Articles

Directly Observed β-H Elimination of Unsaturated PCP-Based Rhodium(III)−Alkyl Complexes

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Received February 4, 1999

The unsaturated PCP-type complexes Rh(L){2,6-($CH_2P^tBu_2$)$_2C_6H_3$}X (L = Et, ^{n}Pr; X = Cl, I) complexes convert upon heating to the corresponding Rh(III)−hydride complexes Rh(H){2,6-($CH_2P^tBu_2$)$_2C_6H_3$}X (X = Cl, I) and ethylene or propylene, products indicative of a β-H elimination process. The ^{i}Pr analogue is observed upon reaction of Rh(η^1-N_2){2,6-($CH_2P^tBu_2$)$_2C_6H_3$} with ^{i}PrI at −10 °C and decomposes readily at room temperature to give Rh(H){2,6-($CH_2P^tBu_2$)$_2C_6H_3$}I and propylene. Analogous alkyl complexes — lacking β-hydrogens — are stable under the applied reaction conditions. The mechanism of this process has been studied by NMR, using ^{13}C and deuterium labeling of the alkyl ligand (L = Et-d_5, $^{13}CH_2$-CH_3). ^{13}C labeling shows that the β-H elimination is irreversible. A deuterium isotope effect of k_{Et}/k_{Et-d_5} = 1.4 and a rate order of Et < ^{n}Pr ≪ ^{i}Pr were observed. The overall process follows first-order kinetics in the Rh(III)−alkyl complexes. The activation parameters for the thermolysis of Rh(Et)(2,6-($CH_2P^tBu_2$)$_2C_6H_3$)I in toluene were determined: $\Delta H^‡$ = 21.2 kcal/mol, $\Delta S^‡$ = −21.1 eu, and $\Delta G^‡_{298\,K}$ = 27.5 kcal/mol.

Introduction

β-H elimination and its microscopic reverse, alkene insertion into metal−hydride bonds, are fundamental processes often invoked as key steps in many catalytic reactions.[1−22] The conversion of a metal−alkyl complex to a metal−hydride species and an olefin is likely to involve the following steps: (i) creation of a vacant site in a cis position to the alkyl ligand, (ii) (reversible) concerted β-H elimination via a nonpolar, four-centered, transition state, and (iii) loss of the coordinated olefin. Generally, unsaturated late transition metal−alkyl complexes readily undergo β-hydrogen elimination and the alkene−hydride intermediates are rarely detected. Examples of alkyl complexes which undergo a rate-determining β-H elimination process are relatively uncommon.[4,18−20,23]

We have previously shown that C−C bond activation of a phosphine-functionalized alkyl−arene by Rh(I) might be driven by β-H elimination (Scheme 1)[24] and that β-H elimination is involved in the generation of PCP-based Rh(I) quinone−methide and methylene−arenium complexes.[25] An unprecedented trans insertion/β-hydrogen elimination with a (PCP)Rh^I complex has been observed and fully characterized kinetically and thermodynamically.[6] Herein, we report the results of a mechanistic study of β-H elimination for several unsaturated Rh(L){2,6-($CH_2P^tBu_2$)$_2C_6H_3$}X (L = Et, ^{i}Pr, ^{n}Pr;

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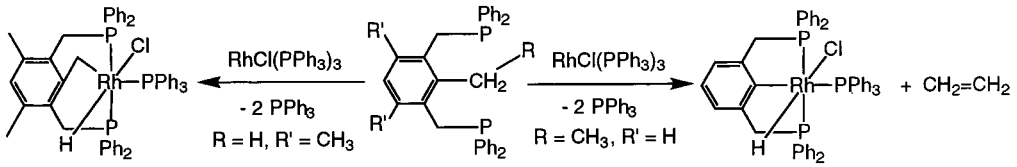
10.1021/om990073v CCC: $18.00
Publication on Web 05/29/1999

Scheme 1



Scheme 2

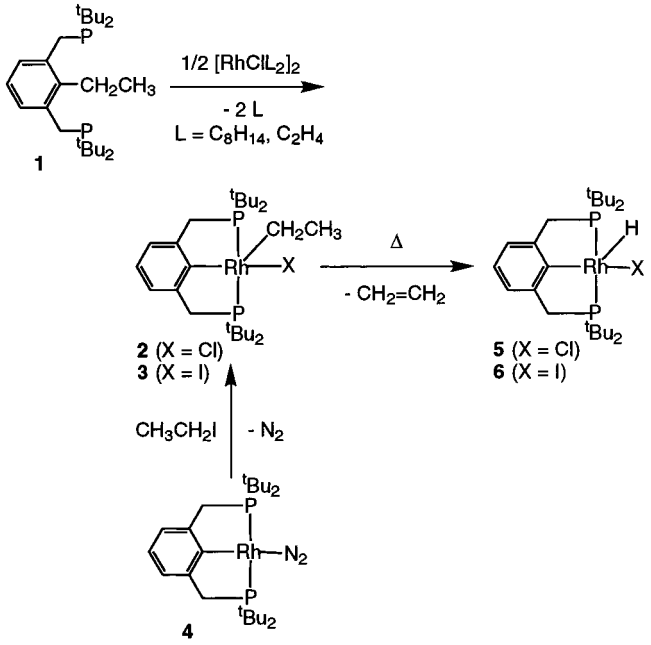
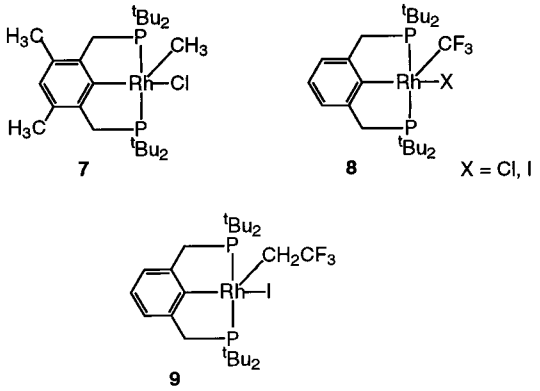


Chart 1



X = Cl, I) complexes by NMR using deuterium and ^{13}C labeling of the alkyl ligand. Our evidence indicates that an irreversible rate-determining β-H cleavage step is involved followed by a facile, irreversible alkene elimination.

