Journal of Organometallic Chemistry, 72 (1974) 211—220
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

POLYSILANE DERIVATIVES OF THE TRANSITION METALS

III*. PREPARATIONS AND SPECTRA OF MANGANESE AND IRON DERIVATIVES

BRIAN K. NICHOLSON** and JAMES SIMPSON***
Department of Chemistry, University of Otago, P.O. Box 56, Dunedin (New Zealand)

(Received December 6th, 1973)

Summary

The preparations of derivatives of $Mn(CO)_5$, $Mn(CO)_4PPh_3$ and π-$Cp(CO)_2Fe$ containing the polysilyl ligands $(Me_3Si)_nMe_{3-n}Si$— (n = 1-3) are presented. The infrared and proton NMR spectra of the compounds are given and for the $Mn(CO)_5$ derivatives, force constants are derived and discussed in terms of the σ-donor/π-acceptor properties of the silyl ligands.

Introduction

Although numerous complexes with bonds between silicon and transition metals are known [1—4], little attention has been given to compounds having polysilyl ligands bound to the metal atom. King et al. [5] reported a series of iron complexes containing straight-chain polysilyl ligands and, in the course of this investigation, a number of communications dealing with organodisilane derivatives have appeared [6—8]. Interest in this field derives from two sources. The nature of the Si—M bond in transition metal systems is the subject of continued speculation, particularly with respect to the involvement of *d*-orbitals on silicon in $(d-d)\pi$ interactions and also the possibility of bonding interactions between carbonyl ligands and the metal-bound silicon atom [9]. There is evidence from other organosilicon systems to suggest that electron delocalisation can occur through the *d*-orbitals of catenated silicon atoms [10-12] and such a process could enhance $(d-d)\pi$ bonding in polysilyl metal systems. Furthermore, the steric requirements of the bulky polysilyl ligands could markedly affect both the geometry of, and the bonding in, Si—M systems.

This paper describes the preparation and spectroscopic properties of manganese and iron complexes incorporating the ligands $(Me_3Si)_nMe_{3-n}Si$— (n = 1-3).

---

[*] For part II see ref. 14.

[**] Present address: School of Molecular Sciences, University of Sussex, Brighton.

[***] To whom correspondence should be addressed.

A preliminary account of part of this work has been published [13] and the molecular structure of one of the compounds, $(Me_3Si)_3SiMn(CO)_5$, has been described [14].

Experimental

All reactions were conducted under dry nitrogen in oven-dried glassware. Solvents were dried over sodium wire, except for THF which was distilled from sodium/benzophenone mixtures prior to use. The silanes Me_5Si_2H [15], Me_5Si_2Cl [16], $(Me_3Si)_3SiH$ [17], $(Me_3Si)_3SiCl$ [18], $(Me_3Si)_4Si$ [19] and $(ClMe_2Si)_4Si$ [20] were prepared by published procedures. $(Me_3Si)_3SiMe$, $Me(Me_3Si)_2SiH$ and $Me(Me_3Si)_2SiCl$ were prepared similarly [21]. The metal carbonyl reagents $BrMn(CO)_5$ [22], $[Mn(CO)_4PPh_3]_2$ [23], $BrMn(CO)_4PPh_3$ [24], $NaMn(CO)_5$ and $NaFe(CO)_2Cp$ [25] were synthesised from $Mn_2(CO)_{10}$ and $[\pi\text{-}CpFe(CO)_2]_2$ purchased from Strem Chemicals Inc.

Infrared spectra were recorded on a Perkin—Elmer Model 225 grating spectrophotometer fitted with a thermocouple detector and NMR spectra on a Varian T60 machine. Analytical data are listed in Table 1 for all the manganese and iron derivatives which were also characterised by mass spectroscopy [26].

