Carbon−Carbon Bond Activation by Rhodium(I) in Solution. Comparison of sp^2-sp^3 vs sp^3-sp^3 C−C, C−H vs C−C, and $Ar-CH_3$ vs $Ar-CH_2CH_3$ Activation

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Abstract: Reaction of $[RhClL_2]_2$ (L = cyclooctene or ethylene) with 2 equiv of the phosphine {1-Et-2,6-$(CH_2P^tBu_2)_2C_6H_3$} (**1**) in toluene results in a selective metal insertion into the strong Ar−Et bond. This reaction proceeds with no intermediacy of activation of the weaker sp^3-sp^3 $ArCH_2-CH_3$ bond. The identity of complex Rh(Et){2,6-$(CH_2P^tBu_2)_2C_6H_3$}Cl (**3**) was confirmed by preparation of the iodide analogue **6** by reaction of the new Rh(η^1-N_2){2,6-$(CH_2P^tBu_2)_2C_6H_3$} (**7**) with EtI. It is possible to direct the bond activation process toward the benzylic C−H bonds of the aryl−alkyl group by choice of the Rh(I) precursor, of the substituents on the phosphorus atoms (^{t}Bu vs Ph), and of the alkyl moiety (Me vs Et). A Rh(III) complex which is analogous to the product of insertion into the $ArCH_2-CH_3$ bond (had it taken place) was prepared and shown not to be an intermediate in the $Ar-CH_2CH_3$ bond activation process. Thus, aryl−C activation by Rh(I) is kinetically preferred over activation of the alkyl−C bond in this system. Moreover, cleavage of an $Ar-CH_2CH_3$ bond, followed by β-H elimination, may be preferred over sp^2-sp^3 C−C activation of an $Ar-CH_3$ group.

Introduction

The insertion of transition metal complexes into C−C bonds in solution is a topic of much current interest.[1−20] We have reported transition metal insertion into strong C−C single bonds in solution and details related to the mechanism of these reactions.[21−29] Recently, we observed catalytic activation of a strong C−C single bond[28] and an unprecedented oxidative addition of a C−C bond of a fluorinated organic substrate.[29] We report here a system that allows the direct observation of an oxidative addition of a strong sp^2-sp^3 Ar−Et bond to Rh(I), affording a new unsaturated Rh(III)−ethyl complex, which upon heating undergoes slow β-H elimination. We also qualitatively compare sp^2-sp^3 vs sp^3-sp^3 C−C, C−H vs C−C, and $Ar-CH_3$ vs $Ar-CH_2CH_3$ carbon−carbon bond activation. Part of this work has been communicated.[25]

Results and Discussion

Preparation of Substrates. The new aryl−ethyl phosphines **1** and **2** were prepared in order to explore the possibility of competitive activation of unstrained sp^2-sp^3 and sp^3-sp^3 C−C single bonds. The synthesis of substrates **1** and **2** is similar to that of other PCP-based ligands.[26,30−33] It consists of lithiation

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(1) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.
(2) For a review, see: Rybtchinski, B.; Milstein, D. *Angew. Chem. Int. Ed.*, in press.
(3) Suggs, J. W.; Jun, C.-H. *J. Chem. Soc., Chem. Commun*. **1985**, 92.
(4) Perthuisot, C.; Jones, W. D. *J. Am. Chem. Soc*. **1994**, *116*, 3647.
(5) Perthuisot, C.; Edelbach, B. L.; Zubris, D. L.; Jones, W. D. *Organometallics* **1997**, *16*, 2016.
(6) Fujimura, F.; Aoki, S.; Nakamura, E. *J. Org. Chem*. **1991**, *56*, 2809.
(7) Suzuki, H.; Takaya, Y.; Takemori, T. *J. Am. Chem. Soc.* **1994**, *116*, 10779.
(8) Lu, Z.; Jun, C.-H.; de Gala, S. R.; Sigalas, M.; Eisenstein, O.; Crabtree, R. H. *Organometallics* **1995**, *14*, 1168.
(9) Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc*. **1998**, *120*, 2843.
(10) Huffman, M. A.; Liebeskind, L. S. *J. Am. Chem. Soc*. **1991**, *113*, 2771.
(11) Nicholls, J. C.; Spencer, J. L. *Organometallics* **1994**, *13*, 1781.
(12) Murakami, M.; Amii, H.; Shigeto, K.; Ito, Y. *J. Am. Chem. Soc*. **1996**, *118*, 8285.
(13) Murakami, K.; Takahasi, K.; Amii, H.; Ito, Y. *J. Am. Chem. Soc*. **1997**, *119*, 9307.
(14) Crabtree, R. H.; Dion, R. P.; Gibboni, D. J.; McGrath, D. V.; Holt, E. M. *J. Am. Chem. Soc*. **1986**, *108*, 7222.
(15) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc*. **1969**, *91*, 5970.
(16) Eilbracht, P. *Chem. Ber*. **1976**, *109*, 1429.
(17) Jones, W. D.; Maguire, J. A. *Organometallics* **1987**, *6*, 1301.
(18) Benfield, F. W. S.; Green, M. L. H. *J. Chem. Soc., Dalton Trans*. **1974**, 1324.
(19) Hemond, R. C.; Hughes, R. P.; Locker, H. B. *Organometallics* **1986**, *5*, 2391.
(20) Yeh, W.-Y.; Hsu, S. C. N.; Peng, S.-M.; Lee, G. H. *Organometallics* **1998**, *17*, 2477.
(21) Gozin, M.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1993**, 699.
(22) Gozin, M.; Aizenberg, M.; Liou, S.-Y.; Weisman, A.; Ben-David, Y.; Milstein, D. *Nature* **1994**, 370.
(23) Gandelman, M.; Vigalok, A.; Shimon, L. J. W.; Milstein, D. *Organometallics* **1997**, *16*, 3981.
(24) Liou, S.-Y.; Gozin, M.; Milstein, D. *J. Am. Chem. Soc*. **1995**, *117*, 9774.
(25) Liou, S.-Y.; Gozin, M.; Milstein, D. *J. Chem. Soc., Chem. Commun*. **1995**, 1965.
(26) Rybtchinski, B.; Vigalok, A.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc*. **1996**, *118*, 12406.
(27) van der Boom, M. E.; Kraatz, H.-B.; Ben-David, Y.; Milstein, D. *J. Chem. Soc., Chem. Commun*. **1996**, 2167.
(28) Liou, S.-Y.; van der Boom, M. E.; Milstein, D. *Chem. Commun*. **1998**, 687.
(29) van der Boom, M. E.; Ben-David, Y.; Milstein, D. *Chem. Commun*. **1998**, 917.
(30) Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020.

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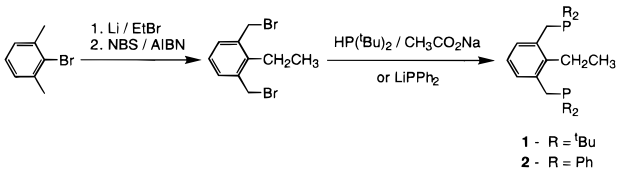
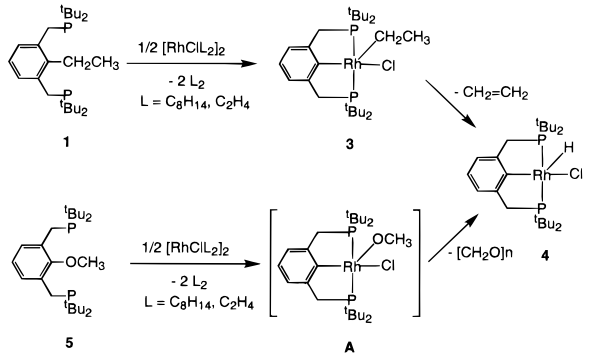
Scheme 1



Scheme 2

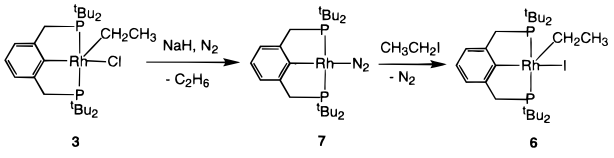


of 2-bromo-1,3-dimethylbenzene, coupling with ethyl bromide, bromination, and reaction with HP^tBu_2 or $LiPPh_2$ (Scheme 1). Compounds **1** and **2** were obtained as white powders and were characterized by ^1H, ^{31}P, and ^{13}C NMR.

