

Reactivity of [TiM₂] (M = Rh, Ir) and [TiIr₃] Early-Late Heterobimetallic Sulfido-Bridged Clusters

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Keywords

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Abstract

Treatment of heterobimetallic sulfido-bridged complexes [Cp(acac)Ti(μ₃-S)₂{M(cod)}₂] (M = Rh (**1**), Ir (**2**)) with the organic acids CX₃COOH (X = F, H) forms the corresponding acetate derivatives [Cp(CX₃COO)Ti(μ₃-S)₂{M(cod)}₂] (X = F, M = Rh (**3**), Ir (**4**); X = H, M = Rh (**5**), M = Ir (**6**)). While complex **3** was easily isolated, compounds **4-6** establish in solution the corresponding equilibria with the starting complexes **1** and **2**. Treatment of **1** with a hydrochloric acid solution in THF generates the heterohexanuclear cationic cluster [{CpTi(μ₃-S)₂Rh₂(cod)₂}]₂(μ-OH)[Cl] (**7**), which is deprotonated with weak bases affording the oxo derivative [{CpTi(μ₃-S)₂{Rh(cod)}₂}]₂(μ₂-O) (**8**). Cluster **8**, and the analogous with the ligand methylcyclopentadienyl [{(CpMe)Ti(μ₃-S)₂{Rh(cod)}₂}]₂(μ₂-O) (**9**), can be synthesized from reaction of the respective complexes [Cp₂Ti(SH)₂] and [(CpMe)₂Ti(SH)₂] with the methoxo-bridged dinuclear complex [Rh(μ-OMe)(cod)]₂ in the presence of water. A preliminary study of the molecular structure of **9** confirmed the formation of an almost linear array of the “Ti–O–Ti” subunit, in which each titanium atom supports two “Rh(cod)” moieties through two sulfido bridges. Further, the heterotetranuclear cluster

$[\text{CpTi}(\mu_3\text{-S})_3\text{Ir}_3(\mu_2\text{-CO})(\text{CO})_3(\text{PMe}_3)_3]$ (**10**) reacts with alkynes at the triiridium metallic triangle. The reactions with activated alkynes, such as dimethylacetylenedicarboxylate (or diethylacetylenedicarboxylate) afford clusters $[\text{CpTi}(\mu_3\text{-S})_3\text{Ir}_3(\mu_2\text{-}\eta^1\text{-RO}_2\text{CC=CCO}_2\text{R})\{\text{C}(\text{O})\text{RO}_2\text{CC=CCO}_2\text{R}\}(\text{CO})_3(\text{PMe}_3)_3]$ (R = Me (**11**), Et (**12**)), which incorporate two molecules of alkyne. The X-ray molecular structure of **11** shows that one alkyne is *cis*-metallated to the metal–metal bonded iridium centres whereas the other is taking part of a iridacyclobutenone moiety resulting from the CO migratory insertion into a iridium-alkyne bond at the third iridium centre. However, reaction of **10** with phenylacetylene stops at the cluster $[\text{CpTi}(\mu_3\text{-S})_3\text{Ir}_3(\mu_2\text{-}\eta^1\text{-PhCCH})(\text{CO})_3(\text{PMe}_3)_3]$ (**13**), which contains only a *cis*-metallated olefin to two metal–metal bonded iridium atoms. The X-ray molecular structure of $[\text{CpTi}(\mu_3\text{-S})_3\text{Ir}_3(\mu_2\text{-}\eta^1\text{-PhCCH})(\text{H})(\text{CO})_3(\text{PMe}_3)_3][\text{BF}_4]$ (**14**), the product resulting from protonation of **13** with $\text{HBF}_4 \cdot \text{OEt}_2$ shows that the $[\text{TiIr}_3]$ core remains intact and that the olefin is indeed *cis*-metallated to the two metal–metal bonded iridium atoms, while the third iridium atom from the metallic triangle becomes protonated.

Introduction

The chemistry of early-late heterobimetallic (ELHB) complexes have been attracting significant attention in recent years due to the synergistic effects associated with the interplay of widely electronically divergent transition metals.¹ The combination of electron-poor and electron-rich transition metals have promoted distinctive reactivity patterns with application in both catalytic and stoichiometric reactions,² including the cooperative activation of small molecules or the exploration of new metal-metal bonds or bonding interaction schemes.³ It has been established that sulfido ligands are able to accommodate the different electronic and coordination environments required for both disparate metals thereby resulting in the stabilization of early-late heterobimetallic species.⁴

The development of rational synthetic methodologies has allowed the preparation of a wide range of metal-sulfur polynuclear compounds and clusters with the required metal-sulfur framework.⁵ In this context, hydrosulfido metal complexes are fundamental precursors for the controlled synthesis of sulfido-bridged homo- and heterometallic clusters.^{6,7} In fact, we have reported the usefulness of the compounds $[\text{Cp}_2\text{Ti}(\text{SH})_2]$ and $[\text{Cp}^{\text{tt}}_2\text{Zr}(\text{SH})_2]$ ($\text{Cp}^{\text{tt}} = \eta^5\text{-1,3-di-}i\text{-tert-butylcyclopentadienyl}$) as precursors for the synthesis of $d^0\text{-}d^8$ sulfido-bridged ELHB complexes or clusters through additive deprotonation reactions with mono- and dinuclear d^8 rhodium and iridium compounds having protonable ligands.⁸ This strategy has led to the preparation of the expected heterotrimeric clusters with a triangular $[\text{ZrM}_2]$ ($\text{M} = \text{Rh}, \text{Ir}$) core capped with two μ_3 -sulfido ligands,⁹ but also unexpected clusters of composition $[\text{TiM}_3]$ ($\text{M} = \text{Rh}, \text{Ir}$), with an incomplete cubane structure,¹⁰ and $[\text{Ti}_2\text{Rh}_4]$ oxo-sulfido clusters, with an incomplete double-fused cubane structure.¹¹ Noteworthy, the carbonyl iridium complex $[\text{Cp}^{\text{tt}}_2\text{Zr}(\mu_3\text{-S})_2\{\text{Ir}(\text{CO})_2\}_2]$ is a precursor for the synthesis of early-late heterotrimetallic (ELHT) clusters with $[\text{ZrIrM}]$ ($\text{M} = \text{Rh}, \text{Pd}, \text{Au}$) metal cores by metal exchange reactions.¹²

We have reported the strong influence of electronic and steric effects imparted by the early metal fragment in the outcome of oxidative addition reactions on $[\text{TiIr}_2]$ and $[\text{ZrRh}_2]$ clusters which has no precedent in dinuclear rhodium or iridium chemistry.¹³ Additionally, reactivity studies on $[\text{ZrM}_2]$ ($\text{M} = \text{Rh}, \text{Ir}$) clusters have shown the reversible opening of the triangular core by 1,2-bis(diphenylphosphane)methane that results in the formation of a bent trinuclear clusters driven by an intramolecular disproportionation process involving the reversible metal-metal bond formation.¹⁴ Encouraged by these

findings, we decided to explore the reactivity of the clusters $[\text{Cp}(\text{acac})\text{Ti}(\mu_3\text{-S})_2\{\text{M}(\text{cod})_2\}]$ (acac = acetylacetonate; cod = 1,5-cyclooctadiene) and $[\text{CpTi}(\mu_3\text{-S})_3\text{Ir}_3(\mu_2\text{-CO})(\text{CO})_3(\text{PR}_3)_3]$, with $[\text{TiM}_2]$ (M = Rh, Ir) and $[\text{TiIr}_3]$ metal cores, respectively.¹⁵ Remarkably, both clusters possess uncommon features that suggest an exciting and unpredictable chemical reactivity. The presence of a replaceable acetylacetonate ligand at the titanium centre in $[\text{TiM}_2]$ clusters renders it as a reactive site. On the other hand, the $[\text{TiIr}_3]$ cluster has a distorted tetrahedral metal framework with short Ir–Ir distances and a weak Ti–Ir interaction with a tetrahedral coordinated iridium centre appropriate for multicentre activation of small molecules.

Results and Discussion

The chemistry project on the synthesis of early-late heterobimetallic (ELHB) complexes driven by bis-hydrosulfido titanium and zirconium metalloligands that we undertook some years ago immediately gave unexpected results. Reaction of complex $[\text{Cp}_2\text{Ti}(\text{SH})_2]$ with the acetylacetonate complexes $[\text{M}(\text{acac})(\text{cod})]$ (cod = 1,5-cyclooctadiene; M = Ir, Rh) gave the early-late heterotrinnuclear complexes $[\text{Cp}(\text{acac})\text{Ti}(\mu_3\text{-S})_2\{\text{M}(\text{cod})_2\}]$ (M = Rh (**1**), Ir (**2**)) with a $[\text{TiM}_2]$ core.^{15a} The formation of these compounds results from a complex reaction involving the deprotonation of the hydrosulfido ligands along with the addition of the late-metal fragments, followed by the release of cyclopentadiene by coordination of acetylacetonate to the titanium centre, probably through a heterodinuclear intermediate. On the other hand, cluster $[\text{CpTi}(\mu_3\text{-S})_3\text{Ir}_3(\mu_2\text{-CO})(\text{CO})_3(\text{PMe}_3)_3]$ (**10**) with a tetranuclear core $[\text{TiIr}_3]$ was obtained from the reaction of $[\text{CpTi}(\text{SH})_2]$ with the methoxy-bridged complex $[\{\text{Ir}(\mu\text{-OMe})(\text{cod})\}_2]$, followed by carbonylation and addition of trimethylphosphane.^{15b}

The presence of the acetylacetonate ligand coordinated to titanium centre in complexes **1** and **2** opens up new modes of reactivity when compared to cluster **10**, in which although the titanium centre has 12 v.e., there is no possibility of accessing to it due to steric reasons. The titanium centre in **1** and **2** has 14 v.e. but the presence of the coordinated acetylacetonate ligand allows directing the reactivity to this metal.

Reactivity of complexes with $[\text{TiM}_2]$ (M = Rh, Ir) cores.

The protonation reactions on $[\text{Cp}(\text{acac})\text{Ti}(\mu_3\text{-S})_2\{\text{M}(\text{cod})_2\}]$ (M = Rh (**1**), Ir (**2**)) should likely release acetylacetonate, therefore creating vacant sites at titanium which

could facilitate the coordination of other substrates. However the electrophilic reagent (H^+) may also protonate the late metals (d^8), a process that could lead to the formation of hydrido complexes, especially in the case of the iridium cluster **2**. In this context it could also be expected the protonation at the sulfido bridges, a process that potentially could lead to the degradation of the heterotrinnuclear structures. In order to explore this scenario we chose a range of acids of different nature, such as trifluoroacetic acid (CF_3COOH), acetic acid (CH_3COOH), hydrochloric acid (HCl) and hexafluorophosphoric acid (HPF_6) as reagents towards the isostructural complexes **1** and **2**.

