Cluster Chemistry. Part 19.[1] Crystal and Molecular Structures of the Complexes $[Ru_3(CO)_{11}\{P(C_6H_{11})_3\}]$, $[Ru_3(CO)_{10}\{P(OMe)_3\}_2]$, and $[Ru_3(CO)_9(PMe_3)_3]$: * Two Examples of Disordered Metal Cores within Ordered Ligand Atom Polyhedra

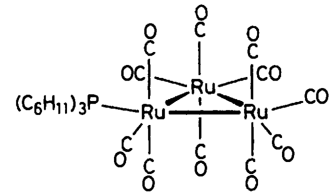
Michael I. Bruce* and Janis G. Matisons
Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia, 5001
Brian W. Skelton and Allan H. White*
Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, W. A. 6009

The crystal and molecular structures of the title complexes are reported. Crystals of the complex $[Ru_3(CO)_{11}\{P(C_6H_{11})_3\}]$ are triclinic, space group $P\bar{1}$, with $a = 17.58(1)$, $b = 17.50(1)$, $c = 12.023(8)$ Å, $\alpha = 69.80(5)$, $\beta = 88.19(5)$, $\gamma = 82.32(5)°$, and $Z = 4$. Refinement of 7 382 data gave residuals $R,R' = 0.042, 0.049$. Crystals of $[Ru_3(CO)_{10}\{P(OMe)_3\}_2]$ are triclinic, space group $P\bar{1}$, with $a = 10.569(4)$, $b = 8.588(3)$, $c = 8.362(3)$ Å, $\alpha = 68.45(3)$, $\beta = 83.07(3)$, $\gamma = 77.06(3)°$, and $Z = 1$. Refinement of 2 773 data gave $R,R' = 0.039, 0.048$. Crystals of $[Ru_3(CO)_9(PMe_3)_3]$ are monoclinic, space group $P2_1/n$, with $a = 20.474(9)$, $b= 12.339(5)$, $c = 11.976(6)$ Å, $\beta = 90.80(4)°$, and $Z = 4$. Refinement of 5 014 data gave $R,R' = 0.037, 0.046$. All complexes contain an Ru_3 core bearing the tertiary phosphine or phosphite ligands in equatorial positions on different metal atoms. The $P(OMe)_3$ and PMe_3 complexes are disordered according to a model in which the central Ru_3 cluster occupies two positions related by a 60° rotation about the inversion centre, while the peripheral atom polyhedron (constructed from the O of CO, and P of the phosphite or phosphine) remains essentially unchanged.

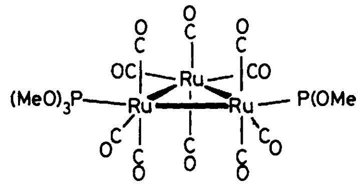
The availability of a large number of mono-, di-, and tri-substituted derivatives of $[Ru_3(CO)_{12}]$ containing Group 5B donor ligands, which were synthesised by the radical ion-initiated reactions described earlier,[2] has enabled us to determine the structural parameters of several of these complexes. In the course of this investigation it became apparent that the solid-state structures of many of these compounds are disordered, but that the disorder could be refined in terms of a model involving two symmetry-related positions of the Ru_3 core within a ligand polyhedron, of which the peripheral atoms (that is, the O of CO, and the P of the phosphite or phosphine) occupy only 12 distinct sites. We have communicated earlier the outlines of these results, and those obtained for similar complexes containing isocyanide ligands;[3] this paper contains the details of the structure analyses of the three title complexes. Of these, $[Ru_3(CO)_{11}\{P(C_6H_{11})_3\}]$ (1) is ordered, while $[Ru_3(CO)_{10}\{P(OMe)_3\}_2]$ (2) and $[Ru_3(CO)_9(PMe_3)_3]$ (3) exhibit the disorder phenomenon. The only previous structural study of a trinuclear ruthenium carbonyl derivative containing a unidentate tertiary phosphine is that of $[Ru_3(CO)_{11}(PPh_3)]$.[4]

Experimental

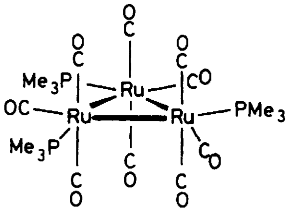
The three complexes were prepared by radical ion-initiated reactions of stoicheiometric amounts of the tertiary phosphine or phosphite with $[Ru_3(CO)_{12}]$, as described earlier.[2] Crystals were obtained from hexane solution.



(1)



(2)



(3)

Crystallography.—For general details and atom-labelling methods used see the preceding paper.

Crystal data for complex (1). $C_{29}H_{33}O_{11}PRu_3$, $M = 891.7$, Triclinic, space group $P\bar{1}$ (C_i^1, no. 2), $a = 17.58(1)$, $b = 17.50(1)$, $c = 12.023(8)$ Å, $\alpha = 69.80(5)$, $\beta = 88.19(5)$, $\gamma =$

---

† 1,1,1,1,2,2,2,2,3,3,3-Undecacarbonyl-3-tricyclohexylphosphine- and 1,1,1,1,2,2,2,3,3,3-decacarbonyl-2,3-bis(trimethyl phosphite)-*triangulo*-triruthenium and tris[tricarbonyl(trimethylphosphine)-ruthenium](3 *Ru–Ru*).

Supplementary data available (No. SUP 23647, 75 pp.): structure factors, thermal parameters, H-atom co-ordinates, phosphine ligand geometries. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Non-hydrogen atom co-ordinates for $[Ru_3(CO)_{11}\{P(C_6H_{11})_3\}]$ (1)

