C(42)	0.4199	0.6288	0.9674	0.061 (2)
C(43)	0.4296	0.7406	0.9353	0.061 (2)
C(44)	0.3886	0.7568	0.8616	0.052 (2)
C(45)	0.3380	0.6612	0.8199	0.047 (2)
C(46)	0.3283	0.5494	0.8519	0.036 (2)
C(51)	0.3329 (4)	0.3984 (6)	0.6342 (3)	0.065 (3)
C(52)	0.2521 (5)	0.3872 (6)	0.5767 (3)	0.075 (3)
C(53)	0.2063 (4)	0.5005 (6)	0.5673 (3)	0.064 (2)
C(54)	0.2579 (4)	0.5805 (5)	0.6213 (3)	0.058 (2)
C(55)	0.3349 (4)	0.5200 (5)	0.6619 (3)	0.058 (2)

Table 2. *Geometric parameters* (Å, °)

Ru(1)—Cl(1)	2.452 (2)	Ru(1)—P(1)	2.275 (2)
Ru(1)—P(2)	2.282 (2)	Ru(1)—C(51)	2.223 (8)
Ru(1)—C(52)	2.227 (8)	Ru(1)—C(53)	2.224 (6)
Ru(1)—C(54)	2.161 (6)	Ru(1)—C(55)	2.167 (6)
Cl(2)—C(3)	1.737 (6)	Cl(3)—C(3)	1.737 (7)
Cl(4)—C(3)	1.711 (8)	P(1)—C(1)	1.834 (6)
P(1)—C(36)	1.827 (4)	P(1)—C(46)	1.839 (3)
P(2)—C(2)	1.856 (5)	P(2)—C(16)	1.832 (3)
P(2)—C(26)	1.850 (3)	C(1)—C(2)	1.525 (7)
C(51)—C(52)	1.398 (9)	C(51)—C(55)	1.421 (9)
C(52)—C(53)	1.399 (10)	C(53)—C(54)	1.404 (8)
C(54)—C(55)	1.372 (8)		
Cl(1)—Ru(1)—P(1)	83.0 (1)	Cl(1)—Ru(1)—P(2)	93.3 (1)
P(1)—Ru(1)—P(2)	83.5 (1)	Cl(1)—Ru(1)—C(51)	101.2 (2)
P(1)—Ru(1)—C(51)	112.7 (2)	P(2)—Ru(1)—C(51)	159.3 (2)
Cl(1)—Ru(1)—C(52)	92.9 (2)	P(1)—Ru(1)—C(52)	147.7 (2)
P(2)—Ru(1)—C(52)	128.8 (2)	C(51)—Ru(1)—C(52)	36.6 (2)
Cl(1)—Ru(1)—C(53)	118.6 (2)	P(1)—Ru(1)—C(53)	158.0 (2)
P(2)—Ru(1)—C(53)	98.6 (2)	C(51)—Ru(1)—C(53)	61.4 (2)
C(52)—Ru(1)—C(53)	36.6 (2)	Cl(1)—Ru(1)—C(54)	154.3 (2)
P(1)—Ru(1)—C(54)	120.7 (1)	P(2)—Ru(1)—C(54)	98.9 (2)
C(51)—Ru(1)—C(54)	62.1 (2)	C(52)—Ru(1)—C(54)	61.9 (2)
C(53)—Ru(1)—C(54)	37.3 (2)	Cl(1)—Ru(1)—C(55)	136.8 (2)
P(1)—Ru(1)—C(55)	99.9 (2)	P(2)—Ru(1)—C(55)	129.9 (2)
C(51)—Ru(1)—C(55)	37.7 (2)	C(52)—Ru(1)—C(55)	62.1 (3)
C(53)—Ru(1)—C(55)	61.9 (2)	C(54)—Ru(1)—C(55)	37.0 (2)
Ru(1)—P(1)—C(1)	108.3 (2)	Ru(1)—P(1)—C(36)	117.7 (1)
C(1)—P(1)—C(36)	106.2 (2)	Ru(1)—P(1)—C(46)	120.7 (1)
C(1)—P(1)—C(46)	102.3 (2)	C(36)—P(1)—C(46)	99.8 (1)
Ru(1)—P(2)—C(2)	109.6 (2)	Ru(1)—P(2)—C(16)	119.7 (1)
C(2)—P(2)—C(16)	104.2 (2)	Ru(1)—P(2)—C(26)	116.5 (1)
C(2)—P(2)—C(26)	104.2 (2)	C(16)—P(2)—C(26)	101.0 (1)
P(1)—C(1)—C(2)	106.4 (4)	P(2)—C(2)—C(1)	108.8 (4)
Cl(2)—C(3)—Cl(3)	109.8 (4)	Cl(2)—C(3)—Cl(4)	111.1 (4)
Cl(3)—C(3)—Cl(4)	111.3 (4)	P(2)—C(16)—C(11)	120.8 (1)
P(2)—C(16)—C(15)	119.2 (1)	P(2)—C(26)—C(21)	119.4 (1)
P(2)—C(26)—C(25)	120.5 (1)	P(1)—C(36)—C(31)	124.3 (1)
P(1)—C(36)—C(35)	115.7 (1)	P(1)—C(46)—C(41)	119.6 (1)
P(1)—C(46)—C(45)	120.4 (1)	Ru(1)—C(51)—C(52)	71.9 (5)
Ru(1)—C(51)—C(55)	69.0 (4)	C(52)—C(51)—C(55)	107.0 (5)
Ru(1)—C(52)—C(51)	71.5 (4)	Ru(1)—C(52)—C(53)	71.5 (4)
C(51)—C(52)—C(53)	108.5 (5)	Ru(1)—C(53)—C(52)	71.8 (4)
Ru(1)—C(53)—C(54)	68.9 (3)	C(52)—C(53)—C(54)	107.3 (5)
Ru(1)—C(54)—C(53)	73.8 (4)	Ru(1)—C(54)—C(55)	71.8 (4)
C(53)—C(54)—C(55)	108.9 (5)	Ru(1)—C(55)—C(51)	73.3 (4)
Ru(1)—C(55)—C(54)	71.3 (4)	C(51)—C(55)—C(54)	108.2 (5)

