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Synthesis and Reactivity of $[PPh_4][MRu_3Cp(CO)_{12}]$ Clusters (M = Mo, W)

Martine Cazanoue, Noël Lugan, Jean-Jacques Bonnet, and René Mathieu*

Laboratoire de Chimie de Coordination du CNRS, Unité No. 8241 liée par convention à l'Université Paul Sabatier, 205, route de Narbonne, 31077 Toulouse Cedex, France

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The clusters $[PPh_4][MRu_3Cp(CO)_{12}]$ (**1a**, M = Mo; **1b**, M = W) have been synthesized in 70–75% yield by the reaction of $[PPh_4][MCp(CO)_3]$ with $Ru_3(CO)_{12}$ in boiling THF. The structure of **1a** has been established: monoclinic; space group C_{2h}^5—$P2_1/c$; a = 12.427 (2) Å, b = 13.637 (4) Å, c = 23.811 (4) Å; β = 86.02 (1)°; Z = 4. The reactivity of **1a**,**b** toward H^+, H_2, and alkynes has been studied. The unstable complexes $(\mu\text{-}H)MRu_3Cp(CO)_{12}$ (**2a**, M = Mo; **2b**, M = W) have been obtained by protonation. Molecular hydrogen reacts with **1a**,**b** in boiling THF to give $[PPh_4][(\mu\text{-}H)_2MRu_3Cp(CO)_{11}]$ (**3a**, M = Mo; **3b**, M = W) in good yield. They are fluxional on the NMR time scale. The alkynes MeC≡CMe or PhC≡CH react with **1a**,**b** in boiling THF to give respectively $[PPh_4][MRu_3Cp(CO)_{10}(\mu_4\text{-}\eta^2\text{-}MeC{\equiv}CMe)]$ (**4a**, M = Mo; **4b**, M = W) and $[PPh_4][MRu_3Cp(CO)_{10}(\mu_4\text{-}\eta^2\text{-}PhC{\equiv}CH)]$ (**5a**, M = Mo; **5b**, M = W). The structure of **4b** has been determined at −150 °C: triclinic; space group C_i^1—$P1$; a = 14.035 (2) Å, b = 14.818 (5) Å, c = 10.311 (3) Å; α = 98.70 (3)°, β = 108.48 (3)°, γ = 86.65 (2)°; Z = 2. It consists of a butterfly arrangement of metal atoms, the tungsten atom being on the hinge and the alkyne being $\mu_4\text{-}\eta^2$ bonded. Compounds **3a**,**b** react also with an excess of the same alkynes affording respectively **4a**,**b** and **5a**,**b** and the corresponding alkenes.

Introduction

Mixed tetranuclear clusters are now very numerous,[1,2] and quite general routes to the synthesis are known.[1,3] In this class of compounds those containing both group 6 and group 8 metals are of particular interest since such metals can have quite different properties, e.g. oxophilicity for a group 6 metal and hydrogen activation ability for a group 8 metal.

Several examples of associating molybdenum or tungsten with osmium are known.[4a-g] To our knowledge, no similar clusters containing ruthenium are known ($HRu_3WCp(CO)_{12}$ was briefly mentioned,[4a] but no further details were published later), and such compounds could have a different reactivity due to weaker Ru–Ru bonds.

In this paper, we present an easy synthesis of the clusters $[PPh_4][MRu_3Cp(CO)_{12}]$ (M = Mo, W) and the study of their reactivity toward acids, molecular hydrogen, and alkynes.

Results and Discussion

Synthesis of the $[PPh_4][MRu_3Cp(CO)_{12}]$ Clusters (M = Mo, W). We have retained the same strategy as that used for the synthesis of $[PPN][CoRu_3(CO)_{12}]$.[5] $Ru_3(CO)_{12}$ reacts readily with $[PPh_4][CpM(CO)_3]$ (M = Mo, W) complexes in boiling tetrahydrofuran to give a dark red solution from which the $[PPh_4][MRu_3Cp(CO)_{12}]$ clusters (**1a**, M = Mo; **1b**, M = W) have been isolated in 70–75% yield.

The same route failed when M = Cr, and only cluster anions of ruthenium were detected. We did not attempt to fully identify them, but proton NMR evidence suggested formation of $[HRu_3(CO)_{11}]^-$ and $[H_3Ru_4(CO)_{12}]^-$ (δ −12.37 and −16.88 for the hydride resonances). No evidence for formation of $[CpCr(CO)_3]_2$ was obtained. It has to be pointed out that reaction of $Ru_3(CO)_{12}$ with $[Mn(CO)_5]^-$ in boiling tetrahydrofuran leads to the formation of $[Ru_6(CO)_{18}]^{2-}$; in this reaction, the intermediate formation of $[HRu_3(CO)_{11}]^-$ was suggested[6] and later demonstrated.[7]

Since hydrogen in some cases[4g,8] may enhance formation of clusters, we have run the same reactions under an hydrogen atmosphere. In every cases (M = Cr, Mo, W), only $[HRu_3(CO)_{11}]^-$ was detected.

The infrared spectra of **1a** and **1b** in solution are very similar in the ν(CO) stretching region, suggesting similar structures, while the proton NMR spectra suggest the presence of one cyclopentadienyl ligand per tetraphenylphosphonium cation.

The precise structure of the clusters was established by an X-ray diffraction study of **1a**. An ORTEP plot of the anionic part of **1a** is shown in Figure 1, and bond distances and angles of interest are gathered in Table I.

The metal framework consists of a tetrahedron in which the Ru_3 triangle is nearly equilateral. The molybdenum atom is assymetrically bonded to this triangle, the Mo(1)–Ru(1) distance being longer than the other two. It is surrounded by the cyclopentadienyl ligand and three carbonyl groups of the semibridging type. The distance from Mo to the plane of the C_5H_5 ring is 1.978 (1) Å. Each ruthenium atom is bonded to three terminal carbonyl groups and interacts with one of the three semibridging carbonyl groups. The structure of **1a** provides a further example in which the $CpM(CO)_3^-$ fragment can be con-

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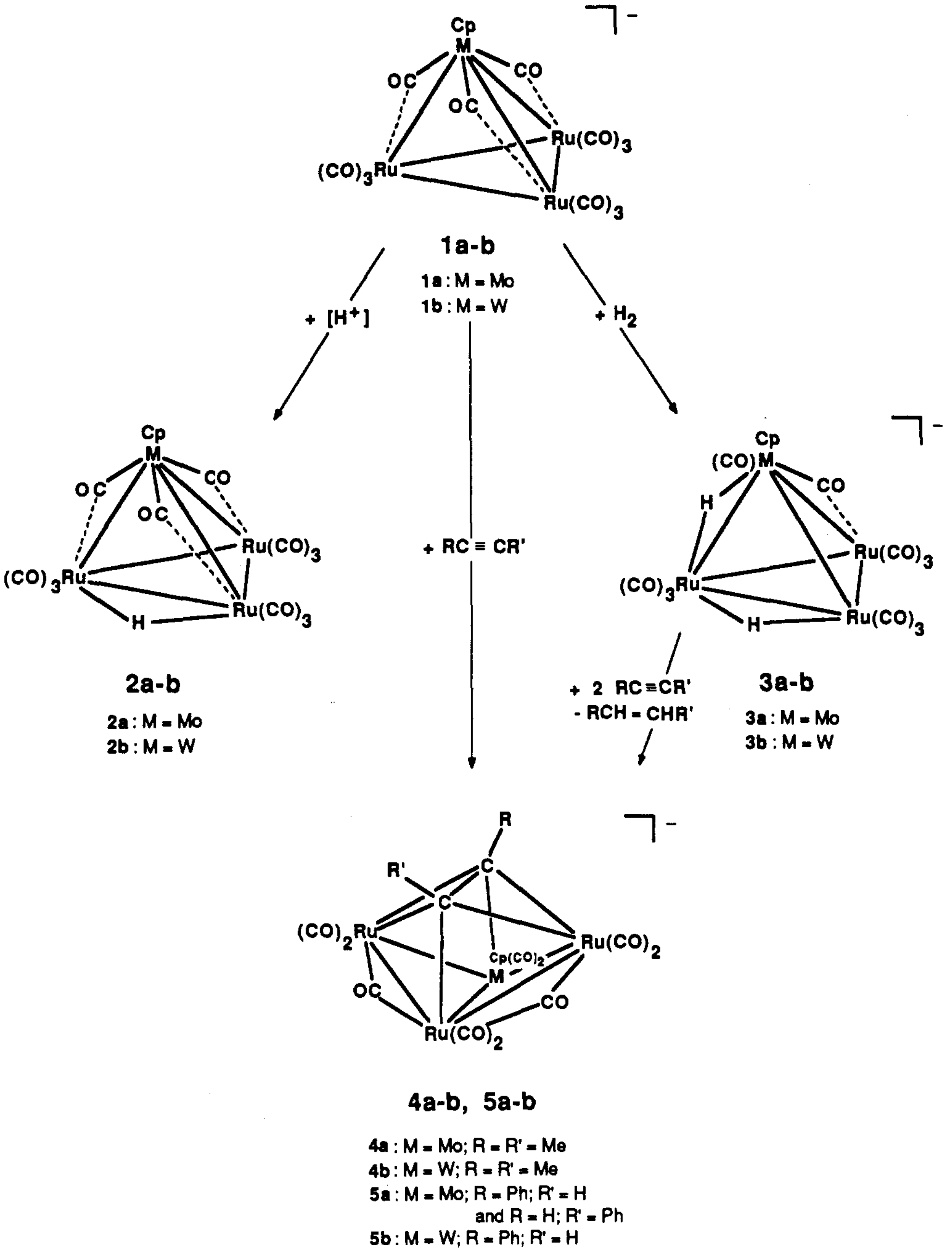
Scheme I



