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Undecacarbonyl(triethylphosphine)- and -(trimethyl phosphite)-*triangulo*-triruthenium, $[Ru_3(CO)_{11}PR_3]$ [R = Et (1), OMe (2)]: Substituent Effects on Ru—Ru and Ru—P Bond Lengths and Some Comments on the Effects of Refinement Models on Ru—C and C≡O Bond Lengths

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Abstract. (1), $[Ru_3(CO)_{11}\{P(C_2H_5)_3\}]$, $M_r = 729{\cdot}5$, triclinic, $P\bar{1}$, $a = 8{\cdot}740\,(2)$, $b = 12{\cdot}056\,(2)$, $c = 12{\cdot}363\,(1)$ Å, $\alpha = 85{\cdot}22\,(1)$, $\beta = 72{\cdot}64\,(1)$, $\gamma = 72{\cdot}73\,(1)°$, $V = 1187{\cdot}3$ Å^3, $D_x = 2{\cdot}04$ g cm^{-3}, $Z = 2$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 19{\cdot}7$ cm^{-1}, $F(000) = 704$, $T = 298$ K, $R = 0{\cdot}0219$ for 4950 observed [$I \geq 3\sigma(I)$] reflections. (2), $[Ru_3(CO)_{11}\{P(OCH_3)_3\}]$, $M_r = 735{\cdot}4$, monoclinic, $P2_1/c$, $a = 16{\cdot}621\,(2)$, $b = 7{\cdot}992\,(2)$, $c = 18{\cdot}124\,(3)$ Å, $\beta = 113{\cdot}36\,(1)°$, $V = 2209{\cdot}9$ Å^3, $D_x = 2{\cdot}21$ g cm^{-3}, $Z = 4$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 21{\cdot}2$ cm^{-1}, $F(000) = 1408$, $T = 298$ K, $R = 0{\cdot}0235$ for 4218 observed [$I \geq 3\sigma(I)$] reflections. Both molecules contain slightly distorted triangular Ru_3 moieties with the phosphine and phosphite ligands equatorially substituted. Each Ru atom has distorted octahedral coordination geometry. The Ru1—Ru2, Ru1—Ru3, Ru2—Ru3 and Ru1—P bond lengths for (1) [values for (2) in square brackets] are: 2·9078 (2) [2·8883 (3)], 2·8648 (2) [2·8685 (3)], 2·8802 (2) [2·8735 (3)] and 2·3489 (5) Å [2·2750 (7) Å] respectively. The corresponding Ru2—Ru1—P bond angles are 112·80 (1)° [103·27 (2)°]. The observed Ru—P distances are consistent with a marked correlation between these distances and the Tolman cone angles for the P ligands in monosubstituted $[Ru_3(CO)_{11}PR_3]$ complexes. Introduction of anisotropic displacement (thermal) parameters for the carbonyl ligands has resulted in small shifts of up to 0·02 Å in the positions of the C atoms towards the O atoms. The shifts are somewhat less than the effects commented upon by Braga & Koetzle [*Acta Cryst.* (1988), **B44**, 151–155].

Introduction. Electronic and steric effects shown by P-donor nucleophiles in their associative reactions with metal carbonyl clusters can be distinguished quantitatively by analysis of the dependence of the rate constants on pK_a and Tolman cone angle data (Tolman, 1977) for the nucleophiles (Brodie, Chen & Poë, 1988; Poë, 1988). Standard or intrinsic reactivities with respect to attack by a standard nucleophile can be obtained. The effects of substituents on the standard reactivities and on the electronic and steric effects can also be obtained so that the reactivity of any given cluster can be quantitatively characterized in this way. It will obviously be of interest to try and correlate reactivity effects of substituents with their structural effects and in the present paper the detailed X-ray analysis of two $[Ru_3(CO)_{11}L]$ clusters [$L = P(OMe)_3$ and PEt_3] used in the kinetic studies are reported and discussed.

Experimental. The preparations of both compounds will be reported in detail elsewhere (Brodie, Chen & Poë, in preparation). Suitable crystals of (1) were obtained from a methanol/hexane solvent mixture (*ca* 1:1) over an extended period; those of (2) from a methanol/methylene dichloride solvent mixture.

Details of the unit-cell and space-group determinations and intensity data collections for both compounds are summarized in Table 1. Lorentz and polarization corrections were applied to all data measured; absorption corrections were not considered necessary in view of the regular shape of the crystals and the magnitude of μ for each compound. Both structures were solved by use of the Patterson function to locate the Ru atoms, and standard least-squares and Fourier methods to locate the remaining non-H atoms. H-atom positions obtained from ΔF maps were allowed to refine in the least squares.

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Table 1. *Experimental details*

Measurements were made using an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator: Mo $K\alpha$ radiation (λ = 0·71069 Å); ω–2θ scans.

