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Methyl-to-Double Bond Migration in Methylene Arenium Rhodium Complexes

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The novel methylene arenium Rh(I)−Me complexes **5** and **10** were prepared by selective protonation of the corresponding xylylene complexes with HBF_4 in cold pentane. These complexes are stable both in the solid state and in solution. Upon reaction with carbon monoxide, the corresponding CO adducts **11** are obtained, which undergo under ambient conditions selective methyl migration to the coordinated double bond of the methylene arenium moiety. This provides an uncommon example of a migratory insertion process in a saturated complex that is promoted by the incoming ligand. No evidence for a concurrent methyl migration to the CO ligand was observed, indicating that the methyl-to-olefin migration is thermodynamically preferred over the carbonylation process. The observed activation entropy ($\Delta S^{\ddagger} = -36.1$ eu) is in good agreement with an organized transition state for the migration process.

Introduction

Methylene arenium metal complexes represent a new family of organometallic compounds that contain a nonlabile, highly electron deficient olefin ligand.[1] The strong back-bonding of a late transition metal center, such as monovalent Rh or Ir, to the positively charged arenium ligand results in an increase of the electrophilicity of the metal center. Electrophilic (normally cationic) metal complexes are highly active in various catalytic transformations involving ligand migration to a coordinated double bond, such as in the polymerization of olefins.[2] For the migratory insertion to take place, the two interacting ligands have to occupy cis-positions.[3] The created empty coordination site in the reaction product makes the β-hydrogen elimination from the newly formed alkyl group an easy process. Addition of another ligand can drive the reaction toward the insertion product.[4] When carbon monoxide is used, CO insertion to give the corresponding acyl complex is likely to take place. This is also the case when both possibilities, alkene polymerization and CO−olefin copolymerization, are available.[5,6] In contrast to the widespread insertion of olefins into the Rh−H bond, examples of olefin insertion into a Rh−Me bond are extremely rare.[7,8] Here we present the synthesis and ligand insertion chemistry of Rh(I) methyl complexes containing the highly electron deficient methylene arenium olefin ligand. These complexes, stable otherwise, upon addition of CO undergo irreversible methyl migration to the olefin, yielding the corresponding ethyl arenium Rh(I) complexes, representing an unexpected ligand-promoted migratory insertion process. Moreover, although instances of Rh−alkyl bond carbonylation are well documented,[9] in our case we found no evidence for methyl migration to the coordinated CO, while a rare, facile, thermodynamically driven methyl migration to the coordinated double bond of the arenium moiety is observed.

Results and Discussion

Protonation of Xylylene Rh(I) Methyl Complexes. We have recently reported the synthesis and characterization of the *o*- and *p*-xylylene Rh(I) complexes **1** and **2**, respectively.[1] Reaction of a 1:1 mixture of these two complexes with an excess (2.5−3 equiv) of trifluoromethane sulfonic acid (triflic acid, HOTf) in methylene chloride resulted in the arenium complex **3**, which was fully spectroscopically characterized and was shown to have most of the positive charge ring localized.[1] When the same mixture was reacted with another strong acid, HBF_4, in pentane at −30 °C, a brown precipitate was immediately formed. NMR analysis in $CDCl_3$ showed two products in an approximate ratio of 1:3: the dicationic methylene arenium complex **4**, similar to **3**, and the methylene arenium Rh methyl complex **5** (Scheme 1).

The ^{31}P NMR spectrum of complex **5** exhibits a doublet at 43.41 ppm ($J_{RhP} = 131.4$ Hz). The protons of

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[1] Vigalok, A.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 477.

[2] For a recent review see: Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428.

[3] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. In *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

[4] Brown, C. K.; Wilkinson, G. *J. Chem. Soc. A* **1970**, 2753.

[5] For a recent review see: Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663.

[6] For comparative analysis of alkyl migration to olefin and carbon monoxide see: Rix, F. C.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 1137.

[7] The k_H/k_{Alkyl} ratio in a Rh(III) olefin complex was found to be more than 10^6: Brookhart, M.; Hauptman, E.; Lincoln, D. M. *J. Am. Chem. Soc.* **1992**, *114*, 10394.

[8] For an example of Rh(III)-catalyzed alkene polymerization see: (a) Flood, T. C.; Wang, L. *J. Am. Chem. Soc.* **1992**, *114*, 3169. (b) Wang, L.; Lu, R. S.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1993**, *115*, 6999.