Results and Discussion

We have recently demonstrated that reaction of the alkene complex $[RhClL_2]_2$ (L = ethylene or cyclooctene) with 2 equiv of the aryl−ethyl phosphine **1** in toluene at 120 °C (~5 min in a sealed tube) resulted in quantitative formation of the *unsaturated* Rh(III)−ethyl complex **2** by selective oxidative addition of the strong sp^2-sp^3 C−C bond (Scheme 2).[24] The sterically demanding ^{t}Bu groups force the Rh(III) complexes to be unsaturated.[26,27] The iodide analogue **3** was prepared by EtI oxidative addition to the dinitrogen complex **4**.[24] While unsaturated alkyl complexes containing β-hydrogens are generally expected to be quite unstable, these complexes are remarkably stable. Nevertheless, thermolysis of **2** and **3** in toluene at 120 °C overnight resulted in the quantitative formation of ethylene and the Rh(III)−hydride complexes **5** and **6**, products indicative of a β-H elimination process. The structures of **5** and **6** were confirmed by comparison with authentic samples. No other complexes were observed by ^1H and ^{31}P NMR. It is remarkable that the C−C bond activation occurs at a much higher rate than the β-H elimination process (Scheme 2).[24]

Complexes **7**−**9**,[28−30] lacking β-hydrogens, are thermally stable under conditions in which **2** and **3** convert to **5** and **6** (Chart 1), suggesting that Rh−C homolysis is an unlikely mechanism for this reaction. Complex **9** was obtained quantitatively by CF_3CH_2I oxidative addition to complex **4** and was unambiguously characterized by ^1H, ^{19}F, and ^{31}P NMR analysis of the product solution. Assignments in the ^1H and ^{19}F NMR spectra were made using $^1H\{^{31}P\}$ and $^{19}F\{^1H\}$ NMR. In the $^{31}P\{^1H\}$ NMR spectrum of **9** one doublet resonance appears at δ 45.13 with $^1J_{RhP} = 109.0$ Hz, indicating that both phosphorus atoms are magnetically equivalent and are coordinated to a Rh(III) center. The Rh−CH_2CF_3 group appears in the ^1H NMR spectrum as a multiplet at δ 3.76, which collapses in the $^1H\{^{31}P\}$ into a double quartet with $^2J_{RhH} = 4.6$ Hz and $^3J_{FH} = 14.3$ Hz. Two sets of resonances are seen for the protons of the ^{t}Bu groups at δ 1.38 and δ 0.97, and resonances of the CH_2 "arms" of the PCP ligand are seen at δ 3.49 and δ 3.00. The Rh−CH_2CF_3 group appears in the $^{19}F\{^1H\}$ NMR as a doublet at δ −54.07 with $^3J_{RhF} = 5.8$ Hz. The similarities in the ^{13}C NMR chemical shifts of the *ipso*-carbon of **9** (δ 169.7, $^1J_{RhC} = 34.3$ Hz) to those of analogous rhodium aryl halide complexes where the X-ray structure is known, Rh(H){2,6-$(CH_2P^tBu_2)_2C_6H_3$}Cl (**5**; δ 166.85),[31] Rh(Me){2,6-$(CH_2P^tBu_2)_2$-3,5-$C_6H(CH_3)_2$}Cl (**7**; δ 168.80),[32] and Rh(Me){2-$(CH_2P^tBu_2)$-6-$(CH_2N(C_2H_5)_2$-3,5-$(CH_3)_2$}Cl (δ 170.04)[33] indicate that the aryl group is directly bound to the metal center trans to the halide ligand. It is known that ^{13}C NMR spectroscopy is a sensitive tool for analyzing electronic

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(30) Complexes **7** and **8**-Cl were obtained by sp^2-sp^3 C−C bond activation,[24,32] while complex **8**-I was prepared by CF_3I oxidative addition to **4**.[29]
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trends in aryl-bound complexes.[34,35] Thus for **9**, the apparently strongest trans director, the trifluoroethyl ligand is trans to the vacant coordination site, in agreement with all crystal structures of analogous square-pyramidal PCP and PCN type rhodium(III) and iridium(III) complexes.[31−33,36−38]

A $^{31}P\{^{1}H\}$ NMR investigation of the thermolysis of **2** and **3** in toluene-d_8 or in dioxane-d_8 at 85 °C in a sealed tube showed that the conversion to the corresponding Rh(III)−hydride complexes **5** and **6** and ethylene is nearly independent of the solvent or the halide. For example, heating **3** in dioxane or toluene at 75 °C resulted in ∼25% conversion to **6** and ethylene after 2 h. Almost identical first-order rate constants at 75 °C were observed: for **2**, $k = 3.16 \times 10^{-5}$ s^{-1} (in toluene-d_8); for **3**, $k = 3.21 \times 10^{-5}$ s^{-1} (in dioxane-d_8).

