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SYNTHESIS AND REACTIONS OF PENTAPHENYLETHYL CARBANION AND SYNTHESES OF ETA(6)-CHROMIUMTRICARBONYL PENTAPHENYLETHANES

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Synthesis and Reactions of Pentaphenylethyl Carbanion and Syntheses of η^6- Chromiumtricarbonyl Pentaphenylethanes

by

Bijaya Misra

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This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

April 13, 1987
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ABSTRACT

Synthesis and Reactions of Pentaphenylethyl Carbanion and Syntheses of η^6-Chromiumtricarbonyl Pentaphenylethanes

by

Bijaya Misra

Advisor: Herman E. Zieger

The synthesis of pentaphenylethyl carbanion by deprotonation of pentaphenylethane with $KOBu^t/BuLi$ at -78°C has been achieved. Chemical Ionisation mass spectrometric analysis of the deuteriopentaphenylethane shows 80% of monodeuteration at the benzylic carbon and 10% of dideuteration at both benzylic and aromatic carbons. Reactions of the anion with electrophiles such as MeI, CO, TMCS and DMS are described. It appears that pentaphenylethyl carbanion undergoes a single electron oxidation to a pentaphenylethyl radical whose limited stability results in fragmented derivatives such as triphenylmethanol and benzophenones.

Two chromiumtricarbonyl coordinated pentaphenylethanes have been synthesised via coupling reactions. Furthermore a number of Arene-$Cr(CO)_3$ complexes have been prepared utilizing two different methods in good to excellent yields. Single crystal X-ray structure analyses of the PPE-CTC complexes have been completed; the ethane bond distance in C(1) and C(2) complexes were found to be 1.615 ± 0.007 A° and 1.620 ± 0.006 A°. The chromiumtricarbonyl unit was found in a staggered orientation with respect to the ring carbons in both complexes. A near staggered conformation of the phenyl rings around the ethane bond have been observed.

A carbon -13 NMR study of pentaphenylethyl carbanion shows no evidence for a thermal decomposition of the anion to a trityllithium. The anions of pentaphenylethane-CTC complexes have been synthesised at room temperature from their hydrocarbon with $KOBu^t$ in DMSO. Carbon -13 NMR of the anion have shown the carbonyl resonances near 241 ppm , a deshielding of 8.2 to 8.4 ppm with respect to that of the hydrocarbons.The Benzylic carbon resonance in PPE(C2)-CTC anion was observed at 105.8 ppm. For PPE(C1)-CTC anion a η^5-chromiumtricarbonyl structure is proposed.

To My Mother

ACKNOWLEDGEMENTS

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TABLE OF CONTENTS

Page

EXPERIMENTAL (continued)

Page

EXPERIMENTAL (continued)

TABLES page

FIGURES page

page

FIGURES (continued)

APPENDIX page

page

APPENDIX (continued)

CARBON NUCLEAR MAGNETIC RESONANCE

INTRODUCTION

Organic carbanions have enjoyed widespread use in synthetic organic chemistry for the deprotonation of weakly acidic substrates as well as the formation of carbon-carbon and carbon-heteroatom bonds[1]. The study of carbanions in solution often is complicated whenever the carbanion of interest is sufficiently basic to react with the solvent. Previous co-workers in our laboratory have studied the coupling reactions of benzylic carbanions[2] and the research presented in this thesis describes the synthesis and reactions of the novel, sterically hindered benzylic system found in the pentaphenylethyl carbanion. In addition it will describe the synthesis and the physical properties of tricarbonylchromium(0) complexes of pentaphenylethane and their deprotonation to pentaphenylethyl carbanion complexes which are stabilized by the appropriately positioned $Cr(CO)_3$ group. The introduction provides an overview of carbanion structure and reactivity in solution followed by a review on the synthesis and reactions of arene-chromiumtricarbonyl complexes.

I) The Structure of Carbanions in Solution:

The influence of aggregation, complexation and solvation on the reactivity of organometallic species is of paramount importance to synthetic organic chemists. A complete summary of all the work in this area that will pertain to discussions in this thesis is contained in selected review articles[3,4,5,6,7].

The effect of ion pairing phenomena on the NMR spectra of carbanions are specially relevant and briefly presented below. The ion pair equilibria experienced by carbanions in solution are shown in Scheme 1. The concentration of free anions present in most solutions of organic ions is small and it is generally found that loose (solvent separated) ion pairs are favoured by small cations such as Li^+, strong coordinating solvents such as DME, and resonance stabilization of the carbanion[6,9,10,11].

$$A^{(-)} + M^{(-)} \rightleftharpoons A^{(-)} \,||\, M^{(+)} \rightleftharpoons A^{(-)} , M^{(+)}$$

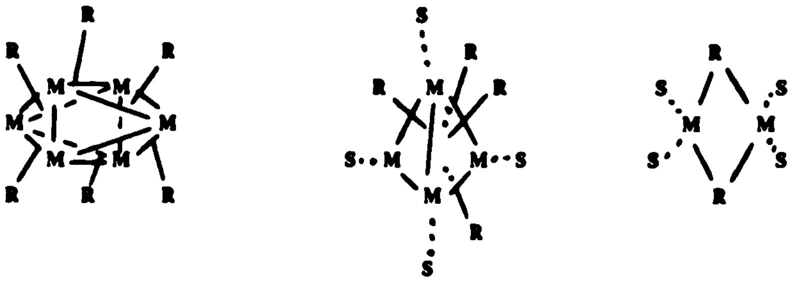
Free Ions	Solvent Separated Ion Pairs(SSIP)	Contact Ion Ion Pairs(CIP)

(SCHEME-1)

The energy required to shift the equilibrium towards solvent separated ions is a balance between the coulombic energy needed to separate the oppositely charged ions and the energy gained from ion dipole interaction between cation and the solvent. Energy required to separate the ions decreases as the size of the π-system of the carbanion increases. The energy gained from the cation solvent interaction is larger for solvents of high coordinating ability and for small cations such as lithium. Since cation solvation results in a large negative ΔS term, lower temperatures also favour the solvent separated ion pairs[5,12,13].

Conventional NMR studies on organolithium species, most notably using ^{13}C and ^{7}Li nuclei, have in recent years revealed many details of ion pair interaction and the aggregate and interaggregate exchange[5,7,10,14-26]. The contact ion pair (CIP)/solvent separated ion pair (SSIP) equilibrium may be followed by observing the change in the α-carbon chemical shift with temperature in benzylic systems[7,10,15,16,18,20]. The signal moves down field as the equilibrium shift from CIP, where most of the negative charge is localized on the α-carbon, to SSIP in which the negative charge is dispersed throughout the π-system. O'Brien[10] observed the formation of

SSIP with the lithium and sodium salts. However the potassium, cesium, and rubidium salts appear to be contact ion pairs for all combinations of solvent, temperature and cation. The tendency of alkyllithium compounds to exist as dimer, tetramer and hexamers[27,28,29] in solution (Fig.1) has



R= n-Bu S= THF M= Li

Fig. 1. Alkyllithium Aggregates

stimulated many NMR experiments. The relationship between ^{13}C relaxation times and molecular motion makes it possible to obtain estimates of the overall size of the aggregate from the relaxation time (τ) data[30,31]. Lithium NMR was first used by T. L. Brown,[32] and numerous authors have since correlated ^{6}Li and ^{7}Li chemical shift and τ data with structural effects in such compounds[5,20,23]. The coupling constants of ^{13}C-^7Li and ^{13}C-^6Li have been used to obtain the information regarding the organolithium aggregate structure[21-25,34]. The magnitude of the coupling constant is an indication of the type of carbon-lithium bonding present (pure ionic bonds should show no coupling[23]) while ^{13}C peak multiplicities may be used to determine the degree of aggregation.

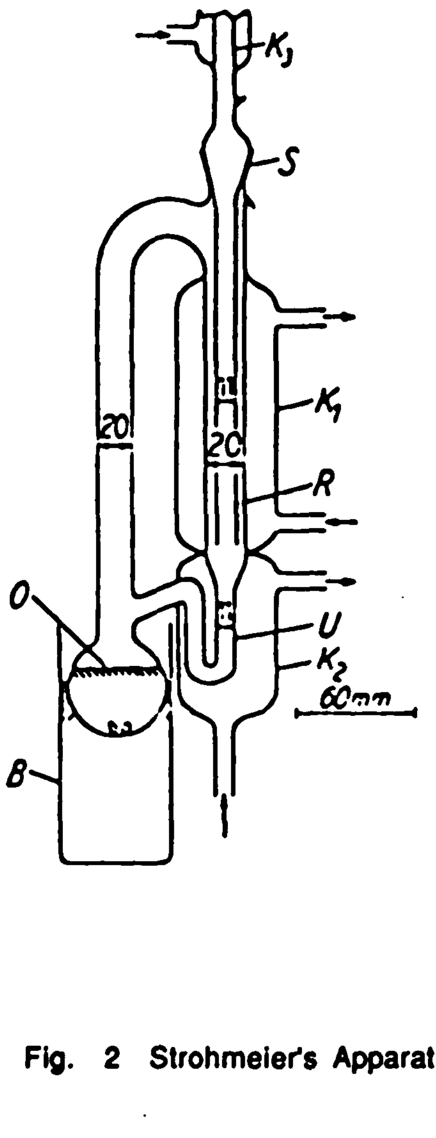
Seebach[25] observed that phenyllithium, vinyllithium and cyclopropyllithium derivatives are dimers while n-BuLi exists as both the dimers and tetramers in equilibrium with the latter being favoured at low temperatures. McGarrity[26] using a rapid injection NMR technique, also observed that n-butyllithium in THF consists of a tetramer in equilibrium with a dimer. The reactions of n-butyllithium in various solvents have been interpreted in terms of an initial rapid dissociation of aggregated butyllithium into monomer which is considered to be the predominantly reactive species[27]. This interpretation is supported by the observed change in reaction order in n-BuLi from approximately 0.33 to 1 in its reaction with the solvent THF as the concentration is lowered from 100 to 1.5 mM. However, McGarrity et al. in their recent NMR study did not observe any evidence for a monomeric n-butyllithium in THF[26].

II) Synthesis of π-arene Chromium(0) Complexes:

Since the discovery [37-41] of arene tricarbonylchromium(0) complexes in the late 1950's, methods of preparation for this class of organometallic compounds have been extensively studied. The parent member of this series, benzene chromiumtricarbonyl, was first obtained by Fischer and Ofele[37] from chromium hexacarbonyl and dibenzene chromium in benzene in a sealed system at 200°C. Later Natta and his group[39] prepared several of these complexes but utilized a pressurized system with intermittent release of carbon monoxide and high temperatures. The most useful preparative method, however, was developed by Nicholls and Whiting[38] which involves heating $Cr(CO)_6$ under reflux in an excess of aromatic compound or with a molar quantity in an inert solvent. In the above procedure the solvents employed are high boiling in nature and one encounters the following major difficulties: 1. Chromium hexacarbonyl possesses an extremely high vapour pressure and sublimes out of boiling solvents. It solidifies readily in the condenser clogging it. 2. The reaction is slow. 3. It is difficult to remove the excess arene or solvent and trace impurities of $Cr(CO)_6$ from the product. With the advent of a sophisticated apparatus by Strohmeier[4]

(Fig. 2), the first problem was solved which allows chromium hexacarbonyl to be recycled. Alternatively $Cr(CO)_3L_3$ ($L=CH_3CN$, NH_3) is reacted with the arene at moderate temperatures, the former is prepared from $Cr(CO)_6$ and acetonitril[43] or ammonia[44].

The use of donor solvents[45,46] allows a decrease in the length of the reaction time via intermediate $Cr(CO)_{6-n}D_n$($n=1$, 2, 3). Alkyl pyridines have been recommended[46] but ethers are still widely used. All the chromium(0)



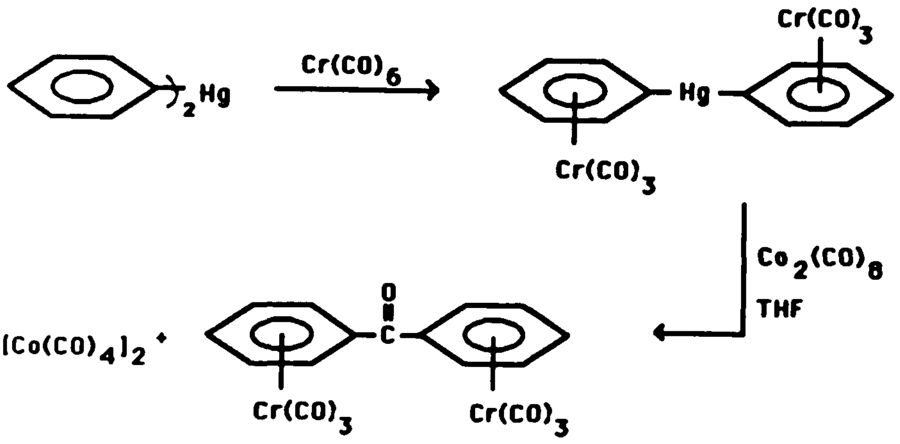
K1 = condenser #1
K2 = condenser #2
K3 = condenser #3
S = S/T joint
R = tube
U = U tube
O = chromium hexacarbonyl
B = heating bath

Fig. 2 Strohmeier's Apparatus

complexes have relatively high temperatures of formation and narrow ranges of thermal stability before reaching the temperature of decomposition. Hence the difficult part lies in the selection of a suitable solvent or solvent mixture for a particular arene. THF alone is an excellent solvent which allows for clean reaction, but the reaction is too slow as a result of its low boiling point[47]. Diglyme is a good donor solvent with a high boiling point that often provides low yields due to decomposition. Mahaffy[48] considered a solvent mixture like dibutyl ether and THF. Top and Jaouen[49] claimed good to excellent yields of π-arene complexes in relatively short reaction time using dibutyl ether and THF. The addition of THF allows one to wash the condenser and recycle the sublimed $Cr(CO)_6$. However, there is a limitation to this method. The complexes of condensed polynuclear aromatic systems like anthracene and naphthalene cannot be prepared in more than 10%. It is known that naphthalene-$Cr(CO)_3$ decomplexes[50] at room temperature just by dissolving in THF due to the weak arene-metal bonds.

Substituent effects seem to play a significant role in the formation of the chromium(0) complexes. Electron donating substituents such as OH, OCH_3 and NH_2 favour the complex formation whereas electron withdrawing groups like Cl and NO_2 inhibit the complexation. In mono substituted benzophenones, the chromiumtricarbonyl moiety sits on the most electron rich ring.

Introduction of two -$Cr(CO)_3$ moieties in a molecule has never been easy until recently. Seyferth[51] has developed a new preparative approach to make the bis chromium(0)tricarbonyl which involves the reaction of $Co_2(CO)_8$ on the known derivatives of biphenyl mercury bis chromium(0) tricarbonyl to yield benzophenone bis chromium(0)tricarbonyl complex (Scheme-2). However, Jaouen's method appeared to be more general and easier to implement. It involves the reaction of an arene with a two mole excess of $Cr(CO)_6$ in dibutyl ether and THF[49].



(SCHEME 2)

III) Reactions of Arene-tricarbonylchromium(0) Complexes:

It is generally accepted that metal-ligand bonding may be divided into two parts, i) the forward coordination in which the ligands donate electrons to the metal and ii) the back donation whereby the filled metal d-orbitals interact with antibonding orbitals of the ligand[53]. P^K measurements have shown that aniline-$Cr(CO)_3$ is a weaker base than aniline and benzoic acid-$Cr(CO)_3$ and phenyl acetic acid-$Cr(CO)_3$ are both stronger acids than the corresponding uncomplexed acids[38]. Dipole moment[54], molecular orbital calculation[55,56,57] and nuclear magnetic resonance spectra[58,59,60,61] support a powerful electron withdrawing effect by the $Cr(CO)_3$ group much like the effect of a nitro substituent in the σ-framework. In general, the complexation by the $Cr(CO)_3$ moiety results in a net decrease in σ-electron density while little perturbation of the π-electron density of the ring occurs[62].

Five general changes in arene reactivity have been observed when a chromiumtricarbonyl moiety is coordinated to an arene system (Fig.3) :

1. nucleophilic aromatic substitution and addition[67-69],
2. enhanced acidity of the arene ring hydrogens[66,70],
3. steric effect of the coordinated metal unit[62,71,72],
4. stabilization of side chain cation site[51,73-75,77-79] and
5. stabilization of side chain anion site.[80,81]

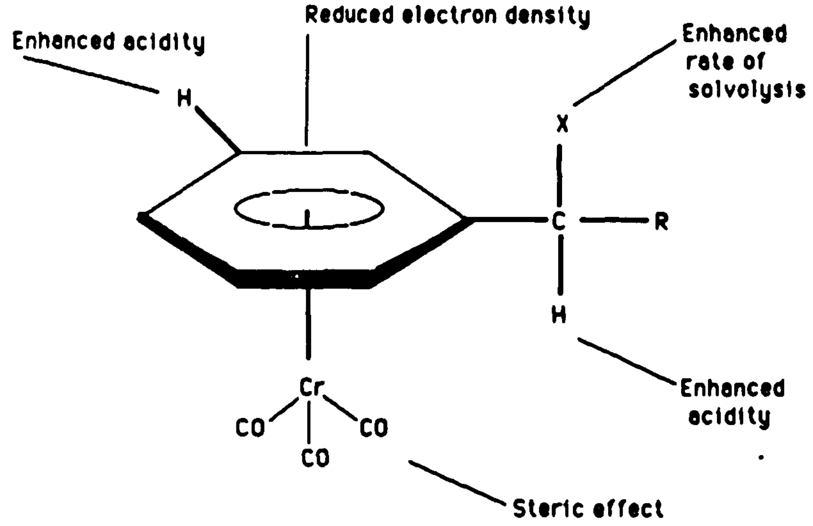
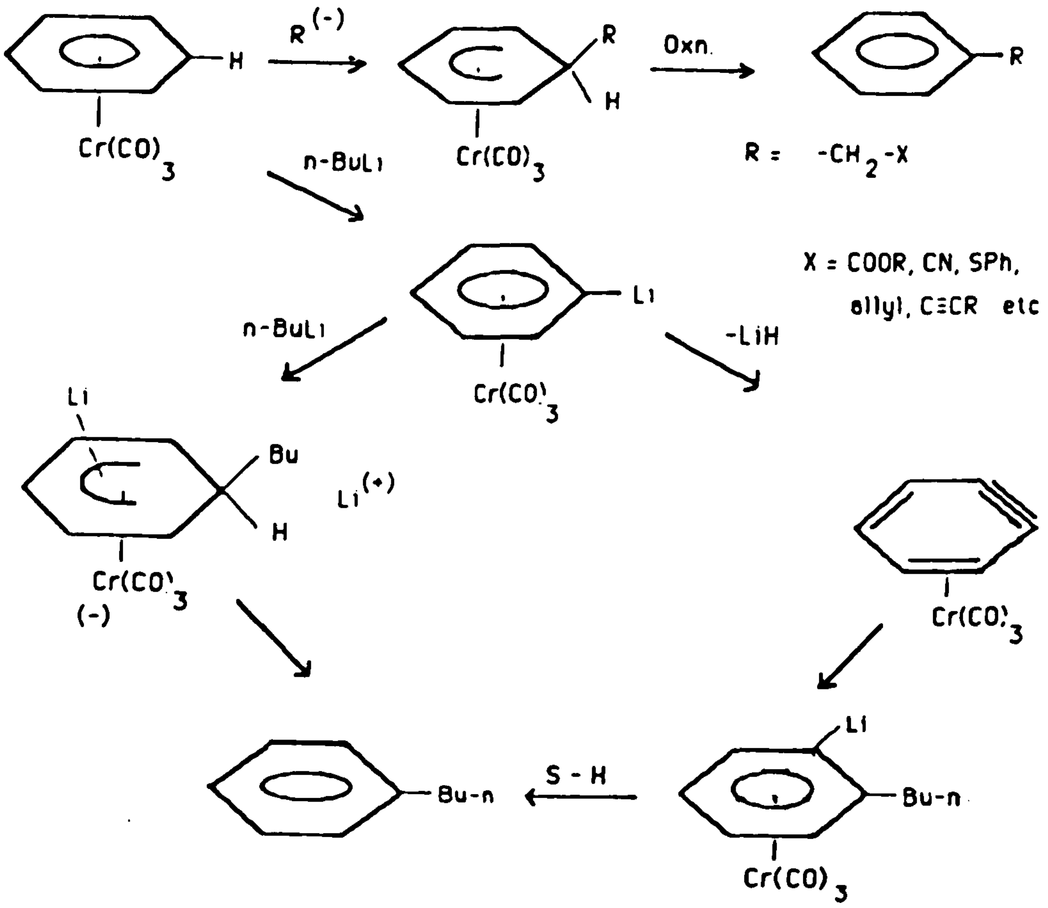


Fig. 3. Effects on arene reactivity of tricarbonylchromium cordination

The presence of a nitro group is known to reverse the reactivity pattern of the aromatic ring allowing the addition of a nucleophile under mild conditions[63]. However the lack of mild and direct methods for attaching and removing the nitro group limits its application as an arene activating substituent. Now it appears that the $-Cr(CO)_3$ grouping with an equivalent electronic effect is the reagent of choice; the ease of complexation and displacement of the chromiumtricarbonyl unit makes these reactions potentially attractive in certain synthetic pathways.

The net nucleophilic displacement of aromatic fluoride and chloride substituents by nucleophiles like $^{(-)}$OR, $^{(-)}$SR has received considerable attention[65]; nucleophiles like butyllithium on the other hand metalate at the position ortho to fluorine in fluorobenzene-$Cr(CO)_3$. Semmelhack[67] studied a wide range of carbon nucleophiles ($P^{Ka} > 20$) that add to the benzene nucleus of the benzene-$Cr(CO)_3$ to yield alkylated products under mild conditions. These reactions often show a regioselectivity which usually is not observed in the reaction of uncomplexed analogues. With strong resonance donors such as alkoxy and amino, meta substitution is always preferred[68,69]. Proton abstraction is the primary reaction with strong bases like MeLi and n-BuLi; s-BuLi gives similar amounts of metalation and nucleophilic addition whereas t-butyllithium undergoes only nucleophilic addition. n-BuLi is also known to undergo[70] nucleophilic addition to benzene-$Cr(CO)_3$ at higher temperatures (0°C and up). Two different reaction pathways have been proposed as shown in Scheme-3. In substituted benzene-$Cr(CO)_3$, n-BuLi selectively metalates at the position meta to the substituents like methyl and ethyl [66,114].

The $Cr(CO)_3$ group has been found to exert a large steric blocking effect which has begun to be exploited by Jaouen et al. in assymetric organic synthesis. Preparation of products with high enantiomeric purity can be achieved by assymetric induction from a chiral arene metal complex[62]. When the functional group undergoing reaction is included in an acyclic ring fused ortho to complexed arene (i.e. indane), reaction occured exclusively from the side exo to the chromiumtricarbonyl[71]. The steric hindrance by $Cr(CO)_3$ is also felt at the benzylic hydrogens during metalation of toluene-$Cr(CO)_3$[70] and indane-$Cr(CO)_3$[72] where only two anti hydrogens exchanged with deuterium in the latter.



(SCHEME 3)

Kinetic studies of ionization reactions[73-75] and p^{Ka} measurements of arene-$Cr(CO)_3$ derivatives have shown great stability of alkylaryl carbocations complexed to $Cr(CO)_3$. Seyferth[51,77] observed an extensive delocalization of the positive charge to $Cr(CO)_3$ unit during the study of (η,η'-diarylcarbonium hexafluorophosphate)bis-(tricarbonylchromium) complexes with nucleophiles like alcohols, amines and highly nucleophilic heterocyclic aromatic compounds. Similar studies have also been reported for 1-p-tolyl ethyl and di-p-tolyl methyl tricarbonylchromium cations[78,79].

The studies on chromiumtricarbonyl complexed benzylic carbanions are mainly due to Jaouen et al[80, 81]. He demonstrated via a DNMR study that there is a substantial distribution of the negative charge on the chromiumtricarbonyl group. In contrast to stabilization of benzylic cation by $Cr(CO)_3$ moiety- a phenomenon[51,79] that seems to involve direct overlap of a filled 3-d orbital with the vacant 2-p orbital at the α-carbon as in Fig.4- the stabilization of benzylic anion is indirect[104]. Indeed such an overlap between a chromium d orbital and the orbital of α-carbon would be destabilizing since both orbitals are filled[81].

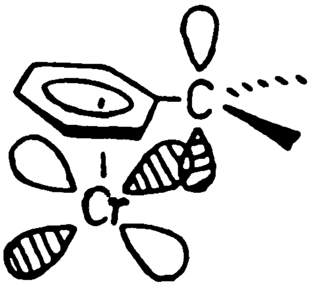


Fig.4. Stabilization of Carbocation by Chromiumtricarbonyl Group

STATEMENT OF PROBLEM

Pentaphenylethane (1) is a stable, easily prepared[144] polyphenylethane of substantial interest as a starting material for the synthesis of hexaphenylethane (HPE). It possesses a benzylic hydrogen atom whose removal with free radical agents is believed to produce the pentaphenylethyl radical which fragments easily to radical or carbenoid products. These unstable intermediates emerge as triphenylmethanol, triphenylmethyl peroxide, diphenyl ketones etc[147].

Removal of a proton by powerful bases to give pentaphenylethyl carbanion (2) does not appear to have been achieved previously. Despite the fact that this benzylic hydrogen atom can be expected to be sterically hindered by adjacent phenyl rings, it was the goal of this thesis to deprotonate pentaphenylethane in order to make the pentaphenylethyl carbanion. Furthermore, it was one of the goals of this thesis at the outset to study the reactions of 2 especially its coupling reactions with organic halides.

When difficulties were enountered in making new carbon to carbon bonds with 2, a chromiumtricarbonyl group was introduced into the aromatic ring with the goal of enhancing the kinetic acidity of the benzylic hydrogen and stabilizing the carbanion by inductive withdrawal of the negative charge on to the chromium atom. Consequently, it became a goal of this study to synthesize η^6-chromiumtricarbonyl pentaphenylethanes and to examine the effects of $Cr(CO)_3$ moiety on the generation and stability of the counterpart carbanions (3, 4) to 2. Carbon-13 NMR studies on 2, 3 and 4 were undertaken in order to correlate the thermal stability of the carbanions with their chemical shifts.

The central ethane bond length in hexaphenylethanes has been the subject of many theoretical calculations and one might imagine that PPE-Cr$(CO)_3$ would be a good approximation to hexaphenylethane. Pentaphenylethane in its solid state exhibits an abnormal ethane bond length (1.606 A°) along with deformation of several bond angles. The ethane bond length for HPE is calculated to be 1.636-1.639 A°.[131] With this in mind it became one of the objectives of this study to determine the ethane bond length of chromiumtricarbonyl coordinated pentaphenylethanes by single crystal X-ray analysis.

RESULTS AND DISCUSSION

I) Synthesis of Pentaphenylethyl Carbanion:

The primary importance of benzylic carbanions as organic intermediates is demonstrated by the development of a variety of methods for their synthesis such as halogen metal exchange[82], reduction of arylalkanes[83], reductive cleavage of methyl ethers[84], transmetalation[85] and deprotonation of weak hydrocarbon acids (i.e. the metalation reaction). The ease of metalating a weak hydrocarbon acid is limited by the requirement of a strongly basic reagent to effect proton detachment. Sometimes solubility problems and reaction of the basic reagents with the solvent hinder the effectiveness of the metalation reaction.

Nonetheless, we decided to attempt the deprotonation of pentaphenylethane (*1*) as a way of generating the pentaphenylethyl carbanion. On the one hand the ethane hydrogen is doubly benzylic like the hydrogens of diphenylmethane; on the other hand the presence of the trityl group suggests that steric hindrance to nucleophilic attack on hydrogen will be high. Unlike the carbanions from diphenyl- and triphenylmethane, the chemistry of the pentaphenylethyl carbanion has received little attention and remains largely unexplored.

Alkyllithiums[86], alkali metal amide[87] and alkali metal hydride in crown ether[88] have been successfully utilized for the deprotonation of diphenylmethane and triphenylmethane with P^{Ka} values of 33.1 and 31.5[89] respectively. Structural similiarities of pentaphenylethane (PPE) with diphenylmethane (DPM) led us to assume that the P^{Ka} of the former would be close to that of the latter and use of conventional metalating systems would enable us to deprotonate pentaphenylethane. Benzylic carbanion colors range from yellow to dark red which make them visually detectable in the reaction medium. For pentaphenylethyl carbanion, we were looking for an orange red to a rust red color similar to that of diphenylmethyllithium.

Table 1 lists the results of the preliminary experiments with various bases, solvents and temperatures. In experiments with n-butyllithium, tetramethylethylene diamine (TMEDA) in THF, t-butyllithium-TMEDA in THF and potassium hydride-18-crown-6 in THF, the solution acquired light pink to light orange colors and when quenched with deuterium oxide, carbon dioxide, methyl iodide or trimethylchlorosilane the color disappeared immediately and the product mixture after isolation was found to be mostly pentaphenylethane. Lithium diisopropyl amide (LDA) and lithium tetramethyl piperidide (LTMP) also were unable to metalate PPE in THF solution. It appears from the above study that PPE is a considerably weaker acid than DPM. One of the main reasons seems to be due to the steric hindrance of the benzylic hydrogen by the phenyl rings.

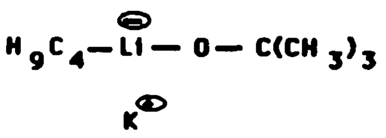
Potassium tertiary butoxide activates butyllithium in an unprecedented manner[90]. When treated with this super base, hydrocarbons in the low acidity range of p^{Ka} 35-50 undergo a clean metalation. Until recently, butyl potassium was believed to be the active metalating species[91,92] in the above system. However, Schlosser[93] in a recent communication demonstrated that butyl potassium and butyllithium/ potassium t-butoxide in THF are two different deprotonating agents. The true nature of the activating species is not clear and several structures have been proposed (*2-5*).

McGarrity recently observed by a rapid injection NMR study that n-butyllithium in the presence of trace amount of alcohol or oxygen in THF exists in the form of mixed alkyllithium-lithium alkoxide complexes with up to three alkoxide ligands. Increased substitution of alkyl ligands in aggregates increases the reactivity of the remaining alkyl group and the aggregate $Bu_2Li_4(OBu)_2$ has comparable reactivity to that of the

Table 1. Metalation of Pentaphenylethane.

Base	Solvent	Temp.(°C)	Color
n-BuLi	Cyclopentane	5-25	yellow
	Cyclopentane/ TMEDA	5-25	yellow
	Ether	0-10	light orange
	Ether/TMEDA	0-10	"
	Ether/TMEDA	-70-0	"
	THF	0-5	light orange
	THF/TMEDA	-70-0	brown
KH	THF	25	-
	THF/crown ether	25	light pink
	THF/crown ether	-70-0	"
t-BuLi	Cyclopentane	25	light orange red
	THF	-70-0	"
LDA	THF	-70-0	-
LTMP	THF	-70-0	-

butyllithium dimer.



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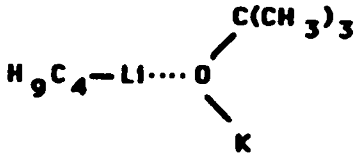

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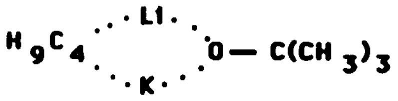

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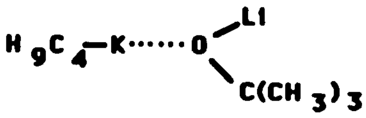


(5)

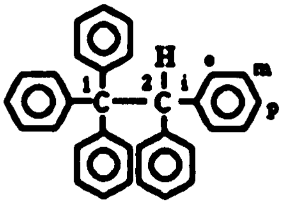
In the beginning of this study we were concerned about the stability of the pentaphenylethyl carbanion taking into account the very low stability of the corresponding radical[95] . Hence all the reactions were carried out at low temperatures. In the trial experiments two moles of the metalating solution were used per mole of the substrate at -78°C in THF and for the first time a dark red solution, the characteristic benzylic carbanion color, was observed. When the carbanion was quenched with deuterium oxide, it gave a mixture of pentaphenylethane and 2-deuteriopentaphenylethane (PPE(D)) in the ratio 20:80. The PPE to PPE(D) ratio was determined using a proton integration method, the benzylic hydrogen at 5.85 ppm vs the aromatic protons near 7.3 ppm.

A carbon magnetic resonance study confirmed the position of the deuterium showing a triplet centered at 58.98 ppm with $^1J_{C\text{-}D} = 16.7$ Hz. The rest of the ^{13}C spectrum was similar to that of pentaphenylethane

(Table 2)[96]. An infrared spectrum of the mixture showed a weak broad band at 2150 cm^{-1} due to the C-D strech.

Table 2. Carbon-13 Chemical Shifts(in δ) of PPE and PPE(D).

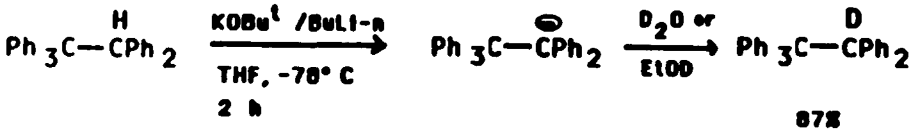
Peak#	PPE($\delta^{13}C$)	PPE(D)($\delta^{13}C$)	Assignments
1.	145.77	145.75	i_1
2.	143.09	143.02	i_2
3.	131.73	131.69	o_{1*}
4	131.44	131.39	o_{2*}
5.	127.37	127.35	m_2
6.	126.94	126.93	m_1
7.	125.85	125.84	$p_{1,2}$
8	62.76	62.67	C_1
9.	59.47	58.98(triplet)	C_2



i= ipso, o= ortho, m= meta, p= para

* our assignments for 1 agree with the literature[96] except the ortho carbons of trityl and benzhydryl benzene rings where it was interchanged based on the intensity of the ^{13}C signals

A series of experiments was carried out to optimise the reaction conditions with respect to the mole ratios of base and the substrate. The results are presented in Table 3. Entry #2 in Table 3 shows that the metalation in the presence of a molar quantity of base was incomplete. The optimum results were obtained with a 40% excess of butyllithium and potassium t-butoxide (Entry #4). Metalation was found to be incomplete at



$$Ph_3C-\overset{H}{C}Ph_2 \xrightarrow[\text{THF, }-78^\circ C,\ 2\ h]{KOBu^t/BuLi\text{-}n} Ph_3C-\overset{\ominus}{C}Ph_2 \xrightarrow[EtOD]{D_2O\text{ or}} Ph_3C-\overset{D}{C}Ph_2 \quad 87\%$$

(eqn. 1)

Table 3*. PPE : PPE(D) Ratio from Deuterolysis of the Pentaphenylethyl Carbanion.

Entry #	Temp.(°C)	Rxn.Time	PPE:Base	PPE:PPE(D)(%)
1.	-95 to -100	5hrs	1 : 2	50 : 50
2.	-78	5hrs	1 : 1	50 : 50
3.	-78	5hrs	1 : 2	13 : 87
4.	-78	5hrs	1 : 1.4	15 : 85
5.	-78	2hrs	1 : 8	13 : 87
6.	-78	2hrs	1 : 1.4	14 : 86
7.	-78	1/2hrs	1 : 1.2	50 : 50
8.	-78	1hr	1 : 1.2	50 : 50
9.	-78	11/2hrs	1 : 1.2	35 : 65
10.	-78	2hrs	1 : 1.2	35 : 65
11.	-78	21/2hrs	1 : 1.2	38 : 62
12.	-78	5hrs	1 : 1.2	36 : 64

* the hydrocarbon solution in THF was approximately 0.11M

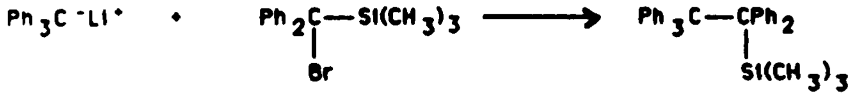
lower temperatures (Entry #1); variation of the quantity of potassium tertiary butoxide (Table 4) and order of mixing also made no difference in the deprotonation ratio. For a qualitative estimation of P^{Ka} of PPE, hydrogen-deuterium exchange under phase transfer catalysis conditions[97] (tetrabutyl ammonium hydrogensulfate, 63% $NaOD/D_2O$ in hexane) was employed with no success.

Table 4*. PPE : PPE(D) Ratios from Deuterolysis of the Pentaphenylethyl Carbanion.

Entry#	Rxn.Time	(PPE/n-BuLi): $KOBu^t$	PPE:PPE(D)
1.	1/2hr	1 : 2	34 : 66
2.	1hr	1 : 2	27 : 73
3.	11/2hrs	1 : 2	26 : 74
4.	2hrs	1 : 2	26 : 74
5.	1/2hrs	1 : 4	25 : 75
6.	1hr	1 : 4	28 : 72
7.	11/2hrs	1 : 4	24 : 76
8.	2hrs	1 : 4	22 : 78

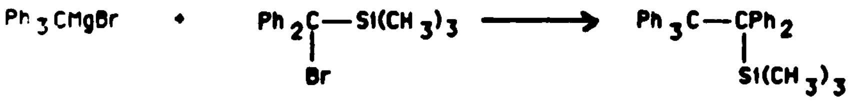
* The hydrocarbon solution in THF was approximately 0.11M

A second method for the generation of pentaphenyl ethyl carbanion by desilylation of pentaphenylethyl trimethyl silane (*8*) with a tetra-alkyl ammonium fluoride or cesium fluoride [98,99] was undertaken. The idea was to secure the carbanion in a mildly basic medium. Accordingly two different approaches were tried for the synthesis of pentaphenylethyl trimethyl silane (*8*). These are shown in equation 2 and 3.



$$Ph_3C^-Li^+ + Ph_2C(Br){-}Si(CH_3)_3 \longrightarrow Ph_3C{-}CPh_2{-}Si(CH_3)_3$$

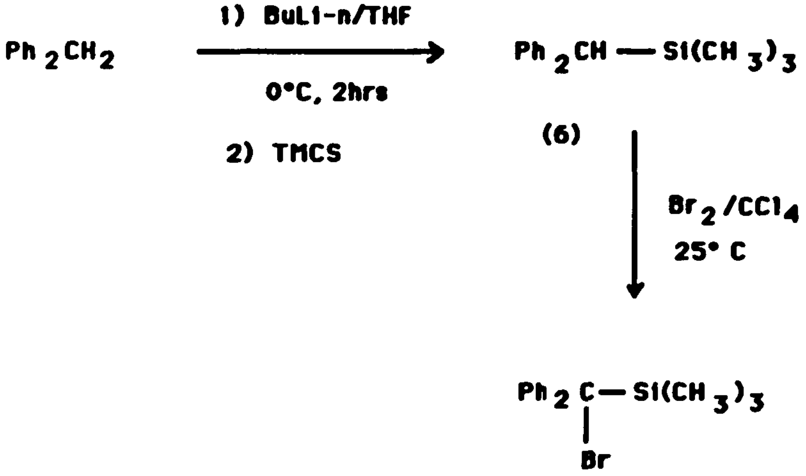
(7) (8) (Eqn. 2)



$$Ph_3CMgBr + Ph_2C(Br){-}Si(CH_3)_3 \longrightarrow Ph_3C{-}CPh_2{-}Si(CH_3)_3$$

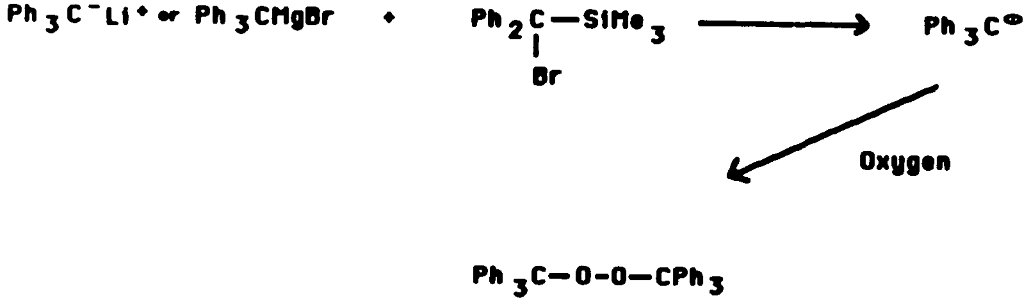
(7) (8) (Eqn. 3)

In both cases upon reaction with diphenyl α-bromomethyltrimethyl silane (*7*)[102], the color of the reaction mixture turned yellow and on work up trityl peroxide (*9*) was the only isolable product (Scheme 5). α-Bromo methyltrimethylsilane (*7*) was synthesized as shown in Scheme 4[100-103]. It appears from the above results that the trityl anion or trityl Grignard undergoes single electron oxidation in presence of diphenyl α-bromomethyl trimethylsilane and gives the more stable trityl radical which reacts with oxygen during work up to afford *9* (Scheme 5).



$$Ph_2CH_2 \xrightarrow[\text{0°C, 2hrs; 2) TMCS}]{\text{1) BuLi-n/THF}} Ph_2CH{-}Si(CH_3)_3 \ (6) \xrightarrow[\text{25° C}]{Br_2/CCl_4} Ph_2C(Br){-}Si(CH_3)_3$$

(SCHEME 4) (7)



(9)

(SCHEME 5)

II) Mass Spectral Analysis of PPE(D):

n-BuLi/KOPe^t was shown to attack exclusively at the benzylic site of the alkylbenzenes[133a] and at the same time to metalate benzene(P^{Ka} = 43[133b]) effectively. In the present system it is reasonable to expect a small amount of ring metalation with BuLi/KOBu^t since the latter is known to deprotonate weak hydrocarbon acids (P^{Ka} upto 50). The ^{13}C and ^{1}H NMR studies on the deuterolysis product (PPE(D)) of pentaphenylethyl carbanion demonstrated respectively the attachment of the deuterium at the benzylic carbon in 85-90% yield. In order to determine the mole percent of deuterium in the ring, the mass spectral analysis of PPE(D) was carried out. Electron Impact ionization technique fragmented the molecular ion peak of PPE hence Chemical Ionization mass spectroscopy procedures using ammonia gas were employed.[150] The mass peaks of PPE(M, M+1, M-1) and PPE(D)(P, P+1, P-1) with their relative abundances are given in table 5.

