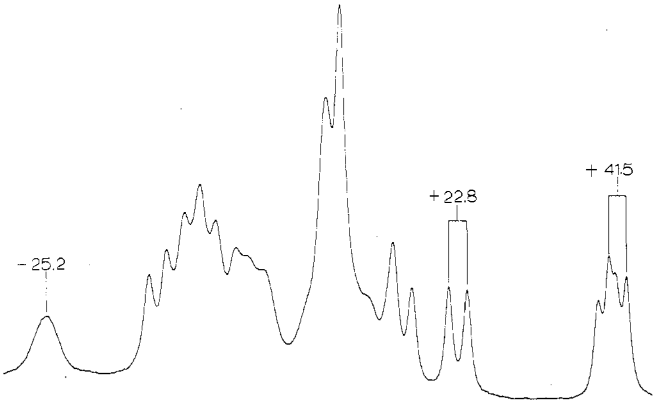

Figure 4. The 70.6-MHz ^{11}B nmr spectrum of $B_{18}H_{20}CNH_2C_6H_{11}$ in acetone solution referenced to $BF_3 \cdot O(C_2H_5)_2$.

sponding to the phenyl and cyclohexyl protons, respectively. We propose that the $CNH_2C_6H_{11}$ group is inserted into one and the $Ni(Ph_2PCH_2CH_2PPh_2)$ group is inserted into the other open face of the B_{18} framework. This gives the most sterically favorable bonding arrangement if framework rearrangements do not occur.

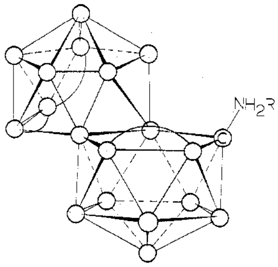

Figure 5. Proposed structure of i-$B_{18}H_{20}CNH_2C_6H_{11}$ ($R = C_6H_{11}$).

Registry No. n-$B_{18}H_{20}Ni(PPh_3)_2$, 36182-42-0; $(CH_3)_4N[n$-$B_{18}H_{20}Co(CO)_3]$, 36182-41-9; $(CH_3)_4N[n$-$B_{18}H_{20}Rh(CO)PPh_3]$, 36465-07-3; n-$B_{18}H_{20}Ni$(diphos), 36182-40-8; n-$B_{18}H_{20}Pd$(diphos), 36182-39-5; i-$B_{18}H_{20}Ni$(diphos), 36182-45-3; i-$B_{18}H_{20}Pt$(diphos), 36182-44-2; i-$B_{18}H_{20}Pd$(diphos), 36182-43-1; n-$B_{18}H_{20}(C_5H_5N)_2$, 12745-16-3; i-$B_{18}H_{20}CNH_2C_6H_{11}$, 12745-15-2; $(i$-$B_{18}H_{18}CNH_2C_6H_{11})Ni$(diphos), 12745-17-4.

Acknowledgments. The authors thank Mr. Ron Garber for some of the ^{11}B nmr measurements. This work was generously supported by the Office of Naval Research.

Contribution from the Naval Research Laboratory, Washington, D. C. 20390, and the John Harrison Laboratory of Chemistry and the Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

Mass Spectral Studies of Some Manganese Carbonyls

F. E. SAALFELD,*[1a] M. V. McDOWELL,[1a] J. J. DeCORPO,[1a,b] A. D. BERRY,[1c] and A. G. MacDIARMID[1c]

Received April 17, 1972

Mass spectral studies have been carried out on a series of manganese carbonyls: $HMn(CO)_5$, $(CH_3)_3SiMn(CO)_5$, and $(CH_3)_3SiMn(CO)_x(PF_3)_{5-x}$ where $x = 2$-5. These studies include measurement of the fragmentation patterns and calculation of heats of formation of the compounds and some of their positive ions from appearance potential measurements. The heats of formation of the compounds are as follows (kcal/mol): $HMn(CO)_5$, -237; $(CH_3)_3SiMn(CO)_5$, -423; $(CH_3)_3SiMn(CO)_4(PF_3)$, -638; $(CH_3)_3SiMn(CO)_3(PF_3)_3$, -823; $(CH_3)_3SiMn(CO)_2(PF_3)_3$, -1023; $(CH_3)_3SiMn(CO)(PF_3)_4$, -1223.

