Coordination of Ethylene to a Zwitterionic Rh(III) Half-Sandwich Complex: Influence of Ambiphilic Ligands on Reactivity

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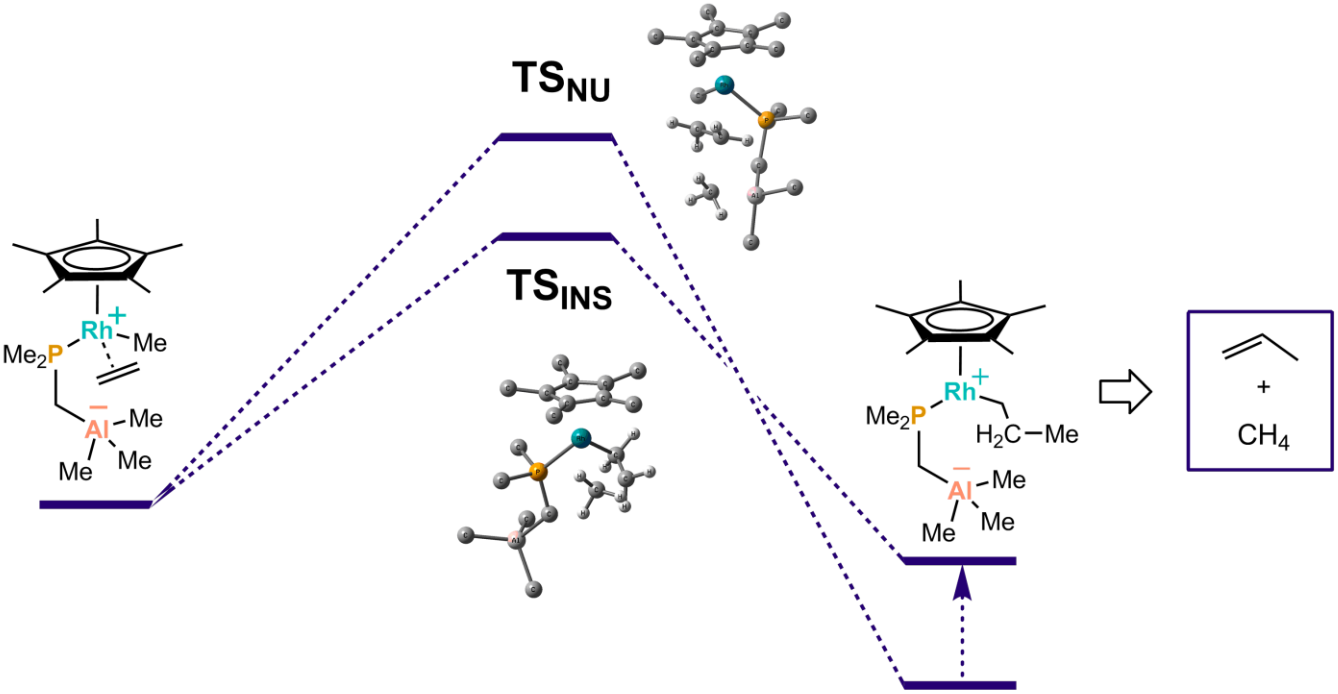


Abstract

The reactivity of Rh(III) half-sandwich complex Cp*RhMe$_2$(κ^P-μ^{Al-Me}PMe$_2$CH$_2$AlMe$_2$) **2** (Cp* = η^5-pentamethylcyclopentadienyl) with ethylene was investigated. Coordination of ethylene (or ethylene-*d*$_4$) gave a mixture of products including as principal species zwitterionic complexes Cp*Rh$^+$Me(C$_2$H$_4$)(PMe$_2$CH$_2$AlMe$_3$$^-$) **4** (or **4**-*d*$_4$) and [Cp*Rh$^+$Me(C$_2H_4$)(PMe$_2CH_2$AlMe$_3$$^-$)][AlMe$_3$] (**4'**), after the abstraction of a Rh-methyl group by the pendant Lewis acid, and base free Cp*RhMe$_2$(PMe$_2$CH$_2$AlMe$_2$) (**5**). Heating this complex at 50 °C results in the generation of propene (or propene-*d*$_{3,4}$), methane (or methane-*d*$_1$), and trace amounts of butene, as organic materials, as well as previously characterized [Cp*RhMe(μ^2-η^2(P,C)-PMe$_2$CH$_2$)]$_2$ (**10**) and rhodium(I) species. Two different pathways for the reactivity of the zwitterionic π-complex were investigated by density functional theory (DFT). It is likely that propene is formed by *β*-hydride elimination from a cationic Rh-propyl fragment that is generated either by insertion of ethylene into a Rh-C bond or by a nucleophilic attack of the methyl-aluminate fragment on coordinated ethylene. After releasing propene, the neutral complex Cp*RhHMe(PMe$_2$CH$_2$AlMe$_2$) **11** is most likely responsible for the reductive elimination of methane.

Introduction

Ambiphilic molecules, having both Lewis acid and base moieties, have gained a lot of importance during the past decade for the activation of small molecules,[1] as sensors,[2] or as ligands for transition metals.[3] While the Lewis acid moiety of ambiphilic ligands has been known to coordinate to late transition metals in a σ-acceptor fashion,[3,4] or to serve as an anchor for incoming substrates,[5] an interest has recently emerged for ambiphilic ligands coordinating in a L → M–X → Z fashion (Chart 1, **A**),[6] L and Z being the Lewis base and Lewis acid moieties, respectively. Although many Lewis acids can interact with precatalysts to form active catalysts,[7] mainly in Ziegler-Natta olefin polymerization[8] but also for C-C bond activation[9] and catalytic hydroboration reactions,[10] the influence of ambiphilic ligands on reactivity has been little studied. In some cases, however, the tethering of the Lewis acid has been shown to significantly enhance the activity of the Lewis acid and the stability of the resulting complexes. In this manner, it was reported that $Me_2PCH_2AlMe_2$ can coordinate nickel(II) indenyl complexes to form a species where the tethered alane activates the Ni–Me moiety (Chart 1, **B**) and induces important rate enhancement for phenylsilane homologation compared to the system with a monodentate phosphine.[11] In addition, the borane moiety in phosphanylborane complex [*trans*-$(Ph_2P(CH_2)_2B(C_8H_{14}))_2$-$Re(CO)_4$][$BF_4$] (Chart 1, **C**) has been shown by Bercaw, Labinger and co-workers to facilitate hydride transfer and induce the reduction of a rhenium-bound carbon monoxide upon addition of molecular hydrogen with a strong phosphazene base[12] or a hydride source, $NaHBEt_3$ or $[HPt(dmpe)_2]^+$.[13]

