Articles

Iridium(III) and Rhodium(III) Complexes Bearing Chelating Cyclopentadienyl−Phosphine Ligands as C−H Activation Catalysts for the Deuteration of Hydrocarbons in D_2O

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The complex Cp*(PMe_3)$IrCl_2$ (**1**) catalyzes H/D exchange between D_2O and water-soluble organic and organometallic molecules in aqueous solution. This complex undergoes a ligand redistribution reaction to produce [Cp*(PMe_3)$_2$IrCl](Cl) and (Cp*$IrCl_2$)$_2$, which is believed to be responsible for an erosion of exchange activity at long reaction times. We therefore have devised strategies for synthesizing metal complexes which feature chelating cyclopentadienyl−phosphine ligands to inhibit the redistribution reaction. Multistep syntheses of the chelating cyclopentadienyl−phosphine complexes (η^5:η^1-$Me_2PCH_2CMe_2C_5H_4$)IrX_2 (X = I (**3**), OTf (**4**)) are reported, as are one-pot procedures for the synthesis of (η^5:η^1-$Me_2PCH_2SiMe_2C_5Me_4$)IrX_2 (X = I (**7**), Br (**8**)) and (η^5:η^1-$Me_2PCH_2SiMe_2C_5Me_4$)RhX_2 (X = I (**11**), Br (**12**)). We further report the preparation of (η^5:η^1-$Me_2PCH_2SiMe_2C_5Me_4$)Ir(OSO_2CF_3)$_2$ (**9**) and [(η^5:η^1-$Me_2PCH_2SiMe_2C_5Me_4$)Ir(OH_2)$_2$](SO_4) (**10**). Complexes **3** and **4** are not catalysts for the exchange of deuterium between D_2O and organic substrates. Although the water-insoluble complexes **7**, **8**, **11**, and **12** are also not active catalysts, the water-soluble complexes bearing the η^5:η^1-$Me_2PCH_2SiMe_2C_5Me_4$ ligand (**9** and **10**) are. These results imply that an electron-rich iridium center promotes catalytic C−H activation. The activities and lifetimes of these complexes in aqueous H/D exchange reactions with unactivated C−H bonds are similar to those of catalysts which do not contain chelating ligands. This suggests that catalyst deactivation occurs even when a chelating ligand is used. The relevance of these results to ligand redistribution reactions of Ir(III) is discussed.

Introduction

Interest in the reactions of transition-metal organometallic complexes in water is due to the possible availability of new reaction modes and the environmentally benign nature of the solvent.[1,2] This area is underdeveloped because many metal−carbon bonds undergo hydrolysis, thereby limiting their roles in innocent ancillary ligand sets or as transient ligands in catalytic reactions. However, late-metal−carbon bonds are much less polar than early-metal−carbon bonds and are therefore more apt to resist this potential decomposition mode. It occurred to us that using late-metal organometallic complexes as catalysts in an aqueous medium would encourage dissociation of anionic ligands, with the prospect of increasing catalytic efficiency. This idea is complementary to the weakly coordinating anion approach[3−7] of recent years.

We recently discovered that Cp*(PMe_3)$IrCl_2$ (**1**) is an active catalyst for the preparation of isotopically labeled organic compounds, using deuterium oxide as both the reaction solvent and deuterium source.[8] Careful observation of the catalyst during the reaction enabled us to identify a ligand redistribution which coincided with a decrease in H/D exchange efficiency (eq 1). On the basis

$$2\text{Cp*}(PMe_3)IrCl_2 \rightleftharpoons [\text{Cp*}(PMe_3)_2IrCl][Cl] + {}^1/_2[\text{Cp*}IrCl_2]_2 \quad (1)$$

of this observation, it seemed that phosphine dissociation from the iridium center may be responsible for the catalyst degradation equilibrium of eq 1, and if so, it should be possible to stabilize the catalyst against this reaction mode by covalently linking the cyclopentadienyl and phosphine ligands.

Metal complexes featuring linked cyclopentadienyl−phosphine ligands have been known for a number of

(1) Hanson, B. E. *Coord. Chem. Rev.* **1999**, *185−186*, 795.
(2) Li, C.-J. *Chem. Rev.* **1993**, *93*, 2023.
(3) Chen, M. C.; Marks, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 11803.
(4) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 133.
(5) Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970.
(6) Thayer, A. M. *Chem. Eng. News* **1995**, *73*, 15.
(7) Strauss, S. H. *Chem. Rev.* **1993**, *93*, 927.
(8) Klei, S. R.; Golden, J. T.; Tilley, T. D.; Bergman, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 2092.

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years, although a ligand featuring permethylation of the cyclopentadienyl ring and methyl substitution at the phosphine has not been reported.[9] Presumably due to their facile synthesis, late-metal complexes of this type are most often encountered with unsubstituted cyclopentadienyl rings and phenyl substitution at the phosphine.[10−12] Mobley and Bergman reported the synthesis of the chiral organoiridium complex [η^5:η^1-1-($Me_2PCH_2CMe_2$)-3-(*t*-Bu)C_5H_3]IrH_2, which was shown to undergo a diastereoselective C−H activation reaction with cyclohexane upon irradiation.[13] More recently, this chiral ligand has been used in the preparation of new iridate complexes which show diastereoselectivity in their reactions with Ph_3SnCl.[14] We describe here the preparation of such ligands (with both permethylated and unsubstituted cyclopentadienyl rings), as well as iridium and rhodium complexes thereof. Furthermore, the aqueous catalytic H/D exchange activity of these new compounds is addressed.

Results

The synthetic procedure developed for the preparation of (η^5:η^1-1-$Me_2PCH_2CMe_2C_5H_4$)IrI_2 followed the strategy of Mobley and Bergman for the preparation of structurally similar, chiral organoiridium complexes.[13] Addition of lithiated trimethylphosphine[15] to 6,6-dimethylfulvene[16] led to a 1:2 mixture of the desired addition product [($Me_2PCH_2CMe_2$)C_5H_4] and the deprotonation product Li[(CH_2(CH_3)CC_5H_4], respectively (eq 2). Treatment of this mixture with NH_4Cl in THF, followed by addition of HCl in Et_2O, deprotonation with NEt_3 in pentane, and finally deprotonation with KH in pentane led to the isolation of [K][($Me_2PCH_2CMe_2$)C_5H_4] (**2**) in 5% overall yield from the starting fulvene. This ligand has been used previously in the synthesis of (η^5:η^1-1-$Me_2PCH_2CMe_2C_5H_4$)Ir(C_2H_4).[17] Reaction of the potassium salt **2** with [Ir(COE)$_2$Cl]$_2$[18] (COE = cyclooctene), followed by oxidation with elemental iodine, afforded the desired Ir(III) complex (η^5:η^1-1-$Me_2PCH_2CMe_2C_5H_4$)-IrI_2 (**3**) in 21% overall yield (eq 3). This complex has appreciable air stability and was purified by column chromatography on silica gel.