TABLE 1

PREPARATIVE DATA FOR THE SILYL METAL CARBONYL COMPOUNDS

Compound	Method	Yield (%)	Analytical data found (calcd.) (%)	
			C	H
$Me_3SiMn(CO)_5$	b	33		
$Me_5Si_2Mn(CO)_5$	c	12	37.30 (36.81)	4.93 (4.60)
$Me_5Si_2Mn(CO)_5$	a	26		
$Me_7Si_3Mn(CO)_5$	c	19	37.79 (37.48)	5.46 (5.46)
$Me_7Si_3Mn(CO)_5$	d	30		
$Me_9Si_4Mn(CO)_5$	c	21	38.09 (38.02)	6.03 (6.11)
$Me_9Si_4Mn(CO)_5$	d	41	38.32 (38.02)	6.33 (6.11)
$Me_3SiMn(CO)_4PPh_3$	c	35	60.16 (59.76)	5.27 (4.78)
$Me_9Si_4Mn(CO)_4PPh_3$	d	8	55.92 (55.03)	6.27 (6.21)
$Me_3SiFe(CO)_2(\pi\text{-}Cp)$	e	62	48.32 (48.00)	5.65 (5.60)
$Me_5Si_2Fe(CO)_2(\pi\text{-}Cp)$	f	48	47.08 (46.75)	6.43 (6.49)
$Me_7Si_3Fe(CO)_2(\pi\text{-}Cp)$	a	30	46.24 (45.90)	7.33 (7.10)
$Me_9Si_4Fe(CO)_2(\pi\text{-}Cp)$	a	18	46.35 (45.28)	7.48 (7.54)
$\{(\pi\text{-}Cp(CO)_2Fe)Me_2Si\}_4Si$	a	5	44.66 (44.63)	4.83 (4.55)

[a] Salt elimination reaction between chlorosilane and metal carbonyl anion. [b] See ref. 28. [c] Hydrogen elimination reaction. [d] Salt elimination reaction between silyl—lithium reagent and manganese carbonyl halide. [e] See ref. 37. [f] See ref. 5.

Hydrogen elimination reactions

$Me_5Si_2Mn(CO)_5$. A mixture of Me_5Si_2H (0.9 g, 6.7 mmol) and $Mn_2(CO)_{10}$ (1.2 g, 3.1 mmol) was heated in a sealed evacuated ampoule for 28 h at 125°. On cooling, the contents of the ampoule were extracted with hexane and the filtered solution concentrated and chilled to precipitate unreacted $Mn_2(CO)_{10}$ The supernatant liquid was chromatographed on silica-gel plates, eluting with hexane, to give two bands; $H_3Mn_3(CO)_{12}$ (R_f 0.5) and impure $Me_5Si_2Mn(CO)_5$ (R_f 0.9). The latter product was dissolved in hexane and extracted with conc. H_2SO_4 at 0°. Separation of the organic layer and removal of solvent at $\approx$ 20°/ 30 mm gave $Me_5Si_2Mn(CO)_5$ (0.25 g, 12%) as a colourless liquid.

$Me(Me_3Si)_2SiMn(CO)_5$ and $(Me_3Si)_3SiMn(CO)_5$ were obtained as white crystals in 19% and 20% yields respectively by similar procedures.

$Me_3SiMn(CO)_4PPh_3$. A mixture of Me_3SiH (0.34 g, 4.6 mmol) and $[Mn(CO)_4PPh_3]_2$ was heated in an evacuated ampoule at 135° for 12 h. The contents of the ampoule were extracted with ether. Solvents was removed from the filtered extract to leave a solid, which was recrystallised from hexane to give $Me_3SiMn(CO)_4PPh_3$ (0.16 g, 35%) as off-white crystals.

$Me_5Si_2Mn(CO)_4PPh_3$ (attempted). Me_5Si_2H (0.3 g, 2.3 mmol) and $[Mn(CO)_4PPh_3]_2$ (0.9 g, 1.05 mmol) were heated together at 140° for 24 h in a sealed, evacuated ampoule. Extraction of the contents with hexane and chromatography of this extract on silica-gel gave an off-white crystalline compound which was identified by analysis, infrared and NMR spectroscopy as $Me_3SiMn(CO)_4PPh_3$. A mass spectrum showed that traces of $Me_5Si_2Mn(CO)_4PPh_3$ were present in the product as an impurity.

Salt-elimination reactions

$Me_5Si_2Mn(CO)_5$. An ether solution of $NaMn(CO)_5$ (2 mmol) was reduced to dryness on the vacuum line. Excess Me_5Si_2Cl (8 mmol) was distilled on to the residue and the mixture stirred for 12 h. Unreacted Me_5Si_2Cl was pumped off and the residue was extracted with hexane. Chromatography of this extract on silica-gel plates gave $Me_5Si_2Mn(CO)_5$ (0.17 g, 26%) as a colourless oil.

