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A New Titanium Alkoxide–Thiolate Complex as a Versatile Heterofunctional Metalloligand

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The titanium complex [TiCp*(OSBz)(OBzSH)] (**1**) has been synthesized by reaction of [TiCp*(Me)$_3$] (Cp* = η^5-C$_5$Me$_5$) with 2-mercaptobenzyl alcohol (H$_2$OSBz). The reaction of complex **1** with H$_2$O gives the dinuclear oxo-bridged complex [{TiCp*(OSBz)}$_2$(μ-O)] (**2**). Complex **1** reacts with [M(μ-OH)(cod)]$_2$ (M = Rh, Ir) to yield the early–late heterobimetallic complexes [TiCp*(OSBz)$_2$M(cod)] {M = Rh (**3**); Ir (**4**)}. Carbon monoxide easily replaces the cod ligand in **3** and **4**, which leads to the corresponding dicarbonyl derivatives [TiCp*(OSBz)$_2$M(CO)$_2$] {M = Rh (**5**); Ir (**6**)}. Compound **5** reacts with PPh$_3$ to yield the monocarbonyl complex [TiCp*(OSBz)$_2$Rh(CO)(PPh$_3$)] (**7**). The molecular structures of complexes **2** and **5** have been established by single-crystal X-ray diffraction studies. The structure of complex **1** and its coordination mode toward a rhodium moiety have been ascertained by means of calculations based on density functional theory.
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Introduction

Early–late heterobimetallic (ELHB) complexes are of interest because of their unique structures and the possibility of cooperative reactivities that originate from the combination of electropositive early metals and electron-rich late metals. These properties have prompted the search for systematic synthetic methods for this class of compounds.[1,2] With regard to the preparation of sulfur-bridged ELHB complexes, several investigations on hydrosulfido complexes[3] have revealed that they behave as potential sulfur metalloligands for the preparation of sulfur-bridged polynuclear complexes.[3–9] A primary requirement to keep these multinuclear cores intact under the reaction conditions is the use of bridging ligands that can firmly connect the metal centres. We have recently reported the synthesis of the titanium alkoxide complex [TiCp*(O$_2$Bz)(OBzOH)] and analyzed the preferences of the Rh(cod) [cod = cyclooctadiene] moiety towards the three alternative coordination sites of the Ti complex, finding out that in the least stable isomer the Rh atom is coordinated by the phenoxido oxygen atoms.[10]

Now we extend our studies to ligands such as deprotonated 2-mercaptobenzyl alcohol with the aim of studying the influence of changing the oxygen atoms of the most-hindered position in the metalloligand, i.e. the phenoxido groups, by sulfur atoms on the coordination preferences of the Rh(cod) moiety. In this sense, because of the high bridging ability and strong affinity that are characteristic of chalcogen atoms with regard to late transition metals [according to the hard and soft acid–base (HSAB) criteria], we would expect that, in spite of the steric hindrance, the late metallic fragment would bind the ligand through the sulfur rather than through the oxygen atoms. Moreover, the combination of hard and soft donors makes the titanoligand potentially able to form complexes with a wide range of metal centres.

Results and Discussion

The piano stool titanium complex [TiCp*(Me)$_3$] reacts with 2-mercaptobenzyl alcohol to yield complex [TiCp*(OSBz)(OBzSH)] (**1**, Scheme 1).

Complex **1** was isolated as a yellow oil and was spectroscopically characterized. It is highly soluble in the most commonly used organic solvents.

The ^{1}H NMR spectrum in C$_6$D$_6$ at room temperature shows a singlet signal at δ = 1.91 ppm corresponding to the Cp* group and several broad signals at 3.48, 5.10, 6.79 and 6.97 ppm assigned to the mercapto proton, to the methylene moieties and to the aromatic protons of the ligands,

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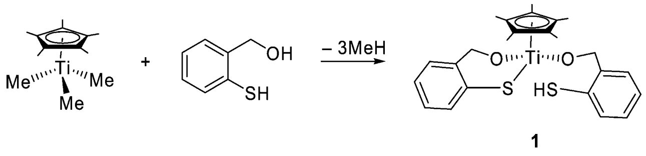
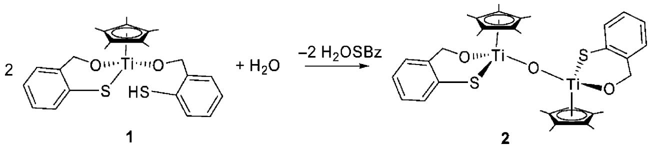


Scheme 1.



Scheme 2.

respectively. The broadness of these signals could be indicative of a fluxional process at this temperature. To clarify this point, a ^{1}H VTNMR experiment was carried out. At 193 K, the ^{1}H NMR spectrum shows two singlet signals corresponding to the Cp* ligand and several broad signals (4.38, 4.61, 5.15 and 5.66 ppm) corresponding to the methylene groups. The broadness of these signals and the overlapping of some of them prevented us from presenting an accurate proposal based on the NMR spectroscopic data.