	Molecule 1			Molecule 2		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Ru(1)	0.050 12(3)	0.758 77(3)	0.187 47(5)	0.422 56(3)	0.251 94(4)	0.376 09(5)
Ru(2)	−0.037 21(4)	0.720 68(5)	0.401 80(6)	0.313 85(4)	0.287 47(4)	0.185 48(6)
Ru(3)	−0.082 01(3)	0.671 18(4)	0.213 07(6)	0.467 28(4)	0.326 86(4)	0.130 21(5)
Phosphine ligand						
P	0.098 9(1)	0.787 4(1)	−0.011 7(1)	0.528 2(1)	0.222 0(1)	0.515 3(2)
C(11)	0.194 9(4)	0.824 9(4)	−0.027 5(6)	0.498 6(4)	0.176 2(4)	0.672 4(5)
C(12)	0.190 8(4)	0.909 8(4)	−0.014 3(6)	0.440 5(5)	0.234 8(5)	0.710 8(7)
C(13)	0.269 0(5)	0.940 5(5)	−0.029 2(7)	0.419 5(6)	0.194 3(5)	0.842 8(7)
C(14)	0.328 7(5)	0.878 2(6)	0.052 7(8)	0.390 5(6)	0.113 5(6)	0.864 9(8)
C(15)	0.333 4(4)	0.795 2(5)	0.036 8(7)	0.448 3(5)	0.055 6(5)	0.827 3(7)
C(16)	0.254 8(4)	0.763 5(4)	0.056 6(6)	0.468 2(4)	0.093 3(4)	0.696 7(6)
C(21)	0.037 8(4)	0.874 4(4)	−0.123 3(5)	0.569 3(4)	0.315 3(4)	0.519 2(6)
C(22)	0.069 7(4)	0.910 6(5)	−0.248 0(6)	0.628 8(6)	0.298 4(5)	0.619 3(8)
C(23)	0.016 8(5)	0.986 9(5)	−0.322 5(6)	0.649 6(6)	0.379 7(6)	0.623 2(8)
C(24)	−0.063 8(5)	0.968 8(5)	0.328 8(7)	0.681 4(6)	0.428 4(6)	0.507 5(9)
C(25)	−0.095 7(5)	0.929 2(5)	−0.206 6(7)	0.626 2(6)	0.445 1(5)	0.405 9(8)
C(26)	−0.042 4(4)	0.853 4(4)	−0.135 7(6)	0.604 4(5)	0.364 5(5)	0.401 8(7)
C(31)	0.110 2(5)	0.703 2(4)	−0.077 0(7)	0.605 0(4)	0.140 9(4)	0.501 2(6)
C(32)	0.167 4(5)	0.713 0(5)	−0.179 0(7)	0.665 9(5)	0.104 7(5)	0.599 0(7)
C(33)	0.166 9(7)	0.648 0(7)	−0.235 1(10)	0.715 2(5)	0.031 1(6)	0.584 5(7)
C(34)	0.171 0(8)	0.565 2(7)	−0.154 5(11)	0.754 1(5)	0.052 0(6)	0.464 9(8)
C(35)	0.115 6(7)	0.555 0(6)	−0.052 7(10)	0.693 7(5)	0.091 2(6)	0.366 8(7)
C(36)	0.119 3(6)	0.618 9(6)	0.007 7(9)	0.646 0(5)	0.165 7(5)	0.382 0(7)
Carbonyl groups						
C(1U)	0.118 7(4)	0.655 7(5)	0.243 2(6)	0.444 8(5)	0.141 5(4)	0.376 5(6)
O(1U)	0.165 1(3)	0.601 4(3)	0.276 4(5)	0.458 6(4)	0.073 2(3)	0.387 9(6)
C(1D)	−0.018 1(4)	0.860 7(4)	0.131 3(6)	0.408 4(6)	0.362 0(5)	0.379 4(8)
O(1D)	−0.052 0(3)	0.924 1(3)	0.093 6(5)	0.398 5(5)	0.423 2(4)	0.394 7(7)
C(12)	0.117 3(4)	0.807 6(5)	0.255 0(7)	0.340 2(5)	0.223 1(6)	0.477 6(7)
O(12)	0.156 8(4)	0.833 6(4)	0.301 5(5)	0.287 6(4)	0.205 6(6)	0.535 6(6)
C(2U)	0.038 8(6)	0.624 4(6)	0.455 8(8)	0.344 7(5)	0.179 5(5)	0.173 4(7)
O(2U)	0.082 2(4)	0.567 6(5)	0.500 4(6)	0.354 9(4)	0.116 3(4)	0.165 1(6)
C(2D)	−0.109 9(5)	0.821 0(5)	0.337 6(7)	0.286 6(5)	0.392 0(6)	0.209 5(9)
O(2D)	−0.153 5(4)	0.878 2(4)	0.311 5(6)	0.264 5(4)	0.453 5(4)	0.216 1(7)
C(21)	0.012 1(6)	0.773 7(7)	0.487 6(9)	0.222 9(5)	0.247 9(6)	0.263 0(8)
O(21)	0.041 9(6)	0.804 5(6)	0.539 0(7)	0.168 5(4)	0.224 9(6)	0.306 5(7)
C(23)	−0.112 6(6)	0.666 9(6)	0.511 6(8)	0.283 5(5)	0.332 8(6)	0.023 3(8)
O(23)	−0.156 6(5)	0.634 7(5)	0.574 4(7)	0.265 6(4)	0.360 0(5)	−0.074 4(6)
C(3U)	−0.011 1(6)	0.572 5(5)	0.273 6(9)	0.496 2(5)	0.212 2(5)	0.144 3(8)
O(3U)	0.025 9(4)	0.509 3(4)	0.303 2(8)	0.518 3(4)	0.150 0(4)	0.143 2(7)
C(3D)	−0.146 0(5)	0.774 6(6)	0.144 9(8)	0.434 4(6)	0.435 9(6)	0.137 8(9)
O(3D)	−0.190 7(4)	0.830 9(4)	0.099 1(7)	0.421 0(5)	0.501 4(4)	0.132 0(8)
C(31)	−0.085 5(5)	0.655 6(5)	0.061 8(8)	0.571 6(5)	0.344 5(6)	0.131 2(7)
O(31)	−0.088 6(5)	0.647 7(4)	−0.025 7(6)	0.634 0(4)	0.356 8(5)	0.123 1(6)
C(32)	−0.166 8(5)	0.618 1(6)	0.295 5(9)	0.453 4(5)	0.364 0(6)	−0.037 8(8)
O(32)	−0.218 2(4)	0.589 3(5)	0.340 8(7)	0.448 8(5)	0.384 2(5)	−0.138 4(6)

82.32(5)°, U = 3 440(4) Å^3, D_m = 1.74(1), Z = 4, D_c = 1.72 g cm^{-3}, F(000) = 1 768, μ_{Mo} = 13.0 cm^{-1}; specimen size 0.27 × 0.30 × 0.08 mm, $2\theta_{max.}$ = 50°. N,N_o = 11 951, 7 382. R,R' = 0.042, 0.049.

Crystal data for complex (2). $C_{16}H_{18}O_{16}P_2Ru_3$, M = 831.5, Triclinic, space group $P\bar{1}$ (C_i^1, no. 2), a = 10.569(4), b = 8.588(3), c = 8.362(3) Å, α = 68.45(3), β = 83.07(3), γ = 77.06(3)°, U = 687.4(4) Å^3, D_m = 2.00(1), Z = 1, D_c = 2.01 g cm^{-3}, F(000) = 404, μ_{Mo} = 16.1 cm^{-1}; specimen size 0.48 × 0.21 × 0.25 mm, $2\theta_{max.}$ = 60°. N,N_o = 4 024, 2 773. R,R' = 0.039, 0.048.

Crystal data for complex (3). $C_{18}H_{27}O_9P_3Ru_3$, M = 783.5, Monoclinic, space group $P2_1/n$ (C_{2h}^5, no. 14), a = 20.474(9), b = 12.339(5), c = 11.976(6) Å, β = 90.80(4)°, U = 3 025(2) Å^3, D_m = 1.71(1), Z = 4, D_c = 1.72 g cm^{-3}, F(000) = 1 536, μ_{Mo} = 16.6 cm^{-1}; specimen size 0.10 × 0.43 × 0.15 mm, $2\theta_{max.}$ = 60°. N,N_o = 8 729, 5 014. R,R' = 0.037, 0.046.

Abnormal features. Complex (1) refined normally. In (2), the molecule was disordered about a centre of symmetry as in compound (2) of the previous paper, both components being refined independently. In (3), minor disorder was found and only the two components of the Ru_3 core were refined with populations P and 1 − P; P converging to 0.932(3).

