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#### Abstract

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## ACS Publications

## Supporting Information

# Thermal and Photochemical Reactions of <br> a Cationic Rhenocene-Acetonitrile Adduct: <br> The First C-H Bond Activation by Rhenocene Cation 

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## Experimental Section

General. All manipulations were performed under an inert atmosphere or under a high vacuum. Rhenocene dihydride $\left[\mathrm{Cp}_{2} \operatorname{Re}(\mathrm{H})_{2}\right](\mathrm{BF} 4)$ was prepared by applying the preparative methods of $\left[\mathrm{Cp}_{2} \mathrm{Re}(\mathrm{H})_{2}\right] \mathrm{Cl}^{1 \mathrm{~b}}$ and $\left[\mathrm{Cp}_{2} \operatorname{Re}(\mathrm{H})_{2}\right]\left(\mathrm{PF}_{6}\right) .{ }^{1 \mathrm{k}}$ Other reagents were used without further purification. Acetonitrile was distilled from $\mathrm{P}_{2} \mathrm{O}_{5}$ twice, then fractionally distilled from $\mathrm{CaH}_{2}$. Diethylether and toluene were distilled from Na-benzophenone ketyl. Dichloromethane was distilled from $\mathrm{CaH}_{2}$. Acetone was distilled from anhydrous $\mathrm{CaSO}_{4}$ (Drierite) and vacuum transferred onto activated $4 \AA$ molecular sieves. Benzene was distilled from Na-benzophenone ketyl and vacuum transferred into a glass tube containing $K$ mirror. Acetone- $d_{6}$ was dried over Drierite and vacuum transferred onto activated $4 \AA$ molecular sieves. Acetonitrile- $d 3$ was dried over $\mathrm{CaH}_{2}$ and vacuum transferred onto activated $4 \AA$ molecular sieves.

Photolysis was performed with an Ushio UM-452 450 W medium pressure Hg lamp placed in a water-cooled, quartz jacket. Sample solutions were irradiated through a Pyrex sleeve.

Synthesis of [Cp2Re(NCMe)](BF4) (2). A Pyrex glass tube ( 15 mm o.d. x 30 $\mathrm{cm})$ was charged with an MeCN solution ( 25 mL ) of $[\mathrm{Cp} 2 \operatorname{Re}(\mathrm{H}) 2](\mathrm{BF} 4)(\mathbf{1})(255 \mathrm{mg}, 0.630$ $\mathrm{mmol})$. The solution was photo-irradiated with a medium pressure mercury lamp for 24 h at 3 ${ }^{\circ} \mathrm{C}$ with stirring. During the reaction, a gas evolution was observed and the colorless solution gradually changed to orange-red. The resulting solution was transferred to a Schrenk tube (50 mL ) and the solvent was removed in vacuo to afford the red solid, which was washed with $\mathrm{Et}_{2} \mathrm{O}(5 \mathrm{~mL} \times 2)$ to yield $\left[\mathrm{Cp}_{2} \operatorname{Re}(\mathrm{NCMe})\right]\left(\mathrm{BF}_{4}\right)(2)(261 \mathrm{mg}, 0.588 \mathrm{mmol}, 93.3 \%)$.

Recrystallization by diffusion of $\mathrm{Et}_{2} \mathrm{O}$ vapor into an MeCN solution of $\mathbf{2}$ in a desiccator gave red needles. ${ }^{1} \mathrm{H}$ NMR ( 300 MHz , acetone-d6): $\delta 2.67$ (s, $3 \mathrm{H}, \mathrm{MeCN}$ ), $5.00(\mathrm{~s}, 10 \mathrm{H}, \mathrm{Cp}$ ). ${ }^{13} \mathrm{C}$ NMR ( 75.5 MHz , acetone-d6): $\delta 5.2(\mathrm{MeCN}), 78.3(\mathrm{Cp}), 129.1(\mathrm{MeCN})$. IR ( KBr , $\mathrm{cm}^{-1}$ ): 3398 (m), 3114 (m), 3052 (m), 1427 (m), 1400 (m), 1353 (w), 1288 (w), 1076 (vs), 987 (vs), 910 (vs), 835 (m), 534 (m), 520 (m), 420 (w). Mass (FAB, m-nitrobenzyl alcohol matrix, Xe): $m / z 358\left(\mathrm{M}^{+}, 85.7\right), 317\left(\mathrm{M}^{+}-\mathrm{MeCN}, 100\right)$. Anal. Calcd for $\mathrm{C}_{12} \mathrm{H}_{13}$ NBF4Re: C, 32.44; H, 2.95; N, 3.15. Found: C, 32.13; H, 3.29; N, 3.13.