$Me(Me_3Si)_2SiMn(CO)_5$. A mixture of $(Me_3Si)_3SiMe$ (0.52 g, 2 mmol) biphenyl (0.16 g) and lithium chips (0.17 g) in THF (30 ml) was stirred for 24 h. The resulting solution of $Me(Me_3Si)_2SiLi$ was filtered from unreacted lithium and cooled to −80°. A solution of $BrMn(CO)_5$ (0.55 g, 2 mmol) in THF (30 ml) was added dropwise and the mixture slowly warmed to room temperature. After removal of solvent, the residue was extracted with pentane and the filtered extract chromatographed on silica-gel plates. The uppermost, colourless band (R_f 0.9) was removed and sublimed at 30°/0.1 mm to give $Me(Me_3Si)_2SiMn(CO)_5$ (0.27 g, 30%).

$(Me_3Si)_3SiMn(CO)_5$ was obtained in 41% yield by a similar procedure using $(Me_3Si)_4Si$.

$(Me_3Si)_3SiMn(CO)_4PPh_3$. A mixture of $(Me_3Si)_4Si$ (0.32 g, 1 mmol), biphenyl (0.1 g) and lithium (0.12 g) in THF (13 ml) was stirred for 24 h. The solution of $(Me_3Si)_3SiLi$ was removed from unreacted lithium and added dropwise to an isomeric mixture of $BrMn(CO)_4PPh_3$ (1.4 mmol) in THF (10 ml) at −80°. After stirring for 1 h at room temperature the THF was removed and the

contents were extracted with hexane. Chromatography of this extract on silica-gel plates, eluting with benzene/hexane (1/9), gave off-white crystals (R_f 0.5) of $(Me_3Si)_3SiMn(CO)_4PPh_3$ (0.05 g 8%).

$(Me_3Si)_3SiFe(CO)_2Cp$. A THF solution containing $NaFe(CO)_2(\pi\text{-}Cp)$ (6 mmol) and $(Me_3Si)_3SiCl$ (5 mmol) was stirred at room temperature for 12 h. Solvent was removed and the residue extracted with hexane. The extract was transferred to a 15 × 1.5 cm column of alumina, elution with hexane giving a yellow solution. Removal of the solvent and sublimation at 80°/0.1 mm gave $(Me_3Si)_3SiFe(CO)_2(\pi\text{-}Cp)$ (0.37 g, 18%) as orange crystals.

A similar procedure using $Me(Me_3Si)_2SiCl$ gave orange crystals of $Me(Me_3Si)_2SiFe(CO)_2(\pi\text{-}Cp)$ in 30% yield.

$[(\pi\text{-}Cp(CO)_2Fe)Me_2Si]_4Si$. A mixture of $NaFe(CO)_2(\pi\text{-}Cp)$ (11 mmol) in THF (60 ml) and $(ClMe_2Si)_4Si$ (1.1 g, 2.5 mmol) was stirred for 18 h. THF was removed under vacuum and the residue extracted with hexane. After filtration this extract was placed on a 15 × 1.5 cm column of alumina. Elution with hexane yielded a trace of ferrocene; continued elution with ether/hexane (3/7) gave a yellow product which was recrystallised from hexane to give yellow crystals of $[(\pi\text{-}Cp(CO)_2Fe)Me_2Si]_4Si$ (0.12 g, 5%).

Results and discussion

Preparative aspects

A. Pentacarbonyl manganese derivatives

The hydrogen elimination reaction of silicon hydrides with dimanganese decarbonyl (eqn. 1) is the standard preparative route to monosilyl derivatives of manganese carbonyl [27-31]. This reaction however was found to be less

$$2R_3SiH + Mn_2(CO)_{10} \rightarrow 2R_3SiMn(CO)_5 + H_2 \qquad (1)$$

successful for the preparation of polysilyl derivatives. Yields were generally poor (Table 1) and the inevitable presence of siloxane impurities made isolation of pure products difficult. The production of siloxane species in these systems was unexpected as the reactions were performed in sealed tubes under rigorously dry and anaerobic conditions. The oxygen for siloxane formation must therefore be presumed to originate from a carbonyl group. The hydride cluster compound $H_3Mn_3(CO)_{12}$ [32] was also isolated as a by-product of these reactions. It has been shown [32] that the analogous rhenium hydride results from the reaction of $Re_2(CO)_{10}$ with molecular hydrogen at 383 K so that the presence of $H_3Mn_3(CO)_{12}$ in these systems is unremarkable.

