Early (Ti, Zr) - Late (Rh, Ir) Heteronuclear Complexes with Bridging Sulfido Ligands.

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Abstract - We report on this account on the controlled synthesis of novel d^0-d^8 early-late heteropolynuclear diolefin and carbonyl clusters. The synthetic approach was based on additive-deprotonation reactions involving the titanium and zirconium bis-hydrosulfido complexes of formula $[Cp_2Ti(SH)_2]$ and $[Cp^{tt}{}_2Zr(SH)_2]$ and appropriate rhodium and iridium diolefin and carbonyl compounds. The significant differences between the resulting early-late complexes and their structures coming from the titanium or zirconium metalloligand precursors are highlighted. The catalytic activity of some representative titanium-rhodium and zirconium-rhodium compounds towards alkene hydroformylation was explored. Interestingly, the heterotetranuclear "$CpTi(\mu_3$-$S)_3Rh_3$" structure was maintained as such under mild conditions.

Keywords: **early-late / heteronuclear / rhodium / iridium / titanium / zirconium / hydroformylation**

Résumé - Complexes Hétéronucléaires Early (Ti, Zr) – Late (Rh, Ir) à Ponts Sulfure. Nous rapportons dans cet article la préparation contrôlée de nouveaux clusters hétéropolynucléaires “early-late” d^0-d^8 portant les ligands oléfine et carbonyle. La réaction de déprotonation-addition a été la méthode de synthèse utilisée et implique la condensation de complexes bis-hydrogénosulfure du titane et du zirconium, de formule $[Cp_2Ti(SH)_2]$ et $[Cp^{tt}{}_2Zr(SH)_2]$, sur les composés adéquats du rhodium et de l’iridium portant les ligands oléfine et carbonyle. Les différences significatives de structure des complexes “early-late” ainsi préparés, dûes à la nature du metalloligand précurseur du titane ou du zirconium employé, sont mises en évidence. L’activité catalytique de quelques composés représentatifs titane-rhodium et zirconium-rhodium dans l’hydroformylation d’alcènes a été mesurée. Il convient de noter que la structure hétérotétranucléaire "$CpTi(\mu_3$-$S)_3Rh_3$" est maintenue comme telle sous des conditions douces de réaction.

Mots-clés: **early-late / hétéronucléaire / rhodium / iridium / titanium / zirconium / hydroformylation**

1. Introduction

In the last two decades important progress has been achieved in the development of rational strategies to control the structures and metal composition of multinuclear transition complexes. Part of this interest is due to the presence of multimetallic coordination sites that could facilitate unique chemical transformations through cooperative or successive interaction of the metal centers with substrate molecules [1-2].

Complexes having two widely divergent metals, one Lewis-acid early transition metal and the other an electron-rich late transition metal, are promising candidates for new stoichiometric and catalytic reactions. Moreover they could model the role of the support in heterogeneously catalyzed reactions [3-4]. If the metal centers could "speak each other", properties such as multifunctionality and cooperative effects should be expected. Nevertheless, the problems found to meet the different coordination environments of both metals in close proximity could be as great as the expectations, and thus synthetic strategies leading to new complexes are highly desirable. A goal is still to find ways to accommodate the different electronic and coordination environments required by the metals in close proximity in order to obtain stable compounds.

Transition metal complexes with bridging sulfur ligands have a broad scope comprising from a widely studied biological systems and applied industrial processes such as hydrodesulfurisation and catalysis to novel chemistry of molecular systems [5-8]. Organometallic early-late heterobimetallic complexes are relatively uncommon and efforts to develop this chemistry have been reviewed recently [9]. In particular, an elegant synthetic approach for early-late heterobimetallic complexes established by Stephan and coworkers, and other groups, involves early-metal complexes acting as metalloligands for late-transition metal species [10]. They include titanium and zirconium complexes with terminal thiolate [11], phosphide [12], and alkoxyalkylphosphine ligands [13], pendant chelating metalloligands [14-15] and also macrocyclic metalloligands [16]. Other useful metalloligands are based on early-metallocene complexes [17] and remarkable synthetic strategies involve the use of bis(cyclopentadienyl)titanacyclobutanes [18-20] or methylcarbene titanium complexes [21] to give methylene bridged early-late heterometallic complexes.

We report in this account recent progress on the preparation and reactivity of early, titanium and zirconium, - late, rhodium and iridium, transition metals sulfido complexes. It is well known the effectiveness of sulfur to behave as a good bridging ligand preventing the undesirable fragmentation of the heteronuclear framework. Our synthetic approach was based on the deprotonation of the bis-hydrosulfido titanium or zirconium complexes [$Cp_2M(SH)_2$] (M = Ti, Zr) by appropriate d^8 rhodium and iridium compounds containing diolefins or carbonyl groups as ancillary ligands. At first glance, the preparation of heterotrinuclear complexes containing the "$Cp_2M(\mu\text{-}S)_2M'_2$" (M´= Rh, Ir) framework should be expected, but this behavior is only favored for zirconium, while the loss of one coordinated cyclopentadienyl ligand from the titanium center is dominant. This loss creates additional coordination vacancies that should facilitate the preparation of complexes of higher nuclearity. We herein report on this rich heterometallic chemistry involving titanium and zirconium as early metals, and rhodium and iridium, as late transition metals.

2. Sulfido-Bridged Titanium-Rhodium and Titanium-Iridium Complexes

2.1. Heterobimetallic $TiRh_3$ and $TiIr_3$ Diolefin Complexes

The reported reactivity of $[Cp_2Ti(SH)_2]$ is very limited since its preparation in 1965 [22]. We initially recognized the ability of this compound to stabilize early-late polynuclear complexes by protonation of appropriate late transition metal complexes. We initially thought that the protonation of $[\{Rh(\mu\text{-}OMe)(diolefin)\}_2]$ (diolefin = 1,5-cyclooctadiene, cod; tetrafluorobenzobarrelene, tfbb) by $[Cp_2Ti(SH)_2]$ would yield heterotrinuclear complexes of the type $[Cp_2Ti(\mu_3\text{-}S)_2\{Rh(diolefin)\}_2]$, but the reaction was more complicated. Monitoring the reaction by ^1H NMR spectroscopy we observed that it proceeds quickly with formation of methanol, free cyclopentadiene and heterotetranuclear complexes of formula $[CpTi(\mu_3\text{-}S)_3\{Rh(diolefin)\}_3]$ as main products [23-24] (Scheme 1).

A similar protocol using $[Cp_2Ti(SH)_2]$ and $[\{Ir(\mu\text{-}OMe)(cod)\}_2]$ was not suitable for the synthesis of the related Ti-Ir complex $[CpTi(\mu_3\text{-}S)_3\{Ir(cod)\}_3]$, since this reaction followed an alternative pathway resulting in the formation of the known cluster $[Ir_3(\mu\text{-}S)_2(\mu\text{-}H)(cod)_3]$ in high yield [25]. As the latter hydridoiridium cluster can be obtained from $[\{Ir(\mu\text{-}Cl)(cod)\}_2]$ and NaHS or H_2S, the titanium complex acts, in fact, as a source of hydrosulfido ligands for iridium, one of which produces the oxidative-addition of the S-H bond leading to the hydrido ligand. To avoid this undesired reaction, we decide to use a deprotonated form of $[Cp_2Ti(SH)_2]$. Thus, $[Cp_2Ti(SH)_2]$ was reacted with butyllithium yielding a green solution of the anionic complex $[Cp_2Ti_2(\mu\text{-}S)_2(S)_2]^{2-}$, that showed identical color and ^1H NMR spectrum than that for the $Na_2[Cp_2Ti_2(\mu\text{-}S)_2(S)_2]$ complex, recently isolated by Kubas [26] from the monodeprotonation of $Cp_2Ti(SH)_2$ with sodium hydride. Solutions of the anion $[Cp_2Ti_2(\mu\text{-}S)_2(S)_2]^{2-}$, prepared in situ, were excellent starting materials for the synthesis of heterometallic iridium-titanium and rhodium-titanium complexes with sulfido bridging ligands providing also an insight on the above reactions. On reacting $[Cp_2Ti_2(\mu\text{-}S)_2(S)_2]^{2-}$ with the chloro-complexes $[\{M(\mu\text{-}Cl)(diolefin)\}_2]$ the compounds $[CpTi(\mu_3\text{-}S)_3\{M(diolefin)\}_3]$ (M = Rh, diolefin = cod, nbd, tfbb; Ir, diolefin = cod) resulted [23]. The complexes were isolated as air stable crystalline solids. Their NMR spectra were consistent with the incomplete cubane structure lacking one vertex, in which the group $[CpTi(S)_3]^{3-}$ capped a trimetallic triangle of the late-metals, as substantiated for $[CpTi(\mu_3\text{-}S)_3\{Rh(tfbb)\}_3]$ by X-ray diffraction methods [24]. This tetrafluorobenzobarrelene complex presented one titanium and three rhodium atoms engaged through three alternated triple-bridging sulfur atoms, each connecting two rhodium atoms to the titanium center. The central $TiRh_3S_3$ core exhibited an incomplete cubane-type structure, with one vacant site close to the three rhodium atoms, and the internal bond angles deviated slightly from the ideal value of 90°. The Rh-Ti separations were in the range 2.912-2.940(3) Å. These distances and the values of the Ti-S-Rh angles are consistent with a week dative interaction from the electron rich d^8 metal to the acid d^0 titanium center. A related oxoderivative of formula $[Cp^*Ti(\mu\text{-}O)_3\{Rh(cod)\}_3]$ was simultaneously reported, but in this case the titanium source was specifically a monocyclopentadienyl compound of formula $[Cp^*TiMe_3]$ [27].

