DALTON

The carboxylate-bridged polymer $[\{Ru_2[\mu\text{-}\eta^2\text{-}OC(R)O]_2(CO)_4\}_n]$ (R = H, Me or Et) as a synthon in the synthesis of dinuclear phosphorus pyridyl-, quinolyl- and bipyridyl-bridged derivatives of ruthenium(I)

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Treatment of $[\{Ru_2[\mu\text{-}\eta^2\text{-}OC(R)O]_2(CO)_4\}_n]$ or its acetonitrile adduct $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}_2(CO)_4(MeCN)_2]$ (R = H, Me or Et) with a two-fold molar equivalent of the phosphorus–nitrogen ligands 2-diphenylphosphinopyridine (dppy), 2-diphenylphosphinoquinoline (dpquin) and 6-diphenylphosphino-2,2′-bipyridine (dpbipy) in alcohol under reflux resulted in the formation of dinuclear products of the type $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}_2(CO)_4(PPh_2R')_2]$ (R′ = pyridyl, quinolyl or bipyridyl) in which the PPh_2R' ligands are monodentate, co-ordinating axially through the phosphorus donor atoms, as established X-ray crystallographically for $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}_2(CO)_4(dppy)_2]$. On the other hand reaction of $[\{Ru_2[\mu\text{-}\eta^2\text{-}OC(R)O]_2(CO)_4\}_n]$ with 2 molar equivalents of dppy or dpquin in toluene under reflux in the presence of NH_4PF_6 and under a slight pressure of carbon monoxide afforded products of the type $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}(CO)_4(\mu\text{-}dppy)_2]PF_6$ or $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}(CO)_4(\mu\text{-}dpquin)_2]PF_6$ in which the dppy or dpquin ligands adopt the bridging co-ordination mode, this mode of co-ordination being confirmed through a crystal structure determination on $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(H)O\}(CO)_4(\mu\text{-}dppy)_2]PF_6$. Reaction of $[\{Ru_2[\mu\text{-}\eta^2\text{-}OC(R)O]_2(CO)_4\}_n]$ with dpbipy in *n*-butanol under reflux likewise afforded products, isolated as their hexafluorophosphate salts, in which the phosphorus–nitrogen ligands are bridging, *viz.* $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}(CO)_2(\mu\text{-}dpbipy)_2]PF_6$, the structure of $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}(CO)_2(\mu\text{-}dpbipy)_2]PF_6$ being established X-ray crystallographically.

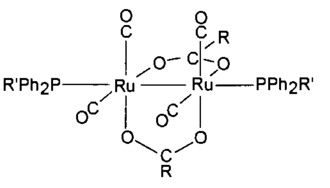
The carboxylate-bridged polymers $[\{Ru_2[\mu\text{-}\eta^2\text{-}OC(R)O]_2(CO)_4\}_n]$ (R = H, Me, Et, Ph, *etc.*), readily synthesized by a number of procedures including the reaction of $[Ru_3(CO)_{12}]$ with the appropriate carboxylic acids,[1] together with their corresponding solvated products $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}_2(CO)_4(solv)_2]$, obtained by treatment of the polymer with donor solvents such as acetonitrile,[1] tetrahydrofuran (thf)[2] or hot alcohol,[3] have been established to be excellent precursors for the synthesis of dinuclear carboxylate-bridged derivatives of ruthenium(I). For instance their reaction with an excess of neutral monodentate donor ligand L such as carbon monoxide, pyridine and tertiary phosphines affords products of the type $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}_2(CO)_4L_2]$.[4,5] Further product types are formed in their reactions with bidentate neutral ligands.[3,6–10] Thus, while the reaction of $[\{Ru_2[\mu\text{-}\eta^2\text{-}OC(R)O]_2(CO)_4\}_n]$ with 2 molar equivalents of $Ph_2PCH_2PPh_2$ (dppm) in alcohol under ambient conditions affords $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}_2(CO)_4(dppm\text{-}P)_2]$, the corresponding reaction under reflux gives $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}(CO)_4(\mu\text{-}dppm)_2]^+$ together with smaller quantities of $[Ru_2\{OC(O)R\}_2(CO)_4(\mu\text{-}dppm)_2]$, the former being readily isolated as its hexafluorophosphate salt. On the other hand reaction of the polymers with strongly chelating ligands such as $Ph_2PC_2H_4PPh_2$ and 2,2′-bipyridine yields products of the type $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}(\mu\text{-}CO)_2(L\text{–}L)_2]^+$ (L–L = $Ph_2PC_2H_4PPh_2$, 2,2′-bipyridine, *etc.*). Significantly the acetate ligand in $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}(CO)_4(\mu\text{-}dppm)_2]^+$ is susceptible to nucleophilic substitution by halide and tetrahydroborate ions, the latter in the presence of carbon monoxide, affording $[Ru_2(\mu\text{-}X)X(CO)_3(\mu\text{-}dppm)_2]$ (X = Cl, Br or I) and $[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-}dppm)_2]$ respectively.[11,12]

With the object of synthesizing dinuclear compounds of ruthenium(I), stabilised to fragmentation by phosphorus, pyridyl and related ligands, the reactions of $[\{Ru_2[\mu\text{-}\eta^2\text{-}OC(R)O]_2(CO)_4\}_n]$ (R = H, Me or Et) with 2-diphenylphosphinopyridine (dppy), 2-diphenylphosphinoquinoline (dpquin) and 6-diphenylphosphino-2,2′-bipyridine (dpbipy) have been investigated.

