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Mixed Ruthenium−Rhodium Carbonyl Cluster Complexes. Synthesis of the Anions $[Ru_3Rh(CO)_{13}]^-$ and $[RuRh_3(CO)_{12}]^-$ and Crystal Structures of Their $[N(PPh_3)_2]^+$ Salts[1]

Alessandro Fumagalli,*[,2a] Mascia Bianchi,[2b] Maria Carlotta Malatesta,[2b] Gianfranco Ciani,[2c] Massimo Moret,[2c] and Angelo Sironi*[,2c]

CNR, Centro di Studio sulla Sintesi e la Struttura dei Composti dei Metalli di Transizione nei Bassi
Stati di Ossidazione, Dipartimento di Chimica Inorganica Metallorganica e Analitica, and
Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università di Milano,
Via G. Venezian 21, 20133 Milano, Italy

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The new anion $[Ru_3Rh(CO)_{13}]^-$ (**1**) has been obtained by reaction of $[Rh(CO)_4]^-$ ($[N(PPh_3)_2]^+$ or $[PPh_4]^+$ salt) with $Ru_3(CO)_{12}$; $[RuRh_3(CO)_{12}]^-$ (**2**) has been derived by oxidative degradation of $[RuRh_4(CO)_{12}]^{2-}$. Their salts, $[N(PPh_3)_2][Ru_3Rh(CO)_{13}]$ (**I**) and $[N(PPh_3)_2][RuRh_3(CO)_{12}]$ (**II**), were characterized by single-crystal X-ray diffraction. Data for **I**: space group $P\bar{1}$, $a = 9.827(2)$ Å, $b = 14.911(2)$ Å, $c = 18.735(3)$ Å, $\alpha = 110.53(1)°$, $\beta = 99.79(2)°$, $\gamma = 91.85(2)°$, R1 = 0.0342, wR2 = 0.0926 for 7257 independent reflections with $I > 3\sigma(I)$. Data for **II**: space group $P2_1/c$, $a = 14.746(3)$ Å, $b = 21.395(4)$ Å, $c = 16.140(4)$ Å, $\beta = 102.95(2)°$, R1 = 0.0582, wR2 = 0.1383 for 4381 independent reflections with $I > 3\sigma(I)$. Both anions have a tetrahedral metal frame; **1** has an idealized C_3 symmetry, with the Rh atom and its unique terminal carbonyl on the 3-fold axis; nine more carbonyls are terminally bonded to the three Ru atoms, while three bridge the Ru−Rh edges. In **2**, which has an idealized C_s symmetry, three carbonyls are terminally bound on the Ru atom, and one, one, and two CO, respectively, on Rh1, Rh2, and Rh3; five more CO bridge all edges but the Ru−Rh3 edge. It is worthy of note that subtle details of the CO ligands stereochemistry allowed the correct labeling of metal centers, otherwise indistinguishable on the basis of good quality X-ray diffraction data only. Compound **1** reacts with PPh_3, yielding the rhodium-substituted $[Ru_3Rh(CO)_{12}(PPh_3)]^-$ (**1a**) (^{31}P NMR; 56.9 ppm (d), $J_{P-Rh} = 188$ Hz). ^{13}C NMR spectrum of **1** is a doublet (207 ppm, $J_{C-Rh} = 17.5$ Hz) consistently with a fluxional behavior with complete CO scrambling, from 295 down to 170 K.

Introduction

Several Ru−Rh carbonyl cluster compounds have been reported in literature, mostly neutral species which also contain hydrido, phosphino, or Cp ligands. Our interest in the study of equilibria between Ru, Rh, and Ru−Rh carbonyl clusters led us to focus particularly on anionic species, where very few homoleptic species have been so far characterized, namely, $[RuRh_4(CO)_{15}]^{2-}$,[3] $[RuRh_5(CO)_{16}]^-$,[4] and the recently reported $[Ru_2Rh_2(CO)_{12}]^{2-}$.[5] We now report two new tetranuclear anions which are the first homoleptic species among the numerous four-metal clusters with an Ru−Rh internal ratio of 3:1[6] or 1:3.[7]

Results and Discussion

(1) Synthesis of the Anions $[Ru_3Rh(CO)_{13}]^-$ and $[RuRh_3(CO)_{12}]^-$. It has been previously reported[5] that the reaction of $Ru_3(CO)_{12}$ with $[Rh(CO)_4]^-$ as the $[PPh_4]^+$ or $[N(PPh_3)_2]^+$ (hereafter PPN) salt yields, as the first detectable mixed-metal species, the dianion $[Ru_2Rh_2(CO)_{12}]^{2-}$ (**3**). The formation of **3** occurs at room temperature within minutes, both under nitrogen and CO, without IR evidence of precursors and independently from the initial relative amounts of the two reactants which, at this early stage of the reaction, are mostly unreacted. Of course, **3** can be obtained with the best yields when the two metals are in the correct 1:1 ratio, according to eq 1:

$$^{2}/_{3}Ru_3(CO)_{12} + 2[Rh(CO)_4]^- \rightarrow [Ru_2Rh_2(CO)_{12}]^{2-} + 4CO \tag{1}$$