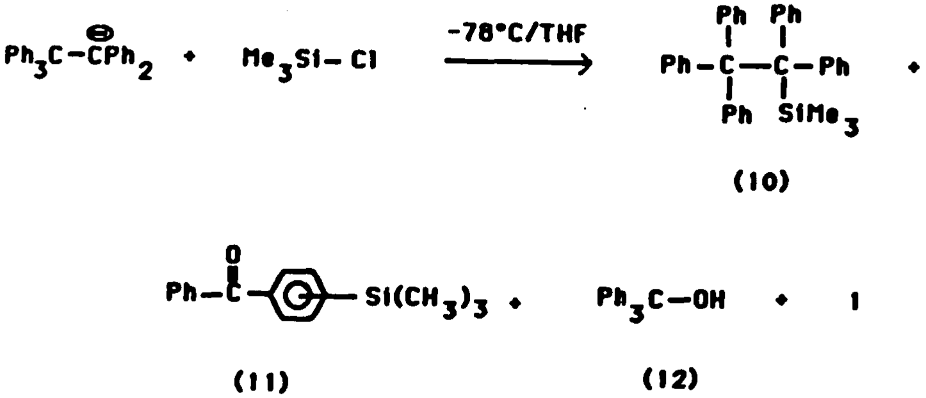
Table 5. Mass Peaks of PPE and PPE(D) with Their Relative Abundances:

a)	M-1 (%)	M (%)	M+1 (%)	M+2 (%)	M+3 (%)
PPE MW 410·NH$_3$	427(13)	428(100)	429(35.9)	430(6.2)	431(0.2)
b)	P-1(%)	P(%)	P+1(%)	P+2(%)	P+3(%)
PPE(D) MW 411·NH$_3$	428(13.4)	429(100)	430(47.0)	431(11.8)	432(1.6)

Preliminary examination of the peak at P+1 (430, 47%) reveals the presence of a dideuteriopentaphenylethane (PPE-d_2) as one of the components in PPE(D). Utilizing the ratios of (M+1)/M and (M-1)/M obtained from parent hydrocarbon (Table 5a) the compositions of PPE, PPE-d_1 and PPE-d_2 in PPE(D) were found to be 10.1, 79.7 and 10.1% respectively.

III) Reactions of Pentaphenylethyl Carbanion with Electrophiles:

Pentaphenylethyl carbanion on reaction with trimethyl chlorosilane (TMCS) afforded an intractable polymeric mixture from which the following compounds were isolated by column chromatography (eqn. 4). Pentaphenylethyltrimethylsilane (*10*, 5%), trimethylsilyl benzophenone (*11*, 35.4%), triphenylmethanol (*12*, 12%) and unreacted pentaphenyl ethane (*1*, 13%).



(eqn. 4)

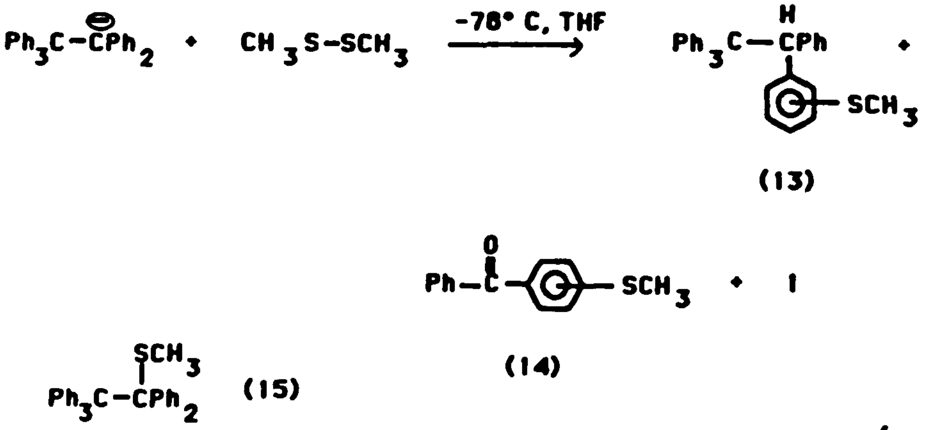
The hydrocarbonsilane (*10*) was identified from its infrared, proton nmr and ^{13}C nmr spectra. Thin layer chromatography of this compound showed the presence of a trace of impurity which could not be removed even after repeated separation through column chromatography and preparative TLC method. The strong evidence for this structure comes from its ^{13}C spectrum, the signals at 68.3 and 65.8 ppm, the former being more intense than the latter, an exact reverse pattern to that of pentaphenylethane. The peak at 68.3 ppm was assigned due to the carbon bearing the trimethylsilyl group which was deshielded due to presence of Si atom function and the peak at 65.8 ppm was due to C(1) also deshielded compared to that of pentaphenylethane.

The silane does not seem to be stable towards acids or bases. The presence of acids in deuterated chloroform appears to cleave the ethane bond in a few days as is evidenced by the disappearance of the characteristic signals at 68.3 and 65.8 ppm of the ethane system in ^{13}C nmr. Bases like alkoxide and amides are known to react rapidly with benzylic silanes and cleave the carbon-silicon bond[105]. The low yield of *10* in this reaction is presumably due to its subsquent reaction with potassium tertiary butoxide and butyllithium which is present atleast in 40% excess in the reaction medium.

Carbon monoxide has been used to convert alkyllithiums to acyllithiums[106]. Because of its small size and linearity, it was hoped that CO would be able to form a new bond at the sterically inacessible benzylic site. When carbon monoxide was bubbled into the anion solution for a period of 5 hrs no appreciable change in color was observed. It was subsequently reacted with trimethylchlorosilane and the products isolated were comparable to that of the trimethylchlorosilane quench reaction and were as follows: silane (*10*, 3.5%), trimethylsilyl benzophenone (*11*, 21.3%), triphenylmethanol (*12*, 10%) and pentaphenylethane (*1*, 10%). It appears that carbon monoxide shows little, if any, reaction with pentaphenylethyl carbanion.

The carbanion color did not disappear on reaction with dimethyldisulfide (DMS) at -78°C and the temperature was raised before hydrolysis. The reaction mixture on column chromatographic separation afforded the following compounds (eqn 5): 1,1,1,2-tetraphenyl 2-thiomethylphenylethane (*13*, 11%), thiomethyl benzophenone (*14*, 2.5%) and pentaphenylethane (*1*, 31%) along with an intractable mixture. Structure *13* was identified from its infrared, proton nmr and ^{13}C nmr spectra and elemental analysis. The ^{13}C spectrum has two peaks at 62.54 and 58.8 ppm

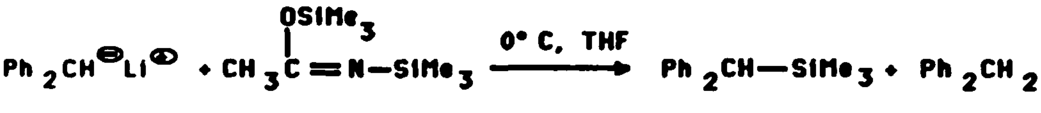
C(1) and C(2) due to the two ethane carbons respectively. The formation of *13* indicates the reaction of the electrophile at the aromatic ring. The desired product pentaphenylethyl methyl sulfide (*15*) could not be isolated.



(eqn. 5)

Methyl iodide decolorized the carbanion solution immediately but the crude reaction mixture did not show an ^1H NMR signal due to the methyl group and purification was not pursued. Dimethyl sulfate on the other hand did not change the carbanion color and on hydrolysis pentaphenylethane was recovered quantitatively.

Bis trimethylsilyl acetamide (BSA, *16*)[107] has been used as a silylating agent for amines and alcohols and an attempt was made to extend its use to carbanion silylation. Pentaphenylethyl carbanion did not react with BSA and pentaphenylethane (96%) was obtained after hydrolysis, however in a blank experiment, BSA silylated diphenylmethyllithium in 50% yield (eqn. 6).



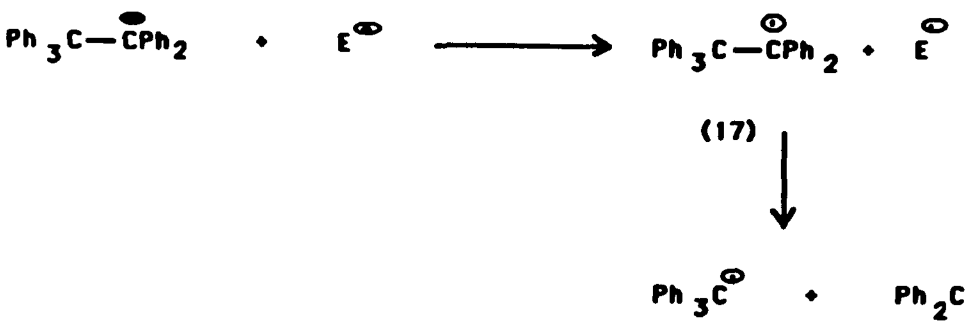
$$Ph_2CH^{\ominus}Li^{\oplus} + CH_3\overset{OSiMe_3}{C}{=}N{-}SiMe_3 \xrightarrow{0°\ C,\ THF} Ph_2CH{-}SiMe_3 + Ph_2CH_2$$

16

(eqn. 6)

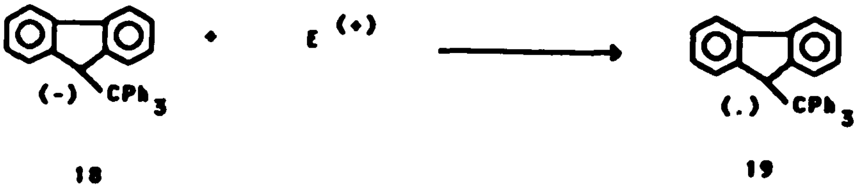
Treatment of a carbanion solution with $(n\text{-}Bu)_3P.CuI/CH_3I$[109] gave triphenylmethanol (*12*, 14%) and a 1:1 mixture of benzophenone and methyl benzophenone (20%).

The isolation of triphenylmethanol and benzophenone derivatives in the foregoing reactions suggests the limited stability of pentaphenylethyl carbanion during its reaction. Apparently Single Electron Oxidation (SET) of pentaphenylethyl carbanion occurs in presence of an electrophile to give pentaphenylethyl radical (*17*) which is known[95] to be an unstable intermediate and cleaves the ethane bond to give trityl and diphenylmethyl fragments (eqn. 7).



(eqn. 7)

Analogous oxidation of 9-trityl fluorene carbanion (*18*) to its radical (*19*) is already known (eqn. 8)[110].



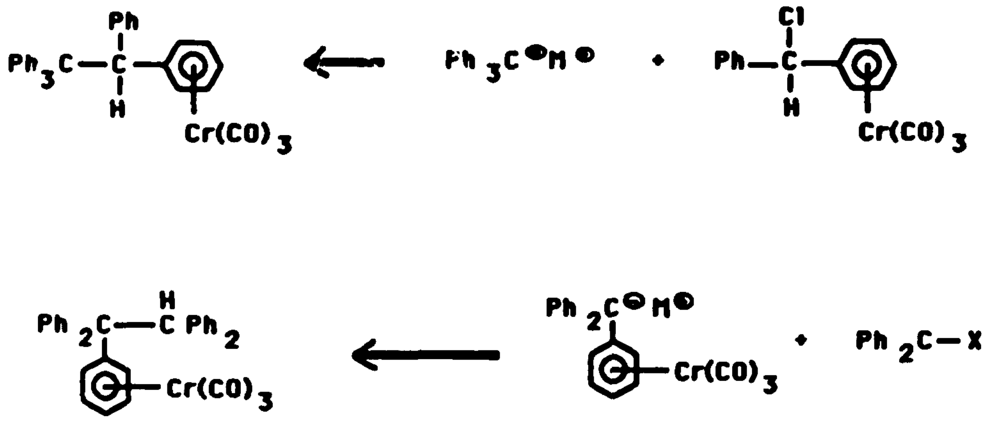
(eqn. 8)

Because of the instability of the pentaphenylethyl carbanion and our inability to make derivatives with classical electrophiles it was decided to explore the effects on the pentaphenylethane system of forming its chromiumtricarbonyl complex (C.T.C.). The chromiumtricarbonyl moiety by virtue of its powerful electron withdrawing effect should enhance the acidity of a benzylic hydrogen and stabilize the carbanion through inductive delocalization of the electronic charge. In addition, it would be interesting to study the influence of the metal unit on the formation and reactions of a sterically hindered carbanion, not to mention on the synthesis of such a chromiumtricarbonyl coordinated complex of an already crowded pentaphenylethane. The following sections describe the synthesis of the hydrocarbons (PPE.C.T.C) and their anions.

IV) Synthesis of Pentaphenylethane Chromiumtricarbonyl Complexes:

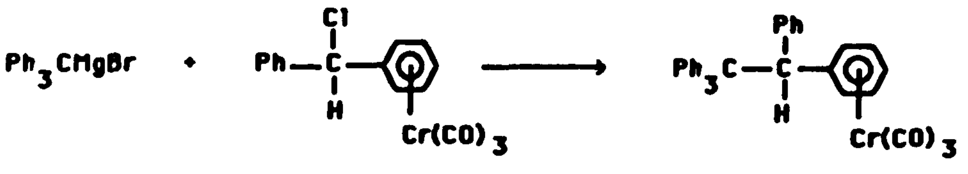
a) Pentaphenylethane(C2)-Chromiumtricarbonyl:

A very large number of chromiumtricarbonyl complexes have been synthesized since their discovery and have been utilized in organic synthesis. These complexes are generally prepared from a substrate, chromiumhexacarbonyl, and a suitable solvent at reflux. The above procedure however was not very promising for the synthesis of the target compounds given the fact that it would yield a mixture of isomeric complexes. Pentaphenylethane is known to decompose to trityl radical and diphenylmethyl radical at moderately elevated temperatures such as 110°C[144b]. An alternative approach for the synthesis of the titled complexes via coupling reactions was planned as shown in Scheme-6.



(Scheme 6)

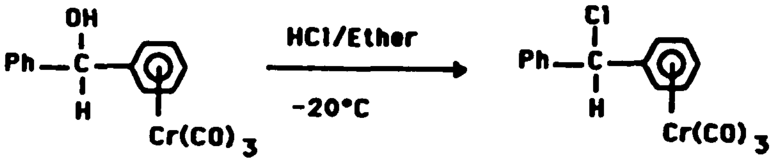
The coupling of trityl Grignard with benzhydryl chloride tricarbonyl chromium (*21*) was carried out analogously to the synthesis of pentaphenyl ethane from trityl Grignard and benzhydryl bromide. From the above reaction the pentaphenylethane-C(2)-tricarbonylchromium (*22*) was isolated in 88% yield which is comparable to that of pentaphenylethane synthesis (eqn. 9).



21 22

(eqn. 9)

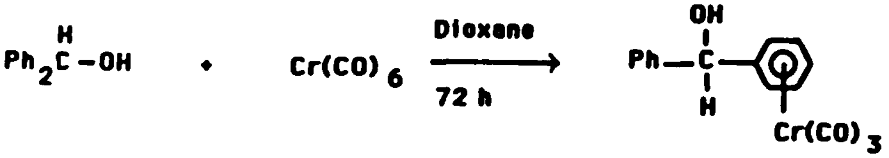
Benzhydryl chloride tricarbonylchromium was prepared according to the literature[73] but with a higher yield under a different set of reaction conditions as shown in eqn. 10. The reaction of benzhydrol chromium tricarbonyl (*23*) with hydrogen chloride at room temperature resulted in decomposition of the complex, however at -20°C the benzhydrylchloride chromium complex was isolated in 92% yield. In the above experiment chasing of excess



23 21

(eqn. 10)

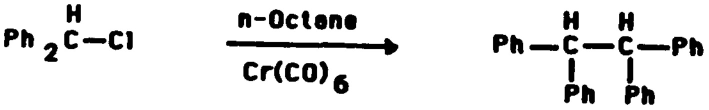
hydrogen chloride by nitrogen gas before removal of the ether seems to be very important, since extensive decomposition of the tricarbonyl complex was observed in one of the runs by straight removal of the solvent after the reaction. Benzhydrol chromiumtricarbonyl was prepared from benzhydrol (*24*) and chromiumhexacarbonyl by boiling in dioxane for 3 days in 60% yield (eqn. 11). Earlier workers synthesized *23* by reduction of benzophenone chromiumtricarbonyl (*25*) with $NaBH_4$[73] or by the reaction of benzhydrol and $Cr(CO)_6$ in dibutyl ether and THF[49]. In both cases either the overall yield is low or requires a cumbersome procedure to isolate the complex.



24 23

(eqn. 11)

A direct synthesis of benzhydryl chloride tricarbonylchromium by the reaction of benzhydryl chloride (*26*) and chromiumhexacarbonyl was not successful; tetraphenylethane (*27*) was isolated as the only product. Dimerization of benzhydryl systems in organometallic reactions is well documented (eqn 12).

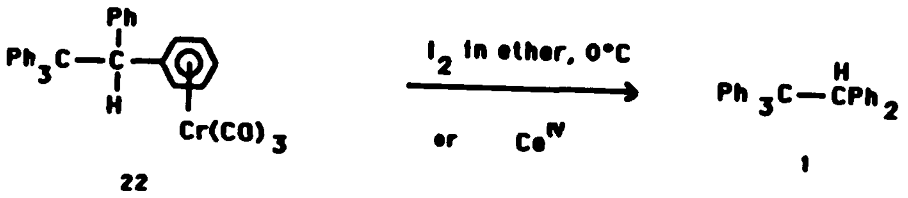


26 27

(eqn 12)

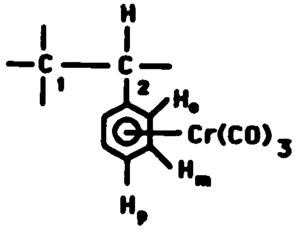
The complex *22* was identified through spectroscopic data, elemental analysis, and its decomplexation to pentaphenylethane by iodine in ether and ceric ammonium nitrate in acetonitrile (eqn. 13).

The infrared spectrum of *22* shows two strong and broad absorption bands due to the carbonyl stretching vibration. The rest of the spectrum was very similar to that of pentaphenylethane. The proton nmr exhibits a



(eqn. 13)

multiplet at 7.2 ppm(20H) due to aromatic and a multiplet at 5 ppm (6H) due to protons in the chromiumtricarbonyl complexed aromatic ring and the benzylic protons. By way of comparision the ^{1}H nmr chemical shift for the complexed benzene ring of diphenylmethane chromiumtricarbonyl is at 5.5 ppm[49]. Moreover in diphenylmethane-$Cr(CO)_3$ the ^{13}C signals for the coordinated ring are found[153] at 112.9, 93.1, 94.3 and 91 ppm. The ^{13}C nmr spectrum of *22* displays two characteristic signals at 63.5 and 58.4 ppm due to the quaternary carbon (C1) and benzylic carbon (C2) respectively. The Nuclear Overhauser Enhancement (NOE) of the carbon signal at 58.4 (C2) ppm by the benzylic hydrogen is clearly visible and was confirmed by a proton coupled ^{13}C INEPT[111] (Insensitive Nuclei Enhancement by Polarization Transfer) experiment. In the INEPT experiment the signals due to quarternary carbon disappear in the carbon spectrum and the carbons with hydrogens show the usual splitting pattern. The two singlets at δ 59.29 and 57.28 were due to the one bond coupling of the carbon with its hydrogen ($^1J_{C\text{-}H} = 127$ Hz) (fig. 5).



$^1J_{C_2-H}$ = 127 Hz

$^1J_{C_o-H_o}$ = 174.7, 174.9 Hz ; $^2J_{C_o-H_m}$ = 6.6 Hz

$^1J_{C_m-H_m}$ = 176.5, 177.0 Hz

$^1J_{C_p-H_p}$ = 170.3 Hz

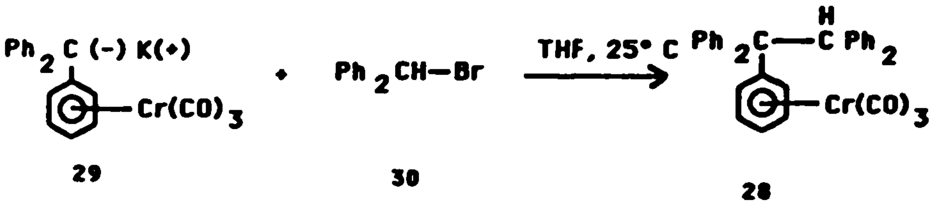
Fig.5.C-H Coupling Constants(22)

There are six signals in the 115-85 ppm range due to six carbons of the complexed aromatic ring shielded by the $Cr(CO)_3$ group (Table 6, pg. 37) The two upfield signals at 87.6 and 86.6 ppm are due to two ortho carbons and the three signals at 100.6, 98.6 and 96.2 ppm are due to two meta and para carbons. The two ortho carbons are identified by their appearance as doublets with a coupling constant 6.6 Hz due to $^2J_{C\text{-}C\text{-}H}$ in the INEPT coupled spectrum. In case of the meta and para carbons the peaks appeared as multiplets and could not be distinguished one from the other from their multiplicities. However, from the magnitude of the C-H coupling constants (Fig. 5) it is reasonable to assign the peak at 96.2 ppm due to the para carbon and the peaks at 100.6 and 98.6 ppm due to two meta carbons. The signals at 112.9 and 232.5 ppm are due to the ipso and the carbonyl carbon respectively and are absent in the INEPT experiment (Fig. 6).

The structure was confirmed by single crystal X - ray structure determination which is presented in detail with the highlights in a later section.

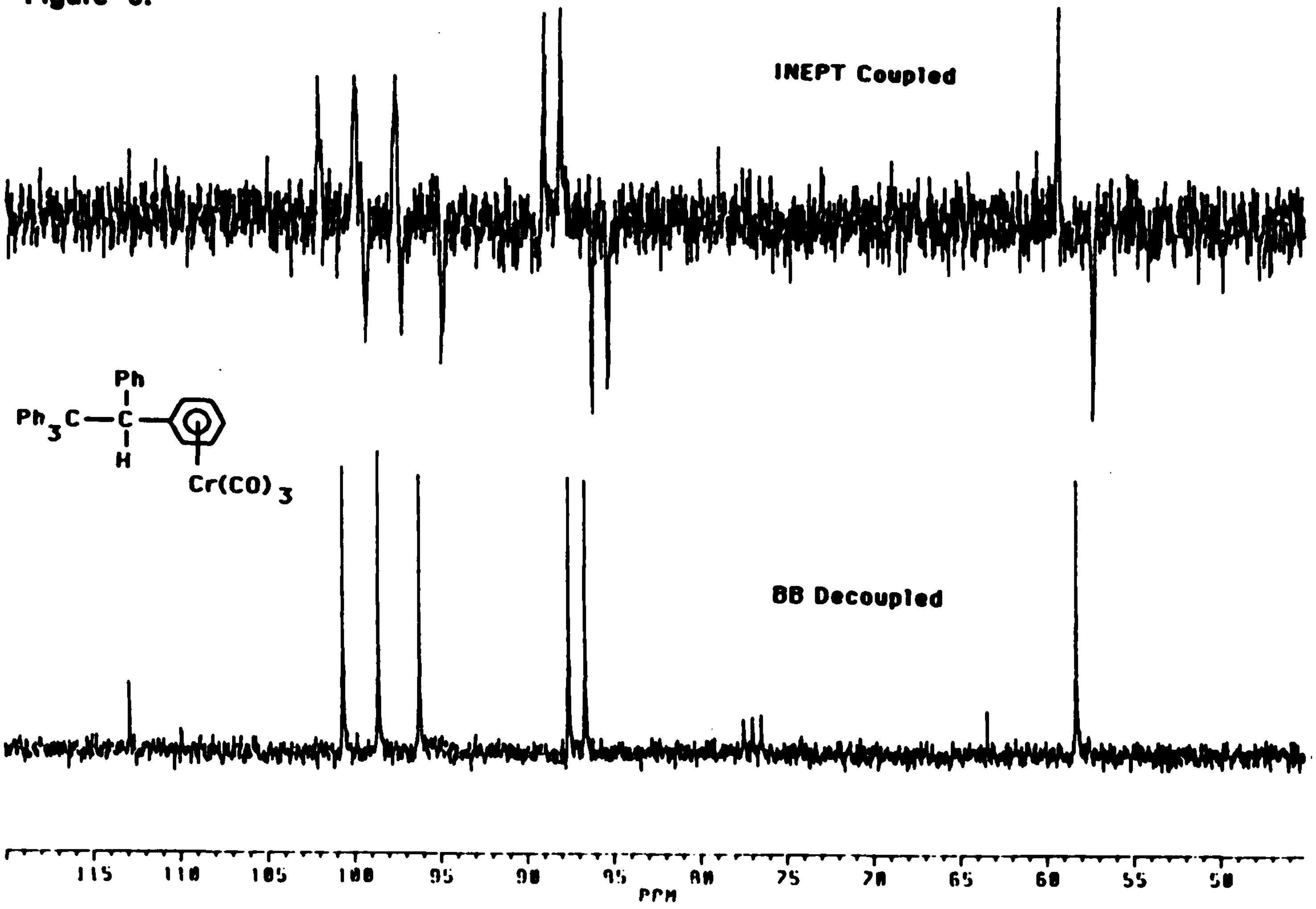
b) Pentaphenylethane(C1)-Chromiumtricarbonyl *(28)* ;

Pentaphenylethane(C1)-chromiumtricarbonyl (*28*) was synthesized in 65.7% yield via the coupling of triphenylmethane chromiumtricarbonyl carbanion (*29*) with benzhydryl bromide (*30*) in THF (eqn 14). Triphenyl-

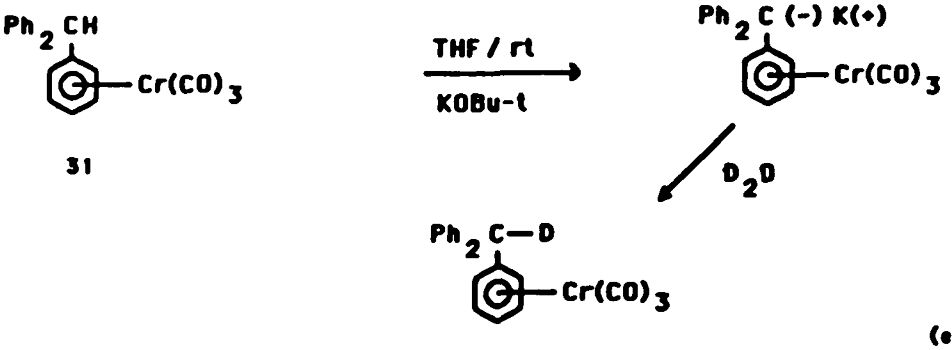


(eqn. 14)

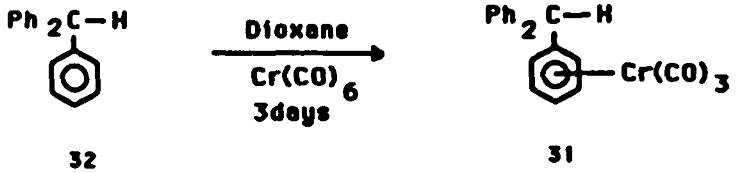
Figure 6:


INEPT Coupled
Ph
Ph3C—C—
H
Cr(CO)3
BB Decoupled
115
110
105
100
95
90
85
80
75
70
65
60
55
50
PPM

methane-$Cr(CO)_3$ carbanion was secured in 80-85% yield by the deprotonation[153] of triphenylmethane-$Cr(CO)_3$ (*31*) with potassium tertiary butoxide in THF at room temperature (eqn 15). Triphenylmethane chromiumtricarbonyl was prepared by the reaction of triphenylmethane (*32*) and $Cr(CO)_6$ at the boiling point of dioxane in 61% yield (eqn. 16). In the present reaction the good yield of coupling product (*28*) seems to be very significant[112] because benzhydryl bromide dimerizes notoriously in organolithium and Grignard coupling reactions.

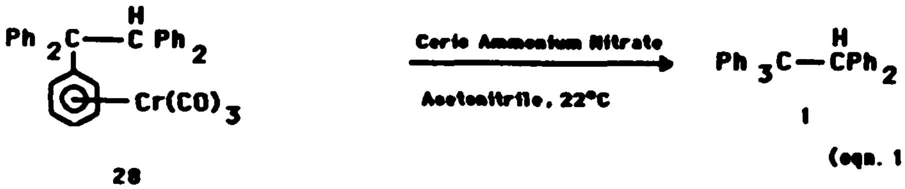


(eqn. 15)



(eqn. 16)

Compound *28* was identified from its infrared, nmr, elemental analysis and by decomplexation to 1 (72%) (eqn. 17).

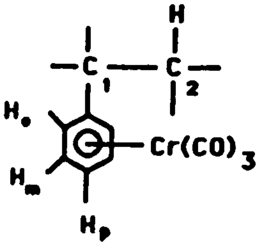


(eqn. 17)

The infrared spectrum showed two strong and broad carbonyl absorption bands near 1960 and 1900 cm^{-1}. The proton nmr spectrum showed a multiplet at 7.2 ppm, a singlet at 5.7 ppm and multiplet at 5.5-4.5 ppm due to the uncomplexed aromatic, benzylic and tricarbonylchromium coordinated ring protons respectively. The carbon NMR spectrum showed signals at 233 ppm due to the carbonyl and 122.1, 98.6, 95.9, 88.2 ppm due to complexed ring carbons. The two signals at 60.6 and 59.8 ppm were the quarternary(C1) and benzylic(C2) carbons respectively, the former being more intense due to NOE by the presence of benzylic hydrogen.

A proton coupled ^{13}C NMR INEPT experiment provided the long range C-H coupling constants which are presented in Fig. 7

It is very interesting to note that *22* exhibits six carbon signals due to the coordinated aromatic ring whereas *28* shows only four signals. The ipso carbon of the coordinated aromatic ring in *28* appears almost 10 ppm down field compared to its counterpart in *22* (table 6). It seems that the ortho and the meta carbons in *22* are magnetically nonequivalent. This may be explained due to restricted rotation of the complexed ring about



$^1J_{C_2-H} = 129.5$ Hz

$^1J_{C_o-H_o} = 175.1$ Hz ; $^2J_{C_o-H_m} = 7.3$ Hz .

; $^3J_{C_o-H_p} = 0.8$ Hz

$^1J_{C_m-H_m} = 171.1$ Hz

$^1J_{C_p-H_p} = 172.9$ Hz

Fig. 7 C-H Coupling Constants(28)

Table 6. ^{13}C Chemical Shifts for Complexes *22* and *28*

PPE-Π-C2-CTC(*22*)	PPE-Π-C1-CTC(*28*)	Assignments
δ .ppm	δ .ppm	
58.35	59.83	C(2)
63.48	60.63	C(1)
86.64		C_{ortho}-Cr
	88.17	C_{ortho}-Cr
87.59		C_{ortho}-Cr
96.17	95.88	C_{para}-Cr
98.56		C_{meta}-Cr
	98.62	C_{meta}-Cr
100.61		C_{meta}-Cr
112.91	122.11	C_{ipso}-Cr
126.35	126.28	C_{para}
127.16	126.93	C_{para}
127.32	127.31	Φ_3C_{meta}
128.10	127.83	Φ_2CH_{meta}
131.02	131.46	Φ_2CH_{ortho}
(131.41)		
131.57	132.06	Φ_3C_{ortho}
140.06	142.59	Φ_2CH_{ipso}
144.92	143.07	Φ_3C_{ipso}
232.48	233.08	carbonyl

C(2)-C(27) (see Fig. 8, page 42) by the presence of $Cr(CO)_3$ group. However, the same argument is also applicable to the isomer *28* where the ortho and meta carbons appear to be equivalent. The very next feature for the above difference recognized was the presence of a chiral center at C(2) in *22* which was absent in *28* . Six signals for the complexed rings have also been observed in the case of benzhydryl chloride and benzhydrol chromium tricarbonyls (*23, 24*). Diastereotopic nature of hydrogens and carbons due to presence of a chiral center in chromiumtricarbonyl complexes have been observed by Trouflet et al[113].

V) Single Crystal X-ray Analyisis:

Strong interactions between phenyl rings are expected to occur in a crowded molecule like pentaphenylethane chromiumtricarbonyl (*22* or *28*). It was hoped that complexation of a -$Cr(CO)_3$ group to the benzene ring would have made the complexed rings more like sp^3 hybridized carbons. In addition we expected transmission of the electron withdrawing character of the Cr atom through the sigma bonding framework to result in a shortening of the ethane bond in *22* and *28* relative to that of the parent hydrocarbon PPE. In order to evaluate the validity of our presumptions, single crystal X-ray structure determinations of *22* and *28* were carried out. The solid state confomations, the orientation of chromiumtricarbonyl on the benzene plane, deformation of bond angles and bond lengths are presented below

a) Pentaphenylethane(C-2)-Chromiumtricarbonyl (22):

X- ray quality crystals were grown from benzene and petroleum ether (1:1, v/v) during three weeks at -17°C in an argon atmosphere. Several attempts to crystallize *22* from a single solvent like benzene, carbon tetrachloride and methylene dichloride alone were without success. The crystals were dried under vacuum and stored in a vial under argon at -17° C. Melting point determination of a small crystal indicated the presence of solvent in the crystal. During the three months before the X-ray data collection, a thin film of Cr^{+3} was deposited on the surfaces of the crystals which were freshly cut before exposure to X-rays. All the diffractometer data were collected at room temperature. The crystal data collection and refinement parameters are summarized in Table 7. Views of solid state comformations are given in Fig. 8, 9 and 10. Coordinates, anisotropic temperature factors, bond distances and bond angles are given in Appendix 1

Table 7. Single Crystal X- Ray Crystallographic Analysis(*22*)

A. Crystal Parameters

formula	$C_{35}H_{26}O_3CrZC_6H_6$(624.72)
crystallization medium	benzene/pet.ether(1:1) at -17°C
crystal size, mm	0.20 X 0.22 X 0.22
cell dimensions	a = 13.525(3) A
	b = 10.678(3) A
	c = 22.448(8) A
	$\alpha = 90.0$
	$\beta = 92.77(3)$
	$\gamma = 90.0$
	V = 3238(2) $A^{\circ 3}$
space group	$P2_1/c$
molecules/unit cell	4
density observed,g/cm^3	1.26
density calculated,g/cm^3	1.28
linear absorption coefficient, cm^{-1}	31.65

B. Refinement Parmeters

number of reflections	3335
nonzero reflections ($I>3.0\sigma$)	2785
R- index = $\sum \| \|Fo\| - \|Fc\| \| / \sum \|Fo\|$	0.053
GOF = $[\sum(Fo^2-Fc^2)^2/(m-s)]^{1/2}$	1.41
scale factor	1.462(2)
secondary extinction coefficient	10(2) X10 $^{-4}$

Table 8. Bond Distances and Bond Angles Involving the Ethane Atoms C(1) and C(2) in Pentaphenylethane(*1*), *22* and *28*)

Bond length in A°

Bond	*22*		*28*		PPE(*1*)[115]	
C(1) - C(2)	1.620	.006	1.615	.007	1.606	.003
C(1) - C(9)	1.533		1.551		1.544	
C(1) - C(3)	1.549		1.545		1.550	
C(1) - C(15)	1.561		1.562		1.563	
C(2) - C(21	1.535		1.531		1.537	
C(2) - C(27)	1.527		1.528		1.531	

Bond Angles (°)

C(2)-C(1)-C(3)	112.0	111.2	114.0
C(2)-C(1)-C(15)	106.7	108.4	107.6
C(2)-C(1)-C(9)	110.1	110.5	109.4
C(3)-C(1)-C(15)	102.9	111.0	102.2
C(3)-C(1)-C(9)	111.2	108.7	110.1
C(9)-C(1)-C(15)	113.8	107.0	113.6
C(1)-C(2)-C(27)	112.8	117.5	113.4
C(1)-C(2)-C(21)	117.4	117.9	118.6
C(21)-C(2)-C(27)	110.5	108.6	109.2

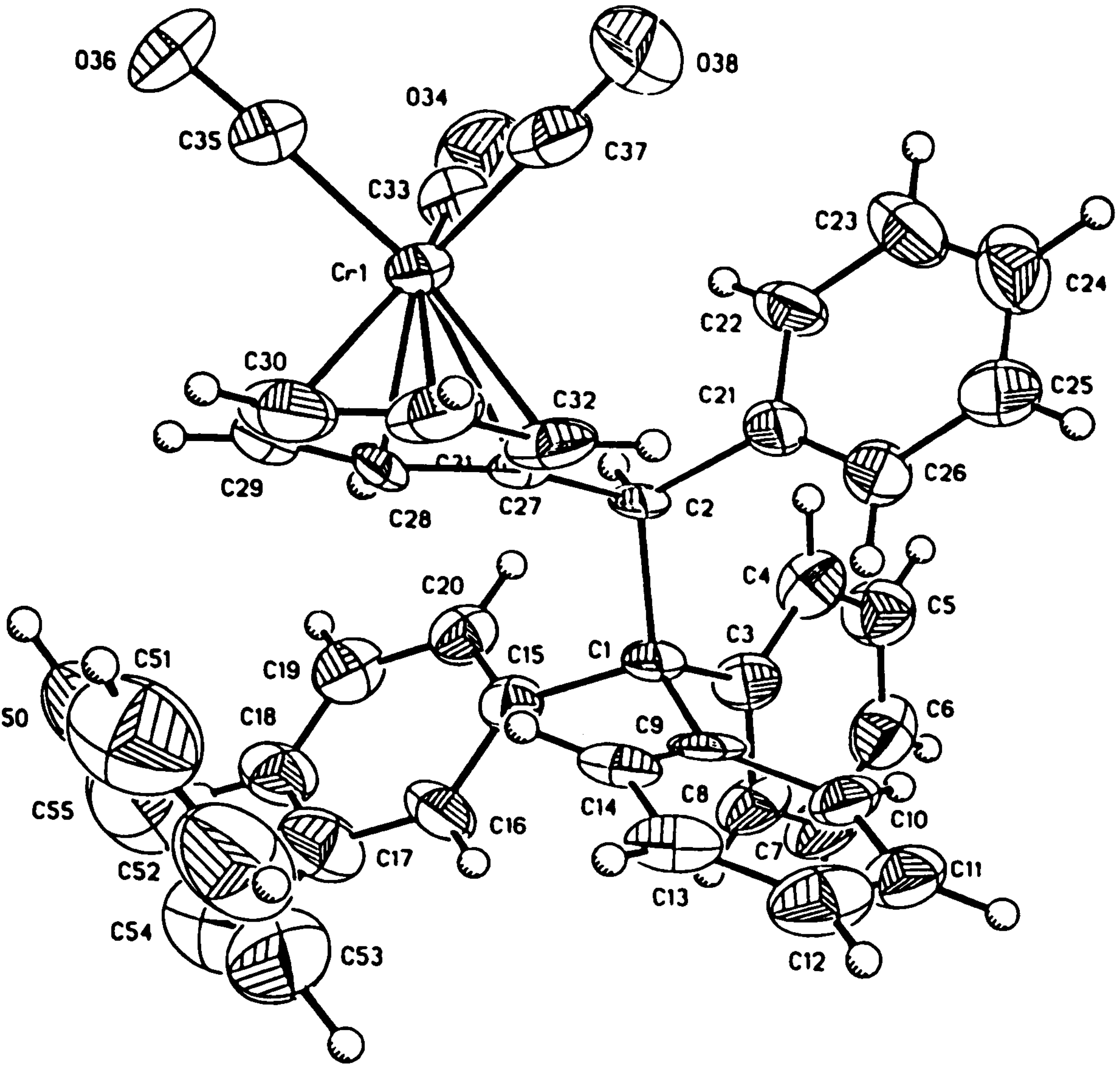
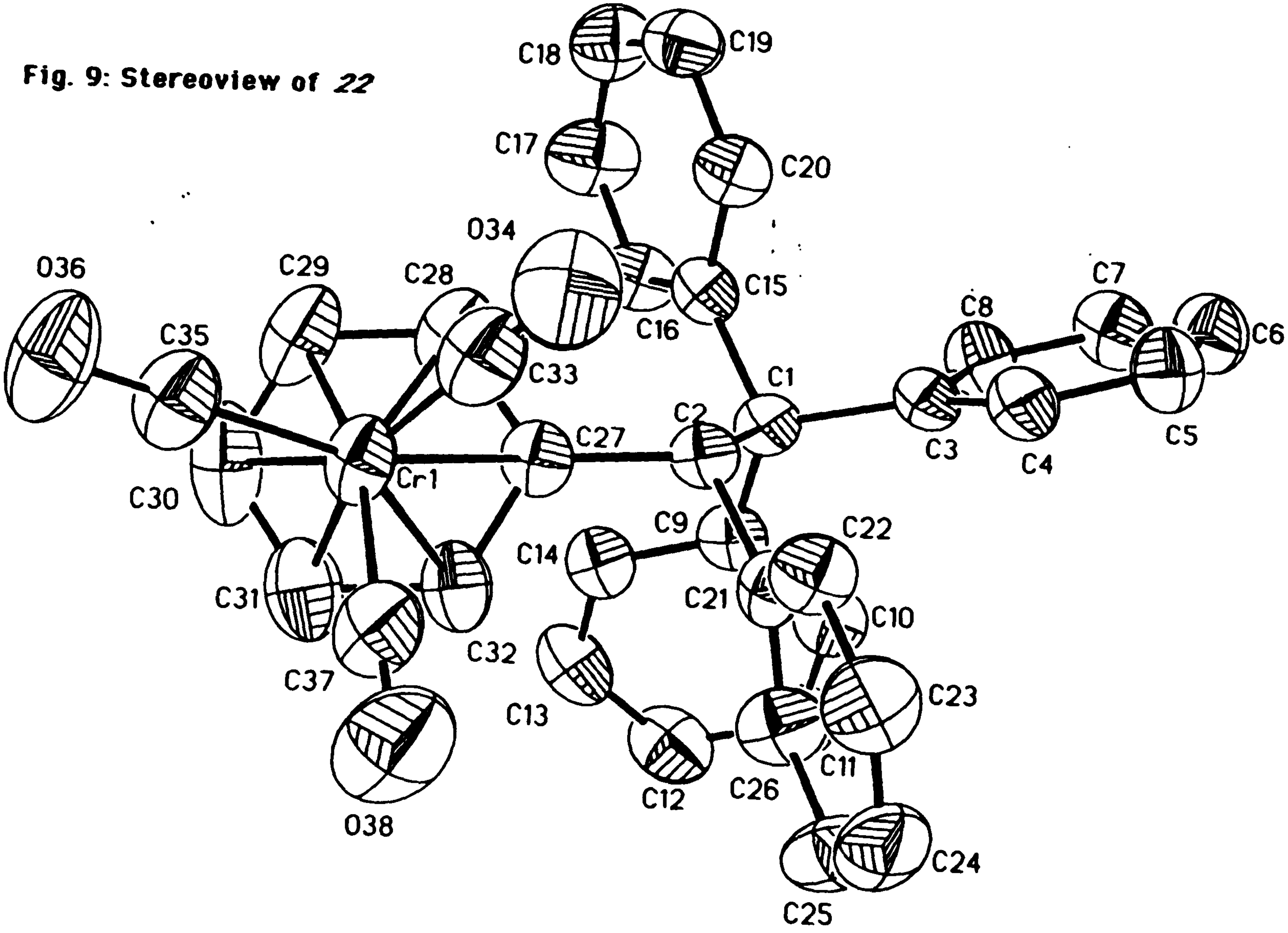


Fig. 8. Stereoview of *22*

Fig. 9: Stereoview of *22*



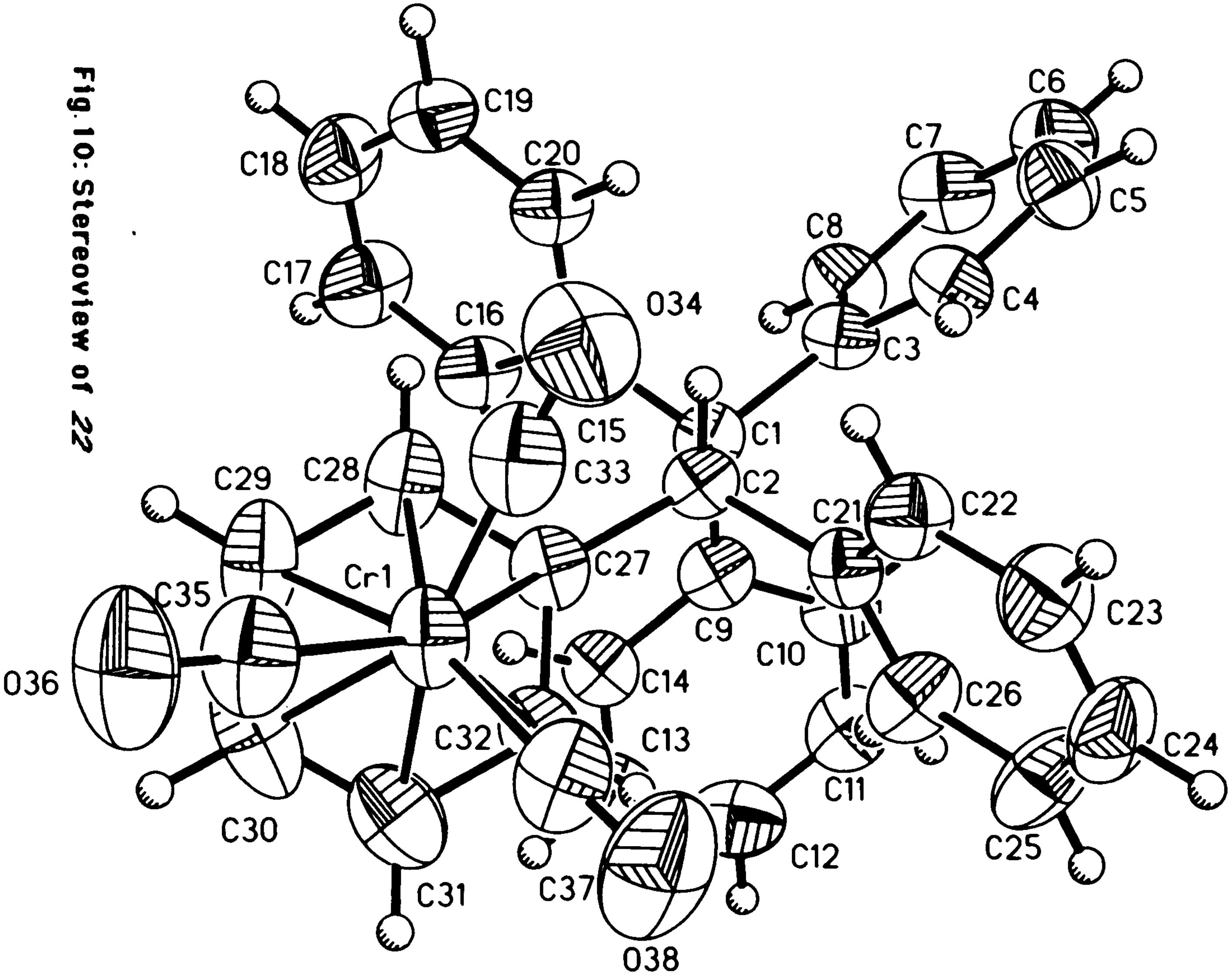
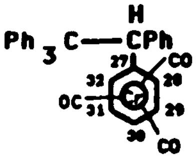


Fig. 10: Stereoview of *22*

The primary difference between pentaphenylethane (*1*) and complex *22* is that the central C(1)-C(2) bond is slightly longer in chromiumtricarbonyl complex at 1.620 A°. This striking and unexpected difference is all the more remarkable when one considers the near identity of the remaining bond distances and angles of *22* shown in Fig. 8 and those reported for *1* (see Table 8). The degree of deformation of the molecule is well documented by the marked deviation of some bond distances and bond angles from their standard values. Of particular relevence are lengthening of C(1)-C(15), 1.561A°; the closure of C(3)-C(1)-C(15) angle, 102.9°; Expansion of C(1)-C(2)-C(21) angle, 117.4 A° and the deformation of the two rings at the center of attachment to the ethane carbon atom as shown by the values C(1)-C(3)-C(4) and C(2)-C(21)-C(26) angles, 125.8° and 125.2° respectively (see Appendix 1, pg. 105). However the angle C(2)-C(27)-C(28) and C(2)-C(27)-C(32), 120.2° and 122.6° respectively for the chromium tricarbonyl complexed aromatic ring seems to be due to that of a normal sp^2 hybridized carbon.