The reactions leading to $[CpTi(\mu_3\text{-}S)_3\{Rh(diolefin)\}_3]$ complexes from $[Cp_2Ti(SH)_2]$ with the methoxorhodium complexes should proceed through a complicated mechanism sensitive to nucleophiles such as methanol, produced in the reactions. Remarkable observations on these syntheses were the incorporation of an extra sulfido ligand in the products, the removal of a cyclopentadienyl ligand initially bonded to titanium and the loss of some titanium from the starting material as unknown cyclopentadienyl products (Scheme 2). The transfer of a sulfido ligand between two titanium atoms requires the intermediacy of species with sulfido ligands bridging two titanium centers. The formation of such dinuclear species and the removal of the cyclopentadienyl ligand in these reactions was exemplified in a simple way by the reaction of $Cp_2Ti(SH)_2$ with BuLi. For this simplest case, monodeprotonation of the titanium complex, either with BuLi or NaH, should take place in a first instance to give the undetected intermediate $[Cp_2Ti(S)(SH)]^-$, followed by a transfer of the proton on the hydrosulfido ligand to one cyclopentadienyl ring. Similarly, $[Cp_2Ti(SH)_2]$ should be deprotonated by $[\{Rh(\mu\text{-}OMe)(cod)\}_2]$ to give methanol and the dinuclear complex $[Cp_2Ti(\mu\text{-}S)(\mu\text{-}SH)Rh(diolefin)]$, **A**. This unobserved intermediary species would lose the cyclopentadienyl ring, as does the anion $[Cp_2Ti(S)(SH)]^-$, either spontaneously or through interaction with methanol. Removal of one Cp ring from the reaction of bis(cyclopentadienyl) titanium complexes with methanol is a well known feature of these kind of compounds [28]. In any case, the dimerization of the resulting species would afford tetranuclear species of formula $[(CpTi)_2(\mu_3\text{-}S)_4\{Rh(diolefin)\}_2]$, **B**, with four sulfido bridging ligands. Complex **B** is also the expected product from the reactions of the anionic complex $[Cp_2Ti_2(\mu\text{-}S)_2(S)_2]^{2-}$ with the chlorocomplexes $[\{M(Cl)(diolefin)\}_2]$. Thus, both synthetic routes have in common this intermediate **B**, which possesses a cubane-type sulfido cluster structure. A further reaction of complex **B** with $[\{M(\mu\text{-}Cl)(diolefin)\}_2]$ or $[\{M(\mu\text{-}OMe)(diolefin)\}_2]$ would lead to the asymmetrical breaking of the sulphido bridges rendering the heterotetranuclear complexes $[CpTi(\mu_3\text{-}S)_3\{M(diolefin)\}_3]$ along with unknown cyclopentadienyltitanium complexes. This simplified mechanism explains the features for both synthetic approaches assuming the simplest intermediates. In particular, the proposed intermediate species, **B**, of formula $[(CpTi)_2(\mu_3\text{-}S)_4\{Rh(cod)\}_2]$ was isolated by reacting the thiotitanate anion, $[Cp_2Ti_2(\mu\text{-}S)_2(S)_2]^{2-}$, with $[\{Rh(\mu\text{-}Cl)(cod)\}_2]$ [29]. The synthesis and molecular structures of cubane-type sulfido clusters have been reported by Hidai and coworkers [29-30], that have confirmed our previous proposal of formation of $[CpTi(\mu_3\text{-}S)_3Rh_3(diolefin)_3]$ by the intermediacy of $[(CpTi)_2(\mu_3\text{-}S)_4\{Rh(diolefin)\}_2]$ and $[Cp_2Ti_2(\mu\text{-}S)_2(S)_2]^{2-}$ compounds, according to Scheme 2. In this context, it is important to mention the development, by Hidai and coworkers, of a variety of rational synthetic approaches for the preparation of cubane type sulfido clusters containing noble metals [30].

2.2. Heterobimetallic $TiRh_3$ and $TiIr_3$ Carbonyl Complexes

Replacement of the diolefin ligands in $[CpTi(\mu_3\text{-}S)_3\{M(diolefin)\}_3]$ (M = Rh, Ir) complexes by carbon monoxide takes place to give the hexacarbonyl compounds $[CpTi(\mu_3\text{-}S)_3\{M(CO)_2\}_3]$ (M = Rh, Ir). The nuclearity and the incomplete cubane framework of the starting materials are maintained in these reactions [23-24]. Reactions of the hexacarbonyl iridium complex with a variety of phosphine and phosphite ligands occurred readily under evolution of carbon monoxide to give the complexes $[CpTi(\mu_3\text{-}S)_3Ir_3(\mu\text{-}CO)(CO)_3(PR_3)_3]$ (PR_3 = PPh_3, PMe_3, $P(OMe)_3$, $PMePh_2$), containing a bridging carbonyl group, as evidenced by a ν(CO) band in the range 1770-1740 cm^{-1} in the IR spectra. Remarkable features in the structure of these compounds, as found for $[CpTi(\mu_3\text{-}S)_3Ir_3(\mu\text{-}CO)(CO)_3\{P(OMe_3)_3\}]$ by X-ray diffraction studies, are a distorted tetrahedral metal framework with short iridium-iridium distances and a tetrahedral coordination of the iridium atom closest to the titanium. The tetrahedral coordination of one iridium atom, together with the equatorial disposition of the phosphite ligands and consequent axial disposition for the carbonyl ligands, and the metal-metal bonding in the triiridium triangle are crucial in explaining the dynamic and chemical behaviour observed for these complexes [23]. While the bridging carbonyl group moves along the triangle, all the iridium centers are successively exchanging their stereochemistry, becoming tetrahedral and interacting with the titanium center. Moreover, the carbonyl exchange in these clusters with external CO is very fast as deduced from ^{13}CO-labeling NMR experiments. However, when the electron-rich tetrahedral iridium center is protonated (Scheme 3) the carbonyl scrambling ceases [23].