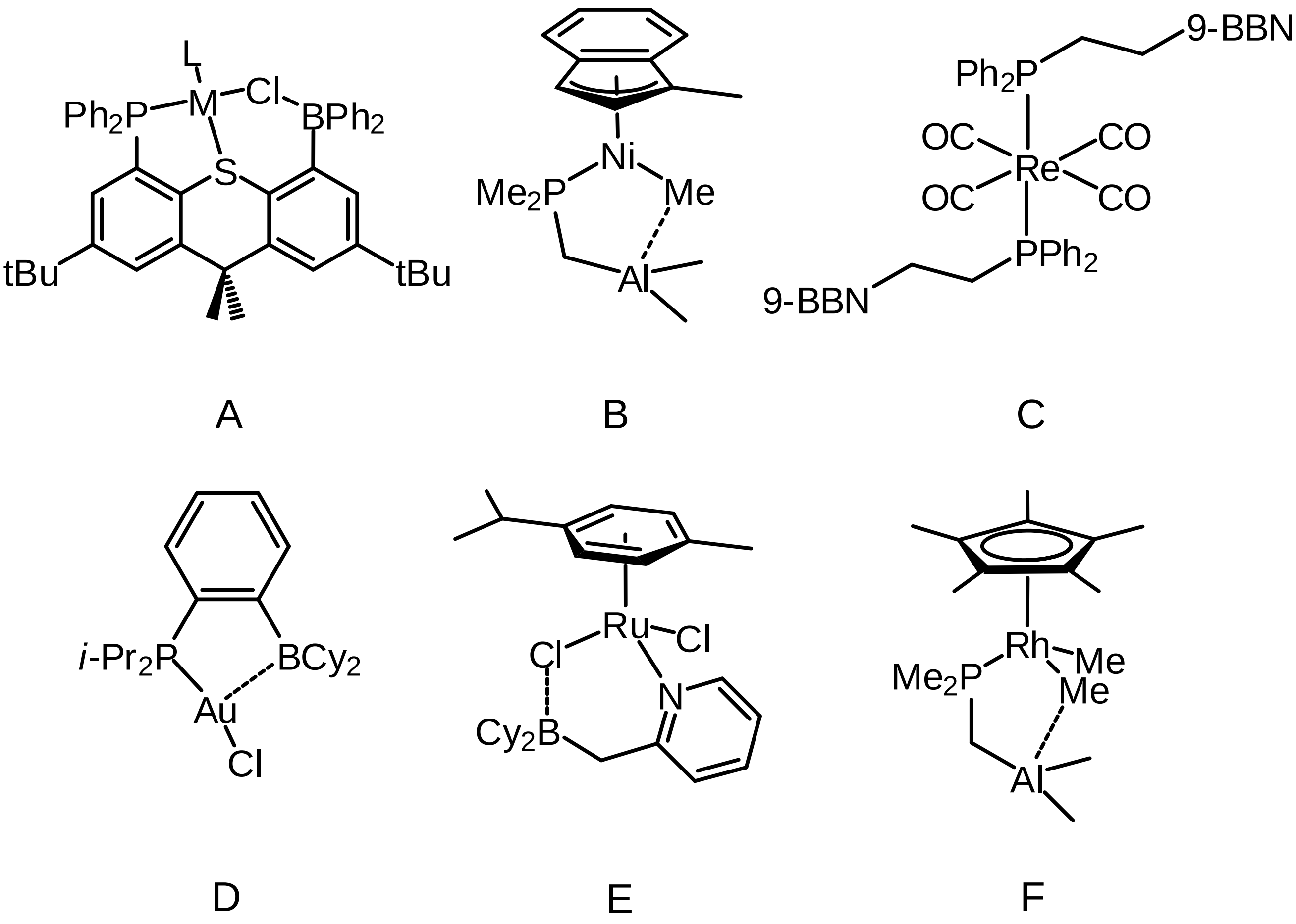
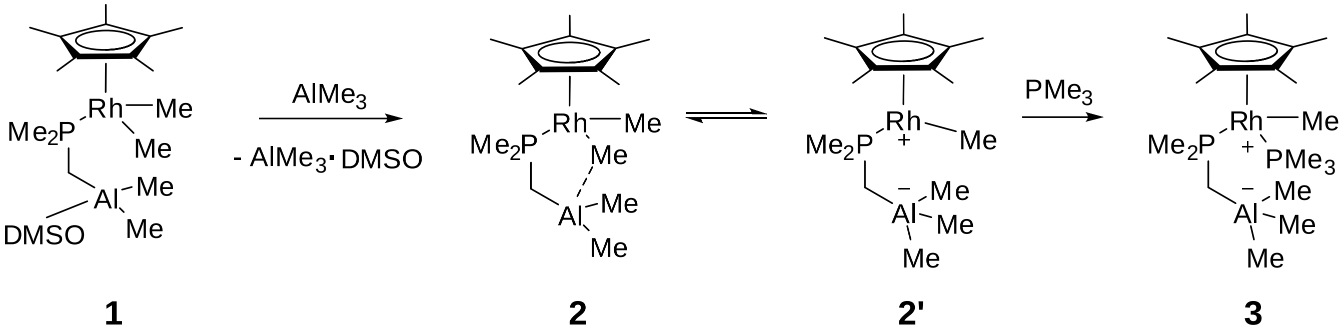


Chart 1.

Bourissou and co-workers have shown that the borane moiety in phosphanyl or picolyl boranes tends to interact with late transition metal complexes either in a L→ M → Z σ acceptor fashion (Chart 1, **D**)[14] or with a L→ M–X → Z acceptor bridging interaction (Chart 1, **E**) (Pd(II) or Rh(I),[15] Ru(II)[16]), which represents a preliminary step in the intramolecular activation of M–X bonds. The phosphanyl alanes, on the other hand, tend to form zwitterionic complexes by abstraction of the X ligand by the alane moiety,[17] while phosphanyl gallium does both depending on the chemical environment.[18] The formation of zwitterionic complexes was also observed for the coordination of *β*–phosphinoethylboranes in Ni–Methyl complexes.[19] Our research group has reported that $Me_2PCH_2AlMe_2$ can be coordinated to a cyclopentadienyl Rh(III) dimethyl complex (Chart 1, **F**)[20] to form complexes of interest in alkane activation.[21] It was shown that the Lewis acid tether plays a crucial role in the activation the Rh-Me bond, so that $Cp^*RhMe_2(\kappa^P\text{-}\mu^{Al\text{-}Me}PMe_2CH_2AlMe_2)$ ionizes to the zwitterionic species $Cp^*RhMe^+(PMe_2CH_2AlMe_3^-)$ as shown by dynamic NMR spe ctroscopy and trapping experiments with PMe_3 (Scheme 1).



Scheme 1.

No ionization was observed with the analogous bimolecular system $Cp^*RhMe_2(PMe_3)$ + $AlMe_3$ under similar conditions; however, the cationic $[Cp^*RhMe(PMe_3)]^+$ analogue can be obtained by exchange of the triflate in $Cp^*RhMe(OTf)(PMe_3)$ with the noncoordinating anion $BAr'_4{}^-$ (Ar' = 3,5-$C_6H_3(CF_3)_3$) by adding $NaBAr'_4$ in CH_2Cl_2 to produce $[Cp^*RhMe(PMe_3)(CH_2Cl_2)]BAr'_4$.[22] This complex is known to activate C-H bonds in C_6H_6 or aldehydes,[23,24] C-C bonds in aryl and alkyl cyanides,[25] and Si-H bonds in silanes.[26] The cationic ethylene complexes $[(\eta^5\text{-}C_5R_5)M(PMe_3)(C_2H_4)H]BF_4$ (M = Co,[27] Rh[28]; R = H, CH_3) can be formed by protonation of the M(I) complexes $(\eta^5\text{-}C_5R_5)M(PMe_3)(C_2H_4)$ with HBF_4. Previous studies have shown that the rhodium complexes easily undergo hydride 1,2-migratory insertion of the coordinated ethylene ligand to produce, in the presence of ethylene, the ethyl ethylene complex $[(\eta^5\text{-}C_5R_5)Rh(PMe_3)(C_2H_4)C_2H_5]BF_4$ (R = H, CH_3) which can in turn undergo either ethyl 1,2-migratory insertion[29] or nucleophilic addition of a PMe_3 molecule (R=H).[30] Evitt and Bergman observed an alternative route with $(\eta^5\text{-}C_5H_5)Co(PPh_3)(CH_3)_2$ where the dissociation of PPh_3 occurs prior to the 1,2-migratory insertion and the elimination of propene and methane.[31a] It should be noted that with electron donating PMe_3, the phosphine dissociation, and consequently the insertion, is unlikely.[31b]

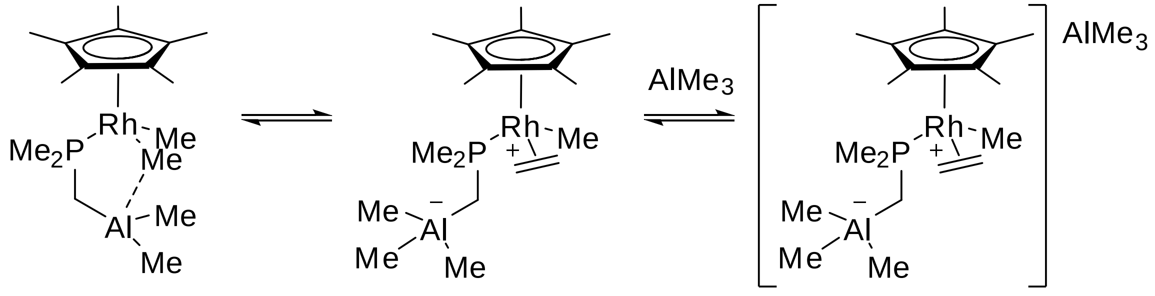
Herein we report that previously reported $Cp^*RhMe_2(\kappa^P\text{-}\mu^{Al\text{-}Me}PMe_2CH_2AlMe_2)$ reacts with ethylene to form π-complexes. In addition to the migratory insertion that was previously observed for the cationic complexes reported by Brookhart,[29] the presence of an aluminate moiety on the ambiphilic ligand makes possible a nucleophilic addition pathway to the π-bound ethylene. Density functional theory was used to determine whether both pathways are accessible with these complexes.

Results and Discussion

Generation and Spectral Characterization of the Ethylene Complex $Cp^*RhMe(C_2H_4)(PMe_2CH_2AlMe_3)$

It was previously observed by NMR spectroscopy that treatment of $Cp^*RhMe_2(PMe_2CH_2AlMe_2{\cdot}DMSO)$ **1** with one equivalent of $AlMe_3$ in benzene-d_6 or toluene-d_8 creates an equilibrium between complex $Cp^*RhMe_2(\kappa^P\text{-}\mu^{Al\text{-}Me}PMe_2CH_2AlMe_2)$ **2** and its zwitterionic analogue $Cp^*Rh^+Me(PMe_2CH_2AlMe_3^-)$ **2'**.[20] Although the neutral complex is the only observed species at 20 ºC according to the ^1H NMR spectrum, trapping of the 16-electron zwitterion can be achieved by the addition of PMe_3 to give $Cp^*Rh^+Me(PMe_3)(PMe_2CH_2AlMe_3^-)$ **3** (Scheme 1). Similarly, $Cp^*RhMe_2(PMe_2CH_2AlMe_2{\cdot}DMSO)$ (**1**) reacts with $AlMe_3$ and excess ethylene (1 atm) in a J-Young NMR tube in benzene-d_6 or toluene-d_8 to generate three new Cp*Rh-containing products, accompanied by residual **2**. (See Electronic Supplementary Information, Fig. S1) It is noteworthy that complex **2** does not react with propene nor styrene under similar conditions.