Phenyl rings were refined as rigid groups using H atoms placed in idealized postions with fixed isotropic $U = 0.08$ Å^2. The $\bar{1}11$ reflection suffered from extinction and was therefore omitted during the refinement process. All structure calculations were performed with the *SHELXTL-Plus* system (Sheldrick, 1990).

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Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71065 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1036]

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A New Polymorph of Tetraruthenium Tridecacarbonyl Dihydride

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Abstract

The tetranuclear ruthenium carbonyl hydride cluster, di-μ-carbonyl-undecacarbonyl-di-μ-hydrido-*tetrahedro*-tetraruthenium(6 *Ru—Ru*), crystallizes in a monoclinic cell with two crystallographically independent $H_2Ru_4(CO)_{13}$ molecules, each with a tetrahedral array of Ru atoms as also previously found in two earlier polymorphs. Two of the Ru—Ru vectors [Ru(2)—Ru(3) 2.790 (1), Ru(2′)—Ru(3′) 2.778 (1) Å and Ru(3)—Ru(4) 2.782 (2), Ru(3′)—Ru(4′) 2.817 (1) Å] are unsymmetrically bridged by carbonyl ligands. The fourth Ru atom, Ru(1), caps the basal plane of Ru(2), Ru(3) and Ru(4) and is unique in that it carries three terminal carbonyl ligands, only.

