Complexes of the Platinum Metals. Part 31.[1] Reactions of Binuclear Ruthenium(II,III) and Rhodium(II) Carboxylates with Chelating Diphosphines; *X*-Ray Crystal Structure of (Acetato-*O,O'*)bis[bis(diphenylphosphino)methane-*P,P'*]ruthenium(II) Tetraphenylborate†

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The chelating diphosphines $Ph_2P(CH_2)_nPPh_2$ (n = 1—3) react with binuclear carboxylato complexes $[Ru_2(O_2CR)_4Cl]$ (R = Me, Et, or Ph) in cold or refluxing benzene to yield products *trans*-$[Ru(O_2CR)_2\{Ph_2P(CH_2)_nPPh_2\}_2]$ and *cis*-$[Ru(O_2CR)_2\{Ph_2P(CH_2)_nPPh_2\}_2]$ respectively, both of which are readily converted to the tetraphenylborate salts $[Ru(O_2CR)\{Ph_2P(CH_2)_nPPh_2\}_2]BPh_4$. Attempts to obtain similar products using samples of $[Ru_2(O_2CR)_4Cl]$ (R = CF_3 or Bu^t), prepared from the corresponding acetate complex by treatment with the appropriate carboxylic acids under vigorous conditions, gave mixtures indicative of incomplete carboxylate exchange. The *trans* complexes $[Ru(O_2CR)_2(Ph_2PCH_2PPh_2)_2]$ react with $NaBH_4$ and CO to afford *cis*- and *trans*-$[RuH_2(Ph_2PCH_2PPh_2)_2]$ and *cis,cis,trans*-$[Ru(O_2CR)_2(CO)_2(Ph_2PCH_2PPh_2)_2]$ respectively. The latter species react with $NaBH_4$ to yield *cis*- and *trans*-$[RuH_2(CO)(Ph_2PCH_2PPh_2)_2]$. Several of these products contain pendant $Ph_2PCH_2PPh_2$ ligands. The corresponding complexes containing $Ph_2P(CH_2)_2PPh_2$ failed to carbonylate even under vigorous conditions. The relationship between chelate ring size and ^{31}P n.m.r. parameters for some of these complexes is discussed. Confirmation that the cations contained in the tetraphenylborate salts are mononuclear and not, as previously suggested elsewhere, binuclear has been provided by an *X*-ray diffraction study of one such salt $[Ru(O_2CMe)(Ph_2PCH_2PPh_2)_2]BPh_4$. The crystals are triclinic, space group $P\bar{1}$ (no. 2), with a = 14.693(5), b = 18.821(4), c = 11.807(3) Å, α = 95.39(2), β = 108.03(2), γ = 92.43(2)°, and Z = 2 at 144(2) K. The complex contains tris(chelate)ruthenium(II) cations with bidentate acetate and bis(diphenylphosphino)methane ligands together with tetraphenylborate anions.

The ruthenium(II,III) carboxylates $[Ru_2(O_2CR)_4Cl]$[2] and their recently reported osmium(III) counterparts $[Os_2(O_2CR)_4Cl_2]$[3] adopt binuclear 'lantern' structures similar to those found for the well known rhodium(II) carboxylates.[4,5] However, they show marked dissimilarities in their behaviour toward neutral donor ligands (L). Whereas the rhodium(II) carboxylates tenaciously retain their integrity, and in most instances merely form axial adducts $Rh_2(O_2CR)_4L_2$,[4,5] the corresponding ruthenium(II,III) complexes cleave readily to form mononuclear ruthenium(II) products.[6] This difference in behaviour has been attributed to the electronic effects of adduct formation which are thought to strengthen the Rh–Rh bonds but weaken the Ru–Ru bonds in binuclear rhodium(II) and ruthenium(II,III) complexes respectively.[7] However, the relative instability of mononuclear rhodium(II) complexes may also contribute to this behaviour pattern. Whereas cleavage of binuclear $Ru^{II,III}$ centres leads directly to formation of stable mononuclear Ru^{II} and Ru^{III} complexes (the latter may subsequently be reduced to Ru^{II}), rupture of the Rh^{II} dimers must be accompanied by a concomitant redox step if unstable, mononuclear rhodium(II) intermediates are to be avoided.

In this paper we report reactions of binuclear ruthenium(II,III) and rhodium(II) carboxylates with chelating diphosphines $Ph_2P(CH_2)_nPPh_2$ (n = 1—3), and describe results which tend to confirm the reactivity pattern noted above. Some of the complexes described are apparently similar to products obtained by Lehmann and Wilkinson[8] during their study of reactions between trinuclear ruthenium(II,III) carboxylates and the same diphosphines.

Experimental

Ruthenium and rhodium chlorides were supplied by Johnson Matthey p.l.c., tetra(μ-acetato)-chlorodiruthenium(II,III),[2] chloro-tetra(μ-propionato)-diruthenium(II,III),[2] and tetra(μ-acetato)-dirhodium(II)[9] were prepared by standard literature procedures. All reactions were performed under nitrogen but products were worked-up in air. Analyses, performed by the Microanalytical laboratory, University College, London, melting points, taken in sealed tubes under nitrogen, and molecular weight data, obtained for $CHCl_3$ solutions using an Hitachi–Perkin-Elmer osmometer, are collected in Table 1. Proton and ^{31}P n.m.r. spectra were measured in $CDCl_3$ solution at 90 and 36.44 MHz respectively using a Bruker HFX 90 spectrometer operating in the Fourier-transform mode and are referenced to internal $SiMe_4$ and external 85% H_3PO_4 respectively. Positive values for ^1H and ^{31}P chemical shifts indicate resonances at low field relative to the reference. Infrared spectra were taken on a Perkin-Elmer 457 grating spectrometer using samples mulled in Nujol. Spectroscopic data are presented in Tables 2 and 3.

Tetra(μ-*benzoato*)-*chlorodiruthenium*(II,III).—Solutions of ruthenium trichloride trihydrate (0.34 g, 1.3 mmol) in 2-methoxyethanol (20 cm³) and lithium chloride (0.34 g, 8.02 mmol) in

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† *Supplementary data available* (No SUP 56541, 8 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Analyses, melting points, and molecular weights

