Synthesis, Reactivity, and Catalytic Activity of Triangular ZrM_2 (M = Rh, Ir) Early-Late Heterobimetallic Complexes

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Summary

Reactions of the zirconium-sulfide metallocene anion $[Cp^{tt}_2ZrS_2]^{2-}$ (Cp^{tt} = η^5-1,3-di-*tert*-butylcyclopentadienyl) with $[\{M(\mu\text{-Cl})(diolefin)\}_2$ gave the d^0-d^8 complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{M(diolefin)\}_2]$ (M = Rh, diolefin = 2,5-norbornadiene (nbd, **1**), 1,5-cyclooctadiene (cod); M = Ir, diolefin = cod) with a triangular ZrM_2 core capped by two symmetrical μ_3-sulfido ligands. The rhodium complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(diolefin)\}_2]$ (diolefin = tetrafluorobenzobarrelene (tfbb), nbd, cod) can also be prepared by the additive-deprotonation reactions of the mononuclear [Rh(acac)(diolefin)] (diolefin = nbd, tfbb) and the dinuclear $[\{Rh(\mu\text{-OH})(cod)\}_2]$ complexes with $[Cp^{tt}_2Zr(SH)_2]$. These compounds exist as two rotamers in solution due to a hindered rotation of the cyclopentadienyl rings and the relative disposition of the substituents of the Cp^{tt} groups in the sandwich moiety. The reaction of $[Cp^{tt}_2Zr(SH)_2]$ with [Ir(acac)(cod)] gave the complex $[Cp^{tt}(acac)Zr(\mu_3\text{-}S)_2\{Ir(cod)\}_2]$ (**5**) with release of HCp^{tt} and coordination of acetylacetonate to the zirconium center. Carbonylation of compounds **1** and **5** yielded $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**6**) and $[Cp^{tt}(acac)Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2]$, respectively, while the complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{M(CO)_2\}_2]$ (M = Rh, Ir) resulted also from the reaction of $[Cp^{tt}_2Zr(SH)_2]$ with $(PPh_3Bz)[MCl_2(CO)_2]$ in the presence of triethylamine. Reactions of the carbonyl complexes with one molar-equiv of bis(diphenylphosphino)methane (dppm) gave the *cisoid* complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{M(CO)\}_2(\mu\text{-dppm})]$ (M = Rh (**9**), Ir) with evolution of carbon monoxide. Monodentate phosphites, $P(OMe)_3$ and $P(OPh)_3$, react with **6** to give mixtures of the *transoid* and *cisoid* isomers $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)(P(OR)_3)\}_2]$, which also exhibit a restricted rotation of the Cp^{tt} rings. The molecular structures of complexes **6** and **9** have been determined by X-ray diffraction methods. Compound **6** in the presence of P-donor ligands, $P(OMe)_3$, $P(OPh)_3$, and

PPh_3, is a precursor of catalyst for the hydroformylation of oct-1-ene under mild conditions of pressure and temperature.

Introduction

Transition metal-sulfur complexes have attracted considerable attention due to the possible relevance to the active sites of metalloenzymes and industrial processes by metal-sulfide catalysts.[1] Sulfido clusters containing metals of the 8-10 groups display a wide potential in homogeneous catalysis [2] owing both to their structural diversity and the strong bridging ability of sulfido ligands to prevent the fragmentation of the metal-sulfur framework.[3] In addition, new reactivity patterns are expected from the combination of widely divergent transition metals in mixed-metal sulfido clusters. Early-late heterobimetallic (ELHB) complexes, containing both electron-poor early transition metals and electron-rich late transition metals in close proximity, should provide multimetallic reaction sites to explore the cooperative heterometallic activation of small molecules and to search for the synergism between the metals in both catalytic[4, 5] and stoichiometric reactions.[6]

The rational construction of sulfur-bridge ELHB complexes requires the design of building blocks suitable for a stepwise synthetic approach. Recently, it has been established that hydrosulfido[3f,7] and hydroxo metal complexes[8] are appropriate to synthesize ELHB complexes. In this context, we have shown that the deprotonations of the bis-hydrosulfido titanium complex $[Cp_2Ti(SH)_2]$ with d^8 rhodium and iridium compounds lead to d^0-d^8 sulfido-bridged complexes.[9] Thus, the reactions of $[Cp_2Ti(SH)_2]$ with $[\{Rh(\mu\text{-OMe})(diolefin)\}_2]$ gave the tetranuclear heterobimetallic clusters $[CpTi(\mu_3\text{-S})_3\{Rh(diolefin)\}_3]$ (diolefin = cod, tfbb),[10] with a corner-sulfido voided incomplete cubane structure, probably through the cubane cluster $[(CpTi)_2(\mu_3\text{-S})_4\{Rh(diolefin)\}_2]$.[11] However, when this reaction was carried out in the presence of water and after carbonylation afforded the oxo-sulfido cluster $[(CpTi)_2(\mu_4\text{-O})(\mu_3\text{-S})_4Rh_4(CO)_6]$ with a

incomplete double-fused cubane structure.[12] By contrast, the additive-deprotonation of $[Cp_2Ti(SH)_2]$ with the diolefin complexes [M(acac)(diolefin)] (M = Rh, Ir; diolefin = cod, tfbb) resulted in the formation of the heterotrinuclear complexes $[Cp(acac)Ti(\mu_3\text{-}S)_2\{M(diolefin)\}_2]$ with elimination of cyclopentadiene.[13] Moreover, these syntheses may be complicated further by the transference of sulfido ligands between the metal centers, such as it was found in the reactions of $[Cp_2Ti(SH)_2]$ with the carbonyl complexes $[M(acac)(CO)_2]$ to give the ion-pair compounds $[Cp_2Ti(acac)][M_3(\mu_3\text{-}S)_2(CO)_6]$ (M = Rh, Ir).[13]

Preliminary experiments with the related zirconium hydrosulfido complex $[Cp_2Zr(SH)_2]$ resulted in extensive sulfido transfer to the d^8 metal centers, being the trimetallic complexes $[M_3(\mu\text{-}S)_2(\mu\text{-}H)(cod)_3]$ and the anionic clusters $[M_3(\mu_3\text{-}S)_2(CO)_6]^-$ (M = Rh, Ir) the outcome of these reactions. We reasoned that the known dimerization[14] of $[Cp_2Zr(SH)_2]$ with extrusion of H_2S probably complicated these reactions. To overcome this problem in the syntheses of ELHB complexes containing zirconium we envisaged that the use of a bulkier zirconium-metallocene hydrosulfido compound could avoid the undesirable reactions. For this purpose we explored successfully[15,16] the capability of $[Cp^{tt}_2Zr(SH)_2]$ ($Cp^{tt} = \eta^5$-1,3-di-*tert*-butylcyclopentadienyl) to generate a sulfido metallaligand. Herein we report on the controlled construction of the diolefin and carbonyl complexes containing the core "$Zr(\mu_3\text{-}S)_2M_2$" as well as the replacement reactions on the carbonyl complexes by P-donor ligands. In addition, the hydroformylation of oct-1-ene under mild conditions using the catalyst precursor $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ is also described.

Results

Syntheses of the Heterotrinuclear Diolefin Complexes.

The double deprotonation of $[Cp^{tt}_2Zr(SH)_2]$ with n-BuLi (in a 1:2 molar ratio) in diethyl ether at temperatures under 0 ºC generated the zirconium-sulfide metallocene anion $[Cp^{tt}_2ZrS_2]^{2-}$

in situ. Reactions of these solutions with the complexes [{M(μ-Cl)(diolefin)}$_2$] gave the d^0-d^8 ELHB complexes [Cp$^{tt}_2$Zr(μ_3-S)$_2${M(diolefin)}$_2$] (M = Rh, diolefin = 2,5-norbornadiene (nbd, **1**), diolefin = 1,5-cyclooctadiene (cod, **3**); M = Ir, diolefin = cod, **4**) with a triangular $ZrRh_2$ or $ZrIr_2$ cores capped by two μ_3-sulfido ligands. The reactions are almost quantitative at temperatures under –20 ºC, but a partial decomposition occurs if the reactions are carried out at room temperature, which is particularly noticeable for the iridium complex.

Alternatively, the acidity of the hydrosulfido ligands in [Cp$^{tt}_2$Zr(SH)$_2$] facilitates the direct synthesis by using other mono- and di-nuclear rhodium complexes that avoid the use of n-BuLi. Thus, the reaction of [Cp$^{tt}_2$Zr(SH)$_2$] with two molar-equiv of [Rh(acac)(nbd)] in methanol gave compound **1** in good yield, while **1** can be also obtained from the reaction of [Cp$^{tt}_2$Zr(SH)$_2$] with [{Rh(μ-Cl)(nbd)}$_2$] in the presence of NEt_3 (Scheme 1). The related compound [Cp$^{tt}_2$Zr(μ_3-S)$_2${Rh(tfbb)}$_2$] (**2**) was cleanly obtained as an orange solid in excellent yield by addition of methanol to a solid mixture of [Cp$^{tt}_2$Zr(SH)$_2$] with two molar-equiv of [Rh(acac)(tfbb)]. However, the additive-deprotonation reactions are not appropriate for the preparation of the related 1,5-cyclooctadiene complexes [Cp$^{tt}_2$Zr(μ_3-S)$_2${M(cod)}$_2$] (**3**, **4**), since the formation of these complexes competes with the transference of the sulfido ligands to the d^8 metal centers. Thus, the reactions of [Cp$^{tt}_2$Zr(SH)$_2$] with [{Rh(μ-OMe)(cod)}$_2$], [Rh(acac)(cod)], and [{Rh(μ-Cl)(cod)}$_2$] in the presence of NEt_3 gave non separable mixtures of **3** and the known[17] hydride trirhodium complex [Rh_3(μ-S)$_2$(μ-H)(cod)$_3$] in variable amounts. Nevertheless, a straightforward and clean synthesis of [Cp$^{tt}_2$Zr(μ_3-S)$_2${Rh(cod)}$_2$] (**3**) consisted in the reaction of [Cp$^{tt}_2$Zr(SH)$_2$] with [{Rh(μ-OH)(cod)}$_2$] in methanol at room temperature. However, the identical reaction of [Cp$^{tt}_2$Zr(SH)$_2$] with one molar-equiv of [{Ir(μ-OH)(cod)}$_2$] in tetrahydrofuran/methanol gave the hydride triiridium complex [Ir_3(μ-S)$_2$(μ-H)(cod)$_3$][18], which was isolated in 90% yield. On the

other hand, the reaction of $[Cp^{tt}_2Zr(SH)_2]$ with two molar-equiv of [Ir(acac)(cod)] in diethyl ether afforded the new complex $[Cp^{tt}(acac)Zr(\mu_3\text{-}S)_2\{Ir(cod)\}_2]$ (**5**) impurified with $[Ir_3(\mu\text{-}S)_2(\mu\text{-}H)(cod)_3]$; complex **5** could be isolated pure as a dark blue solid by recrystallization.

Characterization of the Heterotrinuclear Diolefin Complexes and the Rotamers in Solution

Elemental analyses, mass spectra, and molecular weights data of compounds **1**-**5** were found in accordance with the proposed formulae except for compound **4**, which gave unsatisfactory elemental analyses due presumably to incomplete combustion. Complexes **1**, **2** were found to exist in solution as two species which were unambiguously identified as two rotamers by ^1H, $^{13}C\{^1H\}$, and two-dimensional NMR techniques (*vide infra*). Both rotamers differ in the spatial disposition of the *tert*-butyl groups of both Cp^{tt} rings in the sandwich moiety and correspond to the limiting eclipsed (**a**) and fully staggered (**b**) conformations respectively (Figure 1). In the eclipsed rotamer (**a**) the *tert*-butyl groups of both Cp^{tt} rings are positioned towards the front of the metallocene "clam-shell" while in the fully staggered rotamer (**b**) the *tert*-butyl groups of one of the Cp^{tt} rings are directed towards the back of the metallocene "clam-shell".

The rotamers of the compounds **1** and **2** interconvert in solution producing an equilibrium mixture in which the eclipsed rotamers **1a** (60%) and **2a** (55%) predominate. This interconversion was verified by a saturation transfer experiment on the nbd complex **1**. Both rotamers **3a (**15%) and **3b** (85%) were detected for the cod complex **3** on monitoring the reaction by ^1H NMR, but the staggered rotamer was the sole species isolated for complex **3**. A mixture of both rotamers **4b** and **4a** containing mainly the staggered isomer **4b** (80%) could be isolated for the iridium complex **4**. A remarkable observation is that the eclipsed isomer **4a** decomposes in $CDCl_3$ at room temperature in a period of 4h, which allowed the isolation of the staggered isomer **4b** pure. A further observation is that the staggered rotamers of the cod complexes **3** and **4** do not evolve to the eclipsed rotamers for a period of 24h in solution.

