Oxo-centred Triruthenium Formate Complexes. Diphosphine Adducts of Oxo-centred Triruthenium Acetates †

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Early studies by Mond have been repeated and the oxo-centred formate $[Ru_3O(O_2CH)_6(OH_2)_3][O_2CH]$ obtained. Like its acetate analogue this undergoes a reversible one-electron reduction. It reacts with pyridine (py) to give $Ru(O_2CH)_2(py)_2$ and $Ru(O_2CH)_2(py)_4$ and with carbon monoxide to give $[Ru_3O(O_2CH)_6(OH_2)_2(CO)]$. A sodium salt, $Na[Ru(O_2CH)_3(OH_2)]$, has also been isolated. Interaction of bis(diphenylphosphino)methane (dppm) and 1,2-bis(diphenylphosphino)ethane (dppe) with $[Ru_3O(O_2CMe)_6(MeOH)_3]^{0,1+}$ gives the acetato-bridged dicationic species $[Ru_2(O_2CMe)_4L_2][ClO_4]_2$. Neutral species, $Ru_2(O_2CMe)_4(dppm)_2$, $Ru(O_2CMe)_2$-$(dppm)_2$, and probably $Ru_6O_2(O_2CMe)_{12}(dppe)_3$ have been isolated.

CARBOXYLATE complexes for numerous transition metals of the general formula $M_3O(O_2CR)_6L_3$, where L = unidentate ligand, are well known. We now describe the previously unestablished ruthenium formate and some of its reactions, together with complexes obtained by interaction of the ruthenium(III) oxo-centred acetate with chelating diphosphines.

RESULTS AND DISCUSSION

Oxo-centred Triruthenium Formate and its Derivatives.—The original work of Mond[1] could not be repeated[2,3] and the only established ruthenium formates are the brown dimers $[Ru_2(O_2CH)_4]X$, X = Cl or Br,[3] and $K[Ru_2(O_2CH)_4Cl_2]$, whose structure has been determined.[4] Green intermediates were observed in the reduction of ruthenium halide species by formic acid, but only the polymeric carbonyl halides, $[\{Ru(CO)_2X_2\}_n]$, X = Cl or Br, were isolated.[5] Despite the previous reports to the contrary, *freshly* prepared ruthenium ' hydroxide ' will dissolve in warm aqueous formic acid as stated by Mond and from the solution we have isolated a dark green complex which is evidently the oxo-centred species $[Ru^{III}_3O(O_2CH)_6(OH_2)_3][O_2CH]$ (1). The electronic absorption spectrum (Table 1) is virtually identical to that of the acetate[6] $[Ru_3O(O_2CMe)_6(OH_2)_3]$-$[O_2CMe]$ while the i.r. spectrum has no CO stretches but contains the appropriate carboxylate bands. The compound is paramagnetic with $\mu_{eff.}$ = 3.48 B.M.‡ per Ru_3 unit, corresponding to three unpaired electrons (with some spin–spin interaction *via* the central oxygen).

Like its acetate analogue[6] the formate can be reduced electrochemically and chemically. Cyclic voltammetry and ring-disc polarography (a gold electrode was used since platinum gives irreproducible results) confirmed a one-electron reversible reduction at *ca.* 0.05 V *vs.* s.c.e. (n = 1.12). Complete reduction at this potential gave a light green, extremely air-sensitive solution. Re-oxidation by O_2 gave the dark green starting material. The reduced complex is more conveniently obtained by reduction of H_2O or MeOH solutions by zinc amalgam under argon. The electronic spectrum of the aqueous solution [*ca.* 830 nm, ε *ca.* 1 760; 420(sh) nm, ε *ca.* 1 660 $dm^3 mol^{-1} cm^{-1}$] is similar to that of the acetate[6] and the reduced species is clearly $[Ru_3O(O_2CH)_6(OH_2)_3]$.