	Analysis[b] (%)			
Compound[a]	C	H	M.p./°C	*M*
$[Ru(O_2CMe)(Ph_2PCH_2PPh_2)_2]BPh_4$	72.60 (73.15)	5.45 (5.40)	262[c]	
$[Ru(O_2CMe)\{Ph_2P(CH_2)_2PPh_2\}_2]BPh_4 \cdot CHCl_3$	68.65 (68.00)	5.60 (5.15)	258	1 476 (1 276)
$[Ru(O_2CMe)\{Ph_2P(CH_2)_3PPh_2\}_2]BPh_4 \cdot 0.5CHCl_3$	71.80 (70.90)	5.75 (5.50)	217	
$[Ru(O_2CEt)(Ph_2PCH_2PPh_2)_2]BPh_4$	73.05 (73.30)	5.35 (5.45)	282[c]	
$[Ru(O_2CEt)\{Ph_2P(CH_2)_2PPh_2\}_2]BPh_4$	72.95 (73.55)	5.70 (5.65)	275[c]	1 438 (1 290)
$[Ru(O_2CEt)\{Ph_2P(CH_2)_3PPh_2\}_2]BPh_4 \cdot 0.5CHCl_3$	70.50 (71.05)	6.00 (6.30)	218	
$[Ru(O_2CBu^t)(Ph_2PCH_2PPh_2)_2]BPh_4$	72.15 (73.30)	6.10 (5.70)	255	
$[Ru(O_2CBu^t)\{Ph_2P(CH_2)_2PPh_2\}_2]BPh_4$	73.00 (73.55)	6.30 (5.90)	238	1 287 (1 318)
$[Ru(O_2CPh)(Ph_2PCH_2PPh_2)_2]BPh_4$	73.90 (74.25)	5.65 (5.25)	221	
$[Ru(O_2CCF_3)\{Ph_2P(CH_2)_2PPh_2\}_2]BPh_4$	70.65 (70.45)	5.05 (5.10)	249	
$[Ru(O_2CMe)_2(Ph_2PCH_2PPh_2)_2]$	64.65 (65.65)	5.45 (5.05)	242	
$[Ru(O_2CEt)_2(Ph_2PCH_2PPh_2)_2]$	65.75 (66.20)	5.30 (5.30)	191	
$[Ru(O_2CMe)_2\{Ph_2P(CH_2)_2PPh_2\}_2] \cdot 0.5\ CHCl_3$	64.65 (63.10)	4.90 (5.90)	233	
$[Ru(O_2CPh)_2\{Ph_2P(CH_2)_2PPh_2\}_2]$	70.70 (69.55)	5.20 (5.10)	258	
$[Ru(O_2CMe)_2(CO)_2(Ph_2PCH_2PPh_2)_2]$	64.40 (63.90)	4.80 (5.15)	235	
$[Ru(O_2CEt)_2(CO)_2(Ph_2PCH_2PPh_2)_2]$	66.45 (66.50)	5.00 (5.15)	181	
$[RuH_2(Ph_2PCH_2PPh_2)_2]$	68.90 (68.10)	5.20 (4.65)	239[c]	
$[Rh_2(O_2CMe)_4(Ph_2PCH_2PPh_2)_2]$	55.45 (57.50)	4.65 (4.65)	167—169[c]	
$[Rh_2(O_2CMe)_4\{Ph_2P(CH_2)_2PPh_2\}_2]$	56.90 (58.20)	4.70 (4.85)	178[c]	

[a] Ruthenium compounds sometimes combust badly and give poor analyses.[8] [b] Calculated values in parentheses. [c] With decomposition.

2-methoxyethanol (20 cm^3) were added quickly and successively to a stirred solution of benzoic anhydride (5.6 g, 24.7 mmol) and benzoic acid (25.0 g, 204 mmol) in 2-methoxyethanol (100 cm^3). The mixture was heated to reflux under a stream of oxygen for 8 h. The brown microcrystals which separated were filtered off after standing for 12 h, washed with water, ethanol, chloroform, and finally light petroleum (b.p. 60—80 °C), and then dried *in vacuo* (yield 0.48 g, 51%), m.p. > 285 °C (Found: C, 46.15; H, 2.95; Cl, 4.70. Calc. for $C_{28}H_{20}ClO_8Ru_2$: C, 46.55; H, 2.80; Cl, 4.9%).

Chlorotetra(μ-2,2-*dimethylpropanoato*)-*diruthenium*(II,III).—The corresponding acetate, $[Ru_2(O_2CMe)_4Cl]$ (0.40 g, 0.84 mmol), dissolved in ethanol (75 cm^3), was treated with 2,2-dimethylpropanoic acid (2.5 g, 25mmol). The solution was heated under reflux for 4 h and then reduced to half volume under reduced pressure. The precipitate which deposited was washed with n-hexane and dried *in vacuo* to yield the product as a brown powder (0.43 g, 80%).

Chlorotetra(μ-*trifluoroacetato*)-*diruthenium*(II,III) *and Tetra*(μ-*benzoato*)-*chlorodiruthenium*(II,III).—Attempts to obtain these products by prolonged and repeated treatment of the corresponding acetate with neat trifluoroacetic acid under reflux and with benzoic acid in refluxing methanol–benzene respectively gave brown solids. Since these products are paramagnetic characterisation by n.m.r. was not practical. However, subsequent reactions with diphosphines yielded mixtures which clearly indicate that only partial exchange of carboxylate ligands had been achieved.

Acetatobis[*bis*(*diphenylphosphino*)*methane*]*ruthenium*(II) *Tetraphenylborate*, $[Ru(O_2CMe)(Ph_2PCH_2PPh_2)_2]BPh_4$.—A mixture of bis(diphenylphosphino)methane (0.32 g, 0.84 mmol) in benzene (10 cm^3) and ruthenium(II,III) acetate (0.10 g, 0.21 mmol) suspended in methanol (10 cm^3) was heated under reflux for 50 min. Sodium tetraphenylborate (0.14 g, 0.42 mmol) in methanol (5 cm^3) was added to the cooled green solution; the yellow precipitate which formed was crystallised from dichloromethane–light petroleum (b.p. 60—80 °C) to yield yellow crystals (0.30 g, 57%).

The following new complexes were similarly prepared using the appropriate carboxylato complex and diphosphine: $[Ru(O_2CMe)\{Ph_2P(CH_2)_2PPh_2\}_2]BPh_4 \cdot CHCl_3$ as yellow crystals from chloroform–hexane (70%), $[Ru(O_2CMe)\{Ph_2P(CH_2)_3PPh_2\}_2]BPh_4 \cdot 0.5\ CHCl_3$ as yellow microcrystals from chloroform–hexane (41%), $[Ru(O_2CEt)(Ph_2PCH_2PPh_2)_2]BPh_4$ as yellow microcrystals from dichloromethane–methanol (71%), $[Ru(O_2CEt)\{Ph_2P(CH_2)_2PPh_2\}_2]BPh_4$ as yellow crystals from chloroform–hexane (83%), $[Ru(O_2CEt)\{Ph_2P(CH_2)_3PPh_2\}_2]BPh_4 \cdot 0.5\ CHCl_3$ as yellow crystals from chloroform–hexane (88%), $[Ru(O_2CBu^t)(Ph_2PCH_2PPh_2)_2]BPh_4$ as yellow crystals from dichloromethane–methanol (60%), $[Ru(O_2CBu^t)\{Ph_2P(CH_2)_2PPh_2\}_2]BPh_4$ as yellow crystals from chloroform–hexane (43%), and $[Ru(O_2CPh)(Ph_2PCH_2PPh_2)_2]BPh_4$ as yellow crystals from dichloromethane–hexane (47%).

Attempts to prepare the corresponding complex $[Ru(O_2CPh)\{Ph_2P(CH_2)_3PPh_2\}_2]BPh_4$ in a similar manner using a sample of '$Ru_2(O_2CPh)_4Cl$' obtained by carboxylate exchange gave a product which was shown by ^{31}P n.m.r. to be a *ca.* 1:1 mixture of acetato and benzoato complexes. Similarly, attempts to prepare $[Ru(O_2CCF_3)(Ph_2PCH_2PPh_2)_2]BPh_4$ and the analogous complex $[Ru(O_2CCF_3)\{Ph_2P(CH_2)_3PPh_2\}_3]BPh_4$ gave *ca.* 1:1 mixtures of acetato and trifluoroacetato complexes. Solubility differences permitted isolation of $[Ru(O_2CCF_3)\{Ph_2P(CH_2)_2PPh_2\}_2]BPh_4$ as yellow crystals, by crystallising the *ca.* 1 : 1 mixture from chloroform–hexane (47%).

cis-*Bis*(*acetato*)*bis*[*bis*(*diphenylphosphino*)*methane*]*ruthenium*(II).—A solution of ruthenium(II,III) acetate (0.10 g, 0.21 mmol) in methanol (10 cm^3) was added to bis(diphenylphosphino)methane (0.32 g, 0.84 mmol) in benzene (10 cm^3) and the solution heated under reflux for 1 h. The dark orange solution was evaporated to dryness under reduced pressure and the residue was treated with hexane to yield a yellow solid. This was washed with hexane and diethyl ether and then crystallised from chloroform–hexane as yellow microcrystals (0.36 g, 86%).

