

# Synthesis, Structure, and Reactivity of *ansa*-Rhenocene Complexes

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Received December 14, 1998

Complexes of rhenocene ( $\text{Cp}_2\text{Re}$ ) with substitution at the cyclopentadienyl rings have been prepared from  $\text{Cp}_2\text{Re-Me}$  by dilithiation of the Cp rings followed by reaction with  $\text{Me}_2\text{-SiCl}_2$  or  $\text{Cl}(\text{SiMe}_2)_2\text{Cl}$  to afford *ansa*-bridged species. Protonation of the resulting neutral Re methyl complexes gives thermally labile methyl hydride complexes. The thermal stability of the methyl hydride complex with a single silicon atom in the *ansa* bridge is enhanced with respect to the unbridged analogues.

## Introduction

There is considerable current interest in *ansa*-bridged metallocene complexes due to their utility in the catalysis of stereoregular olefin polymerization reactions.<sup>1</sup> The importance of the *ansa* bridge in the preparation of novel metallocene-based polymers has been investigated by Manners.<sup>2</sup> On a more fundamental level, several groups have recently reported *ansa*-bridged metallocene complexes which show interesting changes in structure or reactivity compared to the corresponding unbridged metallocene complexes.<sup>3</sup> Parkin and co-workers have recently reported changes in reactivity and structure between several *ansa*-bridged zirconium complexes and the  $\text{Cp}^*$  parent complexes.<sup>4</sup> Green and co-workers have investigated the influence of the *ansa* bridge on several group 6 metallocene complexes and have noted dramatic reactivity differences in comparison to the unbridged analogues, most notably in the facility of reductive elimination from alkyl hydride complexes.<sup>5</sup> For example, the presence of an *ansa* bridge in the alkyl hydride complex  $(\eta^5\text{-C}_5\text{H}_4\text{-CMe}_2\text{-}\eta^5\text{-C}_5\text{H}_4)\text{W}(\text{H})\text{CH}_3$  makes elimination of methane significantly slower than in the unbridged parent compound.

In comparison to other metallocenes of the d-block, there are very few reports of rhenocene derivatives. By analogy to the well-known chemistry of photogenerated tungstenocene ( $\text{Cp}_2\text{W}$ ), an interesting chemistry of the rhenocene cation " $\text{Cp}_2\text{Re}^+$ " can be anticipated. The high

reactivity of this 16-electron fragment and the difficulty of finding an unreactive solvent for this chemistry is indicated by our recent observation that chemically generated  $\text{Cp}_2\text{Re}^+$  reacts with methylene chloride even at low temperatures to afford  $[\text{Cp}_2\text{Re}(\text{CH}_2\text{Cl})\text{Cl}]^+$ .<sup>6</sup> Tobita and co-workers have recently demonstrated the utility of rhenocene cation for activation of C–H bonds of benzene by the in situ photolysis of  $[\text{Cp}_2\text{Re}(\text{NCCH}_3)]\text{[BF}_4\text{]}$  in acetone in the presence of benzene.<sup>7</sup> The resulting phenyl hydride cation,  $[\text{Cp}_2\text{Re}(\text{C}_6\text{H}_5)\text{H}]^+$ , is stable in the solid state and undergoes gradual decomposition in solution. Similar results were obtained for thiophene, but the prospects for generality of this interesting C–H bond activation chemistry are not encouraging, since the rhenocene alkyl hydride complexes are known to be quite thermally unstable in solution, decomposing at or below 0 °C by elimination of alkane.<sup>8</sup>

To facilitate the investigation of C–H activation of a greater variety of substrates by " $\text{Cp}_2\text{Re}^+$ " and related fragments, the stability of the products should be increased. We have previously reported that the thermal stability of cationic rhenocene derivatives can be increased by utilization of less nucleophilic anions, such as  $(\text{BAR}'_4)^-$ ; ( $\text{Ar}' = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$ ).<sup>6</sup> On the basis of the observations of Green and co-workers, we expect that further improvements in thermal stability of rhenocene derivatives can be achieved by the incorporation of an *ansa* bridge between the Cp rings. In this paper, we report the synthesis and structural characterization of *ansa*-bridged metallocenes of rhenium and a preliminary exploration of their thermal stability.

