CONFORMATIONAL CONSEQUENCES OF METALLO-METHYL INTERACTIONS: A ^{13}C NUCLEAR MAGNETIC RESONANCE STUDY*

W. ADCOCK*, B.D. GUPTA

School of Physical Sciences, The Flinders University of South Australia, Bedford Park, South Australia, 5042, (Australia)

W. KITCHING,

Department of Chemistry, University of Queensland, Brisbane, Queensland, 4067, (Australia)

D. DODDRELL

School of Science, Griffith University, Nathan, Queensland, 4111 (Australia)

(Received July 10th, 1975)

Summary

A number of model benzyl-organometallic systems have been synthesized and characterised, and their proton-decoupled natural-abundance ^{13}C NMR spectra measured and assigned. A comparison of the ^{13}C chemical shifts of carbons formally *para* to the carbon—metal (C—M) bond strongly supports the importance of hyperconjugative interactions in the neutral ground state for metallo-methyl substituents. Further, an analysis of the carbon—metal coupling constants has defined unambiguously the generality and origin (hyperconjugation) of a new concept, namely, large five-bond carbon—metal coupling in benzylic systems. The utilization of $^5J(^{13}$C—^{117,119}Sn) for structural and stereochemical assignments is demonstrated.

Introduction

Fluorine-19 NMR studies [2-6] on model systems have indicated that when a metallo-methyl substituent is attached to an aromatic ring, it induces substantial changes in the ground state π-electron-density distribution by σ—π conjugation involving the carbon—metal (C—M) bond. The resulting π-charge distribution is characterized by the presence of a formal negative charge at the various conjugated positions relative to the corresponding carbon centers in the hydrogen

---

* A preliminary account of this work has appeared [1].

or carbon analogue (toluene, ethylbenzene or neopentylbenzene when the aromatic ring is benzene).

More recently, analogous ^{13}C chemical shift studies of a number of benzylsilanes [7] and -stannanes [8] have substantiated the importance of this phenomenon in the neutral ground state and, in addition, led to the suggestion that where the metal in question possesses magnetically active isotopes ($I = \frac{1}{2}$) in natural abundance sufficient to give rise to easily detectable long-range spin coupling with ^{13}C, then five-bond carbon—metal coupling constants should be observed which are largely a manifestation of hyperconjugation involving the carbon—metal bond. It is important to note that this proposal was based essentially on the observation that, whereas the relative magnitude of the coupling from $^{117,119}Sn$ to aryl carbons in the phenylstannane system is $^3J_{meta} > ^4J_{para}$, the order is reversed in the benzyl case. Further, in p-tolyltrimethylstannane where hyperconjugative effects (but not in principle p—d interactions) are inoperative, $^5J(^{13}C—^{117,119}Sn)$ was not observed. Thus, on this basis, the proposal as it stands is equivocal since a comparison of coupling constants in different systems through a different number of intervening bonds is highly questionable. Moreover, relative magnitudes of coupling constants can be complicated by the sign of the σ and π contributions to the coupling mechanism [9].

The purpose of the present research was three-fold. Firstly, we wanted to establish unambiguously the origin of the relatively large $^5J(^{13}C—^{117,119}Sn)$ value observed in benzyltrimethylstannane. If our suggestion is correct then $^5J(^{13}C—^{117,119}Sn)$ should show a strong conformational dependence, an absolute pre-requisite for invoking a hyperconjugative mechanism. Consequently, we have syn-
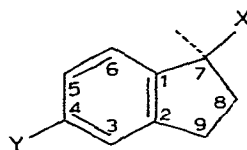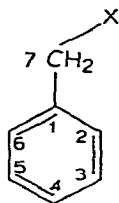
(I) X = Si(CH$_3$)$_3$ (II) X = Ge(CH$_3$)$_3$

(III) X = Sn(CH$_3$)$_3$ (IV) X = Pb(CH$_3$)$_3$

(V) X = HgCH$_2$C$_6$H$_5$ (VI) X = HgCl

(VII) X = Sn(CH$_3$)$_3$; Y = H

(VIII) X = Sn(CH$_3$)$_3$; Y = F
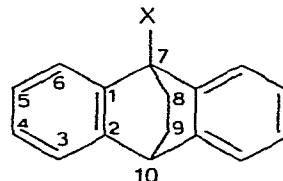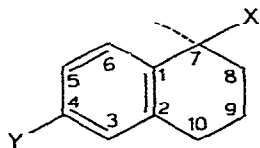
(IX) X = Sn(CH$_3$)$_3$; Y = H

(X) X = Sn(CH$_3$)$_3$; Y = F

(XI) X = H

(XII) X = Sn(CH$_3$)$_3$

thesized and measured the ^{13}C NMR spectra of two model benzylic tin compounds (VII and XII) in which the geometrical relationship of the C—Sn bond with respect to the adjacent aromatic system has been considerably varied: an examination of models indicates that the angle between the C—C—Sn plane and the aromatic ring (dihedral angle θ) in these systems is 60° and 0°, respectively*.

Since our recent studies of benzocycloalkenes have demonstrated convincingly that fluorine substitution is an effective and relatively simple strategy for ^{13}C spectral assignments in such systems [7,11], we have also synthesized compound VIII (a fluorine analogue of VII) in order to unambiguously assign the spectrum of compound VII. Compound XI was synthesized and studied in order to determine the ^{13}C substituent chemical shift (SCS) for $(CH_3)_3Sn$ in compound XII as well as to assist in the spectral assignment of the latter derivative.

An additional feature of model systems, VII and XII, is that because the steric factors associated with the $(CH_3)_3Sn$ group are generally considered not to be extreme (less than CH_3) [12], the ^{13}C SCS for C_3, C_4, and C_5 of the aromatic ring should reflect only the electronic effect of this group. An apparent problem associated with our previous ^{13}C NMR studies [7] of model bicyclic (sila)-indan and -tetralin was that effects related to ring strain made interpretation of the aromatic chemical shifts in terms of the electronic effect of the C—Si bond quite difficult.

Secondly, we wanted to substantiate the generality of the phenomenon that was observed in the benzyl- and phenyltrimethylstannanes [8], namely, that whereas $J_{para} > J_{meta}$ in the former systems, the reverse situation holds for the corresponding phenyl derivatives. Accordingly, we have synthesized and measured the ^{13}C spectra of compounds IV, V, and VI as well as their phenyl analogues**. Compound II was also examined in order to complete the ^{13}C chemical shift study of the metalloidal substituents $((CH_3)_3M$, where M = Si, Ge, Sn, and Pb).

