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Rhodium and Iridium Hydroxide Complexes $[M(\mu\text{-}OH)(COD)]_2$ (M = Rh, Ir) as Versatile Precursors of Homo and Early−Late Heterobimetallic Compounds. X-ray Crystal Structures of $Cp^*Ta(\mu_3\text{-}O)_4[Rh(COD)]_4$ ($Cp^* = \eta^5\text{-}C_5Me_5$) and $[Ir(2\text{-}O\text{-}3\text{-}CN\text{-}4,6\text{-}Me_2\text{-}C_5HN)(COD)]_2$

Rosa Fandos,*,† Carolina Hernández,† Antonio Otero,*,‡ Ana Rodríguez,‡ and Maria José Ruiz†

Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Ciencias del Medio Ambiente, Campus de Toledo Universidad de Castilla-La Mancha, C/ S. Lucas 6, 45001 Toledo, Spain, and Facultad de Químicas, Campus de Ciudad Real, Universidad de Castilla-La Mancha, 13071 Ciudad Real, Spain

José Luis García Fierro and Pilar Terreros

Instituto de Catálisis y Petroleoquímica, CSIC, Cantoblanco, 28049 Madrid, Spain

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The reaction of Cp^*TiMe_3 with 3 equiv of $[Ir(\mu\text{-}OH)(COD)]_2$ affords the new heterometallic organometallic oxide $Cp^*Ti(\mu_3\text{-}O)_3[Ir(COD)]_3$ (**3**). Reaction of Cp^*TaMe_4 with 4 equiv of $[M(\mu\text{-}OH)(COD)]_2$ (M = Rh, Ir) yields complexes $Cp^*Ta(\mu_3\text{-}O)_4[M(COD)]_4$ [M = Rh (**5**), Ir (**6**)]. The structure of compound **5** has been determined by X-ray diffraction. Complexes **5** and **6** react with the alcohol $3\text{-}CN\text{-}4,6\text{-}Me_2\text{-}2\text{-}OH{-}C_5HN$ to yield the corresponding rhodium (**7**) or iridium (**8**) alkoxide complexes. The structure of complex **8** has been determined by X-ray diffraction. Reaction of $[Rh(\mu\text{-}OH)(COD)]_2$ with thiolacetic acid gives rise to a thioacetate complex $[Rh(\mu\text{-}SCOCH_3)(COD)]_2$ (**9**).

Introduction

A great deal of attention has been paid lately to the broad family of hydroxo metal "M−OH" complexes, which are either monomeric,[1] dimeric, or polymeric, due to the interesting reactivity and potential relevance to catalytic reactions.[2] Such complexes can react with protic electrophiles (HX), releasing water and leading to the formation of new M−X bonds, they can act as proton-transfer agents (Brönsted acid), producing heterometallic oxo ($M{-}OH + M'{-}R \rightarrow M{-}O{-}M'$) or carboxylato complexes [($M{-}OH + M'{-}CO^+ \rightarrow M'M_2(\mu_3CO_2)$)],[3] or as Brönsted bases with hydroxide/alkoxide exchange,[4] or they may use their nucleophilic properties, allowing the synthesis of a wide variety of new complexes.[5] The hydroxide ion can also act as a one-electron reducing agent.[6]

Homonuclear μ-oxo-bridged metal complexes have been extensively studied and have greatly contributed to our current understanding of metal−metal interactions. However, systematic attempts to prepare and study heteronuclear μ-oxo-bridged metal complexes have only recently been undertaken.[7] A few examples of extreme $d^0{-}d^8$ associations can be found in the literature.[8]

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† Universidad de Castilla-La Mancha.

‡ Facultad de Químicas, Campus de Ciudad Real.

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Early-metal oxides, such as titania and zirconia, are often employed as support materials for heterogeneous catalysts. The support may provide sufficient surface area to disperse the late-metal atoms or may play an active role in the catalytic reaction giving rise, for instance, to the phenomenon known as strong metal support interaction (SMSI), which dramatically alters both catalyst activity and selectivity.[9]

Heterometallic complexes consisting of both an early oxophilic metal center and a late electron-rich transition metal can be envisaged as model systems for surface compounds or catalytically active sites on an early transition metal oxide supported catalyst.[10] Such complexes can exhibit structural features such as metal–metal bonds or oxygen-bridged metal centers. These complexes may model or mimic a metal–support interaction[11] and could enable the different metals to activate substrates in a cooperative way.

These compounds are important because of the variety of mixed-metal oxides that have found catalytic applications in numerous reactions, including several of commercial importance.[12]

Herein we report the synthesis of several d^0–d^8 heterometallic complexes taking advantage of the ability of rhodium(I) and iridium(I) hydroxo complexes to act as Brönsted acids. Moreover, their reactivity with different protic electrophiles has been explored. This has allowed us to synthesize alkoxide and thioacetate complexes in high yields.