In an attempt to improve the yields of polysilyl derivatives, alternative methods of silicon—metal bond formation were applied, where possible, to the polysilyl species. In particular, syntheses involving salt-elimination reactions proved successful in this respect. Thus reasonable yields of $Me_5Si_2Mn(CO)_5$ were obtained by the reaction of Me_5Si_2Cl with $NaMn(CO)_5$ in the absence of solvents. The same reaction in THF is reported [5] to give no Si—Mn bonded product and our work confirms this finding. Optimum yields of the derivatives $(Me_3Si)_nMe_{3-n}SiMn(CO)_5$ (n = 2 or 3) were obtained by coupling the appropriate silyl—lithium reagent with $BrMn(CO)_5$ in THF. Although other factors are undoubtedly involved, the success of these latter reactions parallel the stabilities of the silyl—lithium species in THF [17]:

$(Me_3Si)_3SiLi > Me(Me_3Si)_2SiLi \gg Me_5Si_2Li$

In contrast to these observations however, a similar reaction with the stable silyl—lithium reagent Ph_3SiLi gave only low yields of the Si—Mn bonded product. In this case, lithium—halogen exchange, leading to the formation of Si—Si and Mn—Mn bonds, predominated even at 193 K.

Purification of the polysilylpentacarbonylmanganese compounds was achieved by chromatography on silica gel followed by sublimation. If the products contained siloxane impurities the purification procedure was more complex. Extraction of a pentane solution of the products with concentrated sulphuric acid removed most of the siloxanes but complete purification in such systems was tedious.

All the $(Me_3Si)_nMe_{3-n}SiMn(CO)_5$ compounds (n = 0-3) could be safely handled in air for short periods and stored indefinitely under nitrogen at 273 K. $Me_5Si_2Mn(CO)_5$ showed the greatest tendency to decompose, the liquid nature of this derivative making it more susceptible to oxidation and hydrolysis.

B. Tetracarbonyl(triphenylphosphine)manganese derivatives

Good yields of $Me_3SiMn(CO)_4PPh_3$ were obtained from a sealed tube reaction between Me_3SiH and $[Mn(CO)_4PPh_3]_2$ at 398 K. Hydrogen elimination reactions with polysilanes however were less straightforward. Using Me_5Si_2H, the major product was found to be $Me_3SiMn(CO)_4PPh_3$ rather than the expected polysilyl compound, while $(Me_3Si)_3SiH$ gave a complex mixture of silyl derivatives that could not be separated chromatographically. It appears that under the conditions necessary for reaction $[Mn(CO)_4PPh_3]_2$ can catalyse Si—Si bond cleavage. Similar rearrangements have been encounterd previously in the presence of organometallic derivatives of the transition metals at temperatures in the range 363-413 K [6, 33, 34].

Attempts to prepare $R_3SiMn(CO)_4PPh_3$ [R_3 = $(Me_3Si)_3$, $(Me_3Si)_2Me$, Me_3SiMe_2] by direct phosphine substitution of the $R_3SiMn(CO)_5$ compounds led to decomposition without extensive carbonyl replacement despite the fact that similar methods have been used successfully to obtain phosphine substituted derivatives of monosilyl manganese pentacarbonyls [28, 30].

The only viable synthetic route to $(Me_3Si)_3SiMn(CO)_4PPh_3$ was found to be the reaction between $(Me_3Si)_3SiLi$ and $BrMn(CO)_4PPh_3$. Even here the yields obtained were low, and an attempt to similarly prepare $Me(Me_3Si)_2SiMn(CO)_4$-PPh_3 gave only traces of the desired product.

C. Attempted preparation of tris[(trimethylsilyl)methyl] pentacarbonylmanganese

Attempts were made to synthesise $(Me_3Si)_3CMn(CO)_5$ for comparison with the polysilyl derivative. Although $Me_3SiCH_2Mn(CO)_5$ has been successfully prepared from the reaction of Me_3SiCH_2Li with $BrMn(CO)_5$ [36], a similar reaction with $(Me_3Si)_3CLi$ gave no C—Mn bonded product. The reaction of $(Me_3Si)_3CBr$ with $NaMn(CO)_5$ was equally unsuccessful. The structure of $(Me_3Si)_3SiMn(CO)_5$ [14] points to a considerable steric interaction between the methyl groups on the β-silicon atoms and the equatorial carbonyl groups. The reduction in length of the M—M′ vector on passing from Si—Mn to C—Mn would be expected to increase such interactions appreciably in $(Me_3Si)_3CMn(CO)_5$, a view that is borne out by examination of molecular models. Our inability to synthesize this molecule may therefore be attributed to these steric interactions.

