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The Anions $[Cp^{tt}_2Zr(\mu\text{-}S)_2M(CO)_2]^-$ (M = Rh, Ir) as Versatile Precursors for the Synthesis of Sulfido-Bridged Early−Late Heterotrimetallic (ELHT) Compounds[†]

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The reaction of $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2]$ ($Cp^{tt} = \eta^5$-1,3-di-*tert*-butylcyclopentadienyl) with dppe (1,2-bis-(diphenylphosphino)ethane) affords the ion-pair compound $[Ir(CO)(dppe)_2][Cp^{tt}_2Zr(\mu\text{-}S)_2Ir(CO)_2]$ (**2**). The related compound $[Rh(dppe)_2][Cp^{tt}_2Zr(\mu\text{-}S)_2Rh(CO)_2]$ (**5**) has been obtained in solution under a carbon monoxide atmosphere by reaction of $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ with dppe through the intermediate heterotrinuclear compound $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(dppe)\}\{Rh(CO)_2\}]$ (**4**). Reaction of the heterodinuclear anion $[Cp^{tt}_2Zr(\mu\text{-}S)_2Ir(CO)_2]^-$, generated *in situ*, with $[Rh(\mu\text{-}Cl)(cod)]_2$, $[RhCl_2(CO)_2]^-$ and $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$ affords the $d^0-d^8-d^8$ early−late compounds $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}\{Rh(cod)\}]$ (**6**), $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}\{Rh(CO)_2\}]$ (**7**), and $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}\{Pd(\eta^3\text{-}C_3H_5)\}]$ (**8**) each with a symmetrical trigonal−bipyramidal $M_3(\mu_3\text{-}S)_2$ heterotrimetallic metal−sulfur core. In the same way, the reaction of $[Cp^{tt}_2Zr(\mu\text{-}S)_2M(CO)_2]^-$ (M = Rh, Ir) with $[AuCl(PPh_3)]$ leads to the preparation of the $d^0-d^8-d^{10}$ early−late compounds $[Cp^{tt}_2Zr(\mu\text{-}S)_2\{Ir(CO)_2\}\{Au(PPh_3)\}]$ (**9**) and $[Cp^{tt}_2Zr(\mu\text{-}S)_2\{Rh(CO)_2\}\{Au(PPh_3)\}]$ (**10**) with an open $M_3(\mu_3\text{-}S)(\mu_2\text{-}S)$ heterotrimetallic metal−sulfur framework. On the other hand, treatment of the bis(hydrosulfido)zirconium compound $[Cp^{tt}_2Zr(SH)_2]$ with triethylamine followed by addition of $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$ or $[AuCl(PPh_3)]$ affords the sulfido-bridged early−late heterobimetallic compounds $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Pd(\eta^3\text{-}C_3H_5)\}_2]$ (**11**) and $[Cp^{tt}_2Zr(\mu\text{-}S)_2\{Au(PPh_3)\}_2]$ (**12**). The molecular structure of complexes **9** and **12** determined by X-ray diffraction methods are also described.

Introduction

Transition-metal sulfido clusters have been attracting significant attention because of their possible relevance to biological systems and industrial metal sulfide catalyst.[1] The controlled construction of sulfido clusters has been a major objective in this field and the development of rational synthetic methods has led to the preparation of a wide range of multimetallic sulfido clusters with the desired metal composition and metal−sulfur framework.[2] In general, the control of the metal composition in mixed-metal sulfido clusters requires suitable building-blocks for cluster growth reactions. For example, the utilization of mononuclear tetrathiometalates, $[MS_4]^{n-}$, as precursors for clusters synthesis has resulted in the formation of a large number of heterometallic sulfido clusters with extraordinary structural varieties.[3] In the same way, the incorporation of heterometal fragments into dinuclear $M_2(\mu\text{-}S)_2S_2$ templates (M = Mo, W, Re)[4] or trinuclear clusters with an incomplete cubane-type geometry[5] are convenient strategies for the synthesis of heterobimetallic and heterotrimetallic cubane-type clusters. Alternative dinuclear precursors for mixed-metal cluster synthesis are bishydrosulfido-bridge complexes via bridged-assisted nuclearity expansion reactions[6] or through condensation processes involving HCl and/or CpH elimination.[7]

[†] This contribution is dedicated to Professor Dr. Karen Mach on the occasion of his 70th birthday.

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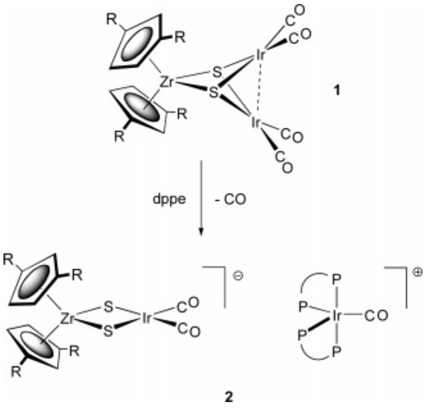
The chemistry of metal−sulfur polynuclear compounds containing widely divergent transition metals, that is, early−late heterometallic compounds,[8] and in particular those containing group 4 transition metals, has been less intensively investigated probably as a consequence of the difficulties to accommodate the different electronic and coordination environments required for both metals. However, it has been established that sulfido ligands are able to stabilize early−late heterobimetallic compounds (ELHB) that contain dinuclear [TiM],[9] trinuclear $[TiM_2]$ (M = Rh, Ir),[10] and tetranuclear $[TiM_3]$[11a−d] and $[Ti_2M_2]$[11e,f] (M = Rh, Ir, Ru) metal cores.

We have recently reported the application of the bis(hydrosulfido)zirconium complex $[Cp^{tt}_2Zr(SH)_2]$ ($Cp^{tt} = \eta^5$-1,3-di-*tert*-butylcyclopentadienyl) for the controlled construction of ELHB heterotrinuclear complexes with an unprecedented triangular $[ZrM_2]$ (M = Rh, Ir) core capped with two μ_3-sulfido ligands.[12] Interestingly, the zirconium-iridium complex $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2]$ is a precursor for the controlled synthesis of Zr−Rh−Ir early−late heterotrimetallic (ELHT) complexes by metal exchange reactions. Although the triangular core is sustained in reactions with monodentate P-donor ligands, we discovered that reaction with 1,2-bis-(diphenylphosphino)ethane (dppe) results in the selective sequestering of one of the iridium atoms of the $[ZrIr_2]$ metal core as the cation $[Ir(CO)(dppe)_2]^+$. The ensuing heterodinuclear anion $[Cp^{tt}_2Zr(\mu\text{-}S)_2Ir(CO)_2]^-$ behaves as a metalloligand for d^8-$[RhL_2]^+$ electrophillic metal fragments affording sulfur-bridge heterotrimetallic complexes of composition [ZrRhIr] with a triangular structure.[13] Noteworthy, several ELHT [TiRuM] (M = Rh, Ir, Pd, Pt) sulfido clusters have been recently synthesized from a bis(hydrosulfido)-bridge heterobimetallic precursor having a [TiRu] metal core.[14]

Scheme 1



We report herein on the synthesis of the heterodinuclear anions $[Cp^{tt}_2Zr(\mu\text{-}S)_2M(CO)_2]^-$ from the trinuclear carbonyl complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{M(CO)_2\}_2]$ (M = Rh, Ir) and their scope and limitations as building-blocks for the preparation of ELHT compounds. A preliminary account of part of this work was previously communicated.[13]

Results and Discussion

Synthesis and Characterization of the Early−Late Heterodinuclear Anions $[Cp^{tt}_2Zr(\mu\text{-}S)_2M(CO)_2]^-$ (M = Rh, Ir). The reaction of $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2]$ (**1**) with dppe (1:2 molar ratio) gave quantitatively the ion-pair compound $[Ir(CO)(dppe)_2][Cp^{tt}_2Zr(\mu\text{-}S)_2Ir(CO)_2]$ (**2**) which was isolated as an air and moisture highly sensitive pale-orange solid in excellent yield. The formation of **2** is a consequence of the sequestering of an iridium metal center in the trinuclear sulfido-bridged $[ZrIr_2]$ compound as the cation $[Ir(CO)(dppe)_2]^+$ (Scheme 1). This species was observed in the $^{31}P\{^1H\}$ NMR spectrum as a single resonance at δ 25.6 ppm ($CDCl_3$) and in the FAB+ mass spectrum at *m*/*z* 989. The resulting heterodinuclear anion $[Cp^{tt}_2Zr(\mu\text{-}S)_2Ir(CO)_2]^-$ was detected in the FAB- mass spectrum at *m*/*z* 757. The ^1H and $^{13}C\{^1H\}$ NMR spectra were in agreement with a C_{2v} structure with a planar arrangement of the "$Zr(\mu\text{-}S)_2Ir$" metal−sulfur core similar to that found in the related heterobimetallic complex $[Cp^*_2Zr(\mu\text{-}S)_2Rh(CO)_2]^-$ ($Cp^* = \eta^5$-pentamethylcyclopenta-dienyl).[15] The monitoring of the reaction by ^1H NMR indicates that the formation of compound **2** is clean and quantitative as no intermediate species were detected when the reaction was carried out with substoichiometric dppe/**1** ratios. In addition, it has been found that the heterodinuclear anion does not react further with neither dppe nor other monodentate P-donor ligands as PPh_3.

The reaction of $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**3**) with dppe (1:2 molar ratio) in dichloromethane gave a dark orange-brown