Thirdly, in anticipation of $^5J(^{13}C—^{117,119}Sn)$ being proved to be stereochemically dependent, we wanted to test its utility for determining the stereochemistry of ill defined structures. Thus, we have synthesized and measured the ^{13}C spectrum of compound IX in which the alicyclic ring is potentially mobile: an examination of Dreiding models indicates that the $(CH_3)_3Sn$ group can occupy either an equatorial ($\theta \sim 30°$) or an axial ($\theta \sim 70°$) position. A consideration of non-bonding interactions as well as stabilizing hyperconjugative interactions suggests that the axial conformer should be favoured. If this is the case, then $^5J(^{13}C—^{117,119}Sn)$ for this system should approach the value observed in compound VII where $\theta \simeq 60°$. Compound X, a fluorine analogue of IX, was prepared and examined for the same reasons expounded above for compound VIII.

In this paper we report the results of our study.

Experimental

The benzyltrimethylmetalloidal derivatives were prepared by a standard procedure as described by Hauser and Hance [13] for benzyltrimethylsilane. The

---

* Model systems VII and XII have been successfully employed in other studies concerning the origin of the electronic effect of metallomethyl substituents [10].

** Sn, Pb, and Hg have magnetically active isotopes ($I = \frac{1}{2}$) in natural abundance sufficient to give rise to easily detectable long-range spin coupling with ^{13}C.

ortho-deuterated derivatives were similarly prepared from *o*-deuterobenzylbromide which was synthesized by standard transformations from *o*-toluidine. The ^1H spectra indicated approximately 70% deuterium incorporation. The indanyl and tetralyl derivatives of tin were prepared by a common procedure as outlined for 1-indanyltrimethylstannane.

Benzyltrimethylsilane (I). Colorless oil, b.p. 76°/20 mm Hg (lit. [14] 191-192°/760 mm Hg). n_D^{25} 1.4920. PMR (CCl$_4$, from (CH$_3$)$_3$Si at δ 0.00): 2.10 (2H, singlet, CH$_2$) and 7.0 (5H, complex, aromatic protons).

Benzyltrimethylgermane (II). Colorless oil, b.p. 100°/30-31 mm Hg (lit. [14] 94-95°/28 mm Hg). n_D^{25} 1.5080. PMR (CCl$_4$, from (CH$_3$)$_3$ Ge at δ 0.00): 2.08 (2H, singlet, CH$_2$) and 6.97 (5H, complex, aromatic protons).

Benzyltrimethylstannane (III). Colorless oil, b.p. 108°/21-22 mm Hg (lit. [15] 87°/9 mm Hg). n_D^{25} 1.5440. PMR (CDCl$_3$, from (CH$_3$)$_3$Sn at δ 0.00): 2.28 (2H, singlet, CH$_2$: *J*(Sn—CH$_2$) 62 Hz; *J*(Sn—CH$_3$) 53 Hz) and 7.20 (5H, complex, aromatic).

Benzyltrimethylplumbane (IV). Colorless oil, b.p. 70-74°/0.07 mm Hg (lit. [14] 124°/13 mm Hg, decomp. n_D^{26} 1.6075. PMR (CCl$_4$, from (CH$_3$)$_3$ Pb at δ 0.00): 2.15 (2H, singlet, CH$_2$; *J*(Pb—CH$_2$) 63 Hz; *J*(Pb—CH$_3$) 55 Hz) and 6.33 (5H, complex, aromatic).

Benzylmercuric chloride (VI). VI was obtained (via a Grignard synthesis) as a white solid, m.p. 102-103° (lit. [16] 104°). PMR (CDCl$_3$, from (CH$_3$)$_4$Si): 3.28 (2H, singlet, CH$_2$; *J*(Hg—CH$_2$) 228 Hz) and 7.20 (5H, complex, aromatic).

1-Indanyltrimethylstannane (VII). 1-Chloroindan (8.5 g; 0.056 mol), prepared according to the method outlined by Pacaud and Allen [17], was added dropwise with stirring to a filtered solution (THF) of trimethyltin lithium (~0.05 mol) [18]. After addition was complete, the reaction mixture was allowed to stir overnight before heating to reflux for an hour. The mixture was then filtered, the solvent evaporated off, and the crude residue distilled under a nitrogen atmosphere to afford a colorless oil (3.4 g; 20%), b.p. 60°/0.1 mm Hg n_D^{23} 1.5632. PMR (CCl$_4$, from (CH$_3$)$_3$Sn at δ 0.00): 2.54 (5H, multiplet, CHCH$_2$CH$_2$) and 7.0 (4H, complex, aromatic). Anal. Found: C, 52.06; H, 6.50. C$_{12}$H$_{18}$Sn calcd.: C, 51.30; H, 6.46%.

1-(5-Fluoroindanyl)trimethylstannane (VIII). 5-Fluoro-1-indanone was prepared by the method outlined by Adcock, Dewar, and Gupta [19] and reduced to 5-fluoro-1-indanol by a standard procedure employing lithium aluminium hydride. The alcohol crystallized from ethanol in fine white crystals, m.p. 40-41°. 1-Chloro-5-fluoroindan was prepared by treating the alcohol with dry hydrogen chloride gas. Distilled as a colorless oil, b.p. 60°/0.5 mm Hg.

1-(5-Fluoroindanyl)trimethylstannane distilled as a colorless oil, b.p. 70°/ 0.1 mm Hg. n_D^{23} 1.5505. PMR (CCl$_4$, from (CH$_3$)$_3$Sn at δ 0.00): 2.54 (5H, multiplet, CHCH$_2$CH$_2$) and 6.78 (3H, complex, aromatic).

1-Tetralyltrimethylstannane (IX). 1-Chlorotetralin was prepared by treating 1-tetralol with dry hydrogen chloride gas. Distilled as a colorless oil, b.p. 92-100°/ 0.9-1.00 mm Hg (lit. [20] 98-100°/2 mm Hg). 1-Tetraallyltrimethylstannane distilled as a colorless oil, b.p. 92-98°/0.3-0.4 mm Hg. n_D^{23} 1.5688. PMR (CCl$_4$, from (CH$_3$)$_3$ Sn at δ 0.00): 1.98 (4H, multiplet, C(2)—H and C(3)—H), 2.80 (3H, multiplet, C(1)—H and C(4)—H) and 6.93 (4H, multiplet, aromatic).

1-(6-Fluorotetraallyl)trimethylstannane (X). 6-Fluoro-1-tetralone was pre-

pared according to the method of Allinger and Jones [21] and reduced to 6-fluoro-1-tetralol, m.p. 50°. The alcohol was converted to 1-chloro-6-fluorotetralin in the usual way. Distilled as a colorless oil, b.p. 76-80°/0.1-0.2 mm Hg.

1-(6-Fluorotetralyl)trimethylstannane distilled as a colorless oil, b.p. 84-88°/0.1-0.2 mm Hg. n_D^{23} 1.5515. PMR (CDCl$_3$, from (CH$_3$)$_3$Sn at δ 0.00): 1.95 (4H, multiplet, C(2)—H and C(3)—H, 2.78 (3H, multiplet, C(1)—H and C(4)—H) and 6.78 (3H, multiplet, aromatic).