Reaction of 2 with PPh3. To a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution ( 5 mL ) of 2 ( $22 \mathrm{mg}, 49 \mathrm{mmol}$ ) was added PPh 3 ( $50 \mathrm{mg}, 0.19 \mathrm{mmol}$ ) and the mixture was stirred for 1 week at room temperature. After the volatiles were removed, the residue was washed with $\mathrm{Et} 2 \mathrm{O}(10 \mathrm{~mL} \times 3)$ to remove the excess PPh 3 to afford $\left[\mathrm{Cp}_{2} \operatorname{Re}(\mathrm{PPh} 3)\right]\left(\mathrm{BF}_{4}\right)(3)(28 \mathrm{mg}, 43 \mathrm{mmol}, 88 \%)$. Complex 3 was characterized by ${ }^{1} \mathrm{H}$ NMR and mass spectra by comparison with the literature values. 1 k

Reaction of 2 with $\boldsymbol{t}_{\mathbf{B u N C}}$. To a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution ( 5 mL ) of $2(62 \mathrm{mg}, 0.14 \mathrm{mmol}$ ) was added t BuNC $(100 \mu \mathrm{l}, 0.88 \mathrm{mmol})$ and the mixture was stirred for 1 week at room temperature. After the volatiles were removed, the residue was washed with $\mathrm{Et} 2 \mathrm{O}(10 \mathrm{~mL} \times 3)$ to afford crude $\left[\mathrm{Cp}_{2} \operatorname{Re}\left(\mathrm{CN}^{t} \mathrm{Bu}\right)\right](\mathrm{BF} 4)(4)(48 \mathrm{mg}, 0.10 \mathrm{mmol}, 71 \%)$. The crude product was recrystallized by layering toluene over the $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution of 4 to give yellow needles. ${ }^{1} \mathrm{H}$ NMR ( 300 MHz , acetone- $\mathrm{d}_{6}$ ): $\delta 1.54$ (s, 9H, ${ }^{\mathrm{t}} \mathrm{BuNC}$ ), 5.26 ( $\mathrm{s}, 10 \mathrm{H}, \mathrm{Cp}$ ). ${ }^{13} \mathrm{C}$ NMR ( 75.5 MHz , acetone- $d_{6}$ ): $\delta 30.0(\mathrm{Me} 3 \mathrm{CNC}), 76.4(\mathrm{Cp})$. Other signals could not be located. IR (KBr, cm-1): 3128 (w), 3106 (w), 2987 (w), 2154 (w), 1486 (w), 1477 (w), 1465 (w), 1457 (w), 1432 (w), 1400 (w), 1373 (w), 1238 (w), 1195 (m), 1078 (s), 1049 (s), 1037 (s), 985 (m), 937 (w), 844 (w), 538 (w), 520 (w), 464 (w), 408 (w). Mass (FAB, m-nitrobenzyl alcohol matrix, Xe): $m / z 400\left(\mathrm{M}^{+}, 49.1\right), 344\left(\mathrm{M}^{+}{ }^{-} \mathrm{Bu}+1,40.2\right)$. Anal. Calcd for $\mathrm{C}_{15} \mathrm{H}_{19} \mathrm{NBF} 4 \mathrm{Re}: \mathrm{C}, 37.05 ; \mathrm{H}, 3.94 ; \mathrm{N}, 3.24$. Found: C, 37.36; H, 4.00; N, 3.24.