The atomic co-ordinates of complexes (1)—(3) are given in Tables 1—3 respectively.

Discussion

Crystal Structure of $[Ru_3(CO)_{11}\{P(C_6H_{11})_3\}]$ (1).—The unit-cell contents comprise discrete molecules of the complex of

Table 2. Non-hydrogen atom co-ordinates for $[Ru_3(CO)_{10}\{P(OMe)_3\}_2]$ (2). All atom populations 0.5

Atom	*x*	*y*	*z*
Ru(1)	0.118 52(5)	0.993 71(6)	0.100 25(7)
Ru(2)	−0.131 66(5)	1.150 05(6)	−0.035 42(7)
Ru(3)	0.005 50(5)	0.842 51(6)	−0.083 96(7)
Carbonyl groups			
C(1U)	0.215(5)	1.057(5)	−0.112(5)
O(1U)	0.276(5)	1.095(5)	−0.216(5)
C(1D)	0.016(1)	0.906(2)	0.312(2)
O(1D)	−0.022(3)	0.871(7)	0.425(5)
C(12)	0.144(2)	1.174(2)	0.161(4)
O(12)	0.162(2)	1.302(3)	0.181(5)
C(2U)	−0.027(1)	1.305(1)	−0.195(1)
O(2U)	0.041(3)	1.397(3)	−0.285(4)
C(2D)	−0.211(4)	0.970(4)	0.137(5)
O(2D)	−0.275(4)	0.881(5)	0.252(5)
C(21)	−0.187(2)	1.300(2)	0.088(3)
O(21)	−0.219(4)	1.388(5)	0.180(6)
C(3U)	0.021(1)	1.025(1)	−0.303(2)
O(3U)	0.049(3)	1.129(6)	−0.449(5)
C(3D)	−0.018(1)	0.683(1)	0.148(1)
O(3D)	−0.015(3)	0.570(3)	0.277(5)
C(31)	0.154(2)	0.692(3)	−0.131(3)
O(31)	0.248(4)	0.610(5)	−0.152(6)
C(32)	−0.128(2)	0.773(2)	−0.166(3)
O(32)	−0.201(2)	0.733(2)	−0.206(4)
Phosphite ligands: two fragments (population 0.5); P common (population 1.0)			
P(1)	0.298 85(10)	0.781 9(1)	0.210 2(1)
O(11)	0.385 6(11)	0.810 7(13)	0.328 0(15)
C(11)	0.364 5(30)	0.886 2(31)	0.445 0(29)
O(12)	0.400 3(10)	0.719 1(19)	0.091 3(18)
C(12)	0.531 7(19)	0.700 7(30)	0.056 4(35)
O(13)	0.255 0(10)	0.617 6(11)	0.332 8(18)
C(13)	0.288 4(33)	0.462 4(45)	0.451 9(62)
O(21)	0.434 0(6)	0.823 1(9)	0.112 4(11)
C(21)	0.498 5(15)	0.756 4(26)	−0.000 4(30)
O(22)	0.288 0(7)	0.875 8(11)	0.334 4(11)
C(22)	0.398 3(37)	0.872 5(54)	0.434 7(46)
O(23)	0.355 8(9)	0.582 0(10)	0.310 4(12)
C(23)	0.303 0(46)	0.493 0(51)	0.425 0(63)

Table 3. Non-hydrogen atom co-ordinates for $[Ru_3(CO)_9(PMe_3)_3]$ (3)

Atom	*x*	*y*	*z*
Ru(1)	0.409 47(2)	0.211 66(3)	0.025 07(3)
Ru(2)	0.289 80(2)	0.191 76(3)	0.143 68(3)
Ru(3)	0.287 99(2)	0.208 29(4)	−0.094 69(3)
Phosphine ligands			
P(1)	0.485 57(8)	0.254 0(1)	−0.111 8(2)
C(11)	0.564 9(3)	0.286 7(5)	−0.056 3(6)
C(12)	0.468 0(3)	0.370 3(6)	−0.201 1(6)
C(13)	0.505 7(3)	0.148 7(6)	−0.212 7(5)
P(2)	0.322 27(9)	0.214 9(1)	0.329 3(1)
C(21)	0.254 5(3)	0.218 2(5)	0.424 7(4)
C(22)	0.365 8(4)	0.340 1(6)	0.364 7(5)
C(23)	0.374 3(3)	0.113 3(5)	0.393 3(4)
P(3)	0.178 85(7)	0.236 6(1)	−0.143 1(1)
C(31)	0.166 5(4)	0.258 2(10)	−0.289 7(6)
C(32)	0.135 3(4)	0.342 9(10)	−0.077 4(10)
C(33)	0.122 8(4)	0.125 5(9)	−0.127 0(8)
Carbonyl ligands			
C(1D)	0.404 1(3)	0.362 0(5)	0.064 8(5)
O(1D)	0.407 5(2)	0.451 1(3)	0.088 1(4)
C(1U)	0.405 9(2)	0.064 7(4)	−0.027 0(4)
O(1U)	0.411 2(2)	−0.021 7(3)	−0.057 5(3)
C(12)	0.467 6(2)	0.182 6(5)	0.144 4(4)
O(12)	0.503 1(2)	0.165 0(4)	0.215 9(3)
C(2D)	0.272 6(3)	0.343 2(5)	0.127 4(4)
O(2D)	0.260 4(2)	0.435 0(3)	0.130 8(4)
C(2U)	0.319 6(2)	0.044 0(4)	0.150 2(4)
O(2U)	0.333 6(2)	−0.043 5(3)	0.164 0(3)
C(23)	0.202 4(2)	0.157 9(5)	0.169 3(4)
O(23)	0.148 8(2)	0.136 3(3)	0.187 3(4)
C(3D)	0.302 3(3)	0.362 5(5)	−0.101 4(5)
O(3D)	0.307 7(3)	0.454 1(4)	−0.115 6(4)
C(3U)	0.268 0(3)	0.059 0(4)	−0.067 2(4)
O(3U)	0.252 2(2)	−0.029 4(3)	−0.063 3(4)
C(31)	0.320 1(3)	0.183 7(6)	−0.236 6(4)
O(31)	0.338 6(2)	0.163 4(5)	−0.323 1(3)
Disordered fragment *			
Ru(12)	0.370 0(3)	0.203 3(6)	0.144 1(6)
Ru(13)	0.367 1(4)	0.217 7(6)	−0.094 1(6)
Ru(23)	0.247 4(3)	0.202 3(6)	0.025 2(6)

* Ruthenium populations: Ru(1,2,3) 0.932(3), 0.936(3), 0.936(3); Ru(12,13,23) 0.054(2), 0.049(1), 0.050(1).

the required stoicheiometry with two molecules constituting the asymmetric unit of the structure. These molecules (Figure 1) differ slightly in the disposition of the cyclohexyl substituents in the phosphine ligand. As expected, the molecule is basically the $[Ru_3(CO)_{12}]$ species with one of the carbonyl groups replaced by the phosphine ligand. Unlike $[Ru_3(CO)_{11}(CNBu^t)]$ described in the previous paper, no disorder of the Ru_3 molecular core is found and this is reflected in the manner in which the axial carbonyl substituents lie more nearly normal to the Ru_3 plane. However, unlike $[Ru_3(CO)_{11}(CNBu^t)]$, the unique substituent here is found to be equatorial rather than axial. This probably reflects the greater effective bulk of the phosphine ligand in which the three substituents are immediately attached to the co-ordinating atom rather than being one atom further removed as is the case in the t-butyl isocyanide. It is of interest to note that, in the present complex, the disposition of the pair of equatorial carbonyl substituents relative to the other two ruthenium atoms is not symmetrical (as measured by the C–Ru–Ru angles). This seems to be a consequence of the unsymmetrical environment of the equatorial substitution site, and the manner of its occupancy by the phosphine, which disposes one of the cyclohexyl groups equatorial but directed toward the more crowded side in that plane wherein the carbonyl group is attached to the same ruthenium atom, while the other two substituents lie above and below the Ru_3 plane in, presumably, the less crowded direction. All cyclohexyl groups adopt the ' chair ' conformation.