Compound	(1), R = Et	(2), R = OMe
Crystal	Orange-red block	Dark-red needles
Crystal size (d in mm)	{001}: 0·082 (20$\bar{1}$), ($\bar{2}$01): 0·082 {010}: 0·130	(101)($\bar{1}0\bar{1}$): 0·225 (011)(01$\bar{1}$) (001) + small (021)(0$\bar{2}$1) + (00$\bar{1}$) } 0·063–0·081
No. of reflections in cell determination/θ range (°)	25/10·6 < θ < 15·5	25/11·5 < θ < 15·2
ω-scan range (°)	0·65 + 0·35tanθ	0·65 + 0·35tanθ
Max. scan time (s)*	80	70
Max. 2θ (°)/quadrants	55/h, $\pm k$, $\pm l$†	55/h, k, $\pm l$
No. of standard reflections/ interval (s)‡	3/6500	3/6000
No. of data collected	5595	5752
No. of unique data§	5357	4894
No. of data with $I \geq 3\sigma(I)$	4950	4218¶
Final R (wR)	0·0219 (0·0312)	0·0235 (0·0301)
Max. Δ/σ in final cycle	0·50	0·15
Weights, value of P‖	0·02	0·025
Extinction correction	4·23 (15) × 10^{-7}	1·70 (5) × 10^{-7}
Max. peak in final ΔF map	0·45 (Near Ru3)	0·53 (Near Ru)
E.s.d. of unit weight, S	1·670	1·285

* Prescan at 10° $\min^{-1}$. Prescan intensity accepted if $I/\sigma(I) \geq 25$, otherwise scan speeds were chosen to give this ratio within the max. scan time specified. Backgrounds by extending the scan by 25% on either side of the peak were measured for half the time taken to collect the peak.

† h, k, $\pm l$ for h = 0.

‡ No systematic fluctuations in intensities were observed.

§ 91 [542] systematically absent or zero $F_{\rm obs}$ data for (1) [(2)] were rejected and 151 symmetry equivalent reflections for (2) [$R_{\rm merge}(F)$ = 0·016] were averaged to give the final numbers of unique data.

¶Four reflections with bad $w\Delta F^2$ values were rejected in final cycles.

‖Weights given by $4F^2[\sigma^2(I) + (pF^2)^2]^{-1}$.

Table 2. *Positional parameters and their estimated standard deviations* (*in parentheses*)

