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# The ruthenium cluster anion [HRu3(CO)8(.mu.-PPh2)2]- as a building block for the assembly of bimetallic tetranuclear clusters: synthesis, structure, fluxionality, and reactivity. Syntheses and structures of [H2Ru3Rh(.mu.-CO)(CO)6(PPh3)2(.mu.-PPh2)(PPhC6H4)] and [H2Ru3Ir(.mu.-CO)(CO)7(PPh3)(.mu.-PPh2)(PPhC6H4)]

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# The Cluster Anion $[HRu_3(CO)_8(\mu\text{-}PPh_2)_2]^-$ as a Building Block for the Assembly of Bimetallic Tetranuclear Clusters: Synthesis, Structure, Fluxionality, and Reactivity. Syntheses and Structures of $[H_2Ru_3Rh(\mu\text{-}CO)(CO)_6(PPh_3)_2(\mu\text{-}PPh_2)(PPhC_6H_4)]$ and $[H_2Ru_3Ir(\mu\text{-}CO)(CO)_7(PPh_3)(\mu\text{-}PPh_2)(PPhC_6H_4)]$

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The anionic cluster $[HRu_3(CO)_8(\mu\text{-}PPh_2)_2]^-$ (1) is obtained from the reaction of $[HRu_3(CO)_{11}]^-$ with $PPh_2H$ in THF solution. The solid-state structure of **1** has been determined by a single-crystal X-ray analysis of the bis(triphenylphosphine)iminium salt. Crystals are triclinic, space group $P\bar{1}$, with $Z = 2$ in a unit cell of dimensions $a = 14.690$ (6), $b = 18.652$ (4), $c = 12.150$ (2) Å, $\alpha = 106.60$ (2), $\beta = 92.17$ (2), $\gamma = 95.89$ (2)°. The structure of **1** shows a triangular metal framework of three ruthenium atoms bound to eight terminal carbonyl groups, with the two $\mu$-phosphido ligands bridging two adjacent Ru–Ru bonds one of which is also bridged by the hydride ligand. In solution the hydride ligand was found to be fluxional by migrating from a phosphido-bridged Ru–Ru bond to the other one as documented by the temperature-dependent $^{31}P$ and $^1H$ NMR spectra. The cluster anion **1** reacts with chloro complexes to give neutral mixed-metal tetranuclear clusters. The reaction of **1** with Wilkinson's catalyst, $(PPh_3)_3RhCl$, leads to the formation of $[H_2Ru_3Rh(\mu\text{-}CO)(CO)_6(PPh_3)_2(\mu\text{-}PPh_2)(PPhC_6H_4)]$ (**2**), and with Vaska's complex, $(PPh_3)_2Ir(CO)Cl$, the cluster $[H_2Ru_3Ir(\mu\text{-}CO)(CO)_7(PPh_3)(\mu\text{-}PPh_2)(PPhC_6H_4)]$ (**3**) is obtained. In spite of the formal analogy of **2** and **3** the structures of the two tetranuclear mixed-metal clusters, determined by X-ray diffraction methods, are entirely different. Crystals of **2** are triclinic, space group $P\bar{1}$, with $Z = 2$ in a unit cell of dimensions $a = 12.074$ (4), $b = 22.972$ (8), $c = 11.506$ (5) Å, $\alpha = 78.55$ (1), $\beta = 101.43$ (1), $\gamma = 101.20$ (1)°. Crystals of **3** are monoclinic, space group $P2_1/a$, with $Z = 4$ in a unit cell of dimensions $a = 19.446$ (4), $b = 18.168$ (8), $c = 14.083$ (6) Å, $\beta = 102.29$ (1)°. The $Ru_3Rh$ core in **2** is in a butterfly arrangement with an orthometalated $PPhC_6H_4$ moiety bridging the Ru–Ru hinge edge and $\eta^3$ interacting with the Rh atom. The $Ru_3Ir$ core in **3** is in a tetrahedral arrangement in which the $PPhC_6H_4$ ligand bridges only a tetrahedral Ir–Ru edge.

## Introduction

Anionic metal complexes in general are suitable building blocks for cluster expansion reactions.[1] By contrast, the use of anionic clusters to build up bigger clusters is rather limited. Recently it was found that the trinuclear cluster anion $[Ru_3(CO)_{11}]^-$ reacts with $Bi(NO_3)_3 \cdot 5H_2O$ to give $HRu_5Bi(CO)_{18}$[2] and $Ru_3(CO)_9Bi_2$,[3] but this method does not provide a general route to mixed-metal $Ru_3M$ clusters since the $Ru_3$ core in $[HRu_3(CO)_{11}]^-$ seems to be quite fragile.[4] However, stabilization of the trinuclear ruthenium framework by bridging or capping ligands favors expansion reactions of anionic ruthenium clusters, exemplified by the reaction of the $\mu_3$-phosphinidene anionic cluster $[HRu_3(CO)_9(\mu_3\text{-}PPh)]^-$[5] with a variety of organometallic halides to give $Ru_3M$ (M = Re, Rh, Ir, Cu, Ag, Au) clusters.[5]

Anionic triruthenium clusters containing phosphorus ligands are quite rare: apart from $[HRu_3(CO)_9(PPh)]^-$[5] the only isolated and well-characterized species is $[HRu_3(CO)_8(PPh_3)(PPhC_6H_4)]^-$, which we reported recently as the final product of the reaction of $[HRu_3(CO)_{11}]^-$ with triphenylphosphine.[6] In this paper we describe the synthesis, structure, and fluxionality of the $\mu_2$-phosphido-bridged cluster anion $[HRu_3(CO)_8(PPh_2)_2]^-$ (1) and its use as a building block for the assembly of tetranuclear $Ru_3M$ mixed-metal clusters.

## Results and Discussion

The anionic cluster $[HRu_3(CO)_{11}]^-$ reacts in THF solution at ambient temperature with diphenylphosphine to give the $\mu_2$-phosphido-bridged derivative $[HRu_3(CO)_8(\mu\text{-}PPh_2)_2]^-$ (1), which can be isolated almost quantitatively as the bis(triphenylphosphine)iminium salt from methanol:

$$[HRu_3(CO)_{11}]^- + 2HPPh_2 \rightarrow \underset{\mathbf{1}}{[HRu_3(CO)_8(PPh_2)_2]^-} + 3CO + H_2$$

**Synthesis, Crystal Structure, and NMR Study of $[(PPh_3)_2N][HRu_3(CO)_8(PPh_2)_2]$.** The product $[(PPh_3)_2N][HRu_3(CO)_8(\mu\text{-}PPh_2)_2]$ is obtained as a red microcrystalline and slightly air-sensitive powder that is soluble only in polar organic solvents such as dichloromethane, tetrahydrofuran, and acetonitrile. Solutions

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0276-7333/90/2309-1670$02.50/0

