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CHEMICAL PROPERTIES OF THE SILICON–IRON BOND IN TRIMETHYLSILYL π-CYCLOPENTADIENYLIRON DICARBONYL

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This investigation was carried out for the purpose of examining the little-studied[1, 2] chemical properties of the silicon–iron bond in $Me_3Si{-}Fe(CO)_2(\pi\text{-}C_5H_5)$ in order to determine how they differed from those of this bond in $(H_3Si)_2Fe(CO)_4$[4] and from those of the silicon–metal bonds in $Me_3Si{-}Co(CO)_4$ and $Me_3Si{-}Mn(CO)_5$[5-7]. The silicon–iron bond in this compound is surprisingly inert and in certain ways it tends to resemble the silicon–phenyl linkage.

When heated *in vacuo* at 160° for one hour, $Me_3Si{-}Fe(CO)_2(\pi\text{-}C_5H_5)$ [τ, 9.64 (Me_3Si) and 5.45 ($\pi\text{-}C_5H_5$), 5% in cyclohexane] did not undergo thermal decomposition. A darkening in color and a trace of $(Me_3Si)_2O$ were apparent after one hour at 200°. When solid $Me_3Si{-}Fe(CO)_2(\pi\text{-}C_5H_5)$ was exposed to 0.7 atmosphere of dry oxygen for four days, approximately 70% of the original material was recovered unchanged.

Solid $Me_3Si{-}Fe(CO)_2(\pi\text{-}C_5H_5)$ underwent no reaction with liquid water (1/5 molar ratio) during one day at room temperature; even when its solution in ether was treated with a 1/6 molar excess of water for one hour at room temperature, it could be recovered quantitatively. Analogously, $Me_3Si{-}Fe(CO)_2(\pi\text{-}C_5H_5)$ was recovered from its solution in methanol (1/1 molar ratio) which had stood at room temperature for one hour.

Unlike $Me_3Si{-}Co(CO)_4$[7] and $Me_3Si{-}Mn(CO)_5$[6], which underwent instantaneous reaction with trimethylamine to form the trimethylsilyl ammonium compounds, $[Me_3Si{-}NMe_3]^+[Co(CO)_4]^-$ and $[Me_3Si{-}NMe_3]^+[Mn(CO)_5]^-$ respectively, $Me_3Si{-}Fe(CO)_2(\pi\text{-}C_5H_5)$ was recovered quantitatively from its solution in trimethylamine (1/2 molar ratio) after one hour at room temperature. This is understandable since $HFe(CO)_2(\pi\text{-}C_5H_5)$ is apparently a much weaker acid than $HCo(CO)_4$ or $HMn(CO)_5$[8].

No reaction occurred during one hour between methyl chloride and $Me_3Si{-}Fe(CO)_2(\pi\text{-}C_5H_5)$ (3/1 molar ratio) which formed a homogeneous solution at room temperature.

$Me_3Si{-}Fe(CO)_2(\pi\text{-}C_5H_5)$ dissolved in a methanolic solution of KOH (molar ratios $Me_3Si{-}Fe(CO)_2(\pi\text{-}C_5H_5)$/KOH/MeOH; 1.0/1.6/15.9) underwent a slow and incomplete reaction during one hour at room temperature. Only 51% of the Me_3Si– groups originally present in the starting compound had appeared as Me_3SiOMe and $(Me_3Si)_2O$[9].

An infrared spectrum of the solid residue remaining after the reaction showed that it contained unchanged $Me_3Si{-}Fe(CO)_2(\pi\text{-}C_5H_5)$ and also the $[Fe(CO)_2(\pi\text{-}C_5H_5)]^-$ ion[10]

When a solution of $Me_3Si{-}Fe(CO)_2(\pi\text{-}C_5H_5)$ in dimethylamine (1/2 molar ratio) was held at room temperature a slow reaction occurred, as evidenced by an NMR study. After one hour 25% of the $Me_3Si{-}$ groups in the starting material were recovered as $Me_3Si{-}NMe_2$ (eq.1); some $(Me_3Si)_2O$ was also formed. Infrared examination of the less volatile products showed unreacted $Me_3Si{-}Fe(CO)_2(\pi\text{-}C_5H_5)$ and $HFe(CO)_2(\pi\text{-}C_5H_5)$[11], together with some $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ [12, 13], presumably formed from the partial decomposition of the latter compound.

$$Me_3Si{-}Fe(CO)_2(\pi\text{-}C_5H_5) + HNMe_2 \rightarrow Me_3Si{-}NMe_2 + HFe(CO)_2(\pi\text{-}C_5H_5) \quad (1)$$

In marked contrast to the above reactions, solid $Me_3Si{-}Fe(CO)_2(\pi\text{-}C_5H_5)$ and anhydrous hydrogen chloride (1/3 molar ratio) underwent an extremely rapid reaction while warming from -196° to room temperature, *viz.*

$$Me_3Si{-}Fe(CO)_2(\pi\text{-}C_5H_5) + HCl \rightarrow Me_3SiCl + HFe(CO)_2(\pi\text{-}C_5H_5) \quad (2)$$

After five minutes at room temperature 82% of the $Me_3Si{-}$ groups in the $Me_3Si{-}Fe(CO)_2(\pi\text{-}C_5H_5)$ employed were recovered as Me_3SiCl and $(Me_3Si)_2O$. $HFe(CO)_2(\pi\text{-}C_5H_5)$ is known to decompose rapidly at room temperature[14], and it seems possible that some of the Me_3SiCl formed may undergo a complex reaction with it to give the small amount of $(Me_3Si)_2O$ isolated, together with other non-volatile silicon-containing species.