Reaction of 2 with $\mathbf{P h C} \equiv \mathbf{C H}$. To an acetone solution ( 5 mL ) of $2(48 \mathrm{mg}, 0.11 \mathrm{mmol}$ ) was added $\mathrm{PhC} \equiv \mathrm{CH}(300 \mathrm{mg}, 2.94 \mathrm{mmol})$ and the mixture was stirred for 2 weeks at room temperature. After removal of volatiles, the residue was washed with $\mathrm{Et}_{2} \mathrm{O}(10 \mathrm{~mL} x 3)$ to afford crude $\left[\mathrm{Cp}_{2} \operatorname{Re}\left(\eta^{2}-\mathrm{PhC} \equiv \mathrm{CH}\right)\right]\left(\mathrm{BF}_{4}\right)(5)(43 \mathrm{mg}, 85 \mathrm{mmol}, 79 \%)$. The crude product
was recrystallized by layering toluene over the $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution of 5 . ${ }^{1} \mathrm{H} \mathrm{NMR}(300 \mathrm{MHz}$, acetone-d 6 ): $\delta 5.64(\mathrm{~s}, 10 \mathrm{H}, \mathrm{Cp}), 6.93(\mathrm{~s}, 1 \mathrm{H}, \mathrm{HC} \equiv \mathrm{CPh}), 7.41-7.52(\mathrm{~m}, 3 \mathrm{H}, \mathrm{HC} \equiv \mathrm{CPh})$, $7.71-7.74(\mathrm{~m}, 2 \mathrm{H}, \mathrm{HC} \equiv \mathrm{CPh}) .{ }^{13} \mathrm{C}$ NMR (75.5 MHz, acetone-d6): $\delta 87.7(\mathrm{Cp}), 129.6(\mathrm{Ph})$, $130.3(\mathrm{Ph}), 133.5(\mathrm{Ph})$. Other signals could not be located. IR (KBr, cm ${ }^{-1}$ ): $3145(\mathrm{~m}), 3126$ (m), 3076 (w), 3050 (w), 1760 (w, $\mathrm{n}_{\mathrm{C} / \mathrm{C}}$ ), 1446 (w), 1434 (m), 1407 (m), 1168 (w), 1120 (s), 1081 ( s$), 1056$ ( s$), 1010$ ( s$), 991$ ( s$), 902$ (m), 854 (m), 767 (m), 729 (m), $694(\mathrm{~m}), 630$ (w), 521 (w). Mass (FAB, m-nitrobenzyl alcohol matrix, Xe): m/z $419\left(\mathrm{M}^{+}, 100\right), 317\left(\mathrm{M}^{+}\right.$ - $\mathrm{PhC} \equiv \mathrm{CH}, 50.6$ ). Anal. Calcd for $\mathrm{C}_{18} \mathrm{H}_{16} \mathrm{BF}_{4} \mathrm{Re}: \mathrm{C}, 42.78$; H, 3.19. Found: $\mathrm{C}, 42.78 ; \mathrm{H}$, 3.26.

Photolysis of 2 in the Presence of $\mathbf{C 6 H}_{6}$. A Pyrex glass tube ( 12 mm o.d. $\times 15 \mathrm{~cm}$ ) equipped with a glass stopcock was charged with $2(198 \mathrm{mg}, 0.446 \mathrm{mmol})$ and was connected to a vacuum line. After acetone $(8 \mathrm{~mL})$ and $\mathrm{C}_{6} \mathrm{H}_{6}(3.5 \mathrm{~mL})$ were vacuum-transferred to the glass tube, the stopcock was closed and the glass tube was disconnected from the vacuum line. The suspension was photo-irradiated with a medium pressure mercury lamp for 1.5 h at $3^{\circ} \mathrm{C}$ with vigorous stirring. During the reaction the color changed from red to pale brown. After the stopcock was opened to fill the vessel with Ar gas, the resulting solution was transferred to the Schrenk tube ( 100 mL ) filled with $\mathrm{Et}_{2} \mathrm{O}(80 \mathrm{~mL})$ to form a pale brown powder. The supernatant liquid was removed by use of a cannula, and the residue was washed with Et 2 O ( 20 $\mathrm{mL} \times 2$ ) and dried in vacuo to give $[\mathrm{Cp} 2 \operatorname{Re}(\mathrm{H}) \mathrm{Ph}](\mathrm{BF} 4)(6)(189 \mathrm{mg}, 0.393 \mathrm{mmol}, 88.1 \%)$. $1_{\mathrm{H}}$ NMR ( 300 MHz , acetone- $d_{6}, 250 \mathrm{~K}$ ): $\delta-12.23(\mathrm{~s}, 1 \mathrm{H}, \operatorname{Re}-H), 5.75(\mathrm{~s}, 10 \mathrm{H}, \mathrm{Cp}), 6.85-$ $6.98(\mathrm{~m}, 3 \mathrm{H}$, meta and para Ph$), 7.46(\mathrm{~d}, 1 \mathrm{H}, J=7.3 \mathrm{~Hz}$, ortho Ph$), 7.69(\mathrm{~d}, 1 \mathrm{H}, J=7.5 \mathrm{~Hz}$, ortho Ph$).{ }^{13} \mathrm{C}$ NMR ( 75.5 MHz , acetone- $d_{6}, 250 \mathrm{~K}$ ): $\delta 86.1(\mathrm{Cp}), 111.4(\mathrm{Ph}), 124.7(\mathrm{Ph})$, $129.0(\mathrm{Ph}), 130.1(\mathrm{Ph}), 147.8(\mathrm{Ph}), 152.0(\mathrm{Ph}) . \mathrm{IR}\left(\mathrm{KBr}, \mathrm{cm}^{-1}\right): 3124(\mathrm{~m}), 3060(\mathrm{~m}), 3031$ (w), 3010 (w), 1571 (m), 1463 (m), 1419 (s), 1375 (w), 1105 (sh), 1051 (vs), 918 (m), 786 (m), 746 (s), 703 (m), $640(\mathrm{~m}), 520(\mathrm{~m}), 414(\mathrm{~m})$. Mass (FAB, m-nitrobenzyl alcohol matrix, $\mathrm{Xe}): \mathrm{m} / \mathrm{z} 395\left(\mathrm{M}^{+}, 39.0\right), 317\left(\mathrm{M}^{+}-\mathrm{C}_{6} \mathrm{H}_{6}, 100\right)$. Anal. Calcd for $\mathrm{C}_{16} \mathrm{H}_{16} \mathrm{BF}_{4} \mathrm{Re}: \mathrm{C}$, 39.93; H, 3.35. Found: C, 39.67; H, 3.26.

