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ROLE OF THE CATION IN THE REACTION OF $Co(CO)_4^-$ WITH $RuCl_3 \cdot xH_2O$. SYNTHESIS AND MOLECULAR STRUCTURE OF THE RUTHENIUM CLUSTER $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}Cl)_4(\mu\text{-}CO)_2(CO)_8]$

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Summary

Reaction of $[PPN][Co(CO)_4]$ with $RuCl_3 \cdot xH_2O$ (4/1 ratio) in THF affords $Ru_3(CO)_{12}$, $[PPN][RuCo_3(CO)_{12}]$, $[PPN][Ru_3Co(CO)_{13}]$ and $[PPN]_2[Ru_4(\mu\text{-}Cl)_4(\mu\text{-}CO)_2(CO)_8]$. The latter has been fully characterized by an X-ray structural analysis. These results are compared with those obtained in the related reaction with $Na[Co(CO)_4]$, which afforded mainly $Na[RuCo_3(CO)_{12}]$.

Introduction

In the synthesis of mixed-metal complexes, tetracarbonylcobaltate has been extensively used as building unit [1]. It is often brought into reaction with halogeno complexes of a second metal, leading to two classes of products. In the first case, one or more $[Co(CO)_4]^-$ groups replace halide(s) of the starting complex, without formal occurrence of a redox reaction [2]. In the second case, a redox reaction occurs, usually accompanied by extensive structural rearrangements [3]. The resulting products may be mono- or poly-nuclear and, in the latter case, homo- or hetero-polymetallic. This will largely depend upon the reaction conditions, such as solvent, temperature and time, and obviously also upon the nature of the complex reacted with the tetracarbonylcobaltate. Finally, the cation associated with $Co(CO)_4^-$ might also have a significant effect, but this has not yet been systematically investigated [4].

The interesting results obtained recently in methanol homologation and methanol carbonylation with cobalt/ruthenium catalysts [5–7] have stimulated considerable interest in the synthesis, characterization, and catalytic properties of mixed ruthenium-cobalt carbonyl clusters [8–11].

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We have previously described the reaction of Na[Co(CO)$_4$] with RuCl$_3 \cdot x$H$_2$O (commercial), yielding the tetrametallic cluster Na[RuCo$_3$(CO)$_{12}$] in 60–70% yield [10]. Metathetical exchange with [PPN][Cl] (PPN = (C$_6$H$_5$)$_3$PNP(C$_6$H$_5$)$_3$) was reported to give [PPN][RuCo$_3$(CO)$_{12}$] in ca. 24% yield (based on Na[RuCo$_3$(CO)$_{12}$]) [12].

For the methanol homologation catalysed by these complexes, Hidai et al. have found that [PPN][RuCo$_3$(CO)$_{12}$] is more selective for ethanol than Na[RuCo$_3$(CO)$_{12}$] [12]. A cation effect has also been reported for the reaction of [RuCo$_3$(CO)$_{12}$]$^-$ with diphenylacetylene [13].

In order to study the influence of the cation associated with Co(CO)$_4$$^-$ on the reactivity of the latter, and also to improve the yields of [PPN][RuCo$_3$(CO)$_{12}$], we have studied the reaction of [PPN][Co(CO)$_4$] with RuCl$_3 \cdot x$H$_2$O, and the results are described below.

Results and discussion

The reaction of [PPN][Co(CO)$_4$] with RuCl$_3 \cdot x$H$_2$O in a 4/1 ratio was carried out in tetrahydrofuran at ca. 60°C. From the resulting orange-yellow solution, the following complexes were isolated: Ru$_3$(CO)$_{12}$, [PPN][RuCo$_3$(CO)$_{12}$], [PPN][Ru$_3$Co(CO)$_{13}$], and [PPN]$_2$[Ru$_4$Cl$_4$(CO)$_{10}$] (eq. 1):

$$\mathrm{RuCl_3 \cdot xH_2O + 4[PPN][Co(CO)_4] \rightarrow Ru_3(CO)_{12} + [PPN][RuCo_3(CO)_{12}] +} \\ \mathrm{[PPN][Ru_3Co(CO)_{13}] + [PPN]_2[Ru_4Cl_4(CO)_{10}] + \ldots} \quad (1)$$