The following new complexes were similarly prepared from the appropriate carboxylato complex and diphosphine: *cis*-$[Ru(O_2CMe)_2\{Ph_2P(CH_2)_2PPh_2\}_2] \cdot 0.5\ CHCl_3$ as yellow microcrystals from chloroform–hexane (71%) and *cis*-$[Ru(O_2CEt)_2\{Ph_2P(CH_2)_2PPh_2\}_2]$ as yellow microcrystals from benzene–hexane (61%).

Table 2. Infrared and ^1H n.m.r. data

R	*n*	$\nu_{asym}(OCO)/cm^{-1}$ [a]	$\nu_{sym}(OCO)/cm^{-1}$ [a]	δ(P)/p.p.m.[b]	*J*(PP′)/Hz	δ(Ph)/p.p.m.	$\delta(CH_2)_n$/ p.p.m.	δ(R)/p.p.m.[b]
(*a*) $[Ru(O_2CR)\{Ph_2P(CH_2)_nPPh_2\}_2]BPh_4$								
Me	1	1 580	1 455	8.24 (t), −11.59 (t)	39.1	7.7—6.8, 6.06	4.5, 3.9	1.8
Me	2	1 580	1 461	59.1, 57.66 (A_2B_2)	18.4	7.7—6.8, 5.8	2.8, 2.1, 1.9, 1.4	0.5
Me	3	1 571	1 455	30.46 (t), 1.61 (t)	31.7	7.8—6.6	2.6, 1.85, 1.56, 1.26	1.36
Et	1	1 578	1 466	7.77 (t). −11.86 (t)	39.1	7.8—6.8, 6.1	4.5, 3.9	2.05 (q), 0.87 (t)
Et	2	1 569	1 465	58.91, 57.68 (A_2B_2)	18.3	7.7—6.7, 5.8	2.8, 2.2, 1.9, 1.4	1.85 (q), 0.2 (t)
Et	3	1 571	1 467	30.93 (t), 1.67 (t)	31.7	7.9—6.7	2.6, 2.0, 1.9, 1.5	0.88 (q), 0.44 (t)
Bu^t	1	1 572	1 458	7.07 (t), −11.53 (t)	37.8	7.7—6.8, 5.9	4.3, 3.8	0.78 (s)
Bu^t	2	1 570	1 472	56.86, 53.75 (A_2B_2)	17.1	7.8—6.8, 5.9	2.4, 2.1, 1.7, 1.5	0.22 (s)
CF_3	1	1 598	1 457	10.05 (t), −12.76 t [c]	39.7	7.8—6.8, 6.1	4.6, 3.9	−75.7 (s)[d]
CF_3	2	1 589	1 461	58.91, 57.70 (A_2B_2)	18.4	—	—	−76.3 (s)[d]
CF_3	3	1 598	1 461	29.96 (t), −0.07 (t)[c]	31.7	8.4—6.5	2.5, 2.3, 2.1	−74.73 (s)[d]
Ph	1	1 580	1 500	8.71 (t), −12.20 (t)	39.1	7.7—6.8, 6.07	4.5, 3.8	—
Ph	3	1 568	1 505	43.39 (t), −4.02 (t)[c]	31.1	—	—	—
(*b*) *cis*-$[Ru(O_2CR)_2\{Ph_2P(CH_2)_nPPh_2\}_2]$								
Me	1	1 570	1 455	8.48 (t), −11.47 (t)	38.9	—	—	—
Me	2	1 600	1 500	59.10, 57.66 (A_2B_2)	18.4	—	—	—
Et	2	1 579	1 468, 1 450	58.91, 57.68 (A_2B_2)	18.3	—	—	—
(*c*) *trans*-$[Ru(O_2CR)_2\{Ph_2P(CH_2)_nPPh_2\}_2]$								
Me	1	1 585	1 373	−6.66 (s)	—	7.37—7.08	5.84	0.79 (s)
Et	1	1 592	1 460, 1 382	−6.23 (s)	—	7.3—7.08	5.87	1.07 (q), 0.07 (t)
CF_3	1	1 670	1 473	−9.11 (s)	—	—	—	—
CF_3	2	1 670	1 483	41.4 (s)	—	—	—	—
Ph	2	1 600	1 550, 1500	58.64 (s)	—	7.82—6.82	5.97	—
(*d*) $[Ru(O_2CR)_2(CO)_2(Ph_2PCH_2PPh_2)_2]$								
Me	1	1 617/1 598	1 396	25.51, −27.25 (AA′ XX′)	27.9	—	—	—
Et	1	1 600	1 432	25.06, −27.34 (AA′ XX′)	32.9, 30.5	7.92, 7.26 6.88	3.76	2.13 (q), 1.07 (t)
(*e*) *cis*- and *trans*-$[RuH_2\{Ph_2P(CH_2)_nPPh_2\}_2]$								
—	1			*cis* {14.05 (t) 0.53 (t)} *trans* 9.24 (s)	27.9	—	—	—
(*f*) $[Rh_2(O_2CR)_4\{Ph_2P(CH_2)_nPPh_2\}_2]$								
Me	1	1 583	1 435	—	—	—	—	—
Me	2	1 582	1 429	—	—	—	—	—

Data for carbonyl and hydride ligands

Complex	$\nu(CO)/cm^{-1}$	$\nu(MH)/cm^{-1}$	^1H and ^{31}P n.m.r.
$[Ru(O_2CMe)_2(CO)_2(Ph_2PCH_2PPh_2)_2]$	2 018/1 980	—	—
$[Ru(O_2CEt)_2(CO)_2(Ph_2PCH_2PPh_2)_2]$	2 040/1 989	—	—
cis- and *trans*-$[RuH_2(Ph_2PCH_2PPh_2)_2]$	—	1 832/1 610	see text
cis- and *trans*-$[RuH_2(CO)(Ph_2PCH_2PPh_2)_2]$	1 931	1 980/1 630	see text

[a] Presence of other bands in region 1 600—1 400 cm^{-1} makes unambiguous assignment of ν(OCO) vibrations difficult. [b] s = Singlet, d = doublet, t = triplet, q = quartet. [c] Spectra taken using 50 : 50 mixtures with corresponding acetate (see text). [d] ^{19}F N.m.r. data.

trans-*Bis(acetato)bis[bis(diphenylphosphino)methane]ruthenium*(II).—A suspension of ruthenium(II,III) acetate (0.10 g, 0.21 mmol) in methanol (10 cm^3) was added to a solution of bis(diphenylphosphino)methane (0.32 g, 0.84 mmol) in benzene (10 cm^3). The mixture was stirred at ambient temperature for 1 h after which time a dark yellow powder precipitated. The solid was crystallised from chloroform–hexane to yield yellow microcrystals (0.20 g, 40%).