The identification of the rotamers is simple by NMR methods, since the eclipsed rotamer **a** (C_{2v} symmetry) possesses equivalent Cp^{tt} rings while they are inequivalent for the staggered isomer **b** (Cs symmetry). For example, the eclipsed minor isomer **4a** displays two resonances, at δ 6.37 and 6.00 ppm, for the cyclopentadienyl protons and a singlet for the *tert*-butyl groups in the ^1H NMR spectrum (Figure 2). The staggered rotamer **4b** displays four resonances for the cyclopentadienyl protons and two singlets for the *tert*-butyl groups. Moreover, the resonances at δ 6.25 and 6.04 ppm correspond to the Cp^{tt} ligand with the *t*-Bu groups directed inwards the $ZrRh_2$ core while the signals at δ 7.15 and 5.78 ppm are due to the cyclopentadienyl protons of the Cp^{tt} ligand with the *t*-Bu groups directed outwards the $ZrRh_2$ core. The pattern of resonances for the cyclopentadienyl protons of the Cp^{tt} ligands of both rotamers **1a**, **2a** and **1b**, **2b** in the ^1H NMR spectra follows a trend similar to that observed for complex **1**. Again it is noticeable the unusual chemical shifts of one of the Cp^{tt} rings of the staggered isomer, as previously observed.[16] The number of signals from the *tert*-butyl groups and the auxiliary nbd and tfbb ligands in the $^{13}C\{^1H\}$ and ^1H NMR spectra corroborate the identification and symmetry of both rotamers. For example, the eclipsed rotamers (**1a**, **2a**) display two doublets for the olefinic carbons in the $^{13}C\{^1H\}$ NMR spectra while the staggered rotamer **2b** shows four signals for the olefinic carbons, in agreement with the lower symmetry. This assignment is evident for the complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{M(cod)\}_2]$ (**3**, **4**) for which the staggered rotamers **b** were isolate pure.

Complex **5** shows the molecular ion at m/z 1032 and the ^1H NMR spectrum display a 1:1:2 ratio for the Cp^{tt}, acac, and cod ligands in agreement with the proposed formulation. The ^1H and the $^{13}C\{^1H\}$ NMR spectra (the full assignment of the signals has been done with the help of the ^{13}C-^1H HETCOR spectrum) indicate the presence of a plane of symmetry containing the $ZrIr_2$ core, which intersects both the acac and Cp^{tt} groups relating both halves. In addition, the

chemical shifts of the signals for the cyclopentadienyl protons (at δ 7.02 and 5.47 indicate that the *t*-Bu groups are directed outwards the $ZrIr_2$ core (Scheme 2).

Synthesis and Characterization of the Carbonyl Complexes.

Carbonylation of $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(nbd)\}_2]$ (**1**) under atmospheric pressure in benzene gave the carbonyl complex $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**6**), which was isolated as an emerald-green microcrystalline solid in good yield. Complex **6** is a remarkably stable compound that can be synthesized directly in excellent yields by reacting $[Cp^{tt}_2Zr(SH)_2]$ with a variety of rhodium-carbonyl complexes. Thus, the reactions of $[Cp^{tt}_2Zr(SH)_2]$ with two molar-equiv of $[Rh(acac)(CO)_2]$ in diethyl ether, with $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ in the presence of a slight excess of NEt_3 in dichloromethane, and with $[\{Rh(\mu\text{-}pz)(CO)_2\}_2]$ gave **6** with yields greater than 90%. The related carbonyl complex $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2]$ (**7**) was obtained from the reaction of $[Cp^{tt}_2Zr(SH)_2]$ with two molar-equiv of the anionic complex $[IrCl_2(CO)_2]^-$ in the presence of a slight excess of NEt_3. Under similar experimental conditions, complex **6** was obtained from $(PPh_3Bz)[RhCl_2(CO)_2]$ in 92% yield.

The $ZrRh_2$ core of the compound $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**6**) has been established by X-ray diffraction methods and the molecular structure is depicted in Figure 3 (see below). The spectroscopic data indicate that complexes **6** and **7** have closely related structures, since a similar pattern of resonances is observed both in the $^{13}C\{^1H\}$ and ^1H NMR spectra in agreement with the C_{2v} symmetry found for **6** in the solid state. It is also noticeable the free rotation of the Cp^{tt} rings in complexes **6** and **7**, which is fast on the time scale of the$^{13}C\{^1H\}$ and ^1H NMR. Accordingly, the four equivalent carbonyl ligands give one signal in the $^{13}C\{^1H\}$ NMR spectra, and both Cp^{tt} ligands are equivalent. In addition, both complexes display three strong ν(CO)

bands for the terminal carbonyl groups in the IR spectra in agreement with the C_{2v} symmetry of the molecules.

The carbonylation of [Cp^{tt}(acac)Zr(μ_3-S)$_2${Ir(cod)}$_2$] (**5**) under atmospheric pressure gave the carbonyl complex [Cp^{tt}(acac)Zr(μ_3-S)$_2${Ir(CO)$_2$}$_2$] (**8**), which was isolated as a golden microcrystalline solid in good yield. The spectroscopic information is compatible with the expected C_s structure resulting from the replacement of each diolefin ligand in **5** by two carbonyl groups (Scheme 2). Interestingly, all the carbonyl groups are isochronous in the $^{13}C\{^1H\}$ NMR spectrum that shows a strong singlet at δ 174.3 ppm. In addition, it displays three strong ν(CO) absorptions in the IR spectrum, as found for the related titanium complexes [Cp(acac)Ti(μ_3-S)$_2${M(CO)$_2$}$_2$] (M = Rh, Ir).[13]

Replacement Reactions of the Carbonyl Complexes.

Carbonyl replacement reactions by P–donor ligands take place quickly at room temperature with evolution of carbon monoxide. The reaction of complex [Cp^{tt}_2Zr(μ_3-S)$_2${Rh(CO)$_2$}$_2$] (**6**) with one molar-equiv of *dppm* in dichloromethane gave a dark-green solution of the compound [Cp^{tt}_2Zr(μ_3-S)$_2${Rh(CO)}$_2$(μ-dppm)] (**9**), which was isolated as a dark-green or black microcrystalline solid in excellent yield. Analogously, the complex [Cp^{tt}_2Zr(μ_3-S)$_2${Ir(CO)}$_2$(μ-dppm)] (**10**) was isolated as an orange crystalline solid from the reaction of [Cp^{tt}_2Zr(μ_3-S)$_2${Ir(CO)$_2$}$_2$] (**7**) with one molar-equiv of dppm.

Complexes **9** and **10** were characterized by elemental analyses, FAB+ mass spectra, and NMR spectroscopy. In addition, the molecular structure of [Cp^{tt}_2Zr(μ_3-S)$_2${Rh(CO)}$_2$(μ-dppm)] (**9**) was determined by X-ray diffraction methods and the molecular diagram is shown in Figure 4. It is noteworthy that the $ZrRh_2$ core is maintained after the replacement of two carbonyl groups by the *dppm* ligand, which bridges the rhodium atoms with a *cisoid* arrangement. The ^1H,

$^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of **9** and **10** reveal the existence of a plane of symmetry in the molecules, which contains the Zr and both sulfido ligands and intersects the M-M vector. This plane produces the equivalence of the carbonyl ligands, the P-donor atoms of the *dppm* ligand and the Cp^{tt} ligands, but the protons in each cyclopentadienyl ring are inequivalent, in agreement with the C_s symmetry found in the solid state for **9**; both complexes also display two strong ν(CO) bands for the terminal carbonyls. Although the spectroscopic data suggest that compounds **9** and **10** have an identical structure, the broadening of the signals observed in the NMR spectra of **9** at room temperature indicates some kind of fluxionality for the rhodium complex.

The reaction of $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**6**) with two molar-equiv of $P(OMe)_3$ gave the complex $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)(P(OMe)_3)\}_2]$ (**11**) under evolution of carbon monoxide. The compound was isolated as a green-apple microcrystalline solid in good yield. Although the FAB+ mass spectrum of **11** showed the mass of the molecular ion, the ^1H NMR spectrum is complicated and evidences a non-selective replacement of the carbonyl ligands by the monodentate P-donor ligands. This and the $^{31}P\{^1H\}$ NMR spectrum (Figure 5a) can be rationalized assuming the existence of the *cisoid* and *transoid* isomers, resulting from the relative disposition of the $P(OMe)_3$ ligands along with a restricted rotation of the Cp^{tt} rings for both isomers (Figure 6). The main species is the eclipsed rotamer *trans*-**11a** (of C_2 symmetry) that displays an AA'XX' spin system centered at δ 139.7 ppm. This signal correlates well with the calculated spectrum (Figure 5b) using the parameters reported in the Experimental Part. The doublet centered at δ 140.2 ppm corresponds to the eclipsed rotamer *cis*-**11a** (C_s symmetry). Finally, the minor staggered rotamers *trans*-**11b** and *cis*-**11b** give rise to four doublets as expected for their lack of symmetry. It is noticeable that the *transoid* isomer is much more abundant than the *cisoid* isomer, while the eclipsed rotamer is largely predominant for the *trans* isomer, and both rotamers are roughly in the same proportion for the *cis* isomer.

The unselective replacement of carbonyl ligands in **6** is also observed in the reaction with other monodentate P-donor ligands. Thus, reaction of **6** with two molar-equiv of $P(OPh)_3$ in toluene gave the complex $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)(P(OPh)_3)\}_2]$ (**12**), which was isolated as a green microcrystalline solid in good yield. When this reaction is performed in $CDCl_3$ and monitored by $^{31}P\{^1H\}$ NMR a *cis*/*trans* mixture of isomers results evident. Although the *transoid* isomer is much more abundant than the *cisoid* isomer, the eclipsed rotamers predominate over the staggered ones in both isomers. The eclipsed rotamer *trans*-**12a** displays the expected AA'XX' spin system while the eclipsed rotamer *cis*-**12a** shows a doublet at δ 121.0 ppm ($^1J_{Rh\text{-}P}$ = 294 Hz) in the $^{31}P\{^1H\}$ NMR spectrum. On the other hand, the staggered rotamer *trans*-**12b** displays an ABXY spin system and the rotamer *cis*-**12b** shows two broad doublets at δ 121.8 and 117.8 ppm with $^1J_{Rh\text{-}P}$ coupling constants of 290 and 298 Hz respectively. Interestingly, the isolated product contains only the *trans* isomer (*trans*-**12a** and *trans*-**12b)** as deducted from the $^{31}P\{^1H\}$ NMR spectrum, indicating that both isomers possess different solubilities. Similarly, the IR spectrum (toluene) of the isolated compound displays only two broad ν(CO) bands at 1995 (m) and 1981 (s) cm^{-1}.

Molecular structures of $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (6) and $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)\}_2(\mu\text{-}dppm)]$ (9).

Good quality monocrystals for X-ray diffraction were grown by slow diffusion of n-hexane into a saturated dichlorometane solution of compound **6** at room temperature. Under these experimental conditions the complex crystallized out as the water solvate. In fact, we have observed that the crystallization process is considerably facilitated by the presence of water. Nevertheless, all the attempts to grow good quality water-free crystals of **6** were unsuccessful.