Treatment of $[Cp(acac)Ti(\mu_3-S)_2\{Rh(cod)\}_2]$ (**1**) with one molar-equiv. of neat CF_3COOH in dichloromethane gave a deep orange solution from which the trifluoroacetate complex $[Cp(CF_3COO)Ti(\mu_3-S)_2\{Rh(cod)\}_2]$ (**3**) was isolated as an orange solid with moderate yield (61%). On the contrary, reaction of $[Cp(acac)Ti(\mu_3-S)_2\{Ir(cod)\}_2]$ (**2**) with CF_3COOH is somewhat more complex. Apparently, the reaction never goes to completion, even using a molar ratio **2**: CF_3COOH of 1:5 or conducting the reactions in refluxing THF. This resulted the isolation of the starting complex mixed with the product resulting from the replacement of the acac ligand by a trifluoroacetate group $[Cp(CF_3COO)Ti(\mu_3-S)_2\{Ir(cod)\}_2]$ (**4**). Inspection of the 1H NMR spectrum of the isolated solids showed, among the resonances corresponding to **2**, a singlet at 6.48 ppm for the cyclopentadienyl ligand together with two broad resonances at 4.47 and 4.31 ppm assigned to the olefinic protons of **4**. Monitoring the reaction of **2** with CF_3COOH by NMR spectroscopy suggests that both species are in equilibrium. Although the addition of increased amounts of trifluoroacetic acid resulted in the displacement of the equilibrium to the formation of **4**, at certain point unidentified iridium hydrido species started to form.

Characterization of complex **3** relied on NMR measurements and elemental analysis. Although the FAB^+ mass spectrum of **3** did not give any useful structural information, molecular weight measurements of **3** in chloroform agreed with the heterotrinnuclear formulation proposed above. The 1H NMR spectrum of **3** in $CDCl_3$ at room temperature confirmed the replacement of acetylacetonate from the titanium centre by a trifluoroacetate group, which should be coordinated in a chelated fashion through the oxygen atoms (Fig. 1). Incorporation of the trifluoroacetate ligand in **3** was confirmed upon inspection of the $^{19}F\{^1H\}$ RMN spectrum, which showed a singlet at -76.89 ppm, and the $^{13}C\{^1H\}$ RMN spectrum that showed a resonance at 128.0 ppm corresponding to

the carboxylate carbon atom. The aromatic region of the ^1H NMR spectrum showed a sharp singlet at 6.55 ppm assigned to the cyclopentadienyl ligand. This chemical shift is comparable to that shown by the precursor **1** (6.53 ppm) which strongly suggests that the coordination environment of titanium did not change noticeably after the transformation **1**→**3**. The C_s symmetry of **3** is clearly reflected in the $^{13}\text{C}\{^1\text{H}\}$ RMN spectrum, which showed four well-defined doublets with coupling constants ($J_{\text{Rh-C}}$) *ca.* 11-12 Hz for the olefinic carbons. The analysis of the spectroscopic information gathered for **3** indicated that the heterotrinnuclear $[\text{Ti}(\mu_3\text{-S})_2\text{Rh}_2]$ core of **1** is maintained upon protonation with CF_3COOH , leading to the replacement of the acac ligand by a trifluoroacetate anionic group.

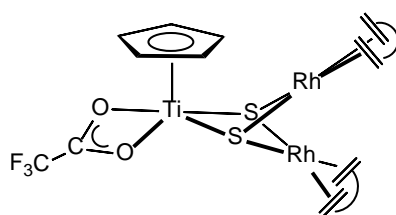
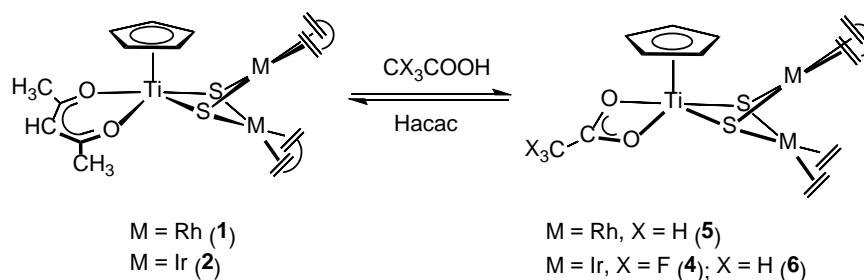


Fig. 1. Proposed structure for cluster $[\text{Cp}(\text{CF}_3\text{COO})\text{Ti}(\mu_3\text{-S})_2\{\text{Rh}(\text{cod})\}_2]$ (**3**).

Reaction of **1** and **2** with a weaker acid, such as acetic acid, also led to the establishment of the respective equilibria between the acetylacetonate and acetate complexes (see Scheme 1). In this way, treatment of a solution of **1** in THF with acetic acid in a 1:1 molar ratio produced a colour change of the solution from dark violet to deep orange. However, work-up led to the quantitative recovery of the starting complex **1**. Monitoring of the aforementioned reaction by NMR spectroscopy allowed us observing that formation of acetate complex $[\text{Cp}(\text{CH}_3\text{COO})\text{Ti}(\mu_3\text{-S})_2\{\text{Rh}(\text{cod})\}_2]$ (**5**) is quantitative when using a slight excess of acetic acid. The ^1H NMR spectrum of this solution showed, along with the resonances from the released acetylacetone, a sharp singlet at 6.46 ppm for the cyclopentadienyl ligand and a singlet at 2.02 ppm for the methyl group of the acetate ligand coordinated to titanium. Among these signals, three multiplets at 4.71 (4H), 4.63 (2H) and 4.52 ppm (2H) corresponding to the olefinic =CH protons were observed, a pattern consistent with a C_s symmetry of the molecule. However, when the reaction is carried out in a 1:1 molar ratio, NMR measurements showed the establishment of the equilibrium illustrated in Scheme 1, with a calculated $K_{\text{eq}} = 1.25$.



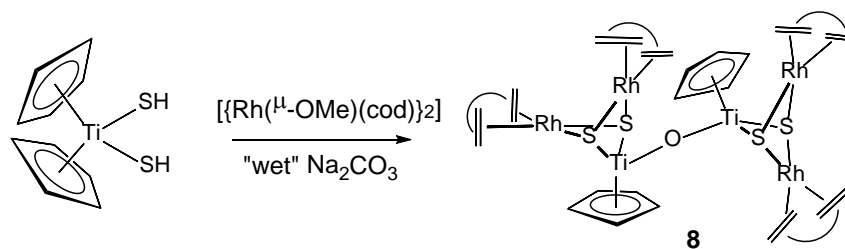
Scheme 1. Equilibria involved in the formation of complexes **4-6**.

Interestingly, the same behaviour was observed on monitoring the reaction of [TiIr₂] complex **2** with acetic acid by NMR spectroscopy. In the presence of an equimolecular amount of acetic acid, complex [Cp(CH₃COO)Ti(μ₃-S)₂{Ir(cod)}₂] (**6**) was formed. The ¹H NMR of the reaction showed, along with the resonances from **2** and free acetylacetonate, a set of signals corresponding to acetate complex **6**; in particular, the cyclopentadienyl protons appeared as a singlet at 6.42 ppm, while the olefinic protons were observed as multiplets at 4.31 (6H) and 4.20 ppm (2H) and the methyl group from the acetate ligand at 2.05 ppm. However, traces of the known heterotetranuclear complex [CpTi(μ₃-S)₃{Ir(cod)}₃] were also observed,^{15b} likely formed as a consequence of side reactions. Addition of an excess of acetic acid to the aforementioned equilibrium allowed displaces it towards **6**. However, on a preparative scale the starting complex **2** was recovered.

The use of a THF solution of HCl gave unexpected results, although only in the case of the rhodium complex **1** we could isolate a discrete complex. Treatment of **1** with a solution of hydrochloric acid in THF in a 1:1 molar ratio at -78 °C gave a deep orange solution from which a dark orange solid **7** was isolated with good yield. The ¹H NMR spectrum of **7** in CDCl₃ at room temperature confirmed the removal of the acac ligand from the titanium centre. Both the number and shape of the resonances from the olefinic protons were distinct from those observed for trifluoroacetate complex **3** and acetate compound **5**, which suggested that complex **7** should have a different structure. The ¹H NMR spectrum of **7** showed a singlet at 6.65 ppm corresponding to the cyclopentadienyl ring, while the =CH protons of the diolefins were observed as two broad signals of an approximate relative intensities of 1:1, with a Cp:cod ratio of 1:2. The shape of the signals observed in the ¹³C{¹H} NMR spectrum of **8** at room temperature indicated that the complex is involved in some dynamic process in solution. In particular, the resonances from the olefinic carbons coordinated to rhodium appeared as unresolved broad signals. However, at 213 K this fluxional behaviour slows down, and the =CH

carbons at this temperature were observed as four distinct doublets ($^1J_{\text{Rh-C}} \sim 10$ Hz). The mass spectrum of **7** showed a peak at m/z : 634 whose isotopic distribution matched with the formula $[\text{Cp}(\text{Cl})\text{Ti}(\text{S})_2\text{Rh}_2(\text{cod})_2]^+$; however the presence of an unsaturated titanium centre (12 v.e.) is unlikely. An hypothetical more stable structure for this compound would correspond to the dimerization product $[\{\text{Cp}(\mu\text{-Cl})\text{Ti}(\mu_3\text{-S})_2\text{Rh}_2(\text{cod})_2\}_2]$, which could be described as a chlorido-bridged $[\text{TiRh}_2]$ cores, or $[\{\text{CpTi}(\mu_3\text{-S})_2\text{Rh}_2(\text{cod})_2\}_2(\mu\text{-OH})]\text{Cl}$ (*vide infra*).

Since no single crystals of **7** were obtained under different conditions, we could not establish its molecular structure by X-ray methods. Therefore we explored the reactivity of **7** with *N*-donor ligands, such as pyridine and triethylamine, in principle expecting a ligand-induced bridge splitting reaction that could lead us to the understanding of its original structure. Complex **7** reacted with pyridine in toluene affording rapidly a microcrystalline violet solid with high yield, which was further characterized as the oxo-derivative $[\{\text{CpTi}(\mu_3\text{-S})_2\{\text{Rh}(\text{cod})\}_2\}_2(\mu_2\text{-O})]$ (**8**) (*vide infra*). At this point we should mention that the heterohexanuclear cluster **8** can be prepared in very good yield from the reaction of $[\text{Cp}_2\text{Ti}(\text{SH})_2]$ with the dinuclear methoxo-bridged complex $[\{\text{Rh}(\mu\text{-OMe})(\text{cod})\}_2]$ (Scheme 2). However, it must be pointed out that when the dirhodium starting complex has been previously recrystallized the aforementioned reaction affords the orange heterotetranuclear cluster $[\text{CpTi}(\mu_3\text{-S})_3\{\text{Rh}(\text{cod})\}_3]$.^{15b} When the starting material $[\{\text{Rh}(\mu\text{-OMe})(\text{cod})\}_2]$ has not been dried over phosphorus pentoxide or simply by adding hydrated sodium carbonate in the reaction with **1**, a purple solution results, from which **8** was isolated in very good yields. Molecular weight measurements of **8** in chloroform gave a mass of 1235, consistent within the experimental error with the formulation $[\text{Cp}_2\text{Ti}_2(\mu\text{-O})(\mu\text{-S})_4\{\text{Rh}(\text{cod})\}_4]$. However, the peak with the highest m/z : 940 in the FAB^+ mass spectrum corresponded to the molecular ion $[\text{CpTi}_2(\mu\text{-O})(\mu\text{-S})_4\{\text{Rh}(\text{cod})\}_3]^+$. The presence of an oxo ligand in complex **8** was also suggested from the chemical shift of the Cp ligands in **8** (δ 6.49 ppm) which is low-field shifted compared to that observed for $[\text{CpTi}(\mu_3\text{-S})_3\{\text{Rh}(\text{cod})\}_3]$ (δ 5.71 ppm).^{10b} On the other hand, the equivalence of the Cp ligands in the ^1H NMR spectrum indicated that **7** was a symmetrical species with a Cp:cod ratio of 1:2, accordingly with the proposed formula. Moreover, the olefinic cod protons gave three signals of relative intensities 2:1:1, which evidenced that the four protons of each cod are non-equivalent.