9,10-Ethano-9,10-dihydro-9-(trimethylstannyl)anthracene (XI). 9-Bromo-9,10-ethano-9,10-dihydroanthracene (4.3 g; 0.15 mol), prepared according to the method outlined by Wilhelm and Curtin [22], in dry tetrahydrofuran (70 ml) at —70° was treated dropwise with t-butyllithium (21 ml; 1.45 M in hexane). The yellow reaction mixture was maintained at —70° for three hours and the yellow precipitate was filtered off at —70°. A solution of trimethyltin chloride (3.0 g; 0.015 mol) in dry tetrahydrofuran (15 ml) was then added dropwise to the yellow filtrate. After addition was complete, the yellow color was discharged. The solution was stirred overnight at —70° before being allowed to warm to room temperature. The THF was evaporated under reduced pressure and the residue extracted with dichloromethane. The inorganic matter was filtered off and the solvent evaporated to afford a product which crystallised from aqueous ethanol as white crystals (3.6 g; 65%) m.p. 105-106° lit. [23] 106-107.5°). PMR (CDCl$_3$, from (CH$_3$)$_3$Sn at δ 0.00): 1.38 (4H, broad singlet, C(15)—H and C(16)—H), 3.88 (1H, broad singlet, C(10)—H) and 6.77 (8H, multiplet, aromatic).

9,10-Ethano-9,10-dihydroanthracene (XII). 9-Bromo-9,10-ethano-9,10-dihydroanthracene (4.3 g; 0.015 mol) was lithiated with t-butyllithium as described above. The mixture was stirred for three hours at —70° before adding water to effect decomposition. The reaction mixture was then extracted with ether and dried; the ether was evaporated to give a product which crystallised from n-pentane as white crystals, m.p. 137-139° (lit. [23] 143-144°). PMR (CDCl$_3$, TMS at δ 0.00): 1.67 (4H, broad singlet, C(15)—H and C(16)—H), 4.30 (2H, broad singlet, C(9)—H and C(10)—H), and 7.17 (8H, multiplet, aromatic).

^{13}C Spectra

A modified Varian HA60IL Spectrometer [24] operating at 15.18 MHz was used to record the spectra of compounds I-Vl as well as the phenyl derivates listed in Table 3. Cyclohexane was used as an internal reference and the chemical shifts converted to the TMS scale by use of the appropriate conversion factor. The spectra of the remaining compounds were obtained on a Bruker Scientific, Inc. WH-90 Fourier transform NMR spectrometer operating at 22.625 MHz. Samples were prepared in deuteriochloroform with TMS as an internal reference.

Results and discussion

Assignments

The ^{13}C NMR data for compound II and compounds IV-XII are listed in Table 1 together with the previously published results for I [7] and III [8]. The spectra for compounds II, IV, V and VI were assigned in the manner previously outlined for compound I and toluene [7]. Spectral assignments for the remaining compounds VII-XII (except XI) were largely determined by experimental facts

TABLE 1

^{13}C NMR PARAMETERS[a,b]

Chemical shifts

Compound	X	Y	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	M—CH$_3$
I	Si(CH$_3$)$_3$		140.4	128.3[c]	128.4[c]	124.2			27.4				−1.9
II	Ge(CH$_3$)$_3$		141.7	127.8[c]	128.4[c]	124.2			26.8				−2.3
III	Sn(CH$_3$)$_3$[d]		142.8	126.8	128.4	123.3			20.4				−10.1
IV	Pb(CH$_3$)$_3$[d]		143.5	126.2	127.7	122.8			25.2				−3.0
V	HgCH$_2$C$_6$H$_5$		145.3	128.0	128.4	123.1							
VI	HgCl[d]		141.2	128.5	128.3	124.7			34.9				
VII	Sn(CH$_3$)$_3$	H	149.1	141.6	124.5	124.4	126.5	122.1	33.4	30.6	33.4		−10.4
VIII	Sn(CH$_3$)$_3$	F	144.5	143.8	111.6	160.7	113.1	122.5	32.2	31.1	33.6		−10.5
IX	Sn(CH$_3$)$_3$	H	142.2	134.3	129.6	123.8	125.9	127.0	31.1	29.7	24.1	31.1	−0.7
X	Sn(CH$_3$)$_3$	F	137.7	136.1	115.6	160.2	112.9	127.9	30.1	29.7	23.3	30.1	−0.9
XI	H		143.8	143.8	123.2	125.5[c]	125.5	123.2	44.1	26.7	26.7	44.1	
XII	Sn(CH$_3$)$_3$		146.9	146.6	123.9	125.5[c]	125.4[c]	125.1	43.0	30.7	29.1	44.8	−8.7

Coupling constants ($J(^{13}C-X)$)

Compound	X	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	M—CH$_3$
III	^{117,119}Sn[e]	36.6	22.6	12.0	14.8			298				322
IV	^{207}Pb	64.6	44.2	26.4	32.4			219				196
V	^{199}Hg	f	55.0	23.2	30.0							
VI	^{199}Hg	151.2	110.0	50.6	62.4							
VII	^{117,119}Sn[e]	32.0	22.0	12.3	15.4	13.0	20.0	333	10.1	f		310
VIII	^{117,119}Sn[e]	f	f	11.0	f	12.8	21.4	333	9.2	f		310
VIII	F	2.4	8.5	22.0	239.7	23.2	7.3	f	f	1.8		
IX	^{117,119}Sn[e]	f	24.6	13.2	15.7	14.0	22.4	346	6.6	19.2	f	310
X	^{117,119}Sn[e]	34.5	f	12.7	f	13.4	23.0	346	f	19.6	f	310
X	F	2.8	6.2	20.8	241.7	20.8	7.3	f	f	f	f	
XII	^{117,119}Sn[e]	5.9	34.1	7.1	>5	>5	34.5	f	f	41.3	f	324

[a] Carbon-13 NMR spectra were obtained for I–VI at 15.18 MHz and for VII–XII at 22.625 MHz. Samples were either neat or concentrated solutions in cyclohexane or chloroform-d. Chemical shifts referenced to TMS (±0.1 ppm). Positive values indicate decreased shielding relative to TMS. Coupling constants in Hertz and are accurate to ±1.0 Hz (or better) except for $J(C(7)–Sn)$ and $J(CH_3–Sn)$ which are no better than ± 5.0 Hz. [b] The carbon-numbering system is as shown on the structural formulas. This system is for convenience only and bears no relation to the numbering system employed for the systematic naming of these compounds. [c] Assignments could be reversed. [d] Assignments confirmed by examination of ortho-deuterated compounds. [e] ^{119}Sn, ^{117}Sn couplings not resolved except for $J(C(7)–Sn)$ and $J(CH_3–Sn)$ [25]. The value quoted for these two couplings constants is for ^{119}Sn coupling. [f] Not observed.

recently established from ^{13}C NMR studies on fluoro-substituted benzocyclo-alkenes [7,11] as well as some model organotin derivatives of fixed molecular geometry*. Firstly, fluoro-substitution in the phenyl ring is characterised by a regular pattern of ^{13}C—^{19}F coupling constants in the aromatic region of the proton-decoupled spectrum, ^1J ($\simeq$245 Hz) $\gg$ ^2J ($\simeq$ 18-20 Hz) > ^3J ($\simeq$ 6-9 Hz) > ^4J ($\simeq$ 1.5-4 Hz). Further, coupling is generally observed ($^4J(^{13}$C—^{19}F $\approx$ 2 Hz) to any *meta* disposed external carbon center which is in a preferred "zig-zag" array. An added benefit of fluorine substitution is the regular and pronounced effect on the ^{13}C chemical shift. The carbon bearing fluorine is quite deshielded (> 30 ppm), whereas carbons *ortho* to fluorine experience quite large upfield shifts ($\simeq$ 14 ppm). Carbons *para* to fluorine are also shielded by a lesser amount ($\simeq$ 5 ppm) whereas *meta* carbons appear to be always deshielded (1-2 ppm).