In contrast to the mentioned $[CpTi(\mu_3\text{-}S)_3Ir_3(\mu\text{-}CO)(CO)_3(PR_3)_3]$ compounds, where a bridging carbonyl was present, a complex of formula $[CpTi(\mu_3\text{-}S)_3Ir_3(CO)_3(PMe_2Ph)_3]$, lacking the bridging carbonyl ligand, was isolated when PMe_2Ph was used [23]. This type of complex is analogous to those resulting from the reactions of monodentate P-donor ligands with the rhodium complex [CpTi(μ_3-S)$_3${Rh(CO)$_2$}$_3$]. These replacement reactions are highly selective. Thus, the more symmetrical C_3 isomers of [CpTi(μ_3-S)$_3${Rh(CO)(PR$_3$)}$_3$] are the only isolated product in the case of monodentate phosphine (PPh$_3$, PMe$_3$ or PCy$_3$) and phosphite ligands (P(OPh)$_3$, P(OMe)$_3$ or P(*o*-OC$_6$H$_4$^{t}Bu)$_3$) [31]. Nevertheless, detailed multinuclear NMR studies at low temperature, have suggested that the formation of [CpTi(μ_3-S)$_3${Rh(CO)(PPh$_3$)}$_3$] from [CpTi(μ_3-S)$_3${Rh(CO)$_2$}$_3$] implied the intermediacy of 62-electron clusters, similar to the isolated iridium complexes, containing a bridging carbonyl ligand and a single Rh-Rh bond as shown in Scheme 4.

The substitution reactions on [CpTi(μ_3-S)$_3${Rh(CO)$_2$}$_3$] with diphosphines are strongly dependent on the nature of the diphosphine. Usually, only one molar-equiv. of diphosphine was easily incorporated into the heterotetranuclear framework (dppp or BINAP); nevertheless, in some cases, the replacement of four of the carbonyl ligands allowed the introduction of two molar-equiv. of 1,2-bis(diphenylphosphino)ethane (dppe). Thus, the reaction with one molar-equiv. of dppe gave the complex [CpTi(μ_3-S)$_3$Rh$_3$(CO)$_4$(μ-dppe)], whilst reaction with two molar-equiv. of the diphosphine gave [CpTi(μ_3-S)$_3$Rh$_3$(μ-dppe)(CO)$_2$(η^2-dppe)] [31]. In the above mentioned reactions the metal "CpTi(μ_3-S)$_3$Rh$_3$" framework was maintained in all replacement transformations.

2.3. Heterobimetallic TiRh$_2$ and TiIr$_2$ Diolefin Complexes

We have commented above on the ability of [Cp$_2$Ti(SH)$_2$] to protonate appropriate d^8 rhodium and iridium compounds yielding heterotetranuclear [CpTi(μ_3-S)$_3${M(diolefin)}$_3$] complexes, in which the group [CpTi(S)$_3$]$^{3-}$ capped a trimetallic triangle of the late-metals. However, if the late metal complexes contain an anionic and good chelating ligand, this is transferred to the titanium, which results in a lower nuclearity of the early-late heteronuclear complexes. Thus, the reaction of [Cp$_2$Ti(SH)$_2$] with [M(acac)(diolefin)] (acac = acetylacetonate) yielded the heterotrinuclear complexes [Cp(acac)Ti(μ_3-S)$_2${M(diolefin)}$_2$] (M = Rh, diolefin = cod, tfbb; M= Ir, diolefin = cod) [32]. The formation of these heterobimetallic complexes resulted from a complex reaction involving the deprotonation of the hydrosulfido ligands along with the addition of the late metal fragments, followed by the release of cyclopentadiene and the coordination of acetylacetonate to the titanium center. Similarly, the reaction of [Cp$_2$Ti(SH)$_2$] with [M(quinol)(diolefin)] (quinol = 8-oxyquinolinate) afforded the complexes [Cp(quinol)Ti(μ_3-S)$_2${M(diolefin)}$_2$] (M = Rh, diolefin = cod, tfbb; M= Ir, diolefin = cod), which incorporate the 8-oxyquinolinate ligand (Scheme 5). These d^0-d^8 trinuclear early-late heterobimetallic complexes exhibit triangular TiRh$_2$ and TiIr$_2$ cores doubly capped by two μ_3-sulfido ligands as substantiated for [Cp(acac)Ti(μ_3-S)$_2${M(diolefin)}$_2$] by X-ray diffraction methods [32]. A tentative mechanism for the formation of the latter complex is presented in Scheme 6, being the first step the monodeprotonation of [$Cp_2Ti(SH)_2$] by one equivalent of [M(acac)(diolefin)] to give dinuclear [$Cp_2Ti(\mu$-S)(μ-SH)M(diolefin)] species, followed by a further reaction with another equivalent of [M(acac)(diolefin)]. However, whether the [$Cp_2Ti(\mu$-S)$_2${M(diolefin)}$_2$] complexes are initially formed and then they react with acacH or the release of CpH takes place before the addition of the second late metal center is still unclear.

2.4. Heterobimetallic $TiRh_2$ and $TiIr_2$ Carbonyl Complexes

The heterobimetallic complexes [Cp(acac)Ti(μ_3-S)$_2${M(cod)}$_2$] (M= Rh, Ir) reacted with carbon monoxide under atmospheric pressure, in dichoromethane, to give the [Cp(acac)Ti(μ_3-S)$_2${M(CO)$_2$}$_2$] complexes. Similarly, the related 8-oxyquinolinate heterotrinuclear complexes [Cp(quinol)Ti(μ_3-S)$_2${M(CO)$_2$}$_2$] were obtained by carbonylation of the diolefin [Cp(quinol)Ti(μ_3-S)$_2${M(cod)}$_2$] complexes .

The reaction of [Cp(acac)Ti(μ_3-S)$_2${M(CO)$_2$}$_2$] with two molar-equiv. of PPh_3 afforded the complex [Cp(acac)Ti(μ_3-S)$_2${M(CO)(PPh_3)}$_2$] after evolution of carbon monoxide (Scheme 7). The rhodium complex was obtained as a 3:5 mixture of the cis and trans isomers, while the formation of a 1:1 mixture was observed for the iridium derivative. The related rhodium and iridium 8-oxyquinolinate complexes [Cp(quinol)Ti((μ_3-S)$_2${M(CO)(PPh_3)}$_2$] were conveniently prepared by reaction of the corresponding tetracarbonyl derivatives [Cp(quinol)Ti((μ_3-S)$_2${M(CO)$_2$}$_2$] with two molar-equiv. of PPh_3. As observed for the acetylacetonate compounds, the formation of both complexes was not selective since the expected four isomers arising from the mutual disposition of the PPh_3 ligands as well as their relative disposition to the 8-oxyquinolinate ligand were observed.

While the reaction of [$Cp_2Ti(SH)_2$] with [M(acac)(diolefin)] gave [Cp(acac)Ti((μ_3-S)$_2${M(diolefin)}$_2$], the analogous reaction with [M(acac)$(CO)_2$] (1:3 molar ratio) in dichloromethane gave the ion-pair product [Cp_2Ti(acac)][$M_3(\mu_3$-S)$_2(CO)_6$]. In particular, the rhodium complex [Cp_2Ti(acac)][$Rh_3(\mu_3$-S)$_2(CO)_6$] was characterised by a X-ray diffraction study. These ion-pair complexes were most probably formed by the intermediacy of an unstable [$Cp_2Ti(\mu_3$-S)$_2${M(CO)$_2$}$_2$] species, retaining two Cp ligands coordinated to titanium, which upon reaction with [M(acac)$(CO)_2$] undergoes a sulfido ligand transfer according to Scheme 8. The anions [$M_3(\mu_3$-S)$_2(CO)_6]^-$ (M= Rh and Ir) have been previously reported and structurally characterised [33].

