Synthesis and Reactions of Octakis(t-butyl isocyanide)dicobalt and Pentakis(t-butyl isocyanide)ruthenium; *X*-Ray Crystal and Molecular Structures of [Co$_2$(Bu^{t}NC)$_8$] and [Ru(Ph$_3$P)(Bu^{t}NC)$_4$]

By Geoffrey K. Barker, Anita M. R. Galas, Michael Green,* Judith A. K. Howard, F. Gordon A. Stone,* Terence W. Turney, Alan J. Welch, and Peter Woodward

(*Department of Inorganic Chemistry, University of Bristol, Bristol* BS8 1TS)

Summary Reduction of [Co(Bu^{t}NC)$_5$]PF$_6$ with K–Hg in tetrahydrofuran affords the complex [Co$_2$(Bu^{t}NC)$_8$], and similarly *trans*-[RuCl$_2$(Bu^{t}NC)$_4$] with Bu^{t}NC, *trans*-[RuCl$_2$(Bu^{t}NC)$_4$] with Ph$_3$P and Bu^{t}NC, and *trans*-[RuCl$_2$(Pr^{i}NC)$_4$] with Pr^{i}NC give [Ru(Bu^{t}NC)$_5$], [Ru(Bu^{t}NC)$_4$(Ph$_3$P)], and [Ru$_2$(Pr^{i}NC)$_9$], respectively; the structures of [Co$_2$(Bu^{t}NC)$_8$] and [Ru(Bu^{t}NC)$_4$(Ph$_3$P)] are established by single crystal *X*-ray diffraction.

Several transition metal complexes with isocyanides as the only ligands are known, particularly cationic species, *e.g.* [Cr(RNC)$_6$]$^{n+}$, [Mn(RNC)$_6$]$^{n+}$, or [Co(RNC)$_5$]$^{n+}$ ($n = 1$ or 2).[1–3] However, this area has not so far developed to give the plethora of structural varieties found with binary metal carbonyls.[4,5] There are as yet, for example, no isocyanide analogues of relatively simple species like [Co$_2$(CO)$_8$] or [Fe$_2$(CO)$_9$]. Nevertheless, the recent isolation of the highly reactive cluster complexes [Ni$_4$(Bu^{t}NC)$_7$][6] and [Pt$_3$(Bu^{t}NC)$_6$][7] suggested that other binary isocyanide compounds of sub-group VIII metals with novel properties might be obtained.

Reaction (room temperature, 12 h) of a tetrahydrofuran (THF) solution of [Co(Bu^{t}NC)$_5$]PF$_6$[3] with potassium amalgam gave (50% yield) orange-red crystalline (from pentane, −78 °C) [Co$_2$(Bu^{t}NC)$_8$].

Crystal data: C$_{40}$H$_{72}$N$_8$Co$_2$, *M* 782·94; orthorhombic, space group $P2_12_12$, $a = 18{\cdot}016(4)$, $b = 12{\cdot}149(4)$, $c = 11{\cdot}381(5)$ Å, $U = 2491{\cdot}4(14)$ Å^3, $Z = 2$ (C_2 symmetry imposed), $D_c = 1{\cdot}044$, $F(000) = 844$, μ(Mo-K_α) = 7·3 cm^{-1}. 2522 out of 4098 reflections (Syntex P2$_1$ diffractometer) measured to $2\theta = 60°$ (Mo-K_α radiation, room temperature) were retained ($I \geqslant 1{\cdot}0\sigma$) and used to solve and refine the structure to a current $R = ca.\ 0{\cdot}07$.†