	x	y	z	B(Å^2)
[Ru$_3$(CO)$_{11}${P(Et)$_3$}]				
Ru1	−0·21746 (2)	0·32591 (1)	0·26751 (1)	2·426 (3)
Ru2	0·12338 (2)	0·17375 (2)	0·20404 (2)	2·941 (4)
Ru3	−0·15676 (2)	0·07888 (1)	0·27927 (2)	2·976 (4)
P1	−0·22986 (7)	0·52364 (5)	0·24865 (5)	2·62 (1)
O11	−0·2229 (3)	0·3417 (2)	0·0199 (2)	5·36 (5)
O12	−0·2060 (2)	0·3505 (2)	0·5089 (1)	4·44 (4)
O13	−0·5887 (2)	0·3542 (2)	0·3512 (2)	4·86 (5)
O21	0·3588 (3)	0·3250 (2)	0·1257 (2)	6·78 (6)
O22	0·3881 (3)	−0·0613 (2)	0·1664 (2)	8·11 (8)
O23	0·1188 (3)	0·1748 (2)	−0·0434 (2)	5·16 (5)
O24	0·1357 (2)	0·1888 (2)	0·4476 (2)	5·18 (5)
O31	0·0587 (3)	−0·1746 (2)	0·2541 (2)	6·35 (6)
O32	−0·5021 (3)	0·0428 (2)	0·3650 (2)	6·51 (6)
O33	−0·1724 (2)	0·0930 (2)	0·5294 (2)	4·82 (5)
O34	−0·1960 (3)	0·0883 (2)	0·0397 (2)	5·91 (5)
C1	−0·3596 (3)	0·6082 (2)	0·3761 (2)	3·93 (6)
C2	−0·3823 (5)	0·7388 (3)	0·3703 (3)	5·41 (8)
C3	−0·3211 (3)	0·6014 (2)	0·1387 (2)	3·92 (6)
C4	−0·5007 (3)	0·6031 (3)	0·1544 (3)	5·22 (7)
C5	−0·0332 (3)	0·5608 (2)	0·2163 (3)	4·06 (6)
C6	0·0490 (3)	0·5371 (3)	0·3112 (3)	5·70 (7)
C11	−0·2128 (3)	0·3286 (2)	0·1101 (2)	3·62 (5)
C12	−0·2030 (3)	0·3350 (2)	0·4189 (2)	3·11 (5)
C13	−0·4491 (3)	0·3462 (2)	0·3190 (2)	3·31 (5)
C21	0·2667 (3)	0·2704 (3)	0·1572 (2)	4·10 (6)
C22	0·2876 (4)	0·0241 (3)	0·1818 (3)	4·87 (7)
C23	0·1093 (3)	0·1756 (2)	0·0504 (2)	3·72 (5)
C24	0·1204 (3)	0·1842 (2)	0·3611 (2)	3·76 (6)
C31	−0·0198 (3)	−0·0803 (2)	0·2633 (3)	4·23 (6)
C32	−0·3750 (3)	0·0580 (2)	0·3333 (2)	4·07 (6)
C33	−0·1589 (3)	0·0922 (2)	0·4354 (2)	3·70 (5)
C34	−0·1755 (3)	0·0889 (2)	0·1263 (2)	4·21 (6)
H11	−0·326 (3)	0·575 (2)	0·437 (2)	3·9 (6)*
H12	−0·473 (4)	0·592 (3)	0·396 (2)	5·7 (8)*
H21	−0·440 (4)	0·765 (3)	0·311 (3)	6·8 (9)*
H22	−0·481 (5)	0·760 (4)	0·445 (3)	11 (1)*
H23	−0·339 (6)	0·760 (4)	0·404 (4)	14 (2)*
H31	−0·326 (3)	0·692 (2)	0·140 (2)	4·1 (6)*
H32	−0·240 (3)	0·561 (2)	0·064 (2)	2·9 (5)*
H41	−0·534 (3)	0·646 (2)	0·093 (2)	4·6 (7)*
H42	−0·566 (5)	0·641 (4)	0·238 (3)	11 (1)*
H43	−0·510 (4)	0·519 (3)	0·138 (3)	9 (1)*
H51	−0·048 (3)	0·644 (2)	0·203 (2)	5·0 (7)*
H52	0·024 (3)	0·508 (2)	0·149 (2)	3·7 (6)*
H61	−0·001 (4)	0·590 (3)	0·357 (3)	7 (1)*
H62	0·162 (4)	0·543 (3)	0·307 (3)	6·8 (9)*
H63	0·056 (4)	0·471 (3)	0·354 (3)	7·0 (9)*
[Ru$_3$(CO)$_{11}${P(OMe)$_3$}]				
Ru1	0·19554 (1)	0·02947 (3)	−0·00051 (1)	2·340 (4)
Ru2	0·34119 (1)	0·23926 (3)	0·00994 (1)	2·460 (4)
Ru3	0·35703 (1)	0·01521 (3)	0·13903 (1)	2·552 (4)
P1	0·08939 (5)	0·0995 (1)	−0·12169 (4)	2·74 (1)
O1	−0·0038 (1)	0·0421 (3)	−0·1267 (1)	3·61 (5)
C1	−0·0824 (2)	0·0659 (6)	−0·1994 (2)	4·93 (9)
O2	0·0903 (1)	0·0107 (3)	−0·2003 (1)	3·69 (5)
C2	0·1530 (2)	0·0554 (6)	−0·2334 (2)	4·81 (8)
O3	0·0762 (2)	0·2872 (3)	−0·1536 (1)	3·86 (5)
C3	0·0669 (2)	0·4250 (5)	−0·1064 (2)	4·52 (9)
C11	0·2393 (2)	−0·1331 (4)	−0·0534 (2)	3·71 (7)
O11	0·2555 (2)	−0·2376 (3)	−0·0884 (2)	5·84 (7)
C12	0·1306 (2)	−0·1443 (4)	0·0215 (2)	3·28 (6)
O12	0·0918 (2)	−0·2514 (3)	0·0313 (2)	5·16 (6)
C13	0·1531 (2)	0·1895 (4)	0·0554 (2)	3·10 (6)
O13	0·1206 (2)	0·2766 (3)	0·0857 (1)	4·64 (5)
C21	0·3002 (2)	0·3608 (4)	−0·0890 (2)	3·35 (6)
O21	0·2775 (2)	0·4312 (3)	−0·1478 (1)	5·11 (6)
C22	0·4579 (2)	0·3289 (4)	0·0662 (2)	3·67 (7)
O22	0·5245 (2)	0·3859 (4)	0·0977 (2)	5·79 (7)
C23	0·2900 (2)	0·4054 (4)	0·0556 (2)	3·19 (6)
O23	0·2631 (2)	0·5155 (3)	0·0784 (1)	4·38 (6)
C24	0·3824 (2)	0·0680 (4)	−0·0423 (2)	3·35 (6)
O24	0·4087 (2)	−0·0180 (3)	−0·0773 (1)	5·03 (6)
C31	0·4747 (2)	0·0454 (4)	0·2144 (2)	3·88 (7)
O31	0·5440 (2)	0·0602 (5)	0·2625 (2)	6·88 (9)
C32	0·3201 (2)	0·1979 (4)	0·1890 (2)	3·56 (7)
O32	0·3042 (2)	0.2984 (3)	0·2248 (1)	5·03 (6)
C33	0·3135 (2)	−0·1465 (4)	0·1928 (2)	3·51 (7)
O33	0·2884 (2)	−0·2393 (3)	0·2252 (2)	5·31 (6)
C34	0·3969 (2)	−0·1559 (4)	0·0858 (2)	3·72 (7)
O34	0·4259 (2)	−0·2604 (3)	0·0613 (2)	5·50 (6)
H11	−0·092 (2)	−0·011 (4)	−0·239 (2)	5·1 (9)*
H12	−0·080 (2)	0·171 (5)	−0·222 (2)	5·0 (9)*
H13	−0·130 (3)	0·046 (6)	−0·188 (3)	10 (2)*
H21	0·124 (4)	0·186 (9)	−0·265 (3)	14 (2)*
H22	0·198 (3)	0·096 (7)	−0·208 (3)	10 (1)*
H23	0·156 (2)	−0·027 (5)	−0·270 (2)	7 (1)*
H31	0·121 (2)	0·428 (5)	−0·049 (2)	6 (1)*
H32	0·023 (3)	0·392 (6)	−0·082 (2)	8 (1)*
H33	0·073 (3)	0·515 (6)	−0·122 (3)	9 (1)*

* Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Full-matrix least-squares refinements minimizing $\sum w\Delta F^2$ (all non-H atoms with anisotropic displacement parameters, extinction corrections included and refined) have converged to the indicated agreement indices. In view of the quality of both data sets further refinements were then repeated with isotropic U values for the C and O atoms (with extinction corrections and weights fixed at their final values) in order to test the effects of the refinement models on bond lengths following the analyses described by Braga & Koetzle (1987, 1988).

All calculations were performed on a PDP 11/23 computer using programs in the Enraf–Nonius *SDP* (Frenz, 1981) package. Scattering factors stored in

Table 3. Ru—Ru *and* Ru—P *bond lengths* (Å) *in monosubstituted phosphine and phosphite complexes* $[Ru_3(CO)_{11}L]$

	L*	Ru1—Ru3	Ru2—Ru3	Ru1—Ru2	Ru1—P	Substituent cone angle (°)	⟨RuRu⟩
(1*a*)	CO	2·8512 (4)	2·8518 (4)	2·8595 (4)		~95	2·8542
(1*d*)	PCy_3	2·878 (2)	2·859 (2)	2·902 (2)	2·425 (3)	170	2·880
		2·875 (2)	2·874 (2)	2·920 (2)	2·430 (3)	170	2·890
(1*b*)	PPh_3	2·876 (3)	2·875 (3)	2·907 (3)	2·380 (6)	145	2·886
(1*c*)	$AsPh_3$	2·850 (1)	2·859 (1)	2·895 (1)	2·464 (1)	142	
(1*i*)	$PPh(OMe)_2$	2·846 (1)	2·858 (1)	2·872 (1)	2·287 (1)	115	2·859
(1*l*)	$P(OCH_2CF_3)_3$	2·859 (1)	2·846 (1)	2·862 (1)	2·254 (1)	≈110	2·856
(1*n*)	$P(OCH_2)_3CEt$	2·858 (1)	2·839 (2)	2·829 (2)	2·238 (1)	101	2·842
	$P(OMe)_3$	2·8685 (3)	2·8735 (3)	2·8883 (3)	2·2750 (7)	107	2·8768
	PEt_3	2·8648 (2)	2·8802 (2)	2·9078 (2)	2·3489 (5)	132	2·8843

* Compound notation corresponds to that used by Bruce, Liddell, bin Shawkataly *et al.* (1988), Bruce Liddell, Hughes, Patrick *et al.* (1988) and Bruce, Liddell, Hughes, Skelton & White (1988). Two independent molecules are present in the asymmetric unit of (1*d*).

the programs were taken from *International Tables for X-ray Crystallography* (1974). The final atomic positional and thermal parameters and bond lengths and bond angles in these and related structures are given in Tables 2–4.[*]

Discussion. With the present two $[Ru_3(CO)_{11}L]$ structures (Figs. 1 and 2) included there are now seven monosubstituted phosphine or phosphite complexes whose structures have been determined, although several bis- and tris-substituted Ru_3 compounds are also known (Forbes, Goodhand, Jones & Hamor, 1979; Bruce, Matisons, Skelton & White, 1983; Chin-Choy, Keder, Stucky & Ford, 1988; Bruce, Liddell, Hughes, Patrick, Skelton & White, 1988; Bruce, Liddell, bin Shawkataly, Hughes, Skelton & White, 1988). Comparisons and comments on the principal structural parameters of the earlier structures with related Os_3 complexes and with the redetermined structure of the parent $[Ru_3(CO)_{12}]$ compound (Churchill, Hollander & Hutchinson, 1977) have been reported (Bruce, Liddell, Hughes, Skelton & White, 1988). In Table 3 we therefore report only data pertaining to the present comparisons of the monosubstituted phosphorus ligand $[Ru_3(CO)_{11}L]$ structures, all of which contain slightly distorted triangular Ru_3 moieties with the P ligands equatorially substituted and with each Ru atom having distorted octahedral coordination geometry.

