Paramagnetic Hydrido- and Chloro-complexes of Iron(I)

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Summary $FeH(dp)_2$ ($dp = Ph_2PCH_2CH_2PPh_2$) has been isolated from the reaction of $FeHCl(dp)_2$ or $[FeH(dp)_2]BPh_4$ with sodium, and $FeCl(dp)_2$ from the reaction of $FeCl_2(dp)$ with stoicheiometric amounts of sodium in the presence of free diphosphine.

FEW paramagnetic transition-metal hydrides have been reported and most have been detected only in solution,[1,2] with two having been isolated in the solid state, $ReHX_2$-*(acac)(PPh*$_3$*)* (X = Cl or I).[3] We report the preparation and characterization of the paramagnetic compounds of iron(I), $FeH(dp)_2$ (I) and $FeCl(dp)_2$(II).

Compound (I) was obtained—red crystals, unstable in air but stable under nitrogen, m.p. 189—190° (decomp.), soluble in non-polar solvents—from the reaction of $FeHCl(dp)_2$[4] or $[FeH(dp)_2]BPh_4$[5] with the stoicheiometric amount of powdered sodium in benzene. The compound was characterised by elemental analysis and by reaction with the stoicheiometric amounts of iodine and hydrochloric acid at room temperature as shown in reactions (1) and (2).

$$FeH(dp)_2 + HCl = FeHCl(dp)_2 + \tfrac{1}{2}H_2 \qquad (1)$$

$$FeH(dp)_2 + \tfrac{1}{2}I_2 = FeHI(dp)_2 \qquad (2)$$

With an excess of hydrochloric acid at 80° (I) reacts according to equation (3). Its i.r. spectrum in Nujol shows a sharp band at 1789 cm^{-1}, assignable to Fe–H stretching. Bulk-susceptibility measurements under nitrogen, by the Faraday method at −175 to 24°, show a magnetic moment of 1·80 B.M. ($\theta = 14{\cdot}5$ K), consistent with the presence of one unpaired electron. The toluene solution of the compound shows a strong e.s.r. signal centred at $g = 2{\cdot}085$, with an almost unresolved hyperfine structure, probably due to the interaction of the unpaired electron of the Fe^I with the phosphorus atoms. Compound (I) is isomorphous with $CoH(dp)_2$.[6]

$$FeH(dp)_2 + 2HCl = FeCl_2(dp) + (dp) + 1{\cdot}5H_2 \qquad (3)$$

Compound (II) was obtained—deep red crystals, m.p. 130° (decomp.), unstable in air, soluble in non-polar solvents—from the reaction of $FeCl_2(dp)$ and (dp) (molar ratio = 1 : 1) with the stoicheiometric amount of powdered sodium in benzene. The compound was characterised by elemental analysis and by treatment with hydrochloric acid as shown in reaction (4).

$$FeCl(dp)_2 + HCl = FeCl_2(dp) + (dp) + \tfrac{1}{2}H_2 \qquad (4)$$

Bulk-susceptibility measurements, made between −174 and 25°, give a magnetic moment of 2·11 B.M. ($\theta = 8$ K). The toluene solution of (II) has a strong e.s.r. signal with a partially resolved hyperfine structure centred at $g = 2{\cdot}075$.

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