[9] (a) Forster, D. *J. Am. Chem. Soc.* **1976**, *98*, 846. (b) Moloy, K. G.; Wegman, R. W. *Adv. Chem. Ser.* **1992**, *230*, 323. (c) Oswald, A. A.; Hendriksen, D. E.; Kastrup, R. V.; Mozeleski, E. J. *Adv. Chem. Ser.* **1992**, *230*, 395. (d) Ojima, I.; Zhang, A.; Korda, A.; Ingallina, P.; Clos, N. *Adv. Chem. Ser.* **1992**, *230*, 277.

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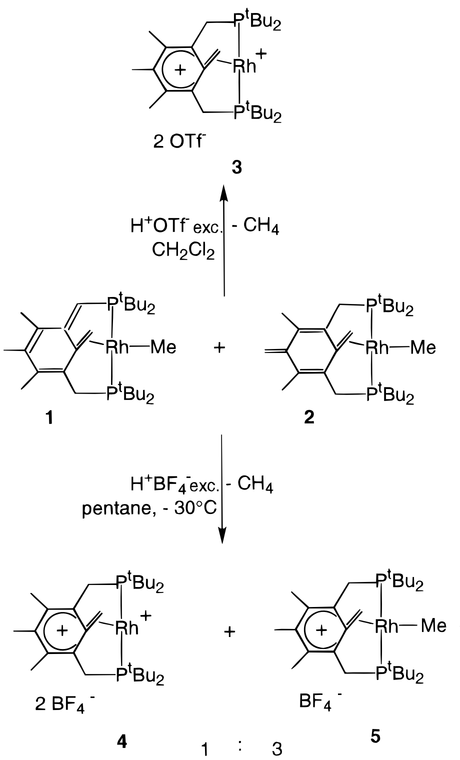
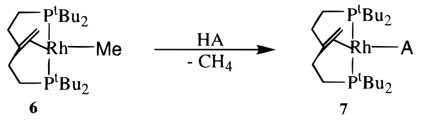
Scheme 1



the coordinated double bond appear in the ^{1}H NMR spectrum as a triplet at 3.89 ppm, whereas the metal-bound methyl group gives rise to a triplet of doublets centered at 1.70 ppm. When **5** was subjected to a large (10−20 equiv) excess of HBF_4 in methylene chloride, a rather slow reaction took place, complex **5** being converted to **4** within several hours. This was surprising, as we expected protonation of an unsaturated Rh(I) methyl complex with a strong acid, followed by methane reductive elimination, to be facile processes.[10] For comparison, we reacted complex **6**,[11] which is analogous to **5**, with strong acids (eq 1). The reactions were instantaneous, with the color changing from dark red to bright yellow due to formation of the corresponding Rh−A complexes **7**.

 (1)

A= OTos (**a**), OTf (**b**), BF_4 (**c**)

The tosylate complex **7a** was crystallized from benzene, giving orange plates. An X-ray structural analysis of **7a** shows weak coordination of the tosylate anion to the rhodium center, Rh(1)−O(5) 2.146(2) Å (Figure 1). Selected bond distances and bond angles are given in Table 1. The coordinated double bond length of 1.407(6) Å is similar to that observed for other Rh(I) PCP type olefin complexes.[11−13] Noteworthy, the rhodium atom is shifted along the double bond toward the least substituted carbon atom with the bond lengths Rh(1)−C(1) and Rh(1)−C(11) being 2.071(3) and 2.134(3) Å, respectively. This asymmetric bonding is similar to the one observed with the corresponding more rigid chelating methylene cyclohexadiene Rh(I) complex.[13]

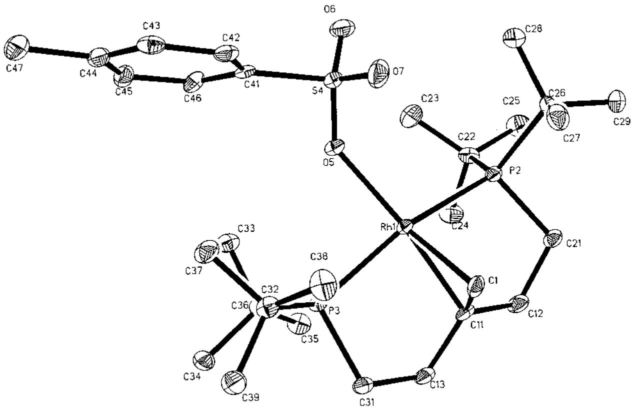


Figure 1. ORTEP view of a molecule of **7a** with the thermal ellipsoids at 50% probability. The hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 7a

