Synthesis, Chemical Reactivity, and X-Ray Molecular Structure of Pentakis(t-butyl isocyanide)iron

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Summary The highly reactive iron(0) complex [Fe(Bu^{t}NC)$_5$] has been synthesised, some oxidative-addition reactions delineated, and the molecular structure established by a single crystal X-ray diffraction study.

ZERO-VALENT complexes of transition metals which do not contain carbonyl ligands are becoming increasingly useful in organometallic syntheses. Herein we describe [Fe(Bu^{t}NC)$_5$], a reactive molecule formally similar to [Fe(CO)$_5$] and the iron analogue of recently discovered[1] [Ru(Bu^{t}NC)$_5$].

Reaction (room temperature, 24 h) of a tetrahydrofuran (THF) solution of FeBr$_2$ and t-butyl isocyanide (excess) with sodium amalgam gave (70% yield) yellow crystalline (from light petroleum, −78 °C) [Fe(Bu^{t}NC)$_5$] (**1**) [ν_{NC} 2 110sh, 2 005s, and 1 830s cm^{-1}; ^{1}H n.m.r.: τ ($C_6D_5CD_3$, −90 °C) 8·72(s); ^{13}C n.m.r.: δ($C_6D_5CD_3$, −80 °C) 197·4 (NCFe) p.p.m.].

Crystal data: $C_{25}H_{45}FeN_5$, M 471·5, monoclinic, space group $P2_1/n$, a = 18·930(8), b = 11·529(3), c = 28·968(8) Å, β = 108·63(1)°, U = 5990·8 Å^3, Z = 8, D_c = 1·05, F(000) = 2048. Current R is 0·105 for 4339 independent reflections (Syntex $P2_1$ diffractometer, Mo-K_α radiation, −80 °C).†

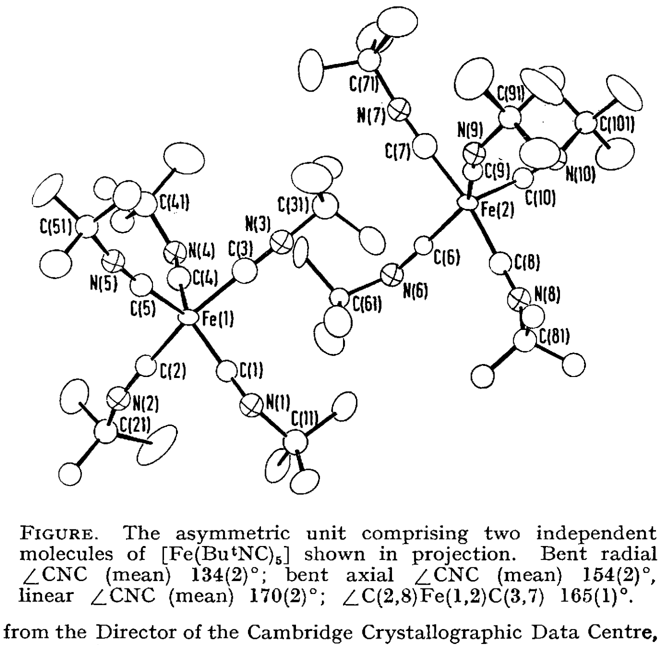

FIGURE. The asymmetric unit comprising two independent molecules of [Fe(Bu^{t}NC)$_5$] shown in projection. Bent radial ∠CNC (mean) 134(2)°; bent axial ∠CNC (mean) 154(2)°, linear ∠CNC (mean) 170(2)°; ∠C(2,8)Fe(1,2)C(3,7) 165(1)°.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

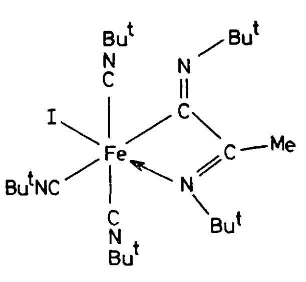
There are two crystallographically independent molecules in an asymmetric unit (Figure) each of which shows marked deviation from idealised trigonal bipyramidal geometry. Notably, the radial ligands [C(1), C(4), and C(5), and C(6), C(9), and C(10)] contain a CFeC angle of 140° [$\angle$C(4)Fe(1)-C(1) and $\angle$C(9)Fe(2)C(6)]. Moreover, C(1) and C(4), and C(9) and C(6) are ligated carbon atoms of isocyanide ligands which show substantial bending [mean 134(2)°] at the nitrogen atoms. One axial ligand on each molecule [C(2) and C(8)] is bent to a lesser degree [mean $\angle$CNC 154(1)°] and is inclined to the radical plane [mean $\angle$CFeC 101(1)°]. The remaining mutually perpendicular radial and axial ligands are essentially linear [mean $\angle$CNC 170(2)°].

The three non-linear isocyanide ligands reflect extensive back-bonding [Fe(3d) $\rightarrow$ (C$\equiv$N)π^*], as found[1] in [Ru(Bu^{t}NC)$_4$(Ph$_3$P)] but in the latter both axial Bu^{t}NC ligands are linear. Evidently complex (**1**) is dynamic in solution down to −80 °C since only one Bu^{t}N*C* resonance is observed in the ^{13}C n.m.r. spectrum. The absorption in the i.r. spectrum at 1 830 cm^{-1} is assigned to $\nu_{N:C}$ of the bent ligands.

