Synthesis and Characterization of *cis*-Di-iodotetrakis(trimethylsilyl isocyanide)iron(II), $[FeI_2(CNSiMe_3)_4]$

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The interaction of FeI_2 with excess Me_3SiNC in tetrahydrofuran yields *cis*-$[FeI_2(CNSiMe_3)_4]$ in high yield. The compound has been characterized by analytical data and by i.r., ^1H, and ^{13}C n.m.r. spectroscopy.

Although there is considerable interest in transition-metal isocyanide complexes,[1] few compounds containing co-ordinated trimethylsilyl isocyanide (Me_3SiNC) as a ligand are known; examples are $[M(CO)_4(CNSiMe_3)]I$ (M = Mn or Re),[2a] $[Mo(CO)_5(CNSiMe_3)]$,[2b,c] and $[Fe(CO)_4(CNSiMe_3)]$.[3] Spectroscopic studies have suggested that the free ligand '$Me_3Si(NC)$' exists mainly as the cyanide Me_3SiCN, with the equilibrium $Me_3SiCN \rightleftharpoons Me_3SiNC$ lying well to the left.[3-7] More recently, however, n.m.r. studies of some silyl and trimethylsilyl pseudohalides have provided convincing evidence that there are no other isomers of Me_3SiCN present in CD_2Cl_2 solution in significant concentration.[8]

In the presence of transition-metal complexes, Me_3SiCN appears to behave differently. Thus, the interaction of '$Me_3Si(NC)$' with $[Fe(CO)_5]$ gives $[Fe(CO)_4(CNSiMe_3)]$[3] which has the properties of a typical isocyanide complex. Few other $Me_3SiNC{-}M$ complexes are known and they are all low-valent complexes which contain carbonyls as the other ligands.[2,3] These observations have prompted us to report the synthesis and characterization of *cis*-di-iodotetrakis(trimethylsilyl isocyanide)iron(II), $[FeI_2(CNSiMe_3)_4]$, which, to our knowledge, is the only example of Me_3SiNC units co-ordinated to a *d*-block transition metal in an oxidation state other than zero or +1 and with ancilliary ligands which are not carbonyls.

Results and Discussion

The interaction of FeI_2[9] in tetrahydrofuran (thf) with a large excess of '$Me_3Si(NC)$' readily gives a dark red solution from which red-brown, crystalline, diamagnetic *cis*-$[FeI_2(CNSiMe_3)_4]$ (1) can be isolated in high yield.

Unlike the t-butyl isocyanide analogue *cis*-$[FeI_2(CNBu^t)_4]$,[10] compound (1) hydrolyses rapidly in moist air and a brown tar is formed. It can be stored indefinitely at ambient temperature under nitrogen or *in vacuo*. It is also considerably less thermally stable and decomposes at 65—67 °C. I.r. spectra (Nujol mull or toluene solution) show two $\nu(N{\equiv}C)$ stretches at 2 130m and 2 050vs cm^{-1}, characteristic of co-ordinated isocyanide,[2,11] and similar to those reported for $[FeI_2(CNBu^t)_4]$.[10]

The i.r. data give no structural information but ^1H and ^{13}C-$\{^1H\}$ n.m.r. data are in accord with a *cis* structure (Figure) since at ambient temperature two singlets (area ratio 1 : 1) are observed in the ^1H n.m.r., and in the ^{13}C-$\{^1H\}$ two isocyanide Me_3SiNC resonances at δ 191.3 and 200.0 p.p.m. are observed.[2,10]

We have so far been unable to obtain single crystals suitable for *X*-ray crystallography.

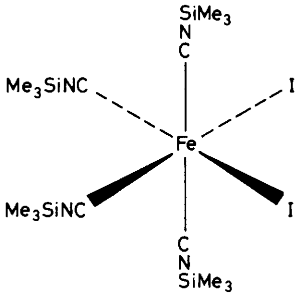

Figure. Structure of $[FeI_2(CNSiMe_3)_4]$ (1)

Experimental

Microanalyses were by Schwartzkopf Microanalytical Laboratory, Woodside, New York. Instruments used were Perkin-Elmer 1330 (i.r.), Varian EM 390 (^1H n.m.r.) and FT 80 (^{13}C n.m.r.) spectrometers.

All operations were performed under nitrogen or *in vacuo*. Trimethylsilyl isocyanide was purchased from Petrarch Systems, Inc.; it was degassed and stored over 4A molecular sieves under nitrogen at −20 °C. FeI_2 was prepared by the literature procedure.[9] Toluene, thf, and hexane were dried over sodium and distilled from Na–benzophenone before use.

cis-$[FeI_2(CNSiMe_3)_4]$.—'$Me_3Si(NC)$' (6.0 cm^3, 45 mmol) was added to a solution of $FeI_2{\cdot}2thf$ (4.64 g, 10 mmol) in thf (80 cm^3) at room temperature. The deep red solution was stirred (10 h), evaporated to dryness under vacuum, and the residue extracted into toluene (50 cm^3). The solution was filtered and evaporated to 10 cm^3 under vacuum. Cooling (−20 °C) yielded a red-brown crystalline mass which was collected, washed with hexane (2 × 20 cm^3), and dried under vacuum. Toluene (35 cm^3) was added and the solution filtered and evaporated to 10 cm^3 under vacuum. Cooling (−20 °C) yielded dark red-brown crystals which were collected, washed with hexane (5 cm^3), and dried under vacuum. Yield 6.0 g, 85%; m.p. 65—67 °C (decomp.) (Found: C, 27.85; H, 5.2; I, 35.1; N, 7.45. Calc. for $C_{16}H_{36}FeI_2N_4Si_4$: C, 27.2; H, 5.1; I, 36.0%); N, 7.95. I.r. (Nujol mull; NaCl plates): 2 130m, 2 050vs br, 1 498w, 1 418w, 1 325w, 1 265m, 1 257s, 1 253s, 1 050w, 845vs br, 766m, 726w, 715w, 692w, and 616m cm^{-1}. N.m.r.: ^1H, δ(p.p.m.) 0.47 (s, 18 H), 0.35 (s, 18 H) (in $[^2H_8]$-toluene at 35 °C and 90 MHz, referenced to $SiMe_4 = 0.0$ p.p.m. as external standard); ^{13}C-$\{^1H\}$, δ(p.p.m.) 200.0 (s, *C*NSiMe$_3$), 191.3 (s, *C*NSiMe$_3$), 0.85 (s, CNSi*Me*$_3$), −0.40

(s, CNSi*Me*$_3$) (in [$^2H_8$]toluene at 35 °C and 20 MHz, referenced to $SiMe_4 = 0.0$ p.p.m.).

Acknowledgements

We thank the Robert A. Welch Foundation and the University of Texas Research Institute for generous financial support.

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Received 5th July 1982; *Paper* 2/1131