Results and Discussion

Synthetic studies

Reaction of the polymer $[\{Ru_2[\mu\text{-}\eta^2\text{-}OC(R)O]_2(CO)_4\}_n]$ or its acetonitrile adduct $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}_2(CO)_4(MeCN)_2]$ (R = H, Me or Et) with 2 molar equivalents of the above ligands, *i.e.* dppy, dpquin and dpbipy, in ethanol or toluene under reflux for short periods of time (less than 4 h) was shown to produce, in moderate to high yields, air-stable, sparingly soluble neutral compounds characterised as $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}_2(CO)_4(PPh_2R')_2]$ **1** (R = H, Me or Et; R′ = pyridyl, quinolyl or bipyridyl). All nine compounds were found to exhibit very similar band patterns in the C–O stretching region of their IR spectra, each pattern comprising four peaks of relative intensity strong, medium, very strong and weak (shoulder) and with the frequencies of corresponding peaks being very similar. These spectra closely resemble those of the axially substituted compounds $[M_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}_2(CO)_4L_2]$ (M = Ru or Os; L = PPh_3, $AsPh_3$, PMe_2Ph, $PMePh_2$, C_5H_5N, MeCN or $Ph_2PCH_2PPh_2\text{-}P$) in the C–O stretching region which is interpreted in terms of the new compounds adopting a similar core structure with each ligand functioning as monodentate and co-ordinating axially.[7,8,13] The $^{31}P\text{-}\{^1H\}$ NMR spectra exhibit well resolved singlets in the range δ 16.9 to 18.1, as expected for a symmetrical structure for these compounds. A crystal structure determination on $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}_2(CO)_4(dppy)_2]$ (see below) has confirmed the structure proposed. The geometry of the $Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}_2(CO)_4$ core in $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}_2(CO)_4(L\text{–}L)_2]$ **1** is the same as that established for the polymer $[\{Ru_2[\mu\text{-}\eta^2\text{-}OC(R)O]_2(CO)_4\}_n]$.[14,15] This reflects that the formation of **1** merely involves the cleavage of the intermolecular Ru-O(carboxylate)-Ru bridges by the attacking nucleophile.



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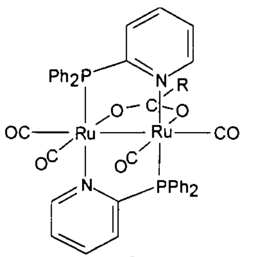

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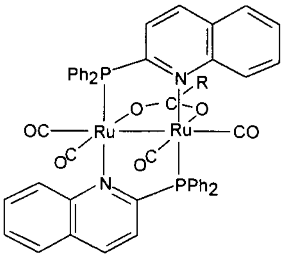

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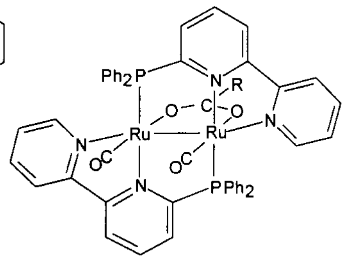

4

One of the carboxylate ligands in $[\{Ru_2[\mu\text{-}\eta^2\text{-}OC(R)O]_2(CO)_4\}_n]$ (R = H, Me or Et) is readily displaced if the reaction of this polymer with 2 molar equivalents of dppy or dpquin is carried out in toluene under reflux in the presence of NH_4PF_6 and carbon monoxide is passed through the solution. The reaction is relatively slow and reaction times of between 4 and 8 h are required. The products which separate from solution were characterised as the cationic species $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}(CO)_4(\mu\text{-dppy})_2]PF_6$ **2** or $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}(CO)_4(\mu\text{-dpquin})_2]PF_6$ **3** in which the phosphorus–nitrogen ligands adopt a bridging co-ordination mode. Four peaks of distinctive band pattern were observed in the C–O stretching region of the IR spectra of these compounds, this band pattern being very similar to that observed in the spectra of the analogous dppm- and dmpm-bridged compounds $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}(CO)_4(\mu\text{-dppm})_2]PF_6$ and $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}(CO)_4(\mu\text{-dmpm})_2]PF_6$ (dmpm = $Me_2PCH_2PMe_2$).[3] The $^{31}P\text{-}\{^1H\}$ NMR spectra of these compounds exhibit well resolved singlets, well down field of compounds of type **1**, consistent again with products of symmetrical structure. A crystal structure determination on $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(H)O\}(CO)_4(\mu\text{-dppy})_2]PF_6$ has confirmed the structural features being proposed for **2** on the basis of the spectroscopic evidence.

Compounds of type **2** or **3** can also be synthesized directly from the corresponding compound of type **1**, simply by refluxing a suspension of the latter in toluene in the presence of NH_4PF_6 and under a very slight pressure of carbon monoxide. This is interpreted in terms of **1** being an intermediate in the formation of **2** or **3**. This conversion involves the migration of the pendant phosphorus–nitrogen ligands from axial to equatorial positions together with the displacement of a carboxylate ion on co-ordination of these ligands to the two rutheniums through their nitrogen atoms.

The phosphorus bipyridyl ligand dpbipy also affords products in which the ligand functions in a bridging co-ordination mode, on reaction with the polymer $[\{Ru_2[\mu\text{-}\eta^2\text{-}OC(R)O]_2(CO)_4\}_n]$ but fairly vigorous reaction conditions are required. Thus reaction of the polymer with 2 molar equivalents of the ligand in *n*-butanol under reflux for at least 3 h and subsequent addition of an excess of NH_4PF_6 led to the separation of a brown product from solution which after crystallisation from acetone–diethyl ether (1:1) was characterised as $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}(CO)_2(\mu\text{-dpbipy})_2]PF_6$ **4**. The IR spectra of these compounds contain two peaks in the C–O stretching region, one of which occurs as a shoulder on the other, while their $^{31}P\text{-}\{^1H\}$ NMR spectra each exhibit a singlet, again well downfield of those observed for the monodentate derivatives and, at the same time, slightly more downfield than those for $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}(CO)_4(\mu\text{-dppy})_2]PF_6$ and $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}(CO)_4(\mu\text{-dpquin})_2]PF_6$. The structure of these compounds has been established unequivocally through a crystal structure determination of $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}(CO)_2(\mu\text{-dpbipy})_2]PF_6$.

