Crystal and Molecular Structure of Di-μ-carbonyl-{μ-carbonyl-bis[(methyldiphenylphosphine)platino]}dicarbonyl(methyldiphenylphosphine)ruthenium(2*Ru–Pt*)(*Pt–Pt*). A Substituted Heteronuclear Cluster Carbonyl of Unexpected Asymmetry

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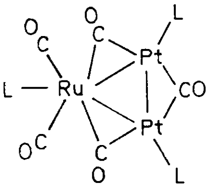
Crystals of the title compound (I) are triclinic, space group $P\bar{1}$, with $Z = 2$ in a unit cell of dimensions: $a = 10.694(3)$, $b = 22.424(7)$, $c = 8.938(2)$ Å, $\alpha = 83.41(2)$, $\beta = 90.02(2)$, $\gamma = 92.42(2)°$. The structure has been elucidated by conventional heavy-atom methods from 5 002 non-zero intensities measured on a diffractometer, and refined to R 0.100. The three metal atoms are bonded to form a triangle which is bridged on all three sides, approximately symmetrically, by carbonyl groups orientated perpendicular to the corresponding metal–metal bond in a coplanar cyclic system. Each Pt atom carries one phosphine ligand with the Pt–P bond in the equatorial plane. The third phosphine is bonded axially to the ruthenium atom and is *trans* to one of the two terminal carbonyl groups also attached to Ru. The equatorial carbonyl group, surprisingly, is not symmetrically placed with respect to the two Ru–Pt bonds, probably for steric reasons; in consequence the two Ru–Pt bond lengths are different [2.707(2) and 2.729(2) Å], the longer bond lying opposite to the larger Pt–Ru–CO angle. Pt–Pt Is 2.647(2), and mean Pt–P 2.262(7) Å.

SUBSTITUTED heteronuclear Ru–Pt cluster carbonyls may be prepared by reaction of low-valent platinum complexes $[Pt(PR_3)_4]$ or $[(Ph_3P)_2Pt(olefin)]$ with $[Ru_3(CO)_{12}]$.[1] Compounds of stoicheiometry $RuPt_2(CO)_5L_3$ ($L = PPh_2Me$) have been shown, from their i.r. and ^1H n.m.r. spectra,[1] to possess the probable structure (I); our X-ray results confirm this overall structure but reveal further that whereas the phosphorus atoms of the ligands attached to the platinum lie in the plane of the metal triangle, that of the ligand attached to ruthenium lies almost perpendicular to this plane.



(I) $L = MePh_2P$

EXPERIMENTAL

Crystals of (I) grow as golden needles along the crystallographic axis c. The one chosen for intensity-data collection was of dimensions 0.04 × 0.07 × 0.19 mm, and was mounted on a Syntex $P2_1$ four-circle autodiffractometer according to methods described earlier.[2] Intensities were collected in the range $3.6° < 2\theta < 45.0°$ with Mo-K_α X-radiation and a graphite monochromator. Scan rates varied from 0.0337 to 0.997° s^{-1} according to the magnitude of the sampled peak count. Six check reflections were remeasured after every 60 intensity measurements and the decay over 152 h crystal-exposure time was 3.5—6.1%; this was not considered sufficient to warrant correction. Reflections for which $I \leqslant 2.5\sigma(I)$ were regarded as unobserved for the purposes of structure solution and preliminary refinement. Of the 5 596 total independent reflections, 3 533 were considered observed and 5 002 had $I > 0$.

Crystal Data.—$C_{44}H_{39}O_5P_3Pt_2Ru$, $M = 1\ 231.5$, Triclinic, $a = 10.694(3)$, $b = 22.424(7)$, $c = 8.938(2)$ Å, $\alpha = 83.41(2)$, $\beta = 90.02(2)$, $\gamma = 92.42(2)°$, $D_m = 1.8(1)$, $Z = 2$, $D_c = 1.93$ g cm^{-3}, $F(000) = 1\ 176$. Space group $P\bar{1}$. Mo-K_α X-radiation (graphite monochromator), $\lambda = 0.71069$ Å; $\mu(\text{Mo-}K_\alpha) = 74.0$ cm^{-1}.