Comment

This compound is the third reported polymorph of $H_2Ru_4(CO)_{13}$. A monoclinic form was reported by

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Yawney & Doedens (1972) and a triclinic form was reported by Rheingold, Haggerty, Geoffroy & Han (1990). Except for differences in the bent semi-bridged carbonyl ligands, the two molecules of the new polymorph are very similar to the previous polymorphs. These two molecules exhibit a wide range of bent semi-bridged metal–carbonyl bond parameters. The θ and ψ parameters for the four semi-bridging CO ligands in this structure obey the Crabtree–Lavin (Crabtree & Lavin, 1986) empirical equation $\theta = n\psi + m$ with $n = 1.52$ and $m = 64.3$. The two bridging hydride ligands were not located but their location can be expected along the longest Ru—Ru edges. The presently reported polymorph has been observed previously in related structures: $[H_2RuOs_3(CO)_{13}]$ (Rheingold, Gates, Scott & Budge, 1987), $[H_2Os_3Fe(CO)_{13}]$ (Churchill, Bueno, Hsu, Plotkin & Shore, 1982), $[H_2FeRu_3(CO)_{13}]$ (Gilmore & Woodward, 1971) and $[H_2FeRu_3(CO)_{13}]$ (Hsu, Bhattacharyya & Shore, 1984).

The extensive polymorphism may be attributed to the low molecular polarity and approximately spherical van der Waals exterior for the title molecule (and its many analogues), thus encouraging a multitude of packing arrangements of similar energies.

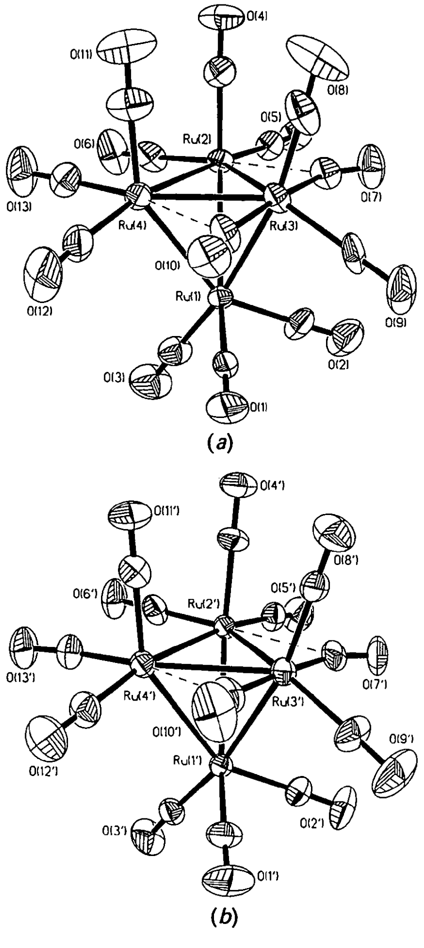

Fig. 1. Thermal ellipsoid diagrams for (*a*) molecule *A* and (*b*) molecule *B*, drawn with 40% probability ellipsoids.

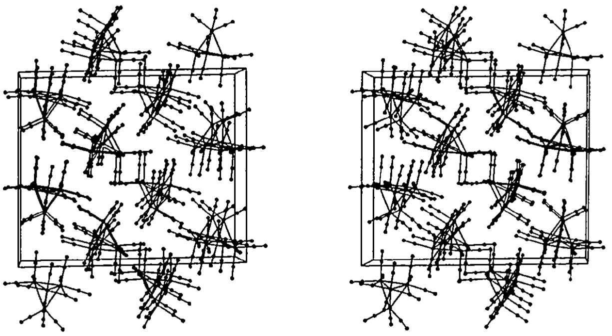

Fig. 2. Unit-cell packing diagram as viewed down the *b* axis.