If some more $Ru_3(CO)_{12}$ is added, thus exceeding the 1:1 Ru−Rh atomic ratio, the initially formed $[Ru_2Rh_2(CO)_{12}]^{2-}$ further reacts, through stages with several unidentified intermediates and with equilibration times of a few hours, to give $[Ru_3Rh(CO)_{13}]^-$ (**1**) together with minor amounts of uncharacterized byproducts:

$$[Ru_2Rh_2(CO)_{12}]^{2-} + {}^{4}/_{3}Ru_3(CO)_{12} \rightarrow 2[Ru_3Rh(CO)_{13}]^- \ (\mathbf{1}) + 2CO \tag{2}$$

It is worth noting that the straightforward stoichiometry in eq 3 (sum of eqs 1 and 2), which is in fact used to synthesize the

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(1) $[N(PPh_3)_2][Ru_3Rh(CO)_{13}]$: ($\mu$-nitrido)bis(triphenylphosphorus) 1,4;2,4;3,4-tris(μ-carbonyl)-1,1,1,2,2,2,3,3,3,4-decacarbonyl-*tetrahedro*-1,2,3-triruthenium 4-rhodiate. $[N(PPh_3)_2][RuRh_3(CO)_{12}]$: ($\mu$-nitrido)-bis(triphenylphosphorus) 1,2;1,3;2,3;2,4;3,4-pentakis(μ-carbonyl)-1,1,1,2,3,4,4-heptacarbonyl-*tetrahedro*-1-ruthenium 2,3,4-trirhodiate.

(2) (a) CNR. (b) Dipartimento di Chimica Inorganica, Metallorganica e Analitica dell'Università di Milano. (c) Dipartimento di Chimica Strutturale e Stereochimica Inorganica dell'Università di Milano.

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anion **1**, would erroneously suggest a clean and rapid reaction of redox condensation:[8]

$$\mathrm{Ru_3(CO)_{12} + [Rh(CO)_4]^- \rightarrow [Ru_3Rh(CO)_{13}]^-\ (\mathbf{1}) + 4CO} \quad (3)$$

This in fact is *not* the case, according to the evidence of a multistep path implying the intermediate $[Ru_2Rh_2(CO)_{12}]^{2-}$.

Reaction 3 cannot be performed under CO (1 atm) because anion (**1**) is readily decomposed with a complex disproportionation to several products, among which $[RuRh_4(CO)_{15}]^{2-}$[3] and $Ru_3(CO)_{12}$ have been identified. Thus, we could not prepare a ^{13}CO-enriched sample of $[PPN][Ru_3Rh(CO)_{13}]$ (see NMR discussion in Section 5 below) by conventional CO exchange in solution; a synthesis was carried out reacting $[PPN][Rh(CO)_4]$ with previously enriched $Ru_3(CO)_{12}$ (^{13}CO *ca*. 15%).

The anion $[Ru_3Rh(CO)_{13}]^-$ is not very stable in solution even under nitrogen, and within a few days, some decomposition may be always observed with slow separation of $Ru_3(CO)_{12}$; apparently the ruthenium carbonyl is involved with **1** in an equilibrium which may be more or less shifted toward its formation also depending on the solvent. However, we could not rationalize this decomposition which significantly varies in extent from case to case.

The reactivity of anion **1** was also tested against various phosphorus ligands. The chelating diphosphines dppm and dppe gave IR evidence of formation of several products, very likely isomers deriving from the substitution of two CO on different metal centers. The reaction with PPh_3 yielded only one substitution product (**1a**) as reported in eq 4:

$$\mathrm{[Ru_3Rh(CO)_{13}]^- + PPh_3 \rightarrow [Ru_3Rh(CO)_{12}(PPh_3)]^-\ (\mathbf{1a}) + CO} \quad (4)$$

The shift of the IR bands of **1a** (with respect to **1**) in the CO-stretching region (see below) is, on average, 15−20 cm^{-1} toward low wavenumbers and consistent with the expected increase of back-donation on a reduced number of carbonyls. Unambiguous evidence of a selective substitution on the rhodium atom was obtained by ^{31}P NMR which gave a doublet ($J_{P-Rh} = 188$ Hz) at 56.9 ppm. We could not crystallize this derivative for structural determination.