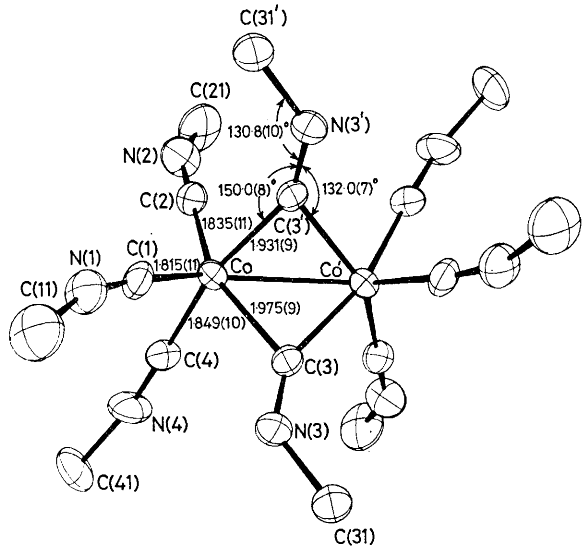

FIGURE 1. The molecule $[Co_2(Bu^tNC)_8]$, together with important molecular parameters, as seen along the crystallographic *c* axis. Methyl groups have been omitted for clarity.

The molecule bestrides a crystallographic C_2 axis along which it is viewed (Figure 1). The Co_2C_8 skeleton closely resembles that of $[Co_2(CO)_8]$[8] insofar as the slightly asymmetric Co–C (bridge) distances average *ca.* 0·1 Å more than the Co–C (terminal) lengths *trans* to them, and inasmuch as the unique Co–C (terminal) separation [Co–C(1)] is the shortest of that type. The equivalence of the terminal ligands (2) and (4) is disturbed, however, by steric influence of the Bu^t group [C(31′)], with the result that (2) bends considerably (154°) at N(2), and the bridging isocyanide (3′) itself leans away (9°) in the CoC(3′)N(3′) plane. For the molecule as a whole the mean Co–C distance is *ca.* 0·03 Å longer than that in $[Co_2(CO)_8]$. Compensation, however, derives from the Co–Co distance being *ca.* 0·066 Å shorter.

In solution, $[Co_2(CO)_8]$ exists in three isomeric forms,[9] and initial studies suggest a related situation with $[Co_2(Bu^tNC)_8]$, which shows a single sharp peak in the ^1H n.m.r. spectrum ($C_6D_5CD_3$, 25 °C) at τ 8·6. On cooling, changes occur typical of a dynamic system.

Reduction (THF, room temperature) of $RuCl_3.3H_2O$ with zinc amalgam in the presence of t-butyl isocyanide affords *trans*-$[RuCl_2(Bu^tNC)_4]$, which is further reduced by sodium amalgam (THF, room temperature) in the presence of an excess of isocyanide to form (25% yield) yellow crystals (−18 °C, light petroleum) of $[Ru(Bu^tNC)_5]$‡ [ν_{NC} 2070sh, 2033s, and 1815s cm^{-1}; ^1H n.m.r.: τ ($C_6D_5CD_3$, +25 to −90 °C) 8·72(s); ^{13}C n.m.r.: τ ($C_6D_5CD_3$–isopentane, −120 °C) 187·54 (N*C*Ru) p.p.m.]. Treatment of $[Ru(Bu^tNC)_5]$ with Ph_3P or direct reduction (Na–Hg, room temperature) of *trans*-$[RuCl_2(Bu^tNC)_4]$ in the presence of isocyanide and Ph_3P affords (70% yield) deep red crystals of $[Ru(Bu^tNC)_4(Ph_3P)]$ [ν_{NC} 2100sh, 2055s, and 1830s cm^{-1}; ^1H n.m.r.: τ ($C_6D_5CD_3$, −90 °C) 8·78(s); ^{13}C n.m.r.: τ ($C_6D_5CD_3$, −90 °C) 191·3 (N*C*Ru) p.p.m.].

Crystal data: $C_{38}H_{51}N_4PRu$, *M* 695·9, monoclinic, space group $P2_1/n$, $a = 12{\cdot}174(4)$, $b = 29{\cdot}193(13)$, $c = 11{\cdot}454(3)$ Å, $\beta = 102{\cdot}62(2)°$, $U = 3972{\cdot}4$ Å^3, $Z = 4$, $D_c = 1{\cdot}17$, $F(000) = 1464$. Current *R* is 0·097 for 1760 independent intensities (Syntex $P2_1$ diffractometer, Mo-K_α radiation, room temperature).†§