Upon removal of the solvent and dissolution of the resulting solid, the three products formed were no longer present and only **2** was observed, suggesting that all compounds depend on the presence of ethylene. Two of these products, **4** and **4'**, present in a 1:1.2 ratio based on the ^1H NMR integrations for the Cp* resonances at δ 0.96 ($^4J_{H\text{-}P}$ = 2.1 Hz) and 0.95 ($^4J_{H\text{-}P}$ = 2.1 Hz), respectively, possess very similar ^1H and $^{31}P\{^1H\}$ NMR spectral properties. Overlapping ^1H NMR resonances corresponding to coordinated ethylene can be observed as two multiplets at δ 2.08 and 1.86. The first complex that was identified is $Cp^{*}Rh^{+}Me(C_2H_4)(PMe_2CH_2AlMe_3^{-})$ (**4**), which is obtained by coordination of ethylene to the cationic rhodium center in the zwitterion **2'**. Some notable features for **4** include the low 114 Hz $^{1}J_{P\text{-}Rh}$ coupling constant observed for the ^{31}P resonance at δ 31.4 which compares to zwitterion **3** ($^{1}J_{P\text{-}Rh}$ = 125 Hz), but is much lower than neutral analogues **1** and **2** ($^{1}J_{P\text{-}Rh}$ = 163 Hz and 159 Hz, respectively).[20] It was observed that the ratio between **4** and **4'** depends on the concentration of $AlMe_3$ in the benzene-d_6 solution, such that at three and ten equivalents, the ratio becomes 1:3.0 and 1:25 (See ESI, Fig. S2.1). We suspect that the complex observed in the presence of excess $AlMe_3$ is an $AlMe_3$ adduct, $[Cp^{*}RhMe(C_2H_4)(PMe_2CH_2AlMe_3)][AlMe_3]$ (**4'**), and by changing $AlMe_3$ and C_2H_4 concentrations, we find a direct correlation between the **4'** over **4** ratio and $AlMe_3$ concentration, K = [**4'**]/[**4**][$AlMe_3$] = 48.3 ± 6.7 M^{-1}.[32] (Scheme 2) Although the exact nature of the interaction is not yet fully understood, the presence of two closely related structures, such as **4** and **4'**, was previously observed for the PMe_3 adduct, $[Cp^{*}Rh^{+}Me(PMe_3)(PMe_2CH_2AlMe_3^{-})]$.[20] Complex **4'** was characterized as the major species in solution in the presence of ten equivalents of $AlMe_3$ by ^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ NMR spectroscopy using selective decoupling of the ^{31}P resonances, and 2D techniques (COSY and HMQC) to accurately assign the resonances (see ESI, Fig. S3). In the ^{1}H NMR spectrum, coordinated ethylene appears as two resonances at δ 2.08 (ddd, 2H, 8.5, 4.7 and 1.8 Hz) and 1.86 (dd, 2H, 8.4 and 1.7 Hz). No $^{3}J_{H\text{-}P}$ coupling is observed for the latter resonance, while the former has a $^{3}J_{H\text{-}P}$ coupling of 4.7 Hz which is removed by selective decoupling of the $^{31}P\{^{1}H\}$ resonance at δ 30.6 ($^{1}J_{P\text{-}Rh}$ = 116 Hz). These signals are not present when the reaction is done with ethylene-d_4; however broad resonances show up at δ 2.05 and 1.84 in the ^{2}H NMR spectrum. (See ESI, Fig. S4) At – 100 °C in dichloromethane-d_2, the ^{1}H NMR resonances of coordinated ethylene in complex $[Cp^{*}RhPMe_3(C_2H_5)(C_2H_4)^{+}][BF_4^{-}]$ were reported at lower field as multiplets at δ 2.70, 2.70, 2.55, and 2.40,[28] which indicates that $Me_2PCH_2AlMe_3^{-}$ in complex **4'** is likely a better donor than PMe_3. The Cp* resonance is extremely high field at δ 0.96 and the Rh-Me resonance accounts for three protons and appears as a doublet of doublets at δ 0.27 ($^{3}J_{H\text{-}P}$ = 5.4 Hz, $^{2}J_{H\text{-}Rh}$ = 2.2 Hz). Although all the Al-Me signals appear as a very broad singlet at δ - 0.34, as previously observed for this family of compounds,[20] the resonances for the phosphanyl alane moieties are in the expected range and diastereotopic signals for the methylene and the methyl groups on the phosphorous are indicative of a chiral metal center.



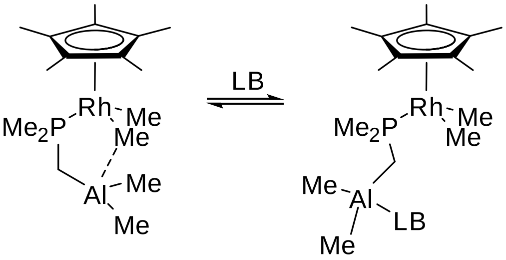
2 **4** **4'**

Scheme 2.

The third complex observed, **5**, is present when lower amounts of $AlMe_3$ are used (1-3 equivalents). This complex has a $^{31}P\{^1H\}$ chemical shift of δ 24.1, with a $^1J_{P\text{-}Rh}$ of 159 Hz. The low field ^1H Cp* resonance (δ 1.88 ppm, $^4J_{H\text{-}P} = 1.9$ Hz) and the fact that the Rh-Me doublet of doublets (δ 0.40, $^3J_{H\text{-}P} = 4.6$ and $^2J_{H\text{-}Rh} = 2.5$ Hz) integrates for 6 protons strongly indicate that it is indeed a neutral $[Cp^*RhMe_2(PR_3)]$ species. The PMe_2 (δ 1.60, $^2J_{H\text{-}P} = 9.3$ Hz) and PCH_2Al (δ 0.65, $^2J_{H\text{-}P} = 13.4$ Hz) resonances can also be observed by ^1H NMR spectroscopy as single resonances, which precludes the presence of a chiral center on the complex, unlike in the case of **4** and **4'**. Based on these spectroscopic evidences, we assume that the complex is a neutral $Cp^*RhMe_2PMe_2CH_2AlMe_2$ species where the Lewis acidic aluminum center no longer interacts with a Rh-Me group. It is clear, however, that the resonances associated with **5** were not observed when only $AlMe_3$ (0.5 – 10 equivalents) was added to **1** in the same temperature range, demonstrating the importance of ethylene in generating **5**. Furthermore, it can be observed that the concentration of **5** varies with the pressure of ethylene, and that the ratio between **5** and **4** is fairly constant (0.83 ± 0.09)[32] at various $AlMe_3$ concentrations and ethylene pressures ranging from one to 6 atm., suggesting that the formation of **5** is also driven by ethylene coordination.

Stabilization of base free Cp*RhMe$_2$(PMe$_2$CH$_2$AlMe$_2$), 5

The stabilization of the Lewis acid of the ambiphilic arm by PMe$_3$ has previously been observed and the adduct Cp*RhMe$_2$(PMe$_2$CH$_2$AlMe$_2$.PMe$_3$), **2*PMe$_3$**, has been spectroscopically characterized.[20] The rhodium bound phosphine has a chemical shift of δ 21.8, with a $^1J_{\text{P-Rh}}$ of 163 Hz. At temperature above 10°C, the resonance for the aluminum bound phosphine at -46.5 ppm is no longer present and the signal at 21.8 ppm becomes broad. The complexity of the mixture at room temperature and the fluxional processes involved prevented further characterization, but at temperatures over 60°C, a signal at δ 23.7 with a $^1J_{\text{P-Rh}}$ of 160.0 Hz was also observed but was not identified at the time. In the absence of a Lewis base, this signal is not present but the addition of dimethylsulfide, which is known to stabilize poorly an interaction with aluminum, gives also the species **5**, both at room and low temperatures (see Supporting Information). On the other hand, diethylether, triethylamine, and DMSO, which all form stable Al-LB adducts, do not yield product **5**. It is thus believed that **5** consists of **2.C$_2$H$_4$** (Scheme **3**, LB = ethylene, dimethylsulfide, or trimethylphosphine), as discussed below.