TABLE 1

Electronic and infrared spectra

Compound	Electronic data, λ/nm (ε/$dm^3 mol^{-1} cm^{-1}$)	I.r.[ν(CO_2), cm^{-1}][a] asym.	sym.
(1) $[Ru_3O(O_2CH)_6(OH_2)_3][O_2CH]$	691 (1 660), 600 (sh) (1 375), 380 (sh) (2 220), 280 (sh) (7 260), 230 (sh) (12 000)[b]	1 555	1 352
(2) $Ru(O_2CH)_2(py)_2$	700 (700), 348 (4 700), 245 (8 310)[c]	1 565	1 345
(3) $Ru(O_2CH)_2(py)_4$	389 (15 475), *ca.* 300 (sh), 248 (11 200)[c]	1 625	
(4) $Ru_3O(O_2CH)_6(OH_2)_2(CO)$	561 (2 236), 390 (sh) (1 455), 300 (sh) (3 400), 227 (sh) (13 360)[c]	1 617	1 350
		1 581	1 390
(5) $Na[Ru(O_2CH)_3(OH_2)]\cdot H_2O$	447 (925), 293 (4 725), 229 (4 880)[b]	1 595	1 320
		1 565	1 335
(6) $[Ru_2((O_2CMe)_2dppm)_4][ClO_4]_2$	700 (130), 390 (sh), 339 (6 780), 256 (67 500)[d]	1 605	1 465
(7) $[Ru_2(O_2CMe)_2(dppe)_4][ClO_4]_2$	711 (120), 353 (3 675), 259 (83 500)	1 625	1 465
(8) $Ru_2(O_2CMe)_4(dppm)_2$	660 (800), 330 (sh), 259 (31 700)[d]	1 585	1 410
(9) $Ru_2(O_2CMe)_4(dppm)_2$	730 (1 080), 605 (sh) (1 000), 417 (sh), 350 (sh), 300 (sh), 261 (59 000)[d]	1 605	1 388
		1 588	1 415
(10) $Ru(O_2CMe)_2(dppm)_2$	420 (400), 340 (sh) (2 460), 300 (sh) (4 485), 263 (48 500)[d]	1 600	1 378
(11) $Ru_6O_2(O_2CMe)_{12}(dppe)_3$	770 (4 500), 620, 420, 350 (sh), 260 (sh) (*ca.* 52 000)[d]	1 555	1 410

[a] KBr disc. [b] In H_2O. [c] In MeOH. [d] In CH_2Cl_2.

We have been unable to isolate this species, however, and addition of CO, PR_3, en, *etc.* (en = ethylenediamine), gave only impure cleavage products. However, addition

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† No reprints available.

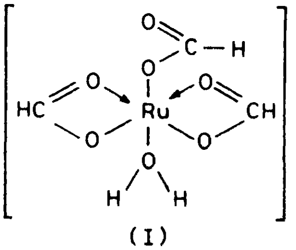
‡ Throughout this paper: 1 B.M. = 9.274 × 10^{-24} A m^2; 1 atm = 101 325 Pa.

of pyridine (py) rapidly gave the orange crystalline $\mathrm{Ru(O_2CH)_2(py)_4}$ (see below).

Attempts to obtain formate analogues of $[\mathrm{Ru^{III}_3O(O_2CMe)_6(py)_3}]^+$ and $[\mathrm{Ru^{II,III,III}O(O_2CMe)_6(PPh_3)_3}]$[6] were unsuccessful. Interaction with pyridine in methanol gave a green solution from which green $\mathrm{Ru^{II}(O_2CH)_2(py)_2}$ (2), which has chelate formato-groups, and on heating orange $\mathrm{Ru(O_2CH)_2(py)_4}$ (3), which has unidentate carboxylate groups, were obtained. These complexes, confirmed by analytical and molecular-weight data, have similar carboxylate analogues.[2]

The interaction of (1) in methanol with CO at 1 atm and room temperature gave a dark purple solution from which $[\mathrm{Ru^{II,III,III}O(O_2CH)_6(OH_2)_2(CO)}]$ (4) could be isolated. This is similar to the acetate analogue[7] in being a non-electrolyte and having inequivalence of the carboxylate groups according to ^{1}H n.m.r. spectra (δ 7.08, 5.66 in $\mathrm{CD_3OD}$) in a 2 : 1 ratio. Whether this inequivalence results from a rearrangement of the formates to both bridging and chelate modes as suggested for the acetate[7a] or whether it results merely from lowering of the symmetry of the complex and π-bonding effects of CO as suggested by Meyer and co-workers,[7b] is unclear. A crystal-structure determination of a complex of this type is desirable.

