Cluster Chemistry. Part 18.† Isocyanide Complexes derived from $[Ru_3(CO)_{12}]$: Crystal and Molecular Structures of $[Ru_3(CO)_{12-n}(CNBu^t)_n]$ (n = 1 or 2) ‡

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Reactions between $[Ru_3(CO)_{12}]$ and isocyanides CNR have given the complexes $[Ru_3(CO)_{12-n}(CNR)_n]$ (R = Bu^t, n = 1, 2, or 3; R = C_6H_{11}, n = 1; R = C_6H_4OMe-*p*, n = 1 or 2; and R = $CH_2SO_2C_6H_4Me$-*p*, n = 3) as orange to red crystalline solids. The crystal structures of $[Ru_3(CO)_{12-n}(CNBu^t)_n]$ (n = 1 or 2) have been determined by *X*-ray diffraction studies, and refined to residuals of 0.035 (4 561 'observed' reflections) and 0.043 (2 849 'observed' reflections) respectively. Crystals of $[Ru_3(CO)_{11}(CNBu^t)]$ are monoclinic, space group $P2_1/c$ with a = 11.948(5), b = 12.108(4), c = 16.621(4) Å, β = 112.74(2)°, and Z = 4; crystals of $[Ru_3(CO)_{10}(CNBu^t)_2]$ are monoclinic, space group $P2_1/a$ with a = 11.910(10), b = 12.831(17), c = 9.565(16) Å, β = 111.84(10)°, and Z = 2. In the latter derivative, the ligand array is 'centrosymmetric' about a crystallographic special position, with the two isocyanide ligands in axial sites; the Ru_3 triangle is disposed about a pair of equally populated centrosymmetrically related dispositions within the ligand array. In $[Ru_3(CO)_{11}(CNBu^t)]$ the isocyanide substituent is also axial; the Ru_3 triangle is similarly disordered but only to the extent of *ca.* 14% within the ligand array. A method for the almost quantitative conversion of $RuCl_3 \cdot xH_2O$ to $[Ru_3(CO)_{12}]$ has been developed consisting of carbonylation of 1% methanol solutions (50—60 atm CO, 125 °C, 16—18 h), recycling the mother-liquors with fresh $RuCl_3 \cdot xH_2O$.

The simple carbonyl-substitution chemistry of the trinuclear ruthenium carbonyl, $[Ru_3(CO)_{12}]$, is dominated by the reactions of Group 5B donor ligands, particularly tertiary phosphines [1] and phosphites,[2] where the usual product is the trisubstituted complex, $[Ru_3(CO)_9(L)_3]$. Until recently, the mono- and di-substituted complexes have been obtained in relatively few instances, by using mild conditions, ligands with bulky groups, such as $P(C_6H_{11})_3$,[3] or as by-products in reactions designed to produce other complexes, such as those with $[Pt(PPh_3)_4]$.[4] Application of radical-ion initiated reactions to the preparation of derivatives of $[Ru_3(CO)_{12}]$ has enabled our knowledge of these complexes to expand rapidly.[5] However, substitution chemistry with carbon-donor ligands is limited to a brief description of the carbene complex $[Ru_3(CO)_{11}\{CNEt(CH_2)_2NEt\}]$,[6] and a mention of the complexes $[Ru_3(CO)_{12-n}(CNBu^t)_n]$ (n = 1—4).[7] This paper details and expands our preliminary communication [8] on the reactions of $CNBu^t$ and related compounds with $[Ru_3(CO)_{12}]$.

Results and Discussion

In a remarkably facile reaction, t-butyl isocyanide reacts with an equimolar amount of the cluster carbonyl $[Ru_3(CO)_{12}]$ in light petroleum at 50 °C for 1—2 h to give a high yield of red $[Ru_3(CO)_{11}(CNBu^t)]$ (1). This complex was readily identified by elemental microanalysis and its spectroscopic properties. In the i.r. spectrum a band at 2 170 cm^{-1} is readily assigned to $\nu(CN)$ and the six-band $\nu(CO)$ spectrum is similar to those of other $[Ru_3(CO)_{11}L]$ molecules. In the ^1H n.m.r. spectrum, the protons of the CMe_3 group resonate as a sharp singlet at δ 1.53, while in the ^{13}C n.m.r. spectrum, all CO groups give rise to a singlet at δ 201.1; the CMe_3 carbons are found at δ 30.1 and 59.0, but the isocyanide carbon was not detected. This simple spectrum indicates that (1) is fluxional at room temperature, and indeed the CO resonance does not change at −100 °C. In this respect the complex resembles the parent $[Ru_3(CO)_{12}]$, which is also fluxional at low temperatures. The solid-state structure of (1) is discussed below.

Reactions with increasing amounts of $CNBu^t$ gave the deep red complexes $[Ru_3(CO)_{12-n}(CNBu^t)_n]$ (n = 1—3). The disubstituted complex (2) shows $\nu(CN)$ at 2 155 cm^{-1}, and also has a six-band $\nu(CO)$ spectrum. The ^1H and ^{13}C n.m.r. spectra are similar to those of (1), although the isocyanide carbons were also observed as a singlet at δ 144.1; again, the spectra indicate that (2) is highly fluxional. The trisubstituted complex (3) is much more sensitive to oxidation than the other two derivatives, and we have not been able to obtain satisfactory microanalytical results. The spectral properties are consistent with substitution at all three metal atoms, with a three-band $\nu(CO)$ spectrum, and a singlet for the CO groups in the ^{13}C n.m.r. spectrum.

The mass spectra of these complexes are detailed in the Experimental section. They are characterised by parent ions which fragment by competitive loss of CO and $CNBu^t$ ligands; the near-equivalence of 3CO (*m/e* 84) and $CNBu^t$ (*m/e* 83) results in a series of 14 ion clusters spaced at approximately 28 units, although overlap of the ion clusters corresponding to $[P - 4CO]^+$ and $[P - CO - CNBu^t]^+$ centred on *m/e* 584, and subsequent fragment ions, is apparent from the different intensity pattern compared with those of $[P - nCO]^+$ (n = 0—3). This suggests that loss of CO and $CNBu^t$ ligands become competitive after initial cleavage of one Ru–CO bond on each metal atom.

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† Part 17, M. I. Bruce, J. G. Matisons, and B. K. Nicholson, *J. Organomet. Chem.*, 1983, **247**, 321.

‡ 3-t-Butyl isocyanide-1,1,1,2,2,2,3,3,3-undecacarbonyl- and 2,3-bis(t-butyl isocyanide)-1,1,1,2,2,2,3,3,3-decacarbonyl-*triangulo*-triruthenium.

Supplementary data available (No. SUP 23646, 38 pp.): structure factors, thermal parameters, H-atom co-ordinates. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. unit employed: 1 atm = 101 325 N m^{-2}.