Introduction

A large number of mass spectral studies of substituted metal carbonyl compounds have been reported in the literature in recent years.[2-20] Substituent effects, such as the σ-donor and π-acceptor properties, have been correlated with observed changes in the ionization potentials of the substituted metal carbonyls.[9-15] Svec and his coworkers[9,18] and Bidinosti and his students[19] have shown that the average ionic bond energies and average neutral bond energies are related. The findings of this report, summarizing the results of a mass spectral study of the compounds $HMn(CO)_5$, $(CH_3)_3SiMn(CO)_5$, and

---

(1) (a) Naval Research Laboratory. (b) NRC-NRL Resident Research Associate 1970-1972. (c) University of Pennsylvania.

(2) (a) F. E. Saalfeld, M. V. McDowell, S. K. Gondal, and A. J. MacDiarmid, *J. Amer. Chem. Soc.*, **90**, 3684 (1968); (b) F. E. Saalfeld, M. V. McDowell, S. K. Gondal, and A. G. MacDiarmid, *Inorg. Chem.*, **7**, 1465 (1968).

(3) F. E. Saalfeld, M. V. McDowell, A. P. Hagen, and A. G. MacDiarmid, *Inorg. Chem.*, **7**, 1665 (1968).

(4) A. G. MacDiarmid, *et al.*, *Pure Appl. Chem.*, **19**, 431 (1969).

(5) A. D. Berry and A. G. MacDiarmid, *Inorg. Nucl. Chem. Lett.*, **5**, 601 (1969).

(6) A. D. Berry, E. R. Carey, A. P. Hagen, A. G. MacDiarmid, F. E. Saalfeld, and B. B. Wayland, *J. Amer. Chem. Soc.*, **92**, 1940 (1970).

(7) A. D. Berry, *et al.*, *J. Amer. Chem. Soc.*, **92**, 1940 (1970).

(8) F. E. Saalfeld, M. V. McDowell, and A. G. MacDiarmid, *J. Amer. Chem. Soc.*, **92**, 2324 (1970).

(9) G. A. Junk, H. J. Svec, and R. J. Angelici, *J. Amer. Chem. Soc.*, **90**, 5758 (1968).

(10) H. J. Svec and G. A. Junk, *Inorg. Chem.*, **7**, 1688 (1968).

(11) W. Hieber and G. Wagner, *Z. Naturforsch. B*, **13**, 339 (1958).

(12) G. A. Junk and H. J. Svec, *J. Chem. Soc. A*, 3171 (1970).

(13) S. Pignataro and F. P. Lossing, *J. Organometal. Chem.*, **11**, 571 (1968).

(14) G. Distefano, G. Innorta, S. Pignataro, and A. Foffani, *J. Organometal. Chem.*, **14**, 165 (1968).

(15) A. Foffani, S. Pignataro, J. Distefano, and G. Innorta, *J. Organometal. Chem.*, **7**, 473 (1967).

(16) D. R. Bidinosti and N. S. McIntyre, *Can. J. Chem.*, **48**, 593 (1970).

(17) G. Distefano, A. Foffani, G. Innorta, and S. Pignataro, presented at the International Conference on Mass Spectrometry, Brussels, Aug 31-Sept 4, 1970.

(18) G. A. Junk and H. J. Svec, *Z. Naturforsch. B*, **23**, 1 (1968).

(19) D. R. Bidinosti and N. S. McIntyre, *Can. J. Chem.*, **45**, 641 (1967).

(20) F. E. Saalfeld, M. V. McDowell, and A. G. MacDiarmid, "Recent Developments in Mass Spectroscopy," K. Ogata and T. Hayakawa, Ed., University Park Press, Baltimore, Md., 1970, p 1073.