The interaction of hydrated $\mathrm{RuCl_3}$ and sodium formate (1 : 2 mol ratio) in 90% formic acid–ethanol (1 : 1) gave, *via* intermediate purple and grey stages over 4—5 h at 70—80 °C, a dark green solution from which a complex similar to (1) could be precipitated by addition of acetone–diethyl ether. It proved difficult to obtain pure, free from sodium salts, and ion-exchange studies suggested a green anionic species was also present. When excess of acid was not used, a yellow diamagnetic solid was obtained as a side product and purified by recrystallisation from aqueous acetone. This compound appears to be $\mathrm{Na[Ru^{II}(O_2CH)_3(OH_2)]\cdot H_2O}$ (5) and we suggest the structure (I) for the anion.

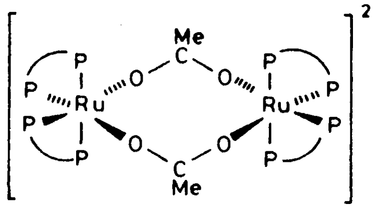


(I)

There is a sharp stretch in the i.r. at 3 620 cm^{-1} while the ^{1}H n.m.r. spectrum (in $\mathrm{D_2O}$) shows two formato-hydrogen singlets (δ 9.08, 5.87 p.p.m.) in a 2 : 1 ratio. Two types of formate groups are confirmed by the i.r. spectrum where the carboxylate bands are split, one value for $\Delta\nu_{(\mathrm{asym}-\mathrm{sym.})}$ being 275 cm^{-1} (unidentate formate), the other 230 cm^{-1}. In cyclic voltammetry this compound shows a reversible one-electron wave (supporting electrolyte: 10^{-3} mol dm^{-3} HCl–10^{-1} mol dm^{-3} KCl; reference electrode: Ag–AgCl; 490 mV *vs.* Ag–AgCl; ΔE_p = 80 mV; working electrode: platinum foil).

Reactions of the Oxo-centred Acetate with Diphosphines.—A number of complexes of the type $[\mathrm{Ru_3O(O_2CMe)_6L_3}]^{0,1+}$ in which L is a unidentate ligand are known.[6,8] We have now studied the interaction of the species L = MeOH with the bidentate diphosphines dppm and dppe, bis(diphenylphosphino)methane and 1,2-bis(diphenylphosphino)ethane respectively.

In alcohol solvents $[\mathrm{Ru_3O(O_2CMe)_6(MeOH)_3}][\mathrm{O_2CMe}]$ reacts to give bright green solutions that contain cationic species. These can be isolated as crystalline salts on addition of $\mathrm{ClO_4}^-$. Analyses, conductivities, and spectroscopic data are consistent with dimeric ruthenium(II) complexes with bridging acetate groups as in (II): P—P = dppm (6), dppe (7).



(II)

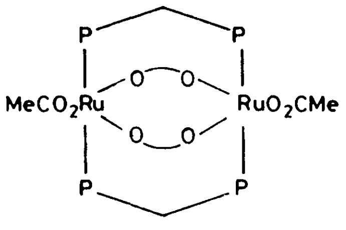
The ^{31}P n.m.r. spectra are of the $\mathrm{A_2B_2}$ type consisting of two triplets while ^{1}H n.m.r. spectra show the acetate groups to be equivalent [singlets, (6), δ 2.05, (7), δ 1.69 p.p.m.].

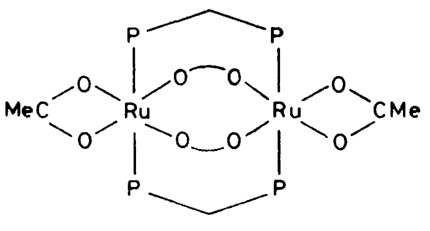
The interaction of $[\mathrm{Ru^{II,III,III}O(O_2CMe)_6(MeOH)_3}]$, and also of $\mathrm{Ru_2(O_2CMe)_4Cl}$, with dppe gave (7) as a side product.