Table 1. Spectroscopic properties of $[M_3(CO)_{12-n}(CNR)_n]$ complexes *

M	Ru	Os	Ru	Os	Ru	Ru	Os	Ru	Os
R	Bu^t	Bu^t	C_6H_4OMe-*p*	C_6H_4OMe-*p*	C_6H_{11}	Bu^t	Bu^t	C_6H_4OMe-*p*	C_6H_4OMe-*p*
n	1	1	1	1	1	2	2	2	2
ν(CN)/cm^{-1}	2 170w	2 177w	2 155w	2 164m	2 155w	2 155w	2 164m	2 154m	2 147m
ν(CO)/cm^{-1}	2 093w	2 100m	2 092w	2 097s	2 092w	2 065w	2 069m	2 093m	2 069m
	2 047s	2 054s	2 071vw	2 055s	2 071vw	2 020s	2 026 (sh)	2 066m	2 056m
	2 040s	2 039s	2 062w	2 040s	2 062w	2 007m	2 024s	2 048s	2 036 (sh)
	2 016m	2 021s	2 049s	2 022s	2 049s	1 996s	2 003 (sh)	2 040s	2 029s
	1 998m	2 005s	2 041vs	2 015 (sh)	2 041vs	1 990m	1 996 (sh)	2 030vs	2 007 (sh)
				2 006s					2 001 (sh)
	1 995m	2 000 (sh)	2 019m	2 002 (sh)	2 019m	1 986m	1 987s	2 022s	1 992s
		1 988s	1 999m	1 990s	1 999m		1 973s	1 997s	1 979s
		1 986 (sh)	1 992m	1 986 (sh)	1 992m		1 966s	1 990s	1 974s
^1H CMe_3/p.p.m.	1.53 (s)	1.5				1.54 (s)	1.5		
^{13}C CMe_3/p.p.m.	30.1 (s)	29.9				30.2 (s)	29.8		
CMe_3/p.p.m.	59.0 (s)					58.3 (s)			
CO/p.p.m.	201.1 (s)	180.7		178.3		204.0 (s)	183.9		180.3

* Data for Os complexes from ref. 9. I.r. spectra were recorded in hexane, n.m.r. in $CDCl_3$.

Similar complexes have been obtained with other isocyanides. Cyclohexyl isocyanide affords $[Ru_3(CO)_{11}\{CN(C_6H_{11})\}]$ (4), whose i.r. spectrum closely resembles that of (1), although the frequency of the ν(CN) band is some 15 cm^{-1} lower. The mono- (5) and di-substituted (6) *p*-methoxyphenyl isocyanide derivatives are yellow and red, respectively, and contain characteristic methoxy-resonances in their ^1H n.m.r. spectra. Again, the ν(CO) spectra are similar to those found previously for $[Ru_3(CO)_{12-n}(L)_n]$ (n = 1 or 2) complexes. The reaction between $[Ru_3(CO)_{12}]$ and *p*-toluenesulphonylmethyl isocyanide contrasts with the above, in that the only product obtained under a variety of conditions was the purple-brown $[Ru_3(CO)_9(CNCH_2SO_2C_6H_4Me\text{-}p)_3]$ (7), which readily crystallised from the reaction mixture. Complex (7) is also unusual in that the i.r. spectrum contains only one broad but strong ν(CO) band, at 1 980 cm^{-1}, in addition to the ν(CN) absorption at 2 168 cm^{-1}.

The i.r. and n.m.r. spectra of some of these complexes are given in Table 1, and are compared with those of similar osmium complexes described recently.[9] It is evident that the various ν(CN) and ν(CO) frequencies are similar in position, but differ markedly in relative intensities when the two series are compared. Similarly, it is found that the ^1H and ^{13}C n.m.r. resonances are not very closely related. The osmium complex exists in two isomeric forms, with axial and equatorial isocyanide substituents. The fluxional process is slowed sufficiently at −60 °C for individual ^{13}C resonances to be assigned, but the weighted mean for the axial isomer is some 20 p.p.m. to lower field than found for (1). The ν(CO) spectra of the two complexes have similar patterns, most bands being shifted to higher frequencies by *ca.* 5—7 cm^{-1} for the Os complexes. Similar comparisons between $[Ru_3(CO)_{12}]$ and $[Os_3(CO)_{12}]$ show that these shifts form part of a general pattern, and indeed are consistent with the replacement of Ru by the heavier Os.

The nature of the substitution product obtained from $[Ru_3(CO)_{12}]$ and simple two-electron donor ligands will depend on a number of factors, of which two practically important ones are the relative magnitudes of the rate constants for the successive reactions [equations (i)—(iii)] and the solubility of the various substituted products. When L = tertiary phosphine, k_2 and k_3 appear to be larger than k_1, *i.e.* reaction (i) is the rate-determining step, and even with a deficiency of tertiary phosphine, $[Ru_3(CO)_9(L)_3]$ is the usual product. However, if the reaction is carried out in a closed system, the partial pressure of CO may become sufficient to enable the intermediate products to be isolated.[10] We have shown also that solubility of the products is an important factor, and that when L = PPh_3, for example, the complex $[Ru_3(CO)_{10}(PPh_3)_2]$ may be readily prepared by using hexane as solvent.[3]

$$[Ru_3(CO)_{12}] + L \xrightleftharpoons{k_1} [Ru_3(CO)_{11}L] + CO \qquad \text{(i)}$$

$$[Ru_3(CO)_{11}L] + L \xrightleftharpoons{k_2} [Ru_3(CO)_{10}(L)_2] + CO \qquad \text{(ii)}$$

$$[Ru_3(CO)_{10}(L)_2] + L \xrightleftharpoons{k_3} [Ru_3(CO)_9(L)_3] + CO \ldots \textit{etc.} \qquad \text{(iii)}$$

Reactions between $[Ru_3(CO)_{12}]$ and some isocyanides evidently have rate constants for reactions (i)—(iii) which allow successive formation (and isolation) of the three substitution products $[Ru_3(CO)_{12-n}(L)_n]$ (n = 1—3). Indeed, in most cases, reaction (iii) is so slow that forcing conditions are required. In one of the limited range of reactions studied, a trisubstituted product (7) was the only product isolated; in this instance the limited solubility of the complex is probably a factor aiding its formation under the reaction conditions we employed.

The ready formation of a monosubstituted derivative of $[Ru_3(CO)_{12}]$ opens up intriguing possibilities for the preparation of further complexes containing two or more different ligands, and as we have reported,[11] the isocyanide is a useful reagent for ' activating ' $[Ru_3(CO)_{12}]$ in several reactions.

Crystal Structures of (1) *and* (2).—The molecular structures of (1) and (2) are shown in Figures 1 and 2, respectively; some bond lengths and angles are listed in Tables 2 and 3. There are no intermolecular contacts shorter than expected in either structure. Both complexes contain an Ru_3 triangle [isosceles for (2)], in which the isocyanide ligands occupy axial sites. All CO groups are terminal.

The contents of the unit cell of $[Ru_3(CO)_{11}(CNBu^t)]$ (1) comprise discrete molecules of the required stoicheiometry with one molecule constituting the asymmetric unit of the structure. As previously reported,[8] the refinement model is complicated by disorder in respect of the ruthenium atoms only, convergence of the initial refinement occurring at *R* 0.07, with three substantial peaks observable in the Ru_3 plane in a