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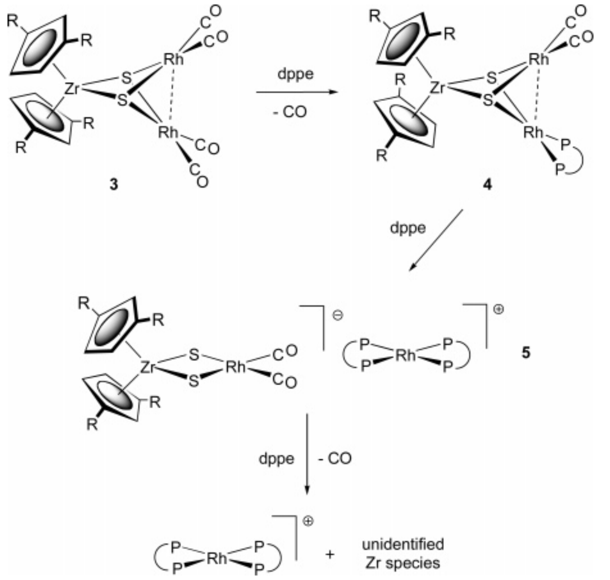
Scheme 2



solution. Analysis of the crude of the reaction by NMR spectroscopy revealed the formation of the heterotrinuclear compound [Cp$^{tt}_2$Zr(μ_3-S)$_2${Rh(dppe)}{Rh(CO)$_2$}] (**4**) and the presence of the cation [Rh(dppe)$_2$]$^+$ (δ 58.23 ppm, $J_{Rh-P} = 133$ Hz)[16] as the only P-containing species but not the expected heterodinuclear anion [Cp$^{tt}_2$Zr(μ-S)$_2$Rh(CO)$_2$]$^-$. In fact, compound **4** was actually isolated from this solution as a dark-brown solid in 40% yield after purification through a short pad of neutral alumina. Compound **4** showed the molecular ion at *m*/*z* 1167 in the FAB+ spectrum and the spectroscopic data were in agreement with a triangular [ZrRh$_2$] structure of C_s symmetry resulting from the replacement of two carbonyl ligands by dppe at the same rhodium center (Scheme 2). The equivalent phosphorus atoms of the η^2-dppe ligand were observed as a doublet at δ 66.4 ppm ($J_{Rh-P} = 184$ Hz) in the ^{31}P{^{1}H} NMR spectrum and the equivalent carbonyl ligands as a doublet at δ 184.3 ppm ($J_{Rh-C} = 70.7$ Hz) in the ^{13}C{^{1}H} NMR spectrum. The presence of a *cis*-Rh(CO)$_2$ fragment was further confirmed in the IR spectrum that showed two strong absorptions at ν(CO) 2029 and 1965 cm^{-1}. The ^{1}H NMR showed four resonances for the cyclopentadienyl protons and two singlets for the *t*-Bu groups as expected for inequivalent Cp^{tt} ligands. The observed pattern of resonances for the protons of both Cp^{tt} rings (td and dt) is a diagnostic for a staggered disposition of both Cp^{tt} ligands (Scheme 2), probably as a consequence of the steric influence of the dppe ligand.[12a] Thus, the resonances at δ 6.50 (t) and 5.72 (d) ppm correspond to the Cp^{tt} ligand with the *t*-Bu groups directed toward the "Rh(CO)$_2$" fragment of the [ZrRh$_2$] core, while the resonances at δ 6.09 (d) and 5.44 (t) are those of the Cp^{tt} ligand with the *t*-Bu groups directed toward the back of the metallocene "clam-shell" and far away from the "Rh(dppe)" fragment.

Unexpectedly, the monitoring by NMR spectroscopy of the reaction of [Cp$^{tt}_2$Zr(μ_3-S)$_2${Rh(CO)$_2$}$_2$] (**3**) with 2 mol equiv of dppe in CDCl$_3$ by NMR spectroscopy ($\approx$ 0.042 M) showed the clean formation of the ion-pair compound [Rh(dppe)$_2$][Cp$^{tt}_2$Zr(μ-S)$_2$Rh(CO)$_2$] (**5**) which has been characterized in solution. The spectroscopic data for the anion [Cp$^{tt}_2$Zr(μ-S)$_2${Rh(CO)$_2$}]$^-$ closely resemble those of the Zr−Ir analogue, and the cation [Rh(dppe)$_2$]$^+$ was observed both in the ^{31}P{^{1}H} NMR spectrum and in the FAB+ at *m*/*z* 899. In addition, the IR spectrum showed two strong absorptions at 2031 and 1971 cm^{-1} in agreement with the presence of a *cis*-Rh(CO)$_2$ fragment. Interestingly, the reaction of **3** with 4 mol equiv of dppe in CDCl$_3$ gave a yellow-brown solution after the complete replacement of the carbonyl ligands (IR evidence) with the cation [Rh(dppe)$_2$]$^+$ as the only phosphorus containing species; however, neither **4** nor the anion of **5** were detected by NMR spectroscopy. These observations are compatible with the sequestering of both rhodium atoms of **3** as the cation [Rh(dppe)$_2$]$^+$ and the probable formation of the dianion [Cp$^{tt}_2$ZrS$_2$]$^{2-}$ that is not stable at room temperature and decompose to unidentified Zr-containing species and free HCp^{tt} (NMR evidence).

The above-described results strongly suggest that the heterotrinuclear compound **4** is an intermediate in the formation of the heterodinuclear ion-pair compound **5**. However, the anion [Cp$^{tt}_2$Zr(μ-S)$_2$Rh(CO)$_2$]$^-$ reacts faster than **4** with dppe under the experimental conditions to give further [Rh(dppe)$_2$]$^+$ (Scheme 2). Nevertheless, it seems that the reaction of [Cp$^{tt}_2$Zr(μ-S)$_2$Rh(CO)$_2$]$^-$ with dppe is inhibited by carbon monoxide as was evidenced by the clean formation of **5** under the standard NMR experimental conditions. In agreement with this, solutions containing the anion [Cp$^{tt}_2$Zr(μ-S)$_2$Rh(CO)$_2$]$^-$ can be prepared *in situ*, by reaction of **3** with 2 mol equiv of dppe under a carbon monoxide atmosphere, and successfully applied to the synthesis of sulfido-bridged ELHT complexes (see later).

It is remarkable that the sequestering of a d^8 metal center in the heterotrinuclear complexes **1** and **3** by dppe results in the formation of the ion-pair compounds **2** and **5**. Both compounds contain analogous heterodinuclear anions [Cp$^{tt}_2$Zr(μ-S)$_2$M(CO)$_2$]$^-$ (M = Rh, Ir) but very different trigonal−bipyramidal and square-planar cations, [Ir(CO)(dppe)$_2$]$^+$ and [Rh(dppe)$_2$]$^+$, respectively. This fact is in agreement both with the outstanding stability of the five-coordinated complex [Ir(CO)(dppe)$_2$]$^+$ against the loss of CO and the failure of the square-planar complex [Rh(dppe)$_2$]$^+$ to react with CO.[17]

Synthesis of Early−Late Zr−Ir−M (M = Rh, Pd, Au) and Zr−Rh−Au Heterotrimetallic Compounds. We have already demonstrated the ability of the anion [Cp$^{tt}_2$Zr(μ-S)$_2$Ir(CO)$_2$]$^-$ to behave as a metalloligand toward cationic [RhL$_2$]$^+$ metal fragments affording the unprecedented Zr−Ir−Rh ELHT complexes as a result of the restoration of the trigonal−bipyramidal metal−sulfur core with a new composition.[13] The reaction of [Ir(CO)(dppe)$_2$][Cp$^{tt}_2$Zr(μ-S)$_2$Ir(CO)$_2$] (**2**) with $^1/_2$ mol equiv of [Rh(μ-Cl)(cod)]$_2$ gave [Cp$^{tt}_2$Zr(μ_3-S)$_2${Ir(CO)$_2$}{Rh(cod)}] (**6**) along with [Ir(CO)(dppe)$_2$]Cl. (Scheme 3) Compound **6** was obtained as yellow-orange microcrystals in good yield after the separation of the iridium byproduct that is insoluble in *n*-pentane. Interestingly, the anion [Cp$^{tt}_2$Zr(μ-S)$_2$Ir(CO)$_2$]$^-$ can be generated *in situ* by the reaction of [Cp$^{tt}_2$Zr(μ_3-S)$_2${Ir(CO)$_2$}$_2$] (**1**) with dppe (1:2 molar ratio) making possible the one-pot synthesis of **6** starting from **1** by the successive addition of dppe and [Rh(μ-Cl)(cod)]$_2$. In the same way, the reaction of **1** with dppe and the anion [RhCl$_2$(CO)$_2$]$^-$ afforded the carbonyl compound [Cp$^{tt}_2$Zr(μ_3-S)$_2${Ir(CO)$_2$}{Rh(CO)$_2$}] (**7**) that was obtained as a green microcrystalline solid in good yield. As expected, compound **7** can be also prepared in excellent yield by carbonylation of **6** at atmospheric pressure (Scheme 3).

The molecular structure of **6** revealed a triangular [ZrIrRh] core capped on both sides by symmetrical μ_3-sulfido ligands. Unusual features of the structure are the short Rh···Ir distance

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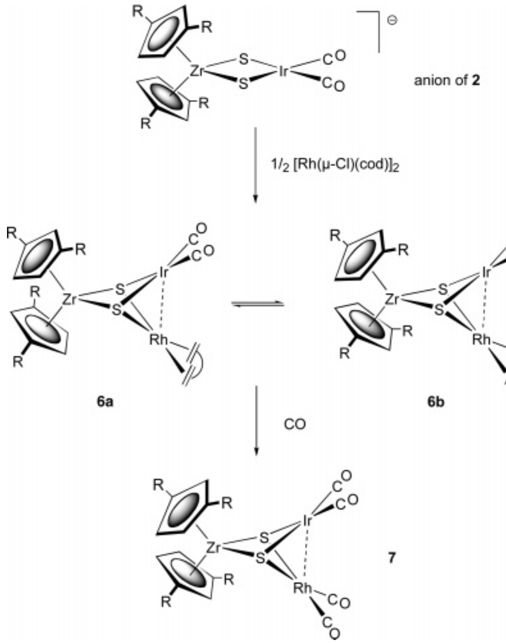
[16] (a) Dorta, R.; Simón, L.; Milstein, D. *J. Organomet. Chem.* **2004**, *689*, 751. (b) Pettinari, C.; Marchetti, F.; Pettinari, R.; Pizzabiocca, A.; Drozdov, A.; Troyanov, S. I.; Vertlib, V. *J. Organomet. Chem.* **2003**, *688*, 216.

[17] Saco, A.; Rossi, M.; Nobile, C. F. *Chem. Commun.* **1966**, 589.

Scheme 3



of 2.8205(10) Å, that lies in the expected range for a metal−metal bond, and the fully staggered relative disposition of both Cp^{tt} ligands.[13] Compound **6** exists in solution as the two limiting rotamers which were unambiguously identified by ^{1}H (Figure 1b), ^{13}C{^{1}H}, and two-dimensional NMR techniques. Both rotamers differ in the spatial disposition of the *tert*-butyl groups of both Cp^{tt} rings in the metallocene moiety and correspond to the limiting fully staggered (**6a**) and eclipsed (**6b**) conformations both of C_s symmetry (Scheme 3). The aromatic protons of both Cp^{tt} ligands in the eclipsed rotamer **6b** display the pattern of resonances, δ 6.69 (t), 6.03 (d) and 6.38 (t), 5.90 (d). However, the rotamer **6a** display a pattern of resonances, δ 6.60 (t), 5.94 (d) and 7.18 (d), 5.83 (t), similar to that found in compound **4** which is a diagnostic for a staggered rotamer.[12a] The interconversion of both rotamers, which was confirmed in the phase-sensitive NOESY spectrum, produces an equilibrium mixture in which the staggered rotamer **6a** predominates (3:1).

The existence of rotamers in compound **6** is a consequence of the restricted rotation induced in the Cp^{tt} ligand close to the more sterically demanding "Rh(cod)" fragment. In fact, this phenomenon was not observed in **7** which contains the fragment "Rh(CO)$_2$" with smaller carbonyl ligands (Figure 1a). The activation parameters for the rotation of the Cp^{tt} ligand obtained by the NMR spin−saturation transfer method in the range of 308−276 K in CDCl$_3$ were $\Delta H^{\ddagger} = 19.2 \pm 1.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = 6.7 \pm 2.6$ eu, that resulted in a $\Delta G^{\ddagger}_{298} = 17.2$ kcal mol^{-1}. This rotational barrier is larger than that observed for metallocene mononuclear complexes containing cyclopentadienyl ligands with bulky substituents[18] and reflects the steric hindrance introduced by the bulky 1,5-cyclooctadiene ligand in the ELHT complex.