Scheme 2. Formation of complex **8**.

As monocrystals of **8** could not be grown up, the analogous compound with the methylcyclopentadienyl ligand was prepared by reaction of $[(\text{MeCp})_2\text{Ti}(\text{SH})_2]$ with $[\{\text{Rh}(\mu\text{-OMe})(\text{cod})\}_2]$ in the presence of water. The product $[(\text{MeCp})_2\text{Ti}_2(\mu_2\text{-O})(\mu_3\text{-S})_4\{\text{Rh}(\text{cod})\}_4]$ (**9**) was isolated as a dark-violet solid in good yield and showed similar spectroscopic properties to those of **8**. Thus, complex **9** showed equivalent MeCp ligands and three signals for the olefinic protons of cod of relative intensity 2:1:1. Confirmation of the presence of an oxo ligand bridging two titanium atoms for **9** was achieved by an X-ray diffraction study on a monocrystal grown from CH_2Cl_2 and hexanes. A preliminary study of the crystalline structure disclosed the atom connectivity of **9** (Fig. 2), which confirmed the presence of a bridging oxo ligand that connects two titanium atoms. Disappointingly the low quality of the single crystal studied prevented further discussion on the relevant structural parameters.

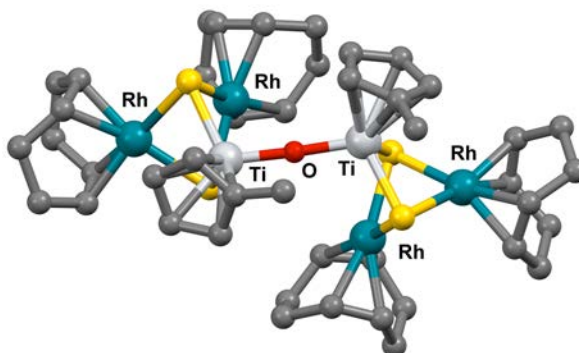


Fig. 2. Representation of the molecular structure of $[(\text{MeCp})_2\text{Ti}_2(\mu_2\text{-O})(\mu_3\text{-S})_4\{\text{Rh}(\text{cod})\}_4]$ (**9**).

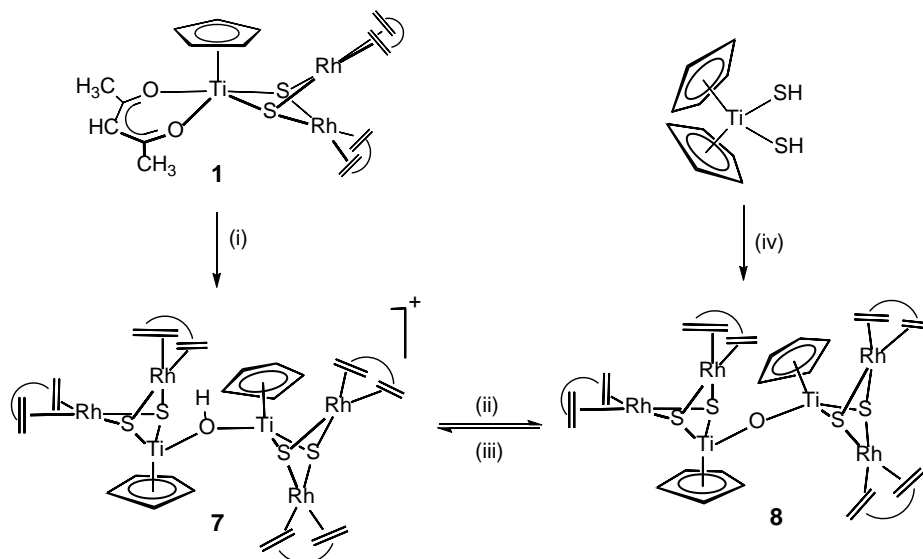
The molecule consists of two trinuclear fragments bridged by an oxygen atom binding the titanium atoms in an almost linear array. Within each trinuclear fragment the titanium and two rhodium atoms are held by two μ_3 -sulfido ligands bridging the three metals. Two sulfur atoms and a 1,5-cyclooctadiene molecule are coordinated to each rhodium atom with square-planar geometries. On the other hand, the titanium metallic

centres are surrounded by pseudo-tetrahedral environments, constituted by the cyclopentadienyl ring, two sulfur atoms and the shared bridging oxo ligand. The global symmetry of complex **9** is C_2 , with the binary axis passing through the oxygen in such a way it relates both heterotrinnuclear $[TiRh_2]$ cores. Therefore, there is clear evidence of an almost linear arrangement of the oxo bridging ligand ($Ti-O-Ti \sim 174^\circ$), a situation well known for d^0 dinuclear $[M(\mu_2-O)M]$ complexes.¹⁶ For instance, complexes $[\{Cp_2Ti(C_9H_7N)\}_2(\mu_2-O)]$,¹⁷ $[\{Cp_2Ti(OCOCF_3)\}_2(\mu_2-O)]$ ¹⁸ and $[\{Cp_2TiCl\}_2(\mu_2-O)]$ ¹⁹ show $Ti-O-Ti$ angles of $174.6(3)^\circ$, $173.3(1)^\circ$ and $173.8(1)^\circ$, respectively, where the linear geometry around oxygen has been explained in terms of a partial double bond character of the $Ti-O$ bonds induced by the π -back donation from the p-filled orbitals at oxygen to the empty d orbitals of the Ti^{IV} centres.

The characterization of clusters **8-9** as oxo derivatives suggested that complex **7** should be an ionic compound formed by two heterotrinnuclear metallic subunits “ $CpTi(\mu_3-S)_2\{Rh(cod)\}_2$ ” linked together through a bridging hydroxo ligand, and it is best formulated as $[\{CpTi(\mu_3-S)_2Rh_2(cod)_2\}_2(\mu_2-OH)]Cl$ (**7**). In fact, conductivity measurements of complex **7** in acetone confirmed its ionic nature, since the values found were in agreement with those expected for a 1:1 electrolyte. Therefore, the aforementioned reaction of **7** with pyridine is based on a deprotonation process of the hydroxo group. As a matter of fact, this reaction can be carried out with different bases such as bipyridine or triethylamine leading to the clean formation of **8**. An indirect proof of the nature of the hydroxo complex **7** comes from its preparation from the oxo complex **8**. In this way, protonation of **8** with HPF_6 afforded compound $[\{CpTi(\mu_3-S)_2Rh_2(cod)_2\}_2(\mu-OH)][PF_6]$, which has been characterized by direct comparison of its spectroscopic properties with **7** (NMR).

These results confirm that protonation of cluster $[Cp(acac)Ti(\mu_3-S)_2\{Rh(cod)\}_2]$ (**1**) with aqueous hydrochloric acid gives the hydroxo derivative $[\{CpTi(\mu_3-S)_2Rh_2(cod)_2\}_2(\mu-OH)][Cl]$ (**7**) and allows speculation about the origin of the hydroxo ligand. Since the THF/HCl mixture was made from an aqueous solution of the commercial acid, it is reasonable to think that the hydroxo ligands come from the water present in the medium. Scheme 3 summarizes the reactions described above, where the proposed structure for cationic cluster **7** is based upon the symmetry observed at low temperature by NMR measurements. The observation of four doublets in the $^{13}C\{^1H\}$

NMR spectrum of **7** at 213 K indicated that both [TiRh₂] subunits are related, a situation that could be explained in terms of a fast pyramidal inversion of the oxygen atom in solution.²⁰ In the ¹H RMN spectrum of **8** the OH proton is hidden in the resonance at 4.54 ppm, while this functional group is also observed in the IR spectrum as a broad band around 3600 cm⁻¹.



Scheme 3. Formation of complexes **7** and **8**. (i) wet HCl; (ii) Py (or NEt₃); (iii) HBF₄; (iv) [{Rh(μ -OMe)(cod)}₂]/wet Na₂CO₃.

On the other hand, when the protonation of complexes **1** and **2** was conducted with a non-coordinating acid in the absence of water the outcome of the reaction changes drastically. In this way, treatment of THF solutions of complexes **1** and **2** with a dry solution of hexafluorophosphoric acid in diethyl ether gave rapidly the known sulfido trinuclear clusters [M₃(μ ₃-S)₂(μ ₂-H)(cod)₃] (M = Rh,²¹ Ir²²) in moderate yields. As a matter of fact, both clusters were easily identifiable by the ¹H NMR spectra since a characteristic triplet at -11.47 ppm and a singlet at -21.48 ppm were observed for the hydrido resonance of the [Rh₃] and [Ir₃] clusters, respectively.

In spite of the very different acid strength of CF₃COOH (*p*K_a = 0.23) and CH₃COOH (*p*K_a = 4.75), most of the reactions described herein lead to the corresponding equilibria between the acetylacetonate starting complexes and the acetate derivatives. As both trifluoroacetate and acetate anions are good ligands, the κ^2 -O,O' coordination to the titanium centre could be anticipated upon protonation of acetylacetonate ligand. Although the aforementioned equilibria can be shifted to the formation of the acetate derivatives in the presence of an excess of the corresponding acid, only in the particular

case of complex $[\text{Cp}(\text{CF}_3\text{COO})\text{Ti}(\mu_3\text{-S})_2\{\text{Rh}(\text{cod})\}_2]$ (**3**) it could be isolated analytically pure. This situation may have its origin in the better affinity of the titanium centre for the acetylacetonate ligand. In this context, this ligand forms a six-membered metallacycle upon coordination to titanium, which is more stable and much less strained than the four-membered metallacycle formed by coordination of the acetate derivatives. Most probably, the isolation of the trifluoroacetate complex **3** is a consequence of both the strong acid character of CF_3COOH and the poor solubility of **3** in the reaction medium.

A plausible mechanism that explains the formation of complex **7** from **1** likely involves the protonation of the acac ligand by H_3O^+ with the release of acetylacetone. Subsequently, the high oxophilicity of the Ti(IV) centre favours the coordination of water rather than the chloride anion. A condensation reaction between two hypothetical water-containing “ $\text{Cp}(\text{H}_2\text{O})\text{Ti}(\mu_3\text{-S})_2\text{Rh}_2(\text{cod})_2$ ” species may lead to the oxo derivative **8**, which is then protonated by the HCl in the medium to yield hydroxo-bridged complex **7**. The presence of water is therefore necessary for the formation of complexes **7-9**, as the source of the hydroxo and oxo ligands.

Reactivity of clusters with $[\text{TiIr}_3]$ cores.