sidered as a six-electron ligand.[9-11] Moreover, the balance of charge is provided by the semibridging carbonyl ligands in agreement with theoretical predictions which show that in the CpM(CO)$_3^-$ fragment, the wave functions that are available for bonding to other fragments involve not only the metal fragment but also the carbonyl C atoms.[10]

Study of the Reactivity of 1a,b. To compare the reactivity of **1a,b** with that of the isoelectronic cluster HOs$_3$WCp(CO)$_{12}$,[4c] we have studied reactions with H$^+$, H$_2$, and alkynes. The results are summarized in Scheme I.

Reactivity toward Proton. Compounds **1a,b** in dichloromethane solution are protonated by trifluoroacetic acid. Crystallization in hexane gives red crystals of **2a** (M = Mo) and **2b** (M = W), which are not very stable, de-

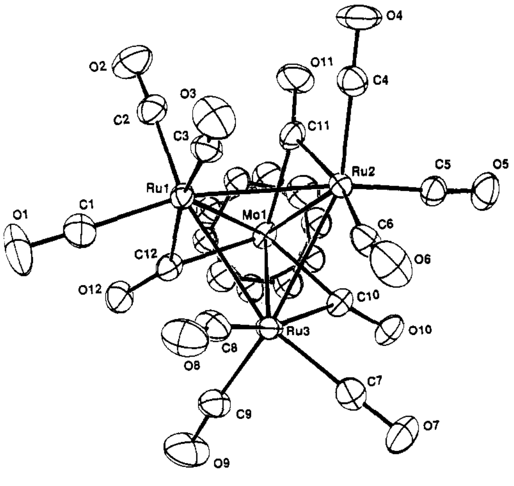


Figure 1. Perspective view of the anionic part of the complex [PPh$_4$][MoRu$_3$Cp(CO)$_{12}$] (**1a**). Vibrational ellipsoids are drawn at the 30% probability level.

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Table I. Bond Distances (Å) and Bond Angles (deg) of Interest for 1a with Esd's in Parentheses

	Bond Distances		
Mo(1)–Ru(1)	2.905 (1)	Ru(3)–C(10)	2.299 (8)
Mo(1)–Ru(2)	2.884 (1)	Mo(1)–C(10)	2.025 (7)
Mo(1)–Ru(3)	2.891 (1)	Mo(1)–C(11)	2.057 (7)
Ru(1)–Ru(2)	2.826 (1)	Mo(1)–C(12)	2.050 (7)
Ru(1)–Ru(3)	2.821 (1)	C(1)–O(1)	1.13 (1)
Ru(2)–Ru(3)	2.823 (1)	C(2)–O(2)	1.14 (1)
Ru(1)–C(1)	1.970 (8)	C(3)–O(3)	1.14 (1)
Ru(1)–C(2)	1.890 (8)	C(4)–O(4)	1.13 (1)
Ru(1)–C(3)	1.912 (7)	C(5)–O(5)	1.13 (1)
Ru(1)–C(12)	2.206 (7)	C(6)–O(6)	1.14 (1)
Ru(2)–C(4)	1.897 (7)	C(7)–O(7)	1.14 (1)
Ru(2)–C(5)	1.904 (8)	C(8)–O(8)	1.14 (1)
Ru(2)–C(6)	1.915 (8)	C(9)–O(9)	1.15 (1)
Ru(2)–C(11)	2.213 (8)	C(10)–O(10)	1.18 (1)
Ru(3)–C(7)	1.893 (8)	C(11)–O(11)	1.18 (1)
Ru(3)–C(8)	1.866 (8)	C(12)–O(12)	1.19 (1)
Ru(3)–C(9)	1.910 (9)		
Mo(1)–(η-C_5H_5) Are in the Range 2.31(3)–2.35(3)			
	Bond Angles		
Ru(1)–Mo(1)–Ru(2)	58.43 (2)	C(4)–Ru(2)–C(11)	84.2 (3)
Ru(1)–Mo(1)–Ru(3)	58.24 (2)	C(5)–Ru(2)–C(6)	96.8 (3)
Ru(2)–Mo(1)–Ru(3)	58.52 (2)	C(5)–Ru(2)–C(11)	94.0 (3)
Mo(1)–Ru(1)–Ru(2)	60.40 (2)	C(6)–Ru(2)–C(11)	168.6 (3)
Mo(1)–Ru(1)–Ru(3)	60.63 (2)	C(7)–Ru(3)–C(8)	91.1 (3)
Ru(2)—Ru(1)–Ru(3)	59.99 (2)	C(7)–Ru(3)–C(9)	101.3 (3)
Mo(1)–Ru(2)–Ru(1)	61.16 (2)	C(7)–Ru(3)–C(10)	81.2 (3)
Mo(1)–Ru(2)–Ru(3)	60.87 (2)	C(8)–Ru(3)–C(9)	95.9 (4)
Ru(1)–Ru(2)–Ru(3)	59.92 (2)	C(8)–Ru(3)–C(10)	99.4 (3)
Mo(1)–Ru(3)–Ru(2)	60.61 (2)	C(9)–Ru(3)–C(10)	164.5 (3)
Mo(1)–Ru(3)–Ru(1)	61.13 (2)	Ru(1)–C(1)–O(1)	178.4 (7)
Ru(1)–Ru(3)–Ru(2)	60.09 (2)	Ru(1)–C(2)–O(2)	177.0 (7)
Mo(1)–C(10)–Ru(3)	83.6 (3)	Ru(1)–C(3)–O(3)	172.3 (7)
Mo(1)–C(11)–Ru(2)	84.9 (3)	Ru(1)–C(12)–O(12)	129.9 (6)
Mo(1)–C(12)–Ru(1)	86.0 (3)	Ru(2)–C(4)–O(4)	178.5 (6)
C(1)–Ru(1)–C(2)	94.9 (3)	Ru(2)–C(5)–O(5)	176.4 (7)
C(1)–Ru(1)–C(3)	97.7 (3)	Ru(2)–C(6)–O(6)	168.0 (6)
C(1)–Ru(1)–C(12)	82.3 (3)	Ru(2)–C(11)–O(11)	129.6 (6)
C(2)–Ru(1)–C(3)	97.3 (3)	Ru(3)–C(7)–O(7)	180 (2)
C(2)–Ru(1)–C(12)	97.7 (3)	Ru(3)–C(8)–O(8)	176.2 (7)
C(3)–Ru(1)–C(12)	165.0 (3)	Ru(3)–C(9)–O(9)	166.8 (7)
C(4)–Ru(2)–C(5)	95.1 (3)	Ru(3)–C(10)–O(10)	127.9 (6)
C(4)–Ru(2)–C(6)	98.3 (3)	Mo(1)–C(10)–O(10)	148.1 (6)
		Mo(1)–C(11)–O(11)	145.2 (6)
		Mo(1)–C(12)–O(12)	143.3 (6)

composing slowly even under inert atmosphere. Both compounds have similar infrared spectra in the ν(CO) stretching region. In addition to absorptions for terminal carbonyl groups, a weak and broad absorption near 1930 cm^{-1} suggests the presence of semibridging carbonyl groups.