In the β-hydride elimination reaction, an initial isomerization or ligand dissociation to create a free coordination site cis to that of the alkyl group is probably required.[21,23,39−42] For example, loss of the phosphine ligand is observed from (η^5-C_5H_5)Fe(PPh_3)-CO(alkyl) prior to β-hydride elimination and subsequent (rate-determining) loss of the coordinated alkene.[39] With Co($PPhMe_2$)$_2$(Et)$_2$(acetylacetonate), the rate-determining β-hydride elimination is again preceded by phosphine dissociation[23] and loss of a phosphine is actually the rate-determining step in the thermolysis of Pt-(PPh_3)$_2$(Bu)$_2$.[40] Loss of an electronegative ligand, X^-, to create a vacant site is reported in the β-hydride elimination reaction of *trans*-Pd(PMe_3)$_2$(Et)X,[43a] and for electron-rich, chelated Pd(II) complexes.[43b] A preequilibrium loss of Cl^- is observed, prior to a rate-determining β-H elimination step for Ir(PR_3)$_2$ClH(OR′) with R = Me, Et, ^{i}Pr and R′ = Me, Et.[21] The air and thermal stability of various PCP complexes lacking β-H's[25,29,44−46] suggests that dissociation of a phosphine is probably not involved in the thermolysis of **2** and **3**. (Complexes **6** and **9** are air-stable in toluene at 85 °C for at least 4 h, while the free ligand **1** is not.) In view of the lack of solvent effect and the very similar rates observed with the chloro and iodo complexes **2** and **3**, halide dissociation is also unlikely to be involved in the β-hydride elimination reaction. Thus, an isomerization of the pentacoordinate complexes to form a vacant site cis to the alkyl ligand, without ligand dissociation, is the likely process here.

The effect of deuterium substitution on the thermolysis rate was determined by comparing the decomposition of **3** and the deuterium-labeled complex Rh(Et-d_5){2,6-($CH_2P^tBu_2$)$_2$$C_6H_3$}I (**10**), which was generated from **4** and CD_3CD_2I. Thermolysis of **10** in toluene at 120 °C overnight resulted in the formation of ethylene-d_4 and the Rh^{III}−D analogue of **6**, which was unambiguously identified by ^{1}H, ^{2}H, and ^{31}P NMR. The ethylene was collected by standard vacuum-line techniques and unambiguously identified by GC. Using nondeuterated toluene, no Rh^{III}−H formation was observed by ^{1}H NMR, showing that the solvent does not contribute to the Rh^{III}−D formed. Likewise, thermolysis of **2** and **3** in deuterated toluene at 120 °C did not result in formation of Rh^{III}−D, although it is known that PCP complexes can activate C−H bonds.[31,44,45,47−51] In addition, H/D exchange between the P^{t}Bu groups and Rh−D or Rh−CD_2CD_3 was not detected.[52] A kinetic isotope effect of $k_H/k_D = 1.4$ was observed at 98 °C in toluene-d_8 (Figure 1), indicating that the rate-determining step is unlikely to be ligand dissociation to create a free coordination site cis to the alkyl group or rearrangement of the complex, but rather a later step such as the β-C−H cleavage or the dissociation of the olefin from the unobserved alkene−hydride species **A**.[53,54] A similar intermediate was postulated in the reaction of an alkene with a (PCP)Ir−$(H)_2$ complex.[50]

Alkene dissociation is often the slow step in thermolysis of metal−alkyl complexes, the actual β-C−H cleavage being relatively fast and reversible. If the β-H elimination is a reversible process via a sterically disfavored intermediate such as **A**, then the equilibrium

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(52) Such an exchange was recently reported for IrD_2{2,6-(CH_2P-$^tBu_2$)$_2$$C_6H_3$} at 25 °C.[50] Cyclometalation of P^{t}Bu ligands was also reported to occur upon treatment of a (PCP)Rh(H)Cl complex with $NaN(SiMe_3)_2$,[31] presumably involving intermediacy of the corresponding Rh(I) complex. We believe that the lack of H/D exchange in the case of the Rh^{III}−D analogue of **6** may be due to the significantly lower electron density on the Rh(III) metal center as compared with the Ir(III) or Rh(I) complexes. Steric hindrance imposed by the halide ligand in the case of **6** may also play a role. It is noteworthy that while a $(PCP)Rh^I$ complex undergoes C−H activation,[49] the corresponding $(PCP)Rh^{III}$(H)Cl complex does not.
(53) For Co(CH_2CX_3)($PPhMe_2$)$_2$(acetylacetonate) and *trans*-Pd(CH_2-CX_3)($PMePh_2$)$_2$ (X = H, D) kinetic isotope effects of 2.3 and 1.4 are observed, respectively.[43] For (η^5-C_5Me_5)Nb(CH_2=CHR)H a kinetic isotope effect of 1.1 ± 0.4 was observed.[4] However, the primary isotope effect for the hydride−olefin insertion was calculated to be in the range of $1.7 \pm 0.6 < k_H/k_D < 2.7 \pm 1.0$. When the thermolysis of Ir(PPh_3)$_2$(CH_2-CD_2R)(CO) was compared to that of Ir(PPh_3)$_2$(CH_2CHDR)(CO), a k_H/k_D value of 2.3 was calculated.[19,20]
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(58) For example, the values of $\Delta H^‡$ are 30.6 and 25.5 kcal/mol for Co($PPMe_2$)$_2$(L)(acetylacetonate) with L = Et, ^{i}Pr, respectively,[23] and $\Delta H^‡$ is 26.0 kcal/mol for *trans*-Pd($PMePh_2$)$_2$(Et)$_2$.[54]