The success in the preparation of Zr−Ir−Rh heterotrimetallic compounds encourages us to apply the same synthetic protocol to the preparation of other ELHT compounds containing groups 10 and 11 metals. The reaction of [Cp$^{tt}_2$Zr(μ-S)$_2$Ir(CO)$_2$]$^-$, generated in situ, with [Pd(μ-Cl)(η^3-C$_3$H$_5$)]$_2$ ($^1/_2$ mol equiv) and [AuCl(PPh$_3$)] gave the compounds [Cp$^{tt}_2$Zr(μ_3-S)$_2${Ir(CO)$_2$}{Pd(η^3-C$_3$H$_5$)}] (**8**) and [Cp$^{tt}_2$Zr(μ-S)$_2${Ir(CO)$_2$}{Au(PPh$_3$)}] (**9**), which were isolated as green and orange microcrystalline solids, respectively, in good yield after the separation of [Ir(CO)(dppe)$_2$]Cl. The compounds gave satisfactory elemental analysis and showed the molecular ion in the FAB+ spectra at *m/z* 904 and 1216, respectively. In addition, the IR spectra in dichloromethane featured two strong absorptions at 2031 and 1959 cm^{-1} (**8**); and, 2029 and 1969 cm^{-1} (**9**), in accordance with the presence of a "cis-Ir(CO)$_2$" fragment. The spectroscopic data for compound **8** showed the presence of two nonconvertible isomers (84:16 ratio) that arise from the spatial disposition of the η^3-allyl ligand in the heterotrimetallic M$_3$(μ_3-S)$_2$ framework (Figure 2).[19] In agreement with this proposal, the aromatic region of the ^{1}H NMR spectrum displayed for each isomer two sets of resonances (triplet and doublet) for the unequivalent Cp^{tt} ligands in accordance with the C_s symmetry of both isomers. Similarly, the η^3-allyl ligand of each isomer showed three resonances (meso, syn, and anti protons) in the ^{1}H NMR spectrum and two in the ^{13}C{^{1}H} NMR spectrum (meso and terminal carbons) indicating that the two halves of the η^3-allyl ligand are related by the symmetry plane in both isomers.

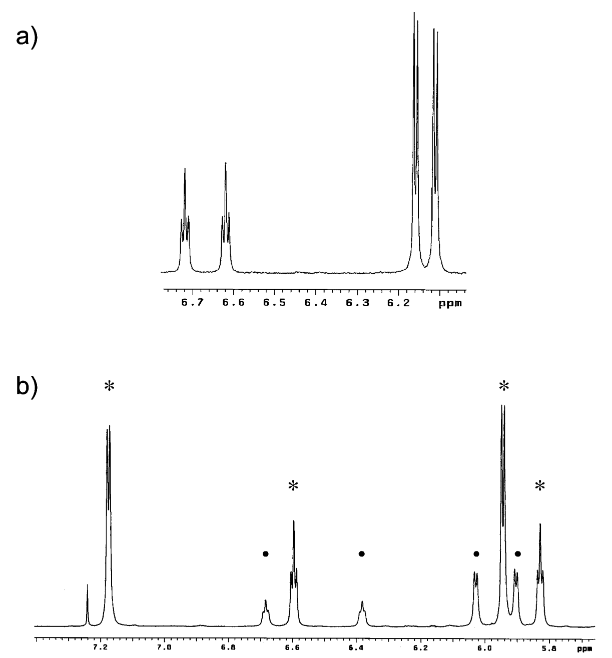


Figure 1. ^{1}H NMR spectra in CDCl$_3$ (aromatic region) of (a) [Cp$^{tt}_2$Zr(μ_3-S)$_2${Ir(CO)$_2$}{Rh(CO)$_2$}] (**7**) and (b) [Cp$^{tt}_2$Zr(μ_3-S)$_2${Ir(CO)$_2$}{Rh(cod)}] (**6**): (∗) staggered rotamer (**6a**), (•) eclipsed rotamer (**6b**).

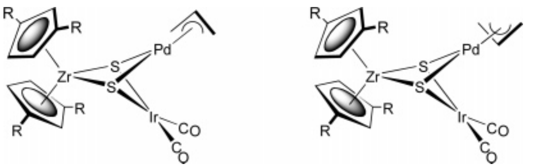


Figure 2. Isomers of compound [Cp$^{tt}_2$Zr(μ_3-S)$_2${Ir(CO)$_2$}{Pd(η^3-C$_3$H$_5$)}] (**8**).

The structure of the compound [Cp$^{tt}_2$Zr(μ-S)$_2${Ir(CO)$_2$}{Au(PPh$_3$)}] (**9**) has been determined by X-ray diffraction methods and is depicted in Figure 3. The structure shows an unusual M$_3$(μ_3-S)(μ_2-S) framework that results from the coordination of the [Au(PPh$_3$)]$^+$ fragment to only one of the sulfido-bridging ligands of the anion [Cp$^{tt}_2$Zr(μ-S)$_2$Ir(CO)$_2$]$^-$. Although the ^{31}P-

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[18] (a) Winter, C. H.; Zhou, X.-X.; Heeg, M. J. *Inorg. Chem.* **1992**, *31*, 1808. (b) Winter, C. H.; Dobbs, D. A.; Zhou, X.-X. *J. Organomet. Chem.* **1991**, *403*, 145. (c) Okuda, J. *J. Organomet. Chem.* **1990**, *397*, C37.

[19] Ciriano, M. A.; Pérez-Torrente, J. J.; Casado, M. A.; Lahoz, F. J.; Oro. L. A. *Inorg. Chem.* **1996**, *35*, 1782.

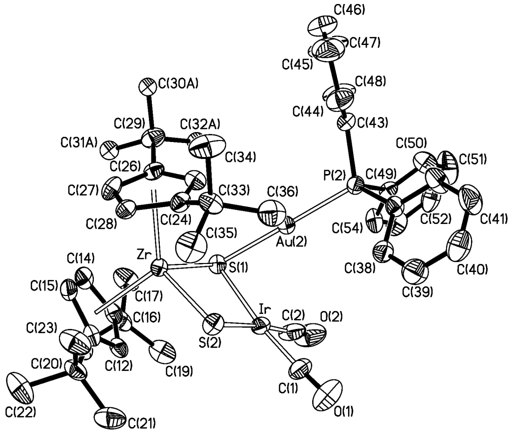


Figure 3. Molecular structure of [$Cp^{tt}{}_2Zr(\mu\text{-}S)_2\{Ir(CO)_2\}\{Au(PPh_3)\}$] (**9**).

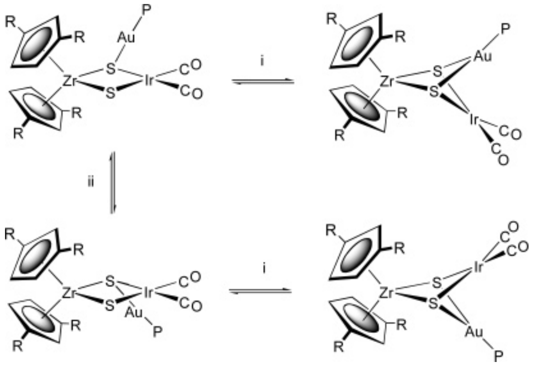
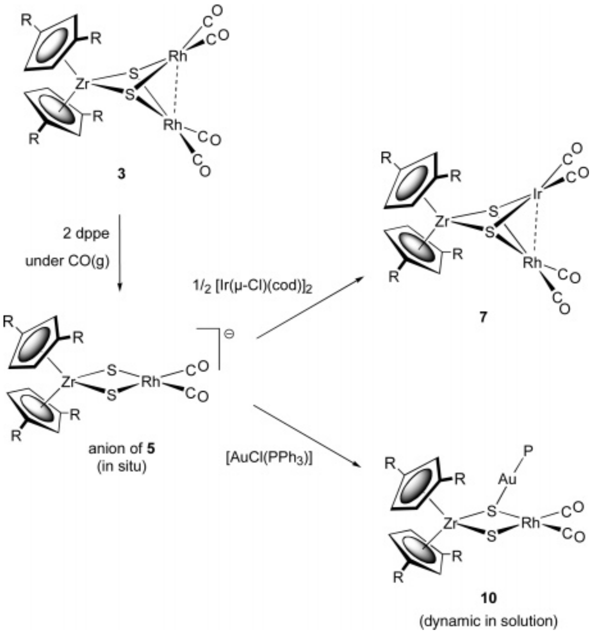


Figure 4. Proposed mechanism for the dynamic behavior observed in compound [$Cp^{tt}{}_2Zr(\mu\text{-}S)_2\{Ir(CO)_2\}\{Au(PPh_3)\}$] (**9**): (i) formation of a $M_3(\mu_3\text{-}S)_2$ metal−sulfur framework, (ii) inversion at the μ_3-sulfido ligand.

Scheme 4



{^1H} NMR spectrum displayed a sharp singlet a δ 33.3 ppm, the ^1H and $^{13}C\{^1H\}$ NMR spectra in $CDCl_3$ at room temperature were not in accordance with the structure found in the solid state as they suggest a higher symmetry structure that probably results from a dynamic behavior involving the [$Au(PPh_3)$]$^+$ fragment. Thus, the aromatic region of the ^1H NNR spectrum showed only two resonances at δ 5.73 (d) and 5.38 (t), indicating both the chemical equivalence of both Cp^{tt} ligands and of the H_4 and H_5 protons of each Cp^{tt}. The Figure 4 displays a plausible mechanism that could give account of the spectroscopic data at room temperature. As the chemical equivalence of the Cp^{tt} ligands is not attained either through the reversible formation of a $M_3(\mu_3\text{-}S)_2$ framework (i) or the ring-flipping of a possible nonplanar [$Zr(\mu\text{-}S)_2Ir$] core with a open-book structure, the inversion of the sulfido ligand bearing the $Au(PPh_3)^+$ fragment must be also invoked (ii). Assuming a planar [$Zr(\mu\text{-}S)_2Ir$] core, the interconversion between both out-of-plane conformations should proceed by a nondissociative mechanism through a planar transition state in which the sulfur donor atom is sp^2 hybridized. Although the sulfur lone-pair inversion could also occur through an alternative dissociative mechanism, the nondissociative mechanism should be more favorable as it has been demonstrated in related bis-thiolate complexes of the type [$Rh(dippe)(\mu\text{-}SR)]_2$ (dippe = 1,2-bis(diisopropylphophino)ethane).[20]