Interaction of the reduced species, $[\mathrm{Ru_3O(O_2CMe)_6(MeOH)_3}]$, in methanol with dppm causes the light green solution to turn dark green and produce a methanol-insoluble precipitate (8), and a methanol-soluble species (9), that can be isolated after evaporation of solvent. Both compounds are non-electrolytes with very similar molecular weights. The ^{31}P n.m.r. of (8) in $\mathrm{CH_2Cl_2}$ shows only a singlet at −7.98 p.p.m., while the i.r. spectrum indicates unidentate acetate: thus all the data are consistent with the formulation $\mathrm{Ru^{II}_2(O_2CMe)_4(dppm)_2}$ having the structure (IIIa).

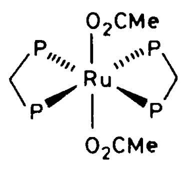
The methanol soluble complex (9) also has a strong ^{31}P singlet at −8.1 p.p.m. but the i.r. spectrum shows no splitting of the carboxylate bands and the $\mathrm{CO_2Me}$ groups are bridging and chelate. The two compounds thus appear to be isomers (IIIa, b) with two bridging acetate ligands, two bridging dppm ligands, but with (8) having a unidentate end acetate and (9) a chelate.

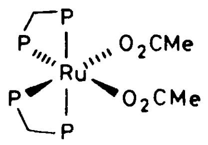
It is to be noted that the ^{31}P n.m.r. spectrum of (9) always contains two weak triplets which have chemical shifts and *J*(P–P) values similar to those of (6) and the compound (10) now to be described. The yellow compound (10), which is a non-electrolyte, is obtained when solutions of $[\mathrm{Ru_2(O_2CMe)_2(dppm)_4}][\mathrm{ClO_4}]_2$ are allowed to stand in $\mathrm{CH_2Cl_2}$ or on attempted recrystallisation of the isomers (8) and (9) (green amorphous products are also formed). Its i.r. spectrum is similar to that of (6) but the carboxylate bands are now characteristic of a unidentate acetate [$\Delta\nu_{(\text{asym.-sym.})} = 222$ cm^{-1}, *cf.* 140 cm^{-1} for (6)]. The ^{31}P n.m.r. spectrum has a singlet at -7.70 p.p.m. (free ligand, 23.6 p.p.m.[9]) and two triplets with the same chemical shifts and J(P–P) as in (6). Since the ratio of singlet to triplet intensities varies with the source, yet all have the same analyses and molecular weights, it seems that there are *cis* and *trans* isomers (IVa, b).


(IIIa) (8)


(IIIb) (9)

The interaction of [$Ru_3O(O_2CMe)_6(MeOH)_3$] with dppe again gave a dark green solution from which on addition of ClO_4^- (7) was obtained and a dark green precipitate that was clearly a mixture. After washing with hot acetone, the residue was extracted with CH_2Cl_2 and from this green solution was obtained a neutral diamagnetic species with a molecular weight of *ca.* 2 250 and analysis corresponding to $Ru_6O_2(O_2CMe)_{12}(dppe)_3$. The ^{31}P n.m.r. spectrum is a singlet at 30.84 p.p.m. (free ligand, 12.5 p.p.m.) [9] and the i.r. spectrum indicates bridging acetates. We suggest that this compound, (11), has two $Ru_3O(O_2CMe)_6$ units linked together by three dppe bridging ligands. Attempts to obtain crystals suitable for *X*-ray study failed even using the technique of allowing [$Ru_3O(O_2CMe)_6(MeOH)_3$] and dppe to warm up slowly from liquid-nitrogen temperature, which was successful in the case of [$Ru_3O(O_2CMe)_6(PPh_3)_3$].[10]


(IVa, singlet ^{31}P)


(IVb, triplets ^{31}P)

Attempts to join two units together by other potentially suitable bifunctional ligands have been unsuccessful giving either insoluble polymeric substances, mixtures, or no reaction. 2-Methoxypyridine gave only dark blue crystals of [$Ru_3O(O_2CMe)_6(2\text{-}OMe\text{-}py)_3$][$ClO_4$] while coordination through N occurs as in the pyridine analogue.