Results and Discussion

Reaction of Cp^*TiMe_3 (**1**) with 3 equiv of $[Ir(\mu\text{-}OH)(COD)]_2$ (**2**) in toluene, at room temperature, affords $Cp^*Ti(\mu_3\text{-}O)_3[Ir(COD)]_3$ (**3**) in 65% yield (eq 1). Complex **3** is moderately air-stable in the solid state, partially soluble in alkanes, and very soluble in toluene or THF.

$$Cp^*TiMe_3 + 3/2[Ir(\mu\text{-}OH)(COD)]_2 \rightarrow Cp^*Ti(\mu_3\text{-}O)_3[Ir(COD)]_3 + 3MeH \quad (1)$$

Complex **3** has been characterized by elemental analysis, ^1H and ^{13}C NMR, and FT IR spectroscopic techniques. The ^1H and ^{13}C NMR spectra are consistent with a structure analogous to that found in the rhodium complex $Cp^*Ti(\mu_3\text{-}O)_3[Rh(COD)]_3$.[10a]

According to the spectroscopic and literature data, complex **3** is proposed to be a tetrametallic compound (Figure 1) in which the titanium has the typical piano-stool shape. It is bonded to the pentamethylcyclopentadienyl group and to three oxygen atoms, each of which is bridging the titanium center and two rhodium atoms. The ^1H NMR spectrum shows two multiplet signals at 3.97 and 4.03 ppm with an integral of 6 H, each of which is assigned to the two sets of olefinic protons in each cyclooctadiene ligand. This also shows that all three of these groups are equivalent. On the other hand, the spectrum shows a singlet at 2.17 ppm, with a relative integral of 15 H, due to the protons of the pentamethylcyclopentadienyl ligand. Two multiplet signals are also observed at 1.55 and 2.08 ppm, with an integral of 12 H, corresponding to the methylene groups of the cyclooctadiene.

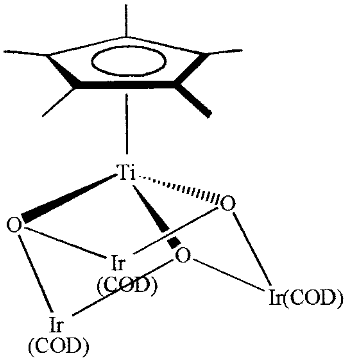

Figure 1. Proposed structure for complex **3**.

As in Cp^*TiMe_3, the methyl groups of Cp^*TaMe_4 (**4**) react with hydroxide complexes of rhodium and iridium. Reaction of complex **4** with 4 equiv of $[M(\mu\text{-}OH)(COD)]_2$ (M = Rh, Ir) in toluene, at room temperature, yields the heterometallic complexes $Cp^*Ta(\mu_3\text{-}O)_4[M(COD)]_4$ [M = Rh (**5**), Ir (**6**)] (eq 2).

$$Cp^*TaMe_4 + 2[M(\mu\text{-}OH)(COD)]_2 \rightarrow Cp^*Ta(\mu_3\text{-}O)_4[M(COD)]_4 + 4MeH \quad (2)$$

$$M = Rh\ (\mathbf{5}),\ Ir\ (\mathbf{6})$$

Complexes **5** and **6** are air-stable in the solid state. They are sparingly soluble in alkanes or toluene and have been characterized by elemental analysis, ^1H and ^{13}C NMR, and FT-IR spectroscopic techniques.

The spectroscopic and analytical data are in agreement with the formation of a pentametallic complex in which each of the four oxygen atoms bridges a tantalum and two rhodium (**5**) or iridium (**6**) centers.

The ^1H NMR spectrum of complex **5** consists of two multiplet signals at 1.33 and 2.15 ppm, corresponding to the methylene groups of the cyclooctadiene ligand, a singlet at 2.66 ppm, assigned to the pentamethylcyclopentadienyl moiety, and two multiplet signals at 3.74 and 3.85 ppm due to the olefinic protons from the cyclooctadiene ligand. It seems that, as in complex **3**, all four cyclooctadiene groups are equivalent. On the other hand, each of the COD ligands has two different olefinic environments: one is that facing the inside of the cavity formed by the $Ta(\mu_3\text{-}O)_4Rh_4$ core, while the other is that facing outside the cavity.

The $^{13}C\{^1H\}$ NMR spectrum is also in agreement with the data discussed above. It consists of a singlet at 12.9 ppm due to the methyl groups in the pentamethylcyclopentadienyl ring, two singlet signals at 30.7 and 30.9 ppm due to the methylene groups of the COD ligand, and two doublet signals at 71.9 and 72.9 ppm with