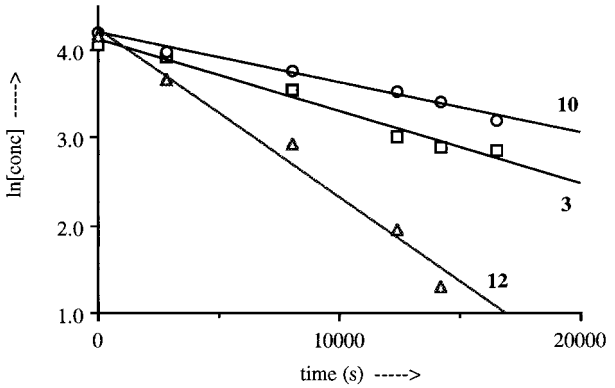
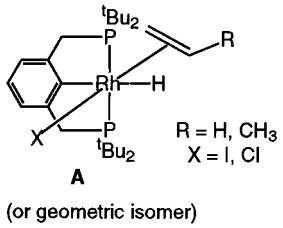


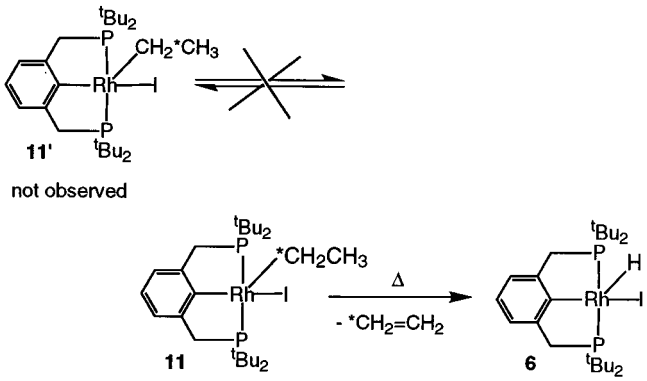
Figure 1. $^{31}P\{^1H\}$ NMR follow-up of thermolysis of **3**, **10**, and **12** (25 mM) in toluene-d_8 at 98 °C.



lies well toward the Rh(III)−alkyl species **2** and **3**. To evaluate the reversibility of the C−H cleavage, the ^{13}C-labeled complex **11** was prepared from **4** and $CH_3{}^{13}CH_2I$ (Scheme 3). The $^{13}CH_2$ resonance is clearly observed in the ^{13}C NMR at δ 18.31 (dt, $^1J_{RhC} = 28.5$, $^2J_{PC} = 4.8$ Hz) and the ^1H NMR at δ 2.38 (m, 2H, $^2J_{RhH} = 2.7$, $^2J_{HH} = 7.2$, $^3J_{PH} = 6.1$, $^1J_{CH} = 140.2$ Hz). The ^{13}C DEPT-135 NMR showed a negative signal, indicative of an even number of protons. ^1H,^{13}C, and ^{31}P NMR follow-up at 80 °C in toluene-d_8 showed only the gradual disappearance of **11** and the simultaneous formation of **6** and $^*CH_2CH_2$. Importantly, we did not observe any ^{13}C incorporation in the CH_3 group of the ethyl ligand (**11′**, Scheme 3),[22] indicating that in this system the *β-hydrogen elimination is irreversible*. Variable-temperature ^1H and ^{31}P NMR (−77 to 40 °C in toluene-d_8) and EXSY experiments were also carried out on complex **2**, but no evidence for a reversible β-H elimination/alkene addition was obtained. Even at low temperatures, no hydrides were observed. Apparently, in this system dissociation of the olefin from an (unobserved) intermediate Rh(III)−olefin complex such as **A** occurs at a much higher rate then insertion of the coordinated ethylene into the Rh(III)−H bond. Thus, alkene dissociation is not rate-determining. Known examples of rate-limiting β-H elimination also lack reversibility of the β-C−H bond cleavage.[4,20,21,23,55,56]

The activation parameters for the conversion of **3** to Rh(H){2,6-($CH_2P^tBu_2$)$_2C_6H_3$}I **6** and ethylene in toluene-d_8 were determined from an Eyring plot (Figure 2): $\Delta H^‡ = 21.2$ kcal/mol, $\Delta S^‡ = -21.1$ e.u, $\Delta G^‡_{298\,K} = 27.5$ kcal/mol. Typically, for reactions where loss of the coordinated alkene is rate-determining, the value for $\Delta S^‡$ is expected to be positive.[57] The observed negative value of $\Delta S^‡$ suggests that the rate-determining step is β-C−H bond cleavage. In support of this, the values of $\Delta H^‡$ and $\Delta G^‡$ are comparable to rare examples where β-H elimination from an alkyl-complex is rate-determining.[18,23,58] The negative $\Delta S^‡$ is also not compatible with a rate-determining ligand (halide or phosphine) loss. In addition, had there been ligand loss *prior* to the rate-determining step, the observed $\Delta S^‡$ value would have been expected to be more positive (since then $\Delta S^‡_{obsd} = \Delta S^‡_{\beta-H} + \Delta S°_{dissociation}$).