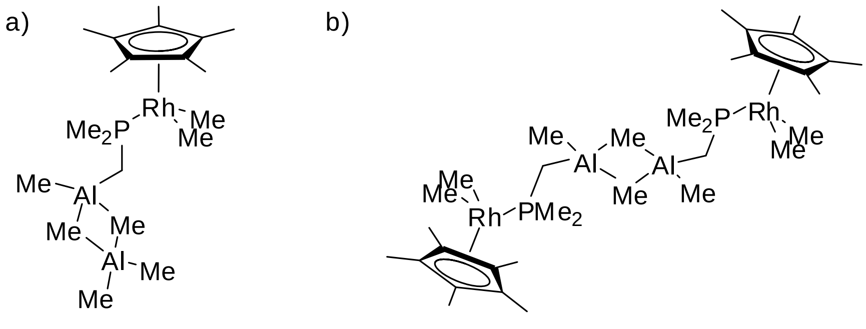


2 **2.LB = 5**

Scheme 3.

The bonding of a Lewis base to the aluminum in **2** to generate **2.LB** is possible. Since the Al-PMe$_3$ interaction was observed only at temperatures below 10°C, it is not abnormal that adducts with weaker Lewis bases, such as ethylene, dimethylsulfide, and triphenylphosphine, would not be detected by NMR spectroscopy. If the exchange rate between bound and free ligand is **2.LB** is very fast, no signal for the bound LB should be observed and in presence of a large excess of LB, which is needed in the case of

SMe_2 and ethylene to observe **2.LB**, no significant shift in their nuclear magnetic spectroscopic of LB should be observed. Because both SMe_2 and ethylene are poor electron donors and because they are far from the metallic core (see Figure S5 for the DFT optimized structures) the spectroscopic features of the organometallic species should be very similar. In fact, the only protons that shift significantly when comparing both adducts are the ones on the methylene fragment of the ambiphilic ligand, being at 0.65 and 0.69 ppm for **2.C_2H_4** and **2.SMe_2**, respectively (Figure S1.5). Although to the best of our knowledge the ethylene aluminum adducts have never been observed, computational studies do establish the possibility of its existence.[33] It was computed that the complexation energy for the adduct $AlMe_3$-ethylene was ranging from -5 to -7 kcal/mol, which according to DFT is close to the cost in energy of the cleavage of the Al-Me-Rh interaction in **2** to generate **2*** (ΔH and ΔG of 7.0 and 4.6 kcal.mol^{-1}, respectively). The transformation of **4** to **2-C_2H_4** was investigated using DFT and was found to be very close to be more or less isothermic with a ΔH of 0.6 kcal.mol^{-1}, which would explain why both species are observed spectroscopically in similar concentrations at low $AlMe_3$ concentrations.[34] However, it cannot be excluded that species **2*** is stabilized by other interactions with $AlMe_3$ (Chart 2a, **5'**) or by three-center-two-electron interactions with an additional **2*** (Chart 2b, **5''**), but since the presence of **2*** is not observed at high $AlMe_3$ concentrations or in the absence of a Lewis base, such a hypothesis is unlikely.



5' **5''**

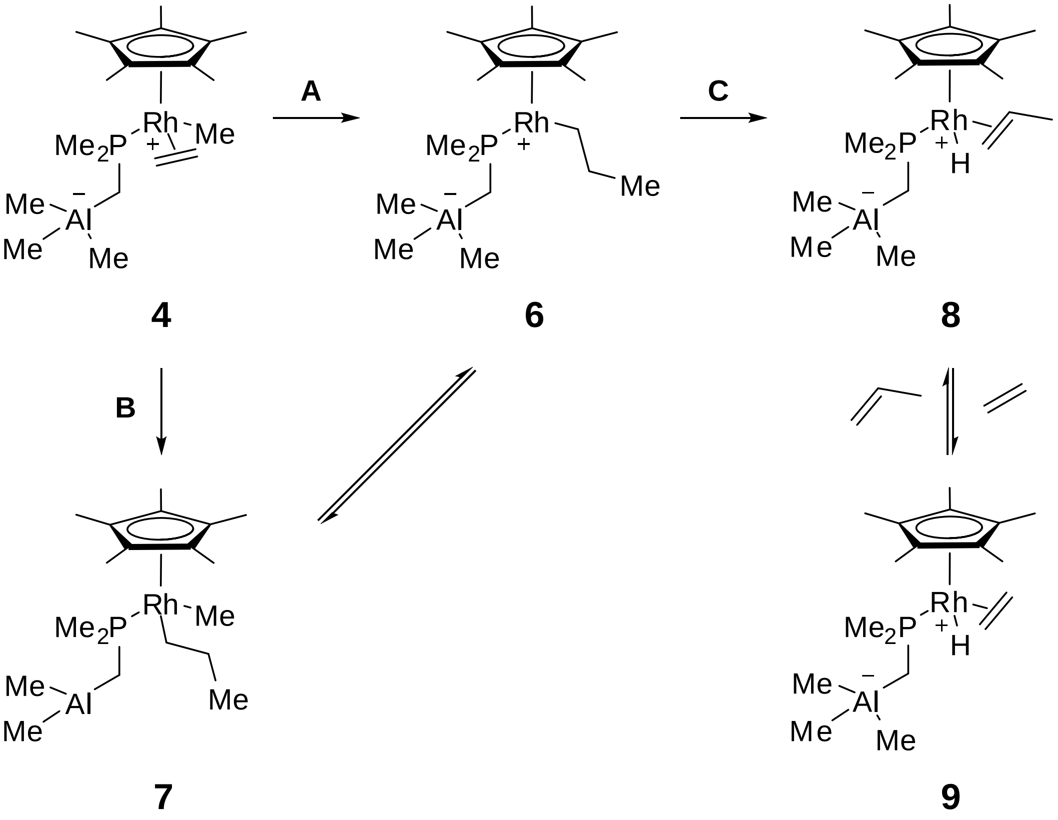
Chart 2.

Reactivity of the Ethylene Complex $Cp^*Rh^+Me(C_2H_4)(PMe_2CH_2AlMe_3^-)$ (4)

When a solution of $Cp^*Rh^+Me(C_2H_4)(PMe_2CH_2AlMe_3^-)$ **4** under 1 – 4 atm. ethylene is heated at 50 °C for 48 hours, the formation of propene and methane can be observed by ^{1}H NMR spectroscopy, with the characteristic vinylic resonances at δ 4.9, 5.0, and 5.7 and the methyl resonance at δ 1.5 for propene, and a single resonance at δ 0.14 for methane. The presence of propene and methane was confirmed by GC/MS analysis (M/z = 42 and M/z = 16, respectively) by direct injection of one mL of the head space of the J-Young NMR tube at room temperature in the GC/MS, which also permitted to identify traces of butene (M/z =56). With deuterated ethylene, under the same conditions, the vinylic resonances of propene did not appear in the ^{1}H NMR spectrum and GC/MS analysis revealed the presence of propene-d_3 (M/z = 45), a significant amount of propene-d_4 (M/z = 46, see ESI for isotopic distribution), and traces of butene-d_8 (M/z = 64). Furthermore, methane-d_1 (δ 0.14, t; $[CH_4]$:$[CH_3D]$ = 3:1) was observed by ^{1}H NMR spectroscopy. The only organometallic complex observed by ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy in benzene-d_6 was $[Cp^*RhMe(\mu^2\text{-}\eta^2(P,C)\text{-}PMe_2CH_2)]_2$ **10** which has a very characteristic $^{31}P\{^1H\}$ NMR signature: δ 21.5 (dd, $^1J_{P\text{-}Rh}$ = 124 Hz, $^2J_{P\text{-}Rh}$ = 28 Hz) (Scheme 5).[20] The residual inorganic materials came out as an insoluble red oil in benzene-d_6.

Dissolution of the red oil in DMSO-d_6 was possible and the $^{31}P\{^1H\}$ NMR spectrum did show two major products. The first species has two phosphorus resonances coming from at least 3 phosphorus atoms at δ 60.0 (dt, $^1J_{P\text{-}Rh}$ = 99 Hz, $^2J_{P\text{-}P}$ = 24 Hz) and δ 11.2 (dd, $^1J_{P\text{-}Rh}$ = 162 Hz, $^2J_{P\text{-}P}$ = 24 Hz), which would suggest the presence of a multimetallic species having a high symmetry. Although the exact nature of this species could not be found, the presence of one very low $^1J_{P\text{-}Rh}$ at 99 Hz and another higher at 162 Hz would suggest that the metal fragments are not at the same oxidation state and/or have different charges. The other product observed by ^{31}P NMR (δ 13.3) has a phosphorus-rhodium coupling constant of 190 Hz, which is typical for a Rh(I) species and is closely related to the coupling constant observed for species $CpRh(C_2H_4)(PMe_3)$ in presence of one equivalent of Al_2Me_6 (≈ 185 Hz).[35] As presented in the later work of Mayer and Calabrese, the very rapid fluxional movements associated with the Al-Me resonances prevent a clean assignation of the ^{1}H NMR spectrum. The high-resolution MS of the crude red oil shows the presence of several Cp*Rh fragments, including [Cp*RhMe]$^+$, [Cp*Rh(PMe$_3$)Me]$^+$, [Cp*Rh(PMe$_3$)$_2$Me]$^+$, [Cp*RhMe(μ^2-η^2(P,C)-PMe$_2$CH$_2$)RhCp*]$^+$, [Cp*RhMe(μ^2-η^2(P,C)-PMe$_2$CH$_2$)(PMe$_3$)RhCp*]$^+$ with M/z observed at 253.05, 329.09, 405.13, 641.14, 717.19, respectively. It should be noted that the presence of PMe$_3$ is associated to the protonolysis of the ambiphilic ligand under the protic conditions of the electron spray ionization mode.