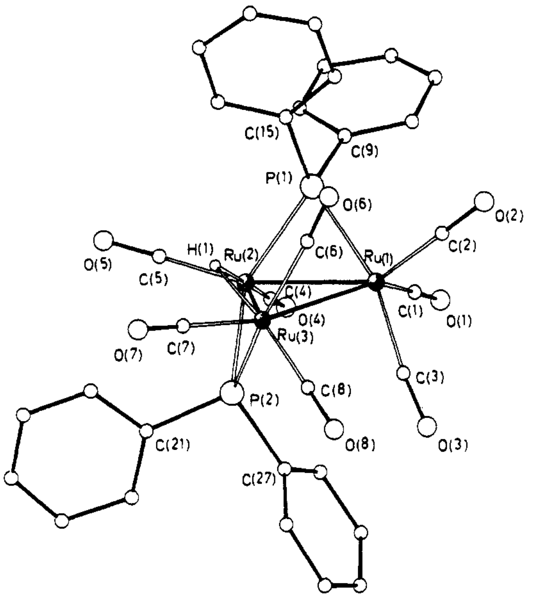


**Figure 1.** View of the structure of the anion of 1 with the atomic numbering scheme.

**Table I. Selected Bond Distances (Å) and Angles (deg) in the Anion 1**

| | | | |
|---|---|---|---|
| | Distances | | |
| Ru(1)-Ru(2) | 2.819 (1) | C(1)-O(1) | 1.15 (1) |
| Ru(1)-Ru(3) | 2.917 (1) | C(2)-O(2) | 1.15 (1) |
| Ru(2)-Ru(3) | 2.870 (1) | C(3)-O(3) | 1.17 (1) |
| P(1)-Ru(1) | 2.357 (3) | C(4)-O(4) | 1.15 (1) |
| P(1)-Ru(2) | 2.308 (3) | C(5)-O(5) | 1.18 (2) |
| P(2)-Ru(2) | 2.317 (3) | C(6)-O(6) | 1.15 (2) |
| P(2)-Ru(3) | 2.382 (3) | C(7)-O(7) | 1.14 (1) |
| Ru(1)-C(1) | 1.88 (1) | C(8)-O(8) | 1.17 (1) |
| Ru(1)-C(2) | 1.90 (1) | P(1)-C(9) | 1.84 (1) |
| Ru(1)-C(3) | 1.90 (1) | P(1)-C(15) | 1.83 (1) |
| Ru(2)-C(4) | 1.84 (1) | P(2)-C(21) | 1.84 (1) |
| Ru(2)-C(5) | 1.83 (1) | P(2)-C(27) | 1.83 (1) |
| Ru(3)-C(6) | 1.93 (1) | Ru(2)-H(1) | 1.82 (6) |
| Ru(3)-C(7) | 1.89 (1) | Ru(3)-H(1) | 1.76 (6) |
| Ru(3)-C(8) | 1.87 (1) | | |
| | Angles | | |
| Ru(2)-Ru(1)-Ru(3) | 60.02 (5) | C(4)-Ru(2)-C(5) | 91.9 (5) |
| Ru(1)-Ru(2)-Ru(3) | 61.69 (5) | P(2)-Ru(3)-C(7) | 101.0 (3) |
| Ru(1)-Ru(3)-Ru(2) | 58.30 (5) | P(2)-Ru(3)-C(8) | 97.6 (4) |
| P(1)-Ru(1)-C(1) | 90.7 (4) | P(2)-Ru(3)-Ru(1) | 84.1 (1) |
| P(1)-Ru(1)-C(2) | 99.2 (4) | P(2)-Ru(3)-Ru(2) | 51.3 (1) |
| P(1)-Ru(1)-Ru(2) | 52.0 (1) | Ru(1)-Ru(3)-C(6) | 71.2 (4) |
| P(1)-Ru(1)-Ru(3) | 88.1 (1) | Ru(1)-Ru(3)-C(8) | 96.1 (4) |
| Ru(2)-Ru(1)-C(1) | 92.3 (4) | Ru(2)-Ru(3)-C(6) | 104.8 (3) |
| Ru(2)-Ru(1)-C(3) | 111.3 (4) | Ru(2)-Ru(3)-C(7) | 117.1 (3) |
| Ru(3)-Ru(1)-C(2) | 111.8 (4) | C(6)-Ru(3)-C(7) | 101.5 (5) |
| Ru(3)-Ru(1)-C(3) | 81.1 (4) | C(6)-Ru(3)-C(8) | 95.4 (5) |
| C(1)-Ru(1)-C(2) | 103.0 (6) | C(7)-Ru(3)-C(8) | 93.5 (5) |
| C(1)-Ru(1)-C(3) | 91.0 (5) | Ru(1)-P(1)-Ru(2) | 74.3 (1) |
| C(2)-Ru(1)-C(3) | 96.6 (5) | Ru(2)-P(2)-Ru(3) | 75.3 (1) |
| P(1)-Ru(2)-C(4) | 96.2 (4) | Ru(1)-C(1)-O(1) | 177 (1) |
| P(1)-Ru(2)-C(5) | 110.7 (4) | Ru(1)-C(2)-O(2) | 176 (1) |
| P(1)-Ru(2)-Ru(1) | 53.6 (1) | Ru(1)-C(3)-O(3) | 173 (1) |
| P(1)-Ru(2)-Ru(3) | 90.2 (1) | Ru(2)-C(4)-O(4) | 178 (1) |
| P(2)-Ru(2)-C(4) | 104.5 (4) | Ru(2)-C(5)-O(5) | 179 (1) |
| P(2)-Ru(2)-C(5) | 104.8 (4) | Ru(3)-C(6)-O(6) | 171 (1) |
| P(2)-Ru(2)-Ru(1) | 87.6 (1) | Ru(3)-C(7)-O(7) | 175 (1) |
| P(2)-Ru(2)-Ru(3) | 53.4 (1) | Ru(3)-C(8)-O(8) | 177 (1) |
| Ru(1)-Ru(2)-C(4) | 96.4 (4) | Ru(2)-H(1)-Ru(3) | 107 (3) |
| Ru(3)-Ru(2)-C(5) | 116.4 (4) | | |

containing 1 are unstable in air and at temperatures higher than 60 °C. The infrared spectra of 1 display six bands in the region of terminal carbonyls. In the $^1H$ NMR spectrum only one hydride is observed as a pseudotriplet; the resonances of the aromatic $PPh_2$ protons are overlaid by those of the protons of the $[(PPh_3)_2N]^+$ cation.

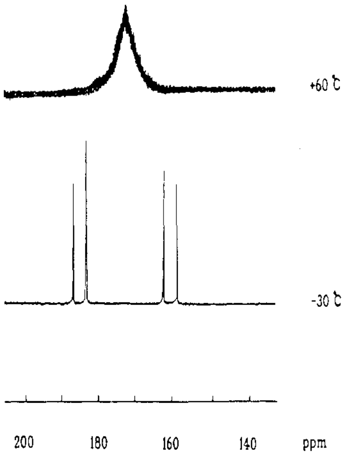


**Figure 2.** Temperature-dependent $^{31}P$ NMR spectra of $[(PPh_3)_2N][HRu_3(CO)_8(PPh_2)_2]$ in $CD_3CN$.

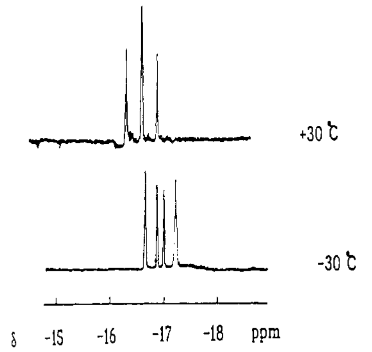


**Figure 3.** $^1H$ NMR spectra (hydride region) of a $CD_3CN$ solution of $[(PPh_3)_2N][HRu_3(CO)_8(PPh_2)_2]$ at different temperatures.

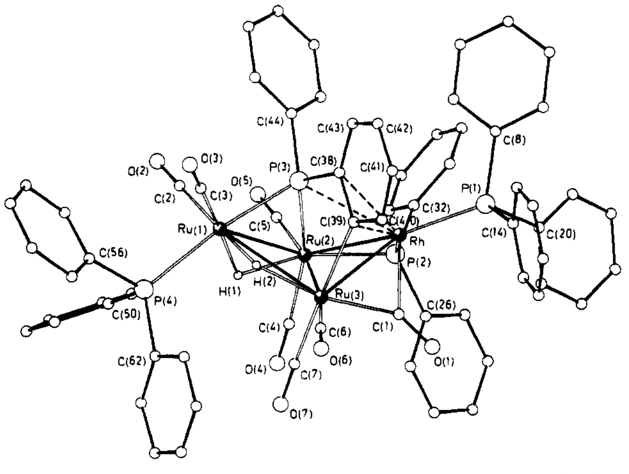


**Figure 4.** View of the structure of 2 with the atomic numbering scheme.

The crystal structure of $[(PPh_3)_2N][HRu_3(CO)_8(\mu\text{-}PPh_2)_2]$ consists of $[(PPh_3)_2N]^+$ cations and $[HRu_3(CO)_8(\mu\text{-}PPh_2)_2]^-$ anions (1), separated by normal intermolecular contacts. The structure of the anion 1 is represented in Figure 1 together with the atomic numbering scheme; selected bond distances and angles are given in Table I. The structure shows a ruthenium triangle of unequal lengths, 2.819 (1), 2.870 (1), and 2.917 (1) Å, with two Ru atoms, Ru(1) and Ru(3), bound to three and the third, Ru(2), to two terminal carbonyl groups. Two phosphido ligands asymmetrically bridge in a slightly asymmetric way the Ru(1)-Ru(2) and Ru(2)-Ru(3) edges of the metal triangle [P(1)-Ru(1) = 2.357 (3) and P(1)-Ru(2) = 2.308 (3), P(2)-Ru(2) = 2.317 (3), and P(2)-Ru(3) = 2.382 (3) Å]. The Ru(1)-P(1)-Ru(2) bridge forms an

**Table II. Selected Bond Distances (Å) and Angles (deg) in 2**

Distances

| | | | |
|---|---|---|---|
| Rh–Ru(2) | 2.866 (1) | C(3)–O(3) | 1.137 (9) |
| Rh–Ru(3) | 2.734 (1) | C(4)–O(4) | 1.143 (9) |
| Ru(1)–Ru(2) | 2.950 (1) | C(5)–O(5) | 1.139 (9) |
| Ru(1)–Ru(3) | 3.125 (1) | C(6)–O(6) | 1.138 (9) |
| Ru(2)–Ru(3) | 2.962 (1) | C(7)–O(7) | 1.136 (10) |
| P(1)–Rh | 2.278 (2) | C(38)–C(39) | 1.423 (8) |
| P(2)–Rh | 2.215 (2) | C(38)–C(43) | 1.406 (10) |
| P(2)–Ru(2) | 2.322 (2) | C(39)–C(40) | 1.418 (10) |
| P(3)–Rh | 2.840 (2) | C(40)–C(41) | 1.389 (11) |
| P(3)–Ru(1) | 2.350 (2) | C(41)–C(42) | 1.377 (11) |
| P(3)–Ru(2) | 2.362 (2) | C(42)–C(43) | 1.371 (11) |
| P(4)–Ru(1) | 2.387 (2) | P(1)–C(8) | 1.838 (7) |
| Rh–C(1) | 2.075 (6) | P(1)–C(14) | 1.847 (7) |
| Ru(3)–C(1) | 2.032 (7) | P(1)–C(20) | 1.851 (7) |
| Ru(1)–C(2) | 1.886 (7) | P(2)–C(26) | 1.845 (6) |
| Ru(1)–C(3) | 1.902 (7) | P(2)–C(32) | 1.848 (7) |
| Ru(2)–C(4) | 1.905 (7) | P(3)–C(38) | 1.805 (7) |
| Ru(2)–C(5) | 1.875 (7) | P(3)–C(44) | 1.829 (6) |
| Ru(3)–C(6) | 1.882 (7) | P(4)–C(50) | 1.823 (7) |
| Ru(3)–C(7) | 1.922 (8) | P(4)–C(56) | 1.841 (7) |
| Rh–C(38) | 2.569 (6) | P(4)–C(62) | 1.838 (7) |
| Rh–C(39) | 2.315 (6) | Ru(1)–H(1) | 1.73 (8) |
| Ru(3)–C(39) | 2.166 (7) | Ru(2)–H(1) | 1.88 (10) |
| C(1)–O(1) | 1.158 (8) | Ru(1)–H(2) | 1.79 (9) |
| C(2)–O(2) | 1.135 (8) | Ru(3)–H(2) | 1.84 (10) |

