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Structure of 1,1,1,1,2,2,2,3,3,3-Decacarbonyl-2,3-μ-[vinylidenebis(diphenylphosphine)-*P*,*P*′]-*triangulo*-triruthenium(0)

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Abstract. $[Ru_3(C_{26}H_{22}P_2)(CO)_{10}]$, $M_r = 979{\cdot}7$, monoclinic, $P2_1/n$, $a = 13{\cdot}043\,(1)$, $b = 12{\cdot}248\,(1)$, $c = 23{\cdot}695\,(1)$ Å, $\beta = 103{\cdot}16\,(1)°$, $V = 3686{\cdot}1$ Å^3, $Z = 4$, $D_m = 1{\cdot}83$, $D_x = 1{\cdot}77$ g cm^{-3}, $\lambda(\mathrm{Mo}\,K\alpha) = 0{\cdot}71069$ Å, $\mu = 13{\cdot}17$ cm^{-1}, $F(000) = 1920$, $T = 293$ K, $R = 0{\cdot}035$ for 4385 observed reflections. The dppee ligand [dppee = vinylidenebis(diphenylphosphine)] bridges one edge of the triruthenium triangle, the phosphine groups occupying equatorial coordination sites. The C=C double-bond length in the dppee ligand is not significantly changed upon coordination.

Introduction. Recent studies have shown that coordination of the dppee ligand leads to the activation of its C=C double bond (Cooper, Hassan, Shaw & Thornton-Pett, 1985; Schmidbaur, Herr, Muller & Riede, 1985). The crystal structures of three complexes containing the dppee ligand have been reported recently; in two of these complexes, $[Fe(CO)_3(dppee)]$ (Clucas, Dawson, Dolby, Harding, Pearson & Smith, 1986) and $[ClAu(dppee)_2AuCl]$ (Schmidbaur *et al.*, 1985), the C=C bond length was found to be very close to the value [1·327 (6) Å] in the free ligand (Schmidbaur, Herr & Riede, 1984), whereas in the complex $[Os_3(CO)_{10}(dppee)]$ (Clucas *et al.*, 1986), the C=C bond appeared to have undergone a significant lengthening [to 1·49 (3) Å]. However, the large e.s.d. for this bond length did not permit any detailed conclusions to be drawn. We therefore undertook the determination of the crystal structure of the ruthenium analogue $[Ru_3(CO)_{10}(dppee)]$ in order to obtain a more accurate picture of the effect of coordination of the dppee ligand across a metal–metal bond.

Experimental. The compound was prepared as described previously (Clucas *et al.*, 1986). Red tabular air-stable crystals were recrystallized from an acetone–ethanol mixture under a stream of nitrogen. Crystal chosen had dimensions 0·3 × 0·25 × 0·15 mm. Accurate lattice parameters and intensities of 6482 reflections measured on a Nonius CAD-4 diffractometer at Queen Mary College, London, with Mo $K\alpha$ radiation. 25 reflections, $1{\cdot}5 < \theta < 25°$, used for cell-parameter determination; no absorption correction $(\sin\theta)/\lambda(\max.) = 0{\cdot}595$ Å^{-1}, $-15 \le h \le 15$, $0 \le k \le 14$, $0 \le l \le 28$. Standard reflections $\bar{3}2\bar{8}$, 610, $\bar{6}\bar{4}1$, 7% random variation in intensity. Number of parameters = 283; in blocked full-matrix refinement; shift/e.s.d. in final cycle ≤0·1. Density measured by flotation in iodomethane/hexachloro-1,3-butadiene. Structure determined from 4385 reflections for which $F > 6\sigma(F)$ using *SHELX*76 (Sheldrick, 1976). Ru atoms located from Patterson map. H atoms in calculated positions on phenyl rings, other H atoms located from Fourier difference map. In least-squares refinement, phenyl rings constrained to have ideal geometry, with individual isotropic U values for C atoms, fixed U values for H atoms. All other atoms except ethylenic C atoms had anisotropic vibration parameters refined. $w = 1/[\sigma^2(F) + 0{\cdot}000429F^2]$. $R = 0{\cdot}035$, $wR = 0{\cdot}0374$. Max. and min. on difference map are 0·93 and −0·50 e Å^{-3}, the former being associated with anisotropic vibrations of the phenyl C atoms. Scattering factors for Ru from *International Tables for X-ray Crystallography* (1974). Program *PLUTO* (Motherwell, 1976) used for figure drawing. All calculations performed on an IBM 3083 computer.