The ^{1}H and ^{13}C NMR spectroscopic data did not allow us to unambiguously propose the coordination mode of the ligands to the titanium centre and we therefore decided to carry out a DFT study in order to get deeper understanding of the nature of complex **1**. Our calculations show that the protonation of a sulfur atom is preferred over that of oxygen by more than 6 kcal/mol, which leaves an uncoordinated thiol group (Ti···S > 4.3 Å) that it is stabilized by a S–H···X (X = O or S) hydrogen bond. Moreover, a *cis* arrangement around the titanium atom (shown in Figure 1) is favoured over a *trans* arrangement by 2.1 kcal/mol. According to these results, and in agreement with the spectroscopic data, we propose that complex **1** is a monomer with two ligands bonded to the titanium centre; one ligand is bonded in a bidentate fashion through the sulfur and oxygen atoms, and the second is an oxygen donor monodentate ligand, as depicted in Scheme 1. The fluxional process observed could therefore be attributed to an S–H···S→S···H–S proton transfer involving coordination of the dangling thiol, and proton transfer and decoordination of the new thiol moiety in a concerted process.[11]

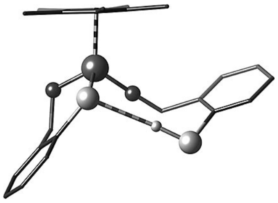


Figure 1. DFT optimized geometry of complex **1** in its most stable conformation (hydrogen atoms omitted for simplicity).

In contrast to the stability observed for [TiCp*(O$_2$Bz)(OBzOH)], complex **1** is extremely moisture sensitive. Complex **1** therefore reacts readily with water to yield the dinuclear oxo-bridged complex **2** (Scheme 2).

Complex **2** was isolated as orange crystals that are soluble in toluene or thf and less soluble in pentane or Et$_2$O. It was characterized by the usual spectroscopic techniques as well as by X-ray diffraction. The molecular structure of **2** is shown in the ORTEP diagram in Figure 2. The crystal data are listed in Table 4, and some important bond lengths and bond angles are shown in Table 1. Complex **2** exhibits a pseudo-tetrahedral geometry around the titanium atoms.

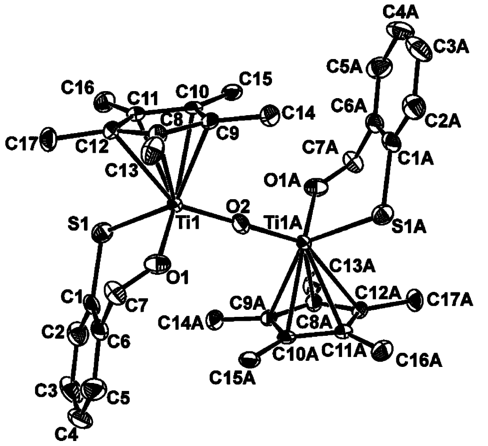


Figure 2. ORTEP diagram of the molecular structure of complex **2**. The hydrogen atoms are omitted for clarity.

Table 1. Bond lengths [Å] and angles [°] for complexes **2** and **5**.

2		**5**	
Bond lengths			
Ti1–O2	1.807(1)	Ti1–O2	1.831(4)
Ti1–O1	1.852(4)	Ti1–O1	1.874(4)
Ti1–S1	2.343(2)	Ti1–S1	2.565(2)
Ti1–C9	2.320(5)	Ti1–S2	2.579(2)
O2–Ti1[a]	1.807(1)	Rh2–C26	1.871(6)
S1–C1	1.789(6)	Rh2–C25	1.888(7)
O1–C7	1.181(8)	Rh2–S2	2.342(1)
		Rh2–S1	2.354(1)
Bond angles			
O2–Ti1–O1	104.9(2)	O2–Ti1–O1	96.7(2)
O2–Ti1–S1	111.39(7)	C26–Rh2–C25	92.1(3)
O1–Ti1–S1	88.9(2)	C26–Rh2–S2	94.0(2)
C1–S1–Ti1	107.3(2)	C25–Rh2–S1	95.8(2)
C7–O1–Ti1	133.8(5)	S2–Rh2–S1	77.80(5)
Ti1–O2–Ti1[a]	180.00(1)	Rh2–S1–Ti1	88.61(5)
		Rh2–S2–Ti1	88.52(5)

[a] Symmetry transformations used to generate equivalent atoms: $-x + 1$, $-y + 2$, $-z + 2$.

In this complex, the Ti–S–C bond angles are significantly smaller (107.4°) than the Ti–O–C bond angles (133.8°). This feature is usual in titanium arylsulfide and alkoxide derivatives[12] and agrees with a Ti–S single bond with sp^3 hybridization in which two lone pairs reside on the sulfur atom and a Ti–O bond with sp^2 hybridization, respectively. Moreover, the Ti–O bond length [Ti1–O2, 1.807(1) Å] is within the range expected for di-μ-oxo-dititanium bridging systems.[13] It is also worth noting that the Ti–O–Ti bond angle is linear (180.0°).