Secondly, trimethylstannyl substitution in aliphatic systems of reasonably fixed geometry is manifested by a sufficiently regular trend of ^{13}C—^{117,119}Sn coupling constants as to be useful for spectral assignments: ^1J ($\simeq$ 300-340 Hz) $\gg$ ^3J ($\simeq$ 10-70 Hz) > ^2J > 12 Hz) > ^4J > 10 Hz). Further, the $(CH_3)_3$Sn shielding effects are also of sufficient regularity to be used in this regard (β ($\simeq$ +4 ppm) > γ ($\simeq$ —0.5 to +3.5 ppm) > α ($\simeq$ +1 ppm) > δ). It should be noted that the vicinal coupling constant, $^3J(^{13}$C—^{117,119}Sn), has been shown to adhere to a Karplus relation [25]. Interestingly, the γ shielding effect of $(CH_3)_3$Sn is also dependent on the dihedral angle, being at a maximum when θ is 180°.

The aromatic carbons and the aliphatic C(9) resonances of compound VIII were readily assigned on the basis of the relative magnitude of the various ^{13}C—^{19}F coupling constants together with the observed chemical shift pattern reported for 5-fluoroindan [7,11]. The remaining carbons, C(7) and C(8), were readily distinguished by the relative magnitude of the associated ^{13}C—^{117,119}Sn coupling. Spectral assignments for the aromatic region of compound VII can then be computed from the chemical shifts of compound VIII by utilizing the established contributions to carbon screenings by fluoro substitution at C(4) in indan. The aliphatic region of VII is readily assigned on the basis of ^{13}C—^{117,119}Sn coupling and their relative intensities (as well as chemical shift considerations). This leads unambiguously to the assignments listed in Table 1 for compound VII. A similar analysis of the aromatic resonance patterns and chemical shifts observed for X, 6-fluorotetralin [7,11] and tetralin [7,11] leads to an unambiguous assignment of the aromatic region for compound IX (Table 1). However, the assignments for the aliphatic carbons (C(7), C(8), C(9) and C(10)) for compounds IX and X were not as straightforward as that for VII and VIII since the expected coupling ($^4J(^{13}$C—^{19}F) to C(10), which would immediately identify this carbon, was not resolved. Further, the situation was complicated by the fact that whereas four resonances were expected, only three were observed. The resonance due to C(7) in these two compounds, however, was readily identified by the associated large one-bond tin—carbon coupling constant. C(8) in compound IX was distinguished by the associated tin—carbon coupling which is of the right order of

---

* Typically, the lines are flanked by tin satellite peaks due to the presence of ^{117}Sn (7.6% natural abundance, $I = \frac{1}{2}$) and ^{119}Sn (8.5% natural abundance, $I = \frac{1}{2}$). Since most of the $J(^{13}$C—^{117}Sn) and $J(^{13}$C—^{119}Sn) long range coupling constants are not large and because the ratio $J(^{13}$C—^{117}Sn/ $J(^{13}$C—^{119}Sn) = 1.046, individual satellite peaks due to each of these isotopes usually cannot be resolved [25].
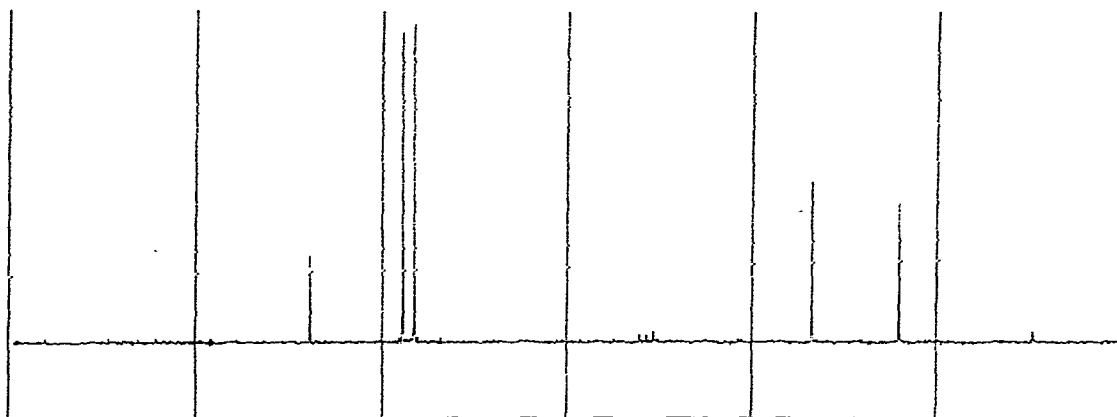
Fig. 1. Proton noise-decoupled ^{13}C FT NMR spectrum of compound XI in CDCl$_3$. Chemical shifts are given relative to internal TMS (Table 1).

magnitude for $^2J(^{13}$C—^{117,119}Sn). This assignment is confirmed by the fact that it leads to an expected large deshielding β-effect. The remaining resonance in the spectrum of compound IX was assigned to C(9) rather than C(10) because of the relatively large associated tin—carbon coupling which is expected for $^3J(^{13}$C—^{117,119}Sn) but not $^4J(^{13}$C—^{117,119}Sn). A consideration of the relative magnitude of γ- and δ-effects for (CH$_3$)$_3$Sn also precludes this resonance from being assigned to C(10). The unusually large intensity of the peak assigned to C(7) for compound IX suggested that C(10) and C(7) are coincidental. This assignment is in accord with an expected small δ-effect. Considering the fact that fluoro substitution at C(4) in tetralin leads to only minor effects to the aliphatic carbon screenings, plus the fact that C(9) is associated with the relatively large $^3J(^{13}$C—^{117,119}Sn), the assignments for C(8), C(9) and C(10) in compound X (Table 1) follow logically from those in IX. Surprisingly, tin—carbon coupling ($^2J(^{13}$C—^{117,119}Sn) was not observed to C(8) in compound X.