Structure Solution and Refinement.—Solution of the Patterson synthesis revealed the locations of the three metal atoms and the three phosphorus atoms. Isotropic refinement with unit weights gave R 0.169 (R' 0.205), and an electron-density difference synthesis revealed all remaining non-hydrogen atom positions. Further isotropic refinement with unit weights gave R 0.088 (R' 0.105). Anisotropic thermal parameters were then introduced for the three metal atoms only, and hydrogen atoms were incorporated at calculated positions (C–H 0.99 Å, U 0.08 Å^2), but because this gave more variables than the least-squares refinement program could cope with simultaneously, two overlapping blocks were defined: (i) scale factor, all temperature factors, and positional parameters for $M_3P_3O_5$ only, followed by (ii) scale factor, all positional parameters, and thermal parameters for $M_3P_3O_5$ only. This choice of variables was made so as to include all with correlation coefficients >0.1 within the same cycle. Next, anisotropy was allowed for $M_3P_3O_5$ and a non-unit weighting scheme devised: $1/w = a + b|F| + c|F|^2$ with $a = 100$, $b = -1.3$, and $c = 0.0068$. Using observed reflections only, as before, and block refinement, this gave R 0.062 (R' 0.072). This refinement was repeated using all 5 002 reflections having $I > 0$. As expected, this made the agreement indices worse but the standard deviations better (R 0.090, R' 0.090). Finally, because of the high X-ray absorption of the crystal (transmission coefficients varied between 0.55 and 0.75) a correction was applied[3] by use of a grid of 10 × 10 × 20. Refinement to convergence gave, surprisingly, a higher agreement index but with no significant change in structural detail (R 0.100, R' 0.106). The results of this last refinement are those given in Tables 1 and 2. The final difference synthesis showed no electron density >1.4 or <-1.7 eÅ^{-3}, except in the neighbourhood of the metal atoms where maxima of 4.1 and minima of -3.4 eÅ^{-3} were observed. In the final least-squares refinement cycle the mean shift-to-error ratio was 0.01. The atomic scattering factors were the analytic types of ref. 4 for platinum and ruthenium (corrected for anomalous dispersion),[5] carbon,

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[1] M. I. Bruce, G. Shaw, and F. G. A. Stone, *Chem. Comm.*, 1971, 1288; *J.C.S. Dalton*, 1972, 1781.

[2] A. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

[3] P. Coppens and R. F. Stewart, ABSORB, part of ref. 7.

[4] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[5] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

TABLE 1

Atomic positional (fractional co-ordinates) and thermal parameters, with estimated standard deviations in parentheses