2.5. Heterobimetallic Ti_2Rh_4 Carbonyl Complexes

The above mentioned $[CpTi(\mu_3\text{-}S)_3\{Rh(CO)_2\}_3]$ complex presenting an incomplete cubane framework, can easily be prepared by carbonylation of $[CpTi(\mu_3\text{-}S)_3\{Rh(cod)\}_3]$, prepared in situ by addition of $[\{Rh(\mu\text{-}OMe)(diolefin)\}_2]$ to $[Cp_2Ti(SH)_2]$ (Scheme 9). However, when the reaction was carried out with either not carefully dried $[\{Rh(\mu\text{-}OMe)(diolefin)\}_2]$, or in the presence of hydrated sodium carbonate, a novel oxo sulfido heteronuclear cluster of formula $[(CpTi)_2(\mu_4\text{-}O)(\mu_3\text{-}S)_4\{Rh_4(CO)_6\}]$ was obtained. This complex reacted with a variety of P-donor ligands to give complexes of formula $[(CpTi)_2(\mu_4\text{-}O)(\mu_3\text{-}S)_4\{Rh_4(CO)_4(PR_3)_2\}]$ (PR_3 = PPh_3, $P(OMe)_3$, $P(OPh)_3$). These unusual oxo sulfido complexes showed an incomplete double cubane-type structure formed by two cubane-type moieties "Rh_2TiS_2O" each with one empty vertex-fused through a common "Rh_2O" face, with the oxide ligand displaying an unusual tetracoordination, as confirmed by X-ray diffraction methods for the triphenylphosphite derivative (Scheme 9) [34]. Most probably the oxide ligand, bridging the two titanium centers, should be formed by reaction with the water present in the reaction medium. The oxophilic character of titanium and the presence of water played a key role on the formation of the oxo cluster. The replacement of the carbonyl groups in $[(CpTi)_2(\mu_4\text{-}O)(\mu_3\text{-}S)_4\{Rh_4(CO)_6\}]$ by P-donor ligands occurred selectively at the two rhodium atoms possesing two sulfido ligands in a cis disposition. Very recently, a $Ti_2Ru_2Pd_2$ hexanuclear oxo sulfido cluster of formula $[(CpTi)_2(Cp^*Ru)_2Pd_2(PPh_3)(\mu_3\text{-}S)_4(\mu_3\text{-}O)(\mu_2\text{-}H)_2]$ has been prepared by reacting the heterotrinuclear cluster $[(CpTiCl_2(Cp^*Ru)\ \{Pd_2(PPh_3)_2\}(\mu_3\text{-}S)(\mu_2\text{-}S)(\mu_2\text{-}H)]$ with water [35].

3. Sulfido-Bridged Zirconium-Rhodium and Zirconium-Iridium Complexes

3.1. Heterobimetallic $ZrRh_2$ and $ZrIr_2$ Diolefin Complexes

We have previously commented that the $[Cp_2Ti(SH)_2]$ complex is an appropriate starting material for the synthesis of early-late complexes of formula $[CpTi(\mu_3\text{-}S)_3\{M(diolefin)\}_3]$. Scheme 2 shows that the loss of one Cp ring is commonly observed. Concerning zirconium, some initial experiments with the related hydrosulfido complex $[Cp_2Zr(SH)_2]$ resulted in extensive sulfido transfer to the d^8 metal centers, giving the trimetallic complexes $[M_3(\mu\text{-}S)_2(\mu\text{-}H)(cod)_3]$ or the anionic clusters $[M_3(\mu_3\text{-}S)_2(CO)_6]^-$ (M = Rh, Ir) as the main outcome of these reactions. We thought that the known dimerization [36] of $[Cp_2Zr(SH)_2]$ with extrusion of H_2S probably complicated these reactions. To overcome this we envisaged that the use of a bulkier zirconium-metallocene hydrosulfido compound, such as [$Cp^{tt}_2Zr(SH)_2$] (Cp^{tt} = η^5-1,3-di-*tert*-butylcyclopentadienyl), could be useful to avoid the undesirable reactions and facilitate the controlled construction of new heterobimetallic $ZrRh_2$ and $ZrIr_2$ complexes. The [$Cp^{tt}_2Zr(SH)_2$] complex 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.

The bishydrosulfido complex [$Cp^{tt}_2Zr(SH)_2$] was prepared by reacting [$Cp^{tt}_2ZrMe_2$], obtained by treatment of [$Cp^{tt}_2ZrCl_2$] with MeLi, with H_2S under pressure [37]. Additive-deprotonation of [$Cp^{tt}_2Zr(SH)_2$] with appropriate rhodium complexes, such as [Rh(acac)(diolefin)], results in the clean formation of heterotrinuclear complexes of formula [$Cp^{tt}_2Zr(\mu_3\text{-}S)_2$\{Rh(diolefin)\}$_2$], without the loss of any coordinated cyclopentadienyl ligand (Scheme 10), although the cycloctadiene derivative resulted impurified with [$Rh_3(\mu\text{-}S)_2(\mu\text{-}H)(cod)_3$]. Nevertheless the [$Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(cod)\}_2$] compound can be effectively prepared by reacting [$Cp^{tt}_2Zr(SH)_2$] with [$\{Rh(\mu\text{-}OH)(cod)\}_2$]. On the other hand, the reaction of [$Cp^{tt}_2Zr(SH)_2$] with two molar-equiv. of [Ir(acac)(cod)] afforded the new complex [$Cp^{tt}(acac)Zr(\mu_3\text{-}S)_2\{Ir(cod)\}_2$] impurified with [$Ir_3(\mu\text{-}S)_2(\mu\text{-}H)(cod)_3$], which could be isolated pure by recrystallization. This reaction implies the replacement of one cyclopentadienyl ring by the acetylacetonate ligand in the zirconium coordination sphere [38]. Related $TiRh_2$ complexes have been described in section 2.3.

A general method for the synthesis of [$Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{M(diolefin)\}_2$] complexes (M = Rh, diolefin = nbd, cod; M = Ir, diolefin =cod) consisted in the reaction of [$\{M(\mu\text{-}Cl)(diolefin)\}_2$] compounds with the zirconium-sulfide metallocene anion [$Cp^{tt}_2ZrS_2]^{2-}$, generated by double deprotonation of [$Cp^{tt}_2Zr(SH)_2$] with BuLi (Scheme 10). These compounds exist in solution as two rotamers, eclipsed and staggered, due to a hindered rotation of the cyclopentadienyl rings and the relative disposition of the Cp^{tt} groups in the sandwich moiety [38]. The two rotamers interconvert for the complexes with diolefin = nbd and tfbb, whilst no interconversion occurs for the cod complexes, which can be isolated as the pure staggered rotamer.

3.2. Heterobimetallic $ZrRh_2$ and $ZrIr_2$ Carbonyl Complexes

Carbonylation of [$Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(nbd)\}_2$] under atmospheric pressure gave the carbonyl complex [$Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2$]. This complex was also prepared 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)$_2$], or with [{Rh(μ-Cl)(CO)$_2$}$_2$] in the presence of a slight excess of NEt$_3$, gave [Cp^{tt}$_2$Zr(μ_3-S)$_2${Rh(CO)$_2$}$_2$]. The ZrRh$_2$ core of the compound [Cp^{tt}$_2$Zr(μ_3-S)$_2${Rh(CO)$_2$}$_2$] has been established by X-ray diffraction methods [37-38]. The related iridium carbonyl complex [Cp^{tt}$_2$Zr(μ_3-S)$_2${Ir(CO)$_2$}$_2$] was obtained from the reaction of [Cp^{tt}$_2$Zr(SH)$_2$] with two molar-equiv of the anionic complex [IrCl$_2$(CO)$_2$]$^-$ in the presence of a slight excess of NEt$_3$ (Scheme 11) [39]. This [Cp^{tt}$_2$Zr(μ_3-S)$_2${Ir(CO)$_2$}$_2$] complex reacted with 1,2-bis(diphenylphosphino)ethane (dppe) yielding selectively the ion-pair [Ir(CO)(dppe)$_2$][Cp^{tt}$_2$Zr(μ-S)$_2$Ir(CO)$_2$]. A related heterobimetallic anion [Cp*$_2$Zr(μ-S)$_2$Rh(CO)$_2$]$^-$ has been previously reported [40]. Apart from the above mentioned reaction, the ZrM$_2$ triangular core in the heterotrinuclear carbonyl clusters [Cp^{tt}$_2$Zr(μ_3-S)$_2${M(CO)$_2$}$_2$] (M = Rh, Ir) is usually maintained in the replacement reactions of carbonyl groups by P-donor ligands. The outcome of these reactions depends on the character of the P-donor ligands. Thus, the replacement reactions with the short-bite bidentate bis(diphenylphosphino)methane (dppm) ligand are stereoselective, and the products [Cp^{tt}$_2$Zr(μ_3-S)$_2${M(CO)}$_2$(μ-dppm)] are cleanly obtained as a single isomer. In contrast, the disubstituted complexes [Cp^{tt}$_2$Zr(μ_3-S)$_2${Rh(CO)(P(OR)$_3$)}$_2$] (P(OR)$_3$ = P(OMe)$_3$ and P(OPh)$_3$) are obtained as mixtures of the transoid and cisoid isomers which exhibit a restricted rotation of the Cp^{tt} rings [38].