Photolysis of 2 in the Presence of Thiophene. A Pyrex glass tube ( 17 mm o.d. x 25 cm ) equipped with a three-way stopcock was charged with $2(354 \mathrm{mg}, 0.797 \mathrm{mmol})$ and
acetone ( 15 mL ) and thiophene $(3.35 \mathrm{~g}, 39.8 \mathrm{mmol})$ were added. The solution was photoirradiated with a medium pressure mercury lamp for 2 h at $3^{\circ} \mathrm{C}$ with vigorous stirring. During the reaction the color changed from red to yellow brown and a precipitate appeared. This precipitate was collected on a Schlenk filter and washed with $\mathrm{Et}_{2} \mathrm{O}(10 \mathrm{~mL} \times 3)$ to give $\left[\mathrm{Cp}_{2} \mathrm{Re}(\mathrm{H})\left(2-\mathrm{C}_{4} \mathrm{H}_{3} \mathrm{~S}\right)\right]\left(\mathrm{BF}_{4}\right)(7)$ as a yellow solid $(82 \mathrm{mg}, 0.17 \mathrm{mmol})$. The filtrate was evaporated and the residual solid was washed with with $\mathrm{Et}_{2} \mathrm{O}(10 \mathrm{~mL} \times 3)$ to give additional 7 ( $229 \mathrm{mg}, 0.470 \mathrm{mmol}$ ). Total yield: $311 \mathrm{mg}\left(0.639 \mathrm{mmol}, 80 \%\right.$ ). ${ }^{1} \mathrm{H}$ NMR ( 300 MHz , acetone-d6): $\delta-11.72(\mathrm{~s}, 1 \mathrm{H}, \operatorname{Re}-H), 5.87(\mathrm{~s}, 10 \mathrm{H}, \mathrm{Cp}), 6.80\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} \mathrm{~J}_{\mathrm{H}-\mathrm{H}}=5.2,3.4\right.$ $\mathrm{Hz}, 4-\mathrm{H}), 6.91\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} J_{\mathrm{H}-\mathrm{H}}=3.4 \mathrm{~Hz},{ }^{4} J_{\mathrm{H}-\mathrm{H}}=0.9 \mathrm{~Hz}, 3-\mathrm{H}\right), 7.42\left(\mathrm{dd}, 1 \mathrm{H},{ }^{3} J_{\mathrm{H}}-\mathrm{H}=\right.$ $\left.5.2 \mathrm{~Hz},{ }^{4} \mathrm{JH}-\mathrm{H}=0.9 \mathrm{~Hz}, 5-\mathrm{H}\right) . \mathrm{IR}\left(\mathrm{KBr}, \mathrm{cm}^{-1}\right): 3126(\mathrm{~s}), 3116$ (sh), 1431 (m), 1419 (s), 1392 (m), 1375 (w), 1286 (w), 1211 (w), 1082 (vs), 1068 (vs), 1061 (vs), 1051 (vs), 1038 (vs), 1012 (s), 1001 (s), 960 (w), 918 (m), 858 (w), 831 (m), 785 (m), 729 (s), 619 (w), 596 (w), 521 (m), 411 (m), 401 (m). Mass (FAB, m-nitrobenzyl alcohol matrix, Xe): m/z 401 $\left(\mathrm{M}^{+}, 58.1\right), 317\left(\mathrm{M}^{+}-\mathrm{C} 4 \mathrm{H}_{4} \mathrm{~S}, 100\right)$. Anal. Calcd for $\mathrm{C}_{14} \mathrm{H}_{14} \mathrm{BF}_{4} \mathrm{ReS}: \mathrm{C}, 34.50 ; \mathrm{H}, 2.90$. Found: C, 34.64; H, 2.94.