Crystal Structure of $[Ru_3(CO)_{10}\{P(OMe)_3\}_2]$ (2).—Crystals of this complex belong to the triclinic crystal system in which two space groups *P*1 and $P\bar{1}$ are possible and indistinguishable on the basis of absences in data. Given that the unit cell can accommodate one molecule only of the cluster, the space group *P*1 which contains no symmetry elements within the

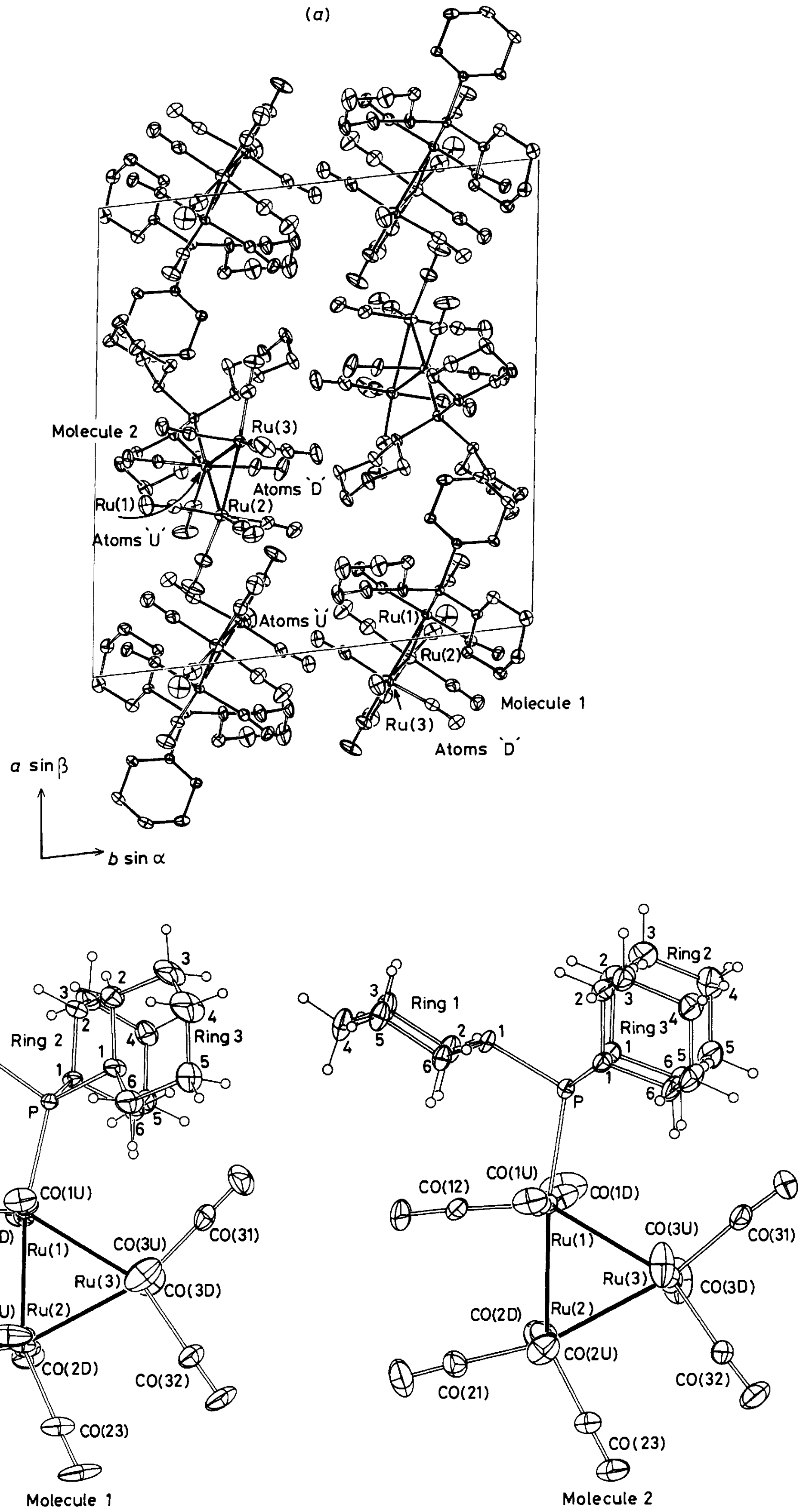


Figure 1. (*a*) Unit-cell contents of (1) projected down *c*; 20% probability thermal ellipsoids are shown for the non-hydrogen atoms. (*b*) Single molecules of (1) projected normal to their Ru_3 planes

