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Deprotonation of $Cp_2Ti(SH)_2$ with Mononuclear Rhodium and Iridium Compounds: A New Route to Trinuclear Early−Late Heterobimetallic Complexes

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The reaction of $Cp_2Ti(SH)_2$ with [M(acac)(diolefin)] (acac = acetylacetonate) yields the complexes [Cp(acac)Ti(μ_3-S)$_2${M(diolefin)}$_2$] (M = Rh, diolefin = 1,5-cyclooctadiene (cod) (**1**); diolefin = tetrafluorobenzobarrelene (tfbb) (**2**); M = Ir, diolefin = cod (**3**)). The formation of the trinuclear heterobimetallic complexes results from a complex reaction involving the deprotonation of the hydrosulfido ligands along with the addition of the late-metal fragment(s), followed by the release of cyclopentadiene and the coordination of acetylacetonate to the titanium center. Similarly, the reaction of $Cp_2Ti(SH)_2$ with [M(quinol)(diolefin)] (quinol = 8-oxyquinolinate) gives the complexes [Cp(quinol)Ti(μ_3-S)$_2${M(diolefin)}$_2$] (M = Rh, diolefin = cod (**4**); tfbb (**5**); M = Ir, diolefin = cod (**6**)), which incorporate the 8-oxyquinolinate ligand. The d^0−d^8 trinuclear early−late heterobimetallic complexes exhibit triangular $TiRh_2$ and $TiIr_2$ cores doubly capped by two μ_3-sulfido ligands. Deprotonation of $Cp_2Ti(SH)_2$ with the mononuclear carbonyl complexes [M(acac)(CO)$_2$] (M = Rh, Ir) yields the ion-pair complexes [Cp_2Ti(acac)][M_3(μ_3-S)$_2$(CO)$_6$] (M = Rh (**7**); M = Ir (**8**)), which result from complete transference of the sulfido ligands to the d^8 metal centers. Carbonylation of the diolefin complexes [Cp(acac)Ti(μ_3-S)$_2${M(diolefin)}$_2$] or [Cp(quinol)Ti(μ_3-S)$_2${M(diolefin)}$_2$] yields the compounds [Cp(acac)Ti(μ_3-S)$_2${M(CO)$_2$}$_2$] (M = Rh (**9**); M = Ir (**10**)) and [Cp(quinol)Ti(μ_3-S)$_2${M(CO)$_2$}$_2$] (M = Rh (**11**); M = Ir (**12**)), respectively. Replacement reactions on the carbonyl complexes with triphenylphosphine give the disubstituted complexes [Cp(acac)Ti(μ_3-S)$_2${M(CO)(PPh$_3$)}$_2$] (M = Rh (**13**); M = Ir (**14**)) or [Cp(quinol)Ti(μ_3-S)$_2${M(CO)(PPh$_3$)}$_2$] (M = Rh (**15**); M = Ir (**16**)), which are obtained as mixtures of *cis* and *trans* isomers. The molecular structures of complexes **1** and **8** have been determined by X-ray diffraction methods.

Introduction

The chemistry of heteropolynuclear complexes containing widely divergent transition metals is of current interest and of relevance to the chemistry involved in certain types of industrial catalytic processes.[1] Among them, complexes with bridging sulfido ligands have a broad scope ranging from biological systems and applied catalysis, such as dehydrosulfurization, to novel chemistry of molecular systems.[2] Moreover, early−late heterometallic complexes, which incorporate electron-poor and electron-rich metals, open possibilities to new reactivity patterns, such as the cooperative heterometallic activation of small molecules, and the exploration of the synergism between the metals in both catalytic[3] and stoichiometric reactions.[4]

An elegant synthetic approach for early−late heterobimetallic complexes (ELHB) established by Stephan and co-workers involves early-metal complexes as metallaligands for late-transition metal species.[5] They include titanium and zirconium complexes with terminal thiolate,[6] phosphide,[7] and alkoxyalkylphosphine ligands,[8] pendant chelating metallaligands,[9] and also

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macrocyclic metallaligands.[10] Other useful metallaligands are based on functionalized cyclopentadienyl groups in early-metallocene complexes,[11] and remarkable synthetic strategies involve the use of bis(cyclopentadienyl)titanacyclobutanes[12] or methylcarbene titanium complexes[13] to give methylene-bridged early−late heterometallic complexes.

A few early−late complexes containing group 4 metals with sulfido bridging ligands have been reported[3d,14] probably because the possible precursors, the early-metal complexes with terminal sulfido groups, are rare.[15] Very recently we have developed a synthetic methodology based on the acid−base chemistry of $Cp_2Ti(SH)_2$ which leads to d^0-d^8 early−late heterometallic complexes. Thus, we have reported that the deprotonation of the bis(hydrosulfido)titanium complex with $[\{Rh(\mu\text{-}OMe)(diolefin)\}_2]$ gives the tetranuclear heterobimetallic complexes $[CpTi(\mu_3\text{-}S_3)\{Rh(diolefin)\}_3]$, in which the group $[CpTi(S)_3]^{3-}$ caps a trimetallic triangle of the late-metals.[16] Moreover, the group $[CpTi(S)_3]^{3-}$, which has no simple precursors in the chemistry of titanium, is a metallaligand generated in these reactions from the cubane clusters $[Cp_2Ti_2(\mu_3\text{-}S)_4\{M(diolefin)\}_2]$ as intermediates and stabilized by coordination to the late-metal fragments. Indeed, a general way to $[CpTi(\mu_3\text{-}S_3)\{M(diolefin)\}_3]$ involves the reactions of the anion $[Cp_2Ti_2(\mu\text{-}S)_2(S)_2]^{2-}$ with the chloro complexes $[\{M(\mu\text{-}Cl)(diolefin)\}_2]$ (M = Rh, Ir).[17] Furthermore, the reactions of $Cp_2Ti(SH)_2$ with rhodium and iridium complexes are sensitive to the presence of oxygen donor ligands such as water, providing in favorable cases the access to oxo-sulfide titanium−rhodium complexes such as $[(CpTi)_2(\mu_4\text{-}O)(\mu_3\text{-}S)_4Rh_4(CO)_4(PR_3)_2]$.[18] Therefore, the course of these complex deprotonation reactions of $Cp_2Ti(SH)_2$ simultaneous with the addition of rhodium and iridium fragments (additive-deprotonation) was unpredictable depending on the oxygen donor ligands in the starting materials to which the proton is transferred.

We describe in this paper the reactions of $Cp_2Ti(SH)_2$ with mononuclear rhodium and iridium complexes containing chelating anionic ligands such as acetylacetonate (acac) and 8-oxyquinolinate (quinol), which lead to a new unexpected type of d^0-d^8 trinuclear heterobimetallic compounds. In addition, some results on the reactivity of the new complexes are also reported.

Results

Reaction of $[Cp_2Ti(SH)_2]$ with [M(acac)(diolefin)] and [M(quinol)(diolefin)]. The reaction of $Cp_2Ti(SH)_2$ with [Rh(acac)(cod)] in toluene (in 1:2 molar ratio) gives the complex $[Cp(acac)Ti(\mu_3\text{-}S)_2\{Rh(cod)\}_2]$ (**1**), which is isolated as a dark violet microcrystalline solid in good yield. The formation of the heterotrinuclear compound is confirmed by the molecular weight and the mass spectrum, where several peaks arising from the molecular ion are observed. The ^1H NMR spectrum of **1** displays a 1:1:2 ratio for the Cp, acac, and cod ligands, respectively, in agreement with the loss of a cyclopentadienyl ligand from the starting titanium complex and the incorporation of an acac ligand. The coordination of the latter to titanium is supported by the downfield shift of the resonance corresponding to the Cp ligand (6.53 ppm) relative to that observed in $[CpTi(\mu_3\text{-}S_3)\{Rh(cod)\}_3]$ (5.71 ppm). In addition, the two strong absorptions at 1580 and 1525 cm^{-1}, observed in the IR spectrum in Nujol, are in agreement with a chelating coordination mode of the acac ligand.[19]

The ^1H and $^{13}C\{^1H\}$ NMR spectroscopic information and the molecular weight in solution are in agreement with the structure found in the solid state (see below). In particular, the plane of symmetry of the molecule

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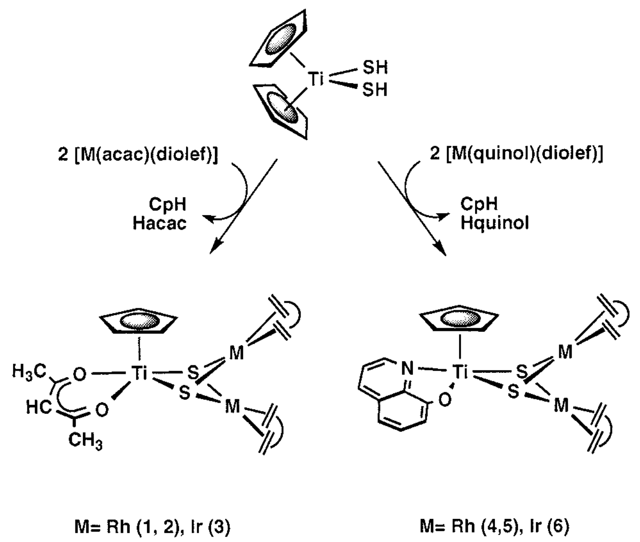
Scheme 1



makes equivalent the methyl and CO groups of acac and two halves of the cod ligands in the ^1H and $^{13}C\{^1H\}$ NMR spectra.

In the same way, the reactions of $Cp_2Ti(SH)_2$ with [Rh(acac)(tfbb)] and [Ir(acac)(cod)] in toluene give the compounds $[Cp(acac)Ti(\mu_3\text{-}S)_2\{Rh(tfbb)\}_2]$ (**2**) and $[Cp(acac)Ti(\mu_3\text{-}S)_2\{Ir(cod)\}_2]$ (**3**), respectively, which are also isolated in high yield (Scheme 1). They have a heterotrinuclear formulation and structure similar to **1**, as deduced from microanalysis, mass spectra, and NMR spectroscopy. In particular, the molecular ion is observed in the mass spectrum of **3** (*m*/*z* 876). In addition, the four signals for the olefinic proton and carbon atoms (=CH) in the ^1H and $^{13}C\{^1H\}$ NMR spectra of both complexes indicate the presence of a symmetry plane that relates the two halves of diolefin ligands.

Mononuclear rhodium and iridium diolefin complexes containing the chelating N,O-donor ligand 8-oxyquinolinate (quinol) behave similarly to the *β*-diketonate (acac) complexes. Thus, the reactions of $Cp_2Ti(SH)_2$ with [Rh(quinol)(cod)] and [Rh(quinol)(tfbb)] (1:2 molar ratio) in dichloromethane lead exclusively to the formation of the heterotrinuclear complexes $[Cp(quinol)Ti(\mu_3\text{-}S)_2\{Rh(cod)\}_2]$ (**4**) and $[Cp(quinol)Ti(\mu_3\text{-}S)_2\{Rh(tfbb)\}_2]$ (**5**), which are isolated in high yield as dark violet solids. Similarly, the heterotrinuclear iridium complex $[Cp(quinol)Ti(\mu_3\text{-}S)_2\{Ir(cod)\}_2]$ (**6**) is obtained in high yield by reaction of $Cp_2Ti(SH)_2$ with [Ir(quinol)(cod)] in dichloromethane (Scheme 1).