The reduced symmetry of the complexed benzene ring is observed from the ring carbon-carbon distances; they range from 1.369 A° to 1.437 A° Fig. 11). Interestingly, the alternate C-C distances are expanded but to different extents. Low temperature(at 80K) X-ray study of benzene chromiumtricarbonyl also reveals[116] similar characteristics; the cis bond



C(27) - C(28) = 1.437 ; C(30) - C(31) = 1.369

C(29) - C(30) = 1.413 ; C(27) - C(32) = 1.397

C(31) - C(32) = 1.401 ; C(28) - C(29) = 1.403

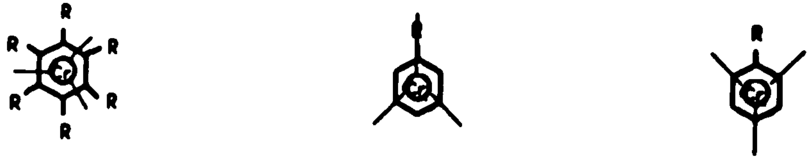
22

Fig. 11

(1.423 A°) (that intersect the projection of Cr-C-O bond on the benzene plane) is found to be longer than the trans bond (1.406 A°) (the bond opposite to the cis bond). Unlike the iron[118] and molybdenum[119]tricarbonyl complexes, the destruction of aromaticity in benzene chromiumtricarbonyl due to -Cr$(CO)_3$ ligand is only partial. The observed alternate stretching of bonds is explained due to the following[116]; the Kekule form with double bonds in trans positions is favoured for energetic reasons. This means a lengthening of the cis bond and shortening of the trans bond. Upon bond formation with chromium the trans bonds are lengthened as is the case with other olefinic bonds coordinated to metal[119]. The resulting trans bond lengths are approximately equal to those in benzene but still somewhat shorter than the cis bond length. The room temperature X-ray diffraction study of benzene chromiumtricarbonyl by Bailey and Dahl, however, did not show any evidence of distortion from D_{6h} symmetry for benzene ring[120].

The individual Cr-C (aromatic) distances range from 2.194 A° to 2.248 A°. Except Cr-C(27), 2.248 A°, all other five Cr-C (phenyl) distances are very close to each other. This means that the chromium atom is displaced slightly away from C(27) from lying directly above the centroid of the benzene ring . The mean Cr-C distance at 2.203 A° is less than and at the low range for those in benzene-Cr$(CO)_3$, 2.229 A°. The correlated mean Cr-C (carbonyl) distance, 1.823 A°, is also less than that of benzene complex. The distance between C(35)-O(36), 1.153 A° is shorter than C(33)-O(34) and C(37)-O(38), 1.165 and 1.162 A° respectively. These unequal chromium carbonyl bond distances are apparently responsible for broad absorptions in their infrared spectrum.

A number of crystal structure determinations established that the tricarbonylchromium derivatives of benzene[116,120], hexamethyl benzene[120], Phenanthrene and dihydrophenanthrene[121,122] adopt the staggered conformation in solid state with respect to the ring carbons. Whereas, $-Cr(CO)_3$ complexes of trinitroanisole[123], o-toludine[124], methyl benzoate[125,126] , 1,2,3-trimethoxy benzene[127], N,N-diethyl aniline[127] and 4- chromanone[128] approximate closely to the eclipsed conformation. The orientation of the Cr-CO vector is explained in terms of the electron withdrawing $-Cr(CO)_3$ moiety[130] as shown in Fig. 12 .



a) R = H, Me

b) R = electron releasing

c) R = electron withdrawing

Fig. 12

The present case is an example of a monosubstituted benzene and one would expect the orientation of Cr-C-O vectors on the benzene skeleton to be either as Fig. 12(b) or (c). But surprisingly, the chromiumtricarbonyl unit is nearly in staggered conformation with respect to ring carbons(Fig. 10) apparently due to predominant steric interaction of phenyl and trityl substitutents.

b) Pentaphenylethane(C-1)-Chromiumtricarbonyl (28):

Crystals for X- ray analysis were grown from a mixture of petroleum ether and benzene (1 : 9, v/v) at 0°C during six weeks. The crystals were very sensitive and develop a green coating due to oxidation of $-Cr(CO)_3$ on exposure to air, light and temperature. All the manipulations were made in a blanket of argon. The diffractometer data collection and refinement parameters are summarized in Table 9. Views of solid state conformations are given in Fig. 13 and 14.

Table 9. Single Crystal X- Ray Crystallographic Analysis(*28*)

A. Crystal Parameters

formula	$C_{35}H_{26}O_3Cr.11/2C_6H_6$(663.76)
crystallization medium	benzene/pet.ether(9:1) at 0°C
crystal size, mm	0.20 X 0.30 X 0.50
cell dimensions	a = 35.177(5) A°
	b = 10.663(2) A°
	c = 18.880(4) A°
	α = 90.0°
	β = 103.71(2)°
	γ = 90.0°
	V = 6880(2) $A^{\circ 3}$
space group	C2/c
molecules/unit cell	8
density calculated, g/cm^3	1.28
linear absorption coefficient, cm^{-1}	31.9

B. Refinement Parmeters

number of reflections	5122
N_o, nonzero reflections ($I>2.0\sigma$)	2929
N_v, no. of variable parameters	404
R- index = $\sum \mid \mid Fo \mid - Fc \mid \mid / \sum \mid Fo \mid$	0.0578
GOF = $[\sum w(Fo-Fc)^2/(N_o-N_v)]^{1/2}$	1.154
R_w= $[\sum w(Fo-Fc)^2/\sum w \mid Fo \mid ^2]^{1/2}$	0.0667

Fig. 13. Stereoview of *28*

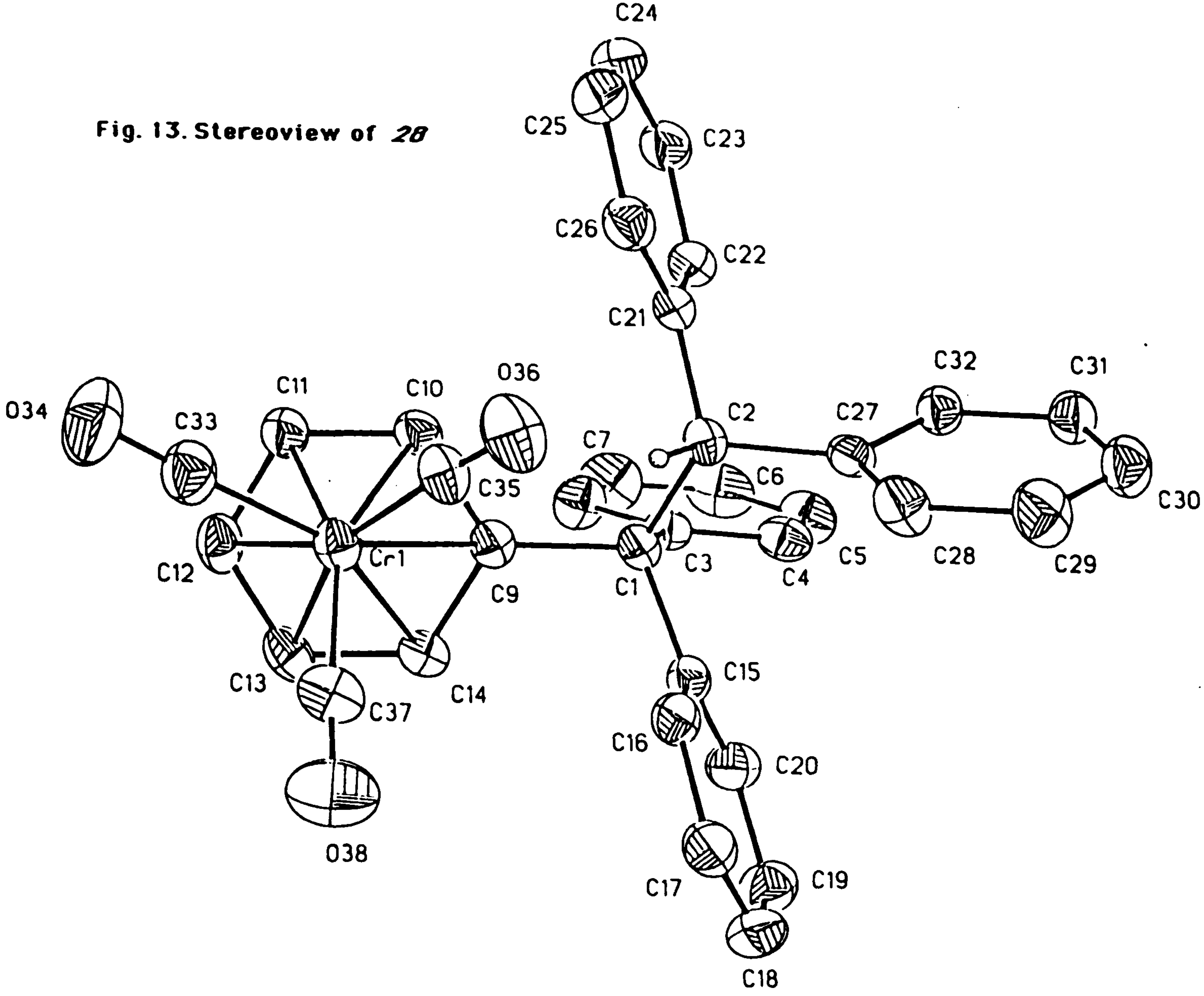
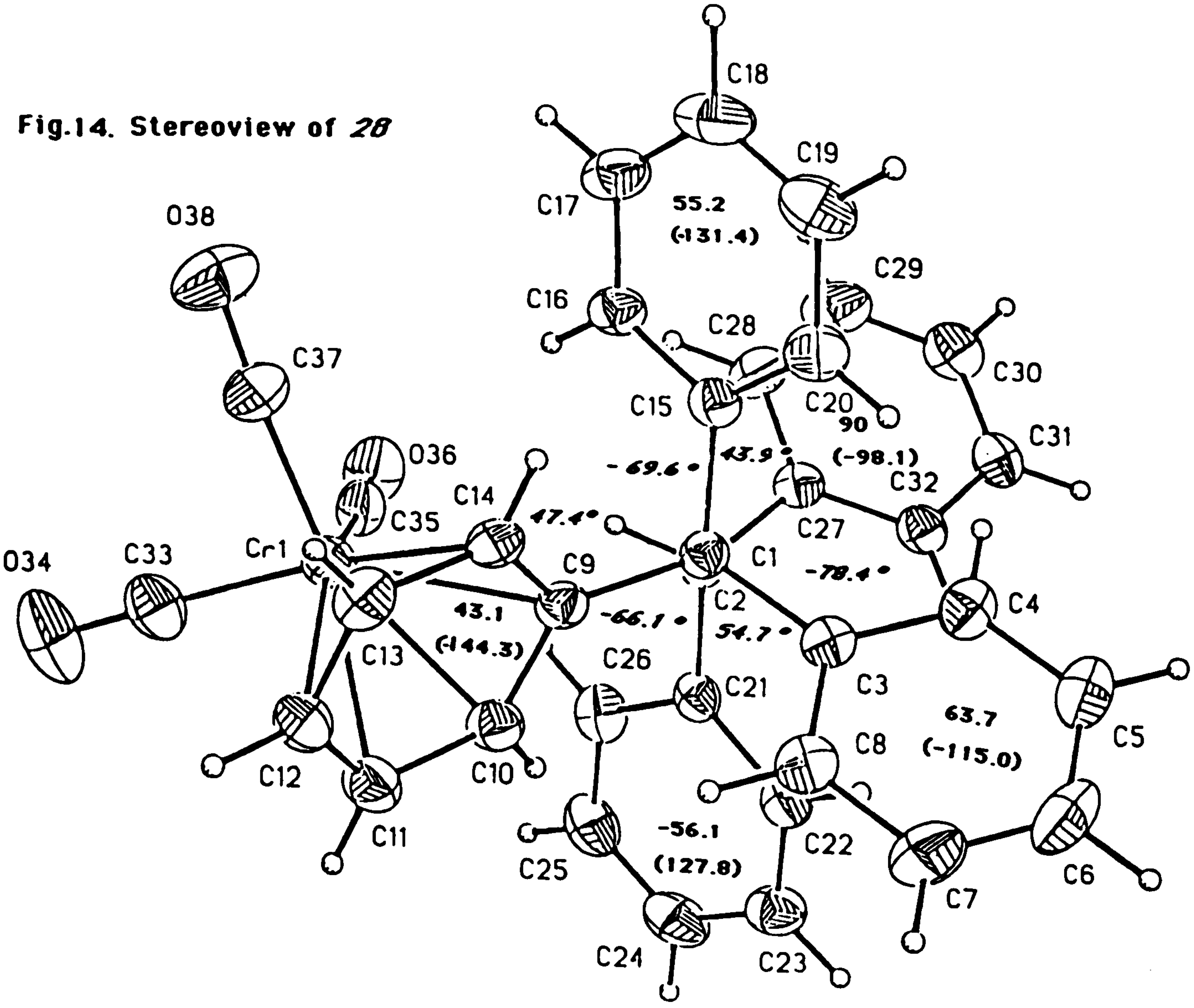
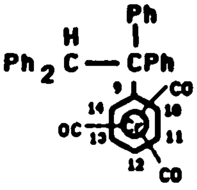


Fig.14. Stereoview of *28*



It is significant to note that the C(1)-C(2) ethane bond is 1.615 A° compared to 1.606 A° for pentaphenylethane. A comparison of properties of *28* with *1* shows very good correspondance for bond distances and modest changes for the bond angles due primarily to the greater steric congestion caused by introducing the $Cr(CO)_3$ group into the trityl portion of the pentaphenylethane (see Table 7).

Fig.13 shows that the chomiumtricarbonyl grouping in *28* is in staggered conformation with respect to benzene carbons similar to complex *22* ; expansion of C(9)-C(10), 1.423 A° and contraction of C(12)-C(13), 1.372 A° relative to benzene C-C distance at 1.400 A° clearly demonstrate the reduction of benzene symmetry upon complexation(Fig. 15). From the Cr-C(ring) distances, it is also observed that the Cr atom is slightly tilted away from C(9).



C(9) - C(10) = 1.423 ; C(12) - C(13) = 1.372

C(11) - C(12) = 1.408 ; C(9) - C(14) = 1.394

C(13) - C(14) = 1.414 ; C(10) - C(11) = 1.397

28

Fig. 15

The conformation of the molecule about the ethane bond may be conveniently described by the angle of torsion about the ethane central bond, φ_c and by those of rotation of the individual phenyl rings, φ_r[131]. Their values are presented in Fig. 14 which shows that the molecule of *28* in this crystal structure is nearly staggered; the $|\varphi_c|$ values being in the range 44-78°. The stereoview of complex *28* along C(1)-C(2) axis is shown in Fig. 14 . The φ_c of *28* are comparable to that of pentaphenylethane except C(27)-C(2) -C(1)-C(3), -78° and C(28)-C(1)-C(2)-C(27), 43.9° where the deviation is 16 to 18° from an ideal value 60° .

In the solid state both the benzylic hydrogen atom and the chromium atom are disposed syn to each other in complex *28* . It would be interesting to study the effect of a remote $Cr(CO)_3$ group on the formation and stabilization of the corresponding benzylic carbanion. This also provides an opportunity to examine the nonbonded interaction, if any, of the chromiumtricarbonyl moiety at close proximity with the benzylic carbanion. The C-13 NMR studies of the carbanions are described in the following section.

VI) ^{13}C NMR Studies on Carbanions:

a) Pentaphenylethyl Carbanion:

It has been observed earlier that pentaphenylethyl carbanion is not stable in the presence of electrophiles with the exception of D_2O or ROD . Even at -78°C reactions occur which produce triphenylmethane- and diphenylmethane derivatives. Such fragmentation products do not measure the thermal stability of the carbanion. The corresponding radical on the other hand is believed to be a thermally unstable species and at room temperature provides trityl radical as one of the decomposition products. The present study was undertaken in order to examine whether pentaphenylethyl carbanion thermally decomposes to give triphenylmethyl carbanion at higher temperatures (> -78°C) prior to a proton capture from the solvent.

Because an anion degradation pathway could rupture the carbanion's ethane bond to give trityl anion and diphenyl carbene, a reference ^{13}C spectrum for trityllithium was recorded at room temperature in THF-d_8 as shown in Fig.16b and the chemical shifts are displayed in Table 10.

It may be seen from the data in table 10 that the chemical shifts of the anion agree well with those in the literature with the exception of the benzylic carbon. This discrepancy is probably due to the presence of hexane in the THF-d_8.

INEPT proton coupled experiments were carried out on both triphenylmethane and its anion to verify the literature chemical shift assignments and to provide model spectra for the analysis of pentaphenylethyl carbanion. The spectra obtained from the INEPT experiments are shown in Fig.17.

In Fig.17a, the separation of triplets labelled 5 and 6 are due to one

FIGURE 16

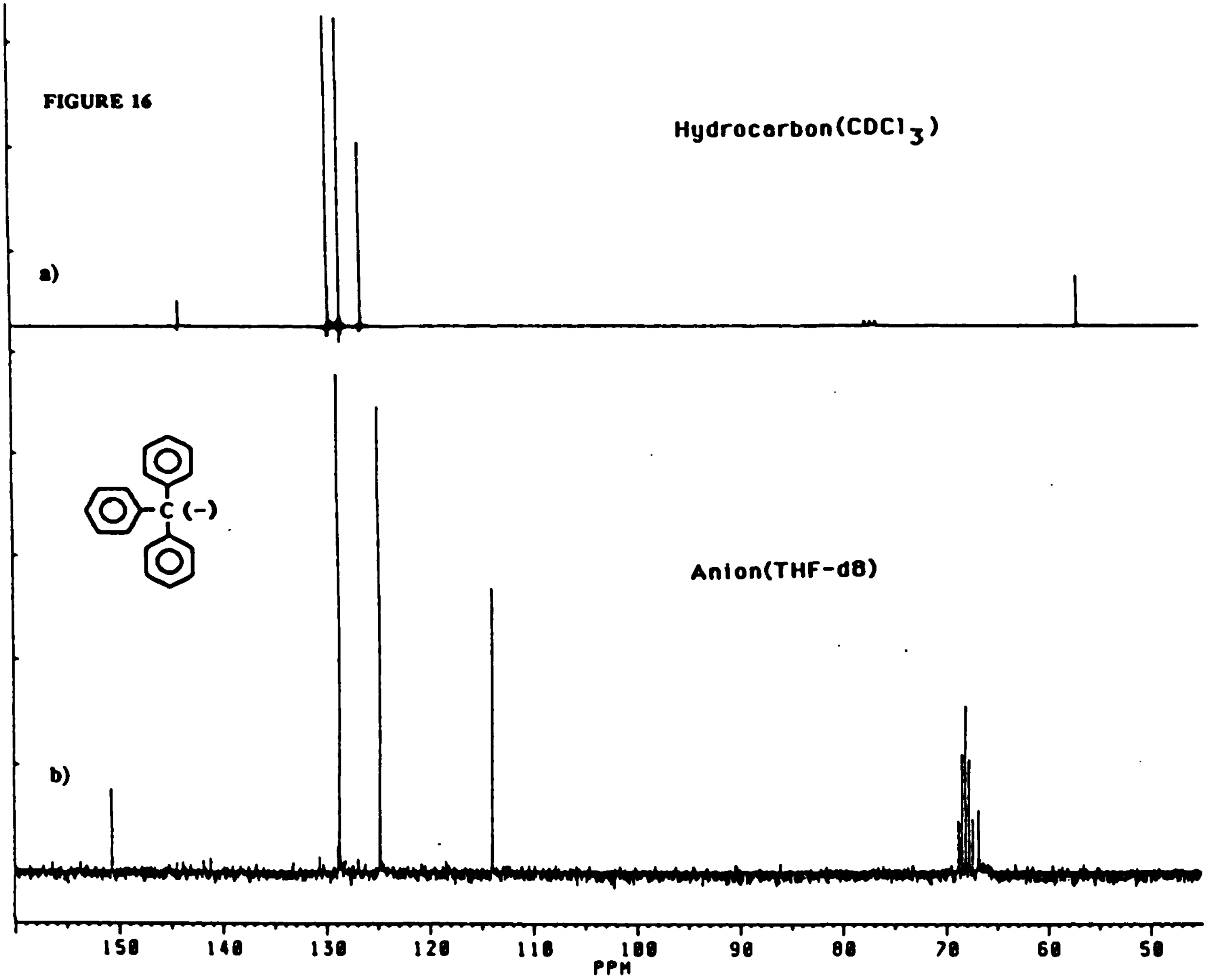

Hydrocarbon(CDCl$_3$)
a)
C (-)
Anion(THF-d8)
b)
150
140
130
120
110
100
90
80
70
60
50
PPM

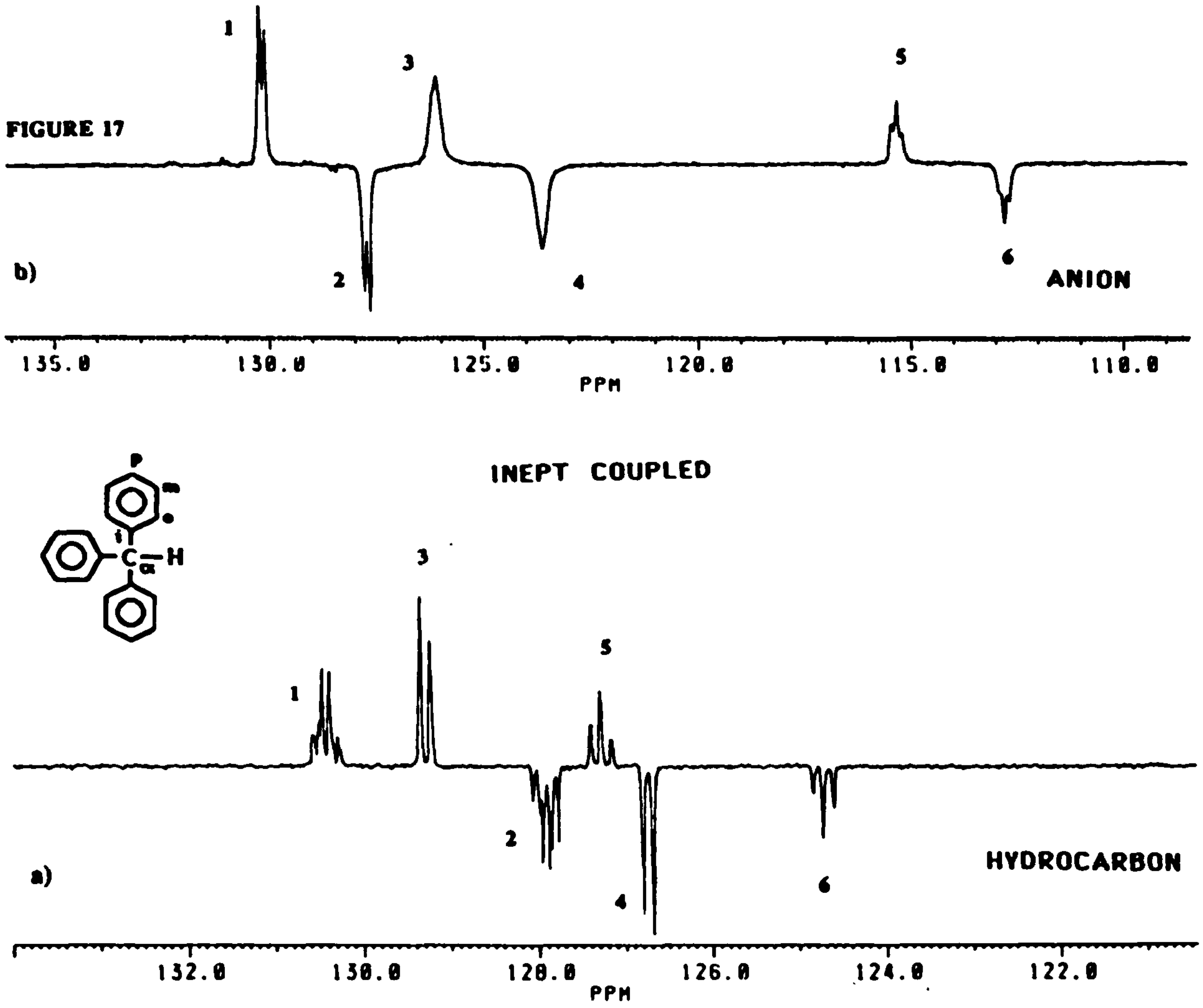
Table 10. Chemical Shifts of Trityllithium and Triphenylmethane

Assignments	C_α	ortho	meta	para	ipso
Anion(THF-d_8 + Hexane)	66.7	124.8	128.7	114.0	150.7
Literature(THF)[132]	91.0	124.4	128.3	113.3	150.5
Hydrocarbon ($CDCl_3$)	56.8	128.3	129.4	126.2	143.9
Literature(THF)[132]	58.2	129.5	130.7	127.5	145.2

bond ($^1J_{Cp\text{-}Hp}$ = 160.3 Hz) and two bond ($^2J_{Cp\text{-}C\text{-}Hm}$ = 7.5 Hz) couplings of the para carbon with para hydrogen and meta hydrogen respectively. The two doublets 3 and 4 are similiarly due to one bond ($^1J_{Co\text{-}Ho}$ =159.8 Hz) and two bond ($^2J_{Co\text{-}C\text{-}Hm}$ = 7.1 Hz) couplings of the ortho carbons with ortho hydrogen and meta hydrogen respectively. The two multiplets 1 and 2 are due to meta carbons which couple unequally to ortho and para hydrogens. and agree well with the literature assignments. However in Fig.17b, the multiplets 1 & 2 and the doublets 3 & 4 were collapsed to clean doublets and unresolved singlets respectively with the retention of the triplets 5 and 6 for the para carbon (the coupling constants are given in table 11). This suggests that in the anion the ortho carbon does not couple with the meta hydrogen and meta carbon does not couple with ortho hydrogen which is not readily conceivable at this stage.

Pentaphenylethyl carbanion was prepared in THF-d_8 solution for the NMR study and the spectrum recorded at room temperature is shown in Fig.18b. The anion spectrum looks very similar to that of the hydrocarbon

FIGURE 17



1
3
5
2
4
6
b)
ANION
135.0
130.0
125.0
120.0
115.0
110.0
PPM
INEPT COUPLED
p
m
o
i
Cα
H
3
5
1
2
4
6
a)
HYDROCARBON
132.0
130.0
128.0
126.0
124.0
122.0
PPM

Table 11. Coupling Constants of Tritylllthium and Triphenylmethane

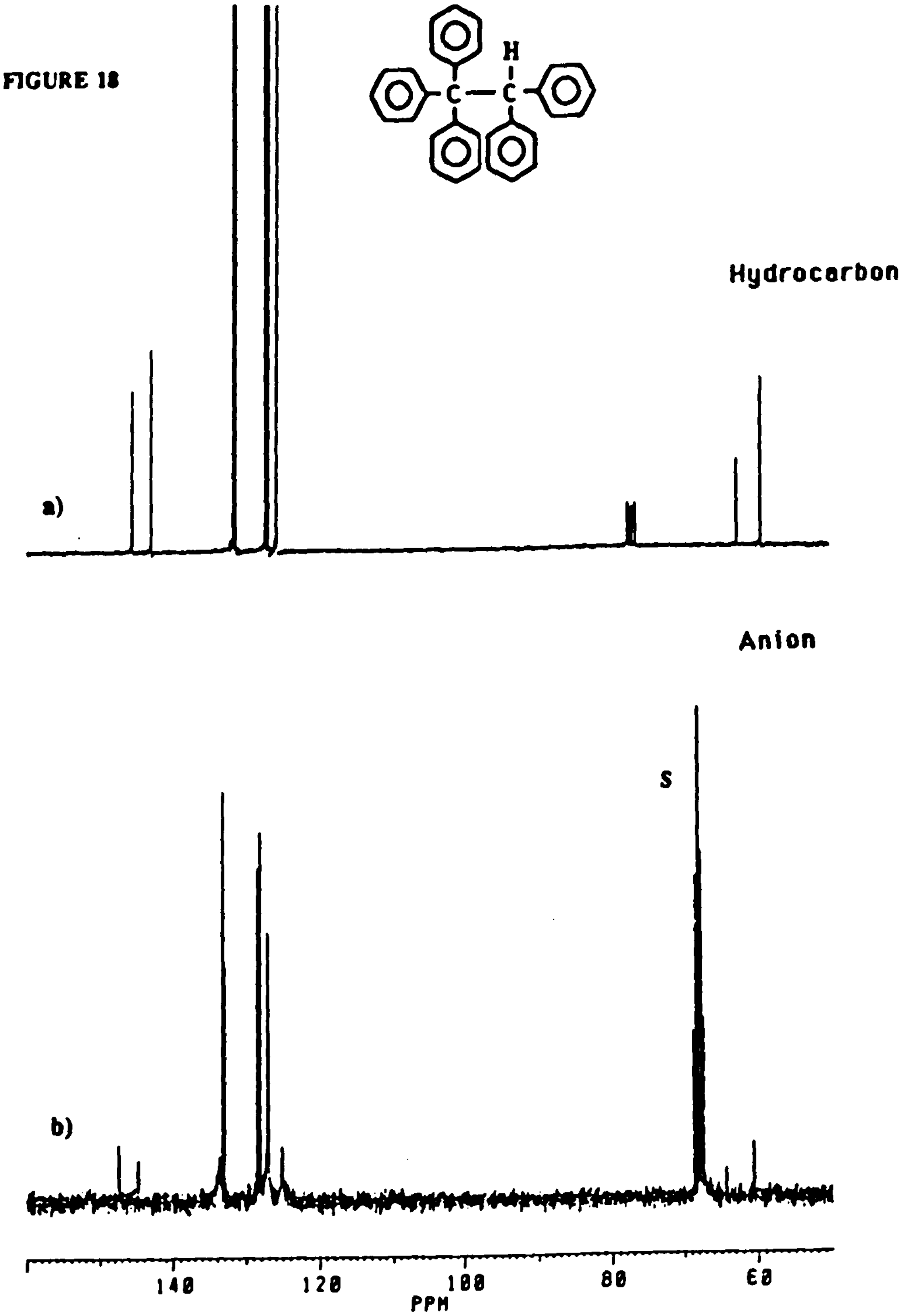
	$^{1}J_{C_o-H_o}$	$^{2}J_{C_o-C-H_m}$	$^{1}J_{C_m-H_m}$	$^{1}J_{C_p-H_p}$	$^{2}J_{C_p-C-H_m}$
Anion	153.3 Hz	-	150.9 Hz	157.2 Hz	7.3 Hz
Hydrocarbon	159.8 Hz	7.1 Hz	162.5 Hz	160.3 Hz	7.5 Hz

(Fig.18a) except the peak at 125.5 ppm. Peaks at 114 and 66.7 ppm could not be observed indicating the absence of triphenylmethyl carbanion species in the solution. When the dark red carbanion solution was hydrolyzed with water, an orange solid was isolated which on proton NMR showed the presence of at least 50% of PPE in the product mixture. The peak at 5.56 ppm was not observed in the proton NMR due to a triphenylmethane. The ^{13}C NMR spectrum was similar to that of PPE with a few additional low intensity signals in the aromatic range due to decompostion of the anion. From this study it appears that the pentaphenylethyl carbanion does not thermally decompose to trityl anion.

b) Pentaphenylethyl(C2)-Chromiumtricarbonyl Carbanion:

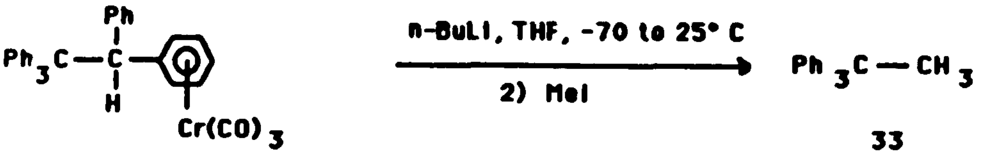
It is well known that the complexation of an aromatic with a tricarbonylchromium group enhances the kinetic acidity of the aromatic hydrogens as well as the benzylic hydrogen atoms. It is also known that alkyllithiums can undergo a nucleophilic addition or metalation at the ring depending on the nature of the base and the reaction temperature. In the present system to effect the metalation only at the benzylic carbon, it is

FIGURE 18



very important to select the right base.

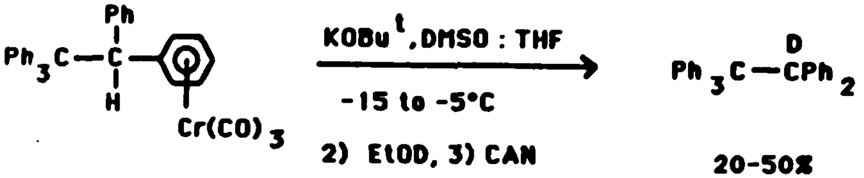
n-Butyllithium reacted with *22* at -70°C with no change in color however, when the temperature was gradually raised, an orange red color appeared at -30°C which deepened to a dark red solution similar to that of a trityllithium. When the anion was reacted with methyl iodide at room temperature , 1,1,1-triphenyl ethane (*33*) was isolated in 40% yield (eqn. 18)



33

(eqn. 18)

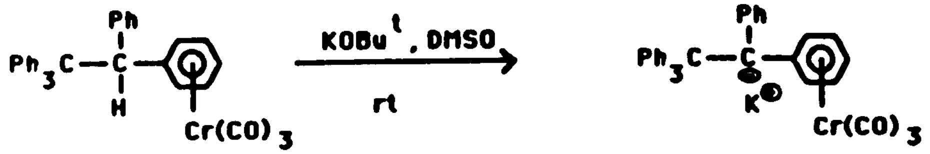
KOBu^t in a mixture of THF and DMSO (7 : 3, v/v) at -15 to -5°C metalated *22* in 20-50% as shown in eqn. 19.



22

(eqn. 19)

Potassium tertiary butoxide on the other hand in DMSO alone at room temperature developed a brown red color with formation of almost a molar quantity of the anion (*34*) (eqn. 20). Bases such as LDA at -70 to -50°C in THF and $LiNH_2$ in liquid ammonia at -30°C were not effective as the deprotonating agent.



22

(eqn. 20)

The anion solution was prepared in DMSO-d_6 for the ^{13}C NMR studies and the spectra was recorded at room temperature during 3-5 hours. The spectrum is shown in Fig.19 & 20 and the chemical shifts are presented in Table 12. The salient features of the anion spectrum are described below.