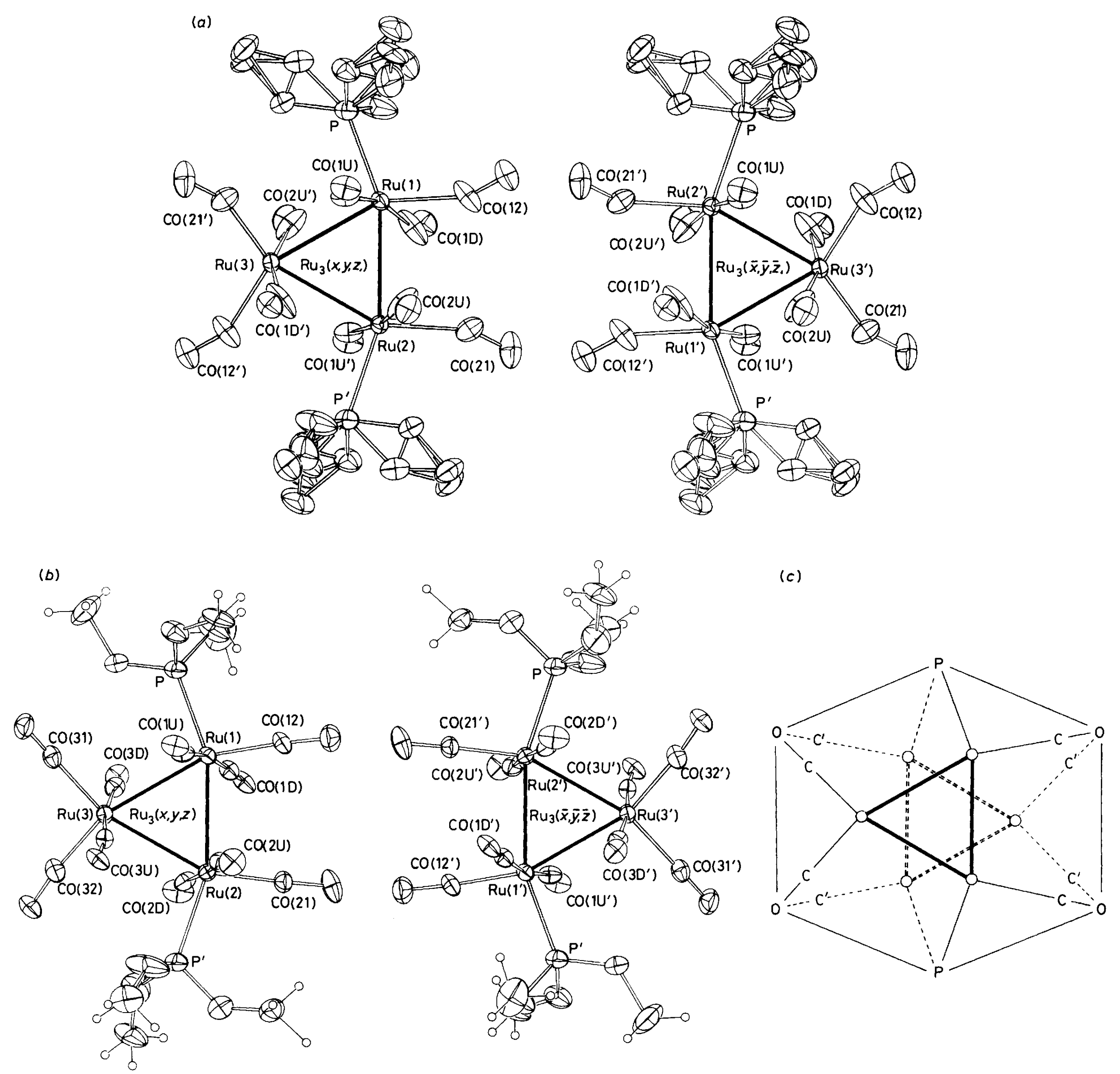


Figure 2. (*a*) The ligand array of (2), *before* its refinement in terms of separate components, with the alternative dispositions of the central Ru_3 triangle. (*b*) Deconvolution of (*a*) as described in the text into a pair of centrosymmetrically related half-molecules; only the phosphorus atoms have populations of 1. (*c*) Co-ordination of CO ligands and P atoms, showing how each Ru_3 triangle can be accommodated within a single peripheral atom polyhedron (portion only shown)

unit cell is a possibility. On the other hand, the space group $P\bar{1}$ has present in the unit cell an inversion centre, requiring that, if the space group be correct, the *molecule* must have an inversion centre which is not the case if it be based on the Ru_3 triangular core. Nevertheless, we have seen in the previous paper another example of the disubstituted system $[Ru_3(CO)_{10}(L)_2]$ in which the periphery of the molecule is so similar to that of its inversion image that it is capable of accommodating two possible dispositions of the Ru_3 core, given that the distortions inherent in the core environment are such that two isomers with very similar ligand arrays are feasible; such a situation is compatible with the known fluxional nature of many of these systems in solution. In the event, we find the correct solution of the present structure to lie in a similar description to that reported for $[Ru_3(CO)_{10}(CNBu^t)_2]$, namely, a centrosymmetrically related pair of disordered molecules, each with population 0.5. Unlike the case of the t-butyl isocyanide derivative, in which the two substituents are axially disposed and attached on opposite sides of the Ru_3 plane to two different ruthenium atoms, here we find that the two phosphine ligands lie equatorially disposed about two different ruthenium atoms in the same cluster (Figure 2). [The equatorial rather than the axial disposition may be a result of the ligand ' effective bulk ' considerations noted as a possible cause for a similar dispositional dissimilarity in some monosubstituted derivatives with analogous ligands under (1) above.] As in $[Ru_3(CO)_{10}(CNBu^t)_2]$, all atoms may be resolved into half-populated components, with the exception

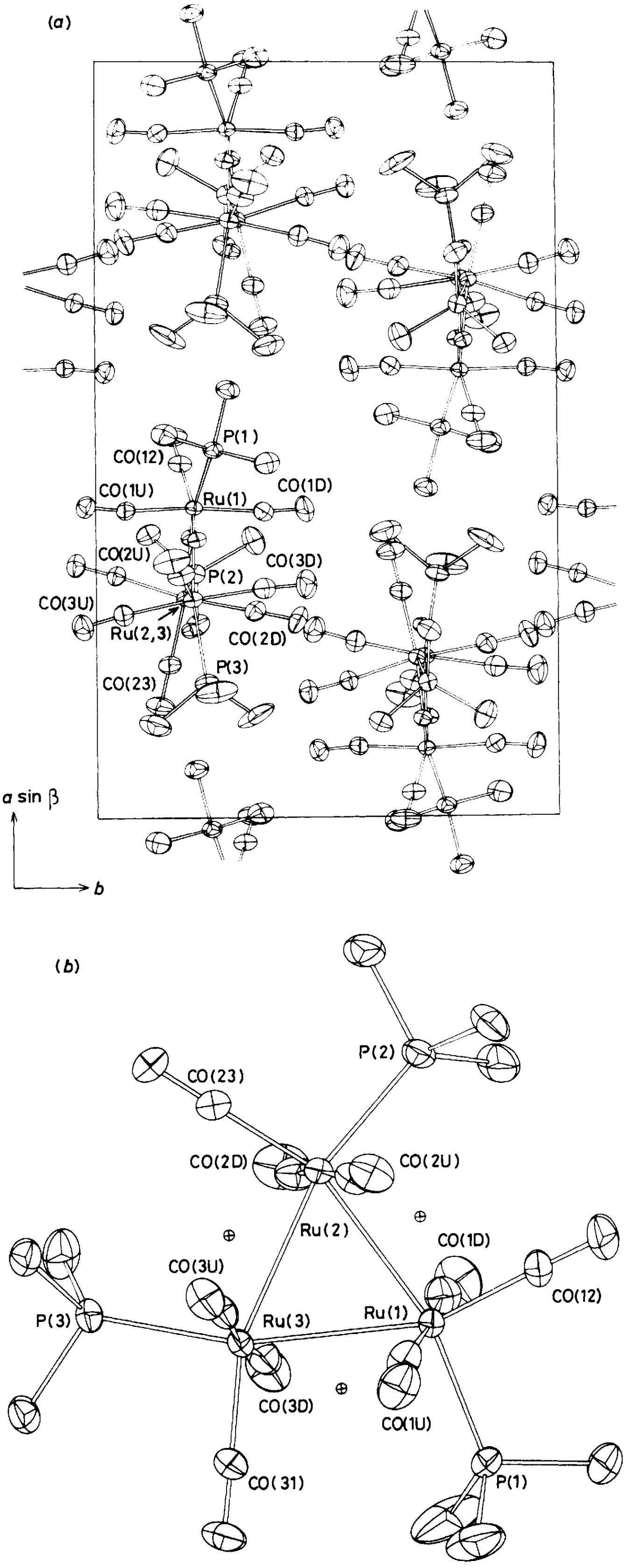


Figure 3. (*a*) Unit-cell contents of (3) projected down *c*; 20% probability thermal ellipsoids are shown for the non-hydrogen atoms. (*b*) A single molecule of (3) projected normal to the Ru_3 plane. The ruthenium atoms of the disordered component (population 0.068) are shown as small spheres