Experimental

Crystal data

$[Ru_4H_2(CO)_{13}]$
$M_r = 770.5$
Monoclinic
$P2_1/c$
$a = 23.125\ (7)$ Å
$b = 9.131\ (2)$ Å
$c = 19.360\ (5)$ Å
$\beta = 91.01\ (3)°$
$V = 4087.3\ (20)$ Å^3
$Z = 8$
$D_x = 2.504$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Cell parameters from 25 reflections
$\theta = 12$–$12.5°$
$\mu = 2.962$ mm^{-1}
$T = 296$ K
Cube
0.42 × 0.40 × 0.36 mm
Dark red
Crystal source: recrystallization from dichloromethane/hexane mixture

Data collection

Siemens *P*4 diffractometer
Wyckoff ω scans
Absorption correction: empirical (ψ scan)
$T_{\min} = 0.130$, $T_{\max} = 0.206$
7780 measured reflections
7042 independent reflections
4937 observed reflections $[F_o > 4.0\sigma(F_o)]$

$R_{\rm int} = 0.056$
$\theta_{\max} = 25°$
$h = -27 \rightarrow 27$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 22$
3 standard reflections monitored every 197 reflections intensity variation: <2%

Refinement

Refinement on *F*
Final $R = 0.056$
$wR = 0.0635$
$S = 1.44$
4937 reflections
541 parameters
$w = [\sigma^2(F_o) + 0.0007F_o^2]^{-1}$
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.89$ e Å^{-3}
$\Delta\rho_{\min} = -1.06$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99, 149)

Computer program(s) used: *SHELXTL-Plus* (Sheldrick, 1990).