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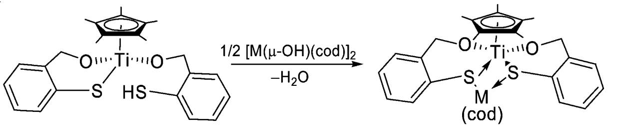
The ^{1}H and ^{13}C NMR spectra show two set of signals corresponding to the O,S ligands. This fact could indicate that the reaction leads to the formation of two isomers of compound **2** (C_i and C_s symmetry) and that both are present in solution but only the C_i isomer could be studied by X-ray diffraction.

The presence of a SH group confers a high reactivity to complex **1** towards metal hydroxido containing species. Complex **1** thus reacts with $[M(\mu\text{-}OH)(cod)]_2$ (M = Rh, Ir) to yield, through a condensation reaction, the heterobimetallic complexes $[TiCp^*(OSBz)_2M(cod)]$ [M = Rh (**3**), Ir (**4**)], (Scheme 3).



1

M = Rh (**3**), Ir (**4**)

Scheme 3.

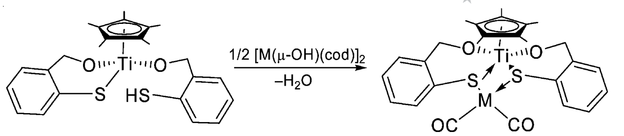
Complexes **3** and **4** are rather stable in air in the solid state, partially soluble in toluene and very soluble in CH_2Cl_2. They were characterized by ^{1}H and ^{13}C NMR spectroscopy as well as analytically. The ^{1}H and ^{13}C NMR spectra are consistent with a symmetric coordination environment of the metal centres. As an example, the ^{1}H NMR spectrum of complex **3** shows two multiplet signals at δ = 2.92 and 4.01 ppm with an integral of 2 H, each one assigned to the two sets of olefinic protons in the cyclooctadiene ligand. In addition, the methylene protons of the cyclooctadiene ligand give rise to multiplet signals at δ = 1.70, 2.05 and 2.35 ppm. The methylene protons of the two equivalent alkoxide groups give rise to two doublet signals at δ = 5.27 and 5.96 ppm, and the aromatic protons to multiplet signals at δ = 7.17 and 7.41 ppm.

These spectroscopic data do not allow us to unequivocally establish whether the rhodium atom is bonded to the two oxygen atoms or to the two sulfur atoms of the metalloligand moiety. However, based on the HSAB principle and given the reactivity reported below, we propose that **3** and **4** are monomeric compounds as drawn in Scheme 3.

To analyze the preferences of the Rh(cod) moiety towards the alternative coordination sites of the Ti starting complex, we carried out a density functional study.

The heterometallic derivatives **3** and **4** react in CH_2Cl_2 at room temperature with excess carbon monoxide, under atmospheric pressure, to yield the corresponding dicarbonyl heterometallic compounds $[TiCp^*(OSBz)_2M(CO)_2]$ [M = Rh (**5**), Ir (**6**)] (see Scheme 4).

Complexes **5** and **6** are soluble in CH_2Cl_2, toluene or thf and less soluble in pentane. Compounds **5** and **6** were spectroscopically and analytically characterized. As an example, the pattern and the relative intensity of the ν(CO) bands at 2052 and 1995 cm^{-1} in the IR spectrum of **5** are as expected for a *cis*-dicarbonyl rhodium(I) complex.[14] Complexes **5** and **6** have C_s symmetry and are expected to display two CO stretching frequencies in the IR spectra, as observed. The averaged value of ν(CO) for **5** is 17 cm^{-1} higher than for the analogous iridium derivative **6**. This is consistent with the well-known periodic trend that third row transition metals are better π bases than those in the second row.



1

M = Rh (**5**), Ir (**6**)

Scheme 4.

The ^{1}H and ^{13}C NMR spectra are also consistent with the proposed structure. The ^{1}H NMR spectrum exhibits an AB pattern for the methylene groups of the two equivalent alkoxide groups, while in the ^{13}C NMR spectrum, the signal corresponding to the two equivalent carbonyl ligands in complex **5** appears at δ = 183.6 ppm.

In order to confirm the proposal, orange crystals suitable for X-ray diffraction of compound **5** were obtained from dichloromethane. The molecular structure was established by an X-ray crystal study. Figure 3 shows an ORTEP diagram, and the most relevant geometrical parameters are summarized in Table 1. The structure is composed of discrete dimetallic (TiRh) molecules.