Discussion. Atom parameters are given in Table 1† and selected bond lengths and angles in Table 2. As shown in Fig. 1, the molecule consists of a triangle of Ru atoms with the dppee ligand bridging one Ru–Ru bond, and coordinated in the equatorial plane. The structure closely resembles that of $[Ru_3(CO)_{10}(Ph_2PCH_2PPh_2)]$ (Coleman, Jones, Dixneuf, Brisson, Bonnet & Lavigne, 1984). The shortest Ru–Ru bond is that bridged by the dppee ligand. This is probably related to the strain induced by the Ru(2)–Ru(3)–P(1)–C(50)–P(2) ring

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† Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a full list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44426 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional coordinates of atoms with e.s.d.'s in parentheses*

$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$

	x	y	z	U_{eq}(Å^2)
Ru(1)	0·12215 (3)	0·14772 (4)	0·09704 (2)	0·0495 (2)
Ru(2)	0·29464 (3)	0·29797 (4)	0·11525 (2)	0·0379 (2)
Ru(3)	0·32925 (3)	0·07660 (4)	0·14931 (2)	0·0359 (2)
P(1)	0·5036 (1)	0·1004 (1)	0·1970 (1)	0·0336 (7)
P(2)	0·4758 (1)	0·3240 (1)	0·1300 (1)	0·0337 (7)
C(1)	0·0106 (5)	0·2272 (7)	0·0481 (3)	0·070 (5)
O(1)	−0·0556 (4)	0·2706 (6)	0·0170 (3)	0·111 (5)
C(2)	0·1498 (5)	0·0666 (6)	0·0314 (3)	0·062 (4)
O(2)	0·1551 (4)	0·0152 (5)	−0·0074 (2)	0·090 (4)
C(3)	0·0582 (5)	0·0219 (7)	0·1212 (3)	0·071 (5)
O(3)	0·0219 (4)	−0·0544 (5)	0·1366 (3)	0·109 (5)
C(4)	0·1080 (5)	0·2326 (6)	0·1637 (3)	0·064 (4)
O(4)	0·0875 (4)	0·2796 (5)	0·2014 (2)	0·088 (4)
C(5)	0·2660 (4)	0·2706 (5)	0·0326 (3)	0·046 (3)
O(5)	0·2486 (3)	0·2659 (4)	−0·0162 (2)	0·062 (3)
C(6)	0·2405 (5)	0·4409 (5)	0·0970 (3)	0·060 (4)
O(6)	0·2083 (5)	0·5269 (4)	0·0870 (3)	0·101 (4)
C(7)	0·3092 (4)	0·3188 (5)	0·1976 (3)	0·051 (4)
O(7)	0·3199 (4)	0·3398 (4)	0·2455 (2)	0·069 (3)
