

## Synthesis and Reactivity of the Hydrido- and Alkylrhenium Methylidene Complexes $\text{Cp}^*(\text{PMe}_3)_2(\text{R})\text{Re}=\text{CH}_2$ ( $\text{R} = \text{H}, \text{CH}_3$ )

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**Abstract:** Protonolysis of the dimethylrhenium(III) compound  $\text{Cp}^*(\text{PMe}_3)_2\text{Re}(\text{CH}_3)_2$  (**3**) led to formation of the highly reactive hydridorhenium methylidene compound  $[\text{Cp}^*(\text{PMe}_3)_2\text{Re}(\text{CH}_2(\text{H}))][\text{OTf}]$  (**4**), which was characterized spectroscopically at low temperature. Although **4** decomposed above  $-30^\circ\text{C}$ , reactivity studies performed at low temperature indicated it was in equilibrium with the coordinatively unsaturated methylrhenium complex  $[\text{Cp}^*(\text{PMe}_3)_2\text{Re}(\text{CH}_3)][\text{OTf}]$  (**2**). Methylidene complex **4** was found to react with  $\text{PMe}_3$  to afford  $[\text{Cp}^*(\text{PMe}_3)_3\text{Re}(\text{CH}_3)][\text{OTf}]$  (**6**) and with chloride anion to give  $\text{Cp}^*(\text{PMe}_3)_2\text{Re}(\text{Me})\text{Cl}$  (**7**). When  $\text{BAR}_f$  anion was added to **4**, the thermally stable methylrhenium methylidene complex  $[\text{Cp}^*(\text{PMe}_3)_2\text{Re}(\text{CH}_2)(\text{CH}_3)][\text{BAR}_f]$  (**8**) was isolated upon warming to room temperature. The mechanisms of formation of both **4** and **8** are discussed in detail, including DFT calculations. The novel carbonyl ligated complex  $\text{Cp}^*(\text{CO})_2\text{Re}(\text{CH}_3)\text{OTf}$  (**12**) was prepared, isolated, and found to not undergo migration reactions to form methylidene complexes.

### Introduction

Surface-bound transition metal methylidenes have been proposed to be intermediates in the Fischer–Tropsch process,<sup>1,2</sup> and homogeneous methylidene complexes undergo methylene-transfer reactions.<sup>3–5</sup> Despite the proven and potential utility of methylidene complexes, detectable methylidenes remain relatively rare. The first stable methylidene complex,  $\text{Cp}_2\text{Ta}(\text{CH}_2)\text{CH}_3$ , was reported by Schrock in 1975,<sup>6–8</sup> and several tantalum methylidenes have been isolated since that initial discovery.<sup>9–14</sup> Isolable complexes bearing terminal methylidene

ligands have been reported since, with metals from groups 6,<sup>4,15–19</sup> 7,<sup>20–23</sup> 8,<sup>24–28</sup> and 9,<sup>29,30</sup> and methylidene ligands have been spectroscopically characterized in a variety of thermally unstable or otherwise nonisolable complexes.<sup>31–40</sup>

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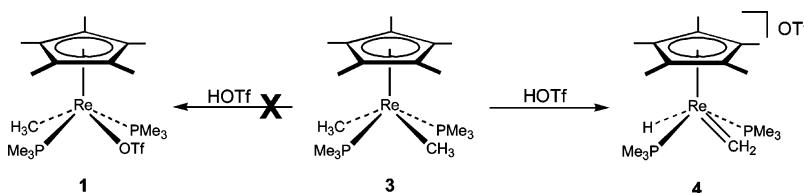
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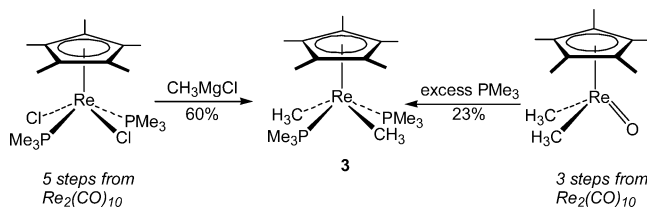
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**Scheme 1.** Formation of Methylidene Hydride Complex **4**

Despite the growing number of known methylidene compounds, accessing terminal methylidene complexes which also bear hydride ligands is particularly difficult. Only two of these complexes have been isolated to date,<sup>9,10,27,41</sup> although others have been observed in low-temperature NMR<sup>42,43</sup> and matrix isolation<sup>44,45</sup> experiments. Reversible  $\alpha$ -hydrogen migration equilibria between methylidene hydride and methyl group species in group 6 complexes were studied extensively by Green and co-workers, but these studies were necessarily based on indirect evidence.<sup>46–49</sup> The first direct observation of  $\alpha$ -hydrogen migration from a methyl group to give a bridging methylidene hydride complex was reported for an osmium cluster by Shapley and Calvert in 1977, and in 1986 Bercaw and co-workers described the formation of the isolable terminal methylidene hydride complex  $\text{Cp}^*\text{Ta}(\text{CH}_2)\text{H}$  by  $\alpha$ -hydrogen migration.<sup>10,50</sup>

In the course of studies originally directed toward the development of new catalysts for C–H activation, we sought to prepare the triflate methylrhodium(III) complex  $\text{Cp}^*(\text{PMe}_3)_2\text{Re}(\text{CH}_3)\text{OTf}$  (**1**) in hopes of accessing the coordinatively unsaturated complex  $[\text{Cp}^*(\text{PMe}_3)_2\text{Re}(\text{CH}_3)][\text{OTf}]$  (**2**). In analogy to the Ir(III) chemistry we have previously reported, we set out to prepare **1** by protonolysis of  $\text{Cp}^*(\text{PMe}_3)_2\text{Re}(\text{CH}_3)_2$  (**3**).<sup>51,52</sup> However, surprisingly, treatment of **3** with HOTf resulted in formation of the thermally sensitive cationic hydridorhenium methylidene complex  $[\text{Cp}^*(\text{PMe}_3)_2\text{Re}(\text{CH}_2)(\text{H})][\text{OTf}]$  (**4**), rather than **1** (Scheme 1). Given the extreme scarcity of methylidene hydride compounds in the literature, our efforts shifted to understanding the mechanism of formation and reactivity of **4**. The results of experimental and theoretical studies addressing these questions are described in this report.