## Results

Reaction of  $\text{Cp}_2\text{ReCH}_3$  (**1**)<sup>9</sup> with 2 equiv of *n*BuLi in THF at 0 °C affords a dilithiated species which was

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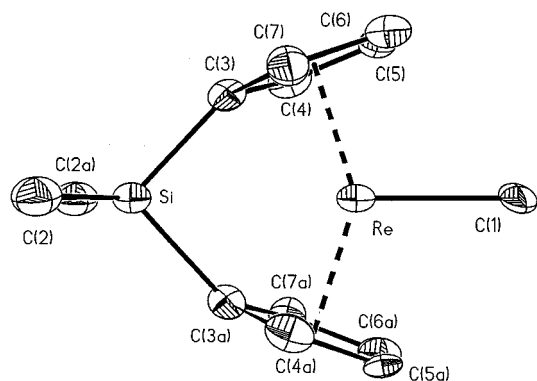
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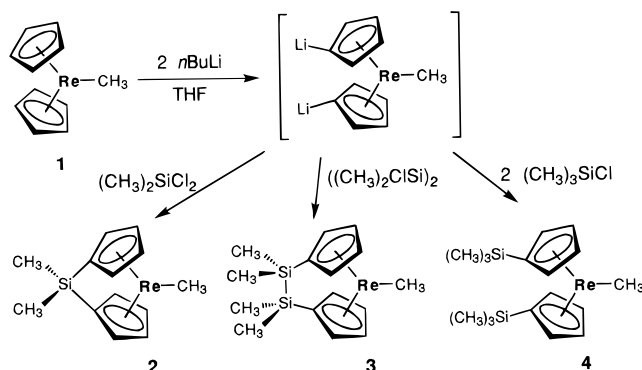
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**Figure 1.** ORTEP representation of  $(\eta^5\text{-C}_5\text{H}_4\text{-SiMe}_2\text{-}\eta^5\text{-C}_5\text{H}_4)\text{ReCH}_3$  (**2**). Thermal ellipsoids are shown at 50% probability. Hydrogen atoms have been omitted for clarity.

**Scheme 1**



immediately derivatized to give *ansa*-bridged complexes in good yield (Scheme 1). When the dilithiated intermediate was treated with a slight excess of  $\text{Me}_2\text{SiCl}_2$ , dark orange crystals of  $\{\eta^5\text{-C}_5\text{H}_4\text{-SiMe}_2\text{-}\eta^5\text{-C}_5\text{H}_4\}\text{ReCH}_3$  (**2**) were isolated in 84% yield after removal of the volatiles followed by sublimation. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **2** are consistent with a  $\text{Cp}_2\text{ReCH}_3$  complex containing a bridging  $\text{-(Si(CH}_3)_2\text{)-}$  group. The  $^1\text{H}$  NMR spectrum of the cyclopentadienyl region reveals two doublet of doublet resonances ( $\delta$  4.82 and 4.21), consistent with the expected AA'BB' spin system ( $J_{\text{HH}} = 1.6$  and 1.9 Hz). The  $^{13}\text{C}$  NMR spectrum of the cyclopentadienyl region contains two doublet resonances ( $\delta$  83.7 and 75.0) which exhibit a large one-bond CH coupling ( $^1J_{\text{CH}} = 180$  Hz). The  $^1\text{H}$  NMR chemical shifts for the 3,4- and 2,5-positions of the cyclopentadienyl rings were assigned by NOE effects between the cyclopentadienyl and methyl groups. The  $^{13}\text{C}$  NMR resonances were assigned by selective  $^1\text{H}$  decoupling experiments.

The procedure used for the synthesis of **2** can be extended to the synthesis of rhenocene derivatives with an *ansa* bridge containing a two-silicon bridge,  $(\eta^5\text{-C}_5\text{H}_4\text{-SiMe}_2\text{-SiMe}_2\text{-}\eta^5\text{-C}_5\text{H}_4)\text{ReCH}_3$  (**3**), and a derivative containing two  $\text{SiMe}_3$  substituents,  $(\text{Me}_3\text{Si-}\eta^5\text{-C}_5\text{H}_4)_2\text{ReCH}_3$  (**4**). Complexes **3** and **4** are isolated as pure solids by sublimation and characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, which gave spectra similar to those of complex **2**.

The molecular structure of complex **2** was confirmed by X-ray crystallography. An ORTEP diagram of the structure is shown in Figure 1. A table of relevant bond distances and angles is given in Table 1. The data

**Table 1.** Selected Bond Distances and Angles for **2**

Distances, Å			
Re–C(1)	2.117(24)	Re–C(3)	2.193(12)
Re–C(4)	2.213(16)	Re–C(5)	2.262(11)
Re–C(6)	2.253(17)	Re–C(7)	2.212(19)
Si–C(3)	1.880(13)	Si–C(2)	1.841(13)
C(3)–C(4)	1.473(18)	C(4)–C(5)	1.373(22)
C(5)–C(6)	1.427(20)	C(6)–C(7)	1.457(22)
C(3)–C(7)	1.439(20)		
Angles, deg			
C(3)–Si–C(3a)	92.9(8)	C(2)–Si–C(2a)	112.2(9)
C(3)–C(7)–C(6)	107.2(12)	C(3)–C(4)–C(5)	107.9(13)
C(5)–C(6)–C(7)	107.0(14)	C(4)–C(3)–C(7)	107.1(11)
C(4)–C(5)–C(6)	110.7(13)	Cp <sub>ent</sub> –M–Cp <sub>ent</sub> ( $\alpha$ )	145.2(16)
Cp <sub>norm</sub> –M–Cp <sub>norm</sub> ( $\beta$ )	140.0(15)	between Cp planes ( $\gamma$ )	40.0(4)

collection and solution procedures are summarized in the Experimental Section.