Atom	x	y	z	$10^2U/\text{Å}^2$ *
Pt(1)	0.322 03(8)	0.315 58 (4)	0.396 71(10)	†
Pt(2)	0.490 26(8)	0.245 90(4)	0.535 63(10)	†
Ru	0.265 38(16)	0.196 48(9)	0.457 61(20)	†
P(1)	0.2643(6)	0.4043(3)	0.2813(7)	†
P(2)	0.6877(6)	0.2343(3)	0.6271(8)	†
P(3)	0.3519(6)	0.1800(3)	0.2192(7)	†
C(1)	0.4977(30)	0.3389(15)	0.4737(35)	6.6(9)
O(1)	0.5687(24)	0.3788(10)	0.4687(33)	†
C(2)	0.4252(21)	0.1565(11)	0.5796(26)	3.7(5)
O(2)	0.4529(19)	0.1110(7)	0.6279(26)	†
C(3)	0.1642(23)	0.2647(11)	0.3459(27)	4.2(6)
O(3)	0.0625(15)	0.2732(8)	0.2886(20)	†
C(4)	0.1733(25)	0.1218(13)	0.4689(30)	5.1(6)
O(4)	0.1208(24)	0.0764(10)	0.4848(27)	†
C(5)	0.2005(22)	0.2123(10)	0.6500(27)	3.8(5)
O(5)	0.1470(24)	0.2257(12)	0.7504(26)	†
C(10)	0.3599(32)	0.4720(15)	0.3180(38)	7.5(9)
C(20)	0.8085(30)	0.2656(14)	0.4893(36)	6.9(8)
C(30)	0.3925(28)	0.2483(13)	0.0864(33)	6.1(7)
C(11)	0.2694(22)	0.4026(11)	0.0749(27)	4.1(6)
C(111)	0.1737(25)	0.3732(12)	0.0089(30)	5.2(7)
C(112)	0.1848(31)	0.3651(15)	−0.1492(37)	7.2(9)
C(113)	0.2880(27)	0.3847(13)	−0.2251(33)	5.9(7)
C(114)	0.3821(35)	0.4143(17)	−0.1675(42)	8.4(10)
C(115)	0.3696(30)	0.4238(14)	−0.0021(36)	6.8(8)
C(12)	0.1042(22)	0.4273(11)	0.3191(26)	4.0(6)
C(121)	0.0407(26)	0.4034(12)	0.4404(31)	5.4(7)
C(122)	−0.0771(37)	0.4182(18)	0.4736(44)	9.0(11)
C(123)	−0.1346(37)	0.4584(18)	0.3800(44)	9.0(11)
C(124)	−0.0777(37)	0.4871(18)	0.2486(44)	9.0(11)
C(125)	0.0459(33)	0.4709(16)	0.2110(39)	7.8(9)
C(21)	0.7340(23)	0.1582(11)	0.6835(27)	4.3(6)
C(211)	0.8087(22)	0.1296(11)	0.6015(26)	4.0(6)
C(212)	0.8296(29)	0.0690(14)	0.6444(35)	6.5(8)
C(213)	0.7800(28)	0.0374(13)	0.7747(34)	6.2(8)
C(214)	0.6985(25)	0.0683(12)	0.8604(30)	5.0(6)
C(215)	0.6734(28)	0.1263(14)	0.8145(34)	6.4(8)
C(22)	0.7295(22)	0.2716(11)	0.7876(26)	4.0(5)
C(221)	0.6556(31)	0.3145(15)	0.8425(37)	7.1(9)
C(222)	0.6900(41)	0.3426(19)	0.9713(48)	10.1(12)
C(223)	0.8006(38)	0.3295(18)	1.0430(45)	9.3(11)
C(224)	0.8696(37)	0.2861(18)	1.0016(44)	9.0(11)
C(225)	0.8391(28)	0.2578(13)	0.8749(33)	6.1(7)
C(31)	0.4932(21)	0.1383(10)	0.2340(25)	3.7(5)
C(311)	0.6096(31)	0.1662(15)	0.2037(37)	7.1(8)
C(312)	0.7221(32)	0.1311(16)	0.2308(38)	7.6(9)
C(313)	0.7111(33)	0.0746(16)	0.2763(39)	7.7(9)
C(314)	0.5976(28)	0.0443(14)	0.3079(34)	6.3(8)
C(315)	0.4904(27)	0.0789(13)	0.2823(33)	6.0(7)
C(32)	0.2542(21)	0.1361(10)	0.0987(26)	3.8(5)
C(321)	0.3055(25)	0.1064(12)	−0.0137(30)	5.1(6)
C(322)	0.2290(27)	0.0768(13)	−0.1088(32)	5.7(7)
C(323)	0.1001(29)	0.0753(14)	−0.0918(35)	6.6(8)
C(324)	0.0447(32)	0.1054(15)	0.0109(39)	7.6(9)
C(325)	0.1261(29)	0.1367(14)	0.1080(35)	6.5(8)

* $B = 8\pi^2U$. † Anisotropic thermal parameters in the form: $\exp\{-2\pi^2[U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl]\}$, with parameters $(\times 10^2)$:

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt(1)	3.21(5)	4.49(6)	3.60(5)	0.62(4)	−0.58(4)	−0.58(4)
Pt(2)	2.86(5)	4.99(6)	3.77(6)	0.49(4)	−0.84(4)	−0.47(4)
Ru	2.55(9)	4.51(12)	3.20(10)	0.28(8)	−0.08(8)	−0.73(8)
P(1)	4.0(4)	4.2(4)	4.3(4)	0.5(3)	−0.8(3)	−0.2(3)
P(2)	3.2(3)	6.3(4)	4.2(4)	0.4(3)	−0.3(3)	−0.3(3)
P(3)	3.2(3)	4.4(4)	3.8(3)	0.7(3)	−0.2(3)	−0.9(3)
O(1)	9.1(17)	5.6(14)	15.9(25)	−3.6(12)	−6.2(17)	2.4(15)
O(2)	7.2(13)	2.1(9)	11.6(17)	1.4(9)	−4.2(12)	1.2(10)
O(3)	3.3(9)	6.7(12)	6.5(12)	0.6(8)	−4.1(9)	−0.3(9)
O(4)	10.8(18)	5.5(13)	9.4(17)	−2.1(12)	4.8(14)	−0.4(12)
O(5)	10.5(19)	11.3(20)	7.3(15)	2.2(15)	4.6(14)	−1.8(14)