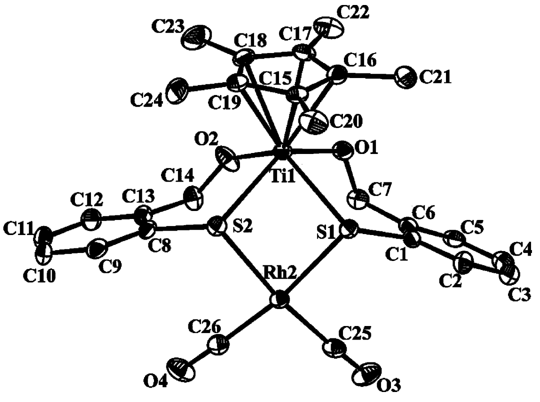
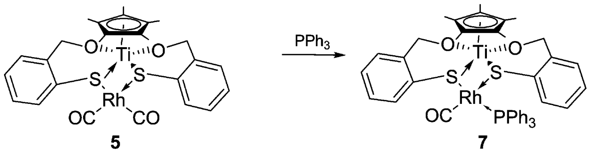


Figure 3. ORTEP diagram of the molecular structure of complex **5**. The hydrogen atoms are omitted for clarity.

The geometry around the titanium atom is that of a square pyramid, while those around the rhodium atoms are almost planar. The Ti–S bond lengths are within the range expected for bridging thiolate ligands.[15]

The intermetallic Rh/Ti distance, 3.439 Å, is long enough to rule out a direct metal–metal interaction.[16] For comparison, the Ti–Rh distance in an alloy of the metals is 2.68 Å, while that involving a highly reduced Rh on titania is 2.55 Å.[17] In the unit cell, two individual $[TiCp^*(OSBz)_2\text{-}Rh(CO)_2]$ molecules are packed together in an up–down fashion and show a Rh···Rh contact of 3.314 Å.

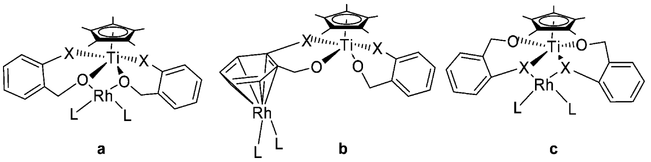
The carbonyl complex **5** reacts with triphenylphosphane at room temperature to give a single product **7**, in which one of the two CO ligands of each $Rh(CO)_2$ fragment is exchanged by the phosphane group (Scheme 5).



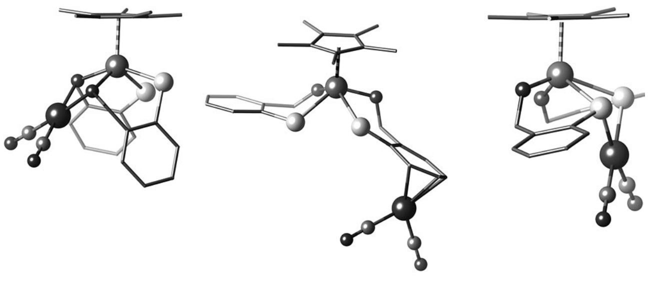
Scheme 5.

Complex **7** is soluble in toluene, CH_2Cl_2 or thf and less soluble in pentane. It has been spectroscopically and analytically characterized. The IR spectrum of complex **7** exhibits one v(CO) band at 1986 cm^{-1}, which is in accordance with the presence of only one carbonyl ligand per metal centre. The ^1H and ^{13}C NMR spectroscopic data indicate a different chemical environment for both alkoxide ligands.

To analyze the preferences of the Rh(cod) and $Rh(CO)_2$ moieties towards the alternative coordination sites of the Ti starting complex (Scheme 1), we carried out a density functional study on the dinuclear complexes [$TiCp^*(OSBz)_2$-RhL_2] (L = cod/2 and CO for **3** and **5**, respectively) with the three coordination modes shown below (Scheme 6), as done in a previous study for X = O.[10b] The optimized structures are shown in Figure 4.



Scheme 6.



a **b** **c**

Figure 4. Optimized structures of three isomers of [$TiCp^*(OSBz)_2$-$Rh(CO)_2$].

The three isomers appear to correspond to minima in the potential energy surface, with relative energies shown in Table 2, together with data for the previously studied [$TiCp^*(O_2Bz)_2Rh(cod)$] complex.[10b] For the latter, the most stable coordination mode for Rh seemed to be through the alkoxide groups (Scheme 6, **a**), followed by that with π coordination from a benzene ring (Scheme 6, **b**), while the least stable isomer is the one in which the Rh atom is coordinated by the phenoxido oxygen atoms (Scheme 6, **c**). However, when the oxygen atoms of the phenolato group are replaced by sulfur, an important change in the relative energies results. The most stable isomer now has the thiophenolato groups coordinated to Rh (Scheme 6, **c**), followed by the isomer with the alkoxide-bonded metal centre (Scheme 6, **a**) and then by the isomer with the π-coordinated aromatic ring (Scheme 6, **b**). The same trends are found if cod is replaced by two carbonyl ligands. It must be noted that the benzene ring in the π-bonded structure presents an allylic η^3-coordination mode and that the corresponding Ti–S bond is significantly elongated. In addition, an alternative π-bonded isomer with a similar energy was found, in which the Ti–S bond is broken and the sulfur atom acquires a thioketone character.