EXPERIMENTAL

Analyses were by the Imperial College Microanalytical Laboratory. Molecular weights were determined on a Perkin-Elmer–Hitachi 115 osmometer. Infrared spectra were recorded on a Perkin-Elmer 597, electronic spectra on a Perkin-Elmer 551, and n.m.r. spectra on a Perkin-Elmer R32 (60 MHz) (^{1}H, hexamethyldisiloxane as external reference) and a Varian XL-100 (^{31}P, in Fourier-transform mode with 85% H_3PO_4 as reference). Conductivity measurements were made on a Mullard Bridge; data in S cm^2 mol^{-1}. Magnetic measurements were made in the solid state using an Evans' balance.

Analytical data are collected in Table 2. Note that ruthenium compounds sometimes combust badly and give unsatisfactory analysis.

Tris(aqua)hexa-μ-formato-μ$_3$-oxo-triruthenium(III) *Formate*, (1).—This is Mond's formate.[1] (*a*). To a concentrated solution of $RuCl_3$(aq) (1 g) in water was added solid K[OH] with ice cooling. The solid was washed free from alkali with cold water and as soon as possible placed in a solution (100 cm^3) of formic acid (90% diluted to 45% with water). On heating for *ca.* 5 h at 80 °C, the solid almost completely dissolved to give a green solution which was then filtered into acetone–diethyl ether (1 : 1) (500 cm^3). After 24 h at -20 °C, the precipitate was collected, washed with acetone and diethyl ether, and dried *in vacuo*.

Yield *ca.* 85%, based on $RuCl_3 \cdot 3H_2O$. The complex is readily soluble in water and slightly soluble in methanol, but is insoluble in other solvents.

(*b*). A solution of $RuCl_3$(aq) (1 g) and sodium formate (4 g) in EtOH (25 cm^3) and formic acid (50 cm^3) (90%) was heated for *ca.* 6 h at 75 °C. The initial red-brown solution quickly turned purple, more slowly grey, then finally a clear dark green. The solution was cooled, filtered, and poured into acetone (250 cm^3)–diethyl ether (100 cm^3) at 0 °C. The precipitate was washed with acetone and diethyl ether and dried *in vacuo*. This product contains NaCl but the spectroscopic and chemical properties are as the complex made in (*a*). On extended heating or at temperatures higher than 75 °C, carbonyl-containing products are obtained.

Sodium Aquatris(formato)ruthenate(II) *Monohydrate*, (5).—A solution of $RuCl_3$(aq) (0.5 g) and sodium formate (1 g) in EtOH (15 cm^3) and formic acid (15 cm^3, 90%) was heated at 75 °C for *ca.* 5 h. The dark yellow precipitate was collected, washed with acetone, dissolved in the minimum of water, and the solution filtered. Addition of acetone precipitated the complex which was redissolved in water and reprecipitated, washed with diethyl ether, and vacuum dried. Yield 0.19 g.

The salt is soluble in water and methanol, insoluble in ethanol, acetone, nitromethane, and diethyl ether. Hydrogen-1 n.m.r. (in D_2O), δ 9.06(2), 5.87(1). The conductivity is somewhat high for a 1 : 1 electrolyte in methanol, probably due to ionisation of co-ordinated water but the molecular weight in water (140) fits well.

Interaction of Oxoformate with Pyridine.—(*a*) *Bis(formato)bis(pyridine)ruthenium*(II), (2). The formate made as for 1(*b*) (0.7 g) was dissolved in methanol (20 cm^3) and pyridine (5 cm^3) and the solution refluxed (2 h). After filtration and evaporation *in vacuo*, the green mass was dissolved in the minimum of acetone and the solution added to excess of light petroleum (40—60%). The precipitate was washed with diethyl ether and vacuum dried to give the green complex. Yield *ca.* 90%.

(*b*) *Bis(formato)tetrakis(pyridine)ruthenium*(II), (3). The formate (0.69 g) in methanol (50 cm^3) under argon was treated with zinc amalgam to give a light green solution which on addition of pyridine turns dark yellow. After filtration and concentration, orange needles were obtained which were recrystallised from ethanol. Yield *ca.* 90%.