Table I. Fragmentation Patterns[a] of Manganese Carbonyl Derivatives

		HMn-	$(CH_3)_3SiMn(CO)_x(PF_3)_{5-x}$			
m/e	Ion	$(CO)_5$[b]	$x = 5$	$x = 4$	$x = 3$	$x = 2$
448	$(CH_3)_3SiMn(CO)_2(PF_3)_3^+$					0.3
433	$(CH_3)_2SiMn(CO)_2(PF_3)_3^+$					0.2
388	$(CH_3)_3SiMn(CO)_3(PF_3)_2^+$				1.1	
375	$Mn(CO)_2(PF_3)_3^+$					0.6
373	$(CH_3)_2SiMn(CO)_3(PF_3)_2^+$				0.7	
360	$(CH_3)_3SiMn(CO)_2(PF_3)_2^+$				1.4	1.4
345	$(CH_3)_2SiMn(CO)_2(PF_3)_2^+$				0.2	
332	$(CH_3)_3SiMn(CO)(PF_3)_2^+$				0.1	0.2
328	$(CH_3)_3SiMn(CO)_4(PF_3)^+$			2.8		
317	$(CH_3)_2SiMn(CO)(PF_3)_2^+$				0.2	
313	$(CH_3)_2SiMn(CO)_4(PF_3)^+$			1.0		
304	$(CH_3)_3SiMn(PF_3)_2^+$					3.6
300	$(CH_3)_3SiMn(CO)_3PF_3^+$			0.1	3.2	
285	$(CH_3)_2SiMn(CO)_3PF_3^+$				0.4	
272	$(CH_3)_3SiMn(CO)_2PF_3^+$			0.05	0.9	0.5
268	$(CH_3)_3SiMn(CO)_5^+$		2.9			
257	$(CH_3)_2SiMn(CO)_2PF_3^+$			0.5	1.1	1.0
253	$(CH_3)_2SiMn(CO)_5^+$		0.7			
244	$(CH_3)_3SiMn(CO)PF_3^+$				0.7	0.6
240	$(CH_3)_3SiMn(CO)_4^+$		0.3	3.0		
229	$(CH_3)_2SiMn(CO)PF_3^+$			1.0	0.7	0.8
225	$(CH_3)_2SiMn(CO)_4^+$		1.0			
216	$(CH_3)_3SiMnPF_3^+$				0.5	0.6
212	$(CH_3)_3SiMn(CO)_3^+$		1.4	0.7	1.0	
201	$(CH_3)_2SiMnPF_3^+$			1.0	0.7	0.6
197	$(CH_3)_2SiMn(CO)_3^+$		0.6			
196	$HMn(CO)_5^+$	7.5				
195	$Mn(CO)_5^+$	1.3				
184	$(CH_3)_3SiMn(CO)_2^+$		0.9	0.9	0.7	0.7
180	$Mn(CO)_2(PF_2)^+$				0.9	0.9
169	$(CH_3)_2SiMn(CO)_2^+$		0.6	0.5		
168	$HMn(CO)_4^+$	0.6				
167	$Mn(CO)_4^+$	0.3	0.1			
156	$(CH_3)_3Si(CO)^+$		1.8	2.3	1.8	1.9
143	$MnPF_3^+$			0.3	1.1	1.1
141	$(CH_3)_2SiMn(CO)^+$		0.3	0.5	0.5	0.5
140	$HMn(CO)_3^+$	2.5				
139	$Mn(CO)_3^+$	2.3	0.2			
128	$(CH_3)_3SiMn^+$		7.3	8.3	7.4	7.0
113	$(CH_3)_2SiMn^+$		1.0	1.6	2.4	2.4
112	$HMn(CO)_2^+$	1.4				
111	$Mn(CO)_2^+$	5.8	0.5			
98	CH_3SiMn^+		0.6	0.6	1.0	1.0
84	$HMn(CO)^+$	8.1				
83	$Mn(CO)^+$	8.8	2.1	1.5	1.8	2.0
73	$(CH_3)_3Si^+$		40.6	32.5	29.8	29.5
70	CH_3Mn^+		3.3	4.1	3.5	3.2
56	HMn^+	7.7				
55	Mn^+	38.6	21.1	14.4	19.8	19.0
45	$CH_3SiH_2^+$			3.2	4.2	3.9
43	CH_3Si^+		3.6	2.3	3.8	3.8
41.5	$Mn(CO)_2^{2+}$	6.1				
28	CO^+/Si^+	5.7	2.4	1.0	3.6	3.9
15	CH_3^+		0.3	0.2	0.2	0.2

[a] Values reported are per cent total ion current summed from *m/e* 12 at 70-eV ionizing current and 0.125-μA trap current. Ion intensities less than 0.05 and isotopic contributions have been omitted.
[b] The sample of $HMn(CO)_5$ was distilled into the mass spectrometer from a probe cooled to -60°.