The following new complexes were similarly prepared using the appropriate carboxylate complex and diphosphine: *trans*-

Table 3. ^{31}P-{^{1}H} N.m.r. data for cations $[Ru(O_2CR)\{Ph_2P(CH_2)_n PPh_2\}_2]^+$ in relation to chelate ring size

n	R	Chelate ring size	$\delta(P_{co\text{-}ord.})$/ p.p.m.[a]	$\delta(P_{free})$/ p.p.m.[b]	Δ/p.p.m.[c]	$^{2}J(PP')$/Hz
1	Me	4	−1.7	−21.5	19.8	39.0
	Et	4	−2.0	−21.5	19.5	39.1
	Bu^t	4	−2.2	−21.5	19.3	37.8
	CF_3	4	−1.3	−21.5	20.2	39.7
	Ph	4	−1.8	−21.5	19.7	39.1
2	Me	5	58.4	−12	76.4	18.4
	Et	5	58.3	−12	70.3	18.3
	Bu^t	5	55.3	−12	67.3	17.1
	CF_3	5	58.3	−12	70.3	18.4
3	Me	6	16.0	−14	30.0	31.7
	Et	6	16.0	−14	30.0	31.7
	CF_3	6	15.0	−14	29.0	31.7
	Ph	6	19.7	−14	33.7	31.1

[a] Average value for ^{31}P nuclei in complex. [b] Value for ^{31}P nuclei in the free ligand. [c] $\delta(P_{co\text{-}ord.}) - \delta(P_{free})$.

$[Ru(O_2CEt)_2(Ph_2PCH_2PPh_2)_2]$ as yellow crystals from chloroform–hexane (67%), *trans*-$[Ru(O_2CCF_3)_2(Ph_2PCH_2PPh_2)_2]$ as yellow crystals from chloroform–hexane (10%), *trans*-$[Ru(O_2CPh)_2\{Ph_2P(CH_2)_2PPh_2\}_2]$ as yellow crystals from chloroform–hexane (35%), and *trans*-$[Ru(O_2CCF_3)_2\{Ph_2P(CH_2)_2PPh_2\}_2]$ as yellow crystals from chloroform–hexane (12%).

Conversion of trans-$[Ru(O_2CEt)_2(Ph_2PCH_2PPh_2)_2]$ *to* $[Ru(O_2CEt)(Ph_2PCH_2PPh_2)_2]BPh_4$.—A suspension of *trans*-$[Ru(O_2CEt)_2(Ph_2PCH_2PPh_2)_2]$ (0.10 g, 0.095 mmol) in methanol–benzene (1%1, 40 cm^3) was heated under reflux for 1 h. The resultant yellow solution was treated with sodium tetraphenylborate (0.14 g, 0.4 mmol) in methanol (5 cm^3) to afford a yellow precipitate which was filtered off and washed with methanol. The product was identified on the basis of i.r. and ^{31}P n.m.r. spectra.

cis,cis,trans-*Bis(acetato)bis[bis(diphenylphosphino)methane]dicarbonylruthenium*(II).—*trans*-$[Ru(O_2CMe)_2(Ph_2PCH_2PPh_2)_2]BPh_4$ (0.2 g, 0.2 mmol) in benzene (30 cm^3) was stirred at ambient temperature with carbon monoxide bubbling through the solution for 4 h. The orange solution was evaporated to dryness and the residue treated with hexane, to yield an off-white solid which formed white crystals from chloroform–hexane (0.18 g, 60%).

The complex *cis,cis,trans*-$[Ru(O_2CEt)_2(CO)_2(Ph_2PCH_2PPh_2)_2]$ was similarly prepared and crystallised from chloroform–hexane (90%).

Treatment of trans-$[Ru(O_2CPh)_2\{Ph_2P(CH_2)_2PPh_2\}_2]$ *with Carbon Monoxide*.—A suspension of *trans*-$[Ru(O_2CPh)_2\{PPh_2(CH_2)_2PPh_2\}_2]$ (0.10 g, 0.088 mmol) in toluene (10 cm^3) was heated under reflux with carbon monoxide bubbling through for 5 h. The yellow solution was evaporated to dryness and the residue treated with hexane to yield a pale yellow solid which was identified by i.r. and ^{31}P n.m.r. as unreacted starting material.

Treatment of $[Ru(O_2CMe)\{Ph_2P(CH_2)_2PPh_2\}_2]BPh_4$ *with Carbon Monoxide*.—A suspension of $[Ru(O_2CMe)\{Ph_2P(CH_2)_2PPh_2\}_2]BPh_4$ (0.1 g, 0.078 mmol) in toluene (10 cm^3) was heated under reflux with carbon monoxide bubbling through the solution for 5 h. The pale yellow solid which precipitated from the cooled solution was identified by its i.r. spectrum as unreacted starting material.

cis- *and* trans-*Bis[bis(diphenylphosphino)methane]dihydridoruthenium*(II).—A solution of *trans*-$[Ru(O_2CEt)_2(Ph_2PCH_2PPh_2)_2]$ (0.15 g, 0.15 mmol) in benzene (7 cm^3) was mixed with sodium tetrahydroborate (0.070 g, 0.2 mmol) in ethanol (20 cm^3) and the mixture then heated under reflux for 2.5 h. An off-white solid precipitated from the cooled solution and was collected, washed successively with methanol, water, methanol, and hexane, then dried *in vacuo* and crystallised from benzene–hexane to form white crystals (0.09 g, 69%).

cis- *and* trans-*Bis[bis(diphenylphosphino)methane](carbonyl)dihydridoruthenium*(II).—A solution of $[Ru(O_2CEt)_2(CO)_2(Ph_2PCH_2PPh_2)_2]$ (0.10 g, 0.093 mmol) in benzene (5 cm^3) was treated with sodium tetrahydroborate (0.05 g, 0.133 mmol) in ethanol (2 cm^3) and the mixture was heated under reflux for 1 h. The yellow solution was evaporated to dryness and then extracted with diethyl ether. The ether extract was concentrated under reduced pressure then diluted with hexane to precipitate a pale yellow solid which was filtered off, washed with hexane, and dried *in vacuo* (0.05 g, 60%).

Tetra(μ-acetato)-bis[bis(diphenylphosphino)methane]dirhodium(II).—A suspension of tetra(μ-acetato)-dirhodium (0.10 g, 0.226 mmol) in methanol (10 cm^3) was treated with bis(diphenylphosphino)methane (0.17 g, 0.45 mmol) in benzene (10 cm^3). The suspension instantly changed from green to orange and after heating under reflux for 2 h the orange solid was filtered off, washed with benzene and methanol, and then dried *in vacuo* (0.19 g, *ca.* 100%).

The complex $[Rh_2(O_2CMe)_4\{Ph_2P(CH_2)_2PPh_2\}_2]$ was similarly prepared as an orange solid (0.19 g, *ca.* 100%).