The two mixed-metal clusters have been described before [8,12], but the Ru$_4$ complex is novel, and was fully characterized by an X-ray analysis, the results of which are reported below. Surprisingly, this reaction gives more products than the corresponding reaction with Na[Co(CO)$_4$] [10] (eq. 2):

$$\mathrm{RuCl_3 \cdot xH_2O + 4\,Na[Co(CO)_4] \rightarrow Na[RuCo_3(CO)_{12}] + \ldots} \quad (2)$$

In the latter case, Na[RuCo$_3$(CO)$_{12}$] was the only carbonyl product isolated (in ca. 60–70% yield). In the present reaction, the formation of [PPN][Ru$_3$Co(CO)$_{13}$] probably results from the condensation of [PPN][Co(CO)$_4$] with Ru$_3$(CO)$_{12}$ [8], itself generated by reductive carbonylation of RuCl$_3 \cdot x$H$_2$O. This is supported by the fact that no Ru$_3$(CO)$_{12}$ was detected nor isolated at the end of reaction 2.

The formation of [PPN][RuCo$_3$(CO)$_{12}$] in an unexpectedly low yield, from the reaction of [PPN][Co(CO)$_4$] was in view of the previous results obtained with Na[Co(CO)$_4$] [9,10]. Unfortunately this complex is somewhat difficult to separate from [PPN][Ru$_3$Co(CO)$_{13}$]. To circumvent this difficulty, we searched for an alternative method, and found that cation exchange between Na[RuCo$_3$(CO)$_{12}$] and [PPN]Cl in water followed by toluene extraction, affords the desired product in yields superior to those reported in the literature [12]. (See Experimental).

The new complex [PPN]$_2$[Ru$_4$Cl$_4$(CO)$_{10}$] observed in reaction 1 comes from partial reduction of the ruthenium precursor. Its molecular geometry is represented in Fig. 1. Selected bond distances and angles, least-squares planes, and positional parameters are given in Tables 1, 2 and 3, respectively. The bridging carbonyls are characterized by IR spectroscopy at relatively low ν(CO) frequencies at 1713 and 1706 cm^{-1}. The four Ru atoms form a distorted tetrahedron with metal–metal separations greater than 3 Å. Two chloride ligands and one CO ligand alternately

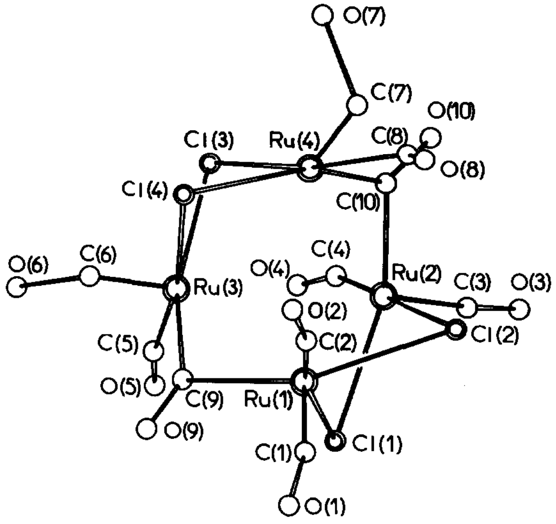

Fig. 1. Diagram of the molecular structure of $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}Cl)_4(\mu\text{-}CO)_2(CO)_8]$. The cation has been omitted for clarity.

bridge all the Ru atoms, and a pseudo C_2 axis passes through the middle of the Cl(1) Cl(2) and Cl(3) Cl(4) vectors. An idealized geometry is represented in Fig. 2a, where four distorted tetrahedrons Ru(1) Ru(2) Ru(3) Ru(4), Cl(1) Cl(2) Cl(3) Cl(4), Ru(1) Ru(2) Cl(1) Cl(2) and Ru(3) Ru(4) Cl(3) Cl(4) can be recognized. The first two interpenetrate, whereas the other two are connected by the C(9) O(9) and C(10) O(10) bridges. Fig. 2b shows another view of the idealised structure of this cluster in which the two nearly planar arrangements Ru(1) Ru(3) Cl(1) Cl(4) and Ru(2) Ru(4) Cl(2) Cl(3) are represented. In this description, if they are considered as planar (Table 2, Planes no. 19 and 20) they are almost parallel to each other, at a distance of 2.38 Å. Furthermore, these arrangements sit on top of each other with a mutual rotation of their Ru–Ru diagonals of ca. 60°.