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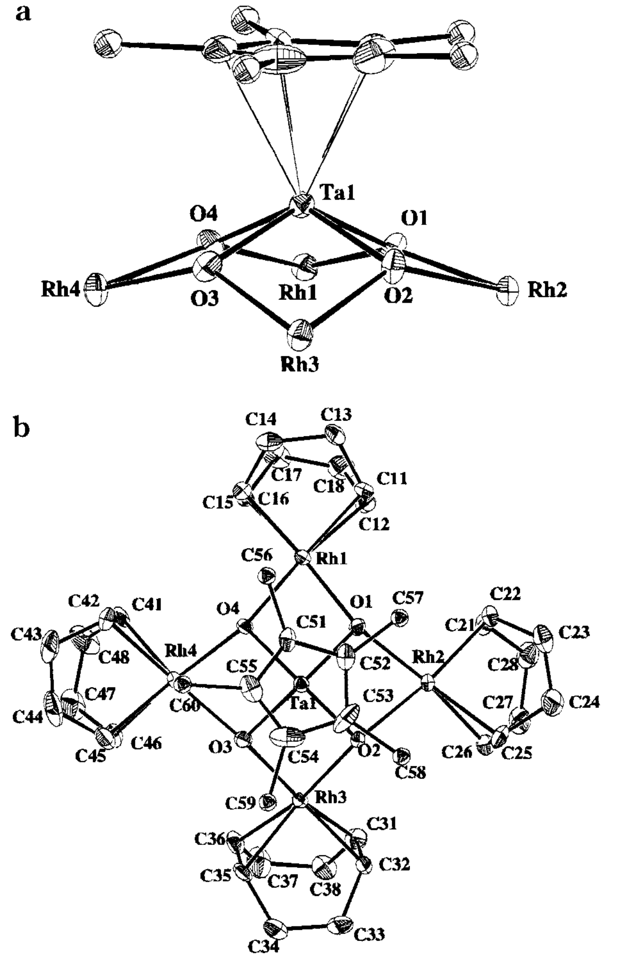

Figure 2. (a) Main framework of the molecular structure of complex **5**. (b) Molecular structure of **5** showing thermal ellipsoids and the labeling scheme.

coupling constants of $^1J_{Rh-C}$ = 14.49 and 14.88 Hz, respectively, corresponding to the olefinic carbon atoms. Both the coupling constants and the chemical shifts observed are typical for Rh(I) complexes.[13] The carbon atoms of the Cp* ring give rise to a singlet at 117.8 ppm.

Compound **5** can be recrystallized from toluene/pentane to give well-formed yellow single crystals. The X-ray structure analysis of **5** confirms the proposed pentametallic nature of the molecule. Figure 2a shows an ORTEP diagram of complex **5** in which the cyclooctadiene ligands have been omitted in order to provide a better view of the metallic cage. Figure 2b displays an ORTEP diagram of the molecule projected onto the pentamethylcyclopentadienyl ring plane. Table 1 lists some selected bond distances and angles.

The structure is built up of discrete pentametallic ($TaRh_4$) organometallic molecules. The pentametallic core forms a square-planar pyramid in which the four μ_3-O oxygen atoms are bridging. The tantalum atom has the usual four-legged piano-stool geometry, while the structure around the rhodium atoms is approximately planar. The rhodium−oxygen bond lengths in **5** [mean value 2.078(8) Å; see Table 1] are somewhat shorter than in the hydroxide complex $[Rh(OH)(P^iPr_3)_2]_2$[2c] but compare well with that found in Cp*Ti(μ_3-O)$_3$[Rh(COD)]$_3$.[10a]

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 5 and 8

distances		angles	
	Compound **5**		
Ta(1)−O(2)	1.942(9)	O(2)−Ta(1)−O(4)	138.0(4)
Ta(1)−O(4)	1.935(8)	O(2)−Ta(1)−O(1)	81.9(3)
Ta(1)−O(1)	1.941(8)	O(4)−Ta(1)−O(1)	79.9(3)
Ta(1)−O(3)	1.953(8)	O(2)−Ta(1)−O(3)	82.9(3)
Ta(1)−Rh(3)	3.0742(12)	O(4)−Ta(1)−O(3)	83.4(3)
Ta(1)−Rh(4)	3.0935(13)	O(1)−Ta(1)−O(3)	134.6(4)
Ta(1)−Rh(1)	3.0949(13)	O(1)−Rh(1)−O(4)	74.7(3)
Rh(1)−O(1)	2.042(8)	O(2)−Rh(2)−O(1)	75.0(3)
Rh(1)−O(4)	2.060(7)	O(3)−Rh(3)−O(2)	77.2(3)
Rh(2)−O(2)	2.090(7)	O(4)−Rh(4)−O(3)	75.9(3)
Rh(2)−O(1)	2.093(8)		
Rh(3)−O(3)	2.060(8)		
Rh(3)−O(2)	2.073(8)		
Rh(4)−O(4)	2.100(8)		
Rh(4)−O(3)	2.106(9)		
Rh(4)−C(46)	2.081(12)		
	Compound **8**		
Ir(1)−C(1)	2.108(9)	O(3)−Ir(1)−N(7)	92.0(2)
Ir(1)−O(3)	2.084(5)	O(4)−Ir(2)−N(5)	92.1(2)
Ir(1)−C(6)	2.104(9)	O(4)−Ir(2)−Ir(1)	72.47(17)
Ir(1)−C(5)	2.093(8)	C(21)−O(3)−Ir(1)	122.0(5)
Ir(1)−C(2)	2.113(9)	C(31)−O(4)−Ir(2)	122.6(5)
Ir(1)−N(7)	2.143(6)	C(22)−N(5)−Ir(2)	120.4(6)
Ir(1)−Ir(2)	3.092(2)	C(21)−N(5)−Ir(2)	119.8(5)
Ir(2)−O(4)	2.077(5)	O(3)−C(21)−N(5)	119.1(7)
Ir(2)−C(14)	2.111(10)	O(3)−C(21)−C(25)	120.4(7)
Ir(2)−C(15)	2.111(8)	N(6)−C(26)−C(25)	176.8(10)
Ir(2)−C(10)	2.119(8)	C(31)−N(7)−Ir(1)	119.8(5)
Ir(2)−C(11)	2.121(8)	C(35)−N(7)−Ir(1)	119.6(5)
Ir(2)−N(5)	2.145(6)	O(4)−C(31)−N(7)	119.7(7)
O(3)−C(21)	1.296(9)	N(8)−C(36)−C(32)	175.2(10)
O(4)−C(31)	1.280(9)		
C(1)−C(2)	1.385(14)		
C(5)−C(6)	1.391(14)		
C(10)−C(11)	1.401(15)		
C(14)−C(15)	1.384(15)		
N(8)−C(36)	1.145(12)		