As proposed from spectroscopic data, complexes **6** and **9** are trinuclear with a triangular $ZrRh_2$ core capped by two μ_3-sulfido ligands; the central skeleton formed by the metals and the

sulfur atoms configures a trigonal bipyramid. The two molecules are structurally analogous, with the sole difference of the substitution of one carbonyl at each Rh by a P atom of the bridging *dppm* ligand. Figures 3 and 4 represent the molecular structures of **6** and **9** together with the atomic labeling schemes, while Tables 1 and 2 collect selected bond distances and angles

In both complexes the Zr atoms exhibit distorted pseudo-tetrahedral geometries being bonded to two bridging sulfur atoms and to two η^5-Cp^{tt} rings. The Zr-Cp^{tt}(centroid) distances, 2.272(2) Å in **6** and 2.302(3), 2. 297(3) Å in **9**, are comparable to the observed values in the closely related heterotrimetallic complex $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2Ir(CO)_2Rh(cod)]$ (2.290(9) and 2.290(13) Å),[16] and longer than the reported distances in mononuclear zirconium thiolate complexes containing unsubstituted Cp rings (range 2.203(3)-2.220(1) Å).[19]

The angles centered on the Zr with the centroids of the Cp^{tt} ligands (G(1)-Zr-G(2), 127.62(7)° in **6** and 126.75(10)° in **9**) are significantly larger than the typical value for a tetrahedral geometry, most probably due to the presence of the bulky *tert*-butyl substituents. The relative dispositions of the Cp^{tt} substituents in both complexes are eclipsed and in the side of the trinuclear core, favoring a smaller G(1)-Zr-G(2) angle than that described in the related Zr-Ir-Rh complex,[16] 129.8(4)°, where the Cp^{tt} rings exhibit a staggered disposition. In fact, the angles G(1)-Zr-G(2) in **6** and **9** are at the lower end of mononuclear zirconium thiolate complexes of the type $Cp_2Zr(SR)_2$ (range 127.7(3)-130.4(1)°).[19]

While complex **6** presents a crystallographically imposed C_{2v} symmetry, and therefore a sole Zr-S distance (2.5214(11) Å), in **9** the two Zr-S bond lengths are different, 2.460(1) and 2.507(1) Å, and reflect the relative asymmetry of the molecule. However, these bond distances in both complexes are comparable to those reported in the Zr-Ir-Rh analogue (2.506(3) and 2.519(3) Å).[16] The angles S-Zr-G (mean value 109.95(4) in **6** and 109.73(4)°in **9**) are quite close to the

ideal value for a tetrahedral geometry. The dihedral angles formed by the LSQ-planes defined by the carbon atoms in the two Cp^{tt} rings are almost identical, 61.63(16) in **6** and 62.1(2)° in **9**.

Without considering a potential Rh···Rh intermetallic interaction, the rhodium atoms exhibit square-planar geometries in both complexes, highly distorted in the case of **9**. The intermetallic Rh(1)···Rh(2) separation, 2.8397(7) Å in **6,** is considerably longer than that observed in **9**, 2.7404(6) Å, most likely due to the additional presence of the bridging diphosphine ligand. In spite of this difference, both intermetallic distances are close to those reported in related complexes where the presence of an attractive intermetallic interaction has been suggested.[20] However, in both complexes the rhodium atoms are out of the LSQ-planes calculated through the coordinated atoms (0.1087(4) Å in **6**, and 0.5712(5), 0.5644(5) Å in **9**) moving away from the other Rh center. These observations suggest the absence of an attractive intermetallic interaction and point towards the bridging system as the cause for the short Rh···Rh separations observed.

The Rh-S bond distances in **6**, 2.3769(11) and 2.4096(11) Å, are significantly shorter than the values observed in **9** (mean value 2.429(1) Å) probably as a consequence of the better π-acceptor character of the carbonyl groups compared to that of the diphosphine. As observed for the Zr-S bond distances, the Rh-S bond lengths in **9** also show the asymmetry of the central $ZrRh_2S_2$ skeleton (see Table 2). The two Rh-P bonds in **9** (mean 2.252(1) Å) are shorter than the values found in the binuclear rhodium complex $[Rh_2Cl_2(CO)_2(dppm)_2]$ (2.3141(9), 2.3315(9) Å).[21]

Catalytic activity

The complex $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**6**) in the presence of different P-donor ligands has been used as catalyst precursor in toluene for the hydroformylation of oct-1-ene under mild conditions of temperature and pressure. The effect of the P/Rh ratio of different monodentate P-

donor ligands in the hydroformylation reaction has been studied and the data obtained from these experiments are presented in Table 3. It is remarkable that the hydrogenation product (octane) has only been observed in trace amounts (< 1%), while 1-nonanal and 2-methyloctanal are exclusively obtained in these reactions; 2-ethylheptanal and 2-propylhexanal were not detected.

When $P(OMe)_3$ was used as modifying ligand (P/Rh = 2) a 79% conversion of 1-octene, at 100 PSI and 353 K, was obtained in 8 h (entry 1). The aldehyde selectivity was 95% with a 76% regioselectivity for the linear aldehyde. Increasing the P/Rh ratio to 4 resulted in an increase of the conversion up to 92% with identical aldehyde selectivity and only slight improvement of the regioselectivity (entry 2). Higher P/Rh ratios provided higher regioslectivity (82%) but significant lower conversion in spite of slight reduction of the isomerization activity (entry 3).

The catalytic system obtained using $P(OPh)_3$ as modifying ligand is much less selective in the hydroformylation of 1-octene as a consequence of the high isomerization activity that produces internal n-octenes (mainly 2-octene isomers). It is noticeable that under the experimental conditions these internal olefins do not react, since neither 2-ehylheptanal nor 2-proylhexanal were detected by GC. Although a significant reduction of the isomerization activity has been observed as the ligand to metal ratio is increased, the optimal ratio found P/Rh = 4 gave a 99% conversion in 8h with a moderate aldehyde selectivity (81%) and 81% regioselectivity for the linear aldehyde (entry 5).

The combinations of the catalytic precursor **6** with other P-donor ligands, such as triphenyl or trialkyl phosphines, gave systems that are much less active for the hydroformylation of oct-1-ene under identical conditions. For example, when PPh_3 was used as modifying ligand (P/Rh = 6) a 32% conversion of 1-octene was attained in 8 h. The aldehyde selectivity was 90% with a 74% regioselectivity for the linear aldehyde (entry 8).

Discussion

The Synthesis of Trinuclear ZrM_2 Early-Late Heterobimetallic Complexes (M = Rh, Ir).

The present study was aimed to prepare new complexes of zirconium and rhodium or iridium of the type early-late d^0-d^8, which could be useful for catalytic processes or reactivity studies. The search for an appropriate zirconium precursor lead us to synthesize[15] the metallocene hydrosulfide complex $[Cp^{tt}_2Zr(SH)_2]$ with two bulky cyclopentadienyl rings. This compound shows a remarkable stability with respect to the elimination of H_2S when compared with the analogous compound $[Cp_2Zr(SH)_2]$, probably because of the steric shielding of the metal atom given by the bulky substituents on the cyclopentadienyl rings. Moreover, the deprotonation of the hydrosulfide groups in $[Cp^{tt}_2Zr(SH)_2]$ was accomplished by reaction with with n-BuLi at low temperature to give solutions that behave as a source of the zirconium-sulfido metallocene $[Cp^{tt}_2ZrS_2]^{2-}$ anion. This species is a rare example of complex of the Group 4 metals containing terminal sulfido ligands,[22] which was not isolated. Evidence of such anion in these solutions comes from the isolation of the new trinuclear complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{ML_2\}_2]$ obtained through its reactions of metathesis with d^8-$[\{MClL_2\}_2]$ (M = Rh, Ir) metal chloride complexes. The heterobimetallic complexes result from the coordination of two d^8-ML_2 metal fragments to both sulfur atoms of the anionic metallaligand to give a predictable triangular disposition of the metals. On the other hand, this result diverges with the deprotonation of $[Cp_2Ti(SH)_2]$ with strong bases[23] to give the dianion $[\{CpTi(S)\}_2(\mu\text{-}S)_2]^{2-}$ with elimination of cyclopentadiene. The latter provides a way to the complexes of the cores "$CpTiS_3M_3$" and "$Cp_2Ti_2S_4M_2$", but in turn, makes inaccessible the related complexes $[Cp_2Ti(\mu_3\text{-}S)_2\{ML_2\}_2]$ through a similar route.

Alternative syntheses of the complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{ML_2\}_2]$ are the additive-deprotonation reactions of $[Cp^{tt}_2Zr(SH)_2]$ with suitable rhodium and iridium complexes. These reactions are strongly sensitive to the ancillary ligands on the d^8-metal complexes used in the

syntheses and to the solvent. As smaller and better π-acceptor the ancillary ligands are the cleanest reaction results, as exemplified by the multiple ways to prepare [$Cp^{tt}_2Zr(\mu_3$-$S)_2\{Rh(CO)_2\}_2$] (**6**) almost quantitatively. On the contrary, the syntheses of the complexes with the bulkiest diolefin cod, [$Cp^{tt}_2Zr(\mu_3$-$S)_2\{M(cod)\}_2$] (**3-4**), are frequently accompanied by the formation of the hydride clusters [$M_3(\mu$-$S)_2(\mu$-$H)(cod)_3$] (M = Rh, Ir)[17, 18] as well as free HCp^{tt} (NMR evidence), due to the transference of the sulfido ligands. Monitoring these reactions evidence that the formation of the dinuclear intermediary species [$Cp^{tt}_2Zr(\mu_2$-$S)(\mu_2$-$SH)M(cod)$] is faster than the further additive-deprotonation to give the ZrM_2 core (Scheme 3) in aprotic solvents. Thus, two of such complexes, [$Cp^{tt}_2Zr(\mu_2$-$S)(\mu_2$-$SH)Rh(nbd)$] and [$Cp^{tt}_2Zr(\mu_2$-$S)(\mu_2$-$SH)Rh(cod)$], were detected by ^1H NMR in the early stages of the reactions of [$Cp^{tt}_2Zr(SH)_2$] with [Rh(acac)(nbd)] and with [$\{Rh(\mu$-$OMe)(cod)\}_2$], respectively, in $CDCl_3$.[24] Since the dinuclear intermediate species from the first step accumulate and then evolve to the final products, the second step is slow in aprotic solvents. Therefore, we believe that the slowness of the second step along with the sensitivity of the intermediate species to the byproducts of these reactions (MeOH, Hacac, $HNEt_3^+$ or H_2O) are the source of the side reactions in aprotic solvents. In methanol, however, the reactions occur faster with two opposite results shown by the quite a clean synthesis of compound **3** from the reaction of [$Cp^{tt}_2Zr(SH)_2$] with [$\{Rh(\mu$-$OH)(cod)\}_2$] and the complete transfer of the sulfido groups in the reaction with the iridium complex in this solvent.

The influence of the solvent in the reactions leading to the early-late heterotrinuclear complexes become evident in the synthesis of the complex [$Cp^{tt}_2Zr(\mu_3$-$S)_2\{Ir(CO)_2\}_2$] (**7**), which is isolated in 72% from the reaction of $[IrCl_2(CO)_2]^-$ with [$Cp^{tt}_2Zr(SH)_2$] in dichloromethane/MeOH. A partial transfer of the sulfide ligands occurs in this mixture of solvents, since the anionic triiridium carbonyl complex $[Ir_3(\mu_3$-$S)_2(CO)_6]^-$ [25] and the methoxo

zirconium complexes $[Cp^{tt}_2Zr(OMe)_2]$ and $[Cp^{tt}_2ZrCl(OMe)]$ [26] are detected in the solution remaining after crystallization by IR and ^1H NMR. However, in the absence of methanol the yield in **7** is considerably reduced (< 20%) because an extensive formation of $[Ir_3(\mu_3\text{-}S)_2(CO)_6]^-$ occurs.

The additive-deprotonation of $[Cp^{tt}_2Zr(SH)_2]$ with the complexes $[M(acac)L_2]$ gives acetylacetone (Hacac) which may interfere in the synthesis of ZrM_2 heterotrinuclear complexes. This is the case of the reaction of $[Cp^{tt}_2Zr(SH)_2]$ with [Ir(acac)(cod)] to give $[Cp^{tt}(acac)Zr(\mu_3\text{-}S)_2\{Ir(cod)\}_2]$ (**5**), which involves the replacement of one cyclopentadienyl ring on the early metal by acetylacetonate. Moreover, this type of replacement has been found to occur in the reactions of $[Cp_2Ti(SH)_2]$ with $[M(acac)L_2]$ to give cleanly the diolefin complexes $[Cp(acac)Ti(\mu_3\text{-}S)_2\{M(diolefin)\}_2]$.[13] Although it might be though that the replacement of Cp by acac occurs in an intermediate step, an independent experiment showed that $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(cod)\}_2]$ (**4**) reacts cleanly with Hacac to give **5**.

A further example of the replacement of one cycopentadienyl ring by acac in $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2]$ (**7**) was observed on monitoring the reaction of $[Cp^{tt}_2Zr(SH)_2]$ with $[Ir(acac)(CO)_2]$ by IR in dichloromethane. The complex $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2]$ (**7**) is formed in the early stages of the reaction, and then $[Cp^{tt}(acac)Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2]$ (**8**) results from the reaction of **7** with the acetylacetone present in the reaction medium. Finally, the reaction is further complicated by the transfer of sulfido ligands to give $[Ir_3(\mu_3\text{-}S)_2(CO)_6]^-$, which become predominant at extended reaction times.