Table 4. Molecular core geometry for $[Ru_3(CO)_{11}\{P(C_6H_{11})_3\}]$ (1); distances (Å) and angles (°). The two values in each entry are for molecules 1 and 2 respectively. For C(NN − 1) with N = 1, read P

	N = 1	N = 2	N = 3
Ru(N)–Ru(N + 1)	2.878(2), 2.875(2)	2.859(2), 2.874(2)	2.902(2), 2.920(2)
Ru(N)–C(NU)	1.947(7), 1.919(8)	1.936(10), 1.949(10)	1.919(9), 1.952(10)
Ru(N)–C(ND)	1.929(7), 1.922(10)	1.959(8), 1.944(11)	1.924(8), 1.951(10)
Ru(N)–C(NN + 1)	1.897(9), 1.871(8)	1.936(10), 1.898(9)	1.933(11), 1.901(9)
Ru(N)–C(NN − 1)	2.425(3), 2.420(3)	1.900(13), 1.914(9)	1.925(10), 1.909(9)
Ru(N − 1)–Ru(N)–Ru(N + 1)	59.29(3), 59.46(5)	60.79(5), 61.05(5)	59.93(4), 59.49(2)
Ru(N − 1)–Ru(N)–C(NU)	91.1(3), 94.5(2)	83.8(3), 90.8(3)	89.2(4), 87.0(3)
Ru(N − 1)–Ru(N)–C(ND)	88.7(2), 85.4(3)	92.3(3), 85.1(3)	90.5(3), 89.3(3)
Ru(N − 1)–Ru(N)–C(NN + 1)	148.6(2), 145.1(3)	155.3(3), 152.6(3)	161.9(3), 167.1(2)
Ru(N − 1)–Ru(N)–C(NN − 1)	109.29(6), 112.86(7)	101.1(3), 104.1(3)	95.4(4), 95.7(3)
Ru(N + 1)–Ru(N)–C(NU)	93.6(2), 89.3(2)	90.3(3), 90.0(3)	86.3(3), 82.2(3)
Ru(N + 1)–Ru(N)–C(ND)	86.6(2), 94.4(3)	88.3(3), 89.2(3)	89.3(3), 90.3(4)
Ru(N + 1)–Ru(N)–C(NN + 1)	89.4(2), 86.2(3)	95.0(3), 91.7(3)	102.0(3), 107.7(2)
Ru(N + 1)–Ru(N)–C(NN − 1)	167.79(8), 171.7(1)	161.4(3), 165.1(3)	155.3(4), 155.0(3)
C(NU)–Ru(N)–C(ND)	179.6(19), 175.6(3)	176.1(5), 175.7(4)	175.1(5), 172.5(4)
C(NU)–Ru(N)–C(NN − 1)	90.8(2), 88.2(2)	91.5(5), 88.3(4)	92.6(4), 93.9(4)
C(NU)–Ru(N)–C(NN + 1)	89.5(4), 90.6(4)	92.3(4), 91.7(4)	90.3(4), 92.1(4)
C(ND)–Ru(N)–C(NN − 1)	88.9(2), 87.7(3)	88.7(4), 91.3(4)	92.3(4), 92.9(4)
C(ND)–Ru(N)–C(NN + 1)	90.8(3), 92.0(4)	91.4(4), 92.6(4)	88.5(4), 90.1(4)
C(NN − 1)–Ru(N)–C(NN + 1)	102.0(2), 101.8(3)	103.4(5), 103.2(4)	102.8(4), 97.1(4)
Carbonyl groups			
C(NU)—O(NU)	1.131(9), 1.15(1)	1.14(1), 1.13(1)	1.15(1), 1.11(1)
C(ND)–O(ND)	1.133(8), 1.14(1)	1.13(1), 1.12(1)	1.16(1), 1.12(1)
C(NN − 1)–O(NN − 1)		1.13(2), 1.13(1)	1.13(1), 1.14(1)
C(NN + 1)–O(NN + 1)	1.133(12), 1.15(1)	1.13(1), 1.14(1)	1.11(1), 1.14(1)
Ru(N)–C(NU)–O(NU)	171.8(8), 173.7(7)	172.3(9), 173.0(8)	171.8(11), 172.5(8)
Ru(N)–C(ND)–O(ND)	173.2(6), 172.2(8)	173.4(8), 172.9(8)	170.9(9), 172.2(9)
Ru(N)–C(NN − 1)–O(NN − 1)		179.3(15), 178.6(11)	177.5(6), 176.5(9)
Ru(N)–C(NN + 1)–O(NN + 1)	176.1(6), 176.9(8)	178.7(11), 179.6(10)	178.7(9), 175.1(8)

not of peripheral groups as was the case with the t-butyl groups, but the phosphorus atom which occupies a fully populated site, and requires half-populated substituents in two different orientations as dictated by the direction of co-ordination to the respective Ru_3 cores. As in the $CNBu^t$ analogue, and for similar reasons, all geometries here need to be taken with a considerable degree of uncertainty; nevertheless, we note the considerable concerted twist distortions of the ruthenium environments about the two-fold axes of the triangle, correlating again with the proportion of disorder.

Crystal Structure of $[Ru_3(CO)_9(PMe_3)_3]$ (3).—The unit-cell contents comprise discrete molecules of the required stoicheiometry with one molecule constituting the asymmetric unit. The molecule, as expected, is basically $[Ru_3(CO)_{12}]$ with three of the carbonyl groups replaced by three phosphine ligands (Figure 3). All three phosphine ligands lie equatorially disposed, probably for the steric reasons inferred above, one per ruthenium, so as to confer pseudo $3/m$ symmetry on the molecule. As with the complex $[Ru_3(CO)_{11}(NCBu^t)]$ discussed in the previous paper, disorder in the Ru_3 core was observed, refinement of the populations showing these to be 0.93_5, $1 - 0.93_5$; the disorder is accompanied by similar twist distortions in the ruthenium environments about the two-fold axes of the Ru_3 triangle.

General Structural Considerations.—In the parent carbonyl, the average Ru–Ru bond length is 2.8515(4) Å.[5] As found with the triphenylphosphine analogue, there are three different Ru–Ru bonds in (1), the longest of which [at 2.902(2), 2.920(2) Å for molecules 1 and 2, see Table 4] is *cis* to the tertiary phosphine. The Ru–Ru bond *trans* to P is 2.878(2), 2.875(2) Å, and that between the $Ru(CO)_4$ moieties 2.859(2), 2.874(2) Å. In $[Ru_3(CO)_{11}(PPh_3)]$, the three distances are identical with those in (1), at 2.907(3), 2.875(3), and 2.876(3) Å. The origins of these differences are not clear, and both electronic and steric explanations can be advanced.