**Scheme 2.** Synthesis of  $\text{Cp}^*(\text{PMe}_3)_2\text{ReMe}_2$  (**3**)

## Results

### Synthesis and Characterization of $\text{Cp}^*(\text{PMe}_3)_2\text{ReMe}_2$ (**3**)

The dark red crystalline compound  $\text{Cp}^*(\text{PMe}_3)_2\text{ReCl}_2$  was synthesized in five previously reported steps from  $\text{Re}_2(\text{CO})_{10}$ .<sup>20,53–56</sup> Treatment of this dichloride complex with methylmagnesium chloride afforded **3** in 60% yield (Scheme 2). Further experiments revealed that dimethyl complex **3** could alternatively be synthesized by treatment of the known compound  $\text{Cp}^*\text{Re}(\text{O})\text{Me}_2$ <sup>57</sup> with excess trimethylphosphine at  $-78$  °C. Although the yield of this reaction is low, this route represents an abbreviated overall synthesis of **3** from commercially available starting materials.

The  $^1\text{H}$  NMR spectrum of **3** exhibits a singlet resonance at 1.48 ppm arising from the  $\text{Cp}^*$  ligand and a triplet at 0.04 ppm corresponding to the metal-bound methyl groups. A virtual triplet resonance at 1.09 ppm indicates two equivalent  $\text{PMe}_3$  ligands, suggesting a trans stereochemistry for this complex.<sup>58</sup> As predicted for such a geometry, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **3** contains a singlet at  $-35.3$  ppm for the two equivalent phosphine ligands.

Dark orange crystals of **3** were obtained by recrystallization from pentane at  $-30$  °C, and a single-crystal X-ray diffraction study of these crystals verified the trans stereochemistry of the compound. An ORTEP diagram of **3** is presented in Figure 1, along with representative bond lengths and angles.

Although not identical, the two Re–P bond lengths (2.333(2)/2.352(2) Å) are quite similar and consistent with reported bond lengths for similar complexes.<sup>59</sup> The P–Re–P angle (105.00(8)°) is somewhat contracted relative to the C–Re–C angle (141.0(3)°), perhaps due to the need to avoid unfavorable steric interactions between the  $\text{PMe}_3$  and the  $\text{Cp}^*$  methyl groups. The Re–C bond distances in **3** (2.236(7)/2.266(7) Å) are similar to reported Re(III)–C(sp<sup>3</sup>) distances in similar complexes.<sup>54,60</sup>

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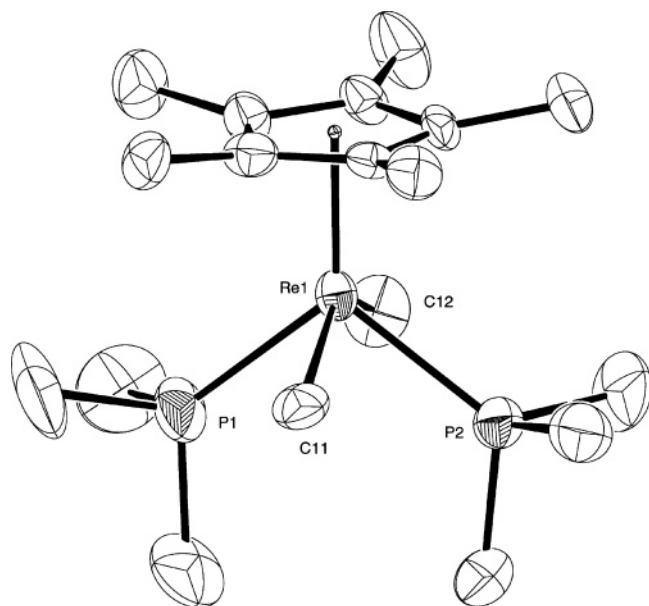
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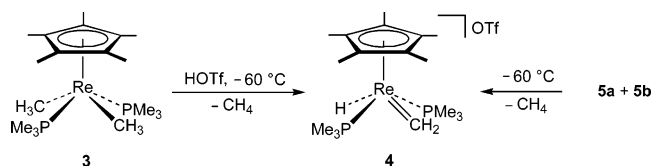
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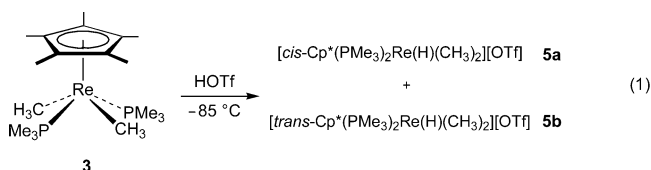
**Figure 1.** ORTEP diagram of one of two identical molecules of **3** located in the unit cell. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Re1–C11, 2.236(7); Re1–C12, 2.266(7); Re1–P1, 2.333(2); Re1–P2, 2.352(2); P1–Re1–P2, 105.00(8); C11–Re1–C12, 141.0(3). Selected analogous bond distances (Å) and angles (deg) for the second molecule of **3** (not pictured): Re2–C29, 2.353(8); Re2–C30, 2.273(7); Re2–P3, 2.552(2); Re2–P4, 2.210(2); P3–Re2–P4, 103.47(8); C29–Re2–C30, 140.1(3).