The anion $[RuRh_3(CO)_{12}]^-$ (**2**), whose possible existence was inferred on the basis of the related known d^8-d^9 mixed species $[OsRh_3(CO)_{12}]^-$,[9] $[FeIr_3(CO)_{12}]^-$,[10] and $[RuIr_3(CO)_{12}]^-$,[11] was obtained by oxidative degradation of the pentanuclear species $[RuRh_4(CO)_{15}]^{2-}$. This procedure, similar to that previously reported for the Os−Rh analogue, uses solutions of I_2 or Cl_2 (respectively, in THF and CH_2Cl_2) to cause selective cleavage of one Rh atom:

$$\mathrm{[RuRh_4(CO)_{15}]^{2-} + X_2 \rightarrow [RuRh_3(CO)_{12}]^- + [Rh(CO)_2X_2]^- + CO\ (X = Cl, I)} \quad (5)$$

The fast reacting Cl_2 seems to give slightly better yields, but the difficulty to have it in solution with a stable titer makes more convenient the use of I_2, which also may be used in a slight excess over the stoichiometric amount. In any case, the reaction, conducted according to eq 5 under nitrogen or CO (1 atm), always gives as a byproduct some $[RuRh_5(CO)_{16}]^-$, very likely because of a side reaction (eq 6), where the just-formed Rh^I derivative gives condensation with some unreacted $[RuRh_4(CO)_{15}]^{2-}$. This hypothesis is supported by the fact that

$$\mathrm{[RuRh_4(CO)_{15}]^{2-} + [Rh(CO)_2X_2]^- \rightleftarrows [RuRh_5(CO)_{16}]^- + 2X^- + CO} \quad (6)$$

addition of excess X^- combined with a CO atmosphere, as reported in the Experimental Section, greatly depresses the formation of $[RuRh_5(CO)_{16}]^-$.

Anion **2** was also obtained from the reaction of $[RuRh_4(CO)_{15}]^{2-}$ with acids which, instead of the expected corresponding hydride(s), induce disproportionation, with metal scrambling:

$$\mathrm{2[RuRh_4(CO)_{15}]^{2-} + 2H^+ \rightarrow [RuRh_3(CO)_{12}]^- + [RuRh_5(CO)_{16}]^- + H_2 + 2CO} \quad (7)$$

This reaction, which is of little synthetic interest, is, however, remarkable because it shows the similarity of the Ru−Rh and Os−Rh systems, as it occurs analogously for $[OsRh_4(CO)_{15}]^{2-}$.[9,12]

It must be also said that the reaction of $Ru_3(CO)_{12}$ and $[Rh(CO)_4]^-$ which has been studied, taking the two reagents in any combination both under nitrogen and CO, never did show any evidence of $[RuRh_3(CO)_{12}]^-$. We also tried what would appear as a feasible redox condensation according to the stoichiometry:

$$\mathrm{{}^1/_2[Ru(CO)_3Cl_2]_2 + 3[Rh(CO)_4]^- \relbar\!\!\times\!\!\rightarrow [RuRh_3(CO)_{12}]^- + 2Cl^- + 3CO} \quad (8)$$

However, this reaction, conducted in THF or MeCN, did *not* work as intended, even in the presence of $AgBF_4$ as chloride acceptor; it yielded instead other products, among which $[RuRh_4(CO)_{15}]^{2-}$ and $[RuRh_5(CO)_{16}]^-$ were identified.

$[RuRh_3(CO)_{12}]^-$ has a limited stability and, in solution under nitrogen, slowly decomposes to give some $[RuRh_5(CO)_{16}]^-$ and other unidentified products. Thus repeated crystallizations by the slow diffusion technique may be not effective in obtaining a very pure product.

(2) Crystal Structure of $[N(PPh_3)_2][Ru_3Rh(CO)_{13}]$. The $[PPN][Ru_3Rh(CO)_{13}]$ salt is isomorphous to the PPN salts of its Fe/Co[13] and Ru/Co[14] homologues and the three cluster anions are strictly isostructural (see Figure 1 for an ORTEP plot of the $[Ru_3Rh(CO)_{13}]^-$ anion). These tetrahedral cluster anions share the presence of a basal metal triangle of d^8 metals capped by an apical d^9 metal (for the title compound: average Ru−Rh and Ru−Ru distances 2.743 and 2.876 Å, respectively). The basal metals bear three terminal carbonyl ligands each, while the apex bears only one terminal CO ligand (for the title compound: Rh−CO is 1.884(6) Å, average Ru−CO is 1.906(14) Å). Three asymmetric μ_2-CO ligands bridge the three basal−apical edges in a propeller-like fashion (for the title compound: average $Rh-C_{bridging}$ and $Ru-C_{bridging}$ distances are 2.026 and 2.159 Å, respectively). Due to this propeller shape, the overall idealized symmetry of the cluster anion (which could

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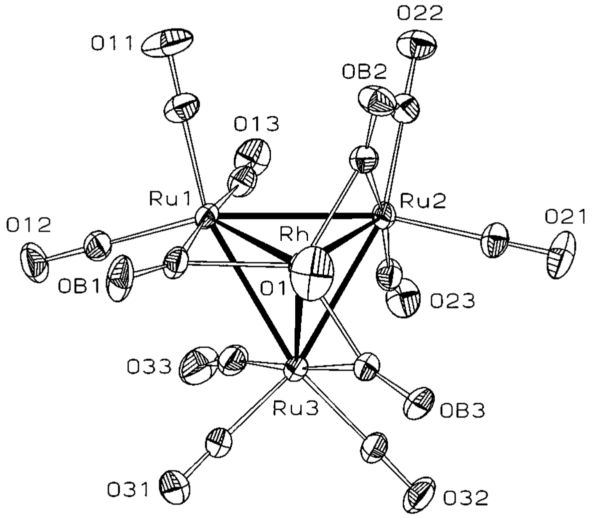

Figure 1. View of the $[Ru_3Rh(CO)_{13}]^-$ anion. The C atoms of the carbonyl groups bear the same numbering as the respective connected O atoms in the crystal structure. The anion has C_3 symmetry with the idealized C_3 axis passing through the Rh atom and the center of the Ru_3 triangle.