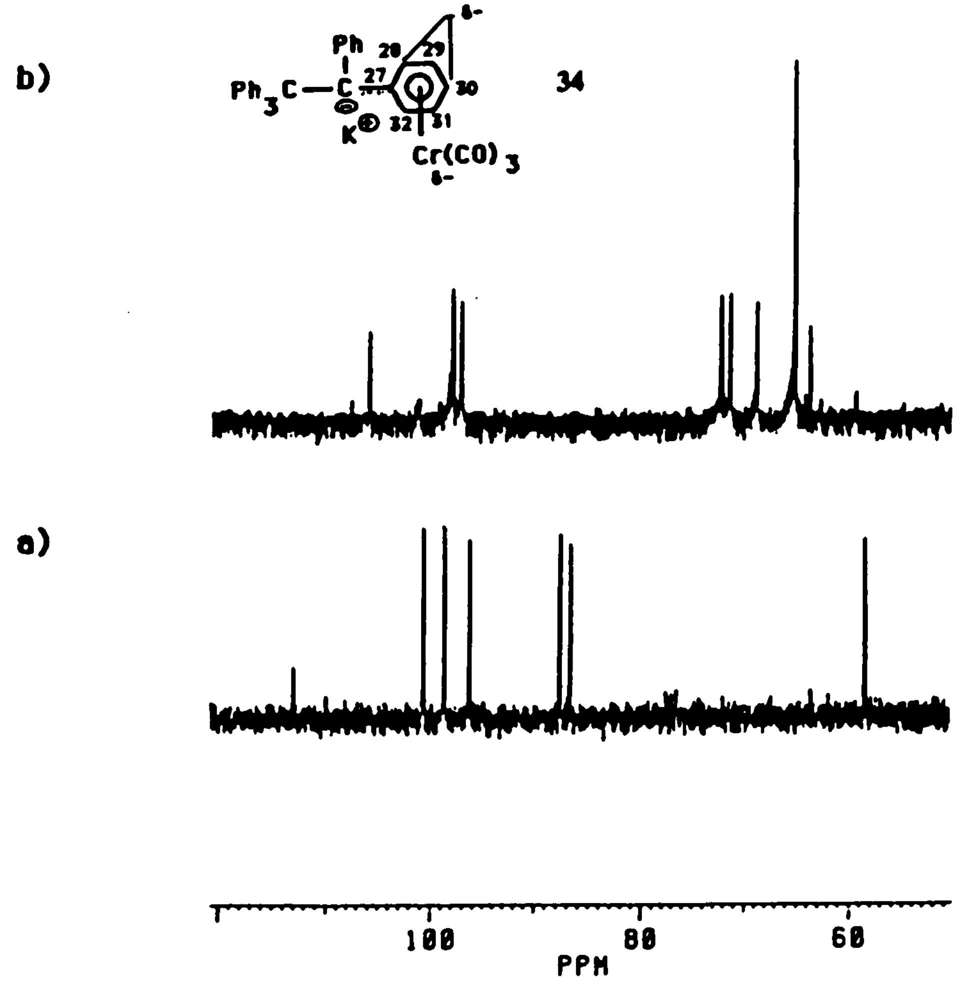
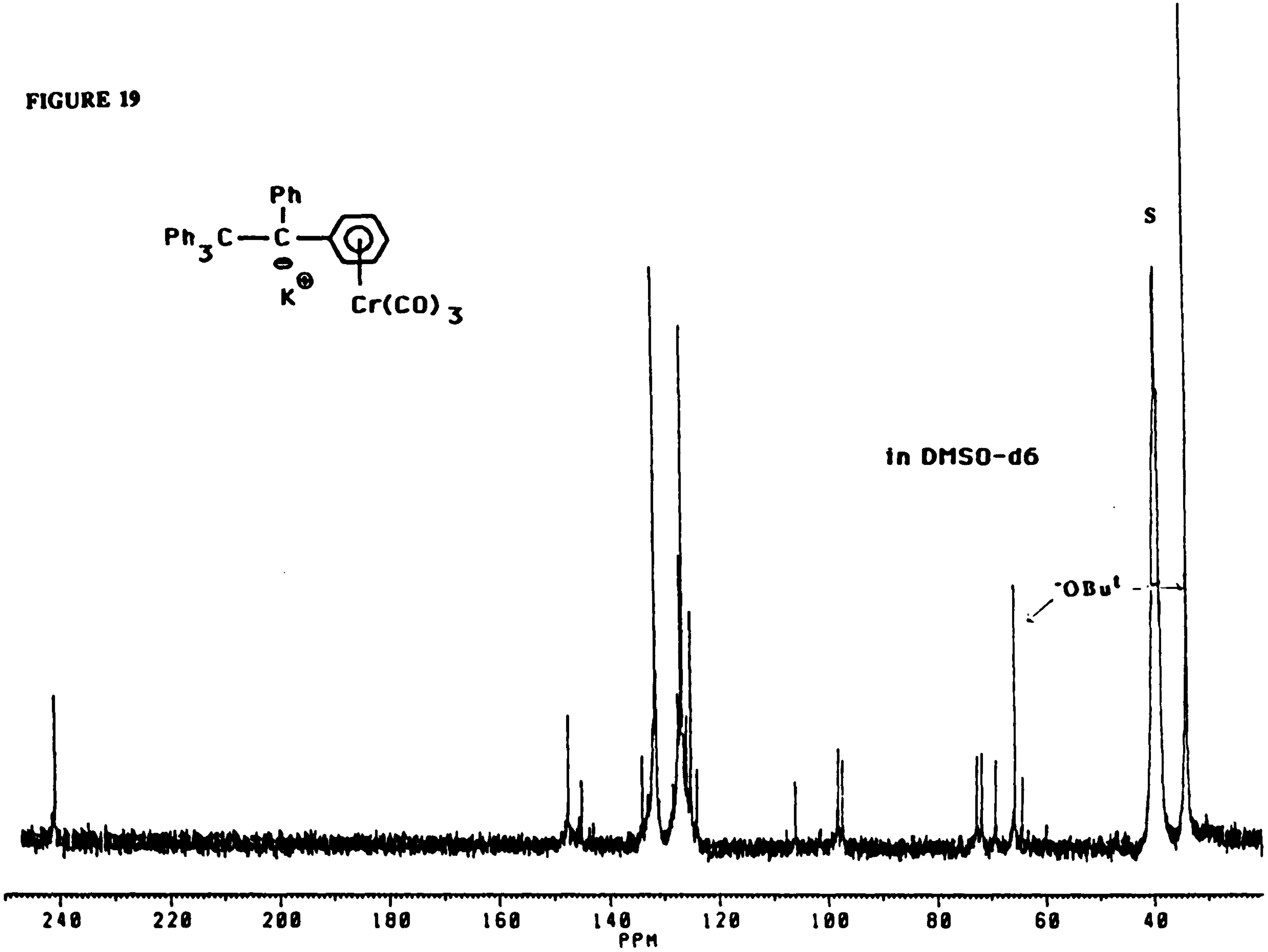


Fig. 20. a) Section of Pentaphenyethane(C2)-Chromiumtricarbonyl in $CDCl_3$
b) Section of PPE-$Cr(CO)_3$ Anion(*34*) in DMSO-d_6 at rt.

FIGURE 19



Ph
Ph3C—C—
K⊕
Cr(CO)3
S
in DMSO-d6
-OBut
240
220
200
180
160
140
120
100
80
60
40
PPM

Table 12. ^{13}C Chemical Shifts for Pentaphenylethyl(C2)-$Cr(CO)_3$ Carbanion

δ.ppm	Assignments
240.70	carbonyl
147.22	Φ_3C_{ipso}
144.82	$\Phi_{ctc}\Phi C_{ipso}$
133.87	C_{ipso}-Cr
131.40	Φ_3C_{ortho}
131.18	$\Phi_{ctc}\Phi C_{ortho}$
(128.22, 127.33, 127.13)	*
126.85	$\Phi_{ctc}\Phi C_{meta}$
126.41	Φ_3C_{meta}
(125.76)	*
124.94	Φ_3C_{para}
123.87	$\Phi_{ctc}\Phi C_{para}$
105.82	C(2) anion
98.04,97.22	C_{meta}-Cr
72.66,71.77	C_{ortho}-Cr
69.20	C_{para}-Cr

* probably due to the presence of unreacted PPEctc.

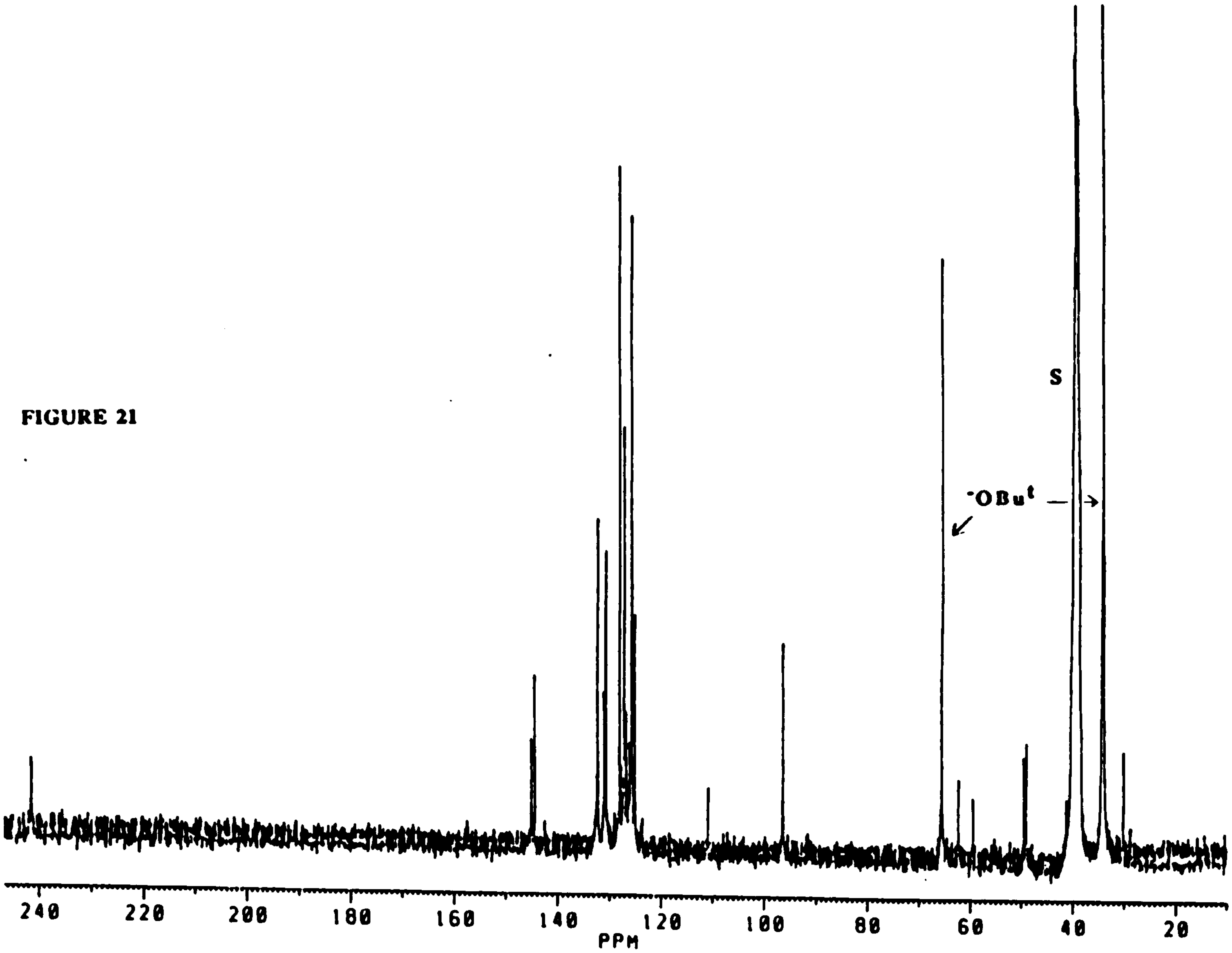
The carbonyl resonance in the anion appears at δ 240.7, an 8 ppm down field shift with respect to the hydrocarbon at δ 232.5 indicating substantial transmittal of the negative charge into the $Cr(CO)_3$ moiety. This is further supported by the shielding[10,81,131] (29 ppm) of the para carbon (C30) at δ 69.2 ppm and shielding (15 ppm) of ortho carbons (C28, C32) at δ 72.7 and 71.8, and deshielding (21 ppm) of the ipso carbon (C27) at δ133.9.[81] The two meta resonances appear at 98.0 and 97.2 ppm. The signal due to the benzylic carbanion was assigned to the peak at δ105.8.[81] In the 128-125 ppm range, a few low intensity peaks were observed which could not be assigned accurately. These δ values compare well to those for the hydrocarbon and have expected multiplicities in the coupled spectrum.

The anion upon hydrolysis afforded the hydrocarbon whose ^{13}C and ^{1}H NMR spectra were identical with spectra for authentic pentaphenyl ethane(C-2)-chromiumtricarbonyl (*22*). Reaction of the anion with methanol-d_1 gave 2-deuteriopentaphenylethane due to the oxidative decomplexation of $Cr(CO)_3$ group during the work up. Coupling reaction of the anion with methyl iodide did not yield a methylated derivative and trimethylchlorosilane decomplexed the anion even at -40°C. The anion (*34*) seems to be a thermally stable species at room temperature since no change in ^{13}C NMR spectrum was observed even after 3 days.

c) Pentaphenylethyl(C1)-Tricarbonylchromium Carbanion:

In pentaphenyethane(C1)-chromiumtricarbonyl (*28*) the $Cr(CO)_3$ group is ligated remote to the anionic site. Furthermore, in the solid state the benzylic hydrogen and the chromium atom are disposed syn to each other (Fig. 13). Thus the structural features of *28* provides a unique opportunity to determine the nonbonded interaction, if any, of the remote chromium tricarbonyl group in the formation and stabilization of the carbanion.

FIGURE 21



Reaction of KOBu^t in DMSO-d_6 with *28* developed a color similar to that of the anion (*34*) during the first few minutes which changed subsequently to a yellow color. The ^{13}C NMR of this solution was recorded during seven to eight hours and the spectra are shown in Fig. 21 and 22 . The chemical shifts are presented in Table 13.

The most striking feature of the carbon spectrum is the carbonyl resonance at 241.4 ppm similar to that of its isomer *34* at 240.7 ppm. This

FIGURE 22

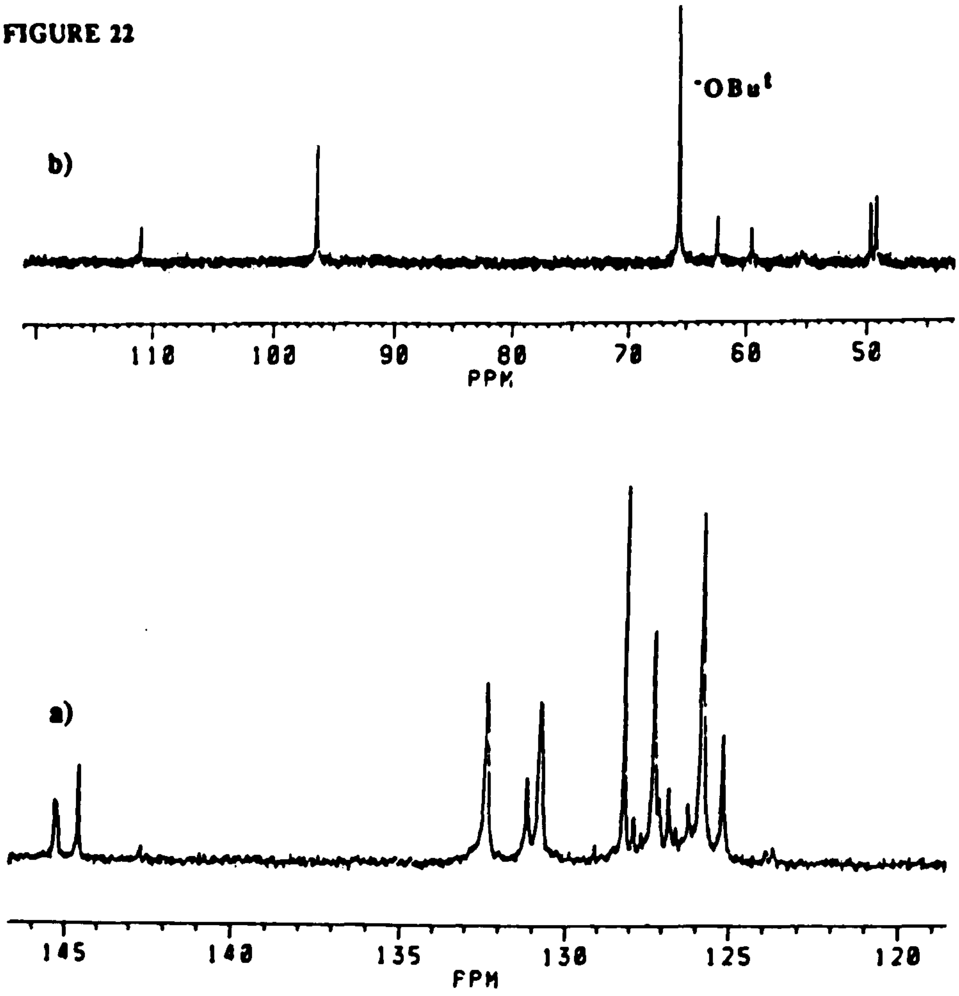


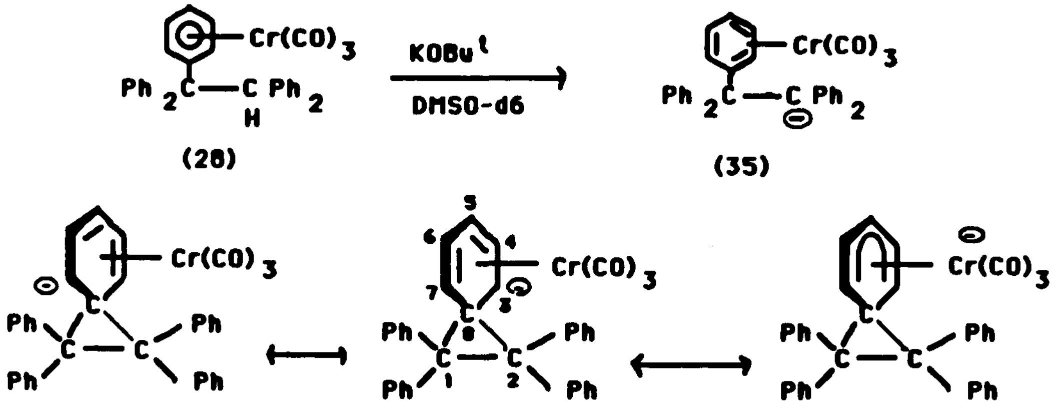
Fig. 22 a) & b). Sections of ^{13}C NMR of *36* in DMSO-d_6 at rt.

Table 13. ^{13}C Chemical Shifts for Pentaphenylethyl(C1)-Cr(CO)$_3$ Carbanion

δ.ppm	Assignments
241.43	carbonyl
145.33, 145.26, 144,62	C_{ipso}
132.40, 131.17, 130.77	C_{ortho}
(128.18)	**
127.89, 127.26, 127.09	C_{meta}
(127.66)	*
126.23, 125.82, 125.19	C_{para}
(126.60)	*
110.96	C(5)
96.50	C(4,6)
62.37	C(1)*
59.52	C(2)*
49.68, 49.18	C(3,7)
30.18	C(8)

* assignments may be interchanged
* low intensity peak and could not be assigned with certainty
** could be due to benzene in the crystal

indicates the possible participation of the remote chromiumtricarbonyl coordinated benzene ring in the delocalization of the carbanionic charge. The presence of five mole excess of KOBu^t in the solution and the low solubility of *28* in DMSO-d_6 prevented obtaining a good signal to noise^{13}C spectrum. The spectrum presented here is obtained by accumulation of 26,500 scans during 7/8 hours. The particular features of the spectrum in support of a bridged pentahapto-chromiumtricarbonyl (*36*) is presented as follows.



(36)

(eqn.21)

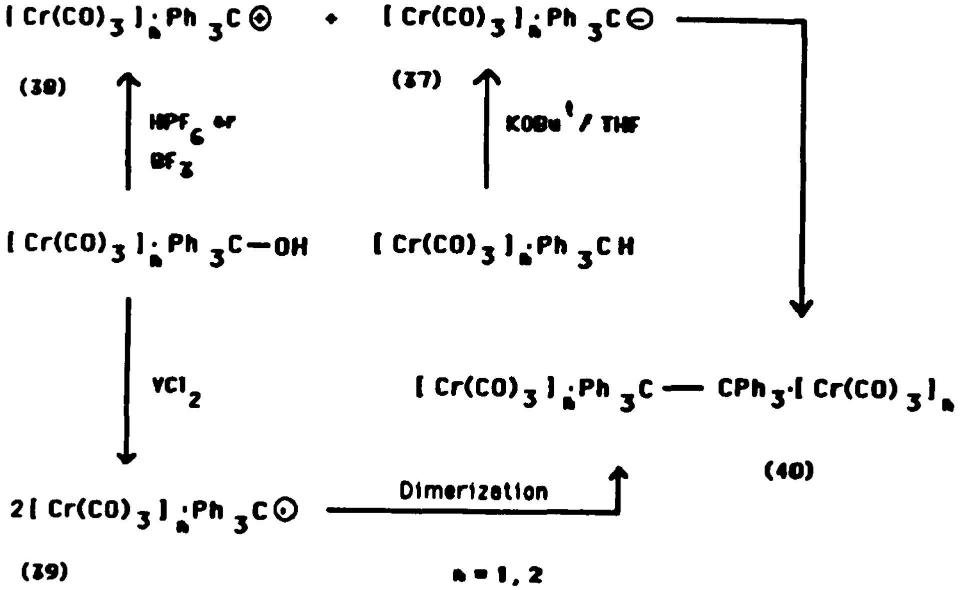
The signals at 49.7 and 49.2 ppm are due to C3 and C7 shielded (39 ppm) with respect to the hydrocarbon at δ 88.2 due to the presence of electronic charges. The C1 and C2 have their resonances at 59.5 and 62.4 ppm of equal intensity. The carbons (C4 and C6) have a strong signal at 96.5 ppm a shielding of only 2 ppm similar to pentaphenylethyl(C2)-chromium tricarbonyl carbaion (*34*). The para carbon (C5) of the complexed ring at 111.0 is deshielded (16 ppm) in contrast to that of its isomer where the para carbon shielded by 29 ppm due to the residence of negative charge. The newly generated tetrahedral carbon appears at 30.2 ppm. In the aromatic region (δ125 to 130), there appeared a few low intensity peaks and the assignments could not be made with certainty. The chemical shifts with their assignments are reported in Table 13.

An attempt to isolate the hydrocarbon by hydrolysis of the anion *36* was not successful. From this preliminary study it appears that the benzylic carbanion interacts with the remote chromiumtricarbonyl complexed benzene ring with the formation of a pentahapto chromiumtricarbonyl complex.

VII) Suggested Extensions for the Synthesis of Chromium tricarbonyl Coordinated Ethanes:

Arnett and his group[134] recently demonstrated that the resonance stabilized carbocations and carbanions undergo direct reaction to produce covalent products by coordination. The reaction of trityl carbanion (*37*) and trityl carbocation (*38*) is probably an unfavourable process for such an interaction. Thermodynamic stability of trityl radical (*39*) over trityl cation and trityl anion is 13.15 and 27.67 K cal/mole[135] respectively and probably is the reason that trityl anion undergoes SET to a trityl radical which subsequently dimerize to a hexadiene dimer. Chromiumtricarbonyl complexation of *37* and *38* may increase the thermodynamic stability of both carbanion and carbocation. However, the extent of relative stabilization of *37* and *38* with respect to the corresponding radical (*39*) is not known. Because of increased thermodynamic stability one hopes that *37* and 38 would be stable in presence of each other for a coordination process and would lead to a covalent bond formation as shown in Scheme 7 .

The presence of chromiumtricarbonyl group in trityl radical (*39*) destroys the aromaticity of the ring to some extent and consequently would hinder the electron delocalization into the para position. The above effect is hoped to work in favour of a α,α coupling similar to that of tris(3,5-di-tertiarybutyl phenyl)methyl[136] to yield chromiumtricarbonyl

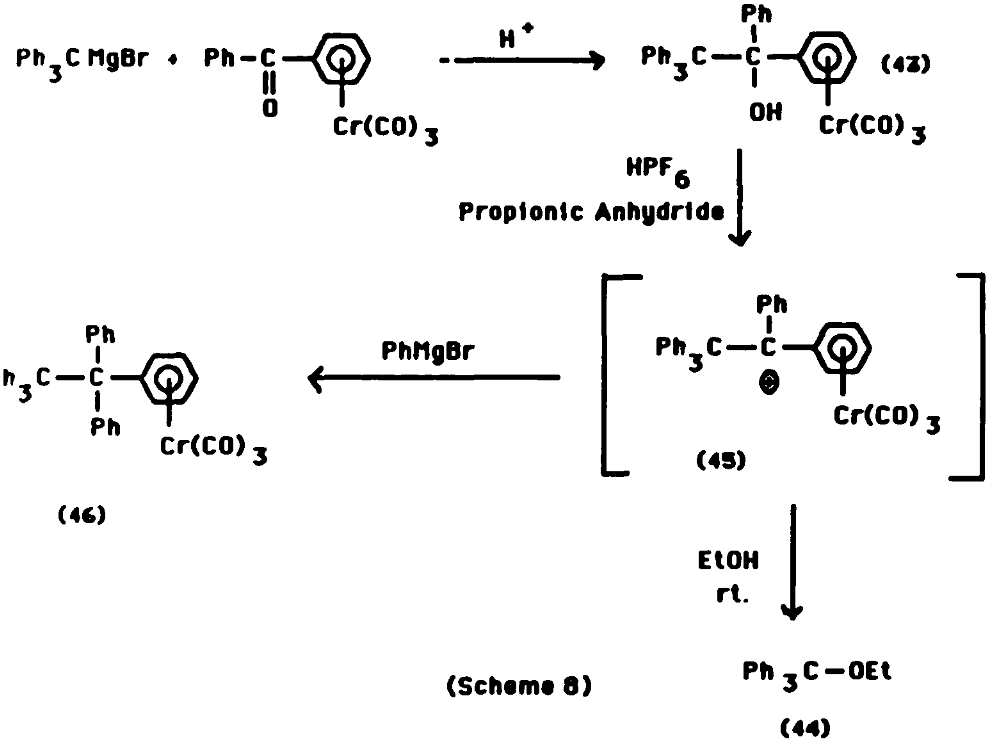


(Scheme 7)

coordinated hexaaryl ethanes over α, p dimer. In these reactions one of the main problems one expects to encounter is the solubility of the chromium complexes since the solubility dramatically decreases with increasing number of $Cr(CO)_3$ groups.

Unlike pentaphenylethyl carbanions, it was hoped that pentaphenyl ethyl carbocation would be more stable towards a chemical reaction. Synthesis of pentaphenylethanol (*41*), the precursor to the cation (*42*), has not been achieved. An attempt was made to synthesize chromiumtricarbonyl coordinated pentaphenylethanol (*43*) by the reaction of benzophenone chromiumtricarbonyl and trityl Grignard (Scheme 8). The infrared of *43* shows the presence of a tertiary -OH group and the expected carbonyl absorptions. A good NMR spectrum could not be obtained because of its insolubility in common organic solvents. Reaction of *43* with HPF_6 in propionic anhydride was carried out at room temperature followed by treatment with absolute ethanol when trityl ethyl ether was isolated in 18%

yield. Apparently pentaphenylethyl carbocation-$Cr(CO)_3$ (*45*) decomposed at room temperature to a trityl cation which reacted with ethanol to yield *44*. It might be possible to synthesize *45* at low temperature and its reaction with phenyl Grignard is likely to yield hexaphenylethane chromiumtricarbonyl (*46*) (Scheme-8).



(Scheme 8)

SUMMARY AND CONCLUSION

The synthesis of pentaphenylethyl carbanion has been achieved by deprotonation of pentaphenyethane with n-BuLi/KOBu^t in THF at -78°C. NMR studies of the product obtained after deuterolysis of the anion revealed that the mixture had at least 87% of deuterium at the benzylic carbon. However the Chemical Ionization mass spectral analysis showed the presence of dideuteriopentaphenylethane (10%) as one of the components in the same mixture.

Reactions of pentaphenylethyl carbanion with MeI, CO, tetrakis tri-n-butylphosphine.CuI/MeI did not yield a coupling product. Trimethyl chlorosilane afforded a very small amount of pentaphenylethyltrimethyl silane (5%); dimethyldisulfide on the other hand thiomethylated in the ring. In the above reactions, triphenylmethanol and benzophenone derivatives were consistently isolated as the fragmented products. Apparently pentaphenylethyl carbanion undergoes a SET in presence of an electrophile to a pentaphenylethyl radical which is known to be an unstable species and cleaves the ethane bond to provide trityl and diphenylmethyls and these fragments subsequently appear as triphenylmethanol and benzophenone derivatives.

To enhance the kinetic acidity of the benzylic hydrogen and to stabilize the carbanion formed by its removal, pentaphenylethane(C2) -chromiumtricarbonyl (1) was synthesized in 88% yield by a novel coupling reaction of trityl Grignard and benzhydryl chloride tricarbonylchromium. Subsequently, in order to determine the effect of remote -$Cr(CO)_3$ moiety on the formation and stabilization of the carbanion, the isomer of 1 pentaphenylethane(C1)-chromiumtricarbonyl (2) was synthesized in 65% yield by the reaction of triphenylmethyl-$Cr(CO)_3$ carbanion with benzhydryl bromide.

Chromiumtricarbonyl coordinated triphenymethyl carbanion was prepared in 80-85% yield at room temperature in THF and KOBu^t. The complex 1 in its ^{13}C NMR exhibited six carbon signals for complexed benzene ring due to magnetically nonequivalent ortho and meta carbons by the presence of a chiral carbon at C2. The chemical shift assignments were made by their coupling constants and multiplicities with the aid of an INEPT proton coupled ^{13}C experiment.

Single crystal X-ray structure analysis for both 1 and **2** were carried out and the particular features of interest are as follows. The central ethane bond lengths are 1.620 A° and 1.615 A° respectively for 1 and **2** which are considerably longer than a normal ethane bond (1.53A°). Upon chromiumtricarbonyl complexation the symmetry of the benzene ring reduced to some extent as evidenced by the alternate long and short bonds. In the solid state the chromiumtricarbonyl group is in a staggered conformation to the benzene carbon skeleton (i.e the projections of the carbonyl bonds on to the complexed ring intersect the alternate C-C bonds). The ethane conformation as a whole is nearly staggered with some deformations in bond angles and quite similar to that of the parent hydrocarbon, pentaphenylethane. In **2** the chromium atom and the benzylic hydrogen are disposed syn to each other.

Pentaphenylethyl(C2)-$Cr(CO)_3$ carbanion (3) was synthesized at room temperature in KOBu^t and DMSO and seems to be thermally stable since no change in its carbon spectrum was observed even after 3 days. The ^{13}C NMR spectrum of the anion exhibited extensive delocalization of the electronic charge on to the -$Cr(CO)_3$ group evidenced by 8 ppm deshielding of the CO resonance with respect to the hydrocarbon. It also displays the expected shielding of ortho and para carbons and deshielding of ipso carbon. The benzylic carbon appeared at 105 ppm. When 1 was reacted with BuLi in THF at room temperature a dark red solution due to trityl anion was observed which upon reaction with methyl iodide afforded 1,1,1-triphenyl ethane. Pentaphenylethyl(C1)-$Cr(CO)_3$ carbanion (4) was similarly synthesized at room temperature with $KOBu^t$ in DMSO-d_6 but the striking observation was the carbonyl resonance at 241 ppm comparable to its isomer 3 at 240.7 ppm. This demonstrates the direct involvment of the remote $Cr(CO)_3$ moiety in the stabilization of the anion. A η^5-bridged structure is proposed for the anion 4. Carbon spectrum of pentaphenylethyl carbanion at room temperature did not show the presence of a trityl carbanion species, the anticipated thermal decomposition product. In a blank experiment tritylithium was synthesized and all the chemical shift assignments were verified by INEPT proton coupled experiments.

EXPERIMENTAL

Materials and Methods:

The following reagents were obtained from the sources indicated and used without additional purification.1,10-Phenanthroline, n-butyl lithium, methyllithium, lithium diisopropylamide, lithium tetramethyl piperidine, potassium hydride, calcium hydride, lithium aluminium hydride, triphenylmethanol, hexafluorophosphoric acid, sodium thiosulfate, phosphorous pentoxide, ceric ammonium nitrate (CAN), thionyl bromide (Aldrich). Deuterium oxide, ethanol-d_1, anhydrous magnesium sulfate, iodine (J.T.Baker). Technical grade hydrogen chloride gas (Matheson). Benzophenone, ammonium chloride, carbon tetrachloride, sodium chloride (Fischer). Chloroform-d_1 containing 1% v/v tetramethylsilane (Norell Inc.). Acetone-d_6, dimethylsufoxide-d_6 (Thompson Packard). Benzhydrol, triphenyl methane (Matheson, Coleman & Hall). Chromiumhexacarbonyl (Strem Chemicals or Alfa Inorganics). Ammonia gas (Matheson). Silicagel (230-400 mesh) for flash chromatography was obtained from Merck and used as received. Alumina 80-200 mesh (Fischer) was activated at 150°C for atleast 24 hrs before use. Silicagel with UV indicator coated plastic plates (Schleicher & Schull, F1500/LS254) were used for routine TLC check.

The normality of n-butyllithium solution was determind by two independent methods[137,138]: 1. Titration with sec.-butanol using 1,10-phenanthroline as indicator as described by Watson and Eastham.[137] 2. Integration of the α-methylene group of n-butyllithium at -0.88 ppm with that of the internal standard benzene at 7.28 ppm as reported by Silveira et al.[138]

The technical grade solvents (methylene chloride, acetone, petroleum ether) were redistilled prior to use. For the chromatographic separation and recrystallization of arene-tricarbonylchromiums such as benzhydrol, triphenylmethanol, triphenylmethane, benzophenone and pentaphenylethane complexes, the dry solvents were degassed using at least five freeze, pump and thaw cycles. Diethyl ether for extraction was obtained by distilling the technical grade material from aqueous sodium hydroxide to remove peroxides. Anhydrous diethyl ether (Mallinckrodt) and tetrahydrofuran (M C&B) were prepared by distilling the technical grade material from a solution of sodium metal and benzophenone under dry argon. Benzene (Fischer) was shaken with concentrated sulfuric acid and distilled from calcium hydride. To make oxygen free benzene, the dry benzene was distilled from sodium and benzophenone under dry argon. Acetonitrile was distilled from phosphorous pentoxide before use. Dioxane (Fischer) was pretreated with lithium aluminium hydride overnight, distilled before its second distillation from sodium metal and benzophenone ketyl. Diglyme (Aldrich) and dibutyl ether (Eastman) were passed through an alumina column to remove the peroxide and then distilled from lithium aluminium hydride. Heptane was stirred over conc. sulfuric acid prior to distillation from calcium hydride.

Potassium tertiary butoxide (Aldrich) was sublimed prior to its use. Methyl iodide (Aldrich), dimethyl disulphide (Eastman) were distilled under nitrogen and kept over molecular sieve (3 A°, Davison). Trimethyl chlorosilane (Aldrich) was distilled under nitrogen before use. Dimethyl sulphate (Eastman) was vacuum distilled (b.p. 52.5°C/6mm) and kept under nitrogen. Tri n-butyl phosphine (Aldrich) was distilled under nitrogen. 18-Crown-6 (Aldrich) was vacuum dried in presence of P_2O_5. Acetyl bromide (Aldrich) was distilled under nitrogen prior to its use.

Deuterated solvents ($CDCl_3$, DMSO-d_6, acetone-d_6) and carbon tetrachloride were degassed by freeze pump and thaw cycles for NMR analysis of the hapto complexes. Absolute ethanol U.S.P was distilled and degassed before use. Cuprous iodide was purified by treatment with decolorizing carbon and precipitating from saturated solution of aqueous potassium iodide, followed by drying in vacuo over conc. H_2SO_4 as described by Kaufmann and Teter[139]. Magnesium turnings were obtained from triplly sublimed magnesium and were used in Grignard syntheses.

Argon (Ar) and nitrogen gas were obtained from Union Carbide Linde Division. Argon was purified by passage through BTS (BASF, R3-11) and P_2O_5 drying towers in a Normag gas purification apparatus (Fig. 23)[140]. Nitrogen gas was dried over a series of towers with sodium hydroxide, self indicating silicagel and drierite in that order. The purified gas was introduced to the desired flask by an all glass manifold. Low temperature experiments (at -78°C) were performed in dry ice and 2-propanol mixtures, lower than -78°C were obtained by heptane and liquid nitrogen mixture.

The term dry and in vacuo refer to treatment with anhydrous magnesium sulphate and removal of the solvent on a Buchler Instruments rotary evaporator at water aspirator pressure unless an alternative technique is specified. Anhydrous reaction conditions were carried out using oven (150°C, overnight) dried or vacuum flame dried glassware under positive pressure of dry nitrogen or argon. Flash Chromatography was performed as described by Still.[141]

Benzhydryl chloride was prepared by the reaction of benzhydrol and thionylchloride[142] at reflux in 91% yield, b.p., 107-110°C at 3 mm. Benzhydryl bromide was prepared either by the reaction of benzhydrol with thionyl bromide (82% yield, m.p., 32-35°C) or by the bromination of diphenyl methane using N-bromo succinimide[143] (96% yield, m.p., 35-36°C). Triphenylmethylbromide was synthesized[144] from triphenylmethanol and acetyl bromide in 70% yield, m.p., 152-154°C. Pentaphenylethane was prepared[144] by the reaction of trityl magnesium bromide with benzhydryl bromide in benzene ether mixture in 80% yield with respect to tritylbromide and in 90% yield with respect to benzhydryl bromide, m.p., 169-71°C (in argon filled sealed capillary tubes)

Instruments:

Single Crystal X-Ray Analysis (*22* and *28*):

A representative crystal was surveyed and a 1-A° data set (maximum sinΘ = 0.5) was collected on a Nicolet R3m/m diffractometer[145]. The diffractometer was equipped with a graphite monochromator and copper Kα radiation (λ = 1.54178A) was employed. Atomic scattering factors were taken from the International Tables for X-Crystallography[146]. All the crystallographic calculations were facilitated by the SHELXTL system. All diffractometer data were collected at room temperature. Pertinent crystal, data collection and refinement parameters are summarized in Table 7.

A trial structure was determined by direct methods. This trial structure refined routinely. Hydrogen positions were calculated wherever possible. The hydrogen parameters were added to the structure factor calculations but were not refined. The shifts calculated in the final cycle of least squares refinement were less than 0.1 of their corresponding standard deviations. The final R-index was 0.053. A final difference Fourier revealed no missing or misplaced electron density.

The refined structure was plotted using the SHELXTL plotting package (Fig. 8, 9 and10). Coordinates, anisotropic temperature factor, distances and angles are given in the Appendix 1(Table S1-S5).

For compound *28* the data set was collected (Sin Θ/λ = 0.544, $2\Theta_{max}$ =114°) on the above model diffractometer[148] equipped with graphite monochromator and copper radiation with a scan speed of

3.91-29.3°/minute. Crystal, data collection and refinement parameters are given in table 9. The largest shift calculated in the final cycle of least square of refinement was 0.5. The final R-index was 0.0578 with a goodness-of-fit (GOF) indicator of 1.154.

The refined structure was plotted using the above software package (Fig. 13 and 14). Coordinates, anisotropic temperature factor, distances and angles are given in the Appendix 1 (Table S6-S11).

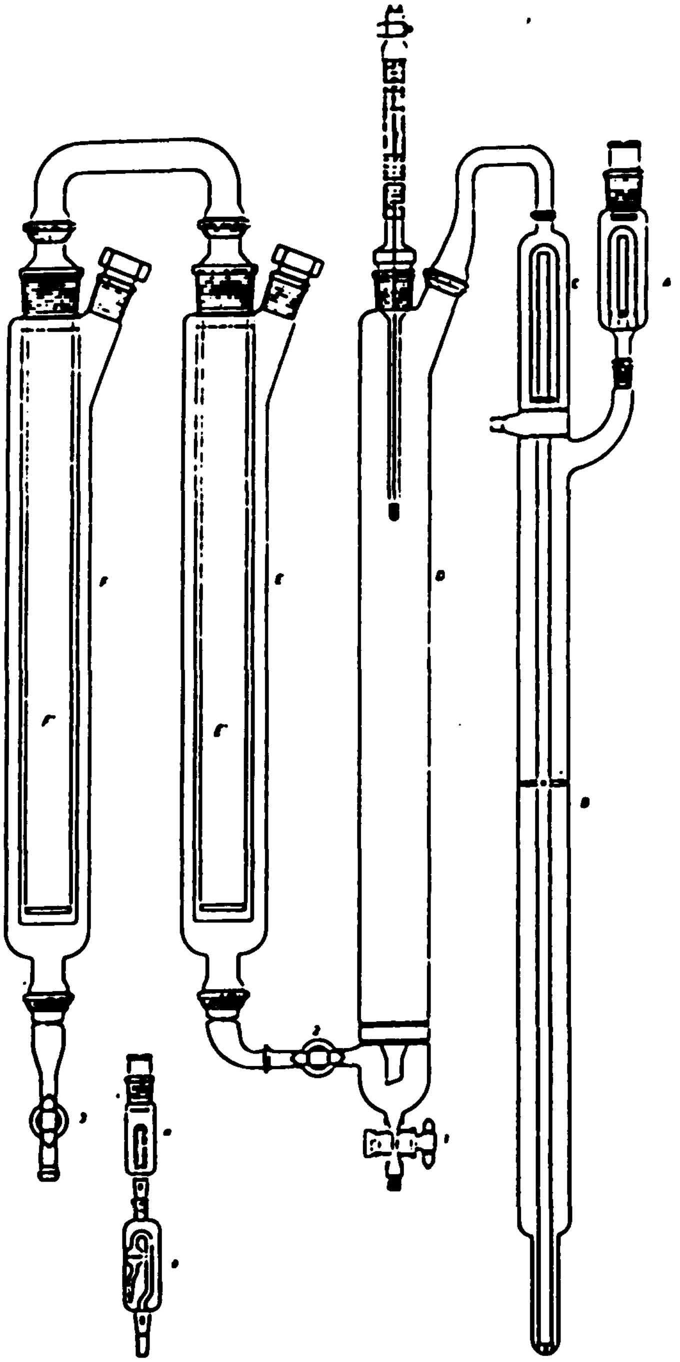
The NMR spectra were obtained on General Electric, QE - 300 MHz and Brucker 250 MHz FT NMR spectrometers. Chemical shifts are reported in δ units, parts per million down field from internal tetramethyl silane for proton spectra. For the ^{13}C spectra the middle peaks of the multiplet due to the deuterated solvents were the references ($CDCl_3$ at 77.0, acetone-d_6 at 29.8, DMSO-d_6 at 39.5 and THF-d_8 at 68.4 ppm).

Gas chromatographic analysis were performed using a Hewlett Packard model 5880 instrument equipped with a hydrogen flame ionization detector. Column diameters were 1/8 " and the lengths were 6 '. 10% SE - 30 on Chromosorb W or OV 101 was used for the packing.

Infrared spectra were taken using a Perkin-Elmer model 1320 spectrophotometer. The infrared spectra of the liquids were obtained from the neat liquid between sodium chloride plates. Solid samples were pulverized with KBr using Wig-L-Bug amagalmater and pressed in to discs.

Elemental analysis were done by Schwarzkopf Laboratory, Woodside, NY and Galbraith Laboratory, Nashville, TN.

All the melting points were obtained using a Mel-Temp melting point apparatus and are uncorrected. The melting points of hapto complexes were obtained in argon filled sealed capillary tubes.



A= Absorption of mercury vapours over sulfur

B= Mercury column excess pressure releif valve

C= Bubble counter

D= Absorption tube with BTS catalyst(1300g)

E= KOH pallets(900g)

E'= Silicagel(400g) with moisture indicator

F= P_2O_5'350g)

F'= $MgClO_4$(400g)

Fig. 23. Normag Gas Purification Apparatus

Preparation of Pentaphenylethyl Carbanion:

To a solution of potassium tertiary butoxide (2.0g, 20 m mol) and pentaphenylethane (2.05g, 5 m mol) in THF (75 mL), n-butyllithium (4 mL, 7 m mol) was added dropwise maintaining the reaction temperature at -78°C with a dry ice/2-propanol mixture. The first drop of BuLi developed an orange red color which disappeared immediately, the color however persisted after few drops of BuLi resulting in a dark red solution. The contents were stirred at the same temperature at least for a period 2h and was then reacted with deuterium oxide or deuterated ethanol. In case of D_2O it took almost 20 minutes for the carbanion color to disappear due to freezing of D_2O. The reaction mixture was extracted into ether, dried and solvent removed under reduced pressure to yield the product (>95%).

The ratio of pentaphenylethane to deuterio pentaphenylethane in the product mixture was determined as follows. The crude product was crystallized from benzene and absolute ethanol to obtain a colorless crystalline solid, melting point range 169-172°C (sealed capillary under argon). 100mg of the mixture was taken in 0.5 mL carbontetrachloride and the product composition was determined using proton integration method (the integration of benzylic proton singlet at 5.85 ppm vs the aromatic multiplet near 7.3 ppm).