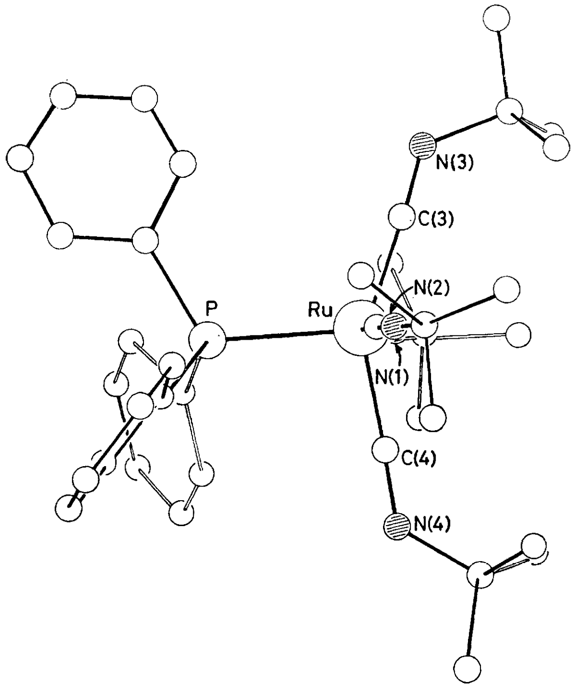

FIGURE 2. Projection of the molecule $[Ru(Bu^tNC)_4(PPh_3)]$ onto the equatorial plane of the molecule. Ru–C_{ax}(mean) 1·93(3); C–N_{ax}(mean), 1·18(4); Ru–C_{eq}(mean), 1·89(2); C–N_{eq}(mean), 1·24(3); and Ru–P, 2·338(8) Å.

A most interesting aspect of the structure (Figure 2) is that two of the isocyanide ligands [C(3) and C(4)] are considerably bent [130(2)°] at the nitrogen. Similar bending, but to a lesser extent, occurs in the complex *trans*-$[Mo(MeNC)_2(Ph_2PCH_2CH_2PPh_2)_2]$ [∠CNMe 156(1)°].[10] With the ruthenium complex the bending can be attributed to

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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.

‡ Highly reactive $[Fe(Bu^tNC)_5]$ has been similarly prepared and an *X*-ray crystallographic study is in hand (J. M. Bassett, J. A. K. Howard, M. Green, and F. G. A. Stone, unpublished results).

§ Crystals of the compound are unstable in air, changing from deep red to yellow. Data were collected rapidly (3 days) during which an overall 30% reduction in intensities of the standard reflections occurred despite enclosure of the sample in a Lindemann tube. This decay was reflected in the high thermal activity of the Bu^t groups.

extensive back-bonding $[\mathrm{Ru}(4d) \rightarrow (\mathrm{C{\equiv}N})\pi^*]$, the molecular geometry being described as essentially trigonal bipyramidal with the phosphorus atom, C(3), and C(4) in the equatorial plane. The axial isocyanide ligands are effectively linear [$\angle$CNC (mean) 169(3)°], although $\angle$CRuC (164°) is $<180°$ and is concave away from the phosphine ligand.

The presumed Berry *pseudo*-rotation process which $[\mathrm{Ru(Bu^tNC)_4(Ph_3P)}]$ readily undergoes must involve pairwise exchange *via* a synchronous bending and straightening of the axial and equatorial isocyanide ligands. The fact that these ligands can act as electron reservoirs, as can nitric oxide, may have implications for catalysis[11] particularly when bonded to clusters.[12]

Reduction (Na–Hg, THF) of *trans*-$[\mathrm{RuCl_2(Pr^iNC)_4}]$ in the presence of $\mathrm{Pr^iNC}$ affords a dinuclear deep red crystalline complex $[\mathrm{Ru_2(Pr^iNC)_9}]$ [ν_{NC} 2140s, 2120sh, 2080sh, 1648s, and 1580s cm^{-1}; ^{1}H n.m.r.: τ ($\mathrm{C_6D_5CD_3}$, room temperature) 6·48 (septet, C*H*Me$_2$) and 8·80 (d, CH*Me*$_2$, $^2J_{HH}$ 6Hz)] which, initial *X*-ray crystallographic studies have shown, is isostructural with $[\mathrm{Fe_2(CO)_9}]$, with a mean Ru–Ru separation of 2·63 Å.

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