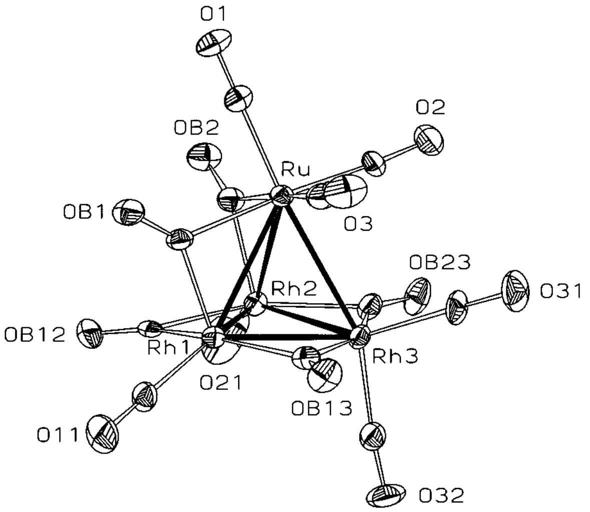

Figure 2. View of the $[RuRh_3(CO)_{12}]^-$ anion. The C atoms of the carbonyl groups bear the same numbering as the respective connected O atoms in the crystal structure. The anion has C_s symmetry; the idealized mirror plane contains the Ru, C1, O1, Rh3, C31, O31, C32, O32, CB12, and OB12 atoms.

have been C_{3v}) is C_3. This is one of the few examples in which clusters from the first- and second-row transition metals are strictly isostructural both with respect to the metal framework and the disposition of the CO ligands about the cluster.

Although the positioning of metals differing by one atomic number is often difficult with single-crystal X-ray techniques, in this work the assignment of the Rh location appears to be substantiated by that of Co in $[Ru_3Co(CO)_{13}]^-$. However, a difference of one electron between two sites may be enough to induce significant perturbations of the overall cluster geometry, which eventually could allow discrimination between two metal atoms on stereochemical grounds. In particular, the comparison of both the local electron bookkeeping and the local stereogeometry of the pertinent atoms can lead to the correct labelling of metal centers, not distinguishable on the basis of even good quality X-ray diffraction data only. For instance, when dealing with two different metals with similar local stereogeometry, the presence of a semibridging carbonyl ligand is particularly informative since the electron-poorer metal, in order to fulfil its ideal EAN and/or to better spread its formal local charge, is expected to have the shortest interaction.[5]

In the present case, we suggest that details of the ligand stereochemistry offer independent evidence for the location of the rhodium atom in the apical position. Indeed, even the overall ligand stereochemistry makes a clear-cut distinction between apical and basal metals (their 1:3 ratio clearly suggests a basal location for the three Ru atoms and an apical location for the Rh atom), but what matters here is to observe that, under the assumption that the μ_2-CO ligands are symmetric, the local electron bookkeeping assigns 10 valence electrons (plus their own) to the basal metal but only 8 (plus its own) to the apical metal. The only way to equidistribute the local valence electrons is to assign the d^8 metals to the basal positions and the d^9 metal (and the charge) to the apical position. The resulting stereochemistry (with symmetric μ_2-COs) fulfills one of the principles at the heart of CO ligand stereochemistry, that is the equalization of the local electron bookkeeping but not equalization of charge.[15] Accordingly, in order to redistribute the "free" charge accumulated in the apical position, we "foresee" the *observed* bending of the μ_2-CO toward the apical d^9 atom. Note that the equalization of the local electron bookkeeping is maintained because the loss (gain) of "free" electrons is compensated by the gain (loss) of "bonding" electrons. With the above arguments we have argued that the observed ligand stereochemistry is coherent with the *proposed* apical location of the d^9 atom, but we cannot yet infer that the observed stereochemistry uniquely suggests that location. Indeed, also a d^9 metal disordered about the three basal positions could afford a similar *averaged disordered* ligand stereogeometry. In such a hypothesis the apical d^8 atom would have two terminal and two bridging COs, which, due to the disorder of the d^9 atom on the three basal sites, would be rotationally disordered over three positions; accordingly, each of the three μ_2CO would have one-third terminal character, and it would appear distorted almost in the observed way. However, the lack of such disorder prompts for the proposed apical location of the d^9 atom.