In the Ru—C≡O moieties in all seven complexes the axial Ru—C distances are clearly longer than the equatorial Ru—C distances due to the *trans* effect of the carbonyl ligand, and the axial Ru—C≡O bond angles are slightly more distorted from 180° than are the corresponding Ru—C≡O equatorial bond angles [see Table 4 and the discussion in Bruce, Liddell, Hughes, Skelton & White (1988)]. Notably, none of the observed Ru—C axial distances in (1) and (2) differ significantly from the average Ru—C axial bond distance in all seven compounds (1·937 Å) (Table 4). In (1) and (2) the longest Ru—Ru bond length is *cis* to the $P(OMe)_3$ and PEt_3 ligands and is partially compensated for by some shortening of the equatorial Ru—C(≡O) bond length at the substituted atom. Similar trends occur for the other monosubstituted complexes with the exception of the complex with the ligand $P(OCH_2)_3CEt$ in which the *cis* Ru—Ru bond is the shortest. Fig. 3 summarizes the average Ru—Ru distance and the range of values as a function of the Tolman cone angle θ (Tolman, 1977) for the P ligand. This correlation is not clear cut. A much better correlation is obtained, however, when the Ru—P distances are plotted against θ. However, the Ru—Ru—P bond angles do not follow the same trends since steric effects are accommodated by several angular distortions and particularly by the displacement of atoms from the planes through the Ru_3 moieties.[*] Equivalently, these distortions can be viewed as a rotation of the octahedral Ru centres about axes through each Ru and the centroid of the Ru_3 triangles (Table 5). [Compare also the discussion of the structure of $(OC)_5Cr[Os(CO)_3PMe_3]_2$ (Davis, Einstein, Johnston & Pomeroy, 1988).] The rotations are much more pronounced as the Ru—P distance decreases as can be seen, for example, in the torsion angles between the axial carbonyl ligands on the same side of the Ru_3 triangle or equivalently between the *cis* equatorial ligands. Thus in (1) and (2) the *cis* L—Ru—Ru—L' torsion angles are $-0{\cdot}6\,(3)$ $[-20{\cdot}4\,(3)]$, $1{\cdot}8\,(3)$ $[-8{\cdot}4\,(4)]$ and $-6{\cdot}6\,(6)°$ $[-7{\cdot}2\,(4)°]$ respectively. Even larger torsion angles are observed for the complexes with $L =$

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[*] Lists of structure factor amplitudes, anisotropic thermal parameters and supplementary bond lengths/bond angles for both compounds have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51941 (36 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

[*] A similar correlation between Mo—P distances and Tolman cone angle has been observed in a series of *cis*-$Mo(CO)_4(PR_3)_2$ compounds. Notably the P—Mo—P angle does not, however, show a similar good correlation due to preferred orientations of the R groups on the phosphines (Cotton, Darensbourg, Klein & Kolthammer, 1982).

Table 4. *Selected bond lengths (Å) and bond angles (°) and the effects of the temperature factor expressions on the refinements on these values*

	$L = \mathrm{PEt}_3$					$L = \mathrm{P(OMe)}_3$				
	Final $R = 0{\cdot}0219$ $wR = 0{\cdot}0312$	Isotropic C + O $R = 0{\cdot}0398$ $wR = 0{\cdot}0576$	$\Delta(\times 10^3)$	U_C	U_O	Final $R = 0{\cdot}0235$ $wR = 0{\cdot}0301$	Isotropic C + O $R = 0{\cdot}0383$ $wR = 0{\cdot}0511$	$\Delta(\times 10^3)$	U_C	U_O
Ru1—C11	1·932 (2)	1·925 (3)	7	3·4	5·2	1·921 (3)	1·907 (4)	14	3·67	5·49
C12	1·927 (2)	1·925 (3)	2	2·9	4·4	1·896 (3)	1·887 (4)	9	3·16	5·20
C13	1·878 (2)	1·871 (3)	7	3·2	4·7	1·930 (3)	1·927 (3)	3	2·91	4·44
Ru2—C21	1·893 (2)	1·882 (3)	11	3·9	6·4	1·911 (3)	1·901 (4)	10	3·19	4·97
C22	1·924 (2)	1·905 (4)	19	4·7	7·6	1·936 (3)	1·916 (4)	20	3·60	5·49
C23	1·937 (2)	1·933 (3)	4	3·8	5·1	1·932 (3)	1·928 (4)	4	3·00	4·39
C24	1·948 (2)	1·947 (3)	1	3·7	5·0	1·937 (3)	1·933 (4)	4	3·19	5·04
Ru3—C31	1·927 (2)	1·912 (3)	15	4·1	6·1	1·905 (3)	1·882 (4)	23	3·73	6·57
C32	1·910 (2)	1·893 (3)	17	4·1	6·4	1·941 (3)	1·931 (4)	10	3·35	5·05
C33	1·944 (2)	1·946 (3)	2	3·5	4·8	1·923 (3)	1·916 (4)	7	3·46	5·20
C34	1·937 (2)	1·934(3)	3	4·1	5·9	1·936 (3)	1·928 (4)	8	3·54	5·41
C11—O11	1·139 (3)	1·140 (4)	−1			1·143 (4)	1·157 (5)	−14		
C12—O12	1·136 (2)	1·140 (3)	−4			1·127 (3)	1·127 (4)	0		
C13—O13	1·142 (3)	1·149 (3)	−7			1·144 (3)	1·146 (4)	−2		
C21—O21	1·148 (3)	1·158 (4)	−10			1·129 (3)	1·131 (4)	−2		
C22—O22	1·124 (3)	1·147 (5)	−23			1·121 (4)	1·141 (5)	−20		
C23—O23	1·139 (3)	1·141 (4)	−2			1·136 (4)	1·141 (4)	−5		
C24—O24	1·124 (3)	1·122 (4)	−2			1·133 (3)	1·144 (4)	−11		
C31—O31	1·135 (3)	1·147 (4)	−12			1·142 (4)	1·159 (5)	−17		
C32—O32	1·127 (3)	1·143 (4)	−16			1·127 (4)	1·136 (5)	−9		
C33—O33	1·134 (3)	1·121 (3)	+13			1·124 (4)	1·135 (5)	−11		
C34—O34	1·138 (3)	1·142 (4)	−4			1·138 (4)	1·143 (5)	−5		
P—O1/C1	1·822 (2)	1·813 (3)				1·583 (2)	1·585 (3)			
—O2/C3	1·831 (2)	1·834 (3)				1·597 (2)	1·597 (3)			
—O3/C5	1·825 (2)	1·827 (3)				1·591 (2)	1·586 (3)			
O1/C1—C1/C2	1·526 (3)	1·540 (5)				1·454 (4)	1·451 (6)			
O2/C3—C2/C4	1·517 (3)	1·508 (5)				1·438 (4)	1·432 (6)			
O3/C5—C3/C6	1·517 (4)	1·510 (5)				1·439 (4)	1·438 (5)			