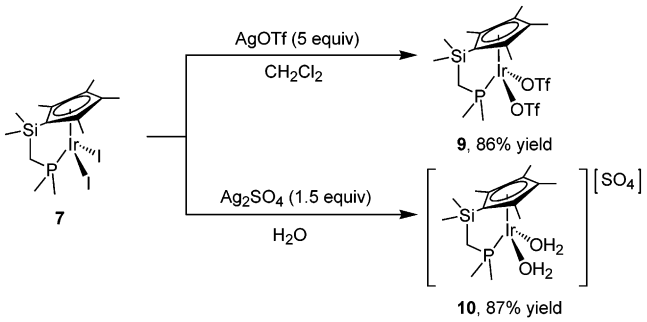
Unfortunately, attempted H/D exchange with Et_2O using D_2O and 5 mol % **3** led to no observable reaction when a mixture of these materials was heated to 135 °C for 40 h. It is noteworthy that **3** is extremely insoluble in D_2O, and this may be responsible for the lack of reactivity. To address this issue, a more water-soluble analogue of **3** was sought.

Anion metathesis of **3** with AgOTf led to the isolation of (η^5:η^1-1-$Me_2PCH_2CMe_2C_5H_4$)Ir(OSO_2CF_3)$_2$ (**4**) in 53% yield after crystallization. Bis(triflate) **4** is significantly more soluble in D_2O than is the diiodide complex **3**. However, heating a mixture of Et_2O, D_2O, and 5 mol % of **4** to 135 °C for 40 h led to no deuterium incorporation into the ether. The likely electronic requirements for C−H activation by the Ir(III) center offer a potential explanation for these observations. It has been previously observed that thermal, stoichiometric C−H activation reactions by Cp*(PMe_3)Ir(Me)OTf are faster with a more electron-rich metal center,[19] as are photochemical C−H activation reactions at an Ir(I) center.[20]

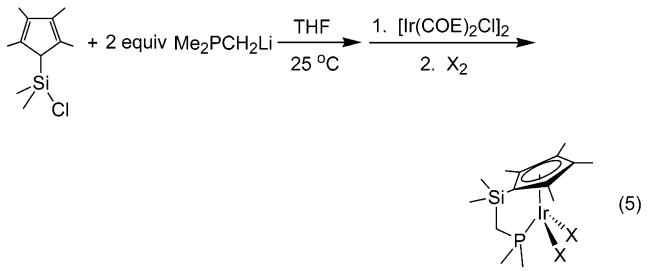
Considering this hypothesis concerning the electronic requirements of the iridium center, a synthetic route to chelating tetramethylcyclopentadienyl−dimethylphosphine complexes was sought. Our first attempt involved addition of lithiated trimethylphosphine to tetramethylpentafulvene[21] in toluene/THF at 0 °C. However, this reaction failed to produce the desired addition product, resulting instead in the formation of a complicated mixture of products. Our next method relied on addition of lithiated trimethylphosphine to the commercially available reagent chlorodimethyl(2,3,4,5-tetramethyl-2,4-cyclopentadien-1-yl)silane. Reaction of 1 equiv of the lithium reagent with the chlorosilane resulted in an approximately 1:1 mixture of the desired addition product (**5**) and the product of subsequent deprotonation by lithiated trimethylphosphine (**6**), as well as unreacted starting material, on the basis of ^{1}H and ^{31}P NMR analysis (eq 4). It was therefore advantageous to use 2 equiv of lithiated trimethylphosphine, one as a nucleo-

(9) Butenschoen, H. *Chem. Rev.* **2000**, *100*, 1527.
(10) Slawin, A. M. Z.; Williams, D. L.; Crosby, J.; Ramsden, J. A.; White, C. *J. Chem. Soc., Chem. Commun.* **1988**, 2491.
(11) Lee, I.; Dahan, F.; Maisonnat, A.; Poilblanc, R. *Organometallics* **1994**, *13*, 2743.
(12) Lefort, L.; Crane, T. W.; Farwell, M. D.; Baruch, D. M.; Kaeuper, J. A.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 3889.
(13) Mobley, T. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 3253.
(14) Paisner, S. N.; Lavoie, G. G.; Bergman, R. G. *Inorg. Chim. Acta*, in press.
(15) Karsch, H. H.; Schmidbaur, H. *Z. Naturforsch.* **1977**, *32B*, 762.
(16) Compton, D. L.; Rauchfuss, T. B. *Organometallics* **1994**, *13*, 4367.
(17) Mobley, T. A. Ph.D. Thesis, University of California, Berkeley, 2001.
(18) van der Ent, A.; Onderdelinden, A. L. *Inorg. Synth.* **1990**, *28*, 90.

Scheme 1



phile and the other as a base. In this manner, combining 2 equiv of lithiated trimethylphosphine with 1 equiv of the silyl chloride, followed by reaction with $[Ir(COE)_2Cl]_2$ and then elemental iodine, yielded the desired chelating ligand complex (η^5:η^1-$Me_2PCH_2SiMe_2C_5Me_4$)IrI_2 (**7**) in 47% isolated yield after silica gel chromatography and recrystallization (eq 5). It was also possible to prepare



the dibromoiridium derivative (η^5:η^1-$Me_2PCH_2SiMe_2C_5Me_4$)$IrBr_2$ (**8**) by oxidation of the presumed "(η^5:η^1-$Me_2PCH_2SiMe_2C_5Me_4$)Ir(COE)" complex with elemental bromine, in 31% overall yield.

Attempted deuteration of Et_2O in D_2O solvent at 135 °C for 40 h catalyzed by 5 mol % of either **7** or **8** led to no observable deuterium incorporation. The insolubility of these complexes in D_2O was a potential reason for this lack of reactivity, and so more water-soluble iridium complexes bearing the chelating tetramethylcyclopentadienyl−dimethylphosphine ligand were desired. Again, anion metathesis was found to be an effective means for changing the solubility. Reaction of diiodoiridium complex **7** with AgOTf in CH_2Cl_2 led to the isolation of (η^5:η^1-$Me_2PCH_2SiMe_2C_5Me_4$)$Ir(OSO_2CF_3)_2$ (**9**) in 86% yield, and treatment of **7** with Ag_2SO_4 in H_2O led to the isolation of [(η^5:η^1-$Me_2PCH_2SiMe_2C_5Me_4$)$Ir(OH_2)_2$](SO_4) (**10**) in 87% yield (Scheme 1). Both bis(triflate) **9** and bis(aquo) complex **10** have greatly improved solubility in D_2O compared to the diiodoiridium starting material **7**.

