

Chemistry of Low-valent Metal Isocyanide Complexes. Part 1. Synthesis of Zerovalent Iron and Ruthenium Complexes. Crystal and Molecular Structures of Tetrakis(*t*-butyl isocyanide)(triphenylphosphine)ruthenium and Pentakis(*t*-butyl isocyanide)iron

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Reduction (Na–Hg, tetrahydrofuran) of *trans*-[RuCl₂(CNBu^t)₄] in the presence of excess of CNBu^t gives [Ru(CNBu^t)₅], which on reaction with PPh₃ affords [Ru(CNBu^t)₄(PPh₃)]. The latter is also formed on reduction of *trans*-[RuCl₂(CNBu^t)₄] with sodium amalgam in the presence of 1 mol equivalent of PPh₃. In order to establish the structural identity of this complex a single-crystal X-ray diffraction study has been made. Crystals of the complex are monoclinic, space group *P*2₁/*c*, *Z* = 4, in a unit cell of dimensions *a* = 12.174(4), *b* = 29.193(13), *c* = 11.454(3) Å, and β = 102.62(2)°. The structure has been refined to *R* 0.094 (*R'* 0.089) for 1 763 reflections. The complex has a trigonal-bipyramidal structure with PPh₃ and two bent CNBu^t [mean C–N–C 130(2)°] ligands occupying equatorial sites, and two essentially linear isocyanides in the axial sites. A similar reduction of FeBr₂ in the presence of excess of CNBu^t, CNPrⁱ, CNEt, or CNC₆H₃Me₂-2,6 affords the crystalline complexes [Fe(CNR)₅] (*R* = Bu^t, Prⁱ, Et, or C₆H₃Me₂-2,6). A single-crystal X-ray diffraction study of [Fe(CNBu^t)₅] has been undertaken. Crystals of the complex are monoclinic, space group *P*2₁/*n*, *Z* = 8, in a unit cell of dimensions *a* = 18.930(8), *b* = 11.529(3), *c* = 28.968(8) Å, and β = 108.63(1)°. The structure has been refined to *R* 0.099 (*R'* 0.129) for 4 339 reflections. There are two crystallographically independent molecules in an asymmetric unit, each of which shows marked deviation from idealised trigonal-bipyramidal geometry, the radial ligands being bent. Reaction of [Fe(CNBu^t)₅] with PPh₃ (1 mol) gives [Fe(CNBu^t)₄(PPh₃)], and treatment of [Fe(CNEt)₅] with CNC₆H₃Me₂-2,6 affords [Fe(CNEt)₃(CNC₆H₃Me₂-2,6)₂]. Reduction of [{OsCl₂(1,5-C₈H₁₂)_n}] with potassium amalgam in the presence of excess of CNBu^t gives [Os(CNBu^t)₃(1,5-C₈H₁₂)]. The structure in solution and dynamic behaviour of these complexes is discussed.

As a ligand, carbon monoxide has largely dominated the chemistry of low-valent transition-metal complexes, except for nickel, palladium, and platinum where many zerovalent complexes are known having tertiary phosphines or olefins as the sole stabilising groups. However, it is increasingly recognised that carbonyl and phosphine groups impose certain limitations on the range of chemical behaviour shown by a metal in a complex compound. Thus the high backbonding characteristics of carbon monoxide makes it less easy to increase the nucleophilicity of metal centres, and although the latter effect can be accomplished by phosphines these ligands tend to be sterically demanding thereby blocking co-ordination sites. With these factors in mind, we have begun to explore the chemistry of low-valent metal isocyanide complexes. Isocyanide molecules cause less steric crowding around a metal than phosphines, yet have a range of bonding modes, *i.e.* terminal, edge-bridging, or face-bridging, comparable with carbon monoxide. Hence, in principle, binary metal isocyanide complexes could have a chemistry as rich as that of metal carbonyls. It is surprising, therefore, that until relatively recently few zerovalent metal complexes had been reported with isocyanide molecules as the only ligands.¹ Among early discoveries² was the synthesis of (aryl isocyanide)-nickel complexes [Ni(CNR)₄],³⁻⁵ and palladium species formulated as [Pd(CNR)₂].^{6,7} Alkyl isocyanide complexes of these metals were subsequently prepared,⁸ and shown to be very reactive towards electrophilic reagents.⁹⁻¹¹

Recently, the cluster complexes [Pt₃(CNBu^t)₆]¹² and [Ni₄(CNBu^t)₇]¹³ have been isolated. The nickel

complex shows catalytic properties,¹⁴ and the platinum complex cleaves certain types of C–C bond.^{15,16} Thus *t*-butyl isocyanide ligands are very effective in promoting high reactivity at these zerovalent metal centres, and the results with platinum and nickel directed our attention^{17,18} to the iron, ruthenium, and osmium subgroup, with a view to synthesising the species [M(CNBu^t)₅] (*M* = Fe, Ru, or Os). These complexes, formally analogous to the pentacarbonyls, would be expected to have an extensive chemistry. Iron complexes [Fe(CNR)₅] (*R* = Bu^t, C₆H₁₁, CH₂·CH, or Me) have been mentioned¹⁹ as products of reactions of iron atoms with isocyanides.

RESULTS AND DISCUSSION

As a preparative route to isocyanide metal complexes, ligand exchange with CO in metal carbonyls has met with only limited success. The complexes [Fe₃(CNR)_{*n*}(CO)_{12-*n*}] (*n* = 1 or 2, *R* = Me; *n* = 1–3, *R* = Bu^t) have been synthesised, but attempts to increase *n* resulted in cluster fragmentation.²⁰ Ruthenium²¹ and osmium analogues²² have also been prepared with *n* = 1–4 for *M* = Ru or Os, *R* = Bu^t, and *M* = Os, *R* = Ph; *n* = 1–3 for *M* = Os, *R* = C₆H₄OMe-*p*; and *n* = 1–2 for *M* = Os, *R* = Me. Pyrolysis of the osmium complexes in refluxing octane gave the cluster complex [Os₆(CNR)_{*n*}(CO)_{18-*n*}] (*n* = 1–5, *R* = Me or Bu^t). However, the successful synthesis of [Fe{P(Ome)₃}₅]^{23,24} and [Fe(CH₂·PMe₂)H(PMe₃)₃]²⁵ by sodium-amalgam reduction of [FeCl₂{P(Ome)₃}₃] and [FeCl₂(PMe₃)₂], respectively, in the presence of excess of ligand, suggested that a similar reduction of isocyanide-

iron and -ruthenium halides might afford $[M(CNR)_5]$ complexes, or even the analogues of the di- and polynuclear carbonyls. Initially our attention was focused on the ruthenium system.

Zinc-amalgam reduction of $RuCl_3 \cdot 3H_2O$ in the presence of an excess of *t*-butyl isocyanide in tetrahydrofuran (thf) as solvent afforded the yellow crystalline complex *trans*- $[RuCl_2(CNBut)_4]$, characterised by elemental analysis and 1H and ^{13}C n.m.r. spectroscopy. In contrast, on heating $RuCl_3 \cdot 3H_2O$ under reflux in ethanol with $CNBut$ a *cis-trans* mixture of $[RuCl_2(CNBut)_4]$ was formed, the white *cis* isomer predominating. Whereas, under a nitrogen atmosphere, the *trans* complex was readily reduced with either sodium or potassium amalgam in the presence of an excess of $CNBut$ in thf as solvent, the less soluble (in thf) *cis*- $[RuCl_2(CNBut)_4]$ did not react under similar conditions. The product of reduction of the *trans*-dichloride was readily extracted into hexane, and concentration at low temperature and cooling gave fine yellow crystals of pentakis(*t*-butyl isocyanide)-ruthenium (1). Both solutions of complex (1) and the crystalline material were found to be extremely air-sensitive. When *trans*- $[RuCl_2(CNBut)_4]$ was reduced in the absence of excess of isocyanide the reaction mixture became red; however, no hexane-soluble material was produced.

Elemental analysis and mass spectroscopy (field-ionisation) both suggested that (1) was the sought for mononuclear pentakis(isocyanide) complex $[Ru(CNBut)_5]$; however, the i.r. spectrum showed, in addition to bands assignable to terminally bonded isocyanide ligands, a band at 1815 cm^{-1} , which could be interpreted as evidence for a bridging isocyanide group. Examination of the 1H and ^{13}C n.m.r. spectra did not clarify the structural problem since only one isocyanide environment was observed down to -120°C .

Despite a number of attempts we could not obtain suitable crystals of (1) for single-crystal X-ray crystallographic studies. As an approach to solving the structural problem, complex (1) was treated with 1 mol equivalent of triphenylphosphine in hexane at room temperature to give (2), it having been previously observed that ligand exchange readily occurred with $^{13}CNBut$. Complex (2) formed red crystals analysing for $[Ru(CNBut)_4(PPh_3)]$.