When $Me_3Si{-}Fe(CO)_2(\pi\text{-}C_5H_5)$ was dissolved in a solution of hydrogen chloride in methanol (molar ratios $Me_3Si{-}Fe(CO)_2(\pi\text{-}C_5H_5)$/HCl/MeOH; 1.00/0.13/4.17) and held for one hour at room temperature, most of the $Me_3Si{-}Fe(CO)_2(\pi\text{-}C_5H_5)$ was recovered unchanged. One may write a hypothetical equation for the methanolysis as

$$Me_3Si{-}Fe(CO)_2(\pi\text{-}C_5H_5) + MeOH \rightarrow Me_3SiOMe + HFe(CO)_2(\pi\text{-}C_5H_5). \quad (3)$$

It is not unreasonable to assume that this reaction is thermodynamically possible as written in view of the strength of the silicon—oxygen bond formed in the product molecule, Me_3SiOMe, and in view of the observation that both $Me_3Si{-}Co(CO)_4$ and $Me_3Si{-}Mn(CO)_5$ undergo rapid methanolysis to give Me_3SiOMe and the corresponding transition metal carbonyl hydride[5, 6]. Since an extensive reaction did not occur in a homogeneous medium when potassium hydroxide or hydrogen chloride was dissolved in a methanolic solution of $Me_3Si{-}Fe(CO)_2(\pi\text{-}C_5H_5)$, it would appear that methanolysis is not strongly catalysed by bases such as potassium hydroxide or by acids such as hydrogen chloride or $MeOH_2^+$ [15, 16]. This indicates that the silicon in $Me_3Si{-}Fe(CO)_2(\pi\text{-}C_5H_5)$ is not readily attacked even by the strong nucleophile OH^-. It also suggests that the silicon—iron bond does not undergo rapid electrophilic attack at the iron by the electrophile, $MeOH_2^+$, but that an attack at the iron by the more strongly electrophilic hydrogen of hydrogen chloride does readily occur (eq.2) Furthermore, the non-reaction of $Me_3Si{-}Fe(CO)_2(\pi\text{-}C_5H_5)$ with trimethylamine and the slow reaction with dimethylamine (eq.1) also indicate that the silicon in the silicon—iron bond is not particularly susceptible to nucleophilic attack by nitrogen. The greater rate of reaction of the silicon—iron bond with hydrogen chloride indicates that the rate-controlling step in the cleavage of this bond might well involve an electrophilic attack at the iron. In this respect the silicon—iron bond is analogous to the silicon—phenyl bond which undergoes electrophilic aromatic attack by hydrogen chloride even at low temperatures[17].

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REFERENCES

1 T.S. Piper, D. Lemal and G. Wilkinson, *Naturwissenschaften*, 43 (1956) 129.
2 R.B. King and K.H. Pannell, *Inorg. Chem.*, 7 (1968) 1510.
3 B.J. Aylett, J.M. Campbell and A. Walton, *Inorg. Nucl. Chem. Lett.*, 4 (1968) 79.
4 M.A. Nasta and A.G. MacDiarmid, Unpublished observations, (1969).
5 Y.L. Baay and A.G. MacDiarmid, *Inorg. Chem.*, 8 (1969) 986.
6 S.K. Gondal, A.G. MacDiarmid, F.E. Saalfeld and M.V. McDowell, *Inorg. Nucl. Chem. Lett.*, in press; A.D. Berry and A.G. MacDiarmid, *ibid.*, in press.
7 J.F. Bald, Jr. and A.G. MacDiarmid, *J. Organometal Chem.*, submitted for publication.
8 M.L. Bruce and F.G.A. Stone, *Angew. Chem., Intern. Ed.*, 7 (1968) 747; R.E. Dessy, R.L. Pohl and R.B. King, *J. Amer. Chem. Soc.*, 88 (1966) 5121; W. Hieber and G. Wagner, *Z. Naturforsch.*, 13b (1958) 339.
9 W.T. Grubb, *J. Amer. Chem. Soc.*, 76 (1954) 3408.
10 R.B. King, K.H. Pannell, C.A. Eggers and L.W. Houk, *Inorg. Chem.*, 7 (1968) 2353.
11 A. Davison, J.A. McCleverty and G. Wilkinson, *J. Chem. Soc.*, (1963) 1133.
12 K. Noack, *J. Inorg. Nucl. Chem.*, 25 (1963) 1383.
13 A.R. Manning, *J. Chem. Soc., A*, (1968) 1319.
14 M.L.H. Green, C.N. Street and G. Wilkinson, *Z. Naturforsch.*, 14b (1959) 738.
15 T. Schedlovsky and R.L. Kay, *J. Phys. Chem.*, 60 (1956) 151.
16 P. Salomaa, *Acta Chem. Scand.*, 11a (1957) 125.
17 G. Fritz and D. Kummer, *Z. Anorg. Allg. Chem.*, 308 (1961) 105.