(3) Crystal Structure of $[N(PPh_3)_2][RuRh_3(CO)_{12}]$. The $[PPN][RuRh_3(CO)_{12}]$ salt is isomorphous to its osmium analogues $[PPN][OsRh_3(CO)_{12}]$, which we have previously characterized.[9] The two cluster anions are isostructural, and most of the considerations, if not all, we have previously made on the Os derivative still hold for the Ru one (see Figure 2 for an ORTEP plot of the $[RuRh_3(CO)_{12}]^-$ anion). **2** has an unusual ligand stereochemistry since the twelve carbonyl groups surrounding the tetrahedral metal skeleton are, in terms of occupied volumes but not of valence electrons, unevenly distributed. In more detail there are five μ_2 carbonyl ligands, bridging all the M−M edges but Ru−Rh3, three out of the seven terminal COs are bound to the Ru atom which thus is connected to five CO ligands while all the Rh atoms are connected to four carbonyls. The overall carbonyl stereochemistry has an idealized C_s symmetry and can be obtained from that of $[Rh_4(CO)_{12}]$ by bending two (formerly) terminal COs toward the apical metal atom and slightly rearranging all the other COs but maintaining their original connectivity.

In the original work on $[OsRh_3(CO)_{12}]^-$ the different scattering factors of Rh and Os allowed the unambiguous labeling of the more crowded vertex of the tetrahedron as Os. In the present case, rhodium and ruthenium can hardly be differentiated on the basis of their X-ray scattering power, and we rely on the isomorphism between the ruthenium and the osmium derivatives. However, we can parallel the discussion made for

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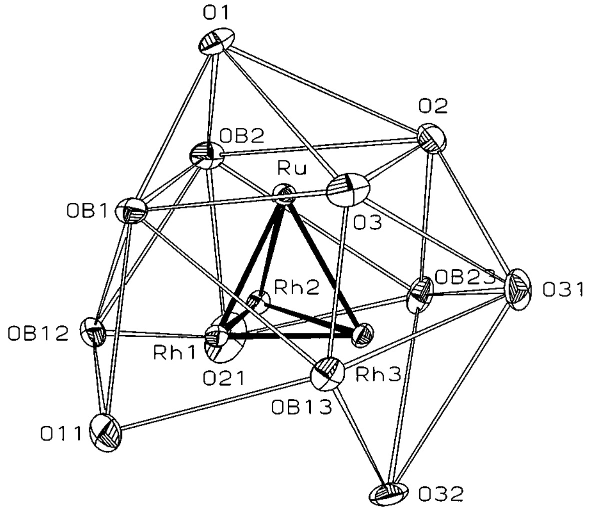

Figure 3. Ligand envelope of $[RuRh_3(CO)_{12}]^-$ obtained by joining the oxygen atoms closer than 5 Å. It does not resemble the icosahedron of the parent $[Rh_{12}(CO)_{12}]$ and clearly shows that the CO ligands, grouping around the apical Ru atom (which carries five COs), leave a hole below the basal face.

$[Ru_3Rh(CO)_{13}]^-$ in order to show that again the comparison of both the local electron bookkeeping and the local stereogeometry of the pertinent atoms can lead to the correct labeling of metal centers. The (formal) substitution of a d^9 atom by an isoelectronic $(d^8)^-$ anion must be (formally) followed by a slight, but visible, reorganization of the ligand envelope in order to delocalize the charge which, otherwise, would be accumulated on the d^8 atom. Such reorganization primarily involves terminal ↔ semibridging ↔ bridging interconversions of some CO ligand but a "second-order" reorganization of the terminal COs is also expected. Starting from the $[Rh_4(CO)_{12}]$ stereochemistry the substitution may occur either at a basal or at the apical position. In the former hypothesis, we expect the μ2-COs strengthen their interactions with the d^8 atom (at the expenses of those with the d^9 atoms),[5] this has been experimentally confirmed by the structures of the $[FeIr_3(CO)_{12}]^-$ [10] and $[RuIr_3(CO)_{12}]^-$.[11] In the latter hypothesis, the apical d^8 atom, which originally would lack bridging COs, is expected to "attract" some COs of the basal moiety establishing semibridging interaction with them; this actually occurs to the title compound and to $[OsRh_3(CO)_{12}]^-$. We have previously offered an explanation for the different stereochemistry of $[RuIr_3(CO)_{12}]^-$ and $[OsRh_3(CO)_{12}]^-$ which holds also for $[RuRh_3(CO)_{12}]^-$;[9] however, what is relevant here is the fact that in both the situations the details of the ligand stereochemistry allow one to reorganize the d^8 atom.

Noteworthy is the optimization of interligand interactions, which is often considered the major factor responsible for the ligand stereochemistry,[16] has little effect here. In fact, the polyhedron defined by the oxygen atoms (see Figure 3) no longer resembles the icosahedron of the parent $[Rh_4(CO)_{12}]$ and clearly shows that the CO ligands are grouped around the apical Ru atom (which carries five COs), leaving empty volumes below the basal face. A similar situation also occurs for $[NiRu_3(CO)_{12}]^{2-}$.[17]

(4) IR Spectra. CO stretchings of anions **1**, **2**, and **1a**, all as PPN$^+$ salts in THF (±2 cm^{-1}), are as follows for **1**, 2065 w, 2016 s, 1992 ms, 1975 ms, 1833 sh, 1819 m cm^{-1}; for **2**, 2071 mw, 2024 s, 2015 ms, 2006 s, 1987 ms, 1949 w, 1848 m, 1836 ms, 1814 mw cm^{-1}; for **1a**, 2046 ms, 2000 s, 1958 ms, 1800 m cm^{-1}.

