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Coordination of a Bifunctional Ligand to a Rhodium(III) Dimethyl Complex: Lewis Acidity Enhancement by Chelation

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The addition of the ambiphilic compound $(Me_2PCH_2AlMe_2)_2$ (**1**) to $Cp^*RhMe_2(DMSO)$ (DMSO = dimethylsulfoxide) (**2**) gives $Cp^*RhMe_2(PMe_2CH_2AlMe_2{\cdot}DMSO)$ (**3**·DMSO). The addition of Lewis acids (LA) such as $La(dbm)_3$ (dbm = dibenzoylmethane) and $AlMe_3$ to a solution of complex **3**·DMSO gives a competition reaction that results in the formation of LA·DMSO and $Cp^*RhMe_2(PMe_2CH_2AlMe_2)$ (**3**). When heated to 40 °C, complex **3** ionizes to a putative zwitterionic species, $Cp^*Rh^+Me(PMe_2CH_2AlMe_3^-)$ (**3′**), which is converted to $[Cp^*Rh(Me)(\mu^2\text{-}\eta^2\text{-}Me_2PCH_2)]_2$ (**4**) irreversibly. Spin saturation transfer experiments demonstrated that the rate of the methyl abstraction by the alane moiety was $0.76 \pm 0.09\ s^{-1}$, while the rate of abstraction of the methyl in $Cp^*RhMe_2(PMe_3)$ by $AlMe_3$ was $0.10 \pm 0.02\ s^{-1}$. The zwitterionic species **3′** could be trapped in solution by addition of PMe_3 to afford both $Cp^*Rh^+Me(PMe_3)(Me_2PCH_2AlMe_3^-)$ (**5**) and $[Cp^*Rh^+Me(PMe_3)(Me_2PCH_2AlMe_2)]AlMe_4^-$ (**6**). When compound **1** was added to complex **3′**, the formation of the zwitterionic complex $Cp^*Rh^+Me(\eta^2\text{-}Me_2PCH_2Al^-Me_2CH_2PMe_2)$ (**7**) was observed.

Introduction

In the past decade, a major emphasis has been put on Lewis acid design in order to enhance catalytic transformations such as olefin polymerization or asymmetric synthesis.[1] One of the strategies that has emerged is the tethering of a Lewis acidic moiety on an ancillary ligand.[2,3] Transition metal complexes bearing such ligands have been reported for early metals,[2] but examples of reactions with late metals are still scarce.[3] While group IV cyclopentadienyl complexes with a pendant borane exhibit some activity in olefin polymerization,[2a−d] to our knowledge, the use of borane- or alane-modified ligands for other chemical transformations is limited to three examples. First, a borane-substituted cyclopentadienyl zirconium complex has recently been used to orient an *N*-methylbenzimidazole substrate for selective C−H activation at a Zr(IV) center.[2f] In this case, the Lewis acid moiety was used as an anchor for substrate coordination, a role that can be related to enzymatic catalysis. Boron-modified phosphine ligands have also been coordinated to late metal catalysts in order to induce specific interactions with various amino olefins, but the catalytic outcome showed only moderate success.[3d−e]

The Lewis acid can also be used as a cocatalyst, since it can interact with a transition metal and/or its ligands. Thus, it was reported that $(Me_2PCH_2AlMe_2)_2$ (**1**) could coordinate nickel(II) indenyl complexes. The presence of compound **1** was found to enhance by 2 orders of magnitude the rate of phenylsilane homologation compared to the system with a monodentate phosphine.[3a] While it was found that the phosphine moiety of the $Me_2PCH_2AlMe_2$ fragment was bound to the metal center, the nature of the interaction between the alane moiety and the ligand sphere was elusive, although clearly important. It was speculated that the role of the Lewis acid in this system was to interact with the Ni-Me moiety (species A, Chart 1).[4] Thus, the tether was playing an important role compared to unchelated alkylaluminum species, since alanes usually inhibit the homologation reactivity. This may be due to interactions that were blocking the reagents from approaching the coordination site, as shown in Chart 1 (species B).

Herein we report that $Me_2PCH_2AlMe_2$ can also be coordinated to a cyclopentadienyl Rh(III) center to form complexes of interest in saturated alkane activation.[5,6] The activity of compounds of general formulation $Cp^*MR(PMe_3)H$ (Cp^* = pentamethylcyclopentadienyl; M = Rh, Ir; R = alkyl, aryl, or H)[7−13] is still far from the one observed for other rhodium and iridium

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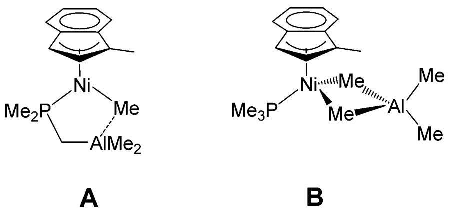
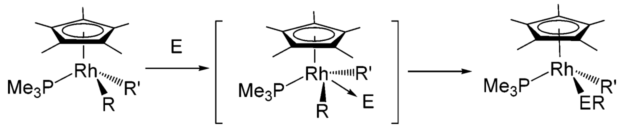
10.1021/om700401c CCC: $37.00

Chart 1



Scheme 1

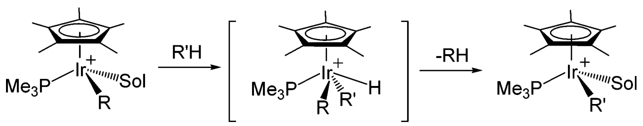


alkane borylation catalysts, although $Cp^*IrH_2(PMe_3)$ was demonstrated to catalyze the borylation of benzene.[8] Indeed, these species with tightly bound phosphines cannot easily undergo further transformation with common reagents such as olefins, since they lack the necessary unoccupied orbital for substrate coordination.[9] In order to solve such a problem, two general strategies have been developed: using electrophilic substrates or ionizing the metal center.

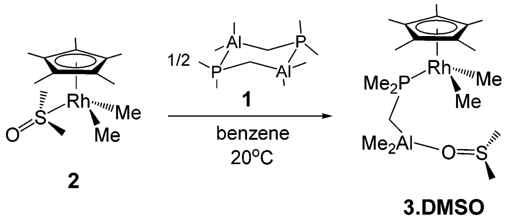
The coordination of nucleophiles such as olefins to electron-rich, saturated organometallic species is difficult; however, compounds of the type $Cp^*MR(PMe_3)H$ have an accessible lone pair on the metal that allows the binding to electrophiles (E). It is therefore possible for unsaturated reagents, such as CS_2 and SO_2, to insert into a metal hydride or metal alkyl bond (Scheme 1). These transformations, however, remain stoichiometric.[10]

The formation of cationic intermediates has been studied with Ir(III) complexes.[11−13] It has led to several stoichiometric C−H bond functionalization reactions of interest under very mild conditions. Presumably, these reactions proceed via an iridium(V) intermediate (Scheme 2). Catalytic activity has also been observed, mainly as C−H/C−D scrambling reactions between various organic substrates and common deuterated solvent molecules.[12] While strong and bulky Lewis acids like tris(perfluorophenyl)borane can efficiently generate cationic species by abstracting the R group from the precursors $Cp^*IrR_2(PMe_3)$ (R = hydride or alkyl), the nucleophilic nature of the metal can cause side reactions.[12d] Indeed, it was observed that soft Lewis acids (LA), such as alanes or alkylmagnesium species, form adducts of general formulation $Cp^*IrH_2(PMe_3)\cdot LA$ when added to $Cp^*IrH_2(PMe_3)$.[13] These interactions may prove counterproductive if these species would ever be used under catalytic conditions.

Scheme 2



Scheme 3



We wish to report that the Cp*Rh(III) complexes obtained from the coordination of an ambiphilic ligand exhibit an ionizing capability that surpassed the untethered bimolecular system. We were able to isolate zwitterionic intermediates that were trapped with PMe_3, whereas the analogous $Cp^*RhMe_2(PMe_3)$ proved inactive when $AlMe_3$ was added under similar conditions. Since this ionization is reversible and the resulting aluminate could also be used as a nucleophile, this bifunctional system may open the door to new reactivity perspectives.

Results

Addition of 0.5 equiv of bifunctional ligand **1** to a 0.5 M solution of $Cp^*RhMe_2\cdot DMSO$ (**2**) in benzene gave a light yellow solution.[14] After 8 h, the volatile materials were removed, affording a highly air-sensitive yellow oil. The spectroscopic characterization and the literature[3a] comparison are consistent with the connectivity expected for $Cp^*RhMe_2(Me_2PCH_2AlMe_2\cdot DMSO)$ (**3**·DMSO) (Scheme 3). The coordination of the phosphine of ligand **1** to rhodium in complex **3**·DMSO is supported by the presence of a doublet at 19.5 ppm ($^1J_{P-Rh}$ = 163 Hz) in the $^{31}P\{^1H\}$ NMR spectrum. A selective decoupling $^1H\{^{31}P\}$ NMR experiment confirmed that the latter resonance was coupling with the Cp*, PMe_2, CH_2, and $RhMe_2$ respectively located at 1.82, 1.44, 0.55, and 0.35 ppm.