D. Cyclopentadienyldicarbonyliron derivatives

Polysilyl derivatives of π-$Cp(CO)_2Fe$ were obtained by coupling $NaFe(CO)_2$-(π-Cp) and the appropriate chlorosilane in THF. Purification by chromatography on alumina and subsequent sublimation gave reasonable yields of the required product. This method, which was originally used to prepare monosilyl [37] and straight-chain polysilyl [5] compounds, can be extended to produce polysilyl species with more than one iron atom per molecule by the use of the appropriate halopolysilane.

All the polysilyl derivatives of cyclopentadienyldicarbonyliron, which ranged in colour from red to yellow, were unaffected by exposure to air in the solid state, although in solution signs of decomposition appeared after several hours in contact with air.

E. Tetracarbonylcobalt derivatives

Hydrogen elimination occurred readily between $Co_2(CO)_8$ and polysilanes at room temperature to give products with infrared spectra entirely consistent with the formation of Si—Co bonded species. Despite the apparent success of the preparative method, the high solubility and low volatility of the resulting tetracarbonyl cobalt compounds necessitated the use of chromatographic isolation techniques. The polysilylcobalt compounds proved particularly susceptible to oxidation and hydrolysis and none of the derivatives could be isolated in the pure state.

Nuclear magnetic resonance spectra

Table 2 lists the proton NMR chemical shift data for the polysilyl metal complexes of manganese and iron. The methyl protons from groups attached to metal-bonded silicon atoms resonate in the range 9.5-9.7τ, while the resonan-

TABLE 2

PROTON NMR CHEMICAL SHIFTS (τ)[a]

Compound	MeSiM	MeSiSi	PPh_3[b]	π-Cp
$Me_3SiMn(CO)_5$	9.53			
$Me_5Si_2Mn(CO)_5$	9.53	9.85		
$Me(Me_3Si)_2SiMn(CO)_5$	9.57	9.79		
$(Me_3Si)_3SiMn(CO)_5$		9.73		
$Me_3SiMn(CO)_4PPh_3$	9.53		3.70	
$(Me_3Si)_3SiMn(CO)_4PPh_3$		9.75	3.70	
$Me_3SiFe(CO)_2(\pi$-$Cp)$	9.64			5.53
$Me_5Si_2Fe(CO)_2(\pi$-$Cp)$	9.57	9.82		5.45
$Me(Me_3Si)_2SiFe(CO)_2Cp$	9.67	9.80		5.39
$(Me_3Si)_3SiFe(CO)_2Cp$		9.73		5.32
$[(Cp(CO)_2Fe)Me_2Si]_4Si$	9.25			5.35

[a] Manganese compounds in CH_2Cl_2, iron compounds in 90% CS_2/10% C_6H_6. [b] Multiplet.

ce of β-silicon substituents is found at higher field, 9.7-9.9τ. For the π-Cp(CO)$_2$Fe derivatives an adsorption is found in the region 5.3-5.9τ due to the five equivalent protons of the C_5H_5 group. This resonance position varied considerably from 5.87τ in benzene to 5.34τ in $CDCl_3$ for the compound Me$_3$SiFe(CO)$_2$(π-Cp), whereas the methyl resonances were virtually independent of the solvent used. No obvious correlation could be found between solvent polarity and the chemical shift of the C_5H_5 protons.

Infrared spectra

A. $R_3SiMn(CO)_5$ molecules

In discussing the infrared spectra of LMn(CO)$_5$ compounds in the carbonyl stretching region, the molecular symmetry is usually taken as C_{4v} although the true symmetry is often lower [27, 38]. For C_{4v} geometry, three infrared active ($2A_1 + E$) and one Raman active (B_1) carbonyl stretching modes are expected [39]. In general, three bands are observed in the 2000 cm^{-1} region of the infrared spectra of R$_3$SiMn(CO)$_5$ compounds and their assignment to the $2A_1$ and E vibrational modes is well established [27]. The highest frequency band is assigned A_1 (2), the most intense band E and the remaining absorption A_1 (1). The intensity of the A_1 (2) band is usually greater than predicted suggesting considerable coupling between the two A_1 modes [39].