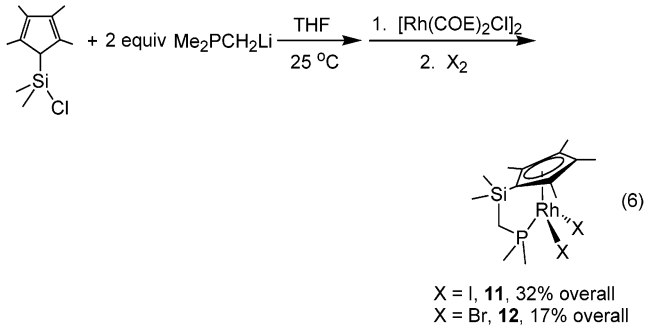
Water-soluble iridium complexes bearing a chelating permethylated cyclopentadienyl−dimethylphosphine ligand were found to be active for H/D exchange catalysis in D_2O solvent at 135 °C for 40 h. Table 1 summarizes the total exchange percentages observed when comparing the chelating complexes to the unbridged complex **1** in the deuteration of Et_2O. Although

Table 1. H/D Exchange Data for Iridium Complexes in Reactions with Et_2O

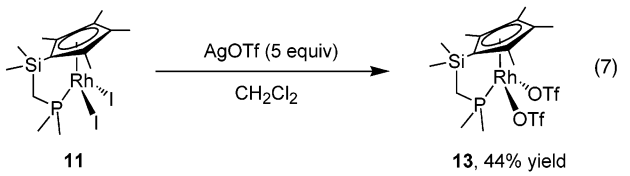
complex	% D incorpn
(η^5:η^1-$Me_2PCH_2SiMe_2C_5Me_4$)$Ir(I)_2$ (**7**)	0
(η^5:η^1-$Me_2PCH_2SiMe_2C_5Me_4$)$Ir(Br)_2$ (**8**)	0
(η^5:η^1-$Me_2PCH_2SiMe_2C_5Me_4$)$Ir(OSO_2CF_3)_2$ (**9**)	33
[(η^5:η^1-$Me_2PCH_2SiMe_2C_5Me_4$)$Ir(OH_2)_2$](SO_4) (**10**)	40
Cp*$(PMe_3)IrCl_2$ (**1**)	36

the water-soluble complexes of the chelating ligand are active for exchange, their activities are comparable to those of the unbridged complex **1**. Complexes **9** and **10** both were observed to undergo decomposition to ^1H and ^{31}P NMR silent materials, making the identification of the decomposition products difficult. It is possible that these chelating complexes undergo a disproportionation reaction that is similar to that observed in the unbridged system, although oligomeric and/or polymeric iridium species result in this case.

Rhodium is often observed to be a more catalytically active metal than iridium.[22] In fact, iridium complexes are often used to probe the mechanisms of rhodium-catalyzed reactions, because the higher stability of the iridium complexes usually allows for isolation.[23] It was therefore hoped that Rh(III) complexes might be more active for H/D exchange catalysis in D_2O. However, using 5 mol % Cp*$(PMe_3)RhCl_2$ in an attempted H/D exchange reaction with *n*-propanol in D_2O at 135 °C for 40 h led to very low levels of incorporation (<10% overall) and precipitation of a black solid (possibly a polymeric rhodium species or bulk metal). We hoped that the chelating ligand would suppress the reaction responsible for precipitation. The synthesis of diiodorhodium complex (η^5:η^1-$Me_2PCH_2SiMe_2C_5Me_4$)RhI_2 (**11**) was performed in a one-pot procedure analogous to the protocol for iridium complex **7** (eq 6). Complex **11** was



obtained in 32% yield over the three-step sequence and displays a ^{31}P NMR chemical shift (δ 13.1, d, J_{Rh-P} = 137 Hz) with coupling to rhodium. When elemental bromine was used instead of iodine, the dibromorhodium complex (η^5:η^1-$Me_2PCH_2SiMe_2C_5Me_4$)$RhBr_2$ (**12**) was obtained in 17% overall yield. Treatment of diiodorhodium complex **11** with AgOTf in CH_2Cl_2 produced the bis(triflate)complex(η^5:η^1-$Me_2PCH_2SiMe_2C_5Me_4$)$Rh(OSO_2CF_3)_2$ (**13**) in 44% yield after two recrystallizations (eq 7).



(19) Tellers, D. M.; Yung, C. M.; Arndtsen, B. A.; Adamson, D. R.; Bergman, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 1400.
(20) Ma, Y.; Bergman, R. G. Unpublished results.
(21) Doering, S.; Erker, G. *Synthesis* **2001**, 43.

Unfortunately, deposition of a black precipitate was observed when complexes **11** and **13** were used in attempted H/D exchange reactions. In both cases there was no observable H/D exchange under standard conditions.

Discussion

After observing the slow disproportionation of the H/D exchange catalyst Cp*(PMe_3)$IrCl_2$ over time at elevated temperatures, we hoped that a chelating cyclopentadienyl−phosphine complex would disproportionate more slowly, leading to longer catalyst lifetimes and higher substrate incorporation of deuterium. A redistribution mechanism involving phosphine (PMe_3) dissociation from the inner coordination sphere of an iridium center should be inhibited by the chelation strategy. However, a pathway that involved interaction of two intact Cp*(PMe_3)$IrCl_2$ molecules, through either electron transfer or a bridging ligand, might not be significantly perturbed by chelation and would instead lead to a similar type of decomposition with the formation of polymetallic species. Literature reports on related systems give varying guidance on this point. For example, a study of chloride ligand redistribution reactions of rhodium and iridium complexes described by Stang et al. gives spectroscopic evidence for a bimetallic intermediate which is responsible for the reactivity.[24] Another report of ligand redistribution within a heterobimetallic complex of ruthenium and osmium also suggests that bridging ligands such as halides promote the behavior.[25] In our system, ligand redistribution may occur via the intermediacy of the bridging complex [Cp*(PMe_3)Ir(μ-Cl)]$_2$($Cl)_2$. Formation of this complex requires chloride dissociation, and it was observed that addition of excess NaCl (10 equiv) inhibited the disproportionation reaction. Unfortunately, it also retards the catalytic H/D exchange. In this context it is interesting to note that the redistribution reaction does not occur in the less polar solvent CD_2Cl_2 under otherwise identical conditions and that there, too, H/D exchange is not observed. The lack of ^1H and ^{31}P NMR spectral resonances for thermally decomposed samples of the chelating complexes studied here is consistent with production of oligomeric and/or polymeric iridium materials in which there are many different types of phosphine environments that are formed in low abundance.