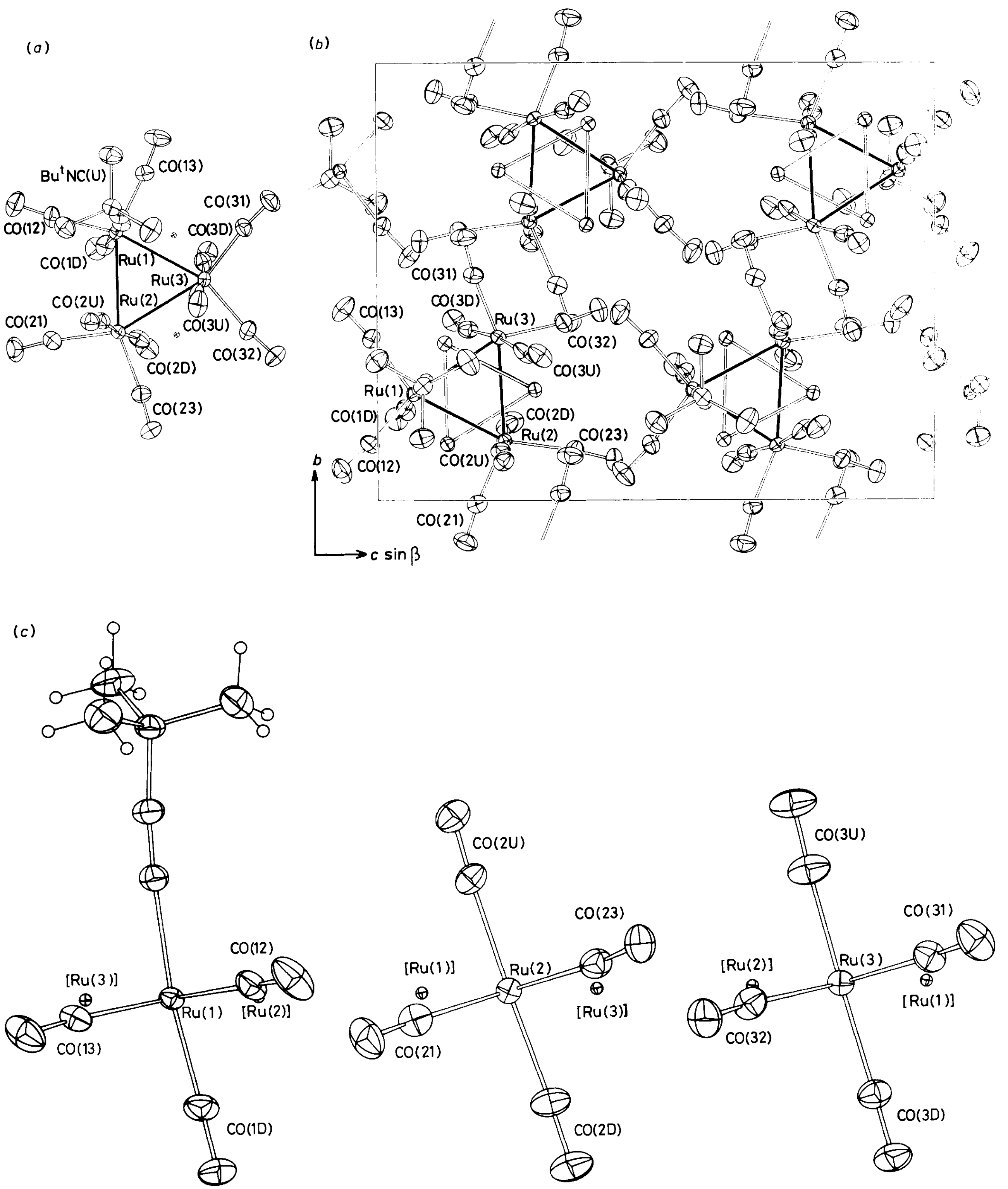


Figure 1. (*a*) Molecular structure of $[Ru_3(CO)_{11}(CNBu^t)]$ (1) showing the atom-numbering scheme. (*b*) Unit-cell contents projected down *c* showing 20% thermal ellipsoids. (*c*) Ruthenium atom environments in projection down the Ru(N)–Ru_3 (centroid) lines

difference map, rotated by 60° relative to the main Ru_3 core. Refinement of these and the ruthenium atoms of the parent core with fractional populations led to a population of the major component of 0.861(1), a value similar to that reported in the earlier study.[8]

Crystals of $[Ru_3(CO)_{10}(CNBu^t)_2]$ (2) belong to space group $P2_1/a$, as determined from the systematic absences present on photographic examination and subsequent diffractometer measurement of the data, imposing the necessity of two molecules in the unit cell with one half comprising the asymmetric unit, generating the other half by the available symmetry operations of unit translation, two-fold screw, or inversion

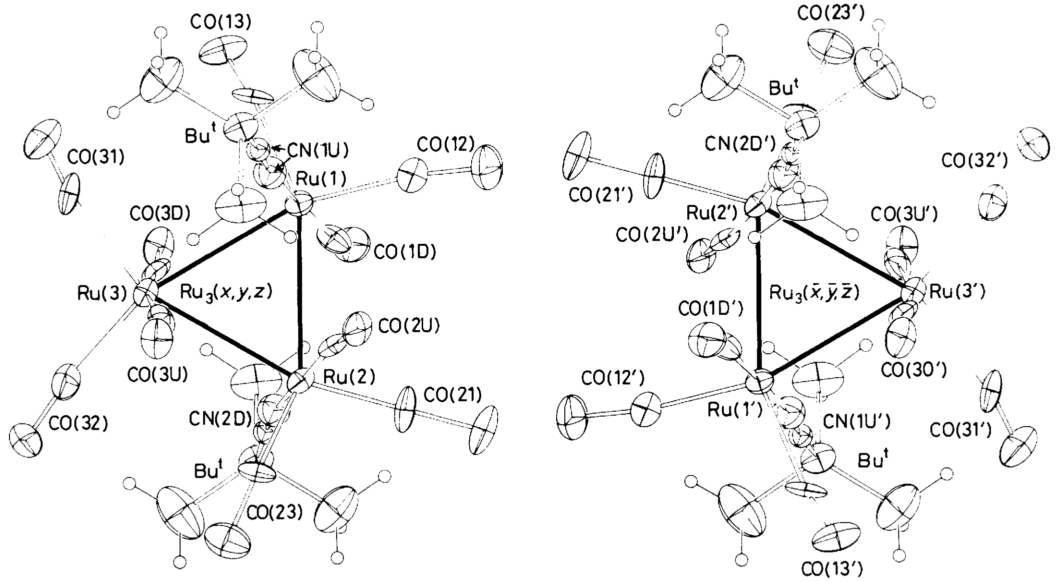


Figure 2. Molecular structure of $[Ru_3(CO)_{10}(CNBu^t)_2]$ (2) showing the atom-numbering scheme

centre. Such restrictions are clearly incompatible with the intrinsic symmetry expected of a molecule based on the above cluster. Nevertheless, the structure has been successfully solved in terms of a molecule which is disordered about the crystallographic centre of symmetry; the description invoked comprises a pair of molecules, each with population 0.5, the second of which is generated from the first by inversion through the centre of symmetry located at the centroid.

In (1), two shorter metal–metal bonds [2.847 7(8), 2.857 5(8) Å] are to Ru(1), to which is bonded the isocyanide; the longer of these is the same as found for $[Ru_3(CO)_{12}]$ [2.854(1) Å].[12] The remaining bond, within the $Ru_2(CO)_8$ fragment, is significantly longer at 2.866 8(11) Å; this lengthening may be associated with the twisting of the two $Ru(CO)_4$ groups about this bond (see later). The average Ru–Ru length [2.856(1) Å] is the same as that found in the parent carbonyl.[12] In (2), the longest bond is that between the two isocyanide-bearing metal atoms, Ru(1)–Ru(2), 2.849(2) Å, whereas those to Ru(3) are considerably shorter, at 2.837(3) Å. Compared with $[Ru_3(CO)_{12}]$, there is a considerable contraction of the metal triangle in (2) [average Ru–Ru, 2.841 Å].

The Ru–CO distances in the $Ru(CO)_4$ groups in (1) lie in the range 1.923(4)—1.961(5) Å, but there are no significant differences observed between the axial and equatorial bond lengths. In the parent carbonyl, such differences are *ca.* 0.02 Å. In both molecules, the shortest Ru–CO distances are those *cis* to the isocyanide ligand on Ru(1). The isocyanide ligands in both complexes are approximately linear. The Ru–C distances [2.041(5) Å in (1), 2.042(7) and 2.040(7) Å in (2)] are longer than those involving carbonyl groups, reflecting the weaker π-acceptor properties of the isocyanide.

The structures of the isocyanide-substituted complexes are unusual in that they show that axial substitution has occurred, in contrast to the situation found for tertiary phosphines, for example. The only other axially substituted M_3 clusters containing simple two-electron donor ligands are the pair of acetonitrile complexes $[Os_3(CO)_{12-n}(NCMe)_n]$ ($n = 1$ or 2).[13] This can be explained by considering the relative *trans* influences of the metal–metal bond and CO, and the electronic properties of the substituting ligands.