Restricted rotation in Trinuclear ZrM_2 Early-Late Heterobimetallic Complexes (M = Rh, Ir).

The introduction of sterically demanding substituents in metallocene complexes result in significant barriers to rotation about the metal-cyclopentadienyl bond.[27] The bulky substituents in bent metallocenes with a wedge-like structure exhibit a strong preference to occupy sites in the

open part of the wedge but repulsions between the subtituents on different rings causes the rings to adopt a mutually staggered conformation.[28] The disposition of the *tert*-butyl groups found in the solid state for mononuclear bent metallocene complexes containing Cp^{tt} ligands ranges from the nearly eclipsed conformation in $[Cp^{tt}_2TiCl_2]$ [29] (torsión angle between the Cp^{tt} rings, C_2-G(1)-G(2)-C_2'), -34.8(3)°) to a partially staggered conformation found in $[Cp^{tt}_2ZrI_2]$ [30] (-119.27°). An intermediate situation has been found in the complex $[Cp^{tt}_2Zr(SH)(OSO_2CF_3)]$ with a torsión angle between the Cp^{tt} rings of 52.4(5)°.[15]

The diolefin complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{M(diolefin)\}_2]$ exist in solution as two rotamers arising from the hindered rotation of the cyclopentadienyl rings about the Cp^{tt}(centroid)-Zr axis. In contrast, the carbonyl compounds $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{M(CO)_2\}_2]$ (**6-7**) show no restriction to the rotation of the Cp^{tt} rings. Therefore, the steric demand of the ancillary ligands (L) on the ML_2 fragments determinates whether the Cp^{tt} ligands can rotate freely or undergo a restricted rotation or they do not rotate at all. An associated fact is that the steric demand of the ancillary diolefin ligands influence also strongly the ratio of both rotamers, Thus, while the eclipsed rotamer prevails in the complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(nbd)\}_2]$ (**1**) and $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(tfbb)\}_2]$ (**2**) the predominance of the staggered results evident for the complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{M(cod)\}_2]$ (**4**). This observation is again in agreement with the larger bulkiness of the 1,5-cyclooctadiene ligands, and reflects that the main contribution to the energetic barrier associated to the rotation of the Cp^{tt} ligands is the steric demand of the ancillary ligands on the d^8 metal centers. The constancy in the ratio of rotamers for compounds **1** and **2**, independent of the synthetic method, strongly suggest that both rotamers interconvert in solution, as it was confirmed experimentally for **1**. In addition, we have found that the temperature has a little effect on the ratio of rotamers, since the proportion of the staggered rotamer in **1** increase from 38 to 41% in the range 273 and 328 K in $CDCl_3$.

The preference for the staggered conformation observed for cod complexes **3** and **4** and the lack of interconversion with the eclipsed isomer indicates that the rotational barrier in these compounds is exceedingly high, and then the rotation of the Cp^{tt} ligands is frozen. Thus, although rotational barriers associated to the rotation of η^5-cyclopentadienyl metal complexes have generally been found to be less than 13 Kcal mol^{-1},[31] the significant steric hindrance produced by a single Rh(cod) fragment in the ELHB complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{ML_2\}_2]$ results in the larger rotational barrier of 17.2 kcal mol^{-1} found for the trimetallic complex $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}\{Rh(cod)\}]$, which exists as two interconverting rotamers in solution.[16]

The replacement of two carbonyl ligands in $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**6**) by P-donor ligands is enough to cause a restricted rotation of the Cp^{tt} ligands in the complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)(P(OR)_3)\}_2]$ (**11-12**) independly of the cone angle of the phosphite ligands (R = Me, 107°, R = Ph, 128°).[32] In sharp contrast, the related complexes containing a bridging *dppm* ligand $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{M(CO)\}_2(\mu\text{-dppm})]$ (**9-10**) show a free rotation of the Cp^{tt} ligands.

In order to ascertain which factors affect to the rotation of the Cp^{tt} ligands in the heterotrinuclear complexes it should be noticed the steric influence of the X groups on the narrow ("back") portion of the zirconocene wedge in bent metallocenes $[Cp_2MX_2]$. It has been shown that the conformation of the Cp^{tt} and Cp' ligands (Cp' = 1,3-bistrimetylsilylcyclopentadienyl) in uranocene complexes $[Cp_2UX_2]$ is directly related to the size of the X ligands.[33] The complexes show an idealized C_{2v} structure (eclipsed conformation) for X = F, Cl, Br, and a C_2 structure (partially staggered conformation) with larger ligands such as as I or Me. In addition, this steric influence is also transferred to the back of the metallocene "clam-shell" in such a way that as larger is the size of the X ligand, the angle between the idealized planes of both Cp ligands results smaller. This effect can be observed in the zirconium chemistry on comparing the complexes $[Cp^{tt}_2ZrCl_2]$ [34] and $[Cp^{tt}_2ZrI_2]$, [30] with angles of 58.9(1)° and 53.04°, respectively.

As far as the $ZrRh_2$ complexes is concerned, the angle between the idealized planes of both Cp^{tt} ligands in the complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**6**) and $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}\{Rh(cod)\}]$ are 61.63(16)º and 53.8(4)º respectively. The angle of 62.1(2)º observed in the complex $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)\}_2(\mu\text{-dppm})]$ (**9**), similar to that of the carbonyl complex, is large enough to allow the free rotation of the Cp^{tt} ligands. An additional difference with the related phosphite complexes **11**, **12** is the bridging coordination mode of the *dppm* ligand. This produces an important contraction of the Rh-Rh separation along with a very distorted coordination environment around the rhodium atoms with small P-Rh-S angles, and prevents the rotation about the Rh-P bonds. These factors working together result in a reduction of the steric encumbrance of the dinuclear subunit "$Rh_2(\mu\text{-}S)_2(\mu\text{-dppm})(CO)_2$" in the complexes **9-10** with reference to "$Rh_2(\mu\text{-}S)_2(CO)_2(P(OR)_3)_2$" in the complexes **11-12**, which seems to be enuogh to allow the free rotation of the Cp^{tt} rings.

Replacement reactions and catalytic activity.

The ZrM_2 triangular core in the heterotrinuclear carbonyl clusters $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{M(CO)_2\}_2]$ (**6-7**) (M = Rh, Ir) is maintained in the replacement reactions of carbonyl by P-donor ligands. The outcome of these reactions depends on the character of the P-donor ligands as exemplified by the reactions with *dppm*, $P(OMe)_3$ and $P(OPh)_3$. Thus, the replacement reactions with the short-bite bidentate *dppm* ligand are stereoselective and the products $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{M(CO)\}_2(\mu\text{-dppm})]$ (**9-10**) are cleanly obtained as a single isomer. In contrast, the disubstituted complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)(P(OR)_3)\}_2]$ (**11-12**) are obtained as a *cis*/*trans* mixture of isomers as the result of the unselective replacement of the carbonyl ligands. The lack of stereoselectivity in the substitution process has also been observed in the tetracarbonyl complexes $[Cp(acac)Ti(\mu_3\text{-}S)_2\{M(CO)_2\}_2]$[13] and $[\{M(\mu_2\text{-}SR)(CO)_2\}_2]$ (M = Rh, Ir),[35] that contain two symmetrically arranged sulfido and thiolate bridging ligands respectively.

In view of the interest in the development of new heterobimetallic catalyst that might lead to increased catalytic activity with enhanced chemo- and regioselectivity in the hydroformylation of alkenes, we have studied the catalytic activity of the cluster $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**6**). Interestingly, certain early-late heterobimetallic systems have been shown to be efficient hydroformylation catalysts.[5] In fact, we have recently described that the tetranuclear early-late heterobimetallic complexes $[CpTi(\mu_3\text{-}S)_3\{Rh(diolefin)\}_3]$ in presence of P-donor ligands are active precursors in the hydroformylation of hex-1-ene and styrene.[5a]

The compound $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**6**) in combination with monodentate P-donor ligands provides catalytic systems which are active in the hydroformylation of oct-1-ene under mild conditions of pressure and temperature. The catalytic systems obtained with phosphite ligands $P(OR)_3$ are much more active than the corresponding with triphenylphosphine (Table #). In addition, the system formed with $P(OMe)_3$ is much more selective than the system obtained with $P(OPh)_3$, giving an aldehyde selectivity of 95% with a regioslectivity close to 80% with the optimal ligand to metal ratio. The investigation of the solutions obtained after the hydroformylation reactions with the precursor **6** shows no evidence of the complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)(P(OR)_3)\}_2]$ (**11-12**), which indicates that the heterotrinuclear complexes are not maintained as such, and most probably they break down to active monomeric rhodium species. This behavior is opposite to the observed in the hydroformylation of hex-1-ene using the catalyst precursor $[CpTi(\mu_3\text{-}S)_3\{Rh(diolefin)\}_3]$ in which PPh_3 gave superior results than the $P(OR)_3$ ligands. High pressure NMR spectroscopic studies have shown that under hydroformylation conditions the 62-electron clusters $[CpTi(\mu_3\text{-}S)_3Rh_3(\mu\text{-}CO)(CO)_4(PPh_3)_2]$ and $[CpTi(\mu_3\text{-}S)_3Rh_3(\mu\text{-}CO)(CO)_3(PPh_3)_3]$ are formed. Interestingly, the resting state of the precursor after the catalysis is the heterotetranuclear compound $[CpTi(\mu_3\text{-}S)_3\{Rh(CO)(PPh_3)\}_3]$, obtained by decarbonylation of the later, which indicated an outstanding stability of the

heterotetranuclear framework.[5]

Concluding Remarks

The zirconium bis-hydrosulfido complex $[Cp^{tt}_2Zr(SH)_2]$ containing the bulky Cp^{tt} ligands is a precursor for the synthesis of d^0-d^8 early-late heterotrinuclear clusters with the cores $ZrRh_2$ and $ZrIr_2$. The controlled synthesis of these compounds can be accomplished through additive-deprotonation reactions involving rhodium and iridium complexes. The clusters possess the predictable triangular structure, which have no precedent in the related titanium chemistry. Some of the compounds exist in solution as two rotamers as a consequence of the hindered rotation of the Cp^{tt} ligands. It is noteworthy that this phenomenon is affected by the steric demand of the ancillary ligands bonded to the d^8 metal fragments, which is transmitted to the metallocene moiety through the modification of the angle between the idealized planes of both cyclopentadienyl ligands.

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 complex $[Cp^{tt}_2Zr(SH)_2]$ was prepared as described previously.[15] Standard literature procedures were used to prepare the mononuclear complexes [M(acac)(diolef)] (M = Rh, diolef = nbd, tfbb;[36] M = Ir, diolef = cod[37]), $[Rh(acac)(CO)_2]$[38] and $(PPh_3Bz)[MCl_2(CO)_2]$ (M = Rh, Ir).[39] The compounds $[\{Rh(\mu\text{-}Cl)(nbd)\}_2]$,[40] $[\{Rh(\mu\text{-}OH)(cod)\}_2]$[41] and $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$[42] were prepared according to previously reported methods, and 1-octene was purchased from Aldrich and was distilled prior to use.

Scientific Equipment. ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian

Gemini 300 spectrometers operating at 300.08, 121.47 MHz 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 (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P) as external reference respectively. Assignments in complex NMR spectra were done by simulation with the program gNMR© v 3.6 (Cherwell Scientific Publishing Limited) for Macintosh. The initial choice of chemical shifts and coupling constants were optimized by successive iterations following a standard least-squares procedure, a numerical assignment of the experimental frequencies was used. IR spectra were recorded on a Nicolet-IR^{TM} 550 spectrometer (4000-400 cm^{-1}. Elemental C, H and N analysis were performed in a 240-C Perkin-Elmer microanalyzer. In several cases we encountered difficulty (as have other investigators)[43] in obtaining satisfactory elemental analyses on zirconium complexes, due presumably to incomplete combustion. Molecular weights were determined with a Knauer osmometer using chloroform solutions of the complexes. 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. Hydroformylation experiments were carried out in a stainless steel magnetically stirred autoclave (100 mL) equipped with a thermocouple and an external heating mantle. The syngas (CO/H_2 = 1) was supplied at constant pressure from a ballast. The drop in pressure in the ballast was monitored using a pressure transducter.