C(8)	0·3162 (4)	−0·0776 (5)	0·1532 (3)	0·052 (4)
O(8)	0·3084 (4)	−0·1704 (4)	0·1538 (2)	0·085 (4)
C(9)	0·3669 (4)	0·0727 (4)	0·0748 (2)	0·043 (3)
O(9)	0·3932 (3)	0·0634 (4)	0·0324 (2)	0·061 (3)
C(10)	0·2794 (4)	0·0917 (5)	0·2195 (3)	0·049 (3)
O(10)	0·2520 (4)	0·0936 (4)	0·2621 (2)	0·069 (3)
C(12)	0·7104 (2)	0·0471 (3)	0·1927 (1)	0·0415 (12)
C(13)	0·7875 (2)	−0·0063 (3)	0·1708 (1)	0·0491 (14)
C(14)	0·7585 (2)	−0·0852 (3)	0·1277 (1)	0·0519 (14)
C(15)	0·6525 (2)	−0·1107 (3)	0·1064 (1)	0·0507 (14)
C(16)	0·5754 (2)	−0·0573 (3)	0·1283 (1)	0·0413 (12)
C(11)	0·6043 (2)	0·0216 (3)	0·1715 (1)	0·0343 (11)
C(22)	0·5055 (3)	0·1448 (3)	0·3134 (2)	0·0673 (17)
C(23)	0·5240 (3)	0·1203 (3)	0·3723 (2)	0·0846 (23)
C(24)	0·5723 (3)	0·0220 (3)	0·3931 (2)	0·0733 (19)
C(25)	0·6021 (3)	−0·0518 (3)	0·3549 (2)	0·0719 (19)
C(26)	0·5835 (3)	−0·0272 (3)	0·2959 (2)	0·0523 (14)
C(21)	0·5353 (3)	0·0710 (3)	0·2752 (2)	0·0427 (12)
C(32)	0·4714 (2)	0·5300 (3)	0·1801 (2)	0·0472 (13)
C(33)	0·5095 (2)	0·6341 (3)	0·1972 (2)	0·0551 (15)
C(34)	0·6027 (2)	0·6707 (3)	0·1842 (2)	0·0548 (15)
C(35)	0·6579 (2)	0·6032 (3)	0·1540 (2)	0·0529 (15)
C(36)	0·6198 (2)	0·4991 (3)	0·1369 (2)	0·0446 (13)
C(31)	0·5265 (2)	0·4625 (3)	0·1499 (2)	0·0376 (11)
C(42)	0·5020 (2)	0·3442 (3)	0·0177 (2)	0·0532 (14)
C(43)	0·5543 (2)	0·3302 (3)	−0·0270 (2)	0·0645 (17)
C(44)	0·6445 (2)	0·2655 (3)	−0·0184 (2)	0·0653 (17)
C(45)	0·6825 (2)	0·2146 (3)	0·0349 (2)	0·0681 (18)
C(46)	0·6302 (2)	0·2286 (3)	0·0797 (2)	0·0514 (14)
C(41)	0·5400 (2)	0·2933 (3)	0·0710 (2)	0·0364 (11)
C(50)	0·5478 (4)	0·2433 (4)	0·1921 (2)	0·0330 (11)
C(51)	0·6211 (5)	0·2876 (5)	0·2337 (3)	0·0510 (15)

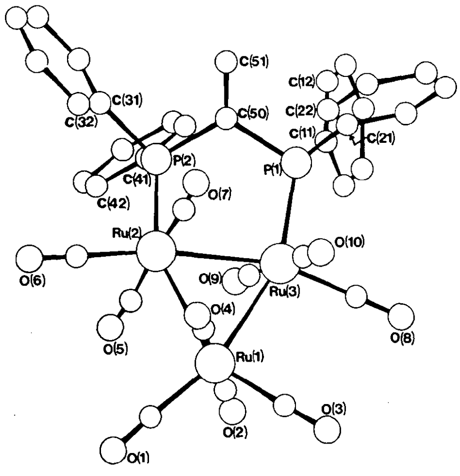

Fig. 1. Molecular structure and atom labelling of $[Ru_3(CO)_{10}\{Ph_2PC(=CH_2)PPh_2\}]$; H atoms have been omitted.