Table 1 Selected interatomic distances (Å) and angles (°) for $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}_2(CO)_4(dppy)_2]$

Ru(1)–Ru(2)	2.720(1)	Ru(1)–P(1)	2.410(2)
Ru(2)–P(2)	2.413(2)	Ru(1)–O(1)	2.118(7)
Ru(2)–O(2)	2.119(6)	Ru(1)–O(3)	2.054(7)
Ru(2)–O(4)	2.071(6)	Ru(1)–C(39)	1.80(1)
Ru(1)–C(40)	1.80(1)	Ru(2)–C(41)	1.84(1)
Ru(2)–C(42)	1.78(1)	O(1)–C(35)	1.27(1)
O(2)–C(35)	1.22(1)	O(3)–C(37)	1.26(1)
O(4)–C(37)	1.28(1)	C(35)–C(36)	1.51(1)
C(37)–C(38)	1.54(2)		
Ru(2)–Ru(1)–P(1)	169.5(1)	Ru(1)–Ru(2)–P(2)	176.6(1)
Ru(2)–Ru(1)–O(1)	83.5(2)	Ru(1)–Ru(2)–O(2)	82.8(1)
Ru(2)–Ru(1)–O(3)	87.4(2)	Ru(1)–Ru(2)–O(4)	84.4(2)
Ru(2)–Ru(1)–C(39)	92.8(3)	Ru(1)–Ru(2)–C(41)	93.0(3)
Ru(2)–Ru(1)–C(40)	89.6(4)	Ru(1)–Ru(2)–C(42)	88.4(3)
P(1)–Ru(1)–O(1)	89.9(2)	P(2)–Ru(2)–O(2)	93.8(2)
P(1)–Ru(1)–O(3)	87.4(2)	P(2)–Ru(2)–O(4)	95.5(2)
P(1)–Ru(1)–C(39)	94.1(3)	P(2)–Ru(2)–C(41)	90.4(3)
P(1)–Ru(1)–C(40)	98.6(4)	P(2)–Ru(2)–C(42)	91.5(3)
O(1)–Ru(1)–O(3)	85.6(3)	O(2)–Ru(2)–O(4)	84.1(3)
O(1)–Ru(1)–C(39)	175.6(4)	O(2)–Ru(2)–C(41)	174.5(3)
O(1)–Ru(1)–C(40)	89.5(5)	O(2)–Ru(2)–C(42)	91.4(3)
O(3)–Ru(1)–C(39)	96.4(5)	O(4)–Ru(2)–C(41)	92.0(4)
O(3)–Ru(1)–C(40)	172.2(5)	O(4)–Ru(2)–C(42)	171.9(3)
C(39)–Ru(1)–C(40)	88.1(7)	C(41)–Ru(2)–C(42)	91.9(4)

Crystal structure determinations

$[Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}_2(CO)_4(dppy)_2]$. The stereochemistry of this compound is illustrated in Fig. 1 and a selection of interatomic distances and angles given in Table 1. The two ruthenium atoms, separated by a distance of 2.720(1) Å corresponding to a formal ruthenium–ruthenium bond, are linked through two bridging acetate ligands *cis* disposed with respect to each other. Two carbonyl groups on each ruthenium atom are co-ordinated mutually *cis* and *trans* to the two bridging acetates while the two phosphorus pyridyl ligands which function as monodentate occupy axial sites on each ruthenium. The complex adopts an essentially eclipsed configuration as reflected by C(39)–Ru(1)–Ru(2)–C(41) and C(40)–Ru(1)–Ru(2)–C(42) torsion angles of 8.5 and 4.6° respectively. The structure is similar to those reported for the carboxylate-bridged compounds $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}_2(CO)_4L_2]$ (R = Me, Pr^n, Ph or 4-FC_6H_4; L = CO, PBu^t_3, py, H_2O or $PhCO_2H$)[15–18] and for the anionic ligand-bridged derivatives $[Ru_2(\mu\text{-}X)_2(CO)_4(PR_3)_2]$ (X = 3,5-dimethylpyrazolato or pyridin-2-onato; R = Bu^t, Ph or *p*-MeC_6H_4).[13,19,20]

$[Ru_2\{\mu\text{-}\eta^2\text{-}OC(H)O\}(CO)_4(\mu\text{-dppy})_2]PF_6$. A perspective view of the cation of this complex is illustrated in Fig. 2 and a selection of interatomic distances and angles given in Table 2. The two ruthenium atoms are bridged by two mutually *trans* dppy ligands as well as by a formate anion. Each ruthenium is also bound to two carbonyl groups, *cis* disposed with respect to each other, with one occupying an equatorial site and the other co-ordinating axially. The local geometry of each ruthenium is essentially octahedral, the sixth site being occupied by the other ruthenium atom, with the angles subtended by *cis*-disposed ligands ranging from 80.8(1) to 98.1(2)°. The ruthenium–ruthenium distance of 2.731(1) Å corresponds to a formal ruthenium–ruthenium bond. The cation is substantially distorted from an eclipsed configuration as reflected by the P(1)–Ru(1)–Ru(2)–N(1) and P(2)–Ru(2)–Ru(1)–N(2) torsion angles of 28.2 and 30.7° respectively. This torsional twist about the ruthenium–ruthenium vector is markedly larger than that