When generated in benzene-d_6 or toluene-d_8, complex **3**·DMSO was stable for several days at 60 °C. The addition of water, alcohols, or primary and secondary amines led to the cleavage of the bond between the aluminum atom and the

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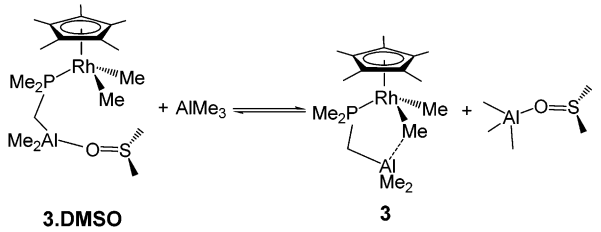
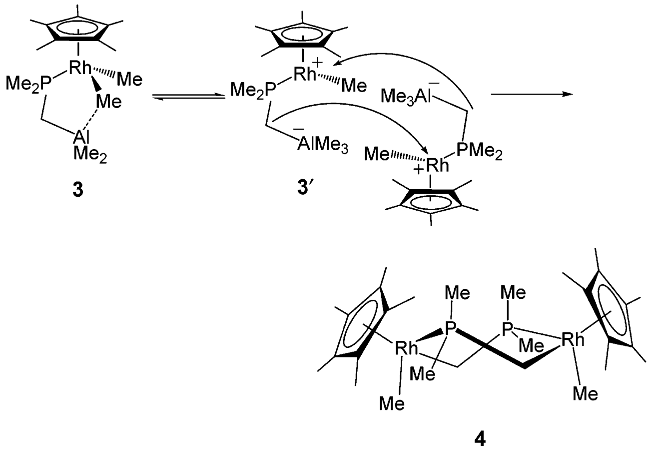
(14) When 2 equiv of DMSO is added to **1**, we observed the formation of ($Me_2PCH_2AlMe_2\cdot DMSO$). The ^1H NMR spectrum of $Me_2PCH_2AlMe_2\cdot DMSO$ exhibits no more $^3J_{H-P}$ coupling for the methylalane and has a $^{31}P\{^1H\}$ NMR resonance closer to free PMe_3. ^1H NMR (benzene-d_6): δ 1.62 (s, DMSO), 1.14 (br s, 6H, PMe_2CH$_2$AlMe$_2$), 2.26 (br d, $^2J_{H-P}$ = 4.2 Hz, 2H, PMe$_2$CH_2AlMe$_2$), −0.32 (br s, 6H, PMe$_2$CH$_2$AlMe_2). $^{31}P\{^1H\}$ NMR (benzene-d_6): δ −61.9 ppm.

Scheme 4



Scheme 5



methylene fragment and generated $Cp^*RhMe_2(PMe_3)$[15] in addition to insoluble residues. The addition of 1 equiv of diphenylsulfoxide, triphenylphosphine oxide, or pyridine to a 0.03 M benzene-d_6 solution of complex **3**·DMSO did not lead to a significant change in the ^{1}H NMR spectrum of the starting material, other than a downfield shift for the DMSO resonance from 1.28 to 1.33, 1.47, and 1.44 ppm, respectively. Thus, the connectivity of the complex likely remains intact, but the acid−base adduct is in equilibrium depending on the nature of the Lewis base. The lack of reactivity between complex **3**·DMSO and alkenes, tertiary amines, or phosphines, such as trimethylphosphine, is notable.

This inactivity of **3**·DMSO was expected considering the strong interaction between alanes and DMSO.[16] In order to use the Lewis acid capability of the aluminum center, it was necessary to remove DMSO from its coordination sphere. In a first attempt, 1 equiv of $La(dbm)_3$ (dbm = dibenzoylmethane) was added to a 0.03 M solution of **3**·DMSO in benzene-d_6. After 5 min, it was possible to observe the emergence of a new series of resonances by ^{1}H NMR spectroscopy, with the same coupling pattern and integration ratio as **3**·DMSO, and a new doublet at 16.8 ppm ($^1J_{P-Rh} = 164$ Hz) in the $^{31}P\{^1H\}$ NMR spectrum. One remarkable feature of this experiment was the broadening of the DMSO methyl resonance at 1.23 ppm, which was almost lost in the baseline. Such a phenomenon can be explained by the formation of $La(dbm)_3$·DMSO and consequently the formation of $Cp^*RhMe_2(PMe_2CH_2AlMe_2)$ (**3**). However, this reaction mixture decomposes rapidly to several intractable species before completion, as shown by the complicated ^{1}H NMR spectrum and by the several new resonances between 8 and 35 ppm by $^{31}P\{^1H\}$ NMR spectroscopy after 1 h of reaction.

As an alternative strategy for removing the sulfoxide, $AlMe_3$ was added to a 0.03 M solution of complex **3**·DMSO in toluene-d_8. The less hindered alane was expected to compete with the bifunctional ligand for the Lewis base and consequently to form $AlMe_3$·DMSO and complex **3**. When 1 or 2 equiv of $AlMe_3$ was added, the ^{1}H NMR spectra after 5 min of reaction at 22 °C indicated that the alane was reacting similarly to $La(dbm)_3$ and forming **3**, since all the resonances of the Rh complex shifted to higher field while maintaining the same coupling patterns. The presence of only one AlMe resonance at −0.36 ppm and of one sharp DMSO resonance at 1.36 ppm suggests that a fast equilibrium depicted in Scheme 4 is taking place. Unlike the reaction of complex **3**·DMSO with the lanthanide complex, this reaction mixture was stable since only traces of ionization (*vide infra*) were observed after 6 h at 22 °C.

Variable-temperature multinuclear NMR studies provided additional insight into the nature of the reaction mixture (Figure 1). As the temperature decreases, the chemical shifts of all resonances for the equilibrium between complexes **3** and **3**·DMSO migrate to lower field and come closer to the one of complex **3**·DMSO. The single resonance for the Al-Me starts to coalesce at −40 °C to give a series of signals that become well defined at −80 °C. Two of the signals correspond to the excess of Al_2Me_6; the chemical shift of the terminal methyl groups is at −0.51 ppm (12 protons) and that of the bridging methyl is at 0.00 ppm (6 protons). One remarkable feature of the low-temperature ^{1}H NMR spectra compared to the spectra of complex **3**·DMSO without added $AlMe_3$, even in the presence of **1**, is that, starting at −40 °C, the resonances corresponding to $Cp^*RhMe_2(PMe_2CH_2AlMe_2)$ are broadening and losing all coupling pattern. By $^{31}P\{^1H\}$ NMR spectroscopy, the resonance of complex **3** at −40 °C (20.3 ppm, $^1J_{P-Rh} = 160$ Hz) can be observed to split at −60 °C into one major broad resonance at 20.8 ppm ($^1J_{P-Rh} = 161$ Hz) and one minor at 19.6 ppm ($^1J_{P-Rh} = 158$ Hz) in an approximate ratio of 7:1. This suggests that the rate of the equilibrium between **3** and **3**·DMSO depicted in Scheme 4 becomes slow enough to observe coalescence, but not slow enough to locate both species by ^{1}H NMR spectroscopy.

Using spin saturation transfer, an exchange between the methyl groups on the aluminum and the ones on rhodium was observed starting at −20 °C when 1 equiv of $AlMe_3$ was added to a solution of complex **3**·DMSO in toluene-d_8. Since the Rh center in complex **3**·DMSO is electronically saturated, such a phenomenon is possible via a degenerate process involving the ionization of the Rh−Me bond by the Lewis acid followed by an alkylation of the Rh^+ cationic intermediate by the aluminate. Similar behavior was observed when 1 equiv of $AlMe_3$ was added to a solution of $Cp^*RhMe_2(PMe_3)$ in benzene-d_6. The rate constant (k) for both processes was determined on the basis of the relative integration intensity of the saturated signal (I) having a T_1 relaxation time using the relation $k = ((1/I) - 1)/T_1$.[17] At 22 °C, the experimental values of T_1 for $Cp^*Rh\mathit{Me}_2(PMe_3)$ and $Cp^*Rh\mathit{Me}_2(PMe_2CH_2AlMe_2)$·DMSO were 5.9 ± 0.2 and 3.0 ± 0.2 s, respectively; the signal intensity ratios were approximately at 62 ± 5% and 31 ± 5% of their respective original values. The rates of exchange were calculated to be 0.76 ± 0.09 s^{-1} for the latter system and 0.10 ± 0.02 s^{-1} for the untethered one. Therefore, addition of a tether increased by almost 1 order of magnitude the rate of ionization of the Rh−Me bond compared to the "blank" reaction with $Cp^*RhMe_2(PMe_3)$. It should be noted that the observation of a spin