There is much current interest in the fluxional properties of metal cluster carbonyls and their derivatives, and an approach to the interpretation of these properties in terms of structure has been made.[14] As noted above, complex (1) is highly fluxional, and a considerable topological perturbation of the parent $[Ru_3(CO)_{12}]$ ligand anti-cuboctahedron is evident; this can be described as a twist of the environment of each ruthenium about the pseudo-two-fold axis which passes through it. Examination of the polyhedron formed by the 11 CO groups and the CN part of the isocyanide ligand [Figure 3(*a*)], and comparison with that found for $[Ru_3(CO)_{12}]$ shows that the polyhedron more closely approximates the icosahedron found for $[Fe_3(CO)_{12}]$ and several $[M_4(CO)_{12}]$ species. We recall that the equivalence of the CO groups in these cluster carbonyls has been explained in terms of rearrangement of the icosahedron by lengthening of edges and concomitant flattening of pairs of two edge-joined triangular faces to form the square faces of the anti-cuboctahedron. Further distortion (by movement of the diagonal apices towards each other) regenerates an icosahedron with apices interchanged.

In (2) similarly, we find that the environments of the ruthenium atoms are perturbed from the $[Ru_3(CO)_{12}]$ anti-cuboctahedral ideal by a set of concerted twists about the two-fold axes of the triangles [Figure 3(*b*)]. While the distortion of the ligand polyhedron results in disorder of the 10 CO groups, the atoms of the two isocyanide ligands in each molecule are located in positions close to (or encompassed by) the thermal ellipsoids of the similar ligands on the centrosymmetric alternative. The structure was thus found to be refinable in terms of a model in which the asymmetric unit was a full molecule with a population 0.5, with only one t-butyl substituent at its periphery having a population of 1. The symmetry of the molecule is a good approximation to 2. Further examination of the structure shows that the oxygen atoms of the disordered CO groups of each molecule occupy similar positions, although the carbon atoms refine separately. Similar observations have been made for several cluster carbonyls including $[Fe_3(\mu\text{-}CO)_2(CO)_{10}]$ [15] and, most recently $[Os_3(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_{10}]$ [16] and we have earlier commented on this feature in the structures of several $[Ru_3(CO)_{12-n}(PR_3)_n]$ complexes as well as those described herein.[17]

The twisting of the $Ru(CO)_4$ groups about the Ru(2)–Ru(3) bond in (1) is then seen to be a method of accommodating the different requirements of the packing of 11 CO groups and one

Table 2. Molecular core geometry for the complex $[Ru_3(CO)_{11}(CNBu^t)]$ (1); distances (Å) and angles (°). N refers to the cyclic permutation 1, 2, 3 (note that for N = 1, ' N − 1 ' is 3; for N = 3, ' N + 1 ' is 1). For C(1U), read C(1)

	N = 1	N = 2	N = 3
Ru(N)–Ru(N + 1)	2.857 5(8)	2.866 8(11)	2.847 7(8)
Ru(N)–C(NU)	2.041(5)	1.940(4)	1.949(6)
Ru(N)–C(ND)	1.940(6)	1.961(5)	1.938(6)
Ru(N)–C(NN + 1)	1.892(4)	1.943(4)	1.923(4)
Ru(N)–C(NN − 1)	1.917(4)	1.942(5)	1.950(4)
Ru(N − 1)–Ru(N)–Ru(N + 1)	60.33(2)	59.67(1)	60.00(2)
Ru(N − 1)–Ru(N)–C(NNU)	89.3(1)	80.3(1)	77.2(1)
Ru(N − 1)–Ru(N)–C(ND)	92.7(1)	96.5(1)	97.0(1)
Ru(N − 1)–Ru(N)–C(NN + 1)	164.3(1)	157.4(1)	156.0(1)
Ru(N − 1)–Ru(N)–C(NN − 1)	92.7(1)	96.2(1)	98.9(1)
Ru(N + 1)–Ru(N)–C(NNU)	96.5(1)	97.1(1)	91.1(1)
Ru(N + 1)–Ru(N)–C(ND)	79.0(1)	78.1(1)	82.1(1)
Ru(N + 1)–Ru(N)–C(N + 1)	105.0(1)	100.9(1)	98.7(1)
Ru(N + 1)–Ru(N)–C(NN − 1)	151.6(1)	152.8(2)	157.3(1)
C(NU)–Ru(N)–C(ND)	173.3(2)	175.1(2)	172.6(2)
C(NU)–Ru(N)–C(NN − 1)	91.5(2)	90.3(2)	92.0(2)
C(NU)–Ru(N)–C(NN + 1)	86.8(2)	91.8(2)	93.4(2)
C(ND)–Ru(N)–C(NN − 1)	94.8(2)	93.8(2)	93.3(2)
C(ND)–Ru(N)–C(NN + 1)	89.5(2)	89.8(2)	90.2(2)
C(NN − 1)–Ru(N)–C(NN + 1)	102.6(2)	105.1(2)	103.6(2)
(*a*) Disordered fragment			
Ru(NN + 1)–Ru(NN − 1)	2.831(3)	2.853(3)	2.856(3)
Ru(N)–Ru(NN + 1)	1.746(2)	1.665(2)	1.537(2)
Ru(N)–Ru(NN − 1)	1.646(2)	1.563(2)	1.767(2)
Ru(NN − 1)–Ru(NN + 1)–Ru(N + 1 N + 2)	60.33(7)	59.45(7)	60.22(7)
(*b*) Carbonyl groups			
C(NU)–O(NU)	*	1.101(6)	1.131(7)
C(ND)–O(ND)	1.149(7)	1.123(6)	1.115(7)
C(NN − 1)–O(NN − 1)	1.118(6)	1.126(6)	1.111(5)
C(NN + 1)–O(NN + 1)	1.108(5)	1.127(5)	1.127(5)
Ru(N)–C(NU)–O(NU)	*	169.1(3)	171.0(4)
Ru(N)–C(ND)–O(ND)	172.6(3)	170.3(3)	172.2(4)
Ru(N)–C(NN − 1)–O(NN − 1)	173.1(4)	173.8(3)	173.2(4)
Ru(N)–C(NN + 1)–O(NN + 1)	174.4(4)	172.8(4)	173.1(4)

* For the t-butyl isocyanide: C(1)–N(1), 1.139(6); N(1)–C(2), 1.465(6); C(2)–C(3,4,5), 1.500(8), 1.505(7), 1.515(6) Å. Ru(1)–C(1)–N(1), 171.4(3); C(1)–N(1)–C(2), 174.1(4); N(1)–C(2)–C(3,4,5), 107.8(3), 108.3(4), 107.6(4); C(3)–C(2)–C(4), 110.8(5); C(3)–C(2)–C(5), 112.1(4); and C(4)–C(2)–C(5), 110.0(4)°.

isocyanide ligand about the Ru_3 cluster, compared with the regular anti-cuboctahedral arrangement adopted by the 12 CO groups in $[Ru_3(CO)_{12}]$.

We believe that the disorder observed in these structures provides further evidence supporting the idea that the fluxional behaviour of metal cluster carbonyls can be rationalised, at least in part, by the movement of the metal-atom cluster within the ligand polyhedron, with some small deformation of the latter, as proposed by Johnson and Benfield.[14] In the present case, we find that it is the peripheral atoms which define the polyhedron. Conversion of one tautomer to another can occur by bending of the M–C–R (R = O or NBu^t) bond.