The more exact description of Fig. 2c illustrates the Ru(1) Ru(3) Cl(1) Cl(4) and Ru(2) Ru(4) Cl(2) Cl(3) butterflies of Ru(1) Ru(3) and Ru(2) Ru(4) hinges. The normal to their wings form an angle of ca. 20° (Table 2, Planes 11, 12 and 13, 14) and are folded towards the inside of the distorted monoclinic antiprismatic cavity. The latter is idealized in Fig. 2d.

The environment about each Ru atom is roughly square-pyramidal, with two Cl ligands and a terminal and a bridging CO ligand forming the square base, a terminal CO being in the apical position (Table 2). This arrangement bears some resemblance to that in $[RuCl(NO)(\mu\text{-}PPh_2)]_4$, in which the nitrosyl ligands occupy the corresponding apical positions, although in this molecule the Ru atoms form a rectangular array [14].

Figure 3 illustrates this square-pyramidal geometry, and shows that the "vacant" sixth coordination site of the Ru atoms is directed toward the centre of the cavity defined above. When the best plane defined only by the four atoms (Cl, Cl, C, C) which form a square about each Ru atom is considered, the metal is found to be out of plane by 0.13 to 0.24 Å, and always toward the apical carbonyl ligand. With a

(Continued on p. 132)

TABLE 1

DISTANCES (Å) AND ANGLES (°) FOR $[PPN]_2[Ru_4(\mu\text{-}Cl)_4(\mu\text{-}CO)_2(CO)_8]$

Ru(1)–Ru(2)	3.255(7)	Ru(3)–Cl(3)	2.66(1)	Ru(1)–C(9)	2.08(4)	C(4)–O(4)	1.32(5)
Ru(1)–Ru(3)	3.059(5)	Ru(3)–Cl(4)	2.49(1)	Ru(2)–C(3)	1.76(6)	C(5)–O(5)	1.11(5)
Ru(1)–Ru(4)	3.840(6)	Ru(4)–Cl(2)	3.84(1)	Ru(2)–C(4)	1.81(4)	C(6)–O(6)	1.23(6)
Ru(2)–Ru(3)	3.831(7)	Ru(4)–Cl(3)	2.50(1)	Ru(2)–C(10)	2.08(5)	C(7)–O(7)	1.38(7)
Ru(2)–Ru(4)	3.055(6)	Ru(4)–Cl(4)	2.69(2)	Ru(3)–C(5)	1.94(4)	C(8)–O(8)	1.19(5)
Ru(3)–Ru(4)	3.185(6)	Cl(1)–Cl(2)	3.35(1)	Ru(3)–C(6)	1.72(5)	C(9)–O(9)	1.20(6)
Ru(1)–Cl(1)	2.51(1)	Cl(1)–Cl(3)	5.35(2)	Ru(3)–C(9)	1.97(5)	C(10)–O(10)	1.20(6)
Ru(1)–Cl(2)	2.83(1)	Cl(1)–Cl(4)	5.73(2)	Ru(4)–C(7)	1.47(6)	P(1)–N(2)	1.59(3)
Ru(1)–Cl(4)	3.88(1)	Cl(2)–Cl(3)	5.66(2)	Ru(4)–C(8)	1.88(4)	P(2)–N(2)	1.54(4)
Ru(2)–Cl(1)	2.70(1)	Cl(2)–Cl(4)	5.38(2)	Ru(4)–C(10)	2.04(5)	P(3)–N(1)	1.64(3)
Ru(2)–Cl(2)	2.47(1)	Cl(3)–Cl(4)	3.33(2)	C(1)–O(1)	1.19(6)	P(4)–N(1)	1.48(2)
Ru(2)–Cl(3)	3.85(1)	Ru(1)–C(1)	1.65(5)	C(2)–O(2)	1.28(6)		
Ru(3)–Cl(1)	3.93(1)	Ru(1)–C(2)	1.84(5)	C(3)–O(3)	1.10(7)		
Ru(1)–Ru(2)–Ru(3)	50.3(1)	Ru(1)–C(1)–O(1)	171(4)	C(5)–Ru(3)–C(9)	90(2)		
Ru(2)–Ru(3)–Ru(4)	50.6(1)	Ru(1)–C(2)–O(2)	170(4)	C(6)–Ru(3)–C(9)	95(2)		
Ru(3)–Ru(4)–Ru(1)	50.6(1)	Ru(2)–C(3)–O(3)	172(4)	C(7)–Ru(4)–C(8)	77(3)		
Ru(4)–Ru(1)–Ru(2)	50.2(1)	Ru(2)–C(4)–O(4)	174(4)	C(7)–Ru(4)–C(10)	83(3)		
Ru(1)–Ru(3)–Ru(4)	75.9(1)	Ru(3)–C(5)–O(5)	171(4)	C(8)–Ru(4)–C(10)	80(2)		
Ru(2)–Ru(4)–Ru(1)	54.9(1)	Ru(3)–C(6)–O(6)	171(4)	C(1)–Ru(1)–Cl(1)	94(2)		
Ru(1)–Cl(1)–Ru(2)	77.3(3)	Ru(4)–C(7)–O(7)	158(5)	C(1)–Ru(1)–Cl(2)	109(2)		
Ru(1)–Cl(2)–Ru(2)	75.4(3)	Ru(4)–C(8)–O(8)	153(4)	C(3)–Ru(2)–Cl(1)	110(2)		
Ru(3)–Cl(3)–Ru(4)	76.0(3)	C(1)–Ru(1)–C(2)	85(2)	C(3)–Ru(2)–Cl(2)	93(2)		
Ru(3)–Cl(4)–Ru(4)	75.8(4)	C(1)–Ru(1)–C(9)	94(2)	C(6)–Ru(3)–Cl(3)	102(2)		
Ru(1)–C(9)–Ru(3)	98(2)	C(2)–Ru(1)–C(9)	93(2)	C(6)–Ru(3)–Cl(4)	87(2)		
Ru(1)–C(9)–O(9)	126(3)	C(3)–Ru(2)–C(4)	84(2)	C(7)–Ru(4)–Cl(3)	97(2)		
Ru(3)–C(9)–O(9)	135(3)	C(3)–Ru(2)–C(10)	89(2)	C(7)–Ru(4)–Cl(4)	114(2)		
Ru(2)–C(10)–Ru(4)	96(2)	C(4)–Ru(2)–C(10)	90(2)	P(1)–N(2)–P(2)	147(2)		
Ru(2)–C(10)–O(10)	129(3)	C(5)–Ru(3)–C(6)	91(2)	P(3)–N(1)–P(4)	144(2)		
Ru(4)–C(10)–O(10)	134(3)						