A combination of off-resonance noise decoupling and chemical shift considerations allowed ready assignment of C(7), C(10) and C(8), C(9) as well as C(1), C(2) in the spectrum of compound XI (Fig. 1). In the absence of a readily available deutero- or fluoro-substituted analogue, Günther and co-workers [26] so called "finger-print" method was crucial for discriminating between C(3), C(6) (C$_\alpha$) and C(4), C(5) (C$_\beta$) of the aromatic ring. This technique is based on the observation that the splitting patterns for the ^{13}C signals in the ^{1}H-coupled spectra of symmetrically ortho-disubstituted benzenes differ characteristically for carbons α and β. An examination of our spectrum (Fig. 2) indicates quite clearly that the splitting pattern is stikingly similar to Günther and co-workers [26] calculated spectra and those of other ortho-disubstituted benzenes for which C$_\alpha$, C$_\beta$ assignments were known i.e., C$_\alpha$ is clearly upfield from C$_\beta$.

The assignments for compound XII follow logically from those determined for XI by considering the shielding effects of (CH$_3$)$_3$Sn substitution as well as the relative magnitude of the various associated tin—carbon coupling constants. C(7) and C(10) were readily distinguished from C(8) and C(9) on chemical shift
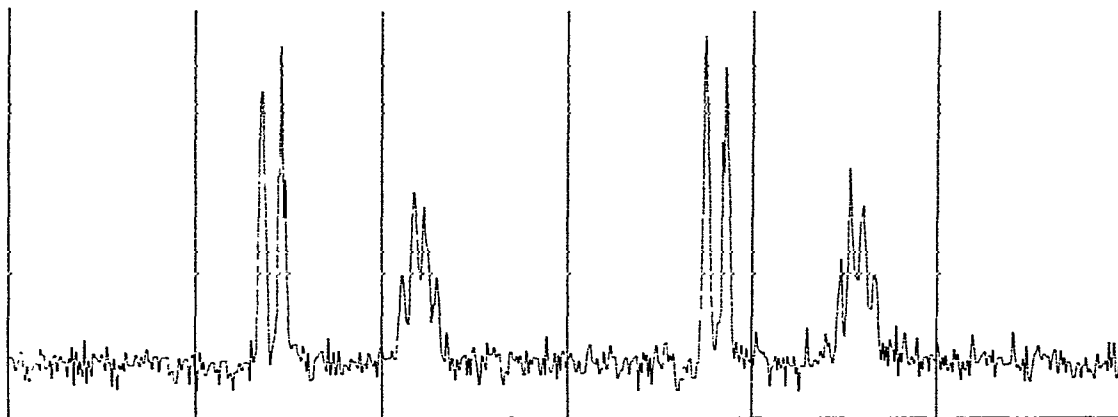
Fig. 2. Proton coupled ^{13}C FT NMR spectrum of the aromatic region (C_α and C_β) of compound XI.

grounds as well as on the basis that α and δ effects are small. However, the expected tin satellites ($^1J(^{13}C—^{117,119}Sn)$ associated with C(7) were not observed and relative signal intensities were employed to define C(7) from C(10), the former being considerably less intense due to a reduction in Overhauser enhancement and the dependence of S/N on T_1 and recycle time in a fourier transform experiment. Although no coupling was observed to the assigned resonance for C(8) (Table 1), the large tin—carbon coupling associated with the resonance assigned to C(9) is characteristic of vicinal carbon—tin centers in an *anti*-coplanar array ($^3J(^{13}C—^{117,119}Sn) \gg {}^2J(^{13}C—^{117,119}Sn)$).

Off-resonance noise decoupling as well as chemical shift and signal intensity considerations allowed ready assignment of the quaternary carbon centers, C(1) and C(2), from the other aromatic carbons (C(3), C(4), C(5) and C(6)). A distinction between C(1) and C(2) was then made on what appears to be a reasonable assumption, namely, that since the C—Sn bond in compound XII lies in the nodal plane of the π-system, the relative magnitude of the two- and three-bond tin—carbon couplings in the aromatic region should be in the order generally observed for relatively rigid aliphatic systems ($^3J(^{13}C—^{117,119}Sn \gg {}^2J(^{13}C—^{117,119}Sn)$). C(6) was readily assigned by the relatively large associated tin—carbon coupling ($^3J(^{13}C—^{117,119}Sn)$) which was anticipated for vicinal centers in a *syn*-coplanar arrangement. It is of interest to note that $^3J(^{13}C—^{117,119}Sn)$ for C(2) and C(6), where the dihedral angle is 180° and 0° respectively, are approximately the same (Table 1). C(3) was distinguished from C(4) and C(5) on chemical shift considerations (δ effect should be small). In the absence of selective deutero substitution, it was not possible to distinguish between the two remaining carbon resonances, C(4) and C(5).

Chemical shifts

Since carbon-13 chemical shifts are considered to be dominated by the paramagnetic term of the perturbational equation for screening constants, certain approximations are necessary if they are to be discussed in terms of charge densities [27]. In particular, a constant average excitation energy term has to be assumed for a series of structurally related compounds and comparisons of chem-

TABLE 2

^{13}C SUBSTITUENT CHEMICAL SHIFTS (SCS)^a

Position	I	II	III	IV	V	VI	VII	IX	XII
Meta C(3)	+0.2^b	+0.2^b	+0.2^b	−0.5^b	+0.2^b	+0.1^b	+0.1^c	+0.4^d	+0.7^e
Meta C(5)							+0.3^c	+0.7^d	−0.1^c
Para C(4)	−1.3^b	−1.3^b	−2.2^b	−2.7^b	−2.4^b	−0.8^b	−1.8^c	−1.4^d	0.0^c

^{a} Positive values imply a downfield shift relative to the appropriate standard. ^{b} Relative to C(3) and C(4) in ethylbenzene [7]. ^{c} Relative to C(3), C(4), and C(5) in indan [11]. ^{d} Relative to C(3), C(4), and C(5) in tetralin [11]. ^{e} Relative to C(3), C(4), and C(5) in compound XI.

ical shifts confined to those carbons sufficiently remote from the substituent such that steric, compressional and bond order effects are not important. Bearing these points in mind, a number of empirical and theoretical correlations have appeared indicating a very close relationship between ^{13}C substituent chemical shifts and charge densities [28,29].

The ^{13}C SCS* for the relevant carbons (C(3) and C(5); C(4)) in compounds I-VII together with those for IX and XII are listed in Table 2. An examination of the data indicates that a number of points are worthy of comment. Firstly, it is clear that replacement of CH_3 in ethylbenzene with the Group IVB metalloidal substituents (compounds I-IV) results in a progressive movement of C(4) to higher field, implying enhanced electron-release from the metallomethyl substituent compared to the alkyl group. The mechanism of this electron release can immediately be attributed to hyperconjugation involving the C—M σ-bond since in compound XII, where θ = zero, the SCS for the $Sn(CH_3)_3$ at C(4) is zero, a result completely in line with the established stereoelectronic requirements of this mechanism but not the π-inductive effect [3-5,10,30,31]. In addition, this result from compound XII, together with the essential constancy of the *meta* SCS (C(3) or C(5)), indicates that σ-inductive or field effects are relatively unimportant for these groups [10].