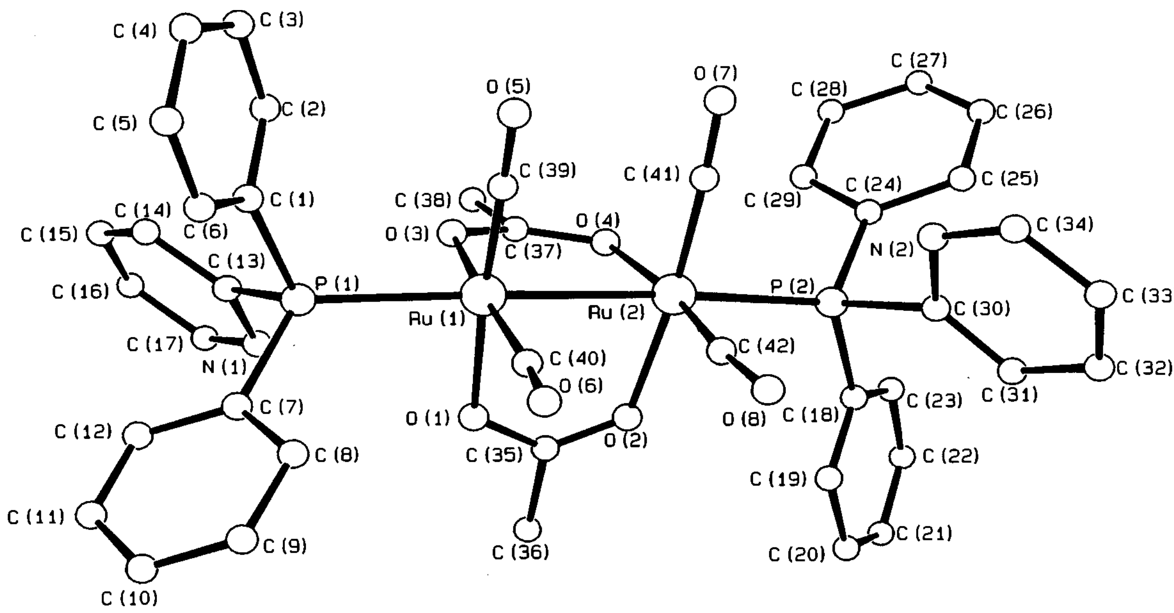

Fig. 1 Molecular structure of $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}_2(CO)_4(dppy)_2]$ showing the atom labelling scheme

Table 2 Selected interatomic distances (Å) and angles (°) for $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(H)O\}(CO)_4(\mu\text{-}dppy)_2]PF_6$

Ru(1)–Ru(2)	2.731(1)	Ru(1)–P(1)	2.287(1)
Ru(1)–O(3)	2.132(3)	Ru(1)–N(2)	2.178(4)
Ru(1)–C(35)	1.960(5)	Ru(1)–C(36)	1.848(5)
Ru(2)–P(2)	2.296(1)	Ru(2)–O(6)	2.151(3)
Ru(2)–N(1)	2.178(4)	Ru(2)–C(37)	1.943(5)
Ru(2)–C(38)	1.841(5)		
Ru(2)–Ru(1)–P(1)	84.8(1)	Ru(1)–Ru(2)–P(2)	83.5(1)
Ru(2)–Ru(1)–O(3)	82.3(1)	Ru(1)–Ru(2)–O(6)	81.5(1)
Ru(2)–Ru(1)–N(2)	88.8(1)	Ru(1)–Ru(2)–N(1)	89.3(1)
Ru(2)–Ru(1)–C(35)	176.2(2)	Ru(1)–Ru(2)–C(37)	173.5(2)
Ru(2)–Ru(1)–C(36)	91.2(1)	Ru(1)–Ru(2)–C(38)	93.5(1)
P(1)–Ru(1)–O(3)	88.6(1)	P(2)–Ru(2)–O(6)	90.7(1)
P(1)–Ru(1)–N(2)	168.3(1)	P(2)–Ru(2)–N(1)	170.1(1)
P(1)–Ru(1)–C(35)	92.8(2)	P(2)–Ru(2)–C(37)	91.8(2)
P(1)–Ru(1)–C(36)	91.8(2)	P(2)–Ru(2)–C(38)	93.0(2)
O(3)–Ru(1)–N(2)	80.8(1)	O(6)–Ru(2)–N(1)	81.5(1)
O(3)–Ru(1)–C(35)	94.8(2)	O(6)–Ru(2)–C(37)	94.3(3)
O(3)–Ru(1)–C(36)	173.5(2)	O(6)–Ru(2)–C(38)	173.4(1)
N(2)–Ru(1)–C(35)	93.1(2)	N(1)–Ru(2)–C(37)	94.9(2)
N(2)–Ru(1)–C(36)	98.1(2)	N(1)–Ru(2)–C(38)	94.2(2)
C(35)–Ru(1)–C(36)	91.7(2)	C(37)–Ru(2)–C(38)	91.0(2)

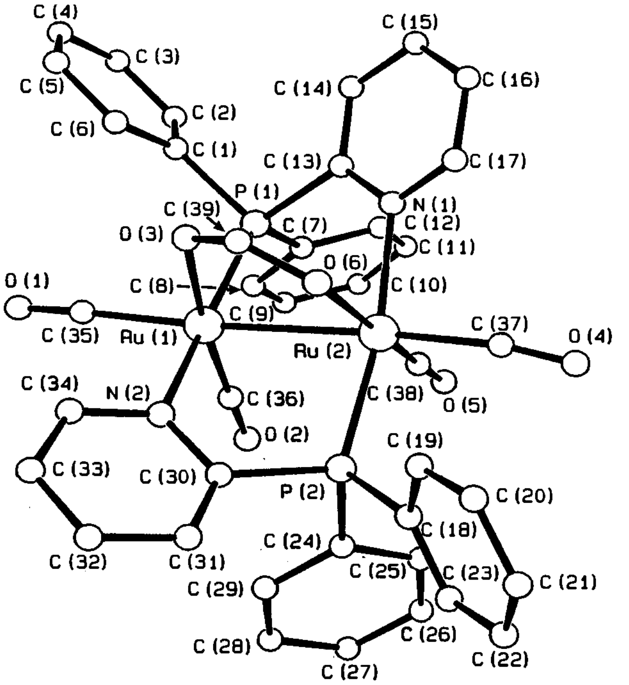

Fig. 2 Structure of the cation in $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(H)O\}(CO)_4(\mu\text{-}dppy)_2]PF_6$ showing the atom labelling scheme

observed in $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$, with corresponding torsion angles of 17.3 and 13.8°,[21] $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}(CO)_4(\mu\text{-}dppm)_2]PF_6$[3] and $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(Ph)O\}(CO)_4\{\mu\text{-}(Pr^iO)_2PN(Et)P(OPr^i)_2\}_2]PF_6$, the latter adopting in fact an almost eclipsed configuration as reflected by the corresponding torsion angles of 0.7 and 1.5° respectively.[22] Significantly, the ruthenium–carbon distances for the axial carbonyls [Ru(1)–C(35) 1.960(5), Ru(2)–C(37) 1.943(5) Å] are substantially longer than those for the equatorial carbonyls [Ru(1)–C(36) 1.848(5), Ru(2)–C(38) 1.841(5) Å], which undoubtedly reflects large differences in the *trans* influence of the formate ion and the adjacent ruthenium atom.