Attempts to extend the derivatization of the dilithiated intermediate to carbon bridges were not successful. Reaction with methylene chloride, methylene bromide, methylene ditosylate, and a variety of other halocarbons and ditosylates led to no tractable products.

Addition of 1 equiv of  $[\text{H}(\text{Et}_2\text{O})_2]\text{B}(\text{Ar})_4$  to complexes **1–4** gives clean formation of cationic methyl hydride complexes **5–8**. The methyl hydride cations have been characterized by  $^1\text{H}$  NMR spectroscopy at 250 K in both  $\text{CD}_2\text{Cl}_2$  and  $\text{CD}_3\text{CN}$ . The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the Si-bridged *ansa* complexes **6–8** are observed to have decreased symmetry compared to the corresponding neutral methyl complexes. The  $^1\text{H}$  NMR spectra of the cyclopentadienyl rings exhibit four broad resonances due to the four chemically inequivalent protons on each ring, although the two rings are still equivalent to each other. Two resonances are observed for the methyl groups of the silicon bridge, which become inequivalent with one group cisoid to the rhenium methyl group and the other cisoid to the hydride.

Colorless solutions of **5–8** were prepared and monitored by  $^1\text{H}$  NMR spectroscopy from 250 K to room temperature. At 250 K complexes **5–8** were indefinitely stable, and  $^{13}\text{C}$  NMR spectra of complexes **5** and **6** were obtained at this temperature without noticeable decomposition. As the solutions were warmed to 0 °C, rapid reaction occurred for complexes **5**, **7**, and **8**. The solutions became dark orange, and the elimination of methane was observed in the  $^1\text{H}$  NMR spectra. Complex **6** was observed to be stable at 0 °C, and decomposition was only evident when the sample was allowed to stand at room temperature:  $t_{1/2} = 2$  h.

## Discussion

The most common synthetic routes to *ansa*-bridged metallocene complexes employ a ligand having two cyclopentadienyl rings joined by a bridging group. A dianionic form of the ligand is reacted with an appropriate metal salt. While this approach is satisfactory, yields are variable and rarely completely satisfactory. A promising alternative to the salt elimination reaction has been reported by Jordan and co-workers<sup>10</sup> and by Collins and co-workers.<sup>11</sup> This approach uses the ap-

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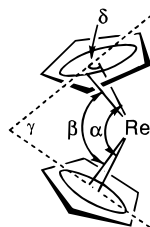
propriate dicyclopentadiene and a metal amide complex. Liberation of amine provides the driving force for the reactions, which afford both chiral and achiral *ansa*-metallocene complexes in excellent yield.

In part due to the lack of a readily available Re(III) precursor, synthetic entries to conventional rhenocene chemistry employ reaction of the cyclopentadienyl anion with either  $\text{ReCl}_4(\text{THF})_2$  or  $\text{ReCl}_5$ .<sup>9</sup> Yields of  $\text{Cp}_2\text{ReH}$  are modest, and our attempts to extend this approach to *ansa*-bridged complexes were unsuccessful.

An alternative methodology starts from unbridged metallocene complexes, which are then derivatized to *ansa* complexes. The metalation of cyclopentadienyl complexes by  $^n\text{BuLi}$  has been reported by several groups.<sup>12</sup> Consistent with our synthetic goals, there have been reports of metalation of sandwich complexes followed by addition of dialkylchlorosilane to generate *ansa*-bridged complexes.<sup>13,14</sup> Since  $\text{Cp}_2\text{Re-H}$  is known to react with alkylolithium reagents to give lithiation at the metal,<sup>9</sup> alkyl derivatives such as  $\text{Cp}_2\text{Re-CH}_3$  present a better starting point for this chemistry.

Dilithiation of  $\text{Cp}_2\text{Re-CH}_3$  gives a very reactive material, which was not isolated. Formulation of this intermediate as  $(\eta^5\text{-C}_5\text{H}_4\text{Li})_2\text{Re-CH}_3$  was confirmed by the formation of complexes **2–4** by reaction with various chlorosilanes. The *ansa*-bridged species are obtained in a state of high purity as very air-sensitive orange crystals by sublimation of the reaction residues. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data are consistent with the structures depicted in Scheme 1. Retention of the methyl group bound directly to Re is indicated by the high-field resonance in both the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. The presence of the bridge connecting the two rings in complexes **2** and **3** is indicated by the reduced symmetry of the Cp rings and appropriate resonances for the Si-bound methyl groups.