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Molecule *A*				
Ru(1)	0.4430 (1)	0.2752 (1)	0.4211 (1)	0.040 (1)
Ru(2)	0.3668 (1)	0.5154 (1)	0.3757 (1)	0.041 (1)
Ru(3)	0.3245 (1)	0.2375 (1)	0.4070 (1)	0.044 (1)
Ru(4)	0.3850 (1)	0.2773 (1)	0.2855 (1)	0.044 (1)
O(1)	0.4594 (5)	−0.0551 (9)	0.4316 (6)	0.081 (4)
O(2)	0.4354 (6)	0.3044 (13)	0.5748 (5)	0.108 (6)
O(3)	0.5712 (5)	0.3453 (14)	0.4177 (7)	0.107 (6)
O(4)	0.2545 (5)	0.5937 (13)	0.3040 (6)	0.096 (5)
O(5)	0.3538 (5)	0.7706 (9)	0.4762 (5)	0.078 (4)
O(6)	0.4416 (6)	0.7092 (11)	0.2880 (7)	0.104 (5)
O(7)	0.2986 (5)	0.4618 (10)	0.5179 (5)	0.081 (4)
O(8)	0.1974 (5)	0.2335 (13)	0.3632 (9)	0.127 (7)
O(9)	0.3180 (6)	0.0573 (12)	0.5378 (6)	0.115 (6)
O(10)	0.3390 (4)	−0.0547 (8)	0.3312 (5)	0.074 (4)
O(11)	0.2730 (5)	0.3171 (13)	0.2025 (7)	0.114 (6)
O(12)	0.4270 (7)	0.0068 (12)	0.2101 (6)	0.132 (7)
O(13)	0.4499 (6)	0.4697 (12)	0.1849 (6)	0.108 (6)
C(1)	0.4533 (5)	0.0700 (14)	0.4286 (6)	0.046 (4)
C(2)	0.4392 (7)	0.2928 (14)	0.5178 (6)	0.065 (5)
C(3)	0.5240 (6)	0.3207 (16)	0.4182 (8)	0.068 (5)
C(4)	0.2966 (7)	0.5637 (14)	0.3295 (7)	0.063 (5)
C(5)	0.3595 (6)	0.6754 (12)	0.4407 (6)	0.053 (4)
C(6)	0.4144 (6)	0.6312 (12)	0.3194 (8)	0.060 (5)
C(7)	0.3146 (6)	0.4095 (12)	0.4683 (7)	0.056 (5)
C(8)	0.2451 (7)	0.2365 (14)	0.3807 (9)	0.073 (6)
C(9)	0.3193 (6)	0.1224 (13)	0.4876 (8)	0.068 (5)
C(10)	0.3400 (6)	0.0668 (14)	0.3521 (7)	0.063 (5)
C(11)	0.3150 (7)	0.3001 (14)	0.2323 (8)	0.076 (6)
C(12)	0.4114 (7)	0.1072 (16)	0.2359 (8)	0.078 (6)
C(13)	0.4255 (7)	0.4029 (15)	0.2241 (7)	0.066 (5)
Molecule *B*				
Ru(1′)	0.1147 (1)	0.7471 (1)	0.2261 (1)	0.035 (1)
Ru(2′)	0.1900 (1)	0.6905 (1)	0.1080 (1)	0.038 (1)
Ru(3′)	0.1278 (1)	0.9492 (1)	0.1203 (1)	0.044 (1)
Ru(4′)	0.0693 (1)	0.6875 (1)	0.0868 (1)	0.040 (1)
O(1′)	0.0120 (5)	0.9147 (14)	0.2812 (6)	0.101 (5)
O(2′)	0.1977 (5)	0.9109 (10)	0.3222 (5)	0.087 (4)
O(3′)	0.1080 (5)	0.4836 (10)	0.3239 (6)	0.083 (4)
O(4′)	0.2161 (5)	0.7632 (12)	−0.0408 (5)	0.083 (4)
O(5′)	0.3156 (4)	0.6769 (13)	0.1570 (6)	0.086 (5)
O(6′)	0.1926 (4)	0.3642 (10)	0.0796 (6)	0.081 (4)
O(7′)	0.2526 (4)	0.9924 (9)	0.1688 (6)	0.075 (4)
O(8′)	0.1518 (5)	1.1023 (12)	−0.0158 (6)	0.096 (5)
O(9′)	0.1125 (7)	1.2110 (12)	0.2130 (6)	0.119 (6)
O(10′)	−0.0006 (5)	1.0045 (11)	0.0890 (8)	0.109 (6)
O(11′)	0.0796 (5)	0.7256 (12)	−0.0673 (5)	0.079 (4)
O(12′)	−0.0613 (4)	0.6837 (14)	0.0925 (6)	0.099 (5)
O(13′)	0.0629 (5)	0.3559 (10)	0.0723 (6)	0.081 (4)
C(1′)	0.0500 (6)	0.8497 (15)	0.2599 (7)	0.064 (5)
C(2′)	0.1672 (5)	0.8495 (12)	0.2859 (6)	0.048 (4)
C(3′)	0.1091 (5)	0.5776 (13)	0.2873 (7)	0.052 (4)
C(4′)	0.2057 (6)	0.7362 (14)	0.0144 (7)	0.055 (5)
C(5′)	0.2691 (5)	0.6859 (13)	0.1364 (7)	0.052 (4)
C(6′)	0.1903 (5)	0.4895 (14)	0.0906 (7)	0.057 (5)
C(7′)	0.2101 (6)	0.9453 (12)	0.1470 (7)	0.056 (5)
C(8′)	0.1427 (7)	1.0455 (12)	0.0353 (7)	0.061 (5)
C(9′)	0.1177 (7)	1.1150 (13)	0.1770 (7)	0.075 (6)
C(10′)	0.0452 (7)	0.9515 (15)	0.0997 (7)	0.071 (6)
C(11′)	0.0753 (6)	0.7125 (13)	−0.0105 (7)	0.054 (5)
C(12′)	−0.0127 (5)	0.6892 (16)	0.0901 (7)	0.062 (5)
C(13′)	0.0687 (5)	0.4831 (13)	0.0773 (7)	0.052 (4)

Table 2. *Bond lengths* (Å) *and angles* (°)