This complex was also formed by reduction (Na-Hg) of *trans*- $[RuCl_2(CNBut)_4]$ in the presence of PPh_3 (1 mol equivalent). However, again a band at 1830 cm^{-1} was evident in the i.r. spectrum, raising doubts about the degree of nuclearity of this complex. Fortunately, suitable crystals for X-ray diffraction studies were obtained, resulting in the establishment of the trigonal-bipyramidal molecular structure shown in Figure 1. Internuclear distances and bond angles are given in Table 1. The triphenylphosphine ligand occupies an equatorial site, together with two of the *t*-butyl isocyanide ligands.

An interesting feature of the structure is that the equatorial isocyanide ligands are considerably bent, *i.e.*

$C(3)N(3)C(7)$ and $C(4)N(4)C(8)$, where the mean C-N-C angle is $130(2)^\circ$. The axial isocyanide ligands are almost linear [C-N-C mean $170(3)^\circ$]. Within the accuracy of data, the degree of bending at the nitrogen is paralleled by a change in the (Ru)C-N and N-C separations, increasing in length as the nitrogen adopts more sp^2 character [(Ru)C-N, N-C axial 1.18, 1.43 Å, compared with 1.25, 1.48 Å, respectively, for the equatorial ligands]. The C(1)-Ru-C(2) angle is significantly less than 180° , being concave away from the phosphine ligand, suggesting a steric effect. Similarly, the C-P-C angles are all less than tetrahedral, a distortion not uncommon with triphenylphosphine ligands. The *t*-butyl groups show the expected tetrahedral geometry within the limitations of the data.

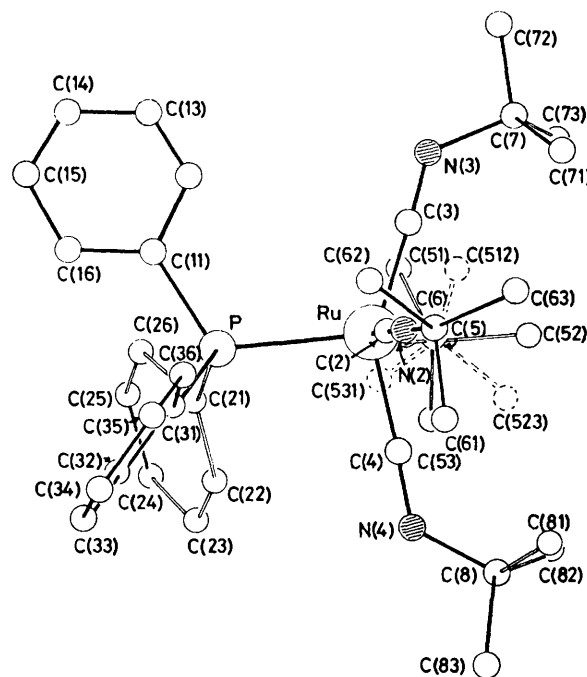


FIGURE 1 Projection of a molecule of $[Ru(CNBut)_4(PPh_3)]$ (2) onto the mean plane of P, C(3), and C(4), and showing the crystallographic numbering system

The extensive bending of the equatorial $CNBut$ ligands provided an explanation for the appearance in the i.r. spectrum of (2) of a band at 1830 cm^{-1} , and suggested that the parent complex (1) very probably contains bent isocyanide ligands also.

We next set out to synthesise and structurally characterise the iron complex $[Fe(CNBut)_5]$ (3). The availability of tetrahydrofuran-soluble anhydrous iron(II) salts avoided the need for the partial reduction step used with the ruthenium system. Reduction of iron(II) bromide* in thf with sodium amalgam in the presence of an excess of $CNBut$ afforded (24 h) a good yield of the required pentakis(*t*-butyl isocyanide)iron (3), isolated from light petroleum (-78°C) as bright yellow air-sensitive crystals, and characterised by ele-

* Reasonable yields were also obtained with iron(II) chloride, but reduction proceeded more slowly.

mental analysis, mass spectroscopy, i.r., ^1H and ^{13}C n.m.r. spectroscopy. Comparison of the i.r. spectra of (1) and (3) suggested that in solution the complexes are isostructural, a conclusion which was supported by the n.m.r. spectra, which showed resonances due to one *t*-butyl isocyanide environment down to -130°C (CF_2Cl_2 - CHCl_2F solutions).

TABLE 1

Internuclear distances (\AA) and bond angles ($^\circ$) (with estimated standard deviations in parentheses) for $[\text{Ru}(\text{CNBu}^t)_4(\text{PPh}_3)]$ (2)

| Bonds | | Angles | |
|--------------------------|----------|------------------|----------|
| Ru-P | 2.334(7) | Ru-P-C(11) | 123.8(8) |
| P-C(11) | 1.84(2) | Ru-P-C(21) | 112.7(8) |
| P-C(21) | 1.81(3) | Ru-P-C(31) | 114.1(8) |
| P-C(31) ^a | 1.86(2) | C(11)-P-C(21) | 99(1) |
| | | C(11)-P-C(31) | 99(1) |
| | | C(21)-P-C(31) | 106(1) |
| Ru-C(1) | 2.00(3) | Ru-C(1)-N(1) | 176(2) |
| C(1)-N(1) | 1.17(4) | P-Ru-C(1) | 95(1) |
| N(1)-C(5) | 1.42(5) | C(1)-N(1)-C(5) | 167(3) |
| C(5)-C(51) | 1.55(6) | N(1)-C(5)-C(51) | 110(3) |
| C(5)-C(52) | 1.53(8) | N(1)-C(5)-C(52) | 108(4) |
| C(5)-C(53) | 1.61(7) | N(1)-C(5)-C(53) | 103(3) |
| C(5)-C(512) ^b | 1.75(10) | N(1)-C(5)-C(512) | 102(4) |
| C(5)-C(523) | 1.44(7) | N(1)-C(5)-C(253) | 105(4) |
| C(5)-C(531) | 1.47(11) | N(1)-C(5)-C(531) | 113(4) |
| Ru-C(2) | 1.92(2) | Ru-C(2)-N(2) | 174(2) |
| C(2)-N(2) | 1.19(4) | P-Ru-C(2) | 101(1) |
| N(2)-C(6) | 1.43(4) | C(2)-N(2)-C(6) | 172(3) |
| C(6)-C(61) | 1.50(4) | N(2)-C(6)-C(61) | 107(2) |
| C(6)-C(62) | 1.58(4) | N(2)-C(6)-C(62) | 111(2) |
| C(6)-C(63) | 1.45(5) | N(2)-C(6)-C(63) | 109(2) |
| Ru-C(3) | 1.86(2) | Ru-C(3)-N(3) | 177(2) |
| C(3)-N(3) | 1.28(3) | P-Ru-C(3) | 112(1) |
| N(3)-C(7) | 1.51(4) | C(3)-N(3)-C(7) | 131(2) |
| C(7)-C(71) | 1.52(5) | N(3)-C(7)-C(71) | 108(2) |
| C(7)-C(72) | 1.56(4) | N(3)-C(7)-C(72) | 104(2) |
| C(7)-C(73) | 1.51(4) | N(3)-C(7)-C(73) | 107(2) |
| Ru-C(4) | 1.91(2) | Ru-C(4)-N(4) | 176(2) |
| C(4)-N(4) | 1.22(3) | P-Ru-C(4) | 101(1) |
| N(4)-C(8) | 1.46(3) | C(4)-N(4)-C(8) | 129(2) |
| C(8)-C(81) | 1.47(5) | N(4)-C(8)-C(81) | 108(2) |
| C(8)-C(82) | 1.46(4) | N(4)-C(8)-C(82) | 113(2) |
| C(8)-C(83) | 1.52(3) | N(4)-C(8)-C(83) | 111(2) |
| | | C(1)-Ru-C(2) | 164(1) |
| | | C(1)-Ru-C(3) | 88(1) |
| | | C(1)-Ru-C(4) | 88(1) |
| | | C(2)-Ru-C(3) | 85(1) |
| | | C(2)-Ru-C(4) | 89(1) |
| | | C(3)-Ru-C(4) | 146(1) |

^a Other molecular parameters associated with the phenyl rings have been deposited (Appendix A). ^b Atoms C(512), C(523), and C(531) indicate alternative positions for the disordered methyl carbon atoms in this Bu^t group.