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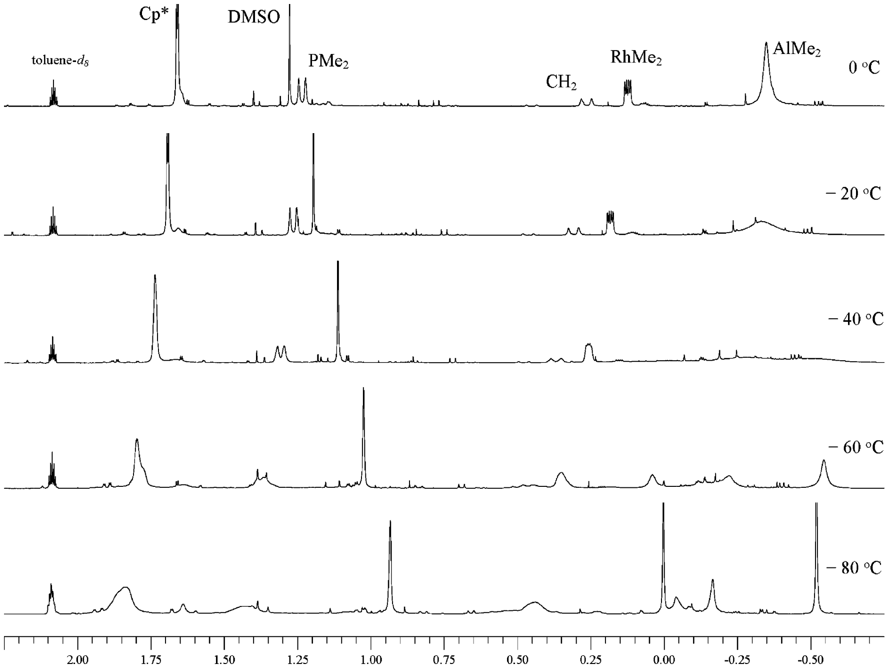

Figure 1. ^{1}H NMR spectra of **3**·DMSO in the presence of 1.5 equiv of AlMe$_3$ at low temperature.

saturation transfer contrasts with the report that alkylalanes do not ionize Cp*IrH$_2$(PMe$_3$) but instead form Cp*IrH$_2$(PMe$_3$)·alane adducts with a direct Ir−Al interaction.[13] It cannot be excluded that such an interaction occurs with the less nucleophilic rhodium analogue as a competitive path to ionization; however, such interaction would not lead to a spin saturation transfer. Still, the constrained geometry of **3** would favor the ionization pathway since the competing formation of a four-membered ring Lewis base−Lewis acid adduct would be unfavored, even if possible, therefore enhancing the reaction rates. Also, while it is still possible for free AlMe$_3$ to interact with complex **3**·DMSO and ionize the metal center, circumstantial evidence suggests that this pathway is unlikely (*vide infra*) and that Cp*RhMe$_2$(PMe$_2$CH$_2$AlMe$_2$) is the active species in solution.

Between −20 and 40 °C, the reaction mixture of complex **3**·DMSO and 1 equiv of AlMe$_3$ gave ^{1}H NMR spectra that were quite different from one temperature to another, with clear changes in chemical shift for all resonances. Since there is no evidence of formation of any new species, such equilibrium, in conjunction with the spin saturation transfer experiment, indicates that the ionization and the DMSO abstraction are both reversible processes, which may also explain the stability of the reaction mixture. However, when the temperature of the reaction mixture was raised to 40 °C, it was possible to observe immediately by ^{31}P{^{1}H} NMR spectroscopy the growth of one species at 21.5 ppm ($^1J_{\mathrm{Rh-P}} = 124$ Hz, $^2J_{\mathrm{Rh-P}} = 28$ Hz). This species became the major one in solution when the temperature was raised to 80 °C. The ^{1}H NMR spectrum was also quite informative, with a Cp* resonance at 1.57 ppm, two virtual triplets at 1.31 and 1.19 ppm for the PMe$_2$, and complex coupling patterns for the Rh-Me and methylene resonances. The species was confirmed to be [Cp*RhMe(μ^2-$\eta^2_{(\mathrm{P,C})}$-PMe$_2$CH$_2$)]$_2$ (**4**) by X-ray crystallography (Figure 2). The six-membered metallacycle possesses a twist-boat conformation caused principally by a small average P−Rh−C angle of 92.1°. In order to minimize steric hindrance, both Cp* rings are in the equatorial position, while the methyl groups on each of the rhodium atoms are in the axial position of the metallacycle. The average Rh−P distance is 2.243(2) Å, while all the Rh−Me and Rh−CH$_2$R distances are within 2.090(7) and 2.101(7) Å. The synthesis and solution characterization of [(PMe$_3$)$_2$Rh(μ^2-$\eta^2_{(\mathrm{P,C})}$-PMe$_2$CH$_2$)]$_2$ had been reported previously,[18] but complex **4** is the first structurally characterized compound bearing [Rh(μ^2-$\eta^2_{(\mathrm{P,C})}$-PR$_2$-CR′$_2$)]$_2$ as a central core. To our knowledge, the only other transition metal complexes bearing a M$_2$P$_2$C$_{(\mathrm{sp}^3)2}$ core to ever be characterized crystallographically are {Cl(PPh$_3$)Pd(μ^2,$\eta^2_{(\mathrm{P,C})}$-CH$_2$P(tBu)Cl)}$_2$,[19] {(dmpe)HRu(μ^2,$\eta^3_{(\mathrm{P,P,C})}$-(Me)$_2PCH_2CH_2$P-(Me)CH$_2$)}$_2$,[20] and {CpNi($\mu^2$,$\eta^2_{(\mathrm{P,C})}$-CH$_2PPh_2$)}$_2$.[21] Only in the Ru complex does the structure show a clear chair conformation; the two other complexes exhibit a major distortion in the metallacycle caused by P−M−C angles close to 90°, like the one observed in complex **4**.

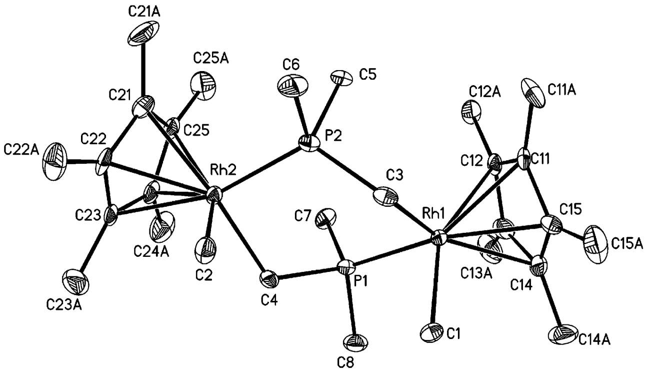

Figure 2. ORTEP diagram of **4**. The hydrogens atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh(1)−C(1) 2.091(7); Rh(1)−C(3) 2.095(7); Rh(1)−P(1) 2.2439(19); Rh(2)−C(2) 2.090(7); Rh(2)−C(4) 2.101(7); Rh(2)−P(2) 2.242(2); C(1)−Rh(1)−C(3) 84.2(3); C(1)−Rh(1)−P(1) 85.1(2); C(3)−Rh(1)−P(1) 92.0(2); C(2)−Rh(2)−C(4) 84.2(3); C(2)−Rh(2)−P(2) 86.6(2); C(4)−Rh(2)−P(2) 92.24(18).

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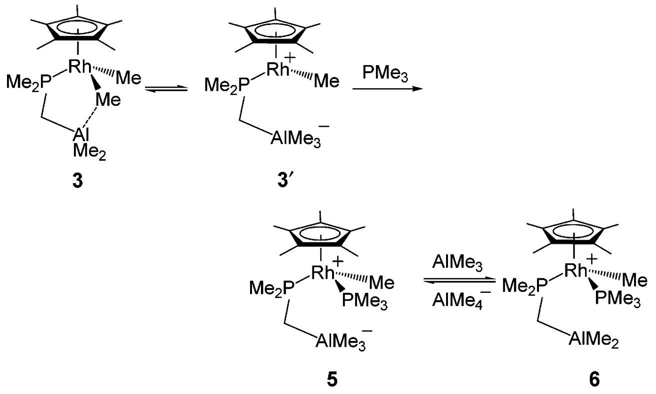
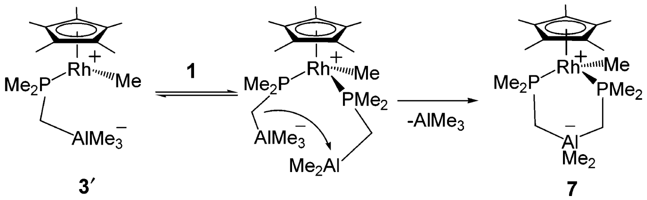
Scheme 6



Scheme 7



The isolation of complex **4** gave added insight into the nature of the bifunctional ligand **1** and further information on its role in complex **3**. A proposed mechanism for the formation of **4** is depicted in Scheme 5. For the metallacycle to form, two conditions need to be met: first, the metal has to be ionized, since a nucleophilic attack on an 18-electron species would otherwise not happen. Second, the presence of an aluminate (AlR_4^-) is required, since the alane moiety in complex **3** is not nucleophilic enough to deliver the fragment $Cp^*RhMe_2PCH_2^-$ and initiate the metallacycle formation. Therefore, the first step of the proposed mechanism for the formation of complex **4** implicates the ionization of the Rh-Me group, which was shown to take place rapidly at lower temperature as observed from the spin saturation transfer experiment, to form a cationic intermediate of the general composition $Cp^*Rh^+Me(PMe_2CH_2AlMe_3^-)$ (**3′**). At lower temperature, the aluminate functionality of zwitterion **3′** serves as a nucleophile to revert to complex **3** in an intramolecular degenerative process. However, zwitterion **3′** can undergo a bimolecular transformation with another zwitterionic species. Instead of delivering a methyl group, the fragment $Cp^*RhMe_2PCH_2^-$ of **3′** can be transferred to another metal center while releasing $AlMe_3$. It is unclear at this point if the formation of complex **4** implies a concerted one-step mechanism or a two-step transformation.