**Scheme 3.** Formation of Hydridorhenium Methylidene Compound **4**



**Observation of Initial Protonation Products.** Treatment of dimethyl compound **3** with 1 equiv of HOTf at room temperature yielded an intractable mixture of products, as did treatment of a dilute solution of **3** with HOTf at  $-78\text{ }^{\circ}\text{C}$ , followed by gradual warming to room temperature. However, when **3** was treated with HOTf at  $-90\text{ }^{\circ}\text{C}$ , variable-temperature NMR spectroscopy conducted at  $-85\text{ }^{\circ}\text{C}$  (without allowing the sample to warm) revealed two new rhenium hydride resonances: one triplet ( $^2J_{\text{HP}} = 48\text{ Hz}$ ) at  $-7.87\text{ ppm}$  and one doublet of doublets ( $^2J_{\text{HP}} = 43, 18\text{ Hz}$ ) at  $-10.45\text{ ppm}$ . A complicated set of multiply split trimethyl phosphine and Cp\* resonances was observed between 1.55 and 1.97 ppm. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of this mixture contained a singlet at  $-32.3\text{ ppm}$  as well as a set of coupled doublets at  $-38.9$  ( $^2J_{\text{PP}} = 20\text{ Hz}$ ) and  $-52.2$  ( $^2J_{\text{PP}} = 20\text{ Hz}$ ) ppm. Although the presence of a mixture of isomers and the extreme thermal instability of these species prevented more conclusive characterization, we propose that these complexes are geometric isomers of the Re(V) protonation product  $[\text{Cp}^*(\text{PMe}_3)_2\text{Re}(\text{H})(\text{CH}_3)_2][\text{OTf}]$  (**5a,b**) (eq 1). We assume complexes **5a,b** adopt capped four-legged piano stool geometries, as have been previously reported in the protonation of tungsten complexes.<sup>61</sup> The complexes **5a** and **5b** are designated as *cis* and *trans* on the basis of the relative

stereochemistry of the trimethylphosphine ligands, deduced from the  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra. However, the complexity of the NMR spectrum of the mixture of **5a,b** prevented more definite assignment of the stereochemistry of these complexes.



### Formation of Cationic Hydridorhenium Methylidene Complex **4**.

When the mixture of **5a** and **5b** was warmed to  $-60\text{ }^{\circ}\text{C}$  in variable-temperature NMR experiments, clean formation of both methane and the hydridorhenium methylidene compound **4** was observed (Scheme 3). Complex **4** could be formed directly by treatment of **3** with 1 equiv of HOTf at  $-78\text{ }^{\circ}\text{C}$  and observation at  $-60\text{ }^{\circ}\text{C}$ , although warming **4** to room temperature resulted in decomposition.

The yield of compound **4** was determined to be 99% on the basis of the starting dimethylrhenium compound **3** (determined by integration of **4** against an internal standard). Although a  $\text{CD}_2\text{Cl}_2$  solution of **4** could be stored at  $-78\text{ }^{\circ}\text{C}$  for a week in a sealed NMR tube without decomposition, multiple products were observed in its  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra immediately upon warming to  $-20\text{ }^{\circ}\text{C}$ .

The  $^1\text{H}$  NMR spectrum of **4** at  $-60\text{ }^{\circ}\text{C}$  exhibits a resonance at  $-7.1\text{ ppm}$  (tt, 1H,  $^3J_{\text{HH}} = 8\text{ Hz}$ ,  $^2J_{\text{HP}} = 56\text{ Hz}$ , Re-H) and a broad resonance at 14.5 ppm, assigned to the rhenium hydride and methylidene protons, respectively. The downfield shift of the methylidene resonance is diagnostic for this group.<sup>20–22</sup> The broadness of the methylidene proton resonance is likely due to hindered rotation around the Re–C bond, as this resonance sharpens to reveal splitting into a broad four-line pattern at  $-30\text{ }^{\circ}\text{C}$ , near the decomposition temperature of the complex.<sup>7,20,37</sup> No decoalescence of this signal is observed at  $-95\text{ }^{\circ}\text{C}$ . The structural assignment of **4** is confirmed by  $^{13}\text{C}\{^1\text{H}\}$  and DEPT NMR spectroscopies. The presence of a resonance at 229.5 ppm in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum that is inverted in the DEPT spectrum confirms the presence of a methylidene carbon in **4**.<sup>62</sup> The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, featuring a singlet at  $-28.1\text{ ppm}$ , indicates that complex **4** possesses a *trans* stereochemistry.

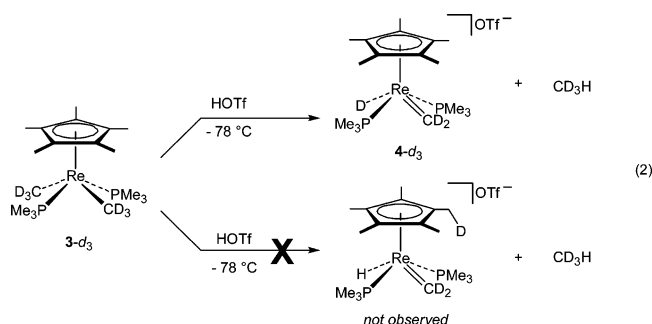
The possibility that reversible  $\alpha$ -hydrogen migration occurs in compound **4** was probed spectroscopically. Surprisingly, spin polarization transfer spectroscopy revealed no evidence of such migration in compound **4** on the NMR time scale at  $-50\text{ }^{\circ}\text{C}$ ; irradiation of the hydride resonance of **4** resulted in no attenuation of the methylidene resonance. The results of a gradient NOESY experiment performed at  $-45\text{ }^{\circ}\text{C}$  were consistent with this finding; no EXSY cross-peaks were observed between the rhenium hydride and methylidene proton resonances in experiments performed with short (400 ms) or long (800 ms) mixing times. As the *trans* stereochemistry of complex **4** predicts, no NOESY cross-peaks were observed between the hydride and methylidene resonances in either NOESY experiment.