Reaction of Pentaphenylethyl Carbanion with Trimethylchlorosilane:

The carbanion was prepared from 6.83g (16.7 mm) of pentaphenyl ethane, 2.85g (25 m mol) of $KOBu^t$ and 12.5 mL of BuLi (25 m mol) in THF (150 mL) at -78°C. After 2h, trimethylchlorosilane (15 mL) was added during ten minutes at the same temperature. The carbanion color disappeared immediately with appearance of a light yellow-green color. The reaction mixture was worked up as before by extracting into a organic

solvent (ether) and removing the solvent in vacuo. The crude reaction mixture (6.52g) was separated by a silicagel column chromatography and the following compounds were isolated in the order of elution:
petrol:benzene (4:1); recovered pentaphenylethane (*1*, 0.9g, 13%);
petrol:benzene (1:1); triphenylmethanol (*12*, 0.52g, 12%), identified by mixed melting point determination and superimposable infrared and nmr spectra with that of an authentic sample;
petrol:benzene (1:4); trimethylsilyl benzophenone (*11*, 1.5g 35.4%);
ir (neat), 2860,1275, 835 cm^{-1} ($SiMe_3$), 1665 cm^{-1} (>CO); ^1H nmr ($CDCl_3$), δ 7.9-7.3(m, aromatic, 9H), 0.25(s, $SiMe_3$, 9H); ^{13}C nmr ($CDCl_3$), δ 196.4 (CO), 146, 137.6, 137.5, 133, 132.2, 129.8, 128.8, 15.9 ($SiMe_3$);
benzene; 1,1,1-triphenyl-2,2-diphenyl-2-trimethylsilyl ethane(*10*, 0.4g, 5%), m.p., 225-27°C (benz./hexane); ir(KBr), 2860, 1260, 1250, 855, 835 cm^{-1}($SiMe_3$); ^1H nmr($CDCl_3$), 7.4-5.7 (m, aromatic, 25H), 0.25 (s, $SiMe_3$, 9H); ^{13}C nmr($CDCl_3$), 186.8, 165.5, 145.7,141.2, 141.0, 139.7, 138.4, 133.2, 131.96, 128.4, 127.6, 127.4, 126.9,126.6, 68.3, 65.8, -1.2 ($SiMe_3$);
the ether washing of the column gave 3.3g of an intractable solid which was left unidentified.

Reaction of Pentaphenylethane Carbanion with Carbon monoxide/TMCS:

Carbon monoxide was bubbled into a 0.11M carbanion solution (obtained from PPE (7.32g), $KOBu^t$ (4.0g) and BuLi (14.3 mL) in THF (150 mL)) for a period of 5h with no apparent change in carbanion color. It was then reacted with trimethylchlorosilane (10 mL) and worked up as before. The products isolated were: pentaphenylethane (*1*, 0.75g, 10%), trimethylsilyl benzophenone (*11*,0.9g, 21%), triphenylmethanol (*12*, 0.5g, 10%), pentaphenylethyltrimethylsilane (*10*, 0.3g, 3.7%) and an intractable mixture 4.3g.

Reaction of Pentaphenylethyl Carbanion with Dimethyldisulfide:

Pentaphenyethyl carbanion was prepared in THF (250 mL) from pentaphenylethane (7.32g, 17.8 mm), KOBu^t (4.0g,35.7mmol) and BuLi (18 mL) at -78°C during 2h. It was quenched with dimethyldisulfide (10 mL), the carbanion color did not change even after 2h at the same temperature hence was raised to -20°C and then hydrolyzed with 5% hydrochloric acid (200 mL) and extracted into ether (2 X 100 mL). The organic layer was separated, washed with $NaHCO_3$ solution (100 mL, 5%) and water (100 mL) successively and dried. Ether was removed under vacuum to give the crude mixture (6.87g) which was separated by flash chromatography. The following compounds were isolated in the order of elution (petrol:benz (4:1), petrol:benz (1:1), petrol:benz (1:3) and ether) respectively.

Recovered pentaphenylethane (*1*, 2.3g, 31%);

1,1,1-triphenyl-2-phenyl-2-thiomethylphenyl ethane (*13*, 0.9g,11%), m.p., 139-42°C (benz/hexane);

Analysis, calculated for $C_{33}H_{28}S$,

calculated	found
C = 86.84%	C = 86.72%
H = 6.14%	H = 6.52%
S = 7.02%	S = 4.58%

Ir (KBr), 2820 cm^{-1}; ^{1}H nmr ($CDCl_3$),δ 7.5-6.8 (m, aromatics, 24H), 5.8 (s, benzylic, 1H), 2.3 (s, SCH_3, 2.8H); ^{13}C nmr($CDCl_3$), δ145.6, 142.9, 139.7, 135.6, 131.9, 131.6, 131.3, 131.2, 127.4, 126.9, 125.9, 62.54, 58.8, 15.4;

thiomethyl benzophenone (*14*, 0.1g, 2.5%), m.p. 60-62° C; ir (KBr), 2820, 1645 cm^{-1}; ^{1}H nmr ($CDCl_3$), 7.8-7.3 (m, aromatics, 9H), 2.5 (s, SCH_3, 2.8H);

^{13} nmr (CDCl$_3$), 195.5, 147.2, 145.2, 137.6, 133.4, 131.9, 130.5, 129.6, 128.0, 127.8, 127.7, 126.9, 124.6, 14.6;
the ether washings gave an intractable mixture which was left unidentified.

Reaction of Pentaphenylethyl Carbanion with Tetrakis Iodo(tri-n-butylposphine)copper(I):

To a solution of tetrakis(tri n-butylposphine) cupper iodide solution (31.85g) in THF (200 mL) at -70°C, the carbanion solution of pentaphenylethane(obtained from 22g, 54 mmol hydrocarbon, 9.1g, 81 m mol KOBu^t, 81 m mol n-butyllithium in THF (300 mL)) at -70°C was added via a cannulla and argon pressure during 0.5h. To the resulting mixture cold methyl iodide was added during 0.3h, the color changed from red-orange to yellow and after 2h it was hydrolyzed with 5N HCl (100 mL) and was extracted into ether (2 X 100 mL). The organic phase was separated dried and the solvent was removed in vacuo. The residue was separated on a silicagel column and the following compounds were isolated. Triphenyl methanol (2.3g,14%) , a 1:1 (by gas chromatography) mixture of benzophenone and methyl benzophenone (4.5g, 20%) and an intractable mixture which could not be purified.

Synthesis of Pentaphenylethane(C-2) tricarbonylchromium (*22*):

A solution of trityl magnesium bromide was prepared from trityl bromide and magnesium in ether and benzene mixture as follows: A solution of trityl bromide (10.03g, 0.031 mol) in benzene (40 mL) was added to magnesium (0.91g, 0.031 g atom) in ether (20 mL) during 10 minutes. The reaction occured immediately upon warming with appearance of a brown color. The reaction was continued on a steam bath for a period of 2h during which most of the magnesium dissolved. It was cooled to room temperature and filtered through a coarse frit to remove the unreacted magnesium. The trityl Grignard was then cooled to 10°C to which benzhydryl chloride tricarbonylchromium (9.3g, 0.027 mol) in benzene (30 mL) was added during 5 minutes. The reaction temperature rose to 15°C and the contents were stirred at room temperature overnight while protecting from light. It was hydrolyzed with saturated ammonium chloride solution (200 mL) and was extracted into ether (2 X 100 mL). The organic layer was separated, dried and filtered to remove the desicant. The solvent was removed in vacuo and the residue was crystallized from benzene and cyclopentane (1:9) to give the titled compound (13.0g) in 88% yield based on benzhydryl chloride chromium tricarbonyl, m.p.,178-178.5°C dec.

Elemental Analysis, calculated for $C_{35}H_{26}CrO_3$,

calculated	found
C = 76.92%	C = 76.34%
	C = 76.21%
H = 4.762%	H = 5.11%
	H = 4.97%

Ir(KBr), 1970-1955 and 1905-1860 cm^{-1} (broad, >CO); ^1H nmr ($CDCl_3$), δ7.2 (m,aromatic, 20H), 5.0 (m, complexed aromatics and the benzylic, 6H); ^{13}C nmr ($CDCl_3$), δ 232.5 (CO), 144.9, 140.1, 131.6, 131.4, 131.0, 128.1, 127.3, 127.2, 126.3, 112.9, 100.6, 98.6, 96.2, 87.6, 86.6, 63.5, 58.4.

Synthesis of Pentaphenylethane(C1)-tricarbonylchromium *(28)*:

A solution of triphenylmethane tricarbonylchromium carbanion in THF (20 mL) was prepared from triphenylmethane tricarbonylchromium (2.05g, 5 mmol) and potassium tertiary butoxide (1.7g, 16 m mol) during 0.3h at room temperature. The orange red carbanion solution was cooled to 0°C to which a solution of benzhydryl bromide (2.6g,16 mmol) in THF (10 mL) was added during 10 minutes when the color changed to cherry red. The contents were stirred overnight at room temperature and then hydrolyzed with saturated sodium chloride solution (200 mL). The organic phase was extracted into ether (2 X 100 mL), dried, filtered and the ether was removed under reduced pressure. The dark oil residue on trituration with petroleum ether (3 X 100 mL) afforded an orange red solid (1.9g, 65.7%) which on recrystallization gave a yellow solid as pentaphenylethaneC(1)-tricarbonylchromium, m.p.,182-3°C (benz:petrol (1:1)).

Elemental Analysis, calculated for $C_{35}H_{26}CrO_3$,

calculated	found
C = 76.92%	C = 76.78%
	C = 76.58%
H = 4.76%	H = 4.76%
	H = 4.98%

Ir(KBr), 1970-1955, 1965-1860 (broad, CO) cm^{-1}; ^1H nmr ($CDCl_3$), δ7.6-7.0(m, aromatic, 20H), 5.7 (s, benzylic, 1H), 5.5-4.5 (m, complexed aromatics, 5H); ^{13}C nmr ($CDCl_3$), δ233 (CO), 143.1, 42.6, 132.1, 131.5, 127.9, 126.9, 126.3, 122.1, 98.6, 95.9, 88.2, 60.6, 59.8.

Decomplexation of Pentaphenylethane tricarbonylchromium (*22*):

a) Iodine method: To a stirred solution of pentaphenylethane chromiumtricarbonyl (0.25g, 0.45 m mol) in ether (30 mL) at 0°C, iodine(0.185g,0.68 m mol) was added and the contents were stirred for 3h at the room temperature. The resulting dark solution was washed with 10% sodium thiosulfate solution (2 X 25 mL) followed by water (2 X 50 mL). The clear organic layer was separated and dried over magnesium sulfate, filtered and the ether were removed under reduced pressure to yield a colorless solid identified as pentaphenylethane (0.105g, 56.9%) by its superimposable ir nmr with that of an authentic sample and mixed melting point determination.

b) Ceric Ammonium Nitrate (CAN) method: 0.5m mol of pentaphenyl ethane chromium complex was dissolved in mixture of ether (5 mL) acetonitrile (5 mL) and to the resulting yellow solution, a 0.2N cericammonium nitrate solution (10g of CAN in 20 mL of water and 80 mL acetonitrile) was added dropwise until the solution became nearly colorless and then slightly yellow. The solution was allowed to stand for .5h and then 100 mL of water was added. The organic portion was extracted into ether (2 X 25 mL) dried, filtered and the ether was removed in vacuo to give pentaphenyl ethane (0.16g, 78%) identified as above.

Decomplexation of *28* by CAN solution:

One mmol (0.546 mg) of pentaphenylethane(C-1)-chromium tricarbonyl was decomplexed by ceric ammonium nitrate solution exactly as described above and the parent hydrocarbon (PPE) was isolated in 72% (0.495g) yield.

Synthesis of Benzhydryl chloride tricarbonylchromium (*21*):

To a solution of benzhydrol tricarbonylchromium (10.0g, 31 mm) in anhydrous ether (250 mL) at -20°C, hydrogen chloride was bubbled for a period of 0.75h during which the yellow solution changed its color to a light coffee red. Nitrogen gas was bubbled into the solution to chase the excess HCl at the same temperature for 1h when the solution acquired a deep yellow color. The ether was removed in vacuo and the residue was crystallized from benzene and petroleum ether (1:9 v/v) to give the titled compound (9.7g, 92%), m.p., 76-77°C dec., lit.[73] 76.5-77.5°C; ir(KBr), 1980-1945,1910-1840 (broad, CO) cm^{-1}; ^{1}H nmr ($CDCl_3$), δ 7.35 (m, aromatic, 5H), 5.28 (m, 6H); ^{13}C nmr ($CDCl_3$), δ 232, 138, 129, 128.8, 127.6, 110.4, 93.4, 92.7, 92.6, 90.8, 90.4, 62.6.

<u>Metalation Studies on Triphenylmethane tricarbonychromium:</u>

Deprotonation of triphenylmethane-$Cr(CO)_3$ at the benzylic carbon was secured in 80-85 % using 3-5 moles of potassium tertiary butoxide in THF at room temperature. The percent formation of the anion was determined by proton nmr integration of the decomplexed product mixture (the aromatic multiplet at 7.5 ppm vs the benzylic singlet at 5.56 ppm) after deuterium oxide quench of the carbanion. ^{13}C nmr spectrum showed a triplet at 56.7 ppm indicating the presence of a deuterium at the benzylic carbon. Salt free methyllithium also deprotonates the triphenylmethane-$Cr(CO)_3$ complex at room temperature in THF up to 60%. A typical run is described as below:

The reaction was carried out under argon atmosphere at room temperature with triphenylmethane-$Cr(CO)_3$ (1 m mol) and potassium tertiary butoxide (5 m mol) in THF (10 mL). An immediate intense orange red color ensued and the mixture was stirred for 0.3h at room temperature followed by D_2O quench. The contents were hydrolyzed by pouring onto water-ether (100 mL each) mixture. The organic layer was separated, dried and concentrated (5 mL) under reduced pressure. The residue was taken in 5 mL acetonitrile and a 0.2N ceric ammonium nitrate solution was added dropwise until the solution became nearly colorless and then slightly yellow. The solution was allowed to stand for 0.5h and then 100 mL of water was added. The organic portion was extracted into 2 X 50 mL ether, dried, filtered and the solvent removed in vacuo. The residue was dissolved in 1 mL $CDCl_3$ and analyzed by proton nmr.

Reaction of Triphenylmethane-chromiumtricarbonyl Carbanion with Benzhydryl chloride:

Triphenylmethane tricarbonylchromium carbanion was prepared from triphenylmethane chromium complex (0.95g, 2.4 mmol) and $KOBu^t$ (0.7g, 6.25 mmol) in THF (20 mL) at room temperature. To the orange red carbanion solution, benzhydryl chloride (1.1g, 5.4 mmol) in THF (5 mL) was added and the reaction was allowed to run overnight. It was hydrolyzed with saturated sodium chloride solution and was extracted into ether. The ether layer was dried, filtered and the solvent was removed in vacuo to yield a residue (1.1g). The residue was triturated with petroleum ether (2 X 25 mL) which afforded 0.8g (85%) of unreacted triphenylmethane tricarbonylchromium identified by mixed melting point determination and superimposable ir and nmr spectra.

Reaction of Tritylllithium with Benzhydryl chloride-tricarbonylchromium:

Trityl carbanion was prepared from 6.8 m mol of triphenyl methane (1.56g) and 3.2 mL of butyllithium in THF (20 mL) at 0-2°C during 1h. To the red carbanion solution benzhydryl chloride tricarbonylchromium (2.3g) was added in THF (5 mL) during 5 minutes. The color changed to orange red and the contents were stirred overnight. The reaction mixture was hydrolyzed and extracted into ether. The ether was completely removed and the residue was taken in cyclopentane (25 mL) and kept at -17°C. A solid was filtered after 2h as triphenylmethane (0.3g, 20%). T.l.c. of the filtrate showed a complex mixture and the identification of the spot due to pentaphenylethane chromium complex was not conclusive. The filtrate on standing at the same temperature did not provide the pentaphenylethane chromium complex (*22*) even after 5 months and the solution gradually turned green.

Formation of Di (bis-tricarbonylchromium benzhydryl)ether:

Benzhydrol bis chromium complex(0.912, 2 m mol) was dissolved in propionic anhydride (5 mL) at room temperature to which 65% hexafluoro phosphoric acid (0.54 mL, 2.2 m mol) in propionic anhydride (3 mL) was added during 5 minutes. The first drop gave a brilliant blue precipitate. The contents were allowed to stir for 0.5h during which the blue color vanished and the solution acquired a green-yellow color. The mixture was poured into ice-water, extracted into ether (2 X 100 mL). A solid insoluble in ether was filtered (0.27g) as the titled ether complex in 29% yield, m.p., 236-8°C dec., lit.[51], 200°C dec. The ether layer upon concentration gave a second crop of 0.33g (36.5%); ir(KBr), 1158 cm^{-1}(C-O-C); ^1H nmr(Acetone-d_6), δ7.8-6.9 (m, 4H), 6.2 (m, 7H), 5.7 (m,10H), 4.2 (m, 1H); ^{13}C nmr (Acetone-d_6), δ 234, 115.3, 99.5, 98.1, 97.6, 90.7, 55.07.

Preparation of Arene-chromiumtricarbonyl complexes:

Two procedures were followed for the synthesis of chromium tricarbonyl complexes of the following compounds: benzhydrol, triphenyl methane, triphenylmethanol, benzophenone, bromobenzene and benzene. Reaction conditions and the results were given in Table 14 and 15.

Method A utilized an apparatus in the early literature by Strohmeier. Method B used wide mouthed flasks fitted with wide bore condensers. The solvents chosen and the isolation procedures followed have the advantage of permitting the isolation of crude tricarbonyl complexes directly from the reaction mixture without requiring the separation through silicagel column[49]. All attempts to utilize the solvents and reaction conditions described by Top and Jaouen could not duplicate the yields they reported.

Procedure A:

Into an argon filled Strohmeier's apparatus (see Fig. 2 , page 5) were introduced 0.02 to 0.05 moles of the substrate and chromium hexacarbonyl (0.02 to 0.06 moles) (see table 14) togather with 150 mL of dioxane. The contents were refluxed for the period of time indicated in table 15. In all cases, except for benzophenone a yellow color developed during first 5 to 10 minutes as the $Cr(CO)_6$ dissolved in the solution; benzophenone showed an intense orange red color.

The temperature in the upper and lower condenser of the Strohmeier's apparatus were maintained at 80°C and 70°C in order to facilitate the recycling of unreacted $Cr(CO)_3$ into the reaction flask through the return siphon.

After reaction appear to be completed, the reaction solution was cooled to 10°C, filtered to remove unreacted $Cr(CO)_6$ and distilled in vacuo to remove all of the solvent. The residue was crystallized from the appropriate solvent(s) to afford crude samples of complex which were further purified from solvent mixtures to produce spectral quality samples.

Procedure B:

In a 250/500 mL wide mouth flask fitted with a wide bore condenser was placed diglyme and THF (3:1 v/v) under nitrogen. The solvent mixture was degassed using at least five freeze, pump and thaw cycles and then arene and $Cr(CO)_6$ were introduced. The duration of the reaction period depends on the substrate as shown in the Table 15. After the reaction the solvents were removed under reduced pressure (5-10 mm) and the residue was crystallized as in the above procedure. In some cases, partial decomposition of the hapto complexes occured indicated by a grey green suspension in the reaction solution. In such cases, after the removal of the solvents, the residue was dissolved in benzene(20 mL) and filtered through celite in an atmosphere of nitrogen. Extensive decomposition resulted when heating the reaction was continued for more than two days. The benzene was removed in vacuo and the residue was treated with an appropriate solvent(s) for crystallization (Table 14). In most of the cases the crystallization took more than two days at -17°C.

The moles of the substrate, the chromiumhexacarbonyl, the solvent, the recovery of the unreacted $Cr(CO)_3$, yields and the melting points are presented in Table 14 and 15. The infrared, proton and carbon NMR data are displayed in Table 16.

Table 14. A List of Prepared Arene-$Cr(CO)_3$ Complexes

Substrate g(mmol)	$Cr(CO)_6$, g(mmol)	Recovered $Cr(CO)_3$ g(%)	Ar-$[Cr(CO)_3]_n$ g(%)	m.p.(°C) (solvent)	Lit.,m.p.(°C)
PhCHOHPh 9.2(50)	11.0(50)	1.6(14.5)	(n=1) 9.59(59)	98-99 (eth./pet.)	99.5-100.5[73] 105[49]
PhCHOHPh 5.4(30)	13.2(60)	-	(n=2) 6.6(48.3)	148-9 (eth./ace.)	160[49] 148-9[51]
Ph_3CH 9.76(40)	13.2(60)	5.3(40)	(n=1) 9.3(61)	153-4 (ben./cyp.)	167[49]
Ph_3COH 10.4(40)	8.8(40)	4.0(45.5)	(n=1)# 5.6(35.4)	139-40 (ben./pet.)	147[49] 139.5-140.5
PhCOPh 3.6(20)	13.2(60)	5.2(39.5)	(n=2)* 0.4(4.4)	164-5 (eth./pet.)	168[49] 164-65[51]
			(n=1)* 4.4(69.6)	87-88 (eth./pet.)	89[73] 88-89[49]
PhBr 120 mL	8.8(40)	-	3.7(30)	109-110 (pet.)	
PhH 10 mL	11.0(50)	6.0(54)	3.3(31)	158-9 (cyp.)	160-1[46] 161-3[70] 166.5[38c]

\# separated through an alumina column(2nd fraction, ben./pet.,1:1 v/v)

* isolated by successive crystalization of the crude product from ether/petroleum ether and benzene/petroleum ether respectively

Table 15 . A List of Prepared Arene-$Cr(CO)_3$ Complexes

Substrate	Arene-$Cr(CO)_3$	Method	Solvent(s)(mL)	Rxn. Period	% Yield
PhCHOHPh	$ArCr(CO)_3$	A	Dioxane(150)	3 days	59
	$Ar[Cr(CO)_3]_2$	B	Diglyme+THF (180) (60)	30 hrs	48
Ph_3CH	$ArCr(CO)_3$	A	Dioxane(150)	3 days	61
Ph_3CHOH	$ArCr(CO)_3$	A	Dioxane(150)	3 days	35
PhCOPh	$ArCr(CO)_3$	A	Dioxane(150)	84 hrs	70
	$Ar[Cr(CO)_3]_2$				4
PhBr (120 mL)	$ArCr(CO)_3$	A	THF(20)	45 hrs	30
PhH	$ArCr(CO)_3$	A	Glyme+Diglyme (25) (125)	64hrs	31

Table 16. Infrared, Proton and ^{13}C NMR Data for Arene-Cr(CO)$_3$ Complexes

Substrate	Arene-[Cr(CO)$_3$]$_n$	Ir(KBr) cm^{-1}	^{1}H NMR (CDCl$_3$), ppm	^{13}C NMR (CDCl$_3$), ppm
PhCHOHPh	n=1	3570(s, OH) 1980-1950 & 1910-1850(CO)	7.4(s,5H, Ar) 5.2(m,6H,Ar-Cr) 2.5(d,1H, OH)	232.8, 141.9 128.7, 128.4 126.4, 115.2 92.4,92.3,92.2 91.8,90.3,66.8
PhCHOHPh	n=2	3590, 3570 3530(s, OH)	5.61(d,2H,Ar-Cr) 5.4(m,1H,Ar-Cr) 5.1(d,1H,Ar-Cr) 2.58(d,1H,CH) 1.58(s,1H,OH)	232.2, 111.8 93.4,92.1,91.1 91.3,91.0,90.9 72.3
Ph$_3$CH	n=1	1890-1950 1910-1850 (br, CO)	7.5-7.1(m,10H) 5.5-4.9(m, 6H)	233.0, 141.3, 128.5, 127.0 114.7, 95.4, 94.4,90.1,54.6
Ph$_3$COH	n=1	3570(s,OH)	7.2(s,10H) 5.5(m,1H) 5.4(d, 2H) 5.3(m,2H) 3.1(s,1H, OH)	232.9,144.8 128.0, 127.9 127.6, 118.4 95.8,95.2,88.5 79.8
PhCOPh	n=2	1648(ArCOAr)	6.5(m, 4H)* 6.2(m, 2H) 5.8(m, 4H)	232.5, 206.3* 97.2,97.0,91.6
PhCOPh	n=1	1651(CO)	7.8(d, 2H) 7.6(d,1H) 7.56(d, 2H) 6.0(d, 2H) 5.62(m,1H) 5.3(m, 2H)	229.9,192.9 135.8,131.7 127.9,127.8 96.2,95.7,94.9 94.7,89.6,89.2
PhBr			5.6-4.9(m)	231.0,98.0, 93.8,93.1,88.5

* deuterated acetone was the solvent

Reaction of Trityl Grignard with Benzophenone chromiumtricarbonyl:

A solution of trityl magnesium bromide was prepared in benzene (20 mL) and ether (10 mL) from 0.48g (0.02 mol) of Mg and 1.75g (0.005 mol) of trityl bromide. The excess magnesium was removed by filtration through a coarse frit and the Grignard was added dropwise to a solution of benzophenone chromiumtricarbonyl (1.1g, 0.003 mol) in benzene (10 mL) during 10 minutes. The reaction temperature shot up to 32°C with a change in color from orange-red to coffee-red. The contents were stirred at room temperature for 1h followed by hydrolysis with saturated NH_4Cl (100mL) solution when a yellow solid separated (1.15g, m.p., 192°C partially melted at 184-186°C) as pentaphenylethanol tricarbonylchromium(*40*); Ir (KBr), 3540 (sharp, OH), 1965, 1875 (broad, CO), 1150 cm^{-1}.

A good NMR spectrum could not be obtained because of its poor solubility in common organic solvents. It dissolved in basic solvents like DMF and DMSO with a change in color to orange red, the characteristic color of a benzophenone chromiumtricarbonyl, apparently due to decomposition *40*. ^{13}C NMR of *40* in DMSO-d_6 at room temperature shows signals at δ 234.25, 232.18,193.38, 144.53, 136.34, 132.82, 129.79, 128.91, 128.80, 128.73, 128.52, 127.84, 126.61,118.74, 98.19, 97.87, 97.63, 94.51, 94.37, 94.24, 93.69, 92.68, 92.29, 72.55, 55.45.

Decomplexation of *40* by Ceric ammonium nitrate :

400 mg of alcohol (*40*) was taken in a mixture of acetone (10 mL)and acetonitrile (5mL) at room temperature to which CAN solution was added until the solution became colorless and then to a light yellow. On standing at room temperature a colorless solid separated as trityl peroxide (*41*, 110 mg, 59.4 %), m.p.,178-179°C. The filtrate upon dilution with water(100 mL) a second portion of the solid separated as benzopinacol (*42*, 75mg, 57.7%),

m.p., 176-78°C. Both *41* and *42* were identified by mixed melting point determinations and superimposable ir with that of the authentic samples.

Reaction of *40* with Hexafluorophosphoric acid :

To the suspension of pentaphenylethanol chromiumtricarbonyl (1.124g, .002 mol) in propionic anhydride (5 mL) at room temperature hexafluorophosphoric acid (0.54 mL, 10% excess) was added via a plastic syringe. The contents were stirred at room temperature for 18h during which the solution acquired a brown-yellow color. All the starting material did not dissolve and an attempt to filter the solids through a fine frit was not successful. Hence, the reaction mixture was treated with absolute ethanol (20 mL) at the same temperature followed by hydrolysis with water (200 mL). The yellow solid separated during hydrolysis was filtered as the starting substance (440 mg, 33%). The organic phase was extracted into ether and ether removed after drying over magnesium sulfate to yield a residue (0.300 mg) which was subsequently purified through a silicagel column. Fraction #3 (hexane) afforded triphenylethyl ether (59 mg, 18%) and was identified by an independant synthesis (1.9 g, 90%), m.p., 78-80°C, Lit.[151], 82.5-83.5°C, from triphenylmethanol (2.0g), conc. sulfuric acid (10 mL) and absolute ethanol (20 mL).

Preparation of Bis-(trimethylsilylmethyl) mercury:

Trimethylsilylmethyl chloride (25.0g, 0.21 mol) in THF (150 mL) was reacted with magnesium 5.54g (10% excess) at room temperature for 2h during which most of the magnesium dissolved. The Grignard solution was filtered to remove the unreacted magnesium and to the filtrate the mercuric chloride (25.75g, .095 mol) in THF (50 mL) was added during 10 minutes. The contents were stirred for 2h and was hydrolyzed with saturated ammonium chloride solution (500 mL). The organic phase was extracted into ether and ether was removed in vacuo. The residue was vacuum distilled to give bis (trimethylsilylmethyl)mercury(29.1g, 77.8%), Lit.[152], 48.5%, b.p., 63.5-64.5°C at 0.65 mm, Lit.[152] 49-50°C at 0.35 mm. Ir (Neat), 2950, 2880, 1285, 960, 945, 820, 760 cm^{-1}; ^1H NMR (C_6D_6), 0.24 (s, 9H, $Si(CH_3)_3$), 0.13 (s, 2H, CH_2); ^{13}C NMR (C_6D_6), 28.05 (CH_2), 2.83 (Si($CH_3)_3$).

Reaction of Trityl Grignard with α-Bromodiphenylmethyltrimethylsilane:

A 0. 58 M trityl Grignard was prepared in benz/ether (300/100 mL) from trityl bromide (75g, 0.23 mol) and magnesium (6.13g, .255 gatom) for the synthesis of pentaphenylethane. A portion of the above solution (50 mL) was reacted with 10.8g, 0.35 mol) of bromosilane at room temperature when a light yellow color developed during the addition of the Grignard solution. The contents were stirred at room temperature overnight followed by hydrolysis with water. A solid separated during hydrolysis was filtered (3.5g, 40.7%) as trityl peroxide, m.p., 171-172°C, Lit.[149]185-186°C.

Reaction of Trityllithium with α-Bromodiphenylmethyltrimethylsilane:

To a solution of trityllithium solution prepared from triphenylmethane (2.44g, 0.01 mol) and BuLi (0.5 ml, 0.011 mol) in THF (30 mL) at 0°C, bromo silane (2.9g, 9.2 mmol) in THF (10 mL) was added during 10 minutes. The red carbanion color disappeared during the addition with formation of a yellow color. The contents were hydrolyzed with water when trityl peroxide was separated as insoluble solid (1.0g, 41%) in both phases and was filtered. The compound was identfied by mixed melting point determination with that of an authentic sample prepared independantly following literature.[149]

Preparation of Carbanion Solution for ^{13}C NMR Studies:

i) Triphenylmethyllithium: In a flame dried, argon filled, septum covered NMR tube (5mm), triphenylmethane (75 mg, 0.33 mmol) was taken in a blanket of argon to which tetrahydrofurane-d_8 (5 mL) from a freshly opened ampule was introduced into the NMR tube via gas tight syringe at room temperature. The triphenylmethane was dissolved in THF-d_8 by shaking the tube several times and n-BuLi (0.3 mL) was added into the clear solution by a syringe. An immediate red color developed at the interface with separation of a precipitate. The supernatant red solution was syringed out to a second NMR tube and proton decoupled and coupled INEPT spectra were recorded at room temperature as shown in Fig. 16 and 17.

ii) Pentaphenyethyllithium at room temperature:

In a 25 mL dry three necked flask, pentaphenylethane (110mg, 0.25 mmol) and potassium tertiary butoxide (45 mg, 0.4 mmol) were placed under argon to which 2 mL of THF-d_8 was added via a syringe. The contents were stirred for several minutes at room temperature to dissolve the solids. The temperature of the reaction mixture was cooled down to -78°C followed by addition of BuLi (0.2 mL, 0.4 mmol) when an immediate red color appeared. The mixture was stirred for 2h while bringing the reaction temperature to 20°C. The above solution (0.5 mL) was placed in a dry NMR tube and the spectra was recorded at room temperature. The typical acquisition parameters for the trityllithium and pentaphenylethyllithium were as follows; carbon NMR studies were carried out using IBM/Brucker 250 FT NMR with a ^{13}C resonance frequency of 62.9 MHz at the field strength. Data were acquired using 16K real data points for a digital resolution of 0.95Hz. A total of 4000-8000 pulses were averaged to produce the spectra shown in Fig.18. Artificial enhancement of the anion resonances was induced by rapid pulsing with short or no delay times. The pulse repetition was thus limited essentially by acquisition time (0.5 sec., 32K, 15625 Hz spectrum). The spectra were obtained with simultaneously broadband proton decoupling at ambient temperatures. The FIDs were multiplied by a exponential weighting function ($e^{-(i-1*LB/2*SW}$, LB= 0.5Hz) for an improvement of S/N. INEPT experiments were carried out utilizing the software supplied by Brucker with the instrument.

iii) Potassium salt of pentaphenylethyl(C-2)-Cr(CO)$_3$:

To degassed DMSO-d6 (3 mL), pentaphenylethyl-Cr(CO)$_3$ (200 mg, 0. 365 m mol) and KOBu^t (120 mg, 1.1 m mol) were added in an argon atmosphere at room temperature. A brick red color developed during first ten minutes and the reaction mixture was stirred at the same temperature for an additional period of 2h. An aliquot (0.5 mL) of the above solution was syringed out to a dry NMR tube and the spectrum was recorded during 5h. No change in resonance frequencies was noticed when the spectrum was recorded again after three days. The anion solution was hydrolyzed with water extracted into ether and ether removed to yield a yellow residue (130 mg), m.p.,165-172°C which on ^{13}C NMR shows the signals at δ 58.3, 63.4, 86.6, 87.6, 96.2 98.6, 100.6, 112.9, 125.8, 126, 127.3, 128.0, 128.1, 128.3, 131.0,131.4, 131.5, 140.1, 144.9, 232.3 due to that of a pentaphenyl ethane(C2)-chromiumtricarbonyl (*22*). The additional low intensity signals in the 135-125 ppm range are probably due to presence of pentaphenylethane ,the decomplexed hydrocarbon.

In a subsequent run (*22* (205 mg), KOBu^t (134 mg) in DMSO-d$_6$ (3 mL)) ^{13}C spectrum of the anion showed no change in resonance frequencies even after 7 days and the anion was hydrolyzed with CH$_3$OD. On usual hydrolytic work up, 2-deuteriopentaphenylethane (85 mg, m.p., 130-145°C) was obtained due to oxidative decomplexation of Cr(CO)$_3$ during work up.

Potassium Salt of Pentaphenylethane(C1)-Cr(CO)$_3$:

PPE(C1)-Cr(CO)$_3$ (115 mg, 0.27 mmol) was dissolved in degassed DMSO-d$_6$(3 mL) at room temperature to which KOBu^t (110 mg) was added with stirring. During first few minutes a brick red color appeared which subsequently changed to light yellow. A aliquot of the above solution was transfered by a gas tight syringe into a NMR tube and the spectrum was recorded during 7-8h and shown in Fig. 21 and 22. The anion was hydrolyzed after 48h and worked up as usual to yield a colorless semisolid (42 mg) whose carbon spectrum has signals at δ 132.4, 132.3, 131.8, 131.4, 130.0, 129.5, 129.2, 129.1, 129.0, 128.9, 128.5, 128.3, 128.0, 127.8, 127.6, 127.5, 127.4, 127.3, 127.2, 127.0, 126.5, 126.4, 126.2, 126.1, 125.9, 125.6, 64.0, 59.0, 30.0, 1.0 probably due to a complex mixture.

The special acquisition parameters for obtaining the carbanion spectra include short pulse angles (25-30°) and no pulse delay to achieve the selective saturation of solvent resonances. The low concentration of the carbanion in the solution required an increase in number of scans needed for obtaining a reasonably good S/N spectrum. The FIDs acquired used 32K computer memory corresponding to 16K real data points in the spectrum after carrying out the Fourier Transform.

APPENDIX I

Table S1. Atomic cordinates (X 10^4) and isotropic thermal parameters (A° X 10^3) for **22**

	X	Y	Z	U
Cr(1)	3284(1)	11920(1)	1779(1)	47(1)*
C(1)	2497(3)	9411(4)	1036(2)	36(1)*
C(2)	2924(3)	9621(3)	1715(2)	36(1)*
C(3)	2896(3)	8191(4)	762(2)	40(1)*
C(4)	3516(3)	7329(4)	1054(2)	47(2)*
C(5)	3869(3)	6306(4)	753(2)	58(2)*
C(6)	3624(3)	6099(4)	162(2)	61(2)*
C(7)	3014(3)	6950(4)	-136(2)	61(20*
C(8)	2665(3)	7972(4)	155(2)	52(2)*
C(9)	1362(3)	9423(4)	1012(2)	40(1)*
C(10)	821(3)	8333(4)	905(2)	47(2)*
C(11)	-199(3)	8312(4)	920(2)	59(2)*
C(12)	-718(3)	9389(5)	1039(2)	64(2)*
C(13)	-201(3)	10474(4)	1132(2)	58(2)*
C(14)	821(3)	10500(4)	1124(2)	44(1)*
C(15)	2960(3)	10455(4)	651(2)	39(1)*
C(16)	2403(3)	11259(4)	281(2)	50(2)*
C(17)	2852(4)	12146(4)	-67(2)	67(2)*
C(18)	3856(4)	12237(4)	-59(2)	64(2)*
C(19)	4434(3)	11409(4)	283(2)	56(2)*
C(20)	3984(3)	10518(4)	630(2)	47(1)*
C(21)	2699(3)	8607(4)	2174(2)	40(1)*
C(22)	3483(3)	8204(4)	2550(2)	50(2)*
C(23)	3336(4)	7341(4)	3000(2)	66(2)*
C(24)	2415(4)	6865(4)	3078(2)	70(2)*
C(25)	1627(4)	7258(5)	2719(2)	69(2)*
C(26)	1770(3)	8123(4)	2268(2)	55(2)*
C(27)	2688(3)	10920(4)	1956(2)	42(1)*
C(28)	3276(4)	11982(4)	1801(2)	56(2)*
C(29)	3038(4)	13176(4)	2012(2)	67(2)*
C(30)	2251(4)	13332(4)	2397(2)	78(2)*
C(31)	1708(4)	12319(4)	2563(2)	66(2)*
C(32)	1933(3)	11127(4)	2348(2)	51(2)*
C(33)	4474(4)	11129(4)	2787(2)	59(2)*
O(34)	5226(3)	10596(4)	2805(2)	87(2)*
C(35)	3851(4)	13188(5)	3230(2)	62(2)*
O(36)	4200(3)	14013(3)	3496(2)	95(2)*
C(37)	3056(4)	11059(4)	3455(2)	61(2)*
O(38)	2727(3)	10477(4)	3882(2)	99(2)*
C(50)	1129(6)	15095(5)	1342(3)	95(3)*

C(51)	249(7)	15012(7)	1549(3)	116(4)*
C(52)	-488(5)	14433(7)	1259(4)	119(3)*
C(53)	-329(5)	13870(6)	738(3)	119(3)*
C(54)	586(5)	13938(7)	515(3)	125(3)*
C(55)	1331(4)	14558(6)	821(3)	101(3)*

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table S2. Bond lengths (A°) for **22**

Cr(1) - C(27)	2.248(4)	Cr(1) - C(28)	2.194(4)
Cr(1) - C(29)	2.194(4)	Cr(1) -C(30)	2.200(5)
Cr(1) - C(31)	2.204(5)	Cr(1) - C(32)	2.196(4)
Cr(1) - C(33)	1.817(5)	Cr(1) - C(45)	1.837(5)
Cr(1) - C(37)	1.815(5)	C(1) - C(2)	1.620(5)
C(1) -C(3)	1.549(5)	C(1) - C(9)	1.533(5)
C(1) - C(15)	1.561(5)	C(2) - C(21)	1.535(5)
C(2) - C(27)	1.527(5)	C(3) - C(4)	1.388(5)
C(3) - C(8)	1.404(5)	C(4) - C(5)	1.382(6)
C(5) - C(6)	1.371(6)	C(6) - C(7)	1.378(6)
C(7) - C(8)	1.367(6)	C(9) - C(10)	1.390(6)
C(9) - C(14)	1.367(6)	C(10) - C(11)	1.381(6)
C(11) - C(12)	1.380(7)	C(12) - C(13)	1.365(7)
C(13) - C(14)	1.384(6)	C(15) - C(16)	1.392(6)
C(15) - C(20)	1.389(6)	C(16) - C(17)	1.386(6)
C(17) - C(18)	1.360(7)	C(18) - C(19)	1.387(6)
C(19) - C(20)	1.387(6)	C(21) - C(22)	1.391(5)
C(21) - C(26)	1.384(6)	C(22) - C(23)	1.390(6)
C(23) - C(24)	1.364(8)	C(24) - C(25)	1.370(7)
C(25) - C(26)	1.392(6)	C(27) - C(28)	1.437(6)
C(27) - C(32)	1.397(6)	C(28) - C(29)	1.403(6)
C(29) - C(30)	1.413(7)	C(30) - C(31)	1.369(7)
C(31) - C(32)	1.401(6)	C(33) - O(34)	1.165(6)
C(35) - O(36)	1.153(6)	C(37) - O(38)	1.162(6)
C(50) - C(51)	1.302(12)	C(50) - C(55)	1.343(10)
C(51) - C(52)	1.319(11)	C(52) - C(53)	1.341(11)
C(53) - C(54)	1.360(9)	C(54) - C(55)	1.363(9)