$(CH_3)_3SiMn(CO)_x(PF_3)_{5-x}$ where $x = 2–5$, concur with the conclusions of Junk, Svec, and Angelici[9] and Foffani, *et al.*[15]

The synthesis of $(CH_3)_3SiMn(CO)_5$ and its reaction with PF_3 have been described previously.[4,5] Pentacarbonylmanganese hydride was prepared by standard reactions.[21] The desired products were separated by vacuum distillation and gas chromatography. While $(CH_3)_3SiMn(CO)_4PF_3$ was obtained in a high degree of purity, it was impossible to isolate $(CH_3)_3SiMn(CO_3)_3(PF_3)_2$ or $(CH_3)_3SiMn(CO)_2(PF_3)_3$ completely free from $(CH_3)_3SiMn(CO)_4PF_3$.

All mass spectral data reported here, except the exact mass measurements, were obtained on a modified Bendix 12-107 time-of-flight mass spectrometer which has been described previously.[22] The reasons for using this mass spectrometer as well as the technique employed for the appearance potential measurements have been cited in a previous publication.[2a] The chemical composition of the positive ions was established from high-resolution mass spectral data obtained with a CEC 21-110 mass spectrometer; it has been assumed that the chemical composition of the positive ions observed with the Bendix mass spectrometer were the same as those observed with the CEC instrument.

The fragmentation patterns of all of the compounds exhibited some temperature dependence, the most temperature-sensitive spectrum being that of $HMn(CO)_5$. For example, when $HMn(CO)_5$ was introduced into the mass spectrometer through a conventional gas inlet system using a molecular leak at 30°, the ratio of the molecular weight ion to the Mn^+ ion was 30:100; whereas, when $HMn(CO)_5$ was introduced into the instrument through a cold probe (-60°) similar to that described by Haddon, *et al.*,[23] this ratio was 90:100. Although the cold probe technique is difficult to employ for mass spectral studies, it was used to check the thermal sensitivity of the compounds studied. In the case of $HMn(CO)_5$, it was used for all of the data reported. The mass spectrum of $HMn(CO)_5$, reported in Table I, agrees well with the spectrum reported by Edgell and Risen,[24] which was also obtained using the cold probe technique.[25] The mass spectra of the other compounds did not change significantly when the mass spectrometer introduction temperature was varied from -60 to +30°.

All mass spectral data obtained for this report have been studied as a function of the ion source temperature and pressure. These data, fragmentation patterns, and appearance potential measurements, together with the mass spectral data reported earlier[20] for the negative ion and neutral fragments, produced by electron impact reactions for these compounds, support the existence of a (d → d)π-back-bonding interaction between the metal atom and the substituent as postulated in previous studies[4] for some substituted cobalt carbonyl compounds.

Results and Discussion

Fragmentation Patterns. The mass spectral data for the manganese compounds, corrected for residual background in the mass spectrometer, are shown in Table I. In addition to the ions reported, other ions with relatively minor abundance (less than 0.5% of the total ion current) were also observed. These were fragment ions formed by the loss of an oxygen atom from one of the carbon monoxide ligands or by loss of a fluorine atom from one of the phosphorus trifluoride moieties. All of the compounds had a readily observable molecular weight ion.

No obvious correlation between the degree of substitution of phosphorus trifluoride for carbon monoxide and the ion current intensities of the PF_3-containing ions is apparent. This is in contrast to the observations reported for the $HCo(CO)_x(PF_3)_{4-x}$ series of compounds.[2a] Moreover, the manganese compounds did not fragment by consecutive losses of carbon monoxide or phosphorus trifluoride ligands in the

---

(21) R. B. King, "Transition Metal Compounds," Vol. I, Academic Press, Inc., New York, N. Y., 1965, p 158.

(22) F. E. Saalfeld and M. V. McDowell, *Inorg. Chem.*, 6, 96 (1967).

(23) W. F. Haddon, E. M. Chait, and F. W. McLafferty, *Anal. Chem.*, **38**, 1968 (1966).

(24) W. F. Edgell and W. M. Risen, *J. Amer. Chem. Soc.*, **88**, 5451 (1966).

(25) W. F. Haddon, private communication, 1968.