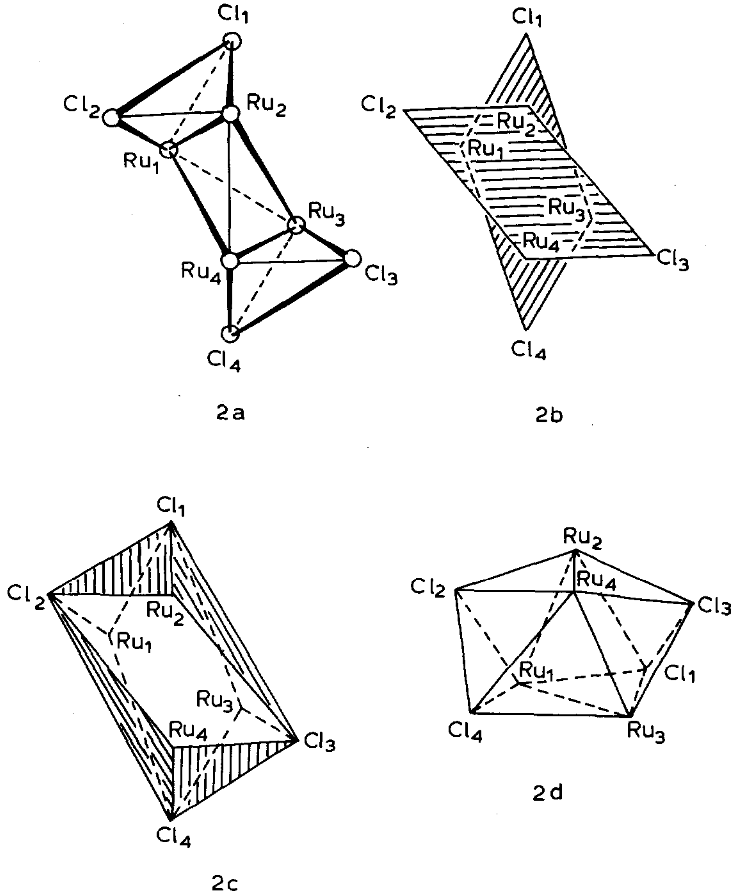

Fig. 2. Idealized view of the framework of $[Ru_4(\mu\text{-}Cl)_4(\mu\text{-}CO)_2(CO)_8]$.