In the slow exchange limit the ^1H NMR in toluene-d_8 at 193 K displays four featureless resonances in a 1:2:1:2 ratio as expected for a $M_3(\mu_3\text{-}S)_2$ (ZrIrAu) core of C_s symmetry. The pairs of resonances at δ 5.77 and 5.64 ppm and δ 5.60 and 5.45 ppm (that correspond to both unequivalent Cp^{tt} ligands) coalesce at the same temperature (δ = 5.60 ppm, T_c = 223 K) giving average resonances at δ 5.62 and 5.58 ppm (1:2 ratio) at 263 K. When the temperature was raised over 303 K both signals became isochronous. The calculated $\Delta G^{\ddagger}_c$ value using the Gutowsky−Holm[21] and the Eyring equations is about 10.7 kcal mol^{-1}. This value lies in the lower limit of the range activation energies for the interconversion of conformers measured in planar dinuclear platinum complexes with thiolato-bridging ligands (13−20 kcal mol^{-1}).[22] Furthermore, such values are in good agreement with the calculated value of 16 kcal mol^{-1} for the compound [$Pt_2(\mu\text{-}SMe)_2(PH_3)_4$]$^{2+}$.[23]

The usefulness of the ELHB compound [$Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2$] (**3**) as a precursor of ELHT complexes by metal-exchange reactions have been demonstrated by the one-pot synthesis of compound [$Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}\{Rh(CO)_2\}$] (**7**). As in the iridium chemistry, the intermediate anionic species [$Cp^{tt}{}_2Zr(\mu\text{-}S)_2Rh(CO)_2$]$^-$ can be formed in situ from **3** and dppe, although a CO atmosphere is required to avoid their decomposition. Thus, the sequential reaction of **3** with dppe (1:2 molar ratio) under a carbon monoxide atmosphere, followed of $^1/_2$ mol equiv of [$Ir(\mu\text{-}Cl)(cod)]_2$ afforded the ELHT compound **7** in 40% yield (Scheme 4). In the same way, the reaction of [$Cp^{tt}{}_2Zr(\mu\text{-}S)_2Rh(CO)_2$]$^-$, generated in situ under the same conditions, with 1 mol equiv of [$AuCl(PPh_3)$] gave the compound [$Cp^{tt}{}_2Zr(\mu\text{-}S)_2\{Rh(CO)_2\}\{Au(PPh_3)\}$] (**10**) that was isolated as an orange microcrystalline solid in 67% yield after the appropriate workup (Scheme 4). The spectroscopic data obtained for compound **10** are closely related with those of compound **9** and consequently, should be isostructural. In particular, the ^1H NMR spectrum in $CDCl_3$ features only two resonances at δ 5.75 (d) and 5.43 (t) ppm suggesting that the mechanism shown in the Figure 4 is also operative in solutions of compound **10**.

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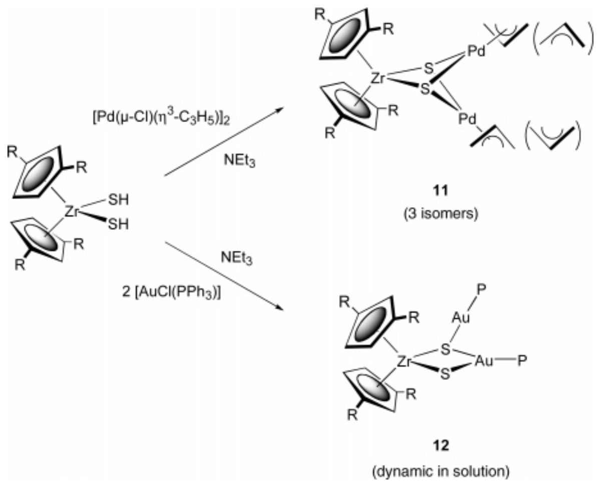
(20) Oster, S. S.; Jones, W. D. *Inorg. Chim. Acta* **2004**, *357*, 1836.

(21) Gutowsky, S. H.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.

(22) (a) Rivera, G.; Bernès, S.; Rodriguez de Barbarin, C.; Torrens, H. *Inorg. Chem.* **2001**, *40*, 5575 and references therein. (b) Mitchell, K. A.; Jensen, C. M. *Inorg. Chem.* **1995**, *34*, 4441. (c) Abel, E. W.; Evans, D. G.; Koe, J. R.; Hursthouse, M. B.; Mazid, M.; Mahon, M. F.; Molloy, K. C. *J. Chem. Soc., Dalton Trans.* **1990**,1697. (d) Orrell, K. G. *Coord. Chem. Rev.* **1989**, *96*, 1.

(23) Aullón, G.; Ujaque, G.; Lledós, A.; Alvarez, S. *Chem. Eur. J.* **1999**, *5*, 1391.

Scheme 5



Synthesis of Trinuclear Early−Late ZrPd$_2$ and ZrAu$_2$ Heterobimetallic Compounds. On the light of the very different trimetallic metal−sulfur framework observed in the described ELHT compounds, M$_3$(μ_3-S)$_2$ and M$_3$(μ_3-S)(μ_2-S), the synthesis of related trinuclear ELHB compounds containing groups 10 and 11 metals has been carried out for structural comparative purposes. The reaction of [Cp$^{tt}{}_2$Zr(SH)$_2$] with [Pd(μ-Cl)(η^3-C$_3$H$_5$)]$_2$ in the presence of triethylamine gave the compound [Cp$^{tt}{}_2$Zr(μ_3-S)$_2${Pd(η^3-C$_3$H$_5$)}$_2$] (**11**) that was isolated as a yellow powder. In the same way, the compound [Cp$^{tt}{}_2$Zr(μ-S)$_2${Au(PPh$_3$)}$_2$] (**12**) was obtained as orange microcrystals from the reaction of [Cp$^{tt}{}_2$Zr(SH)$_2$] with [AuCl(PPh$_3$)] (1:2 molar ratio) and triethylamine (Scheme 5).

Compounds **11** and **12** were isolated in excellent yields and characterized by elemental analysis, FAB+ mass spectra, and NMR spectroscopy. As could be expected, compound **11** exists as three isomers (**11a**, **11b**, and **11c** in 61:34:5 ratio) originated from the different relative orientation of both η^3-allyl ligands in the triangular Zr(μ_3-S)$_2$Pd$_2$ metal−sulfur framework. The information obtained from the ^{1}H NMR and ^{13}C{^{1}H} NMR spectra shows that the isomers **11a** and **11c** have equivalent Cp^{tt} and η^3-allyl ligands in agreement with a C_{2v} symmetry resulting from a symmetrical structural disposition of the η^3-allyl ligands, that is, with the meso carbons of both η^3-allyl ligands inside or outside of the pocket determined by the open-book structural unit "Pd$_2$(μ-S)$_2$". The unsymmetrical disposition of the meso carbons of the η^3-allyl ligands in the pocket (in and out, respectively) results in the isomer **11b** that display unequivalent Cp^{tt} and η^3-allyl ligands in accordance with a C_s symmetry.

The molecular structure of compound **12** has been determined by X-ray crystallography (Figure 5) and displays an open M$_3$(μ_3-S)(μ_2-S) metal−sulfur framework with two different Au(PPh$_3$)$^+$ fragments having gold atoms with linear and planar-triangular coordination environments. However, the ^{31}P{^{1}H} NMR spectrum showed a single resonance at δ 38.1 ppm indicating the chemical equivalence of both Au(PPh$_3$)$^+$ fragments. Besides, the ^{1}H NMR and ^{13}C{^{1}H} NMR spectra also displayed equivalent Cp^{tt} ligands in agreement with a higher symmetry (C_{2v}) than they exhibited in the solid state. These observations suggest that compound **12** is dynamic in solution, probably as a consequence of the mobility of the Au(PPh$_3$)$^+$ fragments on both sulfur atoms of the metallaligand [Cp$^{tt}{}_2$ZrS$_2$]$^{2-}$. A fast equilibrium between structures having Zr(μ_3-S)(μ_2-S)-Au$_2$ and Zr(μ_3-S)$_2$Au$_2$ metal−sulfur frameworks, similar to the proposed for compound **9** (Figure 4i), could easily account for the dynamic behavior observed in compound **12**.

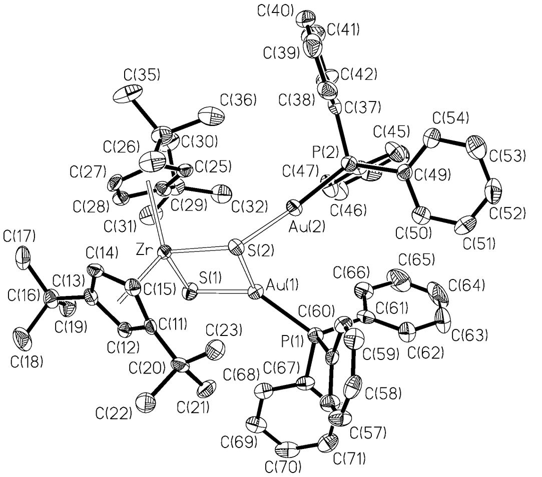


Figure 5. Molecular structure of [Cp$^{tt}{}_2$Zr(μ-S)$_2${Au(PPh$_3$)}$_2$] (**12**).

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Complex [Cp$^{tt}{}_2$Zr(μ-S)$_2${Ir(CO)$_2$}{Au(PPh$_3$)}] (9)

Zr−S(1)	2.523(3)	Zr−S(2)	2.454(3)
Zr−C(11)	2.594(10)	Zr−C(24)	2.630(10)
Zr−C(12)	2.623(9)	Zr−C(25)	2.638(10)
Zr−C(13)	2.637(10)	Zr−C(26)	2.645(9)
Zr−C(14)	2.509(10)	Zr−C(27)	2.542(10)
Zr−C(15)	2.524(11)	Zr−C(28)	2.494(10)
Zr−G(1)[a]	2.282(5)	Zr−G(2)[a]	2.290(5)
Ir−S(1)	2.434(3)	Ir−S(2)	2.370(3)
Ir−C(1)	1.823(13)	Ir−C(2)	1.838(14)
Au(2)−S(1)	2.345(3)	Au(2)−P(2)	2.261(3)
Ir···Au(2)	2.9653(6)	Zr···Ir	3.3055(11)
S(1)−Zr−S(2)	92.30(9)	S(1)−Ir−S(2)	96.66(9)
S(1)−Zr−G(1)[a]	106.47(15)	S(1)−Ir−C(1)	173.3(5)
S(1)−Zr−G(2)[a]	109.69(14)	S(1)−Ir−C(2)	85.6(4)
S(2)−Zr−G(1)[a]	106.46(15)	S(2)−Ir−C(1)	84.2(4)
S(2)−Zr−G(2)[a]	111.06(14)	S(2)−Ir−C(2)	174.8(4)
G(1)−Zr−G(2)[a]	125.67(17)	C(1)−Ir−C(2)	94.1(6)
Zr−S(1)−Au(2)	107.98(10)	S(1)−Au(2)−P(2)	173.39(9)
Zr−S(1)−Ir	83.63(8)	Zr−S(2)−Ir	86.49(9)
Ir−S(1)−Au(2)	76.67(8)		

[a] G(1) and G(2) represent the centroids of the cyclopentadienyl ligands.