Standard Hydroformylation Experiment. In a typical run, a solution of the catalyst precursor $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**6**) (0.017 mmol), containing the phosphine or phosphite ligand (0.20-0.60 mmol), 1-octene (10.2 mmol) and toluene (15.4 mL) was transferred from a Schlenk tube under argon to the autoclave by using a stainless steel cannula. The autoclave was purged with syngas three times at 120 PSI and then pressurized at 50 PSI and heated at 80 ºC. When the thermal equilibrium was reached, the pressure was adjusted at 100 PSI and the mixture stirred for 8 h with the continuous supply of syngas at constant pressure. After the reaction time, the

autoclave was cooled at room temperature and depressurized. The reaction mixture was analysed by gas chromatography with a Hewlett-Packard 5890 equipped with a capillary column (HP, ULTRA 1, 25m x 0.32mm x 0.17 μm) and a flame-ionization detector. The products were quantified by the internal standard method using anisole.

Synthesis of the complexes. [$Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(nbd)\}_2$] (1). **Method A**. To a finely divided solid mixture of [$Cp^{tt}_2Zr(SH)_2$] (0.100 g, 0.195 mmol) and [Rh(acac)(nbd)] (0.115 g, 0.390 mmol) was added 10 mL of methanol at room temperature. The suspension, which turned from yellow to brick-orange within 1 min, was stirred for 30 min. The brick-orange solid was filtered, washed with methanol (5 mL) and vacuum-dried. Yield: 0.148 g (84%). **Method B.** [$Cp^{tt}_2Zr(SH)_2$] (0.100 g, 0.195 mmol) was reacted with triethylamine (60 μL, 0.432 mmol) and [{Rh(μ-Cl)(nbd)}$_2$] (0.090 g, 0.195 mmol) in dichloromethane (10 mL) for 30 min to give a brown cloudy solution. The solvent was removed under vacuum and the residue washed with methanol (10 mL) and diethyl ether (5 mL). The crude was extracted with dichloromethane (20 mL) and then filtered to give a clear brown red solution. Addition of n-hexane (50 mL) and concentration of the solution to *ca* 15 mL afforded the compound as an orange-brown solid which was filtered, washed with n-hexane (10 mL) and dried under vacuum. Yield: 0.105 g (60%). **Method C**. A pale yellow solution of [$Cp^{tt}_2Zr(SH)_2$] (0.100 g, 0.195 mmol) in diethyl ether (10 mL) was reacted with n-butyllithium (156 μL, 2.5 mol·L^{-1}, 0.39 mmol) at -50 ^{o}C. Then, solid [{Rh(μ-Cl)(nbd)}$_2$] (0.090 g, 0.195 mmol) was added to this solution and the temperature was let to increase to -0 ^{o}C for 1 h. The resulting brown-red suspension was evaporated to dryness. Recrystallization of the residue from dichloromethane/n-hexane following the procedure described above gave the compound in 62% yield (0.109 g). Anal. Calcd for $C_{40}H_{58}S_2Rh_2Zr$: C, 53.38; H, 6.49; S, 7.12. Found. C, 53.32; H, 6.78; S, 7.11. MS (FAB$^+$, CH_2Cl_2, m/z): 898 (M^+, 37%), 806 (M^+ - nbd, 14%), 721 (M^+ - Cp^{tt}, 100%). Mol. Weight. Found: 902 (Calcd. 900). ^{1}H

NMR ($CDCl_3$, 293K). Rotamer **1a** (60%) δ: 6.67 (t, 2.4 Hz, 2H, H_2), 5.71 (d, 2.4 Hz, 4H, H_4 and H_5) (Cp^{tt}), 4.26-3.68 (m, 12H, =CH and CH), 1.43-1.33 (m, 4H, $>CH_2$) (nbd), 1.31 (s, 36H, *t*-Bu). Rotamer **1b** (40%) δ: 7.36 (d, 2.6 Hz, 2H, H_4 and H_5), 5.59 (t, 2.6 Hz, 1H, H_2) (Cp^{tt}), 6.61 (t, 2.6 Hz, 1H, H_2), 5.72 (d, 2.6 Hz, 2H, H_4 and H_5) (Cp^{tt}), 4.26-3.68 (m, 12H, =CH and CH), 1.43-1.33 (m, 4H, $>CH_2$) (nbd), 1.32 and 1.24 (s, 18H each, *t*-Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293K). Rotamer **1a** δ: 146.2 (C_1 and C_3), 117.7 (C_2), 107.7 (C_4 and C_5) (Cp^{tt}), 62.8 (d, J_{Rh-C} = 6.5 Hz, $>CH_2$), 57.8 and 51.5 (br d, J_{Rh-C} = 9.2 Hz, =CH), 51.2 and 50.2 (br, CH) (nbd), 34.1 (CMe_3), 32.6 (CMe_3). Rotamer **1b** δ: 148.6 (C_1 and C_3), 139.6 (C_1 and C_3), 121.6 (C_2), 117.3 (C_4 and C_5), 110.0 (C_2), 104.1 (C_4 and C_5) (Cp^{tt}), 63.0 and 62.7 (d, J_{Rh-C} = 6.5 Hz, $>CH_2$), 56.7 and 52.5 (br d, J_{Rh-C} = 9.2 Hz, = *C*H), 49.2 (br, CH) (nbd), 34.3 and 33.7 (CMe_3), 32.9 and 31.9 (CMe_3).

$[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(tfbb)\}_2]$ (2). To a finely divided solid mixture of $[Cp^{tt}_2Zr(SH)_2]$ (0.100 g, 0.195 mmol) and [Rh(acac)(tfbb)] (0.167 g, 0.390 mmol) was added 10 mL of methanol at room temperature. The yellow suspension, which turned progressively dark orange, was stirred for 1 h and then filtered to give a brick-orange powder, which was washed with methanol (5 mL) and dried under vacuum. Yield: 0.212 g (93%). Anal. Calcd for $C_{50}H_{54}F_8S_2Rh_2Zr$: C, 51.41; H, 4.66; S, 5.49. Found. C, 51.17; H, 4.66; S, 5.47. MS (FAB^+, CH_2Cl_2, m/z): 1166 (M^+, 43%), 989 (M^+ - Cp^{tt}, 100%), 940 (M^+ - tfbb, 21%), 714 (M^+ - 2tfbb, 11%). ^1H NMR ($CDCl_3$, 293K). Rotamer **2a** (55%) δ: 6.91 (t, 2.4 Hz, 2H, H_2), 5.92 (d, 2.4 Hz, 4H, H_4 and H_5) (Cp^{tt}), 5.66 and 5.50 (m, 2H each, CH), 4.03-3.80 (m, 8H, =CH) (tfbb), 1.34 (s, 36H, *t*-Bu). Rotamer **2b** (45%) δ: 7.48 (d, 2.4 Hz, 2H, H_4 and H_5), 5.76 (t, 2.4 Hz, 1H, H_2) (Cp^{tt}), 6.85 (t, 2.4 Hz, 1H, H_2), 5.92 (d, 2.4 Hz, 2H, H_4 and H_5) (Cp^{tt}), 5.82, 5.64, 5.47 and 5.45 (m, 1H each, CH), 4.03-3.80 (m, 8H, =CH) (tfbb), 1.35 and 1.21 (s, 18H each, *t*-Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293K). Rotamer **2a** δ:

147.4 (C_1 and C_3), 118.2 (C_2), 109.0 (C_4 and C_5) (Cp^{tt}), 57.0 and 53.9 (d, J_{Rh-C} = 9.7 Hz) (=CH region, tfbb), 34.3 (CMe_3), 32.5 (CMe_3). Rotamer **2b** δ: 149.8 (C_1 and C_3), 141.0 (C_1 and C_3), 122.3 (C_2), 118.2 (C_4 and C_5), 110.7 (C_2), 105.5 (C_4 and C_5) (Cp^{tt}), 57.2, 56.0, 54.3, and 53.5 (d, J_{Rh-C} = 9.9 Hz) (=CH region, tfbb), 33.9 and 34.5 (CMe_3), 32.9 and 31.8 (CMe_3).

$[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(cod)\}_2]$ (3). Method A. A pale yellow solution of $[Cp^{tt}_2Zr(SH)_2]$ (0.056 g, 0.11 mmol) in diethyl ether (10 mL) was reacted with n-butyllithium (130 μL, 1.68 mol·L^{-1}, 0.22 mmol) at -60 °C. Then, solid $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ (0.054 g, 0.11 mmol) was added to this solution and the temperature was let to increase to room temperature for 2 h. The resulting dark-brown suspension was evaporated to dryness and the residue was washed with methanol (3x10mL) to give a black-brown crystalline solid, which was dried under vacuum. Yield: 0.083 g (81 %). **Method B.** To a finely divided solid mixture of $[Cp^{tt}_2Zr(SH)_2]$ (0.100 g, 0.195 mmol) and $[\{Rh(\mu\text{-}OH)(cod)\}_2]$ (0.089 g, 0.195 mmol) was added 10 mL of methanol at room temperature to give a light brown suspension which was stirred for 30 min. The brown solid was filtered, washed with methanol (5 mL) and dried under vacuum. Yield: 0.157 g (86%). Anal. Calcd for $C_{42}H_{66}S_2Rh_2Zr$: C, 54.12; H, 7.14; S, 6.88. Found: C, 53.82; H, 8.02; S, 7.07. MS (FAB^+, CH_2Cl_2, m/z): 930 (M^+, 32%), 822 (M^+ - cod, 25%), 753 (M^+ - Cp^{tt}, 100%), 714 (M^+ - 2cod, 21%). ^1H NMR ($CDCl_3$, 293K). Rotamer **3b** δ: 7.32 (d, 2.6 Hz, 2H, H_4 and H_5), 5.70 (t, 2.6 Hz, 1H, H_2) (Cp^{tt}), 6.48 (t, 2.6 Hz, 1H, H_2), 5.89 (d, 2.6 Hz, 2H, H_4 and H_5) (Cp^{tt}), 4.42 (br m, 6H, =CH), 4.29 (br m, 2H, =CH), 2.7-1.7 (m, 16H, $>CH_2$) (cod), 1.32 and 1.26 (s, 18H each, *t*-Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293K) δ: 148.4 (C_1 and C_3), 139.9 (C_1 and C_3), 121.0 (C_2), 117.0 (C_4 and C_5), 111.0 (C_2), 105.5 (C_4 and C_5) (Cp^{tt}), 79.4, 79.2, 78.2, and 78.1 (d, J_{Rh-C} = 11.5 Hz, =CH, cod), 34.5 and 33.7 (CMe_3), 33.0 and 32.0 (CMe_3), 31.6, 31.0, and 30.9 ($>CH_2$, cod).

A mixture of the staggered (**3b**) and eclipsed (**3a)** rotamers in a 85:15 molar ratio was observed on monitoring the reaction of Method B in $CDCl_3$ by ^1H NMR. Rotamer **3a**: δ : 6.63 (t, 2.4 Hz, 2H, H_2), 5.86 (d, 2.4 Hz, 4H, H_4 and H_5), 1.32 (s, 36H, *t*-Bu).

[$Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(cod)\}_2$] (4). A solution of [$Cp^{tt}_2Zr(SH)_2$] (0.056 g, 0.11 mmol) in diethyl ether (10 mL) at -60º C was treated with n-butyllithium (0.134 mL, 1.68 mol·L^{-1}, 0.225 mmol). Then, solid [{Ir(μ-Cl)(cod)}$_2$] (0.074 g, 0.11 mmol) was added to this solution and the temperature was let to increase to -20º C for 1h. The resulting black-green suspension was evaporated to dryness. The residue was washed with 6 mL of diethyl ether/methanol (1/1) and then with methanol (3x5mL) to give a black-green solid, which was dried under vacuum. Yield: 0.062 g (51 %). Satisfactory elemental analyses could not be obtained for this compound although it was chaaracterized by spectroscopic methods as follows. MS (FAB^+, CH_2Cl_2, m/z): 1110 (M^+, 28%), 933 (M^+ - Cp^{tt}, 100%). ^1H NMR ($CDCl_3$, 293K). Rotamer **4a** (20%) δ : 6.37 (t, 2.7 Hz, 2H, H_2), 6.00 (d, 2.7 Hz, H_4 and H_5), 3.97 (m, 8H, =CH cod), 2.45-2.30, 1.90-1.80 and 1.72 (m, 6H each, $>CH_2$ cod), 1.32 (s, 36H, *t*-Bu). Rotamer **4b** (80%) δ: 7.15 (d, 2.4 Hz, 2H, H_4 and H_5), 5.78 (t, 2.4 Hz, 1H, H_2) (Cp^{tt}), 6.25 (t, 2.4 Hz, 1H, H_2), 6.04 (d, 2.4 Hz, 2H, H_4 and H_5) (Cp^{tt}), 3.93-3.85 (m, 8H, =CH cod), 2.45-2.30, 1.90-1.80 and 1.74 (m, 6H each, $>CH_2$ cod), 1.32 and 1.26 (s, 18H each, *t*-Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293K). Rotamer **4b** δ: 149.9 (C_1 and C_3), 141.3 (C_1 and C_3), 120.1, 119.9 (C_2, C_4 and C_5) 112.5 (C_2), 107.3 (C_4 and C_5) (Cp^{tt}), 64,7, 63.8, 62.6, and 60.5 (=CH, cod), 34.8 and 34.0 (CMe_3), 33.0 and 31.9 (CMe_3), 32.6, 31.7, and 31.3 ($>CH_2$, cod).