Ru—CO angles (anisotropic results)

	(1)	(2)		(1)	(2)		(1)	(2)
C11	172·5 (2)	171·8 (3)	C21	176·9 (2)	178·5 (3)	C31	179·0 (2)	176·6 (3)
C12	173·3 (2)	176·6 (3)	C22	177·3 (3)	177·7 (3)	C32	178·3 (2)	173·5 (3)
C13	177·4 (2)	173·7 (3)	C23	172·8 (3)	172·6 (3)	C33	172·4 (2)	178·9 (3)
			C24	173·0 (2)	172·4 (3)	C34	173·6 (2)	173·7 (3)

Phosphorus ligands (anisotropic results)

	(1)	(2)		(1)	(2)
Ru—P—O1/C1	112·96 (7)	110·55 (8)	O2/C3—P—O3/C5	102·4 (1)	98·2 (1)
—O2/C3	115·53 (8)	118·27 (9)	P—O1/C1—C1/C2	116·9 (2)	121·5 (2)
—O3/C5	117·54 (8)	121·69 (8)	P—O2/C3—C2/C4	114·9 (2)	121·8 (2)
O1/C1—P—O2/C3	102·9 (1)	100·1 (1)	P—O3/O5—C3/C6	114·7 (2)	122·4 (2)
—O3/C5	103·7 (1)	105·2 (1)			
Ru2—Ru1—Ru3	59·85 (1)	59·89 (1)	C21—Ru2—C22	99·6 (1)	102·5 (1)
—P1	112·80 (1)	103·27 (2)	—C23	89·02 (9)	89·9 (1)
—C11	88·46 (7)	87·22 (9)	—C24	90·90 (9)	87·9 (1)
—C12	89·23 (6)	160·66 (9)	C22—Ru2—C23	92·1 (1)	92·3 (1)
—C13	150·11 (6)	93·02 (8)	—C24	92·9 (1)	92·6 (1)
Ru3—Ru1—P1	172·65 (1)	163·15 (2)	C23—Ru2—C24	174·89 (9)	175·0 (1)
—C11	92·19 (6)	90·34 (9)	Ru1—Ru3—Ru2	60·81 (1)	60·40 (1)
—C12	92·54 (6)	101·36 (9)	—C31	155·12 (7)	164·3 (1)
—C13	90·26 (6)	88·45 (8)	—C32	104·14 (7)	91·31 (9)
P1—Ru1—C11	87·13 (7)	89·2 (1)	—C33	86·51 (6)	93·71 (9)
—C12	87·48 (6)	95·46 (9)	—C34	85·93 (7)	88·52 (9)
—C13	97·09 (6)	92·20 (8)	Ru2—Ru3—C31	94·30 (7)	104·0 (1)
C11—Ru1—C12	172·80 (9)	88·3 (1)	—C32	164·95 (7)	88·14 (9)
—C13	92·90 (9)	178·4 (1)	—C33	89·58 (7)	154·05 (9)
C12—Ru1—C13	92·50 (8)	91·0 (1)	—C34	89·95 (7)	88·46 (9)
Ru1—Ru2—Ru3	59·33 (1)	59·72 (1)	C31—Ru3—C32	100·7 (1)	89·7 (1)
—C21	106·91 (8)	104·79 (9)	—C33	94·0 (1)	102·0 (1)
—C22	153·44 (9)	152·6 (1)	—C34	94·4 (1)	89·4 (1)
—C23	87·97 (7)	85·79 (8)	C32—Ru3—C33	89·1 (1)	91·0 (1)
—C24	87·16 (6)	90·43 (9)	—C34	89·2 (1)	176·2 (1)
Ru3—Ru2—C21	166·20 (8)	164·49 (9)	C33—Ru3—C34	171·58 (9)	92·9 (1)
—C22	94·11 (8)	93·0 (1)			
—C23	89·28 (7)	89·60 (8)			
—C24	89·58 (6)	91·25 (9)			

$\mathrm{P(OCH_2)_3CEt}$ and $\mathrm{P(OCH_2CF_3)_3}$ (Bruce, Liddell, Hughes, Skelton & White, 1988).