Scheme 3



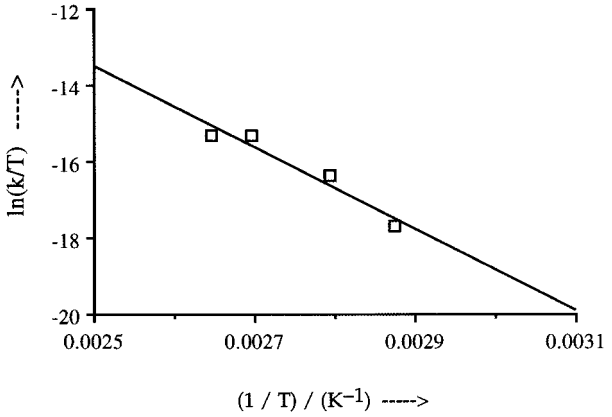
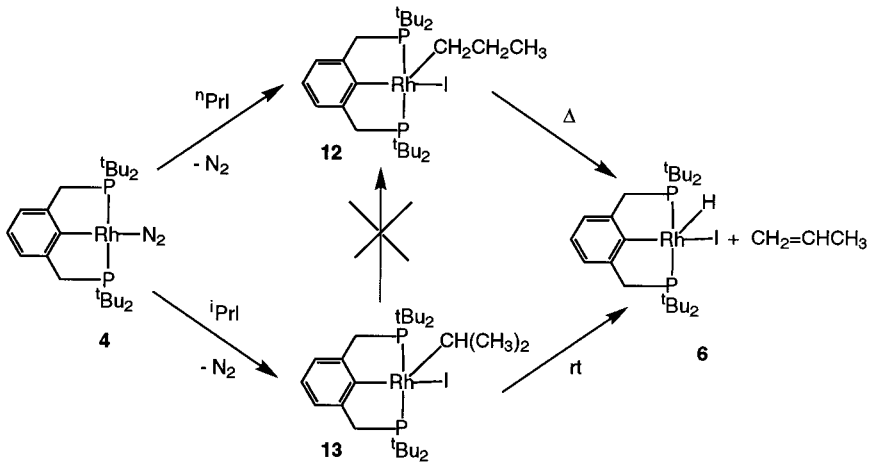


Figure 2. Eyring plot for the conversion of **3** to **6** and ethylene in toluene−d_8 (k = observed rate constant in s^{-1}).

To determine the effect of the alkyl chain on the β-H elimination process, complex **4** was reacted with 1 equiv of ^{n}PrI in toluene or dioxane at room temperature, affording the new complex **12** in excellent yield (~95% by ^{31}P NMR; Scheme 4). The reaction was completed within 30 min, and no intermediates were observed by ^1H and ^{31}P NMR. The ^{31}P NMR of **12** (δ 52.40, $^1J_{RhP} = 122.8$ Hz) is similar to that of **2**, **3**, and **11** (Schemes 2 and 3). Thermolysis of the product solution at 120 °C overnight resulted in the quantitative formation of **6** (by ^1H and ^{31}P) and propylene (by ^1H NMR and GC). $^{31}P\{^1H\}$ NMR investigation of the thermolysis of complexes Rh(Et){2,6-($CH_2P^tBu_2$)$_2C_6H_3$}I (**3**) and Rh(^{n}Pr){2,6-($CH_2P^tBu_2$)$_2C_6H_3$}I (**12**) in toluene at 98 °C shows that the observed rate of the conversion to the corresponding Rh^{III}−H complex **6** is indeed dependent on the alkyl chain, indicating that the rate-determining step involves β-C−H cleavage or dissociation of the olefin (Figure 1). The process is first order in the alkyl iodide complexes **3** and **12**. The conversion to **6** is found to be about 2.5 times faster for the ^{n}Pr complex **12** than for the Et complex **3**.

On addition of 1 equiv of ^{i}PrI to **4** at room temperature, immediate formation of **6** and propylene was observed by ^1H and ^{31}P NMR in almost quantitative yield (Scheme 4). A minor product (~5%), observed in the $^{31}P\{^1H\}$ NMR spectrum at δ 74.5 (d, $^1J_{RhP} = 146.9$ Hz), possibly arises from coordination of the liberated propylene to residual **4** to form Rh(η^2-H_2C=$CHCH_3$){2,6-

Scheme 4



$(CH_2P^tBu_2)_2C_6H_3\}$. The ethylene analogue Rh(η^2-H_2C=CH_2)\{2,6-$(CH_2P^tBu_2)_2C_6H_3$\}, having similar $^{31}P\{^1H\}$ NMR data (d, δ 73.5, $^1J_{RhP} = 152$ Hz), is known.[31] When the reaction is performed at −10 °C, evidence can be seen for the oxidative addition intermediate **13**. The chemical shift and the value of the coupling constant in the $^{31}P\{^1H\}$ NMR spectrum (d, δ 55.01, $^1J_{RhP} = 126.8$ Hz) are indicative of two magnetically equivalent phosphorus nuclei coordinated to a Rh(III) center and are similar to those of **2** (d, δ 54.99, $^1J_{RhP} = 123.8$ Hz), **3** (d, δ 52.63, $^1J_{RhP} = 122.5$ Hz), and **12** (d, δ 52.40, $^1J_{RhP} = 122.8$ Hz). The ^1H NMR shows two new ^{t}Bu moieties as virtual triplets at δ 1.36 and δ 1.16 ($^{3+5}J_{PH} = 12.0$ Hz), respectively.[58] It is therefore likely that this species is the oxidative addition product Rh(^{i}Pr)\{2,6-$(CH_2P^tBu_2)_2C_6H_3$\}I **13**, although further identification by ^1H NMR is hampered by overlap with signals of **4**, **6**, and propylene. When the sample is warmed to room temperature in the NMR probe, complex **13** gradually disappears and the same products are observed as in the room-temperature reaction. There is no evidence for the formation of **12** during the thermolysis of **13**. Importantly, complex **12** is stable under the conditions in which **13** readily undergoes β-H elimination to afford **6** and propylene. It is known that secondary alkyl complexes are often unstable and either do not form[18,60,61] or rapidly isomerize to the more stable 1° alkyl complexes.[62,63] The olefin π-complex **A**, presumably formed after the β-H elimination step, bears two large phosphine ligands. Crowding in the coordination sphere of the metal is expected to favor formation of the ^{n}Pr derivative **12**, which is not observed by ^1H and ^{31}P NMR. This indicates that the β-H elimination with the Rh(III)−propyl species **13** is an irreversible process, the rate of alkene elimination being much faster than its unobserved insertion. The rate of thermolysis of Rh(^{i}Pr)\{2,6-$(CH_2P^tBu_2)_2C_6H_3$\}I (**13**) is much faster than with Rh(^{n}Pr)\{2,6-$(CH_2P^tBu_2)_2C_6H_3$\}I (**12**). The observed reactivity order (^{i}Pr ≫ ^{n}Pr > Et) seems to indicate that the statistical prevalence for β-hydride elimination from a primary C atom is outweighed by a much higher reactivity of the hydrogens bound of a secondary carbon atom. The observed reactivity order can be rationalized in terms of the generally accepted mechanism for β-C−H cleavage.[4,64−66] It is likely that a relatively nonpolar, cyclic transition state with concerted bond making and breaking is involved, where partial positive charge is developed at the β-C and the hydrogen is transferred to the metal with partial hydride character. The bulky ^{t}Bu groups may destabilize the Rh−alkyl ligand in the order ^{i}Pr > ^{n}Pr > Et. Thus, we believe that substitution of H at the β-C by an alkyl group stabilizes the transition state and destabilizes the starting complex (by steric hindrance), leading to the observed reactivity order ^{i}Pr ≫ ^{n}Pr > Et.