Table II. Ionization Potentials

Compound	IP, eV	Compound	IP, eV
$HMn(CO)_5$	8.5 ± 0.1[a]	$(CH_3)_3SiMn(CO)_3(PF_3)_2$	8.1 ± 0.1
$(CH_3)_3SiMn(CO)_5$	8.7 ± 0.2	$(CH_3)_3SiMn(CO)_2(PF_3)_3$	9.1 ± 0.2
$(CH_3)_3SiMn(CO)_4PF_3$	8.7 ± 0.2		

[a] The error represents an estimate of the accuracy of the measurements; the reproducibility of the measurements, based on the standard deviation of the mean of 10 measurements, was better than 0.05 eV in all cases. Therefore, we believe the relative difference between the ionization potentials of these compounds to be real and significant.

Table III. Appearance Potentials and Heats of Formation for Selected Ions from $XMn(CO)_x(PF_3)_{5-x}$[a]

	$XMn(CO^+)_4$	$XMn(CO^+)_3$	$XMn(CO^+)_2$	$XMnCO^+$	XMn^+	$Mn(CO^+)_5$	$Mn(CO^+)_4$	$Mn(CO^+)_3$	$Mn(CO^+)_2$	$MnCO^+$	Mn^+
					$HMn(CO)_5$						
AP, eV	8.7	9.9	10.3	12.7	13.8		11.2	13.2	13.7		17.3
$\Delta H_f°$, kcal/mol	-11	54	80	161	212		6	69	106		(241)[b]
					$(CH_3)_3SiMn(CO)_5$						
AP, eV	9.2	10.2	10.8	12.0	12.8					17.9	21.7
$\Delta H_f°$, kcal/mol	-184	-134	-95	-41	5						(241)[c]
					$(CH_3)_3SiMn(CO)_4PF_3$						
AP, eV	9.9		11.1	12.7							21.9
$\Delta H_f°$, kcal/mol	-184		-103	-40							(241)[d]

[a] X = H or $(CH_3)_3Si$. [b] $\Delta H_f°(Mn^+) = 241$ kcal/mol from ref 27; from this value $\Delta H_f°(HMnCO) = -237$ kcal/mol was calculated and used to calculate the heats of formation for the other ions shown. [c] $\Delta H_f°(Mn^+) = 241$ kcal/mol from ref 27; from this value $\Delta H_f°((CH_3)_3SiMn(CO)_5) = -423$ kcal/mol was calculated. [d] $\Delta H_f°(Mn^+) = 241$ kcal/mol from ref 27; from this value $\Delta H_f°((CH_3)_3SiMn(CO)_4PF_3) = -638$ kcal/mol was calculated.

manner of the cobalt compounds, but rather, the loss of a methyl group from the trimethylsilyl moiety always competed with the loss of a CO or PF_3 ligand. As had been noted previously[2a,26] for other substituted carbonyls, no doubly charged positive ions are observed when PF_3 is incorporated into the metal carbonyl.

Ionization Potentials. The ionization potentials of the manganese compounds are delineated in Table II. The ionization potential of H· is 13.6 eV[27] while that of $(CH_3)_3Si$ has been estimated to be 7.8 eV.[28] The reason the ionization potentials of the compound and of the substituents do not follow the trends reported by Junk, *et al.*,[9] for the compounds $XMn(CO)_5$ (X = Cl, Br, I) may be explained by the presence of back-bonding between the metal and the substituent. For H, back-bonding cannot take place and, qualitatively, electron density in the metal orbital is expected to be greater, causing the compound's ionization potential to be lower than one would predict from the trend noted by Junk. For the $(CH_3)_3Si$ substituent, it is believed that significant $(d \rightarrow d)\pi$ back-bonding is present,[4,6] which removes some of the electron density of the metal orbital and thus raises the ionization potential of the molecule compared to the predicted behavior. Both of these expected trends agree with the experimental observations; thus some support for the existence of back-bonding is gleaned for the manganese compounds.

In comparing the ionization potentials of the $(CH_3)_3SiMn(CO)_x(PF_3)_{5-x}$ series of compounds, a minimum is noted at $x = 3$. A similar trend of ionization potential with PF_3 substitution for CO was observed previously for $HCo(CO)_x(PF_3)_{4-x}$ compounds.[2a] The reason for this behavior is not readily apparent.