The deuterated compound **3-d**<sub>6</sub> was prepared and treated with HOTf at  $-78\text{ }^{\circ}\text{C}$ . Observation of the resulting methylidene

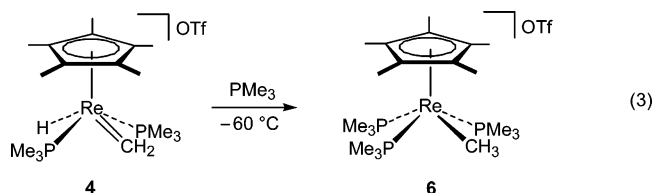
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complex **4-d<sub>3</sub>** by <sup>1</sup>H NMR at  $-60\text{ }^{\circ}\text{C}$  indicated no incorporation of protons into the methylidene or rhenium hydride positions of **4**. Furthermore, no deuterium resonances were observed for the Cp\* group of **4** by <sup>2</sup>H NMR at  $-60\text{ }^{\circ}\text{C}$  (eq 2). When the all proteo-dimethyl compound **3** was treated with DOTf using the procedure describe above, CH<sub>3</sub>D was generated and no deuterium incorporation was observed in **4**.

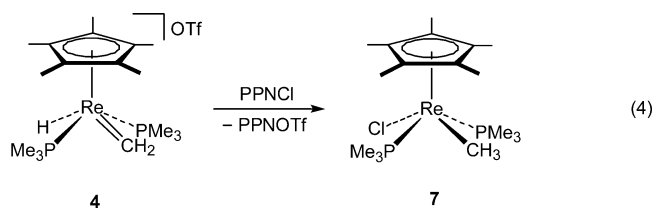


**Reactions with Nucleophiles.** The hydridorhenium methylidene complex **4** was found to react cleanly with the nucleophiles PMe<sub>3</sub> and chloride. However, the reactions occurred with hydrogen rearrangement. The new bonds were formed to the metal to give cationic methylrhenium complexes, rather than to the CH<sub>2</sub> group of the hydridorhenium methylidene. When **4** was generated at  $-78\text{ }^{\circ}\text{C}$  in CD<sub>2</sub>Cl<sub>2</sub> and treated with PMe<sub>3</sub>, [Cp\*(PMe<sub>3</sub>)<sub>3</sub>Re(CH<sub>3</sub>)](OTf) (**6**) was observed in the <sup>1</sup>H NMR spectrum at  $-60\text{ }^{\circ}\text{C}$  (eq 3).



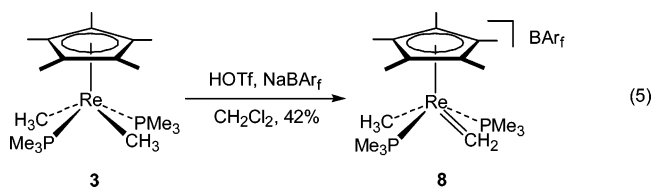
The <sup>1</sup>H NMR spectrum of **6** contains a singlet at 1.69 ppm arising from the Cp\* ligand, a resonance at 1.81 ppm for the PMe<sub>3</sub> ligand *trans* to the metal-bound methyl group, a virtual triplet at 1.42 ppm assigned to the two equivalent PMe<sub>3</sub> ligands *cis* to the methyl group, and a triplet of doublets at 0.43 ppm corresponding to the methyl group bound to rhenium. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum contains a doublet at  $-44.1\text{ ppm}$  assigned to the PMe<sub>3</sub> ligands *cis* to the methyl group, and a triplet at  $-49.7\text{ ppm}$  for the PMe<sub>3</sub> ligand *trans* to the methyl group. The phosphine adduct **6** could not be isolated, as it decomposed upon warming to  $0\text{ }^{\circ}\text{C}$ . The yield for this trapping reaction was determined to be 67% by integration of the <sup>1</sup>H NMR spectrum relative to internal standard.

Compound **4** was also found to react cleanly with chloride anion, and addition of PPnCl (PPN = (Ph<sub>3</sub>P)<sub>2</sub>N) to **4** at  $-78\text{ }^{\circ}\text{C}$  provided Cp\*(PMe<sub>3</sub>)<sub>2</sub>ReMeCl (**7**) in 93% yield (based on internal standard) (eq 4).



The <sup>1</sup>H NMR spectrum of **7** exhibits a singlet at 1.46 ppm arising from the Cp\* ligand, a virtual triplet at 1.20 ppm for the PMe<sub>3</sub> ligands, and a singlet at  $-0.05\text{ ppm}$  assigned to the rhenium-bound methyl group. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum contains only a singlet at  $-30.7\text{ ppm}$ , suggesting a *trans* stereochemistry for this complex. Unfortunately, NMR spectra of this reaction mixture became broad at temperatures above  $-20\text{ }^{\circ}\text{C}$ , and the methyl chloride compound **7** could not be isolated directly from the mixture (presumably due to the presence of free triflate anion). However, the identity of **7** was confirmed by independent synthesis. Treatment of Cp\*(PMe<sub>3</sub>)<sub>2</sub>Re(CH<sub>3</sub>)<sub>2</sub> with 1.0 equiv of HCl allowed for clean isolation of methyl chloride compound **7**. The <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of this compound are identical to those observed when it is accessed directly from **4**.