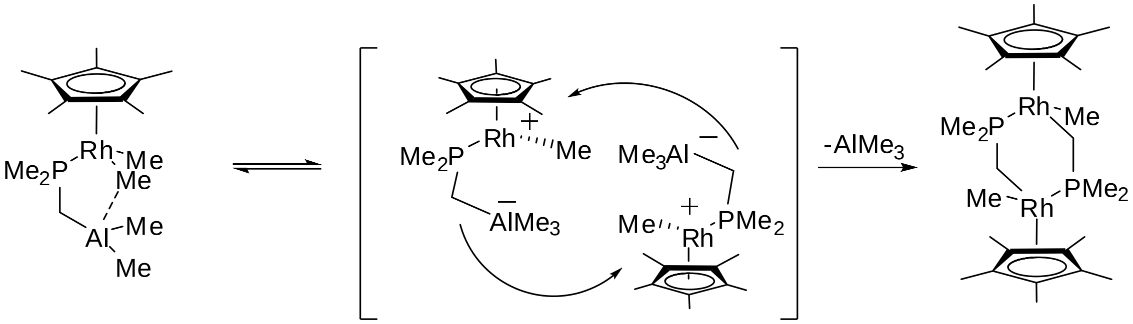
Brookhart and co-workers reported the dimerization of ethylene to butene using the cationic complex [Cp*RhH(C$_2$H$_4$)(PMe$_3$)]BF$_4$ as precatalyst.[29] According to their mechanistic studies, subsequent insertion of ethylene into the hydride, and then into the ethyl fragment thus formed, rapidly generates a rhodium butyl complex that can undergo β-hydride elimination to generate butene and a rhodium hydride species. The latter complex acts as a catalyst for 2-butene formation. An equivalent reaction pathway is expected to occur with the half-sandwich rhodium complex containing the ambiphilic ligand PMe$_2$CH$_2$AlMe$_2$. The formation of propene can be easily explained by the following chain of events (Scheme 4). The formation of the zwitterionic propyl complex Cp*Rh$^+$Pr(PMe$_2$CH$_2$AlMe$_3^-$) **6** could arise from either a methyl 1,2-migratory insertion (**A**) or a nucleophilic attack (**B**) from the methylaluminate moiety in **4** to give neutral Cp*RhMePr(PMe$_2$CH$_2$AlMe$_2$) **7** which can then ionize to zwitterion **6**. Thus, β-hydride elimination of propene (**C**) should occur readily from complex **6** to generate the propene π-complex Cp*RhH(n-C$_3$H$_6$)(PMe$_2$CH$_2$AlMe$_3$) **8**. Since the propene π-complex **8** was not detected from the reaction mixture and the coordination of propene to zwitterion **2’** proved not feasible, the dissociation of the propene is likely favored. In presence of ethylene-d_4, species Cp*RhD(CD$_2$=CDCH$_3$)(PMe$_2$CH$_2$AlMe$_3$) should be formed, with subsequent release of propene-d_3. However, since there is a significant amount of propene-d_4 observed by GC-MS, it can be proposed that isomerization involving intermediate Cp*Rh(CD(CD$_3$)(CH$_3$))(PMe$_2$CH$_2$AlMe$_3$) to generate Cp*RhH(CD$_2$=CDCH$_2$D)(PMe$_2$CH$_2$AlMe$_3$) occurs rapidly. The rhodium hydride complex formed, Cp*RhH(C_2H_4)($PMe_2CH_2AlMe_3$) **9**, should be an efficient catalyst for ethylene dimerization if a path similar to Brookhart's catalytic reaction was followed. However, the trace amount of butene revealed by GC/MS, and absent in the ^{1}H NMR spectrum, combined with the absence of any hydride species, indicates that a lower energy reaction occurs faster than ethylene dimerization.



Scheme 4.

Actually, evidence for at least two other pathways is observed. First, the formation of [Cp*RhMe(μ^2-η^2(P,C)-PMe_2CH_2)]$_2$ **10** proves to be a thermodynamic sink in most reactions involving species Cp*RhMe$_2$($PMe_2CH_2AlMe_2$).[20] Since the ethylene ligand in **4** is labile, generation of the intermediate in Scheme 5 is possible, therefore limiting the activity of the catalyst. However, it is possible to limit the formation of **10** by having larger quantities of $AlMe_3$, as was demonstrated by the 65 % conversion to **10** after 24 hours at 50 °C with one equiv. of $AlMe_3$ compared to the 20 % conversion with ten equivalents in the same conditions. It is presumed that this helps formation of an

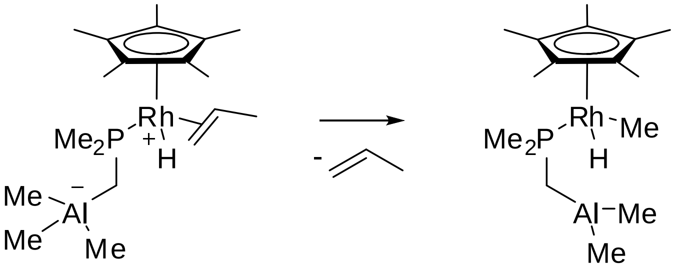
$AlMe_3$ adduct (*vide supra*) which reduces the nucleophilicity of the aluminate moiety of the ambiphilic ligand. Nevertheless, with an excess of $AlMe_3$ the production of butene is not increased.



2 **10**

Scheme 5.

The second pathway involves the reductive elimination of an alkane from $Cp^*RhHMe(PMe_2CH_2AlMe_2)$ **11.** Indeed, the key difference between the zwitterionic and the cationic systems is the possibility to generate the neutral complex **11** from **8** after dissociation of propene (Scheme 6). Jones did show that $Cp^*Rh(PMe_3)(H)(R)$ in various organic solvents undergoes very rapid reductive elimination of alkane or alkene at 25°C,[36] so a pathway involving reductive elimination is likely. Indeed, the observation of a species having a 190 Hz phosphorus-rhodium coupling constant in the red oil formed suggests it. Additionally, at no time and temperature the formation of a rhodium hydride species was observed and once the production of propene was underway, the generation of methane was observed by ^1H NMR. Furthermore, methane-d_1 is generated when the reaction is run with ethylene-d_4.



8 **11**

Scheme 6.

Density functional theory studies.

All products formed in this reaction do not withstand reduced pressure, re-forming **1**, and do not crystallize, making their isolation difficult. Furthermore, the fast dynamic processes involving the methylalane moieties, the extreme sensitivity of the products, and the several degradation pathways observed do not allow for reliable kinetic studies that could give more information on the mechanism at hand in this system. Therefore, density functional theory studies were carried out to support the experimental findings for the generation of propene. The geometry of π-complex **4** was optimized with the B3LYP hybrid functional and the combined SDD(Rh)/6-31g**(C,H,Al,P) basis set and is shown in Figure 1, where most of the hydrogen atoms have been omitted for simplicity. The C-C bond distance for coordinated ethylene of the optimized complex is 1.397 Å, value which falls between those obtained for the $CpRhH(C_2H_4)PH_3$ (1.408 Å,[37] and 1.391 Å[38]) and $CpRhMe(C_2H_4)PH_3$ (1.391 Å)[33] model complexes.