Table S3. Bond angles (°) for **22**

C(27) - Cr(1) - C(28)	37.7(1)	C(27) - Cr(1) - C(29)	67.2(2)
C(28) - Cr(1) -C(29)	37.3(2)	C(27) - Cr(1) - C(30)	79.1(2)
C(28) - Cr(1) - C(30)	67.5(2)	C(29) - Cr(1) - C(30)	37.5(2)
C(27) - Cr(1) - C(31)	66.9(2)	C(28) - Cr(1) - C(31)	79.4(2)
C(29) - Cr(1) - C(31)	66.5(2)	C(30) - Cr(1) - C(31)	36.2(2)
C(27) - Cr(1) - C(32)	36.6(1)	C(28) - Cr(1) - C(32)	66.9(2)
C(29) - Cr(1) - C(32)	78.4(2)	C(30) - Cr(1) - C(32)	66.0(2)
C(31) - Cr(1) - C(32)	37.1(2)	C(27) - Cr(1) - C(33)	94.0(2)
C(28) - Cr(1) - C(33)	89.2(2)	C(29) - Cr(1) - C(33)	113.1(2)
C(30) - Cr(1) - C(33)	150.2(2)	C(31) - Cr(1) - C(33)	159.8(2)
C(32) - Cr(1) - C(33)	122.9(2)	C(27) - Cr(1) - C(35)	157.9(2)
C(28) - Cr(1) - C(35)	120.7(2)	C(29) - Cr(1) - C(35)	91.4(2)
C(30) - Cr(1) - C(35)	87.2(2)	C(31) - Cr(1) - C(35)	110.6(2)
C(32) - Cr(1) - C(35)	147.6(2)	C(33) - Cr(1) - C(35)	89.5(2)
C(27) - Cr(1) - C(37)	112.2(2)	C(28) - Cr(1) - C(37)	149.2(2)
C(29) - Cr(1) - C(37)	160.2(2)	C(30) - Cr(1) - C(37)	122.9(2)
C(31) - Cr(1) - C(37)	94.6(2)	C(32) - Cr(1) - C(37)	90.1(2)
C(33) - Cr(1) - C(37)	86.6(2)	C(35) - Cr(1) - C(37)	89.7(2)
C(2) - C(1) - C(3)	112.0(3)	C(2) - C(1) - C(9)	110.1(3)
C(3) - C(1) - C(9)	111.2(3)	C(2) - C(1) - C(15)	106.7(3)
C(3) - C(1) - C(15)	102.9(3)	C(9) - C(1) - C(15)	113.8(3)
C(1) - C(2) - C(21)	117.4(3)		
C(1) - C(2) - C(27)	112.8(3)	C(21) - C(2) - C(27)	110.5(3)
C(1) - C(3) - C(4)	125.8(3)	C(1) - C(3) - C(8)	117.4(3)
C(4) - C(3) - C(8)	116.7(4)	C(3) - C(4) - C(5)	120.6(4)
C(6) - C(7) - C(8)	120.5(4)	C(5) - C(6) - C(7)	118.3(4)
C(1) - C(9) - C(10)	121.1(3)	C(1) - C(9) - C(14)	122.3(3)
C(10) - C(9) - C(14)	116.5(4)	C(9) - C(10) - C(11)	121.8(4)
C(10) - C(11) - C(12)	120.6(4)	C(11) - C(12) - C(13)	118.4(4)
C(12) - C(13) - C(14)	121.3(4)	C(9) - C(14) - C(13)	121.3(4)
C(1) - C(15) - C(16)	123.4(3)	C(1) - C(15) - C(20)	118.8(3)
C(16) - C(15) - C(20)	117.5(4)	C(15) - C(16) - C(17)	121.2(4)
C(16) - C(17) - C(18)	120.4(4)	C(17) - C(18) - C(19)	119.8(4)
C(18) - C(19) - C(20)	119.8(4)	C(15) - C(20) - C(19)	121.2(4)
C(2) - C(21) - C(22)	117.0(3)	C(2) - C(21) - C(26)	125.2(3)
C(22) - C(21) - C(26)	117.7(4)	C(21) - C(22) - C(23)	120.9(4)
C(22) - C(23) - C(24)	120.2(4)	C(23) - C(24) - C(25)	120.0(4)
C(24) - C(25) - C(26)	120.0(5)	C(21) - C(26 - C(25)	121.2(4)
Cr(1) - C(27) - C(2)	130.5(2)	Cr(1) - C(27) - C(28)	69.1(2)
C(2) - C(27) - C(28)	120.2(3)	Cr(1) - C(27) - C(32)	69.6(2)
C(2) - C(27) - C(32)	122.6(3)	C(28) - C(27) - C(32)	117.2(4)
Cr(1) - C(28) - C(27)	73.2(2)	Cr(1) - C(28) - C(29)	71.3(2)
C(27) - C(28) - C(29)	119.8(4)	Cr(1) - C(29) - C(28)	71.4(2)
Cr(1) - C(29) - C(30)	71.5(3)	C(28) - C(29) - C(30)	120.3(4)

Cr(1) - C(30) - C(29)	71.0(3)	Cr(1) - C(30) - C(31)	72.0(3)
C(29) - C(30) - C(31)	120.3(4)	Cr(1) - C(31) - C(30)	71.8(3)
Cr(1) - C(31) - C(32)	71.1(3)	Cr(30) - C(31) - C(32)	119.7(4)
Cr(1) - C(32) - C(27)	73.8(2)	Cr(1) - C(32) - C(31)	71.8(3)
C(27) - C(32) - C(31)	122.6(4)	Cr(1) - C(33) - O(34)	177.9(4)
C(1) - C(35) - C(36)	177.5(4)	Cr(1) - C(37) - O(38)	177.9(4)
C(51) - C(50) - C(55)	120.6(7)	C(50) - C(51) - C(52)	122.6(7)
C(51) - C(52) - C(53)	119.4(7)	C(52) - C(53) - C(54)	119.1(6)
C(53) - C(54) - C(55)	120.2(6)	C(50) - C(55) - C(54)	118.1(6)

Table S4. Anisotropic thermal parameters (A° x 10^3) for **22**

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cr(1)	68 (1)	42 (1)	30 (1)	-4 (1)	-15 (1)	-4 (1)
C(1)	43 (2)	43 (2)	20 (2)	-1 (2)	-8 (2)	-5 (2)
C(2)	40 (2)	44 (2)	23 (2)	-3 (2)	-6 (2)	-4 (2)
C(3)	42 (2)	49 (3)	28 (2)	-7 (2)	-1 (2)	-0 (2)
C(4)	50 (3)	53 (3)	39 (2)	-10 (2)	-3 (2)	1 (2)
C(5)	67 (3)	53 (3)	54 (3)	-7 (2)	-1 (2)	7 (2)
C(6)	63 (3)	60 (3)	59 (3)	-23 (2)	4 (2)	-7 (2)
C(7)	66 (3)	78 (3)	37 (3)	-26 (2)	-2 (2)	-8 (3)
C(8)	62 (3)	60 (3)	33 (2)	-10 (2)	-5 (2)	4 (2)
C(9)	46 (3)	53 (3)	19 (2)	-1 (2)	-8 (2)	-2 (2)
C(10)	40 (3)	58 (3)	40 (2)	-3 (2)	-9 (2)	-3 (2)
C(11)	59 (3)	68 (3)	49 (3)	-9 (2)	-11 (2)	-16 (2)
C(12)	40 (3)	91 (3)	61 (3)	-14 (3)	-6 (2)	-5 (3)
C(13)	54 (3)	80 (3)	40 (3)	-10 (2)	-7 (2)	17 (3)
C(14)	48 (3)	53 (3)	30(2)	-2 (2)	-10 (2)	3 (2)
C(15)	46 (3)	51 (3)	20(2)	-7 (2)	-4 (2)	1 (2)
C(16)	47 (3)	67 (3)	37(2)	10 (2)	-4 (2)	5 (2)
C(17)	67 (3)	80 (4)	54 (3)	34 (2)	-1 (2)	9 (3)
C(18)	81 (4)	61 (3)	50 (3)	15 (2)	7 (2)	-1 (3)
C(19)	49 (3)	68 (3)	50 (3)	-4 (2)	7 (2)	-6 (2)
C(20)	50 (3)	58 (3)	32(2)	5 (2)	-0 (2)	2 (2)
C(21)	50 (3)	38(2)	30(2)	-9 (2)	-4 (2)	-2 (2)
C(22)	55 (3)	57 (3)	39(2)	8 (2)	-2 (2)	3 (2)
C(23)	83 (4)	69 (3)	47 (3)	18 (3)	-2 (3)	13 (3)
C(24)	108 (4)	60 (3)	42 (3)	12 (2)	13 (3)	-8 (3)
C(25)	86 (4)	83 (4)	37 (3)	7 (3)	2 (2)	-31 (3)
C(26)	64 (3)	69 (3)	30(2)	-1 (2)	-6 (2)	-13 (3)
C(27)	51 (3)	49 (3)	25(2)	-2 (2)	-11 (2)	1(2)
C(28)	90 (3)	47 (3)	28(2)	0 (2)	-13 (2)	-13 (3)
C(29)	112 (4)	44 (3)	44 (3)	5 (2)	-25 (3)	-14 (3)
C(30)	128(5)	54 (3)	50 (3)	-10 (2)	-29 (3)	30 (3)
C(31)	73 (3)	66 (3)	58 (3)	-15 (3)	-13 (2)	12 (3)
C(32)	60 (3)	54 (3)	38(2)	-13 (2)	-13 (2)	5 (2)
C(33)	72 (4)	58 (3)	45 (3)	-6 (2)	-20 (3)	-10 (3)
O(34)	72(2)	83 (3)	104 (3)	-8 (2)	-17 (2)	5 (2)
C(35)	80 (3)	61 (3)	42 (3)	-6 (3)	-20 (2)	-10 (3)
O(36)	133 (3)	72(2)	77 (3)	-23 (2)	-36 (2)	-24 (2)
C(37)	86 (4)	62 (3)	32 (3)	-6 (3)	-10 (2)	-17 (3)
O(38)	156 (4)	91 (3)	50(2)	12 (2)	-4 (2)	-29 (3)

C(50)	108 (6)	71 (4)	101 (5)	6 (4)	-31 (4)	3 (4)
C(51)	118 (6)	136(7)	95 (5)	-15 (5)	14 (5)	36 (6)
C(52)	72 (4)	138 (6)	147(7)	40 (5)	12 (4)	8 (5)
C(53)	104 (5)	92 (4)	156 (6)	2 (4)	-58 (4)	-22 (4)
C(54)	146 (6)	139 (6)	90 (5)	-34 (4)	-8 (4)	22 (5)
C(55)	75 (4)	116 (5)	110 (5)	38(5)	9 (4)	10 (4)

The anisotropic temperature factor exponent takes the form:

$-2\pi^2 (h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$

Table S5. H - Atom cordinates (x 10^4) and isotropic thermal parameters
(A x 10^3) for **22**

	X	Y	Z	U
H(2)	3624	9541	1669	43
H(4)	3695	7461	1468	58
H(5)	4301	5725	963	70
H(6)	3877	5386	-42	74
H(7)	2835	6818	-550	71
H(8)	2233	8553	-56	60
H(10)	1176	7578	824	51
H(11)	-553	7544	846	67
H(12)	-1427	9375	1045	78
H(13)	-556	11229	1212	65
H(14)	1175	11268	1198	49
H(16)	1649	11213	280	60
H(17)	2455	12707	-312	82
H(18)	4168	12845	-303	71
H(19)	5143	11455	284	65
H(20)	4381	9957	874	52
H(22)	4135	8529	2496	57
H(23)	3883	7067	3256	76
H(24)	2310	6267	3388	84
H(25)	975	6933	2773	77
H(26)	1223	8396	2011	67
H(28)	3808	11872	1539	71
H(29)	3421	13885	1897	79
H(30)	2102	14151	1544	82
H(31)	1175	12430	2826	75
H(32)	1550	10418	2463	59
H(50)	1652	15534	1559	113
H(51)	125	15402	1924	143
H(52)	-1134	14384	1417	131
H(53)	-851	13431	522	127
H(54)	710	13548	140	139
H(55)	1977	14607	663	115

Table S6. Atom Coordinates ($X10^4$) and Temperature factors (A° X 10) for **28**

atom	x	y	z	U_{eq}
Cr(1)	980(1)	4390(1)	2003(1)	46(1) *
C(1)	1598(1)	6136(4)	3433(3)	40(2) *
C(2)	1441(1)	5420(4)	4063(2)	42(2) *
C(3)	1660(1)	7548(4)	3606(3)	42(2) *
C(4)	1939(1)	7940(5)	4220(3)	53(2) *
C(5)	1983(2)	9193(5)	4415(3)	69(2) *
C(6)	1754(2)	10076	3185(3)	81(2) *
C(7)	1486(2)	9724(5)	3370(4)	83(2) *
C(8)	1439(2)	8463(5)	3174 (3)	61(2) *
C(9)	1302(1)	5990(4)	2685(3)	41(2) *
C(10)	891(1)	6113(4)	2599(3)	47(2) *
C(11)	634(2)	6131(5)	1910(3)	56(2) *
C(12)	779 (2)	6026(5)	1279(3)	55(2) *
C(13)	1174(2)	5884(4)	1346(3)	51(2) *
C(14)	1432(1)	5871(4)	2046(3)	43(2) *
C(15)	1987(1)	5499(4)	3364(3)	42(2) *
C(16)	1994(1)	4222(4)	3237(3)	46(2) *
C(17)	2322(2)	3650(5)	3105(3)	62(2) *
C(18)	2653(2)	4330(6)	3104(3)	73(3) *
C(19)	2653(2)	5587(6)	3232(3)	70(2) *
C(20)	2320(1)	6185(5)	3351(3)	56(2) *
C(21)	1071(1)	5923(4)	4258(2)	41(2) *
C(22)	1017(1)	7131(5)	4476(3)	50(2) *
C(23)	674 (2)	7485(6)	4666(3)	40(2) *
C(24)	378(2)	6613(7)	4632(3)	69(3) *
C(25)	427(2)	5420(6)	4431(3)	65 (2) *
C(26)	773(1)	5061(5)	4253(3)	54(2) *
C(27)	1741(1)	5099(5)	4768(3)	42(2) *
C(28)	1901(2)	3903(5)	4870(3)	60(2) *
C(29)	2150(2)	3541(5)	5518(3)	72(3) *
C(30)	2243(2)	4360(5)	6089(3)	64(2) *
C(31)	2085(1)	5541(5)	6009(3)	56(2) *
C(32)	1830(1)	5906(5)	5360(3)	47(2) *
C(33)	545(2)	3513(6)	1544(3)	64(2) *
C(34)	265(1)	2957(5)	1276(2)	102(2) *
C(35)	993(2)	3323(5)	2756(3)	52(2) *
C(36)	1008(1)	2588(4)	3211(2)	75(2) *
C(37)	1278(2)	3208(5)	1690(3)	57(2) *
C(38)	1471(1)	2432(4)	1528(3)	91(2) *

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table S7. Bond lengths (A°) for 28

Cr(1) - C(9)	2.272(4)	Cr(1) - C(10)	2.216(5)
Cr(1) - C(11)	2.204(5)	Cr(1) - C(12)	2.226(5)
Cr(1) - C(13)	2.221(5)	Cr(1) - C(14)	2.229(5)
Cr(1) - C(33)	1.826(6)	Cr(1) - C(35)	1.814(6)
Cr(1) - C(37)	1.825(6)	C(1) - C(2)	1.615(7)
C(1) - C(3)	1.545(6)	C(1) - C(9)	1.551(6)
C(1) - C(15)	1.562(7)	C(2) - C(21)	1.531(7)
C(2) - C(27)	1.528(6)	C(3) - C(4)	1.394(6)
C(3) - C(8)	1.385(7)	C(4) - C(5)	1.385(7)
C(5) - C(6)	1.373(8)	C(6) - C(7)	1.365(8)
C(7) - C(8)	1.393(8)	C(9) - C(10)	1.423(7)
C(9) - C(14)	1.394(7)	C(10) - C(11)	1.397(6)
C(11) - C(12)	1.408(8)	C(12) - C(13)	1.372(7)
C(13) - C(14)	1.414(6)	C(15) - C(16)	1.384(7)
C(15) - C(20)	1.385(7)	C(16) - C(17)	1.377(8)
C(17) - C(18)	1.375(9)	C(18) - C(19)	1.361(9)
C(19) - C(20)	1.398(8)	C(21) - C(22)	1.380(7)
C(21) - C(26)	1.394(7)	C(22) - C(23)	1.390(8)
C(23) - C(24)	1.388(9)	C(24) - C(25)	1.351(10)
C(25) - C(26)	1.392(8)	C(27) - C(28)	1.398(7)
C(27) - C(32)	1.387(7)	C(28) - C(29)	1.380(7)
C(29) - C(30)	1.366(8)	C(30) - C(31)	1.371(8)
C(31) - C(32)	1.392(6)	C(33) - O(34)	1.158(7)
C(35) - O(36)	1.154(7)	C(37) - O(38)	1.157(8)

Table S8. Bond angles (°) for **28**

C(9) - Cr(1) - C(10)	36.9	C(9) - Cr(1) - C(11)	66.7
C(10) - Cr(1) - C(11)	36.8	C(9) - Cr(1) - C(12)	78.2
C(10) - Cr(1) - C(12)	66.4	C(11) - Cr(1) - C(12)	37.0
C(9) - Cr(1) - C(13)	66.4	C(10) - Cr(1) - C(13)	77.7
C(11) - Cr(1) - C(13)	65.7	C(12) - Cr(1) - C(13)	35.9
C(9) - Cr(1) - C(14)	36.1	C(10) - Cr(1) - C(14)	65.1
C(11) - Cr(1) - C(14)	77.4	C(12) - Cr(1) - C(14)	65.6
C(13) - Cr(1) - C(14)	37.1	C(9) - Cr(1) - C(33)	154.4
C(10) - Cr(1) - C(33)	117.5	C(11) - Cr(1) - C(33)	90.5
C(12) - Cr(1) - C(33)	90.1	C(13) - Cr(1) - C(33)	115.8
C(14) - Cr(1) - C(33)	152.9	C(9) - Cr(1) - C(35)	96.3
C(10) - Cr(1) - C(35)	95.8	C(11) - Cr(1) - C(35)	120.1
C(12) - Cr(1) - C(35)	156.7	C(13) - Cr(1) - C(35)	158.9
C(14) - Cr(1) - C(35)	122.1	C(33) - Cr(1) - C(35)	85.0
C(9) - Cr(1) - C(37)	117.0	C(10) - Cr(1) - C(37)	153.9
C(11) - Cr(1) - C(37)	154.8	C(12) - Cr(1) - C(37)	117.8
C(13) - Cr(1) - C(37)	92.2	C(14) - Cr(1) - C(37)	92.4
C(33) - Cr(1) - C(37)	88.5	C(35) - Cr(1) - C(37)	84.9
C(2) - C(1) - C(3)	111.2	C(2) - C(1) - C(9)	110.4
C(3) - C(1) - C(9)	108.7	C(2) - C(1) - C(15)	108.4
C(3) - C(1) - C(15)	111.0	C(9) - C(1) - C(15)	107.0
C(1) - C(2) - C(21)	117.9	C(1) - C(2) - C(27)	117.5
C(21) - C(2) - C(27)	108.6	C(1) - C(3) - C(4)	120.3
C(1) - C(3) - C(8)	122.1	C(4) - C(3) - C(8)	117.6
C(3) - C(4) - C(5)	121.6	C(4) - C(5) - C(6)	119.4
C(5) - C(6) - C(7)	120.3	C(6) - C(7) - C(8)	120.4
C(3) - C(8) - C(7)	120.7	Cr(1) - C(9) - C(1)	136.7
Cr(1) - C(9) - C(10)	69.4	C(1) - C(9) - C(10)	122.6
Cr(1) - C(9) - C(14)	70.3	C(1) - C(9) - C(14)	120.7
C(10) - C(9) - C(14)	116.3	Cr(1) - C(10) - C(9)	73.7
Cr(1) - C(10) - C(11)	71.1	C(9) - C(10) - C(11)	121.5
Cr(1) - C(11) - C(10)	72.1	Cr(1) - C(11) - C(12)	72.3
C(10) - C(11) - C(12)	120.3	Cr(1) - C(12) - C(11)	70.6
Cr(1) - C(12) - C(13)	71.9	C(11) - C(12) - C(13)	119.4
Cr(1) - C(13) - C(12)	72.2	Cr(1) - C(13) - C(14)	71.8
C(12) - C(13) - C(14)	120.1	Cr(1) - C(14) - C(9)	73.7
C(1) - C(14) - C(13)	71.2	C(9) - C(14) - C(13)	122.5
C(1) - C(15) - C(16)	119.6	C(1) - C(15) - C(20)	122.2
C(16) - C(15) - C(20)	117.9	C(15) - C(16) - C(17)	121.1
C(16) - C(17) - C(18)	120.9	C(17) - C(18) - C(19)	118.9
C(18) - C(19) - C(20)	120.9	C(15) - C(20) - C(19)	120.4
C(2) - C(21) - C(22)	125.7	C(2) - C(21) - C(26)	116.7
C(22) - C(21) - C(26)	117.5	C(21) - C(22) - C(23)	121.3
C(22) - C(23) - C(24)	119.7	C230 - C(24) - C(25)	119.9
C(24) - C(25) - C(26)	120.3	C(21) - C(26) - C(25)	121.2
C(2) - C(27) - C(28)	120.0	C(2) - C(27) - C(32)	122.8

C(28) - C(27) - C(32)	116.7	C(27) - C(28) - C(29)	122.2
C(28) - C(29) - C(30)	120.2	C(29) - C(30) - C(31)	119.1
C(30) - C(31) - C(32)	120.9	C(27) - C(31) - C(32)	120.8
Cr(1) - C(33) - O(34)	177.6	Cr(1) - C(35) - O(36)	175.8
Cr(1) - C(37) - O(38)	176.4		

Table S9. Anisotropic temperature factors $(AX10^3)$ for **28**

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr(1)	51 (1)	46 (1)	40 (1)	2 (1)	6 (1)	3 (1)
C(1)	46 (3)	40 (3)	34 (3)	-1 (2)	9 (2)	2 (2)
C(2)	47 (3)	40 (3)	37 (3)	-1 (2)	6 (2)	-3 (2)
C(3)	44 (3)	41 (3)	45 (3)	3 (3)	16 (2)	-0 (2)
C(4)	58 (3)	48 (3)	58 (4)	-2 (3)	25 (3)	-10 (3)
C(5)	79 (4)	60 (4)	69 (4)	-16 (3)	23 (3)	-16 (3)
C(6)	105 (5)	45 (3)	104 (5)	-23 (2)	43 (4)	-9 (3)
C(7)	97 (5)	47 (4)	103 (5)	3 (3)	22 (4)	11 (3)
C(8)	62 (4)	49 (3)	69 (4)	-1 (3)	8 (3)	7 (3)
C(9)	47 (3)	33 (3)	41 (3)	4 (2)	8 (2)	6 (2)
C(10)	51 (3)	51 (3)	40 (3)	2 (3)	11 (3)	10 (2)
C(11)	51 (3)	68 (4)	45 (3)	-0 (3)	5 (3)	10 (3)
C(12)	61 (3)	54 (3)	42 (3)	5 (3)	-3 (3)	12 (3)
C(13)	74 (4)	45 (3)	36 (3)	6 (3)	15 (3)	4 (3)
C(14)	51 (3)	35 (3)	45 (3)	4 (2)	17 (2)	4 (2)
C(15)	45 (3)	44 (3)	36 (3)	4 (3)	8 (2)	4 (2)
C(16)	50 (3)	45 (3)	43 (3)	8 (3)	8 (2)	11 (2)
C(17)	71 (4)	65 (4)	48 (4)	4 (3)	12 (3)	29 (3)
C(18)	57 (4)	96 (4)	69 (4)	8 (4)	22 (3)	30 (2)
C(19)	53 (3)	86 (4)	74 (4)	17 (4)	20 (3)	2 (3)
C(20)	54 (3)	59 (3)	59 (4)	3 (3)	20 (3)	3 (3)
C(21)	41 (3)	50 (3)	32 (3)	-1 (2)	8 (2)	-1 (2)
C(22)	49 (3)	57 (3)	45 (3)	-1 (3)	13 (2)	-2 (3)
C(23)	60 (3)	71 (4)	50 (4)	1 (3)	16 (3)	16 (3)
C(24)	47 (3)	103 (5)	59 (4)	11 (4)	18 (3)	10 (2)
C(25)	52 (3)	86 (5)	58 (4)	3 (4)	12 (3)	-12 (3)
C(26)	59 (3)	57 (3)	46 (3)	4 (3)	12 (3)	-7 (3)
C(27)	46 (3)	45 (3)	39 (3)	2 (3)	15 (2)	2 (2)
C(28)	81 (4)	51 (3)	50 (4)	1 (3)	16 (3)	13 (3)
C(29)	93 (5)	60 (4)	61 (4)	21 (3)	16 (4)	28 (3)
C(30)	69 (3)	69 (4)	51 (3)	17 (3)	5 (3)	5 (3)
C(31)	52 (3)	67 (4)	46 (3)	2 (3)	5 (2)	-6 (3)
C(32)	47 (3)	49 (3)	43 (3)	5 (3)	7 (2)	-0 (2)
C(33)	64 (4)	71 (4)	50 (4)	13 (3)	2 (3)	-1 (3)
O(34)	83 (3)	119 (4)	85 (3)	17 (3)	-18 (3)	-40 (3)
C(35)	64 (4)	48 (4)	42 (3)	-3 (3)	7 (3)	-5 (3)
O(36)	109 (3)	52 (2)	58 (3)	11 (3)	10 (2)	-7 (2)
C(37)	73 (4)	44 (3)	61 (4)	2 (2)	27 (3)	-0 (3)
O(38)	107 (4)	54 (3)	124 (4)	-5 (3)	55 (3)	8 (2)

The anisotropic temperature factor exponent takes the form:
$-2\pi^2(h^2a^{*2} U_{11}{}^2 + k^2b^{*2} U_{22} +.... +2hka^*b^*U_{12})$

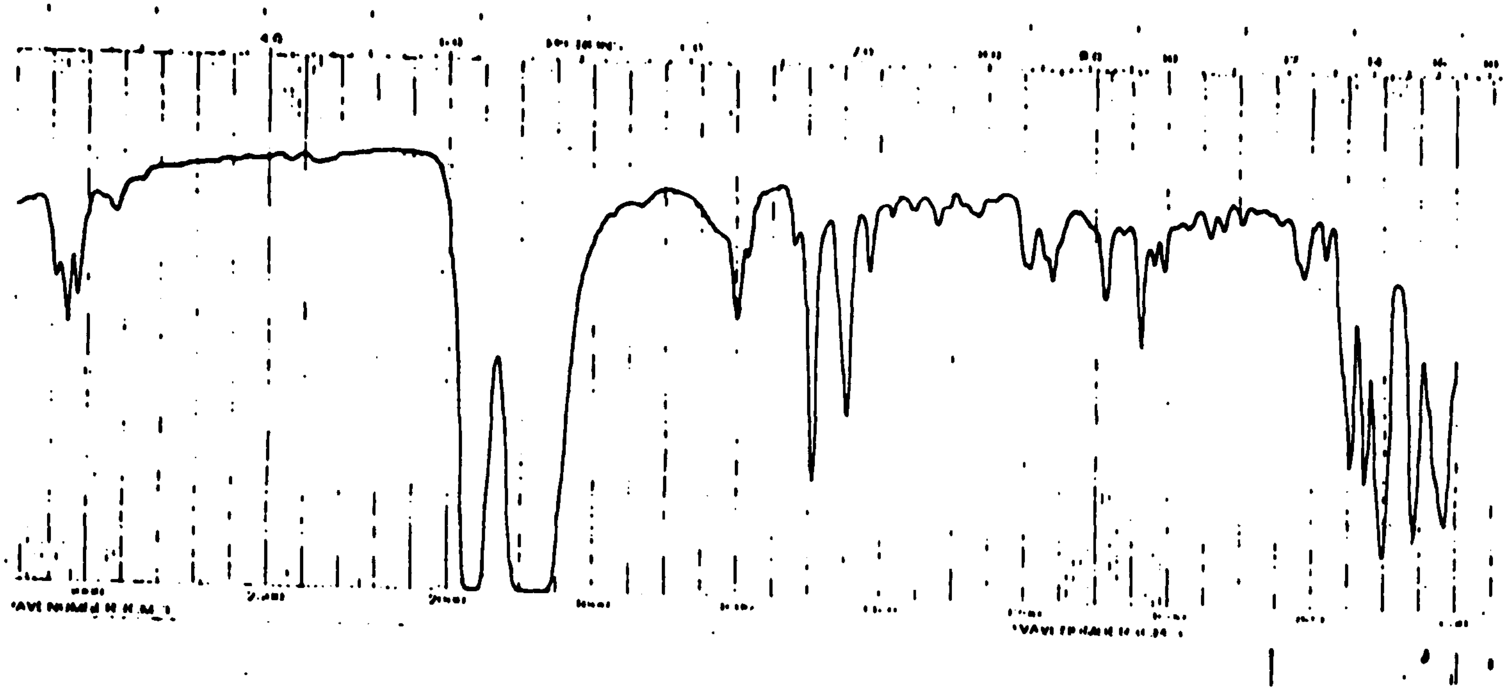
Table S10. Hydrogen coordinates (X 10^4) and temperature factors (A°X10^3) for **28**

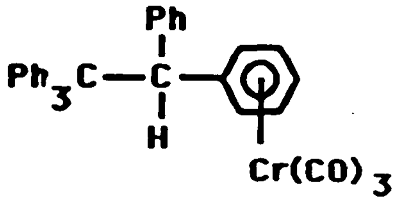
atom	x	y	z	U
H(2)	1373	4655	3794	50
H(4)	2105	7328	4514	64
H(5)	2172	9442	4847	83
H(6)	1782	10946	4119	98
H(7)	1330	10348	3068	102
H(8)	1252	8227	2737	74
H(10)	787	6187	3024	58
H(11)	358	6217	1867	69
H(12)	603	6051	805	66
H(13)	1275	5793	920	62
H(14)	1707	5778	2081	50
H(16)	1767	3726	3240	55
H(17)	2317	2764	3011	74
H(18)	2882	3923	3018	89
H(19)	2884	6070	3237	85
H(20)	2220	7076	3425	68
H(22)	1221	7739	4498	60
H(23)	643	8329	4819	72
H(24)	137	6858	4751	83
H(25)	222	4815	4412	79
H(26)	807	4204	4126	66
H(28)	1837	3311	4477	73
H(29)	2258	2709	5567	85
H(30)	2418	4114	6539	77
H(31)	2150	6123	6408	67
H(32)	1714	6726	5321	56

Table S11. Torsion angles (°) for **28**

C(9) - C(1) - C(2) - H(2)	47.4(0.3)
C(15) - C(1) - C(2) - H(2)	-69.6(0.6)
C(2) - C(1) - C(3) - C(4)	63.7(0.6)
C(2) - C(1) - C(15) - C(16)	55.2(0.5)
C(1) - C(2) - C(21) - C(22)	-56.1(0.6)
C(1) - C(2) - C(27) - C(28)	-98.1(0.6)
C(3) - C(1) - C(2) - C(21)	54.7(0.5)
C(9) - C(1) - C(2) - C(21)	-66.1(0.5)
C(2) - C(1) - C(3) - C(8)	-115.0(0.5)
C(2) - C(1) - C(9) - C(10)	43.1(0.6)
C(2) - C(1) - C(15) - C(20)	-131.4(0.4)
C(1) - C(2) - C(21) - C(26)	127.8(0.4)
C(1) - C(2) - C(27) - C(32)	90.0(0.6)
C(3) - C(1) - C(2) - C(27)	-78.4(0.5)
C(15) - C(1) - C(2) - C(27)	43.9(0.5)
C(2) - C(1) - C(9) - C(14)	-144.3(0.4)

APPENDIX II

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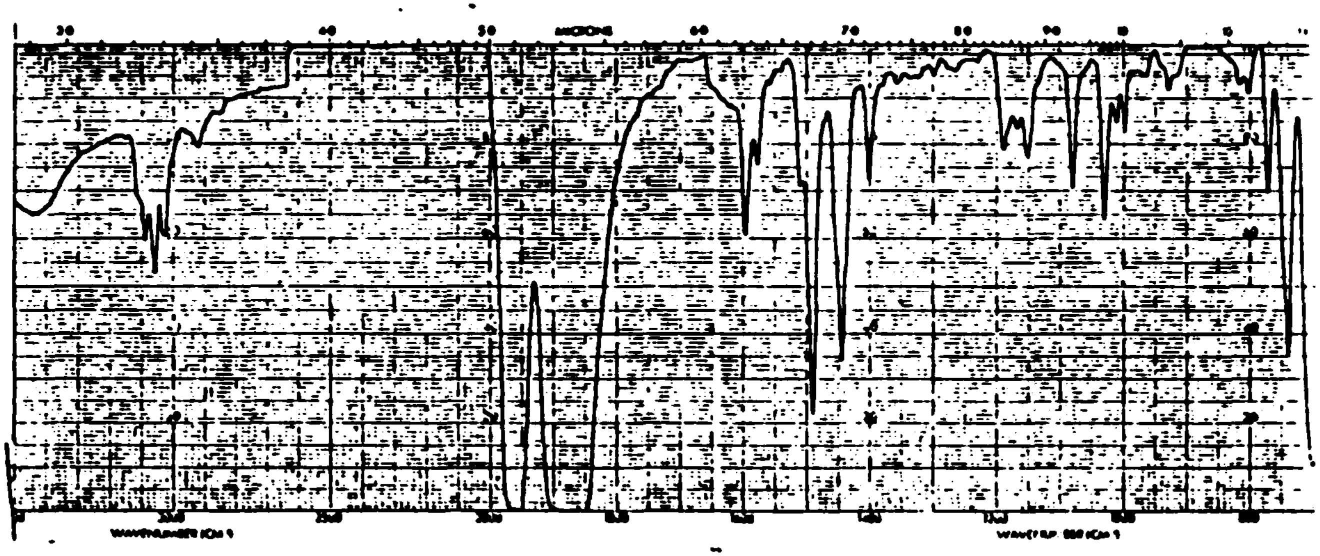
C
H
Cr(CO)3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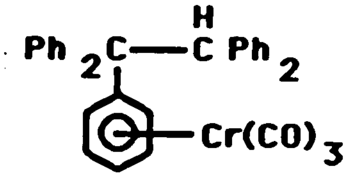
WAVENUMBER (CM-1)


H
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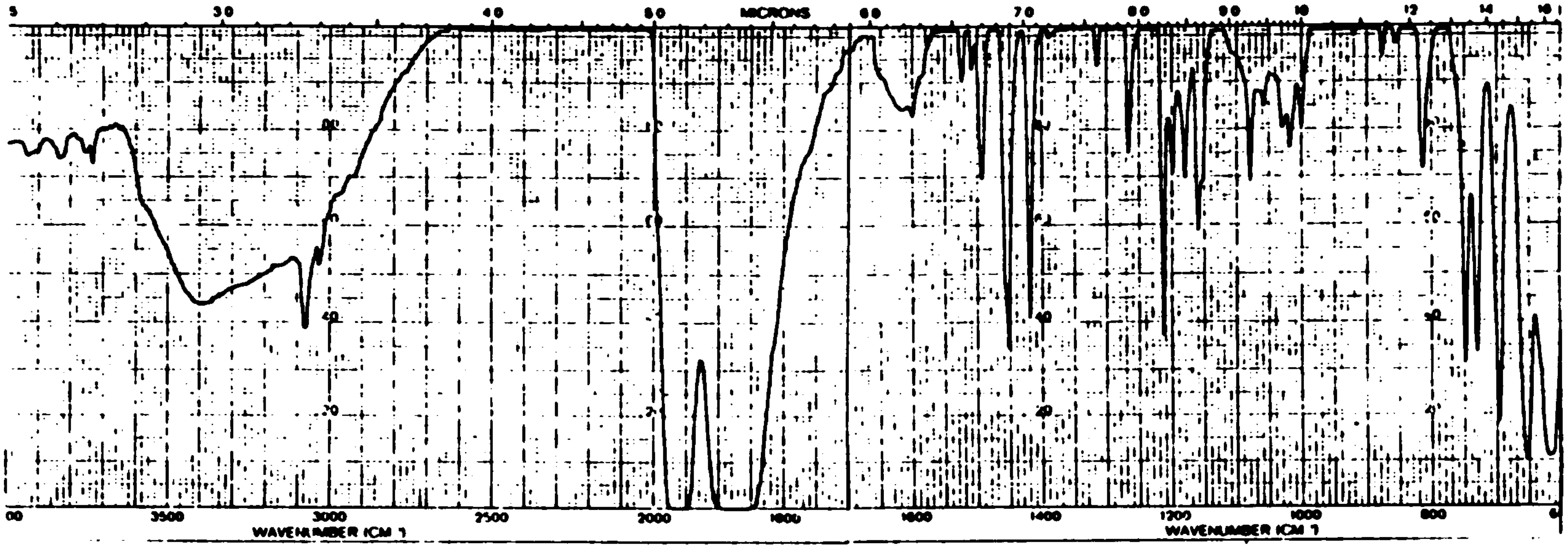
Cr(CO)3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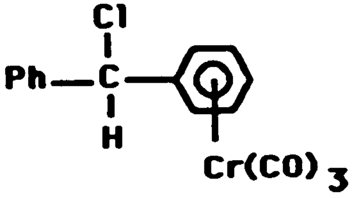
WAVENUMBER (CM⁻¹)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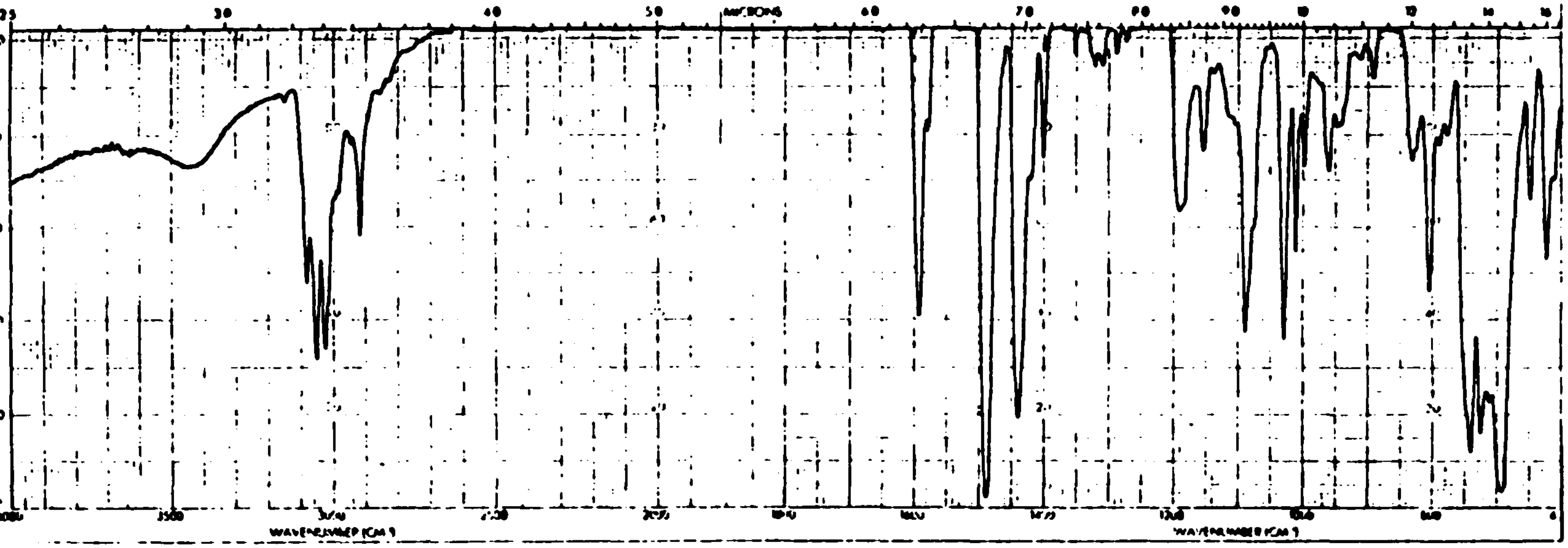
Ph
C
H
Cr(CO)3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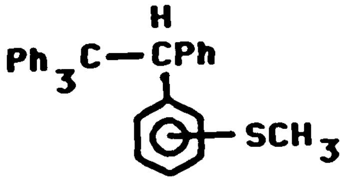
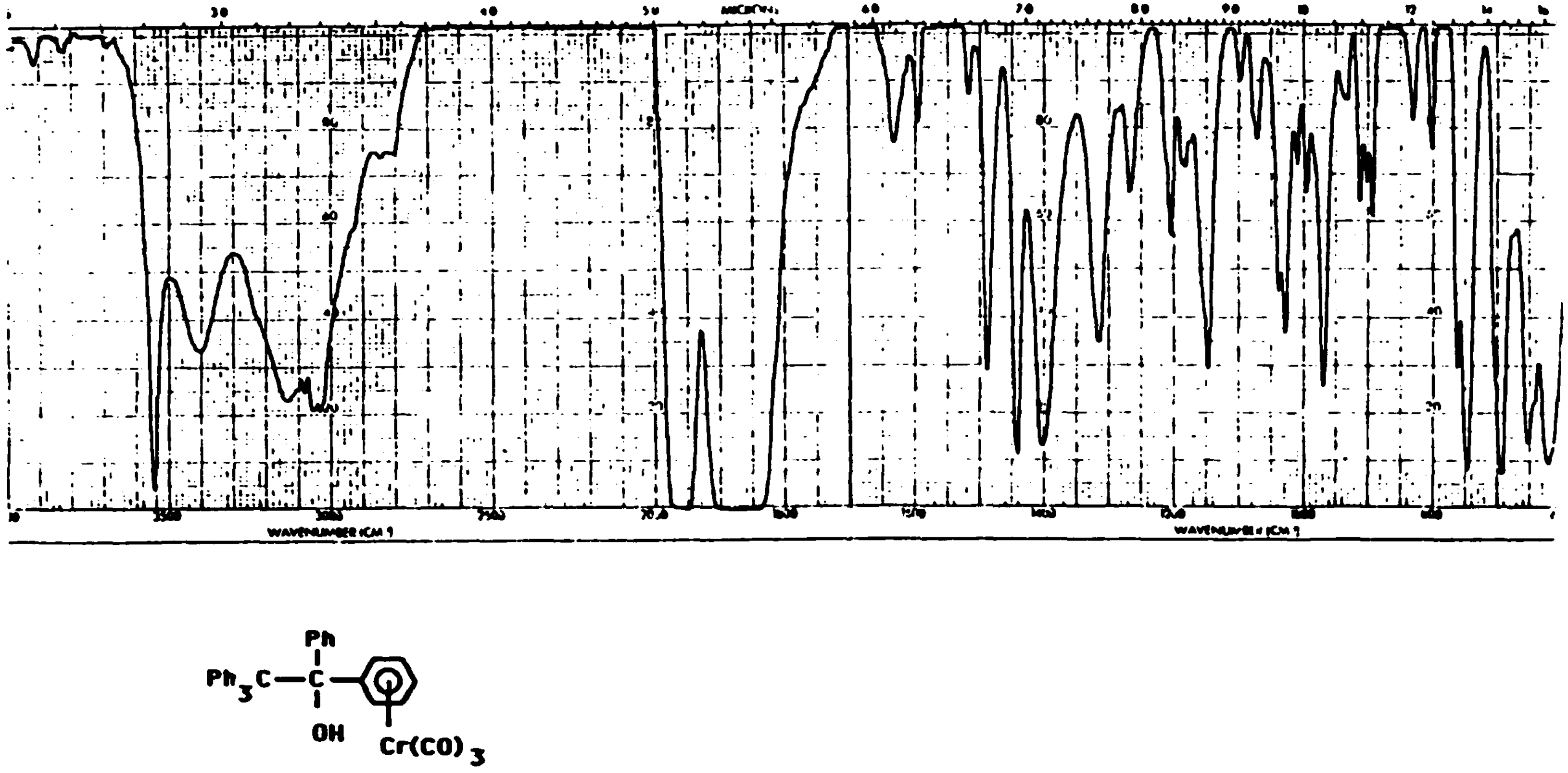
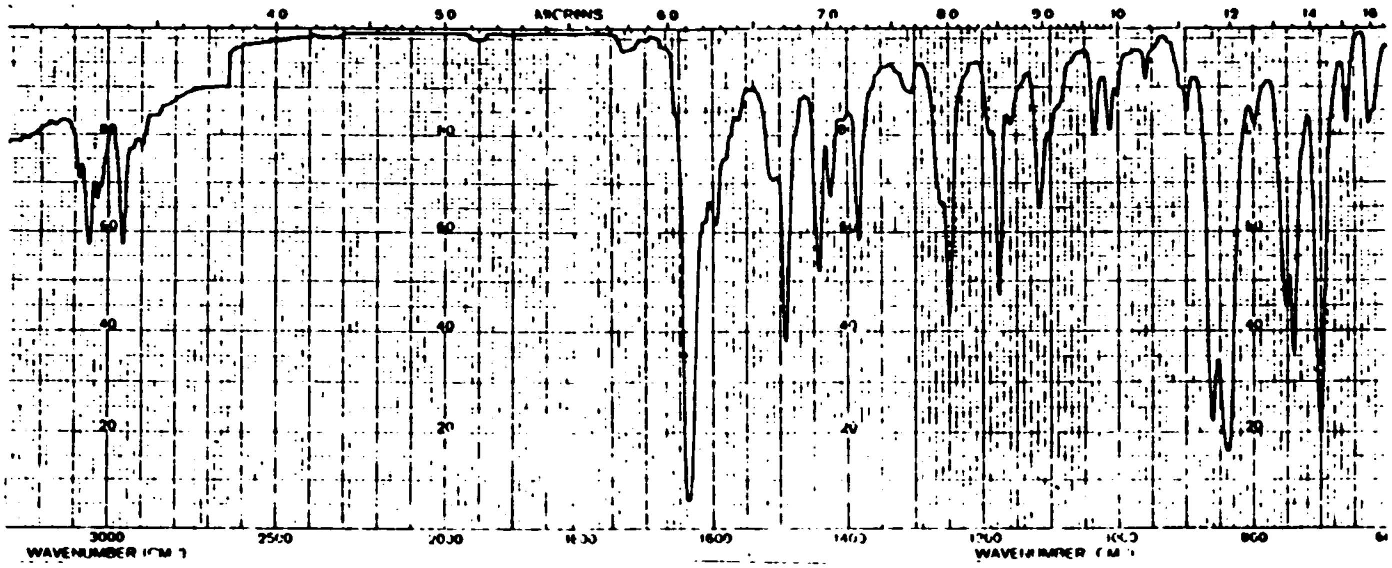
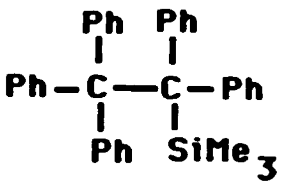
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
WAVENUMBER (CM-1)
WAVENUMBER (CM-1)