(a) Bond Lengths			
Rh(1)−C(1)	2.071(3)	Rh(1)−O(5)	2.146(2)
Rh(1)−C(11)	2.134(3)	Rh(1)−P(2)	1.3557(12)
C(1)−C(11)	1.407(6)	Rh(1)−P(3)	1.3626(11)
(b) Angles			
P(2)−Rh(1)−P(3)	163.10(3)	C(1)−C(11)−Rh(1)	68.1(8)
P(3)−Rh(1)−C(1)	90.04(11)	C(11)−C(1)−Rh(1)	72.9(2)
P(3)−Rh(1)−C(11)	84.23(11)	C(1)−C(11)−C(12)	118.6(3)
C(1)−Rh(1)−C(11)	39.1(2)	O(5)−Rh(1)−P(3)	90.53(8)

As complex **6** is extremely reactive toward strong acids, we attribute the relative inertness of **5** to the electron-withdrawing effect of the arenium ring. The two reaction centers in complexes **1** and **2**—the exocyclic methylene groups and the rhodium center—are both accessible to proton attack, with attack at the former site being in general a least 3 times more preferable. As the methylene groups in (the mixture of) **1** and **2** could differ in their proton affinity, we reacted the *o*-xylylene complex **8**[14] with an excess of HBF_4 in pentane at −30 °C in order to directly compare the reactivity of the metal center and the exocyclic methylene in the protonation reaction. A 1:3 mixture of the corresponding dicationic arenium complex **9** and the methyl arenium Rh(I) complex **10**, respectively, immediately precipitated as a brown solid (Scheme 2). Complexes **9** and **10** possess NMR features similar to those of complexes **4** and **5**, respectively. Since the reaction of complex **10** with an excess of HBF_4 is relatively slow and occurs only within a few hours to give **9**, we can assume that in the xylylene Rh(I) methyl complexes the total reactivity of the exocyclic methylene groups is approximately 3 times higher toward protonation than that of the metal center, as manifested in the ratio between complexes **9** and **10**. Presumably, the unobserved cationic xylylene Rh(I) complex **A** reacts immediately with H^+ at the exocyclic methylene group

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(10) For facile Rh protonation and C−H reductive elimination in a similar chelating system see: Hahn, C.; Spiegler, M.; Herdtweck, E.; Taube, R. *Eur. J. Inorg. Chem.* **1998**, 1425.

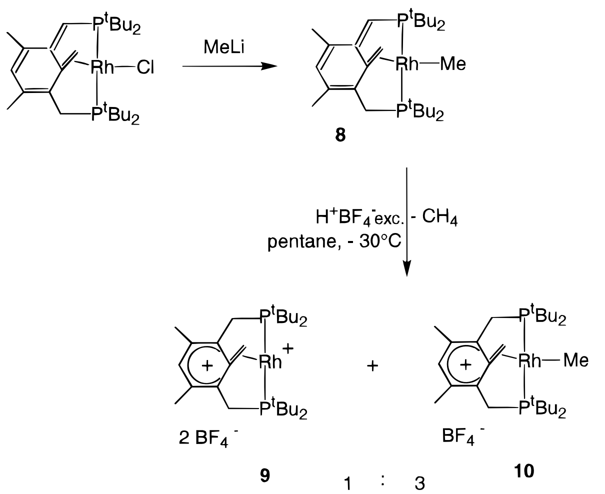
(11) Vigalok, A.; Kraatz, H.-B.; Konstantinovsky, L.; Milstein, D. *Chem. Eur. J.* **1997**, *3*, 253.

(12) Vigalok, A.; Shimon, L. J. W.; Milstein, D. *J. Chem. Soc. Chem. Commun.* **1996**, 1673.