The electronic requirements of the metal center in C−H activation reactions are also relevant to the question of improving the catalytic H/D exchange reaction. It was recently found that electron-donating phosphorus ligands accelerate the stoichiometric C−H activation reactions of Cp*(L)IrMe(X) (L = PMe_3, $P(OMe)_3$; X = OTf, $(CH_2Cl_2)BAr_f$ (BAr_f = B(3,5-$C_6H_3(CF_3)_2)_4$)).[19] It is intriguing that this generalization, originally found for stoichiometric reactions in CH_2Cl_2, apparently holds for catalytic reactions in water.

Conclusion

The ligand redistribution reaction of dichloride complex **1** provided the impetus for developing routes to complexes of cyclopentadienyl ligands which bear a pendant phosphine. The one-pot synthetic procedure used to access chelating complexes **7**, **8**, **11**, and **12** uses readily available materials to generate these complexes. All previously reported syntheses of related chelating cyclopentadienyl−phosphine metal complexes are more involved.[9] These complexes should prove useful in examining reactivity modes of other metal complexes bearing cyclopentadienyl and phosphine ligands, which might benefit from the presence of a ligand bite angle different from that in their unchelated analogues.

Experimental Section

General Procedures. Unless otherwise noted, reactions and manipulations were performed at 25 °C in an inert-atmosphere (N_2) glovebox or using standard Schlenk and high-vacuum or -pressure techniques. Silica chromatography was carried out in air in all cases. Glassware was dried a minimum of 12 h at temperatures of 150 °C or greater. All NMR spectra were obtained using Bruker AMX 400 MHz, AMX 300 MHz, and DRX 500 MHz spectrometers. Infrared (IR) spectra were recorded on samples as KBr pellets using a Mattson Instruments Galaxy 3000 Fourier transform spectrometer. Mass spectrometric (MS) analyses were obtained at the University of California, Berkeley, mass spectrometry facility on Micromass VG Quattro (equipped with ESI source), VT ProSpec, ZAB2-Eq, and 70-FE mass spectrometers. Elemental analyses were performed at the University of California, Berkeley, microanalytical facility on a Perkin-Elmer 2400 Series II CHNO/S analyzer.

Materials. Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Celite (Aldrich) and alumina (Brockman I, Aldrich) were dried at 250 °C for 56 h. Pentane, hexanes, and benzene were passed through a column of activated alumina (A2, 12 × 32, Purifry Co.) collected under and sparged with N_2 prior to use. Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone ketyl under N_2 and sparged with N_2 prior to use. Dichloromethane (Fisher) was either distilled from CaH_2 (Aldrich) under N_2 or passed through a column of activated alumina and collected under and sparged with N_2 prior to use. Deuterated solvents (Cambridge isotope Laboratories) were purified using standard procedures[26] and vacuum-transferred prior to use. The starting materials Cp*(PMe_3)$IrCl_2$,[27] Cp*(PCy_3)$IrCl_2$,[28] $[Ir(COE)_2Cl]_2$,[18] $[Rh(COE)_2Cl]_2$,[18] Me_2PCH_2Li,[15] and 6,6-dimethylfulvene[16] were prepared according to literature procedures. Chlorodimethyl(2,3,4,5-tetramethyl-2,4-cyclopentadien-1-yl)silane was purchased from Aldrich.

H/D Exchange Experiments. Details regarding the performance and analysis of the H/D experiments are given in the Supporting Information to ref 8.

K(η^5:η^1-$Me_2PCH_2CMe_2C_5H_4$) (2). This reagent was prepared by following a procedure similar to that used by Mobley and Bergman for K[1-($Me_2PCH_2CMe_2$)-3-(*t*-Bu)C_5H_3].[17] A 100 mL Schlenk flask was charged with a magnetic stir bar, Me_2PCH_2Li (1.50 g, 18.3 mmol), 40 mL of Et_2O, and 20 mL of THF. To this stirred solution was added 6,6-dimethylfulvene (2.00 g, 18.9 mmol) in 10 mL of THF at room temperature. The

(22) Shriver, D. F.; Atkins, P.; Langford, C. H. *Inorganic Chemistry*, 2nd ed.; Freeman: New York, 1994.
(23) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 2nd ed.; Wiley-Interscience: New York, 1994.
(24) Stang, P. J.; Huang, Y.-H. *J. Organomet. Chem.* **1992**, *435*, 185.
(25) Fleming, M. M.; Pomeroy, R. K.; Rushman, P. *J. Organomet. Chem.* **1984**, *273*, C33.
(26) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: New York, 1988.
(27) Isobe, K.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2003.
(28) Freedman, D. A.; Mann, K. R. *Inorg. Chem.* **1991**, *30*, 836.

reaction mixture was stirred for 5 min, and the solvent was then removed in vacuo to yield a foam which was dissolved in 100 mL of THF. This solution was added to a 250 mL Schlenk flask. To the resulting mixture was added NH_4Cl (1.01 g, 18.9 mmol) and a magnetic stir bar, and the mixture was stirred for 15 h at room temperature. The solution was then concentrated to 50 mL and stirred for an additional 30 min. The solvent was removed in vacuo, and the resulting brown oily solid was extracted with 4 × 50 mL pentane using cannula filtration.

The pentane extract was concentrated in vacuo to give an orange oil, which was then dissolved in 150 mL of Et_2O, added to a 250 mL Schlenk flask along with a magnetic stir bar, and cooled to 0 °C using an ice bath. To this vigorously stirred solution was added 4.0 mL of an ethereal solution of HCl (1.0 M) over the course of 5 min. After the mixture was stirred for an additional 15 min, the solvent was removed in vacuo to afford an oily wax. This wax was washed with 2 × 50 mL of pentane and then suspended in an additional 75 mL of pentane. This solution was magnetically stirred, and NEt_3 (0.75 mL, 55 mmol) was added to it by syringe. The mixture was stirred for 14 h, and the supernatant was then transferred using cannula filtration. The ammonium salts were washed with 50 mL of pentane, and these washings were combined with the supernatant.