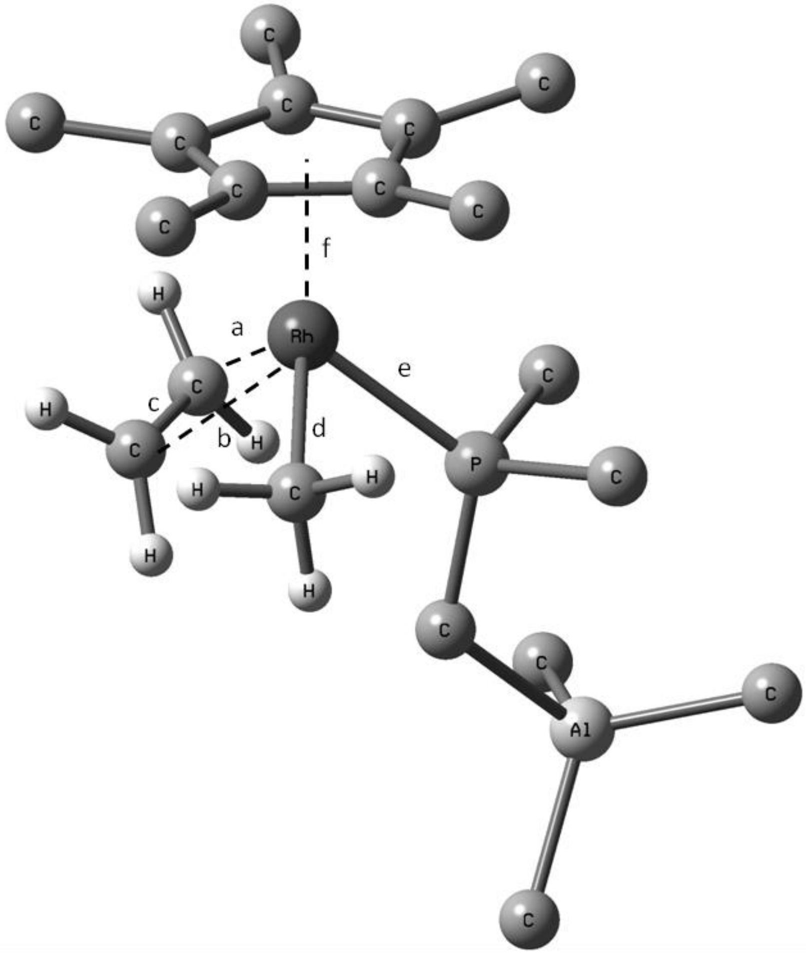


Figure 1. DFT optimized geometry for ethylene π-complex **4** (0.0 kcal.mol^{-1}), B3LYP/SDD(Rh),6-31g**(C,H,Al,P). Most hydrogen atoms were omitted for clarity. Bond distances in Å : a) 2.223; b) 2.196; c) 1.397; d) 2.127; e) 2.362; f) 1.983.

The transition state structures for the methyl 1,2-migratory insertion (**TS$_{\mathbf{INS}}$**) and nucleophilic attack (**TS$_{\mathbf{NU}}$**) have been localized on the potential energy surface and the free energy of activation ($\Delta G^{\ddagger}$) has been evaluated for both mechanistic pathways (Figure 2). Cartesian coordinates as well as energy values for all optimized species can be found in the electronic supplementary information. The relative Gibbs free energies for these species as well as species **6** – **8** and **11** are reported in kcal/mol in Table 1 with complex **4** fixed at 0 kcal.mol^{-1}. For the methyl 1,2-migratory insertion pathway starting from the ethylene complex **4**, the free energy activation barrier was calculated to be 27.5 kcal.mol^{-1}. This barrier is slightly higher than the experimental value of 23.4 ± 0.2 kcal.mol^{-1} obtained by Brookhart and coworkers for the ethyl 1,2-migratory insertion of ethylene in cationic complex $[Cp^*Rh(PMe_3)Me(C_2H_4)]^+$.[29] The barrier values we have computed for the Brookhart system are identical to the experimental values within the precision of the method, which suggest that the relation between **4** and $[Cp^*Rh(PMe_3)Me(C_2H_4)]^+$ is valid (See ESI). The methyl 1,2-migratory insertion pathway leads to the zwitterionic propyl complex **6**, which lies at 5.3 kcal.mol^{-1} lower than π-complex **4** on the potential energy surface. A second pathway that leads to complex **6** was also investigated, which is the nucleophilic attack on coordinated ethylene from one of the Al-Me groups, followed by ionization of the remaining Rh-Me bond by the Lewis acidic Al moiety. The transition state for the nucleophilic attack pathway (**TS$_{NU}$**) lies at 31.5 kcal.mol^{-1} on the potential energy surface and this step results in the formation of the neutral propyl complex $Cp^*RhMePr(PMe_2CH_2AlMe_2)$ **7** which is much lower in energy (- 17.0 kcal.mol^{-1}). Although it is conceivable that complex **7** could be ionized to give 16-electron zwitterion **6** in the path towards the formation of $Cp^*Rh^+H(C_3H_6)(PMe_2CH_2AlMe_3^-)$ (**8**), based on the reactivity of analogous $Cp^*RhMe_2(PMe_2CH_2AlMe_2)$, it is more likely that the reaction follows the methyl 1,2-migratory insertion pathway which has a lower activation barrier ($\Delta\Delta G^\ddagger$ = 4.0 kcal.mol^{-1}) and directly leads to zwitterion **6** (Figure 2). A Mulliken population analysis did not give any diagnostic result as why the 1,2-migratory insertion is slightly favored, but one can observe in the transition state of the nucleophilic attack that the methyl group transfer induces a significant geometry change that will be energetically costly.

Table 1. Calculated relative Gibbs free energy of complexes **4**, **6** – **8**, **11**, and transition state structures

found for both insertion of ethylene (**TS$_{INS}$**) and nucleophilic attack on ethylene (**TS$_{NU}$**)[a]

Complex	Gibbs Free Energy[a] (kcal/mol)
Cp*RhMe(C_2H_4)($PMe_2CH_2AlMe_3$) **4**	0
TS$_{INS}$	27.5
Cp*RhPr($PMe_2CH_2AlMe_3$) **6**	- 5.3
TS$_{NU}$	31.5
Cp*RhMePr($PMe_2CH_2AlMe_2$) **7**	-17.0
Cp*RhH(C_3H_6)($PMe_2CH_2AlMe_3$) **8**	- 9.0
CpRhHMe($PMe_2CH_2AlMe_2$) **11**	- 26.2

[a] Relative to Cp*Rh^+Me(C_2H_4)($PMe_2CH_2Al^-Me_3$) **4**

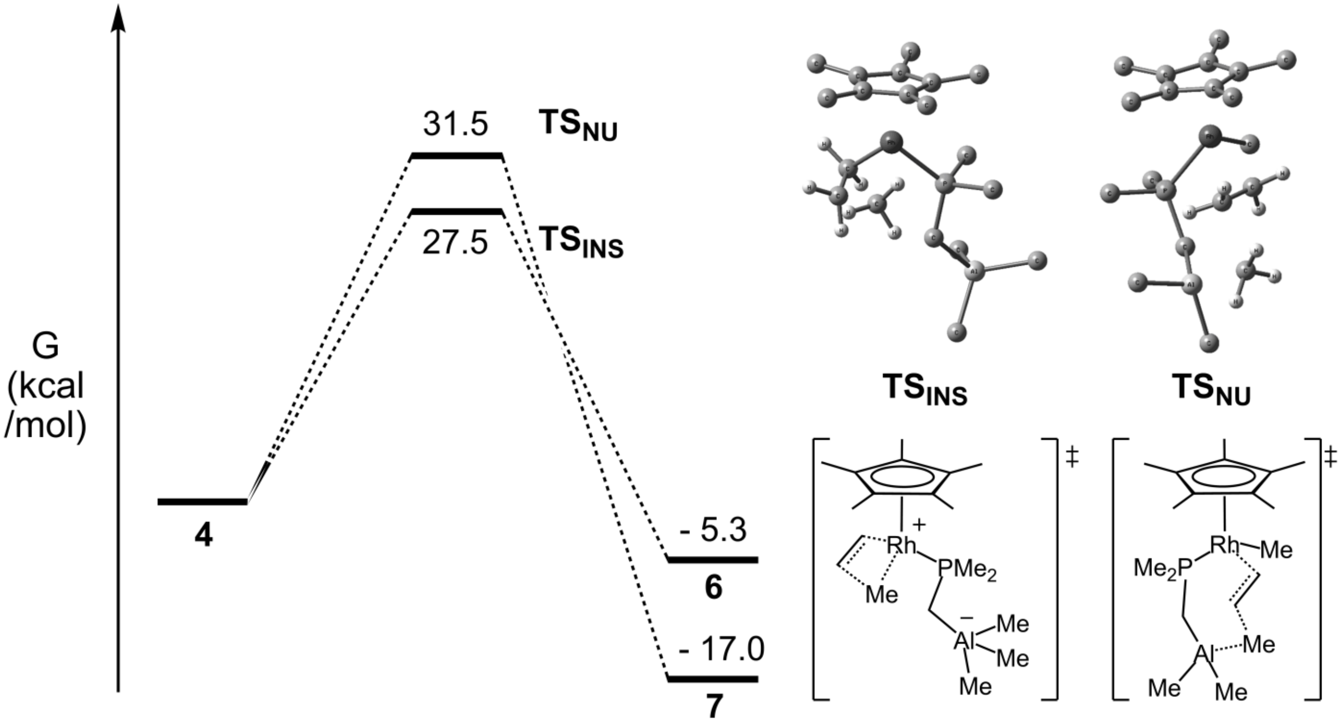
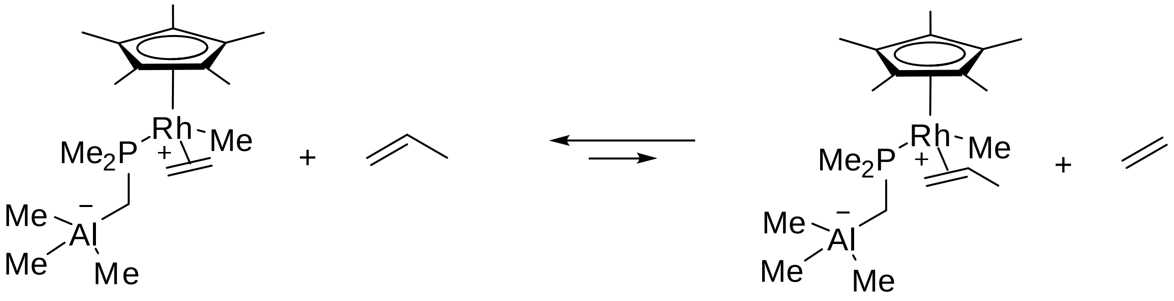


Figure 2. Calculated Gibbs free energy (kcal/mol) diagram of the insertion of ethylene (**TS$_{INS}$**) and the nucleophilic attack on ethylene by an Al-Me group (**TS$_{NU}$**) from complex **4**.