$[Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}(CO)_4(\mu\text{-}dpbipy)_2]PF_6$. The structure of the cation of this complex is illustrated in Fig. 3 and a selection of interatomic distances and angles given in Table 3. The two ruthenium atoms are bridged by two mutually *trans* dpbipy ligands as well as by an acetate group with the two dpbipy ligands functioning as tridentates. A carbonyl group and the other ruthenium atom complete the octahedron around each ruthenium with these two carbonyl groups being situated at equatorial sites *trans* to the acetate group. The ruthenium–ruthenium distance of 2.688(2) Å, which again corresponds to a formal ruthenium–ruthenium single bond, is one of the shortest known for compounds of this type. The cation adopts a partially staggered conformation as reflected by the P(1)–Ru–Ru′–N(1) torsion angle of 22.6°. Both ruthenium atoms have a distorted octahedral geometry with angles subtended by *cis*-disposed ligands ranging from 76.1(2) [N(1′)–Ru–N(2′)] to 106.5(7)° [P(1)–Ru–N(2′)]. This distortion is undoubtedly as a consequence of the restrictive bite of the dpbipy ligands and in particular that of the bipyridyl fragments with this restriction in turn being reflected by the angle associated with the group coordinated at the axial site of 164.3(8)° [Ru′–Ru–N(2′)] and the dihedral angle between the pyridyl rings of the dipyridyl fragment of 11.2°.

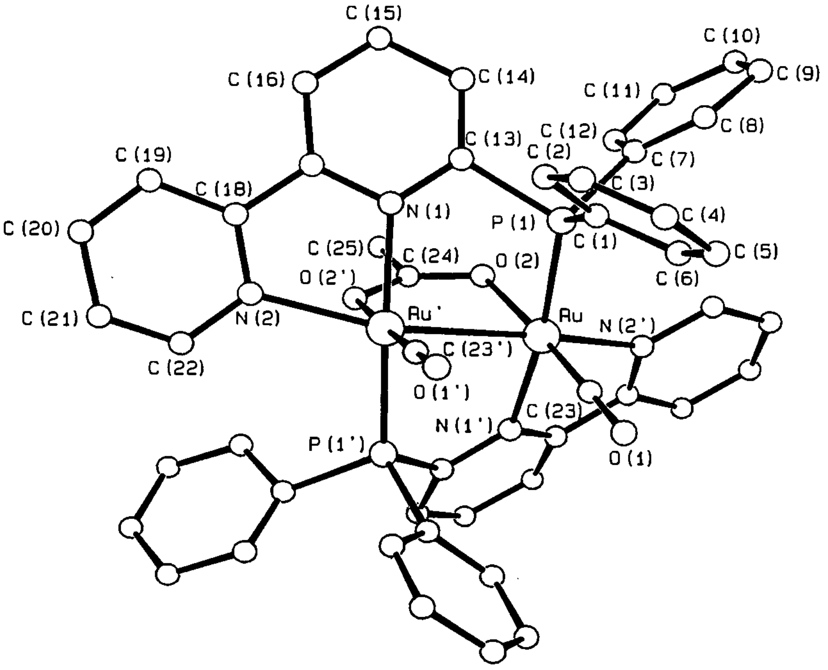

Fig. 3 Structure of the cation in $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}(CO)_2(\mu\text{-dpbipy})_2]PF_6$ showing the atom labelling scheme

Table 3 Selected interatomic distances (Å) and angles (°) for $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}(CO)_2(\mu\text{-dpbipy})_2]PF_6$

Ru–Ru′	2.688(2)	Ru–P(1)	2.250(4)
Ru–O(2)	2.170(11)	Ru–N(1′)	2.120(2)
Ru–N(2′)	2.198(3)	Ru–C(23)	1.78(2)
O(2)–C(24)	1.25(1)	C(24)–C(25)	1.51(3)
Ru′–Ru–P(1)	83.1(3)	Ru′–Ru–O(2)	83.3(6)
Ru′–Ru–N(1′)	92.7(2)	Ru′–Ru–N(2′)	164.3(8)
Ru′–Ru–C(23)	95.5(8)	P(1)–Ru–O(2)	89.2(3)
P(1)–Ru–N(1′)	171.6(4)	P(1)–Ru–N(2′)	106.5(7)
P(1)–Ru–C(23)	92.3(6)	O(2)–Ru–N(1′)	83.1(4)
O(2)–Ru–N(2′)	84.4(3)	O(2)–Ru–C(23)	177.8(6)
N(2′)–Ru–N(1′)	76.1(2)	N(2′)–Ru–C(23)	96.5(2)
N(1′)–Ru–C(23)	95.3(6)		

Experimental

The ligands dppy, dpquin and dpbipy were synthesized according to procedures described previously[23–25] while $[\{Ru_2[\mu\text{-}\eta^2\text{-}OC(R)O]_2(CO)_4\}_n]$ (R = H, Me or Et) were also synthesized according to a literature method.[1] All reactions and manipulations were carried out under an atmosphere of nitrogen using Schlenk techniques. Solvents were purified according to recognised procedures. Infrared spectra were measured on a Shimadzu FTIR-4300 spectrometer, $^{31}P\text{-}\{^1H\}$ NMR spectra on a Varian FT80A instrument and ^1H NMR spectra on a Varian Gemini 200 spectrometer. Relevant spectroscopic data are summarised in Table 4.