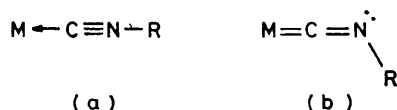
Crystals of (3) suitable for X-ray crystallography were grown from hexane solutions, and analysis of the diffraction data established the structure shown in Figure 2, with the internuclear distances and bond angles given in Table 2. There are two crystallographically independent molecules in an asymmetric unit, each of which shows substantial bending of the radial isocyanide ligands [C(1) and C(4), and C(6) and C(9)] which can be attributed to extensive back bonding from the metal into the anti-bonding orbitals of the isocyanide ligand $[\text{Fe}(3d) \rightarrow \text{C} \equiv \text{N} (\pi^*)]$, similar backbonding occurring with the ruthenium complexes $[\text{Ru}(4d) \rightarrow \text{C} \equiv \text{N} (\pi^*)]$. In the case

TABLE 2

Internuclear distances (\AA) and bond angles ($^\circ$) (with estimated standard deviations in parentheses) for $[\text{Fe}(\text{CNBu}^t)_2]$ (3)

| Bonds | | Angles | |
|----------------|-----------|----------------------|----------|
| (a) Molecule 1 | | | |
| Fe(1)-C(1) | 1.813(7) | C(1)-Fe(1)-C(2) | 89.3(3) |
| Fe(1)-C(2) | 1.811(7) | C(1)-Fe(1)-C(3) | 88.0(3) |
| Fe(1)-C(3) | 1.837(7) | C(1)-Fe(1)-C(4) | 145.2(4) |
| Fe(1)-C(4) | 1.803(10) | C(1)-Fe(1)-C(5) | 111.2(4) |
| Fe(1)-C(5) | 1.835(8) | C(2)-Fe(1)-C(3) | 164.5(4) |
| | | C(2)-Fe(1)-C(4) | 86.8(4) |
| | | C(2)-Fe(1)-C(5) | 101.4(3) |
| | | C(3)-Fe(1)-C(4) | 86.7(4) |
| | | C(3)-Fe(1)-C(5) | 93.8(4) |
| | | C(4)-Fe(1)-C(5) | 103.4(4) |
| C(1)-N(1) | 1.21(1) | Fe(1)-C(1)-N(1) | 178.2(7) |
| N(1)-C(11) | 1.48(1) | C(1)-N(1)-C(11) | 133.1(8) |
| C(11)-C(111) | 1.52(1) | N(1)-C(11)-C(111) | 107.9(7) |
| C(11)-C(112) | 1.50(1) | N(1)-C(11)-C(112) | 107.3(6) |
| C(11)-C(113) | 1.55(1) | N(1)-C(11)-C(113) | 107.8(6) |
| C(2)-N(2) | 1.20(1) | Fe(1)-C(2)-N(2) | 176.7(8) |
| N(2)-C(21) | 1.42(1) | C(2)-N(2)-C(21) | 151.6(9) |
| C(21)-C(211) | 1.58(2) | N(2)-C(21)-C(211) | 107(1) |
| C(21)-C(212) | 1.49(2) | N(2)-C(21)-C(212) | 110.4(8) |
| C(21)-C(213) | 1.51(2) | N(2)-C(21)-C(213) | 109.2(8) |
| C(3)-N(3) | 1.16(1) | Fe(1)-C(3)-N(3) | 178.1(9) |
| N(3)-C(31) | 1.43(1) | C(3)-N(3)-C(31) | 177.1(8) |
| C(31)-C(311) | 1.54(1) | N(3)-C(31)-C(311) | 106.6(7) |
| C(31)-C(312) | 1.53(2) | N(3)-C(31)-C(312) | 110.7(8) |
| C(31)-C(313) | 1.51(1) | N(3)-C(31)-C(313) | 108.9(7) |
| C(4)-N(4) | 1.22(1) | Fe(1)-C(4)-N(4) | 176.9(7) |
| N(4)-C(41) | 1.48(1) | C(4)-N(4)-C(41) | 134.6(8) |
| C(41)-C(411) | 1.43(2) | N(4)-C(41)-C(411) | 112(1) |
| C(41)-C(412) | 1.52(2) | N(4)-C(41)-C(412) | 106.0(9) |
| C(41)-C(413) | 1.57(2) | N(4)-C(41)-C(413) | 107.2(7) |
| C(5)-N(5) | 1.19(1) | Fe(1)-C(5)-N(5) | 176.2(7) |
| N(5)-C(51) | 1.46(1) | C(5)-N(5)-C(51) | 169.2(7) |
| C(51)-C(511) | 1.53(1) | N(5)-C(51)-C(511) | 106.1(8) |
| C(51)-C(512) | 1.52(1) | N(5)-C(51)-C(512) | 108.8(7) |
| C(51)-C(513) | 1.51(1) | N(5)-C(51)-C(513) | 107.9(7) |
| (b) Molecule 2 | | | |
| Fe(2)-C(6) | 1.817(7) | C(6)-Fe(2)-C(7) | 88.0(3) |
| Fe(2)-C(7) | 1.834(8) | C(6)-Fe(2)-C(8) | 89.5(3) |
| Fe(2)-C(8) | 1.835(7) | C(6)-Fe(2)-C(9) | 136.3(4) |
| Fe(2)-C(9) | 1.812(9) | C(6)-Fe(2)-C(10) | 112.9(4) |
| Fe(2)-C(10) | 1.846(9) | C(7)-Fe(2)-C(8) | 167.2(4) |
| | | C(7)-Fe(2)-C(9) | 87.0(4) |
| | | C(7)-Fe(2)-C(10) | 91.5(4) |
| | | C(8)-Fe(2)-C(9) | 86.1(4) |
| | | C(8)-Fe(2)-C(10) | 101.0(3) |
| | | C(9)-Fe(2)-C(10) | 110.6(3) |
| C(6)-N(6) | 1.20(1) | Fe(2)-C(6)-N(6) | 178.4(8) |
| N(6)-C(61) | 1.48(1) | C(6)-N(6)-C(61) | 135.2(8) |
| C(61)-C(611) | 1.48(1) | N(6)-C(61)-C(611) | 109.2(7) |
| C(61)-C(612) | 1.55(2) | N(6)-C(61)-C(612) | 107.4(7) |
| C(61)-C(613) | 1.51(1) | N(6)-C(61)-C(613) | 106.6(7) |
| C(7)-N(7) | 1.18(1) | Fe(2)-C(7)-N(7) | 179.5(9) |
| N(7)-C(71) | 1.41(1) | C(7)-N(7)-C(71) | 165(1) |
| C(71)-C(711) | 1.53(1) | N(7)-C(71)-C(711) | 106.6(7) |
| C(71)-C(712) | 1.55(2) | N(7)-C(71)-C(712) | 106.8(9) |
| C(71)-C(713) | 1.49(1) | N(7)-C(71)-C(713) | 107.9(8) |
| C(8)-N(8) | 1.18(1) | Fe(2)-C(8)-N(8) | 177.4(8) |
| N(8)-C(81) | 1.39(1) | C(8)-N(8)-C(81) | 158.1(8) |
| C(81)-C(811) | 1.54(3) | N(8)-C(81)-C(811) | 113(1) |
| C(81)-C(812) | 1.50(2) | N(8)-C(81)-C(812) | 110(1) |
| C(81)-C(813) | 1.50(3) | N(8)-C(81)-C(813) | 114(1) |
| C(9)-N(9) | 1.20(1) | Fe(2)-C(9)-N(9) | 176.9(6) |
| N(9)-C(91) | 1.47(1) | C(9)-N(9)-C(91) | 136.9(8) |
| C(91)-C(911) | 1.52(2) | N(9)-C(91)-C(911) | 107.3(7) |
| C(91)-C(912) | 1.55(1) | N(9)-C(91)-C(912) | 107.9(7) |
| C(91)-C(913) | 1.57(2) | N(9)-C(91)-C(913) | 107.7(9) |
| C(10)-N(10) | 1.20(1) | Fe(2)-C(10)-N(10) | 174.2(7) |
| N(10)-C(101) | 1.44(1) | C(10)-N(10)-C(101) | 166.3(8) |
| C(101)-C(1011) | 1.55(1) | N(10)-C(101)-C(1011) | 106.8(9) |
| C(101)-C(1012) | 1.53(1) | N(10)-C(101)-C(1012) | 107.2(7) |
| C(101)-C(1013) | 1.55(2) | N(10)-C(101)-C(1013) | 110.6(7) |

of (3) this results in an increase in the sp^2 character of the radial nitrogen atoms N(1), N(4), N(6), and N(9). This is seen not only in the C-N-C angle [mean $135(1)^\circ$], but also in the increase in C-N separation [mean $1.21(1)$ Å], and a shortening, hence multiple-bond character, of the Fe-C bond [mean $1.811(8)$ Å]. A less pronounced bending of a terminally bonded isocyanide ligand has been observed²⁶ in the complex $[\text{Mo}(\text{CNMe})_2(\text{dppe})_2]$ [Me-N-C $156(1)^\circ$, $\nu(\text{NC})$ at 1850 cm^{-1} ; dppe = $\text{Ph}_2\text{-PCH}_2\text{CH}_2\text{PPh}_2$], but the iron and ruthenium systems clearly represent extreme cases, where in valence-bond terms a substantial contribution to the electronic structure is made by the bent canonical form (b):