In an attempt to trap the cationic species formed, PMe_3 and $AlMe_3$ were added to a 0.03 M solution of **3**·DMSO in toluene-d_8. In addition to **3**·DMSO and $PMe_3 \cdot AlMe_3$ (20.5 and −46.1 ppm, respectively by $^{31}P\{^1H\}$ NMR spectroscopy), it was possible to observe at −50 °C one new species when 1 equiv of PMe_3 and 2 equiv of $AlMe_3$ were added. It consisted of one doublet of doublets at 21.8 ppm ($^1J_{Rh-P} = 163$ Hz, $^3J_{P-P} = 19$ Hz) and one doublet at −46.5 ppm ($^3J_{P-P} = 19$ Hz). The chemical shift of the latter signal, which is very close to that of $PMe_3 \cdot AlMe_3$, clearly indicates that its connectivity is close to $PMe_3 \cdot AlMe_2R$. Since the resonance at 21.8 ppm, with a chemical shift close to **3**·DMSO, also has a $^3J_{P-P}$ coupling constant of 19 Hz, it is reasonable to conclude that the species $Cp^*RhMe_2(PMe_2CH_2AlMe_2 \cdot PMe_3)$ (**3**·PMe_3) was present in solution. The ^1H spectrum of this product was quite similar to the one of complex **3**·DMSO, with the exception of a methylalane resonance that appeared as a doublet at −0.40 ppm ($^3J_{H-P} = 7$ Hz). However, when there was more PMe_3 than $AlMe_3$ added, or when the temperature was raised above 10 °C, the doublet observed at −46.5 ppm in the $^{31}P\{^1H\}$ NMR spectra was no longer present and the $^3J_{P-P}$ coupling of the 21.8 ppm resonance also disappeared. A fluxional process was taking place since the half-height width of the latter signal was also broader relative to complex **3**·DMSO. This result clearly contrasts with the lack of reactivity observed between **3**·DMSO and PMe_3 in the absence of $AlMe_3$, once more confirming the efficiency of $AlMe_3$ in removing DMSO from the alane moiety of the bifunctional ligand.

When the reaction mixture containing complex **3′** and PMe_3 was heated to 60 °C or higher, in addition to **4**, two new compounds were observed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, which were attributed to $Cp^*RhMe^+(PMe_3)(Me_2PCH_2AlMe_3^-)$ (**5**) and $[Cp^*RhMe^+(PMe_3)(Me_2PCH_2Al_xMe_y)]AlMe_4^-$ (**6**; $x = 1$ and $y = 2$ or $x = 2$ and $y = 5$) (Scheme 6). The $^{31}P\{^1H\}$ NMR spectra of complexes **5** and **6** are quite characteristic of a rhodium complex bearing two inequivalent phosphines, with the expected pair of doublets of doublets. The $^{31}P\{^1H\}$ chemical shifts of $PMe_2CH_2AlMe_x$ for complexes **5** (minor species) and **6** (major species) are respectively 20.5 and 19.8 ppm, both having a $^1J_{P-Rh}$ of 125 Hz, while the PMe_3 chemical shifts are respectively at 1.4 and 1.3 ppm and have a $^1J_{P-Rh}$ of 156 Hz. In both compounds, both phosphines are coupled with each other with a coupling constant of 47 Hz. When additional $AlMe_3$ was added, only complex **6**, with the phosphine resonances at 16.8 and 1.1 ppm, was observed. The isolation at the solid state and complete characterization of these complexes were however not possible. It is unclear at this point if the $AlMe_x$ resonances observed in **6** can be attributed to a single alane ($AlMe_2$), which could interact with the rhodium methyl group remaining without ionizing it, or to the formation of a dialane (Al_2Me_5), like the one observed in trimethylaluminum. However, the presence of more than one AlMe resonance, the high dependence of the chemical shifts on temperature and $AlMe_3$ concentration for complex **6**, and the known ability for these alkylaluminum species to exhibit alkyl exchange (*vide supra*) strongly suggest that the aluminate moiety can undergo nucleophilic displacement. While the ionization of $Cp^*IrH_2(PMe_3)$ using $B(C_6F_5)_3$ was previously observed,[12d] these results can be contrasted with the reported reactivity of alanes with these organometallic complexes.[13] They are even more remarkable when compared to the *absence of reactivity* of $Cp^*RhMe_2(PMe_3)$ under similar reaction conditions. Indeed, the addition of 2 equiv of $AlMe_3$ with or without 3 equiv of PMe_3-d_9 to a 0.03 M solution of $Cp^*RhMe_2(PMe_3)$ in toluene-d_8 only leads to 3% decomposition after 24 h at 80 °C and 10% decomposition after 24 h at 90 °C, while *no other compounds were observed* by ^1H and $^{31}P\{^1H\}$ NMR. Furthermore, no deuterium incorporation in $Cp^*RhMe_2(PMe_3)$ or phosphine substitution was observed.

When 1 equiv of **1** and 2 equiv of $AlMe_3$ were added to complex **3**·DMSO, a complex reaction mixture was observed by NMR spectroscopy, but when this reaction mixture was heated at 90 °C for 3 days, it was possible to isolate a pentane-soluble yellow powder that proved to be the zwitterionic complex $Cp^*Rh^+Me(Me_2PCH_2Al^-Me_2CH_2PMe_2)$ (**7**) (Scheme 7). The compound is stable in the solid state, but decomposes in solution over the course of a day unless in the presence of a small amount of $AlMe_3$. The chemical shift of the phosphines in the $^{31}P\{^1H\}$ NMR spectrum of complex **7** (14.5 ppm) is upfield compared to those in cationic complexes **5** and **6**, which have resonances at 20.5 and 19.8 ppm, respectively. The $^1J_{P-Rh}$

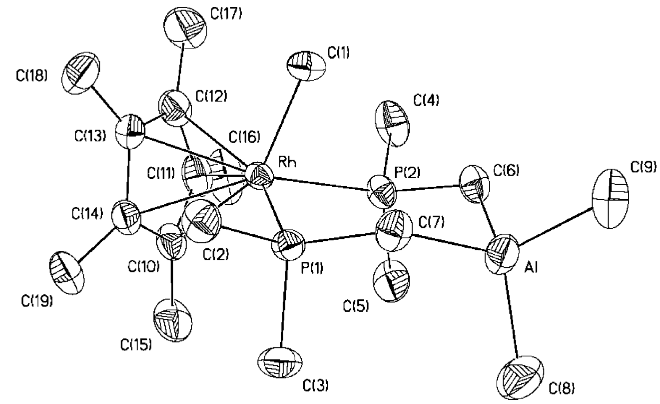


Figure 3. ORTEP diagram of **7**. The hydrogens atoms were omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh−P(1) 2.2750(4); Rh−P(2) 2.2744(4); Rh−P(1) 2.1071(15); C(1)−Rh−P(1) 87.18(5); C(2)−Rh−P(1) 85.78(5); P(1)−Rh−P(2) 94.649(15).

of 137 Hz for complex **7** is significantly lower than those observed for the $PMe_2CH_2AlMe_x$ in cationic species **5** and **6**, suggesting that the Rh−P bonding might be weaker, a consequence of a constrained six-membered metallacycle. The ^1H NMR spectrum of **7** is also quite characteristic, with a Cp* resonance at 1.25 ppm, indicative of strong bonding of the ligand on the cationic metal center. The presence of two virtual triplets at 1.23 and at 1.03 ppm and of two multiplets for the methylene protons indicates that the metallacycle is rigid in solution. Crystals suitable for an X-ray diffraction study were obtained in low yield from pentane at −35 °C, and the molecular structure is shown in Figure 3. The rhodium atom is bonded to Cp*, a methyl group, and an anionic bidentate phosphine $(Me_2PCH_2)_2AlMe_2^-$ in a piano-stool fashion. This chelating ligand type is the first one to be reported in the literature[4] and is reminiscent of the boron analogue $(Ph_2PCH_2)_2BPh_2^-$, first reported by Peters.[22] The Rh−P bond distances are in the expected range for such an interaction at 2.2747(4) Å. The Rh−Me bond length of 2.1071(15) Å in complex **7** is comparable to the distance of 2.106(5) Å for cationic complex $[Cp^*Rh(PMe_3)(Me)(CH_2Cl_2)]^+$ [23] and significantly longer than that of 2.255(4) Å in $Cp^*Rh(PMe_3)MeCl$.[24] The route for the formation of complex **7** also implies the presence of putative **3′**, which can coordinate to $PMe_2CH_2AlMe_2$ to form a zwitterionic intermediate of the form $Cp^*Rh^+Me(PMe_2CH_2AlMe_2)(PMe_2CH_2AlMe_3^-)$. The aluminate moiety of the later compound can in turn deliver the fragment containing the metal center, as observed for the generation of dimeric complex **4**, to give **7** and 1 equiv of $AlMe_3$. No reactivity studies have yet been performed on the latter complex.