The heterotrinuclear formulation of complexes **4**−**6** relies on both the mass and the ^1H and $^{13}C\{^1H\}$ NMR spectra, where a 1:1:2 ratio for the Cp, quinol, and diolefin ligands, respectively, is observed. The introduction of the 8-oxyquinolinate ligand in the heterotrinuclear structure results in the disappearance of the mirror plane, and, in consequence, complexes **4**−**6** have no symmetry. This is easily deduced from the ^1H and $^{13}C\{^1H\}$ NMR of the complexes since, for example, complex **5** exhibits one resonance for each proton and carbon in the molecule. The 8-oxyquinolinate ligand displays a set of six resonances (Figure 1) showing standard J_{H-H} couplings,[20] which have been unequivocally assigned from the H,H-COSY NMR spectrum for complex **4** only, since an identical pattern of resonances is observed in all cases (see Experimental Section). The chemical shift of the Cp resonance in complexes **4**−**6** is similar to that observed in the related acetylacetonate complexes and strongly supports the chelating coordination of the quinol ligand to the titanium center.

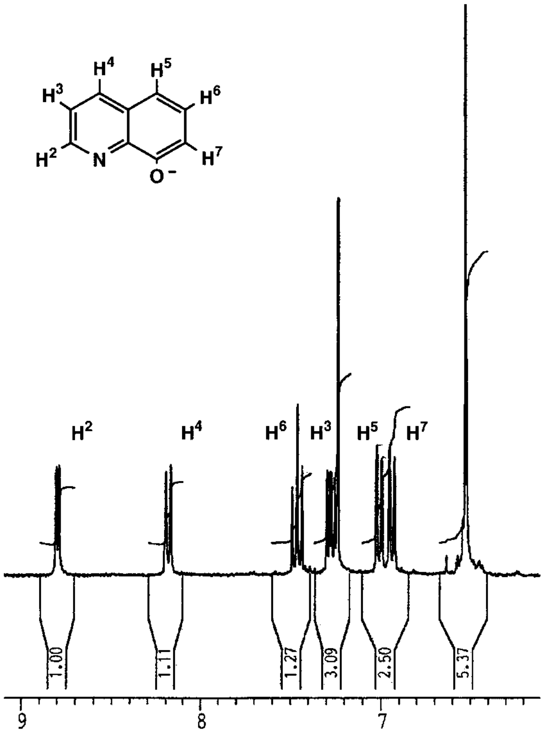


Figure 1. Aromatic region of the ^1H NMR spectrum of $[Cp(quinol)Ti(\mu_3\text{-}S)_2\{Rh(cod)\}_2]$ (**4**) in $CDCl_3$ at 293 K showing the numbering scheme for the 8-oxyquinolinate ligand.

Complexes **2**, **3**, and **4** are dynamic in solution since line-broadening effects are observed at room temperature in the olefinic region of the ^1H NMR spectra, although sharp signals are observed at low temperature. This dynamic behavior is also observed in complex **1** at temperatures higher than room temperature. As the broadening of the signals for the diolefinic ligands are the single feature observed, no further study was carried out.

Structure of $[Cp(acac)Ti(\mu_3\text{-}S)_2\{Rh(cod)\}_2]$ (1). The structure of $[Cp(acac)Ti(\mu_3\text{-}S)_2\{Rh(cod)\}_2]$ (**1**) has been determined by X-ray diffraction methods from a single crystal obtained by slow diffusion of *n*-hexane into a concentrated solution of the complex in toluene at low temperature. The molecule has crystallographically imposed C_s symmetry with the three metals occupying special positions in the symmetry plane (Figure 2). Compound **1** shows a triangular $TiRh_2$ core capped on both sides by two nearly symmetrical μ_3-sulfido ligands. The geometry around the rhodium atoms is square-planar, with the metal atom bonded to both sulfido groups and to two olefinic bonds of an η^4-1,5-cyclooctadiene ligand. The titanium center adopts a typical *four-legged piano stool* arrangement by coordination, apart from the two sulfido ligands, to an η^5-cyclopentadienyl and a chelating acetylacetonate ligand.

Selected bond distances and angles for **1** are summarized in Table 1. The Rh−S bond lengths, 2.3419(7)

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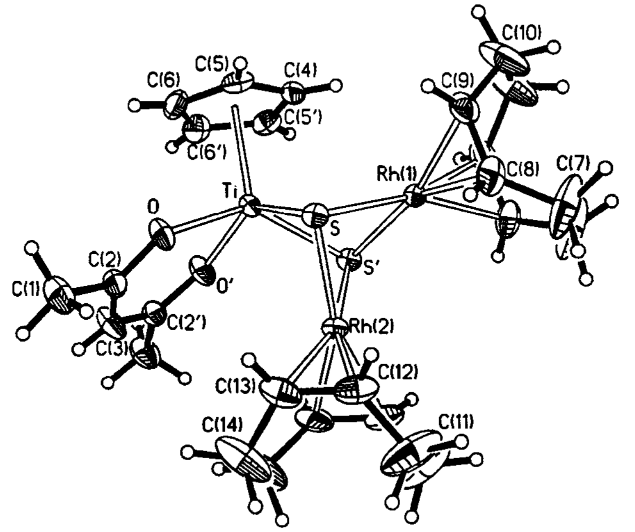

Figure 2. Molecular structure of [Cp(acac)Ti(μ_3-S)$_2${Rh(cod)}$_2$] (**1**) showing the atom-numbering scheme used (symmetry transformation for primed atoms: *x*, 1/2−*y*, *z*).

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 1[a]

Rh(1)···Rh(2)	2.9207(5)		
Rh(1)···Ti	3.1992(8)	Rh(2)···Ti	2.9904(8)
Rh(1)−S	2.3419(7)	Rh(2)−S	2.3333(7)
Rh(1)−C(8)	2.134(3)	Rh(2)−C(12)	2.144(3)
Rh(1)−C(9)	2.143(3)	Rh(2)−C(13)	2.137(3)
C(8)−C(9)	1.382(5)	C(12)−C(13)	1.373(5)
Ti−S	2.3750(8)	Ti−Cp[b]	2.060(3)
Ti−O	2.062(2)	O−C(2)	1.269(3)
Ti−C(4)	2.368(4)	C(1)−C(2)	1.507(4)
Ti−C(5)	2.371(3)	C(2)−C(3)	1.382(4)
Ti−C(6)	2.394(3)		
S−Rh(1)−S′	83.65(3)	S−Rh(2)−S′	84.02(3)
S−Rh(1)−M(1)[c]	94.1(1)	S−Rh(2)−M(2)[c]	94.0(1)
S′-Rh(1)−M(1)[c]	175.1(1)	S′-Rh(2)−M(2)[c]	177.6(1)
S−Ti−Cp[b]	115.21(9)	S−Ti−O′	136.54(6)
S−Ti−O	82.60(6)	O−Ti−Cp[b]	108.12(11)
S−Ti−S′	82.22(2)	O−Ti−O′	81.08(7)
Rh(1)−S−Ti	85.41(2)	Rh(2)−S−Ti	78.85(2)
Rh(1)−S−Rh(2)	77.32(2)		

[a] Primed atoms are related to the unprimed ones by the symmetry transformation *x*, 1/2−*y*, *z*. [b] Cp represents the centroid of the cyclopentadienyl ligand. [c] M(1) and M(2) represent the midpoints of the olefinic bonds coordinated to Rh(1) and Rh(2), respectively.

and 2.3333(7) Å, are statistically slightly different, but compare well with those found in the closely related μ_3-sulfido Rh−Ti heterotetranuclear complex [CpTi(μ_3-S$_3$){Rh(tfbb)}$_3$] (2.311−2.338(4) Å),[16] where each sulfido ligand also bridges two “Rh(diolefin)” moieties to a CpTi group. However these distances are significantly shorter than the values observed in related μ_2-thiolate bridged Rh−Ti complexes as in [Cp$_2$Ti{S(CH$_2$)$_3$PPh$_2$}$_2$Rh]$^+$ (2.349 and 2.380(3) Å)[9a] or in [CpTi{S(CH$_2$)$_3$S}$_2$Rh(nbd)] (mean 2.477(2) Å),[10a] as well as in rhodium homonuclear μ_2-thiolate derivatives [Rh$_4$(μ-PyS$_2$)$_2$(cod)$_4$] (2.391−2.394(1) Å)[21] and [Rh$_3$(μ_3-C$_7$H$_4$NS$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$(tfbb)]$^+$ (2.374−2.383(6) Å).[22] On the other hand, the Ti−S bond distance observed, 2.3750(8) Å, is significantly longer than that observed in the related [CpTi(μ_3-S$_3$){Rh(tfbb)}$_3$] (mean 2.295(3) Å)[16] or in the cluster [{CpTi}$_2$(μ_4-O)(μ_3-S)$_4$ {Rh$_4$(CO)$_4$(P(OPh)$_3$)$_2$}] (average 2.2693(10) Å);[18] the greater electron density of the titatium center in **1**, due to the additional presence of the coordinated acetylacetonate ligand, probably justifies this structural behavior.

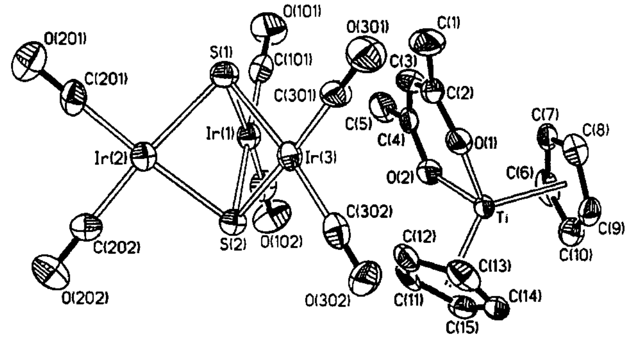

Figure 3. Molecular diagram of the two ionic metal complexes of the compound [Cp$_2$Ti(acac)][Ir$_3$(μ_3-S)$_2$(CO)$_6$] (**8**).

Interestingly the two Rh···Ti separations are markedly different, with values of 3.1992(8) and 2.9904(8) Å. Most probably this asymmetry is fundamentally due to the distinct steric requirements of the two ancillary ligands bonded to the titanium center (Cp and acac), rather than to electronic effects. In fact, the electronic characteristics of both rhodium atoms seem to be quite similar in light of Rh−C, C=C, or Rh−S bond distances, which are identical for both rhodium atoms (as commented above, only Rh−S bond distances are slightly different). Although both distances are well over the values reported for direct Rh−Ti metal−metal bonds,[23] the shortest Rh(2)···Ti separation in **1** is close to the values reported in the related tetranuclear complex [CpTi(μ_3-S$_3$){Rh(tfbb)}$_3$] (2.912−2.940(3) Å)[16] or in dinuclear thiolate[9a,10a] or methylene-bridged[12a,b] Rh−Ti complexes (2.827−2.986(1) Å), where a weak dative interaction from the electron-rich d^8 metal to the acidic d^0 titanium center has been suggested. Thus, from the Rh···Ti geometric parameters (also the Rh−S−Ti bond angles), this weak dative intermetallic interaction could also be present in **1** between Rh(2) and Ti, but the longest Rh(1)···Ti separation clearly rules out this possibility for the second rhodium atom. Some kind of intermetallic interaction between the two d^8 metals could also be suggested from the shorter Rh(1)···Rh(2) distance, 2.9207(4) Å.[24]

Reactions of [Cp$_2$Ti(SH)$_2$] with [M(acac)(CO)$_2$] (M = Rh, Ir). The reaction of Cp$_2$Ti(SH)$_2$ with [Rh(acac)(CO)$_2$] (1:3 molar ratio) in dichloromethane gives the ion-pair product [Cp$_2$Ti(acac)][Rh$_3$(μ_3-S)$_2$(CO)$_6$] (**7**), which is isolated as a brown microcrystalline solid in excellent yield. The related complex [Cp$_2$Ti(acac)][Ir$_3$(μ_3-S)$_2$(CO)$_6$] (**8**) is obtained as dark red microcrystals by reaction of Cp$_2$Ti(SH)$_2$ with [Ir(acac)(CO)$_2$] (Scheme 2). Complex **8** has been characterized by an

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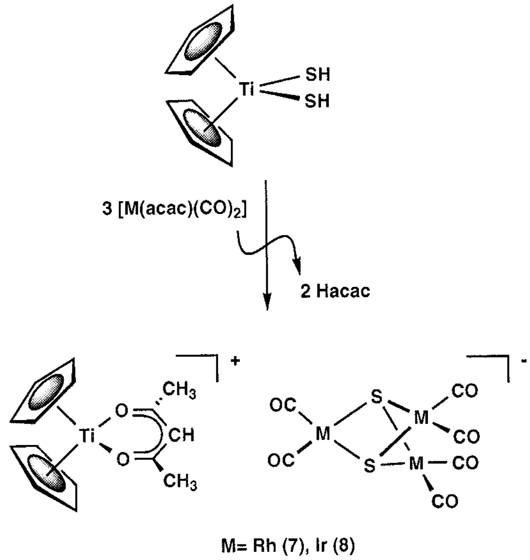
(21) Pérez-Torrente, J. J.; Casado, M. A.; Ciriano, M. A.; Lahoz, F. J.; Oro, L. A. *Inorg. Chem.* **1996**, *35*, 1782.