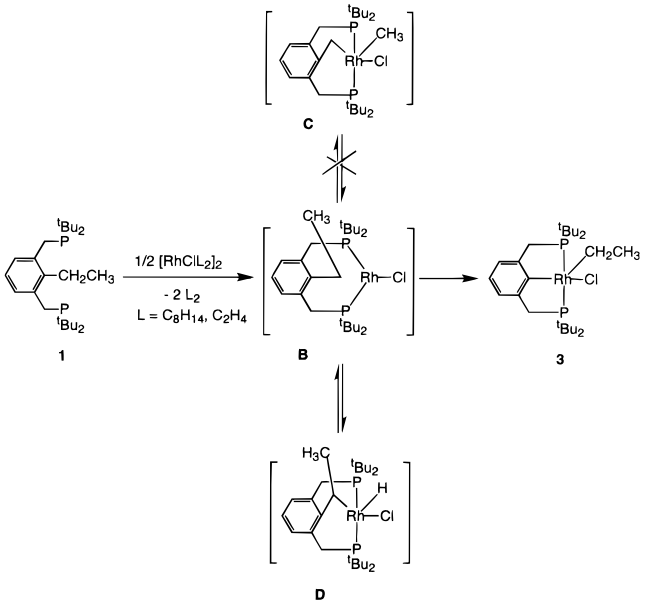
Ar−CH$_2$CH$_3$ vs ArCH$_2$−CH$_3$ Activation with 1. Reaction of the alkene complex $[RhClL_2]_2$ (L = ethylene or cyclooctene) with 2 equiv of **1** in toluene at 120 °C (5 min in a sealed tube) resulted in quantitative formation of the new pentacoordinated Rh(III)−ethyl complex **3** by selective oxidative addition of the strong sp^2-sp^3 C−C bond (compare bond dissociation energy (BDE) of Ph−Et = 96.3 ± 1 kcal/mol; Scheme 2).[34] Complex **3** was characterized by various NMR techniques (vide infra). Thermolysis of **3** in toluene at 120 °C overnight resulted in the quantitative formation of ethylene and the known Rh(III)−hydride complex **4**,[30,35] which was unambiguously identified by ^1H and ^{31}P NMR and by comparison with an authentic sample. The ethylene was observed by ^1H NMR and was collected by standard vacuum line techniques and identified and quantified by GC. Using deuterated toluene, no Rh(III)−D formation was observed by ^2H NMR, indicating that the solvent does not contribute to the Rh(III)−H formed. Oxidative addition of a strong Ar−CH_3 single bond to Rh(I) in solution was observed in our group with other PCP-type systems.[21,22,24−26,28,29] Very recently, we observed metal insertion into the strong sp^2-sp^3 Ar−O bond of an aryl ether **5**,[32,36] which probably occurs via an (unobserved) oxidative addition product Rh(OMe){2,6-($CH_2P^tBu_2$)$_2C_6H_3$}Cl (**A**) followed by β-hydride elimination to give formaldehyde and **4** (Scheme 2).

To confirm the identity of **3**, we prepared the iodide analogue **6** by EtI oxidative addition to the new dinitrogen complex **7**. Reaction of **3** with an excess of NaH in THF under nitrogen at room temperature led to the quantitative formation of the Rh-

Scheme 3



Scheme 4

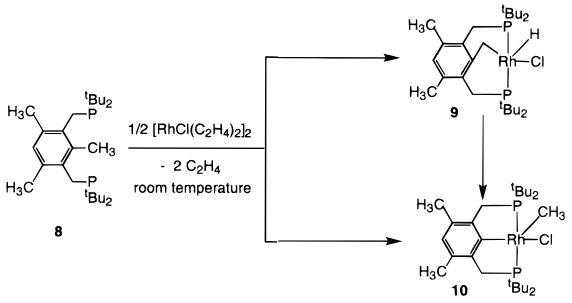


(I)−dinitrogen complex **7** and ethane (Scheme 3).[37] The ethane was collected by standard vacuum line techniques and analyzed by GC. The air-sensitive complex **7** was characterized by ^1H, ^{31}P, and ^{13}C NMR and IR. It exhibits spectroscopic properties similar to those of its iridium analogue (vide infra).[38] No THF coordination was observed in the ^1H NMR, probably as a result of the bulky *tert*-butyl substituents on the phosphorus atoms.[32,39] η^1-N_2 binding to similar *tert*-butyl PCP−Rh(I) complexes competes favorably with CO_2 and even with ethylene.[39] Treatment of **7** with 1 equiv of EtI in toluene or dioxane at room temperature led to the selective formation of **6** in excellent yield (~95%). The reaction was completed within 10 min, and no intermediates were observed by ^1H and ^{31}P NMR. As observed for **3**, thermolysis of the product solution at 120 °C overnight resulted in the quantitative formation of the iodide analogue of **4** (by ^1H, ^{31}P, and ^{13}C NMR) and ethylene (by ^1H NMR and GC).[35]

Mechanistically, coordination of **1** to the metal center is likely to precede the Ar−C bond cleavage step (Scheme 4, **B**). Coordination of both phosphine arms to the metal center was postulated for the Ar−H,[30] Ar−OMe (**5**, Scheme 2),[32,36] Ar−CH_3 (**8**, Scheme 5),[26] and Ar−CF_3[29] analogues of **1** with rhodium(I) and iridium(I) and was observed for similar substrates with platinum(II)[40] and ruthenium(II).[41] Performing the reaction (**1** → **3**) at room temperature resulted in the formation of oligomers, as indicated by ^1H and ^{31}P NMR spectroscopy,

(31) Rybtchinski, B.; Ben-David, Y.; Milstein, D. *Organometallics* **1997**, *16*, 3786.
(32) van der Boom, M. E.; Liou, S.-Y.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 6531.
(33) Weisman, A.; Gozin, M.; Kraatz, H. B.; Milstein, D. *Inorg. Chem.* **1996**, *35*, 1792.
(34) Egger, K. W.; Cocks, A. T. *Helv. Chim. Acta* **1973**, *56*, 1516.
(35) Details about this β-H elimination process will be reported in a forthcoming paper.
(36) van der Boom, M. E.; Liou, S.-Y.; Ben-David, Y.; Vigalok, A.; Milstein, D. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 625.
(37) This compound was probably observed by Kaska et al. in a nonselective dehydrochlorination reaction of **4** with $NaN(SiMe_3)_2$.[43]
(38) Rybtchinski, B. M.Sc. Thesis, The Weizmann Institute of Science, Rehovot, Israel, 1996.
(39) Vigalok, A.; Ben-David, Y.; Milstein, D. *Organometallics* **1996**, *15*, 1839.
(40) van der Boom, M. E.; Gozin, M.; Ben-David, Y.; Shimon, L. J. W.; Frolow, F.; Kraatz, H. B.; Milstein, D. *Inorg. Chem.* **1996**, *35*, 7068.
(41) Dani, P.; Karlen, T.; Gossage, R. A.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1997**, *119*, 11317.