Table 2. Relative energies [kcal/mol] of the three isomers **a**–**c** (Scheme 6) for the complexes [$TiCp^*(OXBz)_2RhL_2$], with L = cod/2 and CO.

X	L	**a**	**b**	**c**
O	cod/2	0.0	21.8	25.3
S	cod/2	20.0	35.0	0.0
S	CO	20.7	45.4	0.0

The fact that the reaction of **1** with 1 equiv. Rh(cod) leads to the thiophenolato complex **3** is in excellent agreement with the higher stability predicted for isomer **c** by our calculations. The higher stability of the thiolato–rhodium isomer is in agreement with the expectations of the HSAB principles.

A closer analysis of their optimized structures shows that substitution of oxygen by sulfur in [$TiCp^*(OXBz)_2Rh(cod)$] produces significant conformational changes in the molecular structure. Thus, the TiS_2Rh ring is significantly more bent than the TiO_2Rh ring and, at the same time, the sulfur atom is more strongly pyramidalized than the oxygen one, as revealed by the bond angle sums around those atoms (Σ_X in Table 3).[18] By comparing the data shown in Table 3 with those for the alternative isomers, we have verified that those geometry changes are associated with the different nature of the donor atom (sulfur versus oxygen) rather than to the coordination mode.

Table 3. Selected parameters for the TiX_2Rh ring in the most-stable isomers of [$TiCp^*(OXBz)_2Rh(cod)$] (X = O for **a**, X = S for **c**).

X	O	S	S
L	cod/2	cod/2	CO
Ti···Rh	3.272	3.593	3.522
Ti–X	2.036	2.631	2.656
Rh–X	2.108	2.436	2.428
Ti–X–X–Rh	157.5	123.3	119.1
Σ_X[a]	352.7	311.9	307.3

[a] Σ_X is the sum of bond angles centred at atom X.

It is interesting to note that there is an intermolecular $Rh^I \cdots Rh^I$ contact (3.31 Å) in the crystal structure of [$TiCp^*(OSBz)_2Rh(CO)_2$]. Since those weak interactions cannot be correctly estimated at the DFT level, we have carried out MP2 calculations in a model neutral complex, by replacing the organic substituents in the experimental structure by hydrogen atoms (Figure 5). The calculated interaction energy, corrected for the basis set superposition error by the counterpoise method, –4.5 kcal/mol, is larger than those previously found for other Rh^I complexes.[19] Such an interaction could impart an extra stabilization to the thiolato–rhodium isomer.

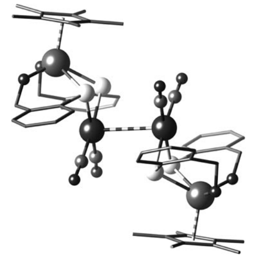


Figure 5. Intermolecular Rh···Rh contact (3.31 Å) in the experimental structure of [TiCp*(OSBz)$_2$Rh(CO)$_2$].

A striking difference between the alkoxide and thiolato complexes is the higher instability of the π-bonded isomer **b** in the latter case (Table 2). In this regard, it must be noted that the benzene ring is coordinated to Rh in that isomer in an allylic η^3 rather than a η^6 mode. A search of the Cambridge Structural Database shows that the η^6-coordination mode for O-substituted phenyl rings is very common. In contrast, the only structurally characterized example of an S-substituted phenyl ring π bonded to Rh^{I} is that of a dibenzothiophene complex, in which the aromatic ring presents an η^4 coordination to Rh.[20] All these data suggest that π coordination of a sulfur-substituted arene to Rh^{I} is not very favourable.

Conclusions

We have shown that the titanium derivative [TiCp*(OSBz)(OSBzH)] can behave as a flexible metalloligand that is able to bind late transition metals to yield the corresponding sulfur-bridged early–late transition-metal compounds. These derivatives are quite stable and react with carbon monoxide, and the heterometallic core remains unchanged. In this Ti(SR)$_2$M core, the metallic centres are quite close but a direct Ti–M interaction is discarded. DFT calculations have allowed us to propose the most-likely structure for the parent mononuclear complex and to explain its different coordination mode to a rhodium moiety than that previously reported for the alkoxide compound.

Experimental Section

General Procedures: The preparation and handling of the described compounds were performed with rigorous exclusion of air and moisture under nitrogen atmosphere by using standard vacuum line and Schlenk techniques. All solvents were dried and distilled under a nitrogen atmosphere. The following reagents were prepared by literature procedures: [TiCp*(Me)$_3$],[21] [Rh(μ-OH)(cod)]$_2$,[22] and [Ir(μ-OH)(cod)]$_2$.[23] Commercially available compounds such as 2-mercaptobenzyl alcohol were used as received from Aldrich. ^{1}H and ^{13}C NMR spectra were recorded on a 200-Mercury Varian Fourier Transform spectrometer. Trace amounts of protonated solvents were used as reference, and chemical shifts are reported in parts per million relative to SiMe$_4$.