(22) Ciriano, M. A.; Pérez-Torrente. J. J.; Viguri, F.; Lahoz, F. J.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Chem. Soc., Dalton Trans.* **1990**, 1493.

(23) Tauster, S. J. *Acc. Chem. Res.* **1987**, *20*, 389. Sakellson, S.; McMillan, M.; Haller, G. L. *J. Phys. Chem.* **1986**, *90*, 1733.

(24) (a) Tejel, C.; Shi, Y.-M.; Ciriano, M. A.; Edwards, A. J.; Lahoz, F. J.; Modrego, J.; Oro, L. A. *J. Am. Chem. Soc.* **1997**, *119*, 6678. (b) Tejel, C.; Villoro, J. M.; Ciriano, M. A.; López, J. A.; Eguizábal, E.; Lahoz, F. J.; Bakhmutov, V. I.; Oro, L. A. *Organometallics* **1996**, *15*, 2967. (c) Ciriano, M. A.; Pérez-Torrente, J. J.; Lahoz, F. J.; Oro, L. A. *J. Chem. Soc., Dalton Trans.* **1992**, 1831.

Scheme 2



X-ray diffraction study, and the structure is shown in Figure 3.

The ion-pair complexes **7** and **8** are 1:1 electrolytes in acetone. The FAB+ mass spectra show the presence of the cation $[Cp_2Ti(acac)]^+$, and the corresponding anions $[M_3(\mu_3\text{-}S)_2(CO)_6]^-$ are observed under FAB− conditions. Spectroscopic data for both complexes are very similar and in agreement with the structure found in the solid state for **8**. The ^1H NMR spectra show the expected 2:1 ratio for the Cp:acac ligands, and the chemical shifts of the Cp resonances closely resemble those found for complexes **1**−**3**, where an acac ligand is also bonded to the titanium center. Moreover, the =CH resonance of the acetylacetonate ligand in complexes **7** and **8** is observed at low field, in agreement with the electrophilic character of the cation $[Cp_2Ti(acac)]^+$. These values are only comparable to that observed in the heterotrinuclear complex $[Cp(acac)Ti(\mu_3\text{-}S)_2\{Rh(tfbb)\}_2]$ (**2**) containing π-acceptor tfbb ligands. Finally, all the carbonyl ligands in the $[M_3(\mu_3\text{-}S)_2(CO)_6]^-$ anions are equivalent, yielding a doublet at 184.9 ppm ($^1J_{Rh-C}$ = 70 Hz) and a singlet at 174.7 ppm in the $^{13}C\{^1H\}$ NMR spectra of complexes **7** and **8**, respectively. In addition, the ^1H and $^{13}C\{^1H\}$ NMR spectra of both complexes also show equivalent methyl and CO groups of the acac ligand, as required by the C_s symmetry of the $[Cp_2Ti(acac)]^+$ cation.

The anions $[M_3(\mu_3\text{-}S)_2(CO)_6]^-$ (M = Rh and Ir) have been previously obtained by several methods and structurally characterized by Garlaschelli et al.[25] The degradation of the clusters $[M_4(CO)_{12}]$ and $[M_6(CO)_{16}]$ with KSCN and potassium polysulfide and the reaction of the anionic complexes $[MCl_2(CO)_2]^-$ (M = Rh, Ir) with $[N(PPh_3)_2]_2S$ give both anions in yields ranging from 60 to 80%. $[Cp_2Ti(acac)]ClO_4$ was prepared by reaction of Cp_2TiCl_2 with $AgClO_4$ in water in the presence of acetylacetone,[26] probably via the intermediate species $[Cp_2Ti(OH)]^+$; however, a crystal structure of compounds containing this cation has not been reported yet.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 8

Anionic Complex			
Ir(1)···Ir(2)	3.0435(14)		
Ir(1)···Ir(3)	3.1198(11)	Ir(2)···Ir(3)	3.076(2)
Ir(1)−S(1)	2.362(3)	Ir(1)−S(2)	2.360(3)
Ir(2)−S(1)	2.364(3)	Ir(2)−S(2)	2.368(2)
Ir(3)−S(1)	2.370(3)	Ir(3)−S(2)	2.358(2)
Ir(1)−C(101)	1.842(11)	Ir(1)−C(102)	1.830(10)
Ir(2)−C(201)	1.851(10)	Ir(2)−C(202)	1.844(10)
Ir(3)−C(301)	1.854(10)	Ir(3)−C(302)	1.869(12)
C(101)−O(101)	1.157(12)	C(102)−O(102)	1.147(11)
C(201)−O(201)	1.135(11)	C(202)−O(202)	1.153(12)
C(301)−O(301)	1.131(11)	C(302)−O(302)	1.133(12)
Ir(2)···Ir(1)···Ir(3)	59.86(5)	S(1)−Ir(1)−S(2)	82.53(9)
S(1)−Ir(1)−C(102)	174.4(3)	S(2)−Ir(1)−C(101)	174.3(3)
S(1)−Ir(1)−C(101)	92.0(3)	S(2)−Ir(1)−C(102)	92.0(3)
Ir(1)···Ir(2)···Ir(3)	61.30(2)	S(1)−Ir(2)−S(2)	82.29(8)
S(1)−Ir(2)−C(202)	174.1(3)	S(2)−Ir(2)−C(201)	175.1(3)
S(1)−Ir(2)−C(201)	94.0(3)	S(2)−Ir(2)−C(202)	92.3(3)
Ir(1)···Ir(3)···Ir(2)	58.84(5)	S(1)−Ir(3)−S(2)	82.39(9)
S(1)−Ir(3)−C(302)	173.2(3)	S(2)−Ir(3)−C(301)	175.8(3)
S(1)−Ir(3)−C(301)	93.6(3)	S(2)−Ir(3)−C(302)	91.0(3)
Cationic Complex			
Ti−Cp(1)^a	2.035(10)	Ti−Cp(2)^a	2.034(10)
Ti−O(1)	1.981(6)	Ti−O(2)	1.969(7)
O(1)−C(2)	1.279(11)	O(2)−C(4)	1.295(11)
C(2)−C(3)	1.40(2)	C(3)−C(4)	1.34(2)
Cp(1)^a−Ti−Cp(2)^a	133.8(4)	Cp(2)^a−Ti−O(1)	106.3(4)
Cp(1)^a−Ti−O(1)	105.9(3)	Cp(2)^a−Ti−O(2)	108.0(4)
Cp(1)^a−Ti−O(2)	106.1(3)	O(1)−Ti−O(2)	86.6(3)
Ti−O(1)−C(2)	129.2(6)	Ti−O(2)−C(4)	128.4(7)
O(1)−C(2)−C(3)	122.0(10)	O(2)−C(4)−C(3)	123.4(10)

[a] Cp(1) and Cp(2) represent the centroids of the two cyclopentadienyl ligands (Cp(1), C(6)−C(10); Cp(2), C(11)−C(15)).

Structure of $[Cp_2Ti(acac)][Ir_3(\mu_3\text{-}S)_2(CO)_6]$ (8). The molecular structure of the complex $[Cp_2Ti(acac)][Ir_3(\mu_3\text{-}S)_2(CO)_6]$ (**8**) has been unambiguously determined by X-ray crystallography on a single crystal obtained by slow diffusion of *n*-hexane into a concentrated solution of **8** in dichloromethane. The compound consists of discrete mononuclear titanium cations $[Cp_2Ti(acac)]^+$ and trinuclear iridium anions $[M_3(\mu_3\text{-}S)_2(CO)_6]^-$ (Figure 3). Selected bond distances and angles are summarized in Table 2.

The anion $[Ir_3(\mu_3\text{-}S)_2(CO)_6]^-$ shows a triangular arrangement of iridium atoms capped on each side by two triply bridging sulfur atoms. Each iridium center displays a square-planar geometry by coordination to two *cis* μ_3-bridging sulfidos and two terminal carbonyl groups. The structure of this anionic complex has been previously reported forming part of the ionic compound $[NMe_3(CH_2Ph)][Ir_3(\mu_3\text{-}S)_2(CO)_6]$;[25a] in this salt, two structurally different trinuclear anions were found in the asymmetric unit: one anion with idealized D_{3h} symmetry (Ir···Ir 3.084−3.088(1) Å) and the second one in which the symmetry is lowered to C_{2v} due to the shortening of two Ir···Ir distances (3.064 and 3.065(1) Å) and the lengthening of the remaining one (3.127(1) Å). In **8**, the three Ir···Ir separations are statistically different, spread out between 3.0435(14) and 3.1198(11) Å, and reducing consequently to C_s, the symmetry of this anion in the solid state. As reported by Garlaschelli et al. in $[NMe_3(CH_2Ph)][Ir_3(\mu_3\text{-}S)_2(CO)_6]$,[25a] these intermetallic separations are clearly longer if

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(25) (a) Pergola, R. D.; Garlaschelli, L.; Martinengo, L.; Demartin, F.; Manassero, M.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1986**, 2463. (b) Galli, D.; Garlaschelli, L.; Ciani, G.; Fumagalli, A.; Martinengo, S.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1984**, 55.

(26) (a) Doyle, G.; Stuart, T. *Inorg. Chem.* **1968**, *7*, 2484. (b) Doyle, G.; Tobias, R. S. *Inorg. Chem.* **1967**, *6*, 1111.

compared with metal−metal bond distances observed in tetra- or hexanuclear iridium carbonyl complexes (2.65−2.80 Å),[27] but are short enough to be indicative of weak intermetallic interactions.[17,28] On the other hand, all the remaining Ir−S (mean 2.364(2) Å), Ir−C (mean 1.848(5) Å), and C−O (mean 1.143(5) Å) *bond* distances are identical and compare well with values reported previously.