Thermochemical Properties. The appearance potentials of several of the fragment ions have been measured and are cited in Table III. Unfortunately, it was impossible to measure the appearance potential of $Mn(CO)_5^+$ from $HMn(CO)_5$ accurately because the resolution of the mass spectrometer was insufficient to resolve $Mn(CO)_5^+$ from the tail of the $HMn(CO)_5$ peak. An estimate of the appearance potential of $Mn(CO)_5^+$ indicates that this value is approximately equal to the ionization potential of $HMn(CO)_5$. Since it was not possible to separate $(CH_3)_3SiMn(CO)_4PF_3$ from $(CH_3)_3SiMn(CO)_2(PF_3)_3$ or $(CH_3)_3SiMn(CO_3)(PF_3)_2$, no meaningful energetic measurements could be made on the fragment ions from these last two substances. However, some of the thermochemical values for these compounds can be estimated from the trends discussed below.

Thermochemical values, such as heats of formation and bond energies, can be calculated using appearance potential values, provided the ion source reaction is known or can be reasonably assumed and appropriate ancillary thermochemical data are available. Information concerning the ion source reactions was obtained by the clastogram method, developed by Kiser.[29] This method, based on the quasiequilibrium theory of mass spectra, delineates which ions are fragmenting and forming other ions. In this study, the following supporting data were employed in the calculations (in kcal/mol): $\Delta H_f°(H) = 52.1$,[30] $\Delta H_f°(CO) = -26.4$,[30] $\Delta H_f°(PF_3) = -226.0$,[31] $\Delta H_f°(Mn^+) = 241$,[20] $\Delta H_f°(MnCO^+) = 187$,[32] $\Delta H_f°((CH_3)_3Si) = -42$.[33] The thermochemical values are summarized in Table III.

It is seen that substitution of a PF_3 moiety for a CO lowers the heat of formation by approximately 200 kcal/mol. Since this difference is the same (within experimental error) as the difference between heats of formation of phosphorus trifluo-

---

(26) R. W. Kiser, M. A. Krassoi, and R. J. Clark, *J. Amer. Chem. Soc.*, 89, 3653 (1967).

(27) J. T. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, and K. Drafl, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. 26 (1969).

(28) R. W. Kiser, "Additions and Corrections to Tables of Ionization Potentials," TID-6142, U. S. Atomic Energy Commission Office of Technical Information, Washington, D. C., June 20, 1962.

(29) R. W. Kiser, "Introduction to Mass Spectrometry and its Applications," Prentice-Hall, Englewood Cliffs, N. J., 1965, p 191.

(30) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, *Nat. Bur. Stand. (U. S.), Circ.*, No. 500 (1952).

(31) H. C. Duus and D. P. Mykyterik, *J. Chem. Eng. Data*, 9, 585 (1964).

(32) R. E. Winters and R. W. Kiser, *J. Phys. Chem.*, 69, 1618 (1965).

(33) Calculated from data presented in G. G. Hess, F. W. Lampe, and A. L. Yergey, *Ann. N. Y. Acad. Sci.*, 136, 106 (1966).

ride and carbon monoxide (-226.0[31] and -26.4 kcal/mol,[30] respectively), the nature of the manganese-to-carbon and the manganese-to-phosphorus bonds must be similar. A similar relationship has been observed previously for a variety of cobalt carbonyl derivatives[2a,34] and in the data reported by Kiser, *et al.*,[26] for the carbonyl derivatives of nickel. It is also pointed out that the data for the heats of formation of the $(CH_3)_3SiMn(CO)_x^+$ ions are internally consistent for the values obtained from $(CH_3)_3SiMn(CO)_5$ and $(CH_3)_3SiMn(CO)_4PF_3$.

Using the relationship noted above (*i.e.*, substitution of PF_3 for CO lowers the ΔH_f° of the ion and the compound by 200 kcal/mol), it is possible to predict the values for the heats of formation of the remaining compounds in this series for which meaningful energetic measurements could not be obtained. These predicted values are as follows (kcal/mol): $\Delta H_f^\circ((CH_3)_3SiMn(CO)_3(PF_3)_2) = -823$, $\Delta H_f^\circ((CH_3)_3SiMn(CO)_2(PF_3)_3) = -1023$, $\Delta H_f^\circ((CH_3)_3SiMn(CO)(PF_3)_4) = -1223$.

Previous results[9,18,19] have shown that the average ionic bond energies are equal to the average neutral bond energies within 0.3 eV. Assuming this holds for the compounds reported here, the neutral hydrogen-manganese bond energy may be estimated using the technique described by Junk, *et al.*[9] This calculation for the H-Mn bond energy gives a value of 0.3 ± 0.5 eV (7 ± 12 kcal/mol), which supports previous claims[35,36] that this bond energy is very low.

