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Stereoselective Oxidative Additions of Iodoalkanes and Activated Alkynes to a Sulfido-Bridged Heterotrinuclear Early–Late ($TiIr_2$) Complex

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The reactions of the early–late trinuclear complex $[Cp(acac)Ti(\mu_3\text{-}S)_2Ir_2(CO)_4]$ (**1**) with electrophiles have been found to occur on the iridium atoms with no other involvement of the early metal than in electronic effects. The reaction with iodine gave two isomers of the diiridium(II) complex $[Cp(acac)Ti(\mu_3\text{-}S)_2Ir_2I_2(CO)_4]$ differentiated by the relative positions of the iodo ligands on the iridium atoms. The reactions with iodoalkanes are highly stereoselective to give one sole isomer of formula $[Cp(acac)Ti(\mu_3\text{-}S)_2Ir_2(R)(I)(CO)_4]$ ($R = CH_3$, CH_2I, CHI_2) with a carbonyl and the iodo ligand trans to the metal–metal bond. The structures of the symmetrical isomer with the iodo ligands trans to the metal–metal bond and that of the compound with $R = CHI_2$ have been solved by X-ray diffraction methods. The stereoselectivity of the oxidative-addition reactions can be rationalized assuming the influence of steric effects of the groups on the titanium center and a radical-like mechanism. Reactions of **1** with the activated acetylenes, dimethylacetylenedicarboxylate and methylacetylenecarboxylate, gave the complexes $[Cp(acac)Ti(\mu_3\text{-}S)_2Ir_2(\mu\text{-}\eta^1\text{-}RC{=}CCO_2Me)(CO)_4]$ ($R = CO_2Me$, H), with the alkyne bridging the two iridium centers as a cis-dimetalated olefin and the C=C bond parallel to the Ir–Ir axis. Two isomers resulting from the disposition of the alkyne along the Ir–Ir vector were observed in solution for the compound with the nonsymmetrical alkyne (R = H), while only one was observed for the compound with $R = CO_2Me$. An exchange, fast in the NMR time scale, of the apical with the equatorial carbonyls occured in the complexes $[Cp(acac)Ti(\mu_3\text{-}S)_2Ir_2(\mu\text{-}\eta^1\text{-}RC{=}CCO_2Me)(CO)_4]$, producing their equivalence in the $^{13}C\{^1H\}$ NMR spectra.

Introduction

Oxidative-addition reactions of XY substrates to unsaturated dinuclear complexes have been extensively studied as models in homogeneous metal-catalyzed transformations of organic substrates.[1] The use of bridging ligands in such systems allows a broad range of intermetallic separations; thus, cooperative effects between both metallic centers are expected to occur.[2] In the case of iridium(I) dinuclear complexes, this results in the formation of metal−metal-bonded Ir(II)−Ir(II) compounds.[3−10] There are only scarce examples of different behavior, such as the reported one-center methyl iodide oxidative addition to give mixed-valence Ir(III)−Ir(I) dinuclear complexes,[10] and the double oxidative addition of different substrates to pyrazolato- and thiolato-bridged complexes to give dinuclear Ir(III)−Ir(III) derivatives.[4,5,8,11] A remarkable example is illustrated by the tauto-

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meric equilibrium reached between the complexes [$L_2(Cl)Ir^{II}(\mu\text{-}Pz)_2Ir^{II}(\eta^1\text{-}CH_2Ph)L_2$] and [$L_2Ir^{I}(\mu\text{-}Pz)_2Ir^{III}(Cl)(\eta^1\text{-}CH_2Ph)L_2$], resulting from the addition of benzyl chloride to the pyrazolato-bridged iridium(I) compound [{Ir(μ-Pz)-L_2}$_2$] (L = CNBu^t).[12]

It is not obvious to generalize about the mechanisms followed by oxidative-addition processes on dinuclear complexes, because many factors govern the profile of these reactions: steric and/or electronic effects from the ancillary and bridging ligands, nature of the alkyl halide[12] (both the organic fragment and the halide), the relative disposition of the metallic centers,[13] etc. However, in several cases it has been proved that oxidative addition of substrates such as alkyl halides to dinuclear iridium systems follows a S_N2 pathway.[7,12] The attack of the more electrophilic fragment to an iridium center affords the cationic intermediate [Ir(III)−Ir(I)]$^+$. Further coordination of the nucleophilic fragment results in the formation of the metal−metal-bonded Ir(II)−Ir(II) complex.[14] Moreover, the stereochemistry of the final product involves a mutual transoid arrangement of the added fragments across the metal−metal bond as a direct consequence of the reaction mechanism. On the other hand, there are only scarce examples of the behavior of polynuclear complexes in oxidative-addition reactions, such as the reported addition of Me$^+$ to a single center in a trinuclear iridium cluster.[15]

Early−late heterometallic complexes are of special interest because they are composed of metals with divergent properties, but only a few studies concerning the behavior of early−late metal complexes in oxidative-addition reactions have been reported. Thus, the complexes [$Cp_2M(\mu\text{-}PEt_2)_2Rh(\eta^5$-indenyl)] (M = Zr, Hf) undergo an oxidative addition of MeI to give the cationic complexes [$Cp_2M(\mu\text{-}PEt_2)_2Rh(Me)$-($\eta^5$-indenyl)]I.[16] Bergman et al. have also shown that the early metal in the dinuclear complex [$Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)_2$] acts as a sink and source of electrons for the late metal through a direct Ta−Ir interaction.[17] Furthermore, the catalytic activity of this complex in the hydrogenation and hydrosilylation of ethylene illustrates very elegantly the cooperative activity between both early and late metals.[18]

We have recently rationalized a synthetic approach for the synthesis of early−late heterobimetallic (ELHB) complexes [$CpTi(\mu_3\text{-}S)_3$\{M(diolefin)\}$_3$] (M = Rh, Ir)[19,20] based on the acid−base chemistry of [$Cp_2Ti(SH)_2$]. The additive deprotonation reactions of [$Cp_2Ti(SH)_2$] with the mononuclear complexes [M(acac)(diolefin)] (M = Rh, Ir) resulted in the formation of the unexpected ELHB complexes [Cp(acac)-Ti(μ_3-S)$_2$\{M(diolefin)\}$_2$] by replacement of one cyclopentadienyl group by an acetylacetonato ligand at the titanium center.[21] It is noticeable that the heterotrinuclear framework, formed by triangular TiM_2 cores doubly capped by two μ_3-sulfido ligands, is maintained upon carbonylation, giving the tetracarbonyl complexes [Cp(acac)Ti(μ_3-S)$_2$\{M(CO)$_2$\}$_2$] (M = Rh, Ir).

Complex [Cp(acac)Ti(μ_3-S)$_2$\{Ir(CO)$_2$\}$_2$] (**1**) resembles the dinuclear dithiolate compound [\{Ir(μ-S(CH$_2$)$_n$S)(CO)$_2$\}$_2$][22] if the fragment “Cp(acac)TiS$_2$” is considered as a S-donor metalloligand that supports the dinuclear moiety “Ir$_2$(CO)$_4$”. The early metalloligand in this [TiIr$_2$] system is expected to exert some steric and electronic influences on the reactivity of the late metals toward electrophiles. Moreover, the structure of such systems allows the existence of weak dative interactions (Ir → Ti) from the electron-rich d^8 metals to the acidic d^0 titanium center.[20,23] Herein we report on the reactivity of complex **1** with several electrophiles such as iodine, alkyl iodides, and activated acetylenes.