Angles

| | | | |
|---|---|---|---|
| Ru(2)–Rh–Ru(3) | 63.81 (4) | Ru(3)–Ru(2)–C(4) | 95.6 (2) |
| Rh–Ru(2)–Ru(3) | 55.94 (4) | Ru(2)–Ru(3)–C(39) | 95.7 (2) |
| Rh–Ru(3)–Ru(2) | 60.25 (4) | Ru(2)–Ru(3)–C(1) | 89.5 (2) |
| Ru(2)–Ru(1)–Ru(3) | 58.27 (4) | Ru(2)–Ru(3)–C(7) | 84.4 (2) |
| Ru(1)–Ru(2)–Ru(3) | 63.82 (4) | C(1)–Ru(3)–C(6) | 97.1 (3) |
| Ru(1)–Ru(3)–Ru(2) | 57.91 (4) | C(1)–Ru(3)–C(7) | 92.9 (3) |
| Rh–Ru(2)–Ru(1) | 100.65 (5) | C(1)–Ru(3)–C(39) | 85.0 (3) |
| Rh–Ru(3)–Ru(1) | 99.43 (5) | C(6)–Ru(3)–C(7) | 89.7 (3) |
| P(1)–Rh–C(1) | 105.6 (2) | C(6)–Ru(3)–C(39) | 90.3 (3) |
| P(2)–Rh–C(1) | 97.7 (2) | Rh–P(2)–Ru(2) | 78.3 (1) |
| P(1)–Rh–P(2) | 105.4 (1) | Ru(1)–P(3)–Ru(2) | 77.5 (1) |
| Ru(3)–Rh–P(2) | 105.5 (1) | Ru(2)–P(3)–C(38) | 124.7 (2) |
| Ru(2)–Rh–C(1) | 91.3 (2) | Ru(2)–P(3)–C(44) | 119.8 (2) |
| P(3)–Ru(1)–C(2) | 90.9 (2) | C(38)–P(3)–C(44) | 104.9 (3) |
| P(3)–Ru(1)–C(3) | 95.8 (2) | Rh–C(1)–Ru(3) | 83.5 (3) |
| P(4)–Ru(1)–C(2) | 89.4 (2) | Rh–C(1)–O(1) | 131.4 (5) |
| P(4)–Ru(1)–C(3) | 94.9 (2) | Ru(3)–C(1)–O(1) | 145.1 (6) |
| C(2)–Ru(1)–C(3) | 95.1 (3) | Ru(1)–C(2)–O(2) | 177.2 (6) |
| P(2)–Ru(2)–C(4) | 95.2 (2) | Ru(1)–C(3)–O(3) | 179.7 (7) |
| P(2)–Ru(2)–C(5) | 99.1 (2) | Ru(2)–C(4)–O(4) | 175.5 (7) |
| P(3)–Ru(2)–C(5) | 94.7 (2) | Ru(2)–C(5)–O(5) | 177.6 (7) |
| P(2)–Ru(2)–P(3) | 102.3 (1) | Ru(3)–C(6)–O(6) | 177.6 (7) |
| C(4)–Ru(2)–C(5) | 92.4 (3) | Ru(3)–C(7)–O(7) | 176.0 (7) |
| Ru(3)–Ru(2)–P(2) | 96.1 (1) | Ru(1)–H(1)–Ru(2) | 110 (5) |
| Ru(3)–Ru(2)–P(3) | 72.8 (1) | Ru(1)–H(2)–Ru(3) | 119 (5) |

angle of 113.6 (1)° with the Ru triangle (P(1) is out of 1.703 (3) Å from it), the Ru(2)–P(2)–Ru(3) bridge forms an angle of 109.9 (1)° (with P(2) out of −1.749 (3) Å). The Ru(2)–Ru(3) edge is also bridged by the hydride ligand, on opposite sides with respect to the phosphido bridge. The dihedral angles formed by the hydride bridge with the metal triangle and the phosphido bridge are 129 (2) and 121 (2)°, respectively. The rather large Ru(3)–Ru(2)–C(5) and Ru(2)–Ru(3)–C(7) angles, 116.4(4) and 117.1 (3)°, are typical of the Ru–H–Ru system and confirm the presence of the hydride bridging the Ru(2)–Ru(3) edge.

**Table III. Selected Bond Distances (Å) and Angles (deg) in 3**

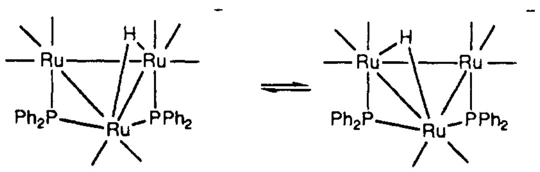
Distances

| | | | |
|---|---|---|---|
| Ir–Ru(1) | 2.875 (1) | P(1)–C(27) | 1.823 (7) |
| Ir–Ru(2) | 2.769 (1) | P(2)–C(10) | 1.802 (7) |
| Ir–Ru(3) | 2.963 (1) | P(2)–C(33) | 1.823 (7) |
| Ru(1)–Ru(2) | 2.818 (1) | P(3)–C(39) | 1.831 (6) |
| Ru(1)–Ru(3) | 2.710 (1) | P(3)–C(45) | 1.814 (9) |
| Ru(2)–Ru(3) | 2.797 (1) | C(1)–O(1) | 1.135 (8) |
| Ir–P(1) | 2.329 (2) | C(2)–O(2) | 1.108 (10) |
| Ir–C(1) | 1.879 (7) | C(3)–O(3) | 1.131 (10) |
| Ir–C(9) | 2.086 (7) | C(4)–O(4) | 1.140 (10) |
| Ru(1)–P(2) | 2.295 (2) | C(5)–O(5) | 1.122 (11) |
| Ru(1)–C(2) | 1.929 (8) | C(6)–O(6) | 1.132 (10) |
| Ru(1)–C(3) | 1.887 (9) | C(7)–O(7) | 1.140 (10) |
| Ru(1)–C(6) | 2.156 (9) | C(8)–O(8) | 1.144 (11) |
| Ru(2)–P(2) | 2.299 (2) | C(9)–C(10) | 1.408 (9) |
| Ru(2)–P(3) | 2.337 (2) | C(10)–C(11) | 1.391 (10) |
| Ru(2)–C(4) | 1.878 (8) | C(11)–C(12) | 1.392 (11) |
| Ru(2)–C(5) | 1.905 (9) | C(12)–C(13) | 1.385 (11) |
| Ru(3)–P(3) | 2.281 (2) | C(13)–C(14) | 1.384 (11) |
| Ru(3)–C(6) | 2.223 (8) | C(9)–C(14) | 1.412 (10) |
| Ru(3)–C(7) | 1.888 (8) | Ir–H(1) | 1.80 (8) |
| Ru(3)–C(8) | 1.871 (8) | Ir–H(2) | 1.77 (9) |
| P(1)–C(15) | 1.832 (7) | Ru(1)–H(1) | 1.82 (9) |
| P(1)–C(21) | 1.822 (7) | Ru(3)–H(2) | 1.98 (8) |

Angles

| | | | |
|---|---|---|---|
| Ru(1)–Ir–Ru(2) | 59.87 (4) | C(7)–Ru(3)–C(8) | 93.0 (3) |
| Ru(1)–Ir–Ru(3) | 55.27 (3) | C(6)–Ru(3)–C(7) | 93.8 (3) |
| Ru(2)–Ir–Ru(3) | 58.29 (3) | C(6)–Ru(3)–C(8) | 89.0 (3) |
| Ir–Ru(1)–Ru(2) | 58.19 (4) | Ru(1)–P(2)–Ru(2) | 75.7 (1) |
| Ir–Ru(1)–Ru(3) | 64.02 (4) | Ru(1)–P(2)–C(10) | 115.7 (2) |
| Ru(2)–Ru(1)–Ru(3) | 60.76 (4) | Ru(2)–P(2)–C(10) | 114.3 (2) |
| Ir–Ru(2)–Ru(1) | 61.94 (4) | Ru(2)–P(3)–Ru(3) | 74.5 (1) |
| Ir–Ru(2)–Ru(3) | 64.34 (4) | Ir–C(1)–O(1) | 172.4 (6) |
| Ru(1)–Ru(2)–Ru(3) | 57.70 (4) | Ru(1)–C(2)–O(2) | 178.6 (8) |
| Ir–Ru(3)–Ru(1) | 60.71 (4) | Ru(1)–C(3)–O(3) | 174.5 (8) |
| Ir–Ru(3)–Ru(2) | 57.37 (3) | Ru(2)–C(4)–O(4) | 178.8 (7) |
| Ru(1)–Ru(3)–Ru(2) | 61.54 (4) | Ru(2)–C(5)–O(5) | 175.9 (8) |
| P(1)–Ir–C(1) | 101.4 (2) | Ru(1)–C(6)–O(6) | 142.4 (7) |
| P(1)–Ir–C(9) | 95.1 (2) | Ru(3)–C(6)–O(6) | 141.0 (7) |
| C(1)–Ir–C(9) | 84.6 (3) | Ru(1)–C(6)–Ru(3) | 76.4 (3) |
| P(2)–Ru(1)–C(2) | 99.9 (3) | Ru(3)–C(7)–O(7) | 178.1 (7) |
| P(2)–Ru(1)–C(3) | 91.5 (3) | Ru(3)–C(8)–O(8) | 177.4 (7) |
| C(2)–Ru(1)–C(3) | 92.9 (3) | Ir–C(9)–C(10) | 118.6 (5) |
| C(2)–Ru(1)–C(6) | 93.5 (3) | Ir–C(9)–C(14) | 125.2 (5) |
| C(3)–Ru(1)–C(6) | 95.8 (3) | C(10)–C(9)–C(14) | 116.3 (6) |
| Ir–Ru(2)–C(4) | 98.7 (3) | C(9)–C(10)–C(11) | 122.6 (6) |
| Ir–Ru(2)–P(2) | 74.9 (1) | P(2)–C(10)–C(9) | 112.5 (5) |
| Ir–Ru(2)–P(3) | 86.0 (1) | P(2)–C(10)–C(11) | 124.8 (5) |
| C(4)–Ru(2)–C(5) | 100.2 (4) | C(10)–C(11)–C(12) | 119.2 (7) |
| P(2)–Ru(2)–C(4) | 95.3 (3) | C(11)–C(12)–C(13) | 119.9 (7) |
| P(2)–Ru(2)–C(5) | 97.4 (3) | C(12)–C(13)–C(14) | 120.6 (7) |
| P(3)–Ru(2)–C(4) | 98.0 (2) | C(9)–C(14)–C(13) | 121.5 (7) |
| P(3)–Ru(2)–C(5) | 97.2 (3) | Ir–H(1)–Ru(1) | 105 (4) |
| P(3)–Ru(3)–C(7) | 100.7 (3) | Ir–H(2)–Ru(3) | 104 (4) |
| P(3)–Ru(3)–C(8) | 90.6 (2) | | |

In solution the hydride bridge in 1 is not rigid: at −30 °C the $^1$H NMR spectrum exhibits the expected double-doublet at δ −16.91 for the hydride resonance due to the coupling with two different phosphorus atoms (Figure 2), at + 30 °C the two phosphorus atoms become indistinguishable for the hydride ligand giving rise to a pseudo-triplet at δ −17.01. These findings are best interpreted by a fast exchange (flipping) of the hydride bridge from the Ru(1)–Ru(2) to the Ru(2)–Ru(3) edge. An intermediate in which Ru(1)–Ru(3) is bridged by the hydride can be ruled out by chemical shift arguments; however, this could be a possible transition state. In accordance with this interpretation a variable-temperature $^{31}$P{$^1$H} NMR study at −30 °C shows two doublet signals for the two phosphido ligands at δ 184.8 and 160.5 {$J(^{31}P-^{31}P)$ = 112 Hz}, which upon increasing the temperature coalesce to give at +60 °C a broad singlet at δ 172.6 (Figure 3). The following is the proposed mechanism for the fluxional behavior of 1 in solution:

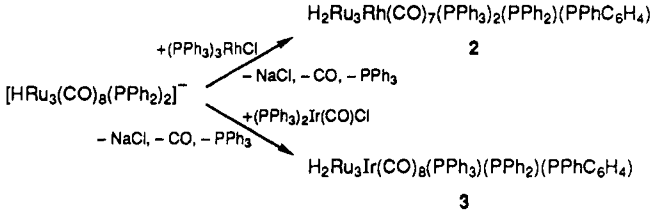


The cluster anion 1 reacts with chloro complexes to give neutral tetranuclear mixed-metal clusters: with Wilkin-

**Table IV. Experimental Data for the X-ray Diffraction Study on 1, 2, and 3**

| | 1 | 2 | 3 |
|---|---|---|---|
| mol formula | $C_{68}H_{51}NO_8P_4Ru_3$ | $C_{67}H_{51}O_7P_4RhRu_3$ | $C_{50}H_{36}IrO_8P_3Ru_3$ |
| mol wt | 1437.26 | 1498.15 | 1353.18 |
| cryst syst | triclinic | triclinic | monoclinic |
| space group | $P\bar{1}$ | $P\bar{1}$ | $P2_1/a$ |
| radiatn | Nb-filtered Mo Kα (λ = 0.71073 Å) | Ni-filtered Cu Kα (λ = 1.541838 Å) | graphite monochromated Mo Kα (λ = 0.71073 Å) |
| *a*, Å | 14.690 (6) | 12.074 (4) | 19.446 (4) |
| *b*, Å | 18.652 (4) | 22.972 (8) | 18.168 (8) |
| *c*, Å | 12.150 (2) | 11.506 (5) | 14.083 (6) |
| α, deg | 106.60 (2) | 78.55 (1) | |
| β, deg | 92.17 (2) | 101.43 (1) | 102.29 (1) |
| γ, deg | 95.89 (2) | 101.20 (1) | |
| *V*, $Å^3$ | 3166 (2) | 3026 (2) | 4861 (3) |
| *Z* | 2 | 2 | 4 |
| $D_{calcd}$, g $cm^{-3}$ | 1.508 | 1.644 | 1.849 |
| *F*(000) | 1444 | 1492 | 2616 |
| cryst dimens, mm | 0.18 × 0.21 × 0.25 | 0.10 × 0.18 × 0.27 | 0.21 × 0.25 × 0.30 |
| linear abs, $cm^{-1}$ | 8.46 | 97.72 | 37.64 |
| diffractometer | Siemens AED | Siemens AED | Philips PW-1100 |
| scan type | $\theta/2\theta$ | $\theta/2\theta$ | $\theta/2\theta$ |
| scan speed, θ/min | 2.5–12 | 2.5/12 | 2.5/12 |
| scan width | $(\theta - 0.6)$ – $(\theta + 0.6 + 0.346 \tan\theta)$ | $(\theta - 0.6)$ – $(\theta + 0.6 + 0.142 \tan\theta)$ | $(\theta - 0.6)$ – $(\theta + 0.6 + 0.346 \tan\theta)$ |
| 2θ range, deg | 6–48 | 6–140 | 6–50 |
| reflns measd | $\pm h,\pm k,l$ | $\pm h,\pm k,l$ | $\pm h,k,l$ |
| std refln | one measd after 50 reflections | | |
| unique total data | 9959 | 11483 | 8609 |
| unique obsd data $[I > 2\sigma(I)]$ | 4046 | 8329 | 6065 |
| *R* | 0.0421 | 0.0446 | 0.0332 |
| $R_w$ | 0.0433 | 0.0590 | 0.0420 |

son's catalyst, $(PPh_3)_3RhCl$, the cluster $[H_2Ru_3Rh(\mu\text{-}CO)(CO)_6(PPh_3)_2(\mu\text{-}PPh_2)(PPhC_6H_4)]$ (**2**) is formed; with Vaska's complex, $(PPh_3)_2Ir(CO)Cl$, the cluster $[H_2Ru_3Ir(\mu\text{-}CO)(CO)_7(PPh_3)(\mu\text{-}PPh_2)(PPhC_6H_4)]$ (**3**) is obtained. Both reactions proceed at room temperature in dichloromethane solution, and the products can be isolated by preparative thin-layer chromatography.



**Syntheses, Crystal Structures, and NMR Studies of $[H_2Ru_3Rh(\mu\text{-}CO)(CO)_6(PPh_3)_2(\mu\text{-}PPh_2)(PPhC_6H_4)]$ (2) and $[H_2Ru_3Ir(\mu\text{-}CO)(CO)_7(PPh_3)(\mu\text{-}PPh_2)(PPhC_6H_4)]$ (3).** The mixed-metal clusters **2** and **3** form dark brown crystals that are only slightly air-sensitive and that dissolve in organic solvents. In spite of their formal analogy, the structures of **2** and **3**, fully elucidated by X-ray diffraction methods, are entirely different, in spite of being in accordance with the 18-electron rule. The structures of **2** and **3** are shown in Figures 4 and 5, respectively; selected bond distances and angles are given in Tables II and III, respectively.

The $Ru_3Rh$ core of **2** is in a butterfly arrangement with the unique metal occupying a wingtip; the Ru–Ru bond distances are the longest, 2.950 (1), 2.962 (1), and 3.125 (1) Å, the two Rh–Ru bond distances being 2.734 (1) and 2.866 (1) Å. The dihedral angle between the two Ru(1)–Ru(2)–Ru(3) and Rh–Ru(2)–Ru(3) wings is 125.5 (1)°. Of the seven carbonyl groups, six are terminal, two for each Ru atom, whereas the seventh one is nearly symmetrically bridging the Rh–Ru(3) edge [Rh–C(1) = 2.075 (6) and Ru(3)–C(1) = 2.032 (7) Å]. The two hydride ligands, H(1) and H(2), bridge respectively the Ru(1)–Ru(2) and Ru(1)–Ru(3) edges of the same wing. The Ru(1)–H(1)–Ru(2) bridge is nearly perpendicular to the wing, whereas the Ru(1)–H(2)–Ru(3) bridge is practically coplanar. The two $PPh_3$ ligands are bound to the Rh and Ru(1) wingtips with the Rh–P(1) bond much shorter, 2.278 (2) Å, than the Ru(1)–P(4) one, 2.387 (2) Å. One of the two bridging phosphido ligands of the starting cluster **1** is migrated from the Ru(2)–Ru(3) edge to the Rh–Ru(2) edge. This bridge in **2** is rather asymmetric [Rh–P(2) = 2.215 (2) and Ru(2)–P(2) = 2.322 (2) Å] and forms a dihedral angle of 138.9 (1)° with the Rh–Ru(2)–Ru(3) wing [P(2) deviates by 1.155 (2) Å from it]. The second phosphido ligand, bridging the Ru(1)–Ru(2) edge in **1**, acts in **2** again as a bridge on the

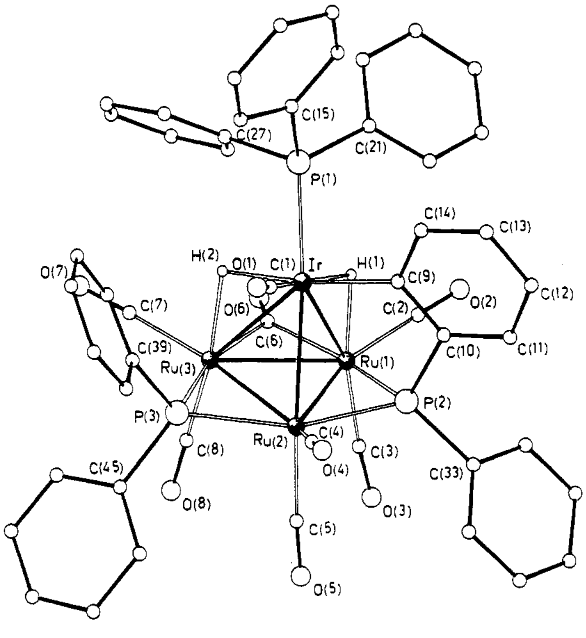


**Figure 5.** View of the structure of **3** with the atomic numbering scheme.

**Table V. Atomic Coordinates (×10$^4$) and Isotropic Thermal Parameters (Å$^2$ × 10$^3$) with Esd's in Parentheses for the Non-Hydrogen Atoms of Anion 1**