The angles contained by the bent radial ligands [C(1)-Fe(1)-C(4) $145.2(4)^\circ$, C(6)-Fe(2)-C(9) $136.2(4)^\circ$] are

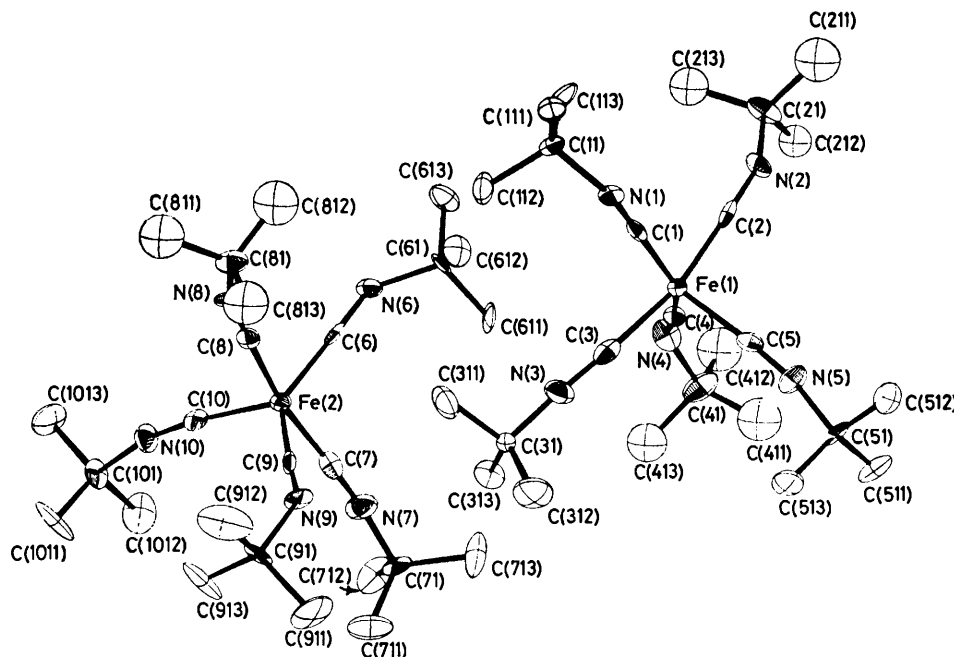


FIGURE 2 The asymmetric unit of $[\text{Fe}(\text{CNBut})_5]$ (3) comprising two independent molecules shown in projection

such that the overall geometry of the molecule is best described as intermediate between square pyramidal and trigonal bipyramidal. The two independent molecules of the asymmetric unit exhibit some differences in molecular geometry, which we attribute, together with the smaller degree of bending of the remaining radial and axial ligands, to distortions arising from packing forces. The 'equatorial' planes defined by Fe(1)C(1)C(4)C(5) and Fe(2)C(6)C(9)C(10) are almost perpendicular to each other (Table 6), with the axial ligand [C(3), *etc.*] of one molecule pointing towards the most open pair of equatorial ligands of the other. The expected tetrahedral geometry is adopted by the *t*-butyl groups.

Extension of the procedure adopted for the synthesis of (3) to the reaction of CNPr^i , CNEt , or $\text{CNC}_6\text{H}_3\text{Me}_2$ -2,6 with FeBr_2 and sodium amalgam resulted in the formation of yellow pentakis(isopropyl isocyanide)-, yellow pentakis(ethyl isocyanide)-, and red pentakis-(2,6-dimethylphenyl isocyanide)-iron, respectively as air-sensitive crystalline complexes (4), (5), and (6), characterised by elemental analysis and i.r. and n.m.r. spectroscopy. In the case of (4) and (5) the i.r. spectra showed again, in addition to terminally bonded isocyanide stretching frequencies, strong bands in the 1830 – 1870 cm^{-1} region, which are assigned to substantially bent isocyanide ligands.

However, in marked contrast, the i.r. spectrum of complex (6) did not have this feature. The isocyanide stretching gave rise to a single broad band centred around the maximum at 1965 cm^{-1} with only a much weaker absorption at 1866 cm^{-1} appearing as a small shoulder. In the light of this observation, it is proposed that the aromatic ring of the ligand plays an important role in

enabling the isocyanide function to accept electron density from the metal into the π^* antibonding orbitals without the necessity of bending at the nitrogen atom. Alternatively, the observed i.r. spectrum may be rationalised by a consideration of the steric requirements of the 2,6-dimethylphenyl isocyanide ligand. As in the case of (1)–(3), the n.m.r. spectra (low temperatures) are consistent with the existence of a dynamic process, which results in an averaging of the different isocyanide environments established by X-ray crystallography in the solid state for (2) and (3) and by i.r. spectroscopy in solution.

Treatment of (3) with 1 mol equivalent of PPh_3 in thf (24 h) gave a deep red solution which afforded red

crystals of $[\text{Fe}(\text{CNBu}^t)_4(\text{PPh}_3)]$ (7). This complex showed similar i.r. and ^1H and ^{13}C n.m.r. characteristics to the ruthenium complex (2). That the isocyanide-displacement reaction is not limited to phosphines was demonstrated by the rapid reaction (30 min) of (5) with 2 mol equivalents of 2,6-dimethylphenyl isocyanide giving bis(2,6-dimethylphenyl isocyanide)tris(ethyl isocyanide)iron (8). The i.r. spectrum of (8) showed bands assignable to both linear and bent isocyanide ligands. The presence of only one isocyanide environment in the n.m.r. spectrum is consistent with a dynamic system, but does not exclude stereochemical rigidity with the three ethyl isocyanide ligands occupying the equatorial sites in a trigonal-bipyramidal structure.

The most likely mechanism for the ligand-substitution reactions of $[\text{M}(\text{CNR})_5]$ ($\text{M} = \text{Fe}$ or Ru) involves reversible dissociative loss of CNR to form the coordinatively unsaturated 16-electron species $[\text{M}(\text{CNR})_4]$, which is captured in the presence of species such as PPh_3 or 2,6-dimethylphenyl isocyanide. It is reasonable to assume that such a dissociative process is slow on the n.m.r. time scale, and that the averaging process responsible for axial and equatorial site exchange is an intramolecular process. Detailed line-shape analysis of the variable-temperature $^{31}\text{P}\{-\text{H}\}$ spectra of all Group 8 d^8 five-coordinate transition-metal phosphite complexes has shown that there is simultaneous exchange of the pair of axial with a pair of equatorial ligands in the intramolecular rearrangement process, *i.e.* a Berry pseudo-rotation mechanism is operative.^{14,27} It is reasonable to suggest that in the d^8 isocyanide complexes a similar low-activation-energy Berry process is also operating, which also involves pairwise exchange which could for the isocyanide complexes occur *via* a synchronous bending and straightening of the axial and equatorial ligands.

In an attempt to prepare $[\text{Os}(\text{CNBu}^t)_5]$, the reduction of $[\{\text{OsCl}_2(1,5\text{-C}_8\text{H}_{12})\}_n]$ with potassium amalgam, in the presence of an excess of CNBu^t , was examined. The pale yellow crystalline product (9), which crystallised from hexane, was obtained in good yield, and was characterised by analysis and mass spectroscopy as (cyclo-octa-1,5-diene)tris(*t*-butyl isocyanide)osmium. Recently, the analogous iron complex has been reported²⁸ as the product of the reaction of CNBu^t with $[\text{Fe}(1,5\text{-C}_8\text{H}_{12})_2]$. As with the iron system, attempts to displace cyclo-octa-1,5-diene from (9) with CNBu^t were unsuccessful. The i.r. spectrum of (9) showed bands consistent with both linear and bent isocyanide ligands. Furthermore, the ^1H and ^{13}C n.m.r. spectra, recorded at -90°C , displayed only one environment for both the isocyanide and cyclo-octa-1,5-diene ligands implying, as with the iron system, stereochemical non-rigidity. However, on the basis of the data at present available it is not possible to comment on the nature of this process.

EXPERIMENTAL

N.m.r. spectra (^1H , hydrogen-1 decoupled ^{13}C and ^{31}P) were recorded on JEOL PFT and PS 100 spectrometers,

with ^{13}C shifts relative to SiMe_4 (0.0 p.p.m.) and ^{31}P shifts relative to H_3PO_4 (external). Infrared spectra were obtained on a Perkin-Elmer 457 spectrophotometer. Molecular weights were established mass spectrometrically with an A.E.I. MS 902 instrument operating at 70 eV.* Experiments were carried out using Schlenk tube techniques under a dry oxygen-free nitrogen atmosphere, with solvents dried and distilled under nitrogen prior to use.