Results

Oxidative-Addition Reactions of Iodine and Iodoalkanes to [Cp(acac)Ti(μ_3-S)$_2$\{Ir(CO)$_2$\}$_2$] (1). The complex **1** reacts with a solution of molecular iodine in dichloromethane (1:1 molar ratio) to give a deep red solution from which the adduct [Cp(acac)Ti(μ_3-S)$_2$Ir$_2$I$_2$(CO)$_4$] (**2**) is isolated in very good yield. The presence of two isomers in a 1:1 ratio was evidenced by the double number of resonances from both cyclopentadienyl and the acetylacetonato ligands in the ^{1}H NMR spectrum of **2**, whereas three ν(CO) bands were observed in the IR spectrum. The resonances observed for both isomers in the ^{13}C\{^{1}H\} NMR spectrum (Figure 1) were only slightly separated, a situation that signals differences only in their stereochemistry. For example, the isomer **2a** (Chart 1) has C_s symmetry and displays two resonances at δ 161.0 and 160.9 ppm for the carbonyl ligands. In contrast, isomer **2b** (Chart 1) has no symmetry and displays four resonances for the carbonyl ligands at δ 162.4, 161.8, 159.1, and 151.9 ppm. The structure of the isomer **2a** was solved by X-ray diffraction methods (see below).

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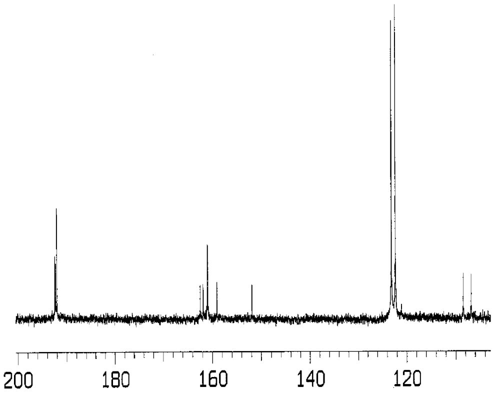
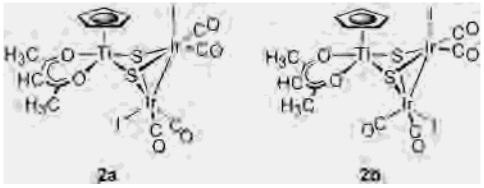


Figure 1. $^{13}C\{^1H\}$ NMR spectrum of the two isomers of complex $[Cp(acac)Ti(\mu_3\text{-}S)_2Ir_2I_2(CO)_4]$ (**2**) in $CDCl_3$ at −55 °C.

Chart 1. Proposed Structures for the Isomers **2a** and **2b**

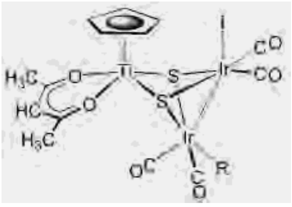


Complex **1** reacts with a wide range of alkyl iodides in conditions that depend on the nature of the substrate used in each case. The reaction of **1** with iodoform in a 1:1 molar ratio gives the heterotrinuclear adduct $[Cp(acac)Ti(\mu_3\text{-}S)_2\text{-}Ir_2(CHI_2)(I)(CO)_4]$ (**3**). Unlike compound **2**, complex **3** exists in solution as one isomer, as evidenced by the ^1H NMR spectrum in $CDCl_3$, which shows a single resonance in the aromatic region for the cyclopentadienyl ligand. In addition, two signals for the methyl groups of the acetylacetonate ligand indicated that complex **3** has no symmetry, while the diiodomethyl fragment ($-CHI_2$) is observed in the ^1H NMR spectrum as a singlet at δ 4.74 ppm and at δ 26.3 ppm in the $^{13}C\{^1H\}$ NMR spectrum. Complex **3** decomposes in a solution of $CDCl_3$ to an equimolar mixture of the diiodo-complexes **2a** and **2b** and other unidentified compounds. To assess the stereochemistry of the formed isomer, the crystal structure of **3** was unambiguously determined by X-ray diffraction methods (see below).

Monitoring the reaction of **1** with methyl iodide by infrared techniques showed that the reaction was very slow, even if a large excess of MeI was used. This reaction afforded the yellow adduct $[Cp(acac)Ti(\mu_3\text{-}S)_2Ir_2(Me)(I)(CO)_4]$ (**4**), which was isolated in good yield after recrystallization from CH_2Cl_2−hexanes. The ^1H NMR spectrum of **4** confirmed the presence of one sole isomer in solution. Thus, the methyl group coordinated to one iridium atom gave a singlet in the ^1H NMR and $^{13}C\{^1H\}$ NMR spectra. The lack of symmetry of this isomer was evidenced by the two signals for the methyl groups of the acetylacetonato ligand in the ^1H NMR and $^{13}C\{^1H\}$ NMR spectra and by four clearly distinguishable resonances for the carbonyl ligands coordinated to the iridium atoms.

Diiodomethane was found to react with **1** only under exposure to ultraviolet light in a quartz tube. Monitoring the reaction by IR indicated that complex **1** was converted cleanly to the adduct $[Cp(acac)Ti(\mu_3\text{-}S)_2Ir_2(CH_2I)(I)(CO)_4]$ (**5**), which was isolated as a red microcrystalline solid. Again, complex **5** was obtained as a sole isomer with no element of symmetry, as indicated by the number of signals due to the cyclopentadienyl, acetylacetonate, and carbonyl ligands in the ^1H and $^{13}C\{^1H\}$ NMR spectra. In particular, the iodomethyl fragment was observed as an AB system centered at δ 3.32 ppm (J_{H-H} = 6.6 Hz) in the ^1H NMR spectrum, which indicates that both protons are diastereotopic. It is noteworthy that complex **5** does not undergo an oxidative isomerization[3b] to the methylene-bridged compound $[Cp(acac)Ti(\mu_3\text{-}S)_2Ir_2(\mu\text{-}CH_2)I_2(CO)_4]$ even under reflux in toluene for a prolonged time.

Chart 2. Proposed Structures for the Complexes **3**−**5**



Complexes **2**−**5** showed three (**2**) and four (**3**−**5**) ν(CO) bands shifted ca. 45 cm^{-1} to higher frequencies relative to complex **1**, which shows three bands in the IR spectrum at 2056(s), 2031(m), and 1983(s) cm^{-1}, in accordance with the local C_{2v} symmetry of the molecular framework.[24,25] This shift is in agreement with an increase in the formal oxidation number of one unit for both iridium atoms, and therefore, complexes **2**−**5** are diiridium(II) complexes with a metal−metal bond. Obviously, the bridging framework was maintained in these oxidative-addition reactions. Nevertheless, the pattern of the ν(CO) bands of complexes **3**−**5** was similar, whereas that of complex **2**, consisting of two isomers, was the same as that of the complexes of C_{2v} symmetry with a sawhorse arrangement of the carbonyl groups. Because the relative intensities of the ν(CO) bands in dinuclear tetracarbonyl complexes are related to the angles formed by the carbonyl groups,[26] the ν(CO) pattern of the complexes **3**−**5** indicates that they possess a similar steric disposition of the ancillary ligands. If we assume that complexes **2b**−**5** are isostructural with complex **3**, which has a carbonyl group trans to the metal−metal bond, we can rationalize the shift of ca. 5 ppm to a higher field of a carbonyl signal relative to the others as characteristic of that type of carbonyl group. Therefore, we can propose reasonably that complexes **2b**−**5** have the structures shown in Charts 1 2, similar to the structure found for complex **3** in the solid state.