Consistent with the shorter Ru—P distance the Ru—P—O bond angles are significantly larger [av. 116·84°] and display more variation in (2) than corresponding Ru—P—C angles in (1). However, the P—O—C bond angles [av. 121·9°] are significantly larger than the P—C—C angles in (1) [av. 115·5°]. Furthermore, the conformation of the phosphine ligand in (1) involves the 'in plane' ethyl group pointing towards the equatorial CO on the *cis* Ru atom [torsion angles τ(Ru2—Ru1—P1—C5) = 7·9;

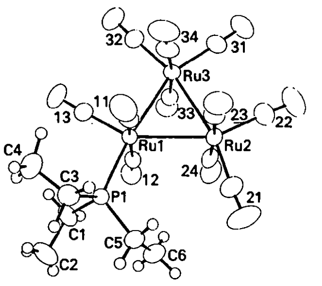

Fig. 1. *ORTEP* view (Johnson, 1965) of compound (1). Thermal ellipsoids are drawn at the 50% probability level; H atoms are drawn with uniform isotropic thermal parameters.

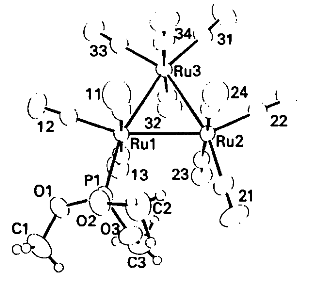

Fig. 2. *ORTEP* view of compound (2).

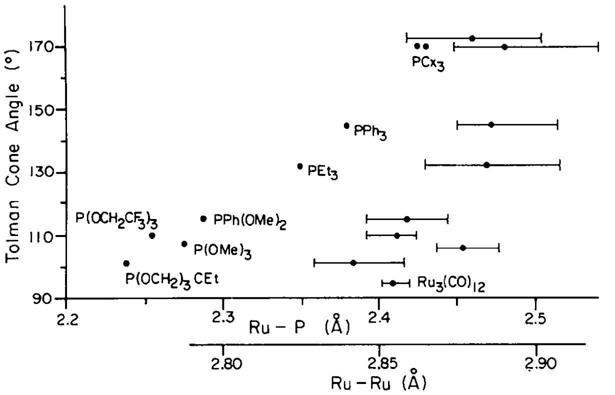

Fig. 3. Correlations of Ru—P and average Ru—Ru bond lengths in monosubstituted phosphine or phosphite complexes [$Ru_3(CO)_{11}PR_3$] with Tolman cone angles for the ligands. (Error bars on the Ru—Ru distances signify the range of values observed.)

τ(Ru3—Ru2—P1—C5) = −10·1°] whereas in (2) the phosphite conformation is such that O2 is virtually perpendicular to the Ru_3 plane [τ(Ru2—Ru1—P1—O2) = 83·5; τ(Ru3—Ru1—P1—O2) = 85·3°] (Figs. 1 and 2).

Following the recent analyses of Braga & Koetzle (1987, 1988) it was decided to test the effects of the refinement model used on the carbonyl bond lengths and other experimental data. The results summarized in Table 4 indicate that the principal observation of the above authors is confirmed for all but one carbonyl group in (1) and (2): namely, that the C atom tends to slide slightly towards the O atom while the *M*···O distance remains unchanged resulting in longer *M*—C and shorter C—O bond lengths in anisotropic temperature factor refinements. However, the magnitudes of the shifts are ≤ 0·023 Å in terms of the Ru—C distances and in many instances are comparable to the e.s.d.'s calculated for each distance.* Significantly, the present shifts are not as large as the changes in bond lengths of 0·02–0·05 Å mentioned by Braga & Koetzle (1987, 1988). In (1) and (2) the largest shifts occur for some but not all of the O atoms with the largest U_{iso} values, and similarly are generally larger for the equatorial CO groups. One notable exception is for the carbonyl Ru3—C33—O33 in (1) in that the anisotropic refinement results in a lengthening of the C33—O33 bond length and perhaps this represents another effect such as unresolved disorder of the C33 site. It is notable that a ΔF map based on the isotropic refinements contains a small residual peak (0·55 e $Å^{-3}$) which was 1·44, 0·54 and 1·65 Å from atoms Ru3, C33 and O33, respectively. This is the highest residual peak close to the Ru_3 triangle but is outranked by 20 other peaks of heights ≤ 1·32 e $Å^{-3}$ close (0·48–0·74 Å) to the O atoms of the carbonyls. In (2) the residual peaks close to the O atoms of the carbonyls and the O atoms of the $P(OMe)_3$ ligand, have heights ≤ 0·90 e $Å^{-3}$ in the isotropic refinement

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* Ru—C≡O angles change by a maximum of 0·5° for (1) and 0·9° for (2).