(5) NMR Spectra. (a) ^{13}C NMR of $[Ru_3Rh(CO)_{13}]^-$. The spectra were obtained in d_8-THF with a sample of $[PPN][Ru_3Rh(CO)_{12}]$ enriched in ^{13}CO at about 10%, prepared from $[PPN][Rh(CO)_4]$ and previously enriched $Ru_3(CO)_{12}$ (^{13}CO *ca.* 15%), according to the Experimental Section. At 295 K, in the carbonyl range, there is only a doublet at 206.8 ppm with $J_{C-Rh} = 17.5$ Hz due to coupling with the Rh atom; this is consistent with complete fluxionality of all 13 carbonyls over the entire cluster. Lowering the temperature to 183 K causes broadening of the doublet with apparent reduction of the J_{C-Rh} to *ca.* 12.5 Hz. At 170 K, very close to freezing point of the solution, only a broad ill-defined peak could be observed without evidence of a solid-like "frozen" structure.

(b) ^{31}P NMR of $[Ru_3Rh(CO)_{12}(PPh)_3]^-$. The spectrum was recorded on the $[PPN]^+$ salt at room temperature in d_6-acetone and gave two resonances at 22.0 ppm (s, $[PPN]^+$) and 56.9 ppm (d, $J_{P-Rh} = 188$ Hz, PPh_3). The latter is consistent with a direct P−Rh bond.[18]

Experimental Section

All operations were carried out under N_2 or CO as specified. Tetrahydrofuran was distilled from sodium benzophenone and propan-2-ol from aluminum isopropoxide. All other analytical-grade solvents were degassed and stored under N_2. $[PPN][Rh(CO)_4]$ and $[PPh_4][Rh(CO)_4]$ were prepared by the published method,[19] and $Ru_3(CO)_{12}$ was obtained commercially. Infrared spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer, using 0.1 mm CaF_2 cells previously purged with nitrogen. ^{13}C and ^{31}P NMR spectra were recorded at 50.3 and 81.0 MHz, respectively, on a Varian instrument.

(1) Synthesis of $[PPN][Ru_3Rh(CO)_{13}]$ (I). $(PPN)[Rh(CO)_4]$ (506.4 mg, 0.67 mmol) and $Ru_3(CO)_{12}$ (430.0 mg, 0.67 mmol) were placed in a Schlenk tube under N_2 atmosphere, and THF (20 mL) was added. After 24 h stirring at room temperature, the red-brown solution was treated with 2-propanol (40 mL) and briefly concentrated in vacuum to induce separation of a small amount of tacky precipitate; the solution was filtered, and the precipitate was discarded. The clear solution was cautiously layered with *n*-hexane (140 mL). When the diffusion was completed (*ca.* 2 weeks), after removal of the decanted mother liquor, the red crystals were washed thoroughly with *n*-hexane and vacuum-dried, yielding 592 mg (67%). The crystals were suitable for X-ray structural determination. Anal. Found: C, 44.49; H, 2.03; N, 1.21. Calcd for $C_{49}H_{30}NO_{13}P_2RhRu_3$: C, 44.97; H, 2.31; N, 1.07. A similar procedure, using $(PPh_4)[Rh(CO)_4]$, applies to the production of the $(PPh_4)^+$ salt which is obtained with comparable yields.

(2a) Synthesis of $[PPN][RuRh_3(CO)_{12}]$ (II). $[PPN]_2[RuRh_4(CO)_{15}]$ (350 mg, 0.174 mmol) was placed in a Schlenk tube under CO atmosphere, and THF (10 mL) was added. A solution of I_2 in THF (0.086 M, 2 mL) was added with ready change of color to red-brown; after 2 h of stirring the solution was treated with 2-propanol (15 mL) and *n*-hexane (15 mL) and, after 10 min of stirring, the precipitated $[PPN][Rh(CO)_2I_2]$ was filtered off and, prior to being discarded, washed with 2-propanol (1 + 1 mL). The clear solution was concentrated in vacuum to *ca* 20 mL; this caused precipitation of some $[PPN][RuRh_5(CO)_{15}]$, which was filtered off to yield the clear orange solution which was cautiously layered with *n*-hexane (60 mL). When the diffusion was completed (*ca.* 1 week), after removal of the decanted mother liquor, the orange crystals were washed thoroughly with *n*-hexane and vacuum-dried; estimated yield *ca.* 40%. Anal. Found: C, 44.55; H, 2.05; N, 1.07. Calcd for $C_{48}H_{30}NO_{12}P_2Rh_3Ru$: C, 44.88; H, 2.35; N, 1.09. It must be said that almost inevitably a few black crystals of