In the structures of both (1) and (2), a number of geometrical vagaries are observed, such as non-linear carbonyl groups. The genuineness of these is uncertain. It is likely that the extent of distortion of the cluster correlates with the rise in population of the disordered component and in (1), the pseudo-atoms which model the carbonyl groups are presumably resultants of the two superimposed molecules, while in (2), where these resultants can be deconvoluted we find that, in a large number of cases, the atomic components of one half of the molecule lie very close to those of the other leading to correlation problems. Stereochemical detail, in (2) in particular, is likely to be ambiguous in its content. Also uncertain from the evidence available is the nature of the disorder: the structure determination offers no certain information as to the time-scale of the effect, *i.e.* whether the two molecular types are ' frozen ' in the lattice or undergoing a dynamic transformation. The time-scale of the *X*-ray diffraction experiment (10^{-18} s) is such that an instantaneous picture is obtained; the recent report [18] of dynamic behaviour in *crystalline* $[Fe_3(CO)_{12}]$ suggests that similar circumstances apply to the molecules described above.

Synthesis of $[Ru_3(CO)_{12}]$.—In the Experimental section we also describe an improved synthesis of the cluster carbonyl $[Ru_3(CO)_{12}]$. In our original synthesis, carbonylation of methanol solutions of hydrated ruthenium trichloride under moderate conditions of pressure ($\leqslant 10$ atm) and temperature (70 °C), in the presence of zinc as a reducing agent and halogen acceptor, gave the carbonyl in *ca.* 70% yield.[19] However, some workers have experienced difficulty in reproducing this synthesis.

Table 3. Molecular core geometry for the complex [$Ru_3(CO)_{10}(CNBu^t)_2$] (2); distances (Å) and angles (°)

	N = 1	N = 2	N = 3
Ru(N)–Ru(N + 1)	2.849(2)	2.837(4)	2.837(3)
Ru(N)–C(NU)	2.042(7)	1.91(2)	1.89(2)
Ru(N)–C(ND)	1.967(19)	2.040(7)	1.98(2)
Ru(N)–C(NN + 1)	1.79(3)	1.99(4)	1.91(3)
Ru(N)–C(NN − 1)	1.79(4)	1.92(2)	2.03(3)
Ru(N − 1)–Ru(N)–Ru(N + 1)	59.85(5)	59.87(6)	60.27(6)
Ru(N − 1)–Ru(N)–C(NU)	85.9(2)	72.4(7)	80.3(8)
Ru(N − 1)–Ru(N)–C(ND)	95.0(5)	104.0(2)	90.6(8)
Ru(N − 1)–Ru(N)–C(NN + 1)	160.8(11)	151.3(15)	160.4(5)
Ru(N − 1)–Ru(N)–C(NN − 1)	93.9(13)	103.4(5)	97.1(9)
Ru(N + 1)–Ru(N)–C(NU)	103.0(2)	95.2(8)	90.9(6)
Ru(N + 1)–Ru(N)–C(ND)	73.2(5)	85.2(3)	77.6(5)
Ru(N + 1)–Ru(N)–C(NN + 1)	105.6(12)	96.9(16)	101.7(5)
Ru(N + 1)–Ru(N)–C(NN − 1)	145.9(13)	160.4(5)	155.6(8)
C(NU)–Ru(N)–C(ND)	174.9(6)	175.4(7)	167.9(8)
C(NU)–Ru(N)–C(NN − 1)	95.6(13)	88.6(8)	94.4(10)
C(NU)–Ru(N)–C(NN + 1)	85.5(8)	95.1(13)	93.0(10)
C(ND)–Ru(N)–C(NN − 1)	89.3(14)	89.6(5)	94.7(9)
C(ND)–Ru(N)–C(NN + 1)	92.1(9)	89.4(12)	93.0(9)
C(NN − 1)–Ru(N)–C(NN + 1)	104.0(17)	102.0(16)	101.8(10)
Carbonyl groups			
C(NU)–O(NU)		1.19(3)	1.09(3)
C(ND)–O(ND)	1.26(3)		1.04(3)
C(NN − 1)–O(NN − 1)	1.25(5)	1.15(6)	1.06(4)
C(NN + 1)–O(NN + 1)	1.29(4)	1.07(4)	1.21(6)
Ru(N)–C(NU)–O(NU)		166.4(22)	169.2(19)
Ru(N)–C(ND)–O(ND)	175.0(16)		169.6(25)
Ru(N)–C(NN − 1)–O(NN − 1)	176.0(31)	171.0(29)	166.6(19)
Ru(N)–C(NN + 1)–O(NN + 1)	173.3(20)	163.5(38)	173.7(25)

For the t-butyl isocyanide groups, values for groups 1 and 2 respectively: C(10,20)–N(10,20), 1.12(1), 1.14(1); N–C, 1.465(8), 1.471(9) Å. Ru–C–N 172.2(6), 174.0(10); C–N–C, 179.6(15), 175.1(9)°.

Common component: C–C(1,2,3), 1.516(7), 1.504(10), 1.503(7) Å; C(1)–C–C(2), 111.9(4); C(2)–C–C(3), 110.3(5); C(3)–C–C(1), 111.0(4)°. (Group 1) N–C–C(1,2,3): 105.2(5), 116.4(5), 101.5(4)°. (Group 2) N–C–C(1,2,3): 109.4(4), 99.8(5), 114.0(4)°.

Exploration of the effects of temperature and pressure on the reaction has shown that the conversion of ruthenium trichloride to the carbonyl proceeds efficiently if the reaction is carried out at 125 °C under carbon monoxide at 50 atm pressure, *in the absence of zinc.* Under these conditions, essentially quantitative conversion occurs, as indicated by our results; in general, we recycle the mother-liquors, which are pale greenish yellow in colour, often up to five times. The carbon monoxide acts as both reducing and carbonylating agent; by-products of the reaction are presumably hydrogen chloride and methyl formate. We note that under milder conditions ($\leqslant$ 10 atm, 70 °C) the major product is the carbonyl chloride, [$\{RuCl_2(CO)_3\}_2$], but this may be accompanied by up to 18% [$Ru_3(CO)_{12}$].[19]

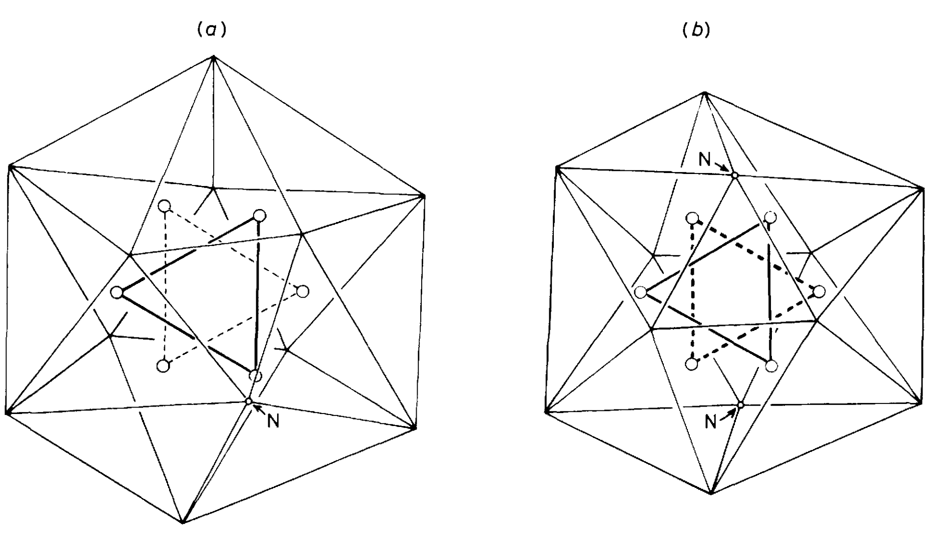
Experimental

Spectroscopic data were obtained with the following instruments: Perkin-Elmer 457 and Jasco IRA 2 (i.r.), Varian Associates T60 (^1H n.m.r.), Bruker WP80 (^1H and ^{13}C n.m.r.), and AEI-GEC MS3074 (mass). Microanalyses were by the Canadian Microanalytical Service, Vancouver.