X-*Ray Structure Analysis of* $[Ru(O_2CMe)(Ph_2PCH_2PPh_2)_2]BPh_4$.—*Crystal data.* $C_{76}H_{67}BO_2P_4Ru$, M = 1 248.2, triclinic, a = 14.693(5), b = 18.821(4), c = 11.807(3) Å, α = 95.39(2), β = 108.03(2), γ = 92.43(2)°, U = 3 082 Å^3 at 144(2) K (by least-squares refinement on diffractometer angles for 22 automatically centred reflections having $8.3 \leqslant \theta \leqslant 10.3°$, λ = 0.710 73 Å), space group $P\bar{1}$ (no. 2), Z = 2, D_c = 1.348 g cm^{-3}. Green-yellow, flat needles elongated along a. Dimensions of crystals used for data collection: 0.37 mm parallel to a; perpendicular distances between members of forms {$(01\bar{1}$} and {001} of 0.051 and 0.088 mm respectively; μ(Mo-K_α) = 3.98 cm^{-1}, F(000) = 1 293.9.

Data collection and processing. CAD4 diffractometer, $\omega/2\theta$ mode with ω scan width = 0.7 + 0.35tanθ, ω scan speed 1.6—5.5 ° min^{-1}, graphite-monochromated Mo-K_α radiation; 11 378 reflections measured ($2.5 \leqslant \theta \leqslant 25°$; $\pm h$, $\pm k$, $+l$), 10 804 unique [merging R = 0.046 after absorption correction (max., min. transmission coefficients 0.98, 0.93)], giving 6 678 with $I \geqslant 3\sigma(I)$. Average change in the 6 intensity standards of −0.5% (no correction).

Structure analysis and refinement. Direct methods (Ru and two P atoms) followed by DIRDIF,[10] an automatic program for the application of direct methods to the solution of structures when part of the structure is known. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic, phenyl and methylene hydrogen atoms in calculated positions (r_{C-H} = 1.00 Å), and methyl hydrogen atoms at positions found in a difference-Fourier map. The B values assigned to the hydrogen atoms were 1.0 A^2 larger than the $B_{equiv.}$ values of the attached carbon atoms as determined at a late stage in the refinement. The weighting scheme $w = 4F_o^2/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$ with $\sigma(F_o)$ from counting statistics gave satisfactory agreement

Table 4. Positional parameters with estimated standard deviations in parentheses for the non-hydrogen atoms of $[Ru(O_2CMe)(Ph_2PCH_2PPh_2)_2]BPh_4$

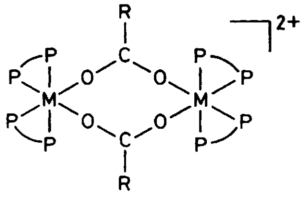
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	0.746 18(4)	0.222 11(3)	0.162 41(5)	C(122)	0.638 8(5)	0.400 8(4)	0.073 7(6)
P(1)	0.603 1(1)	0.274 07(9)	0.158 2(1)	C(123)	0.637 2(5)	0.474 7(4)	0.066 0(6)
P(2)	0.710 5(1)	0.198 02(9)	0.331 4(1)	C(124)	0.592 6(6)	0.516 1(4)	0.133 5(7)
P(3)	0.899 3(1)	0.179 49(9)	0.196 9(1)	C(125)	0.547 7(6)	0.484 2(4)	0.206 8(7)
P(4)	0.857 6(1)	0.313 32(9)	0.261 5(1)	C(126)	0.547 4(5)	0.411 7(4)	0.211 9(6)
O(1)	0.722 7(3)	0.233 9(3)	−0.026 9(4)	C(211)	0.666 9(5)	0.104 6(4)	0.328 0(6)
O(2)	0.671 3(3)	0.135 2(3)	0.022 4(4)	C(212)	0.610 5(5)	0.068 4(4)	0.217 3(6)
C(1)	0.679 5(5)	0.171 7(4)	−0.058 3(6)	C(213)	0.583 6(5)	−0.003 8(4)	0.208 5(7)
C(2)	0.639 0(6)	0.143 4(5)	−0.187 7(7)	C(214)	0.611 5(6)	−0.041 2(4)	0.307 2(8)
C(3)	0.609 0(5)	0.255 9(4)	0.310 1(5)	C(215)	0.666 5(5)	−0.006 0(4)	0.417 4(7)
C(4)	0.962 7(4)	0.257 8(4)	0.297 2(5)	C(216)	0.693 6(5)	0.066 7(4)	0.427 4(6)
C(11)	0.290 4(5)	0.320 7(4)	0.334 4(6)	C(221)	0.779 5(4)	0.219 2(3)	0.488 0(5)
C(12)	0.204 3(5)	0.356 2(4)	0.313 2(6)	C(222)	0.739 9(5)	0.253 2(4)	0.570 0(6)
C(13)	0.159 6(6)	0.380 4(4)	0.203 7(7)	C(223)	0.788 4(5)	0.260 9(4)	0.691 7(6)
C(14)	0.199 0(6)	0.370 8(4)	0.110 4(7)	C(224)	0.878 2(5)	0.236 2(4)	0.736 0(6)
C(15)	0.284 1(6)	0.338 2(5)	0.129 9(7)	C(225)	0.919 5(5)	0.201 3(4)	0.654 7(6)
C(16)	0.327 8(5)	0.314 3(4)	0.239 8(7)	C(226)	0.870 8(5)	0.192 9(4)	0.533 2(6)
C(21)	0.357 7(5)	0.200 9(4)	0.411 6(6)	C(311)	0.956 5(5)	0.164 5(4)	0.079 6(5)
C(22)	0.284 1(6)	0.161 1(4)	0.319 2(7)	C(312)	1.037 6(5)	0.203 3(4)	0.079 2(6)
C(23)	0.291 7(7)	0.091 1(5)	0.271 4(7)	C(313)	1.086 9(5)	0.182 2(5)	−0.001 5(7)
C(24)	0.377 4(7)	0.059 6(5)	0.321 6(9)	C(314)	1.051 5(6)	0.123 0(5)	−0.082 2(7)
C(25)	0.449 7(6)	0.096 7(4)	0.409 2(9)	C(315)	0.968 0(7)	0.084 6(5)	−0.086 7(6)
C(26)	0.441 4(5)	0.166 1(4)	0.455 2(7)	C(316)	0.919 8(6)	0.105 7(4)	−0.004 8(6)
C(31)	0.443 2(5)	0.328 7(4)	0.537 5(6)	C(321)	0.936 8(5)	0.100 9(4)	0.272 8(6)
C(32)	0.484 8(5)	0.387 4(4)	0.499 8(6)	C(322)	0.870 1(5)	0.046 3(4)	0.270 3(6)
C(33)	0.570 2(5)	0.423 7(4)	0.569 7(7)	C(323)	0.898 3(6)	−0.015 4(4)	0.320 8(6)
C(34)	0.620 1(5)	0.403 2(5)	0.682 1(7)	C(324)	0.995 3(6)	−0.023 9(4)	0.372 2(7)
C(35)	0.580 6(5)	0.346 9(4)	0.721 5(7)	C(325)	1.063 4(6)	0.030 3(4)	0.374 6(7)
C(36)	0.495 7(5)	0.311 1(4)	0.650 5(6)	C(326)	1.035 0(5)	0.092 6(4)	0.325 2(6)
C(41)	0.271 1(5)	0.284 1(4)	0.541 6(5)	C(411)	0.879 9(4)	0.376 2(4)	0.162 2(5)
C(42)	0.265 5(5)	0.346 0(4)	0.613 5(6)	C(412)	0.891 3(5)	0.450 2(4)	0.194 0(6)
C(43)	0.205 5(5)	0.349 8(4)	0.685 2(6)	C(413)	0.898 1(6)	0.494 9(4)	0.107 9(6)
C(44)	0.148 5(5)	0.290 3(4)	0.688 9(6)	C(414)	0.895 5(6)	0.467 3(4)	−0.004 4(6)
C(45)	0.152 2(5)	0.226 0(4)	0.619 0(6)	C(415)	0.888 8(5)	0.393 9(4)	−0.033 2(6)
C(46)	0.213 8(5)	0.223 7(4)	0.549 4(6)	C(416)	0.879 7(5)	0.348 8(4)	0.047 3(6)
C(111)	0.489 2(5)	0.233 1(4)	0.056 8(6)	C(421)	0.865 5(5)	0.369 4(3)	0.398 8(6)
C(112)	0.433 8(5)	0.180 7(4)	0.087 7(6)	C(422)	0.941 4(5)	0.368 0(4)	0.503 6(6)
C(113)	0.349 0(5)	0.150 8(4)	0.007 2(6)	C(423)	0.942 6(7)	0.409 9(5)	0.606 8(7)
C(114)	0.317 5(5)	0.172 5(4)	−0.107 4(7)	C(424)	0.871 7(6)	0.455 1(4)	0.606 7(7)
C(115)	0.372 5(5)	0.224 4(4)	−0.139 5(6)	C(425)	0.797 1(5)	0.458 2(4)	0.504 8(7)
C(116)	0.456 4(5)	0.253 9(4)	−0.058 6(6)	C(426)	0.793 0(5)	0.415 4(4)	0.400 1(6)
C(121)	0.594 0(5)	0.369 1(4)	0.146 6(6)	B	0.340 6(6)	0.283 3(4)	0.457 2(7)