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Table 1. Summary of Crystal Data and Structure Refinement Parameters for **1** and **2**

empirical formula	$C_{49}H_{30}NO_{13}P_2RhRu_3$	$C_{48}H_{30}NO_{12}P_2Rh_3Ru$
fw	1308.80	1284.47
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
a, Å	9.827(2)	14.746(3)
b, Å	14.911(2)	21.395(4)
c, Å	18.735(3)	16.140(4)
α, deg	110.53(1)	
β, deg	99.79(2)	102.95(2)
γ, deg	91.85(2)	
V, Å^3	2520.9(7)	4962(2)
Z	2	4
abs coeff, mm^{-1}	1.329	1.403
R1, wR2 indices[a]	0.0342, 0.0926	0.0582, 0.1383

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

Table 2. Bond Lengths (Å) and Angles (deg) for **1**

Rh−Ru(1)	2.7385(7)	Ru(1)−C(12)	1.910(6)
Rh−Ru(2)	2.7324(6)	Ru(1)−C(13)	1.911(6)
Rh−Ru(3)	2.7592(10)	Ru(1)−C(B1)	2.155(5)
Ru(1)−Ru(2)	2.8633(6)	Ru(2)−C(21)	1.896(6)
Ru(1)−Ru(3)	2.8846(8)	Ru(2)−C(22)	1.892(6)
Ru(2)−Ru(3)	2.8809(8)	Ru(2)−C(23)	1.937(6)
Rh−C(1)	1.884(6)	Ru(2)−C(B2)	2.173(5)
Rh−C(B1)	2.028(5)	Ru(3)−C(31)	1.905(7)
Rh−C(B2)	2.037(5)	Ru(3)−C(32)	1.910(6)
Rh−C(B3)	2.014(5)	Ru(3)−C(33)	1.911(7)
Ru(1)−C(11)	1.886(6)	Ru(3)−C(B3)	2.148(6)

O(1)−C(1)−Rh	177.8(6)	O(32)−C(32)−Ru(3)	178.7(5)
O(11)−C(11)−Ru(1)	179.7(7)	O(33)−C(33)−Ru(3)	171.3(6)
O(12)−C(12)−Ru(1)	175.8(7)	O(B1)−C(B1)−Rh	137.1(5)
O(13)−C(13)−Ru(1)	170.9(5)	O(B1)−C(B1)−Ru(1)	141.2(5)
O(21)−C(21)−Ru(2)	179.2(5)	O(B2)−C(B2)−Rh	137.8(4)
O(22)−C(22)−Ru(2)	178.1(5)	O(B2)−C(B2)−Ru(2)	141.2(4)
O(23)−C(23)−Ru(2)	166.7(5)	O(B3)−C(B3)−Rh	136.3(5)
O(31)−C(31)−Ru(3)	178.7(6)	O(B3)−C(B3)−Ru(3)	140.7(5)

Table 3. Bond Lengths (Å) and Angles (deg) for **2**

Ru−Rh(1)	2.879(2)	Rh(1)−C(B1)	1.942(13)
Ru−Rh(2)	2.903(2)	Rh(1)−C(B12)	2.06(2)
Ru−Rh(3)	2.934(2)	Rh(1)−C(B13)	2.06(2)
Rh(1)−Rh(2)	2.725(2)	Rh(2)−C(21)	1.88(2)
Rh(1)−Rh(3)	2.712(2)	Rh(2)−C(B2)	1.944(14)
Rh(2)−Rh(3)	2.697(2)	Rh(2)−C(B12)	2.12(2)
Ru−C(1)	1.93(2)	Rh(2)−C(B23)	2.06(2)
Ru−C(2)	1.91(2)	Rh(3)−C(31)	1.90(2)
Ru−C(3)	1.95(2)	Rh(3)−C(32)	1.86(2)
Ru−C(B1)	2.20(2)	Rh(3)−C(B13)	2.133(14)
Ru−C(B2)	2.214(14)	Rh(3)−C(B23)	2.15(2)
Rh(1)−C(11)	1.89(2)		

O(1)−C(1)−Ru	178.7(13)	O(B2)−C(B2)−Rh(2)	136.2(12)
O(2)−C(2)−Ru	173.6(14)	O(B2)−C(B2)−Ru	135.5(11)
O(3)−C(3)−Ru	175(2)	O(B12)−C(B12)−Rh(1)	141.0(13)
O(11)−C(11)−Rh(1)	177(2)	O(B12)−C(B12)−Rh(2)	137.6(13)
O(21)−C(21)−Rh(2)	177(2)	O(B13)−C(B13)−Rh(1)	143.0(12)
O(31)−C(31)−Rh(3)	174(2)	O(B13)−C(B13)−Rh(3)	136.5(12)
O(32)−C(32)−Rh(3)	174.8(14)	O(B23)−C(B23)−Rh(2)	143.2(12)
O(B1)−C(B1)−Rh(1)	137.7(11)	O(B23)−C(B23)−Rh(3)	137.1(12)
O(B1)−C(B1)−Ru	134.4(10)		

[PPN][$RuRh_5(CO)_{15}$] may be found mixed with the orange crystals of the product; this is due to some decomposition occurring during the crystallization, particularly if performed by the slow diffusion technique. A manual selection of the crystalline product allowed small pure samples to be obtained. The crystals were suitable for X-ray structural determination. A similar procedure, using $(PPh_4)_2[RuRh_4(CO)_{15}]$, applies to the production of the $(PPh_4)^+$ salt.