TABLE 2

Bond lengths (Å) and angles (°)

(*a*) Distances

(i) Metal carbonyl framework

Pt(1)–Pt(2)	2.647(2)
Pt(1)–Ru	2.707(2)
Pt(2)–Ru	2.729(2)
Pt(1)–C(1)	2.07(3)
Pt(2)–C(1)	2.09(3)
C(1)–O(1)	1.14(4)
Pt(1)–C(3)	2.08(2)
Ru–C(3)	2.07(2)
C(3)–O(3)	1.21(3)
Pt(2)–C(2)	2.09(2)
Ru–C(2)	2.19(2)
C(2)–O(2)	1.11(3)
Ru–C(4)	1.90(3)
C(4)–O(4)	1.14(3)
Ru–C(5)	1.93(2)
C(5)–O(5)	1.14(3)

(ii) Methyldiphenylphosphine ligands

Pt(1)–P(1)	2.24(1)
P(1)–C(10)	1.85(3)
P(1)–C(11)	1.85(2)
P(1)–C(12)	1.85(2)
C(11)–C(111)	1.36(4)
C(111)–C(112)	1.45(4)
C(112)–C(113)	1.33(4)
C(113)–C(114)	1.32(5)
C(114)–C(115)	1.52(5)
C(115)–C(11)	1.32(4)
C(12)–C(121)	1.33(3)
C(121)–C(122)	1.36(5)
C(122)–C(123)	1.33(5)
C(123)–C(124)	1.40(5)
C(124)–C(125)	1.43(5)
C(125)–C(12)	1.45(4)
Pt(2)–P(2)	2.28(1)
P(2)–C(20)	1.84(3)
P(2)–C(21)	1.81(2)
P(2)–C(22)	1.79(3)
C(21)–C(211)	1.32(4)
C(211)–C(212)	1.40(4)
C(212)–C(213)	1.39(4)
C(213)–C(214)	1.41(4)
C(214)–C(215)	1.36(4)
C(215)–C(21)	1.44(4)
C(22)–C(221)	1.40(4)
C(221)–C(222)	1.41(6)
C(222)–C(223)	1.37(6)
C(223)–C(224)	1.33(6)
C(224)–C(225)	1.39(5)
C(225)–C(22)	1.43(4)
Ru–P(3)	2.40(1)
P(3)–C(30)	1.86(3)
P(3)–C(31)	1.81(2)
P(3)–C(32)	1.84(2)
C(31)–C(311)	1.38(4)
C(311)–C(312)	1.47(5)
C(312)–C(313)	1.29(5)
C(313)–C(314)	1.38(5)
C(314)–C(315)	1.41(4)
C(315)–C(31)	1.35(4)
C(32)–C(321)	1.39(4)
C(321)–C(322)	1.38(4)
C(322)–C(323)	1.39(4)
C(323)–C(324)	1.35(5)
C(324)–C(325)	1.45(5)
C(325)–C(32)	1.37(4)

(*b*) Angles

(i) Metal carbonyl framework

Pt(1)–Pt(2)–Ru	60.45(5)
Pt(2)–Pt(1)–Ru	61.27(5)
Pt(1)–Ru–Pt(2)	58.28(5)
Pt(2)–Pt(1)–C(1)	51.0(9)
Pt(1)–Pt(2)–C(1)	50.1(9)
Pt(1)–C(1)–Pt(2)	79.0(11)
Pt(1)–C(1)–O(1)	141.1(26)
Pt(2)–C(1)–O(1)	139.1(26)
C(1)–Pt(1)–P(1)	100.9(9)
P(1)–Pt(1)–C(3)	97.7(7)
Pt(1)–C(3)–O(3)	137.7(19)
Ru–C(3)–O(3)	140.7(19)
Ru–C(3)–Pt(1)	81.4(9)
Ru–Pt(1)–C(3)	49.2(7)
Pt(1)–Ru–C(3)	49.4(7)
Ru–C(2)–Pt(2)	79.1(8)
Ru–Pt(2)–C(2)	52.2(6)
Pt(2)–Ru–C(2)	48.7(6)
Pt(2)–C(2)–O(2)	143.1(20)
Ru–C(2)–O(2)	137.6(20)
C(1)–Pt(2)–P(2)	99.6(9)
P(2)–Pt(2)–C(2)	97.9(7)
C(2)–Ru–P(3)	91.9(6)
Pt(2)–Ru–P(3)	89.8(2)
Pt(1)–Ru–P(3)	90.0(2)
C(3)–Ru–P(3)	88.3(7)
C(3)–Ru–C(4)	110.8(11)
C(2)–Ru–C(4)	92.8(10)
C(3)–Ru–C(5)	91.4(10)
C(2)–Ru–C(5)	87.5(9)
C(4)–Ru–C(5)	91.5(11)
P(3)–Ru–C(5)	177.8(7)
P(3)–Ru–C(4)	90.7(9)
Ru–C(4)–O(4)	175.7(25)
Ru–C(5)–O(5)	169.0(22)