Discussion

While bimetallic species have been long known to exhibit some interesting applications in stoichiometric and catalytic homogeneous reactions,[25] the incorporation of some of the more potent main group Lewis acids in the coordination sphere of a transition metal is still underdeveloped. There has been a major interest in boron-based bifunctional ligands in the past few years for potent applications as cocatalysts. However, aluminum compounds have received less attention, probably due to their weaker kinetic stability compared to their boron counterparts and the synthetic challenges related to their isolation. The characterization of the compounds reported in the present study remains a great challenge since they exhibit a highly pyrophoric behavior and, more importantly, have high solubility, which makes their solid-state isolation difficult. However, the high activity of such analogues may prove unique and worth the synthetic challenges involved.

In a previous study, the ambiphilic ligand $Me_2PCH_2AlMe_2$ was used for the first time as a ligand in the presence of weak bases (LB), such as NEt_3 and tmeda (*N*,*N*,*N*,*N*-tetramethylethylenediamine), to form $(1\text{-Me-Ind})NiMe(Me_2PCH_2AlMe_2{\cdot}LB)$.[3a] These Lewis bases proved to be crucial in order to stabilize the alane, but, because of their lability, they did not inhibit the reactivity of the complexes toward silane homologation. However, the strongly donating quinuclidine proved to coordinate strongly to the alane moiety and inhibited the activating effect of the bifunctional ligand. With 18-electron species such as those studied in this report, the associative substitution observed with 16-electron intermediates is disfavored. The types of Rh starting material and the Lewis base are much more critical; therefore, the choice of $Cp^*RhMe_2(DMSO)$ as precursor proved to be crucial. First, the presence of methyl groups on rhodium, instead of the more common halides, is critical to avoid alkylation with the alane moiety in bifunctional ligand **1**. When $[Cp^*RhCl_2]_2$ or $Cp^*RhCl_2(DMSO)$ was used instead of the permethylated precursor, several species were observed by ^1H NMR, which prevented full characterization.[26] Therefore, the necessity of the alkyl groups limited greatly the choice of rhodium precursors. Even if complexes with weaker bases such as **3**·NR_3 (NR_3 = NEt_3 or tmeda) were desirable in order to increase their reactivity and avoid the problems observed with strong bonding between alanes and Lewis bases, the instability of precursors of general formulation $Cp^*RhMe_2{\cdot}NR_3$ makes their preparation difficult.[27]

While the sulfoxide allows a strong stabilization of the alane moiety, it causes a major problem for probing the reactivity of the bifunctional ligand. Irreversible extrusion of this Lewis base is possible with strong Lewis acids such as oxophilic unsaturated lanthanide complexes, but the resulting complexes exhibit low stability. While $AlMe_3$ also competes with **3**·DMSO for the DMSO ligand to make $AlMe_3{\cdot}DMSO$ and complex **3**, the great solubility of the products and the reversibility of this exchange have the advantage of stabilizing **3** while at the same time making the Lewis acid available for subsequent reactivity. The similarity of both DMSO adducts should cause the exchange to be close to thermoneutral. Nevertheless, the reduced steric hindrance for $AlMe_3{\cdot}DMSO$ compared to complex **3**·DMSO and the new stabilizing intramolecular interactions make complex **3** a viable species. The low kinetic barrier for such an equilibrium, as observed by the VT NMR experiments, which gave very broad features even at −80 °C, makes the isolation of species **3** or its zwitterionic analogue **3′** extremely difficult, and it has yet to be done. There are abundant pieces of circumstantial evidence for their presence in solution. Indeed, the reaction rate of $0.76 \pm 0.09\ s^{-1}$ for the abstraction of the Rh-Me group of the reaction mixture of **3**·DMSO and $AlMe_3$

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at 22 °C is significantly faster than for that without the presence of a bifunctional ligand, suggesting an enhancing effect of the tether. Also, the observation of bisphosphine complexes **5** and **6** from trapping experiments with PMe_3 strongly suggests the presence of ionization at the metal center. Finally, the solid-state structures of two new complexes, **4** and **7**, point to the presence of an intermediate connectivity, $Cp^*Rh^+Me(PMe_2CH_2AlMe_3^-)$.

The ionization of Rh(III) alkyl intermediates is not novel, and several precedents have been reported.[28] Other than the scarcity of complexes bearing a bifunctional ligand with an alane moiety, two major reasons make the system reported herein unusual and highly promising. First, the rates of ionization measured for both the bifunctional compound **3** and the bimolecular systems with $Cp^*RhMe_2(PMe_3)$ clearly show an influence of the tether on the activity of the Lewis acid. While the solid-state structures of the intermediates are still unknown, one of the reasons that could explain such different behavior is the geometric constraint caused by the coordination of the Lewis acid moiety on the transition metal in complex **3**. Recent results by Bourissou pointed out that ambiphilic borane ligands could interact with transition metal complexes in two fashions, either by a direct bond with the transition metal in the case of softer gold(I) complexes or by forming μ-Cl bridges with palladium(II) species. The former species is favored, however, because of the five-membered ring formed.[3c] Even if possible, the methylene bridge in **3** impedes the formation of a four-membered metallacycle with direct interactions between the alane and the rhodium(III) species, which is common for $Cp^*IrH_2(PMe_3)$.[13] This constraint makes the formation of μ-Me species more facile, therefore opening the way for faster ionization.

The activity of zwitterionic early metal complexes with pendant borate moieties in ethylene polymerization proved to be at best similar to the nonzwitterionic systems.[2a,b] In the present report, the trapping of the zwitterionic complex **3′** proved to be more facile than for the bimolecular analogue. Indeed, the formation of complexes **5** and **6** was observed immediately when **3** was heated at 60 °C, while no reaction occurred with $Cp^*RhMe_2(PMe_3)$ in the presence of $AlMe_3$ and PMe_3-d_9, even after heating at 90 °C for 24 h. A reason that can be speculated for the lack of functionalization of the latter complex, other than solubility issues, is the high reactivity of the counterion $AlMe_4^-$. The later species is a very good nucleophile and will alkylate back the reactive $[Cp^*RhMe(PMe_3)]^+$ fragment easily, before charge separation occurs. In the zwitterionic species, the intramolecular charge separation can stabilize the resulting complex in a nonpolar solvent, thereby allowing functionalization to occur. While PMe_3-trapped compounds have little catalytic interest, functionalization with unsaturated substrates like olefins could prove useful since the aluminate moiety could participate in further transformations and thereby would induce a productive functionalization of a $Cp^*MRH(PMe_3)$ fragment.

Concluding Remarks

The recent increase in the interest in ambiphilic ligands and their coordination to late transition metals has produced complexes with novel and intriguing metal−ligand interactions. The synthesis of $Cp^*RhMe_2(PMe_2CH_2AlMe_2)$ reported herein has provided additional insights into the reactivity of such bifunctional systems. While there are some setbacks to overcome in order to make complexes with tethered Lewis acids synthetically useful, this ligand design opens the door to several interesting reactivity patterns. The use of cocatalysts or bifunctional ligands has long been concentrated on early metal systems, mainly for olefin polymerization, but our studies reveal that they also have an impact on more electron-rich late transition metal complexes. We are currently investigating the reactivity of species **3′** with unsaturated nucleophiles and working toward a better understanding of the role of the tether in stabilizing the zwitterionic complexes.

Experimental Section

General Comments. All manipulations were conducted under an atmosphere of nitrogen using standard glovebox techniques. Most of the reactions were carried out in a J-Young NMR tube, and therefore NMR conversions are indicated. Dry, deoxygenated solvents were employed for all manipulations. All solvents were distilled from Na/benzophenone, except for DMSO, which was distilled from CaH_2. Benzene-d_6 and toluene-d_8 were purified by vacuum distillation from Na/K alloy. The HRMS were carried out at the Centre Régional de Spectrométrie de Masse at the Université de Montréal. The NMR and Schlenk tubes were silylated prior to usage, using a 10% solution of Me_3SiCl in $CHCl_3$ in order to prevent protonolysis of the *AlMe* moieties. $(Me_2AlCH_2PMe_2)_2$ (**1**),[29] $Cp^*RhMe_2(DMSO)$ (**2**),[30] $Cp^*RhMe_2(PMe_3)$,[15] and $La(dbm)_3$[31] were prepared according to literature procedures. NMR spectra were recorded on a Varian Inova NMR AS400 spectrometer at 400.0 MHz (^1H), 100.0 MHz (^{13}C), and 161.9 MHz (^{31}P) or on a Bruker NMR AC-300 at 300 MHz (^1H) and 75.5 MHz (^{13}C). The temperatures of the VT NMR experiments were measured using a thermocouple inside the probe, which was calibrated with methanol prior to use. On some occasions, the methyl groups on the phosphines appeared as virtual triplets (vt). For all compounds, HMQC and $^1H\{^{31}P\}$ NMR experiments were performed in order to assign the spectra.