Scheme 5



which probably collapsed to monomeric species upon heating. Former studies in our group have shown that coordination of similar di-*tert*-butyl phosphines such as **8** to Rh(I) and Ir(I) complexes occurs at room temperature and controls the overall rate in the activation of an Ar−CH_3 bond (Scheme 5).[26] Likewise, substitution of the olefin (cyclooctene or ethylene) by **1** is probably slow relative to the bond activation. No complexes resulting from C−H or sp^3−sp^3 C−C activation (**D**, **C**; Scheme 4) were observed in the reaction of **1** with $[RhClL_2]_2$ (L = cyclooctene or ethylene) by ^{1}H and ^{31}P NMR.

To evaluate whether activation of the weaker sp^3−sp^3 C−C bond (ΔBDE{Ph−CH_2CH_3 − $PhCH_2$−CH_3} = 24.5 kcal/mol)[34,42] is an intermediate step in the observed sp^2−sp^3 C−C activation process or perhaps a reversible parallel process (**C**, Scheme 4), $[RhCl(C_8H_{14})_2]_2$ (C_8H_{14} = cyclooctene) was reacted with 2 equiv of **1** in C_6D_6 under H_2 (20 psi) at 120 °C for 16 h in a Fischer Porter pressure vessel. Analysis of the reaction solution by ^{1}H and ^{31}P NMR showed exclusive formation of the known Rh(III)−hydride complex **4**,[30] which was identical to an authentic sample. GC analysis of the gas phase showed formation of ethane (∼90%). Only traces of methane were observed (<4%), providing evidence that sp^3−sp^3 C−C cleavage is not involved either on the reaction coordinate or as a side equilibrium. A pathway involving stepwise sp^3−sp^3, sp^2−sp^3 C−C bond cleavage generating 2 equiv of CH_4 and **4** would have been thermodynamically more favorable.[25,34] Thus, in this system, sp^2−sp^3 C−C bond activation is kinetically preferred over that of a sp^3−sp^3 C−C bond.

The possibility of a side equilibrium involving C−H activation (**D**, Scheme 4) cannot be ruled out. However, under appropriate conditions, C−C activation can be kinetically and thermodynamically more favorable than C−H activation.[23,26] Rhodium insertion into an Ar−CH_3 bond becomes more favorable as compared with insertion into an $ArCH_2$−H bond when higher electron density is involved.[24] The reaction of $[RhCl(C_2H_4)_2]_2$ with ligand **8**, having electronic and steric properties similar to those of **1**, resulted in competitive C−H and C−C oxidative addition at room temperature (Scheme 5).[26] In a slower process, **9** undergoes C−H reductive elimination, followed by C−C oxidative addition, to give **10** quantitatively. It is expected that, in the Ar−Et system, **1**, having only two benzylic C−H bonds and considering more steric hindrance imposed by the methyl group, the C−C cleavage is even more competitive with C−H activation.

Identification of Complexes 3, 6, and 7. Complexes **3** and **6** were unequivocally characterized by various NMR techniques and exhibit nearly identical spectroscopic properties. Assignments in the ^{1}H and ^{13}C{^{1}H} NMR spectra were made using ^{1}H{^{31}P}, ^{1}H−^{1}H COSY, NOESY, and ^{13}C-DEPT-135 NMR. In the ^{31}P{^{1}H} NMR spectrum of **3**, one doublet resonance appears at δ 54.99 with $^1J_{RhP}$ = 123.8 Hz, indicating that both

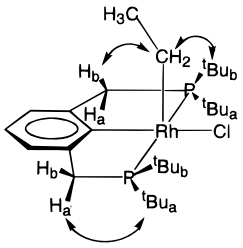


Figure 1. NOE interactions detected for **3**.

phosphorus atoms are magnetically equivalent and coordinated to a Rh(III) center. The structure of **3** is fully supported by ^{1}H and ^{13}C NMR. For instance, the Rh−$\boldsymbol{CH_2}CH_3$ group appears in the ^{13}C{^{1}H} NMR spectrum as a double triplet at δ 16.83, with $^1J_{RhC}$ = 29.1 Hz and cis $^2J_{PC}$ = 4.9 Hz. The Rh−$CH_2\boldsymbol{CH_3}$ group appears as a doublet at δ 23.61, with $^2J_{RhC}$ = 1.4 Hz. In the ^{1}H NMR spectrum, this alkyl group appears as a double triplet at δ 1.24 (3H), with $^3J_{RhH}$ = 2.3 Hz and $^3J_{HH}$ = 7.2 Hz, and as a multiplet at δ 2.40 (2H), with $^2J_{RhH}$ = 2.8 Hz, $^3J_{HH}$ = 7.2 Hz, and cis $^3J_{PH}$ = 7.1 Hz. From the NOESY spectrum, it is possible to unambiguously assign the ^{1}H NMR resonances for **3** and to show that the structure in solution has the ethyl group cis to the aryl group (Figure 1; NOE cross-peaks are seen between H_a and ^{t}Bu$_a$, between H_b and the $\boldsymbol{CH_2}CH_3$, and between ^{t}Bu$_b$ and the $\boldsymbol{CH_2}CH_3$). In the ^{1}H NMR spectrum of **6**, the CH_3 and CH_2 resonances of the ethyl ligand appear at δ 0.89 and 2.38, respectively, and two sets of resonances are seen for the protons of the ^{t}Bu groups and the CH_2 "arms" of the PCP ligand. When the Rh$\boldsymbol{CH_2}CH_3$ protons of **6** were irradiated, selective enhancement of the $RhCH_2\boldsymbol{CH_3}$ signal was observed. A doublet is observed in the ^{31}P{^{1}H} NMR spectrum of **6** at δ 52.75, with $^1J_{RhP}$ = 122.5 Hz. The similarities in the ^{13}C NMR chemical shifts of the *ipso*-carbons 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 (**4**) (δ 166.85),[43] Rh(Me){2,6-$(CH_2P^tBu_2)_2$-3,5-$(CH_3)_2$-C_6H}Cl (**10**) (δ 168.80),[26] Rh(Me){2-$(CH_2P^tBu_2)$-6-$(CH_2N(C_2H_5)_2$-3,5-$(CH_3)_2$-C_6H}Cl (δ 170.04),[23] and **3** (δ 167.57), 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 trends in aryl-bound complexes.[33,44] Thus, for **3** and **6**, the strongest trans director, the ethyl ligand, is trans to the vacant coordination site, in agreement with crystal structures of analogous square-pyramidal PCP- and PCN-type rhodium(III) and iridium(III) complexes.[23,26,38,43,45,46] Theoretical studies predict that the square-pyramidal geometry is preferred for five-coordinated d^6 complexes.[42] The air-sensitive dinitrogen complex **7** is unequivocally characterized by ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR and IR.[37] The ^{1}H NMR spectrum shows two 1:2:1 triplet resonances for the ^{t}Bu and benzylic protons at δ 1.26 and 3.15 (J_{PH} = 6.3 and 3.7 Hz), respectively, which collapse into singlets upon phosphorus decoupling. The ^{31}P-{^{1}H} spectrum exhibits a doublet resonance at δ 81.01 ($^1J_{RhP}$ = 157.9 Hz), indicative of two magnetically equivalent phosphorus nuclei coordinated to a Rh(I) center. The Rh−η^1-N_2 moiety of **7** exhibits a characteristic band in the IR spectrum at

(42) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.