Synthesis of [TiCp*(OSBz)(OSBzH)] (1): To a solution of [TiCp*(Me)$_3$] (0.147 g, 0.64 mmol) in toluene (5 mL) at –40 °C was added 2-mercaptobenzyl alcohol (0.180 g, 1.28 mmol). The mixture was allowed to reach room temperature and then was stirred for 3 h. The solvent was removed under vacuum, and the residue extracted with pentane. After filtration, the solvent was evaporated to yield complex **1** as yellow oil. Yield: 0.280 g, 94%. ^{1}H NMR (C$_6$D$_6$, room temp., 200 MHz): δ = 1.91 (s, 15 H, Cp*), 3.48 (br., 1 H, SH), 5.10 (br., 4 H, OCH$_2$), 6.79 (m, 5 H, Ar), 6.97 (m, 3 H, Ar) ppm. ^{13}C NMR: δ = 11.3 (Cp*), 75.8 (br., O*C*H$_2$), 80.1 (br., O*C*H$_2$), 123.7 (Cp*), 125.2 (br., Ar), 126.8 (br., Ar), 129.8 (br., Ar), 131.0 (br., Ar), 133.4 (br., Ar), 140.0 (br., ipso), 142.8 (br., ipso), 142.9 (br., ipso) ppm.

Synthesis of [{TiCp*(OSBz)}$_2$(μ-O)] (2): To a solution of complex **1** (0.111 g, 0.24 mmol) in toluene (5 mL) at room temperature was added water (4.3 μL, 0.24 mmol). The solution was stirred for 2 h, after which the solvent was removed under vacuum. The residue was extracted with Et$_2$O, and the solution was cooled to –24 °C overnight to yield red crystals of complex **2**. Yield: 0.035 g, 44%. ^{1}H NMR (CDCl$_3$, room temp., 200 MHz): δ = 1.93 (s, 30 H, Cp*), 4.65 (d, J = 12.46 Hz, 1 H, CH$_2$), 4.77 (d, J = 12.46 Hz, 1 H, CH$_2$), 5.51 (d, J = 12.46 Hz, 1 H, CH$_2$), 5.53 (d, J = 12.46 Hz, 1 H, CH$_2$), 6.92 (m, 2 H, Ar), 7.07 (m, 4 H, Ar), 7.30 (m, 1 H, Ar), 7.40 (m, 1 H, Ar) ppm. ^{13}C{^{1}H} NMR: δ = 11.8 (s, Cp*), 79.3 (s, O*C*H$_2$), 124.1 (s, Cp*), 125.7 (s, Ar), 125.8 (s, Ar), 127.1 (s, Ar), 127.3 (s, Ar), 127.7 (s, Ar), 127.8 (s, Ar), 133.3 (s, Ar), 133.7 (s, Ar), 141.5 (s, ipso), 141.7 (s, ipso), 142.2, (s, ipso), 142.4 (s, ipso) ppm. $C_{34}H_{42}O_3S_2Ti_2$ (658.59): calcd. C 62.01, H 6.43, S 9.73; found C 61.84, H 6.55, S 9.53.

Synthesis of [TiCp*(OSBz)$_2$Rh(cod)] (3): To a solution of complex **1** (0.194 g, 0.42 mmol) in toluene was added [Rh(μ-OH)(cod)]$_2$ (0.096 g, 0.21 mmol), and the mixture was stirred at room temperature for 3 h. The solvent was then removed under vacuum, and the residue extracted with CH$_2$Cl$_2$. The solvent was evaporated, and the residue washed with Et$_2$O to yield a yellow complex that was identified as **3**. Yield: 0.195 g, 69%. ^{1}H NMR (CDCl$_3$, room temp., 200 MHz): δ = 1.70 (m, 4 H, cod), 1.81 (s, 15 H, Cp*), 2.05 (m, 2 H, cod), 2.35 (m, 2 H, cod), 2.92 (m, 2 H, cod), 4.01 (m, 2 H, cod), 5.27 (d, J = 13.20 Hz, 2 H, OCH$_2$), 5.96 (d, J = 13.20 Hz, 2 H, OCH$_2$), 7.17 (m, 6 H, Ar), 7.41 (m, 2 H, Ar) ppm. ^{13}C{^{1}H} NMR: δ = 12.6 (s, Cp*), 30.6 (s, cod), 31.1 (s, cod), 75.0 (s, O*C*H$_2$), 83.3 (d, J = 11.0 Hz, cod), 86.0 (d, J = 11.8 Hz, cod), 125.8 (s, Cp*), 127.1 (s, Ar), 127.3 (s, Ar), 127.8 (s, Ar), 134.6 (s, Ar), 135.0 (s, ipso), 143.1 (s, ipso) ppm. $C_{32}H_{39}O_2RhS_2Ti$ (670.57): calcd. C 57.31, H 5.86, S 9.56; found C 56.91, H 5.99, S 9.41.