$Cp^*RhMe_2(PMe_2CH_2AlMe_2{\cdot}DMSO)$ (3·DMSO). Cp^*RhMe_2-DMSO (11 mg, 0.030 mmol) and $(Me_2PCH_2AlMe_2)_2$ (4 mg, 0.015 mmol) were dissolved in benzene-d_6 in an NMR tube. The mixture was left to rest for 7 h for the formation of a pale yellow solution of **3**·DMSO to be complete. The yield was over 95% by ^1H NMR spectroscopy. ^1H NMR (benzene-d_6): δ 1.82 (d, $^4J_{H-P} = 2.0$ Hz, 15H, $C_5\mathit{Me}_5$), 1.44 (dd, $^2J_{H-P} = 9.2$ Hz, $^3J_{H-Rh} = 0.8$ Hz, 6H, $P\mathit{Me}_2CH_2AlMe_2$), 1.30 (s, 6H, DMSO), 0.55 (d, $^2J_{H-P} = 13.5$ Hz, 2H, $PMe_2C\mathit{H}_2AlMe_2$), 0.35 (dd, $^2J_{H-Rh} = 2.3$ Hz, $^3J_{H-P} = 5.0$ Hz, 6H, $Rh\mathit{Me}_2$), −0.36 (s, 6H, $PMe_2CH_2Al\mathit{Me}_2$). ^{13}C NMR (toluene-d_8): δ 95.6 (t, $^1J_{C-Rh} = {}^2J_{C-P} = 3.4$ Hz, C_5Me_5), 36.7 (s, DMSO), 17.6 (dd, $^1J_{C-P} = 28.0$ Hz, $^2J_{C-Rh} = 0.8$ Hz, $P\mathit{Me}_2CH_2AlMe_2$), 13.7 (br, $PMe_2\mathit{C}H_2AlMe_2$), 9.4 (s, $C_5\mathit{Me}_5$), −4.4 (dd, $^1J_{C-Rh} = 30.0$ Hz, $^2J_{C-P} = 14.9$ Hz, $Rh\mathit{Me}_2$), −5.6 (br, $PMe_2CH_2Al\mathit{Me}_2$). $^{31}P\{^1H\}$ NMR (benzene-d_6): 19.5 (d, $^1J_{P-Rh} = 163$ Hz).

$Cp^*RhMe_2(PMe_2CH_2AlMe_2)$ (3) from $AlMe_3$. Trimethylaluminum (3.1 mg, 4.1 μL, 0.043 mmol) was added via syringe into a solution of **3**·DMSO (15 mg, 0.030 mmol) in toluene-d_8 or benzene-d_6. ^1H NMR δ (toluene-d_8, 20 °C): 1.64 (d, $^4J_{H-P} = 2.1$ Hz, 15H, $C_5\mathit{Me}_5$), 1.36 (s, 6H, DMSO), 1.22 (d, $^2J_{H-P} = 9.2$ Hz, 6H, $P\mathit{Me}_2CH_2AlMe_2$), 0.24 (d, $^2J_{H-P} = 14.0$ Hz, 2H, $PMe_2C\mathit{H}_2AlMe_2$), 0.08 (dd, $^2J_{H-Rh} = 2.4$ Hz, $^3J_{H-P} = 5.3$ Hz, 6H, $Rh\mathit{Me}_2$), −0.36 (s, 24H, $Al\mathit{Me}_x$). ^1H NMR (toluene-d_8, −80 °C): δ 1.84

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(br, 15H, $\mathrm{C_5}\mathit{Me_5}$), 1.43 (br, 6H, $\mathrm{P}\mathit{Me_2}\mathrm{CH_2AlMe_2}$), 0.93 (s, 6H, DMSO), 0.85−0.65 (br, 2H, $\mathrm{PMe_2C}\mathit{H_2}\mathrm{AlMe_2}$), 0.44 (br, 6H, $\mathrm{Rh}\mathit{Me_2}$), 0.00 (s, 6H, $\mathrm{Me_2Al}(\mu^2\text{-}\mathit{Me_2})\mathrm{AlMe_2}$), −0.04 (br, 6H, $\mathrm{PMe_2CH_2Al}\mathit{Me_2}$), −0.17 (s, 6H, $\mathit{AlMe_3}\mathrm{\cdot DMSO}$), −0.51 (s, 6H, $\mathit{Me_2}\mathrm{Al}(\mu^2\text{-}\mathrm{Me_2})\mathrm{Al}\mathit{Me_2}$). ^{13}C NMR (benzene-$d_6$, 20 °C): δ 95.8 (t, $^{1}J_{\mathrm{C-Rh}} = {}^{2}J_{\mathrm{C-P}} = 3.5$ Hz, $\mathit{C_5}\mathrm{Me_5}$), 36.6 (s, DMSO), 18.2 (d, $^{1}J_{\mathrm{C-P}} = 27.0$ Hz, $\mathrm{P}\mathit{Me_2}\mathrm{CH_2AlMe_2}$), 13.7 (br, $\mathrm{PMe_2}\mathit{C}\mathrm{H_2AlMe_2}$), 9.4 (s, $\mathrm{C_5}\mathit{Me_5}$), −4.1 (dd, $^{1}J_{\mathrm{C-Rh}} = 28.7$ Hz, $^{2}J_{\mathrm{C-P}} = 13.5$ Hz, $\mathrm{Rh}\mathit{Me_2}$), −6.6 (br, $\mathrm{PMe_2CH_2Al}\mathit{Me_2}$). ^{31}P{^{1}H} NMR (toluene-d_8, 20 °C): δ 19.5 (d, $^{1}J_{\mathrm{P-Rh}} = 159$ Hz).

$\mathrm{Cp^*RhMe_2(PMe_2CH_2AlMe_2)}$ (3) from $\mathrm{La(dbm)_3}$. $\mathrm{La(dbm)_3}$ (13.5 mg, 0.017 mmol) was added into a solution of **3**·DMSO (7.5 mg, 0.015 mmol) in toluene-d_8 or benzene-d_6. ^{1}H NMR (benzene-d_6): δ 1.73 (d, $^{4}J_{\mathrm{H-P}} = 2.1$ Hz, 15H, $\mathrm{C_5}\mathit{Me_5}$), 1.35 (dd, $^{2}J_{\mathrm{H-P}} = 9.0$, $^{3}J_{\mathrm{H-Rh}} = 0.9$ Hz, 6H, $\mathrm{P}\mathit{Me_2}\mathrm{CH_2AlMe_2}$), 1.23 (br, 6H, DMSO), 0.45 (d, $^{2}J_{\mathrm{H-P}} = 13.2$ Hz, 2H, $\mathrm{PMe_2C}\mathit{H_2}\mathrm{AlMe_2}$), 0.32 (dd, $^{2}J_{\mathrm{H-Rh}} = 2.5$ Hz, $^{3}J_{\mathrm{H-P}} = 5.2$ Hz, 6H, $\mathrm{Rh}\mathit{Me_2}$). The methylalane resonance was not located. ^{31}P{^{1}H} NMR (benzene-d_6): δ 16.8 (d, $^{1}J_{\mathrm{P-Rh}} = 166$ Hz).

$[\mathrm{Cp^*RhMe}(\mu^2\text{-}\eta^2_{\mathrm{(P,C)}}\text{-}\mathrm{PMe_2CH_2})]_2$ (4). One equivalent (or more) of $\mathrm{AlMe_3}$ (2.1 mg, 0.030 mmol) was added to a 0.03 M solution of **3**·DMSO (15 mg, 0.030 mmol) in benzene-d_6 or toluene-d_8. The tube was inserted into the probe of a spectrometer and heated at 80 °C. Formation of **4** starts at 40 °C but was mostly complete by the time the temperature reached 80 °C (80% yield). Some yellow crystals of **4** were manually picked from a small crystalline fraction containing as well $\mathrm{Cp^*RhMe_2(PMe_3)}$ that was obtained by slow evaporation of the solvent in a glovebox. ^{1}H NMR (benzene-d_6): δ 1.57 (d, $^{4}J_{\mathrm{H-P}} = 1.7$ Hz, 15H, $\mathrm{C_5}\mathit{Me_5}$), 1.31 (vt, $^{2}J_{\mathrm{H-P}} = 9.4$ Hz, 3H, $\mathrm{P}\mathit{Me_2}$), 1.19 (vt, $^{2}J_{\mathrm{H-P}} = 7.8$ Hz, 3H, $\mathrm{P}\mathit{Me_2}$), 0.79−0.73 (m, $\mathrm{C}\mathit{H_2}$), 0.57−0.45 (m, $\mathrm{C}\mathit{H_2}$), 0.43 (ddd, $^{3}J_{\mathrm{H-P}} = 4.8$ Hz, $^{2}J_{\mathrm{H-Rh}} = 2.4$ Hz, $^{4}J_{\mathrm{H-P}} = 0.8$ Hz, 3H, $\mathrm{Rh}\mathit{Me}$). ^{13}C NMR(benzene-d_6): δ 100.2 (dd, $^{1}J_{\mathrm{C-Rh}} = 5.4$ Hz, $^{2}J_{\mathrm{C-P}} = 2.7$ Hz, $\mathit{C_5}\mathrm{Me_5}$), 21.4 (dd, $^{1}J_{\mathrm{C-P}} = 20.0$ Hz, $^{2}J_{\mathrm{C-Rh}} = 2.1$ Hz, $\mathrm{P}\mathit{Me_2}$), 19.0 (d, $^{1}J_{\mathrm{C-P}} = 27.6$ Hz, $\mathrm{P}\mathit{Me_2}$), 9.6 (s, $\mathrm{C_5}\mathit{Me_5}$), 13.7 (br, $\mathit{C}\mathrm{H_2}$), 0.35 (dd, $^{1}J_{\mathrm{C-Rh}} = 27.8$ Hz, $^{2}J_{\mathrm{C-P}} = 14.0$ Hz, $\mathrm{Rh}\mathit{Me}$). ^{31}P{^{1}H} NMR (benzene-d_6): δ 21.5 (dd, $^{1}J_{\mathrm{P-Rh}} = 124$, $^{2}J_{\mathrm{P-Rh}} = 28$ Hz). HRMS (ESI) calcd for $\mathrm{C_{28}H_{52}P_2Rh_2}$: ($\mathrm{M^+}$) 656.16488, ($\mathrm{M^+ - CH_3}$) 641.14197; found ($\mathrm{M^+}$) 656.16328, ($\mathrm{M^+ - CH_3}$) 641.14103.