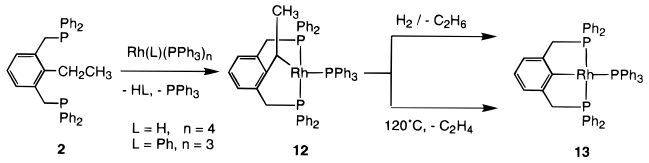
(43) Nemeh, S.; Jensen, C.; Binamira-Soriaga, E.; Kaska, W. C. *Organometallics* **1983**, *2*, 1442.

(44) Van de Kuil, L. A.; Luitjes, H.; Groves, D. M.; Zwikker, J. W.; Van der Linden, J. G. M.; Roelofsen, A. M.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *Organometallics* **1994**, *13*, 468.

(45) Crocker, C. J.; Errington, R. J.; McDonald, W. S.; Odell, K. J.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1979**, 498.

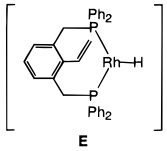
(46) Crocker, C. J.; Empsall, H. D.; Errington, R. J.; Hyde, E. M.; McDonald, W. S.; Markham, R. J.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1982**, 1217.

Scheme 6



$\nu = 2133\ cm^{-1}$. This frequency is close to those observed for other PCP-type Rh(I) complexes: Rh(η^1-N_2){HC($CH_2CH_2P^tBu_2$)$_2$},[39] Rh(η^1-N_2){$CH_3C(CH_2CH_2P^tBu_2)_2$},[47] Rh(η^1-N_2){1-O-2,6-($CH_2P^tBu_2$)$_2$-4-CH_3-C_6H_2},[32] and it is indicative of an "end-on" coordinated dinitrogen complex.[48,49] Very recently, the X-ray structures of [Ir{2,6-($CH_2P^tBu_2$)$_2$$C_6H_3$}]$_2$-($\mu$-$N_2$),[50] [Rh{1-O-2,6-($CH_2P^tBu_2$)$_2$-4-$CH_3$-$C_6H_2$}]$_2$-($\mu$-$N_2$),[32] and Rh($\eta^1$-$N_2$){$CH_3(CH_2CH_2P^tBu_2)_2$}][43] were reported. The N_2 ligand of **7** is readily displaced by CO, affording the carbonyl complex Rh(CO){2,6-($CH_2P^tBu_2$)$_2$$C_6H_3$}, with ^{1}H and ^{31}P NMR and IR spectra identical to those reported in the literature.[30]

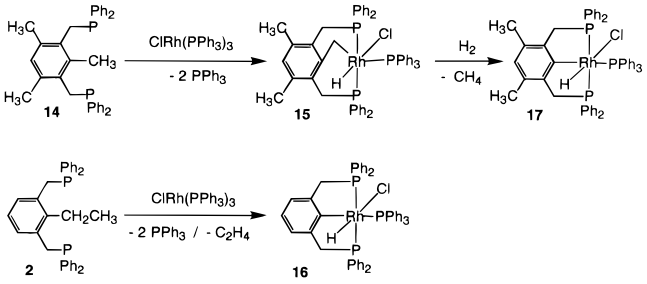
C−H vs C−C Activation. Interestingly, it is possible to direct the bond activation process toward the benzylic protons of the ethyl group by choice of the rhodium(I) precursor and the substituents on the phosphorus atoms (Scheme 6). As recently communicated,[25] reaction of $HRh(PPh_3)_4$ or $PhRh(PPh_3)_3$ with **2** yields the chiral product of C−H activation **12** (Scheme 6), which is analogous to the unobserved **D** (Scheme 4). Reaction of **12** with H_2 (20 psi) at 120 °C resulted in formation of ethane (95% by GC) and **13**, which was unambiguously identified by ^{1}H, ^{31}P, and ^{13}C NMR and by comparison with an authentic sample.[25] The mechanism of the hydrogenolysis of **12** is probably similar to the one reported for the hydrogenolysis of an analogous benzylic Rh(I) complex.[21] Interestingly, thermolysis of **12** at 120 °C in toluene in the absence of H_2 resulted in the quantitative formation of ethylene and **13**. We believe that **12** undergoes (reversible) β-H elimination, giving a Rh(I)−H species **E**. Metal insertion into



the sp^2−sp^2 Ar−C bond followed by C−H elimination and phosphine coordination affords the observed ethylene and **13**. It is known that [Rh(η^1-N_2){$CH_3C(CH_2CH_2P^tBu_2)_2$}] undergoes reversible β-hydride elimination upon N_2 dissociation.[47] While the activation of the C−C bond of biphenylene is known,[4,5,8,20] activation of an unstrained sp^2−sp^2 C−C bond in solution has not been reported. Regardless of the mechanism involved, in both systems **1** and **2**, exclusive sp^2−sp^3 C−C bond cleavage with Rh(I) was observed, showing that this selective bond activation process can take place with significantly different electron density and bulk at the metal center. In system **2**, benzylic C−H activation is kinetically favored over C−C activation.

Ar−CH_2CH_3 vs Ar−CH_3 Activation. Interestingly, reaction of **14** with $ClRh(PPh_3)_3$ results in quantitative C−H activation, forming the thermally stable **15** (up to 150 °C),[24] while reaction of **2** with $ClRh(PPh_3)_3$ (at 120 °C in toluene or benzene in a sealed vessel) results in C−C activation to give **16** and ethylene (91%; Scheme 7), which were identified and quantified by ^{1}H, ^{31}P, and ^{13}C NMR, IR, and X-ray analysis (vide infra) and by GC analysis of the gas phase. Using deuterated solvents, no Rh(III)−D formation was observed by ^{2}H NMR. Very recently, we observed a similar phenomenon with Ni(II).[51] Exclusive benzylic C−H activation occurs upon heating of the ^{i}Pr analogue of **14** with a stoichiometric amount of NiI_2 in ethanol, whereas the ^{i}Pr analogue of **1** and **2** favors Ar−Et activation. Thus, de-ethylation of an arene, which is presumably driven by the β-H elimination process and ethylene release, occurs more readily than Ar−Me cleavage in a similar system.

Scheme 7



Ar−CH_2CH_3 vs ArCH_2−CH_3 Activation with 2. A consecutive sp^3−sp^3, sp^2−sp^3 C−C bond activation pathway of **2** and $ClRh(PPh_3)_3$ under H_2, generating CH_4 and **16**, would most probably involve the intermediacy of a species such as **15** (Scheme 7). Treatment of a THF solution of **15** with H_2 (20 psi) at 80 °C resulted in the formation of methane (>90% by GC) and **17**, which is analogous to **16**. Dehydrochlorination of **17** with MeLi or excess KO^{t}Bu in THF or dioxane resulted in the formation of the known Rh(I) complex Rh{2,6-(CH_2-PPh_2)$_2$-3,5-(CH_3)$_2$-C_6H}(PPh_3) as judged by ^{1}H and ^{31}P NMR.[21] Performing the reaction of **2** with $ClRh(PPh_3)_3$ under H_2 (20 psi) resulted in the formation of ethane and **16**,[25] which has been fully characterized by X-ray analysis (Figure 2).[52,53] Only traces of methane were observed (<4%), indicating that the metal center activates only the sp^2−sp^3 C−C bond in the presence of H_2. Apparently, intermediates analogous to **15** are not involved.