Synthesis of [TiCp*(OSBz)$_2$Ir(cod)] (4): To a solution of complex **1** (0.145 g, 0.31 mmol) in toluene was added [Ir(μ-OH)(cod)]$_2$ (0.098 g, 0.15 mmol), and the mixture was stirred at room temperature for 2 h. The solvent was then removed under vacuum, and the residue extracted with CH$_2$Cl$_2$. The solvent was evaporated, and the residue washed with pentane to yield an orange complex that was identified as **4**. Yield: 0.189 g, 79%. ^{1}H NMR (CDCl$_3$, room temp., 200 MHz): δ = 1.38 (m, 2 H, cod), 1.63 (m, 2 H, cod), 1.83 (s, 15 H, Cp*), 2.04 (m, 2 H, cod), 2.20 (m, 2 H, cod), 2.58 (m, 2 H, cod), 3.64 (m, 2 H, cod), 5.20 (d, J = 13.20 Hz, 2 H, OCH$_2$), 5.90 (d, J = 13.20 Hz, 2 H, OCH$_2$), 7.20 (m, 6 H, Ar), 7.41 (m, 2 H, Ar) ppm. ^{13}C{^{1}H} NMR: δ = 13.3 (s, Cp*), 31.4 (s, cod), 32.5 (s, cod), 68.6 (s, O*C*H$_2$), 71.1 (s, cod), 75.1 (s, cod), 126.7 (s, Cp*), 127.8 (s, Ar), 128.3 (s, Ar), 133.5 (s, ipso), 135.4 (s, Ar), 143.7 (s, ipso) ppm. $C_{32}H_{39}IrO_2S_2Ti$ (759.88): calcd. C 50.58, H 5.17, S 8.44; found C 50.80, H 5.26, S 8.45.

Synthesis of [TiCp*(OSBz)$_2$Rh(CO)$_2$] (5): A solution of complex **3** (0.118 g, 0.17 mmol) in CH$_2$Cl$_2$ was treated with excess CO at room temperature, and the resulting solution was stirred at room temperature for 2 h. The solvent was removed under vacuum, and the residue washed with pentane to yield an orange compound, which was characterized as the dicarbonyl complex **5**. Yield: 0.078 g, 72%.

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IR: ν(C–O) = 2052 (vs), 1995 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$, room temp., 200 MHz): δ = 1.83 (s, 15 H, Cp*), 5.20 (d, J = 13.20 Hz, 2 H, OCH_2), 6.15 (d, J = 13.20 Hz, 2 H, OCH_2), 7.22 (m, 6 H, Ar), 7.60 (m, 2 H, Ar) ppm. ^{13}C{^{1}H} NMR: δ = 12.7 (s, Cp*), 74.3 (s, O*C*H$_2$), 126.8 (s, Cp*), 127.7 (s, Ar), 127.8 (s, Ar), 127.9 (s, Ar), 133.4 (s, Ar), 137.6 (s, ipso), 142.9 (s, ipso), 183.6 (d, J = 70.10 Hz, CO) ppm. $C_{26}H_{27}O_4RhS_2Ti$ (618.40): calcd. C 50.50, H 4.40, S 10.37; found C 49.98, H 4.28, S 10.25.

Synthesis of [TiCp*(OSBz)$_2$Ir(CO)$_2$] (6): A solution of complex **4** (0.102 g, 0.13 mmol) in CH_2Cl_2 was treated with excess CO at room temperature, and the resulting solution was stirred at room temperature for 2 h. The solvent was removed under vacuum, and the residue washed with pentane to yield an orange compound, which was characterized as the dicarbonyl complex **6**. Yield: 0.078 g, 82%. IR: ν(C–O) = 2035 (vs), 1978 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$, room temp., 200 MHz): δ = 1.86 (s, 15 H, Cp*), 5.17 (d, J = 13.56 Hz, 2 H, OCH_2), 6.29 (d, J = 13.56 Hz, 2 H, OCH_2), 7.23 (m, 6 H, Ar), 7.60 (m, 2 H, Ar) ppm. ^{13}C{^{1}H} NMR: δ = 13.3 (s, Cp*), 74.2 (s, O*C*H$_2$), 127.7 (s, Cp*), 128.2 (s, Ar), 128.5 (s, Ar), 128.9 (s, Ar), 134.0 (s, Ar), 143.4 (s, ipso) ppm. $C_{26}H_{27}IrO_4S_2Ti$ (707.72): calcd. C 44.12, H 3.84, S 9.06; found C 44.21, H 3.94, S 9.00.