Although the Ru_3 triangle in complex (2) is isosceles, with bond lengths of 2.845(1), 2.845(1) 2.859(1) Å, there is no simple correlation between the Ru–Ru separation and the disposition of the $P(OMe)_3$ ligands. As expected for complex (3), metal atoms form a near equilateral triangle, of side 2.859(2) Å. The average Ru–Ru distances in (1), (2), and (3) are (2.880, 2.890), 2.850, and 2.859 Å respectively; the greater size of the Ru_3 cores compared with that found in $[Ru_3(CO)_{12}]$ reflects the increase in electron density which occurs on replacement of CO (a good π-acceptor) with a tertiary-phosphine or -phosphite (a good σ-donor). There is no apparent correlation with basicity of phosphine (or phosphite), nor with degree of substitution.

The Ru–P distances are 2.380(6) Å {in $[Ru_3(CO)_{11}(PPh_3)]$}, 2.425(3) and 2.420(3) [in (1)], 2.265(2) and 2.330(1) [in (2)], and 2.330 Å [in (3), average value]. The reason for the large difference in the two $Ru-P(OMe)_3$ distances is not apparent to us. The range of distances appears to be controlled by steric factors, particularly in the case of (1).

Although the differences between individual values are hardly significant, there appears to be a trend in the Ru–CO distances. In all complexes, the Ru–CO(eq) distances are shorter than the Ru–CO(ax) distances by 0.04—0.05 Å; in $[Ru_3(CO)_{12}]$, the difference in averaged values is 0.02 Å. Similarly, the equatorial Ru $\cdots$ O vectors are shorter than the axial Ru $\cdots$ O vectors by *ca.* 0.04 Å.

It is interesting that the introduction of the Group 5 ligand

Table 5. Molecular core geometry for $[Ru_3(CO)_{10}\{P(OMe)_3\}_2]$ (2); distances (Å) and angles (°). For C(13,23) read P as appropriate

	N = 1	N = 2	N = 3
Ru(N)–Ru(N + 1)	2.845(1)	2.859(1)	2.845(1)
Ru(N)–C(NU)	1.89(4)	1.94(1)	1.94(1)
Ru(N)–C(ND)	1.94(1)	1.96(4)	1.94(1)
Ru(N)–C(NN + 1)	1.88(3)	2.265(2)	1.90(2)
Ru(N)–C(NN – 1)	2.330(1)	1.89(2)	1.93(3)
Ru(N – 1)–Ru(N)–Ru(N + 1)	60.32(3)	59.83(3)	59.85(3)
Ru(N – 1)–Ru(N)–C(NU)	79(2)	79.4(3)	73.9(4)
Ru(N – 1)–Ru(N)–C(ND)	94.3(5)	92(1)	98.9(4)
Ru(N – 1)–Ru(N)–C(NN + 1)	155.1(7)	158.11(5)	155.3(9)
Ru(N – 1)–Ru(N)–C(NN – 1)	101.25(5)	99.6(6)	102.1(6)
Ru(N + 1)–Ru(N)–C(NU)	97(1)	98.1(3)	93.4(5)
Ru(N + 1)–Ru(N)–C(ND)	82.5(4)	76(1)	81.2(4)
Ru(N + 1)–Ru(N)–C(NN + 1)	96.7(7)	99.92(4)	100.6(9)
Ru(N + 1)–Ru(N)–C(NN – 1)	159.70(5)	155.1(5)	158.6(8)
C(NU)–Ru(N)–C(ND)	173(2)	171(1)	172.6(5)
C(NU)–Ru(N)–C(NN – 1)	87(1)	90.9(7)	92.0(8)
C(NU)–Ru(N)–C(NN + 1)	95(2)	96.8(3)	93.9(7)
C(ND)–Ru(N)–C(NN – 1)	91.2(3)	93(1)	91.3(7)
C(ND)–Ru(N)–C(NN + 1)	92.0(9)	91(1)	92.1(7)
C(NN – 1)–Ru(N)–C(NN + 1)	102.7(7)	102.0(6)	99.7(11)
Carbonyl groups			
C(NU)–O(NU)	1.02(6)	1.19(3)	1.26(4)
C(ND)–O(ND)	0.95(4)	1.22(5)	1.15(3)
C(NN – 1)–O(NN – 1)		1.23(6)	1.04(4)
C(NN + 1)–O(NN + 1)	1.23(4)		1.12(4)
Ru(N)–C(NU)–O(NU)	171(6)	176(2)	171(2)
Ru(N)–C(ND)–O(ND)	168(4)	169(3)	169(2)
Ru(N)–C(NN – 1)–O(NN – 1)		175(2)	178(3)
Ru(N)–C(NN + 1)–O(NN + 1)	173(3)		173(4)

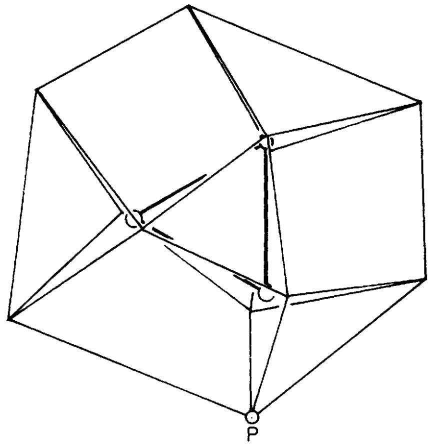
For the phosphite ligands (values for 1 and 2 groups respectively): P–O(1), 1.54(1), 1.60(1); P–O(2), 1.52(1), 1.51(1); P–O(3), 1.54(1), 1.62(1) Å. O(1)–C(1), 1.33(3), 1.32(3); O(2)–C(2), 1.37(2), 1.51(4); O(3)–C(3), 1.34(3), 1.16(4) Å. P–O(1)–C(1), 135(1), 125(1); P–O(2)–C(2), 139(2), 125(2); P–O(3)–C(3), 147(2), 125(2)°. Ru–P–O(1), 118.1(3), 114.3(3); Ru–P–O(2), 120.9(4), 117.4(4); Ru–P–O(3), 110.1(4), 117.9(4)°. O(1)–P–O(2), 101.1(7), 99.4(5); O(2)–P–O(3), 103.3(7), 108.4(5); O(3)–P–O(1), 100.6(7), 95.0(4)°.