analyses. Final *R* and *R′* values are 0.060 and 0.064. Computations were performed on a VAX 11/730 computer using the Enraf-Nonius Structure Determination Package.[11] Scattering factors were from the usual tabulation.[12] Final atomic co-ordinates of non-hydrogen atoms are given in Table 4.

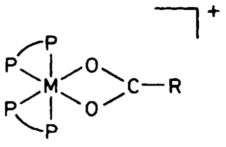
Results and Discussion

Preparation of $[Ru_2(O_2CR)_4Cl]$ *Complexes*.—The ruthenium complexes $[Ru_2(O_2CR)_4Cl]$ used in the present study were either prepared from $RuCl_3 \cdot 3H_2O$, RCO_2H, and $(RCO)_2O$ (R = Me, Et, or Ph) using the original literature method[2] or were obtained from the preformed acetate complex by carboxylate exchange using excess acid RCO_2H or sodium salt RCO_2Na (R = Bu^t, CF_3, or Ph). Samples prepared by the latter method, even after repeated carboxylate exchange cycles subsequently reacted with diphosphines to afford products which in many instances proved to be mixtures indicative of incomplete carboxylate exchange. The retention of acetate ligands in $[Ru_2(O_2CMe)_4Cl]$ is reminiscent of similar behaviour previously reported for the $[Rh_2(O_2CMe)_4]$–CF_3CO_2H systems in which the third and fourth substitutions occur *ca.* 10^2 times less rapidly than the first and second.[13] Stabilisation of the residual acetate linkages in the partially substituted intermediates was proposed to explain the behaviour of the rhodium system and is presumably also responsible for incomplete substitution in the ruthenium acetate. A recent paper reports the use of very vigorous conditions and prolonged reaction times to achieve complete replacement of acetate ligands in $[Ru_2(O_2CMe)_4Cl]$ by $CF_3C(O)NH^-$ anions.[14]

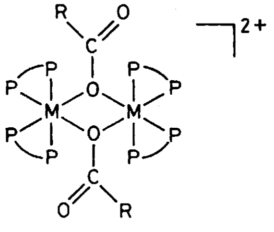
Salts $[Ru(O_2CR)\{Ph_2P(CH_2)_nPPh_2\}_2]BPh_4$ (*n* = 1—3).—The complex cations were obtained by heating the appropriate diphosphine and ruthenium(II,III) carboxylate (R = Me, Et, Bu^t, CF_3, or Ph) under reflux in methanol for 50 min; the salts were precipitated as yellow crystalline solids by addition of sodium tetraphenylborate in methanol solution. They have also been prepared by treatment of *cis*- or *trans*-$[Ru(O_2CR)_2\{Ph_2P(CH_2)_2PPh_2\}_2]$ with sodium tetraphenylborate in benzene–methanol solution. These products have similar stoicheiometry to the previously reported[8] perchlorate salts $[Ru_2(O_2CMe)_2\{Ph_2P(CH_2)_nPPh_2\}_4][ClO_4]_2$ (*n* = 1 or 2) and both sets of complexes display AA′ BB′ or AA′ XX′ patterns in their ^{31}P n.m.r. spectra. However, the perchlorate complexes are des-



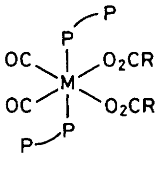
(**I**)



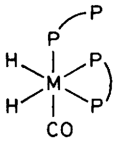
(**II**)



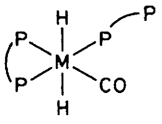
(**III**)



(**IV**)



(**V**)



(**VI**)

cribed as green rather than yellow and, in one instance (n = 2) possess ^{31}P n.m.r. chemical shift values very different to those reported here. In addition molecular-weight data for the tetraphenylborate salts (*ca.* 1 280—1 480) are consistent with the binuclear formulation whereas those reported for the perchlorates (*ca.* 150—170) are anomalously low even for a mononuclear structure. It is therefore by no means certain that we are dealing with directly analogous complexes. As we noted in a previous communication[15] binuclear structures (**I**) of the type proposed for the perchlorate salts seem rather improbable since they involve considerable strain within the bridge and would therefore be expected to be unstable relative to the alternative mononuclear and binuclear structures (**II**) and (**III**) respectively. Complexes containing *O,O*-bridging carboxylate ligands are rare but by no means unknown[16] and structure (**III**) is therefore an entirely feasible alternative to (**I**). In order to differentiate between the three possible structures [(**I**), (**II**), and (**III**)] the *X*-ray crystal structure of one of the tetraphenylborate salts, [Ru(O_2CMe)($Ph_2PCH_2PPh_2$)$_2$]BPh_4, was determined (see below). The structure of the cation (Figure) clearly establishes the mononuclear nature of the salt in the solid state at least.

The high molecular-weight values recorded for the tetraphenylborate salts are obviously at variance with the results of the *X*-ray diffraction study. Possible explanations for the discrepancy include formation of tightly-bound ion pairs or adoption of a binuclear structure, probably (**III**), in solution.

cis- and trans-[Ru(O_2CR)$_2${$Ph_2P(CH_2)_nPPh_2$}$_2$].—One such pair of complexes *cis-* and *trans-*[Ru(O_2CMe)$_2$($Ph_2PCH_2PPh_2$)$_2$] has previously been obtained as an isomer mixture from reduced solutions of [$Ru_3O(O_2CMe)_6(MeOH)_3$][O_2CMe] and the diphosphine in methanol.[8] The examples reported in the present paper were prepared from ruthenium(II,III) carboxylates and the appropriate diphosphines in methanol; reactions performed at ambient temperature afforded the *trans* isomer (^{31}P n.m.r. singlet) and those carried out under reflux yielded the *cis* isomer (^{31}P n.m.r. AA′ XX′ pattern). The ^{31}P n.m.r. pattern of the *cis* isomer is also consistent with the salt formulation [Ru(O_2CR){$Ph_2P(CH_2)_nPPh_2$}$_2$][O_2CR]. However this ionic structure is eliminated by the ^{1}H n.m.r. spectrum of the acetates ($C\mathit{H}_3CO_2$, *one* singlet) and by the poor solubility in polar solvents. Unfortunately the low solubility in polar solvents prevented the collection of meaningful conductivity data.