(ii) Methyldiphenylphosphine ligands

Pt(1)–P(1)–C(10)	117.2(11)
Pt(1)–P(1)–C(11)	109.2(8)
Pt(1)–P(1)–C(12)	117.3(7)
C(10)–P(1)–C(11)	105.8(13)
C(10)–P(1)–C(12)	101.6(14)
C(11)–P(1)–C(12)	104.4(11)
Pt(2)–P(2)–C(20)	112.3(10)
Pt(2)–P(2)–C(21)	117.2(8)
Pt(2)–P(2)–C(22)	117.2(8)
C(20)–P(2)–C(21)	104.2(13)
C(20)–P(2)–C(22)	101.6(13)
C(21)–P(2)–C(22)	102.5(11)
Ru–P(3)–C(30)	116.4(10)
Ru–P(3)–C(31)	113.8(8)
Ru–P(3)–C(32)	117.0(8)
C(30)–P(3)–C(31)	104.8(12)
C(30)–P(3)–C(32)	101.1(12)
C(31)–P(3)–C(32)	101.8(11)

(*c*) Contact distances

C(10) · · · C(115)	3.17(5)
C(10) · · · H(115)	2.69
C(10) · · · C(125)	3.49(5)
C(20) · · · C(211)	3.10(4)
C(20) · · · H(211)	2.61
C(20) · · · C(225)	3.45(4)
C(30) · · · C(311)	3.13(4)
C(30) · · · H(311)	2.66
C(30) · · · C(321)	3.49(4)
C(11) · · · C(125)	3.21(4)
C(111) · · · C(125)	3.33(5)
C(111) · · · C(12)	3.25(4)
C(21) · · · C(225)	3.14(4)
C(215) · · · C(22)	3.27(4)
C(31) · · · C(321)	3.11(4)
C(315) · · · C(321)	3.32(4)
C(315) · · · C(32)	3.24(4)
C(211) · · · C(312)	3.43(4)
C(211) · · · C(313)	3.43(4)
O(1) · · · C(10)	3.30(4)
C(2) · · · C(31)	3.25(3)
O(2) · · · C(21)	3.20(3)
O(2) · · · C(215)	2.92(4)
C(4) · · · C(325)	3.24(4)

TABLE 2 (*Continued*)

C(4) ··· H(325)	2.76	C(221) ··· C(30$^{\text{III}}$)	3.71(4)
C(4) ··· C(32)	3.40(4)	Pt(1) ··· H(113$^{\text{III}}$)	2.94
Pt(1) ··· C(30)	3.40(3)	C(10) ··· H(114$^{\text{IV}}$)	2.93
O(3) ··· H(224$^{\text{I}}$)	2.39	O(2) ··· H(314$^{\text{V}}$)	2.52
C(20) ··· O(3$^{\text{II}}$)	3.24(4)	C(112) ··· H(124$^{\text{VI}}$)	2.72
C(20) ··· C(122$^{\text{II}}$)	3.57(5)	C(112) ··· C(124$^{\text{VI}}$)	3.57(5)

Roman superscripts refer to the following symmetry operations:

I $x - 1, y, z - 1$	IV $1 - x, 1 - y, \bar{z}$
II $x + 1, y, z$	V $1 - x, \bar{y}, 1 - z$
III $x, y, z + 1$	VI $\bar{x}, 1 - y, \bar{z}$

oxygen, and phosphorus, and those of ref. 6 for hydrogen. All computational work was carried out (on the CDC 7 600 of the University of London) with the '*X*-Ray System' of programs.[7] Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21276 (28 pp., 1 microfiche).*