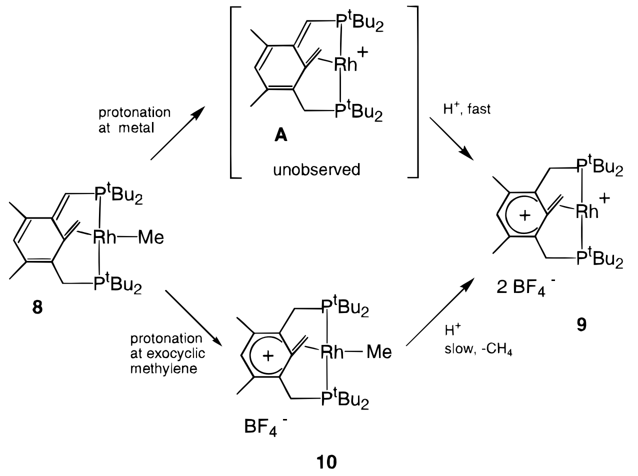
(13) Vigalok, A.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 7873.

(14) Vigalok, A.; Rybtchinski, B.; Shimon, L. J. W.; Ben-David, Y.; Milstein, D. *Organometallics* **1999**, *19*, 895.

Scheme 2



Scheme 3



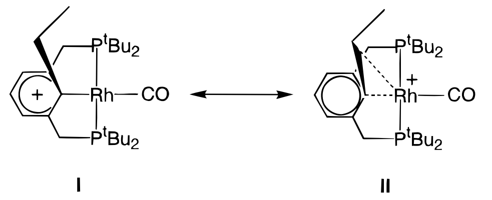
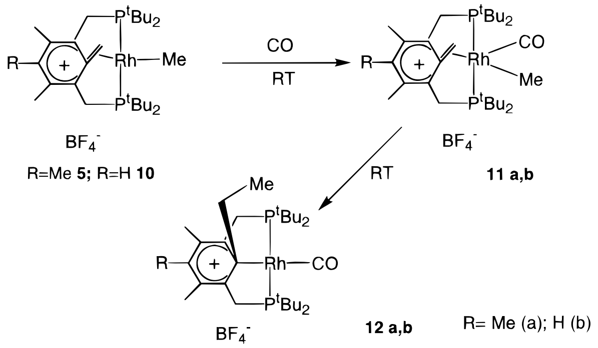
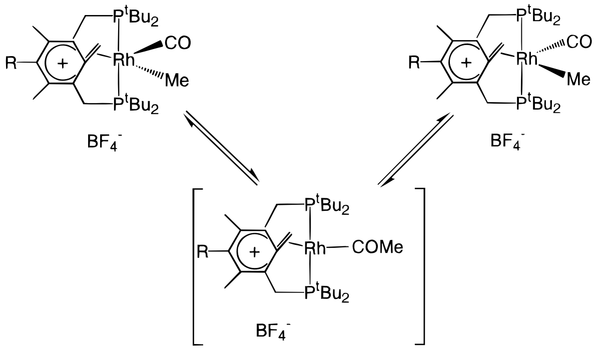


Figure 2.

Scheme 4



Scheme 5



to give the dicationic methylene arenium complexes (Scheme 3).

Methyl-to-Olefin Migration Induced by Carbon Monoxide. When CO was bubbled through a solution of **5** or **10** in $CDCl_3$ for several seconds, formation of the CO adduct **11** was immediately observed[15] with a color change from brown to red. The ^{31}P NMR spectrum of **11a** exhibits a doublet at 56.45 ppm with the $J_{RhP} =$ 100.7 Hz. The ^1H NMR spectrum of **11a** shows signals attributed to both the coordinated methylene group (t, 3.60 ppm) and the Rh$-$CH_3 group (td, 1.77 ppm). Upon standing overnight at room temperature, clean conversion of the CO adduct to the corresponding product of methyl migration to the double bond, complex **12**, took place (Scheme 4).

The *p*-methyl-substituted complex **12a** has been subjected to a single-crystal X-ray analysis. The crystal structure of **12a** has already been reported, and it was shown that the real representation of **12a** is a combination of two resonance forms: the ethyl arenium form **I** and the C$-$C agostic Rh(+) form **II** (Figure 2).[14]