Conclusion

Alkenes are fairly weakly coordinated to Rh\{$CH(CH_2CH_2P^tBu_2)_2$\} and Rh\{2,6-$(CH_2P^tBu_2)_2C_6H_3$\} due to crowding in the coordination sphere of the metal.[31,49] As we reported, the complex stability of Rh(L)\{$CH(CH_2CH_2P^tBu_2)_2$\} is L = H_2 > N_2 > C_2H_4 > CO_2.[49] The ^{31}P NMR and IR data suggest a relatively lower electron density on the metal center in Rh(L)\{2,6-$(CH_2P^tBu_2)_2C_6H_3$\} as compared to the nonaromatic Rh(L)\{$CH(CH_2CH_2P^tBu_2)_2$\} (L = N_2, CO);[26,31,49,67] therefore, back-bonding to ethylene will be even weaker in the postulated intermediate **A**. In addition, Rh(III) complexes of regular olefins are expected to be less stable than those of Rh(I). The surprisingly high thermal stability of the Rh(III)−alkyl complexes **2**, **3**, and **12** and the poor coordination ability of alkenes with the bulky ^{t}Bu-PCP complexes results in fast dissociation of ethylene or propylene. In support of this, the ^{13}C labeling experiment shows that the β-H elimination is irreversible. The observed deuterium isotope effect and the influence of the alkyl chain on the reactivity order clearly reveal that

(59) During the reaction most resonances of **13** in the ^1H NMR are masked by **3**, **6**, ^{i}PrI, and free propylene in the reaction mixture.

(60) Chatt, J.; Coffey, R. S.; Gough, A.; Thompson, D. T. *J. Chem. Soc. A* **1968**, 190.
(61) Wright, D. *J. Chem. Soc., Chem. Commun.* **1966**, 197.
(62) Schwartz, J. *Pure Appl. Chem.* **1980**, 733.
(63) For instance, Yamamoto et al. reported the formation of *trans*-$PdR_2(PMePh_2)_2$ (R = ^{n}Pr, ^{n}Bu) but did not obtain the ^{i}Pr or ^{i}Bu analogues,[18] and Chatt et al. reported the formation of $Pt(PEt_3)_2{}^nPrCl$, while attempts to obtain $Pt(PEt_3)_2{}^iPrCl$ yielded $Pt(PEt_3)_2HCl$.[60]
(64) Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566.
(65) Halpern, J.; Okamoto, T.; Zakhaniev, A. *J. Mol. Catal.* **1976**, *2*, 65.
(66) Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* **1973**, *75*, 7262.
(67) Crocker, C.; Errington, R. J.; Markham, R.; Moulton, C. J.; Odell, K. J.; Shaw, B. L. *J. Am. Chem. Soc.* **1980**, *102*, 4373.

the formation of a vacant coordination site cis to the alkyl ligand is not rate-determining. Attempts to prepare analogous (PCP)Rh^{III}−Et complexes with Ph and ^{i}Pr substituents on the phosphorus atoms failed, suggesting that complexes **2**, **3**, **11**, and **12** are stabilized by the bulky ^{t}Bu groups. Although the observed k_H/k_D value is not high, our evidence indicates that the β-H elimination is rate-determining. Formation of a saturated olefin π-complex such as **A** is sterically unfavorable, contributing to the difficulty of the β-H elimination step. Steric hindrance between the ^{t}Bu groups and the alkyl ligand is expected to follow the same trend as the observed reactivity order (^{i}Pr ≫ ^{n}Pr > Et). The reactivity order and the $\Delta S^{\ddagger}$ value can be rationalized in terms of a cyclic transition state where a partial charge develops at the β-C.[5,64] The value of $\Delta H^{\ddagger}$ is consistent with literature values for related β-H elimination reactions with rate-determining C−H bond cleavage.[53] Remarkably, the overall process (**1** → **3**; Scheme 2) includes fast, selective oxidative addition of a strong C−C bond followed by a relatively slow β-H elimination process from the resulting alkyl ligand in an unsaturated Rh(III) system.