Preparations.—*trans*-Dichlorotetrakis(*t*-butyl isocyanide)ruthenium. Solid $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (1 g, *ca.* 4 mmol) was added to zinc amalgam (3 g, excess) and CNBu^t (4 cm³, 29 mmol) suspended in tetrahydrofuran (50 cm³) at -50°C . The reaction mixture was warmed to room temperature and stirred for 24 h. Filtration, followed by recrystallisation from thf, afforded yellow crystals of *trans*- $[\text{RuCl}_2(\text{CNBu}^t)_4]$ (1.3 g, *ca.* 67%), m.p. 155°C (Found: C, 46.8; H, 8.0; Cl, 15.1; N, 11.3%; *M*, 504. $\text{C}_{26}\text{H}_{36}\text{Cl}_2\text{N}_4\text{Ru}$ requires C, 47.6; H, 7.2; Cl, 14.1; N, 11.1%; *M*, 504); ν_{max} in Nujol at 2 160s,br, 2 090(sh), 1 245m, 1 214s, 770s, 760w, 716w, 575m, and 560m cm⁻¹. N.m.r. resonances: (^1H , [$^2\text{H}_8$]toluene) τ 8.80 (s, invariant at -90°C); (^{13}C , CDCl_3) 31.1 (CNCMe₃) and 56.7 p.p.m. (CNCMe₃).

Pentakis(*t*-butyl isocyanide)ruthenium. *trans*-Dichlorotetrakis(*t*-butyl isocyanide)ruthenium (1.3 g, 2.6 mmol) was added to a stirred suspension of sodium amalgam (50 g, 1%) in CNBu^t (2.0 cm³, 15 mmol) and thf (60 cm³), cooled to -50°C . The reaction mixture was warmed to room temperature and stirring was continued for 48 h. The solvent was removed *in vacuo*, and the residue extracted with hexane (80 cm³). Crystallisation at -18°C afforded yellow crystals of $[\text{Ru}(\text{CNBu}^t)_5]$ (1) (0.3 g, 22%), m.p. $86\text{--}88^\circ\text{C}$ (decomp.) [Found: C, 56.7; H, 8.7; N, 13.3%; *M*, 517 (^{102}Ru). $\text{C}_{25}\text{H}_{45}\text{N}_5\text{Ru}$ requires C, 58.1; H, 8.8; N, 13.6%; *M*, 517]; ν_{max} in hexane at 2 059(sh), 2 032s, 1 832s,br, 1 220(sh), 1 206s, and 1 110s cm⁻¹. N.m.r. resonances: (^1H , [$^2\text{H}_8$]toluene) τ 8.72 (s, invariant down to -90°C); (^{13}C , [$^2\text{H}_8$]toluene) 31.4 (CNCMe₃), 55.4 (CNCMe₃), and 187.5 p.p.m. (CNCMe₃), no change being observed at -120°C ([$^2\text{H}_8$]toluene–isopentane).

Tetrakis(*t*-butyl isocyanide)(triphenylphosphine)ruthenium. (a) *By reduction.* Sodium amalgam (50 g, 1%) was added at room temperature to a stirred solution of *trans*- $[\text{RuCl}_2(\text{CNBu}^t)_4]$ (1.4 g, 2.8 mmol), PPh_3 (0.7 g, 2.8 mmol), and CNBu^t (1 cm³, 8 mmol) in thf (50 cm³). After 14 h the volatile material was removed *in vacuo* from the deep orange solution. The residue was extracted with hexane (50 cm³), which on cooling (-18°C) afforded deep red crystals of $[\text{Ru}(\text{CNBu}^t)_4(\text{PPh}_3)]$ (2) (1.3 g, 70%) (Found: C, 65.7; H, 7.5; N, 8.0. $\text{C}_{38}\text{H}_{51}\text{N}_4\text{PRu}$ requires C, 65.6; H, 7.4; N, 8.0%); ν_{max} in hexane at 2 100(sh), 2 055s, 1 830s,br, 1 590m, 1 235m, 1 220s, 1 095m, 1 038m, 880w, 757m, 745w, and 710s cm⁻¹. N.m.r. resonances: (^1H , [$^2\text{H}_8$]toluene) τ 2.2–2.9 (m, 18 H, PPh) and 8.78 (s, 36 H, CNBu^t) unchanged down to -90°C ; (^{13}C , [$^2\text{H}_8$]toluene, -90°C) 31.1 (CNCMe₃), 55.4 (CNCMe₃), 124–142 (PPh₃), and 191.3 p.p.m. (CNCMe₃); (^{31}P , C_6D_6) $-\text{55.2}$ p.p.m. (s, PPh₃).

(b) *By displacement.* Triphenylphosphine (0.16 g, 0.61 mmol) was added (room temperature) to a solution of (1) (0.2 g, 0.57 mmol) in hexane (20 cm³). A deep orange solution rapidly formed. Cooling (-20°C) gave deep red crystals of (2) (0.33 g, 82%), identical (i.r., n.m.r.) with that described above.

* Throughout this paper: $1\text{ eV} \approx 1.60 \times 10^{-19}\text{ J}$.

Pentakis(*t*-butyl isocyanide)iron. An excess of sodium amalgam (70 g, 1%) was added at room temperature to a stirred solution of anhydrous iron(II) bromide (0.9 g, 4.2 mmol) and CNBu^t (2.0 g, 24 mmol) in thf (40 cm³). After 24 h all the volatile material was removed *in vacuo*, the residue extracted with light petroleum (40 cm³), and the resulting solution filtered through a short column (1 cm) of Florisil. Reduction of the volume of the solvent *in vacuo* and cooling (−78 °C) afforded bright yellow crystals of [Fe(CNBu^t)₅] (3) (1.4 g, 71%) (Found: C, 64.2; H, 9.8; N, 15.2%; *M*, 471. C₂₅H₄₅FeN₅ requires C, 63.7; H, 9.6; N, 14.9%; *M*, 471); ν_{\max} in hexane at 2 110s(sh), 2 005s,br, 1 830s,br, 1 232s, 750m, and 710m, ν_{\max} in Nujol at 2 120s(sh), 2 110s,br, 2 011s,br, 1 836s,br, 1 251s, 1 226s, 896m, 763m, 663w, and 585m cm^{−1}. N.m.r. resonances: (¹H, [²H₆]toluene, −90 °C) τ 8.72(s); (¹³C, CF₂Cl₂–CHCl₂F, −130 °C) 30.7 (CNCMe₃), 59.2 (CNCMe₃), and 209.7 p.p.m. (CNCMe₃).

The following complexes were prepared by essentially the same procedure. Yellow **pentakis(isopropyl isocyanide)iron** (4) (60%) (Found: C, 61.1; H, 9.4; N, 18.1. C₂₀H₃₅FeN₅ requires C, 59.9; H, 8.7; N, 17.5%); ν_{\max} in hexane at 2 060s(sh), 2 020s,br, 1 858s,br, 1 325s, 1 160m, 1 125m, and 805m cm^{−1}. N.m.r. resonances (¹H, [²H₆]acetone, −90 °C) τ 6.15 [septet, 5 H, CNCHMe₂, ²*J*(HH) 6.3] and 8.73 [d, 30 H, CNCHMe₂, ²*J*(HH) 6.3 Hz]; (¹³C, [²H₆]acetone, room temperature) 24.9 (CNCHMe₂), 49.0 (CNCHMe₂), and 197.8 p.p.m. (CNCHMe₂). Yellow **pentakis(ethyl isocyanide)iron** (5) (53%) (Found: C, 56.4; H, 8.0; N, 21.5%; *M*, 331. C₁₅H₂₅FeN₅ requires C, 54.4; H, 7.6; N, 21.2%; *M*, 331); ν_{\max} in diethyl ether at 2 050s,br, 1 830s,br, and 1 330m cm^{−1}. N.m.r. resonances: (¹H, [²H₆]acetone, room temperature) τ 6.52 [q, 10 H, CNCH₂CH₃, ²*J*(HH) 7.0] and 8.75 [t, 15 H, CNCH₂CH₃, ²*J*(HH) 7.0 Hz]; (¹³C, [²H₆]acetone, room temperature) 16.9 (CNCH₂CH₃), 40.3 (CNCH₂CH₃), and 196.2 p.p.m. (CNCH₂CH₃). A shorter reaction time (4 h) and extraction with Et₂O afforded red **pentakis(2,6-dimethylphenyl isocyanide)iron** (6) (85%) (Found: C, 75.8; H, 6.5; N, 10.4. C₄₅H₄₅FeN₅ requires C, 75.9; H, 6.4; N, 9.8%); ν_{\max} in hexane at 2 036s(sh), 1 978vs,br, 1 870m(sh), 1 591m, 763m, and 672m, ν_{\max} in Nujol at 2 040s(sh), 1 965s,br, 1 866m(sh), 1 588m, 770m, and 670m cm^{−1}. N.m.r. resonances: (¹H, [²H₆]acetone, room temperature) τ 2.93 (s, C₆H₃Me₂) and 7.56 (s, C₆H₃Me₂); (¹³C, [²H₆]toluene) 19.4 (Me), 126–137.3 (CNC₆H₃Me₂), and 195.5 p.p.m. (CNC₆H₃Me₂).