The heterobimetallic cluster $[\text{CpTi}(\mu_3\text{-S})_3\text{Ir}_3(\mu_2\text{-CO})(\text{CO})_3(\text{PMe}_3)_3]$ (**10**) has a $[\text{TiIr}_3]$ core composed of three iridium atoms and one titanium centre held together by three μ_3 -sulfido bridges; additionally, a bridging carbonyl ligand is coordinated to two iridium atoms connected by a metal–metal bond, while the third iridium centre has a pseudo tetrahedral geometry with a intermetallic interaction with the titanium atom.^{15b} In this section we will show that complex **10** is able to activate alkynes exclusively at the late metal sites in reactions in which the tetranuclear core remains intact.

Cluster **10** was reacted with activated alkynes such as dimethylacetylenedicarboxylate (DMAD) and diethylacetylenedicarboxylate (DEAD) in a 1:2 molar ratio in toluene at 50 °C to give air stable red solids formulated as $[\text{CpTi}(\mu_3\text{-S})_3\text{Ir}_3(\mu_2\text{-}\eta^1\text{-RO}_2\text{CC=CCO}_2\text{R})\{\text{C}(\text{O})\text{RO}_2\text{CC=CCO}_2\text{R}\}(\text{CO})_2(\text{PMe}_3)_3]$ (R = Me (**11**), Et (**12**)) in high yields. The use of an equimolecular molar ratio of **10**:DMAD led to mixtures of **11** and the starting complex **10**, while no intermediates were detected by NMR spectroscopy. The mass spectra of **11** and **12** showed peaks at m/z 1382 and 1437, respectively, with an isotopic distribution in agreement with the proposed formulae $[\text{CpTi}(\text{S})_3\text{Ir}_3(\text{alkyne})_2(\text{CO})_3(\text{PMe}_3)_3]$ (alkyne = DMAD (**11**), DEAD (**12**), which

confirmed the incorporation of two molecules of alkyne into the heterotetranuclear cluster **10**, upon removal of the bridging carbonyl ligand.

The presence of an iridacyclobutenone fragment in both clusters was unambiguously established by NMR spectroscopy and further confirmed by the determination of the molecular structure of **11** by an X-ray diffraction study. The ^1H NMR spectrum of **11** showed four singlets for the methyl protons of the coordinated alkyne moieties, indicating their chemical non-equivalence in the molecule. This lack of symmetry was also observed by the non-equivalence of the trimethylphosphane ligands, which give as three distinct doublets in the range 1.65-3.84 ppm ($J_{\text{H-P}} = 10.5\text{-}10.8$ Hz). The multinuclear NMR spectra of **12** are virtually identical to those observed for **11**, and therefore both clusters are isostructural. Furthermore, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **11** and **12** showed three resonances, one singlet and two doublets whose large coupling constant ($J_{\text{P-P}} = 107\text{-}108$ Hz) strongly suggested a mutual *transoidal* disposition of the phosphane ligands coordinated to the two iridium centers, which should be metal-metal bonded in order to account for the high values of $J_{\text{P-P}}$. The infrared spectrum of **11** in dichloromethane showed two intense bands at 2042 and 2002 cm^{-1} assigned to the two terminal carbonyl ligands, a weaker stretch at 1720 cm^{-1} ($\nu_{\text{asim}}(\text{CO})$, DMAD) and another intense band at 1699 cm^{-1} due to the ketonic carbonyl group. There is also a weak band at 1568 cm^{-1} assigned to the $\nu(\text{C}=\text{C})$ absorption.

The low field resonances of the carbonyl ligand in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **11** have been assigned unambiguously by using ^{13}CO -labelled techniques. Complex $[\text{CpTi}(\mu_3\text{-S})_3\text{Ir}_3(\mu_2\text{-}\eta^1\text{-RO}_2\text{CC}=\text{CCO}_2\text{R})\{^{13}\text{C}(\text{O})\text{RO}_2\text{CC}=\text{CCO}_2\text{R}\}(\text{CO})_2(\text{PMe}_3)_3]$ (**11***) was prepared from the labelled cluster $[\text{CpTi}(\mu_3\text{-S})_3\text{Ir}_3(\mu_2\text{-}^{13}\text{CO})(^{13}\text{CO})_3(\text{PMe}_3)_3]$ (**10***).^{15b} The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **11*** in CDCl_3 showed after 20 pulses three resonances due to the carbonyl groups. The signals at 174.8 (dd) and 168.4 (m) ppm corresponded to the terminal carbonyl ligands whereas the high field doublet at 154.9 ppm is assigned to the ketonic carbonyl group. The remaining resonances in the spectrum of **11** corresponded to the carbon atoms from the formerly coordinated alkynes, which were observed at 158.1, 166.9, 167.1 and 175.1 ppm.

The molecular structure of **11** has been determined by X-ray diffraction methods from a single crystal obtained from a prolonged standing of a concentrated solution in methanol at -4 °C. Fig. 4 shows a molecular view of cluster **11** and the most significant bond distances and angles are collected in Table 1.

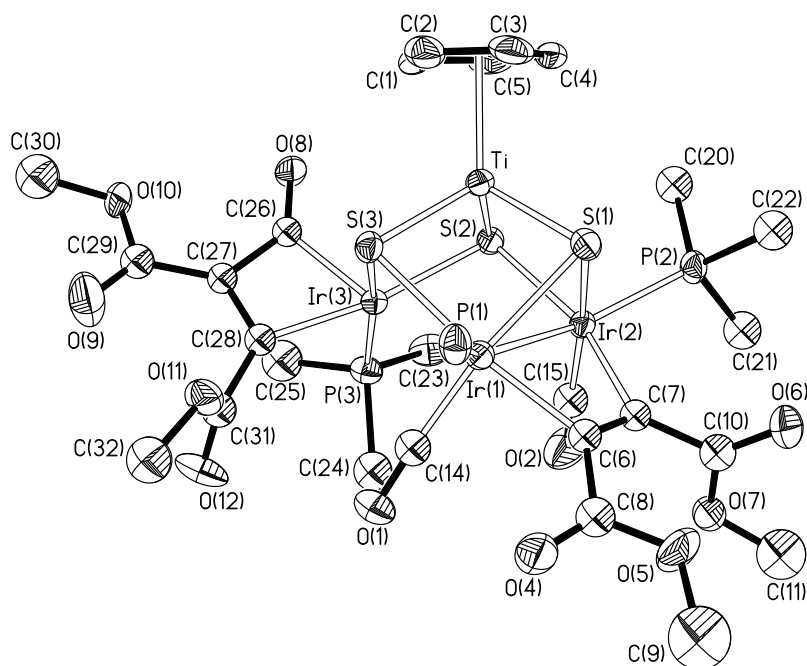


Fig. 4. Molecular structure of cluster **11**. Carbon atoms bonded to the phosphane P(1) atom have been omitted for clarity

Table 1. Selected bond distances (Å) and angles (°) of cluster **11**. G* represents the centroid of the cyclopentadiene ring

Ir(1)–Ir(2)	2.7331(6)	Ir(2)···Ir(3)	3.5726(5)	Ir(3)···Ir(1)	3.2415(5)
Ir(1)–S(1)	2.406(2)	Ir(2)–S(2)	2.474(2)	Ir(3)–S(3)	2.374(2)
Ir(1)–S(3)	2.480(2)	Ir(2)–S(1)	2.385(2)	Ir(3)–S(2)	2.396(2)
Ir(1)–P(1)	2.323(2)	Ir(2)–P(2)	2.324(2)	Ir(3)–P(3)	2.297(3)
Ir(1)–C(6)	2.072(9)	Ir(2)–C(7)	2.070(8)	Ir(3)–C(26)	2.026(9)
Ir(1)–C(14)	1.854(10)	Ir(2)–C(15)	1.845(10)	Ir(3)–C(28)	2.074(9)
Ti–S(1)	2.331(3)	Ti–S(2)	2.278(3)	Ti–S(3)	2.280(3)
Ti–C(1)	2.345(9)	Ti–C(3)	2.364(10)	Ti–C(5)	2.375(10)
Ti–C(2)	2.383(10)	Ti–C(4)	2.366(9)	Ti–G*	2.043(5)
C(6)–C(7)	1.314(12)	C(26)–O(8)	1.222(10)	C(27)–C(29)	1.464(12)
C(6)–C(8)	1.485(12)	C(26)–C(27)	1.456(12)	C(28)–C(31)	1.478(13)
C(7)–C(10)	1.492(13)	C(27)–C(28)	1.341(12)		

S(1)–Ir(1)–S(3)	90.18(7)	S(2)–Ir(2)–S(1)	97.81(8)	S(3)–Ir(3)–S(2)	98.92(8)
S(1)–Ir(1)–P(1)	93.67(8)	S(2)–Ir(2)–P(2)	94.99(8)	S(3)–Ir(3)–P(3)	167.96(8)

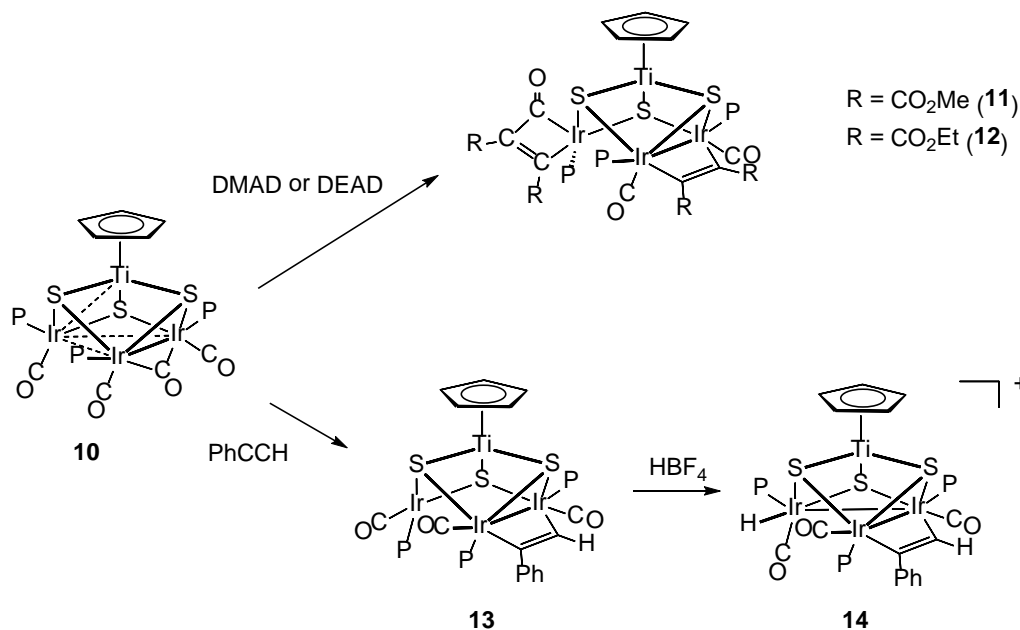
S(1)-Ir(1)-C(6)	83.0(3)	S(2)-Ir(2)-C(7)	164.3(2)	S(3)-Ir(3)-C(26)	92.5(2)
S(1)-Ir(1)-C(14)	165.7(3)	S(2)-Ir(2)-C(15)	89.6(3)	S(3)-Ir(3)-C(28)	82.5(3)
S(3)-Ir(1)-P(1)	87.96(8)	S(1)-Ir(3)-P(2)	95.98(8)	S(2)-Ir(3)-P(3)	91.45(8)
S(3)-Ir(1)-C(6)	172.0(3)	S(1)-Ir(2)-C(7)	82.1(3)	S(2)-Ir(3)-C(26)	106.1(3)
S(3)-Ir(1)-C(14)	96.0(3)	S(1)-Ir(2)-C(15)	165.3(3)	S(2)-Ir(3)-C(28)	169.9(3)
P(1)-Ir(1)-C(6)	96.7(3)	P(2)-Ir(2)-C(7)	100.7(2)	P(3)-Ir(3)-C(26)	90.5(2)
P(1)-Ir(1)-C(14)	99.4(3)	P(2)-Ir(2)-C(15)	96.0(3)	P(3)-Ir(3)-C(28)	88.4(3)
C(6)-Ir(1)-C(14)	89.7(4)	C(7)-Ir(2)-C(15)	87.3(4)	C(26)-Ir(3)-C(28)	63.8(4)
G*-Ti-S(1)	115.33(16)	G*-Ti-S(2)	115.34(17)	G*-Ti-S(3)	116.19(17)
Ti-S(1)-Ir(1)	80.35(8)	Ti-S(2)-Ir(2)	77.36(8)	Ti-S(3)-Ir(3)	77.92(8)
Ti-S(1)-Ir(2)	78.19(8)	Ti-S(2)-Ir(3)	77.50(8)	Ti-S(3)-Ir(1)	79.77(8)
Ir(1)-S(1)-Ir(2)	69.56(6)	Ir(2)-S(2)-Ir(3)	94.36(7)	Ir(1)-S(3)-Ir(3)	83.77(7)
Ir(1)-C(6)-C(7)	110.8(6)	Ir(2)-C(7)-C(6)	109.1(6)	C(6)-C(8)-O(4)	124.9(10)
Ir(1)-C(6)-C(8)	125.0(7)	Ir(2)-C(7)-C(10)	123.0(6)	C(7)-C(10)-O(6)	125.6(9)
C(7)-C(6)-C(8)	123.6(8)	C(6)-C(7)-C(10)	127.9(8)		
Ir(3)-C(26)-O(8)	129.8(7)	C(26)-C(27)-C(28)	101.5(8)	Ir(3)-C(28)-C(27)	98.2(6)
Ir(3)-C(26)-C(27)	96.5(6)	C(26)-C(27)-C(29)	130.7(8)	Ir(3)-C(28)-C(31)	137.8(7)
O(8)-C(26)-C(27)	133.7(8)	C(28)-C(27)-C(29)	127.3(8)	C(27)-C(28)-C(31)	124.0(8)