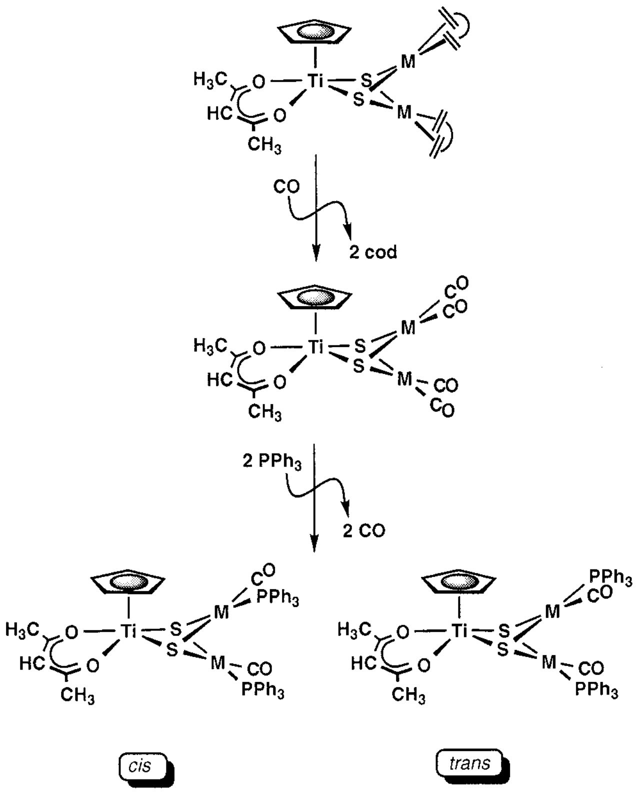
Although a formal valence electron count would render 48 e^- for the anionic complex and a consequent saturated triangular metal cluster structure should be formed, in light of the rather long Ir···Ir separations this anion would be better described as derived from three 16 e^- square-planar Ir(I) moieties sharing two *cis* S atoms and having weak metal−metal interactions. From the different Ir···Ir separations observed, these nonbonding interactions seem to be strongly dependent on intermolecular factors and packing forces.[25]

Considering the Cp ring centroids and the two donor atoms of the acetylacetonate ligand, the titanium exhibits a distorted pseudotetrahedral coordination in the cation $[Cp_2Ti(acac)]^+$. The distortion around the metal arises from the greater steric demand of the Cp ligands compared to that of the acetylacetonate and the chelating nature of the latter ligand. Quite interesting to comment are the differences observed in the titanium coordination sphere between **1** and this cationic complex. While the Ti−Cp(centroid) distances are identical (2.035(10) vs 2.060(3) Å) and the O−Ti−O rather similar (81.08(7)° vs 86.6(3)°), the Ti−O bond distances are markedly different, 2.062(2) in **1** and 1.981(6) and 1.969(7) in **8**. Most likely the comparatively more electrophilic character of this cationic complex strengthens the electronic donation of the acac ligand as evidenced by the shorter Ti−O bond distances in the solid state or by the displacement toward lower field of the =CH resonance of this ligand in the solution ^1H NMR spectra.

Early−Late Heterotrinuclear Carbonyl Complexes. The heterobimetallic complexes $[Cp(acac)Ti(\mu_3\text{-}S)_2\{M(cod)\}_2]$ (M = Rh (**1**) or Ir (**2**)) react with carbon monoxide under atmospheric pressure, in dichoromethane, to give air-sensitive dark red solutions of the complexes $[Cp(acac)Ti(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**9**) and $[Cp(acac)Ti(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2]$ (**10**), respectively (Scheme 3). These carbonyl complexes are isolated as fairly stable black microcrystalline solids in high yield.

The observation of the molecular ions $[Cp(acac)Ti(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]^+$ and $[Cp(acac)Ti(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2]^+$, at *m/z* 594 and 774, respectively, in the FAB mass spectra, confirms that the nuclearity is maintained upon carbonylation. The available spectroscopic information indicates that complexes **9** and **10** have C_s symmetry and evidences that their structures are identical to those of the parent diolefin complexes, replacing the diolefin ligands with two carbonyl groups. As the carbonyl ligands are related by symmetry, two distinct resonances are observed in the $^{13}C\{^1H\}$ NMR spectrum of complex **9**, at δ 183.9 (d, $^1J_{Rh-C} = 72$ Hz) and 183.6 (d, $^1J_{Rh-C} = 71$ Hz). Complexes **9** and **10** display three strong absorptions for terminal carbonyl groups in the IR spectrum, in agreement with the local symmetry of the molecular framework ("$M_2(\mu\text{-}S)_2(CO)_4$", C_{2v}); notwithstanding, four distinct resonances should be observed for the whole C_s symmetry. This observation has already been found in related tetracarbonyl d^8−d^8 dinuclear complexes with bridging thiolate ligands in which the number of absorptions in the IR spectrum is explained by the local molecular symmetry.[29]

Scheme 3



M= Rh (**13**), Ir (**14**)

The related 8-oxyquinolinate heterotrinuclear complexes $[Cp(quinol)Ti(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**11**) and $[Cp(quinol)Ti(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2]$ (**12**) are obtained by carbonylation of the diolefin complexes $[Cp(quinol)Ti(\mu_3\text{-}S)_2\{M(cod)\}_2]$ (**4**, **6**) and isolated as air-sensitive black microcrystalline solids in good yield. Both complexes display the expected set of six resonances for the protons of the 8-oxyquinolinate ligand in the ^1H NMR spectrum and the characteristic downfield-shifted resonance for the cyclopentadienyl ligand. In addition both complexes show three strong absorptions for terminal carbonyls in the IR spectrum.

The reaction of $[Cp(acac)Ti(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**9**) with 2 molar equiv of PPh_3 gives the complex $[Cp(acac)Ti(\mu_3\text{-}S)_2\{Rh(CO)(PPh_3)\}_2]$ (**13**) after evolution of carbon monoxide (Scheme 3). The formation of the disubstituted complex is observed in the FAB mass spectrum and also in the IR spectrum, where the broad band at 1954 cm^{-1} is indicative of monosubstitution at each rhodium center.[21] Complex **13** is obtained as a 3:5 mixture of the

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[27] (a) Garlaschelli, L.; Malatesta, M. C.; Martinengo, S.; Demartin, F.; Manassero, M.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1986**, 777. (b) Demartin, F.; Manassero, M.; Sansoni, M.; Garlaschelli, L.; Raimondi, C.; Martinengo, S. *J. Organomet. Chem.* **1983**, *243*, C10. (c) Ciani, G.; Sironi, A.; Chini, P.; Martinengo, S. *J. Organomet. Chem.* **1981**, *213*, C37.

[28] (a) Pinillos, M. T.; Elduque, A.; López, J. A.; Lahoz, F. J.; Oro, L. A. *J. Chem. Soc., Dalton Trans.* **1991**, 1391. (b) Carmona, D.; Ferrer, J.; Lahoz, F. J.; Oro, L. A.; Reyes, J.; Esteban, M. *J. Chem. Soc., Dalton Trans.* **1991**, 2811.

[29] (a) De Mountazon, D.; Kalck, P. Poilblanc, R. *J. Organomet. Chem.* **1980**, *186*, 121. (b) Palyi, G.; Vizi-Oros, A.; Marko, L.; Marcati, F.; Bor, G. *J. Organomet. Chem.* **1974**, *66*, 295.

cis and *trans* isomers, as deduced from the integral of the Cp resonances in the ^1H NMR spectrum. The *cis* isomer displays two doublets in the $^{31}P\{^1H\}$ NMR spectrum, while the *trans* isomer exhibits two doublets of doublets, showing a J_{P-P} of 9 Hz, a standard value found for long P−P coupling in dinuclear complexes having a mutual *trans* disposition.[30]

The disubstituted iridium complex $[Cp(acac)Ti(\mu_3\text{-}S)_2\{Ir(CO)(PPh_3)\}_2]$ (**14**) is obtained as an air-sensitive violet solid by replacement of two carbonyl ligands by PPh_3 in the complex $[Cp(acac)Ti(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2]$ (**10**). As is found for the rhodium analogue, the synthesis is not selective since a 1:1 ratio of the *cis* and *trans* isomers is isolated. Both isomers are easily identified in the $^{31}P\{^1H\}$ NMR spectrum since the *cis* isomer shows two singlets, while two doublets ($J_{P-P} = 7$ Hz) are observed for the *trans* isomer.

The related rhodium and iridium 8-oxyquinolinate complexes $[Cp(quinol)Ti(\mu_3\text{-}S)_2\{Rh(CO)(PPh_3)\}_2]$ (**15**) and $[Cp(quinol)Ti(\mu_3\text{-}S)_2\{Ir(CO)(PPh_3)\}_2]$ (**16**) are conveniently prepared by reaction of the corresponding tetracarbonyl derivatives $[Cp(quinol)Ti(\mu_3\text{-}S)_2\{M(CO)_2\}_2]$ (M = Rh, **11**; M = Ir, **12**) with 2 molar equiv of PPh_3. As is the case for the acac complexes, the formation of both complexes is not selective since the expected four isomers arising from the mutual disposition of the PPh_3 ligands as well as their relative disposition to the 8-oxyquinolinate ligand are observed. The ratio between the isomers is difficult to establish by ^1H NMR spectroscopy, but the isomers can be distinguished in the $^{31}P\{^1H\}$ NMR spectrum. Thus, for complex **16** the two *cis* isomers display four singlets (two for each isomer), and two doublets ($J_{P-P} = 6-8$ Hz) are observed for each *trans* isomer.

Discussion

Formation of the Trinuclear Heterobimetallic d^0-d^8 Complexes. Assuming the acidity of the hydrosulfido ligands in $Cp_2Ti(SH)_2$, the easy removal of anionic ligands by protonation in rhodium and iridium complexes such as [M(acac)(diolefin)], and the ability of sulfido ligand to bridge several metals, an expected outcome from the reactions between these compounds would be a deprotonation of the first species followed by the addition of two M(diolefin) fragments to give the complexes $[Cp_2Ti(\mu_3\text{-}S)_2\{M(diolefin\}_2]$. However, these reactions are not so simple, although they proceed cleanly to give the heterotrinuclear complexes $[Cp(acac)Ti(\mu_3\text{-}S)_2\{M(diolefin\}_2]$ (M = Rh, Ir) as the exclusive products along with free Hacac and cyclopentadiene. The formation of the new type of early−late compound with $[TiRh_2]$ and $[TiIr_2]$ cores is a fast process, in which no intermediates have been detected, involving a formal replacement of a cyclopentadienyl group from the titanium by a chelating acac ligand and the protons of the hydrosulfido ligands by two M(diolefin) fragments. The results from the reactions of $Cp_2Ti(SH)_2$ with the N,O-chelating 8-oxyquinolinato complex [M(quinol)(diolefin)] evidence that they proceed through an identical pathway.

Closely related reactions are the monodeprotonation of $Cp_2Ti(SH)_2$ either by NaH[15e] or by BuLi[17] to give the dinuclear anion $[Cp_2Ti_2(\mu\text{-}S)_2(S)_2]^{2-}$ and with $[\{Rh(\mu\text{-}OMe)(diolefin)\}_2]$ to give the compounds $[CpTi\{\mu_3\text{-}S)_3\{Rh(diolefin)\}_3]$.[17] All these reactions present as a common feature the removal of a cyclopentadienyl group from the titanium as free cyclopentadiene. The difference is related to the fate of the resulting titanium moiety, which dimerizes in the most simple case, captures a chelating acac ligand, keeping the sulfido groups, or increases the number of sulfido ligands along with the corresponding M(diolefin) moieties.

To complete this general view, the results of some of the reactions of $Cp_2Ti(SH)_2$ with mononuclear rhodium and iridium complexes are strongly dependent on the ancillary ligands of the d^8 metal centers, as shown by those with $[M(acac)(CO)_2]$. In these reactions the cyclopentadienyl groups on the titanium atom are maintained while an acac group is added to form the cation $[Cp_2Ti(acac)]^+$. In addition, the sulfido ligands are transferred to the d^8 metal centers to form the homotrinuclear anions $[M_3(\mu_3\text{-}S)_2(CO)_6]^-$ (M = Rh and Ir). These reactions leading to the ion-pair products $[Cp_2Ti(acac)][M_3(\mu_3\text{-}S)_2(CO)_6]$ are fast and clean processes, although they involve a tremendous ligand redistribution between rhodium (or iridium) and titanium. The deprotonation of $Cp_2Ti(SH)_2$ with $[Rh(quinol)(CO)_2]$ or $[Ir(quinol)(CO)_2]$ also gives ion-pair products, but it seems to follow a different path since a 2:3 mole ratio of the reactants is necessary for the reaction to go to completion. Although the formation of both anions $[M_3(\mu_3\text{-}S)_2(CO)_6]^-$ (M = Rh, Ir) is observed, the cationic species are not well-defined since the spectroscopic data are inconclusive.