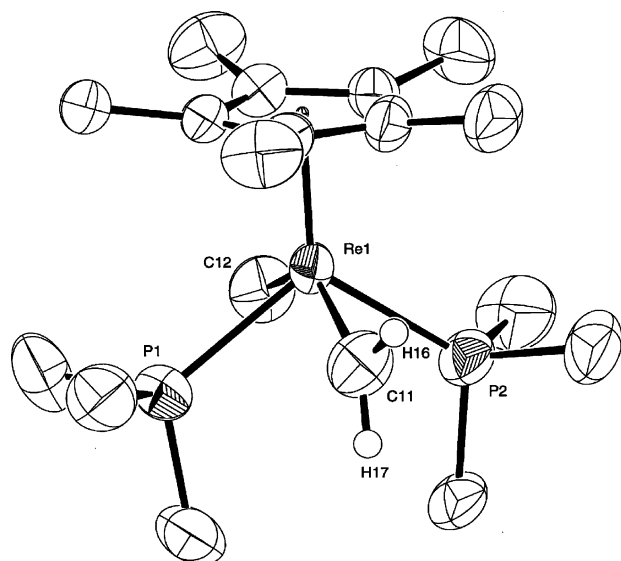
**Isolation of a Thermally Stable Rhenium Methylidene Complex.** Although warming dilute solutions of **4** to room temperature led to formation of complicated mixtures of products, removal of triflate anion from the reaction mixture by precipitation allowed for isolation of a thermally stable methylidene complex. A mixture of dimethyl compound **3** and NaBAR<sub>f</sub> was treated with HOTf in methylene chloride at  $-78\text{ }^{\circ}\text{C}$ , and then warmed slowly to room temperature. This procedure resulted in the formation of the complex [Cp\*(PMe<sub>3</sub>)<sub>2</sub>Re(CH<sub>2</sub>)(CH<sub>3</sub>)](BAR<sub>f</sub>) (**8**), which was isolated by recrystallization in 42% yield (eq 5).



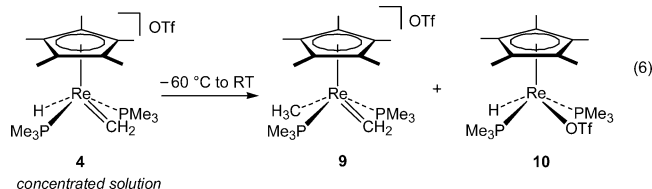
The <sup>1</sup>H NMR spectrum of **8** exhibits a sharp triplet methylidene proton resonance at 14.39 ppm (<sup>3</sup>J<sub>HP</sub> = 20 Hz), and a triplet at 0.30 ppm (<sup>3</sup>J<sub>HP</sub> = 18 Hz) indicates the presence of a rhenium-bound methyl group. X-ray-quality crystals were isolated by cooling a layered methylene chloride/pentane solution of **8** to  $-30\text{ }^{\circ}\text{C}$ . The results of the diffraction study confirmed the identity of this unexpected product (Figure 2). The Re–C bond distance for the CH<sub>2</sub> ligand (2.06 Å) is significantly shorter than that observed for the methyl ligand (2.25 Å). Additionally, the hydrogen atoms on the methylidene carbon were located and refined, and found to be perpendicular to the plane of the Cp\* ring.

It was found that treatment of the dimethyl compound **3** with [H(OEt<sub>2</sub>)<sub>2</sub>](BAR<sub>f</sub>) at  $-78\text{ }^{\circ}\text{C}$  in methylene chloride resulted in formation of **8** upon warming to room temperature, although the complex was not isolated using this procedure. Additionally, if concentrated solutions ( $\sim 0.1\text{ M}$ ) of the hydridorhenium methylidene complex **4** (150 mM) were allowed to warm slowly to room temperature without addition of a BAR<sub>f</sub> anion source, peaks consistent with the formation a triflate methyl methylidene complex (**9**) were observed in the reaction mixture (eq 6).

Unfortunately, these triflate-containing reactions were not as clean as the BAR<sub>f</sub>-based reactions, and it was not possible to isolate **9**. Interestingly, these concentrated triflate anion reactions also revealed formation of one new rhenium hydride species, identified by a <sup>1</sup>H NMR resonance at  $-8.69\text{ ppm}$  (*t*, <sup>2</sup>J<sub>HP</sub> = 55 Hz). On the basis of the multiplicity and coupling constant of



**Figure 2.** ORTEP diagram of **8**. Hydrogens, except for H16 and H17, are omitted for clarity. Selected bond distances (Å) and angles (deg): Re–C12, 2.250(5); Re–C11, 2.064(6); Re–P1, 2.401(2); Re–P2, 2.393(1); P1–Re–P2, 109.54(5); C11–Re–C12, 137.7(3); H16–C11–H17, 108(5); Re–C11–H16, 118(3); Re–C11–H17, 131(3).

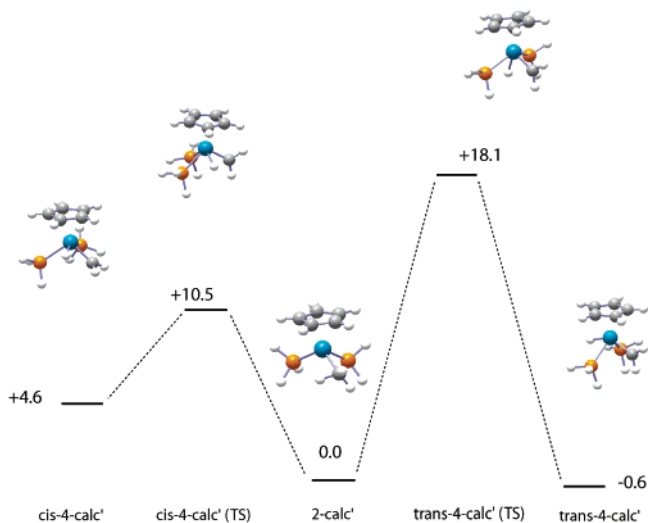


this resonance, as well as the overall stoichiometry of the conversion of **4** to **9**, we postulate that this species is the hydridorhenium triflate complex  $\text{Cp}^*(\text{PMe}_3)_2\text{Re}(\text{H})\text{OTf}$  (**10**).