The molecular structure of **11** shows the presence of two DMAD molecules, one of them is *cis*-dimetallated (C(6) and C(7)), and the other one is taking part of an iridacyclobutenone fragment (C(26)-C(28)). The heterotetranuclear [TiIr₃] core shows an irregular tetrahedral arrangement where each [TiIr₂] face is capped by a triply bridging sulfido ligand. The geometry around the titanium center is pseudo-tetrahedral, adopting a typical three legged piano stool arrangement by coordination of a η^5 -cyclopentadienyl and three sulfido ligands. The Ir(1) and Ir(2) metallic centers have a distorted octahedral geometry, in which the coordination sites are occupied by two sulfur ligands –the S(1) ligand is shared by both iridium centres–, a mutually located *cis* terminal carbonyl and trimethylphosphane ligands (torsional angles through Ir–Ir bond –8.21(18) and –4.5(5)°, respectively), one end of the bridging alkyne ligand bound as a *cis*-metallated olefin, and the Ir–Ir bond. One of the originally acetylenic molecules is bound parallel to the metal–metal bond with *cis*-metallated geometry, in which the parameters involved with the μ_2 - η^1 -olefin binding mode are the expected for this type of coordination.²³ The geometries

around the metallated carbon atoms, C(6) and C(7), are consistent with a slightly distorted sp^2 hybridization and the C(6)–C(7) distance of 1.314(12) Å falls within the range of the distances found in complexes that incorporate *cis*-dimetallated olefins and it is close to that of a carbon–carbon double bond.²⁴

The Ir(3) center displays a severely distorted square pyramidal geometry, with the coordination sites occupied by two sulfur ligands (S(2) and S(3)), the trimethylphosphane ligand, the C(28) carbon atom of the acetylene, and the apical site is occupied by the C(26) ketonic carbonyl ligand. Interestingly, this iridium atom is involved in the formation of an iridacyclobutenone, likely by migratory CO insertion into a Ir–DMAD bond. The formation of this metallacycle is surprising, since mononuclear complexes that incorporate metallacyclobutenones are rare, in spite of their relevance in alkyne coupling processes mediated by transition metals.²⁵ Known examples of these structural motives include complexes of ruthenium,²⁶ iron,²⁷ rhenium²⁸ and iridium,²⁹ all of them resulting from coupling reactions of activated alkynes with carbonyl complexes, and some complexes of platinum³⁰ and cobalt³¹ through insertion reactions in cyclopropanones.

The Ir(1)–Ir(2) separation of 2.7331(6) Å is typical for an Ir–Ir single bond and it is comparable to the values found in Ir–DMAD systems.²³ The Ir–S distances are somewhat different one another and they compare favorably with those found in the parent cluster [CpTi(μ_3 -S)₃Ir₃(μ_2 -CO)(CO)₃(P(OMe)₃)₃].^{15b} The longest Ir–S distances are Ir(1)–S(3) (2.480(2) Å) and Ir(2)–S(2) (2.474(2) Å), which can be explained based on the high *trans* influence of the σ -bonded alkenyl carbons of the *cis*-dimetalated olefin. The Ir(3)–P(3) distance of 2.297(3) Å is shorter than the other two Ir–P distances, 2.323(2) and 2.324(2), probably due to the *trans* influence of the Ir–Ir interaction.³²



Scheme 4. Reactions of cluster **10** with alkynes.

Treatment of **10** with non-activated alkynes such as phenylacetylene gave $[\text{CpTi}(\mu_3\text{-S})_3\text{Ir}_3(\mu_2\text{-}\eta^1\text{-PhC=CH})(\text{CO})_3(\text{PMe}_3)_3]$ (**13**), which was isolated as a red solid in excellent yield. Characterization of **13** relied on spectroscopic NMR multinuclear data, mass spectrometry, IR spectroscopy and elemental analysis. The mass spectrum of **13** showed a peak at m/z 1171 which confirmed that the former tetranuclear $[\text{TiIr}_3]$ core incorporates only one molecule of alkyne. The IR spectrum confirmed the loss of the bridging carbonyl ligand in **10**, since it showed three strong $\nu(\text{CO})$ bands in agreement with the presence of three non-equivalent terminal carbonyl ligands, which were observed as three doublets with different coupling constants ($J_{\text{C-P}} = 11, 14, 40$ Hz) in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. The ^1H NMR spectrum of **13** showed a singlet at 5.96 ppm for the cyclopentadienyl ligand, while three separated doublets assigned for the methyl protons of the trimethylphosphane ligands were observed, which confirmed the lack of symmetry of the molecule. This situation is also reflected in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, which showed a set of three separated multiplets: two doublets at -37.9 ($^4J_{\text{P-P}} = 4$ Hz) and -41.0 ($^3J_{\text{P-P}} = 22$ Hz) and a third doublet of doublets at -73.4 ($^3J_{\text{P-P}} = 22$ Hz, $^4J_{\text{P-P}} = 4$ Hz), an information that suggested a certain degree of electronic communication between the late transition metals. The $=\text{CH}$ proton of the alkyne moiety in **13** was observed at low field (7.84 ppm) as a doublet of doublets, while the carbon atoms of the coordinated alkyne were observed at 101.3 ($=\text{CH}$) and 118.8 ($=\text{CPh}$, $^3J_{\text{C-P}} = 41$ Hz) ppm. The spectroscopic information in solution collected for complex **13** was, however, not enough to propose its

structure unambiguously. All the attempts to grow quality crystals for an X-ray study were not successful.

However, its structure was well established through the full characterization of the cluster formed upon a protonation reaction. Treatment of cluster **13** with an ethereal solution of HBF_4 gave the cationic cluster $[\text{CpTi}(\mu_3\text{-S})_3\text{Ir}_3(\mu_2\text{-}\eta^1\text{-PhCCH})(\text{H})(\text{CO})_3(\text{PMe}_3)_3][\text{BF}_4]$ (**14**) which was isolated as a yellow solid in good yield. We were able to grow quality single crystals suitable for an X-ray diffraction study by slow diffusion of hexane into a concentrated solution of the cluster in THF/dichloromethane. The molecular structure of **14** is shown in Fig. 5 and the most representative bond distances and angles are collected in Table 2.

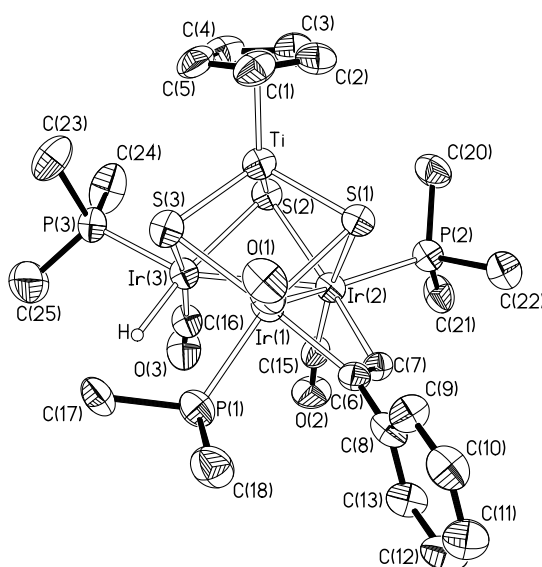


Fig. 5. Molecular structure of cluster **14**.

Table 2. Selected bond distances (Å) and angles (°) of cluster **13**. G* represents the centroid of the cyclopentadiene ring. # Hydride atom has been refined riding on Ir(3) atom.