Syntheses

$[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}_2(CO)_4(dppy)_2]$ (R = H, Me or Et). A suspension of the appropriate carboxylate-bridged polymer $[\{Ru_2[\mu\text{-}\eta^2\text{-}OC(R)O]_2(CO)_4\}_n]$ (R = H, Me or Et) (0.75 mmol) and dppy (0.40 g, 1.5 mmol) in absolute ethanol (15 cm^3) was refluxed for 45 min. The suspension gradually dissolved to be replaced by a yellow-orange precipitate which was filtered off, washed with cold (0 °C) absolute ethanol (5 cm^3) and diethyl ether (5 cm^3) and dried *in vacuo* for 1 h. In cases where the product had not precipitated after 45 min (for R = H), the solvent was carefully removed under reduced pressure until substantial precipitation had been effected. Although all products were isolated sufficiently pure not to require further crystallisation, highly crystalline material could be isolated from a slowly evaporating CH_2Cl_2–ethanol (1 : 1 v/v) solution of the product. Yields: R = H, 60; Me, 75; Et, 75% (Found: C, 51.2; H, 3.7; N, 2.9. Calc. for $C_{40}H_{30}N_2O_8P_2Ru_2$: C, 51.6; H, 3.3; N, 3.0. Found: C, 52.7; H, 4.1; N, 2.6. Calc. for $C_{42}H_{34}N_2O_8P_2Ru_2$: C, 52.6; H, 3.6; N, 2.9. Found: C, 53.4; H, 4.2; N, 2.6. Calc. for $C_{44}H_{38}N_2O_8P_2Ru_2$: C, 53.6; H, 3.9; N, 2.8%).

$[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}_2(CO)_4(dpquin)_2]$ (R = H, Me or Et). A suspension of the appropriate carboxylate-bridged polymer $[\{Ru_2[\mu\text{-}\eta^2\text{-}OC(R)O]_2(CO)_4\}_n]$ (R = H, Me or Et) (0.75 mmol) and dpquin (0.47 g, 1.5 mmol) in toluene (10 cm^3) was refluxed whilst gently passing CO through the solution for 3 h. The suspension gradually dissolved, yielding a bright yellow solution from which the product precipitated. This yellow product was filtered off, washed with diethyl ether (2 × 5 cm^3) and dried *in vacuo* for 2 h. The products were sufficiently pure in all cases so as not to require further crystallisation. Yields: R = H, 80; Me, 90; Et, 70% (Found: C, 55.6; H, 3.5; N, 2.5. Calc. for $C_{48}H_{34}N_2O_8P_2Ru_2$: C, 55.9; H, 3.3; N, 2.7. Found: C, 57.1; H, 3.5; N, 2.8. Calc. for $C_{50}H_{38}N_2O_8P_2Ru_2$: C, 56.7; H, 3.6; N, 2.7. Found: C, 57.2; H, 3.7; N, 2.5. Calc. for $C_{52}H_{42}N_2O_8P_2Ru_2$: C, 57.5; H, 3.9; N, 2.6%).

$[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}_2(CO)_4(dpbipy)_2]$ (R = H, Me or Et). A suspension of the appropriate carboxylate-bridged polymer $[\{Ru_2[\mu\text{-}\eta^2\text{-}OC(R)O]_2(CO)_4\}_n]$ (R = H, Me or Et) (0.3 mmol) and dpbipy (0.21 g, 0.6 mmol) in *n*-butanol (15 cm^3) was refluxed for 3 h. The suspension gradually dissolved affording a clear brown-orange solution at the end of the reaction. The hot solution was filtered quickly and then carefully reduced in volume to *ca.* 5 cm^3 under reduced pressure, yielding the product as a dark orange microcrystalline material. This was filtered off, washed with cold (0 °C) butan-1-ol (2 cm^3) and diethyl ether (10 cm^3) and dried *in vacuo* for 12 h at 40 °C effectively to remove any residual *n*-butanol. The product was recrystallised from a slowly evaporating saturated acetone–ethanol (1 : 1 v/v) solution. Yields: R = H, 60; Me, 70; Et, 70% (Found: C, 55.8; H, 3.5; N, 5.4. Calc. for $C_{50}H_{36}N_4O_8P_2Ru_2$: C, 55.4; H, 3.3; N, 5.2.