The molecular structure of complex **2** was confirmed by X-ray crystallography. No X-ray structure of  $\text{Cp}_2\text{ReCH}_3$  has been reported, but comparison of complex **2** to several other unbridged rhenocene complexes is possible. It is important to clearly define the bond angles involved in comparing various structures, since some confusion exists in the literature on this point. We adopt the definitions of Corey and co-workers<sup>15</sup> as defined in the following diagram:



The Cp–M–Cp bending angles ( $\alpha$  and  $\beta$ ) of complex **2** are approximately  $5^\circ$  smaller than the bending angles

of the unbridged complexes but fall within the range of  $140\text{--}158^\circ$  observed for the crystallographically characterized rhenocene derivatives.<sup>16</sup> This is consistent with the bending angles for group 4 metallocenes reported by Corey and co-workers.<sup>15</sup> The bending angles for structures with a single  $\text{SiMe}_2$  bridge are  $3\text{--}4^\circ$  smaller than the unbridged metallocenes, while the structures with a single  $\text{CMe}_2$  bridge are  $10\text{--}13^\circ$  smaller than the unbridged metallocenes. The difference between the  $\alpha$  and  $\beta$  angles for **2** is  $5^\circ$ , which indicates a slight shift in the angle of the Re to Cp centroid compared to that of Re to the normal of the cyclopentadienyl plane. There is a slight distortion of ring C to Re bond lengths, indicating a subtle shift toward an  $\eta^3$  structure. The Re–C(3) bond distance is the shortest, and the longest Re–C bond distances are to the two carbons which are further from the Si bridge. The most dramatic effect that the  $\text{SiMe}_2$  bridge has upon the structure is the bending of the angle that Si–C(3) makes with the plane of the cyclopentadienyl ring. An unbridged substituent on the Cp ring, such as H or a  $\text{SiMe}_3$  group, normally is found to point slightly away from the other Cp ring. In complex **2**, the constraints of the bridge cause the  $\text{SiMe}_2$  moiety to be shifted significantly toward the metal atom.

We have previously studied methane elimination from the methyl hydride complex **5** resulting from protonation of complex **1** with various acids. On the basis of our observation<sup>6</sup> that the thermal stability of certain cationic rhenocene derivatives is dependent on the nature of the counterion, with the greatest stability achieved with  $\text{B}(\text{Ar})_4^-$ , protonation of **1** with  $[\text{H}(\text{Et}_2\text{O})_2]\text{B}(\text{Ar})_4^-$  was investigated. The rate of methane elimination from the methyl hydride complex **5** is found to be independent of the counterion. This is consistent with our earlier investigation of the mechanism of this reaction, which was found to proceed by rate-determining dissociation of methane.<sup>8</sup>

Motivated by the recent work of Green and co-workers,<sup>5</sup> who report that *ansa*-metallocene complexes of Mo and W alkyl hydrides are significantly stabilized with respect to the unsubstituted analogues, we anticipated that the alkyl hydride complexes of *ansa*-bridged rhenocene such as **6** and **7** would have enhanced thermal stability. Complex **8**, which has two  $\text{SiMe}_3$  substituents, serves as a good comparison to evaluate purely inductive effects of silicon substitution.

The reactivity differences among complexes **5**, **7**, and **8** are subtle, but it appears that the single Si *ansa* bridge in complex **6** significantly increases the thermal stability of the methyl hydride complexes toward methane elimination. Complex **6** was observed to be stable at  $0^\circ\text{C}$ , and decomposition was only evident when the sample was allowed to stand at room temperature;  $t_{1/2}$

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= 2 h. Complexes **5**, **7**, and **8** eliminate methane too rapidly at room temperature to allow observation at this temperature. Green and co-workers have observed a more drastic reactivity difference between  $\text{Cp}_2\text{W}(\text{CH}_3)\text{H}$  and *ansa*-( $\text{Me}_2\text{C}$ ) $\text{Cp}_2\text{W}(\text{CH}_3)\text{H}$ . The parent compounds have been shown to reductively eliminate methane at 40 °C, while the *ansa* complexes show no reactivity up to 150 °C.<sup>5</sup> Green et al. have proposed that this reactivity difference is the result of the ability of the "Cp<sub>2</sub>W" intermediate to attain a parallel structure following reductive elimination of methane and the inability of "*ansa*-Cp<sub>2</sub>W" to attain a parallel structure. This is consistent with the results that we have observed and suggests that the unbridged complexes, **5** and **8**, achieve a parallel ring structure during the transition state of methane reductive elimination. Complex **7**, which contains the double Si bridge, does not constrain the geometry to a bent metallocene and the reactivity is therefore similar to that of the unbridged species. While complex **6** does appear to be more thermally stable than the other complexes, the stability is unfortunately still inadequate for isolation at room temperature.