The observed absorption bands and their assignments for (Me$_3$Si)$_n$Me$_{3-n}$-SiMn(CO)$_5$ (n = 0-3) are given in Table 3. The A_1 (1) band appeared as a shoulder on the E mode for all but the (Me$_3$Si)$_3$SiMn(CO)$_5$ molecule. This showed only two bands in the 2000 cm^{-1} region presumably due to accidental degeneracy of the A_1 (1) and E modes [27]. Our assignments for Me$_3$SiMn(CO)$_5$ agree with those given by previous workers [28, 40].

Many attempts have been made to correlate carbonyl stretching frequencies with electronic distributions in metal carbonyls [41, 42]. Of particular interest has been the likelihood of π-bonding contributions from ligands other than carbon monoxide in substituted systems [43 - 45]. To this end Graham has introduced Δσ and Δπ parameters, derived from carbonyl stretching force constants, which indicate the relative σ-donor/π-acceptor capacities of ligands L in LMn(CO)$_5$

TABLE 3

CARBONYL INFRARED SPECTRA[a], FORCE CONSTANTS[b] AND GRAHAM PARAMETERS[c] FOR RMn(CO)$_5$ COMPOUNDS

R	$A_1(2)$	$A_1(1)$	E	k_1	k_2	Δσ	Δπ
Me$_3$Si	2094	2001	1995	16.20	16.59	−0.55	0.32
Me$_5$Si$_2$	2092	1999	1993	16.29	16.53	−0.76	0.47
Me(Me$_3$Si)$_2$Si	2090	1999	1995	16.30	16.54	−0.75	0.47
(Me$_3$Si)$_3$Si	2091	1998	1998	16.28	16.58	−0.65	0.41
Me[d]	2109	1989	2010	16.11	16.82	0	0
Me$_3$Sn[d]	2089	1998	1991	16.29	16.49	−0.84	0.51

[a] Measured in hexane solution ± 1 cm^{-1}. [b] k_1 And k_2 are axial and equatorial carbonyl stretching force constants in mdyne·Å^{-1}, calculated using the Cotton—Kraihanzel method. Experimental precision ± 0.02. [c] MeMn(CO)$_5$ as reference compound. Precisions are ± 0.08 in Δπ and ± 0.12 in Δσ. [d] From ref. 46.

molecules [46]. Listed in Table 3 are the axial and equatorial carbonyl-bond stretching force constants (k_1 and k_2 respectively) obtained using the Cotton—Kraihanzel method [38] together with the corresponding Graham parameters.

The trends within the series $(Me_3Si)_nMe_{3-n}SiMn(CO)_5$ are consistent with the superposition of two conflicting effects. Starting from the Me_3Si derivative there is an initial increase in σ-donor/π-acceptor ability with β-silicon substitution ($n = 1$) which can be explained in terms of electron release by the Me_3Si group and d-orbital availability for delocalised π-bonding. Further substitution ($n = 2,3$) however, reverses this trend as the steric requirements of the polysilyl ligand increase and non-bonded interactions lengthen the Si—Mn bond. (The Si—Mn bond in $(Me_3Si)_3SiMn(CO)_5$ has been shown [14] to be significantly longer than that in $Me_3SiMn(CO)_5$).

Comparison of our $\Delta\sigma$ and $\Delta\pi$ parameters with those given for other compounds in ref. 46 shows that while the trimethylsilyl and polysilyl ligands act as stronger σ-donor/π-acceptor species than the methyl group, their effect is less than that of Me_3Sn. This can best be explained by considering the σ-donor ability of the Group IV ligand. The established order [47] of electron release by the Me_3M [1] group is Si < Ge < Sn and, in the synergic situation of low-valent transition metal systems an increase in σ-donor strength is likely to be accompanied by an increase in π-acceptor ability if suitable orbitals are available on the ligand. The photoelectron spectra of $CH_3Mn(CO)_5$ and $SiH_3Mn(CO)_5$ have recently beeen interpreted [48] in terms of poor σ-donor ability for the silyl ligand, but no evidence could be adduced in favour of a $(d—d)\pi$ interaction in the Si—Mn bond. While our results support an increased inductive electron release in the sense Sn > Si, the existence of π-contributions to the M—Mn bonds must also be inferred. However, the significant decrease (≈ 30%) in bond order between Si—Mn and M—Mn (M = Ge, Sn) proposed recently [40] on the basis of metal—metal bond stretching force constants and bond energy data derived from mass spectrometric measurements, is not reflected in the results obtained here.