It was already mentioned that *β*-hydride elimination is expected to occur from complex **6** to generate the propene *π*-complex Cp*RhH(C_3H_6)($PMe_2CH_2AlMe_3$) **8**. The calculations show that this reaction is energetically downhill by 3.7 kcal/mol, and that the release of propene to form neutral Cp*RhHMe($PMe_2CH_2AlMe_2$) **11** is again downhill by another 17.2 kcal.mol^{-1}. The propene rhodium interaction was also found to be less stable than the ethylene rhodium bond by 6.9 kcal.mol^{-1} (Scheme 7). In addition to supporting the thermodynamic instability of the propene adduct **8**, it also explain the absence of reactivity between **1** and propene. Attempts to localize a local minimum energy structure for the Rh(I) complex resulting from reductive elimination of methane were unsuccessful.

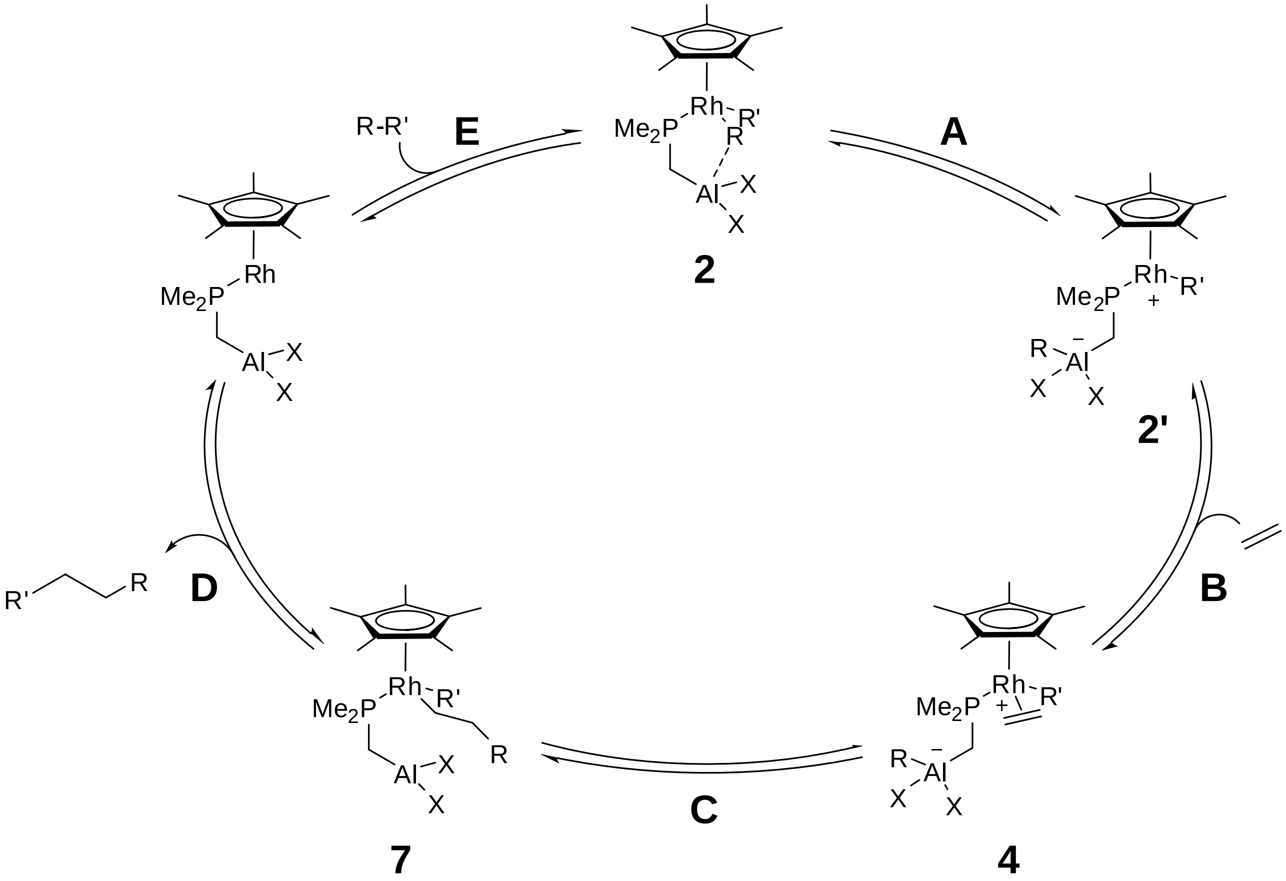


Scheme 7.

Concluding remarks

In summary, it was demonstrated that the zwitterionic complex formed by abstraction of a Rh-methyl group by the pendant Lewis acid in Cp*RhMe$_2$($PMe_2CH_2AlMe_2$) **2** can be trapped by coordination of ethylene to the rhodium centre. While it was expected for this complex to act as catalyst for ethylene dimerization, the presence of the ambiphilic ligand seems to offer a competitive pathway that results in the formation of a series of intractable Cp*Rh-containing species. Based on the simultaneous generation of propene and methane, both of which are partially deuterated when ethylene-*d*$_4$ is used as substrate, we were able to propose a mechanism involving a rapid β-hydride elimination of propene from a propyl fragment after insertion of ethylene in the remaining Rh-C bond. These findings are supported by DFT calculations. The proximity of the intramolecular –AlMe$^-$ counteranion is most likely responsible for the formation of the neutral –RhHMe fragment which accounts for the reductive elimination of methane.

Our prime objective is making a catalytic system that would follow the steps expressed in Scheme 8. In our previous report, we have demonstrated that step **A**, the reversible ionisation of a neutral rhodium complex was possible in the presence of an ambiphilic ligand.[20] In this report, we have demonstrated, by the spectroscopic characterization of **4**, that step **B**, the coordination of ethylene, is also possible. The insertion of ethylene into an Rh-Me bond (step **C**) was also observed, albeit it proved more difficult than with the cationic complexes reported by Brookhart. As for step **D**, we have circumstantial evidence suggesting that this process is occurring (*e.g.* liberation of methane). These various observations demonstrate that the presence of an ambiphilic ligand can open the way for both neutral and ionic reactivities from unique rhodium complexes, which to our knowledge was never reported before. We are currently working on the isolation and characterization of the product(s) resulting from step **D**, which would give invaluable insights on the decomposition process at hand. At this point, it is highly probable that the reactive Rh(I) species formed undergoes an intramolecular oxidation, by cleavage of some bond, presumably from the ambiphilic ligand. We are currently studying several avenues to make more robust complexes and to increase the selectivity of these systems, all of this in order to complete the catalytic cycle.



Scheme 8.

Experimental Section

General Procedures. All manipulations were conducted under an atmosphere of nitrogen using standard glovebox and Schlenk techniques. The reactions were carried out in a J-Young or pressure/vacuum NMR tube. Benzene-*d*$_6$ and toluene–*d*$_8$ were purified by vacuum distillation from Na/K alloy. The GC/MS analyses were done on a HP 5890 series II gas chromatograph equipped with a HP 5989A mass spectrometer in electronic impact mode. The NMR tubes were silylated prior usage, using a 10% solution of Me_3SiCl in $CHCl_3$ in order to prevent protonolysis of the *AlMe* moieties by the surface Si-OH groups. $(Me_2AlCH_2PMe_2)_2$,[39] Cp*$RhMe_2(PMe_2CH_2AlMe_2.DMSO)$ **1** and

$Cp^*RhMe_2(PMe_2CH_2AlMe_2)$ **2**[20] were prepared according to literature procedures. NMR spectra were recorded on a Varian Inova NMR AS400 spectrometer at 400.0 MHz (^1H) and 100.0 MHz (^{13}C) and/or on a Bruker NMR AC-300 at 300 MHz (^1H), 75.5 MHz (^{13}C), and 121.4 MHz (^{31}P). The temperatures of the VT NMR experiments were measured using a thermocouple inside the probe which was calibrated prior its use by determining the difference of chemical shift of a pure sample of methanol. For all compounds, $^1H\{^{31}P\}$ experiments were performed in order to assign the spectra. *Warning: the condensation of ethylene into the J-Young tubes was done using a known volume gas bomb. Care should be taken in avoiding large amounts of solid or liquid ethylene which would lead to explosion of the tube upon warming.*