In the proton NMR spectrum two signals are observed in a 1:5 ratio in the area of hydride and cyclopentadienyl resonances. Moreover, in the case of **2b**, no coupling to ^{183}W was observed in the hydride signal.

Analytical data are consistent with the (μ-H)$MRu_3Cp(CO)_{12}$ formulation for **2a**,**b**. All data are in agreement with a structure similar to that of (μ-H)$WOs_3Cp(CO)_{12}$: the hydride ligand would be in bridging position between two Ru atoms and one or more carbonyl groups would be in semibridging position between the M–Ru bonds.

Reactivity toward Hydrogen. Compounds **1a**,**b** react slowly at room temperature and atmospheric pressure with molecular hydrogen. The reaction is cleaner and faster in boiling tetrahydrofuran to give red **3a** (M = Mo) and **3b** (M = W) in nearly quantitative yield after crystallization. The reaction is not reversible, and heating **3a**,**b** under CO atmosphere has no effect.

Compounds **3a** and **3b** have similar infrared spectra in the ν(CO) stretching region with bands for both terminal and bridging or semibridging carbonyl groups.

In proton NMR spectra at room temperature, resonances of the $[Ph_4]^+$ cation and the cyclopentadienyl and hydride ligands are observed in a 20:5:2 ratio of intensity. Moreover, in the case of **3b**, coupling with the ^{183}W isotope is observed in the hydride resonance.

The chemical analysis is an agreement with the $[PPh_4][(\mu\text{-H})_2MRu_3(CO)_{11}]$ formulation for **3a**,**b**.

All these data suggest for **3a**,**b** a structure analogous to that of the isoelectronic (μ-H)$_3MOs_3Cp(CO)_{11}$ complexes (M = W,[4a] Mo[4g]). Moreover, the observation of only one resonance for the hydride ligands at room temperature suggests (as observed for the osmium analogues) fluxionality of the hydride ligands in **3a**,**b**. The low-temperature (178 K) ^{1}H NMR spectrum of **3a** shows only a slight broadening of the hydride resonance. So it is difficult to decide between very fast exchange and a static molecule in which the two hydride ligands are in equivalent positions (either Ru–Ru or Ru–Mo edges).

In the case of **3b**, low-temperature ^{1}H NMR spectra are more informative. The slow-exchange limit was not reached, but at 188 K a very large resonance was observed which became, upon lowering the temperature to 178 K, two broad signals centered at −15.25 and −17.25 ppm in a 1:1 ratio. The cyclopentadienyl ligand signal remained unchanged at all temperatures.

A similar phenomenon was observed for (μ-H)$_3MoOs_3Cp(CO)_{11}$,[4g] and the slow-exchange-limit proton NMR spectrum for the hydride ligands was in accord with the solid-state structure: the three bridging hydride ligands are located on two Os–Os bonds and one Os–Mo bond.

In our case, observation at room temperature of coupling of the hydride ligand with the ^{183}W nucleus and observation of two resonances at 178 K indicate that for **3b** these two ligands are located on a W–Ru bond and on a Ru–Ru bond.

To summarize, **1a**,**b** have a behavior toward molecular hydrogen similar to that of their protonated analogue (μ-H)$WOs_3Cp(CO)_{12}$. Nevertheless, the reaction seems easier with **1a**,**b**; the osmium analogue had to be refluxed in toluene under hydrogen.

In order to compare further the reactivity of **1a**,**b** with (μ-H)$WOs_3Cp(CO)_{12}$, we have studied reactions involving alkynes.

Reactivity toward Alkynes. The two alkynes employed were MeC≡CMe and PhC≡CH. Reactions in refluxing tetrahydrofuran lead to **4a** (M = Mo) and **4b** (M = W) with MeC≡CMe and to **5a** (M = Mo) and **5b** (M = W) with PhC≡CH, as red-orange crystals in good yield.

The four products have similar infrared spectra in the ν(CO) stretching region, suggesting the presence of terminal and semibridging or bridging carbonyl groups and similar structures.

In the proton NMR spectra of **4a**,**b** (excluding phenyl resonances) one signal is observed for the cyclopentadienyl ligand and two signals of the same intensity are observed for the methyl groups of the alkyne. In the case of **4b**, coupling with ^{183}W is observed in the signal for the CH_3 groups at lower field, showing that part of the alkyne is bonded to the tungsten atom. For **5a**, the situation is more complex, as two signals are observed for the CH and C_5H_5 groups, suggesting the presence of two isomers in a 1:1 ratio. The low-field resonances observed for the CH group are consistent with structures in which the two isomers have groups that are σ-bonded to a metal. For **5b**, only one isomer is detected and no coupling with tungsten is observed for the CH resonance.

These data clearly show that the **4a**,**b** and **5a**,**b** products have structures different from that of the complex resulting

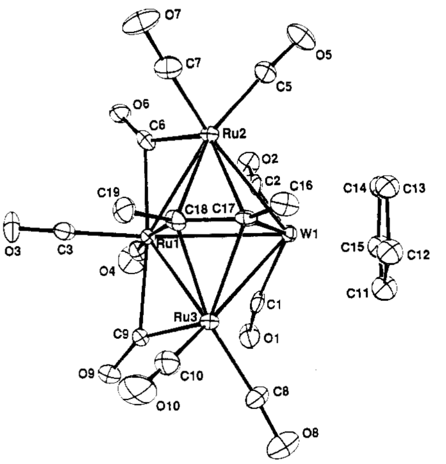

Figure 2. Perspective view of the anionic part of the complex $[PPh_4][WRu_3Cp(CO)_{10}(\mu_4-\eta^2-MeC{\equiv}CMe)]$ (**4b**). Vibrational ellipsoids are drawn at the 50% probability level.

from the reaction of diphenylacetylene with $(\mu-H)WOs_3(CO)_{12}$. In the latter case, the alkyne is μ_3-η^2-bonded to the Os_3 face.[4c]

An X-ray structure determination of **4b** was undertaken to determine precisely the structure of these new clusters.

An ORTEP plot of the anionic part of **4b** is shown in Figure 2, and bond distances and angles of interest are gathered in Table II. There is a butterfly arrangement of Ru_3W atoms with the tungsten atom being on the hinge. The alkyne can be described as σ-bonded to W(1) and Ru(1) and π-bonded to Ru(2) and Ru(3). This is a common situation for products of reactions between alkynes and tetranuclear clusters.[12,13] Furthermore, this structure is in agreement with the proton NMR spectrum of **4b** which showed that the alkyne was bonded to tungsten.

Bond lengths in the metallic frame are typical of butterfly structures. The W(1)–Ru(1) distance is the longest of the W–Ru distances, a general trend for the metal–metal distance for metals in the hinge.

Each ruthenium atom is bonded to two terminal carbonyl groups, and the two Ru–Ru bonds are bridged by carbonyl groups. These two bridging ligands are assymmetrically bonded since they are more tightly bonded to the ruthenium atoms on the "wing tips".