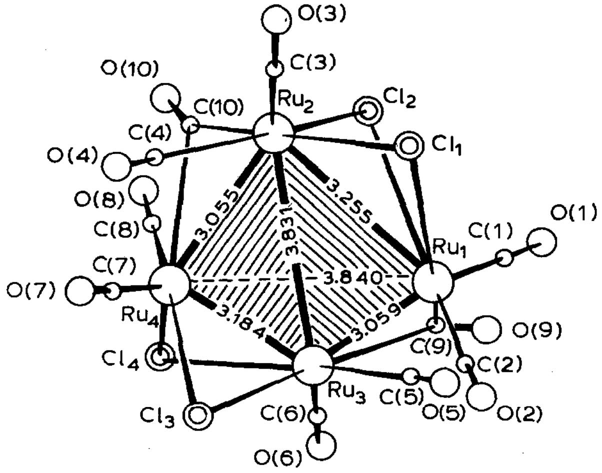

Fig. 3. Idealized structure of $[Ru_4(\mu\text{-}Cl)_4(\mu\text{-}CO)_2(CO)_8]$.

TABLE 2

LEAST-SQUARES PLANES FOR $[\mathrm{PPN}]_2[\mathrm{Ru}_4(\mu\text{-}\mathrm{Cl})_4(\mu\text{-}\mathrm{CO})_2(\mathrm{CO})_8]$ [a]

Plane No.	*A*	*B*	*C*	*D*	Atoms involved	
1	−3.8477	5.2535	−7.0573	−33.2627	Ru(1), Ru(2), Ru(3)	
2	−9.2111	2.6665	−0.4840	−41.3590	Ru(1), Ru(2), Ru(4)	
3	4.4415	−6.6760	−4.9599	−44.8873	Ru(2), Ru(3), Ru(4)	
4	−0.9220	−9.2631	1.6133	−29.7758	Ru(1), Ru(3), Ru(4)	
5	−6.2631	0.3742	2.0536	−22.5641	Ru(1), Ru(2), Cl(1)	
6	0.4834	3.3980	−5.8334	−11.4961	Ru(1), Ru(2), Cl(2)	
7	3.9826	−2.1245	−4.6592	−26.0725	Ru(3), Ru(4), Cl(4)	
8	−2.4340	−5.0742	3.1969	−7.4601	Ru(3), Ru(4), Cl(3)	
9	−0.7861	3.3397	−2.1536	−2.0999	Ru(1), Ru(3), C(9)	
10	−3.5306	2.1411	0.8926	−2.3948	Ru(2), Ru(4), C(10)	
11	−4.5707	−2.4413	−5.6570	−57.5110	Ru(1), Ru(3), Cl(1)	
12	−4.0749	−4.8723	−4.1967	−56.8586	Ru(1), Ru(3), Cl(4)	
13	−4.9807	−3.1650	−4.7003	−77.7712	Ru(2), Ru(4), Cl(2)	
14	−3.1177	−4.4811	−5.3508	−78.7489	Ru(2), Ru(4), Cl(3)	
					Atom distances from plane	
15	−1.5744	2.2136	6.1884	28.0196	Ru(1)	−0.187(4)
					Cl(1)	−0.20(1)
					Cl(2)	0.41(1)
					C(2)	−0.25(2)
					C(9)	0.22(2)
					C(1) [b]	−1.82(2)
					O(1) [b]	−2.96(3)
16	4.1314	4.9008	−1.0799	47.5468	Ru(2)	0.128(4)
					Cl(1)	−0.28(1)
					Cl(2)	0.17(1)
					C(4)	0.22(2)
					C(10)	−0.23(2)
					C(3) [b]	1.85(2)
					O(3) [b]	2.96(3)
17	6.1467	1.8737	−0.6752	21.4311	Ru(3)	−0.128(4)
					Cl(3)	0.27(1)
					Cl(4)	−0.14(1)
					C(5)	−0.17(2)
					C(9)	0.17(2)
					C(6) [b]	−0.185(2)
					O(6) [b]	−3.06(3)
18	0.1012	−0.8998	6.5092	49.5723	Ru(4)	0.101(4)
					Cl(3)	0.16(1)
					Cl(4)	−0.21(1)
					C(8)	0.18(2)
					C(10)	−0.23(2)
					C(7) [b]	1.50(2)
					O(7) [b]	2.87(3)
19	4.3124	3.6872	4.9548	59.1757	Ru(1)	−0.241(4)
					Ru(3)	−0.230(4)
					Cl(1)	0.23(1)
					Cl(4)	0.24(1)