Synthesis of [TiCp*(OSBz)$_2$Rh(CO)(PPh$_3$)] (7): To a mixture of complex **5** (0.091 g, 0.14 mmol) and PPh_3 (0.038 g, 0.14 mmol) was added CH_2Cl_2, and the resulting solution was stirred at room temperature for 2 h. The solvent was removed under vacuum, and the residue extracted with Et_2O. The ether solution was cooled down to –24 °C overnight to yield orange crystals of compound **7**. Yield: 0.080 g, 64%. IR: ν(C–O) = 1986 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$, room temp., 200 MHz): δ = 1.74 (s, 15 H, Cp*), 4.40 (d, J = 12.83 Hz, 1 H, CH_2), 5.06 (d, J = 12.83 Hz, 1 H, CH_2), 5.13 (d, J = 13.92 Hz, 1 H, CH_2), 6.29 (d, J = 12.83 Hz, 1 H, CH_2), 6.50 (m, 1 H, Ar), 6.63 (m, 1 H, Ar), 6.81 (m, 1 H, Ar), 6.95 (m, 1 H, Ar), 7.29 (m, 18 H, Ar), 7.73 (m, 1 H, Ar) ppm. ^{13}C{^{1}H} NMR: δ = 13.0 (s, Cp*), 74.9 (s, O*C*H$_2$), 75.2 (s, O*C*H$_2$), 126.2 (s, Ar), 126.7 (s, Ar), 126.9 (s, Ar), 127.4 (s, Ar), 127.7 (s, Ar), 128.0 (s, Ar), 128.6 (d, J = 10.29 Hz, Ar), 130.3 (d, J = 1.90 Hz, Ar), 133.5 (s, Ar), 133.7 (s, Ar), 134.2 (d, J = 12.19 Hz, Ar), 135.5 (s, Cp*), 138.9 (s, ipso), 144.2 (s, ipso), 144.6, (s, ipso) ppm. ^{31}P{^{1}H} NMR: δ = 38.2 (d, J = 158.24 Hz, PPh_3) ppm. $C_{43}H_{42}O_3PRhS_2Ti$ (852.66): calcd. C 60.57, H 4.96, S 7.51; found C 60.39, H 5.07, S 7.53.

X-ray Crystallography: X-ray data for **2** and **5** were collected on Bruker X8 APEX CCD area detector diffractometers with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) and ω-scan frames covering complete spheres of the reciprocal space (Table 4). The frame data were integrated with the program SAINT,[24] and an absorption correction was performed with the program SADABS.[25] The software package SHELXTL version 6.10[26] was used for space group determination, structure solution and refinement by full-matrix least-squares methods based on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions and refined as riding. CCDC-709646 and CCDC-709647 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details: Density functional calculations were carried out by using the GAUSSIAN03 package.[27] The hybrid density functional B3LYP method was applied.[28] Effective core potentials (ECP) and their associated double-ζ basis set, LANL2DZ, were used for the transition metals (Ti and Rh).[29a] A similar basis set was used for the sulfur atoms, supplemented with an extra d-polarization function.[29b] A split-valence basis set with polarization functions, 6-31G*, was used for the light main group elements (C, H and O).[29c] Geometry optimizations were carried out on the full potential energy surface, without symmetry restrictions. A semiquantitative estimate of the $Rh^I\cdots Rh^I$ interaction energy in a bimolecular aggregate was obtained from MP2 calculations[30a] on the model compound [Rh(HSH···SH)(CO)$_2$] with the experimental structure of **5**, including a counterpoise correction of the basis set superposition error.[30b]

Table 4. Crystal data and structure refinements for **2** and **5**.

	2	**5**
Empirical formula	$C_{34}H_{42}O_3S_2Ti_2$	$C_{26}H_{27}O_4RhS_2Ti$
Formula weight	658.56	618.41
Temperature [K]	180(2)	180(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$Pbca$
a [Å]	11.347(5)	16.941(3)
b [Å]	12.041(5)	13.881(3)
c [Å]	11.697(5)	21.535(4)
β [°]	98.493(8)	
Volume [Å^3]	1580.6(12)	5064.3(16)
Z	2	8
Density (calculated) [g/cm^3]	1.384	1.622
Absorption coefficient [mm^{-1}]	0.670	1.163
F(000)	692	2512
Crystal size [mm]	0.52 × 0.34 × 0.32	0.13 × 0.10 × 0.07
Index ranges	$-12 \le h \le 13$ $-14 \le k \le 14$ $-13 \le l \le 13$	$-22 \le \mathrm{h} \le 22$ $-15 \le \mathrm{k} \le 18$ $-28 \le \mathrm{l} \le 28$
Reflections collected	8393	34402
Independent reflections [R(int)]	2724 [0.0911]	6112 [0.1057]
Data/restraints/parameters	2724/126/192	6112/0/312
Goodness-of-fit on F^2	0.858	1.004
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0727, $wR2$ = 0.1746	R_1 = 0.0563, $wR2$ = 0.1305
R indices (all data)	R_1 = 0.1098, $wR2$ = 0.1922	R_1 = 0.1136, $wR2$ = 0.1602
Largest diff. peak and hole	0.907 and –0.513	0.910 and –1.008

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