X-ray Crystal Structures of $[Cp(acac)Ti(\mu_3\text{-}S)_2Ir_2(I)_2\text{-}(CO)_4]$ (2a) and $[Cp(acac)Ti(\mu_3\text{-}S)_2Ir_2(CHI_2)(I)(CO)_4]$ (3). Single crystals of the complexes were obtained by slow diffusion of *n*-hexane into concentrated solutions of the

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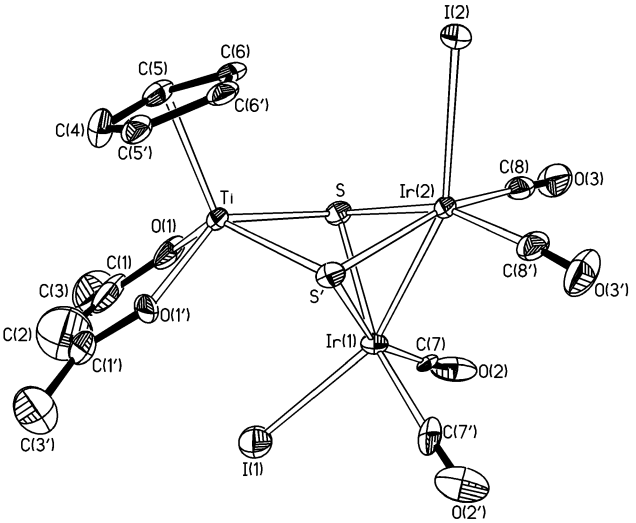


Figure 2. Molecular view of complex [Cp(acac)Ti(μ_3-S)$_2$Ir$_2$I$_2$(CO)$_4$] (**2a**).

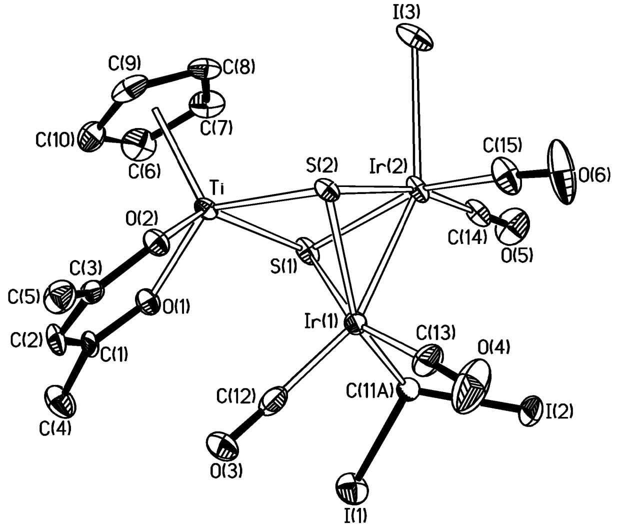


Figure 3. Molecular structure of complex [Cp(acac)Ti(μ_3-S)$_2$Ir$_2$(CHI$_2$)(I)(CO)$_4$] (**3**).

complexes in dichloromethane at 4 °C. The molecular structure of complexes **2a** and **3** are shown in Figures 2 and 3, and selected bond distances and angles are included in Tables 1 and 2.

Both complexes show a triangular [TiIr$_2$] core capped on each side by two μ_3-sulfido ligands in which both iridium centers are joined through a metal−metal bond. The titanium center adopts a typical four-legged piano stool arrangement by coordination to a η^5-cyclopentadienyl, a chelating acetylacetonate, and two sulfido ligands. The Ti−O distances in both complexes are comparable to those observed in the trinuclear complex [Cp$_2$(acac)Ti][Ir$_3$(CO)$_6$(μ_3-S)$_2$] (1.970 and 1.981(7) Å) but are statistically shorter than the value observed in the related TiRh$_2$ compound [Cp(acac)Ti(μ_3-S)$_2$-{Rh(cod)}$_2$] (2.062(3) Å).[20] The small O−Ti−O angles are similar to those of the aforementioned complexes and are a consequence of the chelate coordination mode of the acetylacetonato ligand.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex **2a**[a]

Ir(1)−I(1)	2.6983(15)	Ir(2)−I(2)	2.7469(12)
Ir(1)−S	2.396(3)	Ir(2)−S	2.392(3)
Ir(1)−C(7)	1.955(13)	Ir(2)−C(8)	1.947(12)
Ir(1)−Ir(2)	2.6056(8)	Ti−S	2.436(3)
Ti−O	1.948(9)	Ti−Cp[b]	2.028(6)
I(1)−Ir(1)−Ir(2)	157.70(4)	I(2)−Ir(2)−Ir(1)	157.10(4)
I(1)−Ir(1)−S	108.08(7)	I(2)−Ir(2)−S	106.47(7)
I(1)−Ir(1)−C(7)	90.6(3)	I(2)−Ir(2)−C(8)	92.0(3)
S−Ir(1)−Ir(2)	56.95(7)	S−Ir(2)−Ir(1)	57.12(7)
S−Ir(1)−S′	77.76(13)	S−Ir(2)−S′	7.92(13)
S−Ir(1)−C(7)	91.0(3)	S−Ir(2)−C(8)	89.8(4)
S′−Ir(1)−C(7)	161.1(3)	S′−Ir(2)−C(7)	160.0(4)
C(7)−Ir(1)−Ir(2)	104.2(3)	C(8)−Ir(2)−Ir(1)	103.0(3)
C(7)−Ir(1)−C(7′)	95.5(6)	C(8)−Ir(2)−C(8′)	97.1(8)
S−Ti−O(1)	84.1(3)	S−Ti−O(1′)	136.6(3)
S−Ti−S′	76.28(15)	S−Ti−Cp[b]	114.22(6)
O(1)−Ti−O(1′)	84.4(7)	O(1)−Ti−Cp[b]	109.1(3)

[a] Primed atoms are related to the unprimed ones by the symmetry transformation: *x, 1/2 − y, z.* [b] Cp represents the centroid of the cyclopentadienyl ligand.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex **3**

Ir(1)−S(1)	2.366(2)	Ir(2)−S(1)	2.401(2)
Ir(1)−S(2)	2.4283(19)	Ir(2)−S(2)	2.3776(19)
Ir(1)−C(11)[a]	2.122(10)	Ir(2)−I(3)	2.7491(7)
Ir(1)−C(12)	1.903(10)	Ir(2)−C(14)	1.888(9)
Ir(1)−C(13)	1.906(9)	Ir(2)−C(15)	1.870(10)
Ir(1)−Ir(2)	2.6131(5)		
Ti···Ir(1)	3.1429(15)	Ti···Ir(2)	3.6157(15)
Ti−S(1)	2.413(2)	Ti−S(2)	2.405(2)
Ti−O(1)	1.989(6)	Ti−O(2)	1.977(6)
Ti−Cp[b]	2.024(5)		
S(1)−Ir(1)−Ir(2)	57.41(5)	S(1)−Ir(2)−Ir(1)	56.12(5)
S(1)−Ir(1)−S(2)	78.90(7)	S(1)−Ir(2)−S(2)	79.21(7)
S(1)−Ir(1)−C(11)[a]	83.7(3)	S(1)−Ir(2)−I(3)	107.76(6)
S(1)−Ir(1)−C(12)	106.7(3)	S(1)−Ir(2)−C(14)	92.1(3)
S(1)−Ir(1)−C(13)	160.9(3)	S(1)−Ir(2)−C(15)	155.9(3)
S(2)−Ir(1)−Ir(2)	56.13(5)	S(2)−Ir(2)−Ir(1)	58.00(5)
S(2)−Ir(1)−C(11)[a]	151.1(3)	S(2)−Ir(2)−I(3)	102.55(5)
S(2)−Ir(1)−C(12)	110.0(3)	S(2)−Ir(2)−C(14)	166.7(3)
S(2)−Ir(1)−C(13)	92.7(3)	S(2)−Ir(2)−C(15)	88.3(3)
C(11)[a]−Ir(1)−Ir(2)	95.0(3)	I(3)−Ir(2)−Ir(1)	154.85(2)
C(11)[a]−Ir(1)−C(12)	96.9(4)	I(3)−Ir(2)−C(14)	90.0(3)
C(11)[a]−Ir(1)−C(13)	96.6(4)	I(3)−Ir(2)−C(15)	95.0(3)
C(12)−Ir(1)−Ir(12)	158.9(3)	C(14)−Ir(2)−Ir(1)	108.7(3)
C(12)−Ir(1)−C(13)	92.2(4)	C(14)−Ir(2)−C(15)	95.1(4)
C(13)−Ir(1)−Ir(2)	103.7(3)	C(15)−Ir(2)−Ir(1)	99.8(3)
S(1)−Ti−S(2)	78.44(8)	O(1)−Ti−O(2)	83.2(2)
S(1)−Ti−O(1)	85.56(18)	S(2)−Ti−O(1)	134.25(19)
S(1)−Ti−O(2)	137.75(19)	S(2)−Ti−O(2)	80.83(18)
S(1)−Ti−Cp[b]	111.89(15)	S(2)−Ti−Cp[b]	115.93(16)
O(1)−Ti−Cp[b]	109.8(2)	O(2)−Ti−Cp[b]	110.3(2)