(2b) Synthesis of $(PPh_4)[RuRh_3(CO)_{12}]$ with I_2/LiI Mixture. This method avoids formation of the byproduct $(PPh_4)[RuRh_5(CO)_{16}]$ during the oxidative degradation, but it is somewhat more complicated and the reaction is slower.

$(PPh_4)_2[RuRh_4(CO)_{15}]$ (111 mg, 0.069 mmol) was dissolved in 5 mL of THF in a Schlenk tube under CO atmosphere and treated with 0.75 mL of a THF solution containing I_2 and LiI (respectively 0.01 and 0.04 M); after 18 h of stirring, the solution, checked by IR, showed some residual starting material and was treated with a slight excess of I_2/LiI solution (0.2 mL). After 1 h the reaction appeared complete with no IR evidence of $[RuRh_5(CO)_{16}]^-$, and the solution was treated with (PPh_4)Br in 2-propanol (333 mg in 18 mL) which caused partial precipitation of $[PPh_4][Rh(CO)_2I_2]$ removed by filtration. The clear solution was concentrated in vacuum *ca*. 15 mL; this caused further precipitation of $[PPh_4][Rh(CO)_2I_2]$ which was filtered off to yield a clear orange solution containing the product. The recovery was done by addition of *n*-hexane (15 mL); the decanted precipitate, after removal of the mother liquor with a syringe, was vacuum-dried. This crude product may be purified by extraction with THF (2−3 mL) and then cautiously layered with *n*-hexane. When the diffusion was completed (*ca*. 2 days), after removal of the decanted mother liquor, the orange crystals were washed thoroughly with *n*-hexane and vacuum-dried.

A similar procedure, using $(PPN)_2[RuRh_4(CO)_{15}]$, applies to the production of the $(PPN)^+$ salt.

(3) Synthesis of [PPN][$Ru_3Rh(CO)_{12}(PPh_3)$]. A solution of [PPN][$Ru_3Rh(CO)_{13}$] (43.4 mg, 0.033 mmol) in THF (2 mL) was treated with PPh_3 (9.6 mg, 0.036 mmol). After 10 min stirring, when an IR spectrum revealed completeness of the reaction, the solution was cautiously layered with a mixture of 2-propanol and *n*-hexane (8 + 8 mL). When the diffusion was completed (*ca*. 1 week), after removal of the decanted mother liquor, a red-orange tacky precipitate was recovered, washed with *n*-hexane, and vacuum-dried. The product, dissolved in d_6-acetone, was submitted to ^{31}P NMR.

(4) X-ray Analysis. (a) Collection and Reduction of X-ray Data. A suitable crystal of each compound was chosen and mounted on a glass fiber tip onto a goniometer head. Single-crystal X-ray diffraction data were collected on an Enraf-Nonius CAD4 diffractometer with the use of graphite-monochromatized Mo Kα radiation (0.710 73 Å). The unit cell parameters and an orientation matrix relating the crystal axes to the diffractometer axes were determined by least-squares fit of the setting angles of 25 randomly distributed intense reflections with $10° < \theta < 14°$. The data collections were performed by the ω scan method, at room temperature with variable scan speed (maximum scan time for each reflection: 60 s) and variable scan range out to a maximum 2θ angle of 50°. The crystal stability under diffraction condition was checked by monitoring three standard reflections every 60 min. The measured intensities were corrected for Lorentz, polarization, background, and decay effects and reduced to F^2_{obs}. An empirical absorption correction was applied using ψ scans of three suitable reflections having χ values close to 90°.[20] Selected crystal data are summarized in Table 1.

(b) Solution and Structure Refinement. The structures were solved by direct methods (SIR92)[21] and difference Fourier methods. The structures were refined by full-matrix least-squares against F^2_{obs} using reflections with $F^2_{obs} > 3\sigma(F^2_{obs})$ and the program SHELXL93[22] on a Silicon Graphics Indigo computer. Anisotropic displacement parameters were assigned to all non-hydrogen atoms excluding the phenyl carbon atoms in compound **2**. In that case phenyl moieties were treated as rigid groups with D_{6h} symmetry. All phenyl hydrogens were riding on their parent carbon atoms with individual isotropic displacement parameters 1.2 times that of the pertinent carbon atom. Final bonding parameters are reported in Tables 2 and 3 for compounds **1** and **2**, respectively.

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Supporting Information Available: IR spectra of [PPN][$Ru_3Rh(CO)_{13}$] and [PPN][$RuRh_3(CO)_{12}$] (1 page). X-ray crystallographic files in CIF format for the structure determination of [PPN][$Ru_3Rh(CO)_{13}$] and [PPN][$RuRh_3(CO)_{12}$] are available on the Internet only. Ordering and access information is given on any current masthead page.

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