[Cp^{tt}(acac)$Zr(\mu_3\text{-}S)_2\{Ir(cod)\}_2$] (5). To a yellow solution of [Ir(acac)(cod)] (0.400 g, 1.001 mmol) in diethyl ether (40 mL) was added solid [$Cp^{tt}_2Zr(SH)_2$] (0.256 g, 0.500 mmol). The mixture was refluxed to give a blue-greenish solution in one hour. The solvent was removed

under vacuum and the residue was washed with methanol (2x5 mL) at -78 °C. The crude was extracted with n-pentane (40 mL) and then filtered to give a dark blue solution. Evaporation to dryness under reduced pressure gave the compound as a dark blue powder. Yield: 0.284 g (55%). Anal. Calcd for $C_{34}H_{52}O_2S_2Ir_2Zr$: C, 39.55; H, 5.08; S, 6.21. Found: C, 39.38; H, 5.13; S, 6.19. MS (FAB$^+$, CH_2Cl_2, m/z): 1032 (M^+, 100%), 924 (M^+ - cod, 20%), 855 (M^+ - Cp^{tt} , 67%), 747 (M^+ - cod - Cp^{tt}, 32%). ^{1}H NMR ($CDCl_3$, 293 K) δ: 7.02 (d, 2.7 Hz, 2H, H_4 and H_5, Cp^{tt}), 5.81 (s, 1H, CH, acac), 5.47 (t, 2.7 Hz, 1H, H_2, Cp^{tt}), 3.96 (br m, 8H, =CH), 2.21 (m, 4H, >CH_2) (cod), 2.00 (s, 6H, CH_3, acac), 1.83 (m, 8H, >CH_2), 1.57 (m, 4H, >CH_2) (cod), 1.16 (s, 18H, *t*-Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ 190.5 (*C*O, acac), 144.7 (C_1 and C_3), 108.5 (C_4 and C_5), 107.9 (C_2) (Cp^{tt}), 105.1 (CH, acac), 65.0 and 62.8 (=CH, cod), 33.0 (*C*Me_3), 32.9 and 31.5 (>CH_2, cod), 31.1 (C*Me*$_3$), 26.0 (CH_3, acac).

[$Cp^{tt}_2Zr(\mu_3$-S)$_2${Rh(CO)$_2$}$_2$] (6). Method A. Carbon monoxide was bubbled through a deep red solution of [$Cp^{tt}_2Zr(\mu_3$-S)$_2${Rh(nbd)}$_2$] (0.140 g, 0.156 mmol) in benzene (10 mL) at room temperature for 15 min to give a dark green solution. Then, n-hexane (20 mL) was added and the bubbling was continued for 15 min more to give an emerald green suspension which was kept overnight at 7ºC under CO atmosphere. The suspension was quickly filtered, washed with n-hexane (2x10 mL) and dried under vacuum. Yield: 0.098 g (76%). **Method B**. [Rh(acac)(CO)$_2$] (0.504 g, 1.953 mmol) was added to a yellow solution of [$Cp^{tt}_2Zr(SH)_2$] (0.500 g, 0.977 mmol) in diethyl ether (20 mL). The solution immediately turned dark-green and a solid crystallized out while stirring for 10 min at room temperature. Filtration of the resulting suspension gave the compound as an emerald-green microcrystalline powder after washing with n-hexane (2x10 mL) and drying in vacuo. Yield: 0.753 g (93%). **Method C**. Triethylamine (60 μl, 0.432 mmol) and [{Rh(μ-Cl)(CO)$_2$}$_2$] (0.076 g, 0.196 mmol) were rapidly and succesively added to a vigorously stirred solution of [$Cp^{tt}_2Zr(SH)_2$] (0.100 g, 0.195 mmol) in dichloromethane (5 mL) at room

temperature. The yellow solution turned emerald green inmmediately and a green solid started to precipitate. The reaction mixture was stirred for 5 min and then 10 mL of metanol were added. After stirring for 5 min more the solid was collected by filtration, washed with 10 mL of methanol and dried under vacuum. Yield 0.153 g (95%). **Method D**. [$Cp^{tt}_2Zr(SH)_2$] (0.100 g, 0.195 mmol), triethylamine (60 μl, 0.432 mmol) and (PPh_3Bz)[$RhCl_2(CO)_2$] (0.228 g, 0.391 mmol) were reacted in dichloromethane (5 mL), following the procedure described in method C, to give a green suspension. Work-up as above gave the compound in 92% yield (0.148 g). Anal. Calcd for $C_{30}H_{42}O_4S_2Rh_2Zr$: C, 43.53; H, 5.11; S, 7.75. Found: C, 43.60; H, 5.12; S, 7.82. MS (FAB+, CH_2Cl_2, m/z): 826 (M^+, 29%), 770 (M^+ - 2CO, 39%), 742 (M^+ - 3CO, 34%), 714 (M^+ - 4CO, 100%). ^{1}H NMR ($CDCl_3$, 293K) δ: 6.56 (t, 2.6 Hz, 2H, H_2), 6.03 (d, 2.6 Hz, 4H, H_4 and H_5), 1.31 (s, 36H, *t*-Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ : 185.3 (d, J_{Rh-C} = 73 Hz, *C*O), 148.6 (C_1 and C_3), 121.3 (C_2), 109.0 (C_4 and C_5), 34.6 (*C*Me_3), 32.3 (C*Me*$_3$). IR (CH_2Cl_2, cm^{-1}): ν(CO), 2066 (s), 2041 (s), 1994 (s).

[$Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2$] (7). Triethylamine (290 μl, 2.086 mmol) and finely divided (PPh_3Bz)[$IrCl_2(CO)_2$] (1.315 g, 1.955 mmol) were quickly and successively added to a strongly stirred yellow solution of [$Cp^{tt}_2Zr(SH)_2$] (0.500 g, 0.977 mmol) in 35 mL of dichloromethane/methanol (1/6) at room temperature. The solution became immediately dark green and a apple-green microcrystalline solid started to precipitate. After stirring for 5 min the solid was filtered, washed with methanol (2x10 mL) and diethyl ether (2x10 mL), and dried under vacuum. Yield: 0.708 g (72%). Anal. Calcd for $C_{30}H_{42}O_4S_2Ir_2Zr$: C, 35.80; H, 4.21; S, 6.37. Found: C, 35.37; H, 4.11; S, 6.38. MS (FAB+, CH_2Cl_2, m/z): 1006 (M^+, 93%), 829 (M^+ - Cp^{tt}, 100%). ^{1}H NMR ($CDCl_3$, 293K) δ: 6.74 (t, 2.6 Hz, 2H, H_2), 6.24 (d, 2.6 Hz, 4H, H_4 and H_5), 1.31 (s, 36H, *t*-Bu). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K) δ : 174.7 (*C*O), 150.0 (C_1 and C_3), 127.5 (C_2), 111.0 (C_4 and C_5), 35.1 (*C*Me_3), 32.1 (C*Me*$_3$). IR (CH_2Cl_2, cm^{-1}): ν(CO), 2056 (s),

2027 (s), 1979 (s).

[Cp^{tt}(acac)Zr(μ_3-S)$_2${Ir(CO)$_2$}$_2$] (8). Carbon monoxide was bubbled through a solution of [Cp^{tt}(acac)Zr(μ_3-S)$_2${Ir(cod)}$_2$] (**6**) (0.200 g, 0.194 mmol) in n-pentane (20 mL) to give a golden-brown suspension in 20 min. The suspension was cooled to -78 ^{o}C and then filtered to gave a golden microcrystalline solid which was washed with n-pentane at low temperature and dried under vacuum. Yield: 0.157 g (87%). Anal. Calcd for $C_{22}H_{28}O_6S_2Ir_2Zr$: C, 28.47; H, 3.04; S, 6.91. Found: C, 28.35; H, 3.14; S, 6.83. ^{1}H NMR ($CDCl_3$, 293 K): δ 6.96 (d, 2.5 Hz, 2H, H_4 and H_5, Cp^{tt}), 6.01 (s, 1H, CH, acac), 5.87 (t, 2.5 Hz, 1H, H_2, Cp^{tt}), 2.09 (s, 6H, CH_3, acac), 1.23 (s, 18H, *t*-Bu). ^{13}C{^{1}H} NMR ($CDCl_3$, 293 K,): δ 191.9 (*C*O, acac), 174.3 (Ir-*C*O), 147.0 (C_1 and C_3), 112.3 (C_4 and C_5), 110.7 (C_2) (Cp^{tt}), 107.4 (CH, acac), 33.4 (*C*Me$_3$), 30.9 (C*Me*$_3$), 26.0 (CH_3, acac). IR (CH_2Cl_2, cm^{-1}): ν(CO), 2058 (s), 2033 (s), 1983 (s).

[Cp^{tt}_2Zr(μ_3-S)$_2${Rh(CO)}$_2$(*μ*-dppm)] (9). A solid mixture of [Cp^{tt}_2Zr(μ_3-S)$_2${Rh(CO)$_2$}$_2$] (0.19 g, 0.23 mmol) and dppm (0.088 g, 0.23 mmol) was dissolved in dichloromethane (5 mL) to give a dark green solution with evolution of carbon monoxide. The reaction mixture was stirred for 10 min at room temperature and then n-hexane (15 mL) was added. Concentration of the solution under vacuum to ca 5 mL gave the compound as a black-greenish microcrystalline solid, which was filtered, washed with 2x5 mL of n-hexane and dried under vaccum. Yield: 0.253 g (95%). Anal. Calcd for $C_{53}H_{64}O_2P_2S_2Rh_2Zr$: C, 55.06; H, 5.58; S, 5.55. Found: C, 54.68; H, 5.62; S, 5.47. MS (FAB$^+$, CH_2Cl_2, m/z): 1154 (M^+, 15%), 1126 (M^+ - CO, 6%), 1098 (M^+ - 2CO, 100%). ^{1}H NMR (C_6D_6, 293 K): δ 7.70-6.50 (m, 20H, dppm), 6.19, 5.62 and 5.48 (br, 2H each, H_2, H_4 and H_5, Cp^{tt}), 4.64 and 2.54 (br m, 1H each, >CH_2 dppm), 1.64 and 1.15 (br, 18H each, *t*-Bu). ^{13}C{^{1}H} NMR (C_6D_6, 293 K): δ 193.8 (br d, J_{Rh-C} = 88 Hz, Rh-*C*O), 144.6 and 144.0 (br, C_1 and C_3, Cp^{tt}), 137.2 and 135.4 (d, J_{P-C} = 45 Hz, C_{ipso}), 133.9 (m), 132.1 (m), 129.7

(s), 129.4 (s), 128.7 (m), 127.8 (m) (dppm), 118.2, 106.5 and 106.1 (br, C_2, C_4 and C_5, Cp^{tt}), 34.4 and 33.5 (br s, *C*Me_3), 32.9 and 32.4 (br s, C*Me*$_3$), 28.1 (t, J_{P-C}= 34 Hz, >CH_2 dppm). $^{31}P\{^1H\}$ NMR (C_6D_6, 293 K): δ 24.9 (br d, J_{Rh-P} = 169 Hz). This signal results in a AA'XX' spin system (A = ^{31}P and X = ^{103}Rh) centered at δ 24.7 ppm at 213 K, which has been successfully simulated with the parameters $^1J_{Rh-P}$ = 171 Hz, $^2J_{P-P}$ = 35 Hz and $^3J_{Rh-P}$ = -1.7 Hz. IR (CH_2Cl_2, cm^{-1}): ν(CO), 1962 (s), 1933 (s).