[a] Values for the disordered C(11) atom with major occupancy are stated. [b] Cp represents the centroid of the cyclopentadienyl ligand.

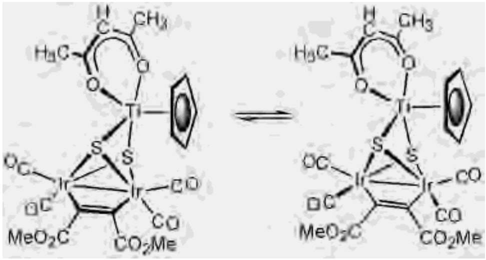
Without considering metal−metal interactions, the geometry around the iridium atoms in both complexes can be described as a slightly distorted square pyramid. For instance, the iridium atom Ir(2) in complex **3** has its apical position occupied by the iodo ligand, and its base is conformed by two mutually cis carbonyl ligands and the two sulfido ligands. In the case of the iridium center Ir(1), the apex is a carbonyl ligand and the base of the pyramid is constituted by a carbonyl ligand, both sulfido ligands, and the diiodomethyl fragment. Both square pyramids are joined through the common edge defined by the two sulfido ligands allowing the formation of an Ir−Ir bond. The main differences concerning the stereochemistry around the iridium centers in both complexes are related to the position of the added fragments. Complex **2a** shows C_{2v} symmetry (crystallographically imposed in the solid state) and has the two iodo ligands located trans to the Ir−Ir metal−metal bond. In contrast, compound **3** possesses the iodo ligand linked to the iridium center adjacent to the cyclopentadienyl ring and trans to the metal−metal bond, while the diiodomethyl fragment remains coordinated to the iridium atom closer to the acetylacetonate ligand. In this way both fragments are in a cisoidal arrangement and complex **3** has no symmetry.

The Ir(1)−Ir(2) separations (2.6056(8) Å in **2a**, 2.6131(5) Å in **3**) fall within the range of metal−metal bond distances, so that each iridium atom has 18 valence electrons to account for the diamagnetism observed in both complexes. These Ir−Ir bond distances are similar to those found for complex $[Ir(\mu\text{-S}^tBu)(I)(CO)_2]_2$ (2.638(1) Å)[25] and for the mixed-bridged dinuclear complex $[Ir(\mu\text{-Pz})(\mu\text{-S}^tBu)(\mu\text{-DMAD})(P(OMe)_3)_2(CO)_2]_2$ (2.614(2) Å).[27g] The values observed for the S−Ir−S angles at both iridium atoms are significantly lower than those observed in complex $[Cp(acac)Ti(\mu_3\text{-S})_2\{Rh(cod)\}_2]$ (84.0(2) and 83.6(2)°), most probably due to contraction imposed by the presence of the Ir−Ir bond.

Reactions of $[Cp(acac)Ti(\mu_3\text{-S})_2\{Ir(CO)_2\}_2]$ (1) with Alkynes. Complex **1** does not react with electron-rich alkynes such as RC≡CPh (R = H, Ph) or $RC{\equiv}CSiMe_3$ (R = H, $SiMe_3$) even under exposure of ultraviolet radiation. However, a fast reaction takes place in toluene at room temperature with acetylenes containing electron-withdrawing groups such as dimethylacetylenedicarboxylate (DMAD) and methylacetylenecarboxylate. The complexes $[Cp(acac)Ti(\mu_3\text{-S})_2Ir_2(\mu\text{-}\eta^1\text{-RC}{=}CCO_2Me)(CO)_4]$ (R = CO_2Me, **6**; R = H, **7**) were obtained as deep-green air-sensitive solids after recrystallization from hexanes in excellent yields. The IR spectra of complexes **6** and **7** showed four ν(CO) bands at similar frequencies than those for the dinuclear iridium(II) complexes **2b**−**5**, suggesting that the oxidative addition of the alkyne occurs across the iridium−iridium axis to give the metal−metal bonded dinuclear complexes **6** and **7**.

Complex $[Cp(acac)Ti(\mu_3\text{-S})_2Ir_2(DMAD)(CO)_4]$ (**6**) exists in solution as a single isomer, which showed two inequivalent methoxy groups of the alkyne in the ^1H NMR spectrum at room temperature, whereas the methyl groups of the acetylacetonato ligand were equivalent. Moreover, the $^{13}C\{^1H\}$ NMR spectrum of **6** at room temperature indicated that the alkyne was coordinated as a cis-dimetalated olefin bridging the two iridium centers with the C=C bond (μ-η^1 coordination mode) parallel to the Ir−Ir axis[27] because the coordination perpendicular to the Ir−Ir vector, in a μ-η^2 fashion, would render equivalent the two CO_2Me groups.[28] Furthermore, the four carbonyl groups give two resonances in the $^{13}C\{^1H\}$ NMR spectrum, whereas the carbon atoms of the C=C bond are inequivalent. These NMR data suggest the presence of a plane of symmetry in the molecule that contains the $[TiIr_2]$ core and the alkyne and associates the carbonyl groups in two sets. However, no such plane exists in the structure that can reasonably be proposed, assuming a distorted octahedral environment of the iridium atoms (Scheme 1), such as that observed in the complex $[Ir_2(\mu\text{-Pz})(\mu\text{-SBu}^t)(DMAD)(CO)_2\{P(OMe)_3\}_2]$.[27g] Therefore, to explain the observed equivalence, a concerted exchange of the carbonyls on each iridium atom has to be admitted. Indeed, the compound is fluxional. Figure 4 shows a fragment of the variable temperature $^{13}C\{^1H\}$ NMR spectra, in which the expected four signals for the carbonyl ligands and two signals for the CO groups of the acac can be observed in the spectrum at −87 °C. Similarly, the signal for the methyl groups in the ^1H NMR spectrum at room temperature splits in two singlets at −87 °C. The activation energy of the fluxional process at the temperature of coalescence was calculated to be 10.6 kcal·mol^{-1} from the separation of the signals of the methyl groups (34 Hz) in the ^1H NMR spectrum at −58 °C.[29]

Scheme 1



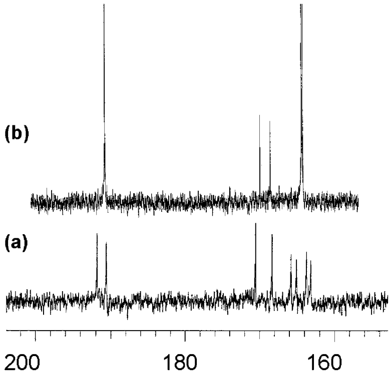


Figure 4. Part of the $^{13}C\{^1H\}$ NMR spectrum of complex $[Cp(acac)Ti(\mu_3\text{-S})_2Ir_2(DMAD)(CO)_4]$ (**6**) at (a) −87 °C and (b) 20 °C.