**DFT Calculations.** The computed structures and energies of the rhenium complexes described above have been investigated using density functional theory (DFT) and compared with the structural data for **3** and **8** to examine the possible reaction pathways leading to formation of the methylidene complexes **4** and **8**. Calculations were performed concurrently with experimental studies, and in several cases, DFT results were used to help guide the course of the experimental work. The first series of calculations (complexes **2-calc**, **3-calc**, **4-calc**, and **8-calc**) were performed on the Cp analogues of compounds **2**, **3**, **4**, and **8**. The geometric parameters computed for  $\text{Cp}(\text{PMe}_3)_2\text{Re}(\text{CH}_3)_2$  (**3-calc**) are presented in Table 1, along with the experimental values for **3** (see Figure 1); reasonable agreement between the two is found. The bond distances in **3-calc** are from 0.01 to 0.04 Å too long, and the calculated bond angles are a few degrees more open than those in the crystal structure of **3**. This is not unexpected, given the hybrid functional used and the replacement of the Cp\* ligand by the simpler Cp group. Errors of this magnitude are also observed for the calculated structure of rhenium methylidene complex  $\text{Cp}(\text{PMe}_3)_2\text{Re}(\text{CH}_3)(\text{CH}_2)^+$  (**8-calc**), with the exception of the Re–C<sub>11</sub> bond length, which is even shorter in the computation (1.94 Å) than in the X-ray structure of **8** (2.06 Å). An error of roughly 0.1 Å is somewhat surprising, as the B3LYP approximation generally does somewhat better than this. However, in agreement with experiment, the computed Re–CH<sub>2</sub> distance of 1.94 Å in **8-calc** is significantly shorter than the Re–CH<sub>3</sub> distance (2.24 Å) in

**Table 1.** Calculated Bond Lengths and Bond Angles from  $\text{Cp}(\text{PMe}_3)_2\text{Re}(\text{CH}_3)^+$  (**2-calc**) and Related Species from DFT Results and X-ray Crystal Structures of the Corresponding Cp\* Species

	Re–Me(H), Å	Re–CH <sub>2</sub> , Å	Re–P, Å	P–Re–P, deg	Me(H)–Re–CH <sub>2</sub> , deg
<b>2-calc</b>	2.14		2.40	104.4	-
<b>3-calc</b>	2.25, 2.26		2.37, 2.40	107.1	144.1
<b>3</b>	2.235, 2.266		2.33, 2.35	105.0	141.0
<b>4-calc</b>	1.67 (H)	1.94	2.41	104.9	135.0
<b>8-calc</b>	2.24	1.94	2.45	106.5	142.0
<b>8</b>	2.250	2.064	2.401	109.5	137.7

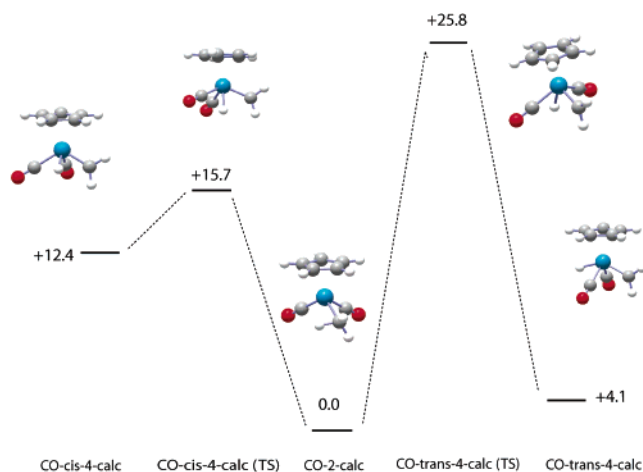


**Figure 3.** Relative energies (kcal/mol) of calculated structures of  $\text{Cp}(\text{PH}_3)_2\text{Re}(\text{CH}_3)^+$  and related species (see text) with phosphorus (orange) and carbon (gray) shown. In the optimized structure for **2-calc'**, the agostic H is shown on the left side of the methyl group positioned in a least-motion sense for the reaction to form **cis-4-calc'**.

this species. The CH<sub>2</sub> ligand of **8-calc** was found to be oriented perpendicular to the plane of the Cp ring, also in agreement with the X-ray structure of **8**.

The calculated structure of  $\text{Cp}(\text{PMe}_3)_2\text{Re}(\text{CH}_3)^+$  (**2-calc**) predicts a C–H agostic interaction between the CH<sub>3</sub> group and the metal center. Two of the Re–C–H bond angles are 116°, whereas the other is 98.8°. The corresponding Re–H distances are 2.79 and 2.55 Å. It was this observation that led us to search for a stable methylidene species (**trans-4-calc**) on the potential surface, and later, to look for complex **4** in the experimental studies described above. Indeed, the stable structure  $\text{Cp}(\text{PMe}_3)_2\text{Re}(\text{CH}_2)\text{H}^+$  (**trans-4-calc**) was found to lie 7.6 kcal/mol below  $\text{Cp}(\text{PMe}_3)_2\text{Re}(\text{CH}_3)^+$  (**2-calc**).