The tungsten atom is surrounded by a η^5-bonded cyclopentadienyl ligand and by two carbonyl groups which interact slightly with the Ru(2) and Ru(3) atoms. The distance to the plane of the cyclopentadienyl ring is 2.0158 (2) Å. The tungsten–alkyne and Ru(1) alkyne σ-bonds are in a range typical for this type of bonding,[4b,14] but the alkyne is asymmetrically π-bonded to the other ruthenium atoms. The Ru(2)–C(17) and Ru(3)–C(17) bonds are longer than the Ru(2)–C(18) and Ru(3)–C(18) bonds, the latter being in the normal range for this type of bonding.[12,14] There is no special feature for the alkyne frame, distances and angles being in the normal range.[12]

To summarize, the reaction of alkynes with **1a,b** leads to substitution of two carbonyl ligands and, unlike the $(\mu-H)WOs_3Cp(CO)_{12}$ cluster, to the opening of one of the Ru–Ru bonds to give a butterfly arrangement of the metal atoms. This different situation is certainly related to weaker metal–metal bonds in **1a,b**.

Table II. Bond Distances (Å) and Angles (deg) of Interest for 4b with Esd's in Parentheses

Bond Distances			
W(1)–Ru(1)	3.084 (1)	Ru(1)–C(9)	2.212 (4)
W(1)–Ru(2)	2.823 (1)	Ru(2)–C(2)	2.618 (5)
W(1)–Ru(3)	2.839 (1)	Ru(2)–C(5)	1.854 (5)
Ru(1)–Ru(2)	2.712 (1)	Ru(2)–C(6)	1.981 (5)
Ru(1)–Ru(3)	2.721 (1)	Ru(2)–C(7)	1.861 (5)
W(1)–C(17)	2.201 (5)	Ru(3)–C(1)	2.652 (5)
Ru(2)–C(17)	2.318 (4)	Ru(3)–C(8)	1.874 (5)
Ru(3)–C(17)	2.325 (4)	Ru(3)–C(9)	1.959 (5)
Ru(1)–C(18)	2.184 (4)	Ru(3)–C(10)	1.871 (5)
Ru(2)–C(18)	2.255 (4)	C(1)–O(1)	1.155 (6)
Ru(3)–C(18)	2.256 (4)	C(2)–O(2)	1.168 (5)
C(16)–C(17)	1.531 (6)	C(3)–O(3)	1.146 (7)
C(17)–C(18)	1.434 (7)	C(4)–O(4)	1.137 (6)
C(18)–C(19)	1.526 (8)	C(5)–O(5)	1.156 (6)
W(1)–C(1)	1.976 (5)	C(6)–O(6)	1.162 (5)
W(1)–C(2)	1.971 (4)	C(7)–O(7)	1.159 (7)
Ru(1)–C(3)	1.867 (5)	C(8)–O(8)	1.146 (6)
Ru(1)–C(4)	1.916 (5)	C(9)–O(9)	1.175 (6)
Ru(1)–C(6)	2.191 (4)	C(10)–O(10)	1.146 (7)
Bond Angles			
Ru(1)–W(1)–Ru(2)	54.45 (2)	Ru(1)–C(9)–Ru(3)	81.2 (2)
Ru(1)–W(1)–Ru(3)	54.51 (2)	C(1)–W(1)–C(2)	86.1 (2)
Ru(2)–W(1)–Ru(3)	89.31 (2)	C(3)–Ru(1)–C(4)	94.9 (2)
Ru(1)–Ru(2)–W(1)	67.68 (2)	C(3)–Ru(1)–C(6)	87.5 (2)
Ru(1)–Ru(3)–W(1)	67.33 (2)	C(3)–Ru(1)–C(9)	87.6 (2)
W(1)–Ru(1)–Ru(2)	57.87 (2)	C(4)–Ru(1)–C(6)	88.6 (2)
W(1)–Ru(1)–Ru(3)	58.16 (2)	C(4)–Ru(1)–C(9)	88.3 (2)
Ru(2)–Ru(1)–Ru(3)	94.17 (3)	C(6)–Ru(1)–C(9)	173.9 (2)
C(17)–W(1)–Ru(1)	67.8 (1)	C(5)–Ru(2)–C(6)	105.8 (2)
C(18)–Ru(1)–W(1)	67.9 (1)	C(5)–Ru(2)–C(7)	89.4 (2)
C(18)–Ru(2)–C(17)	36.5 (2)	C(6)–Ru(2)–C(7)	95.2 (2)
C(18)–Ru(3)–C(17)	36.5 (2)	C(8)–Ru(3)–C(9)	99.6 (2)
C(18)–C(17)–W(1)	111.6 (3)	C(8)–Ru(3)–C(10)	89.5 (2)
C(16)–C(17)–W(1)	126.9 (3)	C(9)–Ru(3)–C(10)	95.9 (2)
C(16)–C(17)–Ru(2)	119.6 (3)	W(1)–C(1)–O(1)	165.5 (5)
C(16)–C(17)–Ru(3)	120.9 (2)	W(1)–C(2)–O(2)	165.8 (5)
Ru(2)–C(17)–Ru(3)	118.0 (2)	Ru(1)–C(3)–O(3)	178.4 (4)
C(17)–C(18)–Ru(1)	112.6 (3)	Ru(1)–C(4)–O(4)	179.6 (5)
C(19)–C(18)–Ru(1)	123.6 (3)	Ru(1)–C(6)–O(6)	134.3 (3)
C(19)–C(18)–Ru(2)	118.5 (3)	Ru(1)–C(9)–O(9)	133.2 (3)
C(19)–C(18)–Ru(3)	117.7 (3)	Ru(2)–C(5)–O(5)	177.6 (5)
Ru(2)–C(18)–Ru(3)	123.8 (2)	Ru(2)–C(6)–O(6)	144.7 (3)
C(18)–C(17)–C(16)	121.5 (4)	Ru(2)–C(7)–O(7)	177.9 (4)
C(17)–C(18)–C(19)	123.9 (4)	Ru(3)–C(8)–O(8)	177.1 (5)
Ru(1)–C(6)–Ru(2)	80.9 (2)	Ru(3)–C(9)–O(9)	145.6 (3)
		Ru(3)–C(10)–O(10)	177.9 (5)

Considering the structure of **4b**, the two isomers observed for **5a** correspond to two situations, one in which the CH part of the alkyne is σ-bonded to Ru and the other in which it is σ-bonded to Mo. Moreover, by comparison with proton NMR data of **5b**, the resonance observed at lower field for the CH group is attributed to the isomer in which the CH group is σ-bonded to one ruthenium atom.

Since compounds **4a,b** and **5a,b** have the structure proposed for the intermediate in the $(\mu-H)WOs_3Cp(CO)_{10}(C_2Ph_2) \rightarrow (\mu-H)WOs_3Cp(CO)_9(\mu_3-CPh)_2$ transformation,[4c] we have checked whether the same type of reaction was observed for these clusters. Heating **4a,b** or **5a,b** to 100 °C leads to decomposition of these clusters and formation of an intractable mixture of compounds, in addition to deposition of metal. No conclusion could be drawn from these results.

Reactivity of 3a,b toward Alkynes. Even though there is no parallel in the chemistry developed for $(\mu-H)_3MoOs_3Cp(CO)_{11}$, we have also tested the reactivity of **3a** and **3b**, respectively, toward MeC≡CMe and PhC≡CH. In the presence of an excess of alkyne, the reactions (in boiling tetrahydrofuran) give **4a,b** and **5a,b** in nearly quantitative yield. It was important to know the fate of the hydride ligands; i.e., was H_2 eliminated, as observed in the case of the reaction of alkynes with $H_2FeRu_3(CO)_{13}$, for instance,[15] or was the alkyne hydrogenated?

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In the case of phenylacetylene, we found that complete reaction requires 2 equiv of the alkyne. Furthermore, GC analysis confirmed the presence of styrene. So, the overall the reaction is

$$\mathbf{3b} + 2PhC\equiv CH \rightarrow \mathbf{5b} + PhCH{=}CH_2$$

We also checked whether **5a,b** reacts with hydrogen. In boiling tetrahydrofuran no reaction was observed under hydrogen.