The reactivity of this new Fe^0 system towards ligand substitution is demonstrated by the observation that treatment of (**1**) with Ph$_3$P, or reduction (sodium amalgam, room temperature, 24 h) of FeBr$_2$ in the presence of isocyanide and triphenylphosphine affords (50% yield) red crystalline (from light petroleum, −78 °C) [Fe(Bu^{t}NC)$_4$(Ph$_3$P)] (**2**) [ν_{NC} 2 100 sh, 2 000s, and 1 840s cm^{-1}; ^{1}H n.m.r.: τ (C_6D_6) 8·8 (s, Bu^t) and 2·1—2·85 (m, Ph); ^{13}C n.m.r.: δ ($C_6D_5CD_3$, −90 °C) 199·7 (NCFe) p.p.m.].

Complex (**1**) also exhibits high reactivity in oxidative-elimination reactions. Thus reaction with n-C_3F_7I in hexane at room temperature produces green crystals (from hexane at −20 °C) of *trans*-[FeI{(CF$_3$)$_2$CF}(Bu^{t}NC)$_4$] (**3**) (70% yield) [ν_{NC} 2 180s and 2 110sh cm^{-1}; ^{1}H n.m.r.: τ (CDCl$_3$) 8·5(s); ^{13}C n.m.r.: δ ($C_6D_5CD_3$) 162·5 (Bu^{t}N*C*), 56·4 (Me$_3$*C*N), and 30·5 (Me) p.p.m.; ^{19}F n.m.r.: δ {(CD$_3$)$_2$CO} 67·8 {d, 6F, CF$_3$, *J*(FF) 11·2 Hz} and 175 p.p.m. {septet, 1F, CF, *J*(FF) 11·2 Hz}]. No evidence for the existence of the n-C_3F_7·Fe derivative was observed in the ^{19}F n.m.r. spectrum. The unusual formation of the (CF$_3$)$_2$CF group suggests the intermediacy in the reaction of an n-perfluoropropyl carbanion species which rearranges *via* fluoride migration to give (**3**).

Methyl iodide and (**1**) in THF at room temperature yield (70%) a brown crystalline adduct (from hexane, −20 °C) (**4**) of composition [Fe(Bu^{t}NC)$_5$·MeI] [ν_{NC} 2 160sh, 2 105s, 2 060sh, 1 635m, and 1 570m cm^{-1}]. The ^{1}H n.m.r. spectrum (C_6D_6) revealed five non-equivalent singlet methyl resonances [τ 8·05 (3H), 8·33 (9H), 8·36 (9H), 8·73 (9H), and 8·75 (18H)], the relative intensities corresponding to one Me group, and three non-equivalent and two equivalent Bu^t groups. The structure shown for (**4**) is compatible with this spectrum, as is the presence of two $\nu_{C=N}$ stretches (1 635 and 1 570 cm^{-1}). Moreover, the ^{13}C n.m.r. spectrum ($C_6D_5CD_3$, −80 °C), partially ^{1}H decoupled, revealed resonances assignable to Fe·*C*(:NBu^t) (194·5), Fe·C(:NBu^t)-*C*(Me) (179·3), FeCN (177·3 and 170·9), and C·*Me* (14·1 p.p.m.). Formation of (**4**) corresponds to initial formation of an Fe–Me bond followed by successive insertion of two isocyanide ligands. A related insertion has been observed in the oxidative-addition reaction of [Ni(Bu^{t}NC)$_4$] with methyl iodide.[2]



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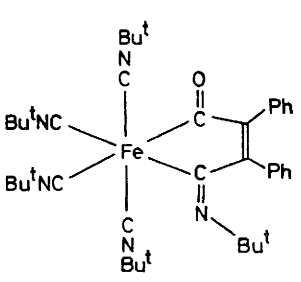

(6)

In contrast, with allyl chloride, complex (**1**) reacts to give (75% yield) pale-yellow microcrystals (from THF-light petroleum at −78 °C) of *trans*-[FeCl(η^1-C_3H_5)(Bu^{t}NC)$_4$] (**5**) [ν_{NC} 2 195sh, 2 130s, and 2 060s and $\nu_{C:C}$ 1 605 cm^{-1}; ^{1}H n.m.r.: τ {(CD)$_3$CO} 8·44 (s, Me), 5·5 (m, CH$_2$), and 3·9 (m, CH); ^{13}C n.m.r.: δ (CD$_3$CN) 151·4 (CH), 103·0 (*C*H$_2$:CH), and 14·4 p.p.m. (CH$_2$Fe)].

Complex (**1**) is also reactive towards some small ring organic compounds. Thus diphenylcyclopropenone affords dark red crystals of composition [Fe(Bu^{t}NC)$_5$·(PhC)$_2$CO] (**6**), the spectroscopic properties [ν_{NC} 2 115s, 2 090sh, and 2 045s and $\nu_{C=O}$ 1 615s, br cm^{-1}; ^{1}H n.m.r.: τ (C_6D_6) 8·0, 8·75, 9·1, and 9·15 (Me); ^{13}C n.m.r.: δ (C_6D_6) 62·1, 58·8, 56·5, and 55·6 p.p.m. (*C*Me$_3$)] suggesting the structure shown. It is proposed that (**1**) reacts with diphenylcyclopropenone to form a metallacyclobutenone[2] which undergoes migration of an iron-bonded carbon atom to a co-ordinated isocyanide group.

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