[$Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)\}_2(\mu\text{-dppm})$] (10). To a suspension of [$Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2$] (0.061 g, 0.061 mmol) in dichloromethane (7 mL) a solution of dppm (0.023 g, 0.061 mmol) in dichloromethane (7 mL) was slowly added to give a brown yellow solution upon evolution of carbon monoxide. After 30 min, the solvent was removed under vacuum and the residue extracted with n-hexane (30 ml) and then filtered. Cooling of the solution to -40 °C gave the compound as orange crystals, which were collected by filtration at low temperature. Yield: 0.057 g (70%). Anal. Calcd for $C_{53}H_{64}O_2P_2S_2Ir_2Zr$: C, 47.69; H, 4.83; S, 4.80. Found: C, 44.09; H, 4.29. MS (FAB^+, CH_2Cl_2, *m/z*, %): 1333 (M^+, 76%), 1278 (M^+- 2CO, 62%), 1157 (M^+- Cp^{tt}, 100%). ^1H NMR ($CDCl_3$, 293 K): δ 7.58 (m, 4H), 7.38 (m, 4H), 7.20 (m, 12H) (dppm), 5.72 (m, 4H), 5.22 (t, 2H) (Cp^{tt}), 3.45 (m, 2H, >CH_2 dppm), 1.29 and 0.99 (s, 18H each, *t*-Bu). ^{31}P NMR ($CDCl_3$, 293 K): δ 11.4 (s). IR (CH_2Cl_2, cm^{-1}): ν(CO), 1965 (s), 1925 (s).

[$Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)(P(OMe)_3)\}_2$] (11). To a solution of [$Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2$] (0.100 g, 0.121 mmol) in toluene (5 mL) was slowly added a solution of $P(OMe)_3$ (28.6μl, 0.242 mmol) in toluene (4 mL) to give a green solution upon evolution of carbon monoxide. The solvent was removed under vacuum and the residue dissolved in n-hexane (3 mL). Stirring of the solution gave the compound as a green-apple microcrystalline solid which was filtered, washed with n-hexane and dried under vaccum. Yield: 0.086 g (70%). Anal. Calcd for

$C_{34}H_{60}O_8P_2S_2Rh_2Zr$: C, 40.04; H, 5.93; S, 6.29. Found: C, 38.28; H, 4.79. MS (FAB$^+$, CH_2Cl_2, m/z): 1019 (M^+, 22%), 962 (M^+ - 2CO, 15%), 838 (M^+ - 2CO - $P(OMe)_3$, 90%). IR (toluene, cm^{-1}): ν(CO), 1978 (m), 1963 (s, br). $^{31}P\{^1H\}$ NMR (C_6D_6, 293 K): Rotamer *trans*-**11a**: δ 139.7 (AA'XX' spin system, $^1J_{Rh-P}$ = 273 Hz, $^3J_{P-P}$ = 3 Hz, $^2J_{Rh-P}$ = -1.3 Hz, $^1J_{Rh-Rh}$ = 17 Hz). Rotamer *cis*-**11a**: δ 140.2 (d, $^1J_{Rh-P}$ = 272 Hz). Rotamers *trans*-**11b** and *cis*-**11b**: δ 140.3 (d, $^1J_{Rh-P}$ = 272 Hz), 139.5 (d, $^1J_{Rh-P}$ = 270 Hz), 139.4 (d, $^1J_{Rh-P}$ = 272), 138.2 (d, $^1J_{Rh-P}$ = 271 Hz).

$[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)(P(OPh)_3)\}_2]$ (12). To a solution of $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (0.048 g, 0.058 mmol) in toluene (5 mL) was slowly added a solution of $P(OPh)_3$ (31 μl, 0.116 mmol) in toluene (4 mL) to give a green solution upon evolution of carbon monoxide. Work-up as above gave the compound as a green-apple microcrystalline solid which was filtered, washed with n-hexane and dried under vaccum. Yield: 0.052 g (64%). Anal. Calcd for $C_{64}H_{72}O_8P_2S_2Rh_2Zr$: C, 55.21; H, 5.21; S, 4.61. Found: C, 55.02; H, 5.43; S, 4.42. MS (FAB$^+$, CH_2Cl_2, m/z): 1390 (M^+, 27%), 1024 (M^+ - 2CO - $P(OPh)_3$, 94%), 931 (M^+ - 2CO - $P(OPh)_3$ – OPh, 100%). IR (toluene, cm^{-1}): ν(CO), 1995 (s, br), 1981 (m, br). $^{31}P\{^1H\}$ NMR (C_6D_6, 293 K): Rotamer *trans*-**12a**: δ 118.6 (AA'XX' spin system, $^1J_{Rh-P}$ = 296 Hz, $^3J_{P-P}$ = 3 Hz, $^2J_{Rh-P}$ = -1.5 Hz, $^1J_{Rh-Rh}$ = 21 Hz). Rotamer *trans*-**12b**: δ 119.36 and 119.28 ppm (ABXY, spin system, $^1J_{Rh-P}$ = 296 Hz, $^3J_{P-P}$ = 8 Hz, $^2J_{Rh-P}$ = -8.4 Hz, $^1J_{Rh-Rh}$ = 24 Hz).

Structural determination of complexes 6 and 9. Single crystals for the X-ray diffraction studies were grown by slow diffusion of n-hexane into concentrated solutions of the complexes in dichloromethane (-20 °C) (**9**) or dichloromethane/acetonitrile (**6**) in the freezer. A summary of crystal data, data collection, and refinement parameters for the structural analysis is given in Table 4. A green (**6**) or a black crystal (**9**) were glued to a glass fibre and mounted on Bruker SMART APEX or Bruker AXS-SMART diffractometer, respectively. Both instruments were

equipped with CCD area detectors and data were collected using graphite-monochromated Mo Kα radiation (λ= 0.71073 Å) and low-temperature equipment (100 K for **6** and 150 K for **9**). Cell constants for **6** were obtained from the least-squares refinement of three-dimensional centroids of 3383 reflections in the range 4.6 ≤ 2θ ≤ 56.4°and from 150 reflections in the region 4.6 ≤ 2θ ≤ 38° for **9**. Data were measured through the use of CCD recording of ω rotation frames (0.3° each). All data were corrected for Lorentz and polarization effects. Absorption correction for **6** was applied by using the SADABS routine[44] and the DIFABS strategy[45] for **9.** Both were integrated with the Bruker SAINT program.[46]

Structures were solved by Patterson (**6**) or direct methods (**9**)**.** Both structures were completed by subsequent difference Fourier techniques and refined by full-matrix least-squares on F^2 (SHELXL-97)[47] with initial isotropic thermal parameters. One solvation water molecule per dinuclear complex was observed in **6**. Two cristallographically independent molecules and two solvent molecules (CH_2Cl_2) were detected for **9**. Anisotropic thermal parameters were used in the last cycles of refinement for all non-hydrogen atoms in **6**, except for the oxygen of the water molecule and for all non-hydrogen atoms in **9**, except carbon atoms involved in a disordered phenyl group and those atoms of the solvent molecule. A model of rotational disorder based on two alternative positions was assumed for the disordered phenyl group of **9**. Two 'CCl_2' moieties of complementary occupancy factors (0.54(1) and 0.46(1)) were also included to account for the disordered solvent molecule. Hydrogen atoms were included in calculated positions in both **6** and **9** and refined with positional and thermal parameters riding on carbon atoms. Atomic scattering factors were used as implemented in the program.[47]

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for complexes **6** and **9** is available. This material is available free of charge via the Internet at http://pubs.acs.org.

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Table 1. Selected Bond Distances (Å) and angles (deg) for complex **6**

Rh···Rh'	2.8397(7)	Zr-S	2.5214(11)
Rh···Zr	3.3302(7)	Zr-C(3)	2.591(4)
Rh-S	2.3769(11)	Zr-C(4)	2.621(4)
Rh- S'	2.4096(11)	Zr-C(5)	2.639(4)
Rh-C(1)	1.868(5)	Zr-C(6)	2.505(4)
Rh-C(2)	1.858(5)	Zr-C(7)	2.484(4)
		Zr- G*	2.272(2)
S-Rh- S'	84.18(4)	S-Zr-S'	79.02(5)
S-Rh-C(1)	170.76(14)	S-Zr-G*	111.97(6)
S'-Rh- C(1)	91.97(14)	S-Zr-G'*	107.88(6)
S-Rh-C(2)	89.47(15)	G-Zr-G'*	127.62(7)
S'-Rh-C(2)	173.15(15)		
C(1)-Rh-C(2)	93.9(2)		
Rh-S-Rh'	72.77(3)	Rh-C(1)-O(1)	176.7(4)
Rh-S-Zr	85.61(3)	Rh-C(2)-O(2)	177.8(4)
Rh-S'-Zr	84.93(3)		

*G and G' represent the centroids of the cyclopentadienyl ligands.

Table 2. Selected Bond Distances (Å) and angles (deg) for the complex **9***

Rh(1)···Zr(1)	3.3378(11)	3.2963(10)	Rh(2)···Zr(1)	3.3219(10)	3.3638(10)
Rh(1)···Rh(2)	2.7399(9)	2.7410(9)			
Rh(1)-P(1)	2.255(2)	2.246(2)	Rh(2)-P(2)	2.257(2)	2.248(2)
Rh(1)-S(1)	2.440(2)	2.467(2)	Rh(2)-S(1)	2.414(2)	2.408(2)
Rh(1)-S(2)	2.422(2)	2.396(2)	Rh(2)-S(2)	2.437(2)	2.450(2)
Rh(1)-C(27)	1.818(9)	1.827(9)	Rh(2)-C(28)	1.837(9)	1.789(9)
Zr(1)-S(1)	2.461(2)	2.458(2)	Zr(1)-S(2)	2.507(2)	2.507(2)
Zr(1)-G(1)$^{\#}$	2.295(4)	2.310(4)	Zr(1)-G(2)$^{\#}$	2.302(4)	2.292(4)
P(1)-Rh(1)-S(1)	149.44(8)	147.66(8)	P(2)-Rh(2)-S(1)	147.45(8)	150.47(8)
P(1)-Rh(1)-S(2)	85.53(8)	85.53(8)	P(2)-Rh(2)-S(2)	87.71(8)	87.78(7)
P(1)-Rh(1)-C(27)	96.8(3)	96.3(3)	P(2)-Rh(2)-C(28)	96.0(3)	95.5(3)
S(1)-Rh(1)-S(2)	84.42(7)	84.39(7)	S(1)-Rh(2)-S(2)	84.63(7)	84.50(7)
S(1)-Rh(1)-C(27)	96.0(3)	96.2(3)	S(1)-Rh(2)-C(28)	95.0(3)	96.3(3)
S(2)-Rh(1)-C(27)	174.4(3)	175.3(3)	S(2)-Rh(2)-C(28)	173.4(3)	171.4(3)
S(1)-Zr(1)-S(2)	82.19(7)	82.29(7)	G(1)-Zr(1)-G(2)$^{\#}$	126.86(15)	126.64(14)
S(1)-Zr(1)-G(1)$^{\#}$	109.27(13)	108.48(11)	S(2)-Zr(1)-G(1)$^{\#}$	109.96(12)	110.59(11)
S(1)-Zr(1)-G(2)$^{\#}$	111.14(11)	111.83(11)	S(2)-Zr(1)-G(2)$^{\#}$	108.41(11)	108.16(11)
Rh(1)-S(1)-Rh(2)	68.73(6)	68.41(6)	Rh(1)-S(2)-Rh(2)	68.66(6)	68.88(6)
Rh(1)-S(1)-Zr(1)	85.86(7)	84.03(6)	Rh(1)-S(2)-Zr(1)	85.23(7)	84.46(7)
Rh(2)-S(1)-Zr(1)	85.90(7)	87.46(7)	Rh(2)-S(2)-Zr(1)	84.41(7)	85.47(6)
Rh(1)-C(27)-O(1)	176.8(8)	177.0(8)	Rh(2)-C(28)-O(2)	176.4(8)	178.9(9)

*Values in the second column are for the second crystallographically independent molecule. $^{\#}$G(1) and G(2) represent the centroids of the cyclopentadienyl ligands.