Table 4 Infrared and ^{31}P-{^{1}H} NMR spectroscopic data

Compound	$\tilde{\nu}$(CO)^a/cm^{-1}	$\tilde{\nu}$(CO$_2$)^a/cm^{-1}	^{31}P-{^{1}H} NMR^b
$[\mathrm{Ru_2\{\mu\text{-}\eta^2\text{-}OC(H)O\}_2(CO)_4(dppy)_2}]$	2025s, 1981m, 1952vs, 1914w (sh)	1572s	16.91 (s)
$[\mathrm{Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}_2(CO)_4(dppy)_2}]$	2027s, 1981m, 1953vs, 1913w (sh)	1571s	16.88 (s)
$[\mathrm{Ru_2\{\mu\text{-}\eta^2\text{-}OC(Et)O\}_2(CO)_4(dppy)_2}]$	2027s, 1977m, 1952vs, 1912w (sh)	1574s	17.02 (s)
$[\mathrm{Ru_2\{\mu\text{-}\eta^2\text{-}OC(H)O\}_2(CO)_4(dpquin)_2}]$	2033s, 1978m, 1945vs, 1913w (sh)	1567s	18.09 (s)
$[\mathrm{Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}_2(CO)_4(dpquin)_2}]$	2032s, 1978m, 1950vs, 1913w (sh)	1568s	17.50 (s)
$[\mathrm{Ru_2\{\mu\text{-}\eta^2\text{-}OC(Et)O\}_2(CO)_4(dpquin)_2}]$	2034s, 1978m, 1950vs, 1912w (sh)	1570s	17.53 (s)
$[\mathrm{Ru_2\{\mu\text{-}\eta^2\text{-}OC(H)O\}_2(CO)_4(dpbipy)_2}]$	2026s, 1989m, 1952vs, 1912w (sh)	1575s	17.62 (s)^c
$[\mathrm{Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}_2(CO)_4(dpbipy)_2}]$	2025s, 1989m, 1953vs, 1914w (sh)	1572s	17.79 (s)^c
$[\mathrm{Ru_2\{\mu\text{-}\eta^2\text{-}OC(Et)O\}_2(CO)_4(dpbipy)_2}]$	2025s, 1981m, 1952vs, 1913w (sh)	1566s	17.80 (s)^c
$[\mathrm{Ru_2\{\mu\text{-}\eta^2\text{-}OC(H)O\}(CO)_4(\mu\text{-}dppy)_2]PF_6}$	2021m, 1995vs, 1964s, 1942w	1557w	45.03 (s)
$[\mathrm{Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}(CO)_4(\mu\text{-}dppy)_2]PF_6}$	2027m, 2004vs, 1969s, 1950w	1541m	45.24 (s)
$[\mathrm{Ru_2\{\mu\text{-}\eta^2\text{-}OC(Et)O\}(CO)_4(\mu\text{-}dppy)_2]PF_6}$	2023m, 1999vs, 1968s, 1951w	1550m	45.91 (s)
$[\mathrm{Ru_2\{\mu\text{-}\eta^2\text{-}OC(H)O\}(CO)_4(\mu\text{-}dpquin)_2]\ PF_6}$	2060m, 1986vs, 1947s, 1920w	1556w	47.22 (s)
$[\mathrm{Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}(CO)_4(\mu\text{-}dpquin)_2]PF_6}$	2056m, 1992vs, 1953s, 1920w	1553w	47.34 (s)
$[\mathrm{Ru_2\{\mu\text{-}\eta^2\text{-}OC(Et)O\}(CO)_4(\mu\text{-}dpquin)_2]PF_6}$	2061m, 1982vs, 1951s, 1926w	1552m	47.31 (s)
$[\mathrm{Ru_2\{\mu\text{-}\eta^2\text{-}OC(H)O\}(CO)_2(\mu\text{-}dpbipy)_2]PF_6}$	1934vs, 1899m (sh)	1557m	45.03 (s)
$[\mathrm{Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}(CO)_2(\mu\text{-}dpbipy)_2]PF_6}$	1930vs, 1890m (sh)	1551m	45.24 (s)
$[\mathrm{Ru_2\{\mu\text{-}\eta^2\text{-}OC(Et)O\}(CO)_2(\mu\text{-}dpbipy)_2]\ PF_6}$	1942vs, 1903m (sh)	1576m	45.91 (s)

[a] Recorded in CH_2Cl_2. Abbreviations: v = very, s = strong, m = medium, w = weak, sh = shoulder. [b] δ in ppm relative to H_3PO_4. Recorded in CD_2Cl_2 unless otherwise specified. Abbreviation: s = singlet. [c] Recorded in [$^2H_6$]acetone.

Table 5 Crystallographic data

	$[\mathrm{Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}_2(CO)_4\text{-}(dppy)_2}]$	$[\mathrm{Ru_2\{\mu\text{-}\eta^2\text{-}OC(H)O\}(CO)_4\text{-}(\mu\text{-}dppy)_2]PF_6}$	$[\mathrm{Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}(CO)_2\text{-}(\mu\text{-}dpbipy)_2]PF_6}$
Formula	$C_{42}H_{34}N_2O_8P_2Ru_2$	$C_{39}H_{29}F_6N_2O_6P_3Ru_2$	$C_{48}H_{37}F_6N_4O_4P_3Ru_2$
M	958.83	1030.72	1142.90
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P2/a$ (no. 13)
a/Å	9.484(2)	12.979(4)	14.743(4)
b/Å	13.146(3)	16.224(5)	9.985(3)
c/Å	16.838(6)	19.922(5)	17.249(6)
α/°	82.10(2)	—	—
β/°	87.85(2)	108.93(2)	91.34
γ/°	77.62(2)	—	—
U/Å^3	2031(2)	3968(1)	2538(1)
Z	2	4	2
D_c/g cm^{-3}	1.568	1.725	1.495
F(000)	964	2048	1128
μ/cm^{-1}	8.64	9.11	7.47
Crystal size/mm	0.40 × 0.32 × 0.30	0.63 × 0.20 × 0.10	0.42 × 0.19 × 0.33
Measured reflections	5872	5927	5655
Independent reflections	5230	4887	3231
Observed reflections [$I > 3\sigma(I)$]	4582	4067	2198
No. variables	512	524	305
Weights (*g*)	0.0010	0.0007	0.014
R	0.070	0.031	0.077
R′	0.086	0.033	0.084
Δ/σ (maximum)	0.150	0.014	0.152
Δρ/e Å^{-3}	1.10	0.43	0.95

Weighting scheme: $w = 1/[\sigma^2(F) + gF^2]$. $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, $R' = \Sigma w^{\frac{1}{2}}(|F_o| - |F_c|)/\Sigma w^{\frac{1}{2}}F_o$.

Found: C, 55.9; H, 3.7; N, 4.7. Calc. for $C_{52}H_{40}N_4O_8P_2Ru_2$: C, 56.1; H, 3.6; N, 5.0. Found: C, 56.7; H, 3.6; N, 4.6. Calc. for $C_{54}H_{44}N_4O_8P_2Ru_2$: C, 56.8; H, 3.9; N, 4.9%).