Tetrakis(*t*-butyl isocyanide)(triphenylphosphine)iron. Triphenylphosphine (0.6 g, 2.3 mmol) was added to a solution of (3) (1.1 g, 2.3 mmol) in dry degassed thf (30 cm³) and stirred for 24 h at room temperature. The volatile material was removed *in vacuo* from the resulting deep red solution, and the residue extracted with light petroleum (40 cm³). Filtration and cooling (−20 °C) afforded deep red crystals of [Fe(CNBu^t)₄(PPh₃)] (7) (0.7 g, 47%) (Found: C, 69.1; H, 7.9; N, 10.0; P, 3.8. C₃₈H₅₁FeN₄P requires C, 70.1; H, 7.8; N, 8.6; P, 4.7%); ν_{\max} in hexane at 2 100s(sh), 2 000s,br, 1 830s,br, 1 210m(sh), 1 200s, 1 170(sh), 1 150s, 1 115m, 730s, and 685s cm^{−1}. N.m.r. resonances: (¹H, C₆D₆, room temperature) τ 2.1–2.85 (m, PPh) and 8.8 (s, CNCMe₃); (¹³C, [²H₆]toluene, −90 °C) 31.6 (CNCMe₃), 55.6 (CNCMe₃), 141.1 [d, FePC, *J*(PC) 34], and 199.7 p.p.m. [d, FeCN, *J*(PC) 14 Hz]; and (³¹P, C₆D₆, room temperature) −78.7 p.p.m.

Bis(2,6-dimethylphenyl isocyanide)tris(ethyl isocyanide)-

iron. 2,6-Dimethylphenyl isocyanide (0.53 g, 4 mmol) was added to a stirred solution of (5) (0.66 g, 2 mmol) in diethyl ether (15 cm³) at room temperature. After 30 min the bulk of the solvent was removed *in vacuo* from the red solution, the last drops of liquid being withdrawn at 0 °C with a syringe leaving a red-orange microcrystalline product which was washed with successive portions of cold diethyl ether–light petroleum (1 : 1, 3 × 10 cm³) before drying *in vacuo* to give crystals of [Fe(CNEt)₃(CNC₆H₃Me₂-2,6)₂] (8) (0.72 g, 75%) (Found: C, 65.3; H, 6.8; N, 14.0. C₂₇H₃₃FeN₅ requires C, 67.1; H, 6.8; N, 14.5%); ν_{\max} in diethyl ether at 2 050m(sh), 2 030m(sh), 1 945s,br, 1 860m(sh), and 1 590m cm^{−1}. N.m.r. resonances: (¹H, [²H₆]acetone, room temperature) τ 3.1–3.3 (m, 6 H, C₆H₃Me₂), 6.31 [q, 6 H, CNCH₂CH₃, ²*J*(HH) 7.3], 7.57 (s, 12 H, Me), and 8.65 [t, 9 H, CNCH₂CH₃, ²*J*(HH) 7.3 Hz]; (¹³C, [²H₆]acetone, room

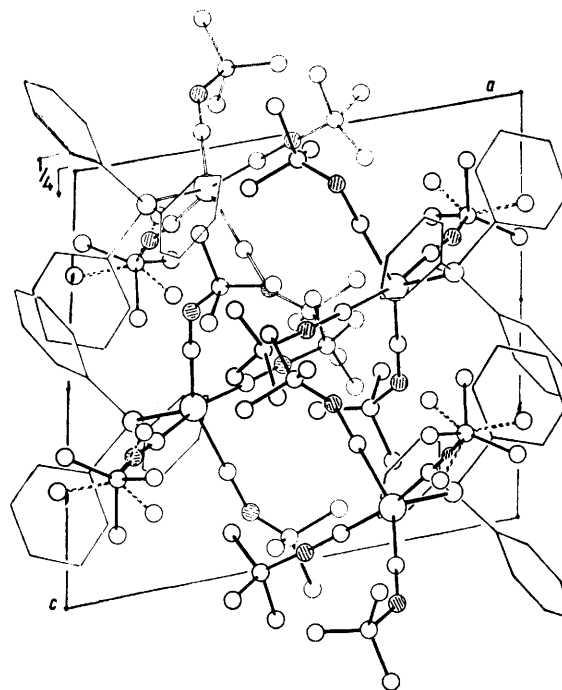


FIGURE 3 Contents of the unit cell of complex (2) viewed down the *b* axis towards the origin, with phenyl rings shown in an abbreviated form for clarity

temperature) 16.4 (CNCH₂CH₃), 19.3 (C₆H₃Me₂), 39.8 (CNCH₂CH₃), 123–133 (C₆H₃), 196.5 (CNC₆H₃Me₂-2,6), and 198.3 p.p.m. (CNEt).

(Cyclo-octa-1,5-diene)tris(*t*-butyl isocyanide)osmium. A mixture of [(OsCl₂(1,5-C₈H₁₂))_n] (0.25 g, 0.7 mmol), potassium amalgam (50 g, 1%), and CNBu^t (1.0 cm³, 7 mmol) in thf (20 cm³) was stirred for 24 h at room temperature. Volatile material was removed *in vacuo*, and the residue, extracted with hexane; cooling (−18 °C) afforded pale yellow crystals of [Os(CNBu^t)₃(1,5-C₈H₁₂)] (9) (0.3 g, 81%), m.p. 102–105 °C (Found: C, 50.2; H, 7.2; N, 7.6%; *M*, 538. C₂₃H₃₉N₃Os requires C, 50.4; H, 7.2; N, 7.7%; *M*, 547); ν_{\max} in Nujol at 2 127s, 2 099s, 2 062s, 1 825s, 1 316w, 1 236m, 1 212m, 870w, 745w, and 723w cm^{−1}. N.m.r. resonances: (¹H, [²H₆]toluene, room temperature) τ 6.18 (s,br, 4 H, CH:CH), 7.13 (s,br, 8 H, CH₂), 8.68 (s, 27 H, CNCMe₃); (¹³C, [²H₆]toluene, −95 °C) 31.3 (CNCMe₃), 36.6 (CH₂), 55.2 (CNCMe₃), 60.3 (CH:CH), and 160.5 p.p.m. (CNCMe₃).

Crystal-structure Determinations of Complexes (2) and (3).—The ruthenium complex (2) grows as air-sensitive deep red prisms from hexane, changing to yellow on exposure to air, whereas bright yellow crystals of (3) are converted rapidly into a brown oil in air. Hence the crystals to be used for data collection were sealed in Lindemann glass capillaries under nitrogen gas. Despite this, after 3 d of rapid data collection on (2), the crystals became yellow, ceased to diffract, and exhibited an overall 30% reduction in the intensities of the standard reflections

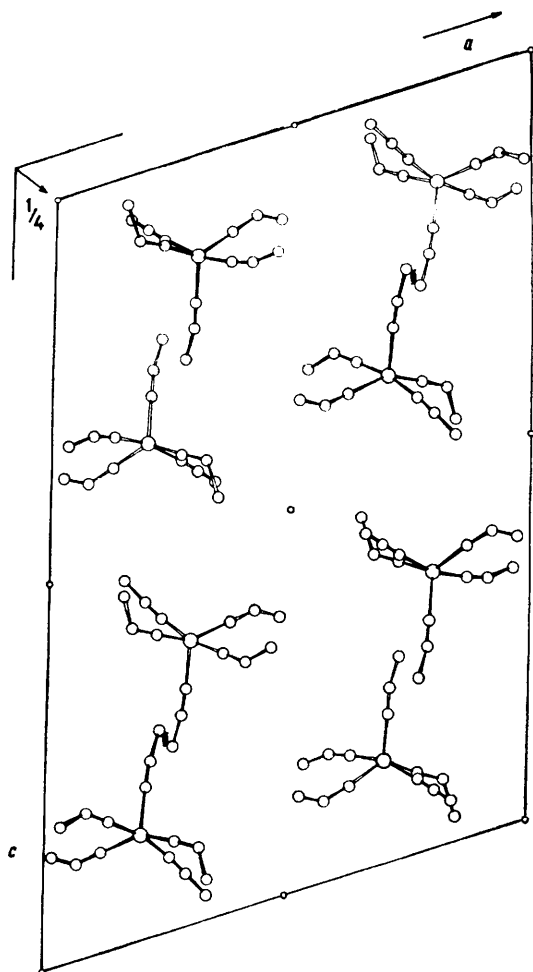


FIGURE 4 Contents of the unit cell of complex (3) viewed down the b axis towards the origin, with methyl groups omitted for clarity

during this period. A similar sudden cessation of diffraction occurred for (3) before data collection was finished, and a second crystal was required for completion. Corrections were applied to compensate for the observed decay in both data sets, and the differences in intensities arising from the use of two crystals in the case of (3).