The intermetallic Rh−Ta distances [mean value 3.0873(13) Å] are somewhat longer than that in the complex Cp*Ta(μ_2-S)$_2$(μ_3-S){Rh(COD}$_2$[14] (2.953 Å), but are sufficiently short that a direct metal−metal interaction is possible.

The distance from the tantalum atom to the Cp* ring centroid is 2.233(4) Å, a value that is normal for monocyclopentadienyltantalum complexes.[15] The tantalum−oxygen bond lengths [mean value 1.943(8) Å; see Table 1] are within the normal range expected for Ta−μ_3-O bonds.[16]

Compounds **5** and **6** react with 3-cyano-4,6-dimethyl-2-hydroxypyridine, in C_6D_6, to yield a rhodium or iridium alkoxide complex (**7** or **8**) together with an unidentified tantalum complex (eq 3).

$$\begin{aligned} &4[\text{3-CN-4,6-Me}_2\text{-2-OH}-\text{C}_5\text{HN}] + \\ &\quad \text{Cp*Ta}(\mu_3\text{-O})_4[\text{M(COD)}]_4 \rightarrow \\ &\quad 2[\text{M(2-O-3-CN-4,6-Me}_2-\text{C}_5\text{HN)(COD)}]_2 + \\ &\quad \text{“Cp*TaO}_2\cdot x\text{H}_2\text{O”} \qquad (3) \end{aligned}$$

$$\text{M} = \text{Rh } (\mathbf{7}),\ \text{Ir } (\mathbf{8})$$

Complexes **7** and **8** can be synthesized in a more straightforward reaction from the hydroxide complexes [M(μ-OH)(COD)]$_2$ (M = Rh, Ir) and the corresponding alcohol (eq 4). These two complexes are quite soluble in toluene but less soluble in Et_2O or alkanes. They have

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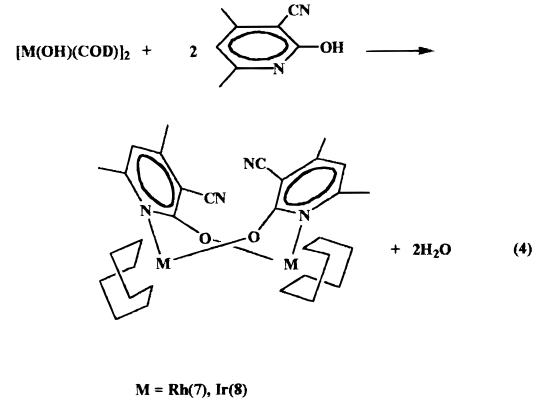
[13] Mackenzie, P. B.; Coots, R. J.; Grubbs, R. H. *Organometallics* **1989**, *8*, 8.



been characterized by elemental analysis, ^{1}H and ^{13}C NMR, and FT-IR spectroscopic techniques.

The ^{1}H and ^{13}C NMR spectra of **7** and **8** show that all four olefinic protons are nonequivalent. For instance, the ^{1}H NMR spectrum of complex **7** shows several multiplet signals between 1.27 and 2.92 ppm due to the methylene groups of the COD ligand. Two singlet signals appear at 1.68 and 3.00 ppm, which can be assigned to the methyl groups of the alkoxide ligand. The multiplet signals associated with the olefinic protons of the COD moiety appear at 2.69, 3.95, 4.81, and 5.42 ppm. The only aromatic proton on the alkoxide ligand gives rise to a singlet at 5.38 ppm.