In conclusion, this study shows that the clusters **1a,b** have a chemistry that is quite similar to that of their osmium analogues. The main difference is that in reactions involving alkynes one Ru–Ru bond is opened, a result which is not unexpected considering that a Ru–Ru bond is weaker than an Os–Os bond.

Experimental Section

General Comments. All reactions were performed under a nitrogen atmosphere by using standard Schlenk tube techniques. Infrared spectra were recorded with a Perkin-Elmer 225 spectrometer in dichloromethane solution for ionic complexes and in hexane solution for neutral ones. ^1H NMR spectra were obtained with a Bruker WH90 spectrometer at room temperature and on a Bruker WM250 instrument for low-temperature experiments. The $[PPh_4][CpM(CO)_3]$ complexes (M = Cr, Mo, W) were prepared by exchange of the cation of $Na[CpM(CO)_3]$ salts[16] with $[PPh_4]Br$. $Ru_3(CO)_{12}$ was synthesized by the published procedure.[17]

Synthesis of $[PPh_4][MRu_3Cp(CO)_{12}]$ (1a, M = Mo; 1b, M = W). To $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol) dissolved in tetrahydrofuran was added $[PPh_4][CpMo(CO)_3]$ or $[PPh_4][CpW(CO)_3]$ (91 mg or 97 mg, respectively, 0.16 mmol), and the solution was refluxed for 1 h. During this time, the solution turned dark red. It was then evaporated to dryness, and the residue was crystallized from a 1:1 mixture of CH_2Cl_2/MeOH at −20 °C affording the following.

1a: dark red crystals (127 mg, 70% yield); IR ν(CO) 2052 m, 2005 s, 1960 m, 1920 w (sh) cm^{-1}; ^1H NMR ($(CD_3)_2CO$) δ 8.04, 7.94 ($[PPh_4]^+$), 5.32 (C_5H_5). Anal. Calcd for $C_{41}H_{25}O_{12}PMoRu_3$: C, 43.19; H, 2.19. Found: C, 42.78; H, 1.95.

1b: dark red crystals (140 mg, 75% yield); IR ν(CO) 2047 m, 2000 s, 1970 m, 1940 w (sh) cm^{-1}; ^1H NMR ($(CD_3)_2CO$) δ 8.04, 7.95 ($[PPh_4]^+$), 5.36 (C_5H_5). Anal. Calcd for $C_{41}H_{25}O_{12}PWRu_3$: C, 40.10; H, 2.03. Found: C, 39.92; H, 1.98.

Synthesis of $(\mu$-H)$MRu_3Cp(CO)_{12}$ (2a, M = Mo; 2b, M = W). To **1a** or **1b** (50 mg) dissolved in 5 mL of dichloromethane was added an excess of trifluoroacetic acid (ca. 0.1 mL). The solution was stirred for 1 h and then evaporated to dryness. Extraction of the residue with 4 × 10 mL of hexane and concentration of the extracts to 10 mL gave the following after cooling to −20 °C.

2a: red crystals (20 mg, 60% yield); IR ν(CO) 2087 m, 2055 s, 2040 s, 2010 m, 1997 m, 1930 w cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.51 (C_5H_5), −20.10 (H). Anal. Calcd for $C_{17}H_6O_{12}MoRu_3$: C, 25.47; H, 0.75. Found: C, 25.10; H, 1.21.

2b: red crystals (25 mg, 70% yield); IR ν(CO) 2087 m, 2052 s, 2042 s, 2010 m, 2000 m, 1928 w cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.48 (C_5H_5), −20.46 (H). Anal. Calcd for $C_{17}H_6O_{12}WRu_3$: C, 22.95; H, 0.67. Found: C, 22.62; H, 1.12.

Synthesis of $[PPh_4][(\mu$-H$)_2MRu_3Cp(CO)_{11}]$ (3a, M = Mo; 3b, M = W). **1a** or **1b** (100 mg) was dissolved into 20 mL of boiling tetrahydrofuran, and a small stream of hydrogen was bubbled through the solution for 30 min. During this time, the solution turned from dark to light red. Evaporation of the solvent and crystallization of the residue from CH_2Cl_2/CH_3OH (1:1) at −20 °C gave the following.

3a: red crystals (80 mg, 85% yield); IR ν(CO) 2054 m, 2012 s, 1992 s, 1970 sh, 1945 sh, 1785 w, 1740 w cm^{-1}; ^1H NMR ($(CD_3)_2CO$, 20 °C) δ 8.04, 7.93 ($[PPh_4]^+$), 5.13 (C_5H_5), −16.14 (2 H). Anal. Calcd for $C_{40}H_{27}O_{11}PMoRu_3$: C, 43.12; H, 2.42. Found: C, 42.75; H, 2.30.

Table III. Experimental Data for X-ray Studies

	1a	**4b**
formula	$C_{41}H_{25}O_{12}PMoRu_3$	$C_{43}H_{31}O_{10}PRu_3W$
fw, amu	1139.77	1225.75
a, Å	12.427 (2)	14.035 (2)
b, Å	13.637 (4)	14.818 (5)
c, Å	23.811 (4)	10.311 (3)
α, deg		98.70 (3)
β, deg	86.02 (1)	108.48 (3)
γ, deg		86.65 (2)
V, Å^3	4025	2010
Z	4	2
ρ_{calcd}, g·cm^{-3}	1.881	2.025
space group	monoclinic, $C^5_{2h}P2_1/c$	triclinic, C^1_iP1
t, °C	22	−150
radiatn	graphite monochromated, Mo Kα, λ(Mo Kα_1) = 0.7093 Å	
linear abs coeff, cm^{-1}	14.8	40.9
transmissn factors[a]	90.30–99.97	61.33–99.90
receiving aperture, mm	4 × 4	4 × 4
takeoff angle, deg	3.2	2.0
scan speed, deg·min^{-1}	2.0	2.0
scan mode	ω	$\omega/2\theta$
scan range, deg	1.0 below Kα_1 to 1.0 above Kα_2	1.0 below Kα_1 to 1.0 above Kα_2
2θ limit, deg	2–44	2–50
data collected	5459	7374
unique data used in final refinement, $F_o^2 > 3\sigma(F_o^2)$	4062	6333
final no. of variables	332	326
weighting scheme,[b] p	0.01	0.02
R (on F_o, $F_o^2 > 3\sigma(F_o^2)$)[c]	0.031	0.024
R_w (on F_o, $F_o^2 > 3\sigma(F_2^2)$)[d]	0.035	0.027
error in observn of unit weight, e^2	2.39	1.83

[a] Ψ-scan method. [b] Weghting scheme: $1/\sigma^2$ where $\sigma^2(F) = \sigma^2 + (pF^2)^2$. [c] $R = \sum||F_o| - |F_c|/\sum|F_o|$. [d] $R_w = \sum w(|F_o| - |F_c|)^2/(\sum w|F_o|^2)]^{1/2}$.

3b: red crystals (90 mg, 90% yield). IR ν(CO) 2047 m, 2005 s, 1985 s, 1965 m, 1936 w, 1840 w cm^{-1}; ^1H NMR ($(CD_3)_2CO$, 20 °C) δ 8.04, 7.94 ($[PPh_4]^+$), 4.99 (C_5H_5), −15.99 (2 H, J_{WH} = 29.4 Hz). Anal. Calcd for $C_{40}H_{27}O_{11}PWRu_3$: C, 39.97; H, 2.25. Found: C, 39.76; H, 2.31.

Synthesis of $[PPh_4][MRu_3Cp(CO)_{10}(\mu_4$-$\eta^2$-$MeC\equiv CMe)]$ (4a, M = Mo; 4b, M = W) and $[PPh_4][MRu_3Cp(CO)_{10}(\mu_4$-$\eta^2$-$PhC\equiv CH)]$ (5a, M = Mo; 5b, M = W). To **1a** or **1b** (100 mg) was added respectively a slight excess of the alkyne $MeC\equiv CMe$ (**4a,b**) or $PhC\equiv CH$ (**5a,b**) in 20 mL of tetrahydrofuran. Refluxing for 2 h afforded orange-red solutions. Evaporation of the solvent and crystallization from a 1:1 CH_3OH/CH_2Cl_2 mixture gave the following.