Computational details

The density functional theory calculations were carried out with the B3LYP hybrid functional as implemented in the G03 program.[40] B3LYP is Becke's three parameter functionals (B3)[41] with the non-local correlation provided by the LYP expression[42] and VWN functional III for local correlation.[43] A combined basis set was used for all Gaussian calculations: the SDD basis set with Stuttgart/Dresden ECPs was used for Rh[44] along with the 6-31g(d,p) basis set for C, P, Al, and H (a single set of first polarization functions were added to each atom).[45] The tight geometry optimizations were performed without symmetry constraints and with the use of the modified GDIIS algorithm.[46] Vibrational analyses were performed to confirm the optimized stationary points as true minima on the potential energy surface or as transition states, and to obtain the zero-point energy and thermodynamic data. The free Gibbs energies, G, were calculated for T = 298.15 K. For every transition state, the reaction path in both directions was followed using the intrinsic reaction coordinate (IRC).[47]

$[Cp^*RhMe(C_2H_4)(Me_2PCH_2AlMe_3)]$ (4), **$[Cp^*RhMe(C_2H_4)(Me_2PCH_2AlMe_3)]AlMe_3$ (4')** and **$[Cp^*RhMe_2(Me_2PCH_2AlMe_2.L)]$ (5).** One equivalent of $AlMe_3$ (2.1 mg, 0.030 mmol) was added to a 0.03 M solution of **1** (15 mg, 0.030 mmol) in benzene-d_6 in a J-Young NMR tube. The solution was then degassed by three freeze-pump-thaw cycles using a Schlenk line and ethylene gas (1 atm.) was then condensed at – 196 °C by gas transfer using a known volume gas bomb. **(4)** δ ^{1}H NMR (benzene-d_6): 2.08 (m, 2H, C_2H_4), 1.86 (m, 2H, C_2H_4), 1.00 (d(br), $^{2}J_{H\text{-}P}$ = 10.5 Hz, 6H, $PMe_2CH_2AlMe_3$), 0.96 (d, $^{4}J_{H\text{-}P}$ = 2.1 Hz, 15H, C_5Me_5), 0.32 (m, 2H, $PMe_2CH_2AlMe_3$), 0.27 (m, 3H, Rh*Me*), 0.23 , – 0.27 (s, -$AlMe_3$). $^{31}P\{^{1}H\}$ NMR (benzene-d_6): 31.4 (d, $^{1}J_{P\text{-}Rh}$ = 114 Hz). **(4')** δ ^{1}H NMR (benzene-d_6): 2.08 (m, 2H, C_2H_4), 1.86 (m, 2H, C_2H_4), 1.08 (d, $^{2}J_{H\text{-}P}$ = 10.5 Hz, 3H, $PMe_2CH_2AlMe_3$), 1.07 (d, $^{2}J_{H\text{-}P}$ = 10.4 Hz, 3H, $PMe_2CH_2AlMe_3$), 0.95 (d, $^{4}J_{H\text{-}P}$ = 2.1 Hz, 15H, C_5Me_5), 0.32 (m, 2H, $PMe_2CH_2AlMe_3$), 0.27 (m, 3H, Rh*Me*), – 0.27 (s, -$AlMe_3$). $^{31}P\{^{1}H\}$ NMR (benzene-d_6): 30.7 (d, $^{1}J_{P\text{-}Rh}$ = 116 Hz). **(5)** δ ^{1}H NMR (benzene-d_6): 1.88 (d, $^{4}J_{H\text{-}P}$ = 1.9 Hz, 15H, C_5Me_5), 1.60 (d, $^{2}J_{H\text{-}P}$ = 9.3 Hz, 6H, $PMe_2CH_2AlMe_3$), 0.65 (d, $^{2}J_{H\text{-}P}$ = 13.4 Hz, 2H, $PMe_2CH_2AlMe_2$), 0.40 (dd, $^{3}J_{H\text{-}P}$ = 4.6 Hz, $^{2}J_{H\text{-}Rh}$ = 2.5 Hz, 6H, RhMe_2), – 0.27 (s, -$AlMe_2$). $^{31}P\{^{1}H\}$ NMR (benzene-d_6): 24.1 (d, $^{1}J_{P\text{-}Rh}$ = 159 Hz).

[Cp*RhMe(C_2H_4)($Me_2PCH_2AlMe_3$)]$AlMe_3$ (4'). Ten equivalents of $AlMe_3$ (21 mg, 0.300 mmol) were added to a 0.03 M solution of **1** (15 mg, 0.030 mmol) in benzene-d_6 in a J-Young NMR tube. The solution was then degassed by three freeze-pump-thaw cycles using a Schlenk line and ethylene gas (4 atm) was then condensed at – 196 °C by gas transfer using a known volume gas bomb. NMR yield of 85%. δ ^{1}H NMR (benzene-d_6): 2.08 (ddd, $^{3}J_{H\text{-}H(trans)}$ = 8.5 Hz, $^{3}J_{H\text{-}P}$ = 4.7 Hz, $^{3}J_{H\text{-}H(cis)}$ or $^{2}J_{H\text{-}Rh}$ = 1.8 Hz, 2 H, C_2H_4), 1.86 (dd, $^{3}J_{H\text{-}H(trans)}$ = 8.4 Hz, $^{3}J_{H\text{-}H(cis)}$ or $^{2}J_{H\text{-}Rh}$ = 1.7 Hz, 2 H, C_2H_4), 1.03 (d, $^{2}J_{H\text{-}P}$ = 10.4 Hz, 3H, $PMe_2CH_2AlMe_3$), 1.02 (d, $^{2}J_{H\text{-}P}$ = 10.3 Hz, 3H, $PMe_2CH_2AlMe_3$), 0.96 (d, $^{4}J_{H\text{-}P}$ = 2.1 Hz, 15H, C_5Me_5), 0.32 (dd, $^{2}J_{H\text{-}P}$ = $^{2}J_{H\text{-}H}$ = 13.7 Hz, 1H, $PMe_2CH_2AlMe_3$) , 0.27 (dd, $^{3}J_{H\text{-}P}$ = 5.4 Hz, $^{2}J_{H\text{-}Rh}$ = 2.2 Hz, 3H, Rh*Me*), 0.23 (dd, $^{2}J_{H\text{-}P}$ = $^{2}J_{H\text{-}H}$ = 13.7 Hz, 1H, $PMe_2CH_2AlMe_3$), – 0.34 (s, -$AlMe_3$). δ ^{13}C NMR (benzene-d_8): 102.1 (br, C_5Me_5), 58.6 (d, $^{1}J_{C\text{-}Rh}$ or $^{2}J_{C\text{-}P}$ = 8.3 Hz, C_2H_4), 14.6 (d, $^{1}J_{C\text{-}P}$ = 14.3 Hz, $PMe_2CH_2AlMe_3$), 14.2 (d, $^{1}J_{C\text{-}P}$ = 14.8 Hz, $PMe_2CH_2AlMe_3$), 12.5 (br, $PMe_2CH_2AlMe_3$), 7.9 (s, C_5Me_5), 3.5 (dd, $^{1}J_{C\text{-}Rh}$ or $^{2}J_{C\text{-}P}$ = 23.4 Hz, 10.0 Hz, Rh*Me*), –7.0 (br, AlMe_3). $^{31}P\{^{1}H\}$ NMR (benzene-d_6): 30.6 (d, $^{1}J_{P\text{-}Rh}$ = 116 Hz).

Generation of propene and methane from Cp*RhMe(C_2H_4)($Me_2PCH_2AlMe_3$) (4). Ten equivalents of $AlMe_3$ (21 mg, 0.300 mmol) were added to a 0.03 M solution of **1** (15 mg, 0.030 mmol) in benzene-*d*$_6$ in a J-Young NMR tube. The solution was then degassed by three freeze-pump-thaw cycles using a Schlenk line and ethylene gas (4 atm) was then condensed at – 196 ºC by gas transfer using a known volume gas bomb. The sample was heated for 48 hours at 50 ºC after which propene[48] and methane (or methane-*d*)[49] were identified based their characteristic ^1H NMR resonances. The presence of propene (M=42) (or propene-*d*$_{3,4}$, M=45,46) was also confirmed by GCMS after injection of one mL of the head space of the J-Young NMR tube at room temperature.

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Supporting Information Available: NMR characterization for compounds **4**, **4’** and **5**. Cartesian coordinates and energy for compounds **4**, **6** – **8** and **11**, ethylene, propene, and Cp*RhMe(CH_3CHCH_2)($PMe_2CH_2AlMe_3$). DFT results for the insertion of C_2H_4 in **[Cp*RhEt(C_2H_4)PMe_3]**$^+$.

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approximation are bound to exhibit weakness in the evaluation of ΔG and of ΔS for bimolecular systems that contain soft vibrational modes, such as for transition metal complexes.

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