3.3. Heterotrimetallic ZrIrRh Carbonyl Complexes

Interestingly, the heterodinuclear anion [Cp^{tt}$_2$Zr(μ-S)$_2$Ir(CO)$_2$]$^-$ is capable of acting as a metalloligand towards d^8 metal centres allowing the syntheses of novel Zr-Ir-Rh heterotrimetallic complexes (Scheme 11). Thus, this anion reacted with [{Rh(μ-Cl)(cod)}$_2$] yielding the complex [Cp^{tt}$_2$Zr(μ_3-S)$_2${Ir(CO)$_2$}{Rh(cod)}], that has been characterized by X-ray diffraction methods. The structure showed a triangular ZrIrRh core capped on both sides by two symmetrical μ_3-sulfido ligands. Although no significant d^0-d^8 bonding interactions are detected, the Rh···Ir distance, 2.8205(10) Å, suggested the presence of a significative d^8-d^8 metal-metal interaction. A remarkable feature of this heterometallic complex is the fully staggered relative disposition of the Cp^{tt} ligands observed in the solid state, while in CDCl$_3$ solution two interconverting rotamers are detected in a 3:1 ratio. The major rotamer showed a staggered disposition of the *tert*-butyl groups, as found in the solid state, whilst the spectroscopic information for the minor isomer suggested an eclipsed conformation. As expected, the carbonylation of [Cp^{tt}$_2$Zr(μ_3-S)$_2${Ir(CO)$_2$}{Rh(cod)}] gave the heterotrimetallic compound [Cp^{tt}$_2$Zr(μ_3-S)$_2${Ir(CO)$_2$}{Rh(CO)$_2$}] (Scheme 11). This complex can also be obtained in one pot synthesis by successive additions of dppe and the anion $[RhCl_2(CO)_2]^-$ to the heterobimetallic $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{Ir(CO)_2\}_2]$ compound [39].

4. Catalytic activity

The importance of heterometallic complexes for homogeneous catalysis is based on the reasonable expectation that two or more adjacent metal centers may offer possibilities for cooperative reactivity and synergism. In particular, some early-late Zr-Rh and Ti-Rh heterobimetallic systems have been shown to be efficient hydroformylation catalysts [41-43].

The heterotetranuclear $[CpTi(\mu_3\text{-}S)_3\{Rh(diolefin)\}_3]$ complexes, in the presence of phosphorus ligands, were found to be active catalyst precursors in the hydroformylation of 1-hexene and styrene. Thus, 1-hexene was hydroformylated at 5 bar and 353K (P/Rh ratio = 2 or 4) with a 96% conversion to aldehydes and a 77% regioselectivity for the linear aldehyde. A higher P/Rh ratio provided a better selectivity for the linear aldehyde (85%) although lower conversions were obtained. Taking into account the equilibrium observed between the different heterotetranuclear species containing carbonyl and phoshine ligands (Scheme 4), and in order to know which of those intermediates were formed under CO pressure, a high pressure NMR spectroscopic study was carried out. Thus, the $^{31}P\{^1H\}$ NMR spectrum of a solution of $[CpTi(\mu_3\text{-}S)_3\{Rh(cod)\}_3]$ and PPh_3 (P/Rh = 2), after being pressurized to 2.5 bar of carbon monoxide, showed an equilibrium between the species $[CpTi(\mu_3\text{-}S)_3Rh_3(\mu\text{-}CO)(CO)_4(PPh_3)_2]$ and $[CpTi(\mu_3\text{-}S)_3Rh_3(\mu\text{-}CO)(CO)_3(PPh_3)_3]$ at 213K. The latter species became predominant when the P/Rh ratio was increased to 6. Most probably, the variation of the active species could be the reason for the higher selectivity and lower conversion observed using this P/Rh ratio in the hydroformylation reaction. Interestingly, the $^{31}P\{^1H\}$ NMR and IR spectra of the solutions obtained at the end of the hydroformylation experiments showed the presence of the heterotetranuclear $[CpTi(\mu_3\text{-}S)_3\{Rh(CO)(PPh_3)\}_3]$ species indicating that the heterotetranuclear framework is maintained under hydroformylation conditions.

The complex $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ in the presence of monodentate P-donor ligands was also an active catalyst precursor for hydroformylation of oct-1-ene under mild conditions of pressure and temperature. The catalytic systems obtained with phosphite ligands were much more active than the corresponding with triphenylphosphine. In addition, the system formed with trimethylphosphite was much more selective than the system obtained with triphenylphosphite, giving an aldehyde selectivity of 95% with a regioslectivity close to 80%. The spectroscopic analysis of the solutions obtained after the hydroformylation reactions with the $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ precursor showed no evidence for the presence of the complexes $[Cp^{tt}{}_2Zr(\mu_3\text{-}$

S)$_2${Rh(CO)(P(OR)$_3$)}$_2$], indicating that the heterotrinuclear complexes are not maintained as such, and most probably break down to active monomeric rhodium species. This behavior is opposite to that observed in the hydroformylation of alkenes using the catalyst precursor [CpTi(μ_3-S)$_3${Rh(diolefin)}$_3$], indicating an outstanding stability of the heterotetranuclear framework.

5. Concluding Remarks

The controlled syntheses of novel d^0-d^8 early-late tri-, tetra-, and hexa-nuclear diolefin and carbonyl clusters with the cores $TiRh_2$, $TiIr_2$, $ZrRh_2$, $ZrIr_2$, ZrRhIr, $TiRh_3$, $TiIr_3$, and Ti_2Rh_4, were accomplished through additive-deprotonation reactions involving the titanium and zirconium bis-hydrosulfido complexes of formula [$Cp_2Ti(SH)_2$] and [$Cp^{tt}{}_2Zr(SH)_2$] and appropriate rhodium and iridium diolefin and carbonyl compounds. Some of the titanium-rhodium and zirconium-rhodium complexes are active catalyst precursors for hydroformylation of alkenes. All the observations pointed out that the heterotetranuclear "CpTi(μ_3-S)$_3$Rh$_3$" framework was maintained under hydroformylation conditions.

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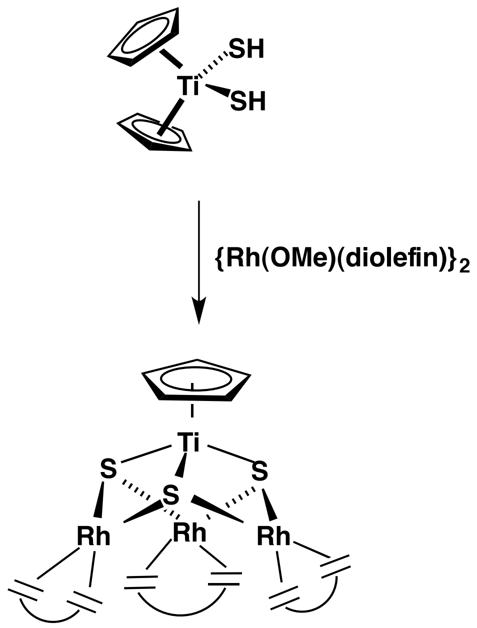