Secondly, the order of electron release from the C—M bonds indicated by the ^{13}C probe for the neutral ground state (Pb > Sn > Ge ~ Si) is similar to the order observed by Traylor and co-workers [15] in their studies on charge-transfer frequencies and certain hydride abstraction reactions where positively charged species are involved. However, it is important to note that since σ—π interactions involving the C—M bond are expected to act on demand, the effect is much more pronounced in situations where electron deficiency is being generated in the adjacent substrate [15]. This point is dramatically exemplified by a comparison of the σ$^+$ values** ($CH_2Si(CH_3)_3$: −0.4; $CH_2Ge(CH_3)_3$: −0.4; $CH_2Sn(CH_3)_3$: −0.45; $CH_2Pb(CH_3)_3$: −0.52; $CH_2HgCH_2C_6H_5$: −0.5) determined from the ^{13}C chemical shift data (Table 1) with those derived from charge transfer measurements [15]

---

* The ^{13}C substituent chemical shift (SCS) is defined as the difference (ppm) between the ^{13}C chemical shift of the substituted compound and that of the appropriate carbon in the parent hydrocarbon. Positive signs imply deshielding, negative signs shielding.

** Calculated utilizing the correlation line generated between *para* ^{13}C SCS (determined using benzene as the parent hydrocarbon) and σ$^+$ [28].

$(CH_2Si(CH_3)_3: -0.66; CH_2Sn(CH_3)_3: -0.90; CH_2Pb(CH_3)_3: -1.08; CH_2HgCH_2C_6H_5: -1.12)$.

Thirdly, it is of interest to note that the para-C(4) ^{13}C SCS for compounds I, II, III, V, VII and IX (Table 1) parallel the ^{19}F SCS (ppm)* for p-FC$_6$H$_4$-CH$_2$Si(CH$_3$)$_3$ (1.90) [2], p-FC$_6$H$_4$CH$_2$Ge(CH$_3$)$_3$ (1.90) [2], p-FC$_6$H$_4$CH$_2$Sn(CH$_3$)$_3$ (2.60) [2], p-FC$_6$H$_4$CH$_2$HgCH$_2$C$_6$H$_5$ (2.80) [2], VIII (2.14) and X(2.15) respectively. A good correspondence between these two different probes has previously been demonstrated in other situations where π-electron effects are dominant [32]. Interestingly, the ^{19}F probe is again shown to be the more sensitive monitor of ground state π-electron density perturbations [32]. Most importantly, however, the results from both probes clearly establish the importance of hyperconjugative carbon—metal interactions in the neutral ground state, a point that has been questioned [31]. Recent studies have also confirmed the importance of this phenomenon with regard to electron-withdrawal in the ground state [19].

Finally, it can be seen (Table 1) that the electron-releasing effect of CH$_2$HgCl is substantially less than CH$_2$HgCH$_2$C$_6$H$_5$, a result previously noted from ^{19}F studies [2]. This observation can be readily ascribed to a decrease in the effective electropositivity of mercury on replacing an alkyl group by the more electronegative chlorine atom.

Coupling constants

The carbon—metal coupling constants are listed in Tables 1 and 3. A scrutiny of the data brings to light a number of important factors. First, it can be seen that when the metal is directly bonded to the phenyl system (Table 3), ^{meta}J(C—M) is not only greater than ^{para}J(C—M) by large factors, but larger than $^{ortho}J$(C—M). Recent studies on phenylthallium derivatives have indicated that the same feature is also observed for carbon—thallium coupling [33]. Thus in all cases known embodying substantial variations in the nature of the

TABLE 3

COUPLING CONSTANTS $(J(^{13}C{-}X))$ FOR SOME PHENYL ORGANOMETALLICS^{a,b}

Entry	Formula	X	$J(^{13}$C-X)				Reference
			C(1)	C(2)	C(3)	C(4)	
I	(C$_6$H$_5$)$_2$Sn(CH$_3$)$_2$	^{117,119}Sn	486(464)	36.8	47.2	10.8	[8]
II	C$_6$H$_5$Sn(CH$_3$)$_3$	^{117,119}Sn	450	35.4	45.4	10.0	[8]
III^c	C$_6$H$_5$Pb(CH$_3$)$_3$	^{207}Pb	364	63.4	68.8	16.2	This work
IV^c	(p-CH$_3$C$_6$H$_4$)$_4$Pb	^{207}Pb	488.4	69.6	83.2	18.8	This work
V^d	(C$_6$H$_5$)$_2$Hg	^{199}Hg	1218	86.3	100.2	18.0	This work

^{a} Coupling constants in Hertz. ^{b} The carbon-numbering system is based on the understanding that the metallosubstituent is attached to C(1). ^{c} Compounds available from another investigation [40]. ^{d} Rather similar values have been reported [41], but the basis for their assignments was unclear. Our values have been confirmed by examination of bis(meta-deuterophenyl)mercury.

* The fluorine-19 NMR spectra of VIII and X were measured in benzene with a Varian A56/60 operating at 56.4 M.Hz. The SCS quoted are upfield relative to p-fluoroethylbenzene (5.15 ppm upfield from fluorobenzene in benzene as solvent) for the para-substituted-fluorobenzenes, and upfield relative to 5-fluoroindan and 6-fluorotetralin for VIII and X respectively.
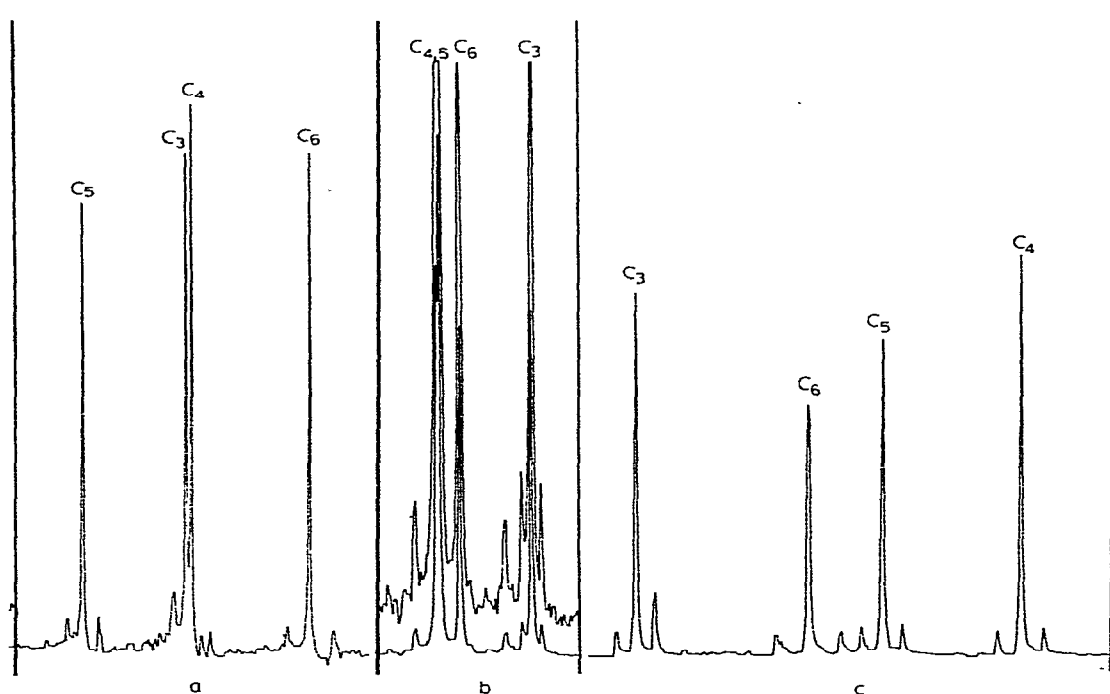
Fig. 3. Proton noise-decoupled ^{13}C FT NMR spectra of the aromatic region (C(3), C(4), C(5) and C(6)) of (a) compound VII, (b) compound XII, (c) compound IX.