TABLE 2

Analytical data and some properties

Compound	Colour	M.p. (θ_c/°C)	Analysis (%) [a] C	H	N/P	*M*
(1)	Blue-green	160 (decomp.)	11.7	1.9		82 [b]
			(12.2)	(1.9)		
(2)	Dark green	45	42.7	4.4	7.2	340 (349.3)
			(41.3)	(3.6)	(8.0)	
(3)	Orange	decomp. >240	49.0	4.3	11.0	470 (507.5) [d]
			(52.0)	(4.4)	(11.0)	
(4)	Purple	decomp. >50	11.5	1.6		
			(12.9)	(1.5)		
					Na H_2O	
(5)	Yellow		12.2	2.5	7.4 12.2	375 [c]
			(12.2)	(2.4)	(7.8) (12.2)	
(6)	Dark green	250 (decomp.)	59.3	4.6	12.0 [e]	171 [f]
			(59.6)	(4.6)	(12.0)	
(7)	Light green	240 (decomp.)	60.1	4.8	11.2 [g]	152 [f]
			(60.4)	(4.9)	(11.7)	
(8)	Dark green	185 (decomp.)	58.2	4.6	9.4	1 260 (1 210) [d]
			(57.1)	(4.7)	(10.3)	
(9)	Light green	210 (decomp.)	60.8	4.9	10.3	1 230 (1 210) [d]
			(57.7)	(4.7)	(10.3)	
(10)	Yellow	225 (decomp.)	65.8	5.2	12.0	910 (990) [d]
			(65.7)	(5.1)	(12.5)	
(11)	Dark green	240 (decomp.)	47.1	4.3	6.8	2 200 (2 542) [d]
			(48.1)	(4.3)	(7.3)	

[a] Calculated values are given in parentheses. [b] In H_2O. [c] In MeOH. [d] In CH_2Cl_2. [e] Cl = 3.6% (3.5). [f] In CH_3NO_2. [g] Cl = 3.6% (3.4).

The compound is also obtained when the bis(pyridine) complex, (2), in acetone is evaporated at *ca.* 50 °C when the solution deposits orange crystals on cooling.

Bis(aqua)carbonylhexaformato-μ_3-oxo-triruthenium(II,III,III), (4).—Through a solution of the formate (0.3 g) in methanol (100 cm^3) at ambient temperatures was bubbled slowly carbon monoxide for 24 h. The solution which slowly becomes purple was then filtered into light petroleum (300 cm^3, b.p. 40—60 °C) and held at −20 °C for 2 days. The purple precipitate (*ca.* 30 mg) was collected, washed with light petroleum, and vacuum dried. It is soluble in water, alcohols, and acetone, insoluble in CH_2Cl_2, $MeNO_2$, and light petroleum. Hydrogen-1 n.m.r.: δ 7.08(2), 5.66(1).

Reactions of Ruthenium Oxoacetate.—The complexes $[Ru_3O(O_2CMe)_6(MeOH)_3][O_2CMe]$ and $[Ru_3O(O_2CMe)_6(MeOH)_3]$ were prepared as described.[7b,11]

(*a*) *Bis(acetato)tetrakis[bis(diphenylphosphino)methane]diruthenium*(II) *perchlorate*, (6). A solution of the acetate (0.5 g) in warm ethanol (80 cm^3) was added dropwise to a stirred suspension of dppm (0.37 g) in ethanol (20 cm^3) at 40 °C. After 12 h, the clear green solution was filtered and lithium perchlorate (0.2 g) added. On standing, dark green crystals were obtained (*ca.* 100 mg) and these were washed with EtOH and diethyl ether and vacuum dried. The salt is soluble in acetone, $CHCl_3$, CH_2Cl_2, and $MeNO_2$, insoluble in water, diethyl ether, and benzene. N.m.r.: ^1H, δ 7.5(br), 2.45 (CH_2), 2.05 (CH_3); ^{31}P (CH_2Cl_2), two triplets, J(P–P) = 39.4 Hz, 7.75, −12.27.

(*b*) *Bis(acetato)bis[bis(diphenylphosphino)methane]ruthenium*(II), (10). This compound may be obtained from (*i*) concentrated solutions of (6) above in CH_2Cl_2 on slow evaporation over a period of 1—2 weeks and (*ii*) the green reaction products of dppm with the reduced oxoruthenium acetate (see below).

The yellow crystals can be separated from other materials present by washing with acetone in which impurities are soluble.