The possibilities for interconversion between **4** and **2** were examined with calculations on a further simplified model, where the PMe<sub>3</sub> ligands were replaced with PH<sub>3</sub> groups (complexes **2-calc'**, **trans-4-calc'**, and **cis-4-calc'**). An even stronger C–H agostic interaction is apparent in the model methyl cation  $\text{Cp}(\text{PH}_3)_2\text{Re}(\text{CH}_3)^+$  (**2-calc'**) compared to the PMe<sub>3</sub> case **2-calc**: **2-calc'** has an elongated methyl C–H bond of 1.17 Å and a short 2.01 Å Re–H contact with an acute Re–C–H angle of 72°. The relative energies for the **calc'** series of compounds, including electronic plus zero-point energy corrections at 0 K from calculated vibrational frequencies, are shown in Figure 3. The relative energies were determined for structures that are all either local minima or true transition states. Other computed thermochemical energy differences, such as relative free energies



**Figure 4.** Relative energies (kcal/mol) of calculated structures of  $\text{Cp}(\text{CO})_2\text{Re}(\text{CH}_3)^+$  and related species.

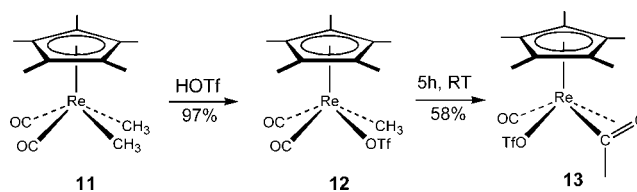
at 298 K, differed very little (less than 1 kcal/mol) from the energies presented in the figure.

The *trans*-hydridorhenium methylidene complex *trans-4-calc'* lies slightly lower (0.6 kcal/mol) in energy than the methyl species *2-calc'*. (Recall that for the calculated  $\text{Cp}/\text{PMe}_3$  species the methylidene *trans-4-calc* was 7.5 kcal/mol lower than *2-calc*.) We also located a stable cis isomer, *cis-4-calc'*, which lies 4.6 kcal/mol above *2-calc'* and 5.2 kcal/mol above the trans form, *trans-4-calc'*. Two transition states were identified. The transition structure *cis-4-calc'*(TS), which is 10.5 kcal/mol above the methyl cation *2-calc'*, leads to the complex *cis-4-calc'*. The second intermediate, *trans-4-calc'*(TS), which is at 18.1 kcal/mol above *2-calc'*, lies along the pathway to the trans species *trans-4-calc'*. The former transition state resembles a “least motion” migration of the proton from the agostic methyl proton to the methylidene structure. The latter structure, *trans-4-calc'*-(TS), actually involves passing the proton underneath the Re center between the P–Re–P linkage, generating a hydride ligand in a location trans to the Cp ligand at the barrier *en route* to the *trans* structure.

Calculations were also performed on the Cp models with carbonyl-ligated rhenium centers (complexes *CO-2-calc*, *CO-trans-4-calc*, and *CO-cis-4-calc*). As shown in Figure 4, it is not energetically favorable for the methyl cation in this series,  $\text{Cp}(\text{CO})_2\text{Re}(\text{CH}_3)^+$  (*CO-2-calc*), to undergo hydride migration to form the hydridorhenium methylidene complex *trans-Cp*( $\text{CO})_2\text{Re}(\text{CH}_2)\text{H}^+$  (*CO-trans-4-calc*). Instead, we find *CO-trans-4-calc* to be 4.1 kcal/mol less stable than the corresponding methylrhenium complex *CO-2-calc*, and the cis isomer *cis-Cp*( $\text{CO})_2\text{Re}(\text{CH}_2)\text{H}^+$  (*CO-cis-4-calc*) is once again higher in energy, at 12.4 kcal/mol. The calculated transition state conversion to *CO-cis-4-calc* is at 15.7 kcal/mol, while the corresponding transition state conversion to the trans complex *CO-trans-4-calc* is even higher, at 25.8 kcal/mol.

The above calculations have dealt with the various possible pathways between the methylidene complex **4** and methyl cation species **2**. As noted in eq 1 and Scheme 3, the methylidene compound **4** was observed experimentally upon protonation of the neutral dimethyl complex **3** via the observed protonated intermediates **5a** and **5b**. Here we consider briefly the relative energies involved when the calculated protonated complex  $\text{CpL}_2\text{Re}(\text{CH}_3)_2\text{H}^+$  (**5-calc**) eliminates  $\text{CH}_4$  to yield the methyl cation

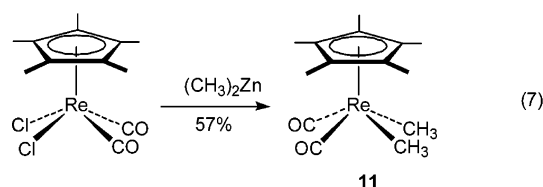
**Scheme 4.** Formation of Methylrhenium Triflate Complex **12** and Migration to Acyl Complex **13**



$\text{CpL}_2\text{Re}(\text{CH}_3)^+$  (**2-calc**). The energy for this process, evaluated at the respective theoretical minima, is found to be favorable in both cases (−16.3 kcal/mol for  $\text{L} = \text{PH}_3$  species and −17.2 kcal/mol for  $\text{L} = \text{CO}$  species). As discussed above, the subsequent step to form the methylidene species is favorable for the phosphine complex *trans-4-calc* but unfavorable for the CO complex *CO-trans-4-calc*.