C—M bond (M = Sn, Pb, Hg and Tl), no example of ^{para}J(C—M) > ^{meta}J(C—M) has been identified. However, it is abundantly clear from the data in Table 1 that when a methylene group is interposed between the phenyl ring and the metal a dramatic change in the order of events occurs, namely ^{para}J(C—M) > ^{meta}J(C—M). Hence, it appears that a rather special and important contribution to the coupling mechanism is operating in benzylic but not in the related phenyl compounds. That this phenomenon has its origin in carbon—metal (σ—π) hyperconjugation, and is a ground state property of some significance, is strikingly exemplified by a comparison of the coupling data for compound XII* with the data for compound VII. Note that in XII where the dihedral angle (θ) is zero, ^{5}J(C(4)—Sn) is not observed (Fig. 3b) and must be less than 5 Hz (width of C(4), C(5) resonance peak), whereas in VII where $\theta \simeq 60°$, ^{5}J(C(4)—Sn) is 15.4 Hz (Fig. 3a)! This striking result suggests that the long-range coupling ^{5}J(C—M) in benzylic systems is being determined predominantly by a π-electron contribution to the coupling mechanism which is enhanced when direct access to the metal s orbitals is possible via σ—π interactions. Confirmation of this conclusion

---

* Although the benzylic carbon in compound XII is not strictly the same type as that in III, VII or IX (quaternary carbon compared to secondary and tertiary centers), studies have shown that successive methyl substitution of the methylene carbon in III does not alter the relative magnitude of the coup-ling constants i.e. ^{para}J(C—Sn) remains substantially greater than ^{meta}J(C—Sn) [34].
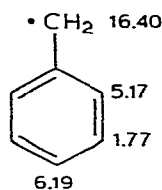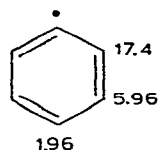
Fig. 4.

Fig. 5.

is provided by the fact that in β-phenethyltrimethyltin*, where structural features preclude σ—π interactions, coupling is only observed at the quaternary carbon atom (vicinal to tin) of the phenyl ring.

An interesting point with regard to the origin of long-range coupling ^5J(C—M) in benzylic systems is the comparison of the hyperfine splitting constants, ∂H_i (in G) in benzyl (Fig. 4) and phenyl radicals [36] (Fig. 5), where in the latter, the unpaired electron is located largely in a σ-type orbital. As expected for a conjugative interaction, $aH_{para} > aH_{meta}$ in the benzyl radical, but in the phenyl radical, $aH_{para} < aH_{meta}$. These results are similar to the coupling constants above for the benzyl and phenyl organometallics.

Secondly, the similar value of ^5J(C(4)—Sn) for compounds III and VII implies that the average or effective dihedral angle (θ) in the mobile monocyclic species $ArCH_2Sn(CH_3)_3$ must approach 60°. This was expected, for if C—Sn hyperconjugation is important, it must tend to increase this angle in order to maximize the resulting stabilization. Presumably, in mobile electron-deficient species, where electronic demands on the C—M σ-bond are much larger than the neutral ground state [10,15], the effective dihedral angle (θ) must approach 90° (the most favoured orientation for maximum σ—π interactions). The importance of hyperconjugative interactions in determining ground state conformations of mobile systems is exemplified by a recent X-ray crystallographic determination [37], photoelectron spectral [38] and theoretical studies [39].

Thirdly, the similar values of ^5J(C(4)—Sn) for compounds VII (15.4 Hz; Fig. 3a) and IX (15.7 Hz; Fig. 3c) indicate that the effective dihedral angle (θ) for the conformationally mobile tetralin system must also be ≃ 60°. This can only be achieved if the predominant conformation has the $Sn(CH_3)_3$ group axially disposed, the preferred orientation for a maximum hyperconjugative interaction. The magnitude of the vicinal coupling constant ^3J(C(9)—Sn) (19.2 Hz), which has been shown to adhere to a Karplus relation with respect to the dihedral angles (ϕ) about the C—C bond [25], unambiguously confirms this conclusion: when $Sn(CH_3)_3$ is equatorially and axially disposed in 9 then ϕ is 180° and 70° (approximately), respectively. Note that in XII where ϕ is 180°, ^3J(C(9)—Sn) is 41.3 Hz. It is worthwhile to note that the conclusions regarding the geometries of III and IX are strongly supported by the appropriate relative chemical shifts (^{13}C and ^{19}F) given above.

---

* The ^{13}C NMR data for $C_6H_5CH_2CH_2Sn(CH_3)_3$ are as follows, δ (ppm) rel., to TMS and (J(C—Sn)-(Hz)): C_{ipso}, 145.6 (45.0); C_{ortho}, 129.2; C_{meta}, 128.7; C_{para}, 126.5; C_α, 33.8 (19.0); C_β, 13.4 (not determined) [35].

Finally, the relatively small value for the two-bond coupling constant $^2J(C(1)-Sn)$ (5.9 Hz) observed in compound XII compared to those observed in III, VII and IX (Table 1), indicates a substantial π-electron contribution to the coupling mechanism for $^2J(C(1)-Sn)$ in the latter compounds.