| | *x/a* | *y/b* | *z/c* | *U* |
|---|---|---|---|---|
| Ru(1) | 1749 (1) | 1492 (1) | 453 (1) | 47.8 (4)[a] |
| Ru(2) | 1850 (1) | 2262 (1) | −1233 (1) | 42.2 (4)[a] |
| Ru(3) | 3124 (1) | 2790 (1) | 757 (1) | 42.0 (3)[a] |
| P(1) | 2164 (2) | 1043 (1) | −1456 (2) | 45 (1)[a] |
| P(2) | 1867 (2) | 3371 (1) | 246 (2) | 43 (1)[a] |
| O(1) | −238 (6) | 869 (5) | −255 (7) | 95 (5)[a] |
| O(2) | 2436 (7) | 275 (5) | 1379 (8) | 107 (5)[a] |
| O(3) | 1169 (6) | 2431 (4) | 2768 (7) | 85 (4)[a] |
| O(4) | −106 (6) | 1844 (5) | −2151 (10) | 129 (6)[a] |
| O(5) | 2350 (6) | 2764 (6) | −3308 (8) | 102 (6)[a] |
| O(6) | 4208 (5) | 1483 (4) | 850 (7) | 79 (4)[a] |
| O(7) | 4754 (5) | 3918 (4) | 746 (7) | 78 (4)[a] |
| O(8) | 3102 (6) | 3401 (5) | 3351 (7) | 103 (5)[a] |
| C(1) | 522 (9) | 1101 (7) | −12 (10) | 73 (6)[a] |
| C(2) | 2193 (8) | 754 (7) | 1061 (9) | 66 (5)[a] |
| C(3) | 1399 (7) | 2114 (6) | 1866 (11) | 63 (5)[a] |
| C(4) | 640 (8) | 2015 (6) | −1783 (11) | 75 (6)[a] |
| C(5) | 2161 (8) | 2564 (6) | −2494 (10) | 62 (5)[a] |
| C(6) | 3740 (8) | 1928 (6) | 779 (9) | 60 (5)[a] |
| C(7) | 4121 (7) | 3500 (6) | 705 (8) | 49 (5)[a] |
| C(8) | 3090 (8) | 3154 (7) | 2353 (11) | 67 (5)[a] |
| C(9) | 1450 (7) | 226 (5) | −2446 (8) | 50 (3) |
| C(10) | 1100 (8) | −365 (6) | −2056 (10) | 74 (4) |
| C(11) | 575 (9) | −1008 (8) | −2872 (12) | 99 (5) |
| C(12) | 429 (9) | −995 (7) | −3950 (12) | 94 (4) |
| C(13) | 788 (9) | −438 (7) | −4370 (12) | 92 (4) |
| C(14) | 1306 (8) | 197 (7) | −3600 (10) | 76 (4) |
| C(15) | 3314 (7) | 787 (5) | −1773 (8) | 50 (3) |
| C(16) | 3632 (8) | 203 (6) | −1399 (9) | 70 (3) |
| C(17) | 4541 (9) | 22 (7) | −1589 (10) | 85 (4) |
| C(18) | 5063 (10) | 407 (7) | −2148 (11) | 93 (4) |
| C(19) | 4791 (9) | 947 (7) | −2586 (11) | 100 (5) |
| C(20) | 3881 (8) | 1152 (6) | −2378 (9) | 71 (3) |
| C(21) | 2107 (6) | 4257 (5) | −127 (8) | 45 (3) |
| C(22) | 2868 (7) | 4350 (6) | −754 (8) | 54 (3) |
| C(23) | 3069 (8) | 4994 (6) | −1105 (9) | 72 (4) |
| C(24) | 2519 (8) | 5528 (7) | −848 (10) | 76 (4) |
| C(25) | 1763 (8) | 5484 (6) | −254 (9) | 74 (4) |
| C(26) | 1548 (7) | 4835 (5) | 136 (8) | 55 (3) |
| C(27) | 963 (7) | 3594 (6) | 1238 (9) | 55 (3) |
| C(28) | 1178 (8) | 4147 (6) | 2284 (10) | 73 (4) |
| C(29) | 487 (10) | 4352 (8) | 3078 (12) | 108 (5) |
| C(30) | −349 (10) | 3976 (7) | 2768 (11) | 97 (4) |
| C(31) | −592 (10) | 3428 (7) | 1773 (12) | 100 (5) |
| C(32) | 90 (7) | 3234 (6) | 958 (9) | 65 (3) |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

**Table VI. Atomic Coordinates (×10$^4$) and Isotropic Thermal Parameters (Å$^2$ × 10$^3$) with Esd's in Parentheses for the Non-Hydrogen Atoms of the Cation of 1**

| | *x/a* | *y/b* | *z/c* | *U* |
|---|---|---|---|---|
| P(3) | 6555 (2) | 2895 (1) | 3769 (2) | 39 (1)[a] |
| P(4) | 7598 (2) | 2728 (1) | 5787 (2) | 41 (1)[a] |
| N(1) | 7373 (5) | 2745 (4) | 4515 (6) | 44 (3)[a] |
| C(33) | 6742 (6) | 2454 (5) | 2296 (7) | 41 (2) |
| C(34) | 6204 (8) | 2589 (6) | 1434 (10) | 79 (4) |
| C(35) | 6333 (9) | 2236 (7) | 279 (11) | 100 (4) |
| C(36) | 6984 (8) | 1768 (6) | 15 (11) | 84 (4) |
| C(37) | 7528 (8) | 1633 (6) | 822 (10) | 84 (4) |
| C(38) | 7399 (7) | 1972 (6) | 2007 (9) | 66 (3) |
| C(39) | 5444 (6) | 2540 (5) | 4063 (8) | 44 (3) |
| C(40) | 5015 (7) | 1835 (5) | 3387 (9) | 62 (3) |
| C(41) | 4183 (8) | 1551 (7) | 3683 (10) | 87 (4) |
| C(42) | 3782 (8) | 1936 (6) | 4624 (10) | 82 (4) |
| C(43) | 4190 (7) | 2623 (6) | 5311 (9) | 65 (3) |
| C(44) | 5012 (6) | 2926 (5) | 5012 (8) | 50 (3) |
| C(45) | 6539 (6) | 3888 (5) | 3948 (7) | 42 (2) |
| C(46) | 5753 (7) | 4169 (5) | 3692 (8) | 59 (3) |
| C(47) | 5793 (7) | 4953 (6) | 3820 (9) | 70 (3) |
| C(48) | 6581 (8) | 5399 (7) | 4182 (9) | 80 (4) |
| C(49) | 7369 (8) | 5130 (6) | 4432 (9) | 76 (4) |
| C(50) | 7354 (7) | 4368 (6) | 4318 (8) | 62 (3) |
| C(51) | 8770 (6) | 3139 (5) | 6196 (8) | 44 (3) |
| C(52) | 9071 (7) | 3481 (5) | 7349 (9) | 63 (3) |
| C(53) | 9981 (8) | 3787 (6) | 7655 (10) | 73 (3) |
| C(54) | 10562 (8) | 3741 (6) | 6818 (9) | 70 (3) |
| C(55) | 10309 (8) | 3415 (6) | 5684 (10) | 77 (4) |
| C(56) | 9389 (7) | 3112 (5) | 5392 (9) | 59 (3) |
| C(57) | 7490 (6) | 1784 (5) | 5878 (8) | 45 (3) |
| C(58) | 7898 (7) | 1611 (6) | 6795 (9) | 62 (3) |
| C(59) | 7787 (7) | 882 (6) | 6867 (10) | 73 (3) |
| C(60) | 7234 (8) | 335 (7) | 6050 (10) | 81 (4) |
| C(61) | 6800 (8) | 487 (7) | 5150 (10) | 85 (4) |
| C(62) | 6927 (7) | 1218 (6) | 5051 (9) | 72 (3) |
| C(63) | 6900 (6) | 3249 (5) | 6843 (7) | 44 (3) |
| C(64) | 6971 (6) | 4034 (5) | 7050 (8) | 51 (3) |
| C(65) | 6380 (7) | 4452 (6) | 7794 (8) | 62 (3) |
| C(66) | 5729 (7) | 4099 (6) | 8286 (9) | 67 (3) |
| C(67) | 5657 (8) | 3332 (6) | 8102 (9) | 77 (4) |
| C(68) | 6244 (7) | 2902 (6) | 7364 (8) | 67 (3) |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

same edge but through one of the phenyl rings is involved in an orthometalation with the Ru(3) atom [Ru(3)–C(39) = 2.166 (7) Å]. The Ru(1)–P(3)–Ru(2) bridge is symmetrical [Ru(1)–P(3) = 2.350 (2) and Ru(2)–P(3) = 2.362 (2) Å] and forms a dihedral angle of 88.5 (6)° with the Ru triangle. The phosphinidene ligand is bonded to all four metal atoms, as through the C(38)–C(39) bond of the orthometalated ring it is also involved in a $\pi$ interaction with the Rh atom [Rh–C(38) = 2.569 (6) and Rh–C(39) = 2.315 (6) Å]. By considering the short Rh–P(3) distance, 2.840 (2) Å, the delocalized double bonds of the orthometalated ring could be extended also to the P(3)–C(38) bond, so that a $\eta^3$ interaction of the phosphinidene ligand with the Rh atom can be envisaged. The Ru(2)–P(3)–C(38)–C(39)–Ru(3) and Ru(1)–P(3)–C(38)–C(39)–Ru(3) rings adopt "envelope" conformations at Ru(2), and Ru(1), respectively, which are −1.120 (1) and 1.775 (1) Å out from the mean plane through the other four atoms. The orthometalated ring forms an angle of 9.1 (2)° with the plane through P(3), C(38), C(39), and Ru(3), P(3), and Ru(3) deviating by 0.182 (2) and 0.378 (1) Å, respectively, from the ring plane.

Differently from **2**, the Ru$_3$Ir metal core of **3** is in a pseudotetrahedral arrangement, the Ru–Ru distances are 2.710 (1), 2.797 (1), and 2.818 (1) Å, and the Ru–Ir distances are 2.769 (1), 2.875 (1), and 2.963 (1) Å. Seven carbonyl groups are terminal, one bound to the Ir atom, two to each Ru atom; the eighth carbonyl nearly symmetrically bridges the Ru(1)–Ru(3) edge [Ru(1)–C(6) = 2.156 (9) Å and Ru(3)–C(6) = 2.223 (8) Å]. The two hydride ligands, H(1) and H(2), bridge the two Ru(1)–Ir and Ru(3)–Ir edges, respectively, and occupy cis positions [H(1)–Ir–H(2) = 94 (4)°] of the octahedral environment of Ir including also C(1), C(9), P(1), and Ru(2) [H(1) and H(2) deviate by 0.05 (8) and 0.22 (8) Å from the mean plane through Ir, C(1), C(9), H(1), and H(2)]. The Ir–H(1)–Ru(1) bridge forms angles of 163 (3) and 126 (4)° with the Ir–Ru(1)–Ru(2) and Ir–Ru(1)–Ru(3) faces, respectively; the Ir–H(2)–Ru(3) bridge forms angles of 151 (3) and 136 (3)° with the Ir–Ru(2)–Ru(3) and Ir–Ru(1)–Ru(3), respectively. The PPh$_3$ ligand is bonded to the Ir atom [Ir–P(1) = 2.329 (2) Å]. A phosphido ligand bridges slightly asymmetrically [Ru(2)–P(3) = 2.337 (2) and Ru(3)–P(3) = 2.281 (3) Å] the Ru(2)–Ru(3) edge and is almost coplanar with the Ru triangle, undergoing a remarkable rearrangement with respect to the starting cluster **1**. The second phosphido ligand symmetrically bridges [Ru(1)–P(2) = 2.295 (2) and Ru(2)–P(2) = 2.299 (2) Å] the same Ru(1)–Ru(2) edge of the starting cluster **1**, but now it is involved through one of the aromatic rings in the orthometalation with the Ir atom [Ir–C(9) = 2.086 (7) Å]. Also the Ru(1)–P(2)–Ru(2) phosphido bridge is almost coplanar