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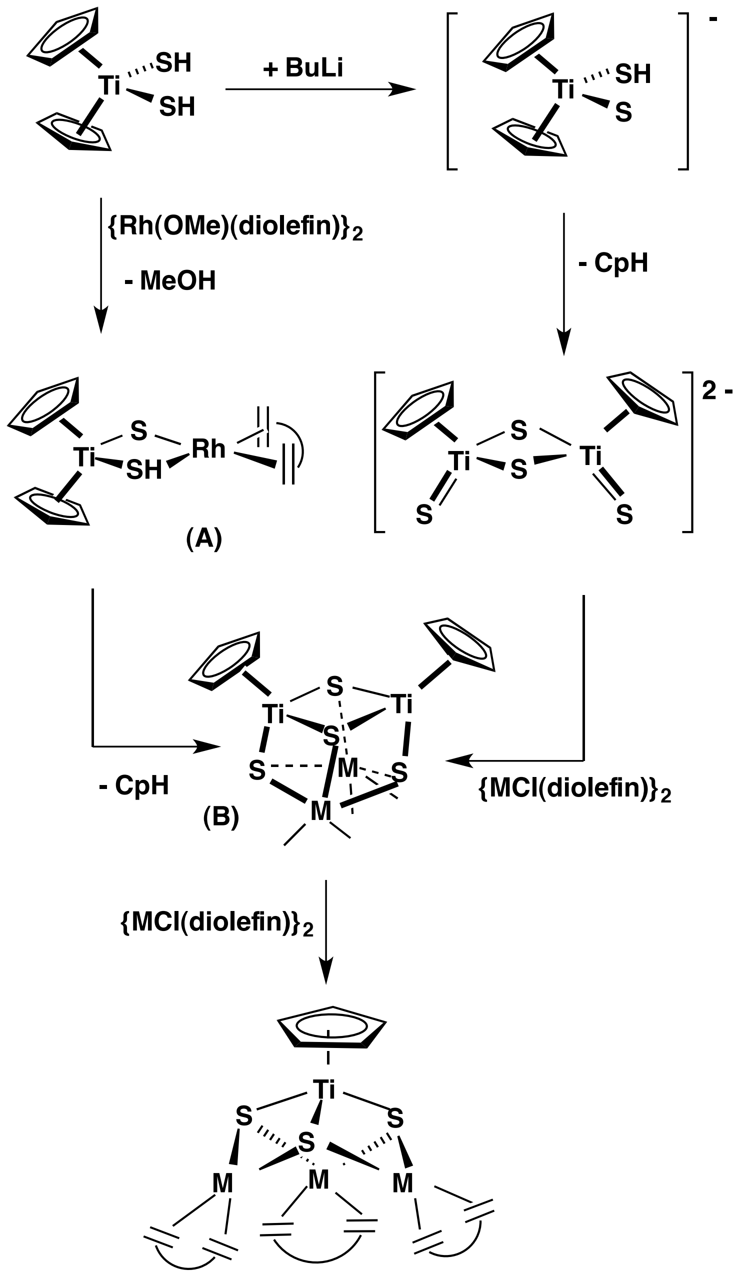
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SH
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-
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- CpH
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Rh
(A)
Ti
S
S
Ti
S
S
2 -
Ti
S
Ti
S
S
M
S
M
(B)
- CpH
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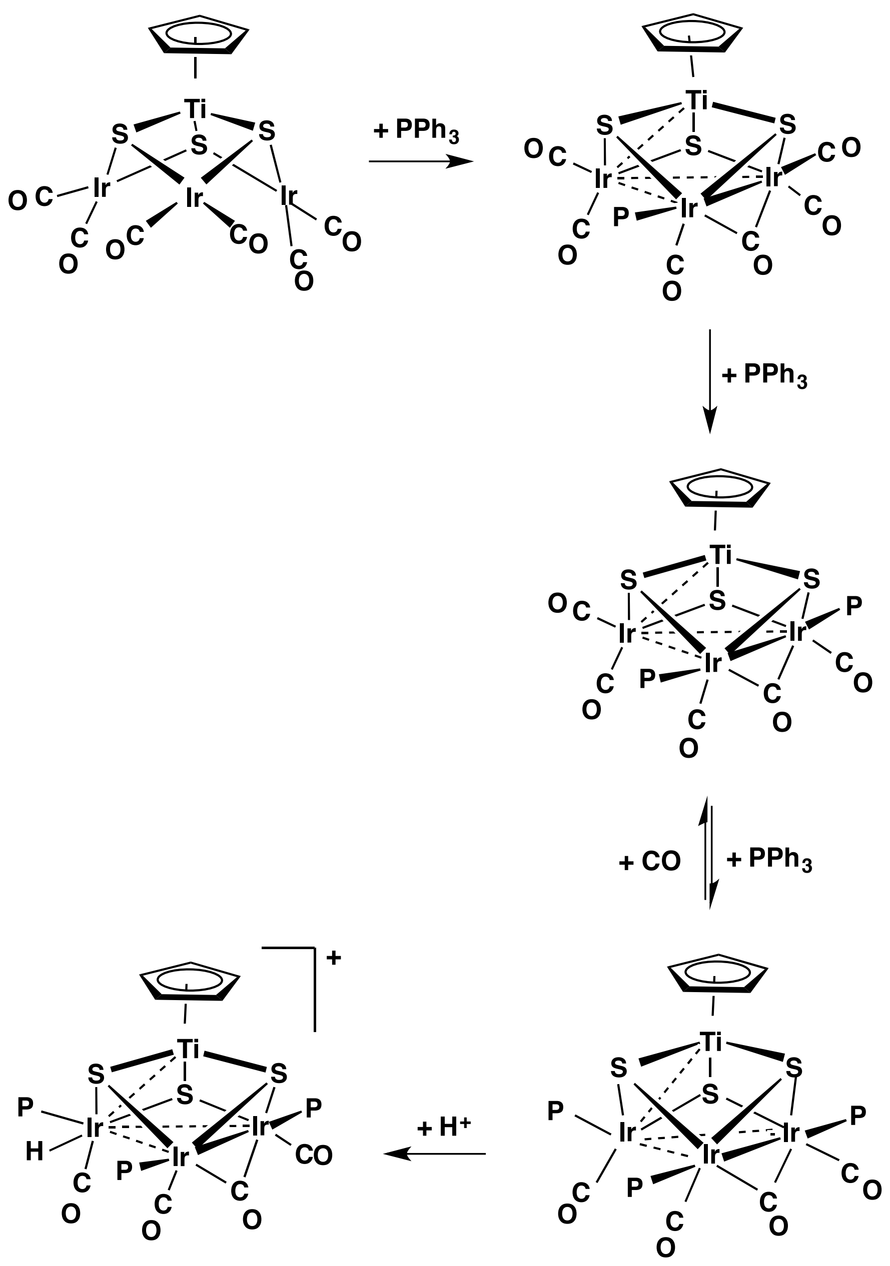
{MCl(diolefin)}2
Ti
S
S
S
M
M
M

Scheme 2



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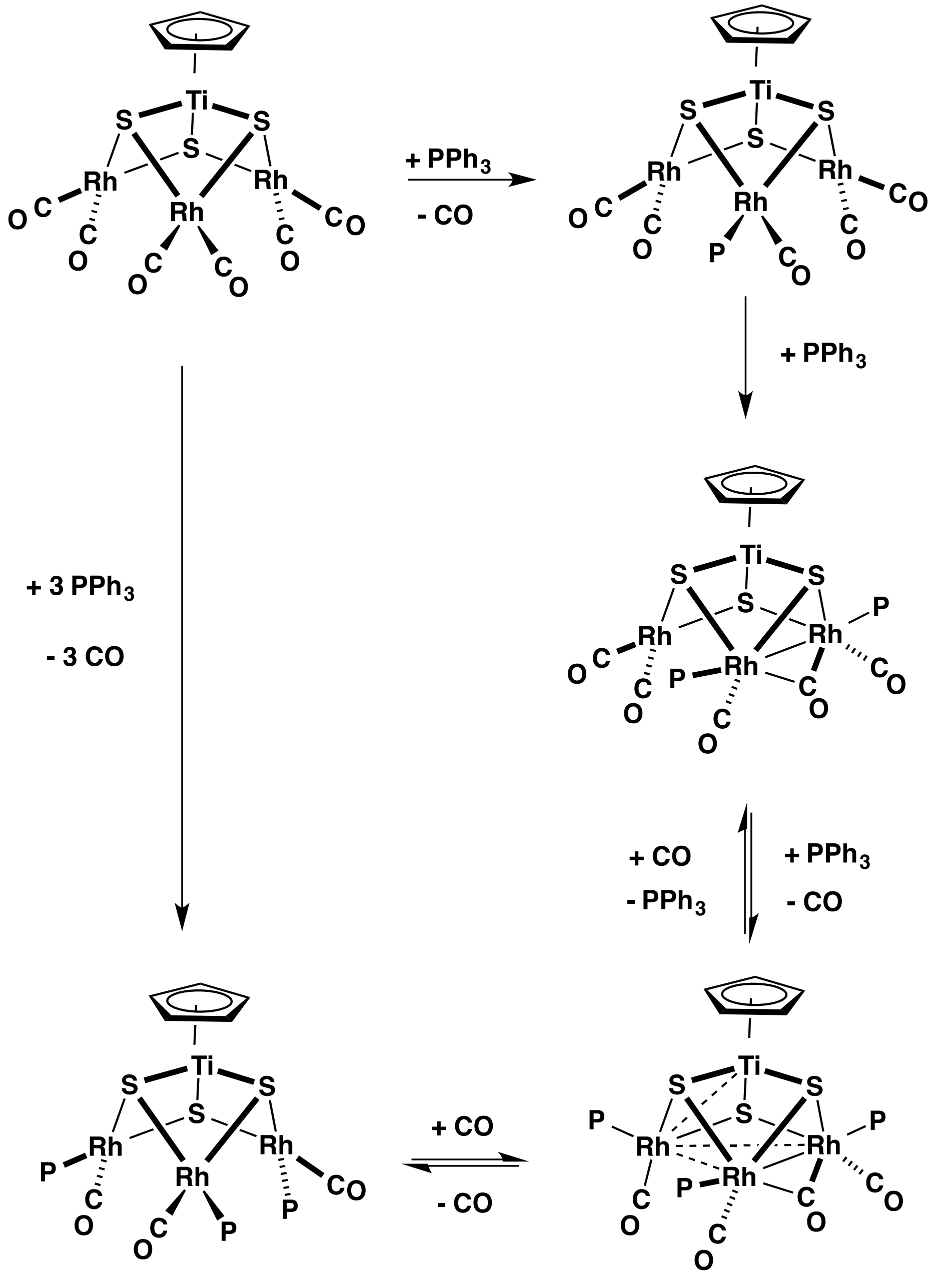