$\mathrm{Cp^*RhMe_2(PMe_2CH_2AlMe_2\cdot PMe_3)}$ (3·PMe$_3$). Two equivalents of $\mathrm{AlMe_3}$ (4.2 mg, 0.060 mmol) was added to a 0.03 M solution of **3**·DMSO (15 mg, 0.030 mmol) in toluene-d_8. The NMR tube was capped with a septum, and 1 equiv of $\mathrm{PMe_3}$ (3.0 μL, 2.2 mg, 0.030 mmol) was syringed into the solution. The NMR tube was cooled to −50 °C in the probe of the spectrometer. ^{1}H NMR (toluene-d_8, −50 °C): δ 1.83 (d, $^{3}J_{\mathrm{H-P}} = 1.8$ Hz, 15H, $\mathrm{C_5}\mathit{Me_5}$), 1.38 (d, $^{2}J_{\mathrm{H-P}} = 10.9$ Hz, 6H, $\mathrm{P}\mathit{Me_2}\mathrm{CH_2AlMe_2}$), 0.55 (d, $^{2}J_{\mathrm{H-P}} = 13.6$ Hz, 2H, $\mathrm{PMe_2C}\mathit{H_2}\mathrm{AlMe_2}$), 0.35 (dd, $^{3}J_{\mathrm{H-P}} = 5.1$ Hz, $^{2}J_{\mathrm{H-Rh}} = 2.4$ Hz, 6H, $\mathrm{Rh}\mathit{Me_2}$), 0.32 (d, $^{3}J_{\mathrm{H-P}} = 6.8$ Hz, 9H, $\mathrm{PMe_2CH_2AlMe_2\cdot P}\mathit{Me_3}$), −0.40 Hz (d, $^{3}J_{\mathrm{H-P}} = 6.5$ Hz, 6H, $\mathrm{PMe_2CH_2Al}\mathit{Me_2}\mathrm{\cdot PMe_3}$). ^{31}P{^{1}H} NMR (toluene-d_8, −50 °C): δ 21.8 (dd, $^{1}J_{\mathrm{P-Rh}} = 163$ Hz, $^{3}J_{\mathrm{P-P}} = 19$ Hz, $\mathit{P}\mathrm{Me_2CH_2AlMe_2}$), −46.5 (d, $^{3}J_{\mathrm{P-P}} = 19$ Hz, $\mathrm{PMe_2CH_2AlMe_2\cdot}\mathit{P}\mathrm{Me_3}$).

$\mathrm{Cp^*RhMe(PMe_3)(Me_2PCH_2AlMe_3)}$ (5) and $[\mathrm{Cp^*RhMe(PMe_3)(Me_2PCH_2AlMe_2)}]\mathrm{AlMe_4}$ (6). Two equivalents of $\mathrm{AlMe_3}$ (4 mg, 0.060 mmol) was added to a 0.03 M solution of **3**·DMSO (15 mg, 0.030 mmol) in toluene-d_8. The NMR tube was capped with a septum, and 3 equivalents of $\mathrm{PMe_3}$ (8.9 μL, 6.6 mg, 0.090 mmol) was added via a syringe. The tube was inserted into the probe of a spectrometer and heated to 60 °C. **5**: NMR yield of 25%. ^{1}H NMR (toluene-d_8, 100 °C): δ 1.40 (d, $^{2}J_{\mathrm{H-P}} = 10.3$ Hz, 3H, $\mathrm{P}\mathit{Me_2}\mathrm{CH_2AlMe_3}$), 1.33 (t, $^{3}J_{\mathrm{H-Rh}} = 2.4$ Hz, 15H, $\mathrm{C_5}\mathit{Me_5}$), 0.89 (d, $^{2}J_{\mathrm{H-P}} = 9.6$ Hz, 9H, $\mathrm{RhP}\mathit{Me_3}$), 0.47 (d, $^{2}J_{\mathrm{H-P}} = 13.3$ Hz, 2H, $\mathrm{PMe_2C}\mathit{H_2}\mathrm{AlMe_3}$), −0.14 to −0.20 (m , 3H, $\mathrm{Rh}\mathit{Me}$), −0.47 (s, 9H, $\mathrm{-AlMe_3}$). ^{13}C NMR (toluene-d_8, 20 °C): δ 101.3 (q, $^{1}J_{\mathrm{C-Rh}} = {}^{2}J_{\mathrm{C-P}} = 2.5$ Hz, $\mathit{C_5}\mathrm{Me_5}$), 18.3 (m, $\mathrm{P}\mathit{Me_2}\mathrm{CH_2AlMe_3}$), 17.5 (d, $^{1}J_{\mathrm{C-P}} = 30.4$ Hz, $\mathrm{RhP}\mathit{Me_3}$), 11.5 (br, $\mathrm{PMe_2}\mathit{C}\mathrm{H_2AlMe_3}$), 10.2 (s, $\mathrm{C_5}\mathit{Me_5}$), −5.2 (m, $\mathrm{Rh}\mathit{Me}$), −8.2 (br, $\mathrm{Al}\mathit{Me_3}$). ^{31}P{^{1}H} NMR (toluene-d_8, 100 °C): δ 20.5 (dd, $^{1}J_{\mathrm{P-Rh}} = 125$ Hz, $^{2}J_{\mathrm{P-P}} = 47$ Hz, $\mathit{P}\mathrm{Me_2CH_2AlMe_3}$), 1.4 (dd, $^{1}J_{\mathrm{P-Rh}} = 156$ Hz, $^{2}J_{\mathrm{P-P}} = 47$ Hz, $\mathrm{Rh}\mathit{P}\mathrm{Me_3}$). **6**: NMR yield of 35%. ^{1}H NMR (toluene-d_8, 100 °C): δ 1.33 (t, $^{3}J_{\mathrm{H-Rh}} = 2.4$ Hz, 15H, $\mathrm{C_5}\mathit{Me_5}$), 1.25 (d, $^{2}J_{\mathrm{H-P}} = 10.2$ Hz, 3H, $\mathrm{P}\mathit{Me_2}\mathrm{CH_2AlMe_2}$), 0.90 (d, $^{2}J_{\mathrm{H-P}} = 9.6$ Hz, 9H, $\mathrm{RhP}\mathit{Me_3}$), 0.41 (d, $^{2}J_{\mathrm{H-P}} = 13.9$ Hz, 1H, $\mathrm{PMe_2C}\mathit{H_2}\mathrm{AlMe_2}$), 0.39 (d, $^{2}J_{\mathrm{H-Rh}} = 13.6$ Hz, 1H, $\mathrm{PMe_2C}\mathit{H_2}\mathrm{AlMe_2}$), −0.14 to −0.20 (m, 3H, $\mathrm{Rh}\mathit{Me}$), −0.49 (s, 3H, $\mathrm{-Al}\mathit{Me_2}$), −0.50 (s, 3H, $\mathrm{-Al}\mathit{Me_2}$). ^{13}C NMR (toluene-$d_8$, 20 °C): δ 101.4 (q, $^{1}J_{\mathrm{C-Rh}} = {}^{2}J_{\mathrm{C-P}} = 2.5$ Hz, $\mathit{C_5}\mathrm{Me_5}$), 18.3 (m, $\mathrm{P}\mathit{Me_2}\mathrm{CH_2AlMe_3}$), 17.5 (d, $^{1}J_{\mathrm{C-P}} = 30.4$ Hz, $\mathrm{RhP}\mathit{Me_3}$), 11.5 (br, $\mathrm{PMe_2}\mathit{C}\mathrm{H_2AlMe_3}$), 10.3 (s, $\mathrm{C_5}\mathit{Me_5}$), −5.2 (m, $\mathrm{Rh}\mathit{Me}$), −8.2 (br, $\mathrm{Al}\mathit{Me_3}$). ^{31}P{^{1}H} NMR (toluene-d_8): δ 19.8 (dd, $^{1}J_{\mathrm{P-Rh}} = 125$ Hz, $^{2}J_{\mathrm{P-P}} = 47$ Hz, $\mathit{P}\mathrm{Me_2CH_2AlMe_2}$), 1.3 (dd, $^{1}J_{\mathrm{P-Rh}} = 156$ Hz, $^{2}J_{\mathrm{P-P}} = 47$ Hz, $\mathrm{Rh}\mathit{P}\mathrm{Me_3}$). For both **5** and **6**, one of the diastereotopic $\mathrm{PMe_2}$ overlapped with the Cp* resonance and their location was confirmed by HMQC.