4a: orange-red crystals (65 mg, 65% yield); IR ν(CO) 2025 m, 1975 sh, 1967 s, 1950 sh, 1907 m, 1855 w, 1815 w cm^{-1}; ^1H NMR ($(CD_3)_2CO$) δ 8.04, 7.93 ($[PPh_4]^+$), 5.83 (C_5H_5), 3.40 (CH_3), 2.85 (CH_3). Anal. Calcd for $C_{43}H_{31}O_{10}PMoRu_3$: C, 45.38; H, 2.72. Found: C, 44.92; H, 2.68.

4b: orange-red crystals (70 mg, 70% yield); IR ν(CO) 2023 m, 1972 sh, 1965 s, 1950 sh, 1905 m, 1855 w, 1815 w cm^{-1}; ^1H NMR ($(CD_3)_2CO$) δ 8.04, 7.93 ($[PPh_4]^+$), 5.93 (C_5H_5), 3.36 (CH_3, J_{WH} = 3.5 Hz), 2.88 (CH_3). Anal. Calcd for $C_{43}H_{31}O_{10}PRu_3W$: C, 42.12; H, 2.53. Found: C, 41.56; H, 2.32.

5a: orange-red crystals (50 mg, 50% yield); IR ν(CO) 2027 m, 1982 sh, 1975 s, 1952 m, 1915 m, 1870 w, 1825 w cm^{-1}; ^1H NMR ($(CD_3)_2CO$) δ 10.62 (H), 8.44 (H), 8.04, 7.93 ($[PPh_4]^+$), 7.12 (C_6H_5), 5.69 (C_5H_5), 5.02 (C_5H_5). Anal. Calcd for $C_{47}H_{31}O_{10}PMoRu_3$: C, 47.59; H, 2.61. Found: C, 47.50; H, 2.57.

5b: orange-red crystals (50 mg, 45% yield); IR ν(CO) 2023 m, 1977 sh, 1970 s, 1948 m, 1915 m, 1877 w, 1842 w, 1820 w cm^{-1}; ^1H NMR ($(CD_3)_2CO$) δ 10.18 (H), 8.04, 7.93 ($[PPh_4]^+$), 7.04 (C_6H_5), 5.77 (C_5H_5). Anal. Calcd for $C_{47}H_{31}O_{10}PRu_3W$: C, 44.31; H, 2.43. Found: C, 43.92; H, 2.52.

Crystallographic Studies. Crystals of **1a** and **4b** suitable for X-ray diffraction were obtained through recrystallization from dichloromethane/methanol solution at −18 °C. Data were col-

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Table IV. Final Atomic Coordinates and U_{eq}/U_{iso} ($\times 10^2$ Å^2) for Compound 1a

atom	x/a	y/b	z/c	U_{eq}/U_{iso}
Ru(1)	0.36674 (4)	0.85528 (4)	0.09542 (2)	3.60 (3)
Ru(2)	0.21698 (4)	0.74768 (4)	0.15488 (2)	3.67 (3)
Ru(3)	0.41180 (4)	0.81287 (4)	0.21059 (2)	3.78 (4)
Mo(1)	0.41665 (5)	0.65503 (4)	0.12975 (2)	3.81 (4)
C(1)	0.4672 (6)	0.9566 (6)	0.0809 (3)	5.7 (5)
O(1)	0.5249 (5)	1.0179 (5)	0.0717 (3)	9.8 (5)
C(2)	0.3425 (6)	0.8175 (6)	0.0192 (3)	5.3 (5)
O(2)	0.3328 (5)	0.7943 (5)	−0.0269 (2)	8.4 (5)
C(3)	0.2418 (6)	0.9363 (6)	0.0992 (3)	4.6 (5)
O(3)	0.1741 (4)	0.9928 (4)	0.0990 (3)	6.8 (4)
C(4)	0.0924 (6)	0.7710 (5)	0.1061 (3)	4.9 (5)
O(4)	0.0184 (4)	0.7870 (5)	0.0771 (2)	7.5 (4)
C(5)	0.1577 (6)	0.6386 (6)	0.1920 (3)	4.9 (5)
O(5)	0.1232 (4)	0.5714 (4)	0.2114 (2)	7.3 (4)
C(6)	0.1910 (6)	0.8434 (6)	0.2112 (3)	4.8 (5)
O(6)	0.1575 (4)	0.8999 (4)	0.2408 (2)	7.5 (4)
C(7)	0.3817 (6)	0.7984 (6)	0.2870 (3)	5.2 (5)
O(7)	0.3636 (5)	0.7896 (5)	0.3330 (2)	8.2 (4)
C(8)	0.5594 (6)	0.8214 (7)	0.2305 (3)	5.9 (6)
O(8)	0.6485 (5)	0.8264 (6)	0.2457 (3)	10.3 (5)
C(9)	0.3898 (6)	0.9504 (6)	0.1998 (3)	5.2 (5)
O(9)	0.3765 (5)	1.0331 (5)	0.2044 (3)	7.5 (4)
C(10)	0.3917 (6)	0.6453 (6)	0.2127 (3)	4.7 (5)
O(10)	0.3819 (4)	0.5950 (4)	0.2522 (2)	6.6 (4)
C(11)	0.2700 (6)	0.6587 (6)	0.0841 (3)	5.2 (5)
O(11)	0.2194 (4)	0.6284 (5)	0.0441 (2)	7.9 (4)
C(12)	0.5160 (6)	0.7707 (5)	0.1148 (3)	4.6 (5)
O(12)	0.6077 (4)	0.7923 (4)	0.1089 (2)	6.0 (4)
C(13)	0.561 (2)	0.582 (1)	0.089 (2)	6.1 (6)
C(14)	0.464 (2)	0.552 (1)	0.058 (2)	6.3 (5)
C(15)	0.403 (2)	0.497 (1)	0.095 (2)	8.9 (6)
C(16)	0.462 (2)	0.493 (1)	0.149 (2)	6.1 (5)
C(17)	0.559 (2)	0.546 (1)	0.144 (2)	6.3 (5)
C(13)′	0.527 (3)	0.576 (1)	0.068 (1)	4.8 (5)
C(14)′	0.429 (3)	0.523 (1)	0.068 (1)	6.7 (6)
C(15)′	0.420 (3)	0.484 (1)	0.123 (1)	6.6 (5)
C(16)′	0.513 (3)	0.513 (1)	0.157 (1)	6.4 (5)
C(17)′	0.579 (3)	0.570 (1)	0.123 (1)	7.3 (6)
P	0.9612 (1)	0.7406 (1)	0.37259 (7)	3.4 (1)
C(18)	0.8406 (3)	0.7316 (3)	0.4090 (2)	3.6 (2)
C(19)	0.8466 (3)	0.7387 (3)	0.4675 (2)	4.3 (2)
C(20)	0.7531 (3)	0.7306 (3)	0.4965 (2)	5.3 (2)
C(21)	0.6537 (3)	0.7154 (3)	0.4668 (2)	5.8 (2)
C(22)	0.6477 (3)	0.7084 (3)	0.4083 (2)	5.6 (2)
C(23)	0.7412 (3)	0.7164 (3)	0.3793 (2)	4.1 (2)
C(24)	0.9260 (4)	0.7391 (3)	0.2992 (2)	3.7 (2)
C(25)	0.9264 (4)	0.8245 (3)	0.2670 (2)	4.8 (2)
C(26)	0.8940 (4)	0.8214 (3)	0.2098 (2)	6.2 (2)
C(27)	0.8612 (4)	0.7329 (3)	0.1847 (2)	6.2 (2)
C(28)	0.8609 (4)	0.6475 (3)	0.2169 (2)	6.0 (2)
C(29)	0.8932 (4)	0.6505 (3)	0.2741 (2)	5.1 (2)
C(30)	1.0540 (3)	0.6418 (3)	0.3875 (1)	3.4 (2)
C(31)	1.1313 (3)	0.6243 (3)	0.3489 (1)	4.8 (2)
C(32)	1.2094 (3)	0.5520 (3)	0.3599 (1)	5.4 (2)
C(33)	1.2102 (3)	0.4973 (3)	0.4094 (1)	5.2 (2)
C(34)	1.1328 (3)	0.5148 (3)	0.4480 (1)	5.3 (2)
C(35)	1.0547 (3)	0.5870 (3)	0.4370 (1)	4.3 (2)
C(36)	1.0258 (3)	0.8525 (3)	0.3941 (2)	3.4 (2)
C(37)	1.1381 (3)	0.8582 (3)	0.3981 (2)	4.8 (2)
C(38)	1.1891 (3)	0.9450 (3)	0.4161 (2)	5.8 (2)
C(39)	1.1277 (3)	1.0260 (3)	0.4300 (2)	6.1 (2)
C(40)	1.0154 (3)	1.0203 (3)	0.4259 (2)	6.3 (2)
C(41)	0.9644 (3)	0.9335 (3)	0.4080 (2)	5.5 (2)