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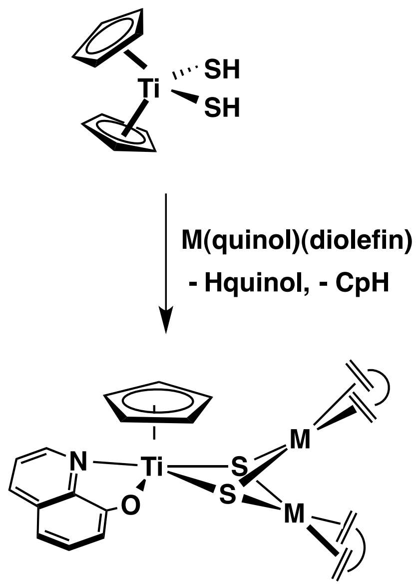

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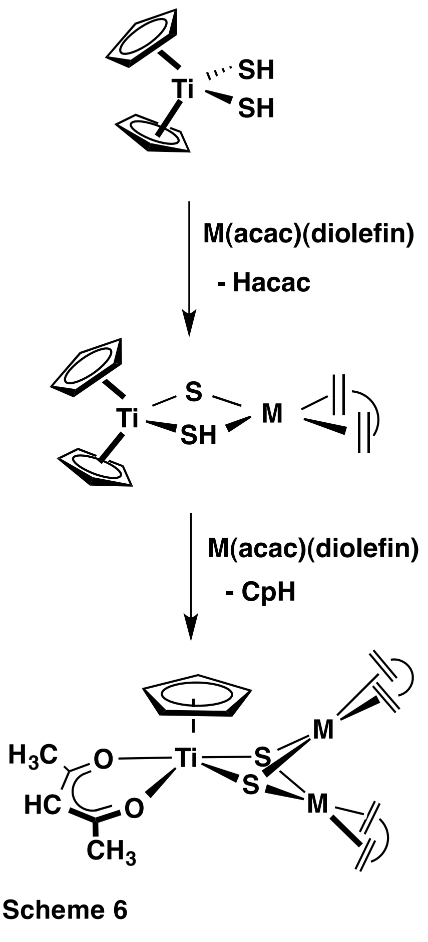

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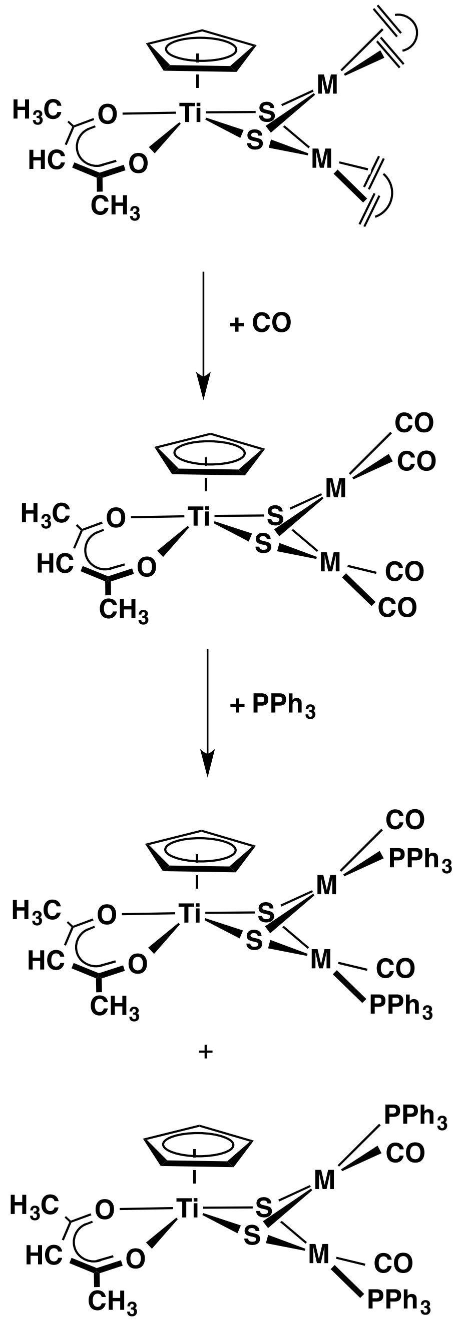
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S
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M
M
HC
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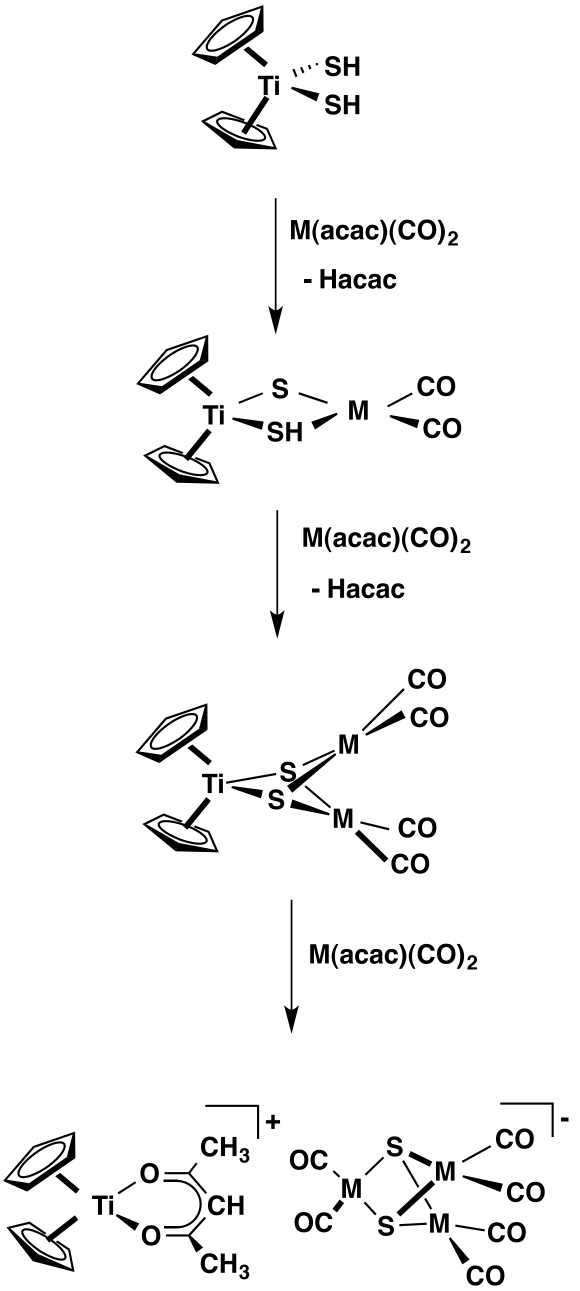
CO
PPh3
+
PPh3
CO
CO
PPh3