Complex $[Cp(acac)Ti(\mu_3\text{-S})_2Ir_2(\mu\text{-HC}{=}CCO_2Me)(CO)_4]$ (**7**) exists in solution as a pair of isomers in a 1:1 ratio, as observed by ^1H NMR spectroscopy. Thus, the ^1H NMR spectrum of **7** shows two resonances for both the cyclopentadienyl and the CH protons of the acetylacetonato ligand,

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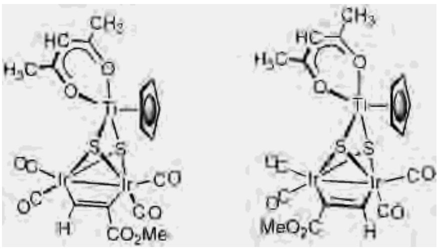
(28) (a) Choi, N.; Conole, G.; King, J. D.; Mays, M. J.; McPartlin, M.; Stone, C. L. *J. Chem. Soc., Dalton Trans.* **2000**, 295. (b) McAdam, C. J.; Duffy, N. W.; Robinson, B. H.; Simpson, J. *J. Organomet. Chem.* **1997**, *527*, 179. (c) Stichbury, J. C.; Mays, M. J.; Davies, J. E.; Raithby, P. R.; Shields, G. P. *J. Chem. Soc., Dalton Trans.* **1997**, 2309. (d) Edwards, A. J.; Mack, S. R.; Mays, M. J.; Mo, C.-Y.; Raithby, P. R.; Rennie, M.-A. *J. Organomet. Chem.* **1996**, *519*, 243.

Chart 3



i.e., one for each isomer. Moreover, both species apparently have C_s symmetry, because the methyl groups of the acetylacetonato ligands display one signal for each isomer. Most probably the exchange of the carbonyl groups proposed for **6** also occurs in both isomers to observe averaged species with C_s symmetry. Interestingly, the isomers show a pattern of the ν(CO) bands similar to that of complex **6**, and consequently the framework should be identical. Therefore, both isomers result from the two arrangements of the methyl propiolate moiety along the metal−metal bond shown in Chart 3.

Discussion

Stereoselective Activation of Iodoalkanes by [Cp(acac)-Ti(μ_3-S)$_2${Ir(CO)$_2$}$_2$] (1). The aim of this study was to investigate the influence of an early metal on the feasibility of oxidative-addition reactions using an early−late heteronuclear complex possessing a molecular framework of the late metals comparable with the well-known dinuclear thiolate iridium complexes.[4,21,30] For this purpose, the heterotrinuclear system [Cp(acac)Ti(μ_3-S)$_2${Ir(CO)(PR$_3$)}$_2$] would be a good candidate to explore the reactions with electrophiles. The complex **1** was chosen although it incorporates only π-acid carbonyl ligands. Thus, the basicity of the iridium centers is less than in other dinuclear systems that bear more basic ancillary ligands. For instance, the related dinuclear thiolate-bridged complex [{Rh(μ-SBu^t)(CNBu^t)$_2$}$_2$] oxidatively adds methylene chloride to give the product of a two-center four-electron oxidative-addition reaction [{Rh(μ-SBu^t)(Cl)(CNBu^t)$_2$}$_2$(μ-CH$_2$)].[31] In this case, the powerful electron-donating isocyanide ligands strongly increase the nucleophilicity of the metallic centers in such way that they react even with chloroalkanes.

It is now well established that the complex **1** reacts with iodine and several iodoalkanes to produce a two-fragment two-center oxidative addition of the substrates with the concomitant formation of an iridium−iridium bond. The addition of alkyl iodides, such as CHI_3, CH_2I_2, and CH_3I, to **1** is stereoselective. In these cases, 10 different isomers, without taking into account their enantiomers, might result upon the oxidative addition of the nonsymmetrical electrophiles, depending on the relative orientation of the added fragments. However, only one isomer was detected both in solution and in the solid state. From the structure of complex **3**, it is apparent that the smaller (and the less electrophilic) fragment, the iodo ligand, is located trans to the metal−metal bond, coordinated to the iridium center closer to the cyclopentadienyl ring. The diiodomethyl fragment coordinates to the other iridium center (the one situated closer to the acetylacetonato ligand) in such a way that it becomes cis to the metal−metal bond. This disposition of the added fragments is not frequent because they adopt a trans arrangement relative to the metal−metal bond in most of the dinuclear iridium systems.[3−9]

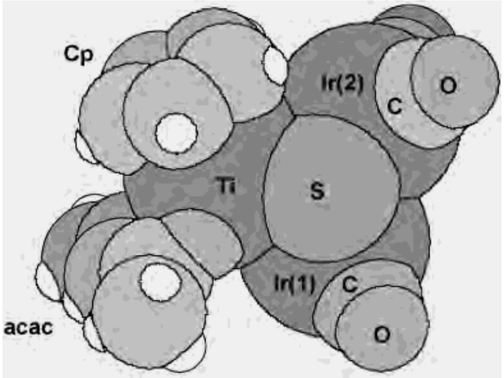


Figure 5. Simulated space-filling model for the complex [Cp(acac)Ti-(μ_3-S)$_2${Ir(CO)$_2$}$_2$] (**1**).

On the contrary, the reaction of **1** with iodine gave two isomers in a 1:1 ratio, which is not surprising because the addition of I_2 to complex **1** may give statistically up to five different isomers together with their corresponding enantiomers. One of the isomers, **2a**, corresponds to the adduct in which both iodo ligands are located trans to the metal−metal bond, and we believe that the isomer **2b** has a stereochemistry identical to that of complexes **3**−**5**, shown in the X-ray structure of complex **3**. Most probably this is a consequence of the reaction pathway followed in their formation.

Mechanistic Considerations. Complex **1** does not react with good electrophiles such as CF_3OSO_2Me. This result suggests that the S_N2 mechanism for the oxidative-addition processes studied on **1** could not be operative because the first step of this mechanism involves the electrophilic attack (E^+) to one of the metallic centers giving a cationic intermediate, which in the case of the dinuclear system [{Ir(μ-Pz)(CO)(P^{i}Pr$_3$)}$_2$] has been structurally characterized.[14] Figure 5 shows a simulated space-filling molecular model for the compound **2**. It shows that the ring of the acetylacetonate ligand coordinated to the titanium is on the square-planar environment of the close Ir(1) atom, creating a shield that hinders the accessibility of the substrates to that face of the Ir(1) atom in the direction of the d_{z^2} orbital.