Isotopic Fractionation in the Reaction of 2 with $\mathrm{C}_{6} \mathrm{H}_{6} / \mathrm{C}_{6} \mathrm{D}_{6}$. An NMR tube equipped with a high vacuum stopcock was charged with $2(7.0 \mathrm{mg}, 16 \mathrm{mmol})$. A $1: 1$ molar mixture of $\mathrm{C}_{6} \mathrm{H}_{6} / \mathrm{C}_{6} \mathrm{D}_{6}(100 \mathrm{~mL})$ was added to the tube in a glove box and the tube was connected to a vacuum line. After the suspension was degassed by freeze-pump-thaw technique, acetone ( 0.4 mL ) was vacuum transferred to the tube and the stopcock was closed. The tube was disconnected from the vacuum line and was photo-irradiated with a medium pressure mercury lamp at $3^{\circ} \mathrm{C}$ for 45 min . Volatiles were removed in vacuo from the reaction mixture and the tube was connected again to the vacuum line. Acetone- $d_{6}$ was vacuum transferred to the tube and then it was sealed. Careful measurement of the integral of its ${ }^{1} \mathrm{H}$ NMR spectrum showed formation of $[\mathrm{Cp} 2 \operatorname{Re}(\mathrm{H}) \mathrm{Ph}](\mathrm{BF} 4)(6)$ and $\left[\mathrm{Cp} 2 \operatorname{Re}(\mathrm{D}) \mathrm{C}_{6} \mathrm{D} 5\right](\mathrm{BF} 4)(6-$ $\left.d_{6}\right)$ in the ratio of $1.09: 1.00$.

Treatment of 6 with Acetone-d6. An NMR tube was charged with 6 ( $10 \mathrm{mg}, 21$ $\mathrm{mmol})$ and connected to a vacuum line. Acetone $-d_{6}$ was vacuum transferred to the tube, which was subsequently flame sealed. The solution was allowed to stand at room temperature and the
change was monitored by ${ }^{1} \mathrm{H}$ NMR spectroscopy periodically. The color of the solution changed from pale brown to deep purple. After 1 day, the ${ }^{1}$ H NMR spectrum showed mainly two singlets at $\delta 4.78$ and 5.88 ppm besides the signal of benzene at $\delta 7.35 \mathrm{ppm}$. The signal of 6 completely disappeared at this stage. The resulting complexes could not be identified.

Reaction of 6 with MeCN. An NMR tube was charged with $2(7.0 \mathrm{mg}, 16 \mathrm{mmol})$ and connected with a vacuum line. Acetone- $d_{6}(0.4 \mathrm{~mL})$ and benzene $(0.1 \mathrm{~mL})$ were vacuum transferred to the tube, which was subsequently flame sealed. The solution was photoirradiated for 30 min to afford 6 . The complete formation of $\mathbf{6}$ and the corresponding amount of MeCN was confirmed by the ${ }^{1} \mathrm{H}$ NMR spectrum. The resulting solution was allowed to stand at room temperature and the change was monitored by ${ }^{1} \mathrm{H}$ NMR spectroscopy. The color of the solution changed from pale brown to red. After 2 days, $\mathbf{6}$ disappeared entirely and $\mathbf{2}$ was found to be formed in ca. $80 \%$ yield from the ${ }^{1} \mathrm{H}$ NMR spectrum.