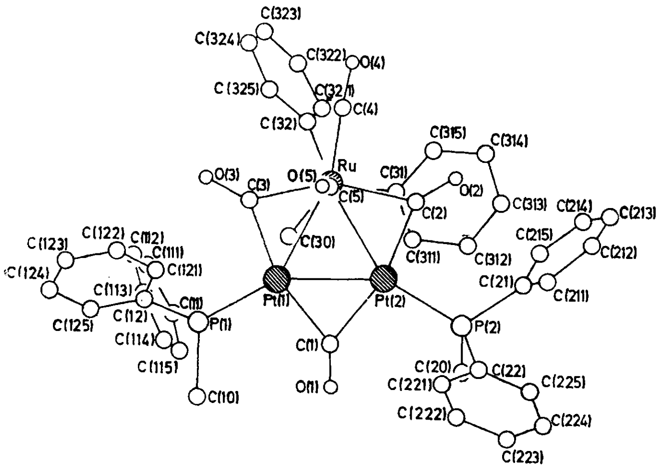

FIGURE 1 The molecular structure viewed perpendicular to the plane of the metal-atom ring showing the atom numbering system used. Phosphorus P(3) of the third phosphine ligand is obscured by ruthenium

RESULTS AND DISCUSSION

The overall configuration of (I) is shown in Figure 1 and the contents of a unit cell in Figure 2. The central framework, comprising the three metal atoms, the three bridging carbonyl groups, one terminal carbonyl group on the ruthenium, and the phosphorus atoms on each of the platinum atoms, is substantially planar (Table 3). The remaining two ligands (phosphine and terminal carbonyl) are both attached to ruthenium and lie mutually *trans* in a direction approximately perpendicular to the plane of the $RuPt_2$ ring. The skeleton of the molecule thus possesses an approximate mirror plane perpendicular to the $RuPt_2$ plane passing through the Ru atom and the midpoint of the Pt–Pt bond.

Inspection of the detailed molecular geometry (Table 2), however, reveals some anomalous features. First, the two Ru–Pt bond lengths differ by some 10σ [Ru–Pt(1) 2.707(2), Ru–Pt(2) 2.729(2) Å], and concomitantly the carbonyls which bridge these bonds have different Ru–C distances [Ru–C(2) 2.195(23), Ru–C(3) 2.072(24) Å]; secondly, the equatorial terminal carbonyl group on ruthenium does not lie in the (approximate) mirror plane but is displaced towards Pt(2) until C(3)–Ru–C(4) has enlarged to 110.8(11) and C(4)–Ru–C(2) shrunk to 92.8(10)°. While we can 'explain' these differences only tentatively we can at least put them into the perspective of the bonding situation in this metal cluster.

TABLE 3

Equations of some least-squares planes;* distances (Å) of relevant atoms from these planes are given in square brackets

Plane (1): Pt(1), Pt(2), Ru, P(1), P(2), C(1)—(4), O(1)—(4)

$$-4.156x + 6.607y + 8.082z = 3.901$$

[Pt(1) 0.053, Pt(2) 0.016, Ru −0.007, P(1) −0.054, P(2) −0.143, C(1) 0.099, O(1) 0.027, C(2) 0.051, O(2) 0.025, C(3) −0.039, O(3) −0.023, C(4) −0.026, O(4) 0.021]

Plane (2): Pt(1), Pt(2), Ru

$$-4.163x + 6.129y + 8.115z = 3.813$$

[P(1) −0.153, P(2) −0.151, C(1) 0.037, O(1) −0.055, C(2) 0.079, O(2) 0.077, C(3) −0.068, O(3) −0.057, C(4) 0.018, O(4) 0.087]

* In the form $Ax + By + Cz = D$ where x, y, and z are fractional co-ordinates.

If the central bonding is regarded as multicentred and delocalised, the oxidation states of all the metal atoms as zero, and the valence orientations trigonal for platinum and trigonal bipyramidal for ruthenium, the main orbital interactions will then take place near the centres of the triangles formed by the carbonyl bridges and the metal–metal bonds. The bonding around the Ru atom can be described as somewhat distorted away from the ideal trigonal bipyramid with its equal equatorial angles towards square pyramidal.