Sulfido Ligand Transfer versus Cyclopentadiene Elimination. The formation of early−late heterobimetallic complexes always competes with the ligand transfer of the potential bridging ligands to the d^8 metal centers. This is particulary frequent in the case of thiolato ligands, so that some thiolate ligand transfer reactions from thiolatotitanocene or thiolatozirconocene complexes have been recently used to prepare the corresponding thiolato complexes of the late transition metals Co, Rh, Pd, and Pt.[31] These ligand transfer reactions are believed to proceed through an associative pathway involving a heterobimetallic intermediate where the ligand redistribution takes place.[31b]

The difference in the reactions leading either to the complexes $[Cp(acac)Ti(\mu_3\text{-}S)_2\{M(diolefin)\}_2]$ or to the ion-pair complexes $[Cp_2Ti(acac)][M_3(\mu_3\text{-}S)_2(CO)_6]$ involves the release of cyclopentadiene versus a sulfido ligand transfer process. Notably, the fate of the reactions in one or the other direction is dictated by the character of the ancillary ligands on the mononuclear complexes, since the sulfide transfer process is only observed for the carbonyl case. A reliable approach to the formation of both types of complexes is presented in Scheme 4, which rationalizes the results. The reactions start with

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[30] Jiménez, M. V.; Sola, E.; López, J. A.; Lahoz, F. J.; Oro, L. A. *Chem. Eur. J.* **1998**, *4*, 1398.

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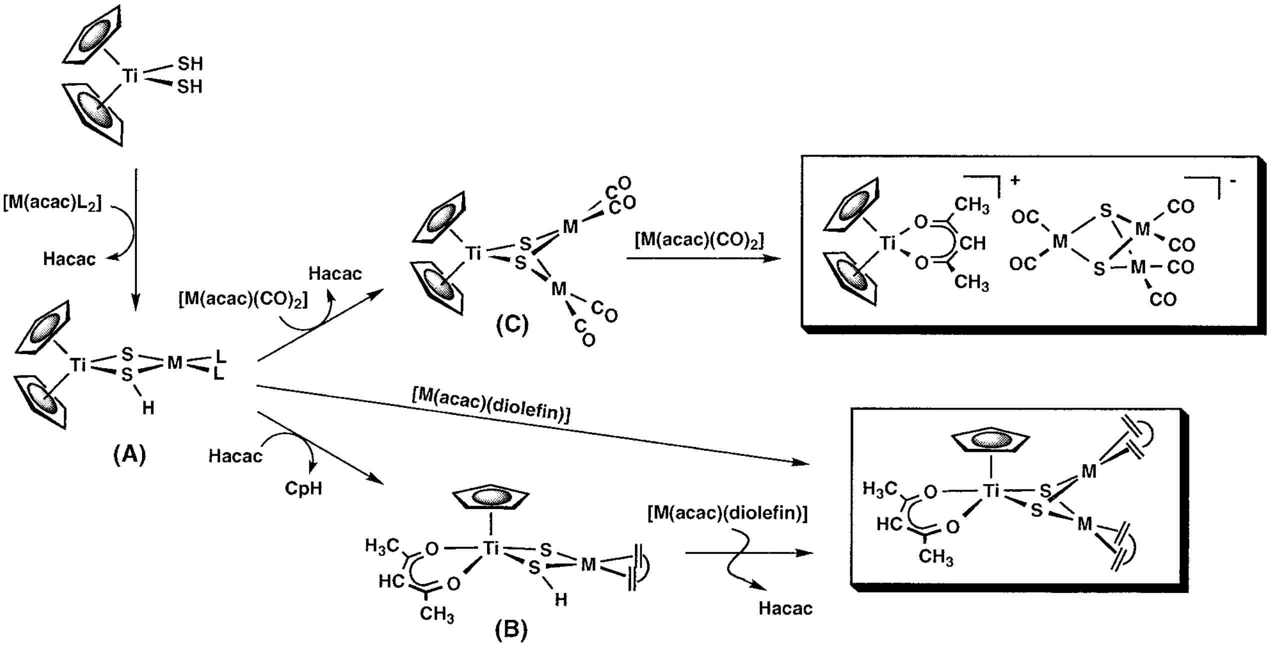
Scheme 4



a first common step: the monodeprotonation of $Cp_2Ti(SH)_2$ by 1 equiv of $[M(acac)L_2]$ (L_2 = diolefin or $(CO)_2$), as occurs when a strong base is used, to give the intermediary species $[Cp_2Ti(\mu\text{-}S)(\mu\text{-}SH)ML_2]$ (**A**) and free acacH.

For the diolefinic complexes, this intermediate **A** could react either with the Hacac present in the medium to give the new heterodinuclear intermediate $[Cp(acac)Ti(\mu\text{-}S)(\mu\text{-}SH)ML_2]$ (**B**) or directly with [M(acac)(diolefin)] with transfer of the acac ligand from rhodium to titanium and elimination of cyclopentadiene to give the final products. Transfer of ligands between metals is a well-documented reaction involving polynuclear intermediates. In the first instance a further reaction with a second equivalent of [M(acac)(diolefin)] should finally produce the trinuclear complexes $[Cp(acac)Ti(\mu_3\text{-}S)_2\{M(diolefin)\}_2]$.

The reaction with Hacac is also open for the intermediate $[Cp_2Ti(\mu\text{-}S)(\mu\text{-}SH)M(CO)_2]$, but it would not account for the results. Most probably, the deprotonation of the hydrosulfide ligand with $[M(acac)(CO)_2]$ to give the heterotrinuclear complex $[Cp_2Ti(\mu_3\text{-}S)_2\{ML_2\}_2]$ (**C**) occurs. As the formation of **C** competes with the cyclopentadiene elimination, this step is crucial to produce the difference between both types of reactions. The strong π-acceptor ligands on the d^8 center in **A** should disfavor the cyclopentadiene elimination, while they promote the deprotonation of the hydrosulfido ligand by $[M(acac)(CO)_2]$. A further reaction of this species with the outcoming Hacac would degrade the heterotrinuclear structure via Ti−S bond cleavage to give the cation $[Cp_2Ti(acac)]^+$, and the probable anionic dinuclear species $[M_2(\mu\text{-}S)(\mu\text{-}SH)(CO)_4]^-$ is deprotonated by the third equivalent of $[M(acac)(CO)_2]$ to give the anion $[M_3(\mu_3\text{-}S)_2(CO)_6]^-$ observed in the final product.

Although the compounds $[Cp(acac)Ti(\mu_3\text{-}S)_2\{M(diolefin)\}_2]$ could be also formed from an intermediary species such as **C** with L_2 = diolefin, the reaction of **C** with Hacac is unlikely for steric reasons. The proposal of the species **A** and **C** is consistent with the existence of related dinuclear heterobimetallic complexes such as $[Cp_2Ti(\mu\text{-}SH)_2Mo(CO)_4]$,[32] $[Cp^*{}_2Zr(\mu\text{-}S)_2Rh(CO)_2]^-$,[3d] and $[Cp^{tt}{}_2Zr(\mu\text{-}S)_2\{M(CO)_2\}_2]$ (Cp^{tt} = 1,3-bis(*tert*-butyl)cyclopentadienyl).[33]

The driving force for the ligand transfer from d^0 to d^8 can be attributed to the hard and soft mismatching between the titanocene moiety and the bridging sulfide ligand.[34] However, it is well-known that the Lewis acidity of the late transition metal centers in early−late heterobimetallic thiolato complexes facilites the Ti−S bond cleavage and consequently the ligand transfer process.[31c] In the present case, the sulfido ligand transfer could be a consequence of the instability of the heterotrinuclear intermediate $[Cp_2Ti(\mu_3\text{-}S)_2\{M(CO)_2\}_2]$ probably due to the presence of the strong π-acceptor carbonyl ligands.

As far as the cyclopentadiene elimination is concerned, the simplest pathway consists of an intramolecular proton transfer from the hydrosulfide ligand to the cyclopentadienyl group in the dinuclear hydrosulfido complex $[Cp_2Ti(\mu\text{-}SH)(\mu\text{-}S)Rh(diolefin)]$ (**A**) (Scheme 5). This step is likely in the proposed deprotonation of $Cp_2Ti(SH)_2$ with $[\{Rh(\mu\text{-}OMe)(diolefin)\}_2]$, for which this intermediate **A** was also proposed.[17] Nevertheless, this intermediate **A** is susceptible to the attack at the titanium center by protonic nucleophiles in the reaction medium such as methanol, water, and Hacac. A further transfer of the proton on the nucleophile to the Cp ring would also produce the elimination of cyclopentadiene in all these processes (pK_a(Hacac) = 9.0; pK_a(HCp) = 15.0). Moreover, this most probable alternative pathway would explain the bonding of the nucleophile (acac) to the titanium center and the sensitivity of these reactions to the reaction medium.[18] Indeed, the removal of a cyclopentadienyl ligand by electrophilic attack is a well-documented process.[35]

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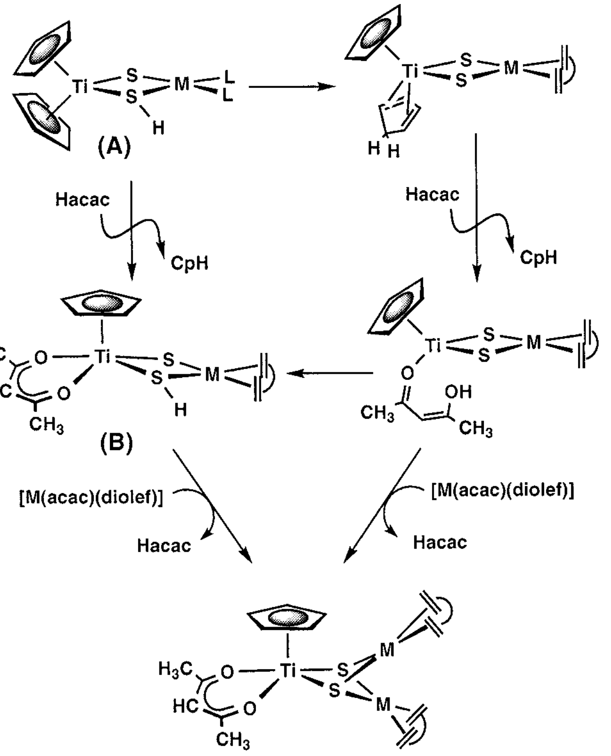
Scheme 5



Replacement Reactions. Although the carbonyl complexes [Cp(acac)Ti(μ_3-S)$_2${M(CO)$_2$}$_2$] are not accessible by the direct reaction of the complexes [M(acac)(CO)$_2$] with Cp$_2$Ti(SH)$_2$, they can be isolated by carbonylation of any of the diolefin complexes [Cp(acac)Ti(μ_3-S)$_2${M(diolefin)}$_2$]. In the same way, the tetracarbonyl complexes [Cp(quinol)Ti(μ_3-S)$_2${M(CO)$_2$}$_2$] are obtained by carbonylation of the heterotrinuclear diolefin complexes under atmospheric pressure.

