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Metal Atom Synthesis and Structure of (η^6-Toluene)bis(trichlorosilyl)iron Dihydride: An Unusual Iron(IV) Complex

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There are very few well-characterized Fe(IV) complexes that have been reported, and generally they exhibit limited thermal stability unless considerable steric bulk in the attached ligands is available. Examples described are Fe(1-norbornyl)$_4$,[1] Fe[(t-BuMe$_2$SiNCH$_2$CH$_2$)$_3$N]CN,[2] and Fe(Cp)(H)(CO)(SiCl$_3$)$_2$.[3] Widespread interest in such high oxidation state iron continues,[4,5] and we report here a unique Fe(IV) compound with π-arene, hydride, and trichlorosilyl ligands.

For several years we have investigated the synthesis and chemistry of π-arene complexes of Ni(II),[6,7] Co(II),[8] Cr(II),[9] and Cr(IV)[10] complexes and have noted the peculiar stabilizing ability of electron-demanding σ-bound SiCl$_3$, SiF$_3$, and C$_6$F$_5$ ligands when combined with the donating ability of the η^6-arene group, e.g., (η^6-toluene)Ni(SiCl$_3$)$_2$,[7] (η^6-toluene)Cr(CO)$_2$(SiCl$_3$)$_2$,[9] and (η^6-toluene)Cr(CO)(H)$_2$(SiCl$_3$)$_2$.[10] This background led us to attempt the synthesis of analogous iron complexes. A series of organometallic wet chemical approaches failed before we turned to the metal atom vapor approach.[11]

Iron vapor (1.5 g) was codeposited with excess toluene (~90 g) at −196 °C forming "toluene solvated iron atoms".[12] Then HSiCl$_3$ (~50 g) was distilled in and the matrix warmed to −78 °C and held there for 2 h followed by warming slowly to room temperature and stirring overnight. The reaction mixture was filtered through Celite under argon, volatiles were removed in vacuo, and the resultant yellow solid was recrystallized from a toluene/hexane mixture to yield yellow crystals of (η^6-toluene)-Fe(H$_2$)(SiCl$_3$)$_2$ (0.15 g, 1.3% based on Fe vaporized).

$$\mathrm{Fe_{vapor}} + 2\mathrm{C_6H_5CH_3} \rightarrow \text{“}(\mathrm{C_6H_5CH_3})_2\mathrm{Fe}\text{”} \xrightarrow{2\mathrm{HSiCl_3}} (\eta^6\text{-toluene})\mathrm{Fe(H)_2(SiCl_3)_2}$$

The X-ray structure shows that (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$ exists as a four-legged piano stool where the SiCl$_3$ and H ligands serve as legs and η^6-arene serves as the seat (Figure 1).[13a,b] The SiCl$_3$ groups are *trans*, as are the hydrides. The bond distances between Fe and the arene C atoms range from 2.111(1) to 2.182(2) Å, with the distance from the Fe to the ring (center) equal to 1.62 Å. The Fe-Si distances are 2.222(2) and 2.218(2) Å, and the Fe-H lie between 1.50(6) and 1.72(9) Å (a fuller discussion of structural parameters will be reported later). The ^{1}H NMR of this diamagnetic compound dissolved in C$_6$D$_6$ showed a singlet for the hydrides at −17.15 ppm, a multiplet for the bound arene at 4.6–5.4 ppm (arene protons), and a singlet at 1.45 ppm (methyl protons). The IR spectrum showed ν_{FeH} at 1930 cm^{-1}.

A Mössbauer spectrum at room temperature (Figure 2) in zero field showed a doublet as expected with $\Delta E_Q = 0.91$ mm/s

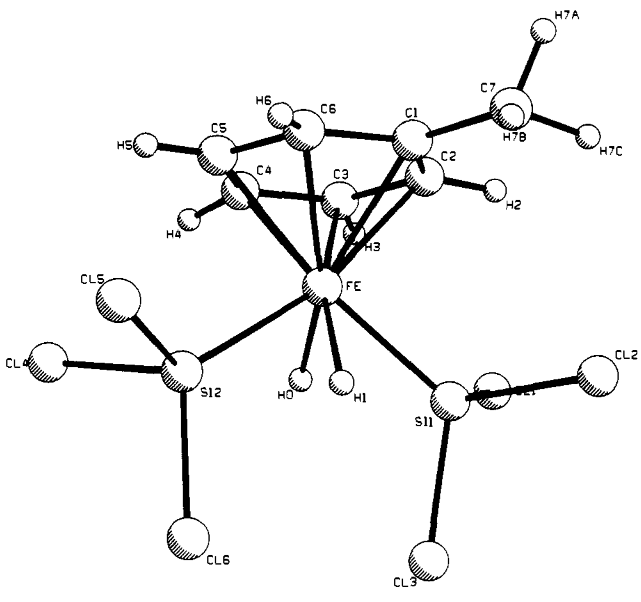

Figure 1. PLUTO drawing of (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$ with atom-labeling scheme. Selected bond distances (Å) and angles (deg) are Fe–Si1, 2.222(2); Fe–Si2, 2.218(2); Fe–C1, 2.182(7); Fe–C2, 2.148(6); Fe–C3, 2.119(7); Fe–C4, 2.111(6); Fe–C5, 2.128(6); Fe–C6, 2.137(6); Fe–H0, 1.50(6); Fe–H1, 1.72(9); Si1–Fe–Si2, 108.77(7); Si1–Fe–H0, 60(2); Si1–Fe–H1, 65(2); Si2–Fe–H0, 74(2); Si2–Fe–H0, 58(3); H0–Fe–H1, 84(4).