Experimental Section

General Procedures. All reactions were carried out under nitrogen in a Vacuum Atmospheres glovebox (DC-882) equipped with a recirculation (MO-40) "Dri Train" or under argon using standard Schlenk techniques. Oxygen levels (<2 ppm) were monitored with Et_2Zn (1 M solution in hexane, Aldrich); water levels (<2 ppm) were monitored with $TiCl_4$ (neat, BDH Chemicals). Solvents were reagent grade or better, dried, distilled, and degassed before introduction into the glovebox, where they were stored over activated 4 Å molecular sieves. The deuterated solvents CF_3CH_2I, CD_3CD_2I, and $CH_3{}^{13}CH_2I$ were purchased from Aldrich. The solvents were degassed and stored over 4 Å activated molecular sieves in the glovebox. $[RhClL_2]_2$ (L = cyclooctene, ethylene) was prepared by a published procedure.[68,69] Rh(η^1-N_2){2,6-$(CH_2P^tBu_2)_2C_6H_3$} (**4**) was prepared from Rh(L){2,6-$(CH_2P^tBu_2)_2C_6H_3$}Cl (L = H, Et) and NaH or KH under a nitrogen atmosphere.[24] The Rh−ethyl complexes **2** and **3** were prepared as previously described.[24] Reaction flasks were washed with deionized water, followed by acetone, and then oven-dried prior to use. GC analyses were performed on a Varian 3300 gas chromatograph equipped with a molecular sieve column.

Spectroscopic Analysis. The ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded at 400.19, 161.9, and 100.6 MHz, respectively, on a Bruker AMX 400 NMR spectrometer. ^{1}H, ^{19}F, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ spectra were also recorded at 250.17, 235.4, 101.3, and 62.9 MHz, respectively, on a Bruker DPX 250 NMR spectrometer. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. The ^{1}H and ^{13}C NMR chemical shifts are relative to tetramethylsilane; the resonance of the residual protons of the solvent was used as the internal standard h_1 (7.15 ppm, benzene; 7.26 ppm, chloroform; 7.09 ppm, toluene) and all-d solvent peaks (128.0 ppm, benzene; 77.0 ppm, chloroform; 20.4 ppm, toluene), respectively. ^{31}P NMR chemical shifts are relative to 85% H_3PO_4 in D_2O at δ 0.0 (external reference) with shifts downfield of the reference considered positive. Assignments in the ^{1}H, ^{19}F, and $^{13}C\{^1H\}$ NMR were made using $^1H\{^{31}P\}$, $^{19}F\{^1H\}$, and ^{13}C DEPT-135 NMR. All measurements were carried out at 298 K unless otherwise specified. Ph_3PO was used as an internal standard for integration. IR spectra were recorded as films between NaCl plates on a Nicolet 510 FT spectrometer.

(68) Herdé, J. L.; Senoff, C. V. *Inorg. Nucl. Chem. Lett.* **1971**, 1029.
(69) Cramer, R. *Inorg. Chem.* **1962**, *1*, 722.

Formation of Rh(CF_3CH_2){2,6-$(CH_2P^tBu_2)_2C_6H_3$}I (9). A stoichiometric amount of CF_3CH_2I (8 mg, 0.038 mmol) was added to a yellow benzene-d_6 solution (1 mL) of **4** (20 mg, 0.038 mmol) at room temperature, which turned immediately dark red. A small excess (2−4 equiv) of CF_3CH_2I can be used as well. NMR analysis of the product solution showed the quantitative formation of **9**. Removal of the volatiles in vacuo afforded a red solid in quantitative yield. ^{1}H NMR (C_6D_6): δ 7.03 (m, 3H, Ar H), 3.76 (m, 2H, CH_2CF_3), 3.49 (left part of vtABq, $^2J_{HH}$ = 17.3 Hz, $^2J_{PH}$ = 4.2 Hz, 2H, CH_2P), 3.00 (right part of vtABq, $^2J_{HH}$ = 17.2 Hz, $^2J_{PH}$ = 4.4 Hz, 2H, CH_2P), 1.38 (vt, $^2J_{PH}$ = 6.5 Hz, 18H, $C(CH_3)_3$), 0.97 (vt, $^2J_{PH}$ = 6.1 Hz, 18H, $C(CH_3)_3$). $^{19}F\{^1H\}$ NMR (C_6D_6): δ −54.07 (d, $^1J_{RhF}$ = 5.8 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 45.13 (d, $^1J_{RhP}$ = 109.0 Hz). FD-MS: $[M - I]^+$ m/z 578.6.