In many compounds of type MX_2Y_3 (X axial, Y equatorial) it is found that two of the M–Y bonds are equal in length but enclose an angle >120°, while the third M–Y bond is longer.[8-11] The distortions in $[RuPt_2(CO)_5(PPh_2Me)_3]$ fit in well with this picture: the largest equatorial interligand angle [C(3)–Ru–C(4)] lies opposite to the longest bond, in the sense that such lengthening must affect both Ru–Pt(2) and Ru–C(2) because of the multicentred delocalised nature of the bonding.

The reasons for the asymmetric disposition of the equatorial Ru–CO group [C(4)–O(4)] are probably steric (Table 2) and arise because of severe restraints imposed on the ligands of the phosphorus P(3) *cis* to C(4)–O(4) on the same ruthenium. The position of C(4) is deter-

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

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mined by its distances from C(325) and H(325), both of which are notably short. This distance cannot be decreased (which would make the position of the carbonyl group more symmetrical) without simultaneously decreasing the C(321)–C(31) distance which is already short. Moreover, C(31) is directly bonded to P(3), and therefore rather rigidly held. There are also many other short interligand contacts among the phosphine ligands, leaving little flexibility (in particular in the positioning of the phenyl rings). It is not clear, however, why the phosphine on the ruthenium adopts an axial rather than an equatorial site, unless the mechanism of formation of the molecule predetermines this stereochemistry. The geometry of the rest of the molecule calls for little comment. The Pt–Pt distance [2.647(2) Å] lies in the expected range,[12-15] but is notably shorter than the means (2.79 and 2.75 Å) determined[16] for the two types of carbonyl-bridged Pt–Pt bonds in the 'butterfly' molecule [$Pt_4(\mu_2\text{-}CO)_5(PPhMe_2)_4$]. In (I) the mean C–O bond lengths for the terminal and bridging carbonyl groups do not differ significantly [overall mean C–O 1.15(4) Å] while the Pt–C (bridging carbonyl) distance is almost the same whether the other metal is Ru or Pt [overall mean 2.08(3) Å]; in each bridge the carbonyl group lies perpendicular to the corresponding metal–metal bond. The Pt–P distances are normal [mean 2.262(7) Å], but for all the phosphines the L–P–L angles tend to be less than, and the M–P–L angles greater than, the ideal tetrahedral value. This is readily understood on the basis of electronegativity effects, which will tend to concentrate electron density nearer to phosphorus in the M–P bonds and nearer to carbon in the P–C bonds. The few fairly short interligand contacts (Table 2) explain any departures from this pattern.

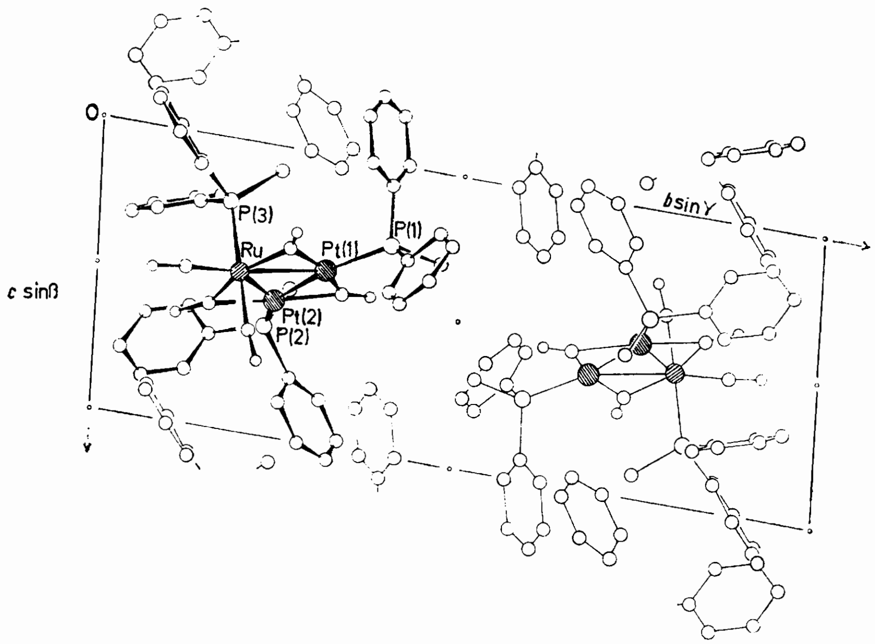

FIGURE 2 The contents of the triclinic unit cell viewed in projection down *a*, looking away from the origin (note that the projection given in Figure 1 is of the right-hand molecule of this diagram).

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