	Molecule *A*	Molecule *B*
Ru(1)—Ru(2)	2.938 (1)	2.944 (1)
Ru(1)—Ru(3)	2.772 (2)	2.778 (1)
Ru(1)—Ru(4)	2.928 (2)	2.928 (1)
Ru(1)—C(1)	1.894 (13)	1.892 (14)
Ru(1)—C(2)	1.881 (13)	1.907 (12)
Ru(1)—C(3)	1.919 (14)	1.955 (12)
Ru(2)—Ru(3)	2.790 (1)	2.778 (1)
Ru(2)—Ru(4)	2.825 (1)	2.814 (1)
Ru(2)—C(4)	1.893 (15)	1.900 (13)
Ru(2)—C(5)	1.937 (12)	1.903 (12)
Ru(2)—C(6)	1.887 (13)	1.865 (13)
Ru(2)—C(7)	2.383 (13)	2.488 (14)
Ru(3)—Ru(4)	2.782 (2)	2.817 (1)
Ru(3)—C(7)	1.983 (12)	1.964 (14)
Ru(3)—C(8)	1.896 (15)	1.902 (13)
Ru(3)—C(9)	1.888 (14)	1.887 (13)
Ru(3)—C(10)	1.924 (14)	1.945 (16)
Ru(4)—C(10)	2.548 (14)	2.488 (14)
Ru(4)—C(11)	1.914 (16)	1.905 (13)
Ru(4)—C(12)	1.931 (15)	1.898 (13)
Ru(4)—C(13)	1.909 (14)	1.875 (12)
O(1)—C(1)	1.152 (15)	1.143 (18)
O(2)—C(2)	1.115 (17)	1.135 (16)
O(3)—C(3)	1.115 (18)	1.114 (16)
O(4)—C(4)	1.118 (18)	1.128 (16)
O(5)—C(5)	1.118 (15)	1.144 (16)
O(6)—C(6)	1.134 (17)	1.165 (16)
O(7)—C(7)	1.141 (17)	1.146 (17)
O(8)—C(8)	1.147 (19)	1.141 (17)
O(9)—C(9)	1.139 (18)	1.126 (17)
O(10)—C(10)	1.181 (16)	1.179 (19)
O(11)—C(11)	1.131 (21)	1.113 (16)
O(12)—C(12)	1.108 (19)	1.126 (16)
O(13)—C(13)	1.132 (19)	1.173 (15)
Ru—Ru—Ru (av.)	60 ± 4	60 ± 4
Ru—C—O(term.) (av.)	177 ± 2	176 ± 4
Ru(2)—Ru(1)—C(1)	146.6 (3)	146.9 (4)
Ru(3)—Ru(1)—C(1)	90.4 (4)	91.4 (4)
Ru(4)—Ru(1)—C(1)	97.5 (3)	97.9 (4)
Ru(2)—Ru(1)—C(2)	101.3 (4)	100.3 (4)
Ru(3)—Ru(1)—C(2)	92.6 (5)	92.6 (4)
Ru(4)—Ru(1)—C(2)	149.6 (5)	149.8 (4)
C(1)—Ru(1)—C(2)	90.9 (5)	92.6 (6)
Ru(2)—Ru(1)—C(3)	114.2 (4)	112.2 (4)
Ru(3)—Ru(1)—C(3)	170.9 (4)	169.2 (4)
Ru(4)—Ru(1)—C(3)	113.9 (4)	112.6 (4)
C(1)—Ru(1)—C(3)	95.5 (6)	97.0 (5)
C(2)—Ru(1)—C(3)	94.2 (7)	93.9 (5)
Ru(1)—Ru(2)—C(4)	145.1 (4)	145.9 (4)
Ru(3)—Ru(2)—C(4)	90.7 (4)	90.2 (4)
Ru(4)—Ru(2)—C(4)	91.3 (4)	94.0 (4)
Ru(1)—Ru(2)—C(5)	115.3 (4)	111.0 (4)
Ru(3)—Ru(2)—C(5)	120.7 (4)	119.4 (4)
Ru(4)—Ru(2)—C(5)	176.0 (4)	171.4 (4)
C(4)—Ru(2)—C(5)	92.7 (6)	94.6 (6)
Ru(1)—Ru(2)—C(6)	103.8 (4)	108.5 (4)
Ru(3)—Ru(2)—C(6)	147.7 (4)	148.9 (4)
Ru(4)—Ru(2)—C(6)	88.8 (4)	88.4 (4)
C(4)—Ru(2)—C(6)	95.7 (6)	92.4 (6)
C(5)—Ru(2)—C(6)	90.6 (5)	91.3 (5)
Ru(1)—Ru(2)—C(7)	77.4 (3)	73.1 (3)
Ru(3)—Ru(2)—C(7)	44.2 (3)	43.4 (3)
Ru(4)—Ru(2)—C(7)	103.6 (3)	103.5 (3)
C(4)—Ru(2)—C(7)	90.5 (5)	92.6 (5)
C(5)—Ru(2)—C(7)	76.5 (5)	76.0 (5)
C(6)—Ru(2)—C(7)	166.0 (5)	166.7 (5)
Ru(1)—Ru(3)—C(7)	88.1 (4)	84.9 (4)
Ru(2)—Ru(3)—C(7)	56.9 (4)	60.4 (3)
Ru(4)—Ru(3)—C(7)	117.8 (4)	120.3 (3)
Ru(1)—Ru(3)—C(8)	168.0 (5)	165.6 (4)
Ru(2)—Ru(3)—C(8)	106.8 (4)	102.5 (4)
Ru(4)—Ru(3)—C(8)	105.8 (5)	106.6 (4)
C(7)—Ru(3)—C(8)	92.5 (6)	92.7 (6)
Ru(1)—Ru(3)—C(9)	93.7 (4)	95.0 (4)
Ru(2)—Ru(3)—C(9)	135.5 (4)	143.3 (5)
Ru(4)—Ru(3)—C(9)	144.3 (4)	138.7 (5)
C(7)—Ru(3)—C(9)	86.4 (5)	89.5 (6)
C(8)—Ru(3)—C(9)	98.3 (6)	99.1 (5)
Ru(1)—Ru(3)—C(10)	87.8 (4)	92.2 (4)
Ru(2)—Ru(3)—C(10)	123.2 (4)	119.9 (4)
Ru(4)—Ru(3)—C(10)	62.5 (4)	59.7 (4)
C(7)—Ru(3)—C(10)	175.0 (6)	176.6 (6)
C(8)—Ru(3)—C(10)	92.1 (6)	90.5 (6)
C(9)—Ru(3)—C(10)	91.2 (6)	88.9 (7)
Ru(1)—Ru(4)—C(10)	74.1 (3)	78.8 (3)
Ru(2)—Ru(4)—C(10)	101.6 (3)	101.5 (4)
Ru(3)—Ru(4)—C(10)	42.0 (3)	42.5 (4)
Ru(1)—Ru(4)—C(11)	148.5 (5)	149.0 (4)
Ru(2)—Ru(4)—C(11)	96.6 (4)	93.1 (4)
Ru(3)—Ru(4)—C(11)	92.1 (5)	94.8 (4)
C(10)—Ru(4)—C(11)	90.3 (5)	90.2 (5)
Ru(1)—Ru(4)—C(12)	107.2 (5)	108.0 (4)