Intensity data were recorded at room temperature for (2) and at -80°C for (3) on a Syntex $P2_1$ four-circle diffractometer in the range $2.9 \leq 2\theta \leq 50^\circ$, based on methods described earlier.²⁹ From a total of 3 304 (2) and 7 374 (3) intensities, 1 763 and 4 339, respectively, were deemed observable for $I \geq 2\sigma(I)$, $\sigma(I)$ being the standard deviation of the measured intensity based on counting statistics. Only these data, corrected for Lorentz and polarization,

but not for X -ray absorption effects, were used in the solution and refinement of the two structures.

Crystal data. (2), $\text{C}_{38}\text{H}_{51}\text{N}_4\text{PRu}$, $M = 695.9$, Monoclinic, space group $P2_1/c$, $a = 12.174(4)$, $b = 29.193(13)$, $c = 11.454(3)$ Å, $\beta = 102.62(2)^\circ$, $U = 3\,972.4$ Å³, $D_m = 1.10$ g cm⁻³ (floatation), $Z = 4$, $D_c = 1.17$ g cm⁻³, $F(000) = 1\,464$, Mo- K_α X -radiation, graphite monochromator (λ 0.710 69 Å), $\mu(\text{Mo-}K_\alpha) = 40.6$ cm⁻¹.

(3), $\text{C}_{25}\text{H}_{45}\text{FeN}_5$, $M = 471.5$, Monoclinic, space group $P2_1/n$, $a = 18.930(8)$, $b = 11.529(3)$, $c = 28.968(8)$ Å, $\beta = 108.63(1)^\circ$, $U = 5\,990.8$ Å³, $D_m = 1.02$ g cm⁻³ (floatation), $Z = 8$, $D_c = 1.05$ g cm⁻³, $F(000) = 2\,048$, Mo- K_α X -radiation, graphite monochromator (λ 0.710 69 Å), $\mu(\text{Mo-}K_\alpha) = 5.38$ cm⁻¹.

Structure solution and refinement. The positions of the two independent Fe atoms (3) and of Ru and P (2) were determined from Patterson syntheses, all remaining light non-hydrogen atoms then being located from successive difference-Fourier syntheses. The molecular configurations (Figures 1 and 2) were refined by full-matrix least squares

TABLE 3

Final positional (fractional co-ordinate) parameters for the non-hydrogen atoms in complex (2), with estimated standard deviations in parentheses

| Atom | X | Y | Z |
|----------|------------|------------|------------|
| Ru | 0.294 8(2) | 0.120 9(1) | 0.099 9(2) |
| P | 0.153 5(6) | 0.175 0(2) | 0.099 6(5) |
| C(1) | 0.213(3) | 0.069(1) | 0.160(2) |
| N(1) | 0.166(2) | 0.038(1) | 0.190(2) |
| C(5) | 0.133(3) | -0.004(1) | 0.236(3) |
| C(51) | 0.021(5) | -0.020(2) | 0.156(4) |
| C(52) | 0.238(6) | -0.034(2) | 0.275(5) |
| C(53) | 0.094(6) | 0.123(2) | 0.355(4) |
| C(512) * | 0.193(8) | -0.044(3) | 0.156(7) |
| C(523) * | 0.188(8) | -0.004(2) | 0.361(6) |
| C(531) * | 0.011(8) | -0.007(3) | 0.224(7) |
| C(2) | 0.403(2) | 0.157(1) | 0.040(2) |
| N(2) | 0.477(2) | 0.177(1) | 0.011(2) |
| C(6) | 0.574(2) | 0.196(1) | -0.025(2) |
| C(61) | 0.642(3) | 0.220(1) | 0.082(2) |
| C(62) | 0.539(3) | 0.234(1) | -0.124(3) |
| C(63) | 0.634(3) | 0.159(1) | -0.069(3) |
| C(3) | 0.277(2) | 0.089(1) | 0.044(2) |
| N(3) | 0.260(2) | 0.069(1) | -0.145(1) |
| C(7) | 0.322(3) | 0.030(1) | -0.188(2) |
| C(71) | 0.444(3) | 0.044(1) | -0.175(2) |
| C(72) | 0.265(3) | 0.024(1) | -0.323(2) |
| C(73) | 0.308(3) | -0.012(2) | -0.114(2) |
| C(4) | 0.383(2) | 0.128(1) | 0.258(2) |
| N(4) | 0.437(2) | 0.135(1) | 0.360(2) |
| C(8) | 0.531(2) | 0.110(1) | 0.431(2) |
| C(81) | 0.626(3) | 0.112(1) | 0.370(3) |
| C(82) | 0.505(3) | 0.061(1) | 0.443(3) |
| C(83) | 0.568(3) | 0.130(1) | 0.556(2) |
| C(11) | 0.041(2) | 0.187(1) | -0.032(2) |
| C(12) | 0.017(2) | 0.154(1) | -0.120(2) |
| C(13) | -0.063(3) | 0.158(1) | -0.219(2) |
| C(14) | -0.120(2) | 0.199(1) | -0.237(2) |
| C(15) | -0.103(2) | 0.233(1) | -0.158(2) |
| C(16) | -0.020(2) | 0.226(1) | -0.058(2) |
| C(21) | 0.068(2) | 0.162(1) | 0.207(2) |
| C(22) | 0.123(2) | 0.159(1) | 0.328(2) |
| C(23) | 0.061(3) | 0.147(1) | 0.416(2) |
| C(24) | -0.048(3) | 0.133(1) | 0.379(3) |
| C(25) | -0.102(3) | 0.135(1) | 0.262(3) |
| C(26) | -0.046(2) | 0.149(1) | 0.177(2) |
| C(31) | 0.206(2) | 0.234(1) | 0.133(2) |
| C(32) | 0.182(2) | 0.261(1) | 0.266(2) |
| C(33) | 0.230(2) | 0.305(1) | 0.249(2) |
| C(34) | 0.297(2) | 0.323(1) | 0.176(2) |
| C(35) | 0.314(2) | 0.298(1) | 0.077(2) |
| C(36) | 0.269(2) | 0.254(1) | 0.061(2) |

* Disordered methyl C atoms; site occupancy factor $\frac{1}{2}$.

for (2) with only the Ru and P having anisotropic temperature factors, and by blocked-matrix least squares for (3), with most atoms refining anisotropically. The rapid decay of the crystal of (2) resulted in relatively low accuracy data, which is reflected in high thermal parameters for almost all light atoms and in the errors of their associated molecular

TABLE 4

Final positional (fractional co-ordinate) parameters for the non-hydrogen atoms in complex (3), with estimated standard deviations in parentheses