All spectroscopic data indicate that the alkoxide ligand is bidentate and is coordinated to the metal center by the oxygen and the pyridinic nitrogen atoms. On the other hand, the fact that all the olefinic protons have a different environment suggests that **7** and **8** are dimer complexes analogous to the complexes reported by Rodman and Mann.[17]

The X-ray structural determination of complex **8** agrees with the proposed binuclear nature. An ORTEP view of the molecule together with the atom-labeling scheme is shown in Figure 3. Table 1 lists the most significant intramolecular distances and bond angles along with their standard deviations.

The geometry around each metal center is distorted square-planar. Each iridium center is bonded to a chelating η^4-COD ligand, to a pyridine nitrogen, and to an oxygen from the other bridging pyridinolate groups. The iridium atoms are situated out of these planes by 0.1523(6) and 0.2271(6) Å. These slight deviations of the metal atom from an ideal square-planar coordination with respect to the other metal atom suggest a clear intermetallic interaction between the iridium centers. The eight-membered (MNCO)$_2$ ring adopts a twisted tube conformation in which the Ir–Ir distance is 3.092(2) Å, which is 0.150 Å shorter than that in the analogous complex reported by Rodman and Mann [Ir(2-O-6-MeC$_5$H$_3$N)(COD)]$_2$.[17]

The coordination planes of the two metals are inclined with respect to each other with a dihedral angle of 55.4(3)°.

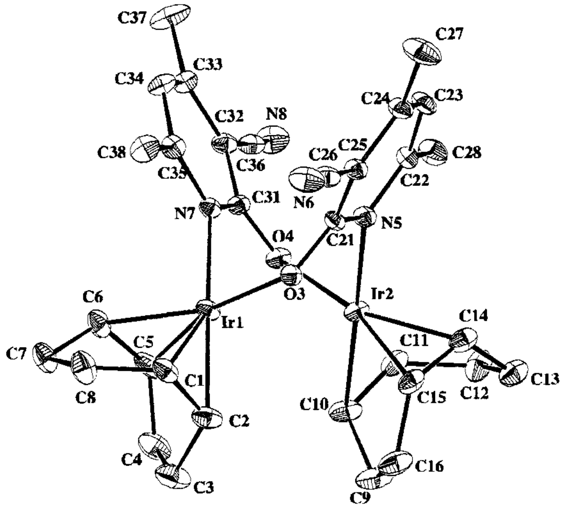
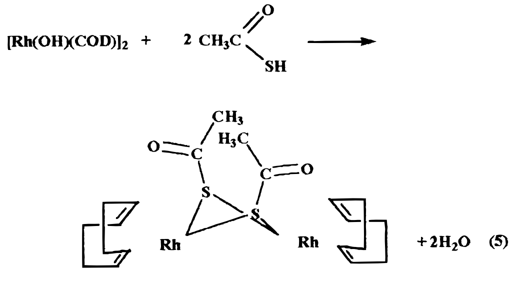


Figure 3. Molecular structure of **8** showing thermal ellipsoids and the labeling scheme.

The Ir–N and Ir–O distances average 2.144(6) and 2.080(5) Å, respectively, and these are slightly longer than those found in Rodman's complex [2.130(8) and 2.066(6) Å, respectively]. The COD ligand is coordinated to the iridium center in the usual η^4- bonding mode, and the C–C distances are within the expected range for Ir(I) complexes.

Complex [Rh(μ-OH)(COD)]$_2$ reacts with thiolacetic acid to render a rhodium thioacetate complex **9** (eq 5).



9

Many reported Rh and Ir carboxylate and thiocarboxylate complexes are monomeric with the ligands bound in a monohapto and/or a dihapto fashion.[18] They can also act as bridging groups[19] in dimeric compounds.[20] This versatility makes these compounds good candidates as catalysts in homogeneous reactions because coordination vacancies at the metal center are easily produced.[21] The reactivity of group 12 metal thiocarboxylates has been used to prepare valuable metal sulfide materials by thiocarboxylic anhydride elimination.[22]

Complex **9** is rather soluble in toluene but is less soluble in pentane. It decomposes slowly in toluene

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Table 2. Crystal Data and Structure Refinement for 5 and 8

	5	8
empirical formula	$C_{42}H_{63}O_4Rh_4Ta$	$C_{32}H_{38}Ir_2N_4O_2$
fw	1224.51	895.06
temp	293(2) K	293(2) K
wavelength	0.71070 Å	0.71070 Å
cryst syst, space group	monoclinic, $P2_1/n$	triclinic, $P\bar{1}$
unit cell dimens	$a = 17.678(5)$ Å	$a = 10.561(4)$ Å, $\alpha = 80.76(5)°$
	$b = 11.5590(10)$ Å, $\beta = 103.630(9)°$	$b = 10.988(3)$ Å, $\beta = 70.11(4)°$
	$c = 20.4740(10)$ Å	$c = 15.450(10)$ Å, $\gamma = 61.37(2)°$
volume	4065.8(12) $Å^3$	1479.8(12) $Å^3$
Z, calcd density	4, 2.000 g/cm^3	2, 2.009 g/cm^3
abs coeff	43.10 cm^{-1}	90.20 cm^{-1}
$F(000)$	2400	856
cryst size	0.2 × 0.2 × 0.4 mm	0.1 × 0.2 × 0.25 mm
limiting indices	$0 \leq h \leq 23, 0 \leq k \leq 15, -27 \leq l \leq 26$	$0 \leq h \leq 13, -12 \leq k \leq 14, -19 \leq l \leq 20$
no. of data/restraints/params	9778/0/435	7134/0/361
goodness-of-fit on F^2	0.971	1.025
final R indices $[I > 2\sigma(I)]$	R1 = 0.0548, wR2 = 0.0873	R1 = 0.0417, wR2 = 0.0962

