Notes

Protonation of Pentakis(t-butyl isocyanide)iron

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Reaction of pentakis(t-butyl isocyanide)iron with the hydrido-metal carbonyls [MnH(CO)$_5$] and [OsH$_2$(CO)$_4$] affords the salts [FeH(CNBu^t)$_5$][Mn(CO)$_5$] and [FeH(CNBu^t)$_5$][OsH(CO)$_4$], respectively. Protonation of [Fe(CNBu^t)$_5$] with anhydrous HBF$_4$·2Et$_2$O yields [FeH(CNBu^t)$_5$][BF$_4$].

We have recently synthesised and structurally characterised the zerovalent iron and ruthenium compounds [M(CNBu^t)$_5$] (M = Fe or Ru).[1] These complexes were prepared in the expectation that they would be very reactive towards a variety of substrate molecules. In the case of the iron compound this has been confirmed by oxidative reactions with alkyl, allyl, benzyl, fluoroalkyl, and pentafluorophenyl halides.[2] Many of the products of these reactions result from the initial oxidative processes being followed by isocyanide ligand insertion into carbon–iron bonds. As part of this study we investigated reactions between [Fe(CNBu^t)$_5$] and the hydrido(carbonyl) compounds [MnH(CO)$_5$] and [OsH$_2$(CO)$_4$], and the results are herein described. Contrary to our expectation that insertion of iron into the H–Mn and H–Os bonds would occur to afford complexes containing covalent metal–metal bonds, the reactions followed a different course.

RESULTS AND DISCUSSION

Pale yellow solids (1) and (2) precipitate immediately on mixing pentane solutions of [Fe(CNBu^t)$_5$] with [MnH(CO)$_5$] and [OsH$_2$(CO)$_4$] respectively. Examination of the i.r. spectra of these two products revealed almost identical absorptions assignable to ν(NC) but at an increase (*ca.* 200 cm^{-1}) in frequency consistent with an oxidation from Fe^0 to Fe^{II}. Moreover, the low-energy NC stretching vibrations at 2 005 and 1 830 cm^{-1} in the spectrum[1] of the parent complex [Fe(CNBu^t)$_5$] were absent, but recognisable CO bands due to the anions [Mn(CO)$_5$]$^-$ and [OsH(CO)$_4$]$^-$ were present in the region 1 850—2 000 cm^{-1}. Microanalysis, together with ^{1}H n.m.r. studies showing Bu^t groups in two environments in a ratio of 4 : 1, indicated no loss of isocyanide ligands in the reactions, and supported assignment of the compounds as the salts [FeH(CNBu^t)$_5$][Mn(CO)$_5$] (1) and [FeH(CNBu^t)$_5$][OsH(CO)$_4$] (2). Moreover, the ^{1}H n.m.r. spectrum of (1) also showed a resonance at τ 20.0, while that of (2) had signals at τ 20.25 and 20.4. The latter was temperature dependent in contrast to the former, hence the resonance at τ 20.4 is tentatively ascribed to the five-co-ordinate anion [OsH(CO)$_4$]$^-$. The protonation of [Fe(CNBu^t)$_5$] by [MnH(CO)$_5$] or [OsH$_2$(CO)$_4$] is reminiscent of the reaction of [Ru(CNBu^t)$_5$] with *nido*-2,3-Me$_2$-2,3-C$_2$B$_4$H$_6$ which affords[3] the salt [RuH(CNBu^t)$_5$][*nido*-2,3-Me$_2$-2,3-C$_2$B$_4$H$_5$].

Reaction of (1) with methyl iodide yields [MnMe(CO)$_5$] and [FeH(CNBu^t)$_5$]I (3). Not unexpectedly, the spectroscopic properties of (3) were indistinguishable from those of the cations of (1) and (2), except that the absence of carbonyl bands in the i.r. spectrum enabled identification of the Fe–H stretch at 1 817 cm^{-1}.

A more orthodox attempted protonation of [Fe(CNBu^t)$_5$] using aqueous HBF$_4$ in diethyl ether gave the aquo-complex [Fe(CNBu^t)$_5$(OH$_2$)][BF$_4$]$_2$ (4) as the product with release of hydrogen. Under stringently anhydrous conditions treatment of [Fe(CNBu^t)$_5$] with HBF$_4$·2Et$_2$O in tetrahydrofuran at −50 °C gave [FeH(CNBu^t)$_5$][BF$_4$] (5).

EXPERIMENTAL

All manipulations were performed under a dry nitrogen atmosphere by using standard Schlenk or vacuum techniques. All solvents were dried prior to use. Infrared spectra were recorded in Nujol using a Perkin-Elmer 457 spectrophotometer with bands calibrated with respect to the 1 601 cm^{-1} absorption of polystyrene film. N.m.r. spectra were measured with JEOL PS- and PFT-100 spectrometers.