TABLE 2 (continued)

Plane No.	*A*	*B*	*C*	*D*	Atom distances from plane	
20	4.0180	3.8019	4.9901	76.2790	Ru(2)	0.195(4)
					Ru(4)	0.193(4)
					Cl(2)	−0.19(1)
					Cl(3)	−0.19(1)
21	1.6357	−6.4506	3.9709	3.8063	Ru(1)	0.00
					Ru(3)	−0.075(4)
					Cl(2)	0.01(1)
					Cl(3)	0.06(1)
22	−4.3778	4.6024	2.5544	15.5120	Ru(2)	0.342(4)
					Ru(4)	0.208(4)
					Cl(1)	−0.31(1)
					Cl(4)	−0.24(1)

Dihedral angles between planes (°)

Planes	Angle	Planes	Angle	Planes	Angle
1–2	55	9–10	62	15–17	103
3–4	56	11–12	21.7	15–18	31
1–4	52	13–14	18	16–18	105
2–3	52	15–16	93	19–20	2.3
5–6	108	16–17	33	21–22	120
7–8	109	17–18	97		

[a] Equation of the planes is of the form $Ax + By + Cz = D$. [b] This atom was not used in defining the plane.

TABLE 3

FRACTIONAL ATOMIC COORDINATES $(\times 10^4)$ (with estimated standard deviations) FOR $[PPN]_2[Ru_4(\mu\text{-}Cl)_4(\mu\text{-}CO)_2(CO)_8]$

Atom	*x/a*	*y/b*	*z/c*
Ru(1)	4482(3)	559(3)	1735(2)
Ru(2)	5068(3)	2286(4)	2380(2)
Ru(3)	2351(3)	1741(3)	2420(2)
Ru(4)	4434(4)	873(4)	3220(2)
Cl(1)	4362(10)	2422(10)	1387(4)
Cl(2)	6573(10)	528(10)	2076(4)
Cl(3)	2553(10)	2531(9)	3321(4)
Cl(4)	2957(10)	4(10)	2998(5)
P(1)	7926(10)	4722(10)	4025(5)
P(2)	8942(11)	2268(11)	4307(5)
P(3)	9850(10)	7316(10)	995(5)
P(4)	11857(10)	5969(10)	334(5)
N(1)	10699(26)	6411(26)	586(12)
N(2)	8599(27)	3408(29)	4011(13)
C(1)	4680(35)	45(36)	1152(19)
O(1)	4703(28)	−367(28)	752(14)
C(2)	4897(38)	−890(41)	1990(19)
O(2)	5037(24)	−1887(26)	2127(12)
C(3)	6026(39)	2926(39)	2402(20)
O(3)	6618(25)	3339(24)	2354(12)

TABLE 3 (continued)

Atom	x/a	y/b	z/c
C(4)	3987(38)	3651(39)	2526(18)
O(4)	3153(26)	4647(26)	2588(12)
C(5)	1831(35)	3148(36)	2011(18)
O(5)	1432(22)	4003(23)	1824(10)
C(6)	969(38)	1820(35)	2470(18)
O(6)	−57(29)	2007(27)	2458(13)
C(7)	4766(43)	702(42)	3773(26)
O(7)	4716(25)	441(24)	4302(13)
C(8)	5953(41)	−231(42)	3206(21)
O(8)	6651(24)	−1159(24)	3167(11)
C(9)	2732(36)	943(36)	1768(18)
O(9)	2184(26)	839(26)	1423(12)
C(10)	5328(34)	1840(34)	3178(17)
O(10)	5732(25)	2188(25)	3496(12)

total of 66 electrons, this cluster can be formally described as a mixed-valence complex with 2 Ru(I) and 2Ru(II) and 6 metal–metal bonding electrons, giving an average formal bond order of 0.5 between the metals, in agreement with their rather large separation.

Since we did not find this unusual complex in reaction 2, it is conceivable that its successful isolation in reaction 1 results in part from kinetic factors related to a cation effect. Further work is in progress to investigate the role of $[Ru_4(\mu\text{-}Cl)_4(\mu\text{-}CO)_2(CO)_8]^{2-}$ as a possible intermediate in the redox reactions described.