The filtrate was concentrated in vacuo to afford 255 mg of an orange oil. This oil was dissolved in 10 mL of pentane and added to a 20 mL vial, along with a magnetic stir bar. To the stirred solution was added solid KH (141 mg, 3.52 mmol), and the solution was stirred for 36 h. The resulting suspension was then filtered through a fritted-glass funnel (medium porosity), and the solids were washed with 100 mL of Et_2O. The solvent was removed in vacuo to afford the product as a sticky, light yellow foam. Trituration with pentane, followed by drying in vacuo, afforded a foam which could be converted to a powder by grinding with a metal spatula. The yield of K(η^5:η^1-$Me_2PCH_2CMe_2C_5H_4$) was 311 mg (5% from the starting fulvene). ^{1}H NMR (500 MHz): δ 5.43 (s, 4H, $Me_2PCH_2CMe_2C_5H_4$), 1.72 (s, 2H, $Me_2PCH_2CMe_2C_5H_4$), 1.21 (s, 6H, $Me_2PCH_2CMe_2C_5H_4$), 0.86 (d, J_{P-H} = 3 Hz, 6H, $Me_2PCH_2CMe_2C_5H_4$). ^{13}C{^{1}H} NMR (126 MHz): δ 131.3 (d, J_{P-C} = 4 Hz, $Me_2PCH_2CMe_2C_5H_4$), 103.8 (s, $Me_2PCH_2CMe_2C_5H_4$, 101.5 (s, $Me_2PCH_2CMe_2C_5H_4$), 51.7 (d, J_{P-C} = 9 Hz, $Me_2PCH_2CMe_2C_5H_4$), 36.2 (d, J_{P-C} = 13 Hz, $Me_2PCH_2CMe_2C_5H_4$), 33.4 (d, J_{P-C} = 7 Hz, $Me_2PCH_2CMe_2C_5H_4$), 16.4 (d, J_{P-C} = 11 Hz, $Me_2PCH_2CMe_2C_5H_4$). ^{31}P{^{1}H} NMR (162 MHz): δ −58.0. IR: 3056, 2950, 2894, 1657, 1603, 1459, 1423, 1373, 1355, 1291, 1243, 1170, 1031, 940, 907, 782, 711 cm^{-1}. A satisfactory elemental analysis for this potassium salt could not be obtained.

(η^5:η^1-$Me_2PCH_2CMe_2C_5H_4$)IrI_2 (3). A 100 mL Schlenk flask was charged with $[Ir(COE)_2Cl]_2$ (135 mg, 0.154 mmol), 15 mL of THF, and a magnetic stir bar. To this stirred suspension was added a solution of K(η^5:η^1-$Me_2PCH_2CMe_2C_5H_4$) (67.8 mg, 0.308 mmol) in 5 mL of THF over the course of 30 s. The resulting mixture was stirred for 30 min, and then the solvent was removed in vacuo. To the residue was added 20 mL of CH_2Cl_2 on a Schlenk line, and the flask was cooled to 0 °C. A solution of I_2 (78.1 mg, 0.308 mmol) in 10 mL of CH_2Cl_2 was also cooled to 0 °C and then added by cannula transfer, over the course of 10 min. The resulting 30 mL of dark red-brown solution was stirred for 15 min and then was poured onto a SiO_2 column (3 cm × 15 cm) that had been saturated with pentane. The unreacted I_2 was removed by elution with pentane, and then the eluent was changed to 4:1 Et_2O/CH_2Cl_2. An orange band was eluted and the resulting solution concentrated using a rotary evaporator. The remaining solvent was removed from the orange residue in vacuo, leaving a red residue which was recrystallized at −35 °C from a CH_2Cl_2 solution layered with pentane. This procedure afforded analytically pure red crystals of **3** in 21% yield (40.1 mg, 0.0639 mmol). ^{1}H NMR (500 MHz): δ 5.83 (s, 2H, C_5H_4), 5.53 (s, 2H, C_5H_4), 3.07 (d, J_{P-H} = 10 Hz, 2H, CH_2CMe_2), 2.07 (d, J_{P-H} = 12 Hz, 6H, $Me_2PCH_2CMe_2$), 1.43 (s, 6H, $Me_2PCH_2CMe_2$). ^{13}C{^{1}H} NMR (126 MHz): δ 118.4 (s, C_5H_4), 92.2 (d, J_{P-C} = 9 Hz, C_5H_4), 73.7 (s, C_5H_4), 64.4 (d, J_{P-C} = 36 Hz, $Me_2PCH_2CMe_2$), 36.3 (s, $Me_2PCH_2CMe_2$), 27.6 (d, J_{P-C} = 10 Hz, $Me_2PCH_2CMe_2$), 21.3 (d, J_{P-C} = 39 Hz, $Me_2PCH_2CMe_2$). ^{31}P{^{1}H} NMR (162 MHz): δ −17.3. IR: 3066, 2963, 1443, 1372, 1283, 1092, 953, 922, 901, 813, 732, 690 cm^{-1}. Anal. Calcd for $C_{11}H_{18}PIrI_2$: C, 21.06; H, 2.89. Found: C, 21.19; H, 2.84.

(η^5:η^1-$Me_2PCH_2CMe_2C_5H_4$)$Ir(OSO_2CF_3)_2$ (4). A 20 mL scintillation vial was charged with (η^5:η^1-$Me_2PCH_2CMe_2C_5H_4$)-IrI_2 (**3**; 120 mg, 0.191 mmol), a magnetic stir bar, and 10 mL of CH_2Cl_2. With stirring, the AgOTf (246 mg, 0.955 mmol) was added in portions over the course of 30 s. After all the AgOTf was added, the vial was protected from ambient light by wrapping it in aluminum foil. The reaction mixture was stirred magnetically for 18 h at room temperature. The mixture was then filitered through a fritted-glass funnel (medium porosity), and the solids were washed with 3 mL of CH_2Cl_2. The filtrate was concentrated in vacuo, the solid residue was redissolved in 2 mL of CH_2Cl_2, and the solution filtered through a Fiberglas plug into a 20 mL vial and then layered with 10 mL of pentane. The vial was capped and the solution stored at −35 °C for 24 h. The yellow crystals that formed were isolated by removing the supernatant with a pipet, and the remaining solvent was removed from the solid in vacuo. The yield of pure **4** was 67.5 mg (0.101 mmol, 53%). ^{1}H NMR (500 MHz): δ 6.40 (s, 2H, C_5H_4), 5.99 (s, 2H, C_5H_4), 3.02 (d, J_{P-H} = 11 Hz, 2H, CH_2CMe_2), 1.83 (d, J_{P-H} = 13 Hz, 6H, $Me_2PCH_2CMe_2$), 1.48 (s, 6H, $Me_2PCH_2CMe_2$). ^{13}C{^{1}H} NMR (126 MHz): δ 115.5 (d, J_{P-C} = 6 Hz, C_5H_4), 98.1 (d, J_{P-C} = 7 Hz, C_5H_4), 61.4 (s, C_5H_4), 58.0 (d, J_{P-C} = 36 Hz, $Me_2PCH_2CMe_2$), 37.3 (s, $Me_2PCH_2CMe_2$), 27.5 (d, J_{P-C} = 10 Hz, $Me_2PCH_2CMe_2$), 13.5 (d, J_{P-C} = 34 Hz, $Me_2PCH_2CMe_2$), CF_3 group not detectable. ^{31}P{^{1}H} NMR (162 MHz): δ 27.1. ^{19}F NMR (376.5 MHz): −77.0. IR: 1327, 1237, 1181, 1022, 959, 927, 843, 636, 516 cm^{-1}. Anal. Calcd for $C_{13}H_{18}PIrO_6S_2F_6$: C, 23.25; H, 2.70. Found: C, 23.28; H, 2.56.