The heterotrinuclear core [TiM$_2$] in the carbonyl complexes is maintained upon replacement of two carbonyls ligands by triphenyphosphine. However, the reactions are not stereoselective since the complexes [Cp(acac)Ti(μ_3-S)$_2${M(CO)(PPh$_3$)}$_2$] are obtained as a *cis/trans* mixture of isomers (M = Rh, 5:3; M = Ir, 1:1). Interestingly, an identical isomer ratio for the rhodium complex is observed when the synthesis is carried out directly from [Rh(acac)(CO)(PPh$_3$)] and Cp$_2$Ti(SH)$_2$. The lack of stereoselectivity is also observed in the synthesis of the complexes [Cp(quinol)Ti(μ_3-S)$_2${M(CO)(PPh$_3$)}$_2$], which are obtained as a mixture of four isomers. The reactivity of the heterotrinuclear carbonyl complexes is closely related to the d^8−d^8 dinuclear thiolato complexes [{M(μ_2-SR)(CO)(PPh$_3$)}$_2$] (M = Rh and Ir), where the disubstituted complexes are also isolated as the *cis/trans* isomer mixture.[36] The lack of selectivity in these substitution processes contrasts with that observed for other di- and tetranuclear complexes supported by N,S-donor ligands, where the preferential substitution of the carbonyls *trans* to sulfur is observed.[21]

Concluding Remarks

The deprotonation of Cp$_2$Ti(SH)$_2$ with mononuclear rhodium and iridium complexes containing anionic ligands has proved to be a convenient synthetic route for the construction of new d^0−d^8 early−late heterotrinuclear complexes having [TiRh$_2$], [TiIr$_2$], [TiRh$_3$], and [TiIr$_3$] cores. The ancillary ligands on the mononuclear complexes (diolefin versus carbonyl) play a key role in the outcome of the reactions, since the heterobimetallic complexes result for the former, while the transfer of the sulfido ligands occurs for the latter. In addition, the products from the additive-deprotonation of Cp$_2$Ti(SH)$_2$ are strongly dependent on the anionic ligand in the starting rhodium and iridium complexes (methoxide versus acetylacetonate), which in turn control the nuclearity of the early−late complexes.

Experimental Section

General Methods. All manipulations were performed under an inert atmosphere (nitrogen or argon) using Schlenk-tube techniques. Solvents were dried by standard methods and distilled under nitrogen immediately prior to use. Molecular weights were determined with a Knauer osmometer using chloroform solutions. Carbon, hydrogen, and nitrogen analyses were performed in a Perkin-Elmer 2400 microanalyzer. IR spectra were recorded with a Nicolet-IR 550 (4000−400 cm^{-1}) spectrophotometer with the bands calibrated against the sharp peak (1601.4 cm^{-1}) of a polystyrene film. Mass spectra were recorded in a VG Autospec double-focusing mass spectrometer operating in the FAB mode. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on Varian spectrometers operating at 299.95 and 300.13 MHz for ^{1}H. Chemical shifts are referenced to SiMe$_4$ and H$_3$PO$_4$.

Starting Materials. Standard procedures were used to prepare the rhodium[37] and iridium acetylacetonate complexes [Rh(acac)(cod)], [Rh(acac)(tfbb)], [Rh(acac)(CO)$_2$], [Rh(acac)(CO)(PPh$_3$)], [Ir(acac)(cod)],[38] and [Ir(acac)(CO)$_2$].[39] The 8-oxyquinolate complexes [Rh(quinol)(cod)], [Rh(quinol)(tfbb)], [Ir(quinol)(cod)], [Rh(quinol)(CO)$_2$], and [Ir(quinol)(CO)$_2$] were prepared according to the previously reported method.[40] Cp$_2$Ti(SH)$_2$ was prepared following the literature procedure.[32]

Synthesis of the Complexes. [Cp(acac)Ti(μ_3-S)$_2${Rh(cod)}$_2$] (1). Cp$_2$Ti(SH)$_2$ (0.196 g, 0.806 mmol) was added to a solution of [Rh(acac)(cod)] (0.500 g, 1.612 mmol) in toluene (6 mL). The resulting violet solution was stirred for 30 min to give a violet microcrystalline solid, which was filtered, washed with hexane, and dried under vacuum (0.425 g). The filtrate was concentrated under vacuum, and then hexane (5 mL) was added to give an additional fraction. Yield (overall): 0.500 g (89%). Anal. Calcd for C$_{26}$H$_{36}$O$_2$Rh$_2$S$_2$Ti (%): C, 44.72; H, 5.19. Found: C, 44.36; H, 4.90. MS (FAB+, CH$_2$Cl$_2$, *m/z*): 599 (M$^+$ − acac, 70), 487 (M$^+$ − acac − cod, 60). Mol Weight. Found: 690 (calcd 698). ^{1}H NMR (CDCl$_3$, 293 K): 6.53 (s, 5H, Cp), 5.70 (s, 1H, CH, acac), 4.64 (m, 2H), 4.40 (m, 2H), 4.31 (m, 2H), 4.23 (m, 2H) (=CH, cod), 2.56 (m, 2H), 2.10−2.19 (m, 8H), 2.02−1.96 (m, 6H) (>CH$_2$, cod), 2.00 (s, 6H, CH$_3$, acac). ^{13}C{^{1}H} NMR (CDCl$_3$, 293 K): 188.8 (CO, acac), 114.6 (Cp), 102.6 (CH, acac), 81.9 (d, J_{Rh-C} = 11 Hz), 80.9 (d, J_{Rh-C} = 10 Hz), 80.4 (d, J_{Rh-C} = 11 Hz), 79.1 (d, J_{Rh-C} = 11 Hz) (=CH, cod), 32.3, 31.7, 31.4, 30.9 (>CH$_2$, cod), 26.2 (CH$_3$, acac).

[Cp(acac)Ti(μ_3-S)$_2${Rh(tfbb)}$_2$] (2) was obtained as a beige microcrystalline solid by reaction of [Rh(acac)(tfbb)] (0.200 g,

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0.467 mmol) and $Cp_2Ti(SH)_2$ (0.057 g, 0.234 mmol) following the procedure described above. Yield: 0.189 g (87%). Anal. Calcd for $C_{34}H_{24}F_8O_2Rh_2S_2Ti$ (%): C, 43.71; H, 2.59. Found: C, 43.67; H, 2.55. ^1H NMR ($CDCl_3$, 223 K): 6.72 (s, 5H, Cp), 6.15 (s, 1H, CH, acac), 5.78 (m, 1H), 5.40 (m, 2H), 5.23 (m, 1H) (CH, tfbb), 4.43 (m, 2H), 4.06 (m, 2H), 3.94 (m, 4H) (=CH, tfbb), 2.14 (s, 6H, CH_3, acac). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 223 K): 189.3 (CO, acac), 139.3 (dm, J_{C-F} = 241 Hz), 138.0 (dm, J_{C-F} = 250 Hz) (CF, tfbb), 128.8 (br), 128.6 (br), 128.3 (br), 128.0 (br) (tfbb), 115.5 (Cp), 103.6 (CH, acac), 59.4 (d, J_{Rh-C} = 8 Hz), 59.0 (d, J_{Rh-C} = 10 Hz), 58.9 (d, J_{Rh-C} = 9 Hz), 58.6 (d, J_{Rh-C} = 9 Hz) (=CH, tfbb), 41.7, 40.8, 40.3, 40.0 (CH, tfbb), 25.1 (CH_3, acac).

[Cp(acac)Ti(μ_3-S)$_2${Ir(cod)}$_2$] (3) was prepared as a gray microcrystalline solid from [Ir(acac)(cod)] (0.200 g, 0.501 mmol) and $Cp_2Ti(SH)_2$ (0.061 g, 0.250 mmol) following the procedure described above. Yield: 0.192 g (87%). Anal. Calcd for $C_{26}H_{36}Ir_2O_2S_2Ti$ (%): C, 35.61; H, 4.14. Found: C, 35.44; H, 3.94. MS (FAB+, CH_2Cl_2, *m/z*): 876 (M^+, 55), 776 (M^+ − acac, 40). ^1H NMR (CD_2Cl_2, 293 K): 6.52 (s, 5H, Cp), 5.85 (s, 1H, CH, acac), 4.37 (m, 2H), 3.90 (m, 6H) (=CH, cod), 2.00 (s, 6H, CH_3, acac), 2.10−1.70 (m, 16H, >CH_2, cod). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): 188.6 (CO, acac), 115.4 (Cp), 103.1 (CH, acac), 66.2 (br), 64.7 (br) (=CH, cod), 33.7 (br), 32.7 (br), 32.0 (br), 31.5 (br) (>CH_2, cod), 31.5 (CH_3, acac).

[Cp(quinol)Ti(μ_3-S)$_2${Rh(cod)}$_2$] (4). [Rh(quinol)(cod)] (0.200 g, 0.583 mmol) was reacted with $Cp_2Ti(SH)_2$ (0.071 g, 0.291 mmol) in dichloromethane (10 mL) to give a purple solution. This solution was stirred for 1 h and then concentrated under vaccum to ca. 1 mL. Slow addition of hexane gave the compound as a violet solid, which was filtered, washed with hexane, and dried under vaccum. Yield: 0.188 g (87%). Anal. Calcd for $C_{30}H_{35}NORh_2S_2Ti$ (%): C, 48.46; H, 4.74; N, 1.88. Found: C, 48.15; H, 4.90; N, 1.90. MS (FAB+, CH_2Cl_2, *m/z*): 743 (M^+, 100), 678 (M^+ − Cp, 25), 635 (M^+ − cod, 35), 527 (M^+ − 2cod, 65). ^1H NMR ($CDCl_3$, 293 K): 8.80 (dd, H^2), 8.18 (dd, H^4), 7.46 (dd, H^6), 7.28 (dd, H^3), 7.01 (dd, H^5), 6.94 (dd, H^7) (J_{2-3} = 4.9 Hz, J_{2-4} = 1.3 Hz, J_{3-4} = 8.2, J_{5-6} = 8.0 Hz, J_{5-7} = 0.7 Hz and J_{6-7} = 7.8) (quinol), 6.53 (s, 5H, Cp), 4.77 (m, 2H), 4.65 (m, 1H), 4.45 (m, 1H), 4.32 (m, 3H), 3.29 (m, 1H) (=CH), 2.54−1.25 (m, 16H, >CH_2) (cod). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): 165.0, 149.8, 143.6, 137.5, 130.8, 130.4, 121.0 (quinol), 114.4 (Cp), 112.0, 111.4 (quinol), 85.6 (br), 83.2 (br), 81.7 (br), 81.6 (br), 80.5 (br), 79.7 (br), 79.1 (br) (=CH, cod), 31.7 (br), 31.0 (s), 30.7 (s) (>CH_2, cod).