$\mathrm{Cp^*RhMe(Me_2PCH_2AlMe_2CH_2PMe_2)}$ (7). $\mathrm{Cp^*RhMe_2\cdot DMSO}$ (40 mg, 0.089 mmol) and $\mathrm{(Me_2PCH_2AlMe_2)_2}$ (26 mg, 0.098 mmol) were mixed in 3 mL of toluene. The dark yellow solution was left to stand for 18 h. Trimethylaluminum (19.5 mg, 0.27 mmol) was then added, and the mixture was heated to 70 °C for 72 h. The volatile materials were removed under reduced pressure, and the yellow residue was extracted with small portions of pentane. Crystals appeared upon cooling the solution at −35 °C. NMR yield 80%, isolated yield 15% (6 mg, 0.013 mmol). ^{1}H NMR (benzene-d_6): δ 1.25 (t, $^{4}J_{\mathrm{H-P}} = 2.3$ Hz, 15H, $\mathrm{C_5}\mathit{Me_5}$), 1.23 (vt, $^{2}J_{\mathrm{H-P}} = 8.7$ Hz, 6H, $\mathit{Me_2}\mathrm{PCH_2AlMe_2CH_2P}\mathit{Me_2}$), 1.03 (vt, $^{2}J_{\mathrm{H-P}} = 10.3$ Hz, 6H, $\mathit{Me_2}\mathrm{PCH_2AlMe_2CH_2P}\mathit{Me_2}$), 0.35−0.45 (m, 2H, $\mathrm{Me_2PC}\mathit{H_2}\mathrm{AlMe_2C}\mathit{H_2}\mathrm{PMe_2}$), 0.16−0.05 (m, 2H, $\mathrm{Me_2PC}\mathit{H_2}\mathrm{AlMe_2C}\mathit{H_2}\mathrm{PMe_2}$), 0.13 (dt, $^{2}J_{\mathrm{H-Rh}} = 2.3$ Hz, $^{3}J_{\mathrm{H-P}} = 4.7$ Hz, 3H, $\mathrm{Rh}\mathit{Me}$), −0.12 (s, 3H, $\mathrm{Me_2PCH_2Al}\mathit{Me_2}\mathrm{CH_2PMe_2}$), −0.23 (s, 3H, $\mathrm{Me_2PCH_2Al}\mathit{Me_2}\mathrm{CH_2PMe_2}$). ^{13}C NMR (benzene-$d_6$): 99.9 (q, $^{1}J_{\mathrm{C-Rh}} = {}^{2}J_{\mathrm{C-P}} = 3.3$ Hz, $\mathit{C_5}\mathrm{Me_5}$), 22.0 (dd, $^{1}J_{\mathrm{C-P}} = 12.0$ Hz, $^{2}J_{\mathrm{C-Rh}} = 10.4\ 8$ Hz, $\mathrm{P}\mathit{Me_2}\mathrm{CH_2AlMe_2}$), 20.5 (dd, $^{1}J_{\mathrm{C-P}} = 16.9$ Hz, $^{2}J_{\mathrm{C-Rh}} = 14.6$ Hz, $\mathrm{P}\mathit{Me_2}\mathrm{CH_2AlMe_2}$), 13.7 (br, $\mathrm{PMe_2}\mathit{C}\mathrm{H_2AlMe_2}$), 9.3 (s, $\mathrm{C_5}\mathit{Me_5}$), −6.5 (dt, $^{1}J_{\mathrm{C-Rh}} = 25.8$ Hz, $^{2}J_{\mathrm{C-P}} = 12.4$ Hz, $\mathrm{Rh}\mathit{Me}$), −6.9 (br, $\mathrm{Al}\mathit{Me_2}$). ^{31}P{^{1}H} NMR (benzene-d_6): δ 14.5 (d, $^{1}J_{\mathrm{P-Rh}} = 137$ Hz). HRMS (ESI) calcd for $\mathrm{C_{19}H_{40}AlP_2Rh}$: ($\mathrm{M^+ - CH_3}$) 445.12410; found ($\mathrm{M^+ - CH_3}$) 445.12456.

$\mathrm{Cp^*RhMe_2(PMe_3)}$ with $\mathrm{AlMe_3}$ and $\mathrm{PMe_3}$-d_9. $\mathrm{Cp^*RhMe_2(PMe_3)}$ (10 mg, 0.035 mmol) was dissolved in toluene-d_8, and 2 equiv of $\mathrm{AlMe_3}$ was added (5 mg, 0.070 mmol). Three equivalents of $\mathrm{PMe_3}$-d_9 (12.0 μL, 0.10 mmol) was syringed into the solution. The NMR tube was heated to 60 °C for 24 h, 70 °C for 36 h, 80 °C for 24 h, and 90 °C for 48 h. ^{1}H and ^{31}P{^{1}H} NMR spectra were taken at regular intervals.

Crystallographic data. Crystallographic data are reported in Table 1. Single crystals were coated with Paratone-N oil, mounted using a glass fiber, and frozen in the cold nitrogen stream of the goniometer. For **7**, a hemisphere of data was collected on a Bruker AXS P4/SMART 1000 diffractometer using ω and θ scans with a scan width of 0.3° and 10 s exposure times. For **4**, the data were collected on a Bruker SMART APEX II diffractometer. The data were reduced (SAINT)[32] and corrected for absorption (SADABS).[33] The structure was solved and refined using SHELXS-97 and SHELXL-97.[34] All non-H atoms were refined anisotropically. The hydrogen atoms were placed at idealized positions. Neutral atom scattering factors were taken from the *International Tables for X-Ray Crystallography*.[35] All calculations and drawings were performed using the SHELXTL package.[36] The final model was

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[32] *SAINT* Version 7.07a; Bruker AXS Inc.: Madison, WI, 2003.

[33] Sheldrick, G. M. *SADABS* Version 2004/1; Bruker AXS Inc.: Madison, WI, 2004.

[34] Sheldrick, G. M. *SHELXS-97 and SHELXL-97. Programs for the refinement of crystal structures*; University of Gottingen: Germany, 1997.

[35] *International Tables for X-Ray Crystallography, Vol C*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordecht, 1992; pp 219−222 and 500−502.

Table 1. Crystallographic Data for Compounds 4 and 7

	4	**7**
formula	$C_{28}H_{52}P_2Rh_2$	$C_{19}H_{40}AlP_2Rh$
fw	656.46	460.34
size (mm)	0.34 × 0.28 × 0.08	0.575 × 0.40 × 0.35
cryst syst	monoclinic	monoclinic
space group	$P2(1)/c$	$P2(1)/n$
a (Å)	23.467(7)	9.2217(4)
b (Å)	8.227(5)	15.0671(8)
c (Å)	15.370(3)	16.9934(8)
α, β, γ (deg)	90, 92.090(6), 90	90, 95.495(1), 90
V (Å^3)	2965(2)	2350.3(2)
Z	4	4
wavelength (Å)	0.71073	0.71073
D_{calc} (g·cm^{-3})	1.470	1.301
F_{000}	1360	968
temp (K)	193(2)	183(1)
no. of unique/total reflns	6311/6311	5248/15 986
R_{int}	0.000	0.0173
final R indices [$I > 2\sigma(I)$]	R1 = 0.0410 wR2 = 0.1113	R1 = 0.0210 wR2 = 0.0559
goodness of fit ($\lvert\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(N_o - N_v)\rvert^{1/2}$)	1.238	1.059
max. and min. peaks in final diff map (e$^-$/Å^3)	1.161/−0.991	0.840/−0.232

checked for either missed symmetry or voids in the crystal structure using the PLATON software.[37] None were found. The crystal structures gave a satisfactory chekcif report.

Compound **4** was found to have a twin. Two different orientations were found using CELL_NOW. There is one 180° rotation around reciprocal axis 1 0 0. The transformation matrix was 1 0 0; 0 −1 0; 0 0 −1 according to the original cell. The BASF factor was 0.42.

Crystallographic data have been deposited with CCDC (CCDC No. 637305 for compound **4** and CCDC No. 637304 for compound **7**). These data can be obtained upon request from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, e-mail: deposit@ccdc.cam.ac.uk, or via the Internet at www.ccdc.cam.ac.uk.

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Supporting Information Available: Selected ^1H and $^{31}P\{^1H\}$ NMR spectra of **3**·DMSO, **3**, **4**, **5**, **6**, and **7** are available free of charge via the Internet at http://pubs.acs.org.

OM700401C

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(36) *SHELXTL*, Version 6.12; Bruker AXS: Madison, WI, 2001.

(37) Spek, A. L. *PLATON*, *A Multipurpose Crystallographic Tool*; University of Utrecht: Utrecht, The Netherlands, 2005.