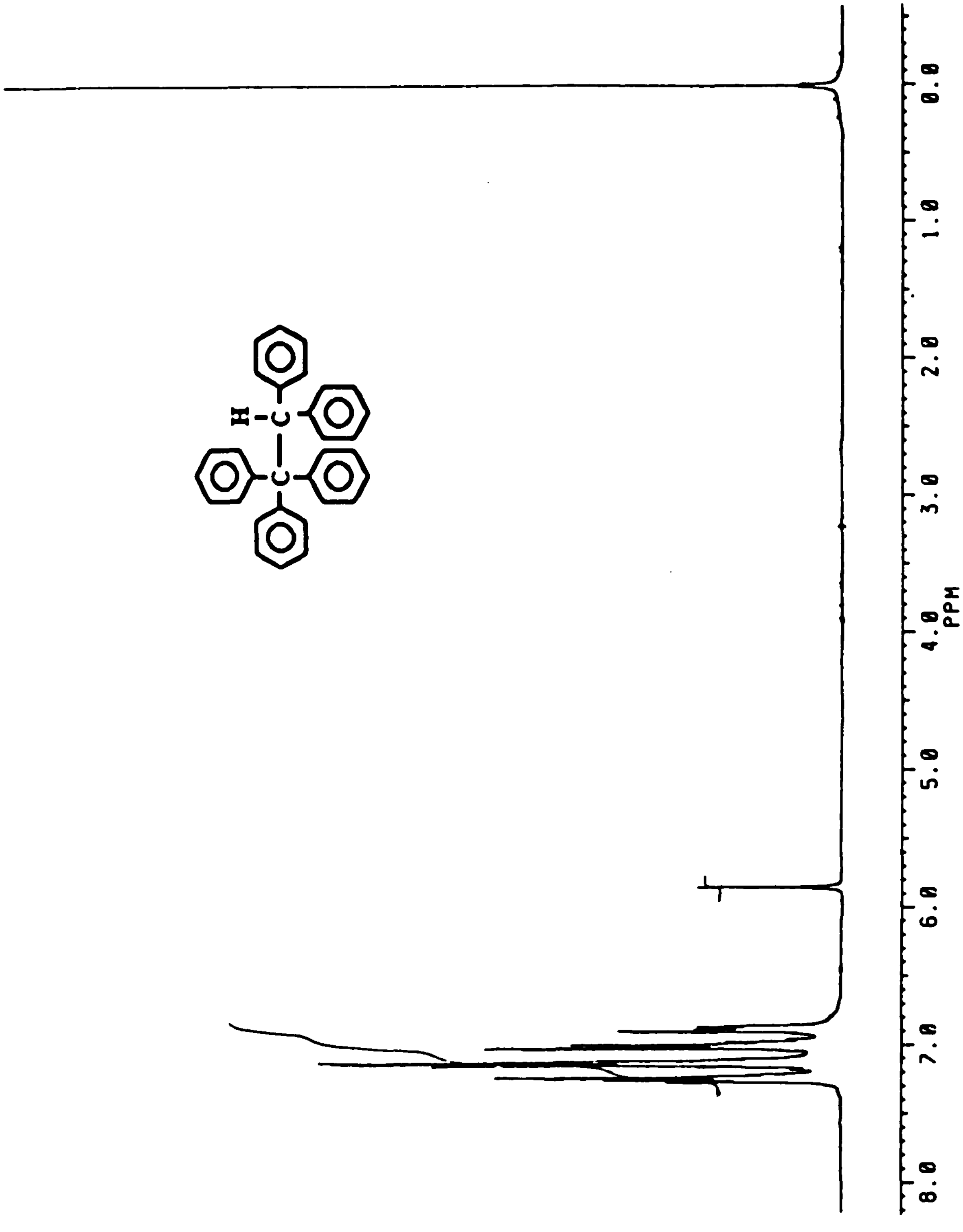

H
Ph3C—CPh
SCH3

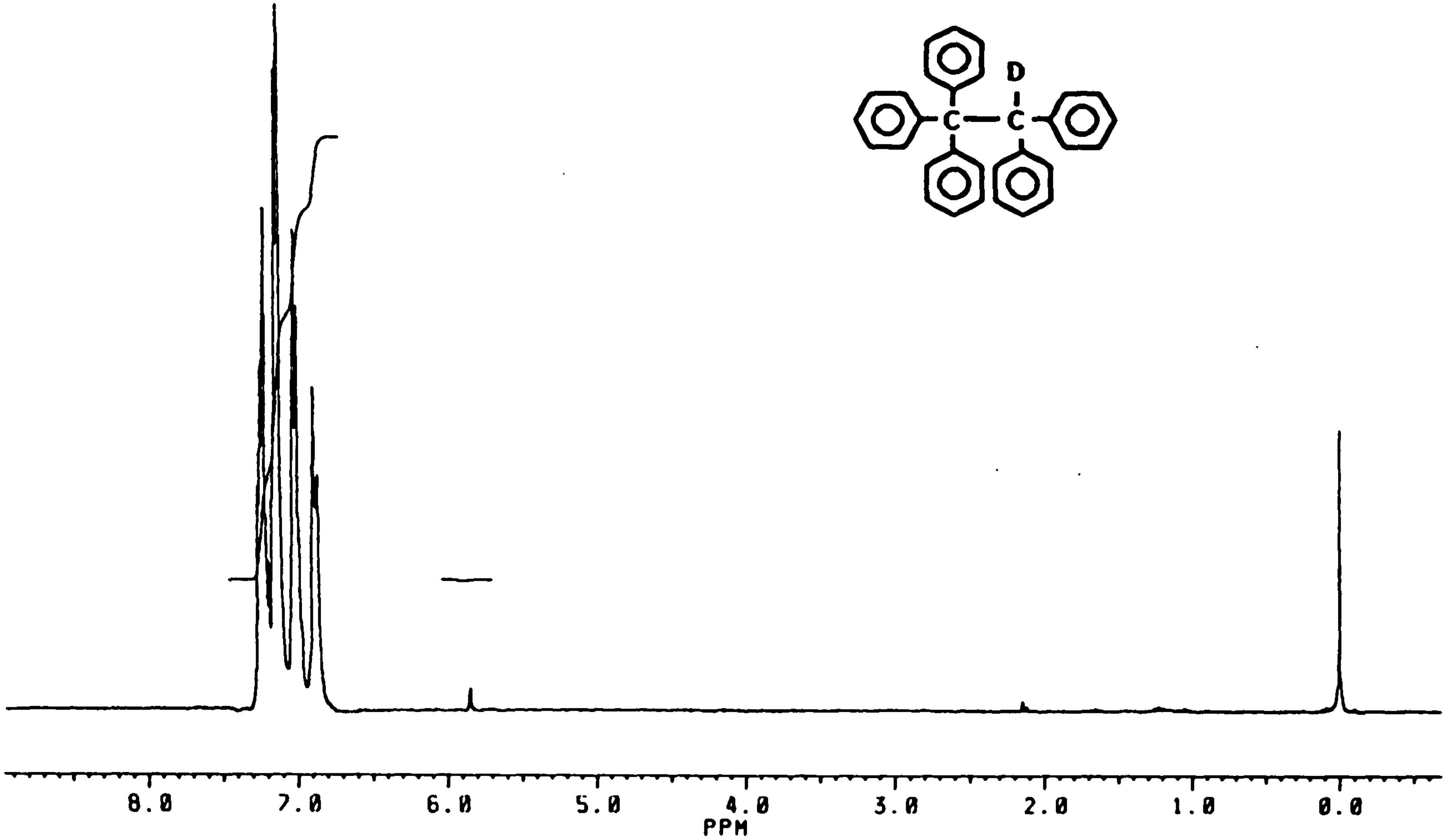

3.0
4.0
5.0
MICRONS
6.0
7.0
8.0
9.0
10
12
14
16
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
WAVENUMBER (CM-1)
WAVENUMBER (CM-1)
Ph
Ph3C
C
OH
Cr(CO)3

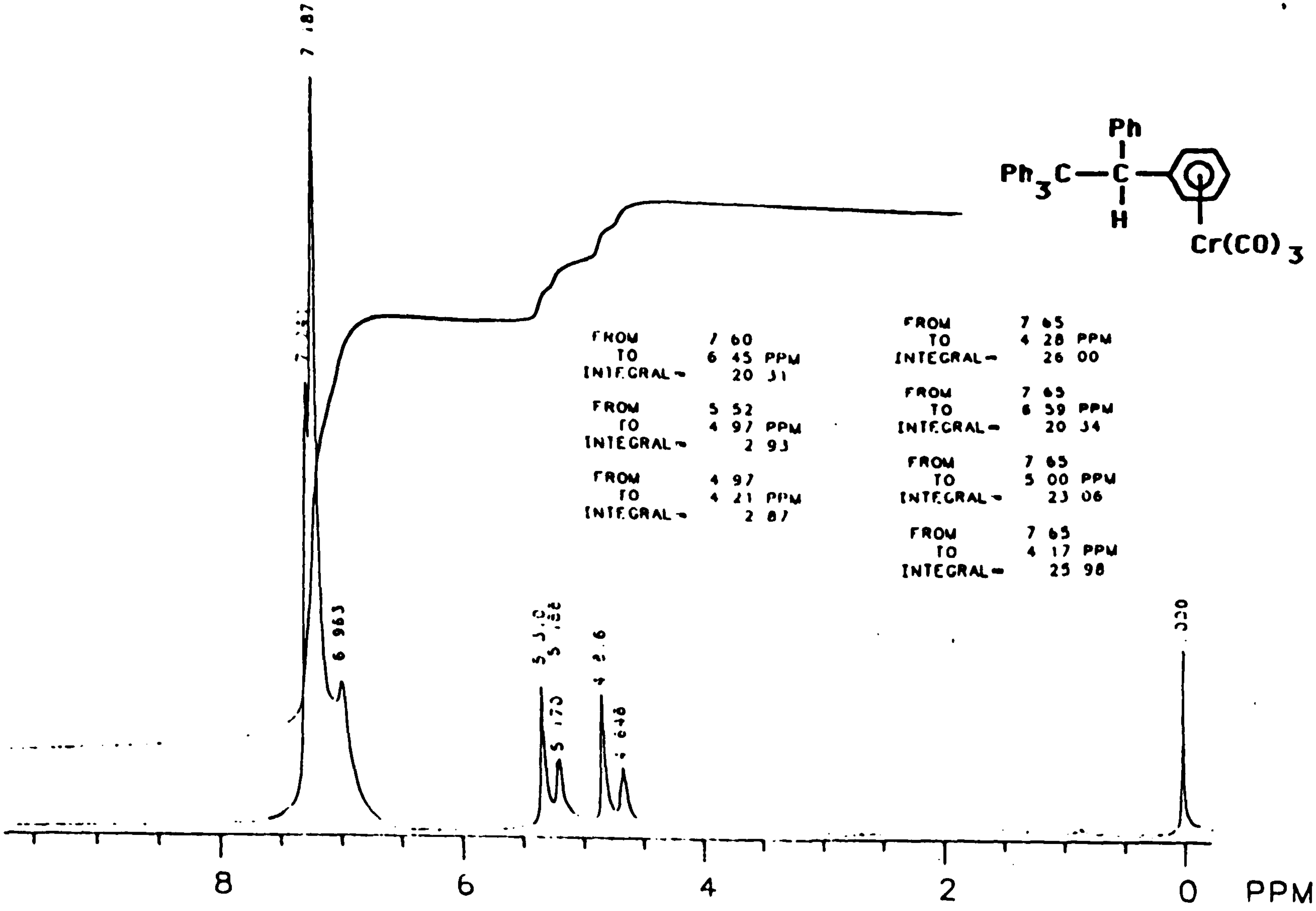


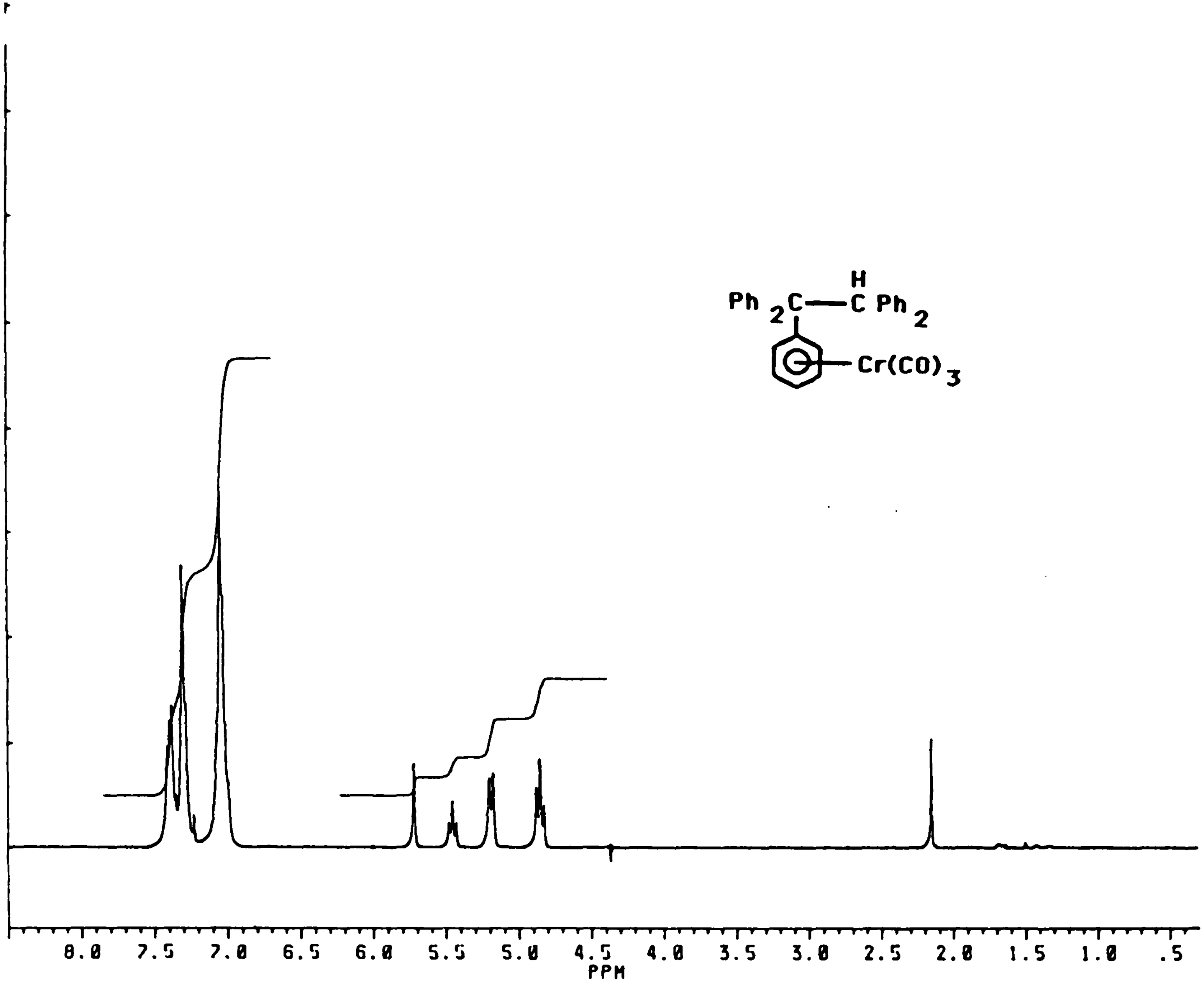


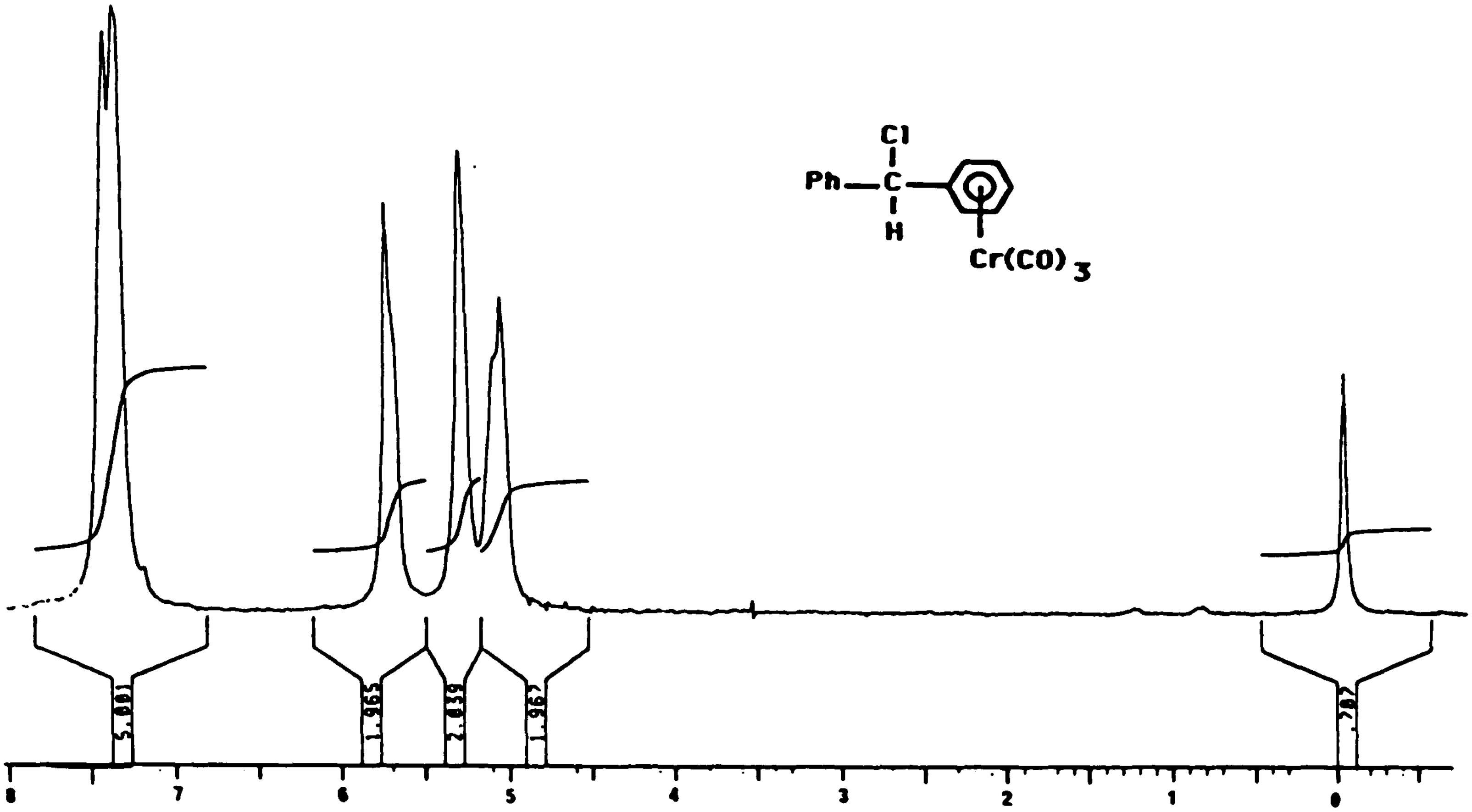
$$\mathrm{Ph_3C{-}CPh_2SiMe_3}$$


H
C
C
0.0
1.0
2.0
3.0
4.0
PPM
5.0
6.0
7.0
8.0


D
C
C
8.0
7.0
6.0
5.0
4.0
PPM
3.0
2.0
1.0
0.0


7 187
6 963
5 173
4 648
.000
Ph
Ph3C—C—
H
Cr(CO)3
FROM 7 60
TO 6 45 PPM
INTEGRAL= 20 31
FROM 5 52
TO 4 97 PPM
INTEGRAL= 2 93
FROM 4 97
TO 4 21 PPM
INTEGRAL= 2 87
FROM 7 65
TO 4 28 PPM
INTEGRAL= 26 00
FROM 7 65
TO 6 59 PPM
INTEGRAL= 20 34
FROM 7 65
TO 5 00 PPM
INTEGRAL= 23 06
FROM 7 65
TO 4 17 PPM
INTEGRAL= 25 98
8
6
4
2
0
PPM


H
Ph2C—CPh2
Cr(CO)3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
PPM



Cl
Ph
C
H
Cr(CO)3
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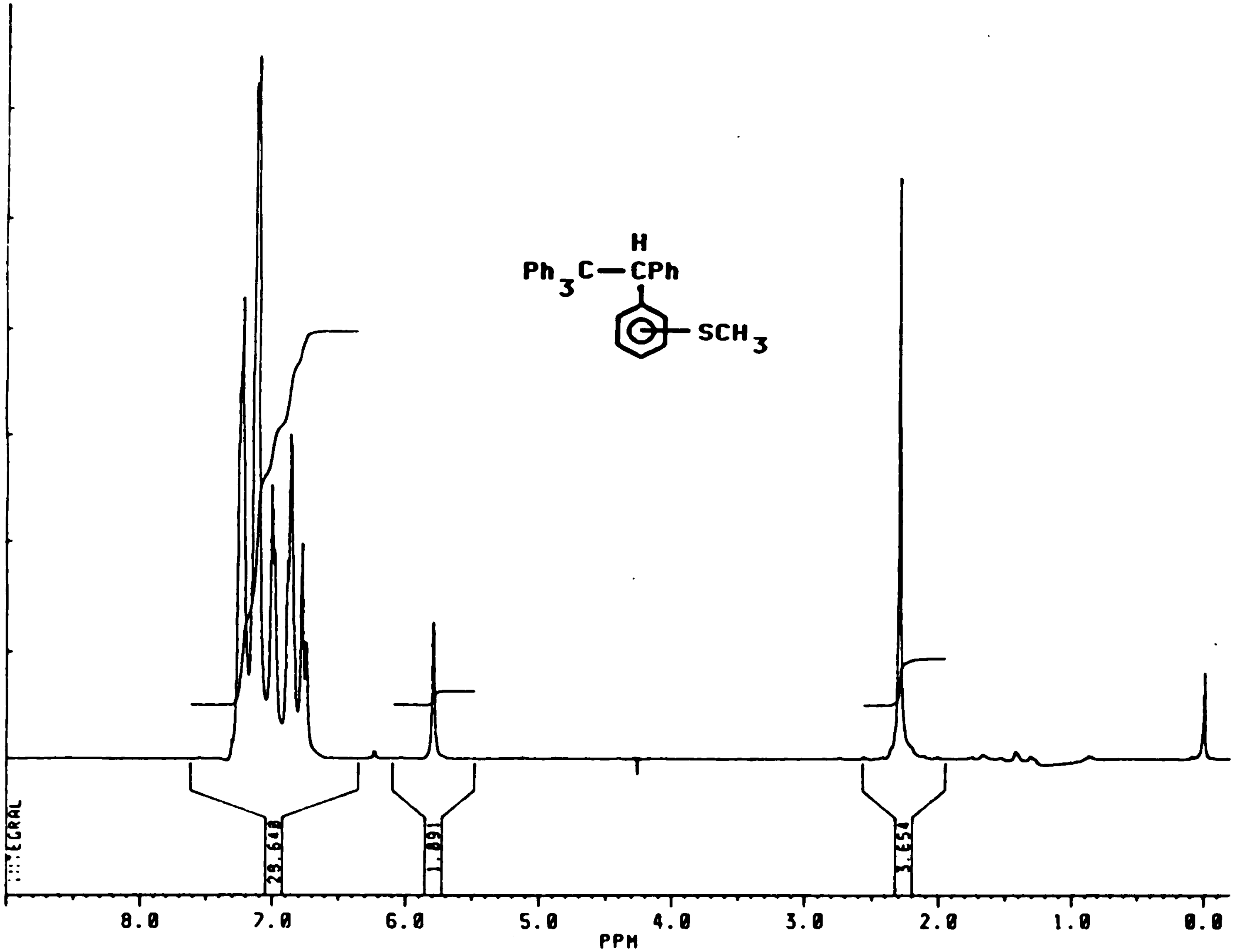
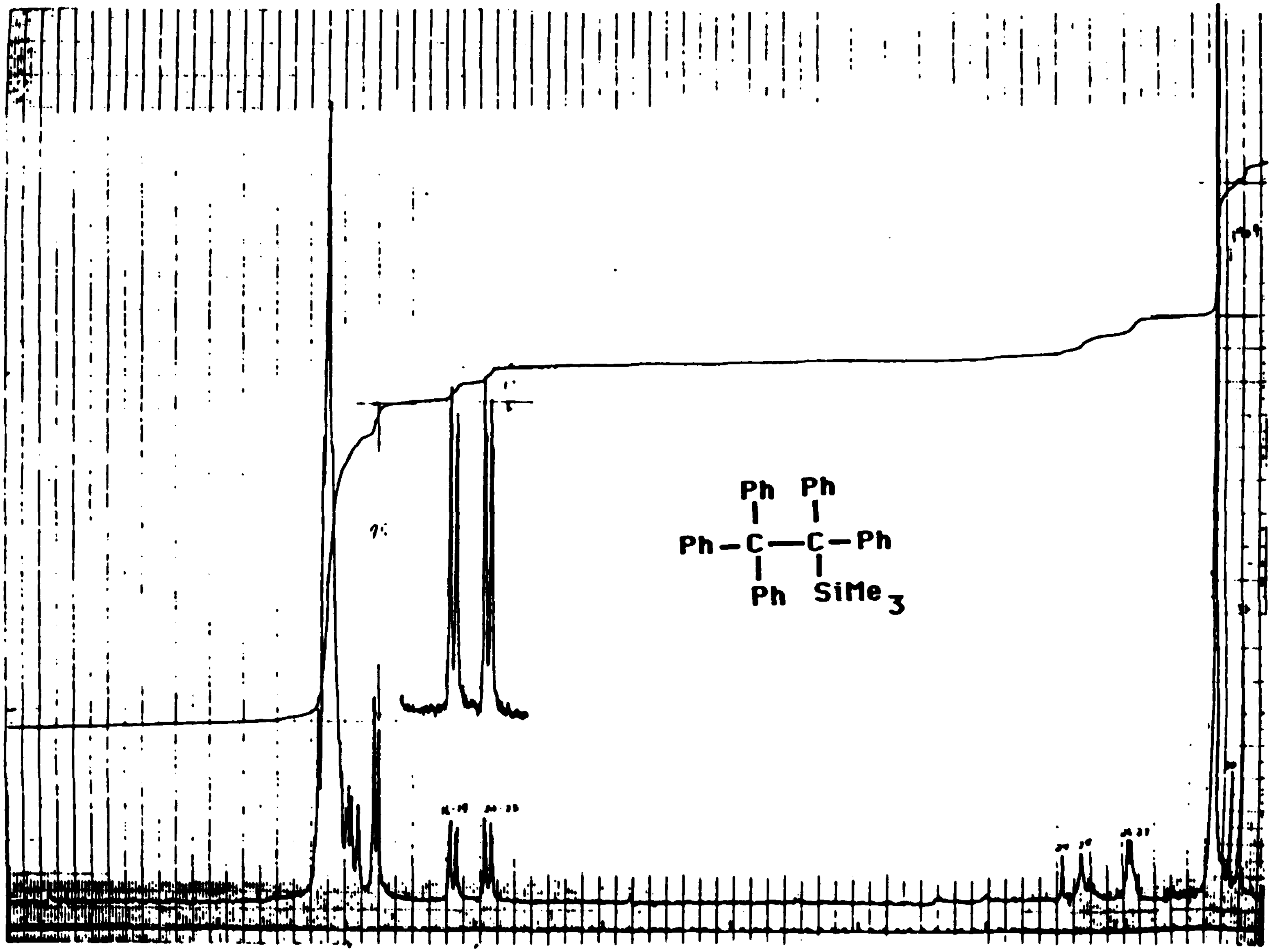
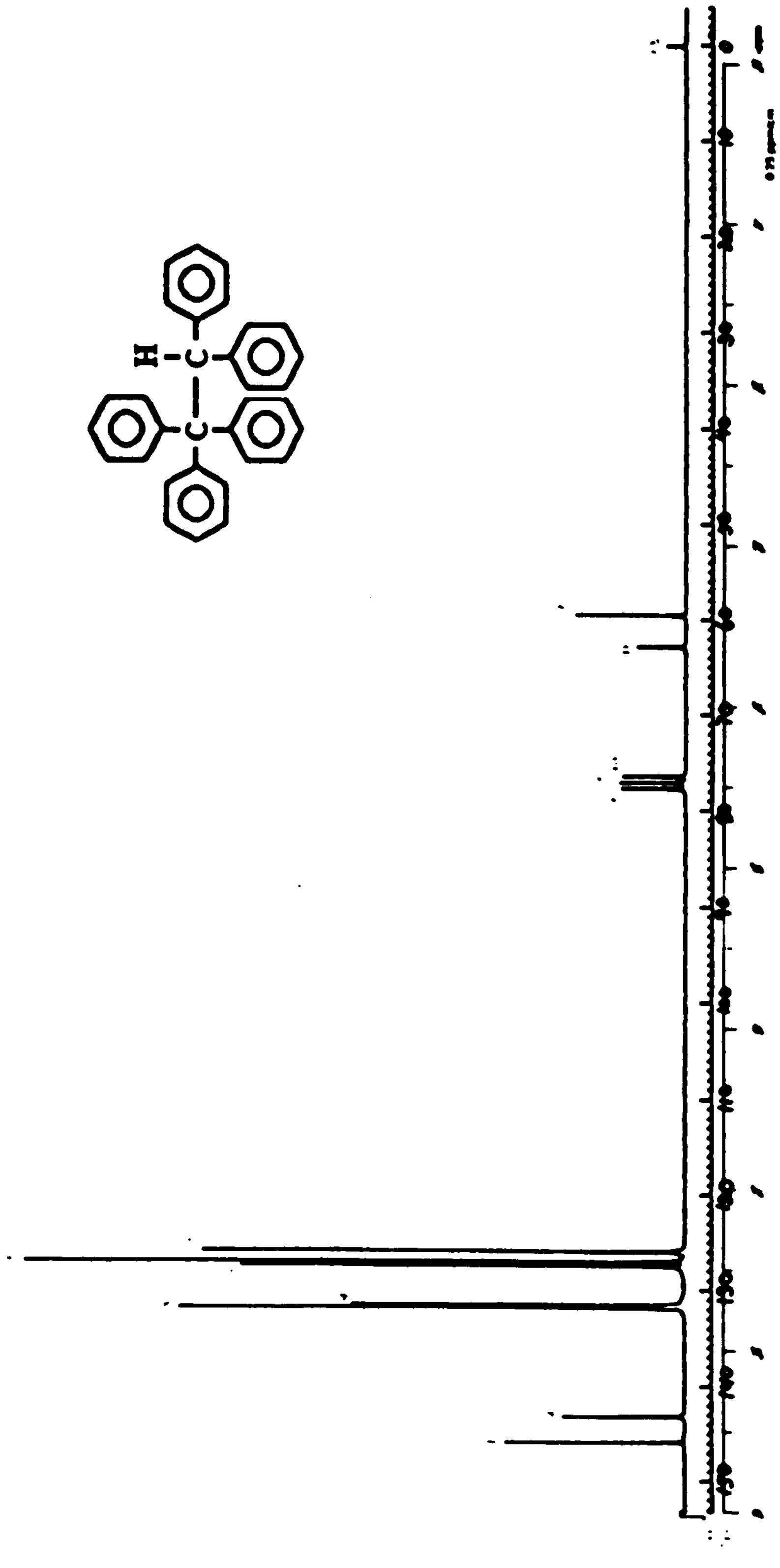
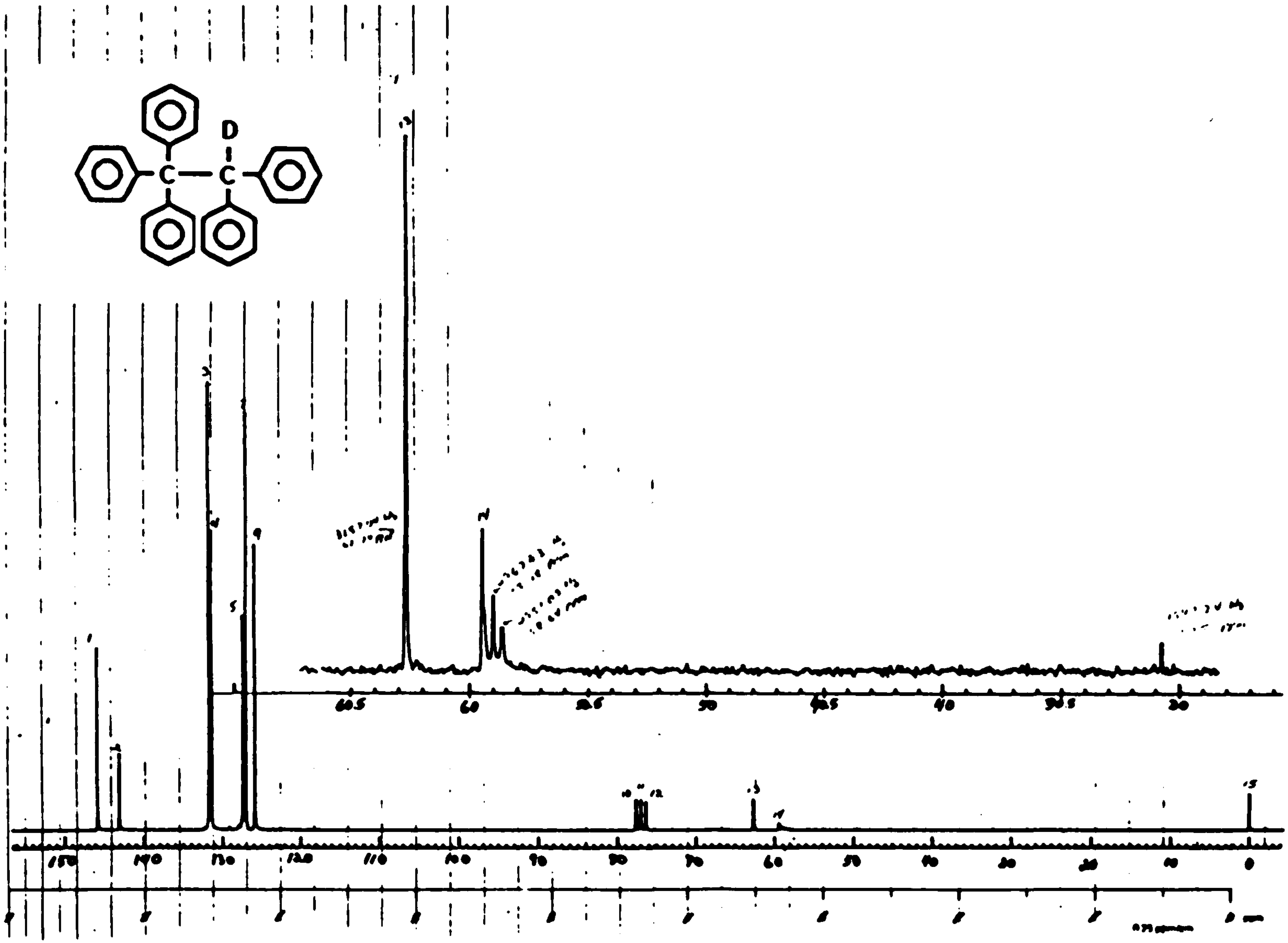
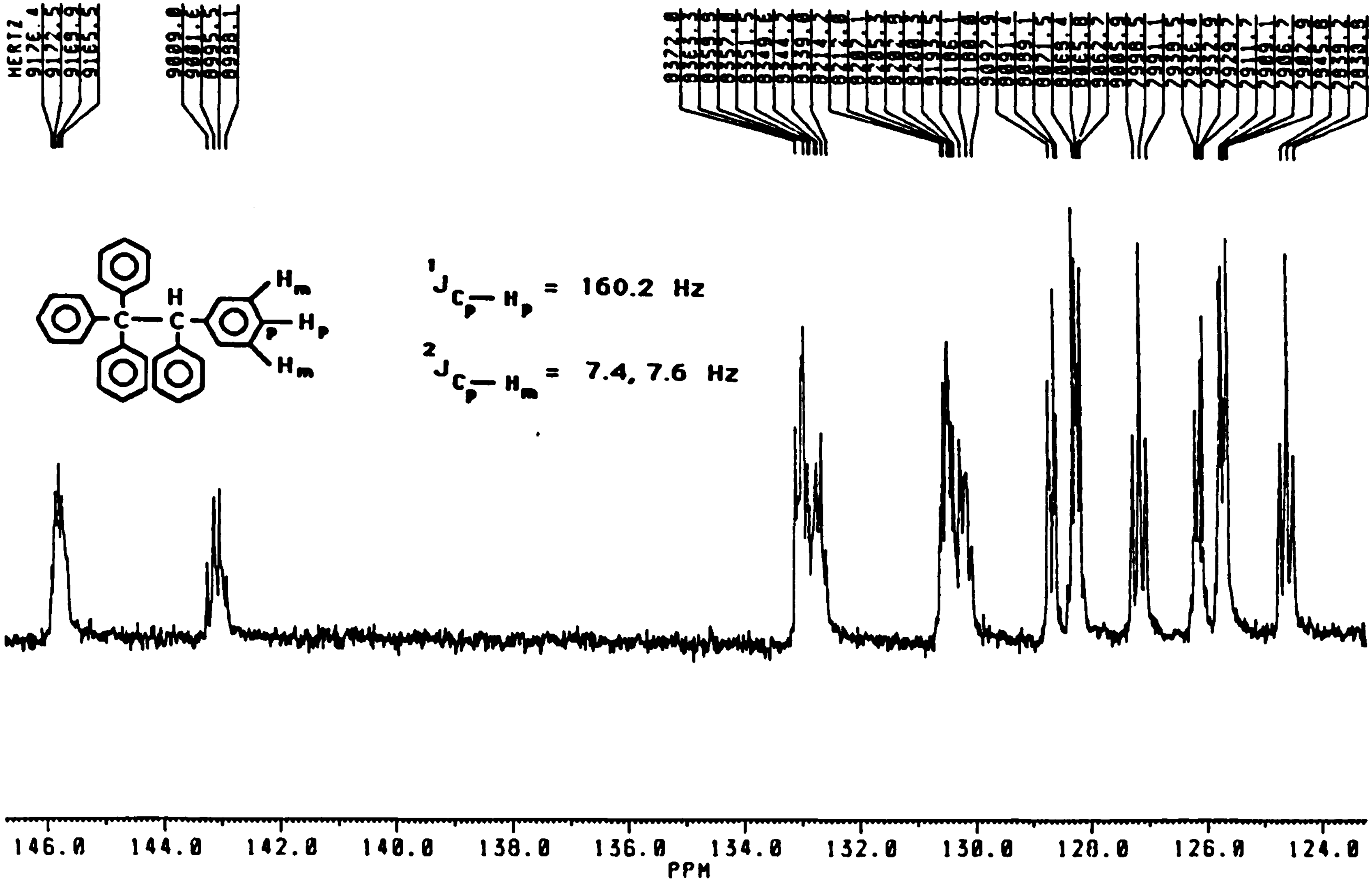
1.965
2.039
1.962
.787
8
7
6
5
4
3
2
1
0


Ph3C—CPh
H
SCH3
INTEGRAL
29.648
1.091
3.654
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM


Ph
Ph
Ph—C—C—Ph
Ph
SiMe3

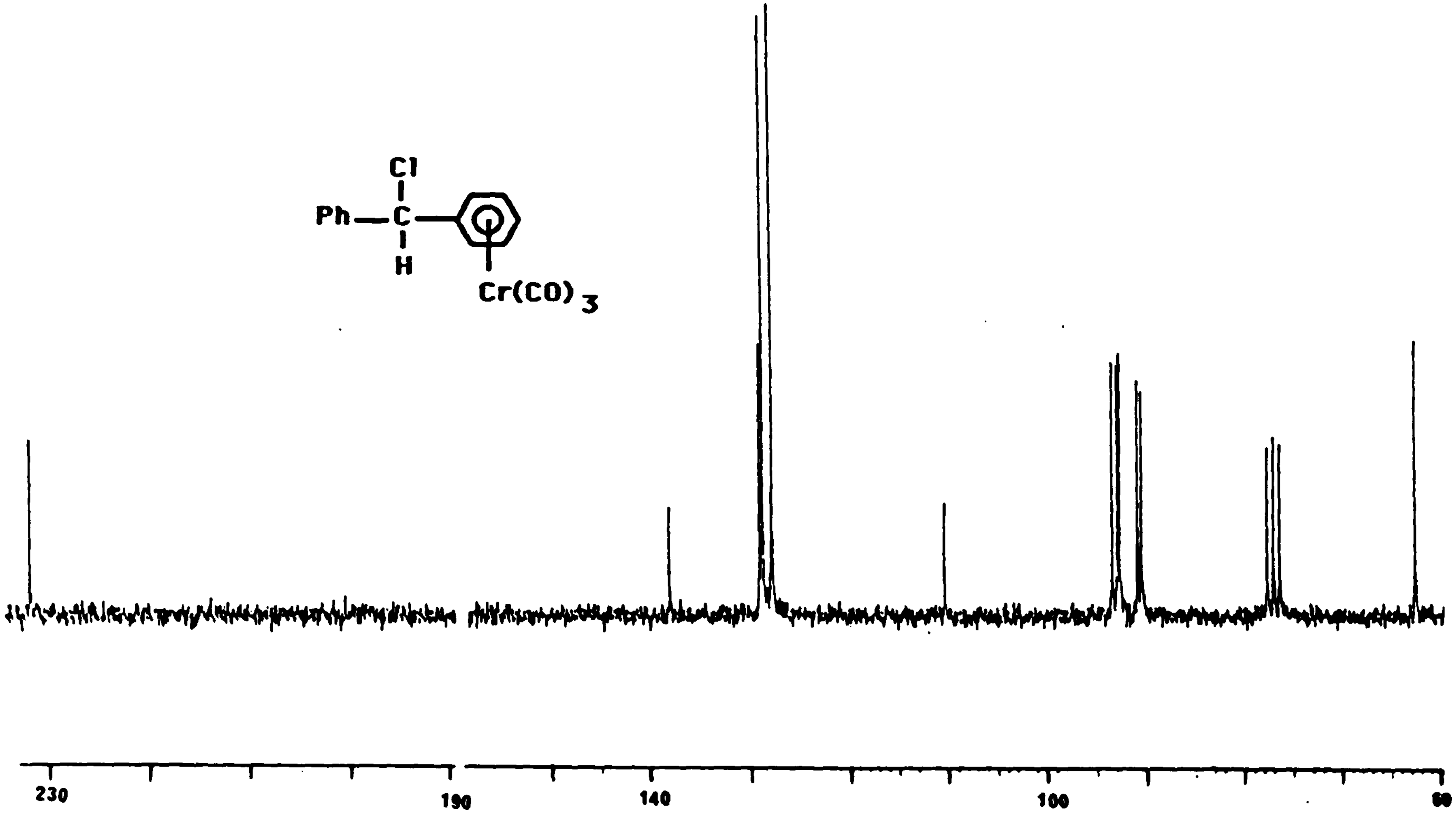

H
C
C

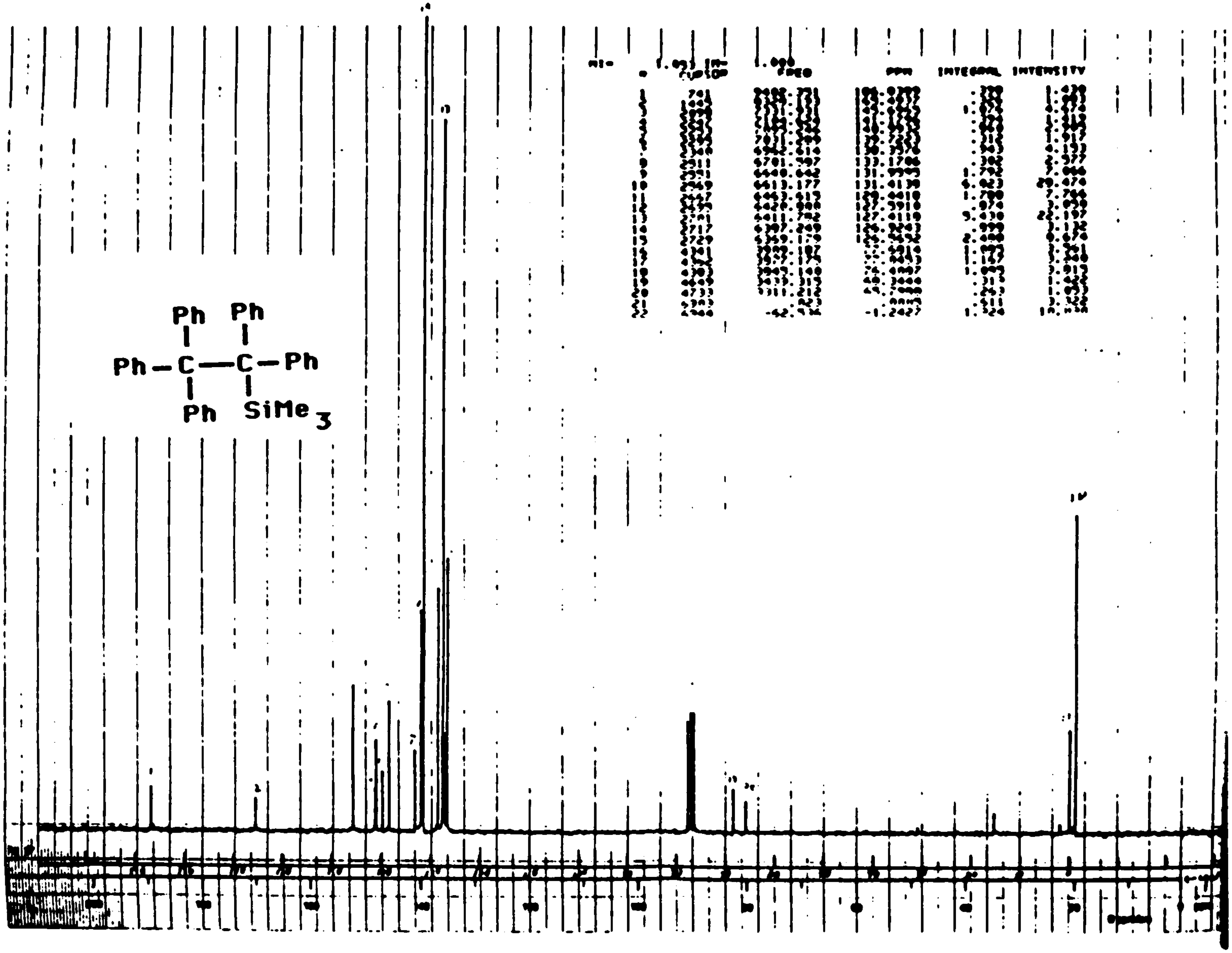

D
C
C
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

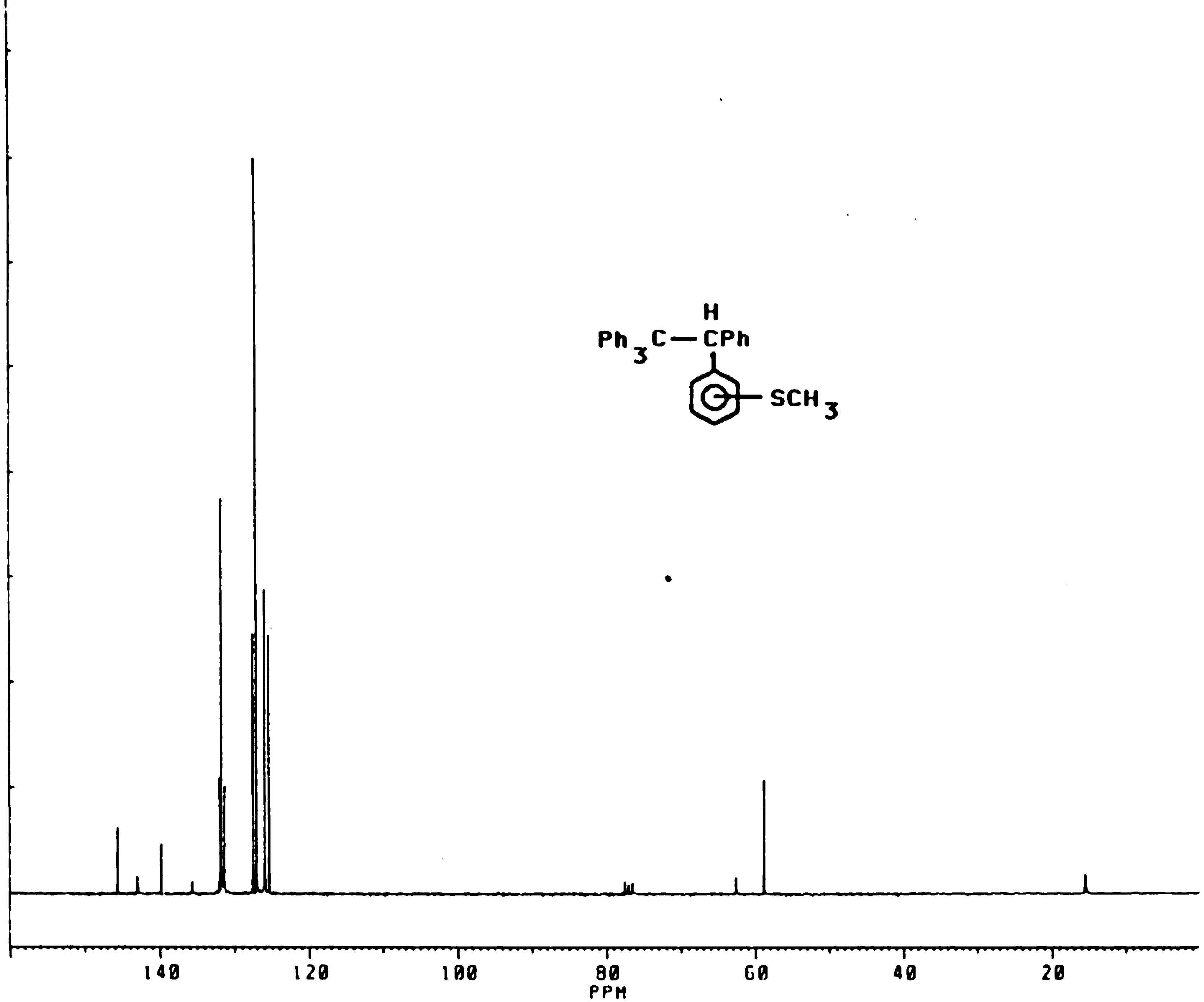


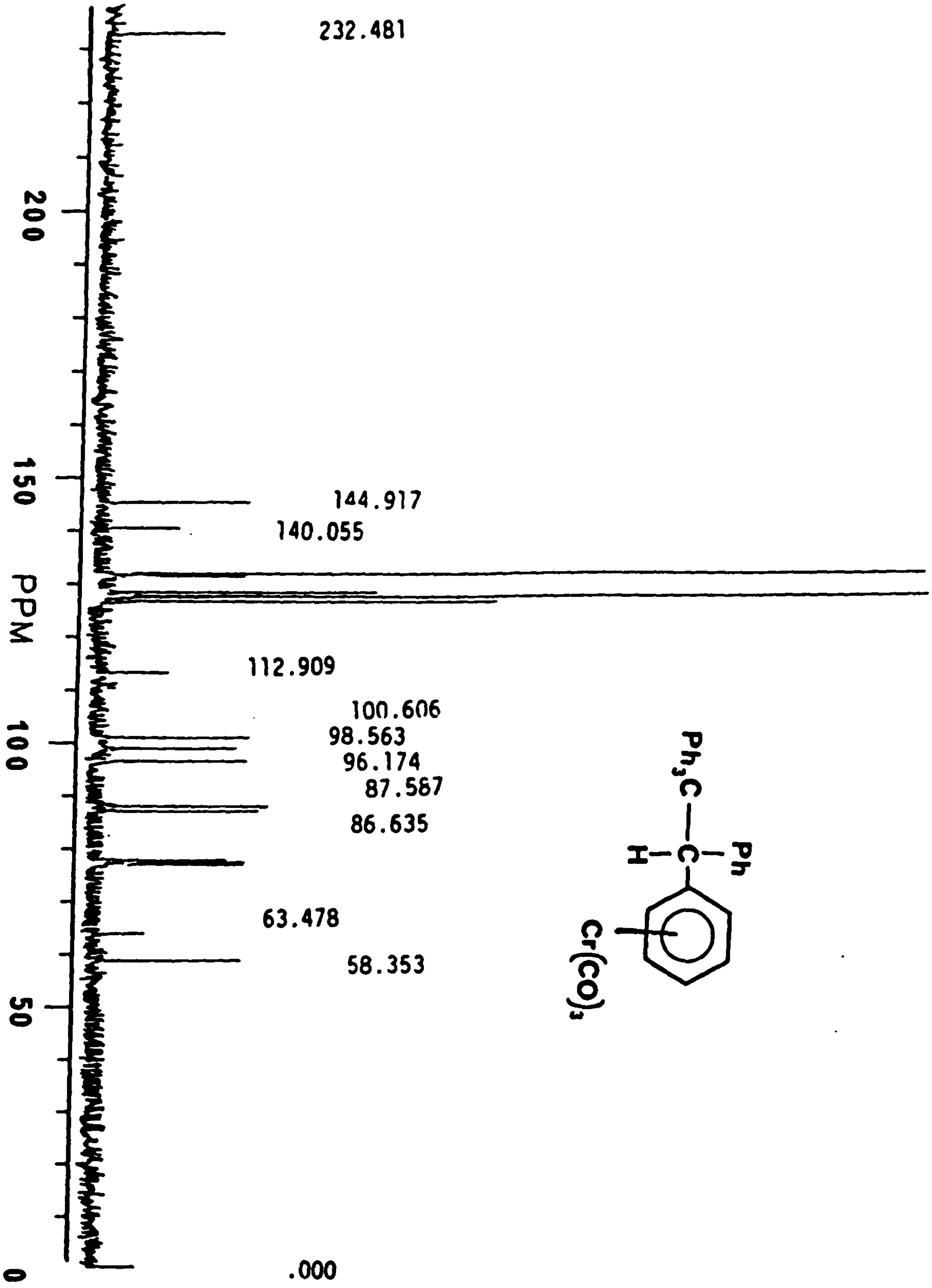
$^1J_{C_p-H_p}$ = 160.2 Hz

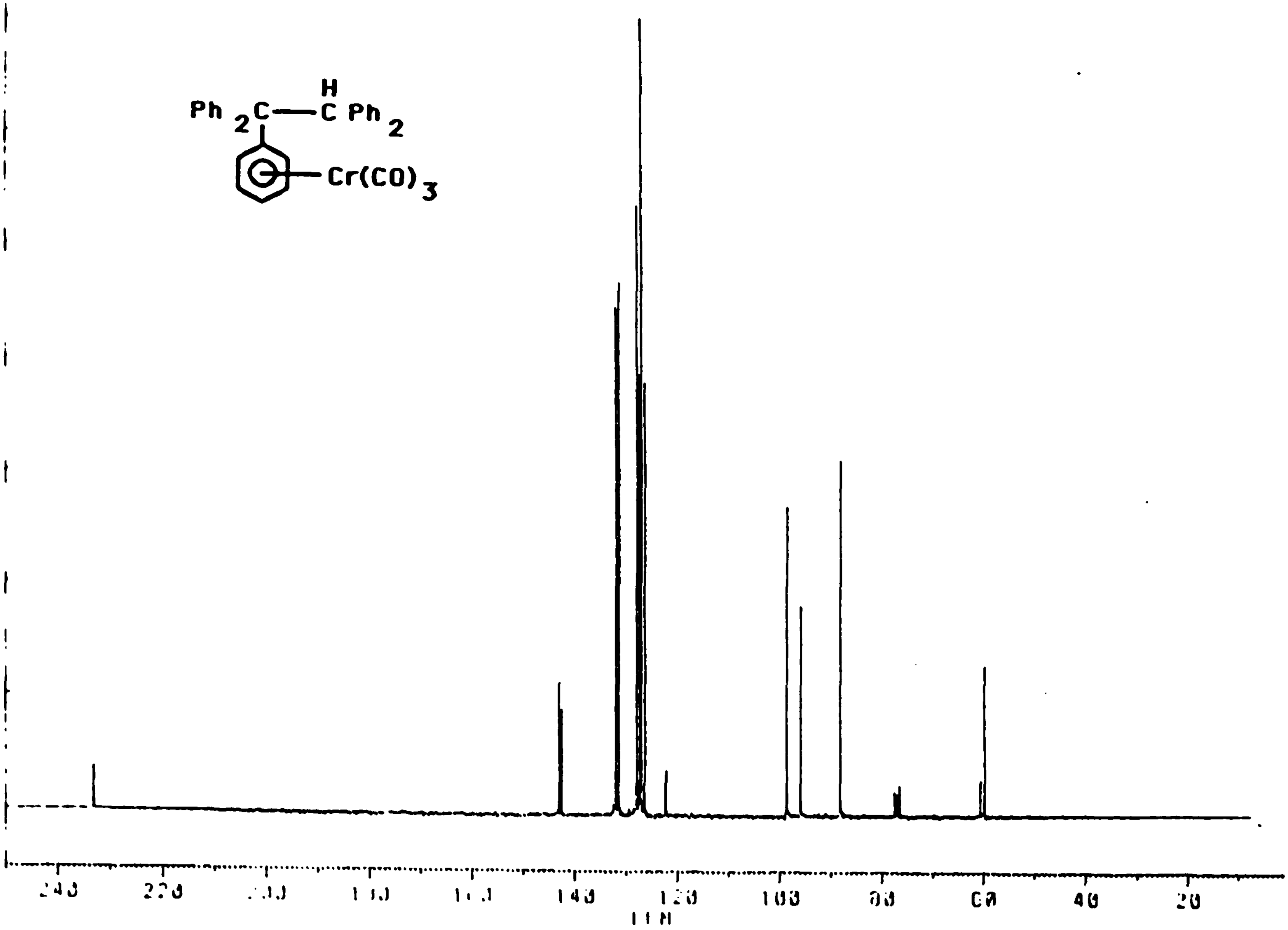
$^2J_{C_p-H_m}$ = 7.4, 7.6 Hz


Cl
Ph
C
H
Cr(CO)3
230
190
140
100
60


Ph
Ph
Ph—C—C—Ph
Ph
SiMe3
INTEGRAL
INTENSITY


H
Ph3C—CPh
SCH3
140
120
100
80
PPM
60
40
20


232.481
144.917
140.055
112.909
100.606
98.563
96.174
87.587
86.635
63.478
58.353
.000
200
150
PPM
100
50
0
Ph
Ph$_3$C—C—H
Cr(CO)$_3$


Ph2C—CH Ph2
Cr(CO)3
240
220
200
180
160
140
120
100
80
60
40
20
PPM

REFERENCES

1. Stowell, J. C., "Carbanions in Organic Synthesis", John Wiley and Sons, New York,1979
2. a) Angres, I.; Zieger, H. E. J. Org. Chem. 1975,40, 1457. b) Zieger, H. E.; Mathisen, D. E. J. Am. Chem. Soc. 1979,101, 2207. c) Bright, D. A. ; Mathisen, D. E.; Zieger, H. E. J. Org. Chem. 1982,47, 3521. d) Zieger, H. E.; Angres, I.; Maresca, L. J. Am. Chem. Soc. 1973,95, 8201
3. Buncel, E. and Durst, T., "Comprehensive Carbanion Chemistry", PartA, Structure and reactivity; Elsevier, New York, 1980
4. Szwarc, M., "Carbanions, Living Polymers and Electron transfer process", Wiley Interscience, New York, 1968
5. Young, R. N. Progress in NMR Spect. 1979,12,261
6. Hogen-Esch, T. E. Adv.Phys. Org.Chem. 1977, 15,153
7. Velthorst, N. H. Pure Appl. Chem. 1979, 51, 85
8. a) Smid, J., in "Ions and Ion Pairs in Organic Reactions", M. Szwarc, Ed.,Wiley Interscience, New York,1972, Vol.1;
   b) Smid, J. Angew. Chem. Int. Ed. Engl. 1972 ,11,112
9. Szwarc, M. ; Streitweiser, A.; Mowery, P. in "Ions and Ion Pairs in Organic Reaction", Szwarc, M., Ed., Wiley Interscience, New York, 1974, Vol.2
10. O'Brien, D. H.; Russel, C. R.; Hart, A. J. J. Am. Chem. Soc. 1979, 10, 633
11. Grutzner, J. B.; Lawor, J. M.; Jackman, L. M. J. Am. Chem. Soc. 1972, 94, 2306
12. Streitweiser, A., Jr. ; Shen, C. C. C. Tetrahedron Lett. 1979, 327
13. Parkes, H. M.; Young, R. N. J. Chem. Soc., Perkin Trans. II, 1980, 1137
14. Jackman, L. M.; Szeuerenyi, N. M. J. Am. Chem. Soc. 1977, 99, 4954
15. Van der Giessen , J.; Gooijer, C.; Maclean, C.; Velthorst, N. H. Chem. Phys. Lett. 1978, 55, 33
16. Edlund, U. Org. Magn. Res. 1979,12, 661
17. Schlosser, M.; Stahle, M. Angew. chem. Int. Ed. Engl. 1980,19,487
18. O'Brien, D. H., in " Comprehensive Carbanion Chemistry ", Part A, Structure and Reactivity; Buncel, E. and Drust, T., Eds., Elsevier, New

York, 1980

19. Greifenstein, L. G.; Lambert, J. B.; Neinhuis, R. N.; Drucker, G. F. ; Pagani, G. A. J. Am. Chem. Soc. 1981,103, 7753

20. Fraenkel, G.; Hallden-Abberton, M. P. J. Am. Chem. Soc. 1981,103, 5657

21. Fraenkel, G.; Fraenkel, A. M.; Geckle, J. J.; Schloss, F. J. Am. Chem. Soc., 1979,101 , 4745

22. Siegel, H.; Hitbrunner, H.; Seebach, D. Angew. Chem. Int. Ed. Engl. 1979,19, 785

23. Clark, T.; Chandrasekher, J.; Schleyer, P. v. R. J. Chem. Soc. Chem. Comm., 1980, 672

24. Fraenkel, G.; Heinrich, M.; Hewitt, J. M. ; MSu, B.; Geckel, M. J. J. Am. Chem. Soc., 1980 ,102, 3345

25. Seebach, D.; Hassig, R.; Gabriel, J. Helv. Chim. Acta. 1983, 66, 308

26. McGarrity, J. F.; Ogle, C. A. J. Am. Chem. Soc. 1985, 107,1805

27. Wakefield, B. J., "The Chemistry of Organolithium Compounds", Pergamon Press, Oxford, 1974

28. Margerison, D.; Newport, J. P. Trans. Faraday Soc. 1963, 59, 2058

29. Oliver, J. P. Adv. Organomet. Chem. 1977, 15, 253

30. Boere, R. T.; Kidd, G. Ann. Rep. on NMR Spect. 1982, 12, 319

31. Gradjean, J.; Laszlo, P. Mol. Phys. 1975, 30, 413

32. Brown, T. L.; Dickerhoff, D. W.; Bafus, D. A. J. Am. Chem. Soc. 1962, 84, 1371

33. a) Sherr, P. A.; Hogan, R. J.; Oliver, J. P. J. Am. Chem. Soc., 1974, 96, 6055. b) Wehrli, F.W. Org. Magn. Res. 1978 ,11,106

34. Seebach, D.; Seigel, H.; Gabriel, J.; Hassig, R. Helv. Chim. Acta. 1980, 63, 2046

35. Holm, T. Acta. Chem. Scand., Ser.B 1978, B32, 162

36. McGarrity, J. F.; Ogle, C. A.; Brich, Z.; Loosli, H. R. J. Am. Chem. Soc. 1985, 107, 1810

37. Fischer, E. O.; Ofele, K. Angew. Chem. 1957, 69, 715. Chem. Ber. 1957, 90, 2532

38. a) Nicholls, B.; Whiting, M. C. Proc. Chem. Soc. 1958, 152. b) J. Chem .Soc. 1958, 287. c) J. Chem. Soc. 1951, 551

39. Natta, G.; Ercolli, R.; Calderazzo, F. Chim. Ind (Milan) 1958, 40, 287

40. Fischer, E. O.; Ofele, K. Z. Naturforsch B 1958,13, 458

41. Fischer, E. O.; Ofele, K.; Essler, H.; Frohlich, W.; Mortensen, J. P. ; Semmling, W. Chem.Ber. 1958, 91, 2763

42. Strohmeier, W. Chem. Ber. 1961, 94, 2490

43. Tate, D. P.; Knipple, W. R.; Augl, J. M. Inorg. Chem. 1962, 1, 433

44. Razuvaev, G. A.; Artemov, A. N.; Aladjin, A. A.; Sirotkin, N. I. J. Organomet. Chem. 1976,111,131

45. Pruett, R. L.; Wyman, J. E.; Rink, D. R.; Parts, L. U.S.Patent 1968, 3378569. Chem. Abstr. 1968, 69, 77512. Chem.Abstr. 1968, 69, 59376

46. Rausch, M. D. J. Org. Chem. 1974, 39,1787

47. Anderson, W. P.; N. HSV; Stranger, C. W.; Munson, B. J. Organomet. Chem. 1974, 69, 249

48. Mahaffy, C. A. L.; Pauson, P. L. Inorg. Synth. 1979,19, 154

49. Top, S.; Jaouen, G. J. Organomet. Chem. 1979,182, 381

50. Yagupsky, G.; Cais, M. Inorg. Chim. Acta 1959 ,12, L27

51. Seyferth, D.; Merola, J. S.; Eschbach, C. S. J. Am. Chem. Soc. 1978,100, 4129

52. Trahanovsky, W. S.; Hall, R. A. J. Organomet. Chem. 1975, 96, 71

53. Orgel, L. E.," An Introduction to Transition Metal Chemistry ", Wiley New York, pp132-170, 1960

54. Fischer, E. O.; Schriener, S. Chem. Ber. 1959, 92, 939

55. Carrol, D. G.; McGlynn, S. P. Inorg. Chem. 1968, 7,1285

56. Brown, D. A.; Rawlinson, R. M. J. Chem. Soc. A. 1969,1530

57. Saillard, J. Y.; Choplin F.; Kaufmann, G.; Grandjean, D. J. Mol. Struct.1974, 23, 363,

58. Price, J. T.; Sorensen, T. S. Can. J. Chem. 1968, 46, 515

59. McFarlane, W.; Grim, S. O. J. Organomet. Chem. 1966, 5,147

60. Emanuel, R. V.; Randall, E. W. J. Chem. Soc.A 1969, 3002

61. Fritz, H. P.; Kreiter, C. G. J. Organomet. Chem. 1967, 7, 427

62. Jaouen, G. Ann. N. Y. Aca. Sci. 1977 ,295, 59

63. Semmelhack, M F. Ann. N. Y. Aca. Sci. 1977, 295, 36

64. Bunnett, J. F. Quart. Rev. Chem. Soc. 1958,12, 1

65 a) Brown, D. A.; Raju, J. R. J. Chem. Soc. A 1966, 40. b) Bunnett, J. F.; Hermann, H. J. Org. Chem. 1971, 36, 4081. c) Semmelhack, M. F.; Hall, H.T. J. Am. Chem. Soc. 1974, 96, 7091, 7092

66. Card, R. J.; Trahanovsky, W. S. J. Org. Chem. 1980, 45, 2560

67. a) Semmelhack, M. F.; Hall, H. T.; Yoshifuji, M.; Clark, G. J. Am. Chem. Soc. 1975, 97, 1247. b) Semmelhack, M. F.; Hall H. T. ; Yoshifuji, M. ibid. 1976,98, 6387. c) Semmelhack, M. F.; Clark, G. ; Yoshifuji, M. Abstracts,The First Chemical Congress of North American Continent, Maxico City,1975. d) Semmelhack, M. F.; Hall, H. T.; Yushifuji, M.; Clark, G. J. Am. Chem. Soc. 1977, 99, 1246. e) Semmelhack, M. F., in " New Applications of Organometallic Reagents in Organic Synthesis ", Seyferth, D, Ed., Elsevier, Amsterdam,The Natherlands, pp 361-395 1976. f) Semmelhack, M. F.; Hall, H. T., Jr.; Farina, R. ; Yoshifuji, M.; Clark, G.; Bargar, T.; Hirotsu, K.; Clardy, J. J. Am Chem. Soc. 1979, 101, 3535. g) Semmmelheck, M. F.; Clark, G. R.; Gracia, J. L.; Harrison, J. J.; Thebtaranonth, Y.; Wulff, W. ; Yamashita, A. Tetrahedron 1981, 37, 3957

68. a) Semmelhack, M. F.; Clark, G. J. Am. Chem. Soc. 197, 99, 1675. b) Semmelhack, M. F.; Yamashita, A. ibid 1980,102, 5924

69. Semmelhack, M. F.; Clark, G.; Farina, R.; Saeman, M. J. Am. Chem. Soc. 1979,101, 217

70. Card, R. J.; Trahanovsky, W. S. J. Org. Chem. 1980, 45, 2555

71. a) Caro, B.; Jaouen, G. Tetrahedron. Lett. 1974,1229, 2061. b) Jaouen, G.; Caro, B.; LeBihan, J. Compt. Rend. Acad. Sci. Paris.Ser. 1972, C274, 904

72. Trahanovsky, W.S.; Card, R. J. J. Am. Chem. Soc. 1972 ,94, 2897

73. Holms, J. D.; Jones, D. A. K.; Pettit, R. J. Organomet. Chem. 1965, 4, 324

74. Ceccon, A. J. Organomet. Chem. 1971, 29, C19

75. a) Bly, R. S.; Veazey, R. L. J. Am. Chem. Soc. 1969, 91, 4221. b) Bly, R. S.; Strickland, R. C.; Swindell, R. T.; Veazey, R. L. ibid 1970 92, 3722. c) Ceccon, A.; Gobbo, A.; Venzo, A. J. Organomet.Chem. 1978,162, 311

76. Trahanovsky, W. S.; Wells, D. K. J. Am. Chem. Soc. 1969, 91, 5870, 5871

77. Seyferth, D.; Eschbach, C. S. J. Organomet. Chem. 1975, 94, C5

78. Acampora, M.; Ceccon, A.; Farra, M. D.; Giacometti, G.; Rigatti, G. J. Chem. Soc., Perkin II, 1977, 483

79. a) Acampora, M.; Ceccon, A.; Farra, M. D.; Giacometti, G. J. Chem. Soc., Chem. Comm. 1975, 871

80. Jaouen, G.; Top, S.; McGlinchey, J. J. Organomet. Chem., 1980, 195, C5

81. Top, S.; Jaouen, G.; Sayer, B. S.; McGlinchey, M. J. J. Am. Chem. Soc. 1983, 105, 6426

82. Wakafield, B. J., " The Chemistry of Organolithium Compounds ", Pergamon Press, Oxford,1974

83. Schmidt, F., in " Houben-Wely, Methoden der Organischen Chemie ", Vol. 6/2, E. Muller, Ed., Verlag Press, Stuttgart,1963, pp5

84. a) Gilman,H.; McNinch, H. A.; Wittenberg, D. J. Org. Chem. 1958, 23, 2044. b) Gilman, H.; Mcninch, H. J. Org. Chem. 1961, 26, 3723. c) Takahashi, K.; Takai, M.; and Asami, R. Org. Mag. Res. 1971, 3, 539

85. a) Waack, R.; McKeever, L. D.; Doran, M. J. Chem. Soc. ,Chem. Comm. 1969,117. b) Waack, R.; Doran, M.; Baker, E.; Olah, G. A. J. Am. Chem.Soc. 1966, 88, 1272. c) Waack, R.; Doran, M. J. Am. Chem. Soc. 1963, 85, 1651. d) Gilman, H.; Rosenberg, R. J. Org. Chem. 1959,24, 2063. e) Seyferth, D.; Suzuki, R.; Murphy, C. J.; Sabet, C. R. J. Organomet. Chem. 1964, 2, 431

86. Menon, B.; Buncel, E. J. Organomet. Chem. 1978 ,159, 35 and references therein

87. Buncel, E.; Menon, B. J. Organomet. Chem. 1977,141, 1

88. a) Buncel, E.; Menon, B. J. Chem. Soc.,Chem. Comm. 1976, 648; b) Buncel, E.; Menon, B. J. Am. Chem. Soc. 1977, 99, 4457

89. Streitwieser, A., Jr.; Murdoch, J. R.; Hafelinger, G.; Chang, C. J. J. Am. Chem. Soc. 1973, 95, 4248

90. a) Schlosser, M. J. Organomet. Chem. 1967 ,8, 9. b) Schlosser, M. ; Hartmann, J. Angew. Chem. Int. Ed. Engl. 1973 ,12, 508. c) Schlosser, M.; David, V. Helv. Chim. Acta 1974, 57,1567. d) Hartmann, J.; Schlosser, M. Helv. Chim. Acta 1976, 59, 453.

91. a) Lochmann, L.; J. Pospisil; Lim, D. Tetrahedron Lett. 1966, 257. b) Lochmann, L. ; Lim, D. J. Organomet. Chem. 1971, 28,153

92. Corey, E. J.; Eckrich,T. M. Tetrahedron Lett. 1983, 24, 3165

93. a) Schlosser, M.; Strunk, S. Tetrahedron Lett. 1984, 25, 741. b) Lehmann, R.; Schlosser, M. Tetrahedron Lett. 1984, 25, 745

94. McGarrity, J. F.; Ogle, C. A.; Brich, Z.; Loosli, H. R. J. Am. Chem. Soc. 1985, 107, 1810

95. Smith, W. B.; Harris, M. C. J. Org. Chem. 1980, 45, 355

96. Proulx, T. W.; Smith, W. B. J. Magn. Res. 1976, 23, 477

97. Feldman, D.; Halpern, M.; Robinovitz, M. J. Org. Chem. 1985, 50, 1746 and references therein

98. Sakurai, H. Tetrahedron Lett. 1978, 19, 3043

99. Vedejes, E.; West, F. G. J. Org. Chem. 1983, 48, 4773

100. Diphenylmethyltrimethylsilane (6) was prepared in 99% yield, m.p. 68-69°C, Lit.^{101} 74.5-75.5°C by reacting diphenylmethyllithium with trimethylchlorosilane, ^{1}HNMR($CDCl_3$), δ 7.2(m,10H), 3.5(s,1H), .02(s,9H); ^{13}CNMR($CDCl_3$), δ 142.88, 128.71, 128.26, 125.06, 46.1, -1.67

101. Hauser, C. R.; Hance, C. R. J. Am. Chem. Soc. 1951, 73, 5846

102. Diphenyl α-bromo methyltrimethylsilane was prepared by the reaction of 6 with Br_2 in CCl_4 at room temperature in 69.6% yield, b.p., 163-6°C/5 mm, Lit.^{103} 166.5-167°C/4mm

103. Hauser, C. R.; Hance, C. R. J. Am. Chem. Soc. 1952, 74, 5091

104. a) Dosser, P. J.; Eaborn, C.; Walton, D. R. M. J. Organomet. Chem. 1974, 71, 207. b) Ceccon, A.; Romanin, A.; Gentiloni, M.; Venzo, A. J. Organomet. Chem. 1977, 127, 315. c) Khandkarova, V. S.; Gubin, S. P. J. Organomet. Chem. 1970, 22, 149

105. Hauser, C. R.; Hance, C. R. J. Am. Chem. Soc. 1951, 73, 5846

106. Trzupek, L. S.; Newirth, T. L.; Kelly, E. G.; Sbarati, N. E.; Whitesides, G. M. J. Am. Chem. Soc. 1973, 95, 8118 and references therein

107. Prepared according to literature,^{108} BSA (91.6g, 45%), b.p. 68-69°C at 33mm, lit., b.p., 71-73°C at 35 mm; N-trimethylsilyl acetamide (35.0g, 26.5%), b.p. 79-80°C, m.p. 40°C, lit., 105-107°C at 35 mm

108. a) Klebe, J. F.; Finkbeiner, H.; White, D. M. J. Am. Chem. Soc. 1966, 88, 3390. b) Birkofer, L.; Ritter, A.; Giessler, W. Angew. Chem. 1963, 75, 93

109. Whitesides, G. M.; Fischer, W. F., Jr. ; Fillipo, J. S., Jr.; Basche R. W. ; House, H. O. J. Am. Chem. Soc. 1972, 91, 4871 and references therein

110. Smith, W.B.; Harris, M. C. J. Org. Chem. 1983, 48, 4957

111. Morris, G. A.; Freeman, R. J. Am. Chem. Soc. 1979, 101, 760

112. Reaction of diphenylmethyl bis chromiumtricarbonyl carbanion with methyl iodide and benzoyl chloride affords moderate yields of the coupling products; Jaouen, G.; Top, S.; McGlinchey, M. J. J.

Organomet. Chem. 1980,195, C5

113. Tiroufiet, J.; Besancon, J.; Mabon, F.; Martin, L. Org. Magn. Res. 1976, 8, 444 and references therein

114. a) Boutonnet, J.; Rose-Munch, F.; Rose, E.; Robert, F. J. Organomet. Chem. 1985, 297, 185. b) Fukui, M.; Ikeda T.; Oishi, T. Tetrahedron Lett. 1982, 23, 1605

115. Destro, R.; Pilati, T.; Simonetta, M. J. Am. Chem. Soc. 1978, 100, 6507

116. Rees, B.; Coppens, P. Acta. Cryst. 1973, B29, 2515

117. Davis, R. E.; Pettit, R. J. Am. Chem. Soc. 1970, 92, 716

118. Cotton, F. A.; La Prade, M. D. J. Am. Chem. Soc. 1968, 90, 5418

119. Manojlovic-Muir, L.; Muir, K. W.; Ibers, J. A. Discuss. Faraday Soc. 1969, 47, 84

120. Bailey, M. F.; Dahl, L. F. Inorg. Chem. 1965, 4, 1314

121. Deuschl, H.; Hoppe, W. Acta. Cryst. 1964,17, 800

122. Muir, K.; Ferguson, G.; Sim, G. A. Chem. Comm. 1966, 465

123. Carter, O. L.; McPhail, A.T.; Sim, G. A. J. Chem. Soc. A 1966, 822

124. Carter, O. L.; McPhail, A.T.; Sim, G. A. J. Chem. Soc., A 1967, 228

125. Saillard, J. Y.; Grandjean, D. Acta. Cryst. 1976, B32, 2285

126. Carter, O. L.; McPhail. A.T.; Sim, G. A. J. Chem. Soc.A 1967, 1619

127. Saillard, J. Y.; Grandjean D.; Maix, P. Le.; Jaouen, G. Nouveau J. Chimie 1981, 5, 153

128. Stewart, K. R.; Levine, S. G.; McPhail, A. T. J. Organomet. Chem. 1984, 263, 45

129. Boutonnet, J.; Rose-Munch, F.; Rose, E.; Jeannin Y.; Robert, F. J. Organomet. Chem. 1985, 297, 185

130. For a theoretical discussion see Albright, T. A.; Hofmann, P. ; Hoffmann, R. J. Am. Chem. Soc. 1977, 99, 7546

131. Hounshell, W. D.; Doughetry, D. A.; Hummel, J. P.; Mislow, K. J. Am. Chem. Soc. 1977, 99, 1916

132. Takahashi, K.; Kondo, Y.; Asami, R. Org. Magn. Res. 1974, 6, 580

133. a) Wilhelm, D.; Clark, T.; Schleyer, P. v. R.; Courtneidge, J. L. ; Davies, A. G. J. Am. Chem. Soc. 1984,106, 361. b) Streitweiser, A. Jr.;

Scannon P. J.; Niemeyer, H. M. J. Am. Chem. Soc. 1972, 94. 7936

134. a)Troughton, E. B.; Molter, K. E. ; Arnett, E. M. J. Am. Chem. Soc. 1984, 106. 6726. b) Arnett, E. M. ; Troughton, E. B., Tettrahedron. Lett. 1983, 24. 3299. c) Arnett, E. M.; Troughton, E. B.; McPhail , A. T.; Molter, K. E. J. Am. Chem. Soc. 1983, 105. 6172. d) Okomoto, K.; Kitagawa, T.; Takeuchi, K.; Takahashi, K. J. Chem. Soc., Chem. Commun. 1985, 173

135. Bank, S.; Ehrlich, C. L.; Zubieta, J. A. J. Org. Chem. 1979, 44.1454

136. Kahr, B.; Engen, D. V.; Mislow, K. J. Am. Chem. Soc. 1986, 108. 8305

137. a) Watson, S. C.; Eastham, J. F. J. Organomet. Chem. 1967, 9. 165. b) Ellison, R. A.; Griffin, R.; Kotsonis, F. N. J. Organomet. Chem. 1972, 36, 209. c) Semmelhack, M. F.; Hall, H. T., Jr.; Frina, R.; Yoshifuji, M.; Clark, G.; Bargar, T.; Hrotsu, K.; Clardy, J. J. Am. Chem. Soc. 1979, 102. 3535

138. Silveira, A., Jr.; Bretherick, H. D., Jr.; Negishi, E. J. Chem. Ed. 1979, 56. 560

139. Kauffman, G. B.; Teter, L. A. Inorg. Synth. 1963, 7. 9

140. Otto. Fritz, BmbH, Feldstraβe, 6238 Hofheim am Tanus, West Germany sell an apparatus for the ultra high purification of peramanent gases. The apparatus has been described in detail in Chemie fur Labor und Betrieb 1975, 8 ,305. One of its principal advantage is a safety device for over and under atmosperic pressure(fig. 23)

141. Still, W. C.; Kahn, M.; Mitra, A. J. Org. Chem. 1978, 43. 2923

142. Gilman, H.; Kirby, J. E. J. Am. Chem. Soc. 1926, 48. 1736

143. Dauben, H. J., Jr.; McCoy, L. L. J. Am. Chem. Soc. 1959, 81, 5405

144. a) Bachmann, W. E. J. Am. Chem. Soc. 1933, 55. 3005; b) Bachman, W. E.; Wiselogle, F.Y. J. Am. Chem. Soc. 1937,59. 354

145. The X-ray was done by Dr. Jon Bordner at Pfizer Central Research , Groton, Connectcut

146. International Tables for Crystallography; Kynoch; Birmingham,1962; Vol. 3, pp, 204-214

147. Tomboulian, P.; Stehower, K. J. Org. Chem. 1968, 33. 1509

148. The structure determination was carried out by Dr. Michael Chaing at Columbia University, NY

149. Gomberg, M. Ber. 1900, 33. 3154

150. The Mass Spectral Data were obtained from Columbia University, NY.

151. Smith, H. A.; Smith, R. J. J. Am. Chem. Soc. 1948, 70, 2400

152. Seyferth, D.; Freyer, W. J. Org. Chem. 1961, 26, 2604

153. Ceccon, A.; Gambaro, A.; Venzo, A. J. Organomet. Chem. 1984, 275, 209