Experimental

All manipulations were performed in Schlenk-type flasks under nitrogen. Solvents were distilled under nitrogen and dried before to use. Nitrogen (Air Liquide purified grade) was passed through BASF R3-11 catalyst and molecular sieve columns to remove residual oxygen and water.

Infrared spectra were recorded in the region 4000–400 cm^{-1} on a Perkin–Elmer 398 spectrophotometer as KBr pellets. The UV spectra were recorded on a Beckman Acta 111 spectrophotometer (CH_2Cl_2 solutions).

Reaction of [PPN][Co(CO)$_4$] with RuCl$_3$ · xH$_2$O

To a stirred solution of $RuCl_3 \cdot xH_2O$ (0.270 g, ~ 1.0 mmol) in THF (40 ml) was added a solution of [PPN][$Co(CO)_4$] (2.800 g, 3.9 mmol) in THF. The green solution was stirred for 24 h at room temperature and then warmed to 60°C. A gradual change in colour occurred and the reaction was stopped after 5–6 h when the solution had turned orange-yellow. The solution was filtered and evaporated under reduced pressure. Extraction of the solid residue with hexane gave $Ru_3(CO)_{12}$. Toluene extraction yielded [PPN][$RuCo_3(CO)_{12}$] and [PPN][$Ru_3Co(CO)_{13}$], which were separated by fractional crystallization from diethylether/hexane. The solid left after the toluene extraction contained some [PPN][$Co(CO)_4$] and [PPN][$Ru_4(\mu\text{-}Cl)_4(\mu\text{-}CO)_2(CO)_8$], which was purified by successive recrystallizations from CH_2Cl_2/hexane, in which it is less soluble. The yellow air-stable product was obtained in 5–10% yield in three experiments. (m.p. 224–226°C) IR ν(CO): 2041w, 2008vs, 1998sh, 1954m, 1934vs, 1929sh, 1713s, 1706s cm^{-1}. Visible spectrum: λ_{max}: 419, 560sh nm. Anal. Found: C, 50.9; H, 2.8; N, 2.00. $C_{82}H_{60}Cl_4N_2O_{10}P_4Ru_4$ (M = 1903.3) calcd.: C, 51.70; H, 3.15; N, 1.50%.

Preparation of [PPN][RuCo$_3$(CO)$_{12}$]

A solution of [PPN]Cl (0.178 g, 0.31 mmol) in hot water (20 ml) was added to a well stirred solution of Na[$RuCo_3(CO)_{12}$] (0.200 g, 0.31 mmol) in water (30 ml) at 60°C. An orange powder separated. After 2 h stirring the product was extracted into toluene (50 ml) and the toluene extract was then evaporated in vacuo. Crystallization of the solid residue in diethylether/hexane gave [PPN][$RuCo_3(CO)_{12}$] as dark red crystals: yield 0.280 g, 81.1% (m.p. 210–215°C) IR ν(CO) 2061w, 1995vs, 1962s, 1840w, 1815sh, 1811s, 1800s cm^{-1}. Visible spectrum: λ_{max}: 392, 450sh nm. Anal. Found: C, 50.09; H, 2.61; N, 1.21. $C_{48}H_{30}NO_{12}PRuCo_3$ (M = 1152) calcd.: C, 50.04; H, 2.60; N, 1.21%.

X-ray structural determination for [PPN]$_2$[Ru$_4$(μ-Cl)$_4$(μ-CO)$_2$(CO)$_8$] *

Single crystals of the complex were grown from CH_2Cl_2/hexane at −15°C. Triclinic space group $P\bar{1}$, a 12.787(4), b 13.257(4), c 25.553(5) Å, α 85.92(2), β 87.62(2), γ 65.20(2)°, U 3918 Å^3, $Z = 2$, D_c 1.35 g cm^{-3}, $F(000) = 1900$, α(Mo-K_α) 74 cm^{-1}. Current R 0.078 (R_w 0.062) for 2235 unique reflections [$F_0 > 2\sigma(F_0)$] measured on a Nonius CAD4 diffractometer ($6 < 2\theta < 60°$). The structure was solved by Patterson and Fourier methods and refined by full matrix least-squares with non H atoms anisotropic (phenyl C isotropic), H atoms were not located nor introduced in the calculation of the structure factors. The phenyl groups of [PPN]$^+$ were refined as rigid groups and were treated alternately with the anionic moiety of the molecule.

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