**Table VII. Fractional Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) with Esd's in Parentheses for the Non-Hydrogen Atoms of 2**

| | *x/a* | *y/b* | *z/c* | *U* | | *x/a* | *y/b* | *z/c* | *U* |
|---|---|---|---|---|---|---|---|---|---|
| Rh | 3260 (1) | 2283 (1) | 1710 (1) | 25.3 (1)[a] | C(27) | 4875 (6) | 1977 (3) | 5132 (7) | 45 (2) |
| Ru(1) | 528 (1) | 3212 (1) | 2287 (1) | 27.0 (2)[a] | C(28) | 5817 (7) | 1912 (4) | 6035 (7) | 54 (2) |
| Ru(2) | 1832 (1) | 2231 (1) | 3455 (1) | 26.1 (1)[a] | C(29) | 6171 (8) | 1356 (4) | 6408 (8) | 64 (2) |
| Ru(3) | 3166 (1) | 3355 (1) | 2348 (1) | 28.0 (1)[a] | C(30) | 5607 (8) | 870 (4) | 5880 (8) | 65 (2) |
| P(1) | 4168 (1) | 1880 (1) | 580 (1) | 29.1 (5)[a] | C(31) | 4682 (7) | 941 (4) | 4970 (7) | 49 (2) |
| P(2) | 3082 (1) | 1600 (1) | 3346 (1) | 27.6 (5)[a] | C(32) | 2420 (6) | 807 (3) | 3305 (6) | 36 (1) |
| P(3) | 946 (1) | 2450 (1) | 1431 (1) | 28.9 (5)[a] | C(33) | 1903 (7) | 488 (4) | 4267 (7) | 48 (2) |
| P(4) | 282 (1) | 3893 (1) | 3501 (2) | 31.9 (5)[a] | C(34) | 1392 (8) | −104 (4) | 4275 (8) | 60 (2) |
| O(1) | 5477 (4) | 2923 (2) | 2821 (5) | 49 (2)[a] | C(35) | 1378 (8) | −382 (4) | 3324 (8) | 62 (2) |
| O(2) | −1740 (4) | 2462 (3) | 2742 (5) | 58 (2)[a] | C(36) | 1877 (8) | −76 (4) | 2351 (8) | 62 (2) |
| O(3) | −403 (5) | 3950 (3) | −77 (5) | 74 (2)[a] | C(37) | 2397 (6) | 523 (3) | 2341 (7) | 45 (2) |
| O(4) | 2734 (6) | 2383 (3) | 6062 (5) | 67 (3)[a] | C(38) | 1701 (5) | 2770 (3) | 188 (6) | 32 (2)[a] |
| O(5) | −158 (6) | 1307 (3) | 4179 (7) | 87 (3)[a] | C(39) | 2736 (5) | 3159 (3) | 533 (6) | 32 (2)[a] |
| O(6) | 4398 (5) | 4592 (3) | 1479 (6) | 71 (3)[a] | C(40) | 3350 (6) | 3469 (3) | −397 (6) | 42 (3)[a] |
| O(7) | 3909 (6) | 3631 (3) | 4907 (5) | 66 (3)[a] | C(41) | 2909 (7) | 3417 (4) | −1589 (7) | 55 (3)[a] |
| C(1) | 4502 (5) | 2911 (3) | 2504 (6) | 33 (2)[a] | C(42) | 1900 (7) | 3041 (4) | −1893 (6) | 52 (3)[a] |
| C(2) | −902 (6) | 2753 (3) | 2549 (6) | 37 (2)[a] | C(43) | 1301 (7) | 2708 (4) | −1022 (6) | 46 (3)[a] |
| C(3) | −56 (6) | 3672 (3) | 806 (6) | 42 (2)[a] | C(44) | −267 (6) | 1922 (3) | 821 (6) | 35 (1) |
| C(4) | 2441 (6) | 2331 (3) | 5075 (6) | 41 (2)[a] | C(45) | −1225 (7) | 2129 (4) | 91 (7) | 48 (2) |
| C(5) | 610 (6) | 1647 (3) | 3916 (7) | 44 (3)[a] | C(46) | −2151 (8) | 1735 (4) | −360 (8) | 62 (2) |
| C(6) | 3916 (6) | 4127 (3) | 1784 (7) | 43 (2)[a] | C(47) | −2131 (8) | 1127 (4) | −87 (8) | 63 (2) |
| C(7) | 3596 (6) | 3517 (3) | 3968 (7) | 42 (3)[a] | C(48) | −1201 (8) | 911 (4) | 620 (8) | 65 (2) |
| C(8) | 3260 (6) | 1483 (3) | −597 (6) | 37 (1) | C(49) | −263 (7) | 1307 (3) | 1092 (7) | 47 (2) |
| C(9) | 3699 (6) | 1311 (3) | −1482 (6) | 42 (2) | C(50) | −330 (6) | 3550 (3) | 4851 (6) | 39 (2) |
| C(10) | 2992 (7) | 1008 (4) | −2354 (8) | 56 (2) | C(51) | −866 (7) | 3894 (4) | 5374 (8) | 58 (2) |
| C(11) | 1838 (8) | 876 (4) | −2334 (8) | 61 (2) | C(52) | −1368 (9) | 3631 (4) | 6388 (9) | 72 (3) |
| C(12) | 1377 (8) | 1039 (4) | −1453 (8) | 63 (2) | C(53) | −1404 (8) | 3026 (4) | 6850 (8) | 60 (2) |
| C(13) | 2081 (6) | 1345 (3) | −595 (7) | 42 (2) | C(54) | −859 (7) | 2693 (4) | 6331 (8) | 57 (2) |
| C(14) | 5148 (6) | 2451 (3) | −264 (6) | 36 (1) | C(55) | −345 (6) | 2943 (3) | 5344 (7) | 45 (2) |
| C(15) | 6126 (6) | 2738 (3) | 378 (7) | 46 (2) | C(56) | −803 (6) | 4359 (3) | 2696 (6) | 40 (2) |
| C(16) | 6827 (7) | 3217 (4) | −207 (8) | 57 (2) | C(57) | −589 (8) | 4968 (4) | 2319 (8) | 57 (2) |
| C(17) | 6562 (8) | 3400 (4) | −1407 (8) | 59 (2) | C(58) | −1476 (9) | 5270 (5) | 1657 (9) | 72 (3) |
| C(18) | 5612 (7) | 3131 (4) | −2061 (8) | 60 (2) | C(59) | −2530 (9) | 4967 (5) | 1400 (9) | 76 (3) |
| C(19) | 4881 (7) | 2649 (4) | −1491 (7) | 49 (2) | C(60) | −2768 (9) | 4371 (5) | 1779 (9) | 76 (3) |
| C(20) | 5095 (5) | 1323 (3) | 1387 (6) | 33 (1) | C(61) | −1922 (8) | 4057 (4) | 2452 (8) | 58 (2) |
| C(21) | 5893 (7) | 1481 (4) | 2390 (7) | 50 (2) | C(62) | 1543 (6) | 4429 (3) | 4011 (6) | 40 (2) |
| C(22) | 6621 (7) | 1072 (4) | 3030 (8) | 57 (2) | C(63) | 1897 (7) | 4486 (4) | 5205 (8) | 56 (2) |
| C(23) | 6531 (8) | 524 (4) | 2718 (8) | 60 (2) | C(64) | 2918 (9) | 4869 (5) | 5564 (10) | 78 (3) |
| C(24) | 5703 (8) | 357 (4) | 1754 (8) | 63 (2) | C(65) | 3521 (9) | 5191 (5) | 4676 (10) | 77 (3) |
| C(25) | 5004 (7) | 766 (4) | 1108 (7) | 51 (2) | C(66) | 3208 (8) | 5136 (4) | 3498 (8) | 64 (2) |
| C(26) | 4294 (5) | 1490 (3) | 4583 (6) | 33 (1) | C(67) | 2208 (7) | 4743 (4) | 3146 (8) | 53 (2) |

[a] Equivalent isotropic $U$ defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

with the Ru triangle. Differently from **2** the phosphinidene ligand does not interact with the fourth metal atom, Ru(3). The dihedral angle between the orthometalated ring and the Ir–C(9)–C(10)–P(2) plane is of 3.9 (2)° with Ir and P(2) −0.060 (1) and 0.134 (2) Å out from the ring plane, which is practically perpendicular to the Ir–Ru(1)–Ru(2) and Ru(1)–Ru(2)–Ru(3) faces. The Ir–C(9)–C(10)–P(2)–Ru(2) and Ir–C(9)–C(10)–P(2)–Ru(1) rings adopt "envelope" conformations at Ru(2) and Ru(1), respectively, which are 1.417 (1) and −1.389 (1) Å out from the plane through the other four atoms.

Both **2** and **3** give rise to six infrared absorptions in the region of terminal carbonyls, the bridging $\mu_2$-CO ligand is identified in **2** by a weak band at 1777 cm$^{-1}$; in **3** a band at 1900 cm$^{-1}$ suggests a "semibridging" character of a carbonyl ligand. In accordance with the X-ray structure determination the $^{31}P\{^1H\}$ NMR spectrum of **2** shows two double doublets of doublets $\{J(^{31}P–^{31}P) = 12$ Hz, $J(^{31}P–^{31}P) = 6$ Hz; $J(^{103}Rh–^{31}P) = 164$ Hz; $J(^{31}P–^{31}P) = 153$ Hz, $J(^{31}P–^{31}P) = 12$ Hz, $J(^{103}Rh–^{31}P) = 8$ Hz$\}$ for the two $\mu_2$-phosphorus nuclei, a doublet $\{J(^{31}P–^{31}P) = 153$ Hz$\}$ for the $PPh_3$ ligand bonded to Ru, and a double doublet $\{J(^{31}P–^{31}P) = 6$ Hz, $J(^{103}Rh–^{31}P) = 214$ Hz$\}$ for the $PPh_3$ ligand bonded to Rh; in the spectrum of **3** the resonances of the two $\mu_2$-phosphorus atoms appear as doublets $\{J(^{31}P–^{31}P) = 198$ Hz$\}$, whereas the $PPh_3$ ligand causes a singlet.