Molecular Structures of [Cp$^{tt}{}_2$Zr(μ-S)$_2${Ir(CO)$_2$}{Au(PPh$_3$)}] (9) and [Cp$^{tt}{}_2$Zr(μ-S)$_2${Au(PPh$_3$)}$_2$] (12). Good quality single crystals suitable for X-ray diffraction experiments were obtained by slow diffusion of *n*-hexane into concentrated solutions of the compounds in dichloromethane (**9**) or toluene (**12**). Molecular drawings of both complexes together with the labeling schemes used are displayed in Figures 3 (**9**) and 5 (**12**); selected bond distances and angles are collected in Tables 1and 2, respectively.

Both complexes are trinuclear having two different μ_2-S and μ_3-S sulfido groups as the only supporting bridging ligands and exhibit very similar structures with an identical central skeleton Zr(μ_2-S)(μ_3-S)MAu. The sole difference between the two molecular structures concerns the metal fragment doubly bridged to the Zr atom: an "Ir(CO)$_2$" moiety in **9** and a "Au(PPh$_3$)" fragment in **12**.

In both complexes the Zr atoms show identical pseudotetrahedral environments, being bonded to the two bridging sulfur atoms and to two η^5-Cp^{tt} rings. The major deviations from this ideal tetrahedral coordination affect the G(1)−Zr−G(2) (G represent the centroids of Cp^{tt} rings) bond angles, 125.67(17) (**9**) and 127.80(9)° (**12**) and, on the other side, the S(1)−Zr−S(2) angles, 92.30(9) and 101.85(5)°, which are significantly

Table 2. Selected Bond Distances (Å) and Angles (deg) for the Complex $[Cp^{tt}{}_2Zr(\mu\text{-}S)_2\{Au(PPh_3)\}_2]$ (12)

Zr−S(1)	2.4290(15)	Zr−S(2)	2.5345(14)
Zr−C(11)	2.688(5)	Zr−C(24)	2.658(5)
Zr−C(12)	2.630(5)	Zr−C(25)	2.647(5)
Zr−C(13)	2.580(5)	Zr−C(26)	2.665(5)
Zr−C(14)	2.539(5)	Zr−C(27)	2.552(5)
Zr−C(15)	2.572(5)	Zr−C(28)	2.517(5)
Zr−G(1)*	2.312(2)	Zr−G(2)*	2.318(2)
Au(1)−S(1)	2.3746(14)	Au(2)−S(2)	2.2984(13)
Au(1)−S(2)	2.5555(14)	Au(2)−P(2)	2.2502(14)
Au(1)−P(1)	2.2738(16)		
Au(1)···Au(2)	3.0053(4)	Zr···Au(1)	3.0985(6)
S(1)−Zr−S(2)	101.85(5)	S(1)−Au(1)−S(2)	102.77(5)
S(1)−Zr−G(1)*	105.75(7)	S(1)−Au(1)−P(1)	133.20(5)
S(1)−Zr−G(2)*	109.11(7)	S(2)−Au(1)−P(1)	120.50(5)
S(2)−Zr−G(1)*	102.73(7)	S(2)−Au(2)−P(2)	170.41(5)
S(2)−Zr−G(2)*	106.60(7)	Zr−S(2)−Au(1)	75.00(4)
G(1)−Z−-G(2)*	127.80(9)	Zr−S(2)−Au(2)	116.92(5)
Zr−S(1)−Au(1)	80.33(4)	Au(1)−S(2)−Au(2)	76.30(4)

* G(1) and G(2) represent the centroids of the cyclopentadienyl ligands.

larger and smaller, respectively, than the typical values for a tetrahedral geometry. The large values of the angles centered on Zr with the centroids of Cp^{tt} ligands, G(1)−Zr−G(2), probably reflect the high steric hindrance of the bulky aromatic rings, although these values are to some extent smaller than those reported in related mononuclear complexes such as $[Cp^{tt}{}_2ZrI_2]$ (133.0°)[24] or $[Cp^{tt}{}_2Zr(SH)(OTf)]$ (129.78(15)°).[12b] The relative disposition of the Cp^{tt} substituents presents the bulky *tert*-butyl substituents toward the internal side of the trinuclear core in both structures, although both conformations are slightly different (Figures 3 and 5). Complex **9** exhibits the two η^5-C_5 rings slightly rotated one to each other (C(25)−G(1)···G(2)−C(12) −41.9(10)°) with the *tert*-butyl substituents maintaining a similar staggered situation along the G(1)···G(2) direction.[12b] In the case of **12**, the two η^5-C_5 rings are nearly eclipsed (C(26)−G(1)···G(2)−C(12), −7.7(8)°) but the *tert*-butyl groups are alternated on different carbon atoms (C(25)−G(1)···G(2)−C(12), −86.7(8)°), always toward the most open side of the zirconium coordination sphere.

Both Zr-G (Cp^{tt} centroids) distances are identical within each complex, 2.286(4) (**9**) and 2.315(2) Å (**12**), and comparable to those reported in other related trinuclear complexes such as $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)\ \{Ir(CO)_2\}\{Rh(cod)\}]$ (**7**) (2.290(9) and 2.290(13) Å)[13] or $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)\{Rh(CO)\}_2(\mu\text{-dppm})]$ (2.302(3) and 2.297(3) Å),[12a] but longer than the observed distances in mononuclear zirconium thiolate complexes (range 2.203(3)−2.220(1) Å)[25] or in the related complex $[Cp^{tt}{}_2Zr(SH)(OTf)]$ (2.237(4) and 2.239(5) Å).[12b]

The two Zr−S bond lengths are different in both complexes—with the Zr-(μ_2-S) distance significantly shorter that the Zr-(μ_3-S) analogue—reflecting the asymmetry of both molecules. The values observed for the μ_3-S bridging ligand compare well with those observed in the heterotrinuclear complex **7** (2.506(3) and 2.519(3) Å).[13] The central $Zr(\mu\text{-}S)_2M$ cores are roughly planar in both molecules as evidenced by the dihedral angle between planes defined by the two $M(\mu\text{-}S)_2$ fragments (ZrS_2 vs S_2M; 10.69(9)° in **9**, and 3.32(5)° in **12**).

Without considering potential intermetallic interactions, the iridium atom in **9** exhibits a slightly distorted square-planar geometry with the metal bonded to the two bridging sulfido ligands and to two terminal carbonyls. The metal atom 0.0135(5) Å is out of the mean coordination plane calculated through the four iridium-bonded atoms, moving away from the gold atom Au(2), suggesting the absence of any attractive Ir···Au interaction, despite the relatively short intermetallic separation (Ir···Au(2), 2.9653(6) Å). In the case of **12**, the (μ_2-S)(μ_3-S) doubly bridged gold atom Au(1) shows a distorted trigonal-planar geometry with three different coordination bond angles, but summing nearly the ideal value of 360° (356.5(5)°). The Au···Au separation, 3.0053(4) Å, slightly over the intermetallic separation observed in metallic gold (2.884 Å) and shorter than the sub-van der Waals distances in intermolecular Au−Au complexes (ca. 3.05 Å),[26] supports the presence of a classical aurophillic interaction, as has been suggested for other structurally related heterometallic sulfido complexes such as $[Pt_2(PPh_3)_4(\mu\text{-}S)(\mu_3\text{-}S)Au(PPh_3)]$ (3.103(1) Å) and $[Pt_2(PPh_3)_4(\mu_3\text{-}S)_2Au_2(\mu\text{-dppm})]^{2+}$ (2.916(1) Å)[27] or in the homometallic thiolate $[Au_2(MNT)\{P(OPh)_3\}]$ (MNT = dicyanoethene-1,2-dithiolate) (2.991(1) Å).[28]

The coordination of the P and S atoms to the Au(2) centers can be considered as quasi-linear (S−Au−P, 173.39(9)° (**9**) and 170.41(5)° (**12**)), and they exhibit very similar Au−P and Au−S bond lengths to those observed in related complexes (2.257(3) and 2.309(2) Å in $[Pt_2(C_6F_5)_2(PPh_3)(\mu_3\text{-}S)\{AuPPh_3\}_2]$ for instance).[29]

Concluding Remarks

The heterodinuclear anions $[Cp^{tt}{}_2Zr(\mu\text{-}S)_2M(CO)_2]^-$ can be obtained from the reaction of the trinuclear early−late heterobimetallic compounds (ELHB) $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{M(CO)_2\}_2]$ (M = Rh, Ir) with 1,2-bis-(diphenylphosphino)ethane (dppe). In contrast with the outstanding inertness of the Zr−Ir compound in substitution reactions, the Zr−Rh is labile and must be generated under a carbon monoxide atmosphere. Interestingly, both species behave as metallaligands for several electrophillic metal fragments resulting in the controlled synthesis of unusual sulfido-bridged early−late heterotrimetallic compounds (ELHT). Interestingly, the anionic species can be generated in situ allowing the one-pot synthesis of trinuclear ELHT from ELHB and dppe, through a metal exchange methodology. In this way, we have synthesized ELHT sulfido-bridged compounds that contain d^0−d^8−d^8 (Zr−Ir−Rh, Zr−Ir−Pd) and d^0−d^8−d^{10} (Zr−Ir−Au, Zr−Rh−Au) trimetallic cores.

The geometry of the metal−sulfur framework in the ELHT compounds is largely determined by the electronic configuration of the incoming metal. The d^8-$[ML_n]^+$ (M = Rh, Ir, Pd) metal fragments produce heterotrinuclear structures with a symmetrical trigonal−bipyramidal $M_3(\mu_3\text{-}S)_2$ metal−sulfur core, although an open $M_3(\mu_3\text{-}S)(\mu_2\text{-}S)$ metal−sulfur framework results from the incorporation of the d^{10}-$[Au(PPh_3)]^+$ fragment. The formation of an open metal−sulfur framework is driven for the preference of the d^{10} metal for a linear coordination, whereas d^8 metal fragments, that prefer a square-planar geometry, adopt the compact trigonal−bipyramidal framework. The Zr−M−Au (M = Rh, Ir) compounds are dynamic as a consequence of the mobility of the $[Au(PPh_3)]^+$ fragment on the sulfur atoms of the $[Zr(\mu\text{-}S)_2M]$ precusor. This behavior has been observed in the related trinuclear ELHB compound of core $[ZrAu_2]$ that also adopts an open metal−sulfur framework in the solid state.

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Experimental Section

General Methods. 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. The complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{M(CO)_2\}_2]$ (M = Rh, Ir) and $[Cp^{tt}_2Zr(SH)_2]$ were prepared as described previously.[12] $[Rh(\mu\text{-}Cl)(cod)]_2$,[30] $[Ph_3PBz][RhCl_2(CO)_2]$,[31] $[Pd(\mu\text{-}Cl)(\eta^3\text{-}C_3H_5)]_2$,[32] and $[AuCl(PPh_3)]$[33] were prepared by standard literature procedures.