The new benzylic Rh(III)−methyl complex **19** was prepared in order to evaluate unambiguously whether activation of the sp^3−sp^3 C−C bond of **2** occurs in the absence of H_2. Complex **19** is the iodide analogue of the expected product of Rh(I) insertion into the $ArCH_2$−CH_3 bond of **2** and $ClRh(PPh_3)_3$. Treatment of a THF solution of **15** with excess Et_3N or KO^{t}Bu resulted in the formation of the known complex **18** (>90 and 40% yield by ^{1}H and ^{31}P NMR, respectively), which can be obtained quantitatively by reaction of **14** with $HRh(PPh_3)_4$ or $PhRh(PPh_3)_3$ in THF at room temperature.[21] Oxidative addition of CH_3I to **18** in toluene at room temperature in a sealed tube leads to exclusive formation of **19** and PPh_3, which were characterized by ^{1}H, ^{31}P, and ^{13}C NMR and FD-MS. The ^{1}H NMR shows clearly the presence of the $ArCH_2Rh$ and Rh−CH_3 moieties, which appear at δ 2.25 (dt, $^3J_{PH} = 8.3$ Hz, $^2J_{RhH}$

(47) Vigalok, A.; Kraatz, H.-B.; Konstantinovsky, L.; Milstein, D. *Chem. Eur. J.* **1997**, *3*, 253.
(48) Busetto, C.; Dalfonso, A.; Maspero, F.; Perego, G.; Zazzetta, A. *J. Chem. Soc., Dalton Trans* **1977**, *1828*.
(49) Thorn, D. L.; Tulip, T. H.; Ibers, J. A. *J. Chem. Soc., Dalton Trans*. **1979**, 2022.
(50) Lee, D. W.; Kaska, W. C.; Jensen, C. M. *Organometallics* **1998**, *17*, 1.
(51) van der Boom, M. E.; Ben-David, Y.; Milstein, D., manuscript in preparation.
(52) Gozin, M. Ph.D. Thesis, The Weizmann Institute of Science, Rehovot, Israel, 1995.
(53) A similar structure of a 3,5-lutidine-based PCP Rh(I) complex was reported recently.[33]

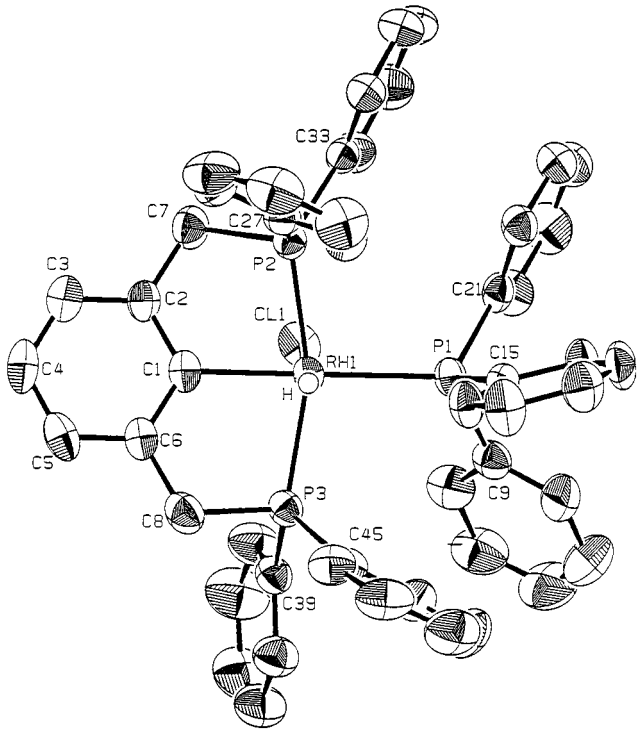
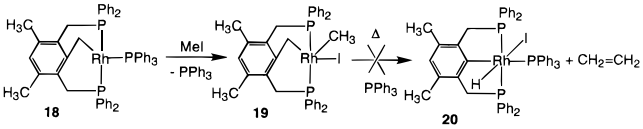


Figure 2. ORTEP view of **16**. Selected bond lengths (Å): Rh(1)−Cl(1) = 2.514(1); Rh(1)−P(1) = 2.400(1); Rh(1)−P(2) = 2.322(1); Rh(1)−P(3) = 2.319(1); Rh(1)−C(1) = 2.090(4). Selected bond angles (deg): P(1)−Rh(1)−P(2) = 99.92(4); P(1)−Rh(1)−P(3) = 98.75(4); P(2)−Rh(1)−P(3) = 157.19(4); P(1)−Rh(1)−C(1) = 177.9(1); Cl(1)−Rh(1)−P(1) = 90.62(4); Cl(1)−Rh(1)−P(2) = 88.37(4); Cl(1)−Rh(1)−P(3) = 104.43(4); Cl(1)−Rh(1)−C(1) = 91.3(1); Rh(1)−C(1)−C(2) = 120.7(3); Rh(1)−C(1)−C(6) 121.8(3).

Scheme 8



= 1.1 Hz, 2H) and δ 1.65 (vq, $^3J_{PH}$ = 4.5 Hz, $^2J_{RhH}$ = 3.1 Hz, 3H), respectively. The $^{31}P\{^1H\}$ spectrum exhibits a doublet resonance at δ 28.9 ($^1J_{RhP}$ = 127.5 Hz), indicative of two magnetically equivalent phosphorus nuclei coordinated to a Rh(III) center. The $^{13}C\{^1H\}$ NMR shows clearly the presence of the Rh(III)−CH_3 moiety at δ 7.90 (bd, $^1J_{RhC}$ = 30.8 Hz) and in the ^{13}C-DEPT-135 NMR, a positive signal is observed, indicative of an odd number of protons. $^{13}CH_3I$ was used as well to unambiguously assign this moiety in the ^{1}H and ^{13}C NMR. Complex **19** is stable in solution at room temperature for 24 h but decomposes slowly upon heating of the product solution at 70 °C (in a sealed tube). However, compounds indicative of Ar−C bond cleavage such as **20** are not observed. Thus, cleavage of the $ArCH_2-CH_3$ bond is most probably not involved either on the reaction coordinate or as a side equilibrium in the thermolysis of **12** (Scheme 6) or in the reaction of **2** with $ClRh(PPh_3)_3$ (Scheme 7).