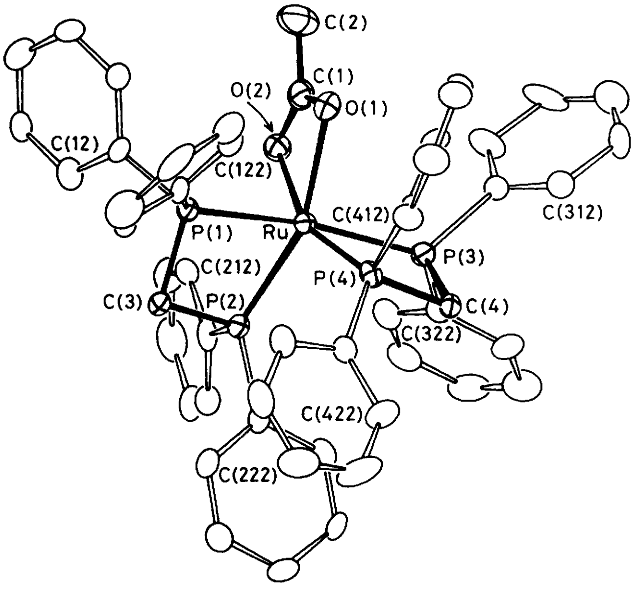


Figure. Perspective view of the complex cation [Ru(O_2CMe)($Ph_2PCH_2PPh_2$)$_2$]$^+$. Ellipsoids represent 50% contours of atomic displacement, and H atoms have been omitted for the sake of clarity

cis- and trans-[RuH_2($Ph_2PCH_2PPh_2$)$_2$].—Treatment of *trans-*[Ru(O_2CEt)$_2$($Ph_2PCH_2PPh_2$)$_2$] with $NaBH_4$ in benzene–ethanol under reflux for 2.5 h affords an off-white precipitate which forms white crystals from benzene–hexane. Analytical and spectroscopic data establish the species present as *cis-*[RuH_2($Ph_2PCH_2PPh_2$)$_2$][ν(RuH) at 1 832 cm^{-1} (broad); δ(RuH) −7.5 (d of quartets), $^2J(PH)_{trans}$ 72.6, $^2J(PH)_{cis}$ 18.2 Hz; ^{31}P-{^{1}H} n.m.r. AA′ XX′ pattern] and *trans-*[RuH_2($Ph_2PCH_2PPh_2$)$_2$][ν(RuH) 1 610 cm^{-1}; δ(RuH) −4.8 (quintet), $^2J(PH)_{cis}$ 19.4 Hz; ^{31}P-{^{1}H} n.m.r. singlet]. The same product mixture has previously been obtained by Chaudret *et al.*[17] from [Ru(C_8H_{12})(C_8H_8)] and $Ph_2PCH_2PPh_2$ under hydrogen but was incorrectly formulated as a single trinuclear complex [Ru_3H_6($Ph_2PCH_2PPh_2$)$_6$]. This formulation was corrected by the original workers[18] and by the present authors.[15]

Attempted carbonylation of this mixture in benzene (1 atm CO, 25 °C, and reflux) merely increased the proportion of the *trans* isomer. However, the anticipated carbonyl products have been obtained by an alternative route (see below).

cis,cis,trans-[Ru(O_2CR)$_2$(CO)$_2$($Ph_2PCH_2PPh_2$)$_2$] (R = Me *or* Et).—These complexes were obtained as white crystals by carbonylation of the species *trans-*[Ru(O_2CR)$_2$($Ph_2PCH_2PPh_2$)$_2$] in benzene at ambient temperature. Their i.r. spectra each display a pair of strong carbonyl absorptions (*ca.* 2 020 and 1 980 cm^{-1}) indicative of a *cis* pair of carbonyl ligands, and carboxylate bands (*ca.* 1 600 and 1 400 cm^{-1}) consistent with the presence of monodentate carboxylate ligands. The ^{31}P-{^{1}H} n.m.r. spectra each consist of an AA′ XX′ pattern with δ(P) *ca.* 25 and −27 p.p.m. The latter value is similar to that found for

Table 5. Selected bond lengths (Å) and angles (°) for $[Ru(O_2CMe)(Ph_2PCH_2PPh_2)_2]BPh_4$*

Ru–P(1)	2.342(2)	P(3)–C(4)	1.819(6)
Ru–P(2)	2.292(2)	P(3)–C(311)	1.834(6)
Ru–P(3)	2.347(2)	P(3)–C(321)	1.819(7)
Ru–P(4)	2.277(2)	P(4)–C(4)	1.862(6)
Ru–O(1)	2.187(4)	P(4)–C(411)	1.829(6)
Ru–O(2)	2.197(4)	P(4)–C(421)	1.818(6)
P(1)–C(3)	1.832(6)	O(1)–C(1)	1.273(8)
P(1)–C(111)	1.816(7)	O(2)–C(1)	1.256(8)
P(1)–C(121)	1.814(7)	C(1)–C(2)	1.493(9)
P(2)–C(3)	1.851(6)	C(11)–B	1.647(11)
P(2)–C(211)	1.838(7)	C(21)–B	1.647(11)
P(2)–C(221)	1.808(6)	C(31)–B	1.658(11)
		C(41)–B	1.631(11)

P(1)–Ru–P(2)	72.26(6)	Ru–P(3)–C(4)	95.0(2)
P(1)–Ru–P(3)	171.04(6)	Ru–P(3)–C(311)	123.3(2)
P(1)–Ru–P(4)	101.27(6)	Ru–P(3)–C(321)	124.0(2)
P(1)–Ru–O(1)	91.8(1)	C(4)–P(3)–C(311)	107.5(3)
P(1)–Ru–O(2)	92.8(1)	C(4)–P(3)–C(321)	107.6(3)
P(2)–Ru–P(3)	102.05(6)	C(311)–P(3)–C(321)	98.0(3)
P(2)–Ru–P(4)	93.53(6)	Ru–P(4)–C(4)	96.2(2)
P(2)–Ru–O(1)	158.5(1)	Ru–P(4)–C(411)	112.9(2)
P(2)–Ru–O(2)	106.0(1)	Ru–P(4)–C(421)	128.5(2)
P(3)–Ru–P(4)	71.80(6)	C(4)–P(4)–C(411)	106.0(3)
P(3)–Ru–O(1)	95.4(1)	C(4)–P(4)–C(421)	106.7(3)
P(3)–Ru–O(2)	95.4(1)	C(411)–P(4)–C(421)	104.3(3)
P(4)–Ru–O(1)	103.9(1)	Ru–O(1)–C(1)	91.2(4)
P(4)–Ru–O(2)	158.7(1)	Ru–O(2)–C(1)	91.2(4)
O(1)–Ru–O(2)	59.4(2)	O(1)–C(1)–O(2)	118.2(6)
Ru–P(1)–C(3)	94.8(2)	O(1)–C(1)–C(2)	120.6(6)
Ru–P(1)–C(111)	119.9(2)	O(2)–C(1)–C(2)	121.2(7)
Ru–P(1)–C(121)	120.2(2)	P(1)–C(3)–P(2)	95.8(3)
C(3)–P(1)–C(111)	107.5(3)	P(3)–C(4)–P(4)	94.9(3)
C(3)–P(1)–C(121)	109.5(3)	C(11)–B–C(21)	105.8(6)
C(111)–P(1)–C(121)	103.9(3)	C(11)–B–C(31)	110.5(6)
Ru–P(2)–C(3)	95.9(2)	C(11)–B–C(41)	110.5(6)
Ru–P(2)–C(211)	114.1(2)	C(21)–B–C(31)	111.6(6)
Ru–P(2)–C(221)	130.4(2)	C(21)–B–C(41)	111.5(6)
C(3)–P(2)–C(211)	109.6(3)	C(31)–B–C(41)	107.0(5)
C(3)–P(2)–C(221)	104.1(3)		
C(211)–P(2)–C(221)	101.2(3)		