Physical Measurements. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Gemini 300 spectrometer operating at 300.08, 121.47, and 75.46 MHz, respectively. Chemical shifts are reported in parts per million and referenced to $SiMe_4$ using the residual resonances of the deuterated solvents (^1H and ^{13}C) and 85% H_3PO_4(^{31}P) as external reference, respectively. IR spectra were recorded on a Nicolet-IR 550 spectrometer. Elemental C, H, and N analysis were performed in a 2400 Perkin-Elmer microanalyzer. 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-nitrobenzylic alcohol (NBA) was used as matrix.

Synthesis of the Complexes. $[Ir(CO)(dppe)_2][Cp^{tt}_2Zr(\mu\text{-}S)_2Ir(CO)_2]$ (2). A solid mixture of $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2]$ (0.075 g, 0.075 mmol) and dppe (0.060 g, 0.150 mmol) was dissolved in dichloromethane (3 mL) at room temperature to give a brown-yellow solution with evolution of carbon monoxide. The addition of *n*-hexane (20 mL) gave an orange suspension that was concentrated under vacuum to ca. 15 mL. The suspension was filtered, washed with *n*-hexane (5 mL), and dried under vacuum to give an orange powder. Yield: 0.131 g (98%). ^1H NMR ($CDCl_3$, 293 K): δ 7.70−6.80 (m, 40H, dppe), 5.57 (d, J_{H-H} = 2.4 Hz, 4H, H_4 and H_5, Cp^{tt}), 4.76 (t, J_{H-H} = 2.4 Hz, 2H, H_2, Cp^{tt}), 2.1 (m, 8H, $>CH_2$, dppe), 1.21 (s, 36H, Cp^{tt}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 25.6 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 186.3 (m, CO, $[Ir(CO)(dppe)_2]^+$), 179.6 (CO, $[Cp^{tt}_2Zr(\mu\text{-}S)_2Ir(CO)_2]^-$), 140.0 ($C_1$ and C_3, Cp^{tt}), 132.6 (br m), 131.1 (s), 128.6 (br s) (dppe), 108.0 (C_2), 99.8 (C_4 and C_5), 33.3 (CMe_3), 31.6 (CH_3) (Cp^{tt}), 30.8 (m, CH_2, dppe). MS (FAB$^+$, $CDCl_3$, *m/z*): 989 (M$^+$ − CO, 100%). MS (FAB$^-$, $CDCl_3$, *m/z*): 757 (M$^-$, 100%). IR (CH_2Cl_2, cm^{-1}): ν(CO), 2004 (vs), 1947 (sh), 1931 (vs).

$[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(dppe)\}\{Rh(CO)_2\}]$ (4). A solid mixture of $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (0.100 g, 0.121 mmol) and dppe (0.096 g, 0.242 mmol) was dissolved in dichloromethane (2 mL) at room temperature to give an orange-brown solution with evolution of carbon monoxide. The solution was stirred for 15 min and the filtered on neutral alumina (4 cm × 2 cm). The dark orange-brown solution was concentrated under vacuum to ca. 1 mL. Slow addition of diethyl ether (3 mL) gave a red-brown microcrystalline solid. Concentration of the suspension under vacuum and addition of *n*-hexane (5 mL) gave the compound as a dark-brown solid that was washed with *n*-hexane and dried under vacuum. Yield: 0.057 g (40%). Anal. Calcd for $C_{54}H_{66}O_2P_2Rh_2S_2Zr$: C, 55.42; H, 5.68; S, 5.48. Found: C, 55.38; H, 5.46; S, 5.32. ^1H NMR ($CDCl_3$, 293 K): δ 7.96 (m, 4H), 7.71 (m, 4H), 7.47−7.30 (set of m, 12H) (Ph, dppe), 6.50 (t, J_{H-H} = 2.5 Hz, 2H, H_4 and H_5), 6.09 (d, J_{H-H} = 2.3 Hz, 1H, H_2), 5.72 (d, J_{H-H} = 2.5 Hz, 2H, H_4 and H_5), 5.44 (t, J_{H-H} = 2.3 Hz, 1H, H_2) (Cp^{tt}), 2.53 and 1.88 (m, 2H each, $>CH_2$, dppe), 1.36 and 0.89 (s, 18H each, ^tBu) (Cp^{tt}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 184.3 (d, J_{Rh-C} = 70.7 Hz, CO), 147.7 and 139.2 (C_1 and C_3, Cp^{tt}), 133.1 (br, C_o or C_m), 131.2 (br d, C_i), 131.0 (C_p), 128.6 (br, C_o or C_m) (dppe), 129.6 (C_2), 122.9 (C_4 and C_5), 117.9 (C_2), 103.2 (C_4 and C_5) (Cp^{tt}), 34.7 and 33.0 (CMe_3), 32.9 and 31.9 (CH_3) (Cp^{tt}), 28.6 (br m, J_{C-P} = 12 Hz, $>CH_2$, dppe). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 66.4 ppm (d, J_{Rh-P} = 184 Hz). MS (FAB$^+$, CH_2Cl_2, *m/z*): 1167 (M$^+$, 15%), 1112 (M$^+$ − 2CO, 100%). IR (CH_2Cl_2, cm^{-1}): ν(CO) 2029 (s), 1965 (s).

$[Rh(dppe)_2][Cp^{tt}_2Zr(\mu\text{-}S)_2Rh(CO)_2]$ (5). ^1H NMR ($CDCl_3$, 293 K): δ 7.35 (m, 10H), 7.23−7.15 (m, 30H) (dppe), 5.54 (d, 4H, J_{H-H} = 2.4 Hz), 4.91 (t, 2H, J_{H-H} = 2.4 Hz) (Cp^{tt}), 2.10 (m, 8H, $>CH_2$, dppe), 1.26 (36H, ^tBu, Cp^{tt}). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 58.23 ppm (d, J_{Rh-P} = 133 Hz). IR ($CDCl_3$, cm^{-1}): ν(CO), 2031 (vs), 1971 (vs). MS (FAB$^+$, $CDCl_3$, *m/z*): 899 ($[Rh(dppe)_2]^+$, 100%).

$[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}\{Rh(cod)\}]$ (6). A solid mixture of $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2]$ (0.200 g, 0.199 mmol) and dppe (0.159 g, 0.398 mmol) was dissolved in dichlomethane (5 mL) at room temperature to give a brown solution with evolution of carbon monoxide. Further reaction with solid $[Rh(\mu\text{-}Cl)(cod)]_2$ (0.049 g, 0.100 mmol) gave a lighter solution which was stirred for 5 min. The solvent was removed under vacuum, and the residue was extracted with *n*-pentane (3 × 20 mL). Filtration of the solution over celite gave a brown-orange solution that was concentrated under vacuum to ca. 5 mL and cooled at −78 °C while stirring. The solid that quickly deposited was filtrated and washed with *n*-pentane (5 mL) at −78 °C to give an yellow-orange microcrystalline powder. Yield: 71% (0.137 g). Anal. Calcd for $C_{36}H_{54}O_2S_2IrRhZr$: C, 44.61; H, 5.62; S, 6.62. Found: C, 44.70; H, 6.02; S, 6.55. ^1H NMR ($CDCl_3$, 293 K). Rotamer **6a**: δ 7.18 (d, J_{H-H} = 2.4 Hz, 2H, H_4 and H_5), 6.60 (t, J_{H-H} = 2.4 Hz, 1H, H_2), 5.94 (d, J_{H-H} = 2.4 Hz, 2H, H_4 and H_5), 5.83 (t, J_{H-H} = 2.4 Hz, 1H, H_2) (Cp^{tt}), 4.42 and 4.19 (m, 2H each) (=CH, cod), 2.7−2.4 (m, 2H), 2.2−1.9 (m, 4H), 1.8−1.6 (m, 2H) ($>CH_2$ cod), 1.32 and 1.26 (s, 18H each, Cp^{tt}). Rotamer **6b**: δ 6.69 and 6.38 (t, J_{H-H} = 2.4 Hz, 1H each, H_2), 6.03 and 5.90 (d, J_{H-H} = 2.4 Hz, 2H each, H_4 and H_5) (Cp^{tt}), 4.42 and 4.19 (m, 2H each, =CH, cod), 2.7−2.4 (m, 2H), 2.2−1.9 (m, 4H), 1.8−1.6 (m, 2H) ($>CH_2$ cod), 1.31 and 1.30 (s, 18H each) (Cp^{tt}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K). Rotamer **6a**: δ 177.7 (CO), 150.0 and 142.2 (C_1 and C_3), 127.6 (C_2), 119.7 (C_4 and C_5), 110.0 (C_2), 105.5 (C_4 and C_5) (Cp^{tt}), 84.0 and 80.6 (d, J_{Rh-C} = 11.5 Hz) (=CH cod), 34.8 and 34.0 (CMe_3), 32.7 and 31.8 (CH_3) (Cp^{tt}), 31.7 and 30.6 ($>CH_2$ cod). Rotamer **6b**: δ 178.3 (CO), 147.2 and 147.1 (C_1 and C_3), 123.8 and 120.7 (C_2), 109.5 and 108.8 (C_4 and C_5) (Cp^{tt}), 85.9 and 80.6 (d, J_{Rh-C} = 11.5 Hz) (=CH cod), 34.5 and 34.4 (CMe_3), 32.3 and 32.2 (CH_3) (Cp^{tt}), 31.6 and 30.2 ($>CH_2$, cod). MS (FAB$^+$, CH_2Cl_2, *m/z*): 968 (M$^+$, 100%), 791 (M$^+$ − Cp^{tt}, 92%). IR (CH_2Cl_2, cm^{-1}): ν(CO) 2023 (s), 1954 (s).