Ir(1)–Ir(2)	2.8044(5)	Ir(2)···Ir(3)	2.9344(6)	Ir(3)···Ir(1)	3.2100(6)
Ir(1)–S(1)	2.379(2)	Ir(2)–S(2)	2.474(2)	Ir(3)–S(3)	2.360(2)
Ir(1)–S(3)	2.414(3)	Ir(2)–S(1)	2.380(2)	Ir(3)–S(2)	2.437(2)
Ir(1)–P(1)	2.297(3)	Ir(2)–P(2)	2.297(2)	Ir(3)–P(3)	2.262(3)
Ir(1)–C(6)	2.089(9)	Ir(2)–C(7)	2.055(8)	Ir(3)–H [#]	1.6036(4)
Ir(1)–C(14)	1.848(10)	Ir(2)–C(15)	1.859(10)	Ir(3)–C(16)	1.845(10)

Ti-S(1)	2.284(3)	Ti-S(2)	2.278(3)	Ti-S(3)	2.277(3)
Ti-C(1)	2.345(9)	Ti-C(3)	2.331(11)	Ti-C(5)	2.348(9)
Ti-C(2)	2.371(10)	Ti-C(4)	2.327(10)	Ti-G*	2.026(5)
C(6)-C(7)	1.332(12)	C(6)-C(8)	1.467(12)	C(8)-C(9)	1.389(12)

S(1)-Ir(1)-S(3)	97.37(8)	S(2)-Ir(2)-S(1)	91.33(8)	S(3)-Ir(3)-S(2)	97.95(8)
S(1)-Ir(1)-P(1)	165.64(9)	S(2)-Ir(2)-P(2)	94.51(8)	S(3)-Ir(3)-P(3)	93.76(9)
S(1)-Ir(1)-C(6)	81.1(2)	S(2)-Ir(2)-C(7)	170.6(3)	S(3)-Ir(3)-H [#]	82.72(6)
S(1)-Ir(1)-C(14)	97.9(3)	S(2)-Ir(2)-C(15)	101.5(3)	S(3)-Ir(3)-C(16)	167.1(3)
S(3)-Ir(1)-P(1)	93.26(9)	S(1)-Ir(3)-P(2)	90.71(8)	S(2)-Ir(3)-P(3)	100.16(9)
S(3)-Ir(1)-C(6)	163.7(2)	S(1)-Ir(2)-C(7)	82.4(2)	S(2)-Ir(3)-H [#]	171.29(6)
S(3)-Ir(1)-C(14)	97.1(3)	S(1)-Ir(2)-C(15)	166.3(3)	S(2)-Ir(3)-C(16)	94.5(3)
P(1)-Ir(1)-C(6)	86.0(2)	P(2)-Ir(2)-C(7)	92.5(3)	P(3)-Ir(3)-H [#]	88.45(7)
P(1)-Ir(1)-C(14)	90.3(3)	P(2)-Ir(2)-C(15)	93.2(3)	P(3)-Ir(3)-C(16)	87.3(3)
C(6)-Ir(1)-C(14)	99.3(4)	C(7)-Ir(2)-C(15)	84.3(4)	H [#] -Ir(3)-C(16)	84.5(3)
G*-Ti-S(1)	113.27(19)	G*-Ti-S(2)	118.23(19)	G*-Ti-S(3)	114.79(19)
S(1)-Ti-S(2)	99.12(10)	S(2)-Ti-S(3)	105.21(10)	S(3)-Ti-S(1)	104.24(10)
Ti-S(1)-Ir(1)	78.79(8)	Ti-S(2)-Ir(2)	78.69(8)	Ti-S(3)-Ir(3)	78.75(8)
Ti-S(1)-Ir(2)	80.57(8)	Ti-S(2)-Ir(3)	77.13(8)	Ti-S(3)-Ir(1)	78.21(9)
Ir(1)-S(1)-Ir(2)	72.20(6)	Ir(2)-S(2)-Ir(3)	73.39(6)	Ir(1)-S(3)-Ir(3)	84.50(8)
Ir(1)-C(6)-C(7)	108.1(6)	Ir(1)-C(6)-C(8)	129.7(6)	C(7)-C(6)-C(8)	122.2(8)
Ir(2)-C(7)-C(6)	113.4(7)				

The tetrametallic core [TiIr₃] supported by three bridging sulfido ligands is maintained in cluster **14** and it is comparable to that shown by cluster **11**. However, the intermetallic distances at the metal triangle in **14** are different from those observed in cluster **11**. While in both structures, the iridium atoms involved in the bonding of the alkyne, Ir(1) and Ir(2), are clearly metal–metal bonded (2.7331(6) (**11**) and 2.8044(5) Å (**14**)), and the Ir(1)···Ir(3) separations are both similar in the range of non-bonded intermetallic separations (3.2415(5) (**11**) vs. 3.2100(6) Å (**14**), the Ir(2)···Ir(3) separations are significantly different, with values from 3.5726(5) (**11**) to 2.9344(6) Å (**14**), the later one suggesting some kind of intermetallic interaction.

The geometry around the Ir(1) and Ir(2) centers are distorted trigonal bipyramids if the metal–metal bond is not taken into account. As in **11**, the geometry of Ir(3) is a distorted square-pyramidal defined by the two sulfur atoms (S(2) and S(3)), a terminal carbonyl and the phosphane ligands, and a hydrido ligand *trans* to S(2). The whole geometry in the Ir₃ triangle results to be very similar in both structures except for the separation Ir(1)–Ir(3) commented above. However, it is noteworthy the mutually *trans* disposition of the phosphane ligands observed in the Ir(1)–Ir(2) dinuclear subunit in **14** (P(1)–Ir(1)–Ir(2)–P(2) torsion $-138.45(13)^\circ$), that is in clear contrast with the *cis* arrangement exhibited in **11** (torsion $-8.21(18)^\circ$). The alkyne is *cis*-metallated to the two bonded iridium atoms, with the double bond C=C parallel to the Ir(1)–Ir(2) axis. The bonding scheme of the coordinated phenylacetylene contrasts with other iridium clusters, in which the alkyne tends to interact with a third iridium centre, showing a $\mu_3\text{-}\eta^3$ -coordination mode.³³

The multinuclear NMR data for cluster **13** nicely fit with the structure found in the solid state. The hydrido ligand was observed as a doublet at -15.92 ppm, whose coupling constant value ($J_{\text{H-P}} = 11.2$ Hz) indicated a *cis* location respect to the phosphane, while the cyclopentadienyl ligand appeared as a singlet at 5.97 ppm. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **13** reflected the structural situation found in complex **12**. In this way, three resolved multiplets were observed, where the larger coupling constant ($J_{\text{P-P}}$) of 38 Hz corresponded to those phosphorus coordinated to the iridium atoms involved in the metal–metal bond in a *cisoidal* disposition. The carbonyl ligands were observed in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum as separate multiplets, and in the IR spectrum as three strong bands in the region of terminal carbonyls. It is obvious that the protonation process has focused exclusively at the iridium atom not involved in the alkyne coordination in cluster **13**, and therefore this situation strongly support the structural proposal for **13** shown in Scheme 3.

In conclusion, we have shown the reactivity of compact heterobimetallic clusters supported by sulfido ligands. The presence of acetylacetonate ligand in clusters with [TiM₂] (M = Rh, Ir) cores allows performing reactivity exclusively at the titanium centre. In this way, the protonation reactions always results in an attack at the acac ligand although the outcome of the reactions is very much dependent on the nature of the acid. Interestingly, the reaction with wet HCl allows the preparation of a series of oxo- and hydroxo-hexanuclear derivatives. On the contrary, the reactivity of the clusters with a [TiIr₃] core is focused at the late transition metals. The reaction with phenylacetylene

gives a species with a *cis*-metallated alkyne and an unaffected iridium atom. On the other hand, activated alkynes allow isolating complexes which incorporate two alkynes: one *cis*-metallated and the other taking part of an iridacyclobutenone fragment.

Experimental Section

All manipulations were performed under a dry argon atmosphere using Schlenk-tube techniques. Solvents were dried by standard methods and distilled under argon immediately prior to use. Carbon and hydrogen analyses were performed in a Perkin-Elmer 2400 microanalyzer. IR spectra were recorded with a Nicolet-IR 550 (4000-400 cm^{-1}) spectrophotometer as Nujol mulls between polyethylene sheets or in solution in a cell with NaCl windows. Molecular weights were determined with a Knauer osmometer using chloroform solutions. Conductivities were measured in ca. $5 \times 10^{-4} \text{ mol dm}^{-3}$ acetone solutions using a Phillips 9501/01 conductimeter. Mass spectra were recorded in a VG Autospec double-focusing mass spectrometer operating in the FAB⁺ mode. Ions were produced with the standard Cs⁺ gun at ca. 30 kV; 3-nitrobenzyl alcohol (NBA) was used as matrix. ¹H, ¹³C{¹H}, and ³¹P{¹H} spectra were recorded on Varian UNITY, Bruker ARX 300, and Varian Gemini 300 spectrometers operating at 299.95, 75.47 and 121.49 MHz; 300.13, 75.47 and 121.49 MHz; and 300.08, 75.46 and 121.47 MHz, respectively. Chemical shifts are reported in ppm and referenced to Me₄Si using the signal of the deuterated solvent (¹H and ¹³C) as external references. The clusters [Cp(acac)Ti(μ₃-S)₂{M(cod)}₂] (**1-2**)^{15a} and [CpTi(μ₃-S)₃Ir₃(μ-CO)(CO)₃(PMe₃)₃] (**10**)^{15b} were prepared as described previously. The compounds [Cp₂Ti(SH)₂]³⁴ and [(MeCp)₂Ti(SH)₂]³⁵ were prepared according to established procedures.

Preparation of [Cp(CF₃COO)Ti(μ₃-S)₂{Rh(cod)}₂] (3**).** Addition of CF₃COOH (10 μL, 1.536 g mL⁻¹, 0.135 mmol) to a solution of **1** (0.085 g, 0.122 mmol) in methylene chloride (10 mL) gave an orange solution within few minutes. After stirring for 1 h the solution was concentrated to ca. 2 mL under vacuum and addition of hexanes afforded a dark orange solid which was filtered off under argon, washed with hexanes and then vacuum-dried. Yield: 0.053 g (61%). IR (CH₂Cl₂, cm⁻¹): ν(CF₃COO), 1620 (vs), 1722 (s). ¹H NMR (CDCl₃, 293 K): δ 6.55 (s, 5H, Cp), 4.80 (m, 4H, =CH), 4.72 (m, 2H, =CH),

4.59 (m, 2H, =CH), 2.50-2.00 (m, 16H, CH₂) (cod). ¹⁹F{¹H} RMN (CDCl₃, 293K): δ –76.89 (CF₃COO). ¹³C{¹H} RMN (CDCl₃, 293K): δ 128.0 (CF₃COO), 114.1 (Cp), 87.8 (d, *J*_{Rh-C} = 11 Hz), 85.6 (d, *J*_{Rh-C} = 11 Hz), 83.5 (d, *J*_{Rh-C} = 11 Hz), 82.4 (d, *J*_{Rh-C} = 12 Hz), (=CH, cod), 31.8, 31.6, 31.3, 31.1 (>CH₂, cod). Mol. weight (CHCl₃): Found, 712, Calcd. 735. Anal. Calcd for C₂₃H₂₉F₃O₂Rh₂S₂Ti: C, 38.78; H, 4.10. Found: C, 38.56; H, 3.90.

Reaction of 2 with CF₃COOH. Addition of CF₃COOH (20 μL, 1.536 g mL⁻¹, 0.285 mmol) to a solution of **2** (0.050 g, 0.057 mmol) in CD₂Cl₂ (0.5 mL) gave an orange solution within few minutes. NMR measurements at this point showed the presence of **2** and complex [Cp(CF₃COO)Ti(μ₃-S)₂{Ir(cod)}₂] (**4**) in a 2:3 molar ratio. Characteristic resonances for **4** in the ¹H NMR spectrum are as follows: 6.48 (s, 5H, Cp), 4.47 (m, 4H), 4.31 (m, 4H) (=CH cod).

Reaction of 1 with CH₃COOH. Addition of CH₃COOH (4 μL, 1.049 g mL⁻¹, 0.072 mmol) to a solution of **1** (0.025 g, 0.036 mmol) in CD₂Cl₂ (0.5 mL) gave a dark orange solution within few minutes. NMR measurements at this point showed complete transformation to complex [Cp(CH₃COO)Ti(μ₃-S)₂{Rh(cod)}₂] (**5**). Characteristic resonances for **5** in the ¹H NMR spectrum are as follows: 6.46 (s, 5H, Cp), 4.71 (m, 4H), 4.63 (m, 2H), 4.52 (m, 2H) (=CH cod), 2.02 (s, 3H, CH₃).