[Cp(quinol)Ti(μ_3-S)$_2${Rh(tfbb)}$_2$] (5) was obtained as a violet microcrystalline solid by reaction of [Rh(quinol)(tfbb)] (0.200 g, 0.423 mmol) with $Cp_2Ti(SH)_2$ (0.052 g, 0.211 mmol) in dichloromethane (10 mL) following the procedure described above. Yield: 0.170 g (82%). Anal. Calcd for $C_{38}H_{23}F_8NORh_2S_2Ti$ (%): C, 46.40; H, 2.37; N, 1.43. Found: C, 46.48; H, 1.83; N, 1.42. MS (FAB+, CH_2Cl_2, *m/z*): 979 (M^+, 65), 914 (M^+ − Cp, 25), 836 (M^+ − quinol, 10), 753 (M^+ − tfbb, 55), 527 (M^+ − 2tfbb, 70), 462 (M^+ − 2tfbb − Cp, 45). ^1H NMR ($CDCl_3$, 293 K): 8.67 (dd, H^2), 8.32 (dd, H^4), 7.69 (dd, H^6), 7.32 (dd, H^3), 7.27 (d, H^5), 7.14 (d, H^7) (J_{2-3} = 4.9 Hz, J_{2-4} = 1.1 Hz, J_{3-4} = 9.2, J_{5-6} = 7.9 Hz and J_{6-7} = 7.8) (quinol), 6.75 (s, 5H, Cp), 5.78 (m, 1H, CH), 5.43 (m, 1H, CH), 5.30 (m, 1H, CH), 4.54 (br s, 2H, =CH), 4.40 (br s, 1H, =CH), 4.02 (br s, 2H, =CH), 3.91 (br s, 1H, =CH), 3.86 (br s, 1H, =CH), 3.44 (m, 1H, CH), 2.63 (br s, 1H, =CH) (tfbb). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): 164.6 (quinol), 150.2 (br), 150.1 (br) (tfbb), 143.7, 140.3, 140.0 (quinol), 139.7 (dm, J_{C-F} = 248 Hz), 138.6 (dm, J_{C-F} = 249 Hz) (tfbb), 131.1, 130.6 (quinol), 128.6 (br), 128.3 (br) (tfbb), 121.0 (quinol), 115.9 (Cp), 112.6, 112.5 (quinol), 64.7 (br), 61.8 (br), 61.5 (br), 60.5 (br), 59.5 (br), 59.0 (br), 58.5 (br) (=CH, tfbb), 41.2, 40.8, 40.4, 40.1 (CH, tfbb).

[Cp(quinol)Ti(μ_3-S)$_2${Ir(cod)}$_2$] (6). [Ir(quinol)(cod)] (0.100 g, 0.225 mmol) was reacted with $Cp_2Ti(SH)_2$ (0.027 g, 0.112 mmol) in dichloromethane (10 mL) to give a dark solution. Workup as above gave the complex as a dark gray solid. Yield: 0.075 g (72%). Anal. Calcd for $C_{30}H_{35}Ir_2NOS_2Ti$ (%): C, 39.08; H, 3.83; N, 1.52. Found: C, 38.91; H, 3.61; N, 1.55. MS (FAB+, CH_2Cl_2, *m/z*): 921 (M^+, 70), 855 (M^+ − Cp, 70), 808 (M^+ − cod, 40), 775 (M^+ − quinol, 55), 744 (M^+ − cod − Cp, 47), 705 (M^+ − 2cod, 45), 665 (M^+ − cod − quinol, 50). ^1H NMR ($CDCl_3$, 293 K): 8.77 (dd, H^2), 8.22 (dd, H^4), 7.47 (dd, H^6), 7.28 (dd, H^3), 7.02 (dd, H^5), 6.91 (dd, H^7) (J_{2-3} = 4.9 Hz, J_{2-4} = 1.3 Hz, J_{3-4} = 8.2, J_{5-6} = 8.0 Hz, J_{5-7} = 0.9 Hz and J_{6-7} = 7.9) (quinol), 6.51 (s, 5H, Cp), 4.36 (m, 3H), 4.12 (m, 1H), 4.00 (m, 1H), 3.94 (m, 1H), 3.82 (m, 1H), 2.79 (m, 1H) (=CH, cod), 2.47 (m, 3H), 2.00 (m, 2H), 1.75 (m, 6H), 1.45 (m, 2H), 1.20 (m, 1H), 1.05 (m, 1H), 0.35 (m, 1H) (>CH_2, cod).

[Cp_2Ti(acac)][Rh$_3$(μ_3-S)$_2$(CO)$_6$] (7). The addition of $Cp_2Ti(SH)_2$ (0.063 g, 0.258 mmol) to a solution of [Rh(acac)$(CO)_2$] (0.200 g, 0.775 mmol) in dichloromethane (10 mL) gave a dark red solution, which turned brown in 30 min. Concentration of the solution to ca. 1 mL and slow addition of hexane gave the compound as a brown microcrystalline solid, which was filtered, washed with hexane, and dried under vaccum. Yield: 0.197 g (93%). Anal. Calcd for $C_{21}H_{17}O_8Rh_3S_2Ti$ (%): C, 30.83; H, 2.09. Found: C, 30.87; H, 1.93. MS (FAB+, CH_2Cl_2, *m/z*): 277 (M^+, 35). MS (FAB−, CH_2Cl_2, *m/z*): 541 (M^-, 35), 513 (M^- − CO, 15), 485 (M^- − 2CO, 7), 457 (M^- − 3CO, 7). Λ_M (Ω^{-1} cm^2 mol^{-1}): 134 (acetone, 4.89 × 10^{-4} M). ^1H NMR (CD_2Cl_2, 293 K): 6.67 (s, 10H, Cp), 6.18 (s, 1H, CH acac), 2.29 (s, 6H, CH_3, acac). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 293 K): 195.7 (CO, acac), 184.9 (d, J_{Rh-C} = 70 Hz, CO), 122.1 (Cp), 106.8 (CH), 26.8 (CH_3) (acac). IR (CH_2Cl_2, cm^{-1}): ν(CO), 2029 (s), 1977 (s).

[Cp_2Ti(acac)][Ir$_3$(μ_3-S)$_2$(CO)$_6$] (8) was obtained as a dark red solid by reaction of [Ir(acac)$(CO)_2$] (0.150 g, 0.432 mmol) with $Cp_2Ti(SH)_2$ (0.035 g, 0.144 mmol) in dichloromethane following the procedure described above. Yield: 0.144 g (92%). Anal. Calcd for $C_{21}H_{17}Ir_3O_8S_2Ti$ (%): C, 23.22; H, 1.58. Found: C, 23.15; H, 1.42. MS (FAB+, CH_2Cl_2, *m/z*): 277 (M^+, 35). MS (FAB-, CH_2Cl_2, *m/z*): 809 (M^-, 100), 781 (M^- − CO, 15), 752 (M^- − 2CO, 5), 724 (M^- − 3CO, 10). Λ_M (Ω^{-1} cm^2 mol^{-1}): 128 (acetone, 5.03 × 10^{-4} M). ^1H NMR (acetone-d_6, 293 K): 6.89 (s, 10H, Cp), 6.35 (s, 1H, CH, acac), 2.30 (s, 6H, CH_3, acac). $^{13}C\{^1H\}$ NMR (acetone-d_6, 293 K): 196.5 (CO, acac), 174.7 (CO), 123.7 (Cp), 107.3 (CH), 26.8 (CH_3) (acac). IR (CH_2Cl_2, cm^{-1}): ν(CO), 2024 (s), 1969 (s).

[Cp(acac)Ti(μ_3-S)$_2${Rh(CO)$_2$}$_2$] (9). Carbon monoxide was bubbled through a solution of [Cp(acac)Ti(μ_3-S)$_2${Rh(cod)}$_2$] (**1**) (0.100 g, 0.143 mmol) in dichloromethane (10 mL) to give a dark red solution in 5 min. Bubbling was maintained in order to concentrate the solution to ca. 2 mL. Addition of hexane (5 mL) gave a black microcrystalline solid, which was isolated by filtration, washed with hexane, and then vacuum-dried. Yield: 0.075 g (88%). Anal. Calcd for $C_{14}H_{12}O_6Rh_2S_2Ti$ (%): C, 28.59; H, 2.06. Found: C, 28.33; H, 2.02. MS (FAB+, CH_2Cl_2, *m/z*): 594 (M^+, 30), 566 (M^+ − CO, 35), 538 (M^+ − 2CO, 40), 510 (M^+ − 3CO, 34), 482 (M^+ − 4CO, 100). ^1H NMR ($CDCl_3$, 293 K): 6.68 (s, 5H, Cp), 5.96 (s, 1H, CH), 2.07 (s, 6H, CH_3) (acac). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): 189.9 (CO, acac), 183.9 (d, J_{Rh-C} = 72 Hz, CO), 183.6 (d, J_{Rh-C} = 71 Hz, CO), 118.4 (Cp), 105.9 (CH, acac), 25.8 (CH_3, acac). IR (CH_2Cl_2, cm^{-1}): ν(CO), 2066 (s), 2044 (s), 1998 (s); ν(CO, acac), 1558 (s), 1528 (s).

[Cp(acac)Ti(μ_3-S)$_2${Ir(CO)$_2$}$_2$] (10) was obtained as a black microcrystalline solid by carbonylation of [Cp(acac)Ti(μ_3-S)$_2${Ir(cod)}$_2$] (**3**) (0.220 g, 0.251 mmol) in dichloromethane following the procedure described above. Yield: 0.169 g (87%). Anal. Calcd for $C_{14}H_{12}Ir_2O_6S_2Ti$ (%): C, 21.86; H, 1.57. Found: C, 21.78; H, 1.48. MS (FAB+, CH_2Cl_2, *m/z*): 774 (M^+, 45), 716 (M^+ − 2CO, 25), 690 (M^+ − 3CO, 10), 660 (M^+ − 4CO, 12). ^1H NMR ($CDCl_3$, 293 K): 6.75 (s, 5H, Cp), 6.05 (s, 1H, CH), 2.09 (s, 6H, CH_3) (acac). IR (CH_2Cl_2, cm^{-1}): ν(CO), 2056 (s), 2031 (s), 1983 (s); ν(CO, acac), 1553 (s), 1530 (s).

[Cp(quinol)Ti(μ_3-S)$_2${Rh(CO)$_2$}$_2$] (11). Carbon monoxide was bubbled through a dichloromethane solution (10 mL) of

[Cp(quinol)Ti(μ_3-S)$_2${Rh(cod)}$_2$] (**4**) (0.100 g, 0.134 mmol) to give a violet solution. The solution was concentrated under carbon monoxide to ca. 1 mL, and then hexane (5 mL) was added. The black solid was collected by filtration, washed with hexane, and then dried under vacuum. Yield: 0.067 g (78%). Anal. Calcd for $C_{18}H_{11}NO_5Rh_2S_2Ti$ (%): C, 33.83; H, 1.73; N, 2.19. Found: C, 33.65; H, 1.56; N, 2.15. ^{1}H NMR ($CDCl_3$, 293 K): 8.81 (d, H^2), 8.34 (d, H^4), 7.55 (dd, H^6), 7.48 (dd, H^3), 7.22 (d, H^5), 6.99 (d, H^7) (J_{2-3} = 4.9 Hz, J_{3-4} = 8.1, J_{5-6} = 7.9 Hz and J_{6-7} = 7.8) (quinol), 6.62 (s, 5H, Cp). IR (CH_2Cl_2, cm^{-1}): ν(CO), 2069 (s), 2047 (vs), 2004 (vs).

[Cp(quinol)Ti(μ_3-S)$_2${Ir(CO)$_2$}$_2$] (12) was obtained as a black microcrystalline solid by carbonylation of [Cp(quinol)Ti(μ_3-S)$_2${Ir(cod)}$_2$] (**6**) (0.100 g, 0.108 mmol) in dichloromethane following the procedure described above. Yield: 0.066 g (74%). Anal. Calcd for $C_{18}H_{11}Ir_2NO_5S_2Ti$ (%): C, 26.44; H, 1.36; N, 1.71. Found: C, 26.32; H, 1.31; N, 1.68. MS (FAB+, CH_2Cl_2, *m/z*): 820 (M$^+$, 8), 789 (M$^+$ − CO, 10), 734 (M$^+$ − 3CO, 7), 705 (M$^+$ − 4CO, 12). ^{1}H NMR ($CDCl_3$, 293 K): 8.73 (d, H^2), 8.39 (d, H^4), 7.58 (dd, H^6), 7.51 (dd, H^3), 7.27 (d, H^5), 6.98 (d, H^7) (J_{2-3} = 4.9 Hz, J_{3-4} = 8.12, J_{5-6} = 8.1 Hz and J_{6-7} = 7.8) (quinol), 6.75 (s, 5H, Cp). IR (CH_2Cl_2, cm^{-1}): ν(CO), 2058 (s), 2035 (vs), 1987 (vs).