Table 6. Molecular core geometry for $[Ru_3(CO)_9(PMe_3)_3]$ (3); distances (Å) and angles (°). For C(NN – 1) read P(1,2,3) as appropriate

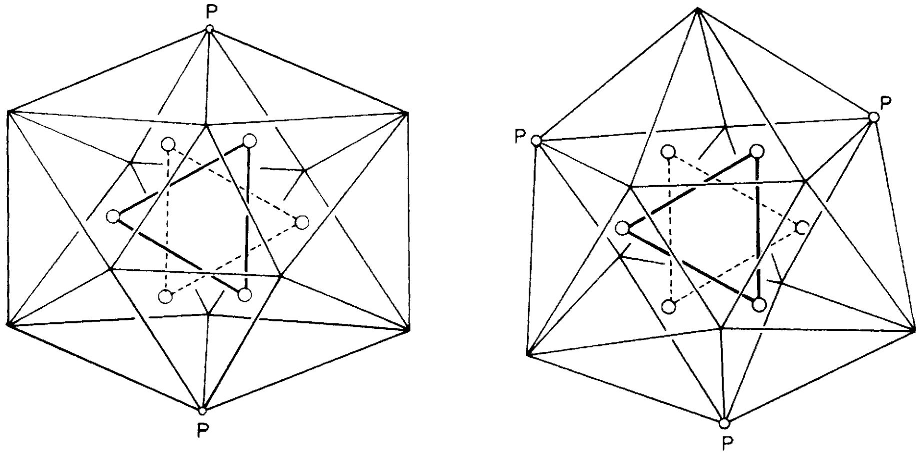
	N = 1	N = 2	N = 3
Ru(N)–Ru(N + 1)	2.860(1)	2.862(2)	2.854(1)
Ru(N)–C(NU)	1.919(5)	1.924(5)	1.917(6)
Ru(N)–C(ND)	1.919(6)	1.911(6)	1.927(6)
Ru(N)–C(NN + 1)	1.881(5)	1.869(5)	1.856(5)
Ru(N)–C(NN – 1)	2.336(2)	2.328(2)	2.327(2)
Ru(N – 1)–Ru(N)–Ru(N + 1)	60.11(4)	59.85(2)	60.05(3)
Ru(N – 1)–Ru(N)–C(NU)	78.1(1)	80.1(1)	76.1(2)
Ru(N – 1)–Ru(N)–C(ND)	94.9(2)	91.4(2)	96.4(2)
Ru(N – 1)–Ru(N)–C(NN + 1)	156.4(1)	158.7(1)	154.4(2)
Ru(N – 1)–Ru(N)–C(NN – 1)	103.63(6)	103.21(5)	104.98(4)
Ru(N + 1)–Ru(N)–C(NU)	93.0(1)	96.2(1)	96.6(2)
Ru(N + 1)–Ru(N)–C(ND)	84.7(2)	80.1(2)	82.8(2)
Ru(N + 1)–Ru(N)–C(NN + 1)	98.3(2)	100.6(2)	98.3(2)
Ru(N + 1)–Ru(N)–C(NN – 1)	162.18(6)	160.56(5)	161.84(7)
C(NU)–Ru(N)–C(ND)	172.9(2)	171.4(2)	171.6(2)
C(NU)–Ru(N)–C(NN – 1)	90.3(2)	89.5(1)	88.9(2)
C(NU)–Ru(N)–C(NN + 1)	95.0(2)	94.9(2)	94.6(3)
C(ND)–Ru(N)–C(NN – 1)	89.9(2)	91.6(2)	89.3(2)
C(ND)–Ru(N)–C(NN + 1)	91.9(2)	93.4(2)	93.8(3)
C(NN – 1)–Ru(N)–C(NN + 1)	98.9(2)	97.4(2)	98.5(2)
Disordered fragment			
Ru(NN + 1)–Ru(NN – 1)	2.858(10)	2.869(10)	2.860(10)
Ru(N)–Ru(NN + 1)	1.652(7)	1.659(7)	1.624(7)
Ru(N)–Ru(NN – 1)	1.662(7)	1.648(7)	1.670(7)
Ru(NN + 1)–P(NN + 1)	2.31(3)	2.51(5)	2.36(4)
Ru(NN – 1)–Ru(NN + 1)–Ru(N + 1 N + 2)	59.9(2)	59.9(2)	60.2(2)

Table 6 (*continued*)

Carbonyl groups	N = 1	N = 2	N = 3
C(NU)–O(NU)	1.133(6)	1.128(6)	1.138(7)
C(ND)–O(ND)	1.135(7)	1.161(7)	1.148(8)
C(NN + 1)–O(NN + 1)	1.137(7)	1.152(6)	1.136(7)
Ru(N)–C(NU)–O(NU)	172.4(4)	172.8(4)	171.5(5)
Ru(N)–C(ND)–O(ND)	173.2(5)	172.0(5)	173.2(5)
Ru(N)–C(NN + 1)–O(NN + 1)	179.5(14)	179.0(7)	176.5(6)



[Ru$_3$(CO)$_{11}${P(C$_6$H$_{11}$)$_3$}] (1)



[Ru$_3$(CO)$_{10}${P(OMe)$_3$}$_2$] (2)

[Ru$_3$(CO)$_9$(PMe$_3$)$_3$] (3)

Figure 4. Idealized ligand polyhedra for the three complexes. The apices of the polyhedra lie at the carbonyl oxygen or ligand phosphorus atoms as appropriate and the location of the Ru$_3$ triangle is displayed. Complex (1) approximates to a cuboctahedron, while (2) and (3) form distorted icosahedra

Table 7. Deviations (Å) of immediately adjoining ' in-plane ' atoms from the Ru plane

	Compound/molecule			
	(1)/1	(1)/2	(2)	(3)
C(12)	−0.05	0.20	−0.72	−0.32
C,P(13)	0.19	−0.14	0.36	0.31
C(21)	0.13	−0.06	0.46	−0.29
C,P(23)	−0.16	0.09	−0.36	0.41
C(31)	0.02	0.03	0.52	−0.46
C(32)	−0.04	−0.12	0.41	0.44

results in the peripheral atom polyhedra of these complexes (Figure 4) moving away from the anti-cuboctahedron found in [Ru$_3$(CO)$_{12}$] towards the icosahedron found for [Fe$_3$(CO)$_{12}$]. This change is not accompanied by the formation of bridging carbonyls, however; instead, as described above, concerted twist distortions about the Ru–Ru bonds occur (Table 7). The fluxional properties of these complexes have not yet been studied; we have earlier suggested [3] that the particular disorder found for (3) may be related to the movement of the Ru$_3$ core within the peripheral atom polyhedron in other complexes, such as [Ru$_3$(CO)$_{11}$(CNBu^t)], which are known to be highly fluxional. In any event, the present determinations have uncovered two more examples of this phenomenon, and suggest that other systems reported as being disordered might be refined using this model.

Acknowledgements

We gratefully acknowledge support of this work by a grant from the Australian Research Grants Committee.

References

1 Part 18, M. I. Bruce, J. G. Matisons, R. C. Wallis, J. M. Patrick, B. W. Skelton, and A. H. White, preceding paper.
2 M. I. Bruce, D. C. Kehoe, J. G. Matisons, B. K. Nicholson, P. H. Rieger, and M. L. Williams, *J. Chem. Soc., Chem. Commun.*, 1982, 442.
3 M. I. Bruce, B. K. Nicholson, and A. H. White, *J. Organomet. Chem.*, 1982, **240**, C33.
4 E. J. Forbes, N. Goodhand, D. L. Jones, and T. A. Hamor, *J. Organomet. Chem.*, 1979, **182**, 143.
5 M. R. Churchill, F. J. Hollander, and J. P. Hutchinson, *Inorg. Chem.*, 1977, **16**, 2655.

Received 30*th December* 1982; *Paper* 2/2191