Reaction of 2 with CH₃COOH. Addition of excess of CH₃COOH (16 μL, 1.049 g mL⁻¹, 0.280 mmol) to a solution of **2** (0.025 g, 0.028 mmol) in CD₂Cl₂ (0.5 mL) gave a dark orange solution within few minutes. NMR measurements at this point showed complete transformation to complex [Cp(CH₃COO)Ti(μ₃-S)₂{Ir(cod)}₂] (**6**). Characteristic resonances for **6** in the ¹H NMR spectrum are as follows: 6.42 (s, 5H, Cp), 2.05 (s, 3H, CH₃).

Preparation of [(CpTi(μ₃-S)₂{Rh(cod)}₂)(μ-OH)][Cl] (7**).** A solution of wet hydrochloric acid in THF (2.23 N, 81 μL, 0.180 mmol) was added to a solution of **1** (0.126 g, 0.180 mmol) in THF (10 mL) at –78 °C. When the resulting mixture reached room temperature an orange solid began to crystallize out, which was isolated by filtration and washed with pentane. The mother liquors were concentrated to ca. 3 mL

and upon addition of pentane a second fraction of an orange solid precipitated. This was filtrated under argon, washed with pentane and then dried under vacuum. Yield: 0.081 g (72%). IR (nujol): $\nu(\text{OH})$, 3600 (w). ^1H NMR (CDCl_3 , 293 K): δ 6.65 (s, 10H, Cp), 4.89 (m, 8H, =CH), 4.54 (m, 9H, =CH and OH), 2.74 (m, 4H, >CH₂), 2.35-2.07 (m, 28H, >CH₂) (cod). $^{13}\text{C}\{^1\text{H}\}$ RMN (CDCl_3 , 213K): δ 115.4 (Cp), 87.4 (d, $J_{\text{Rh-C}} = 10$ Hz), 85.5 (d, $J_{\text{Rh-C}} = 11$ Hz), 81.2 (d, $J_{\text{Rh-C}} = 10$ Hz), 81.1 (d, $J_{\text{Rh-C}} = 11$ Hz) (=CH, cod), 31.8, 31.4, 31.4, 31.1 (> CH₂, cod). FAB(+): m/z (%) 634 ($\text{M}^+ - \text{OH} - \text{CpTiS}_2\{\text{Rh}(\text{cod})\}_2 + \text{Cl}$, 100), 599 ($\text{M}^+ - \text{OH} - \text{CpTiS}_2\{\text{Rh}(\text{cod})\}_2$, 90), 488 ($\text{M}^+ - \text{OH} - \text{CpTiS}_2\{\text{Rh}(\text{cod})\}_2 - \text{cod}$, 87). Λ_{M} ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$): 163 (acetone, $5.03 \cdot 10^{-4}$ M). Anal. Calcd for $\text{C}_{42}\text{H}_{59}\text{ClORh}_4\text{S}_4\text{Ti}_2$: C, 40.29; H, 4.75. Found: C, 40.11; H, 4.55.

Preparation of $[\{\text{CpTi}(\mu_3\text{-S})_2\{\text{Rh}(\text{cod})\}_2\}(\mu\text{-O})]$ (8). Addition of solid $[\text{Cp}_2\text{Ti}(\text{SH})_2]$ (0.100 g, 0.413 mmol) to a solution of $[\{\text{Rh}(\mu\text{-OMe})(\text{cod})\}_2]$ (0.200 g, 0.413 mmol) in wet methylene chloride gave a violet solution from which a violet solid began to crystallize out upon 5 min. of stirring. The suspension was stirred for an additional hour and the microcrystalline solid was filtered off under argon, washed with pentane and then dried under vacuum. Yield: 0.200 g (80%). ^1H NMR (CDCl_3 , 293 K): δ 6.49 (s, 10H, Cp), 4.69 (m, 8H, =CH), 4.62 (m, 4H, =CH), 4.43 (m, 4H, =CH), 2.58-1.94 (set of m, 32H, >CH₂) (cod). FAB(+): m/z (%) 940 ($\text{M}^+ - \text{Rh} - \text{cod} - \text{Cp}$, 100%), 794 ($\text{M}^+ - 2\text{Rh} - \text{cod}$, 50), 751 ($\text{M}^+ - \text{Rh} - 2\text{cod} - \text{Ti} - \text{Cp} - \text{S}$, 80), 652 ($\text{M}^+ - 2\text{Rh} - 3\text{cod} - \text{S}$, 70), 578 ($\text{M}^+ - \text{Rh} - 3\text{cod} - \text{Ti} - 2\text{Cp} - \text{S}$, 95). Mol. weight (CHCl_3): Found, 1215. Calcd. 1235. Anal. Calcd for $\text{C}_{42}\text{H}_{58}\text{ORh}_4\text{S}_4\text{Ti}_2$: C, 41.53; H, 4.81. Found: C, 41.23; H, 4.56.

Preparation of $[\{(\text{MeCp})\text{Ti}(\mu_3\text{-S})_2\{\text{Rh}(\text{cod})\}_2\}(\mu\text{-O})]$ (9). Addition of solid $[(\text{MeCp})_2\text{Ti}(\text{SH})_2]$ (0.112 g, 0.413 mmol) to a solution of $[\{\text{Rh}(\mu\text{-OMe})(\text{cod})\}_2]$ (0.200 g, 0.413 mmol) in wet methylene chloride gave a violet solution which was stirred for 1 h. Evaporation of the solvent to ca. 2 mL and slow addition of pentane afforded a violet microcrystalline solid which was filtered off under argon, washed with pentane and then dried under vacuum. Yield: 0.203 g (79%). ^1H NMR (CDCl_3 , 293 K) δ : 6.52 (t, 4H, MeCp), 6.28 (t, 4H, MeCp), 4.66 (m, 8H, =CH), 4.61 (m, 4H, =CH), 4.45 (m, 4H, =CH) (cod), 2.26 (s, 6H, MeCp), 1.83-2.59 (set of m, 32H, >CH₂) (cod). Anal. Calcd for $\text{C}_{44}\text{H}_{62}\text{ORh}_4\text{S}_4\text{Ti}_2$: C, 42.53; H, 5.03. Found: C, 42.37; H, 4.99.

[CpTi(μ_3 -S)₃Ir₃(μ_2 - η^1 -DMAD){C(O)MeO₂CC=CCO₂Me}(CO)₂(PMe₃)₃] (11). A solution of cluster **10** (0.083 g, 0.074 mmol) in toluene (10 mL) was treated with DMAD (22 μ L, 0.93 g mL⁻¹, 0.148 mmol). The resulting mixture was stirred for 30 minutes at 50 °C to give a red solution which was concentrated under reduced pressure until ca. 1 mL. Addition of hexanes gave a red solid that was filtered, washed with hexanes and then vacuum-dried. Yield: 0.091 g (89%). IR (CH₂Cl₂, cm⁻¹): ν (CO), 2043 (s), 2002 (vs); ν (CO₂), 1720 (s), 1699 (vs); ν (C=C), 1568 (s). ¹H RMN (CDCl₃, 293K): δ 5.97 (s, 5H, Cp), 3.84, 3.63, 3.59, 3.57 (s, 3H each, OCH₃), 3.84 (d, J_{H-P} = 10.5 Hz, 9H), 1.98 (d, J_{H-P} = 10.8 Hz, 9H), 1.65 (d, J_{H-P} = 10.8 Hz, 9H) (PMe₃). ³¹P{¹H} RMN (CDCl₃, 293K) δ : -33.6 (s), -73.6 (d, J_{P-P} = 107 Hz), -88.1 (d, J_{P-P} = 107 Hz). ¹³C{¹H} RMN (CDCl₃, 293K): δ 175.1 (CO₂CH₃), 174.8 (dd, ² J_{C-P} = 7 Hz, ³ J_{C-P} = 4 Hz, Ir-CO), 174.3 (m, =CC(O)Ir), 168.4 (m, Ir-CO), 167.1 (CO₂CH₃), 166.9 (CO₂CH₃), 158.1 (CO₂CH₃), 154.9 (d, ² J_{P-C} = 6 Hz, =CC(O)Ir), 154.0 (m, C=CC(O)Ir), 120.9 (C=C), 110.3 (C=C), 105.0 (Cp), 51.6, 51.6, 51.3, 51.1 (OCH₃), 19.2 (d, J_{C-P} = 28 Hz), 18.8 (d, J_{C-P} = 35 Hz), 18.7 (d, J_{C-P} = 33 Hz) (PMe₃). FAB(+): m/z (%) 1382 (M⁺, 40), 1354 (M⁺-CO, 30), 1326 (M⁺-2CO, 45), 1240 (M⁺-DMAD, 100). Anal. Calcd for C₂₉H₄₄Ir₃O₁₁P₃S₃Ti(%): C, 25.20; H, 3.21. Found: C, 25.15; H, 3.15.

[CpTi(μ_3 -S)₃Ir₃(μ_2 - η^1 -DEAD){C(O)EtO₂CC=CCO₂Et}(CO)₂(PMe₃)₃] (12). Cluster **12** was obtained as a red solid by reaction of **10** (0.100 g, 0.089 mmol) with DEAD (28 μ L, 1.063 g mL⁻¹, 0.178 mmol) in toluene (10 mL) following the procedure described for complex **11**. Yield: 0.109 g (85%). IR (CH₂Cl₂, cm⁻¹): ν (CO), 2050 (s), 2000 (vs); ν (CO₂), 1717 (s); ν (C=C), 1605, 1568 (s). ¹H RMN (CDCl₃, 293K): δ 5.97 (s, 5H, Cp), 4.34 (m, 2H, OCH₂), 4.18 (m, 2H, OCH₂), 4.05 (m, 4H, OCH₂), 1.98 (d, J_{H-P} = 10.3 Hz, 9H), 1.66 (d, J_{H-P} = 10.8 Hz, 9H), 1.55 (d, J_{H-P} = 11.0 Hz, 9H) (PMe₃), 1.34 (t, 3H, J_{H-H} = 7.1 Hz, CH₃), 1.22 (t, J_{H-H} = 7.3 Hz, 3H, CH₃), 1.20 (t, J_{H-H} = 7.1 Hz, 3H, CH₃), 1.17 (t, J_{H-H} = 7.1 Hz, 3H, CH₃). ³¹P{¹H} RMN (CDCl₃, 293K): δ -33.2 (s), -73.0 (d, J_{P-P} = 108 Hz), -86.6 (d, J_{P-P} = 108 Hz). ¹³C{¹H} RMN (CDCl₃, 293K): δ 174.8 (m, OC-Ir), 174.7 (CO₂CH₃), 174.0 (m, =CC(O)Ir), 168.6 (m, Ir-CO), 166.3 (CO₂CH₃), 166.2 (CO₂CH₃), 158.2 (CO₂CH₃), 154.9 (d, ² J_{C-P} = 6 Hz, =CC(O)Ir), 154.0 (m, C=CC(O)Ir), 120.6 (C=C), 109.5 (C=C), 105.0 (Cp), 60.8, 60.3, 60.1, 59.7 (s, OCH₂), 19.3 (d, J_{C-P} = 33 Hz), 18.8 (d, J_{C-P} = 39 Hz), 18.7 (d, J_{C-P} = 34 Hz) (PMe₃), 14.2, 14.1 (CH₃). FAB(+):

m/z (%) 1437 (M^+ , 15), 1410 (M^+-CO , 7), 1381 (M^+-2CO , 5), 1268 (M^+-DEAD , 100).
Anal. Calcd for $C_{33}H_{52}Ir_3O_{11}P_3S_3Ti$ (%): C, 27.55; H, 3.64. Found: C, 27.35; H, 3.45.3