Ru(2)—Ru(4)—C(12)	168.0 (5)	169.6 (4)
Ru(3)—Ru(4)—C(12)	118.9 (4)	117.5 (4)
C(10)—Ru(4)—C(12)	77.3 (5)	76.3 (6)
C(11)—Ru(4)—C(12)	95.3 (6)	97.1 (6)
Ru(1)—Ru(4)—C(13)	109.9 (4)	106.1 (4)
Ru(2)—Ru(4)—C(13)	90.2 (4)	91.7 (4)
Ru(3)—Ru(4)—C(13)	149.8 (4)	150.4 (4)
C(10)—Ru(4)—C(13)	167.9 (5)	166.7 (5)
C(11)—Ru(4)—C(13)	91.1 (6)	91.3 (5)
C(12)—Ru(4)—C(13)	90.6 (6)	90.4 (6)
Ru(2)—C(7)—Ru(3)	78.9 (5)	76.2 (4)
Ru(2)—C(7)—O(7)	129.8 (9)	128.2 (9)
Ru(3)—C(7)—O(7)	151.4 (10)	155.6 (10)
Ru(3)—C(10)—Ru(4)	75.5 (4)	77.9 (5)
Ru(3)—C(10)—O(10)	161.4 (12)	156.4 (12)
Ru(4)—C(10)—O(10)	122.7 (10)	125.6 (11)