* Values in parentheses are estimated standard deviations in the least significant digit.

the free diphosphine (*ca.* −23 p.p.m.). These data establish the *cis,cis,trans*-stereochemistry (**IV**) with pendant $Ph_2PCH_2PPh_2$ ligands.

In sharp contrast, attempts to form carbonyl complexes by carbonylation of the 1,2-bis(diphenylphosphino)ethane derivatives *cis*- and *trans*-$[Ru(O_2CR)_2(Ph_2PCH_2CH_2PPh_2)_2]$ (R = Ph or Me) gave unreacted starting material even when refluxing toluene was employed as solvent. However, this result is not too surprising since $Ph_2P(CH_2)_2PPh_2$ is a much better chelating agent than $Ph_2PCH_2PPh_2$ and is therefore expected to be much less amenable to partial displacement by carbon monoxide.[19]

The complex salts $[Ru(O_2CMe)\{Ph_2P(CH_2)_nPPh_2\}_2]BPh_4$ (n = 1 or 2) also failed to carbonylate under fairly vigorous conditions (CO, 1 atm, benzene, reflux). Presumably the positive charge of the cations militates against co-ordination of the strong π-acceptor carbonyl ligand.[20]

cis- and trans-$[RuH_2(CO)(Ph_2PCH_2PPh_2)_2]$.—Treatment of $[Ru(O_2CEt)_2(CO)_2(Ph_2PCH_2PPh_2)_2]$ with $NaBH_4$ in boiling ethanol affords after work-up a pale yellow solid. Analytical and ^{1}H n.m.r. data establish the species present as the isomers *cis*-$[RuH_2(CO)(Ph_2PCH_2PPh_2)_2]$ (**V**) [^{1}H n.m.r.: δ(RuH), −8.04 (d of t), $^2J(PH)_{trans}$ 86.7, $^2J(PH)_{cis}$ 15.9 Hz] and *trans*-$[RuH_2(CO)(Ph_2PCH_2PPh_2)_2]$ (**VI**) [^{1}H n.m.r.: δ(RuH), −5.59 (quartet), $^2J(PH)_{cis}$ 22.6 Hz].

$[Rh_2(O_2CMe)_4\{Ph_2P(CH_2)_nPPh_2\}_n]$ (n = 1 or 2).—Vigorous treatment of $[Rh_2(O_2CMe)_4]$ with diphosphines $Ph_2P(CH_2)_nPPh_2$ (n = 1 or 2) failed to disrupt the lantern structure. The rather intractable orange products deposited proved to be too insoluble for recrystallisation or study by n.m.r. spectroscopy. However, colour and analytical data strongly support their formulation as simple bis(diphosphine) adducts of binuclear rhodium(II) acetate. Current views on reasons for the failure of binuclear rhodium(II) carboxylates to undergo cleavage on treatment with donor ligands have been noted in the introduction to this paper. An additional factor in the present case may be the extremely low solubility of the adducts involved.

X-*Ray Crystal Structure of* $[Ru(O_2CMe)(Ph_2PCH_2PPh_2)_2]BPh_4$.—The structure determination was undertaken to establish the mononuclear structure of the complex cations present in this and some related salts. This objective has been achieved. The structure consists of discrete cations, $[Ru(O_2CMe)(Ph_2PCH_2PPh_2)_2]^+$, and BPh_4^- anions. The stereochemistry and atomic labelling system for the complex cation are shown in the Figure, selected bond lengths and bond angles for the complex salt are listed in Table 5. The geometry about the six-co-ordinate ruthenium(II) centre deviates substantially from regular octahedral due to steric constraints imposed by the four-membered chelate rings. The angle subtended by the acetate ligand is 59.4(2)° and those subtended by the two diphosphines are 72.26(6) and 71.80(6)°. In the comparable structure of $[Ru(O_2CMe)(PMe_2Ph)_4]PF_6$ the O–Ru–O angle is 58.7(4)° and the angles between *cis* pairs of phosphines, P–Ru–P range from 91.0(2) to 98.9(1)°.[21] Ruthenium–oxygen and ruthenium–phosphorus bond distances vary little between the two structures. The most noticeable difference concerns the Ru–P distances for the mutually *trans* P-donor atoms which fall from 2.43(1) and 2.42(1) Å in $[Ru(O_2CMe)(PMe_2Ph)_4]^+$ to 2.347(2) and 2.342(2) Å in $[Ru(O_2CMe)(Ph_2PCH_2PPh_2)_2]^+$. The change presumably reflects the steric compression along the P–Ru–P axis imposed by the chelate diphosphine ligands. This effect is much less marked for the Ru–P linkages *trans* to acetate. These are already short (*ca.* 2.30 Å)[21] because of the weak *trans* influence of the acetate ligand and show little evidence of further compression in the case of the diphosphine complex.

Relationship between Chelate Ring Size and ^{31}P-{^{1}H} *N.M.R. Parameters for the Complexes* $[Ru(O_2CR)\{Ph_2P(CH_2)_nPPh_2\}_2]BPh_4$.—The ^{31}P-{^{1}H} n.m.r. parameters of chelate diphosphine ligands including Δ [the difference between δ(P) values for the free and chelated diphosphine] and $^2J(PP')$ (the coupling between the P donor atoms of the chelated diphosphine) have recently been shown to be remarkably dependent upon the chelate ring size.[22,23] In particular chelates involving five-membered rings usually have larger values for Δ and smaller values for $^2J(PP')$ than their more highly strained four- and six-membered counterparts. Reasons for this behaviour have been discussed in a recent review.[24] Data assembled in Table 3 for the salts $[Ru(O_2CR)\{Ph_2P(CH_2)_nPPh_2\}_2]BPh_4$ appear to conform to this scheme and thus support our conclusions concerning the chelate nature of the diphosphine ligands involved.

Acknowledgements

We thank the S.E.R.C. and UNESCO for financial support (to E.B.B. and P.A.H. respectively) and Johnson Matthey plc for generous loans of ruthenium trichloride. The *X*-ray diffractometer and the computer used in this research were acquired under N.S.F. and N.I.H. grants. C. P. B. thanks University of Kentucky for leave.

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Received 9*th August* 1985; *Paper* 5/1394