(η^5:η^1-$Me_2PCH_2SiMe_2C_5Me_4$)IrI_2 (7). A 20 mL scintillation vial was charged with chlorodimethyl(2,3,4,5-tetramethyl-2,4-cyclopentadien-1-yl)silane (192 mg, 0.893 mmol), tetrahydrofuran (7 mL), and a magnetic stir bar. To this stirred solution was added Me_2PCH_2Li (146 mg, 1.79 mmol) in portions over the course of 1 min. The solution was exposed to vacuum over the course of 1 h, during which time free PMe_3 was removed and the solvent volume was reduced to 2 mL. To this solution was then added 4 mL of a THF slurry of $[Ir(COE)_2Cl]_2$ (400 mg, 0.893 mmol) dropwise, and the resulting slurry adopted a brown-orange color. This mixture was stirred for 10 min, and then solid iodine (227 mg, 0.893 mmol) was added to the vial. The mixture darkened slightly during this addition, and it was stirred for 30 min. The vial was taken from the glovebox, and the solution was pipetted onto a silica column (15 cm × 3 cm) that had been saturated with pentane. Pentane was used as the eluent, and all solvent collected prior to the collection of the orange band was discarded (this includes any unreacted iodine). The eluent was then changed to 3:1 Et_2O/CH_2Cl_2, and the orange band was collected. The solvent was removed in vacuo to give an orange-red solid which was recrystallized at −35 °C from CH_2Cl_2/pentane to give **7** as an analytically pure red crystalline compound (295 mg, 0.422 mmol, 47%). ^{1}H NMR (500 MHz): δ 2.25 (d, J_{P-H} = 14 Hz, 2H, $Me_2PCH_2SiMe_2$), 2.10 (m, 12H, overlapping $Me_2P-CH_2SiMe_2$ and C_5Me_4), 2.01 (s, 6H, C_5Me_4), 0.53 (s, 6H, $Me_2CH_2SiMe_2$). ^{13}C{^{1}H} NMR (126 MHz): δ 108.9 (d, J_{P-C} = 9 Hz, C_5Me_4), 89.2 (s, C_5Me_4), 87.6 (s, C_5Me_4), 36.1 (d, J_{P-C} = 24 Hz, $Me_2PCH_2SiMe_2$), 23.4 (d, J_{P-C} = 40 Hz, $Me_2PCH_2SiMe_2$), 13.4 (s, C_5Me_4), 11.4 (d, J_{P-C} = 3 Hz, C_5Me_4), 0.35 (d, J_{P-C} = 6 Hz, $Me_2PCH_2SiMe_2$). ^{31}P{^{1}H} NMR (162 MHz): δ −28.5. ^{29}Si NMR (INEPT, 99 MHz): 0.95. IR: 2950, 2915, 2853, 1445, 1378, 1092, 1029, 913, 838, 778 cm^{-1}. Anal. Calcd for $C_{14}H_{26}SiPIrI_2$: C, 24.04; H, 3.75. Found: C, 24.12; H, 3.53.

(η^5:η^1-$Me_2PCH_2SiMe_2C_5Me_4$)$Ir(OSO_2CF_3)_2$ (8). A 20 mL scinitillation vial was charged with diiodoiridium complex **7** (126 mg, 0.180 mmol), 10 mL of CH_2Cl_2, and a magnetic stir bar. To this stirred solution was added AgOTf (232 mg, 0.901 mmol) in portions over 30 s. The reaction mixture was protected from ambient light with aluminum foil and stirred for 18 h. The dark brown reaction mixture was then filtered through a fritted-glass funnel (medium porosity), and the solids were washed with 3 mL of CH_2Cl_2. The filtrate was concentrated in vacuo, the brown residue dissolved in 4 mL of CH_2Cl_2, and the solution filtered through a Fiberglas plug. The resulting solution was layered with 15 mL of pentane and stored at −35 °C for 24 h, affording dark crystals. The supernatant was decanted, the crystals were washed with 3 mL of pentane, and the remaining solvent was removed from the solid in vacuo. This yielded 115 mg (0.155 mmol, 86%) of analytically pure **8**. ^{1}H NMR (500 MHz): δ 2.19 (d, J_{P-H} = 15 Hz, 2H, $Me_2PCH_2SiMe_2$), 1.93 (d, J_{P-H} = 4 Hz, 6H, C_5Me_4), 1.78 (d, J_{P-H} = 12 Hz, 6H, $Me_2PCH_2SiMe_2$), 1.61 (s, 6H, C_5Me_4), 0.60 (s, 6H, $Me_2PCH_2SiMe_2$). ^{13}C{^{1}H} NMR (126 MHz): δ 116.5 (d, J_{P-C} = 8 Hz, C_5Me_4), 85.3 (s, C_5Me_4), 80.13 (s, C_5Me_4), 29.8 (d, J_{P-C} = 25 Hz, $Me_2PCH_2SiMe_2$), 15.8 (d, J_{P-C} = 33 Hz, $Me_2PCH_2SiMe_2$), 13.3 (s, C_5Me_4), 10.4 (s, C_5Me_4), 0.0 (d, J_{P-C} = 33 Hz, $Me_2PCH_2SiMe_2$). ^{31}P{^{1}H} NMR (162 MHz): δ 7.2. ^{29}Si NMR (INEPT, 99 MHz): δ 5.2. IR: 3091, 2976, 2922, 1629, 1265, 1170, 1032, 962, 926, 639, 577, 518 cm^{-1}. Anal. Calcd for $C_{16}H_{26}SiPIrO_6S_2F_6$: C, 25.84; H, 3.52. Found: C, 25.69; H, 3.31.