solution to yield unidentified complexes. It has been characterized by elemental analysis and the usual spectroscopic methods. The ^{1}H NMR spectrum shows multiplet signals at 1.67 and 2.14 ppm, and these are assigned to the methylene protons of the COD ligand. A singlet at 1.99 ppm is assigned to the methyl group of the thioacetate moiety, while the olefinic protons of the COD ligand give rise to a multiplet at 4.82 ppm. The ^{13}C NMR data show a singlet signal at 31.5 ppm, which is assigned to the methylene group of the COD ligand. A singlet is also observed at 37.7 ppm corresponding to the methyl group, while olefinic carbons give rise to a doublet at 80.6 ppm ($^1J_{Rh-C} = 11.44$ Hz). Finally, the carboxylic carbon atom gives a singlet at 201.7 ppm.

All these data indicate that complex **9** is a dimer in which the thioacetate ligand is coordinated only through the sulfur atom bridging the two rhodium centers. Given that Rh(I) is a soft acid, coordination through the softer base, S, is expected. IR data support this hypothesis.[23]

In conclusion, we would like to point out the broad possibility that hydroxo complexes of late transition metals offer the opportunity to prepare either homo- or heterometallic complexes. On one hand, it has been possible to synthesize several heterometallic organometallic oxides that can be envisaged as models for metals supported on reducible oxides, allowing an insight into the phenomenon known as strong metal support interaction (SMSI). On the other hand, hydroxo complexes of rhodium and iridium, acting as Brönsted bases, allowed us to prepare alkoxide and thioacetate complexes.

Experimental Section

General Procedures. All reactions were carried out under nitrogen using Schlenk techniques. Solvents were dried and deoxygenated prior to use.

The following reagents were prepared by literature procedures: Cp^*TiMe_3,[24] Cp^*TaMe_4,[25] $[Rh(\mu\text{-}OH)(COD)]_2$,[26] $[Ir(\mu\text{-}OH)(COD)]_2$.[2e] The commercially available compounds MeLi in diethyl ether, thiolacetic acid, and 3-cyano-4,6-dimethyl-2-hydroxypyridine were used as received from Aldrich.

Elemental analyses were performed with a Perkin-Elmer 2400 microanalyzer. IR spectra were recorded in the region 4000−400 cm^{-1} with a Nicolet Magna-IR 550 spectrophotometer as Nujol mulls using PET cells.

^{1}H and ^{13}C NMR spectra were obtained on a 200 MHz Mercury Varian Fourier Transform spectrometer. Trace amounts of protonated solvents were used as references, and chemical shifts are reported in units of parts per million relative to $SiMe_4$.

Synthesis of $Cp^*Ti(\mu_3\text{-}O)_3[Ir(COD)]_3$ (3). A solution of Cp^*TiMe_3 (0.053 g, 0.23 mmol) in 2.5 mL of toluene, at −20 °C, was added to solid $[Ir(\mu\text{-}OH)(COD)]_2$ (0.203 g, 0.32 mmol). The mixture was allowed to reach room temperature and was stirred for 2 h. After this time the solvent was removed under vacuum and the residue washed twice with 2 mL of pentane. Yield: 0.156 g, 64%. IR (Nujol/PET, cm^{-1}): 1321 (m), 1295 (m), 1203 (w), 1000 (s), 960 (s), 673 (vs), 560 (m), 536 (m), 498 (m). ^{1}H NMR (C_6D_6): δ 1.55 (m, 12 H, CH_2), 2.08 (m, 12 H, CH_2), 2.17 (s, 15 H, Cp*), 3.97 (m, 6 H, =CH), 4.03 (m, 6H, =CH) $^{13}C\{^1H\}$ NMR (C_6D_6): δ 11.7 (s, CH_3), 31.8 (s, CH_2), 31.9 (s, CH_2), 57.7 (s, =CH), 64.5 (s, =CH), 120.1 (s, $C-CH_3$). Anal. Calcd for $C_{34}H_{51}O_3Ir_3Ti$: C, 36.06; H, 4.54. Found: C, 36.35; H, 4.43.