Reaction of 6 with C $_{6} D_{6}$. An NMR tube was charged with $\mathbf{6}(10 \mathrm{mg}, 10 \mathrm{mM})$ and connected to a vacuum line. After acetone $-d_{6}(0.4 \mathrm{~mL})$ and $\mathrm{C}_{6} \mathrm{D}_{6}(0.1 \mathrm{~mL}, \mathrm{ca} .1 \mathrm{mmol})$ was vacuum transferred to the tube, it was flame-sealed. The mixture was allowed to stand for 3 days at room temperature. The reaction was monitored periodically by ${ }^{1} \mathrm{H}$ NMR spectroscopy in which the signals of hydride and phenyl ligands in 6 gradually decreased and the signal of free $\mathrm{C}_{6} \mathrm{H}_{6}$ appeared. After 3 days 6 was completely converted to $\left[\mathrm{Cp}_{2} \operatorname{Re}(\mathrm{D}) \mathrm{C}_{6} \mathrm{D}_{5}\right](\mathrm{BF} 4)$.

Reaction of [Cp2 $\operatorname{Re}(H) P h](B F 4)$ (6) with 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU). To a $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10 \mathrm{~mL})$ suspension of $6(58 \mathrm{mg}, 0.12 \mathrm{mmol})$ was added DBU ( 22 $\mathrm{mg}, 0.14 \mathrm{mmol}$ ) and the mixture was stirred for 10 min at room temperature. The solution changed from colorless to yellow. After removal of volatiles, the residue was extracted with hexane ( $10 \mathrm{~mL} \times 2$ ). The solvent was removed in vacuo from the extract to afford Cp 2 RePh (8) as a yellow solid. Recrystallization of 8 from pentane at $-60^{\circ} \mathrm{C}$ gave analytically pure crystals ( $33 \mathrm{mg}, 84 \mathrm{mmol}, 70 \%$ ). ${ }^{1} \mathrm{H}$ MNR ( $300 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D} 6$ ): $\delta 3.97$ (s, 10H, Cp), 6.98$7.09(\mathrm{~m}, 3 \mathrm{H}, \mathrm{Ph}$ (meta and para) ), 8.05-8.08 (m, 2H, Ph (ortho)); ( 300 MHz , acetoned 6 ):
$\delta 4.33$ ( $\mathrm{s}, 10 \mathrm{H}, \mathrm{Cp}$ ), 6.77-6.71 (m, 3H, Ph (meta and para) ), 7.82-7.85 (m, 2H, Ph (ortho)). ${ }^{13} \mathrm{C}$ NMR ( $75.5 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ): $\delta 71.8(\mathrm{Cp}), 122.3(\mathrm{Ph}), 127.6(\mathrm{Ph}), 132.6(\mathrm{Ph})$, 147.9 (Ph). IR (KBr, $\mathrm{cm}^{-1}$ ): 3078 (w), 3045 (w), 1562 (w), 1454 (w), 1419 (w), 1336 (w),
$1095(\mathrm{~m}), 1054(\mathrm{~m}), 1016(\mathrm{~m}), 998(\mathrm{~m}), 935(\mathrm{~m}), 821(\mathrm{~m}), 781(\mathrm{~m}), 734(\mathrm{~s}), 700(\mathrm{~s}), 580$ (w). Mass (FAB): m/z 394 ( $\mathrm{M}^{+}, 100$ ). Anal. Calcd for $\mathrm{C}_{16} \mathrm{H}_{15 \mathrm{Re}: ~ C, ~ 48.84 ; ~ H, ~ 3.84 . ~}^{\text {. }}$ Found: C, 48.86; H, 4.07.

Reaction of $\mathrm{Cp}_{2} \mathrm{RePh}$ (8) with HBF4. To an $\mathrm{Et}_{2} \mathrm{O}(6 \mathrm{~mL})$ solution of $\mathbf{8 ( 5 0 \mathrm { mg } \text { , }}$ 0.13 mmol ) was added several drops of $\mathrm{HBF}_{4} \cdot \mathrm{Et}_{2} \mathrm{O}$ until the yellow color of the solution vanished entirely. Immediately after that, white precipitates formed. After the solution was removed by use of cannula, the white residue was washed with $\mathrm{Et}_{2} \mathrm{O}(5 \mathrm{~mL} \times 2)$ and dried in vacuo to yield $6(54 \mathrm{mg}, 0.11 \mathrm{mmol}, 85 \%)$.