All reactions were carried out under nitrogen, although in general, reaction products were worked up in air. Chromatography was carried out on columns of Florisil or alumina and preparative t.l.c. on plates (20 × 20 cm) coated with Kieselgel G (Merck). Solvents were dried and distilled before use. Light petroleum was of b.p. 40—60 °C; ' petroleum spirit ' refers to that fraction of b.p. 100—120 °C. High-pressure reactions were carried out in a stainless steel autoclave (Baskerville and Lindsay), internal volume 1 000 cm^3, equipped with a removable glass liner.

Reactions of [$Ru_3(CO)_{12}$] *with Isocyanides.*—(*a*) *t-Butyl isocyanide*, $CNBu^t$. (i) A mixture of the ruthenium carbonyl (706 mg, 1.10 mmol) and t-butyl isocyanide (100 mg, 1.20 mmol) was refluxed in cyclohexane (110 cm^3) for 2 h. Evaporation of solvent and chromatography (Florisil) afforded two fractions. A yellow band was eluted with light petroleum. Crystallisation (light petroleum) then afforded orange crystals of [$Ru_3(CO)_{12}$] (114 mg, 16%). The second fraction, an orange-red band, was eluted with light petroleum. Crystallisation (light petroleum) then afforded red *crystals* of [$Ru_3(CO)_{11}(CNBu^t)$] (1) (576 mg, 82%), m.p. 114—116 °C [Found: C, 27.6; H, 1.3; N, 1.9%; *M* (mass spectrometry), 696. $C_{16}H_9NO_{11}Ru_3$ requires C, 27.7; H, 1.3; N, 2.0%; *M*, 696]. Mass spectrum (most intense ion of cluster): *m/e* 696m, 667vw, 640m, 609m, 584s, 556s, 528s, 500s, 470s, 444s, 416s, 386s, 357s, 329s, and 305s.

(ii) A suspension of ruthenium carbonyl (500 mg, 0.78 mmol) and t-butyl isocyanide (130 mg, 1.56 mmol) in petroleum spirit (80 cm^3) was heated under reflux for 30 min. The solvent was removed, and the residue chromatographed (Florisil). An orange-red band was eluted with petroleum spirit. Crystallisation (light petroleum) then afforded red



$[Ru_3(CO)_{11}(CNBu^t)]$ (1) $[Ru_3(CO)_{10}(CNBu^t)_2]$ (2)

Figure 3. Peripheral atom polyhedra for (1) and (2); O (of CO) or N (of $CNBu^t$) atoms are at each apex

crystals of $[Ru_3(CO)_{11}(CNBu^t)]$ (1) (80 mg, 15%). A second fraction, a red-orange band, was eluted with petroleum spirit. Crystallisation from light petroleum gave deep red *crystals* of pure $[Ru_3(CO)_{10}(CNBu^t)_2]$ (2) (410 mg, 70%), m.p. 90—91 °C [Found: C, 31.5; H, 2.4; N, 3.7%; *M* (mass spectrometry), 751. $C_{20}H_{18}N_2O_{10}Ru_3$ requires C, 32.0; H, 2.4; N, 3.7%; *M*, 751]. ^{13}C N.m.r. ($CDCl_3$): δ 204.0 (s, CO), 144.1 (s, C≡N), 58.3 (s, *C*Me₃), 30.2 (s, C*Me*₃). Mass spectrum (most intense ion of cluster): *m/e* 751m, 723vw, 694m, 666m, 640s, 611s, 582s, 556s, 526s, 498s, 467s, 441s, 413s, 386s, 357s, 330s, and 305s.

(iii) A mixture of $[Ru_3(CO)_{10}(CNBu^t)_2]$ (48 mg, 0.06 mmol) and t-butyl isocyanide (5 mg, 0.06 mmol) was warmed in cyclohexane (30 cm³) for 10 min. The trisubstituted complex $[Ru_3(CO)_9(CNBu^t)_3]$ (3) was identified spectroscopically. Infrared (C_6H_{12}): ν(CN) 2 139m; ν(CO) 2 040m, 1 998s, and 1 971s cm⁻¹. ^1H N.m.r. (C_6D_6): δ 1.04 (s, CMe₃). ^{13}C N.m.r. (C_6D_6): δ 208.0 (s, CO), 57.8 (s, *C*Me₃), 30.0 (s, C*Me*₃).

(*b*) *Cyclohexyl isocyanide*, $CN(C_6H_{11})$. A mixture of the ruthenium carbonyl (650 mg, 1.02 mmol) and cyclohexyl isocyanide (130 mg, 1.19 mmol) in tetrahydrofuran (thf) (100 cm³) was heated at 70 °C for 135 min. Evaporation of the solvent and chromatography (Florisil) afforded four fractions. An orange band was eluted with light petroleum. Crystallisation (light petroleum) afforded orange crystals of $[Ru_3(CO)_{12}]$ (320 mg, 49%) identified by i.r. spectroscopy. A second fraction, an orange band, was eluted with light petroleum. Crystallisation (light petroleum) afforded orange *crystals* of $[Ru_3(CO)_{11}\{CN(C_6H_{11})\}]$ (4) (161 mg, 22%), m.p. 139—141 °C [Found: C, 30.0; H, 1.5; N, 1.9%; *M* (mass spectrometry), 722. $C_{18}H_{11}NO_{11}Ru_3$ requires C, 30.0; H, 1.5; N, 1.9%; *M*, 722]. ^1H N.m.r. [$(CD_3)_2CO$]: δ 1.14 (m, C_6H_{11}). Mass spectrum (most intense ion of cluster): *m/e* 722s, 700vw, 686m, 666w, 641s, 613s, 582s, 555s, 529s, 501s, 471s, 442s, 417s, 389s, 361s, 329s, and 305s. A red fraction, in very low yield, was eluted with light petroleum. The i.r. in cyclohexane gave bands at ν(CN) 2 165m; ν(CO) 2 071m, 2 046m, 2 037 (sh), 2 023vs, 1 994s, 1 984s, and 1 975s cm⁻¹. The fourth fraction, eluted with diethyl ether, afforded pink translucent crystals (14 mg), m.p. 80—83 °C (Found: C, 42.6; H, 5.1; N, 3.4%). Infrared (C_6H_{12}): ν(CN) 2 167w; ν(CO) 2 073m, 2 060w, 2 048s, 2 040s, 2 026vs, 1 995s, 1 987m, and 1 968m cm⁻¹. ^1H N.m.r. [$(CD_3)_2CO$]: δ 1.14 (m, C_6H_{11}). The latter two products were not further identified.

(*c*) p-*Methoxyphenyl isocyanide*, CNC_6H_4OMe-*p*. (i) A mixture of the ruthenium carbonyl (200 mg, 0.31 mmol) and *p*-methoxyphenyl isocyanide (60 mg, 0.45 mmol) in thf (100 cm³) was vigorously stirred at 65 °C for 3 h. Evaporation of the solvent and chromatography (Florisil) afforded three fractions. A yellow-orange band was eluted with light petroleum. Crystallisation (light petroleum) afforded orange *crystals* of $[Ru_3(CO)_{12}]$ (62 mg, 31%) identified by i.r. spectroscopy. This was followed by a yellow band and crystallisation (light petroleum) afforded a yellow *powder* of $[Ru_3(CO)_{11}(CNC_6H_4OMe$-*p*)] (5) (45 mg, 23%), m.p. 147—148 °C (Found: C, 30.8; H, 0.8; N, 1.9. $C_{19}H_7NO_{12}Ru_3$ requires C, 30.7; H, 0.9; N, 1.9%). ^1H N.m.r. ($CDCl_3$): δ 7.56, 7.38, 7.10, and 6.82 (m, 4 H, C_6H_4); 5.83 (s, 3 H, OMe). A third light red fraction was eluted with light petroleum–diethyl ether (1 : 1). Crystallisation from light petroleum–diethyl ether (the complex is both heat- and air-sensitive, decomposing above 50 °C to an insoluble black residue) afforded a light red *powder* of $[Ru_3(CO)_{10}(CNC_6H_4OMe$-*p*$)_2]$ (6) (32 mg, 16%) {Found: C, 37.0; H, 2.3; N, 2.8%; *M* [$(CH_3)_2CO$], 889. $C_{26}H_{14}N_2O_{12}Ru_3$ requires C, 36.8; H, 1.7; N, 3.3%; *M*, 851}.