We anticipate that *ansa*-rhenocene alkyl hydride complexes with a more constrained structure, such as that provided by a single carbon bridge, may be isolable at room temperature. Synthetic efforts directed toward this goal are continuing.

## Conclusions

A high-yield synthesis for the first *ansa*-bridged complexes of rhenocene has been developed. The addition of  $\text{Me}_2\text{SiCl}_2$  or  $(\text{Me}_2\text{Si})_2\text{Cl}_2$  to a THF solution of  $(\eta^5\text{-C}_5\text{H}_4\text{Li})_2\text{ReCH}_3$  generates *ansa*-bridged complexes with one or two silicon dimethyl groups, respectively. The structure of  $(\eta^5\text{-C}_5\text{H}_4\text{-SiMe}_2\text{-}\eta^5\text{-C}_5\text{H}_4)\text{ReCH}_3$  was confirmed by X-ray diffraction. Rhenocene methyl hydride complexes have been generated by protonation and characterized at low temperature by NMR spectroscopy. Methane elimination from these complexes occurs below ambient temperature, although  $[(\eta^5\text{-C}_5\text{H}_4\text{-SiMe}_2\text{-}\eta^5\text{-C}_5\text{H}_4)\text{Re}(\text{CH}_3)\text{H}][\text{B}(\text{Ar}')_4]$  has been observed to be more stable at room temperature than analogous unbridged complexes. This increased stability is attributed to the *ansa* bridge, which restricts formation of the favored transition state for reductive elimination.

## Experimental Section

All manipulations were conducted with rigorous exclusion of air and water using standard high-vacuum Schlenk and drybox techniques. Chlorinated solvents were distilled from  $\text{CaH}_2$ . Hydrocarbon solvents were distilled from Na/K benzophenone ketyl. Deuterated solvents (Cambridge Isotope Laboratories) were dried and stored in the same manner as their protio analogues. All solvents were vacuum-transferred immediately prior to use. Reagent grade chemicals were used as received unless stated otherwise.  $\text{ReCl}_4(\text{THF})_2$ ,<sup>17</sup>  $\text{Cp}_2\text{-ReCH}_3$ ,<sup>9</sup> and  $[\text{H}(\text{Et}_2\text{O})_2][\text{B}(\text{Ar}')_4]$ <sup>18</sup> were prepared using literature procedures.  $\text{Me}_3\text{SiCl}$  was used as received from Aldrich.  $(\text{Me}_2\text{-Si})_2\text{Cl}_2$  (Gelest) and  $\text{Me}_2\text{SiCl}_2$  (Aldrich) were degassed and

dried over silica gel which was activated by heating to 300 °C under vacuum.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker AC-200, AF-300, and WM-500 spectrometers. Samples were contained in sealed or Teflon-valved tubes at ambient probe temperature unless otherwise indicated. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts ( $\delta$ ) are referenced to the deuterated solvent relative to  $\text{SiMe}_4$ . Unless otherwise noted, all NMR spectra were recorded in  $\text{CD}_2\text{-Cl}_2$ . In complexes **5**–**8**, resonances due to the  $\text{B}(\text{Ar}')_4$  anion are listed only for complex **5**. The <sup>1</sup>H and <sup>13</sup>C resonances due to this anion are identical in all complexes reported here. The cyclopentadienyl protons of rhenocene complexes have been observed to relax slowly, and a relaxation delay of 120 s is required to observe appropriate integrals. Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta, Canada.