Synthesis of $Cp^*Ta(\mu_3\text{-}O)_4[Rh(COD)]_4$ (5). A solution of Cp^*TaMe_4 (0.045 g, 0.12 mmol) in 2 mL of toluene was added to solid $[Rh(\mu\text{-}OH)(COD)]_2$ (0.101 g, 0.22 mmol). The suspension was stirred, at room temperature, for 1 h, and the solvent was evaporated under vacuum. After washing the residue twice with pentane the yellow solid isolated was characterized as **5**. Yield: 0.087 g, 64%. IR (Nujol/PET, cm^{-1}): 1324 (s), 1298 (s), 948 (m), 689 (m), 560 (vs). ^{1}H NMR (C_6D_6): δ 1.33 (m, 16 H, CH_2), 2.15 (m, 16 H, CH_2), 2.66 (s, 15 H, Cp*), 3.74 (m, 8 H, =CH), 3.85 (m, 8 H, =CH) $^{13}C\{^1H\}$ NMR (C_6D_6): δ 12.9 (s, CH_3), 30.7 (s, CH_2), 30.9 (s, CH_2), 71.9 (d, $^1J_{Rh-C} = 14.49$ Hz, =CH), 72.9 (d, $^1J_{Rh-C} = 14.88$ Hz, =CH), 117.8 (s, $C-CH_3$). Anal. Calcd for $C_{42}H_{63}O_4Rh_4Ta$: C, 41.20; H, 5.18. Found: C, 41.50; H, 5.11.

Synthesis of $Cp^*Ta(\mu_3\text{-}O)_4[Ir(COD)]_4$ (6). A solution of Cp^*TaMe_4 (0.057 g, 0.15 mmol) in 2.5 mL of toluene was added to solid $[Ir(\mu\text{-}OH)(COD)]_2$ (0.181 g, 0.28 mmol). The suspension was stirred, at room temperature, for 2 h, and the solvent was evaporated under vacuum. After washing the residue twice with pentane the yellow compound was identified as **6**. Yield: 0.132 g, 59%. IR (Nujol/PET, cm^{-1}): 1321 (s), 1299 (s), 892 (m), 646 (m), 571 (vs). ^{1}H NMR (C_6D_6): δ 1.17 (m, 16 H, CH_2), 2.02 (m, 16 H, CH_2), 2.41 (s, 15 H, Cp*), 3.88 (m, 8 H, =CH), 4.06 (m, 8 H, =CH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 12.7 (s, CH_3), 31.8 (s, CH_2), 32.0 (s, CH_2), 55.2 (s, =CH), 56.2 (s, =CH), 120.5 (s, $C-CH_3$). Anal. Calcd for $C_{42}H_{63}O_4Ir_4Ta$: C, 31.89; H, 4.01. Found: C, 32.27; H, 4.02.

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Reaction of [Rh(μ-OH)(COD)]$_2$ with 3-Cyano-4,6-dimethyl-2-hydroxypyridine. A suspension of [Rh(μ-OH)(COD)]$_2$ (0.035 g, 0.077 mmol) in 3 mL of toluene was reacted with 3-cyano-4,6-dimethyl-2-hydroxypyridine (0.023 g, 0.155 mmol) during 3 h. After this time the solution was filtered and the solvent partially removed under vacuum. Slow condensation of pentane into the above solution gave 0.043 g (78%) of an orange crystalline solid, which was identified as complex **7**. IR (Nujol/PET, cm^{-1}): 2215 (s), 1584 (vs), 1545 (s), 1321 (m), 1303 (m), 1216 (s), 1103 (m), 995 (m), 960 (m), 820 (s), 792 (m), 771 (m), 655 (m), 627 (m), 494 (m). ^{1}H NMR (C$_6$D$_6$): δ 1.27 (m, 1 H, CH$_2$), 1.44 (m, 1 H, CH$_2$), 1.68 (s, 3 H, CH$_3$), 1.73 (m, 2 H, CH$_2$), 1.88 (m, 1 H, CH$_2$), 2.51 (m, 2 H, CH$_2$), 2.69 (m, 1 H, =CH), 2.92 (m, 1 H, CH$_2$), 3.00 (s, 3 H, CH$_3$), 3.95 (m, 1 H, =CH), 4.81 (m, 1 H, =CH), 5.38 (s, 1 H, CH), 5.42 (m, 1 H, =CH). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 19.6 (s, *C*H$_3$), 24.9 (s, *C*H$_3$), 28.9 (s, *C*H$_2$), 30.3 (s, *C*H$_2$), 32.0 (s, *C*H$_2$), 33.4 (s, *C*H$_2$), 72.6 (d, $^1J_{Rh-C}$ = 14.65 Hz, =*C*H), 73.62 (d, $^1J_{Rh-C}$ = 14.19 Hz, =*C*H), 77.5 (d, $^1J_{Rh-C}$ = 12.36 Hz, =*C*H), 89.5 (d, $^1J_{Rh-C}$ = 13.73 Hz, =*C*H), 98.1 (s, *C*−CN) 113.9 (s, *C*H), 116.5 (s, *C*N), 154.2 (s, *C*−CH$_3$), 160.1 (s, *C*−CH$_3$), 174.7 (s, *C*−O). Anal. Calcd for C$_{32}$H$_{38}$N$_4$O$_2$Rh$_2$: C, 53.64; H, 5.34; N, 7.82. Found: C, 53.39; H, 5.45; N, 7.75.