Table V. Final Coordinates and U_{eq}/U_{iso} ($\times 10^2$ Å^2) for Compound 4b

atom	x/a	y/b	z/c	U_{eq}/U_{iso}
W(1)	0.28218 (1)	0.18145 (1)	−0.23544 (2)	1.52 (1)
Ru(1)	0.16115 (2)	0.23141 (2)	−0.03141 (3)	1.49 (2)
Ru(2)	0.31784 (2)	0.11159 (2)	0.01593 (3)	1.42 (2)
Ru(3)	0.07346 (3)	0.15248 (3)	−0.29610 (4)	1.78 (2)
C(1)	0.1935 (4)	0.2886 (3)	−0.2789 (4)	2.4 (2)
O(1)	0.1596 (3)	0.3587 (2)	−0.3069 (4)	3.3 (2)
C(2)	0.3574 (3)	0.2600 (3)	−0.0658 (5)	2.3 (2)
O(2)	0.4093 (2)	0.3145 (2)	0.0157 (3)	2.8 (2)
C(3)	0.0829 (3)	0.2191 (3)	0.0812 (5)	2.0 (2)
O(3)	0.0354 (3)	0.2094 (3)	0.1502 (4)	3.7 (2)
C(4)	0.1740 (3)	0.3611 (3)	0.0175 (5)	2.4 (3)
O(4)	0.1816 (3)	0.4382 (2)	0.0457 (4)	4.3 (2)
C(5)	0.4560 (3)	0.1045 (3)	0.0520 (5)	2.0 (2)
O(5)	0.5416 (2)	0.1004 (2)	0.0697 (4)	3.0 (2)
C(6)	0.2936 (3)	0.2158 (3)	0.1469 (5)	1.9 (2)
O(6)	0.3245 (2)	0.2554 (2)	0.2577 (3)	2.5 (2)
C(7)	0.3275 (3)	0.0244 (3)	0.1319 (5)	2.3 (2)
O(7)	0.3359 (3)	−0.0284 (3)	0.2072 (4)	4.0 (2)
C(8)	0.0261 (4)	0.1853 (4)	−0.4743 (5)	3.0 (3)
O(8)	−0.0063 (3)	0.2071 (3)	−0.5818 (4)	5.1 (3)
C(9)	0.0199 (3)	0.2552 (3)	−0.1958 (4)	2.2 (2)
O(9)	−0.0474 (2)	0.3069 (2)	−0.2005 (3)	3.0 (2)
C(10)	−0.0382 (4)	0.0776 (4)	−0.3390 (5)	2.9 (3)
O(10)	−0.1073 (3)	0.0330 (3)	−0.3616 (4)	4.3 (2)
C(16)	0.2194 (3)	−0.0376 (3)	−0.2685 (5)	2.2 (2)
C(17)	0.2116 (3)	0.0614 (3)	−0.2033 (4)	1.6 (2)
C(18)	0.1555 (3)	0.0856 (3)	−0.1084 (5)	1.8 (2)
C(19)	0.0979 (3)	0.0171 (3)	−0.0658 (5)	2.6 (3)
P(1)	0.31758 (8)	0.60822 (7)	−0.3471 (1)	1.66 (5)
C(11)	0.2944 (2)	0.1787 (2)	−0.4581 (3)	3.0 (1)
C(12)	0.3081 (2)	0.0874 (2)	−0.4289 (3)	2.9 (1)
C(13)	0.3969 (2)	0.0835 (2)	−0.3152 (3)	2.5 (1)
C(14)	0.4381 (2)	0.1724 (2)	−0.2742 (3)	2.5 (1)
C(15)	0.3748 (2)	0.2313 (2)	−0.3625 (3)	2.9 (1)
C(21)	0.3456 (2)	0.7011 (2)	−0.4211 (3)	1.92 (9)
C(22)	0.2790 (2)	0.7264 (2)	−0.5428 (3)	2.4 (1)
C(23)	0.3005 (2)	0.8005 (2)	−0.5972 (3)	2.8 (1)
C(24)	0.3888 (2)	0.8493 (2)	−0.5301 (3)	2.6 (1)
C(25)	0.4554 (2)	0.8241 (2)	−0.4084 (3)	2.5 (1)
C(26)	0.4338 (2)	0.7500 (2)	−0.3539 (3)	2.1 (1)
C(31)	0.2696 (2)	0.6511 (2)	−0.2079 (3)	1.89 (9)
C(32)	0.2963 (2)	0.7382 (2)	−0.1363 (3)	2.7 (1)
C(33)	0.2585 (2)	0.7728 (2)	−0.0285 (3)	3.2 (1)
C(34)	0.1942 (2)	0.7202 (2)	0.0076 (3)	2.8 (1)
C(35)	0.1675 (2)	0.6331 (2)	−0.0640 (3)	2.4 (1)
C(36)	0.2052 (2)	0.5985 (2)	−0.1717 (3)	2.3 (1)
C(41)	0.2238 (2)	0.5375 (2)	−0.4721 (3)	1.74 (9)
C(42)	0.1254 (2)	0.5705 (2)	−0.5180 (3)	2.5 (1)
C(43)	0.0517 (2)	0.5164 (2)	−0.6178 (3)	2.7 (1)
C(44)	0.0762 (2)	0.4293 (2)	−0.6717 (3)	2.7 (1)
C(45)	0.1746 (2)	0.3963 (2)	−0.6257 (3)	2.2 (1)
C(46)	0.2484 (2)	0.4504 (2)	−0.5259 (3)	1.78 (9)
C(51)	0.4288 (2)	0.5412 (2)	−0.2845 (3)	1.72 (9)
C(52)	0.5106 (2)	0.5443 (2)	−0.3330 (3)	2.5 (1)
C(53)	0.5942 (2)	0.4881 (2)	−0.2879 (3)	3.0 (1)
C(54)	0.5961 (2)	0.4287 (2)	−0.1942 (3)	2.6 (1)
C(55)	0.5144 (2)	0.4255 (2)	−0.1457 (3)	2.6 (1)
C(56)	0.4307 (2)	0.4817 (2)	−0.1909 (3)	2.4 (1)

lected on an Enraf-Nonius CAD4 diffractometer at 22 °C for compound **1a** and at −150 °C[18] for compound **4b**. For each compound, cell constants were obtained by the least-squares refinement of the setting angles of 25 reflections in the range 24° < 2θ(Mo Kα_1) < 28°. For compound **1a**, the space group was determined by careful examination of systematic extinctions in the listing of the measured reflections. Data reductions were carried out by using the SDP crystallographic computing package.[19] Table III present further crystallographic information.