Registry No. $HMn(CO)_5$, 16972-33-1; $(CH_3)_3SiMn(CO)_5$, 26500-16-3; $(CH_3)_3SiMn(CO)_4(PF_3)$, 33989-27-4; $(CH_3)_3SiMn(CO)_3(PF_3)_2$, 36087-62-4; $(CH_3)_3SiMn(CO)_2(PF_3)_3$, 36087-61-3; $(CH_3)_3SiMn(CO)(PF_3)_4$, 36087-60-2.

(34) F. E. Saalfeld, M. V. McDowell, and A. G. MacDiarmid, *J. Mass Spectrom. Ion Phys.*, in press.

(35) W. F. Edgell, C. Magee, and G. Gallup, *J. Amer. Chem. Soc.*, **78**, 4185 (1956).

(36) W. F. Edgell and R. Summitt, *J. Amer. Chem. Soc.*, **83**, 1772 (1961).

Contribution from the Department of Chemistry,
California State University, Los Angeles, California 90032

Nuclear Magnetic Resonance Studies of Silicon-Nitrogen Compounds

S. CHAN, S. DiSTEFANO, F. FONG, H. GOLDWHITE,* P. GYSEGEM, and E. MAZZOLA

Received April 28, 1972

Variable-temperature proton magnetic resonance spectra were studied for a number of compounds containing silicon-nitrogen bonds in which potentially diastereotopic methyl groups were attached to nitrogen. Even at very low temperatures the methyl groups remained equivalent. It is concluded that rotational barriers about silicon-nitrogen bonds are lower than those about phosphorus- or sulfur-nitrogen bonds in analogous systems.

Introduction

There have recently been extensive studies by dynamic nuclear magnetic resonance spectroscopy of stereochemical phenomena in compounds containing sulfur-nitrogen[1,2] and phosphorus-nitrogen[3-5] bonds, which have been successfully interpreted in terms of a substantial rotational barrier about these bonds. We decided to extend these studies to the adjacent element in the third row of the periodic table, namely, silicon, and to look for rotational barriers about silicon-nitrogen bonds by dynamic proton magnetic resonance studies.

To this end we synthesized a number of compounds containing silicon attached to a dimethylamino group, including several chiral compounds. In these compounds if either inversion at nitrogen or rotation about the silicon-nitrogen bond were sufficiently slowed, the methyl groups attached to nitrogen would become diastereotopic and would, in principle at least, give rise to distinct magnetic resonance signals.

Experimental Section

Proton magnetic resonance spectra were determined on Varian A-60 and HA-100 spectrometers equipped with variable-temperature probes. The compounds used in this study were prepared by published methods,[6,7] and their physical and spectral properties agreed with published values.

Results

The results are presented in Tables I and II.

Discussion

As the results indicate, even at temperatures as low as −130°, there was no indication of the presence of diastereotopic methyl groups on nitrogen in the dimethylamino compounds or diastereotopic protons on the methylene groups in the aziridine and *N*-ethyl compounds examined. The experimental equivalence of the groups observed can have a number of possible explanations. It might be that the methyl groups are, in fact, diastereotopic but that the chemical shift difference due to the adjacent asymmetric silicon center is so small that the peaks are not seen as separate (*i.e*, $\Delta\delta$ must be less than about 0.5 Hz). This seems implausible in view of the large number of compounds studied, the large chemical shift differences induced in analogous systems containing chiral phosphorus[3-5] or sulfur[1,2] centers, and the

(1) J. M. Lehn and J. Wagner, *Chem. Commun.*, 1298 (1968).

(2) M. Raban and F. B. Jones, Jr., *J. Amer. Chem. Soc.*, **93** 2692 (1971).

(3) D. Imbery and H. Friedbolin, *Z. Naturforsch. B*, **23**, 759 (1968).

(4) A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, **92**, 5206 (1970).

(5) H. Goldwhite and D. G. Rowsell, *Chem. Commun.*, 713 (1969).

(6) S. S. Washburne and W. R. Peterson, Jr., *J. Organometal. Chem.*, **21**, 59 (1970).

(7) S. Chan, S. DiStefano, F. Fong, H. Goldwhite, P. Gysegem, and E. Mazzola, *Syn. Inorg. Metal-Org. Chem.*, **2**, 13 (1972).