References

1 W. Adcock, B.D. Gupta, W. Kitching, D. Doddrell and M. Geckle, J. Amer. Chem. Soc., 96 (1974) 7360.
2 W. Adcock, B.F. Hegarty, W. Kitching and A.J. Smith, J. Organometal. Chem., 12 (1968) 21; W. Kitching, W. Adcock and B.F. Hegarty, Aust. J. Chem., 21 (1968) 2411; A.J. Smith, W. Adcock and W. Kitching, J. Amer. Chem. Soc., 92 (1970) 6140.
3 A.R. Bassindale, C. Eaborn, D.R.M. Walton and D.J. Young, J. Organometal. Chem., 20 (1969) 49.
4 W. Adcock, S.Q.A. Rizvi and W. Kitching, J. Amer. Chem. Soc., 94 (1972) 3657.
5 W. Kitching, A.J. Smith, W. Adcock and S.Q.A. Rizvi, J. Organometal. Chem., 42 (1972) 373.
6 C.W. Fong and M.D. Johnson, J. Chem. Soc. Perkin II, (1973) 986; D. Dodd, M.D. Johnson and C.W. Fong, J. Chem. Soc. Dalton, (1974) 58.
7 S.Q.A. Rizvi, B.D. Gupta, W. Adcock, D. Doddrell and W. Kitching, J. Organometal. Chem., 63 (1973) 67.
8 D. Doddrell, M.L. Bullpitt, C.J. Moore, C.W. Fong, W. Kitching, W. Adcock and B.D. Gupta, Tetrahedron Lett., (1973) 665.
9 R.M. Lynden-Bell and R.K. Harris, Nuclear Magnetic Resonance Spectroscopy, Nelson, London, 1969, 101-120.
10 C.G. Pitt, J. Organometal. Chem., 23 (1970) 35; W. Hanstein, H.J. Berwin and J.G. Traylor, J. Amer. Chem. Soc., 92 (1970) 7476.
11 W. Adcock, B.D. Gupta, T.C. Khor, D. Doddrell, D. Jordan and W. Kitching, J. Amer. Chem. Soc., 96 (1974) 1595; W. Adcock, B.D. Gupta, T.C. Khor, D. Doddrell and W. Kitching, J. Org. Chem., submitted.
12 D.D. Davis, A.J. Swimatis and G.L. Robertson, J. Organometal. Chem., 46 (1972) C9.
13 C.R. Hauser and C.R. Hance, J. Amer. Chem. Soc., 73 (1951) 5846.
14 N. Hagihara, M. Kumada and R. Okawara, Handbook of Organometallic Compounds, W.A. Benjamin Inc., New York, 1969.
15 W. Hanstein, H.J. Berwin and T.G. Traylor, J. Amer. Chem. Soc., 92 (1970) 829.
16 A.N. Nesmeyanov and K.A. Kocheshkov (Eds.), Methods of Elemento-Organic Chemistry, North-Holland Publishing Company, Amsterdam, 1967, vol. 4, p. 22.
17 R.A. Pacaud and C.F.H. Allan, Org. Synthesis, Coll. Vol. II, Wiley-Interscience, New York, 1943, p. 336.
18 C. Tamborski, F.E. Ford and E.J. Soloski, J. Org. Chem., 28 (1963) 237.
19 W. Adcock, M.J.S. Dewar and B.D. Gupta, J. Amer. Chem. Soc., 95 (1973) 7353.
20 G. Baddeley, J.W. Rasburn and R. Rose, J. Chem. Soc., (1958) 3168.
21 N.L. Allinger and E.S. Jones, J. Org. Chem., 27 (1962) 70.
22 M. Wilhelm and D.Y. Curtin, Helv. Chim. Acta, 40 (1957) 2129.
23 H.J. Berwin, Ph.D. Thesis, University of California at San Diego, 1970.
24 D. Doddrell, F.B. Hanson, A. Marker, R.J. Kenny and N.V. Riggs, Aust. J. Chem., 27 (1974) 2175.
25 D. Doddrell, I. Burfitt, W. Kitching, M. Bullpitt, R.J. Mynott, J.L. Considine, H.G. Kuivila and R.H. Sarma, J. Amer. Chem. Soc., 96 (1974) 1640;
26 H. Günther, H. Schmickler and G. Jikeli, J. Magn. Resonance, 11 (1973) 344; G. Jikeli, W. Herrig and H. Günther, J. Amer. Chem. Soc., 96 (1974) 323.
27 J.B. Stothers. Carbon-13 NMR Spectroscopy, Academic Press, N.Y. 1972, Chapter 4 and ref. therein.
28 G.L. Nelson, G.C. Levy and J.D. Cargioli, J. Amer. Chem. Soc., 94 (1972) 3089.
29 D.T. Clark, Chem. Commun., (1966) 390 and ref. therein; W.F. Reynolds, I.R. Peat, M.H. Freedman, and J.R. Lyerla, Can. J. Chem., 51 (1973) 1857; D.A. Dawson and W.F. Reynolds, Can. J. Chem., 53 (1975) 373 and ref. therein; H.C. Clark and J.E.H. Ward, J. Amer. Chem. Soc., 96 (1974) 1741.
30 A. Schweig, U. Weidner and G. Manuel, J. Organometal. Chem., 67 (1974) C4 and ref. therein; G.T. Hartman and T.G. Traylor, Tetrahedron Lett., (1975) 939; N.C. Cutress, A.R. Katritzky, C. Eaborn, D.R.M. Walton and R.D. Topsom, J. Organometal. Chem., 43 (1972) 131; P.K. Bischof, M.J.S. Dewar, D.W. Goodman and T.B. Jones, J. Organometal. Chem., 82 (1974) 89; T.G. Traylor, H.J. Berwin, J. Jerkunica and M.L. Hall, Pure Appl. Chem., 30 (1972) 599.
31 C. Eaborn, T.A. Emokpae, V.I. Sidorov and R. Taylor, J. Chem. Soc. Perkin II, (1974) 1454.
32 W. Adcock, M. Aurangzeb, W. Kitching, N. Smith and D. Doddrell, Aust. J. Chem., 27 (1974) 1817.
33 W. Kitching, D. Praeger, C.J. Moore, D. Doddrell and W. Adcock, J. Organometal. Chem., 70 (1974) 339; L. Ernst, J. Organometal. Chem., 82 (1974) 319; W. Kitching, C.J. Moore, D. Doddrell and W. Adcock, J. Organometal. Chem., 94 (1975) 469.

34 M. Geckle, Private communication.

35 M. Bullpitt, Unpublished work.

36 H. Fischer, Z. Naturforsch, 20 (1965) 488; P.H. Kosai, E. Hedaya and E.B. Whipple, J. Amer. Chem. Soc., 91 (1969) 4364.

37 R.D. Bach, A.T. Weibel, W. Schmonsees, and M.D. Glick, J. Chem. Soc. Chem., Commun., (1974) 961.

38 H. Schmidt, A. Schweig, F. Mathey and G. Müller, Tetrahedron, 31 (1975) 1287 and ref. therein.

39 P.A. Scherr, M.D. Glick, J.H. Siefert and R.D. Bach, J. Amer. Chem. Soc., 97 (1975) 1782 and ref. therein.

40 D. Doddrell, K.G. Lewis, C.E. Mulquiney, W. Adcock, W. Kitching and M. Bullpitt, Aust. J. Chem., 27 (1974) 417.

41 F.J. Weigert and J.D. Roberts, J. Amer. Chem. Soc., 91 (1969) 494.