Summary and Conclusions

We observed directly metal insertion into a strong $Ar-CH_2-CH_3$ bond prior to β-H elimination and have shown that sp^2-sp^3 C−C bond activation in this system is kinetically preferable to the unobserved sp^3-sp^3 C−C bond activation with rhodium(I), regardless of the bulk and the electron density at the metal center. sp^3-sp^3 C−C bond activation is not involved, either as a side equilibrium or as an intermediate process, even in the presence of H_2, which could have driven the overall process to a thermodynamically more favorable consecutive sp^3-sp^3, sp^2-sp^3 C−C bond activation process forming methane.[25,34] Thus, the reason for the preference of ethane (in the presence of H_2) or ethylene formation is kinetic. The iodide analogue **19** of the expected product of metal insertion into the sp^3-sp^3 C−C bond was prepared and shown not to be an intermediate in the sp^2-sp^3 Ar−C bond activation process. Although the $Ar-CH_2-CH_3$ bond is substantially stronger than the $ArCH_2-CH_3$ bond (compare BDE values of $Ph-CH_2CH_3$ = 96.3 ± 1 kcal/mol, $PhCH_2-CH_3$ = 71.8 ± 1 kcal/mol),[34,42] selective insertion into the Ar−C bond takes place, indicating that this process is product controlled, and it is likely that BDE(Ar−M + M−CH_2-CH_3) − BDE($ArCH_2$−M + M−CH_3) > ∼20 kcal/mol. The Ar−Rh bond is known to be quite strong.[54,55] The chelate ring size formed may also play a role, although both the five- and six-membered chelates are very stable. The higher accessibility and lower directionality of the sp^2-sp^3 vs the sp^3-sp^3 C−C bond are kinetic factors that undoubtedly favor activation of the Ar−C bond. Although kinetic studies were not performed here, a mechanism involving a nonpolar three-centered transition state is likely to be operative for the Rh(I) insertion into the $Ar-CH_2CH_3$ bond, as shown for the direct Rh(I) insertion into the Ar−CH_3 bond of **8**.[26] The remarkably stable unsaturated Rh(III)−CH_2CH_3 complexes **3** and **6**, obtained by selective insertion of Rh(I) into the Ar−C bond or by oxidative addition of EtI to a dinitrogen complex **7**, are isostructural with previously postulated Rh(III)−OCH_3 species **A** involved in Ar−O bond activation.[32,36] It is noteworthy that sp^2-sp^3 C−O activation by Rh(I) in **5** is kinetically preferred over sp^3-sp^3 C−O bond activation, while Pd(II) exclusively activates the adjacent sp^3-sp^3 C−O bond.[32,36] Our observations show that cleavage of an $Ar-CH_2CH_3$ bond, followed by β-H elimination, may be preferred over sp^2-sp^3 C−C activation of an Ar−CH_3 group. Thus, systems might be designed to selectively activate unstrained C−C bonds of substrates having β-Hs, while similar compounds—but lacking β-H's—undergo exclusively C−H activation.

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), and 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. Deuterated solvents were purchased from Aldrich and were degassed and stored over 4 Å activated molecular sieves in the glovebox. $[RhClL_2]_2$ (L = cyclooctene or ethylene) was prepared by a published procedure.[56,57] 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, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded at 400.19, 161.9, and 100.6 MHz, respectively, on a Bruker AMX 400 NMR spectrometer. ^{1}H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ spectra were also recorded at 250.17, 101.3, and 62.9 MHz,

(54) Martinho-Simoes, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629.
(55) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc*. **1984**, *106*, 1650.
(56) Herdé, J. L.; Senoff, C. V. *Inorg. Nucl. Chem. Lett*. **1971**, 1029.
(57) Cramer, R. *Inorg. Chem*. **1962**, *1*, 722.

respectively, on a Bruker DPX 250 NMR spectrometer. All chemical shifts (δ) are reported in ppm and coupling constants (J) are in hertz. 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 an internal standard h_1 (δ 7.15 benzene; 7.26 chloroform; 7.09 toluene) and *all-d* solvent peaks (δ 128.0 benzene; 77.0 chloroform; 20.4 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 and ^{13}C{^{1}H} NMR were made using ^{1}H{^{31}P}, ^{1}H$-^1$H COSY, and ^{13}C-DEPT-135 NMR. All measurements were carried out at 298 K. 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.

Formation of 1 and 2. (a) Synthesis of 2-Ethyl-1,3-dimethylbenzene. A solution of 2-bromo-1,3-dimethylbenzene (18.1 g, 97.5 mmol) in ether (20 mL) was added dropwise to a cold (0 °C) *n*-butyllithium solution (1.6 M in hexane, 80 mL) in a 250-mL three-necked round-bottom flask equipped with an argon inlet, dropping funnel, and magnetic bar. The resulting reaction mixture was refluxed overnight, cooled to room temperature, and filtered. The residue was washed with cold pentane (3 × 25 mL) and dried in a vacuum, affording 2-lithio-1,3-dimethylbenzene as a white solid in quantitative yield (11 g). A solution of ethyl bromide (21.3 g, 195 mmol) in THF (50 mL) was added dropwise to a stirred suspension of 2-lithio-1,3-dimethylbenzene (11 g, 97.5 mmol) in THF (150 mL) at − 60 °C in a 500-mL Schlenk flask. The reaction mixture was warmed to room temperature and stirred overnight. The THF was removed by rotary evaporation, and the residue was dissolved in CH_2Cl_2 (300 mL), washed with water (3 × 100 mL), and dried again. Distillation (90−92 °C/0.20 mmHg) afforded a colorless oil (4.6 g, 35%). ^{1}H NMR ($CDCl_3$): δ 6.88 (s, 3H, Ar*H*), 2.55 (q, $^3J_{HH}$ = 7.5 Hz, 2H, C*H*$_2$CH$_3$), 2.21 (s, 6H, C*H*$_3$), 1.01 (t, $^3J_{HH}$ = 7.6 Hz, 3H, CH$_2$*CH*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 141.5, 136.3, 128.7, 126.0 (all s, Ar), 23.2 (s, *C*H$_2$CH$_3$), 20.1 (s, *C*H$_3$), 13.8 (s, CH$_2$*C*H$_3$).

(b) Synthesis of 2-Ethyl-1,3-dibromomethylbenzene. A mixture of 2-ethyl-1,3-methylbenzene (3.6 g, 27 mmol), NBS (9.6 g, 54 mmol), and AIBN (∼0.1 g) in CCl_4 (150 mL) was refluxed for 5 h in a 500-mL three-necked round-bottom flask equipped with an argon inlet and condenser. After filtration, the solution was washed with water (3 × 25 mL), treated with $MgSO_4$, filtered, and concentrated by rotary evaporation. The residue was stored overnight at − 20 °C, affording a white lacrimatory solid which was filtered, washed with cold cyclohexane (3 × 25 mL), and dried in a vacuum (7.2 g, 91%). This product was further purified by distillation (110 °C/0.16 mmHg) and by column chromatography using hexane as eluent (3.1 g, 39%). ^{1}H NMR ($CDCl_3$): δ 7.21 (d, $^3J_{HH}$ = 7.6 Hz, 2H, Ar*H*), 7.05 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Ar*H*), 4.43 (s, 4H, CH$_2$Br), 2.80 (q, $^3J_{HH}$ = 7.6 Hz, 2H, C*H*$_2$CH$_3$), 1.21 (t, $^3J_{HH}$ = 7.6 Hz, 3H, CH$_2$*CH*$_3$). ^{13}C NMR ($CDCl_3$): δ 142.4, 136.8, 131.9, 127.1 (all s, Ar), 31.7 (s, CH$_2$Br), 22.0 (s, *CH*$_2$-CH$_3$), 15.7 (s, CH$_2$*CH*$_3$).

(c) Phosphination. For 1: The phosphination with HP^{t}Bu$_2$ to afford **1** was done according to literature procedures.[26,30,32] ^{31}P{^{1}H} ($CDCl_3$): δ − 31.5 (s). ^{1}H NMR ($CDCl_3$): δ 7.25 (m, 2H, ArH), 6.90 (t, 1H, ArH), 3.10 (q, 2H, $^3J_{HH}$ = 7.4 Hz, C*H*$_2$CH$_3$), 2.82 (s, 4H, CH$_2$P), 1.41 (t, 3H, $^3J_{HH}$ = 7.5 Hz, CH$_2$*CH*$_3$), 1.06 (s, 36H, C(C*H*$_3$)$_3$). **For 2:** A solution of 2-ethyl-1,3-bis(bromomethyl)benzene (1.8 g, 6.0 mmol) in THF (120 mL) was added dropwise to a cold THF solution (−78 °C, 30 mL) of $LiPPh_2$ (2.4 g, 13 mmol) in a 250-mL three-necked round-bottom flask equipped with an argon inlet and a dropping funnel. The solution was warmed to room temperature and stirred overnight. The reaction mixture was concentrated by rotary evaporation, toluene was added (100 mL), and the solution was filtered and concentrated again. The residue was dissolved in $CHCl_3$ (100 mL), filtered, and concentrated by rotary evaporation. The residue was recrystallized from pentane to afford a white solid **2** (2.8 g, 92%). ^{31}P{^{1}H} ($CDCl_3$): δ −11.7 (s). ^{1}H NMR ($CDCl_3$): δ 7.6−6.8 (m, 23H, ArH), 3.38 (s, 4H, CH$_2$P), 2.95 (q, $^3J_{HH}$ = 7.5 Hz, 2H, C*H*$_2$CH$_3$), 1.34 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH$_2$*CH*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 141.5−125.5 (Ar), 34.0 (d, $^1J_{PC}$ = 16.8 Hz, CH$_2$P), 22.8 (t, $^4J_{PC}$ = 4.8 Hz, *CH*$_2$CH$_3$), 15.3 (t, $^5J_{PC}$ = 1.8 Hz, CH$_2$*CH*$_3$).