(η^5:η^1-$Me_2PCH_2SiMe_2C_5Me_4$)$IrBr_2$ (9). A procedure identical with that described for **7** was utilized, up to the step where iodine is added, with the exception that the reagent quantities were as follows: chlorodimethyl(2,3,4,5-tetramethyl-2,4-cyclopentadien-1-yl)silane (95.9 mg, 0.446 mmol), Me_2PCH_2Li (73.2 mg, 0.892 mmol), $[Ir(COE)_2Cl]_2$ (200 mg, 0.223 mmol). The resulting mixture was stirred for 10 min, and then elemental bromine (22.9 μL, 0.446 mmol) was added to the vial by syringe. The mixture darkened slightly during this addition, and the mixture was stirred for 30 min. The vial was taken from the glovebox, and purification of the product was carried out using column chromatography and recrystallization conditions as described for **7**. This led to the isolation of **9** as analytically pure black crystals (84.9 mg, 0.138 mmol, 31%). ^{1}H NMR (500 MHz): δ 2.18 (d, J_{P-H} = 14 Hz, 2H, $Me_2PCH_2SiMe_2$), 1.87 (m, 18H, overlapping $Me_2PCH_2SiMe_2$ and C_5Me_4), 0.55 (s, 6H, $Me_2PCH_2SiMe_2$). ^{13}C{^{1}H} NMR (126 MHz): δ 110.2 (d, J_{P-C} = 10 Hz, C_5Me_4), 86.9 (d, J_{P-C} = 5 Hz, C_5Me_4), 85.0 (d, J_{P-C} = 3 Hz, C_5Me_4), 34.7 (d, J_{P-C} = 24 Hz, $Me_2PCH_2SiMe_2$), 18.5 (d, J_{P-C} = 38 Hz, $Me_2PCH_2SiMe_2$), 12.5 (s, C_5Me_4), 9.7 (d, J_{P-C} = 3 Hz, C_5Me_4), 0.20 (d, J_{P-C} = 6 Hz, $Me_2PCH_2SiMe_2$). ^{31}P{^{1}H} NMR (162 MHz): δ −18.5. ^{29}Si NMR (INEPT, 99 MHz): δ 2.4. IR: 2981, 2924, 1403, 1256, 1079, 1024, 951, 919, 848, 822, 784, 749 cm^{-1}. Anal. Calcd for $C_{14}H_{26}SiPIrBr_2$: C, 27.77; H, 4.33. Found: C, 28.09; H, 4.03.

[(η^5:η^1-$Me_2PCH_2SiMe_2C_5Me_4$)$Ir(OH_2)_2$](SO_4) (10). In the air, a 20 mL scintillation vial was charged with the diiodoiridium complex **7** (131 mg, 0.188 mmol), 10 mL of H_2O, and a magnetic stir bar. To this stirred solution was added Ag_2SO_4 (130 mg, 0.417 mmol) in portions over the course of 30 s. The reaction mixture was protected from ambient light using aluminum foil, stirred for 4 h, and then filtered through a fritted glass funnel (medium porosity). The filtrate was concentrated in vacuo, and the orange-yellow residue was extracted with 2 mL of acetone and filtered through a Fiberglas plug. The filtrate was concentrated in vacuo to leave a spectroscopically pure yellow foam (94.0 mg, 0.163 mmol, 87%). ^{1}H NMR (500 MHz, D_2O): δ 2.31 (d, J_{P-H} = 15 Hz, 2 H, $Me_2PCH_2SiMe_2$), 1.73 (d, J_{P-H} = 3 Hz, 6 H, C_5Me_4), 1.61 (d, J_{P-H} = 12 Hz, 6 H, $Me_2PCH_2SiMe_2$), 1.58 (s, 6 H, C_5Me_4), 0.49 (s, 6H, $Me_2PCH_2SiMe_2$). ^{13}C{^{1}H} NMR (126 MHz, D_2O): δ 112.4 (d, J_{P-C} = 8 Hz, C_5Me_4), 86.1 (s, C_5Me_4), 81.3 (s, C_5Me_4), 27.7 (d, J_{P-C} = 28 Hz, $Me_2PCH_2SiMe_2$), 13.5 (d, J_{P-C} = 34 Hz, $Me_2PCH_2SiMe_2$), 11.3 (s, C_5Me_4), 8.2 (s, C_5Me_4), −1.8 (s, $Me_2PCH_2SiMe_2$). ^{31}P{^{1}H} NMR (162 MHz, D_2O): δ 2.0. ^{29}Si NMR (INEPT, 99 MHz, D_2O): δ 5.3. IR: 3433, 2975, 2913, 2818, 1512, 1400, 1255, 1143, 1028, 919, 849, 642, 620 cm^{-1}. Although this complex could be crystallized at −35 °C from CH_3OH/Et_2O, analytically pure material and satisfactory MS data (electrospray) could not be obtained.

(η^5:η^1-$Me_2PCH_2SiMe_2C_5Me_4$)RhI_2 (11). A procedure identical with that described for **7** was performed, with the exception that the reagent quantities were as follows: chlorodimethyl(2,3,4,5-tetramethyl-2,4-cyclopentadien-1-yl)silane (120 mg, 0.558 mmol), Me_2PCH_2Li (91.4 mg, 1.12 mmol), $[Rh(COE)_2Cl]_2$ (200 mg, 0.279 mmol), and iodine (142 mg, 0.558 mmol). Purification of the product was carried out using column chromatography and recrystallization conditions as described for **7**. This led to the isolation of **11** as analytically pure brown-black crystals (110 mg, 0.180 mmol, 32%). ^{1}H NMR (500 MHz): δ 2.20 (m, 8H, $Me_2PCH_2SiMe_2$ and C_5Me_4), 2.03 (d, J_{P-H} = 11 Hz, 6H, $Me_2PCH_2SiMe_2$), 2.01 (s, 6H, C_5Me_4), 0.54 (s, 6H, $Me_2PCH_2SiMe_2$). ^{13}C{^{1}H} NMR (126 MHz): δ 112.6 (dd, J_{P-C} = 3 Hz, J_{Rh-C} = 8 Hz, C_5Me_4), 97.5 (s, C_5Me_4), 97.2 (dd, J_{P-C} = 4 Hz, J_{Rh-C} = 5 Hz, C_5Me_4), 35.9 (d, J_{P-C} = 15 Hz, $Me_2PCH_2SiMe_2$), 25.3 (d, J_{P-C} = 34 Hz, $Me_2PCH_2SiMe_2$), 14.2 (s, C_5Me_4), 11.8 (d, J_{P-C} = 3 Hz, C_5Me_4), 0.91 (d, J_{P-C} = 6 Hz, $Me_2PCH_2SiMe_2$). ^{31}P{^{1}H} NMR (162 MHz): δ 13.1 (d, J_{Rh-P} = 137 Hz). ^{29}Si NMR (INEPT, 99 MHz): δ −0.6. IR: 2967, 2906, 1402, 1255, 1080, 1022, 948, 913, 842, 817, 780, 739 cm^{-1}. Anal. Calcd for $C_{14}H_{26}SiPRhI_2$: C, 27.56; H, 4.30. Found: C, 27.24; H, 4.07.