$[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}\{Rh(CO)_2\}]$ (7). Method A. Carbon monoxide was slowly bubbled through a stirred brown-orange solution of $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}\{Rh(cod)\}]$ (0.102 g, 0.105 mmol) in diethyl ether (10 mL) at room temperature for 15 min to give a green suspension. Then, cold *n*-pentane (10 mL) was added, and the suspension was quickly filtrated, washed with *n*-pentane (2 × 10 mL), and dried under vacuum to give a green microcrystalline powder. Yield: 0.095 g (98%). **Method B**. A brown solution of $[Ir(CO)(dppe)_2][Cp^{tt}_2Zr(\mu\text{-}S)_2Ir(CO)_2]$ was prepared from $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2]$ (0.249 g, 0.247 mmol) and dppe (0.197 g, 0.495 mmol) in dichloromethane (10 mL) at room temperature. Further reaction with solid $[Ph_3PBz][RhCl_2(CO)_2]$ (0.144 g, 0.247 mmol) gave a green suspension which was stirred for 5 min. Then, methanol (15 mL) was added, and the suspension was filtrated, washed with methanol (2 × 5 mL), and diethyl ether (2 × 5 mL), and dried under vacuum to give a green microcrystalline powder. Yield: 70% (0.159 g). Anal. Calcd for $C_{30}H_{42}O_4S_2IrRhZr$: C, 39.29; H, 4.62; S, 6.99. Found: C, 38.90; H, 4.57; S, 7.09. ^1H NMR ($CDCl_3$, 293 K): δ 6.72 and 6.62 (t, J_{H-H} = 2.5 Hz, 1H each, H_2), 6.16 and 6.11 (d, J_{H-H} = 2.5 Hz, 2H each, H_4 and H_5), 1.31 and 1.30 (s, 18H each) (Cp^{tt}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 184.9 (d, J_{Rh-C} = 74 Hz, CO), 175.4 (CO), 149.4 and 149.1 (C_1 and C_3), 126.2 and 122.5 (C_2), 110.1 and 110.0 (C_4 and C_5), 34.9 and 34.8

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(*C*Me$_3$), 32.2 (CH$_3$) (Cp^{tt}). MS (FAB+, CH$_2$Cl$_2$, *m/z*): 916 (M$^+$, 46%), 860 (M$^+$ − 2CO, 100%), 739 (M$^+$ − Cp^{tt}, 49%). IR (CH$_2$Cl$_2$, cm^{-1}): ν(CO) 2062 (s), 2031 (s), 1996 (m), 1971 (m).

[Cp$^{tt}_2$Zr(μ_3-S)$_2${Ir(CO)$_2$}{Pd(η^3-C$_3$H$_5$)}] (8). To a brown-yellow dichloromethane solution of [Ir(CO)(dppe)$_2$][Cp$^{tt}_2$Zr(μ-S)$_2${Ir(CO)$_2$}] (0.149 mmol, 5 mL), prepared in situ as described above, was added solid [Pd(μ-Cl)(η^3-C$_3$H$_5$)]$_2$ (0.027 g, 0.075 mmol) to give immediately a dark red solution. The solution was stirred for 5 min, and the solvent was removed under vacuum. The greenish residue was extracted with toluene (4 × 10 mL), and the resulting suspension was filtrated on neutral alumina (4 × 2 cm). The red filtrate was then evaporated to dryness under vacuum and dissolved in dichloromethane (5 mL). Addition of *n*-hexane (10 mL) and concentration under vacuum to ca. 5 mL gave a pale green microcrystalline solid that was washed with cold *n*-hexane (5 mL) and dried under vacuum. Yield: 0.112 g (83%). Anal. Calcd for C$_{31}$H$_{47}$O$_2$S$_2$IrPdZr: C, 41.11; H, 5.23; S, 7.08. Found: C, 41.53; H, 5.90; S, 7.02. ^{1}H NMR (CDCl$_3$, 293 K). Isomer **8a** (84%): δ 6.48 and 6.05 (br t, J_{H-H} = 2.4 Hz, 1H each, H$_2$), 6.01 and 5.89 (br d, J_{H-H} = 2.4 Hz, 2H each, H$_4$ and H$_5$) (Cp^{tt}), 5.14 (m, 1H, H$_{meso}$), 4.01 (d, J_{H-H} = 6.9 Hz, 2H, H$_{syn}$), 2.71 (d, J_{H-H} = 12.6 Hz, 2H, H$_{anti}$) (C$_3$H$_5$), 1.32 and 1.22 (s, 18H each, CH$_3$ Cp^{tt}). Isomer **8b** (16%): δ 6.53 and 6.14 (br t, J_{H-H} = 2.4 Hz, 1H each, H$_2$), 6.08 and 5.92 (br d, J_{H-H} = 2.4 Hz, 2H each, H$_4$ and H$_5$) (Cp^{tt}), 5.08 (m, 1H, H$_{meso}$), 4.23 (d, J_{H-H} = 6.9 Hz, 2H, H$_{syn}$), 2.81 (d, J_{H-H} = 12.3 Hz, 2H, H$_{anti}$) (C$_3$H$_5$), 1.31 and 1.29 (s, 18H each, CH$_3$ Cp^{tt}). ^{13}C{^{1}H} NMR (CDCl$_3$, 293 K). Isomer **8a**: δ 175.7 (s, CO), 147.5 and 146.6 (s, C$_1$ and C$_3$), 124.1 and 117.1 (s, C$_2$) (Cp^{tt}), 111.5 (s, C$_{meso}$, C$_3$H$_5$), 108.3 and 108.0 (s, C$_4$ and C$_5$ Cp^{tt}), 65.8 (s, C$_{term}$, C$_3$H$_5$), 34.6 and 34.3 (s, *C*Me$_3$), 32.1 and 31.9 (s, CH$_3$) (Cp^{tt}). Isomer **8b** δ: 175.9 (s, CO), 147.3 and 147.2 (s, C$_1$ and C$_3$), 123.2 and 116.8 (s, C$_2$) (Cp^{tt}), 114.1 (s, C$_{meso}$, C$_3$H$_5$), 108.2 (s, C$_4$ and C$_5$ Cp^{tt}), 64.3 (s, C$_{term}$, C$_3$H$_5$), 34.6 and 34.5 (s, *C*Me$_3$), 32.3 and 32.1 (s, CH$_3$) (Cp^{tt}). MS (FAB+, CH$_2$Cl$_2$, *m/z*): 904 (M$^+$, 26%), 863 (M$^+$ − C$_3$H$_5$, 16%), 848 (M$^+$ − 2CO, 12%), 807 (M$^+$ − C$_3$H$_5$ − 2CO, 36%), 727 (M$^+$ − Cp^{tt}, 100%). IR (CH$_2$Cl$_2$, cm^{-1}): ν(CO), 2031 (s), 1959 (s).

Synthesis of [Cp$^{tt}_2$Zr(μ-S)$_2${Ir(CO)$_2$}{Au(PPh$_3$)}] (9). To a brown-yellow dichloromethane solution of [Ir(CO)(dppe)$_2$][Cp$^{tt}_2$Zr(μ-S)$_2${Ir(CO)$_2$}] (0.148 mmol, 5 mL), prepared in situ as described above, was added solid [AuCl(PPh$_3$)] (0.073 g, 0.148 mmol) to give immediately a deep red solution that was stirred for 5 min. Evaporation of the solution to dryness under vacuum, extraction of the deep orange residue with diethyl ether (5 × 10 mL), and filtration of the resulting suspension over neutral alumina (4 × 2 cm) gave a clear deep red solution. The solution was concentrated under vacuum to ca. 5 mL and *n*-hexane (15 mL) was added. Further concentration under vacuum to ca. 10 mL gave an orange microcrystalline solid that was filtrated, washed with *n*-hexane (5 mL) and dried under vacuum. Yield: 0.130 g (72%). Anal. Calcd for C$_{46}$H$_{57}$O$_2$S$_2$PAuIrZr: C, 45.38; H, 4.72; S, 5.27. Found: C, 45.56; H, 4.49; S, 5.55. ^{1}H NMR (CDCl$_3$, 293 K): δ 7.38−7.58 (m, 15H, PPh$_3$), 5.73 (d, J_{H-H} = 2.5 Hz, 4H, H$_4$ and H$_5$), 5.38 (t, J_{H-H} = 2.5 Hz, 2H, H$_2$), 1.18 (s, 36H, CH$_3$) (Cp^{tt}). ^{31}P{^{1}H} NMR (CDCl$_3$, 293 K): δ 33.3 (s). ^{13}C{^{1}H} NMR (CDCl$_3$, 293 K): δ 174.2 (s, CO), 144.1 (s, C$_1$ and C$_3$, Cp^{tt}), 134.2 (d, J_{P-C} = 13.8 Hz, C$_o$ or C$_m$), 131.6 (d, J_{P-C} = 2.8 Hz, C$_p$), 129.9 (d, J_{P-C} = 57.1 Hz, C$_i$), 129.2 (d, J_{P-C} = 11.6 Hz, C$_o$ or C$_m$) (PPh$_3$), 111.3 (s, C$_2$), 102.7 (s, C$_4$ and C$_5$), 33.9 (s, *C*Me$_3$), 31.5 (s, CH$_3$) (Cp^{tt}). MS (FAB+, CH$_2$Cl$_2$, *m/z*): 1216 (M$^+$, 12%), 1160 (M$^+$ - 2CO, 8%), 1039 (M$^+$ - Cp^{tt}, 100%). IR (CH$_2$Cl$_2$, cm^{-1}): ν(CO), 2029 (s), 1960 (s).

[Cp$^{tt}_2$Zr(μ-S)$_2${Rh(CO)$_2$}{Au(PPh$_3$)}] (10). A solid mixture of [Cp$^{tt}_2$Zr(μ_3-S)$_2${Rh(CO)$_2$}$_2$] (0.100 g, 0.121 mmol) and dppe (0.096 g, 0.242 mmol) was dissolved in dichloromethane (3 mL) under a carbon monoxide atmosphere at room temperature to give an orange-brown solution which was stirred for 15 min. The addition of solid [AuCl(PPh$_3$)] (0.060 g, 0.121 mmol) gave immediately a bright orange solution which was stirred for 15 min and filtered on neutral alumina (4 × 2 cm). The orange filtrate was evaporated to dryness under vacuum and dissolved in a 1:2 mixture of diethyl ether/hexane (5 mL). Cooling of the solution to 258 K gave the compound as an orange microcrystalline solid that was filtered, washed with cold *n*-hexane (5 mL), and dried under vacuum. Yield: 0.100 g (67%). Anal. Calcd for C$_{46}$H$_{57}$O$_2$PAuRhS$_2$Zr: C, 48.97; H, 5.09; S, 5.68. Found: C, 49.19; H, 4.01; S, 5.30. ^{1}H NMR (CD$_2$Cl$_2$, 293 K): δ 7.60−7.49 (m, 15H, PPh$_3$), 5.75 (d, J_{H-H} = 2.5 Hz, 4H, H$_4$ and H$_5$), 5.43 (t, J_{H-H} = 2.5 Hz, 2H, H$_2$), 1.23 (s, 36H, CH$_3$) (Cp^{tt}). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 293 K): δ 34.0 (s). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 293 K): δ 186.3 (d, J_{Rh-P} = 71 Hz, CO), 143.5 (s, C$_1$ and C$_3$, Cp^{tt}), 134.4 (d, J_{P-C} = 13.8 Hz, C$_o$ or C$_m$), 131.8 (d, J_{P-C} = 2.3 Hz, C$_p$), 130.1 (d, J_{P-C} = 56.6 Hz, C$_i$), 129.3 (d, J_{P-C} = 11.3 Hz, C$_o$ or C$_m$) (PPh$_3$), 110.7 (s, C$_2$), 102.8 (s, C$_4$ and C$_5$), 34.0 (s, *C*Me$_3$), 31.6 (s, CH$_3$) (Cp^{tt}). MS (FAB+, CH$_2$Cl$_2$, *m/z*): 1070 (M$^+$ − 2CO, 65%), 949 (M$^+$ − Cp^{tt}, 80%), 893 (M$^+$ − Cp^{tt} − 2CO, 45%). IR (CH$_2$Cl$_2$, cm^{-1}): ν(CO), 2041 (s), 1977 (s).