| Atom | X | Y | Z |
|-------------------|-------------|--------------|-------------|
| Molecule 1 | | | |
| Fe(1) | 0.299 97(6) | 0.332 05(8) | 0.636 12(4) |
| C(1) | 0.227 2(4) | 0.338 8(7) | 0.611 8(3) |
| N(1) | 0.177 3(4) | 0.407 6(5) | 0.595 5(2) |
| C(11) | 0.156 5(4) | 0.483 7(7) | 0.551 9(3) |
| C(111) | 0.094 9(5) | 0.564 5(8) | 0.555 3(3) |
| C(112) | 0.127 0(6) | 0.406 8(9) | 0.508 1(3) |
| C(113) | 0.227 9(6) | 0.548 3(9) | 0.550 6(4) |
| C(2) | 0.364 1(4) | 0.348 2(7) | 0.663 6(3) |
| N(2) | 0.408 4(4) | 0.424 3(6) | 0.680 1(2) |
| C(21) | 0.466 1(5) | 0.499 9(8) | 0.677 6(4) |
| C(211) | 0.475 4(9) | 0.596 5(14) | 0.717 8(6) |
| C(212) | 0.539 8(7) | 0.438 6(11) | 0.693 8(4) |
| C(213) | 0.450 1(8) | 0.541 0(13) | 0.625 6(5) |
| C(3) | 0.240 9(5) | 0.126 4(7) | 0.593 5(3) |
| N(3) | 0.204 6(4) | 0.060 8(6) | 0.565 7(3) |
| C(31) | 0.159 8(5) | -0.024 1(7) | 0.533 4(3) |
| C(311) | 0.106 3(7) | 0.042 7(9) | 0.490 4(4) |
| C(312) | 0.113 4(8) | -0.092 9(10) | 0.558 5(5) |
| C(313) | 0.209 9(6) | -0.101 3(8) | 0.515 3(3) |
| C(4) | 0.378 5(5) | 0.158 5(7) | 0.626 9(3) |
| N(4) | 0.430 7(4) | 0.110 9(6) | 0.618 5(2) |
| C(41) | 0.483 4(6) | 0.017 4(8) | 0.642 2(3) |
| C(411) | 0.472 0(9) | -0.022 9(14) | 0.686 0(6) |
| C(412) | 0.560 2(11) | 0.059 3(16) | 0.643 5(6) |
| C(413) | 0.466 8(8) | -0.088 4(12) | 0.606 3(5) |
| C(5) | 0.289 6(4) | 0.160 4(7) | 0.690 2(3) |
| N(5) | 0.284 9(4) | 0.108 5(6) | 0.724 6(2) |
| C(51) | 0.268 1(5) | 0.032 1(7) | 0.760 0(3) |
| C(511) | 0.338 4(6) | -0.040 3(9) | 0.782 8(4) |
| C(512) | 0.250 6(6) | 0.106 2(8) | 0.798 4(3) |
| C(513) | 0.204 6(6) | -0.046 7(8) | 0.732 7(4) |

(b) Molecule 2

| | | | |
|---------|--------------|--------------|-------------|
| Fe(2) | 0.202 85(6) | -0.024 48(8) | 0.361 86(4) |
| C(6) | 0.274 8(4) | 0.080 8(6) | 0.390 9(3) |
| N(6) | 0.323 1(4) | 0.149 5(5) | 0.409 2(2) |
| C(61) | 0.355 6(5) | 0.200 1(7) | 0.458 5(3) |
| C(611) | 0.398 8(6) | 0.109 6(8) | 0.492 2(3) |
| C(612) | 0.289 9(6) | 0.244 4(9) | 0.475 0(4) |
| C(613) | 0.403 4(5) | 0.300 6(8) | 0.453 5(3) |
| C(7) | 0.266 8(5) | -0.138 5(7) | 0.394 7(3) |
| N(7) | 0.308 1(5) | -0.211 9(6) | 0.415 5(3) |
| C(71) | 0.340 2(6) | -0.314 4(7) | 0.440 2(3) |
| C(711) | 0.277 9(7) | -0.405 2(9) | 0.429 0(5) |
| C(712) | 0.401 7(6) | -0.352 4(9) | 0.418 8(4) |
| C(713) | 0.372 2(6) | -0.286 5(12) | 0.493 0(4) |
| C(8) | 0.135 2(4) | 0.094 1(6) | 0.342 1(3) |
| N(8) | 0.089 9(4) | 0.168 3(5) | 0.330 2(2) |
| C(81) | 0.037 4(4) | 0.248 1(7) | 0.334 4(3) |
| C(811) | -0.011 8(15) | 0.295 6(23) | 0.284 7(10) |
| C(812) | 0.075 8(13) | 0.353 4(20) | 0.361 7(8) |
| C(813) | -0.021 8(14) | 0.198 1(23) | 0.353 0(8) |
| C(9) | 0.130 3(5) | -0.100 8(7) | 0.377 9(3) |
| N(9) | 0.083 7(4) | -0.149 7(6) | 0.390 8(2) |
| C(91) | 0.024 1(5) | -0.234 0(7) | 0.370 1(3) |
| C(911) | 0.023 2(8) | -0.317 0(11) | 0.410 8(5) |
| C(912) | -0.049 9(6) | -0.166 4(10) | 0.349 7(5) |
| C(913) | -0.042 0(7) | -0.298 3(10) | 0.327 3(4) |
| C(10) | 0.208 2(4) | -0.076 1(7) | 0.302 7(3) |
| N(10) | 0.214 9(4) | -0.118 0(6) | 0.266 5(2) |
| C(101) | 0.228 5(5) | -0.192 3(7) | 0.230 4(3) |
| C(1011) | 0.156 9(6) | -0.265 6(11) | 0.208 3(5) |
| C(1012) | 0.294 0(7) | -0.271 4(11) | 0.256 7(4) |
| C(1013) | 0.254 4(7) | -0.119 2(9) | 0.190 1(4) |

parameters. Attempts to locate methyl-group hydrogen atoms were unsuccessful, but those for the phenyl carbon atoms were introduced at calculated positions and not refined. In the early stages of refinement the magnitude of the isotropic temperature factors for the methyl carbons C(51), C(52), and C(53), together with the significant residual peaks in the electron-density difference synthesis, led to the introduction of a disordered model for this Bu^t group, with $\frac{2}{3} : \frac{1}{3}$ occupancy of the two alternative sites. This gave a satisfactory refinement in terms of molecular geometry, a featureless difference density in this region, and stable thermal parameters for all six partial carbon atoms.

The low temperature employed for data collection from complex (3) helped to improve the accuracy, but again location of the hydrogen atoms was unsuccessful, and introduction of anisotropic thermal parameters for all Bu^t carbon atoms resulted in an oscillating and unstable refinement. Rotational disorder for certain Bu^t groups was suspected but not proved; hence the offending carbon atoms were allowed isotropic thermal parameters only [*viz.* C(211), C(212), C(213); C(411), C(412), C(413); and C(811), C(812), C(813)]. The final refinement for (3) used only those data (3 891) with $w\Delta F < 3.0$. For both structures, weights were applied according to the scheme $1/w = \sigma(F_o) + \alpha(F_o)$, where $\alpha = 0.01$ (2) and 0.12 (3) and $\sigma(F_o)$ is the estimated standard deviation in $|F_o|$. This gives adequate weight analyses in terms of $|F_o|$ and $|\sin \theta|$. Refinement converged at R 0.094 (R' 0.089) for (2), and R 0.099 (R' 0.129) for (3). Molecular packing diagrams for (2) and (3) are shown in Figure 3 and 4, respectively. Mean (and maximum) shift-to-error ratios were 0.04 (0.70) for (2) and 0.21 (1.44) for (3). Final electron-density difference syntheses showed no peaks > 0.6 or < 0.4 e Å⁻³ for (2) nor > 1.0 or < 0.3 e Å⁻³ for (3). Atomic scattering factors used were those of ref. 30 for Ru and Fe, of ref. 31 for P, C, and N, and of ref. 32 for H. Corrections for the effects of anomalous dispersion were made to those for Ru, Fe, and P.³⁰

Computational work was carried out using the *X*-ray

TABLE 5

Molecular planes for complex (2) in the form $Ax + By + Cz = D$, where x, y, z are fractional co-ordinates, with deviations (Å) from the planes in square brackets

Plane 1: Ru, P, C(3), C(4), N(3), N(4)

$$7.780x + 20.180y - 5.368z = 4.191$$

$$[C(7) - 0.08, C(8) - 0.16, C(1) - 1.98, C(2) 1.89, N(1) - 3.14, N(2) 3.04]$$

Plane 2: Ru, P, C(2)

$$2.912x + 7.664y + 9.850z = 2.769$$

$$[N(2) 0.08, C(1) - 0.04, N(1) - 0.12, C(6) 0.15, C(5) - 0.08]$$

$$\text{Angle between planes: } 88.9^\circ$$

TABLE 6

Molecular planes for complex (3) in the form $Ax + By + Cz = D$, where x, y, z are fractional co-ordinates, with deviations (Å) from the planes in square brackets

Plane 1: Fe(1), C(1), C(4), C(5)

$$8.358x + 7.982y + 11.581z = 11.7$$

$$[Fe(1) 0.03, C(1) - 0.01, C(4) - 0.01, C(5) - 0.01]$$

Plane 2: Fe(2), C(6), C(9), C(10)

$$9.852x - 8.376y + 7.501z = 4.951$$

$$[Fe(2) - 0.03, C(6) 0.012, C(9) 0.01, C(10) 0.01]$$

$$\text{Angle between planes: } 89^\circ$$

system of programs at the University of London Computing Centre. Final atomic co-ordinates are given in Tables 3 and 4, and the equations of some least-squares planes in Tables 5 and 6. The observed and calculated structure factors, thermal and molecular parameters associated with the phenyl rings in complex (2) (Appendix A), and the temperature parameters for complex (3) (Appendix B) are available as Supplementary Publication No. SUP 22465 (33 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

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