Formation and Thermolysis of Rh(Et){2,6-(CH$_2$P^{t}Bu$_2$)$_2$C$_6$H$_3$}Cl (2). A C_6D_6 solution (1 mL) of **1** (30 mg, 0.71 mmol) and $[RhClL_2]_2$ (L = C_2H_4 or C_8H_{14}) (25 mg, 0.035 mmol) was loaded into a 5-mm screwcap NMR tube and heated for 5 min at 120 °C. The resulting deep red solution was analyzed by ^{1}H, ^{1}H{^{31}P}, ^{1}H$-^1$H COSY, NOESY, ^{31}P{^{1}H}, ^{13}C{^{1}H}, and ^{13}C-DEPT-135 NMR, showing the quantitative formation of **2** and C_8H_{14} or C_2H_4. Continued heating for 16 h resulted in the quantitative formation of the known Rh(H){2,6-(CH$_2$P^{t}Bu$_2$)$_2$C$_6$H$_3$}-Cl (**4**) and ethylene, as judged by ^{1}H and ^{31}P NMR and GC.[30,35] Addition of an authentic sample to the solution resulted in overlap of signals in ^{1}H and ^{31}P NMR. The reaction was also performed in a sidearm flask to allow quantitative analysis of the gas phase by GC. ^{1}H NMR (C_6D_6): δ 1.17 (vt, $^3J_{PH}$ = 6.0 Hz, 18H, C(CH$_3$)$_3$), 1.24 (dt, $^3J_{RhH}$ = 2.3 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, RhCH$_2$C*H*$_3$), 1.35 (vt, $^3J_{PH}$ = 6.0 Hz, 18H, C(CH$_3$)$_3$), 2.40 (m, $^2J_{RhH}$ = 2.8 Hz, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 7.1 Hz, 2H, RhC*H*$_2$CH$_3$), 3.07 (ABq, ΔAB = 34.0 Hz, $^2J_{HH}$ = 17.6 Hz, $^2J_{PH}$ = 3.5 Hz, 4H, CH$_2$P), 7.0 (m, 3H, ArH). ^{13}C{^{1}H} NMR (C_6D_6): δ 16.83 (dt, $^1J_{RhC}$ = 29.1 Hz, $^2J_{PC}$ = 4.9 Hz, Rh*C*H$_2$CH$_3$), 23.61 (d, $^2J_{RhC}$ = 1.4 Hz, RhCH$_2$*C*H$_3$), 29.71 (vt, $^2J_{PC}$ = 2.2 Hz, C(*C*H$_3$)$_3$) 31.10 (vt, $^2J_{PC}$ = 2.3 Hz, C(*C*H$_3$)$_3$), 33.01 (dvt, $^2J_{RhC}$ = 2.7 Hz, $^1J_{PC}$ = 8.9 Hz, CH$_2$P), 36.49 (dvt, $^2J_{RhC}$ = 1.6 Hz, $^1J_{PC}$ = 6.6 Hz, *C*(CH$_3$)$_3$), 36.76 (vt, $^1J_{PC}$ = 7.4 Hz, *C*(CH$_3$)$_3$), 122.88 (dt, J_{RhC} = 1.1 Hz, J_{PC} = 8.6 Hz, C$_{meta}$), 130.30 (s, C$_{para}$), 150.16 (dt, $^2J_{RhC}$ = 1.0 Hz, $^2J_{PC}$ = 8.7 Hz, C$_{ortho}$), 167.57 (dt, $^1J_{RhC}$ = 35.8 Hz, $^2J_{PC}$ = 1.9 Hz, C$_{ipso}$). ^{31}P{^{1}H} NMR (C_6D_6): δ 54.99 (d, $^1J_{RhP}$ = 123.8 Hz, 2P).

Formation and Thermolysis of Rh(Et){2,6-(CH$_2$P^{t}Bu$_2$)$_2$C$_6$H$_3$}I (6). EtI (3 mg, 0.019 mmol) was added to a yellow C_6D_6 solution (1 mL) of **5** (10 mg, 0.019 mmol). The red reaction solution was loaded into a 5-mm screwcap NMR tube and analyzed by ^{1}H, ^{1}H$-^1$H NOE, ^{1}H{^{31}P}, and ^{31}P{^{1}H} NMR. The reaction was completed within 10 min, and no intermediate compounds were observed. Continued heating for 16 h resulted in the formation of Rh(H){2,6-(CH$_2$P^{t}Bu$_2$)$_2$C$_6$H$_3$}I and ethylene (∼95%), as judged by ^{1}H and ^{31}P NMR and GC analysis of the solution.[35] The reaction was also performed in a sidearm flask to allow quantitative analysis of the gas phase by GC. ^{1}H NMR (C_6D_6): δ 0.89 (dt, $^3J_{RhH}$ = 2.4 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, RhCH$_2$C*H*$_3$), 1.16 (vt, $^2J_{PH}$ = 6.1 Hz, 18H, C(CH$_3$)$_3$), 1.42 (vt, $^3J_{PH}$ = 6.3 Hz, 18H, C(CH$_3$)$_3$), 2.38 (m, $^2J_{RhH}$ = 2.7 Hz, $^2J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 6.1 Hz, 2H, RhC*H*$_2$CH$_3$), 3.12 (ABq, ΔAB = 9.2 Hz, $^2J_{HH}$ = 17.8 Hz, $^2J_{PH}$ = 3.7 Hz, 4H, CH$_2$P), 7.1 (m, 3H, ArH). ^{31}P{^{1}H} NMR (C_6D_6): δ 52.63 (d, $^1J_{RhP}$ = 122.5 Hz). FD-MS: (M^+ − I) 524.8.