(ii) A mixture of $[Ru_3(CO)_{12}]$ (526 mg, 0.82 mmol) and CNC_6H_4OMe-*p* (379 mg, 2.85 mmol) in thf (90 cm³) was refluxed, with vigorous stirring, for 3 h. Evaporation of the solvent and chromatography (Florisil) afforded three fractions. A yellow fraction, eluted with light petroleum, was crystallised (light petroleum) affording yellow crystals of $[Ru_3(CO)_{11}(CNC_6H_4OMe$-*p*)] (98 mg, 16%) identified by i.r. spectroscopy. A red fraction, eluted with diethyl ether, was crystallised (light petroleum–diethyl ether) affording a light red powder of $[Ru_3(CO)_{10}(CNC_6H_4OMe$-*p*$)_2]$ (361 mg, 52%) identified by i.r. spectroscopy. A third brown fraction was eluted with methanol, giving a brown product (117 mg), m.p. 121 °C. Infrared (CH_2Cl_2): ν(CO) 2 054m, 2 031s, 1 969s br cm⁻¹. This product is believed to be a decomposition product of the disubstituted complex.

(*d*) p-*Toluenesulphonylmethyl isocyanide*, $CNCH_2SO_2C_6H_4$-Me-*p*. (i) A mixture of the ruthenium carbonyl (160 mg, 0.25

Table 4. Atomic co-ordinates for complex $[Ru_3(CO)_{11}(CNBu^t)]$ (1)

Atom	*x*	*y*	*z*
Ru(1) [a]	0.153 26(3)	0.245 50(3)	0.064 60(2)
C(1)	−0.004 6(4)	0.265 2(3)	0.083 3(3)
N(1)	−0.099 4(3)	0.269 5(3)	0.084 1(2)
C(2)	−0.223 0(3)	0.263 3(3)	0.081 9(3)
C(3)	−0.223 2(4)	0.318 0(5)	0.162 8(3)
H(3A)	−0.299 6(—)	0.315 5(—)	0.166 9(—)
H(3B)	−0.163 6(—)	0.285 7(—)	0.215 3(—)
H(3C)	−0.200 2(—)	0.397 0(—)	0.166 5(—)
C(4)	−0.257 8(4)	0.143 5(4)	0.079 3(4)
H(4A)	−0.197 8(—)	0.105 8(—)	0.130 2(—)
H(4B)	−0.333 8(—)	0.135 6(—)	0.081 9(—)
H(4C)	−0.255 8(—)	0.105 5(—)	0.029 4(—)
C(5)	−0.306 2(4)	0.321 2(5)	−0.000 3(3)
H(5A)	−0.300 5(—)	0.286 9(—)	−0.051 9(—)
H(5B)	−0.389 3(—)	0.315 2(—)	−0.007 1(—)
H(5C)	−0.287 0(—)	0.397 2(—)	−0.001 7(—)
C(1D)	0.303 1(4)	0.209 1(4)	0.051 1(3)
O(1D)	0.384 9(3)	0.188 5(3)	0.033 6(2)
C(12)	0.073 9(4)	0.130 5(3)	−0.013 9(3)
O(12)	0.024 7(4)	0.069 4(3)	−0.065 0(2)
C(13)	0.118 9(3)	0.372 3(3)	−0.010 1(3)
O(13)	0.100 1(3)	0.439 5(3)	−0.059 7(2)
Ru(2) [a]	0.284 76(3)	0.137 34(3)	0.226 63(2)
C(2U)	0.120 5(3)	0.114 6(3)	0.219 4(3)
O(2U)	0.035 2(3)	0.090 1(3)	0.225 2(2)
C(2D)	0.447 4(4)	0.173 6(4)	0.231 7(2)
O(2D)	0.544 5(3)	0.179 6(3)	0.238 8(2)
C(21)	0.283 9(4)	−0.008 3(4)	0.177 4(3)
O(21)	0.291 2(4)	−0.095 2(3)	0.155 9(2)
C(23)	0.351 4(4)	0.115 1(4)	0.352 2(3)
O(23)	0.382 5(3)	0.092 9(3)	0.423 3(2)
Ru(3) [a]	0.275 78(3)	0.373 76(3)	0.217 07(2)
C(3U)	0.151 9(4)	0.338 6(4)	0.262 4(2)
O(3U)	0.080 6(2)	0.332 4(3)	0.291 3(2)
C(3D)	0.391 9(4)	0.392 1(3)	0.162 8(3)
O(3D)	0.462 5(3)	0.413 1(3)	0.136 9(2)
C(31)	0.206 1(4)	0.515 5(3)	0.173 2(3)
O(31)	0.170 5(3)	0.602 1(3)	0.155 9(2)
C(32)	0.395 1(4)	0.407 1(4)	0.333 5(3)
O(32)	0.464 9(3)	0.435 4(3)	0.396 5(2)
Ru(12) [b]	0.225 1(2)	0.129 6(2)	0.125 0(1)
Ru(23) [b]	0.330 4(2)	0.254 7(2)	0.281 8(1)
Ru(13) [b]	0.190 3(2)	0.361 1(2)	0.120 9(1)

[a] Population: 0.861(1). [b] Population: 0.139(1).

Table 5. Non-hydrogen atom co-ordinates for $[Ru_3(CO)_{10}(CNBu^t)_2]$ (2). Populations are 0.5, except for the t-butyl group

Atom	*x*	*y*	*z*
Ru(1)	0.091 02(5)	0.098 84(4)	1.057 55(6)
Ru(2)	−0.102 16(5)	−0.024 39(4)	1.075 51(6)
Ru(3)	0.003 82(5)	−0.074 48(4)	0.862 97(6)
Carbonyl groups			
C(1D)	0.159(2)	0.015(1)	1.242(2)
O(1D)	0.210(2)	−0.034(2)	1.364(2)
C(12)	0.093(3)	0.215(3)	1.162(2)
O(12)	0.103(2)	0.293(2)	1.252(2)
C(13)	0.236(4)	0.098(3)	1.041(5)
O(13)	0.337(1)	0.104(1)	1.028(1)
C(2U)	−0.169(2)	0.105(1)	0.984(2)
O(2U)	−0.233(3)	0.176(2)	0.921(3)
C(21)	−0.118(2)	0.023(1)	1.258(2)
O(21)	−0.114(4)	0.059(4)	1.369(6)
C(23)	−0.254(4)	−0.105(3)	0.979(5)
O(23)	−0.339(1)	−0.133(1)	0.902(1)
C(3U)	−0.131(2)	0.003(1)	0.739(3)
O(3U)	−0.218(2)	0.035(1)	0.666(2)
C(3D)	0.147(2)	−0.133(1)	1.025(2)
O(3D)	0.227(2)	−0.169(2)	1.094(3)
C(31)	0.088(2)	−0.059(1)	0.728(2)
O(31)	0.146(4)	−0.040(4)	0.651(6)
C(32)	−0.078(3)	−0.214(2)	0.799(2)
O(32)	−0.118(2)	−0.289(2)	0.792(2)
t-Butyl isocyanide: separate components			
C(1U)	0.007 9(6)	0.188 6(5)	0.871 3(8)
N(1U)	−0.030 4(3)	0.246 8(6)	0.778 7(8)
C(2D)	−0.019 1(6)	−0.156 4(5)	1.184 2(8)
N(2D)	0.020 0(6)	−0.230 4(6)	1.255 6(8)
t-Butyl isocyanide: mutual component (population 1.0)			
C	−0.080 8(4)	0.323 5(3)	0.658 0(4)
C(1)	−0.216 7(4)	0.309 0(4)	0.603 0(6)
C(2)	−0.035 5(7)	0.318 8(6)	0.530 9(7)
C(3)	−0.043 2(6)	0.424 2(4)	0.742 8(8)