Although there are many examples of rhodium-catalyzed carbonylation reactions, examples of olefin polymerization or oligomerization assisted by rhodium complexes are exceedingly rare.[8] In the case of the methyl arenium complexes **5** and **10** no methyl migration to the olefin takes place until carbon monoxide is added. Interestingly, no subsequent β-hydrogen elimination occurs in **12**, showing that the migration product is the thermodynamically stable product in this system. The methyl group migration to the double bond of the arenium moiety is obviously promoted by the CO coordination. To make the migratory insertion process possible, the two reacting groups must be mutually cis to each other. The incoming CO could provide this type of geometry. However, NOE analysis of **11** at low temperatures showed no mutual effect of the methylene and methyl group protons. Although lack of an observed effect cannot rule out the possibility of the mutual cis orientation in **11**, it might be indicative of an unfavorable configuration. Alternatively, the necessary cis positioning might be achieved by rapid insertion of the CO ligand into the Rh$-$Me bond followed by decarbonylation with an exchange in positions between the CO and Me (Scheme 5). Irreversible methyl migration to the double bond would drive the whole process toward complex **12**. However, we did not detect any (CO migration) reactivity upon cooling of **11** to -65 °C, as monitored by multinuclear NMR techniques. ^{31}P NMR follow-up of the conversion of **11** into **12** showed a smooth transformation that obeyed first-order kinetics. Running the reaction under 5 atm of CO had no effect on the reaction rate, indicating that there is no CO

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[15] The dicationic CO rhodium adducts from **4** or **9** were also observed (ref 14).

dissociation at the preequilibrium stage. Kinetic measurements at different temperatures yielded the activation parameters $\Delta H^{\ddagger} = 12.6$ kcal/mol; $\Delta S^{\ddagger} = -36.1$ eu. As expected for a highly organized transition state, the entropy of activation is considerably negative.

Thus, the overall methyl migration to the double bond in methylene arenium rhodium complexes is promoted by coordination of an extra ligand (carbon monoxide). The reaction is irreversible, complex **12** being stable in both the solid state and in solution.

Summary

We have prepared 16e Rh(I) methyl complexes containing the electron-deficient methylene arenium moiety. These complexes do not undergo methyl migration to the olefin. Addition of carbon monoxide results in saturated CO adducts which slowly undergo migration of the methyl ligand to the methylene group, giving ethyl arenium Rh(I) carbonyl complexes. Thus, it is demonstrated that the incoming ligand (CO) actually promotes the migratory insertion process. Unexpectedly, alkyl migration to the coordinated double bond is thermodynamically more favorable over the alkyl group migration to CO (to give the corresponding metal−acyl complex), which was not observed under the reaction conditions. The observed highly negative value for the entropy of activation indicates an organized transition state for the methyl migration process.

Experimental Section

General Procedures. All operations with air- and moisture-sensitive compounds were performed in a nitrogen-filled glovebox (Vacuum Atmospheres with an MO-40 purifier). All solvents were reagent grade or better. Pentane, benzene, and THF were distilled over sodium/benzophenone ketyl. All solvents were degassed and stored under high-purity nitrogen after distillation. All deuterated solvents (Aldrich) were stored under high-purity nitrogen on molecular sieves (3 Å).

^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded at 400, 162, and 100 MHz, respectively, using a Bruker AMX400 spectrometer. ^{1}H and ^{13}C chemical shifts are reported in ppm downfield from TMS and referenced to the residual solvent h_1 (7.24 ppm chloroform-*d*, 7.15 ppm benzene-d_6) and all-*d* solvent peaks (77.00 ppm chloroform, 128.00 ppm benzene), respectively. ^{31}P chemical shifts are in ppm downfield from H_3PO_4 and referenced to an external 85% phosphoric acid sample. All measurements were performed at 20 °C unless otherwise specified.

Synthesis and Characterization of Compounds 5−12. Synthesis of the Rh−Me Methylene Arenium Complex 5. To a pentane solution (2 mL) of a 1:1 mixture of the *o*- and *p*-xylylene Rh−Me complexes **1** and **2**[1] (20 mg, 0.036 mmol), respectively, was added 1.5 equiv of HBF_4 (in dioxane solution). The clear red solution immediately turned turbid yellow, and a dark brown oily precipitate was deposited on the walls of the reaction vial. The pentane layer was decanted, and the resulting solid was washed twice with pentane (2 × 1 mL) and then dissolved in CH_2Cl_2. Filtration and evaporation of the solvent gave a mixture of **5** and the dicationic Rh(I) complex **4** (this cationic complex possesses the same NMR data as **3**) in a ratio of 3:1, as was revealed by the ^{31}P{^{1}H} NMR spectroscopy. Owing to the very similar solubility properties in organic solvents (methylene chloride, THF) of complexes **4** and **5**, it was impossible to separate them by solubility differences in these solvents or by fractional crystallization from mixtures of these solvents with pentane.