Formation and Thermolysis of Rh(L){2,6-$(CH_2P^tBu_2)_2C_6H_3$}I (10−12; L = CD_3CD_2, $CH_3{}^{13}CH_2$, ^{n}Pr). The preparation and spectroscopic data of the alkyl complexes **10**, **11**, and **12** are nearly identical with those reported for complex **3**.[24] A stoichiometric amount (0.019 mmol) of the desired alkyl iodide was added with a microsyringe to a yellow toluene, benzene, or dioxane solution (1 mL) of **4** (10 mg, 0.019 mmol). The red solution was loaded into a 5 mm screw-cap NMR tube and analyzed by various NMR techniques. The reactions were completed within 30 min, and no intermediate compounds were observed. Heating at 120 °C for 16 h resulted in the formation of Rh(H){2,6-$(CH_2P^tBu_2)_2C_6H_3$}I (**6**) and ethylene or propylene (>90%), as judged by ^{1}H and ^{31}P NMR spectroscopy and GC analysis of the gas phase using standard Schlenk techniques. Authentic samples were used to confirm the identity of the products formed. Rh(D){2,6-$(CH_2P^tBu_2)_2C_6H_3$}I was formed in the case of L = CD_3CD_2. The reactions were also performed in sealed sidearm flasks to allow quantitative analysis of the gas phase by GC. Spectral data for **6**: ^{1}H NMR (toluene-d_8) δ 7.0 (m, 3H, Ar H), 3.05 (vtABq, $^2J_{HH}$ = 17.2 Hz, $^2J_{PH}$ = 3.8 Hz, 4H, CH_2P), 1.29 (vt, $^2J_{PH}$ = 6.7 Hz, 36H, $C(CH_3)_3$), −28.75 (dt, J_{RhH} = 50.9 Hz, J_{PH} = 12.2 Hz); $^{31}P\{^1H\}$ NMR (toluene-d_8) δ 75.48 (d, $^1J_{RhP}$ = 112.9 Hz); $^{13}C\{^1H\}$ NMR (toluene-d_8) δ 166.85 (dt, $^1J_{RhC}$ = 32.9 Hz, $J_{PC} \approx$ 1 Hz, C_{ipso}), 151.45 (dt, $J_{RhC} \approx$ 1 Hz, J_{PC} = 9.1 Hz, C_{ortho}), 124.00 (s, C_{para}), 12.28 (dt, $J_{RhC} \approx$ 1 Hz, J_{PC} = 8.6 Hz, C_{meta}), 36.46 (vt, J_{PC} = 7.6 Hz, $C(CH_3)_3$), 35.51 (dvt, J_{RhC} = 2.4 Hz, J_{PC} = 11.0, CH_2P), 30.26 (vt, J_{PC} = 2.4 Hz, $C(CH_3)_3$), 29.85 (vt, J_{PC} = 2.4 Hz, $C(CH_3)_3$). Spectral data for **12**: ^{1}H NMR (toluene-d_8) δ 7.0 (m, 3H, Ar H), 3.10 (vtABq, $^2J_{HH}$ = 19.2 Hz, $^2J_{PH}$ = 3.5 Hz, 4H, CH_2P), 1.41 (vt, $^2J_{PH}$ = 6.1 Hz, 18H, $C(CH_3)_3$), 1.16 (vt, $^2J_{PH}$ = 6.1 Hz, 18H, $C(CH_3)_3$), resonances of the alkyl group cannot be assigned properly; $^{31}P\{^1H\}$ NMR (toluene-d_8) δ 52.40 (d, $^1J_{RhP}$ = 122.8 Hz).

Reaction of Rh(η^1−N_2){2,6-$(CH_2P^tBu_2)_2C_6H_3$} 4 with ^{i}PrI. A stoichiometric amount of ^{i}PrI (2 μl, 0.020 mmol) was added with a microsyringe to a yellow toluene-d_8 solution (1 mL) of **4** (10 mg, 0.019 mmol). The red reaction solution was loaded into a 5 mm screw-cap NMR tube and immediately analyzed by ^{1}H and ^{31}P NMR techniques, showing formation of **6** (95% by ^{31}P NMR) and propylene. The reactions were also performed in sealed sidearm flasks to allow quantitative analysis of the gas phase by GC using standard Schlenk techniques. A minor product (~5%) is also observed in the $^{31}P\{^1H\}$ NMR spectrum at δ 74.5 (d, $^1J_{RhP}$ = 146.9 Hz). When the reaction was performed at −10 °C (in the NMR probe), an intermediate formulated as **13** was observed. Selected spectral data: $^{31}P\{^1H\}$ NMR (toluene-d_8) δ 55.01 (d, $^1J_{RhP}$ = 126.8 Hz); ^{1}H NMR (toluene-d_8) δ 1.16 and δ 1.36 (both vt, $^{3+5}J_{PH}$ = 12.0 Hz, $C(CH_3)_3$).[59] Raising the temperature to room temperature results in the quantitative formation of **6** and propylene. Formation of **12**, which is stable under the applied reaction conditions, was not observed by ^{1}H and ^{31}P NMR.

NMR Investigation of the Thermolysis of Rh(L){2,6-$(CH_2P^tBu_2)_2C_6H_3$}I, (L = CH_3CH_2, CD_3CD_2, $CH_3{}^{13}CH_2$, ^{n}Pr). A solution of an alkyl complex (10 mg) in 0.6 mL of toluene-d_8

or dioxane-d_8 was loaded into a 5 mm screw-cap NMR tube, equipped with a septum. For each set of experiments, samples of the rhodium−alkyl complexes were prepared from the same batch of Rh(η^1-N_2){2,6-($CH_2P^tBu_2$)$_2C_6H_3$} (**4**). The tube was heated in an oil bath and monitored by ^1H and ^{31}P NMR atroom temperature. Complex **3** was heated at 75, 80, 85, 98, and 105 °C (Figure 2). Complexes **10** and **12** were heated at 98 °C (Figure 1); complex **11** was heated at 80 °C. ^{13}C NMR was also used in the case of L = $CH_3{}^{13}CH_2$. Analysis of the gas phase by GC and comparison with an authentic sample showed formation of ethylene and propylene, which were also observed by NMR. In time, formation of complexes **5** and **6** became visible, while complexes **10**−**12** gradually disappeared.

Acknowledgment. This work was supported by The Israel Science Foundation, Jerusalem, Israel, and by the MINERVA Foundation, Munich, Germany. C.L.H. acknowledges Shell and the EPSRC for funding her visit to Israel. D.M. is the holder of the Israel Matz Professorial Chair in Organic Chemistry.

OM990073V