B. $R_3SiMn(CO)_4PPh_3$ molecules

The symmetry of *trans*-LL′M(CO)$_4$ compounds is taken to be C_{4v}, from which a single infrared-active (E) and two Raman-active (A_1 and B_1) carbonyl stretching modes are predicted [39]. The infrared spectra of the $R_3SiMn(CO)_4PPh_3$ molecules show one very intense absorption at ≈ 1945 cm^{-1} and this is assigned to the E mode. In addition, two weak bands are observed at higher frequencies which may be assigned to the formally forbidden A_1 and B_1 vibrations. Table 4 lists the observed frequencies for $Me_3SiMn(CO)_4PPh_3$ and $(Me_3Si)_3SiMn(CO)_4PPh_3$ together with the force constant, k, calculated using the Cotton—

TABLE 4

INFRARED SPECTRA[a] AND FORCE CONSTANTS[b] FOR $RMn(CO)_4PPh_3$

R	A_1	B_1	E	k
Me_3Si	2043(w)	1979(w)	1945(vs)	15.81
$(Me_3Si)_3Si$	2042(w)	1983(w)	1946(vs)	15.83

[a] Measured in hexane solution, ± cm^{-1}. [b] In mdynes. $Å^{-1}$.

TABLE 5

INFRARED SPECTRA OF $R_3SiFe(CO)_2(\pi\text{-}Cp)$ MOLECULES[a]

Compound	ν(CO) absorptions	
$Me_3SiFe(CO)_2(\pi\text{-}Cp)$	1998	1945
$Me_5Si_2Fe(CO)_2(\pi\text{-}Cp)$	1998	1947
$Me(Me_3Si)_2SiFe(CO)_2(\pi\text{-}Cp)$	1998	1949
$(Me_3Si)_3SiFe(CO)_2(\pi\text{-}Cp)$	1999	1951
$[(\pi\text{-}Cp(CO)_2Fe)Me_2Si]_4Si$	1997	1947

[a] Measured in hexane solution, ± 1 cm^{-1}.

Kraihanzel approximation [38]. There is little difference between the vibrational frequencies and hence the force constants for the two compounds but, for a given silyl ligand, the k value is lower than the equivalent k_2 parameter in the corresponding $R_3SiMn(CO)_5$ molecule (see Table 3). This observation is the expected effect of replacing a carbonyl group by the weaker π-acceptor ligand PPh_3.

C. $R_3SiFe(CO)_2(\pi\text{-}Cp)$ molecules

All the $R_3SiFe(CO)_2(\pi\text{-}Cp)$ compounds studied exhibited the two intense absorption bands expected for the carbonyl region. The frequencies observed are given in Table 5. The small but regular shift to high frequency of the low energy vibration as the number of silicon atoms in the ligand increases is probably due to steric rather than electronic variations.

Acknowledgements

We wish to thank the New Zealand Universities' Grants Committee for financial support and a Postgraduate Scholarship (to B.K.N.). The gift of chlorosilanes from Midland Silicones Ltd. is also gratefully acknowledged.

References

1 N.S. Vyazankin, G.A. Razuvaev and O.A. Kuglaya, Organometal. Chem. Rev. A, 3 (1968) 323.
2 J.F. Young, Advan. Inorg. Chem. Radiochem., 11 (1968) 91.
3 E.H. Brookes and R.J. Cross, Organometal. Chem. Rev. A, 6 (1970) 227.
4 H.G. Ang and P.T. Lau, Organometal. Chem. Rev. A, 8 (1972) 235.
5 R.B. King, K.H. Pannell, C.R. Bennett and M. Ishaq, J. Organometal. Chem., 19 (1967) 327.
6 A. Brookes, S.A.R. Knox and F.G.A. Stone, J. Chem. Soc. A, (1971) 3469.
7 W. Malisch, J. Organometal. Chem., 39 (1972) C28.
8 A.G. MacDiarmid, unpublished results quoted in Ref. 5.
9 A.D. Berry, E.R. Corey, A.P. Hagen, A.G. MacDiarmid, F.E. Saalfeld and B.B. Wayland, J. Amer. Chem. Soc., 92 (1970) 1940 and references quoted therein.
10 H. Saturai, S. Deguchi, M. Yamagata, S-I. Morimoto, M. Kira and M. Kumada, J. Organometal. Chem., 18 (1969) 285.
11 M.A. Cook, C. Eaborn and D.R.M. Walton, J. Organometal. Chem., 23 (1970) 85.
12 N.C. Cutress, A.R. Katritzky, C. Eaborn, D.R.M. Walton and R.D. Topsom, J. Organometal. Chem., 43 (1972) 131.
13 B.K. Nicholson and J. Simpson, J. Organometal. Chem., 32 (1971) C29.
14 B.K. Nicholson, J. Simpson and W.T. Robinson, J. Organometal. Chem., 47 (1973) 403.
15 J.V. Urenovitch and R. West, J. Organometal. Chem., 3 (1965) 138.
16 H. Sakurai, K. Tominga, T. Watanabe and M. Kumada, Tetrahedron Lett., (1966) 5493.
17 H. Gilman and C.L. Smith, J. Organometal. Chem., 14 (1968) 91.
18 H. Gilman and R.L. Harrell, J. Organometal. Chem., 5 (1966) 199.
19 H. Gilman and C.L. Smith, J. Organometal. Chem., 8 (1967) 245.
20 M. Kumada, H. Sakurai and T. Watanabe, J. Organometal. Chem., 9 (1967) P11.