**( $\eta^5\text{-C}_5\text{H}_4\text{-SiMe}_2\text{-}\eta^5\text{-C}_5\text{H}_4$ )Re-CH<sub>3</sub> (**2**).** A small glass vessel with an 8 mm Kontes valve was charged with  $\text{Cp}_2\text{ReCH}_3$  (274 mg, 0.83 mmol). THF (20 mL) was vacuum-transferred to the vessel and warmed to 0 °C. Under an argon flow, 2 equiv of *n*-BuLi (1.03 mL, 1.6 M, 1.65 mmol) was added via syringe. The solution was stirred at 0 °C for 45 min. Under an argon flow,  $\text{Me}_2\text{SiCl}_2$  (101  $\mu\text{L}$ , 0.83 mmol) was added via syringe and the mixture was stirred at 0 °C for 15 min. The solvent was removed in vacuo. Sublimation of the residue affords 320 mg of dark orange crystals (84%). <sup>1</sup>H NMR:  $\delta$  4.82 (d of d, 4H,  $J_{\text{HH}} = 1.6$ ,  $J_{\text{HH}} = 2.0$  Hz,  $\eta^5\text{-C}_5\text{H}_4$ ), 4.21 (d of d, 4H,  $J_{\text{HH}} = 1.6$ ,  $J_{\text{HH}} = 2.0$ ,  $\eta^5\text{-C}_5\text{H}_4$ ), 0.28 (s, 3H,  $\text{ReCH}_3$ ), 0.18 (s, 6H,  $\text{Si}(\text{CH}_3)_2$ ). <sup>13</sup>C NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  83.7 (d of quart,  $J_{\text{CH}} = 180$ ,  $J_{\text{CH}} = 6.6$  Hz,  $\eta^5\text{-C}_5\text{H}_4$ ), 75.0 (d of quart,  $J_{\text{CH}} = 183$ ,  $J_{\text{CH}} = 7$ ,  $\eta^5\text{-C}_5\text{H}_4$ ), 28 (s,  $\eta^5\text{-C}_5\text{H}_4$ ), -5.2 (quart,  $J_{\text{CH}} = 121$ ,  $\text{Si}(\text{CH}_3)_2$ ), -34.0 (quart,  $J_{\text{CH}} = 127$ ,  $\text{ReCH}_3$ ). Anal. Calcd for  $\text{C}_{13}\text{H}_{17}\text{ReSi}$ : C, 40.29; H, 4.42. Found: C, 40.31; H, 4.61.

**( $\eta^5\text{-C}_5\text{H}_4\text{-SiMe}_2\text{-SiMe}_2\text{-}\eta^5\text{-C}_5\text{H}_4$ )Re-CH<sub>3</sub> (**3**).** The procedure used for complex **2** was followed. To the dilithiated intermediate generated from 50 mg of  $\text{Cp}_2\text{ReCH}_3$  in THF solution was added 1 equiv of  $\text{ClSiMe}_2\text{-SiMe}_2\text{Cl}$ . After removal of the solvent, 58 mg of complex **3** was obtained in 56% yield by sublimation (56% yield). <sup>1</sup>H NMR:  $\delta$  4.42 ("t", 4H,  $J_{\text{HH}} = 1.7$  Hz,  $\eta^5\text{-C}_5\text{H}_4$ ), 4.37 ("t", 4H,  $J_{\text{HH}} = 1.7$ ,  $\eta^5\text{-C}_5\text{H}_4$ ), 0.36 (s, 3H,  $\text{ReCH}_3$ ), 0.25 (s, 12H,  $\text{Si}(\text{CH}_3)_2$ ). <sup>13</sup>C NMR:  $\delta$  83.91 (d of q,  $J_{\text{CH}} = 181$ ,  $J_{\text{CH}} = 7$  Hz,  $\eta^5\text{-C}_5\text{H}_4$ ), 71.24 (d of q,  $J_{\text{CH}} = 180$ ,  $J_{\text{CH}} = 7$ ,  $\eta^5\text{-C}_5\text{H}_4$ ), 75.01 (s,  $\eta^5\text{-C}_5\text{H}_4$ ), -1.4 (q,  $J_{\text{CH}} = 121$ ,  $(\text{Si}(\text{CH}_3)_2)_2$ ), -36.77 (q,  $J_{\text{CH}} = 129$ ,  $\text{ReCH}_3$ ). Anal. Calcd for  $\text{C}_{15}\text{H}_{23}\text{-ReSi}_2$ : C, 40.42; H, 5.20. Found: C, 40.41; H, 5.15.

**( $\text{Me}_3\text{Si-}\eta^5\text{-C}_5\text{H}_4$ )<sub>2</sub>Re-CH<sub>3</sub> (**4**).** This compound was prepared as described above, but the dilithiated intermediate prepared from 120 mg of  $\text{Cp}_2\text{ReCH}_3$  was reacted with an excess of trimethylsilyl chloride, which was added to the reaction mixture by vacuum transfer at -78 °C. The solution was slowly warmed to room temperature, and the volatiles were removed in vacuo. The solid was sublimed at 60 °C under dynamic vacuum to give 150 mg of **4** as an orange solid (87%). <sup>1</sup>H NMR:  $\delta$  4.52 ("t", 4H,  $J_{\text{HH}} = 1.9$ ,  $\eta^5\text{-C}_5\text{H}_4$ ), 3.52 ("t", 4H,  $J_{\text{HH}} = 1.9$ ,  $\eta^5\text{-C}_5\text{H}_4$ ), 0.19 (s, 18H,  $\text{Si}(\text{CH}_3)_3$ ), 0.18 (s, 3H,  $\text{ReCH}_3$ ). <sup>13</sup>C NMR:  $\delta$  83.9 (d of q,  $J_{\text{CH}} = 176$ ,  $J_{\text{CH}} = 8$ ,  $\eta^5\text{-C}_5\text{H}_4$ ), 68.7 (d of q,  $J_{\text{CH}} = 180$ ,  $J_{\text{CH}} = 6$ ,  $\eta^5\text{-C}_5\text{H}_4$ ), 0.58 (q,  $J_{\text{CH}} = 119$ ,  $\text{Si}(\text{CH}_3)_3$ ), -36.3 (quart,  $J_{\text{CH}} = 128$ ,  $\text{ReCH}_3$ ). Anal. Calcd for  $\text{C}_{17}\text{H}_{29}\text{ReSi}_2$ : C, 42.92; H, 6.14. Found: C, 42.94; H, 6.05.