Reactions of [Fe(CNBu^t)$_5$].—(a) *With* [MnH(CO)$_5$]. A stirred solution of [Fe(CNBu^t)$_5$] (0.58 g, 1.23 mmol) in pentane (10 cm^3) was treated dropwise with [MnH(CO)$_5$] (0.24 g, 1.23 mmol) in pentane (10 cm^3). The yellow coloured *microcrystalline* product which precipitated was washed with pentane (4 × 10 cm^3), dried *in vacuo*, and recrystallised from diethyl ether to give 0.79 g (96%) of [FeH(CNBu^t)$_5$][Mn(CO)$_5$] (1), m.p. 115—118 °C decomp. (Found: C, 53.0; H, 7.2; N, 10.8. C$_{30}$H$_{46}$FeMnN$_5$O$_5$ requires C, 53.9; H, 6.9; N, 10.5%); $\nu_{max.}$ at 2 135vs, 2 060m(sh) (NC), 1 885vs, and 1 858vs (CO) cm^{-1}; ^{1}H n.m.r. (CD$_3$C$_6$D$_5$, room temperature), τ 8.40 (s, 9 H, Bu^t), 8.45 (s, 36 H, Bu^t), and 20.0 (s, 1 H, FeH).

(b) *With* [OsH$_2$(CO)$_4$]. The cream coloured *microcrystalline* compound [FeH(CNBu^t)$_5$][OsH(CO)$_4$] (2) (0.4 g, 90%), m.p. 120—122 °C decomp. (Found: C, 44.0; H, 6.4; N, 8.6. $C_{29}H_{47}FeN_5O_4Os$ requires C, 44.9; H, 6.1; N, 9.0%); $\nu_{max.}$ at 2 135vs, 2 055m(sh) (NC), 2 000s, 1 946s, and 1 873vs, br (CO) cm^{-1}; ^{1}H n.m.r. [$(CD_3)_2CO$, room temperature], τ 8.42 (s, 9 H, Bu^t), 8.48 (s, 36 H, Bu^i), 20.25 (s, 1 H, FeH), and 20.40 (s, 1 H, OsH); was prepared in a similar manner from [Fe(CNBu^t)$_5$] (0.28 g, 0.6 mmol) and [OsH$_2$(CO)$_4$] (0.2 g, 0.7 mmol).

(c) *With aqueous* HBF$_4$. A stirred solution of [Fe(CNBu^t)$_5$] (0.34 g, 0.7 mmol) in diethyl ether (20 cm^3) was treated dropwise with aqueous tetrafluoroboric acid (0.5 cm^3, 40%), affording a yellow oil with some gas evolution. The supernatant liquid was removed and the oil washed with diethyl ether (4 × 10 cm^3) giving a yellow solid which was recrystallised from CH_2Cl_2–Et_2O at −78 °C affording [Fe(CNBu^t)$_5$(OH$_2$)][BF$_4$]$_2$ (4) (0.4 g, 89%), m.p. 165—167 °C decomp. (Found: C, 45.2; H, 7.1; N, 10.5. $C_{25}H_{47}B_2F_8FeN_5O$ requires C, 45.3; H, 7.1; N, 10.6%); $\nu_{max.}$ at 3 400m, br (OH), 2 200vs, br (NC), 1 650w, br (OH) cm^{-1}. ^{1}H n.m.r. [$(CD_3)_2CO$, room temperature], τ 8.30 (s, 36 H, Bu^t) and 8.46 (s, 9 H, Bu^t).

(d) *With anhydrous* HBF$_4$. To a stirred solution of [Fe(CNBu^t)$_5$] (0.5 g, 1.1 mmol) in tetrahydrofuran (20 cm^3) at −40 °C was added $HBF_4 \cdot 2Et_2O$ (four drops). After 30 min, warming to room temperature, pentane (20 cm^3) was added. The supernatant liquid was removed, and the pale yellow residue washed with pentane–diethyl ether (1 : 1, 3 × 10 cm^3). Recrystallisation of the solid from tetrahydrofuran–pentane gave pale yellow *microcrystals* of [FeH(CNBu^t)$_5$][BF$_4$] (5) (0.47 g, 84%), m.p. 111—115 °C decomp. (Found: C, 53.0; H, 8.0; N, 11.3. $C_{25}H_{46}BF_4FeN_5$ requires C, 53.7; H, 8.3; N, 12.5%); $\nu_{max.}$ at 2 135vs, 2 065m(sh) (NC), and 1 817w (FeH) cm^{-1}; ^{1}H n.m.r. [$(CD_3)_2CO$, −50 °C], τ 8.44 (s, 9 H, Bu^t), 8.50 (s, 36 H, Bu^t), and 20.45 (s, 1 H, FeH); ^{13}C n.m.r. [^{1}H-decoupled, $(CD_3)_2CO$, −50 °C], δ 30.4, 30.7 (CNC*Me*$_3$), 57.9, 58.1 (CN*C*Me$_3$), 157.9, and 158.2 p.p.m. (*C*NBu^t).

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