5: ^{31}P{^{1}H} NMR (C_6D_6; δ, ppm) 43.41 (δ, $J_{RhP} = 131.4$ Hz); ^{1}H NMR 3.89 (td, $J_{PH} = 8.5$ Hz, $J_{RhH} = 1.5$ Hz, 2H, C=CH_2), 3.23 (AB m, 4H, CH_2−P), 2.36 (s, 6H, Ar−CH_3), 1.95 (s, 3H, Ar−CH_3), 1.70 (td, $J_{PH} = 5.3$ Hz, $J_{RhH} = 1.7$ Hz, 3H, Rh−CH_3), 1.49 (vt, $J_{PH} = 6.5$ Hz, 18H, t-Bu), 1.23 (vt, $J_{PH} = 6.6$ Hz, 18 H, t-Bu); ^{13}C{^{1}H} NMR 161.26 (br s, *Ar*), 143.60 (s, *Ar*), 134.58 (t, $J_{PC} = 4.3$ Hz, *Ar*), 110.66 (td, $J_{PC} = 4.0$ Hz, $J_{RhC} = <1$ Hz, *C*=CH$_2$), 41.47 (m, C=*C*H$_2$), 36.5 (m, two overlapped *C*(CH$_3$)$_3$), 30.45 (t, $J_{PC} = 2.8$ Hz, C(*C*H$_3$)$_3$), 29.26 (br s, C(*C*H$_3$)$_3$), 22.57 (t, $J_{PC} = 9.5$ Hz, *C*H$_2$−P), 19.36 (s, Ar−*C*H$_3$), 16.95 (s, 2 Ar−*C*H$_3$), 5.54 (dt, $J_{RhC} = 32.0$ Hz, $J_{PC} = 3.7$ Hz, Rh−CH$_3$).

Carbonylation of 5. CO (1 mL) was briskly bubbled through a $CDCl_3$ solution of **5** (in a mixture with the dicationic **4**), resulting in the immediate color change from brown to red. The ^{31}P and ^{1}H NMR spectroscopy revealed clean conversion of **5** to the new CO adduct **11a**: ^{31}P{^{1}H} NMR ($CDCl_3$; δ, ppm)-56.45 (d, $J_{RhP} = 100.7$ Hz); ^{1}H NMR 3.60 (br t, $J_{PH} = 10.0$ Hz, 2H, C=CH_2), 3.35 (AB quart., $J_{HH} = 15.7$ Hz, 4H, CH_2−P), 2.28 (s, 6H, 2 Ar−CH_3), 2.10 (s, 3H, Ar−CH_3), 1.77 (td, $J_{PH} = 4.1$ Hz, $J_{RhH} = 3.1$ Hz, 3H, Rh−CH_3), 1.49 (vt, $J_{PH} = 6.5$ Hz, 18H, t-Bu), 1.28 (vt, $J_{PH} = 6.7$ Hz, 18 H, t-Bu).

Conversion of 11a into 12a. Upon standing at room temperature for 8 h, the CO adduct **11a** was quantitatively converted into the ethyl arenium complex **12a**: ^{31}P{^{1}H} NMR ($CDCl_3$; δ, ppm) 20.78 (d, $J_{RhP} = 102.5$ Hz); ^{1}H NMR 3.73 (AB m, 4H, CH_2−P), 3.51 (quart., $J_{HH} = 7.1$ Hz, 2H, CH$_3$CH_2), 2.39 (t, $J_{PH} = 1.8$ Hz, 6H, 2 Ar−CH_3), 2.16 (s, 3H, Ar−CH_3), 1.47 (vt, $J_{PH} = 7.2$ Hz, 18H, t-Bu), 1.23 (vt, $J_{PH} = 7.1$ Hz, 18 H, t-Bu), 0.81 (t, $J_{HH} = 7.1$ Hz, 3H, CH$_2$CH_3). Complexes **11b** and **12b** were prepared analogously to complexes **11a** and **12a**, respectively, and had nearly identical NMR spectra.