mmol) and $CNCH_2SO_2C_6H_4Me$-*p* (49 mg, 0.25 mmol) was refluxed in benzene (40 cm^3) for 12 h. Chromatography (Florisil) afforded two fractions. An orange band was eluted with light petroleum and crystallisation (light petroleum) yielded orange crystals of $[Ru_3(CO)_{12}]$ (85 mg, 53%). The second band, purple-brown in colour, was eluted with methanol. Crystallisation from acetone–light petroleum afforded purple-brown *crystals* of $[Ru_3(CO)_9(CNCH_2SO_2C_6H_4Me\text{-}p)_3]$ (7) (80 mg, 28%) (Found: C, 36.9; H, 2.9; N, 3.8. $C_{36}H_{27}N_3O_{15}Ru_3S_3$ requires C, 37.9; H, 2.4; N, 3.7%). Infrared (Nujol): ν(CN) 2 168m; ν(CO) 1 980s cm^{-1}.

(ii) A mixture of the ruthenium carbonyl (160 mg, 0.25 mmol) and $CNCH_2SO_2C_6H_4Me$-*p* (147 mg, 0.75 mmol) was refluxed in benzene (40 cm^3) for 12 h. The solution was allowed to cool, and the purple-brown crystals that deposited were recrystallised (acetone–light petroleum) to afford $[Ru_3(CO)_9(CNCH_2SO_2C_6H_4Me\text{-}p)_3]$ (7) (175 mg, 61%), identical with the product obtained above.

Preparation of $[Ru_3(CO)_{12}]$.—A solution of $RuCl_3{\cdot}xH_2O$ (4 g) in methanol (300 cm^3), in an autoclave, was pressurised to 40 atm with CO. The solution was heated at 125 °C for 20 h, the working CO pressure increasing to *ca.* 55 atm. The reaction mixture was allowed to cool, the CO vented, and the bright orange *crystals* of $[Ru_3(CO)_{12}]$ were collected (2.6 g). Hydrated ruthenium trichloride (2.6 g) was added to the mother-liquor and the reaction repeated to yield 2.4 g of the ruthenium carbonyl cluster. The latter procedure was followed two more times, total yield of $[Ru_3(CO)_{12}]$ being 9.84 g (from 11.44 g of ruthenium trichloride), m.p. 144—145 °C (decomp.) [Found: C, 22.4%; *M* (mass spectrometry), 641. $C_{12}O_{12}Ru_3$ requires C, 22.5%; *M*, 641]. Infrared (C_6H_{12}): ν(CO) 2 062vs, 2 030s, and 2 004 cm^{-1}.

Another series of experiments was carried out using six consecutive 7.0 g charges of $RuCl_3{\cdot}xH_2O$ in methanol (700 cm^3), with an initial CO pressure of 53—60 atm, and heating at 125 °C for between 16.0 and 18.5 h, to give a total yield of 38.4 g of $[Ru_3(CO)_{12}]$. On another occasion, 45.5 g of $RuCl_3 \cdot xH_2O$ were similarly converted to 42.4 g of $[Ru_3(CO)_{12}]$ (each charge in 700 cm^3 methanol, initial pressure 60—65 atm, heating at 125 °C for 17 h).

The three sets of experiments described above result in a virtually quantitative conversion of $RuCl_3 \cdot xH_2O$ to $[Ru_3(CO)_{12}]$; however, we and others have noted that the yield from the first charge is often only moderate to good, for reasons which are not clear to us at present. However, if we follow a procedure of adding to the mother-liquor, a weight of $RuCl_3 \cdot xH_2O$, *equal* to the weight of $[Ru_3(CO)_{12}]$ obtained, and recarbonylating, reproducible yields of the carbonyl are obtained. The actual yields are *ca.* 91—99% based on the monohydrate.

Crystallography.—General details given below apply generally to the structure determinations reported in this and the following paper.

For each compound, a unique data set was measured within a $2\theta_{max.}$ limit predetermined by the extent of the data, using Syntex $P\bar{1}$ and $P2_1$ four-circle diffractometers equipped with monochromatic Mo-K_α radiation ($\lambda = 0.710\ 6_9$ Å) and operating in conventional $2\theta/\theta$ scan mode at 295 K. N Independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered ' observed ' and used in the refinement after absorption correction. Although, in most cases, the scale of the refinement precluded the use of full-matrix least-squares methods, block sizes in the block-diagonal refinements were as large as possible, embracing the molecular core, together with any related disordered components. Anisotropic thermal parameters were likewise used to the extent that was meaningfully feasible to do so for all non-hydrogen atoms in each structure. Hydrogen atoms (x,y,z,U) were included at constrained estimates. Residuals (R,R') quoted at convergence are with reflection weights $[\sigma^2(F_o) + 0.0005\ (F_o)^2]^{-1}$. Neutral-atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion $(f'f'')$.[20] Computation used the *X*-RAY 76 program system[21] implemented on a Perkin-Elmer 3240 computer.

Atom labelling adopted is as follows. The three atoms of the triangle are labelled Ru(N) = Ru(1), Ru(2), and Ru(3). Ligand (L) atoms L(NU) and L(ND) are attached to Ru(N) and lie ' Up ' (U) or ' Down ' (D) relative to the Ru_3 plane. Ligand atoms L(NN′) lie in or close to the Ru_3 plane attached to Ru(N) but directed outwards from the Ru_3 triangle on the side of Ru(N′). Disordered ruthenium atoms Ru(NN′) lie midway between Ru(N) and Ru(N′).

Crystal data for complex (1). $C_{16}H_9NO_{11}Ru_3$, $M = 694.5$, Monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), $a = 11.948(5)$, $b = 12.108(4)$, $c = 16.621(4)$ Å, $\beta = 112.74(2)°$, $U = 2\ 218(2)$ Å^3, $D_m = 2.08(1)$, $Z = 4$, $D_c = 2.08$ g cm^{-3}, $F(000) = 1\ 328$, $\mu_{Mo} = 19.2$ cm^{-1}; specimen size 0.21 × 0.16 × 0.48 mm, $2\theta_{max.} = 65°$. $N,N_o = 8\ 057, 4\ 561$. $R,R' = 0.035, 0.046$.

Crystal data for complex (2). $C_{20}H_{18}N_2O_{10}Ru_3$, $M = 749.6$, Monoclinic, space group $P2_1/a$ (variant of C^5_{2h}, no. 14), $a = 11.910(10)$, $b = 12.831(17)$, $c = 9.565(16)$ Å, $\beta = 111.84(10)°$, $U = 1\ 357(3)$ Å^3, $D_m = 1.82(1)$, $Z = 2$, $D_c = 1.83$ g cm^{-3}, $F(000) = 728$, $\mu_{Mo} = 15.7$ cm^{-1}; specimen size 0.45 × 0.22 × 0.13 mm, $2\theta_{max.} = 65°$. $N,N_o = 4\ 928, 2\ 849$. $R,R' = 0.043, 0.052$.

Abnormal features. In (2), the solution of the structure showed the molecule to be disordered about the centre of symmetry; the two components of the molecule were refined independently, as indicated in the table of co-ordinates, with 50% populations. In (1), disorder was also found but only perceptibly so in the molecular core; Ru_3 fragments were refined with variable population P and $1 - P$, P converging to 0.861(1). Crystals of (2) were of poorer quality, with wide linewidths, perhaps a consequence of disorder, hindering precise cell determination.

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