The positions of the two hydride ligands in **2** and **3** are assigned on the basis of the X-ray and the $^1H$ NMR data. For **2** two resonances are observed in the region of $\mu_2$-hydride ligands; the signals appear as multiplets due to the $^1H–^1H$, $^{31}P–^1H$, and $^{103}Rh–^1H$ couplings. Because of the $^1H–^1H$ couplings $\{J(^1H–^1H) = 6$ Hz$\}$ the two $\mu_2$-H ligands can be assumed to bridge two metal–metal bonds involving the same ruthenium atom. For **3**, the $^1H$ NMR spectrum shows two $\mu_2$-hydride signals, too; one exhibiting a double doublet multiplicity due to the coupling with two different P atoms $\{J(^{31}P–^1H) = 10$ Hz, $J(^{31}P–^1H) = 6.5$ Hz$\}$, the other appearing as a pseudoquartet caused by coupling with three phosphorus nuclei by very similar $^{31}P–^1H$ coupling constants $\{J(^{31}P–^1H) = 8$ Hz$\}$. A selective homospin decoupling experiment proves the two hydride resonances to be independent from another; the lack of $^1H–^1H$ coupling suggests that the hydride ligand bridging the Ir–Ru(3) bond in the solid state moves to the Ru(2)–Ru(3) edge in solution. Because of the $^{31}P–^1H$ coupling with $PPh_3$ ligand the double doublet at $\delta$ −14.90 is attributed to the hydride bridging the Ir–Ru(1) bond, and the pseudoquartet at $\delta$ −18.33 is assigned to the mobile one.

## Experimental Section

**General Techniques, Reagents, and Physical Measurements.** All reactions were carried out under an atmosphere of purified nitrogen. Solvents were distilled from drying agents and deoxygenated prior to use. Preparative thin-layer chromatography was performed using 20 × 20 cm plates coated with Merck silica gel 60 GF. $Na[HRu_3(CO)_{11}]$ was prepared by use of a published procedure;[7] other reagents were commercially available. Nuclear magnetic resonance spectra were taken on a Bruker WP 80, WP 200, and JEOL FX 90 Q spectrometer. A Perkin-Elmer 1720 instrument was used to record Fourier transformation infrared spectra. Microanalyses were performed using a Carlo Erba elemental analyzer 1106.

**Preparation of $[(PPh_3)_2N][HRu_3(CO)_8(PPh_2)_2]$.** A solution of 0.5 mmol of $Na[HRu_3(CO)_{11}]$, prepared from 320 mg (0.5 mmol) of $Ru_3(CO)_{12}$ and 80 mg (2.0 mmol) of $NaBH_4$ in 50 mL of THF, was combined with 0.15 mL (1.0 mmol) of $HPPh_2$ and stirred for 6 h at 20 °C. After removal of the solvent the residue, $Na[HRu_3(CO)_8(PPh_2)_2]$, was dissolved in 30 mL of methanol; addition of 210 mg (0.5 mmol) of $[(PPh_3)_2N]Cl$ caused the precipitation of $[(PPh_3)_2N][HRu_3(CO)_8(PPh_2)_2]$, isolated by decantation as a red powder. The product was recrystallized from a dichloromethane–ether solution and dried in vacuo to give dark red crystals, yield 561 mg (78%); IR ($\nu$(CO), cm$^{-1}$, $CH_3CN$) 2034 m, 1986 vs, 1964 vs (br), 1922 m (br), 1900 sh; $^1H$ NMR (+30 °C, $CD_3CN$) $\delta$ 6.23–8.15 (m, 50), −17.01 (t, 1, 22.3 Hz); $^{31}P$ NMR $\delta$ −30 °C, $CD_3CN$) 184.8 (d, 112 Hz), 160.5 (d, 112 Hz). Anal. Calcd for $C_{68}H_{51}NO_8P_4Ru_3$: C, 56.82; H, 3.58; N, 0.98. Found: C, 56.64; H, 3.48; N, 0.91.

**Preparation of $H_2Ru_3Rh(CO)_7(PPh_3)_2(PPh_2)(PPhC_6H_4)$ (2) and $H_2Ru_3Ir(CO)_8(PPh_3)(PPh_2)(PPhC_6H_4)$ (3).** A solution of 0.5 mmol of $(PPh_3)_3RhCl$ or of $(PPh_3)_2Ir(CO)Cl$, respectively, in 200 mL of $CH_2Cl_2$ was added to a solution of 0.5 mmol of $Na[HRu_3(CO)_8(PPh_2)_2]$, freshly prepared as described above, in 100 mL of dichloromethane. The mixture was stirred for 5 h (**2**) or 24 h (**3**), respectively. After removal of the solvent, the residue was dissolved in 10 mL of dichloromethane and separated by preparative thin-layer chromatography using $CH_2Cl_2$/cyclohexane (2:3) as the eluant. The products were extracted from the brown main band each with dichloromethane and recrystallized from $CH_2Cl_2$/pentane (**2** 1:2; **3** 1:1).

**2**: brown crystals, yield 315 mg (42%); IR ($\nu$(CO), cm$^{-1}$, $CH_2Cl_2$) 2037 m, 2019 vs, 1996 vs, 1980 sh, 1957 w, 1940 sh, 1777 w; $^1H$ NMR (+30 °C, $CDCl_3$) $\delta$ 6.20–7.92 (m, 49), −12.23 (m, 1), −16.64 (m, 1); $^{31}P$ NMR (+30 °C, $CDCl_3$) $\delta$ 192.5 (d, d, d, 164 Hz, 12 Hz, 6 Hz), 106.9 (d, d, d, 153 Hz, 12 Hz, 8 Hz), 35.1 (d, d; 215.6 Hz), 31.9 (d; 153 Hz). Anal. Calcd for $C_{67}H_{51}O_7P_4RhRu_3$: C, 53.71; H, 3.43. Found: C, 54.15; H, 3.70.

**3**: chocolate-brown crystals, yield 231 mg (35%); IR ($\nu$(CO), cm$^{-1}$, $CH_2Cl_2$) 2051 s, 2015 vs, 1994 s, 1963 sh, 1948 sh, 1919 sh, 1900 w (sh); $^1H$ NMR (+30 °C, $CDCl_3$) $\delta$ 6.20–7.89 (m,34), −14.90 (d, d, 1, 10 Hz, 6.5 Hz), −18.33 (q, 1, 8 Hz); $^{31}P$ NMR (+30 °C, $CDCl_3$) $\delta$ 303.5 (d, 195 Hz), 287.9 (d, 195 Hz), 1.25 (s). Anal. Calcd for $C_{50}H_{36}IrO_8P_3Ru_3$: C, 44.38; H, 2.68. Found: C, 45.16; H, 2.77.

**X-ray Data Collections, Structure Determinations, and Refinements for 1, 2, and 3.** Single crystals of the bis(triphenylphosphine)iminium salt of **1** were obtained by recrystallization from a dichloromethane–diethyl ether mixture. Single crystals of **2** and **3** were obtained by recrystallization from dichloromethane–pentane mixtures. The crystallographic data are summarized in Table IV. Unit cell parameters were determined from the $\theta$ values of 30 carefully centered reflections having $9 < \theta < 15°$ (**1**), $21 < \theta < 39°$ (**2**), and $11 < \theta < 17°$ (**3**). Data were collected at room temperature, the individual profiles having been analyzed following Lehmann and Larsen.[8] The structure amplitudes were obtained after the usual Lorentz and polarization reduction.[9] A correction for absorption was applied to **2** and **3** (maximum and minimum values for the transmission factors were 1.1537 and 0.8973 for **2**, 1.216 and 1.000 for **3**).[10] Only the observed reflections were used in the structure solution and refinement.

**Table VIII. Fractional Atomic Coordinates (×10$^4$) and Isotropic Thermal Parameters (Å$^2$ × 10$^3$) with Esd's in Parentheses for the Non-Hydrogen Atoms of 3**