If the S_N2 mechanism were operative for the reactions of the system [TiIr$_2$], it would imply that the more electrophilic fragment would become coordinated to the iridium center Ir(2), which has a more accessible axial position. However, this is not in accordance with the position of the fragment CHI_2^+, which is coordinated to the iridium center Ir(1) in the molecular structure of complex **3**. Furthermore, we

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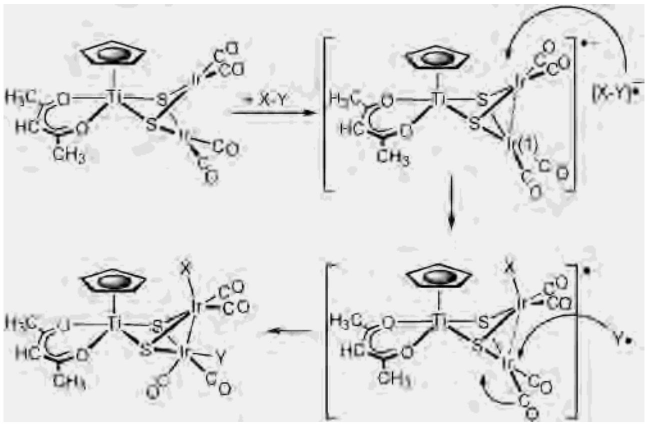
Scheme 2. Proposed Mechanism for the Oxidative Addition of Substrates X−Y to [Cp(acac)Ti(μ_3-S)$_2${Ir(CO)$_2$}$_2$] (**1**)



believe that steric influences in the [TiIr$_2$] system may direct the profile of these reactions and would be responsible for the observed stereoselectivity. Assuming a radical-like mechanism for these oxidative-addition reactions, the complex [Cp(acac)Ti(μ_3-S)$_2${Ir(CO)$_2$}$_2$] can undergo one-electron oxidation by the electrophile (CHI$_3$) to generate the radicals [Cp(acac)Ti(μ_3-S)$_2${Ir(CO)$_2$}$_2$]$^{\bullet+}$ and [CHI$_3$]$^{\bullet-}$ (Scheme 2). A further abstraction of iodine from the halocarbon radical by the species [TiIr$_2$]$^{\bullet+}$ would result in the formation of the organometallic radical [Cp(acac)Ti(μ_3-S)$_2$Ir$_2$(I)(CO)$_4$]• with an incipient metal−metal bond. Finally, the halocarbon radical [CHI$_2$]• approaches the second metallic center through the accessible face (the pocket of the complex), moving one carbonyl ligand coordinated to Ir(1) to the axial position (trans to the metal−metal bond) to give the observed stereochemistry. This radical-like mechanism explains reasonably well the stereoselectivity of the oxidative addition of alkyl iodides to complex **1**, assuming that the steric effects from the acetylacetonate ligand play a significant role.

This mechanism is also consistent with the oxidative addition of iodine to complex **1**. Regarding the isomers of the complex **2**, the stereochemistry of **2a** agrees well with that shown by the dinuclear systems [{Ir(μ-SBu^t)(CO)(I)L}$_2$] (L = PR$_3$), in which the added fragments adopt a typical trans arrangement. Moreover, a radical pathway has been proposed for the oxidative addition of iodine to the thiolate-bridged dinuclear complex [{Ir(μ-SBu^t)(CO)L}$_2$].[4] In our case, the formation of the isomer **2b** is indicative of the difficulty of the iodine radical to reach the external face of the Ir(1) atom in the radical complex (Scheme 2), although the smaller size of the iodine atom relative to the iodoalkyl fragments allows the formation of the isomer **2a**.

The reactions of the complex **1** with the activated alkynes DMDA and methylacetylenecarboxylate give the compounds [Cp(acac)Ti(μ_3-S)$_2$Ir$_2$(μ-η^1-RC=CCO$_2$Me)(CO)$_4$] corresponding to an oxidative addition of the alkyne across the Ir−Ir axis. In these cases, the uptake of the alkyne also occurs in a stereoselective fashion, but the stereochemistry of the adducts is distinct to that observed in the activation of iodoalkanes by complex **1**. The reason for this behavior has to be found in the site of the attack on **1** by the alkyne. Judging by the results, the alkyne approaches complex **1** through the pocket of the complex created by the two "Ir(CO)$_2$" fragments rather than the external face of the iridium atoms. Then, two carbonyl ligands, each one with iridium center, move toward the opposite side of the complex, both becoming located trans to the metal−metal bond, while the alkyne becomes bonded to both iridium atoms occupying two cisoid positions. A similar reaction and coordination mode of the alkyne results from the addition of DMAD to the mixed-bridging complex [Ir$_2$(μ-Pz)(μ-SBu^t)(CO)$_2${P(OMe)$_3$}$_2$], although the phosphite ligands migrate to the positions trans to the metal−metal bond there.[27g] Moreover, activated acetylenes add to the thiolate complexes of the type [{Ir(μ-SBu^t)(CO)L}$_2$] in a μ-η^1 coordination mode,[30] although unfortunately a representative structure determined by X-ray methods was not achieved.

The fluxionality of the complexes with alkynes **6** and **7** showing a process of low activation energy is somewhat surprising. In a related case,[30b] a Berry pseudorotation at one of the metal centers had been proposed to explain the equilibrium between the cisoid and transoid isomers of [Ir$_2$(μ-SBu^t)$_2$(DMDA)(CO)$_2$L$_2$]. That means an easy cleavage of the iridium−iridium bond. In our case, the movement involves the concerted exchange of the apical and equatorial carbonyl groups on both iridium atoms while the bridging framework is maintained, with the *cis*-metalated olefin moving between the two axial positions. The stereochemical changes involve a weakening of the iridium−iridium bond to leave pentacoordinated iridium centers, and therefore, the activation energy would be related to the metal−metal bond energy.

To conclude, complex **1** is less reactive than the related dinuclear thiolate iridium systems. Thus, while the oxidative addition of iodine to **1** stops at the Ir(II) oxidation stage, the double oxidative addition leading to the Ir(III) complexes occurs with the thiolate systems.[4,22] Moreover, while diiodomethane adds readily to [{Ir(μ-*t*-BuS)(CO)L}$_2$], affording methylene-bridged iridium(III) compounds,[32] complex **1** gives the iodomethyl−iridium(II) complex (**3**). Furthermore, the latter compound does not evolve to the methylene-bridged iridium(III) complex, which would be feasible through an internal oxidative addition, despite the close proximity of the iodomethyl group to both iridium centers. These features are indicative that the early metal exerts an electronic influence on the late metals, reducing their nucleophilicity independently of producing steric effects that result in stereoselective oxidative-addition reactions.

Experimental Section

All reactions were carried out under argon using standard Schlenk techniques or in a quartz tube. The UV irradiation was performed with a 125 W UV−vis lamp from Photochemical Reactors Ltd. Complex **1** was prepared as previously reported.[20] All the chemicals were reagent grade and used without further purification. Before use, all solvents were dried and distilled by standard methods. Carbon and hydrogen analyses were performed in a Perkin-Elmer 2400 microanalyzer. IR spectra were recorded with a Nicolet-IR

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(32) El Amane, M.; Maisonnat, A.; Dahan, F.; Pince, R.; Poilblanc, R. *Organometallics* **1985**, *4*, 773.

550 (4000−400 cm^{-1}) spectrophotometer as Nujol mulls between polyethylene sheets or in solution in a cell with NaCl windows. 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. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Varian UNITY, Bruker ARX 300, and Varian Gemini 300 spectrometers operating at 299.95 and 75.47, 300.13 and 75.47, and 300.08 and 75.46 MHz, respectively. Chemical shifts are reported in parts per million and referenced to Me_4Si using the signal of the deuterated solvent (^{1}H and ^{13}C) as references, respectively. The temperatures of the probe were calibrated using the separation of the residual signals of CD_3OD.