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Ru(1)–Ru(2)	2·862 (1)	Ru(3)–Ru(1)–Ru(2)	59·64 (2)
Ru(1)–Ru(3)	2·840 (1)	Ru(3)–Ru(2)–Ru(1)	59·79 (2)
Ru(2)–Ru(3)	2·836 (1)	Ru(2)–Ru(3)–Ru(1)	60·57 (2)
Ru(1)–C(1)	1·908 (7)	Ru(1)–C(1)–O(1)	176·6 (7)
Ru(1)–C(2)	1·947 (8)	Ru(1)–C(2)–O(2)	172·5 (6)
Ru(1)–C(3)	1·902 (8)	Ru(1)–C(3)–O(3)	178·4 (5)
Ru(1)–C(4)	1·935 (8)	Ru(1)–C(4)–O(4)	171·9 (5)
Ru(2)–C(5)	1·937 (6)	Ru(2)–C(5)–O(5)	172·9 (5)
Ru(2)–C(6)	1·900 (7)	Ru(2)–C(6)–O(6)	178·9 (6)
Ru(2)–C(7)	1·933 (7)	Ru(2)–C(7)–O(7)	174·4 (5)
Ru(3)–C(8)	1·901 (7)	Ru(3)–C(8)–O(8)	177·9 (6)
Ru(3)–C(9)	1·939 (6)	Ru(3)–C(9)–O(9)	174·8 (5)
Ru(3)–C(10)	1·928 (7)	Ru(3)–C(10)–O(10)	175·4 (5)
Ru(2)–P(2)	2·331 (1)		
Ru(3)–P(1)	2·316 (1)		
C(11)–P(1)	1·840 (4)		
C(21)–P(1)	1·839 (4)		
C(31)–P(2)	1·843 (4)		
C(41)–P(2)	1·824 (4)		
C(50)–P(1)	1·855 (5)	C(50)–P(1)–Ru(3)	111·9 (1)
C(50)–P(2)	1·842 (5)	C(50)–P(2)–Ru(2)	111·2 (2)
C(50)–C(51)	1·323 (7)	P(1)–C(50)–P(2)	116·6 (2)

and is in agreement with the hypothesis (Coleman *et al.*, 1984) that there is some correlation between the mean value for the intracyclic Ru–Ru–P angles [in this case Ru(2)–Ru(3)–P(1) 95·4 and Ru(3)–Ru(2)–P(2) 89·9°] and this short Ru(2)–Ru(3) bond distance. Axial Ru–C bond lengths (av. 1·937 Å) are longer than equatorial Ru–C bonds (av. 1·903 Å), in agreement with the values found in $[Ru_3(CO)_{10}(Ph_2PCH_2PPh_2)]$ (Coleman *et al.*, 1984) and $[Ru_3(CO)_{12}]$ (Churchill, Hollander & Hutchinson, 1977).

The coordinated dppee ligand shows little change in bond lengths and angles from those found for the free ligand (Schmidbaur *et al.*, 1984). Thus, the C=C bond length [C(50)=C(51) 1·323 (7) Å] and the P(1)–C(50)–P(2) angle [116·6 (2)°] compare well with the values found for the free ligand [1·327 (6) Å and 119·0 (3)°]. Therefore there is no evidence for any C=C bond lengthening in the coordinated dppee ligand. Furthermore, the ligand plane defined by P(1), C(50) and P(2) is found to be tilted with respect to the triangular Ru-atom plane at an angle of 32·2°, implying no interaction between the metal–metal bonding and the ligand double bond. We therefore suggest that the apparent C=C bond lengthening observed in the isomorphous osmium complex $[Os_3(CO)_{10}(dppee)]$ (Clucas *et al.*, 1986) is an artifact of the low-accuracy crystal structure determination rather than a real chemical effect.

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References

Churchill, M. R., Hollander, F. J. & Hutchinson, J. P. (1977). *Inorg. Chem.* **16**, 2655–2659.

Clucas, J. A., Dawson, R. H., Dolby, P. A., Harding, M. M., Pearson, K. & Smith, A. K. (1986). *J. Organomet. Chem.* **311**, 153–162.