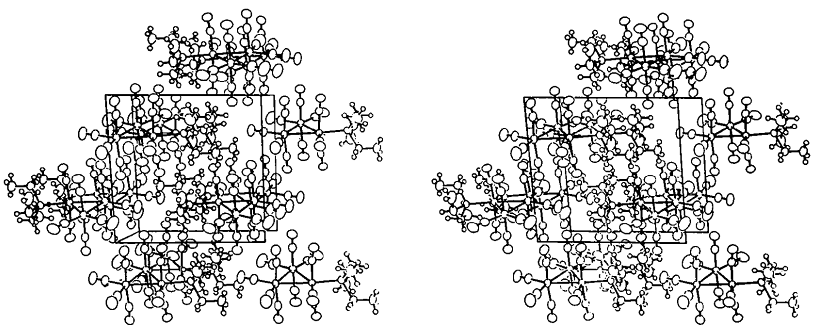

Fig. 4. Stereoscopic view of the crystal packing in compound (1) down *a*. The origin is in the top left-hand corner with *b* across and *c* down the page.

Table 5. *Selected torsion angles* (°) *and atom deviations* (Å) *from* Ru_3 *planes*

Torsion angles in square brackets and the second column of the corresponding atomic deviations are the values for compound (2).

C13[C12]—Ru1—Ru2—C21	178·4 (2)	[163·9 (3)]	C13[C12]—Ru1—Ru3—C31	179·2 (3)	[168·4 (4)]
—C22	−0·6 (3)	[−20·4 (3)]	—C32[C33]	−0·5 (1)	[−6·9 (1)]
P1—Ru1—Ru2—C21	−1.0 (1)	[−1·4 (1)]	C21—Ru2—Ru3—C31	174·6 (4)	[175·2 (3)]
—C22	−180·0 (3)	[174·2 (2)]	—C32[C33]	−6·6 (6)	[−7·2 (4)]
P1—Ru1—Ru3—C31	1·8 (3)	[−8·4 (4)]	C22—Ru2—Ru3—C31	−0·4 (2)	[−4·2 (1)]
—C32[C33]	−178·0 (2)	[176·2 (1)]	—C32[C33]	178·5 (4)	[173·4 (2)]

		Deviation				Deviation				Deviation	
	P1	0·013 (1)	−0·022 (1)	C12	C13	−1·923 (2)	−1·924 (3)	C24	C23	−1·945 (3)	−1·925 (3)
C1	O3	−1·298 (3)	−0·866 (2)	O12	O13	−3·048 (2)	−3·054 (3)	O24	O23	−3·064 (2)	−3·054 (2)
C2	C3	−1·331 (3)	−2·265 (4)	C13	C12	0·005 (2)	0·165 (3)	C31		0·009 (3)	0·058 (4)
C3	O2	1·533 (3)	1·368 (2)	O13	O12	−0·002 (2)	0·320 (3)	O31		0·019 (3)	0·069 (3)
C4	C2	1·853 (3)	2·047 (4)	C21		0·040 (3)	0·027 (3)	C32	C33	−0·012 (3)	−0·062 (3)
C5	O1	−0·202 (3)	−0·482 (2)	O21		0·094 (2)	0·068 (3)	O32	O33	−0·018 (3)	−0·116 (3)
C6	C1	−1·580 (3)	−0·526 (4)	C22		−0·004 (3)	−0·081 (3)	C33	C32	−1·940 (3)	−1·938 (3)
C11		1·928 (2)	1·917 (3)	O22		0·007 (3)	−0·153 (3)	O33	O32	−3·064 (2)	−3·056 (3)
O11		3·054 (2)	3·052 (3)	C23	C24	1·936 (3)	1·937 (3)	C34		1·930 (3)	1·935 (3)
				O23	O24	3·069 (2)	3·056 (2)	O34		3·060 (2)	3·069 (3)

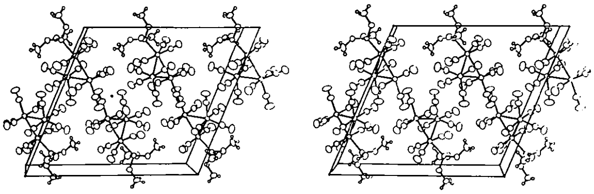

Fig. 5. Stereoscopic view of the crystal packing in compound (2) down *b*. The origin is in the top left-hand corner with *a* down and *c* across the view.

ΔF maps. In both compounds the anisotropic refinements effectively eliminate these residual peaks so that the final ΔF maps contain only peaks of *ca* 0·5 e $Å^{-3}$ close to the Ru atoms (Table 1).

Preliminary work with the program *THMA*11 (Maverick & Trueblood, 1988) has indicated corrections of 0·0044–0·0055 Å to the Ru—C distances and of 0·0026–0·0031 Å to the C—O distances when (2) is treated as rigid [$R_{(U)} = \sum w\Delta U_{ij}^2/\sum wU_{ij}(\mathrm{obs})^2 = 0{\cdot}25$, however].

Views of the crystal packing in (1) and (2) are given in Figs. 4 and 5. The shortest intermolecular O···O and O···H contacts are 3·022 [O13···O21 ($-1+x, y, z$)] and 2·60 Å [O12···H12 ($-1-x, 1-y, 1-z$)] in (1) with corresponding values of 2·934 [O11···O21 ($x, -1+y, z$)] and 2·62 Å [O3···H11 ($-x, \frac{1}{2}+y, -\frac{1}{2}-z$)] in (2). These distances are generally comparable to the intramolecular O···O and O···H contacts.

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