[Cp(acac)Ti(μ_3-S)$_2$Ir$_2$I$_2$(CO)$_4$] (2). A solution of iodine (0.016 g, 0.062 mmol) in dichloromethane (5 mL) was added dropwise to a solution of **1** (0.048 g, 0.062 mmol) in dichloromethane (5 mL), resulting in a fast color change from deep orange to dark red. The solution was stirred for 30 min, and then the volume was concentrated to ca. 1 mL under reduced pressure. Addition of hexanes (10 mL) afforded a red microcrystalline solid, which was collected by filtration, washed with hexanes, and then vacuum-dried. Yield: 0.057 g (89%). Anal. Calcd for $C_{14}H_{12}I_2Ir_2O_6S_2Ti$ (%): C, 16.38; H, 1.18. Found: C, 16.34; H, 1.08. MS (FAB$^+$, *m/z*, %): 1026 (M$^+$, 12), 928 (M$^+$ − acac, 13), 899 (M$^+$ − I, 40), 871 (M$^+$ − I − CO, 27), 843 (M$^+$ − I − 2CO, 15), 815 (M$^+$ − I − 3CO, 15), 787 (M$^+$ − I − 4CO, 20%). IR (cyclohexane, cm^{-1}): ν(CO), 2097 (s), 2073 (m), 2046 (s); ν(CO, acac), 1556 (m), 1531 (m). ^{1}H NMR ($CDCl_3$, 20 °C) δ: 6.79, 6.77 (s, Cp), 6.00, 5.98 (s, C*H*), 2.16, 2.15 (s, CH_3) (acac). ^{13}C{^{1}H} NMR ($CDCl_3$, −55 °C) δ: 192.4 (**2b**), 192.3 (**2b**), 192.0 (**2a**) (CO, acac), 162.4 (**2b**), 161.8 (**2b**), 161.0 (**2a**), 160.9 (**2a**), 159.1 (**2b**), 151.9 (**2b**) (Ir−*C*O), 123.1, 122.3, (Cp), 108.4, 106.8 (CH, acac), 26.4, 26.3 (CH_3, acac).

[Cp(acac)Ti(μ_3-S)$_2$Ir$_2$(CHI$_2$)(I)(CO)$_4$] (3). To a deep-orange solution of **1** (0.053 g, 0.068 mmol) in dichloromethane (10 mL) was added solid CHI_3 (0.027 g, 0.068 mmol). The color of the solution changed immediately from deep orange to dark red. After 30 min, the volume of the solution was concentrated to ca. 1 mL under reduced pressure. Addition of hexanes afforded a red microcrystalline solid, which was collected by filtration, washed with hexanes, and then vacuum-dried. Yield: 0.060 g (75%). Anal. Calcd for $C_{15}H_{13}I_3Ir_2O_6S_2Ti$ (%): C, 15.44; H, 1.12. Found: C, 15.54; H, 0.80. MS (FAB$^+$, *m/z*): 1166 (M$^+$, 5), 1039 (M$^+$ − I, 15), 1011 (M$^+$ − I − CO, 33), 983 (M$^+$ − I − 2CO, 100), 955 (M$^+$ − I − 3CO, 15), 927 (M$^+$ − I − 4CO, 30), 899 (M$^+$ − CHI_2, 20), 871 (M$^+$ − CHI_2 − CO, 15%). IR (CH_2Cl_2, cm^{-1}): ν(CO), 2089 (s), 2070 (s), 2037 (s), 2030 (sh); ν(CO, acac), 1556 (m), 1530 (m). ^{1}H NMR ($CDCl_3$, 20 °C) δ: 6.75 (s, 5H, Cp), 6.00 (s, 1H, C*H*, acac), 4.74 (s, 1H, C*H*I$_2$), 2.17, 2.15 (s, 3H, C*H*$_3$, acac). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C) δ: 192.6, 191.8 (CO, acac), 165.6, 163.2, 162.8, 159.9 (Ir−*C*O), 122.0 (Cp), 106.1 (CH, acac), 26.4, 26.2 (CH_3, acac), 26.3 (CHI_2).

[Cp(acac)Ti(μ_3-S)$_2$Ir$_2$(CH$_3$)(I)(CO)$_4$] (4). A solution of **1** (0.050 g, 0.065 mmol) in a mixture of dichloromethane (5 mL) and methyl iodide (5 mL) was set aside for 10 h at room temperature to give a deep-yellow solution. The volatiles were removed under reduced pressure, and the remaining brown solid was recrystallized from dichloromethane and hexanes to afford a yellow solid. Yield: 0.054 g (91%). Anal. Calcd for $C_{15}H_{15}IIr_2O_6S_2Ti$ (%): C, 19.70; H, 1.65. Found: C, 19.63; H, 1.58. MS (FAB$^+$, *m/z*): 915 (M$^+$, 12), 787 (M$^+$ − I, 100%), 760 (M$^+$ − I − CO, 35), 732 (M$^+$ − I − 2CO, 19), 703 (M$^+$ − I − 3CO, 50), 675 (M$^+$ − I − 4CO, 25%). IR (CH_2Cl_2, cm^{-1}): ν(CO), 2083 (s), 2063 (s), 2026 (s), 2012 (sh); ν(CO, acac), 1556 (m), 1530 (m). ^{1}H NMR ($CDCl_3$, 20 °C) δ: 6.74 (s, 5H, Cp), 5.89 (s, 1H, C*H*, acac), 2.14, 2.10 (s, 3H, C*H*$_3$, acac), 1.24 (s, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C) δ: 191.5, 191.2 (CO, acac), 166.0, 164.4, 164.1, 158.7 (Ir−*C*O), 120.9 (Cp), 105.1 (CH, acac), 26.2, 26.1 (CH_3, acac), −28.8 (s, CH_3).

[Cp(acac)Ti(μ_3-S)$_2$Ir$_2$(CH$_2$I)(I)(CO)$_4$] (5). A solution of **1** (0.061 g, 0.079 mmol) and CH_2I_2 (8 μL, 0.100 mmol) in toluene (5 mL) was placed in a quartz tube and stirred next to a UV−vis lamp (125 W) for 90 min. The resulting dark-red solution was concentrated under vacuum to ca. 1 mL, and after addition of hexanes, a red microcrystalline solid was formed. The solid was collected by filtration, washed with hexanes, and then vacuum-dried. Yield: 0.070 g (87%). Anal. Calcd for $C_{15}H_{14}I_2Ir_2O_6S_2Ti$ (%): C, 17.31; H, 1.36. Found: C, 17.30; H, 1.31. MS (FAB$^+$, *m/z*): 1040 (M$^+$, 5), 913 (M$^+$ − I, 17), 885 (M$^+$ − I − CO, 33), 859 (M$^+$ − I − 2CO, 14), 829 (M$^+$ − I − 3CO, 8), 801 (M$^+$ − I − 4CO, 21%). IR (CH_2Cl_2, cm^{-1}): ν(CO), 2087 (s), 2066 (m), 2031 (s); ν(CO, acac), 1556 (m), 1530 (m). ^{1}H NMR ($CDCl_3$, 20 °C) δ: 6.74 (s, 5H, Cp), 5.94 (s, 1H, C*H*, acac), 3.44, 3.22 (AB system, 2H, J_{AB} = 6.6 Hz, C*H*$_2$I), 2.14 (s, 6H, C*H*$_3$, acac). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C) δ: 192.2, 191.6 (s, CO, acac), 165.2, 163.4, 158.4 (Ir−*C*O), 121.6 (s, Cp), 105.8 (s, CH, acac), 26.2, 26.1 (s, CH_3, acac), −45.7 (s, CH_2I).