**( $(\eta^5\text{-C}_5\text{H}_5)_2\text{Re}(\text{CH}_3)\text{H}][\text{B}(\text{Ar}')_4]$  (**5**).** A sealable NMR tube was charged with  $(\eta^5\text{-C}_5\text{H}_5)_2\text{ReCH}_3$  (**1**; 6 mg, 0.018 mmol) and  $[\text{H}(\text{Et}_2\text{O})_2][\text{B}(\text{Ar}')_4]$  (18.3 mg, 0.018 mmol). Methylene chloride-*d*<sub>2</sub> (0.5 mL) was vacuum-transferred into the tube. The tube was kept at -78 °C until it was placed in the NMR probe. <sup>1</sup>H NMR ( $\text{CD}_2\text{Cl}_2$ , 250 K):  $\delta$  7.74 (m, 8H, *o*-B(Ar')<sub>4</sub>); 7.58 (m, 4H, *p*-B(Ar')<sub>4</sub>); 5.30 (s, 10H,  $\eta^5\text{-C}_5\text{H}_5$ ); 0.53 (s, 3H, Re-CH<sub>3</sub>); -11.88 (s, 1H, Re-H). <sup>13</sup>C{<sup>1</sup>H} NMR ( $\text{CD}_2\text{Cl}_2$ , 250 K):  $\delta$  162.2 (quart,  $^1J_{\text{CB}} = 50$  Hz, B(Ar')<sub>4</sub> ipso); 135.2 (d,  $^1J_{\text{CH}} = 159$ , *o*-B(Ar')<sub>4</sub>); 129.3 (quart,  $^2J_{\text{CF}} = 30$ , *m*-B(Ar')<sub>4</sub>); 125.0 (quart,  $^1J_{\text{CF}} = 272$ , B(Ar')<sub>4</sub> CF<sub>3</sub>); 118.0 (d of t,  $^1J_{\text{CH}} = 166$ ,  $^3J_{\text{CF}} = 4$ , *p*-B(Ar')<sub>4</sub>); 84.0 ( $\eta^5\text{-C}_5\text{H}_5$ ); -40.1 (Re-CH<sub>3</sub>).

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**[( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-SiMe<sub>2</sub>- $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)Re(CH<sub>3</sub>H)][B(Ar')<sub>4</sub>] (6).** A sealable NMR tube was charged with { $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-Si(CH<sub>3</sub>)<sub>2</sub>- $\eta^5$ -C<sub>5</sub>H<sub>4</sub>}ReCH<sub>3</sub> (**2**; 8 mg, 0.021 mmol) and [H(Et<sub>2</sub>O)<sub>2</sub>][B(Ar')<sub>4</sub>] (21 mg, 0.021 mmol). CD<sub>2</sub>Cl<sub>2</sub> was vacuum-transferred to the tube. The tube was kept at -78 °C until it was placed in the NMR probe. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 250 K): 5.81 (s, 2H,  $\eta^5$ -C<sub>5</sub>H<sub>4</sub>); 5.72 (s, 2H,  $\eta^5$ -C<sub>5</sub>H<sub>4</sub>); 5.32 (s, 2H,  $\eta^5$ -C<sub>5</sub>H<sub>4</sub>); 4.92 (s, 2H,  $\eta^5$ -C<sub>5</sub>H<sub>4</sub>); 0.53 (s, 3H, Re-CH<sub>3</sub>); 0.35 (s, 3H, Si-CH<sub>3</sub>); 0.30 (s, 3H, Si-CH<sub>3</sub>); -10.47 (s, 1H, Re-H). <sup>13</sup>C{<sup>1</sup>H} NMR (250 K): 114.7 ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>); 89.5 ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>); 84.4 ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>); 73.5 ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>); 49.5 (ipso  $\eta^5$ -C<sub>5</sub>H<sub>4</sub>); -6.3 (SiCH<sub>3</sub>); -6.4 (SiCH<sub>3</sub>); -41.0 (ReCH<sub>3</sub>).