COLEMAN, A. W., JONES, D. F., DIXNEUF, P. H., BRISSON, C., BONNETT, J.-J. & LAVIGNE, G. (1984). *Inorg. Chem.* **23**, 952–956.
COOPER, G. R., HASSAN, F., SHAW, B. L. & THORTON-PETT, M. (1985). *J. Chem. Soc. Chem. Commun.* pp. 614–616.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
MOTHERWELL, W. D. S. (1976). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
SCHMIDBAUR, H., HERR, R., MULLER, G. & RIEDE, J. (1985). *Organometallics*, **4**, 1208–1213.
SCHMIDBAUR, H., HERR, R. & RIEDE, J. (1984). *Chem. Ber.* **117**, 2322–2327.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

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Tris(3-methylpyridinium) Decavanadate Monohydrate

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Abstract. $[C_6H_8N]_3[V_{10}H_3O_{28}].H_2O$, $M_r = 1260\cdot8$, monoclinic, $P2_1/n$, $a = 7\cdot293$ (3), $b = 21\cdot82$ (2), $c = 23\cdot526$ (8) Å, $\beta = 96\cdot37$ (3)°, $V = 3721$ (4) Å^3, $Z = 4$, $D_m = 2\cdot3$ (1) (by flotation in $CHBr_3/CCl_4$), $D_x = 2\cdot25$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1\cdot93$ mm^{-1}, $F(000) = 2480$, room temperature, $R = 0\cdot069$ for 4100 observed reflections. The decavanadate anion is similar to others already described. The severe distortions in the VO_6 octahedra are mainly due to the internal Coulombic repulsion. One molecule of 3-methylpyridine is partially disordered. Intermolecular hydrogen bonding probably exists.

Introduction. As part of a general study of the crystal chemistry of polyanions of organic bases (Arrieta, Gili & Lorente, 1984, and references therein) we have solved the structure of the title compound.

Experimental. Yellow-brown platy crystals have been synthesized from acidic aqueous media following the method described by Arrieta *et al.* (1984). The chemical analysis of V, C, H and N gave the following calculated (experimental) results: V_2O_5 72·06 (71·75), C 17·12 (17·15), H 2·29 (2·28), N 3·33% (3·50%). Vanadium was analysed as V_2O_5 after calcination at 823 K for two hours; data collected from crystal approximately 0·2 × 0·1 × 0·2 mm; cell parameters determined by least squares from the setting angles of 15 reflections ($10 < 2\theta < 25°$); 5503 independent reflections measured; Syntex $P2_1$ diffractometer, graphite-monochromated Mo $K\alpha$ radiation, ω scans up to $2\theta = 47°$; one standard reflection (101) measured every 50 showed only random deviations from mean intensity; Lp corrections applied but no correction for absorption; 4100 reflections $[I \geq 2\cdot5\sigma(I)]$ considered observed and included in refinement; index range $h \pm 7$, k 0–24, l 0–26; structure solved with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), an E map showed the decavanadate anion except for two O atoms. All remaining (non-H) atoms from three ΔF syntheses; refinement by least squares with *SHELX*76 (Sheldrick, 1976), unit weights, $\sum(\Delta F)^2$ minimized, completed with anisotropic thermal parameters, the H atoms were not taken into account; final $R = 0\cdot069$; scattering factors from *International Tables for X-ray Crystallography* (1974) and the anomalous-scattering factors from Cromer & Liberman (1970); max. $\Delta/\sigma = 0\cdot90$ [for y, C(64)]; max. and min. electron densities in final difference map + 2·5 and + 1·05 e Å^{-3} (this high value of the residual electron density should be related to the 116 H atoms in the unit cell which we have not considered).

Discussion. Table 1† gives the final atomic parameters with their B_{eq} values. Fig. 1 shows the numbering of the decavanadate anion and the arrangement of different V

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† Lists of structure factors, anisotropic thermal parameters, angles of the decavanadate anion, distances and angles of the disordered organic molecule, intermolecular distances and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44413 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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