| | *x/a* | *y/b* | *z/c* | *U* |
|---|---|---|---|---|
| Ir | 1932 (1) | 694 (1) | 2532 (1) | 29.1 (1)[a] |
| Ru(1) | 3417 (1) | 738 (1) | 3354 (1) | 33.1 (2)[a] |
| Ru(2) | 2880 (1) | 152 (1) | 1491 (1) | 34.5 (2)[a] |
| Ru(3) | 2951 (1) | 1667 (1) | 1849 (1) | 35.9 (2)[a] |
| P(1) | 1269 (1) | 1331 (1) | 3460 (1) | 33.0 (6)[a] |
| P(2) | 3132 (1) | −464 (1) | 2951 (1) | 34.0 (6)[a] |
| P(3) | 2501 (1) | 1110 (1) | 398 (1) | 36.6 (6)[a] |
| O(1) | 787 (3) | 135 (3) | 909 (4) | 55 (2)[a] |
| O(2) | 3753 (3) | 603 (4) | 5553 (4) | 78 (3)[a] |
| O(3) | 4925 (3) | 429 (4) | 3261 (5) | 87 (3)[a] |
| O(4) | 1978 (4) | −1061 (4) | 411 (5) | 89 (3)[a] |
| O(5) | 4268 (3) | −179 (5) | 936 (5) | 103 (4)[a] |
| O(6) | 3692 (3) | 2405 (3) | 3857 (4) | 72 (2)[a] |
| O(7) | 2468 (3) | 3234 (3) | 1375 (5) | 73 (3)[a] |
| O(8) | 4315 (3) | 1917 (4) | 1208 (4) | 80 (3)[a] |
| C(1) | 1229 (4) | 381 (4) | 1478 (5) | 40 (3)[a] |
| C(2) | 3628 (4) | 661 (4) | 4752 (6) | 50 (3)[a] |
| C(3) | 4362 (4) | 578 (4) | 3275 (6) | 52 (3)[a] |
| C(4) | 2321 (4) | −601 (4) | 810 (5) | 49 (3)[a] |
| C(5) | 3748 (4) | −38 (5) | 1114 (5) | 56 (3)[a] |
| C(6) | 3481 (4) | 1923 (5) | 3373 (6) | 54 (3)[a] |
| C(7) | 2645 (4) | 2644 (4) | 1567 (5) | 49 (3)[a] |
| C(8) | 3805 (4) | 1828 (4) | 1473 (5) | 49 (3)[a] |
| C(9) | 1791 (3) | −336 (4) | 3116 (4) | 34 (2)[a] |
| C(10) | 2371 (3) | −816 (4) | 3340 (5) | 35 (2)[a] |
| C(11) | 2330 (4) | −1506 (4) | 3752 (5) | 41 (3)[a] |
| C(12) | 1694 (4) | −1735 (4) | 3956 (6) | 50 (3)[a] |
| C(13) | 1111 (4) | −1279 (4) | 3740 (5) | 49 (3)[a] |
| C(14) | 1153 (4) | −597 (4) | 3318 (5) | 42 (3)[a] |
| C(15) | 320 (4) | 1151 (4) | 3171 (5) | 41 (2) |
| C(16) | −42 (4) | 1208 (4) | 2224 (5) | 47 (2) |
| C(17) | −769 (4) | 1066 (5) | 1982 (6) | 60 (2) |
| C(18) | −1110 (5) | 859 (5) | 2694 (7) | 69 (3) |
| C(19) | −763 (5) | 772 (5) | 3633 (7) | 72 (3) |
| C(20) | −39 (4) | 930 (4) | 3890 (6) | 56 (2) |
| C(21) | 1526 (4) | 1211 (4) | 4772 (5) | 40 (2) |
| C(22) | 1293 (4) | 1713 (5) | 5394 (6) | 62 (2) |
| C(23) | 1476 (5) | 1635 (5) | 6386 (7) | 69 (3) |
| C(24) | 1922 (4) | 1066 (5) | 6781 (6) | 58 (2) |
| C(25) | 2138 (4) | 561 (5) | 6173 (6) | 58 (2) |
| C(26) | 1945 (4) | 633 (4) | 5185 (5) | 44 (2) |
| C(27) | 1334 (3) | 2325 (4) | 3327 (5) | 39 (2) |
| C(28) | 1938 (4) | 2677 (4) | 3818 (6) | 53 (2) |
| C(29) | 2040 (5) | 3425 (5) | 3678 (6) | 65 (2) |
| C(30) | 1561 (4) | 3821 (5) | 3023 (6) | 66 (2) |
| C(31) | 968 (5) | 3474 (5) | 2499 (6) | 64 (2) |
| C(32) | 846 (4) | 2725 (5) | 2667 (6) | 57 (2) |
| C(33) | 3837 (4) | −1132 (4) | 3325 (5) | 45 (2) |
| C(34) | 4138 (4) | −1194 (4) | 4301 (5) | 50 (2) |
| C(35) | 4719 (4) | −1655 (5) | 4623 (7) | 66 (2) |
| C(36) | 4986 (5) | −2021 (5) | 3926 (7) | 76 (3) |
| C(37) | 4695 (5) | −1974 (5) | 2977 (7) | 74 (3) |
| C(38) | 4099 (4) | −1519 (5) | 2639 (6) | 62 (2) |
| C(39) | 1582 (3) | 1288 (4) | −190 (5) | 39 (2) |
| C(40) | 1179 (4) | 1826 (4) | 96 (6) | 54 (2) |
| C(41) | 472 (5) | 1907 (5) | −355 (6) | 67 (3) |
| C(42) | 187 (5) | 1447 (5) | −1111 (7) | 70 (3) |
| C(43) | 578 (5) | 916 (5) | −1436 (7) | 68 (3) |
| C(44) | 1278 (4) | 826 (4) | −948 (6) | 52 (2) |
| C(45) | 2941 (4) | 1313 (4) | −585 (5) | 48 (2) |
| C(46) | 3305 (5) | 788 (5) | −972 (7) | 68 (3) |
| C(47) | 3678 (5) | 988 (6) | −1728 (8) | 86 (3) |
| C(48) | 3643 (6) | 1694 (6) | −2025 (8) | 93 (3) |
| C(49) | 3264 (5) | 2214 (6) | −1683 (8) | 90 (3) |
| C(50) | 2909 (5) | 2022 (5) | −941 (7) | 70 (3) |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The structures were solved by direct and Fourier methods and refined first by full-matrix least-squares with isotropic thermal parameters and then by blocked (**1**) and full-matrix (**2** and **3**) least-squares analysis with anisotropic thermal parameters. The hydrides in all three compounds were clearly localized in the final difference Fourier maps and refined isotropically; all other hy-

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(7) Süss-Fink, G. *Inorg. Synth.* **1986**, *24*, 168–169.

(8) Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr. Theor. Gen. Crystallogr.* **1974**, *A30*, 580–584.

(9) Data reduction, structure solution, and refinement were performed on the Cray X-MP/12 and X-MP/48 computers of the "Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale" (CINECA, Casalecchio Bologna) and on the GOULD POWERNODE 6040 of the "Centro di Studio per la Strutturistica Diffrattometrica" del C.N.R., Parma, using the SHELX-76 system of crystallographic computer programs (Sheldrick, G. M. Program for crystal structure determination; University of Cambridge, England, 1976).

(10) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1983**, *39*, 158–166. Ugozzoli, F. *Comput. Chem.* **1987**, *11*, 109–120.

drogen atoms were placed at their geometrically calculated positions (C-H = 1.00 Å) and refined "riding" on the corresponding carbon atoms. The final cycles of refinement were carried out on the basis of 463 (1), 478 (2), and 418 (3) variables; after the last cycles, no parameters shifted by more than 0.86 (1), 0.50 (2), and 0.81 (3) esd. The biggest remaining peaks in the final difference maps were equivalent to about 0.52 (1), 0.97 (2), and 0.81 (3) e/Å$^3$. In the final cycles of refinement a weighting scheme, $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$, was used; at convergence the $K$ values were 0.335 (1), 0.544 (2), and 0.366 (3), and the $g$ values 0.0013 (1), 0.0033 (2), 0.0018 (3). The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref 11. The final atomic coordinates for the non hydrogen atoms are given in Tables V (anion 1), VI (cation 1), VII (2), and VIII (3). The atomic coordinates of the hydrogen atoms are given in Tables SI (1), SII (2), SIII (3); the thermal parameters in Tables SIV and SV (1), SVI (2), and SVII (3) (see supplementary material paragraph).

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**Registry No.** [$(PPh_3)_2N$][**1**], 126294-88-0; Na[**1**], 126294-91-5; **2**, 126294-89-1; **3**, 126294-90-4; Na[$HRu_3(CO)_{11}$], 71936-71-5; $Ru_3(CO)_{12}$, 15243-33-1; $(PPh_3)_3RhCl$, 14694-95-2; $(PPh_3)_2Ir(CO)Cl$, 14871-41-1; Ru, 7440-18-8; Ir, 7439-88-5; Rh, 7440-16-6.

**Supplementary Material Available:** Tables SI, SII, and SIII (atomic coordinates and isotropic thermal parameters for the hydrogen atoms) and Tables SIV, SV, SVI and SVII (thermal parameters for the non-hydrogen atoms) (113 pages); tables of observed and calculated structure factors (108 pages). Ordering information is given on any current masthead page.

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(11) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

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# Reactivity Patterns for Multisite-Bound Acetylides. Nucleophilic Attack at the α-Carbon in $\mu_2$-$\eta^2$-Acetylides. Bridging 2-Amino-1-metallaphenethylidene Complexes via Addition of Primary Amines to $M_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)$ (M = Fe, Ru, Os)

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The binuclear σ–π-acetylides $M_2(CO)_6(\mu_2\text{-}\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)$ (**1a**, M = Fe; **1b**, M = Ru; **1c**, M = Os) react with cyclohexylamine to form the two-carbon-bridged iminium complexes $M_2(CO)_6[\mu_2\text{-}C\{NHR\}CH(Ph)](\mu\text{-}PPh_2)$ (**3a–c**, R = c-$C_6H_{11}$) in all three cases by attack at the α-carbon of the acetylide of **1** and proton transfer across the acetylide triple bond. The new ligands in **3a–c** are 2-(cyclohexylamino)-1-metallaphenethylidene derivatives with a carbene-like carbon atom coordinated to one metal and an sp$^3$ carbon atom, derived from $C_\beta$ of the acetylide attached to the second metal. Analogous complexes $M_2(CO)_6[\mu_2\text{-}C\{NH(i\text{-}Pr)\}CH(Ph)](\mu\text{-}PPh_2)$ (M = Ru, **5b**; M = Os, **5c**) have been characterized from the reactions of **1b** and **1c** with isopropylamine. Complex **1a** only also forms the product of β-acetylide addition $M_2(CO)_6[\mu_2\text{-}CHC(NRH)Ph](\mu\text{-}PPh_2)$. The entire triad of two-carbon-bridged products from **1a–c** with cyclohexylamine, $M_2(CO)_6[\mu_2\text{-}C\{NH(Cy)\}CH(Ph)](\mu\text{-}PPh_2)$ (**3a–c**), have been characterized by IR and $^1$H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy and by single-crystal X-ray diffraction. Crystals of **3b**,**c** are monoclinic space group $P2_1/c$ with the following unit cell dimensions: **3b**, $a$ = 10.076 (3), $b$ = 17.290 (4), $c$ = 20.807 (4) Å, $\beta$ = 102.18 (2)°, $Z$ = 4; **3c**, $a$ = 10.164 (2), $b$ = 17.126 (5), $c$ = 20.691 (5) Å, $\beta$ = 99.44 (2)°, $Z$ = 4. The two structures were solved by the heavy-atom method and refined to the following $R$ and $R_w$ values: **3b**, $R$ = 0.030, $R_w$ = 0.035 on 4372 observed diffractometer data; **3c**, $R$ = 0.035, $R_w$ = 0.038 on 4051 observed data. Comparison with the structure of **3a** determined earlier shows that all three molecules are isostructural, with M–M bond lengths of 2.628 (1) Å for **3a**, 2.7896 (4) Å for **3b**, and 2.8197 (5) Å for **3c**. Changes in the metal–hydrocarbyl interactions down the triad are discussed.

## Introduction

As a $C_2$ hydrocarbyl with the highest degree of unsaturation and unsurpassed versatility as a bridging ligand, the alkynyl or acetylide ligand continues to attract attention.[1] Mononuclear $\eta^1$-acetylides have been shown to react with electrophiles at the β-carbon atom to form vinylidenes that can, in turn, be converted to other hydrocarbyls.[2] Theoretical calculations by Kostic and Fenske[3] suggest that this sequence of reactions has components of orbital and charge control. The reactivity of $\mu_3$-$\eta^2$-acetylides toward nucleophiles, which has been studied extensively by Deeming and co-workers[4] and ourselves,[5] is dominated by attack at $C_\alpha$ although reaction at $C_\beta$ has been observed.[4a] Semiempirical CNDO calculations by Grannozzi et al.[6] have indicated that the regiospecificity of these reactions is charge controlled.

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