Scheme 7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CO
CO
M
Ti
S
S
M
CO
CO
M(acac)(CO)$_2$
+
Ti
O
O
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CH$_3$
-
OC
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M
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S
M
M
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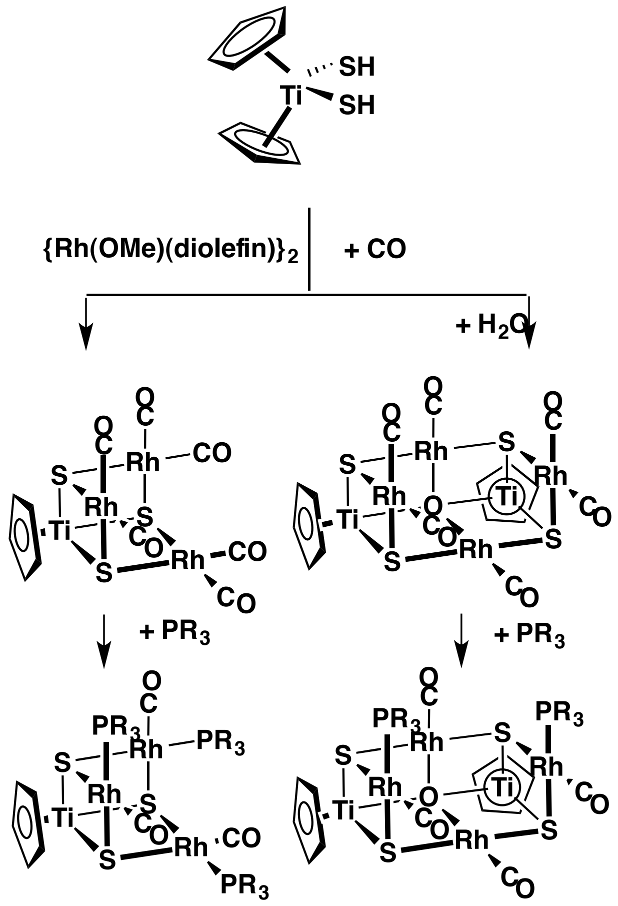
CO
CO
CO

Scheme 8



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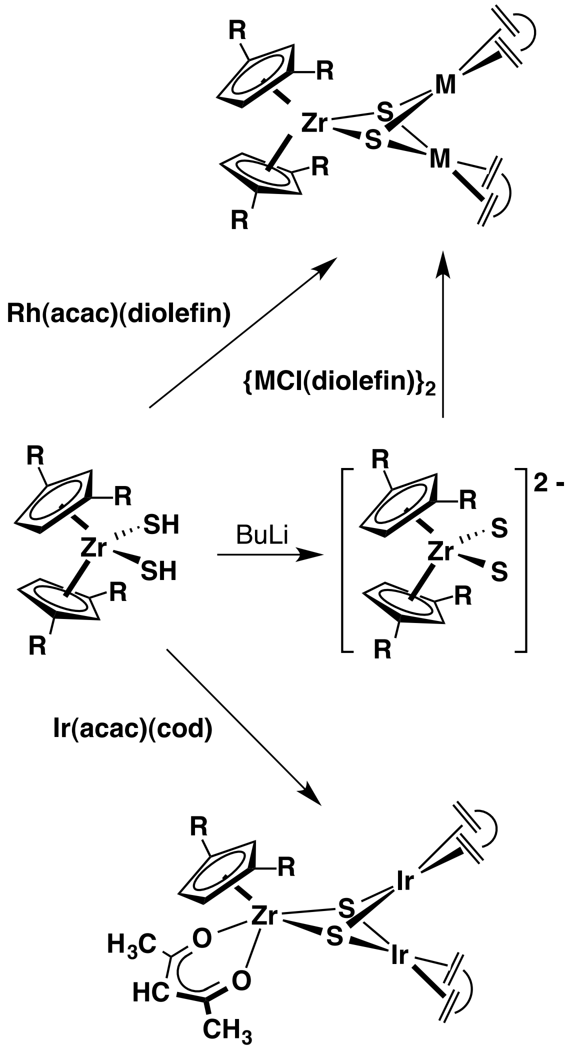
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SH
Zr
SH
R
R
BuLi
R
R
S
Zr
S
R
R
2 -
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Zr
S
S
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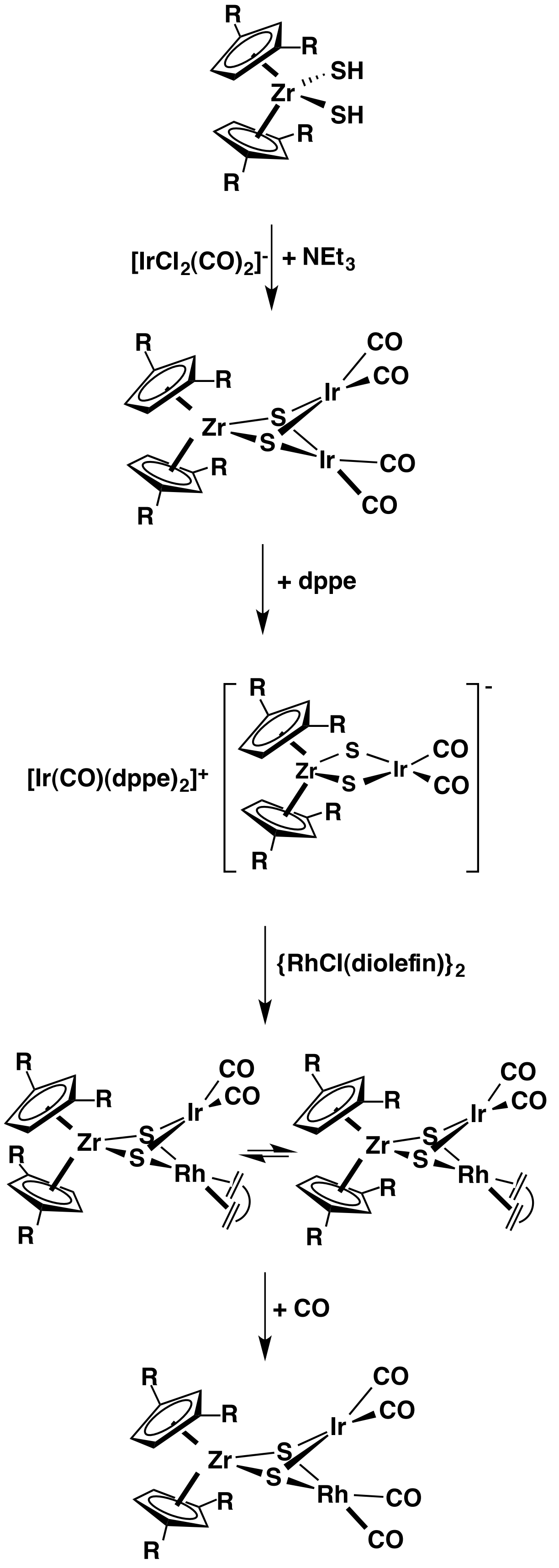
O
O
HC
CH3

Scheme 10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R
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R
CO
Ir
Zr
S
S
R
Ir
CO
R
CO
+ dppe
R
R
S
CO
[Ir(CO)(dppe)$_2$]$^+$
Zr
Ir
S
CO
R
R
{RhCl(diolefin)}$_2$
R
CO
R
CO
R
Ir
CO
R
CO
Zr
S
Ir
S
Zr
S
R
S
Rh
Rh
R
R
R
+ CO
R
CO
R
CO
Ir
S
Zr
S
Rh
CO
R
R
CO

Scheme 11