$[\mathrm{Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}(CO)_4(\mu\text{-}dppy)_2]PF_6}$ (R = H, Me or Et). A suspension of the appropriate carboxylate-bridged polymer $[\{\mathrm{Ru_2[\mu\text{-}\eta^2\text{-}OC(R)O]_2(CO)_4}\}_n]$ (R = H, Me or Et) (0.23 mmol), dppy (0.125 g, 0.46 mmol) and NH_4PF_6 (0.075 g, 0.46 mmol) in toluene (15 cm^3) was refluxed whilst gently passing CO through the solution for 4 h (for R = H and Me) or 6 h (for R = Et). During this time the solution first turned orange and then yellow with separation of a bright yellow precipitate. The reaction mixture was cooled to room temperature and the solid filtered off, washed with diethyl ether (2 × 5 cm^3) and dried *in vacuo*. Further product was obtained by reducing the volume of the filtrate to *ca.* 3 cm^3 and keeping it at −25 °C for 12 h. The combined products were crystallised from a slowly evaporating saturated CH_2Cl_2–ethanol (1 : 1 v/v) solution to afford a bright yellow crystalline material, isolated as described above. Yields: R = H, 65; Me, 70; Et, 65% (Found: C, 45.9; H, 2.9; N, 2.7. Calc. for $C_{39}H_{29}F_6N_2O_6P_3Ru_2$: C, 45.5; H, 2.8; N, 2.7. Found: C, 45.7; H, 3.2; N, 2.8. Calc. for $C_{40}H_{31}F_6N_2O_6P_3Ru_2$: C, 46.0; H, 3.0; N, 2.7. Found: C, 46.3; H, 3.4; N, 2.8. Calc. for $C_{41}H_{33}F_6N_2O_6P_3Ru_2$: C, 46.5; H, 3.1; N, 2.7%).

$[\mathrm{Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}(CO)_4(\mu\text{-}dpquin)_2]PF_6}$ (R = H, Me or Et). A suspension of the appropriate carboxylate-bridged polymer $[\{\mathrm{Ru_2[\mu\text{-}\eta^2\text{-}OC(R)O]_2(CO)_4}\}_n]$ (0.23 mmol), dpquin (0.145 g, 0.46 mmol) and an excess of NH_4PF_6 (0.30 g, 1.84 mmol) in toluene (15 cm^3) was refluxed whilst gently passing CO through the solution for 8 h. During this time the suspension slowly dissolved yielding a yellow solution from which a yellow product precipitated. The solution was cooled and the product filtered off. It was washed with diethyl ether (2 × 5 cm^3) and dried *in vacuo*. Further product could not be isolated from the mother-liquor, removal of the solvent under reduced pressure yielding the corresponding compounds containing pendant dpquin ligands. Yields: R = H, 10; Me, 15; Et, 5% (Found: C, 49.9; H, 2.8; N, 2.5. Calc. for $C_{47}H_{33}F_6N_2O_6P_3Ru_2$: C, 49.9; H, 2.9; N, 2.5. Found: C, 50.5; H, 3.6; N, 2.5. Calc. for $C_{48}H_{35}F_6N_2O_6P_3Ru_2$: C, 50.4; H, 3.1; N, 2.5. Found: C, 50.5; H, 3.3; N, 2.6. Calc. for $C_{49}H_{37}F_6N_2O_6P_3Ru_2$: C, 50.8; H, 3.2; N, 2.4%).

$[Ru_2\{\mu\text{-}\eta^2\text{-}OC(R)O\}(CO)_2(\mu\text{-dpbipy})_2]PF_6$ (R = H, Me or Et). A suspension of the appropriate carboxylate-bridged polymer $[\{Ru_2[\mu\text{-}\eta^2\text{-}OC(R)O]_2(CO)_4\}_n]$ (0.3 mmol) and dpbipy (0.205 g, 0.6 mmol) in *n*-butanol (10 cm^3) was refluxed at 120 °C for 24 h. The solution slowly changed from orange-yellow through to dark brown. The reaction solution was cooled to room temperature and filtered. A hot solution of NH_4PF_6 (0.105 g, 0.65 mmol) in butan-1-ol was added dropwise with stirring to precipitate the product as a brown powder. This was filtered off, washed with diethyl ether (5 × 5 cm^3) and dried *in vacuo* for 12 h at 40 °C effectively to remove any residual *n*-butanol. Recrystallisation of the product from acetonitrile–diethyl ether (1 : 1 v/v) at −25 °C afforded the analytically pure product as dark brown needles. Yields: R = H, 70; Me, 80; Et, 65% (Found: C, 49.9; H, 3.0; N, 4.7. Calc. for $C_{47}H_{35}F_6N_4O_4P_3Ru_2$: C, 50.0; H, 3.1; N, 5.0. Found: C, 50.0; H, 3.7; N, 4.7. Calc. for $C_{48}H_{37}F_6N_4O_4P_3Ru_2$: C, 50.4; H, 3.3; N, 4.9. Found: C, 50.4; H, 3.1; N, 4.7. Calc. for $C_{49}H_{39}F_6N_4O_4P_3Ru_2$: C, 50.9; H, 3.4; N, 4.8%).

Crystallography

Crystal data for $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}_2(CO)_4(dppy)_2]$, $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(H)O\}(CO)_4(\mu\text{-dppy})_2]PF_6$, and $[Ru_2\{\mu\text{-}\eta^2\text{-}OC(Me)O\}(CO)_2(\mu\text{-dpbipy})_2]PF_6$ as well as details of the structure solution and refinement are summarised in Table 5.

Intensity data were collected at 295 K on a CAD4 diffractometer by the variable-speed ω–2θ scan method in the range $3 \leqslant 2\theta \leqslant 46°$ with Mo-Kα radiation ($\lambda = 0.710\,69$ Å) the data being corrected for absorption by the ψ-scan method.[26] The structures were solved by standard Patterson methods and subsequently completed by Fourier recycling and full-matrix least-squares refinement based on *F*.[27] Non-hydrogen atoms were assigned anisotropic thermal factors and the hydrogen atoms a single common thermal factor; the latter were placed in calculated positions. Neutral atom scattering factors were used with corrections for anomalous dispersion.[28]

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