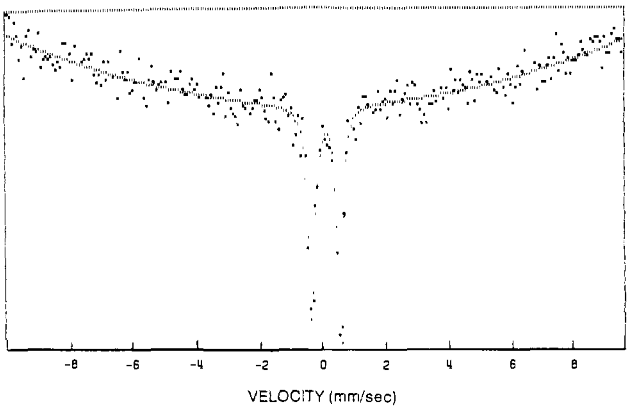

Figure 2. Mössbauer spectrum at room temperature with least-squares fit for (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$. $\delta = 0.25$ mm/s; $\Delta E_Q = 0.91$ mm/s.

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(13) (a) Crystal data: single crystals of (η^6-toluene)Fe(H)$_2$(SiCl$_3$)$_2$ at −160 °C are monoclinic, space group $P2_1/a$ (No. 14) with $a = 12.232(2)$ Å, $b = 8.591(1)$ Å, $c = 13.873(2)$ Å, $\beta = 92.66(2)°$, $V = 1456.3(6)$ Å^3, and $Z = 4$ [$d_{\mathrm{calcd}} = 1.910$ g/cm^3, μ(Cu Kα = 201.84 cm^1]. A total of 2076 independent reflections ($2\theta_{\max} = 112.7°$) were collected using $2\theta/\omega$ scans with graphite-monochromated Cu Kα radiation. The structure parameters have been refined to convergence, $R = 0.056$, $R_w = 0.073$ (based on F) for reflections with $I > 0.01\sigma(I)$. (b) Anal. calcd for C$_7$H$_{10}$FeCl$_6$Si$_2$: C, 20.07; H, 2.41; Si, 13.41; Fe, 13.33; Cl, 50.78. Found: C, 19.47; H, 2.50; Si, 12.08; Fe, 13.33; Cl, 49.66.

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and $\delta = 0.25$ mm/s (relative to α-Fe), consistent with the Fe(IV) oxidation state.[14]

The stability of this compound apparently relies on the closed-shell 18-electron configuration. If toluene is considered to occupy three coordination sites and the σ-bound ligands occupy four sites, this is a seven-coordinate compound. It is surprisingly stable thermally and oxidatively (short air exposures can be tolerated; slow decomposition above 120 °C). Another stability-enhancing characteristic is probably due to the synergistic push–pull of electron density discussed earlier for other similar monoarene complexes bearing strongly electron demanding σ-bound ligands.[15]

Indeed, there are very few examples of (η^6-arene)ML_4 complexes in the literature, perhaps the best being Mo(II) systems.[16,17] Bonding analysis by extended Hückel calculations for 18-electron (benzene)ML_4 complexes suggests that the b_1 and b_2 orbitals merge together until they become degenerate if both *trans* L–M–L angles are equal.[15] Also, the $2a_1$ orbital is greatly destabilized in an ML_4 fragment (*vs* ML_2). The b_2 and $b_1\pi$ orbitals of benzene form a strong bonding interaction with b_2 and b_1 of ML_4. Also, the $a_1\pi$ level of benzene together with $1a_1$ and $2a_1$ in ML_4 create a set of three orbitals, two of which are filled, and the a_2 level of ML_4 is slightly stabilized by benzene a_2.

It is reasonable to assume a similar MO picture for this new 18-electron (arene)FeL_4 system, and further analysis of bonding will be presented later. At this time, our most important conclusion is that under the right conditions Fe(IV) 18-electron compounds can be quite stable, and this stability is not dependent on extremely bulky ligands.

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Supplementary Material Available: Tables of data collection information, atom coordinates, anisotropic thermal parameters, bond lengths, bond angles, and torsion angles for (η^6-toluene)-$Fe(H)_2(SiCl_3)_2$ (12 pages); listing of structure factor amplitudes for (η^6-toluene)$Fe(H)_2(SiCl_3)_2$ (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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