(η^5:η^1-$Me_2PCH_2SiMe_2C_5Me_4$)$RhBr_2$ (12). A procedure identical with that described for **7** was utilized up to the step where iodine is added, with the exception that the reagent quantities were as follows: chlorodimethyl(2,3,4,5-tetramethyl-2,4-cyclopentadien-1-yl)silane (120 mg, 0.558 mmol), Me_2PCH_2Li (91.4 mg, 1.11 mmol), and $[Rh(COE)_2Cl]_2$ (200 mg, 0.279 mmol). The resulting mixture was stirred for 10 min, and then elemental bromine (28.6 μL, 0.558 mmol) was added to the vial by syringe. The mixture darkened slightly during this addition, and it was stirred for 30 min. The vial was taken from the glovebox, and purification of the product was carried out using column chromatography and recrystallization conditions as described for **7**. This led to the isolation of **12** as analytically pure black crystals (50.1 mg, 0.0971 mmol, 17%). ^{1}H NMR (500 MHz): δ 2.17 (d, J_{P-H} = 15 Hz, $Me_2PCH_2SiMe_2$), 1.91 (d, J_{P-H} = 5 Hz, 6 H, C_5Me_4), 1.82 (d, J_{P-H} = 13 Hz, 6 H, $Me_2PCH_2SiMe_2$), 1.79 (s, 6H, C_5Me_4), 0.54 (s, 6 H, $Me_2PCH_2SiMe_2$). ^{13}C{^{1}H} NMR (126 MHz): δ 114.2 (dd, J_{P-C} = 3 Hz, J_{P-C} = 10 Hz, C_5Me_4), 95.7 (d, J_{P-C} = 8 Hz, C_5Me_4), 94.6 (dd, J_{P-C} = 3 Hz, J_{P-C} = 9 Hz, C_5Me_4), 34.4 (d, J_{P-C} = 15 Hz, $Me_2PCH_2SiMe_2$), 20.5 (d, J_{P-C} = 33 Hz, $Me_2PCH_2SiMe_2$), 12.95 (s, C_5Me_4), 10.2 (d, J_{P-C} = 3 Hz, C_5Me_4), 0.70 (d, J_{P-C} = 6 Hz, $Me_2PCH_2SiMe_2$). ^{31}P{^{1}H} NMR (162 MHz): δ 19.6 (d, J_{Rh-P} = 137 Hz). ^{29}Si NMR (INEPT, 99 MHz): δ 0.6. IR: 2968, 2920, 1515, 1401, 1330, 1256, 1078, 1022, 952, 917, 847, 821, 784, 748, 618 cm^{-1}. Anal. Calcd for $C_{14}H_{26}SiPRhBr_2$: C, 32.58; H, 5.08. Found: C, 32.58; H, 4.99.

(η^5:η^1-$Me_2PCH_2SiMe_2C_5Me_4$)$Rh(OSO_2CF_3)_2$ (13). A 20 mL scinitillation vial was charged with diiodorhodium complex **11** (87.7 mg, 0.144 mmol), 10 mL of CH_2Cl_2, and a magnetic stir bar. To this stirred solution was added AgOTf (185 mg, 0.712 mmol) in portions over 30 s. The reaction mixture was protected from ambient light with aluminum foil and stirred for 18 h. The dark brown reaction mixture was then filtered through a fritted-glass funnel (medium porosity), and the solids were washed with 3 mL of CH_2Cl_2. The filtrate was dried in vacuo, the brown residue was dissolved in 4 mL of CH_2Cl_2, and the solution filtered through a Fiberglas plug. The resulting solution was layered with 15 mL of pentane and stored at −35 °C for 24 h. The supernatant was decanted, and the red-orange crystals were washed with 3 mL of pentane and then dried in vacuo. Two such recrystallizations were

necessary to obtain analytically pure material, yielding 41.8 mg (0.0639 mmol, 44%) after purification. ^{1}H NMR (500 MHz): δ 2.25 (d, J_{P-H} = 16 Hz, 2H, $Me_2PCH_2SiMe_2$), 1.90 (d, J_{P-H} = 5 Hz, 6H, C_5Me_4), 1.73 (d, J_{P-H} = 13 Hz, 6H, $Me_2PCH_2SiMe_2$), 1.58 (d, J_{P-H} = 2 Hz, 6H, C_5Me_4), 0.63 (d, J_{P-H} = 2 Hz, 6H, $Me_2PCH_2SiMe_2$). ^{13}C{^{1}H} NMR (126 MHz): δ 120.5 (dd, J_{P-C} = 4 Hz, J_{Rh-C} = 5 Hz, C_5Me_4), 94.0 (m, C_5Me_4), 91.8 (d, J_{Rh-C} = 13 Hz, C_5Me_4), 30.1 (d, J_{P-C} = 18 Hz, $Me_2PCH_2SiMe_2$), 17.0 (d, J_{P-C} = 26 Hz, $Me_2PCH_2SiMe_2$), 15.2 (s, C_5Me_4), 13.2 (s, C_5Me_4), 10.4 (d, J_{P-C} = 3 Hz, $Me_2PCH_2SiMe_2$), CF_3 group not detectable. ^{31}P{^{1}H} NMR (162 MHz): δ 31.0 (d, J_{Rh-P} = 139 Hz). ^{29}Si NMR (INEPT, 99 MHz): δ 4.2. IR: 2989, 2932, 1528, 1291, 1230, 1171, 1028, 919, 845, 637, 517 cm^{-1}. Anal. Calcd for $C_{16}H_{26}SiPRhO_6S_2F_6$: C, 29.36; H, 4.73. Found: C, 28.98; H, 3.86.

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