The compound is soluble in CH_2Cl_2 and $CHCl_3$ but insoluble in alcohols, acetone, $MeNO_2$, and diethyl ether. N.m.r.: ^1H ($CDCl_3$), 7.5(br) (Ph), 2.51(br) (CH_2), 1.11(br) (Me); ^{31}P (CH_2Cl_2), −7.70(s) plus two triplets with same J(P–P) as (6).

(*c*) *Tetrakis(acetato)bis[bis(diphenylphosphino)methane]diruthenium*(II), (8) *and* (9). The compound $[Ru_3O(O_2CMe)(MeOH)_3][O_2CMe]$ (0.415 g) in methanol (60 cm^3) was reduced (3 h) with zinc amalgam under argon and the resulting light green solution added to dppm (0.58 g, 1 : 3 ratio). The ligand dissolves and the solution becomes dark green. After stirring for 12 h, the light green precipitate (0.22 g) of the isomer (8) was collected, washed with methanol and diethyl ether, and dried *in vacuo*. N.m.r.: ^1H ($CDCl_3$), 7.41, 2.31 (br multiplet), 2.0, 1.46(s); ^{31}P (CH_2Cl_2), −8.1(s), two triplets, 7.79, −12.14, J(P–P) = 39.4 Hz.

The solution was evaporated and the dark green oil dissolved in CH_2Cl_2. The filtered solution was evaporated and the dark green isomer (9) washed with diethyl ether and vacuum dried. Yield 0.5 g. The compound is soluble in alcohol, acetone, CH_2Cl_2, $MeNO_2$, and tetrahydrofuran. N.m.r.: ^1H ($CDCl_3$), 7.1 (br multiplet), 1.56, 0.74(s), 1.17 (multiplet); ^{31}P (CH_2Cl_2), −7.98(s).

(*d*) *Bis(acetato)tetrakis*[1,2-*bis(diphenylphosphino)ethane*]-*diruthenium*(II) *perchlorate*, (7). The acetate (0.5 g) in ethanol (50 cm^3)–methanol (25 cm^3) was added dropwise to a warm (80 °C) solution of dppe (0.38 g) in ethanol (50 cm^3) and the mixture refluxed for 30 min. Addition of Li[ClO_4] (70 mg) and cooling with addition of diethyl ether (50 cm^3) gave small green crystals which were washed with ethanol and diethyl ether and vacuum dried.

The compound is soluble in CH_2Cl_2, $CHCl_3$, and $MeNO_2$, insoluble in diethyl ether and alcohols.

The compound can also be obtained by interaction of dppe (1.6 g) with the reduced acetate (0.52 g) in methanol (50 cm^3) at room temperature for 12 h under argon. The green precipitate [(11), below] is removed and the salt precipitated by Li[ClO_4] from the green solution. It may also be obtained by interaction of $Ru_2(O_2CMe)_4Cl$ (0.21 g) in MeOH (20 cm^3) and dppe (0.18 g) in MeOH (10 cm^3)–acetone (10 cm^3); an initial violet colour disappears and after 1 h Li[ClO_4] is added to precipitate the salt. N.m.r.: ^{31}P (CH_2Cl_2), two triplets −2.90, −3.00, J(P–P) = 15.0 Hz.

Dodecakis(acetato)tris[1,2-*bis(diphenylphosphino)ethane*]-*di*-μ_3-*oxo-hexaruthenium*, (11).—The solution of acetate (0.415 g) in methanol (50 cm^3) reduced with zinc amalgam (5 g) for 4 h was added to solid dppe (0.6 g) under argon. The mixture was stirred for 12 h and the green solid collected and washed with methanol and hot acetone. The solid (0.63 g) was then Soxhlet extracted with CH_2Cl_2 to give a green solution which on evaporation gave the complex (0.1 g) which was washed with diethyl ether and vacuum dried. It is soluble in CH_2Cl_2, $CHCl_3$, and $MeNO_2$, but insoluble in acetone, diethyl ether, and methanol. There is also a green CH_2Cl_2-insoluble residue but in the presence of additional dppe this rapidly dissolves to give a solution containing (11) as major product, together with some acetone–light petroleum-soluble materials that we could not separate. N.m.r.: ^{31}P (CH_2Cl_2), 30.84(s).

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