Formation of Rh(η^1-N$_2$){2,6-(CH$_2$P^{t}Bu$_2$)$_2$C$_6$H$_3$} (7). To a solution of **3** (40 mg, 0.071 mmol) in THF (5 mL) was added excess of NaH (35 mg, 1.3 mmol). The suspension was stirred for 24 h at room temperature. The mixture was filtered and dried under vacuum. The resulting solid was dissolved in benzene (10 mL), and the solution was filtered again. Complex **7** was obtained as a yellow air-sensitive solid after evaporation of the benzene. Passing CO through a benzene (3 mL) solution of **7** for 15 min resulted in quantitative formation of Rh-(CO){2,6-(CH$_2$P^{t}Bu$_2$)$_2$C$_6$H$_3$}, as judged by ^{1}H and ^{31}P NMR and IR.[30] ^{1}H NMR (C_6D_6): δ 1.26 (vt, $^2J_{PH}$ = 6.3 Hz, 36H, C(CH$_3$)$_3$), 3.15 (vt, $^2J_{PH}$ = 3.7 Hz, 4H, CH$_2$P), 7.1 (m, 3H, ArH). ^{13}C{^{1}H} NMR (C_6D_6): δ 35.18 (vt, $^2J_{PC}$ = 6.6 Hz, C(*C*H$_3$)$_3$), 36.36 (dvt, $^2J_{RhC}$ = 6.6 Hz, $^1J_{PC}$ = 10.1 Hz), 120.73 (t, J_{PC} = 9.8 Hz, Ar), 123.57 (s, Ar), 128.53 (s, Ar), 157.79 (dt, J_{RhC} = 3.6 Hz, J_{PC} = 12.8 Hz, Ar). ^{31}P{^{1}H} NMR (C_6D_6): δ 81.01 (d, $^1J_{RhP}$ = 157.9 Hz). IR (film): ν = 2133 cm^{-1}, (s, N≡N).

Hydrogenolysis of the Ar−C Bond in 15. A THF solution (30 mL) of **15** (60 mg, 0.066 mmol) was loaded into a 90 cm^3 Fischer Porter pressure vessel, pressurized with H_2 (20 psi), and heated for 12 h at 80 °C. The gas phase was removed using a vacuum line and analyzed quantitatively by GC. The reaction mixture was concentrated to 5 mL. Addition of cold pentane (20 mL) resulted in precipitation of an orange powder, which was filtered off and dried under high vacuum to give >90% yield of **17**. The analogous complex **16**, lacking the two methyl substituents in the 3 and 5 positions of the aromatic ring, has similar spectroscopic features.[25] ^{31}P{^{1}H} NMR (THF): δ 46.6 (dd, $^1J_{RhP}$ = 111.1 Hz, $^2J_{PP}$ = 24.5 Hz, 2P), 19.8 (dt, $^1J_{RhP}$ = 82.2 Hz, 1P). Addition of MeLi (1.2 equiv) or KO^{t}Bu (5 equiv) to the

product solution at room temperature resulted in quantitative formation of Rh{2,6-$(CH_2PPh_2)_2$-3,5-$(CH_3)_2$-C_6H}(PPh_3), as judged by ^1H and ^{31}P NMR.

Thermolysis of Complex 12. A toluene-d_8 solution (1 mL) of **12** (10 mg) was loaded into a 5-mm screwcap NMR tube and heated for 3 days at 120 °C. ^1H and ^{31}P NMR analysis showed the quantitative formation of **13**.[25] Addition of an authentic sample to the solution resulted in overlap of signals in ^1H and ^{31}P NMR. Ethylene was observed by ^1H NMR and GC. The reaction was also performed in a sidearm flask to allow quantitative analysis of the gas phase by GC.

Formation and Thermolysis of Complex 19. To a toluene-d_8 solution (1 mL) of **18**[21] (10 mg, 0.024 mmol) was injected 3 μL (0.048 mmol) of CH_3I (or $^{13}CH_3I$) by a microsyringe at room temperature. ^1H and ^{31}P NMR analysis of the reaction mixture after 30 min showed exclusive formation of **19** and PPh_3. The red solution was dried under vacuum to remove excess of CH_3I, and the resulting red oil was redissolved in toluene-d_8 (1 mL). The product was not separated from PPh_3. Complex **19** is stable at room temperature in solution but slowly decomposes at 70 °C (24 h for ∼90% decomposition). Compounds indicative of Ar−C bond cleavage were not observed. ^1H NMR (toluene-d_8): δ 7.4−6.5 (m, ArH of **19** and PPh_3), 3.3 (left part of ABq, $^2J_{HH}$ = 13.7 Hz, $^2J_{PH}$ = 3.8 Hz, 2H, CH_2P), 2.7 (right part of ABq, $^2J_{HH}$ = 13.7 Hz, $^2J_{PH}$ = 4.4 Hz, 2H, CH_2P), 2.25 (td, $^3J_{PH}$ = 8.3 Hz, $^2J_{RhH}$ = 1.1 Hz, 2H, $ArCH_2Rh$), 1.65 (m, $^3J_{PH}$ = 4.5 Hz, $^2J_{RhH}$ = 3.1 Hz, 3H, $RhCH_3$), 1.54 (s, 6H, $ArCH_3$). $^{31}P\{^1H\}$ NMR (toluene-d_8): δ 28.9 (d, $^1J_{RhP}$ = 127.5 Hz, **19**), −4.71 (bs, PPh_3). $^{13}C\{^1H\}$ NMR (toluene-d_8): δ 139−126 (CAr of **19** and PPh_3), 27.71 (vt, $^1J_{PC}$ = 12.2 Hz, CH_2P), 22.41 (bd, $^1J_{RhC}$ = 15.8 Hz, $ArCH_2Rh$), 19.45 (s, $ArCH_3$), 7.90 (bd, $^1J_{RhC}$ = 30.8 Hz, $RhCH_3$). FD-MS: m/z = 760 (M^+), correct isotope pattern.

X-ray Crystal Structure Determination of Complex 16. A crystal was analyzed (at 298 K) on a PW1100/20 Philips four-circle computer-controlled diffractometer, Mo Kα (λ = 0.710 69 Å) radiation with a graphite crystal monochromator in the incident beam. The unit cell dimensions were obtained by a least-squares fit of 24 centered reflections in the range of $11 < \theta < 14°$. Intensity data were collected using the $\omega-2\theta$ technique to a maximum 2θ of 46°. The scan width, $\Delta\omega$, for each reflection was $1.00 + 0.35 \tan\theta$, with a scan speed of 2.1 deg/min. Background measurements were made for a total of 20 s at both limits of each scan. Three standard reflections were monitored every 60 min. No systematic variations in intensities were found. Intensities were corrected for Lorentz and polarization effects. All non-hydrogen atoms were found by using the SHELXS-80 direct method analysis.[58] After several cycles of refinements,[59] the positions of the hydrogen atoms were calculated, except HRh, and added to the refinement process. Refinement proceeded to convergence by minimizing the function $\sum w(|F_o| - |F_c|)^2$. A final difference Fourier synthesis map showed several peaks less than 0.3 e/Å^3 scattered about the unit cell without a significant feature. The discrepancy indices $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|^2]^{1/2}$ are presented with other crystallographic data in Table 1. An ORTEP view, selected bond angles, and distances of the molecular structure are shown in Figure 2.

Table 1. Crystallographic Data for Complex **16**

formula	$C_{50}H_{43}P_3RhCl\cdot(CD_3)_2CO$
fw	880.79
space group	$P2_1/n$
a, Å	16.052(5)
b, Å	20.434(5)
c, Å	14.519(2)
β, deg	104.43(2)
V, Å^3	4612.1(9)
D_{calcd}, g cm^{-3}	1.34
T, K	298
Z	4
μ(Mo Kα), cm^{-1}	5.61
no. of unique reflections	6637
no. of reflections with $I > 3\sigma(I)$	4667
R	0.031
R_w	0.039

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Supporting Information Available: Tables of crystallographic data and structure refinement, atomic coordinates, bond lengths and angles anistropic displacement parameters, and hydrogen atom coordinates for **16** (11 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(58) Sheldrick, G. M. *SHELXTL*, An integrated system for solving, refining and displaying crystal structures from diffraction data; University of Göttingen, Germany, 1980.

(59) All crystallographic computing was done on a VAX computer at the Hebrew University of Jerusalem, Israel, using TEXSAN structure analysis software.