Protonation of Complex 6. To a red solution of **6** (20 mg, 0.041 mmol) in 1 mL of THF was added 8 mg (0.042 mmol) of HOTos·H_2O in 2 mL of THF, resulting in an immediate color change to yellow. The solvent was evaporated, and the resulting yellow solid was washed with pentane, giving 25 mg (95%) of pure **7a**: ^{31}P{^{1}H} NMR (C_6D_6; δ, ppm) 64.82 (d, $J_{RhP} = 129.3$ Hz); ^{1}H NMR 8.07 (d, $J_{HH} = 7.5$ Hz, 2H), 6.87 (br s, 2H), 2.23 (br s, 2H, doublet in ^{1}H{^{31}P} spectrum, $J_{RhH} = 2.2$ Hz, Rh-(CH_2=C)), 1.96 (s, 3H), 1.26 (vt, $J_{PH} = 6.5$ Hz, 18H, t-Bu), 1.21 (vt, $J_{PH} = 6.1$ Hz, 18H, t-Bu); ^{13}C{^{1}H} NMR 77.07 (dt, $J_{RhC} = 18.1$ Hz, $J_{PC} = 3.7$ Hz, Rh(CH$_2$=*C*)), 34.01 (d of br t, $J_{RhC} = 17.9$ Hz, Rh(*C*H$_2$=C)), 35.60 (m, *C*H$_2$(CH$_2$−P) overlapped with *C*(CH$_3$)$_3$)), 34.96 (td, $J_{RhC} = 1.0$ Hz, $J_{PC} = 6.7$ Hz, *C*(CH$_3$)$_3$), 30.56 (t, $J_{PC} = 2.6$ Hz, C(*C*H$_3$)$_3$)), 29.50 (t, $J_{PC} = 2.9$ Hz, C(*C*H$_3$)$_3$)), 21.11 (s, *C*H$_3$−Ar), 16.89 (br t, $J_{PC} = 7.2$ Hz, *C*H$_2$−P).

Complexes **7b** and **7c** were prepared analogously and possess similar NMR data. Complex **7c**: Anal. Found (Calc) C 47.21 (46.99), H 8.40 (8.25).

Protonation of Complex 8. The methylene arenium complex **8** was prepared analogously to the closely related complex **1**[1] by reacting the corresponding chloride complex[14] with MeLi. Consequent addition of 3−5 equiv of HBF_4 in pentane at −30 °C resulted in formation of complexes **9** and **10** in a 3:1 ratio. Complexes **9** and **10** show NMR signals nearly identical to those of **4** and **5**, respectively. As with complexes **4** and **5**, attempts to separate between **9** and **10** were not successful because of their very similar solubility properties.

X-ray Structural Analysis of 7a. Complex **7a** was crystallized from benzene at room temperature. Crystal data: $C_{29}H_{53}O_3P_2RhS$, orange plates, 0.3 × 0.3 × 0.1 mm^3, monoclinic, $P2_1$, $a = 9.745(2)$ Å, $b = 14.841(3)$ Å, $c = 11.449(3)$ Å, $\beta = 109.04(3)°$, from 25 reflections, $T = 110$ K, $V = 1565.2(5)$ Å^3, $Z = 2$, Fw = 646.62, $D_c = 1.372$ Mg/m^3, $\mu = 0.742$ mm^{-1}.

Data collection and treatment: Rigaku AFC5R four-circle diffractometer, Mo Kα, graphite monochromator ($\lambda = 0.71073$ Å), 7530 reflections collected, $1.88° \le \theta \le 27.64°$, $-12 \le h \le 12$, $0 \le k \le 19$, $-14 \le l \le 14$, ω scan method, scan width = 1.2°, scan speed 12°/min, typical half-height peak width =

0.25°, 3 standards were collected 39 times each, with a 3% change in intensity, 3714 independent reflections ($R_{\mathrm{int}} = 0.036$).

Solution and refinement: The structure was solved by direct methods (SHELXS-92). Full-matrix least-squares refinement was based on F^2 (SHELXL-93). Hydrogens were calculated from difference Fourier map and refined in a riding mode with the exception of H1A and H1B on C1, which were located and refined independently. A total of 346 parameters with one restraint, final $R_1 = 0.0275$ (based on F^2) for data with $I > 2\sigma I$ and $R_1 = 0.0304$ for all data based on 3708 reflections, goodness-of-fit on $F^2 = 1.062$, largest electron density = 0.834 e/Å^{-3}.

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Supporting Information Available: Text describing the crystal structure determination of **7a**, an ORTEP diagram of **7a**, tables of crystal data and structure refinement details, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates for complex **7a**; copies of ^{1}H NMR spectra of complexes **4**, **5** (in a mixture), **11a**, and **12a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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