[Cp$^{tt}_2$Zr(μ_3-S)$_2${Pd(η^3-C$_3$H$_5$)}$_2$] (11). To a yellow solution of [Cp$^{tt}_2$Zr(SH)$_2$] (0.100 g, 0.195 mmol) in CH$_2$Cl$_2$ (5 mL) was successively added NEt$_3$ (55 μL, 0.396 mmol) and [Pd(μ-Cl)(η^3-C$_3$H$_5$)]$_2$ (0.072 g, 0.196 mmol) at room temperature to give an orange solution that was stirred for 5 min. The solvent was removed under vacuum, and the residue was extracted with diethyl ether (25 mL) and then filtered over celite. The solution was evaporated to dryness, and the residue was washed with *n*-pentane (5 mL) at −78 °C and then dried under vacuum to give a yellow powder. Yield: 94% (0.147 g). Anal. Calcd for C$_{32}$H$_{52}$S$_2$Pd$_2$Zr: C, 47.75; H, 6.51; S, 7.97. Found: C, 47.33; H, 6.60; S, 7.36. ^{1}H NMR (C$_6$D$_6$, 293 K). Isomer **11a** (61%): δ 5.81 (t, J_{H-H} = 2.9 Hz, 2H, H$_2$), 5.52 (d, J_{H-H} = 2.9 Hz, 4H, H$_4$ and H$_5$) (Cp^{tt}), 4.80−4.66 (m, 2H, H$_{meso}$), 3.79 (d, J_{H-H} = 6.9 Hz, 4H, H$_{syn}$), 2.58 (d, J_{H-H} = 12.6 Hz, 4H, H$_{anti}$) (C$_3$H$_5$), 1.41 (s, 36H, CH$_3$ Cp^{tt}). Isomer **11b** (34%): δ 5.91 and 5.83 (t, J_{H-H} = 2.4 Hz, 1H each, H$_2$), 5.57 and 5.55 (d, J_{H-H} = 2.4 Hz, 2H each, H$_4$ and H$_5$) (Cp^{tt}), 4.56−4.80 (m, 2H, H$_{meso}$), 4.15 and 3.72 (d, J_{H-H} = 6.9 Hz, 2H each, H$_{syn}$), 2.65 and 2.51 (d, J_{H-H} = 12.3 Hz, 2H each, H$_{anti}$) (C$_3$H$_5$), 1.47 and 1.40 (s, 18H each, CH$_3$ Cp^{tt}). Isomer **11c** (5%): δ 5.94 (t, J_{H-H} = 2.4 Hz, 2H, H$_2$), 5.61 (d, J_{H-H} = 2.4 Hz, 4H, H$_4$ and H$_5$) (Cp^{tt}), 4.56−4.80 (m, 2H, H$_{meso}$), 4.04 (d, J_{H-H} = 6.6 Hz, 4H, H$_{syn}$), 2.59 (d, J_{H-H} = 12.6 Hz, 4H, H$_{anti}$) (C$_3$H$_5$), 1.46 (s, 36H, CH$_3$ Cp^{tt}). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 293 K). Isomer **11a**: δ 143.7 (s, C$_1$ and C$_3$), 114.5 (s, C$_2$) (Cp^{tt}), 110.1 (br s, C$_{meso}$, C$_3$H$_5$), 105.6 (s, C$_4$ and C$_5$ Cp^{tt}), 61.6 (s, C$_{term}$, C$_3$H$_5$), 34.1 (s, *C*Me$_3$), 32.0 (s, CH$_3$) (Cp^{tt}). Isomer **11b**: δ 144.4 and 143.7 (s, C$_1$ and C$_3$), 114.1 and 113.9 (br s, C$_2$) (Cp^{tt}), 111.3 and 109.6 (s, C$_{meso}$, C$_3$H$_5$), 105.9 and 105.6 (br s, C$_4$ and C$_5$ Cp^{tt}), 61.5 and 61.2 (s, C$_{term}$, C$_3$H$_5$), 34.3 and 34.1 (s, *C*Me$_3$), 32.4 and 32.1 (s, CH$_3$) (Cp^{tt}). Isomer **11c**: δ 144.5 (s, C$_1$ and C$_3$), 113.5 (br s, C$_2$) (Cp^{tt}), 110.9 (s, C$_{meso}$, C$_3$H$_5$), 105.9 (br s, C$_4$ and C$_5$ Cp^{tt}), 61.1 (s, C$_{term}$, C$_3$H$_5$), 34.3 (s, *C*Me$_3$), 32.5 (s, CH$_3$) (Cp^{tt}). MS (FAB+, CH$_2$Cl$_2$, *m/z*): 803 (M$^+$ − H, 9%), 763 (M$^+$ − C$_3$H$_5$, 34%), 627 (M$^+$ − Cp^{tt}, 100%).

[Cp$^{tt}_2$Zr(μ-S)$_2${Au(PPh$_3$)}$_2$] (12). To a yellow solution of [Cp$^{tt}_2$Zr(SH)$_2$] (0.100 g, 0.195 mmol) in CH$_2$Cl$_2$ (5 mL) was successively added NEt$_3$ (60 μL, 0.432 mmol) and [AuCl(PPh$_3$)] (0.193 g, 0.391 mmol) at room temperature to give an orange solution that was stirred for 5 min. The solution was concentrated under vacuum to ca. 2 mL, and then methanol (20 mL) was added. The resulting suspension was concentrated to ca. 10 mL, filtrated, washed with methanol (2 × 10 mL), and dried under vacuum to give a yellow orange micocrystalline solid. Yield: 0.273 g (98%). Anal. Calcd for C$_{62}$H$_{72}$P$_2$S$_2$Au$_2$Zr: C, 52.13; H, 5.08; S, 4.49. Found: C, 51.92; H, 4.96; S, 4.97. ^{1}H NMR (C$_6$D$_6$, 293 K): δ 7.68−7.54 (m, 12H, H$_o$), 6.98−6.88 (m, 18H, H$_m$ and H$_p$) (PPh$_3$), 5.99 (t, J_{H-H} = 2.4 Hz, 2H, H$_2$), 5.75 (d, J_{H-H} = 2.4 Hz, 4H, H$_4$ and H$_5$), 1.58 (s,

Table 3. Crystal Data, Data Collection, and Refinement for Complexes 9 and 12

	9	**12**
empirical formula	$C_{46}H_{57}AuIrO_2PS_2Zr$	$C_{62}H_{72}Au_2P_2S_2Zr$
fw	1217.39	1428.41
cryst size, mm	0.38 × 0.15 × 0.11	0.29 × 0.23 × 0.16
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$ (No. 19)	$P2_1/n$ (No.14)
a, Å	14.805(2)	10.3440(7)
b, Å	17.604(2)	38.998(3)
c, Å	18.045(3)	13.9883(9)
β, deg	90	96.2520(10)
V, A^3	4703.1(11)	5609.2(7)
Z	4	4
D_{calcd}, g cm^{-3}	1.719	1.691
μ, mm^{-1}	6.308	5.570
no. of measd reflns	9336 ($2.12 \leq \theta \leq 25.00$)	40793 ($1.8 \leq \theta \leq 28.68$)
no. of unique reflns	8249 (R_{int}= 0.0374)	13280 (R_{int}= 0.0620)
min, max transm fact	0.385, 0.500	0.298, 0.408
no of data/ restraints/ params	8249/ 12/ 496	13280/ 0/ 634
GOF (all data)[a]	1.012	0.917
$R_1(F)$ ($F^2 \geq 2\sigma(F^2)$)[b]	0.0439	0.0439
$wR_2(F^2)$ (all data)[c]	0.0808	0.0594

[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 6610 (**9**) and 9380 **(12)** 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 $P = [\max(0, F_o{}^2) + 2F_c{}^2]/3$.

36H, CH_3) (Cp^{tt}). $^{31}P\{^1H\}$ NMR (C_6D_6, 293 K): δ 38.1 (s). $^{13}C\{^1H\}$ NMR (C_6D_6, 293 K): δ 143.6 (s, C_1 and C_3, Cp^{tt}), 134.7 (d, $J_{P-C} = 14.3$ Hz, C_o or C_m), 132.6 (d, $J_{P-C} = 50.7$ Hz, C_i), 130.6 (d, $J_{P-C} = 2.3$ Hz, C_p), 128.8 (d, $J_{P-C} = 11.0$ Hz, C_o or C_m) (PPh_3), 110.0 (s, C_2), 102.5 (s, C_4 and C_5), 34.4 (s, CMe_3), 31.7 (s, CH_3) (Cp^{tt}). MS (FAB+, CH_2Cl_2, m/z): 1425 ($M^+ - H$, 16%), 1249 ($M^+ -$ Cp^{tt}, 100%), 1163 ($M^+ - PPh_3$, 12%), 935 ($M^+ - SAuPPh_3$, 92%).

Crystal Structure Determination of [Cp$^{tt}{}_2$Zr(μ-S)$_2$\{Ir(CO)$_2$\}\{Au(PPh$_3$)\}] (9) and [Cp$^{tt}{}_2$Zr(μ-S)$_2$\{Au(PPh$_3$)\}$_2$] (12). A summary of crystal data, data collection and refinement parameters are given in Table 3. X-ray data were collected for both complexes at low temperature (200(2) K for **9** and 173(2) for **12**) on a Siemens P4 (**9**) and a Bruker SMART APEX CCD (**12**) diffractometers. Data were collected using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Absorption correction for **12** was applied by using the SADABS routine[34] and the psi-scan method[35] in the case of **9**. Both structures were solved by direct methods, completed by subsequent difference Fourier techniques, and refined by full-matrix least-squares on F^2 (SHELXL-97)[36] with initial isotropic thermal parameters. Anisotropic thermal parameters were used in the last cycles of refinement for all non-hydrogen atoms except for carbon atoms involved in a disordered tert-butyl substituent in **9**. A model of rotational disorder based on two alternative positions was assumed for the disordered group. Hydrogen atoms were included in calculated positions in both structures and were refined with positional and thermal parameters riding on carbon atoms. No hydrogen atoms were included for the disordered group in **9**. All the highest electronic residuals were smaller than 1.0 e/Å^3 and were observed in close proximity to the metal atoms. In **9**, the Flack parameter was refined as a check of the correct absolute structure determination ($x = 0.142(8)$).[37]

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of complexes [Cp$^{tt}{}_2$Zr(μ-S)$_2$\{Ir(CO)$_2$\}\{Au(PPh$_3$)\}] (**9**) and [Cp$^{tt}{}_2$Zr(μ-S)$_2$\{Au(PPh$_3$)\}$_2$] (**12**). This material is available free of charge via the Internet at http://pubs.acs.org.

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