Table 3. Hydroformylation of 1-octene using the complex $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**6**) as catalyst precursor. [a]

Run	Ligand	P/Rh	Conversion [b] (%)	Selectivity (%) [b]		% n
				Aldehyde	Isomerisation	
1	$P(OMe)_3$	2	79	95	5	76
2	$P(OMe)_3$	4	92	95	5	78
3	$P(OMe)_3$	6	80	98	2	82
4	$P(OPh)_3$	2	66	71	29	80
5	$P(OPh)_3$	4	99	81	19	81
6	$P(OPh)_3$	6	99	82	18	82
7	PPh_3	4	27	93	7	75
8	PPh_3	6	32	90	10	74

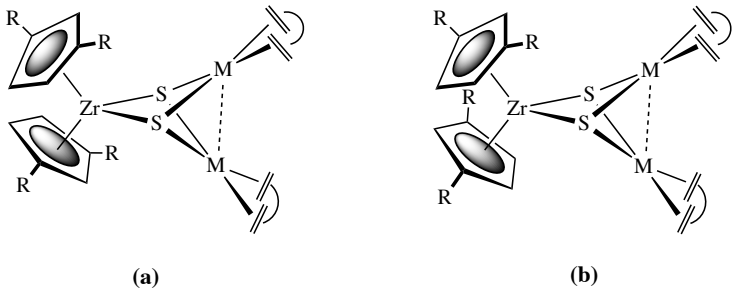
[a] *Reaction conditions:* 100 PSI (CO/H_2, 1/1), 353 K, t = 8 h. 1-octene (10.2 mmol, 0.6M), $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (0.017 mmol, 1 mM). [b] Determined by GC.

Table 4. Crystal data, Data Collection and Refinement for complexes **6** and **9**

	6	**9**
empirical formula	$C_{30}H_{42}O_4Rh_2S_2Zr \cdot H_2O$	$C_{53}H_{64}O_2P_2Rh_2S_2Zr \cdot CH_2Cl_2$
fw	845.81	1241.07
cryst size,mm	0.252 x 0.116 x 0.064	0.36 x 0.20 x 0.20
crystal system	monoclinic	triclinic
space group	*P*2/n (No.13)	*P*-1 (No. 2)
a, Å	12.6643(12)	11.1621(5)
b, Å	9.4235(9)	22.1108(11)
c, Å	13.4335(13)	22.1713(11)
α, °	90	87.408(1)
β, °	95.247(2)	88.050(1)
γ, °	90	84.023(1)
V, A^3	1596.5(3)	5434.3(5)
Z	2	4
D_{calcd}, gcm^{-3}	1.760	1.517
μ, mm^{-1}	1.509	1.061
no. of measd reflns	10461 ($2.1 \leq \theta \leq 28.5$)	44437 ($2.6 \leq \theta \leq 30.1$)
no. of unique reflns	3696 (R_{int}= 0.0302)	18474 (R_{int}= 0.0698)
min, max transm fact	0.737 , 0.910	0.7012 , 0.8158
no of data/restraints/param	3328/0/193	12892/0/1188
GOF(all data)[a]	1.098	1.061
$R_1(F)$ ($F^2 \geq 2\sigma(F^2)$)[b]	0.0431	0.0711
$wR_2(F^2)$ (all data)[c]	0.1154	0.1435

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

Captions to the Figures



(a) (b)

Figure 1. The two limiting rotamers observed in solution for the complexes $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{M(diolefin)\}_2]$: (a) eclipsed rotamer ($C_{2v}$ symmetry), (b) staggered rotamer (C_s symmetry).

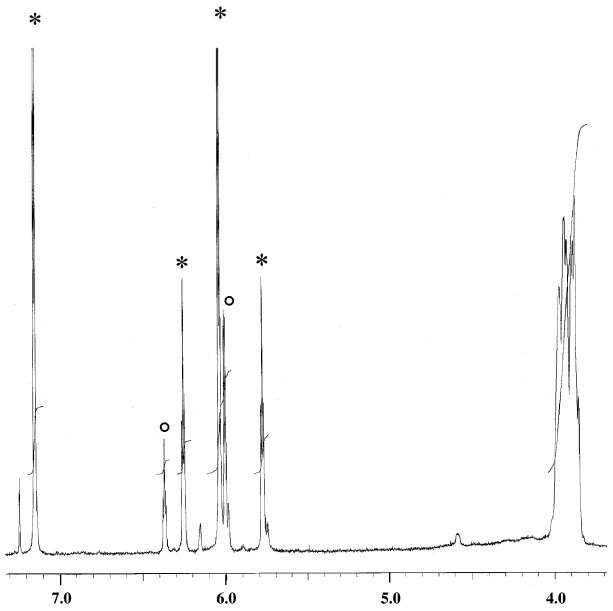


Figure 2. Part of the ^1H NMR spectrum of $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Ir(cod)\}_2]$ (**4**) in $CDCl_3$ showing the signals of the cyclopentadienyl and olefinic protons of cod (* eclipsed rotamer, ° staggered rotamer). Residual resonances are due to $CHCl_3$ and decomposition products.

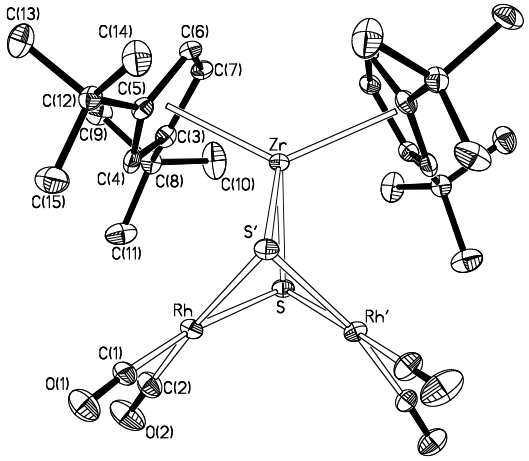


Figure 3. Molecular structure of $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**6**).

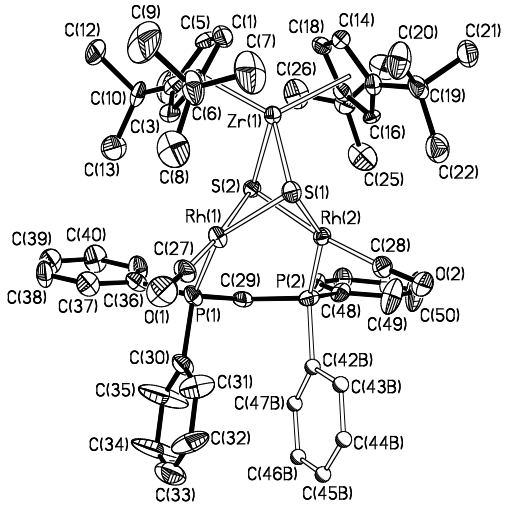


Figure 4. View of the molecular structure of $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)\}_2(\mu\text{-dppm})]$ (**9**). One of the phenyl rings of the dppm ligand is disordered (C(42B)-C(47B)).

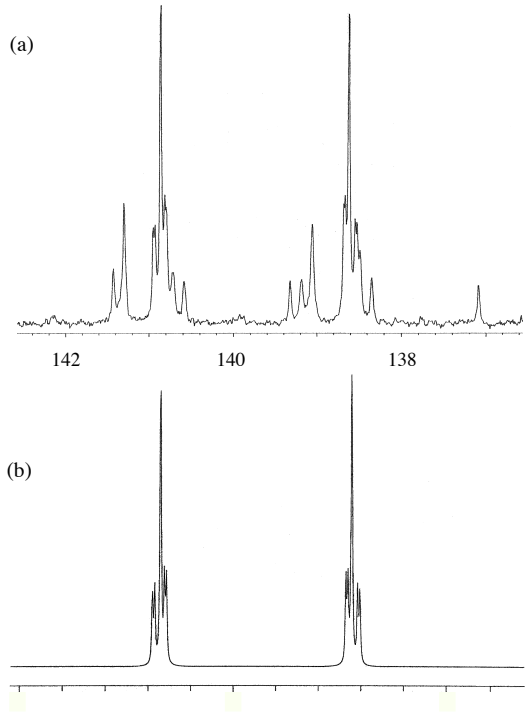


Figure 5. a) $^{31}P\{^{1}H\}$ NMR spectrum of $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)(P(OMe)_3)\}_2]$ (**11**) showing the presence of the *cis*/*trans* isomers with the corresponding rotamers. b) Calculated $^{31}P\{^{1}H\}$ NMR spectrum for the AA'XX' spin system observed for the eclipsed rotamer of the *trans* isomer (*trans*-**11a**).

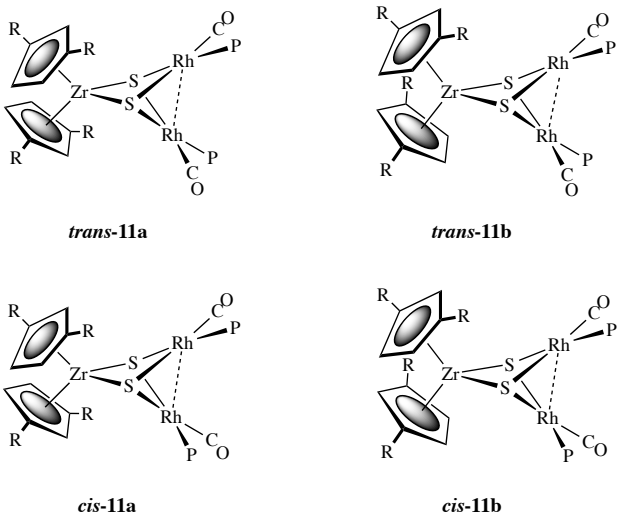
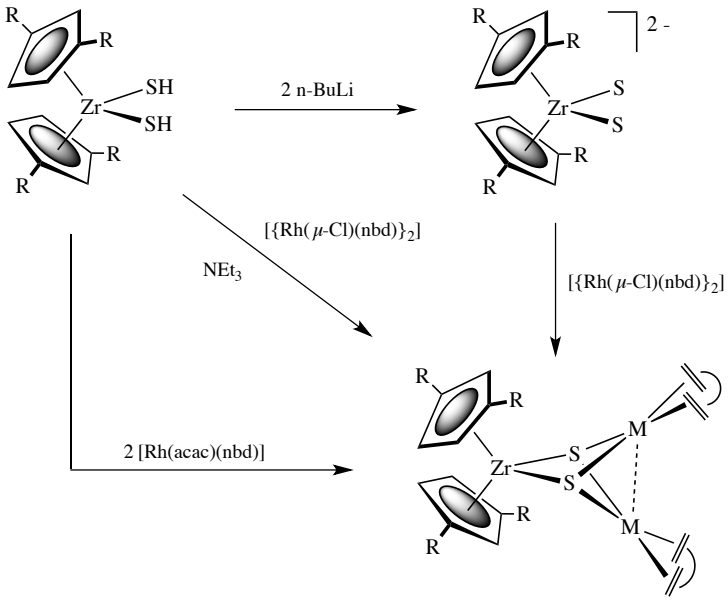
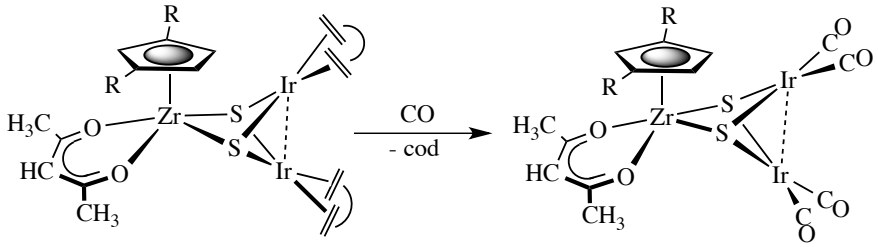


Figure 6. *Cis*/*trans* isomers of the compounds $[Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)(P(OR)_3)\}_2]$ (**11-12**) with the corresponding eclipsed and staggered rotamers.

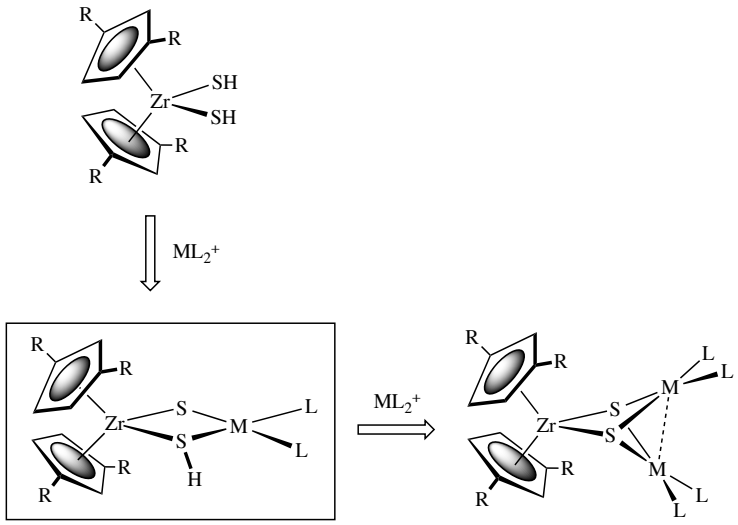


Scheme 1



5 **8**

Scheme 2



Scheme 3