21 B.K. Nicholson, Ph.D. Thesis, University of Otago, (1973).
22 E.W. Abel and G. Wilkinson, J. Chem. Soc., (1959) 1501.
23 A.C. Osborne and M.H.B. Stiddard, J. Chem. Soc., (1964) 634.
24 P.W. Jolly and F.G.A. Stone, J. Chem. Soc., (1965) 5259.
25 R.B. King, Advan. Organometal. Chem., 2 (1964) 157.
26 B.K. Nicholson and J. Simpson, to be published.
27 W. Jetz, P.B. Simmons, J.A.J. Thomson and W.A.G. Graham, Inorg. Chem., 5 (1966) 2217.
28 A.D. Berry and A.G. MacDiarmid, Inorg. Nucl. Chem. Lett., 5 (1969) 601.
29 O. Kahn and M. Bigorgne, C.R. Acad. Sci., Ser. C, 266 (1968) 792.
30 R.R. Schrieke and B.O. West, Inorg. Nucl. Chem. Lett., 5 (1969) 141.
31 R.R. Schrieke and B.O. West, Aust. J. Chem., 22 (1969) 49.
32 B.F.G. Johnson, R.D. Johnston, J. Lewis and B.H. Robinson, J. Organometal. Chem., 10 (1967) 105.
33 H.D. Kaesz, S.A.R. Knox, J.W. Koepke and R.B. Saillant, Chem. Commun., (1967) 477.
34 K. Yamamoto, H. Okinoshima and H. Kumada, J. Organometal. Chem., 23 (1970) C7.
35 H. Sakurai, A. Hosomi and M. Kumada, Chem. Commun. (1969) 4.
36 B. Wozniak, J.D. Ruddick and G. Wilkinson, J. Chem. Soc. A, (1971) 3116.
37 T.S. Piper, D. Lemal and G. Wilkinson, Naturwissenschaften, 43 (1956) 129.
38 F.A. Cotton and C.S. Kraihanzel, J. Amer. Chem. Soc., 84 (1962) 4432.
39 D.M. Adams, Metal—Ligand and Related Vibrations, Arnold, London, 1967.
40 R.A. Burnham and S.R. Stobart, J. Chem. Soc., Dalton Trans., (1973) 1269.
41 L.M. Haines and M.H.B. Stiddard, Advan. Inorg. Chem. Radiochem., 12 (1969) 53.
42 L.M. Bower and M.H.B. Stiddard, J. Chem. Soc. A, (1968) 2264.
43 D.J. Patmore and W.A.G. Graham, Inorg. Chem., 6 (1967) 981.
44 J.A.J. Thomson and W.A.G. Graham, Inorg. Chem., 6 (1967) 1875.
45 O. Kahn and M. Bigorgne, J. Organometal. Chem., 10 (1967) 137.
46 W.A.G. Graham, Inorg. Chem., 7 (1968) 315.
47 J.G.A. Luyten and G.J.M. van der Kerk, Organometallic Compounds of the Group IV Elements, Vol. 1, Part II, Dekker, New York, 1968, p. 91.
48 S. Cradock, E.A.V. Ebsworth and A. Robertson, J. Chem. Soc., Dalton Trans., (1973) 22.