[Cp(acac)Ti(μ_3-S)$_2$Ir$_2$(μ-η^1-DMAD)(CO)$_4$] (6). A solution of **1** (0.050 g, 0.065 mmol) in toluene (10 mL) was treated with dimethylacetylenedicarboxylate (0.027 g, 0.068 mmol), immediately giving a dark-green solution. After 30 min, the volume of the solution was concentrated to ca. 1 mL under reduced pressure, and gave a dark-green solid upon addition of hexanes. The solid was collected by filtration, washed with hexanes, and then vacuum-dried. Yield: 0.048 g (81%). Anal. Calcd for $C_{20}H_{18}Ir_2O_{10}S_2Ti$ (%): C, 26.26; H, 1.98. Found: C, 26.02; H, 1.90. MS (FAB$^+$, *m/z*): 914 (M$^+$, 8), 883 (M$^+$ − OCH_3, 12), 799 (M$^+$ − $2CO_2CH_3$, 8), 772 (M$^+$ − DMAD, 40), 716 (M$^+$ − DMAD − 2CO, 30), 688 (M$^+$ − DMAD − 3CO, 18), 659 (M$^+$ − DMAD − 4CO, 22). IR (CH_2Cl_2, cm^{-1}): ν(CO), 2075 (s), 2054 (vs), 2015 (s) 2008 (sh); ν(CO$_2$Me), 1705 (s); ν(CO, acac), 1560 (m), 1531 (m). ^{1}H NMR ($CDCl_3$, 20 °C) δ: 6.34 (s, 5H, Cp), 5.74 (s, 1H, C*H*, acac), 3.78, 3.74 (s, 3H, CO$_2$C*H*$_3$), 2.03 (s, 6H, C*H*$_3$, acac). ^{13}C{^{1}H} NMR ($CDCl_3$, 20 °C) δ: 191.7 (CO, acac), 170.4, 169.0 (*C*O$_2$Me), 164.8, 164.6 (Ir−CO), 117.1 (Cp), 106.3 (CH, acac), 103.7, 100.9 (C═C), 52.3 (O*C*H$_3$), 26.2 (*C*H$_3$, acac).

[Cp(acac)Ti(μ_3-S)$_2$Ir$_2$(μ-η^1-HC═CCO$_2$Me)(CO)$_4$] (7). 7 was prepared from **1** (0.050 g, 0.065 mmol) and methyl propiolate (5.71 mg, 6 μL, 0.068 mmol) in toluene (10 mL) following the procedure described for **6**. Yield: 0.049 g (89%). Anal. Calcd for $C_{18}H_{16}Ir_2O_8S_2Ti$ (%): C, 25.23; H, 1.88. Found: C, 25.15; H, 1.78. MS (FAB$^+$, *m/z*): 857 (M$^+$, 15), 773 (M$^+$ − CH_3O_2CCCH, 80), 716 (M$^+$ − CH_3O_2CCCH − 2CO, 45), 661 (M$^+$ − CH_3O_2CCCH − 4CO, 35). IR (CH_2Cl_2, cm^{-1}): ν(CO), 2070 (s), 2047 (vs), 2009 (s) 2003 (sh); ν(CO$_2$Me), 1721 (m); ν(CO, acac), 1556 (m), 1532 (m). ^{1}H NMR ($CDCl_3$, 20 °C) (mixture 1:1 of two isomers) δ: 9.15, 9.05 (s, ═C*H*−Ir), 6.33, 6.32 (s, Cp), 5.72, 5.70 (s, C*H*, acac), 3.75, 3.73 (s, CO$_2$C*H*$_3$), 2.03, 2.01 (s, C*H*$_3$, acac). ^{13}C{^{1}H} NMR ($CDCl_3$, −60 °C) δ: 191.6 (*C*O, acac), 171.9 (*C*O$_2$Me), 165.3, 165.2 (Ir−*C*O), 116.6 (Cp), 103.6 (*C*H, acac), 103.6, 100.7 (H*C*═C), 97.7, 94.7 (HC═*C*), 52.6 (O*C*H$_3$), 26.5 (*C*H$_3$, acac).

Structural Determination of Complexes 2a and 3. A summary of crystal data, data collection, and refinement parameters for the structural analysis of both complexes is given in Table 3. A brown (**2a**) or a black crystal (**3**) were glued to a glass fiber and mounted on Bruker SMART APEX diffractometer. The instrument was equipped with CCD area detector, and data were collected using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at low

Table 3. Crystal Data, Data Collection, and Refinement for Complexes **2a** and **3**

	2a	**3**
empirical formula	$C_{14}H_{12}I_2Ir_2O_6S_2Ti{\cdot}CH_2Cl_2$	$C_{15}H_{13}I_3Ir_2O_6S_2Ti{\cdot}0.5(H_2O)$
fw	1111.38	1175.38
cryst size, mm	0.34 × 0.22 × 0.13	0.30 × 0.26 × 0.19
cryst syst	orthorhombic	monoclinic
space group	*Pnma* (no. 62)	$P2_1/n$ (no. 14)
a, Å	14.4291(9)	11.4230(8)
b, Å	9.9988(6)	16.7818(12)
c, Å	18.2839(12)	13.6965(10)
α, deg	90	90
β, deg	90	109.4930(10)
γ, deg	90	90
V, A^3	2637.9(3)	2475.1(3)
Z	4	4
D_{calcd}, g cm^{-3}	2.798	3.154
μ, mm^{-1}	13.089	14.982
no. of measd reflns	16328 ($1.8 \leq \theta \leq 28.44$)	14305 ($1.99 \geq \theta \leq 26.00$)
no. of unique reflns	3300 ($R_{int} = 0.0289$)	4839 ($R_{int} = 0.0297$)
min, max transm fact	0.064, 0.181	0.055, 0.168
no. of data/ restraints/params	3300/30/154	4839/6/269
GOF (all data)[a]	1.159	1.063
$R_1(F)$ ($F^2 \geq 2\sigma(F^2)$)[b]	0.0532	0.0337
$wR_2(F^2)$ (all data)[c]	0.1231	0.0756

[a] GOF = $(\sum[w(F_o^2 - F_c^2)^2]/(n - p))^{1/2}$, where n and p are the number of data and parameters. [b] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$ for 3059 **(2a)** and 4421 (**3**) observed reflections. [c] $wR_2(F^2) = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2])^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ and $P = [\max(0, F_o^2) + 2F_c^2]/3$.

temperature (100 (**2a**) or 110 K (**3**)). Cell constants for **2a** were obtained from the least-squares refinement of three-dimensional centroids of 6643 reflections (4.64° ≤ 2θ ≤ 56.39°) and from 6304 reflections (4.50° ≤ 2θ ≤ 56.32°) for **3**. Data were measured through the use of CCD recordings of ω rotation frames (0.3° each). Both data were integrated with the Bruker SAINT program with Lorentz and polarization corrections.[33] Absorption correction was applied by using the SADABS routine.[34]

Structures were solved by direct methods. Both structures were completed by subsequent difference Fourier techniques and refined by full-matrix least-squares on F^2 (SHELXL-97)[34] with initial isotropic thermal parameters. One solvation CH_2Cl_2 molecule per trinuclear complex was observed in **2a**; half a water molecule was detected for **3**. Anisotropic thermal parameters were used in the last cycles of refinement for all non-hydrogen atoms in **2a**, except for a disordered Cl atom of the CH_2Cl_2 molecule. In **3**, anisotropic displacement parameters were used in the last cycles of refinement for all non-hydrogen atoms, except for the C atom involved in a disordered CHI_2 moiety and the oxygen atom of the solvation water molecule. A model of disorder based on two alternative positions was assumed for the CH_2Cl_2 molecule in **2a** and also for the CHI_2 moiety in **3** (two C atoms of fixed complementary occupancy factors, 0.8 and 0.2 were included). Hydrogen atoms were included in calculated positions in both structures and refined with positional and thermal parameters riding on carbon atoms. Atomic scattering factors were used as implemented in the program.[35]

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Supporting Information Available: An X-ray crystallographic file in CIF format for complexes **2a** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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