[CpTi(μ_3 -S) $_3$ Ir $_3$ (μ_2 - η^1 -PhCCH)(CO) $_3$ (PMe $_3$) $_3$] (13). Cluster **13** was prepared by reaction of **10** (0.10 g, 0.089 mmol) with phenylacetylene (10.9 μ L, 0.93 g mL $^{-1}$, 0.100 mmol) in toluene (10 mL) at 90 °C for 2 h. Work up as described above gave the cluster as a red solid. Yield: 0.96 g (90%). IR (nujol, cm $^{-1}$): ν (CO), 1983 (vs), 1973 (vs), 1880 (s); ν (C=C), 1604 (w). 1H NMR (CDCl $_3$, 293K): δ 7.84 (dd, $^3J_{H-P}$ = 19.0 Hz, $^4J_{H-P}$ = 1.8 Hz, 1H, PhC=CH), 7.17 (t, 2H, H_m Ph), 7.09 (d, 2H, H_o Ph), 7.00 (t, 1H, H_p Ph), 5.96 (s, 5H, Cp), 1.76 (d, $^2J_{H-P}$ = 10.8 Hz, 9H), 1.74 (d, $^2J_{H-P}$ = 10.3 Hz, 9H), 1.51 (d, $^2J_{H-P}$ = 9.8 Hz, 9H) (PMe $_3$). 1H NMR (C $_6$ D $_6$, 293K): δ 8.09 (dd, $^3J_{H-P}$ = 19.0 Hz, $^4J_{H-P}$ = 2.1 Hz, 1H, PhC=CH), 7.46 (dd, 2H, H_o Ph), 7.22 (t, 2H, H_m Ph), 7.00 (t, 1H, H_p Ph), 5.99 (s, 5H, Cp), 1.74 (d, $^2J_{H-P}$ = 11.0 Hz, 9H), 1.49 (d, $^2J_{H-P}$ = 10.3 Hz, 9H), 1.09 (d, $^2J_{H-P}$ = 9.8 Hz, 9H) (PMe $_3$). $^{31}P\{^1H\}$ NMR (CDCl $_3$, 293K): δ -37.9 (d, $^4J_{P-P}$ = 4 Hz), -41.0 (d, $^3J_{P-P}$ = 22 Hz), -73.4 (dd, $^3J_{P-P}$ = 22 Hz, $^4J_{P-P}$ = 4 Hz). $^{13}C\{^1H\}$ NMR (CDCl $_3$, 293K): δ 182.3 (d, $^2J_{P-C}$ = 14 Hz, CO), 173.0 (m, CO), 154.8 (ddd, $^3J_{C-P}$ = 40 Hz, $^2J_{C-P}$ = 11 Hz, $^4J_{C-P}$ = 3 Hz, CO), 150.6 (C_{ipso}), 128.0 (C_o), 126.0 (C_m), 124.7 (C_p) (Ph), 118.8 (d, $^2J_{C-P}$ = 10 Hz, =CPh), 104.3 (Cp), 101.3 (=CH), 22.0 (d, $^1J_{C-P}$ = 41 Hz), 21.4 (dd, $^1J_{C-P}$ = 39 Hz, $^4J_{C-P}$ = 2 Hz), 17.5 (d, $^1J_{C-P}$ = 31 Hz) (PMe $_3$). FAB(+): m/z (%) 1171 (M^+-CO , 33), 1144 (M^+-2CO , 44), 1116 (M^+-3CO , 50). Anal. Calcd for $C_{25}H_{38}Ir_3O_3P_3S_3Ti$ (%): C, 25.02; H, 3.19. Found: C, 24.96; H, 3.05.

[CpTi(μ_3 -S) $_3$ Ir $_3$ (μ_2 - η^1 -PhCCH)(H)(CO) $_3$ (PMe $_3$) $_3$][BF $_4$] (14). A red suspension of **13** (0.075 g, 0.062 mmol) in diethyl ether (10 mL) was treated with HBF $_4$ ·Et $_2$ O (16 μ L, 54% in Et $_2$ O, 1.19 g mL $^{-1}$, 0.062 mmol) at room temperature. Upon addition a light yellow precipitate was formed almost immediately and the mixture was stirred for 10 minutes. The suspension was filtered and the yellow powder washed twice with diethyl ether and then vacuum-dried. Yield: 0.068 g (85%). IR (nujol, cm $^{-1}$): ν (CO), 1992 (s), 1965 (vs), 1946 (vs); ν (C=C), 1605 (s). 1H NMR (CDCl $_3$, 293K): δ 7.24 (m, 3H, H_m), 7.18 (d, 2H, H_o), 6.97 (t, 1H, H_p), 7.00 (t, 1H, H_p) (Ph), 5.97 (s, 5H, Cp), 1.98 (d, $^2J_{H-P}$ = 11.9 Hz, 9H), 1.80 (d, $^2J_{H-P}$ = 11.2 Hz, 9H), 1.64 (d, $^2J_{H-P}$ = 10.8 Hz, 9H) (PMe $_3$), -15.92 (d, J_{H-P} = 11.2 Hz, Ir-H). $^{31}P\{^1H\}$ NMR (CDCl $_3$, 293K): δ -36.3 (d, $^4J_{P-P}$ = 9 Hz), -48.0 (d, $^3J_{P-P}$ = 38 Hz), -61.5 (dd, $^3J_{P-P}$ = 38 Hz, $^4J_{P-P}$ = 9 Hz). $^{13}C\{^1H\}$ NMR (CDCl $_3$, 293K): δ 171.3

(d, $^2J_{P-C} = 16$ Hz, CO), 170.4 (d, $^2J_{P-C} = 15$ Hz, CO), 154.7 (m, CO), 149.0 (C_{ipso}), 128.7 (C_o), 126.5 (C_m), 126.3 (C_p) (Ph), 106.9 (m, =CPh), 105.3 (Cp), 93.0 (m, =CH), 21.8 (d, $^1J_{C-P} = 42$ Hz), 20.1 (d, $^1J_{C-P} = 42$ Hz), 18.3 (d, $^1J_{C-P} = 39$ Hz) (PMe_3). Anal. Calcd for $C_{25}H_{39}BF_4Ir_3O_3P_3S_3Ti$ (%): C, 23.31; H, 3.05. Found: C, 23.21; H, 3.12.

Crystal Structure Determination of Clusters $[CpTi(\mu_3-S)_3Ir_3(\mu_2-\eta^1-DMAD)\{C(O)MeO_2CC=CCO_2Me\}(CO)_2(PMe_3)_3]$ (11) and $[CpTi(\mu_3-S)_3Ir_3(\mu_2-\eta^1-PhCCH)(H)(CO)_3(PMe_3)_3][BF_4]$ (14). Single crystals for the X-Ray diffraction studies were grown from a methanol concentrated solution of **11** maintained at low temperature ($-4^\circ C$) or by slow diffusion of hexane into a solution of **14** in a mixture of THF/dichloromethane. X-ray diffraction data were collected at 200(2) K on a Siemens P4 (**11**) or at 100(1) K on a SMART APEX CCD (**14**) diffractometers equipped with graphite-monochromated Mo- K_α radiation ($\lambda = 0.71073$ Å); a $\omega/2\theta$ scan technique to a 2θ maximum of 50° was used for **11**, while narrow ω rotations (0.3°) were used for **14**. In the case of **11** the orientation matrix and unit cell dimensions were determined by least-squares fit from a set of high angle carefully centred reflections (78 reflect., $12.5 \leq \theta \leq 22.5^\circ$); for **14** a least-square refinement for 7375 unique good-shaped reflections ($2.35 \leq \theta \leq 25.05^\circ$) gave us unit cell parameters. Data were corrected for Lorentz and polarisation effects, and for absorption using a numerical Gaussian³⁶ (**11**) or an empirical³⁷ (**14**) methods. The structures were solved by Patterson methods, and refined, by full matrix least-squares on F^2 , with SHELXL-97.³⁸ Both structures were refined first with isotropic and later with anisotropic displacement parameters for non-disordered non-H atoms. Specific relevant details on each structure are described below. CCDC 1406027 and 1406028 contain the supplementary crystallographic data for this paper.

Crystal data for **11**: $C_{29}H_{44}Ir_3O_{11}P_3S_3Ti \cdot 0.5 CH_3OH$; $M = 1398.25$; red-orange prismatic block $0.54 \times 0.35 \times 0.21$ mm³; monoclinic, $P21/n$; $a = 11.6293(14)$, $b = 22.841(2)$, $c = 16.855(2)$ Å, $\beta = 101.485(9)^\circ$; $Z = 4$; $V = 4387.4(9)$ Å³; $D_c = 2.117$ g·cm⁻³; $\mu = 9.548$ mm⁻¹; min. and max. absorption correct. Fact. 0.041 and 0.157; $2\theta_{max} = 50.0^\circ$; 9671 reflect. collected, 7646 unique ($R_{int} = 0.0471$); number of data/restraints/parameters 7646/0/484; final GOF 1.044; $R_1 = 0.0354$ (5987 reflections, $I > 2\sigma(I)$); $wR(F^2) = 0.0868$ for all data. A methanol solvent molecule was observed in the crystal structure. All hydrogens (except those of the methanol) were included in calculated positions and refined with riding parameters.

Crystal data for **14**: $C_{25}H_{39}BF_4Ir_3O_3P_3S_3Ti \cdot C_4H_8O \cdot C_6H_{14}$; $M = 1446.24$; orange elongated block $0.48 \times 0.17 \times 0.14 \text{ mm}^3$; triclinic, $P-1$; $a = 11.6018(13)$, $b = 14.2931(16)$, $c = 14.5957(16) \text{ \AA}$, $\alpha = 73.832(2)$, $\beta = 69.723(2)$, $\gamma = 75.525(2)^\circ$; $Z = 2$; $V = 2148.7(4) \text{ \AA}^3$; $D_c = 2.235 \text{ g}\cdot\text{cm}^{-3}$; $\mu = 9.752 \text{ mm}^{-1}$; min. and max. absorption correct. fact. 0.097 and 0.193; $2\theta_{\text{max}} = 50.16^\circ$; 21254 reflect. collected, 7582 unique ($R_{\text{int}} = 0.0368$); number of data/restraints/parameters 7582/6/442; final GOF 0.965; $R_1 = 0.0411$ (5939 reflections, $I > 2\sigma(I)$); $wR(F^2) = 0.1016$ for all data. A THF molecule was clearly identified in the residuals map; two carbon atoms were observed disordered in two positions of identical occupancy. Hydrogen atoms were included in calculated positions and refined with a usual riding model. The hydride ligand was obtained from the difference Fourier map, but refined with geometrical restrictions. At this stage, some intense residuals over $2 \text{ e}^-/\text{\AA}^3$ were observed; after several trials trying to configure a disordered solvent molecule without any success, SQUEEZE program³⁹ was used to evaluate available space and electron density (259 \AA^3 and 55e^- approx.). Eventually a highly disordered hexane molecule was assumed to be present in this spatial region.

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