[Cp(acac)Ti(μ_3-S)$_2${Rh(CO)(PPh$_3$)}$_2$] (13). Method A: Solid PPh_3 (0.044 g, 0.168 mmol) was added to a solution of [Cp(acac)Ti(μ_3-S)$_2${Rh(CO)$_2$}$_2$] (**9**) (0.050 g, 0.084 mmol) to give a violet solution and evolution of carbon monoxide. The solution was stirred for 30 min and the solvent removed under vacuum to give a violet residue, which was washed with cold hexane and dried under vacuum. Yield: 0.075 g (84%). Method B: [Rh(acac)(CO)(PPh$_3$)] (0.076 g, 0.154 mmol) was reacted with $Cp_2Ti(SH)_2$ (0.019 g, 0.077 mmol) in dichloromethane to give a violet solution. Workup as above gave the complex as a violet solid. Yield: 0.067 g (82%). Anal. Calcd for $C_{48}H_{42}O_4P_2Rh_2S_2Ti$ (%): C, 54.25; H, 3.98. Found: C, 54.20; H, 3.87. MS (FAB+, CH_2Cl_2, *m/z*): 963 (M$^+$ − acac, 25), 935 (M$^+$ − CO − acac, 15), 907 (M$^+$ − 2CO − acac, 57), 673 (M$^+$ − 2CO − PPh$_3$ − acac, 43). ^{1}H NMR ($CDCl_3$, 293 K): 7.77−7.13 (m, PPh$_3$), 6.33 (s, Cp), 6.30 (s, Cp), 5.59 (s, CH), 2.09 (s, CH$_3$), 2.03 (s, CH$_3$), 1.96 (s, CH$_3$), 1.64 (s, CH$_3$) (acac) (two isomers). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): 38.5 (d, J_{Rh-P} = 169 Hz), 33.6 (d, J_{Rh-P} = 164 Hz) (*cis* isomer); 36.4 (dd, J_{Rh-P} = 169 Hz, J_{P-P} = 9 Hz), 34.7 (dd, J_{Rh-P} = 165 Hz, J_{P-P} = 9 Hz) (*trans* isomer). IR (CH_2Cl_2, cm^{-1}): ν(CO), 1954 (vs); ν(CO, acac), 1580 (s), 1526 (s).

[Cp(acac)Ti(μ_3-S)$_2${Ir(CO)(PPh$_3$)}$_2$] (14) was obtained by reaction of [Cp(acac)Ti(μ_3-S)$_2${Ir(CO)$_2$}$_2$] (**10**) (0.063 g, 0.081 mmol) with PPh_3 (0.043 g, 0.163 mmol) in dichloromethane (10 mL). Workup as above (method A) gave the complex as a black solid. Yield: 0.080 g (79%). Anal. Calcd for $C_{48}H_{42}Ir_2O_4P_2S_2Ti$ (%): C, 46.45; H, 3.41. Found: C, 46.39; H, 3.39. MS (FAB+, CH_2Cl_2, *m/z*): 1240 (M$^+$, 80), 973 (M$^+$ − PPh$_3$, 72). ^{1}H NMR ($CDCl_3$, 293 K): 7.70−7.13 (m, PPh$_3$), 6.33 (s, Cp), 6.32 (s, Cp) 5.60 (s, CH), 2.05 (s, CH$_3$), 1.91 (s, CH$_3$), 1.51 (s, CH$_3$) (acac) (two isomers). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): 20.4 (s), 20.3 (s) (*cis* isomers), 19.4 (d, J_{P-P} = 7 Hz), 17.7 (d, J_{P-P} = 7 Hz) (*trans* isomer). IR (CH_2Cl_2, cm^{-1}): ν(CO), 1952 (vs), 1934 (vs); ν(CO, acac), 1578 (s), 1528 (s).

[Cp(quinol)Ti(μ_3-S)$_2${Rh(CO)(PPh$_3$)}$_2$] (15). [Cp(quinol)Ti(μ_3-S)$_2${Rh(CO)}$_2$] (**11**) (0.080 g, 0.125 mmol) was reacted with PPh_3 (0.066 g, 0.250 mmol) in dichloromethane (10 mL) to give a garnet solution and evolution of carbon monoxide. The solution was stirred for 30 min and the solvent removed under vacuum to give a violet microcrystalline residue, which was washed with cold hexane and dried under vacuum. Yield: 0.115 g (83%). Anal. Calcd for $C_{52}H_{41}NO_3P_2Rh_2S_2Ti$ (%): C, 56.38; H, 3.73; N, 1.26. Found: C, 56.15; H, 3.40; N, 1.31. MS (FAB+, CH_2Cl_2, *m/z*): 1108 (M$^+$, 10), 1079 (M − CO, 35), 1051 (M$^+$ − 2CO, 8), 789 (M$^+$ − 2CO − PPh$_3$, 100), 526 (M$^+$ − 2CO − 2PPh$_3$, 50). ^{1}H NMR ($CDCl_3$, 293 K): 9.20 (d, J_{H-H} = 7.2 Hz), 8.22 (d, J_{H-H} = 7.3 Hz), 7.81−6.71 (m, PPh$_3$ + quinol), 6.28, 6.21, 6.14 (s, Cp) (four isomers). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): 37.4 (d, J_{Rh-P} = 168 Hz), 36.2 (d, J_{Rh-P} = 166 Hz), 35.8 (d, J_{Rh-P} = 162 Hz), 35.2 (d, J_{Rh-P} = 165 Hz) (*cis* isomers); 36.8 (d of m, J_{Rh-P} = 168 Hz), 36.3 (d of m, J_{Rh-P} = 168 Hz, J_{P-P} = 10 Hz) (*trans* isomers). IR (CH_2Cl_2, cm^{-1}): ν(CO), 1958 (vs).

Table 3. Crystallographic Data for Complexes 1 and 8

	1	8
chem formula	$C_{26}H_{36}O_2Rh_2S_2Ti$	$C_{21}H_{17}Ir_3O_8S_2Ti$
fw	698.39	1085.97
cryst size, mm	0.41 × 0.33 × 0.33	0.23 × 0.16 × 0.11
cryst syst	orthorhombic	monoclinic
space group	*Pnma* (no. 62)	$P2_1/n$ (no. 14)
a, Å	17.593(2)	9.379(3)
b, Å	11.6592(7)	14.912(8)
c, Å	12.9790(10)	18.946(5)
β, deg	90.0	93.39(7)
V, Å^3	2662.3(4)	2645.1(18)
Z	4	4
ρ_{calcd}, g cm^{-3}	1.742	2.727
μ, mm^{-1}	1.696	15.536
no. of measd reflns	2681 ($2\theta \le 50°$)	5487 ($2\theta \le 50°$)
no. of unique reflns	2466 (R_{int} = 0.0215)	4682 (R_{int} = 0.0309)
min, max trasm fact	0.752, 0.894	0.153, 0.429
no. data/restraints/ params	2465/0/189	4677/0/322
$R(F)$ ($F^2 \ge 2\sigma(F^2)$)^a	0.0230	0.0346
$wR(F^2)$ (all data)^b	0.0620	0.0679

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ for 2261 (**1**) or 3433 (**8**) observed reflections. [b] $wR(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ (a = 0.0276, b = 4.3535 (**1**) and a = 0.0267, b = 0.3735 (**8**)), where $P = [\max(F_o^2, 0) + 2F_c^2)]/3$.

[Cp(quinol)Ti(μ_3-S)$_2${Ir(CO)(PPh$_3$)}$_2$] (16) was obtained as a dark brown solid by reaction of [Cp(quinol)Ti(μ_3-S)$_2${Ir(CO)}$_2$] (**12**) (0.100 g, 0.122 mmol) with PPh_3 (0.064 g, 0.244 mmol) in dichloromethane (10 mL) following the procedure described above. Yield: 0.133 g (85%). Anal. Calcd for $C_{52}H_{41}Ir_2NO_3P_2S_2Ti$ (%): C, 48.56; H, 3.21; N, 1.09. Found: C, 48.32; H, 3.02; N, 1.05. MS (FAB+, CH_2Cl_2, *m/z*): 1287 (M$^+$, 50), 1023 (M$^+$ − PPh$_3$, 80), 995 (M$^+$ − PPh$_3$ − CO, 30), 705 (M$^+$ − 2CO − 2PPh$_3$, 50). ^{1}H NMR ($CDCl_3$, 293 K): 9.10 (d, J_{H-H} = 7.1 Hz), 8.70 (d, J_{H-H} = 7.3 Hz), 8.20 (d, J_{H-H} = 7.3 Hz) (quinol), 8.00−7.00 (m, PPh$_3$ + quinol), 6.34, 6.35, 6.31, 6.24 (s, Cp) (four isomers). ^{31}P{^{1}H} NMR ($CDCl_3$, 293 K): 21.7 (d, J_{P-P} = 6 Hz), 21.6 (d, J_{P-P} = 6 Hz) (*trans* isomer), 20.5, 20.4, 20.1, 20.0 (s, *cis* isomers), 17.9 (d, J_{P-P} = 8 Hz), 17.5 (d, J_{P-P} = 8 Hz) (*trans* isomer). IR (CH_2Cl_2, cm^{-1}): ν(CO), 1998 cm^{-1} (s).

Determination of Crystal Structures of [Cp(acac)Ti(μ_3-S)$_2${Rh(cod)}$_2$] (1) and [Cp$_2$Ti(acac)][Ir$_3$(μ_3-S)$_2$(CO)$_6$] (8). Single crystals for the X-ray diffraction studies were obtained by slow diffusion of *n*-hexane into concentrated solutions of the complexes in toluene at low temperature (**3**) or in dichloromethane (**8**). A summary of crystal data, intensity collection, and refinement parameters is reported in Table 3. The violet (**1**) or dark red (**8**) crystals used for the X-ray analysis were glued to a glass fiber, mounted on a Siemens-P4 diffractometer, and irradiated with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Cell constants were obtained from the least-squares fit on the setting angles of 25 reflections ($20° \le 2\theta \le 40°$) (**1**) or 44 reflections ($20° \le 2\theta \le 35.6°$) (**8**). A complete set of independent reflections with 2θ up to 50° ($-20 \le h \le 0$, $-13 \le k \le 1$, and $-15 \le l \le 0$ for **1**, and $-11 \le h \le 1$, $-17 \le k \le 1$, and $-22 \le l \le 22$ for **8**) was measured at 173(2) K for each crystal, using the $\omega/2\theta$ scan technique. Three standard reflections were monitored every 100 measurements throughout data collection as a check on crystal and instrument stability; no decay was observed. Both data were corrected for Lorentz and polarization effects.

Reflections were also corrected for absorption using an empirical method (Ψ-scan).[41]

Both structures were solved by Patterson and subsequent difference Fourier techniques (SHELXTL-PLUS)[42] and refined by full-matrix least-squares on F^2 (SHELXL-97).[43] Anisotropic displacement parameters were included for all non-hydrogen atoms. Hydrogen atoms were included in the last cycles of refinement, most of them from observed (**1**) or calculated positions (**8**). All were refined with positional and displacement riding parameters. The function minimized was $\sum[w(F_o^2 - F_c^2)^2]$. The calculated weighting scheme was $1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2,0) + 2F_c^2)]/3$; all the refinements converged to reasonable R factors (see Table 3). The highest residual electron density peaks, weaker than 1.00 e/Å^3 in both structures, were situated in close proximity to the metal atoms and have no chemical sense. Scattering factors were used as implemented in the refinement program.[43]

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Supporting Information Available: An X-ray crystallographic file, also in CIF format, for complexes **1** and **8** is available. This material is available free of charge via the Internet at http://pubs.acs.org.

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