Lists of structure factors, anisotropic thermal parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55959 (34 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1022]

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Structure of an Iridium(I) Complex of Tris(2,6-dimethoxyphenyl)phosphine, $[Ir(C_8H_{12})(C_5H_5N)(P\{2,6\text{-}(CH_3O)_2C_6H_3\}_3)][PF_6]$

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Abstract

The structure of (η^4-1,5-cyclooctadiene)(pyridine)[tris(2,6-dimethoxyphenyl)phosphine]iridium(I) hexafluorophosphate shows approximately square-pyrimidal geometry at the Ir atom with one of the methoxy groups of the phosphine ligand being weakly bound in the apical position [Ir···O = 2.724 (6) Å].

Comment

We have been interested for some time in the structures and solution conformations of cationic iridium–phosphine complexes, particularly of rather hindered phosphines (Abbassioun, Hitchcock & Chaloner, 1989, 1990; Abbassioun, Chaloner, Hitchcock & Koziorowski, 1991; Chaloner, Hitchcock & Reisinger, 1992). Many such complexes have been used as catalysts for homogeneous hydrogenation of hindered alkenes (Crabtree, 1979). There has been considerable interest in the use of the basic hindered phosphine tris(2,4,6-trimethoxyphenyl)phosphine (TMPP) (Wada & Higashizaki, 1984) as a ligand in organometallic chemistry, and a number of structures of complexes have been determined (Dunbar, Haefner & Pence, 1989; Chen & Dunbar, 1990, 1991; Dunbar, Haefner & Burzynski, 1990; Dunbar, Haefner & Quillevéré, 1990; Haefner, Dunbar & Bender, 1991). The related ligand tris(2,6-dimethoxyphenyl)phosphine may be expected to be equally sterically demanding, but a little less basic. There has been little structural work on derivatives of this phosphine; only the structures of the free phosphine (Livant, Sun & Webb, 1991) and the phosphine selenide (Allen, Bell, March & Nowell, 1990) have been determined.

The complex (I) was prepared by reaction of $[Ir(cod)(py)_2][PF_6]$ with tris(2,6-dimethoxyphenyl)phosphine (Crabtree & Moorehouse, 1986) and its structure is shown in Fig. 1. The Ir atom adopts distorted square-pyramidal geometry, partly resulting from the bulk of the phosphine ligand. There is one short contact between an ether O atom and the metal centre, Ir···O2 = 2.724 (6) Å, and the ether may be described as occupying an approximately apical site in the square-based pyramid. The Ir atom is some 0.17 Å above the square-basal plane. The metal–oxygen distance is quite long by comparison with other related interactions. For example, in $[Rh(\eta^3\text{-TMPP})_2][BF_4]_2$ the Rh···O distances are 2.398 (5) and 2.201 (6) Å, in $[Rh(CO)(\eta^2\text{-TMPP})(TMPP)][BF_4]$ they are 2.319 (7) and 2.611 (7) Å (Haefner, Dunbar & Bender, 1991) and in $[RhCl_3(Me_2AsC_6H_4\text{-}2\text{-}OMe)_2]$ they are 2.24 Å (Graziani, Bombieri, Volponi, Panattoni & Clark, 1969). True bonds to alkoxide ligands are considerably shorter, typically of the order of 2.0 Å for $[Ir\{(Me_3C)_2PC_6H_4\text{-}2\text{-}O\}_2]$ and related complexes (Mason, Thomas, Empsall, Fletcher, Heys, Hyde, Jones & Shaw, 1974). The relatively long bond between the ether and the metal suggests that this will be labile in solution. The

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