**[( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-SiMe<sub>2</sub>-SiMe<sub>2</sub>- $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)Re(CH<sub>3</sub>H)][B(Ar')<sub>4</sub>] (7).** A sealable NMR tube was charged with ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-SiMe<sub>2</sub>-SiMe<sub>2</sub>- $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)ReCH<sub>3</sub> (**3**; 3 mg, 0.0067 mmol) and [H(Et<sub>2</sub>O)<sub>2</sub>][B(Ar')<sub>4</sub>] (6.8 mg, 0.0067 mmol). CD<sub>2</sub>Cl<sub>2</sub> was vacuum-transferred to the tube. The tube was kept at -78 °C until it was placed in the NMR probe. <sup>1</sup>H NMR (250 K): 5.44 (s, 2H,  $\eta^5$ -C<sub>5</sub>H<sub>4</sub>); 5.38 (s, 2H,  $\eta^5$ -C<sub>5</sub>H<sub>4</sub>); 5.32 (s, 2H,  $\eta^5$ -C<sub>5</sub>H<sub>4</sub>); 4.31 (s, 2H,  $\eta^5$ -C<sub>5</sub>H<sub>4</sub>); 0.63 (s, 3H, Re-CH<sub>3</sub>); 0.42 (s, 6H, Si-CH<sub>3</sub>); 0.40 (s, 6H, Si-CH<sub>3</sub>); -12.00 (s, 1 H, Re-H).

**[(Me<sub>3</sub>Si- $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Re(CH<sub>3</sub>H)][B(Ar')<sub>4</sub>] (8).** A sealable NMR tube was charged with {(CH<sub>3</sub>)<sub>3</sub>Si- $\eta^5$ -C<sub>5</sub>H<sub>4</sub>}<sub>2</sub>Re(CH<sub>3</sub>)ReCH<sub>3</sub> (**4**; 12 mg, 0.025 mmol) and [H(Et<sub>2</sub>O)<sub>2</sub>][B(Ar')<sub>4</sub>] (26 mg, 0.025 mmol). CD<sub>2</sub>Cl<sub>2</sub> was vacuum-transferred to the tube. The tube was kept at -78 °C until it was placed in the NMR probe. <sup>1</sup>H NMR (250 K): 5.58 (br, 2H,  $\eta^5$ -C<sub>5</sub>H<sub>4</sub>); 5.41 (br, 2H,  $\eta^5$ -C<sub>5</sub>H<sub>4</sub>); 4.79 (m, 4H,  $\eta^5$ -C<sub>5</sub>H<sub>4</sub>); 0.40 (s, 3H, ReCH<sub>3</sub>); 0.25 (s, 18H, Si-(CH<sub>3</sub>)<sub>3</sub>); -12.1 (s, 1H, Re-H).

**X-ray Structure Determination for ( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>-Si(CH<sub>3</sub>)<sub>2</sub>- $\eta^5$ -C<sub>5</sub>H<sub>4</sub>)ReCH<sub>3</sub> (2).** Crystals were generated upon sublimation of the crude reaction material at 50 °C to a probe cooled with ice water under dynamic vacuum. An orange needle of dimensions 0.15 × 0.20 × 0.35 mm was placed in a nitrogen

stream at 183 K on an Enraf-Nonius CAD4 diffractometer using Mo K $\alpha$  radiation with a graphite monochromator ( $\lambda$  = 0.710 73 Å). An orientation matrix was determined from 20 reflections in the range  $24^\circ \leq 2\theta \leq 32^\circ$ . Monoclinic symmetry (space group *C2/c*) was indicated on the basis of systematic absences. The cell parameters are  $a$  = 11.242(2) Å,  $b$  = 14.118(3) Å,  $c$  = 7.885(2) Å,  $\beta$  = 108.19(3)°,  $V$  = 1188.9(4) Å<sup>3</sup> ( $Z$  = 4). A high- $\chi$  reflection was scanned to provide for an absorption correction, reducing the equivalency disagreement from 9% to 3%. The decay was negligible. Reduction of the data was carried out using XCAD4, and all further work was carried out using the Siemens version of SHELX. The structure was solved primarily from the Patterson map, as refinement on the Re was obtained. The weighting scheme required a correction of 0.005. Hydrogens were introduced by calculation. The methyl carbon attached to the Re atom showed a large ellipsoid, and by modeling disorder of the hydrogens bonded to the carbon, it was considerably reduced. A final  $R$  value of 6.3% with a GOF of 1.14 was obtained (data/parameter = 981/71).

**Acknowledgment.** We thank the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. C.E.R. is grateful to the University of Washington for a Ritter Fellowship. We thank Dr. David Barnhart for assistance with X-ray crystallography.

**Supporting Information Available:** Details of the structure determination for complex **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM9810145