Reaction of [Ir(μ-OH)(COD)]$_2$ with 3-Cyano-4,6-dimethyl-2-hydroxypyridine. A mixture of [Ir(μ-OH)(COD)]$_2$ (0.030 g, 0.048 mmol) and 3-cyano-4,6-dimethyl-2-hydroxypyridine (0.020 g, 0.135 mmol) in 2 mL of toluene was stirred at room temperature for 3 h. The solution was filtered and the solvent partially removed under vacuum. Slow condensation of pentane onto the toluene solution yielded complex **8** as dark purple crystals (0.032 g, 75%). IR (Nujol/PET, cm^{-1}): 2226 (s), 1598 (vs), 1542 (s), 1307 (m), 1225 (s), 1150 (m), 1097 (m), 1000 (m), 828 (m), 791 (w), 657 (w), 627 (w), 510 (w), 504 (w). ^{1}H NMR (C$_6$D$_6$): δ 1.05 (m, 1 H, CH$_2$), 1.19 (m, 1 H, CH$_2$), 1.44 (m, 1 H, CH$_2$), 1.57 (m, 1 H, CH$_2$), 1.63 (s, 3 H, CH$_3$), 1.80 (m, 1 H, CH$_2$), 2.30 (m, 2 H, CH$_2$), 2.48 (m, 1 H, =CH), 2.72 (m, 1H, CH$_2$), 2.77 (s, 3 H, CH$_3$), 3.83 (m, 1 H, =CH), 4.37 (m, 1 H, =CH), 5.26 (s, 1 H, CH), 5.41 (m, 1 H, =CH). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 19.5 (s, *C*H$_3$), 24.5 (s, *C*H$_3$), 29.4 (s, *C*H$_2$), 30.5 (s, *C*H$_2$), 32.7 (s, *C*H$_2$), 34.1 (s, *C*H$_2$), 55.9 (s, =*C*H), 56.6 (s, =*C*H), 58.8 (s, =*C*H), 75.8 (s, =*C*H), 99.3 (s, *C*−CN) 115.8 (s, C−*C*N), 116.1 (s, *C*H), 154.4 (s, *C*−CH$_3$), 159.5 (s, *C*−CH$_3$), 173.8 (s, *C*−O). Anal. Calcd for C$_{32}$H$_{38}$N$_4$O$_2$Ir$_2$: C, 42.94; H, 4.28; N, 6.26. Found: C, 43.03; H, 4.27; N, 6.22.

Reaction of [Rh(μ-OH)(COD)]$_2$ with Thiolacetic Acid. To a suspension of [Rh(μ-OH)(COD)]$_2$ (0.085 g, 0.19 mmol) in 3 mL of toluene was added CH$_3$COSH (28 μL, 0.37 mmol). After 1 h the solvent was removed under vacuum and the residue washed twice with pentane to yield 0.065 g of a red solid which was characterized as complex **9** (61%). IR (Nujol/PET, cm^{-1}): 2340 (w), 2090 (w), 2020 (w), 1679 (vs), 1348 (s), 1304 (m), 1109 (s), 1078 (m), 941 (m), 615 (m). ^{1}H NMR (C$_6$D$_6$): δ 1.67 (m, 8 H, CH$_2$), 1.99 (s, 6 H, CH$_3$) 2.14 (m, 8 H, CH$_2$), 4.82 (m, 8 H, =CH). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 31.5 (s, *C*H$_2$), 37.7 (s, *C*H$_3$), 80.6 (d, $^1J_{Rh-C}$ = 11.44 Hz, =*C*H), 201.7 (s, *C*S). Anal. Calcd For C$_{20}$H$_{30}$O$_2$S$_2$Rh$_2$: C, 41.97; H, 5.28. Found: C, 42.09; H, 5.33.

X-ray Structure Determination for 5 and 8. Intensity data were collected on a NONIUS-MACH3 diffractometer equipped with a graphite monochromator [Mo Kα radiation (λ = 0.71073 Å)] using an $\omega/2\theta$ scan technique to a maximum value of 56°. The final unit cell was determined from 25 well-centered high-angle reflections that were widely scattered in reciprocal space. Data were corrected for Lorentz and polarization effects, and absorption correction was carried out on the basis of an azimuthal scan.[27] The structures were solved by direct methods,[28] and refinement was carried out by full-matrix least-squares.[29] For **5**, isotropic temperature parameters were considered for C56−C60 and anisotropic parameters on the remaining atoms. For **8** all non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculation positions but were not refined. Weights were optimized in the final cycles. Atomic scattering factors were taken from ref 30. Crystallographic data and selected bond parameters are collected in Table 2. Other detailed data are supplied in the Supporting Information.

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Supporting Information Available: Crystallographic data, final atomic coordinates for the non-hydrogen atoms, bond distances and angles, anisotropic thermal parameters, and final atomic coordinates for the hydrogen atoms for **5** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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