The structures were solved and refined by using combination of the SDP crystallographic computing package[19] and the SHELX-76 package.[20] The position of metal atoms and P atoms in each structure was determined by direct methods. All remaining non-hydrogen atoms were located by the usual combination of full-matrix least-squares refinement and difference electron density syntheses. The cyclopentadienyl ring attached to the Mo atom in the structure of **1a** was found to be disordered. Carbon atoms of cyclopentadienyl rings in this structure were

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(18) Designed by Bonnet, J.-J.; Askenazy, S., commercially available from Soterem Z. I. de Vic, 31320 Castanet-Tolosan, France.

(19) *Enraf-Nonius Structure Determination Package*, 4th ed.; Frenz, B. A. & Associated, Inc.: College Station, TX; Enraf-Nonius: Delft, The Netherlands, 1981.

(20) Sheldrick, G. M. SHELX-76, *Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.

subsequently refined with an occupancy factor of 0.5.

Atomic scattering factors were taken from the usual tabulations.[21] Anomalous dispersion terms for W, Ru, Mo, and P atoms were included in F_c.[22] Empirical absorption correction were applied in each instance.[23] The final refinements were conducted by using the SHELX-76 program. All non-hydrogen atoms were allowed to vibrate anisotropically, except carbon atoms of cyclopentadienyl and phenyl rings which were refined as isotropic rigid groups in order to reduce the number of variable parameters (C_5H_5, C–C = 1.420 Å; C_6H_5, C–C = 1.395 Å). Hydrogen atoms, except those attached to the disordered cyclopentadienyl ring in **1a**, were entered in idealized positions (C–H = 0.97 Å) and held fixed during refinements. Scattering factors for the hydrogen atoms were taken from Stewart et al.[24]

Final atomic coordinates and 10^2U_{eq} (or 10^2U_{iso}) for non-hydrogen atoms of compounds **1a** and **4b** are given in Tables IV and V, respectively. Tables S1 and S2 list the thermal parameters ($\times 10^2$) for atoms of **1a** and **4b**, respectively, which were refined anisotropically.[25] Structure amplitudes ($10|F_o|$ vs $10|F_c|$) for the two structures are available in Tables S3 and S4.[25]

Acknowledgment. We thank Johnson-Matthey for generous loan of ruthenium chloride.

Registry No. **1a**, 116698-72-7; **1b**, 116698-74-9; **2a**, 116698-75-0; **2b**, 116698-76-1; **3a**, 116698-78-3; **3b**, 116698-80-7; **4a**, 116698-88-5; **4b**, 116698-90-9; **5a** (isomer 1), 116698-82-9; **5a** (isomer 2), 116698-86-3; **5b**, 116698-84-1; $Ru_3(CO)_{12}$, 15243-33-1; $[PPh_4][CpMo(CO)_3]$, 91463-50-2; $[PPh_4][CpW(CO)_3]$, 91482-94-9; MeC≡CMe, 503-17-3; PhC≡CH, 536-74-3.

Supplementary Material Available: Tables S1 and S2, anisotropic thermal parameters for compounds **1a** and **4b**, respectively (2 pages); Tables S3 and S4, structure factor amplitudes (×10) for compounds **1a** and **4b**, respectively (51 pages). Ordering information is given on any current masthead page.

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[21] Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4, Table 2.2B.

[22] Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4, Table 2.3.1.

[23] North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr. Sect. A: Cryst. Phys. Diffr., Theor Gen. Crystallogr.* **1968**, *A24*, 351.

[24] Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

[25] See paragraph at the end of paper regarding supplementary material.

Organometallic Chemistry of Sulfinic Acids. Highly Stereo- and Regioselective Intramolecular Hydroplatinations. X-ray Crystal Structure of $(Ph_3P)_2Pt[\textit{trans}\text{-}SO_2CH(CH_3)CH_2CH(CH_2CH_3)]$

John S. Hallock, Angela S. Galiano-Roth, and David B. Collum*

Baker Laboratory, Department of Chemistry, Cornell University, Ithaca, New York 14853-1301

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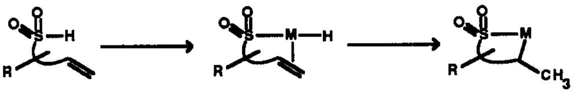
Reactions of sulfinic acids with platinum(0) and platinum(II) complexes are described. *p*-Tolylmethanesulfinic acid reacts with tetrakis(triphenylphosphine)platinum, $(Ph_3P)_4Pt$, to afford *trans*-$(Ph_3P)_2Pt(H)SO_2R$ (R = CH_2-*p*-tolyl) in 70% yield. $(COD)Pt(CH_3)SO_2R$ (COD = 1,5-cyclooctadiene; R = CH_2-*p*-tolyl, 77% yield), $(COD)Pt(CH_3)SO_2R$ (R = *p*-tolyl, 53% yield), and *cis*-$(Ph_3P)_2Pt(CH_3)SO_2R$ (R = *p*-tolyl, 91% yield) were prepared analogously from the corresponding L_2PtMe_2 complexes. Treatment of *cis*-$(Ph_3P)_2Pt(CH_3)_2$ with butene-4-sulfinic acid and pentene-4-sulfinic acid afforded isomerically pure chelates $(Ph_3P)(CH_3)Pt(\eta^3\text{-}SO_2CH(R)CH_2CH_2CH{=}CH_2)$ (R = H, 33% yield; R = CH_3, 31% yield). Reaction of *cis*-$(Ph_3P)_2Pt(CH_3)_2$ with hexene-5-sulfinic acid afforded the unchelated derivative $(Ph_3P)_2(CH_3)Pt(\eta^1\text{-}SO_2CH(CH_3)CH_2CH_2CH_2CH{=}CH_2)$ (22% yield). Intramolecular hydrometalations were observed upon treatment of $(Ph_3P)_4Pt$ with unsaturated sulfinic acids. Butene-4-sulfinic acid was converted to $(Ph_3P)_2PtSO_2CH_2CH_2CH(CH_3)$ (69% yield). Pentene-5-sulfinic acid afforded metallacyclohexane $(Ph_3P)_2PtSO_2CH_2CH_2CH_2CH(CH_3)$ (37% yield), which upon heating, isomerized to a metallacyclopentane, $(Ph_3P)_2PtSO_2CH_2CH_2CH(CH_2CH_3)$, in 27% yield. Pentene-4-sulfinic acid afforded $(Ph_3P)_2Pt[\textit{cis}\text{-}SO_2CH(CH_3)CH_2CH(CH_3)]$ (37% yield, >20:1 stereoselectivity), which upon heating afforded $(Ph_3P)_2Pt[\textit{trans}\text{-}SO_2CH(CH_3)CH_2CH(CH_3)]$ in 56% yield and >20:1 stereoselectivity. Hexene-5-sulfinic acid afforded the metallacyclohexane $(Ph_3P)_2PtSO_2CH(CH_3)CH_2CH_2CH(CH_3)$ (47% yield) as a cis/trans mixture of unassigned stereochemistry. Upon heating, both isomers isomerized to $(Ph_3P)_2Pt[\textit{trans}\text{-}SO_2CH(CH_3)CH_2CH(CH_2CH_3)]$ in 36% yield and >20:1 stereoselectivity. Stereochemical assignments of all metallacyclopentanes derived from a molecular structure determination of $(Ph_3P)_2Pt[\textit{trans}\text{-}SO_2CH(CH_3)CH_2CH(CH_2CH_3)]$. The metallacycle crystallized in $P2_1/c$ space group with cell parameters a = 10.563 (1) Å, b = 9.733 (17) Å, c = 36.362 (42) Å, β = 94.59°, Z = 4, and R_w = 9.8%. Attempts to deinsert SO_2 from the platinum sulfinates failed to afford the corresponding metal alkyls.

Introduction

The rise of organotransition metals to prominence in organic synthesis has produced a steadily increasing need to understand and control the stereochemistry of substrate functionalizations. We describe herein a study of intramolecular hydrometalations of unsaturated sulfinic acids (eq 1). The observed high and complementary kinetic and thermodynamic stereoselectivities may shed some light on the stereoselective hydrometallations implicated in internally directed hydrosilylations,[1] hydroacylations,[2] hy-



(1)