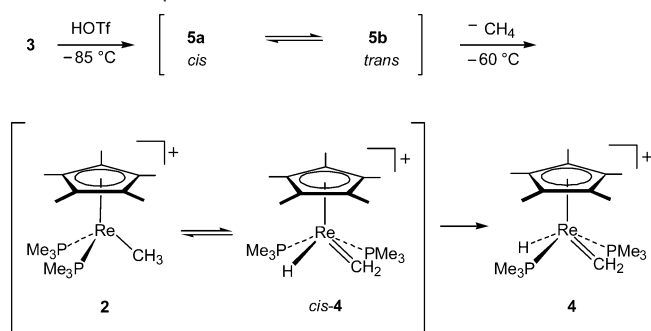
Finally, we note that all of the preceding calculations have been carried out on singlet potential energy surfaces. We have examined the lowest-lying triplet state of the coordinatively unsaturated  $\text{Cp}(\text{PH}_3)_2\text{Re}(\text{CH}_3)^+$  species *2-calc'*. This state corresponds to a d–d excitation of the low-spin Re(III) complexes described above, leading to a  $5d^4$  configuration with two unpaired electrons. The triplet energy is found to be extremely low, only 6.4 kcal/mol above the ground-state singlet of *2-calc'*. In the triplet state, the  $\text{CH}_3$  group does not behave in an agostic manner, but rather exhibits normal C–H bonds and Re–C–H bond angles and a Re–H distance of no less than 2.72 Å. The energy of the triplet state is actually lower than that of the transition states for conversion of *2-calc'* into the *trans*- or *cis*-methylidene complexes *trans-4-calc'* and *cis-4-calc'*. These results suggest even lower pathways might possibly be sampled if spin–orbit coupling effects could induce singlet–triplet potential energy curve-crossings, a possibility that is beyond the scope of the present studies. By contrast, the triplet state for the carbonylated species *CO-2-calc* is quite high in energy (38 kcal/mol).

**Synthesis of Carbonyl Complexes.** To test the calculation-based predictions about the reactivity of the carbonyl complexes, we prepared the dicarbonyl compound  $\text{Cp}^*(\text{CO})_2\text{Re}(\text{CH}_3)_2$  (**11**). Although this compound has been prepared previously, a somewhat improved procedure for its synthesis is described below.<sup>60,63</sup> The dichloride compound  $\text{Cp}^*(\text{CO})_2\text{ReCl}_2$  was prepared in five steps from commercially available starting materials according to previously reported procedures. Addition of 1.2 equiv of dimethylzinc to the dichloride complex afforded the *cis*-dimethylrhenium complex **11** (eq 7).



Treatment of **11** with HOTf led to clean formation of the methyl triflate complex  $\text{Cp}^*(\text{CO})_2\text{Re}(\text{CH}_3)\text{OTf}$  (**12**) (Scheme 4). The  $^1\text{H}$  NMR spectrum of **12** contains a singlet at 1.14 ppm assigned to the  $\text{Cp}^*$  methyl groups and a singlet at 0.39 ppm corresponding to the rhenium-bound methyl ligand. The rhe-

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**Scheme 5.** Proposed Mechanism of Formation of **4**

nium-bound methyl carbon exhibits a  $^{13}\text{C}\{^1\text{H}\}$  NMR signal at  $-19.41$  ppm. As predicted by DFT calculations, no methyldene species were detected in the reaction mixture.

The dicarbonyl methylrhenium triflate complex **12** was found to be moderately unstable in solution at room temperature, and over the course of several hours it was converted cleanly to a new product, **13**. The  $^1\text{H}$  NMR spectrum of **13** contained a singlet at 1.25 ppm corresponding to the Cp\* ligand, and a singlet integrating to three protons at 1.20 ppm for a new methyl group. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **13** was found to contain no upfield rhenium–methyl groups, but a resonance at 22.25 ppm was assigned to the new acyl methyl group. Finally, the IR spectrum of **13** revealed a new stretching frequency at  $1385\text{ cm}^{-1}$ . On the basis of these data, the structure of **13** is tentatively assigned as the  $\eta^2$ -acyl complex depicted in Scheme 4.

## Discussion

The formation of hydridorhenium methylidene complex **4** is proposed to occur by the mechanism depicted in Scheme 5. Protonation of the rhenium dimethyl complex **3** leads to formation of the observed rhenium(V) hydride complexes **5a,b**. The observation of the dialkylrhenium(V) hydride complexes **5a,b** is relevant not only to the mechanism of formation of **4**, but also to C–H activation reactions reported previously by our group.<sup>51,52</sup> In particular, we have accumulated some evidence that analogous dialkyl hydrido Ir(V) complexes are reasonable intermediates in our Ir(III)-mediated C–H activation reactions.<sup>64</sup> The observation of the dialkylrhenium(V) hydride complexes **5a,b** provides an additional argument for the intermediacy of analogous species in our Ir(III)-mediated C–H activation reactions.

We propose that reductive elimination of methane from the complex **5b** (which should have mutually cis methyl and hydride ligands) leads to the formation of the unobserved methyl cation **2**, which undergoes  $\alpha$ -hydrogen migration to form **4**. As other  $\alpha$ -hydrogen migration reactions are known to proceed with cis stereochemistry,<sup>42,65–67</sup> we suggest that the unobserved intermediate **cis-4** may be an intermediate on the pathway to formation of **4** (Scheme 5), although the DFT calculations show complex **4** to be the thermodynamically preferred species. As described in the Introduction, literature precedent supports this

proposed mechanism.<sup>9,10,44–50,65,68–72</sup> The DFT calculation of a transition state for the direct conversion of **2-calc** into **4-calc** (without the intermediacy of **cis-4-calc**) raises the intriguing possibility that, in this system, the  $\alpha$ -hydrogen migration reaction from **2** proceeds directly to the trans isomer **4**.

The formation of **4** is a marked departure from the chemistry of the isoelectronic iridium methyl triflate complex Cp\*(PMe<sub>3</sub>)–Ir(CH<sub>3</sub>)OTf reported by our group.<sup>51</sup> We propose that the increased electron density afforded the rhenium center by its additional phosphine ligand allows for the migration chemistry to occur with complex **2**.<sup>73</sup> It is also possible that the added steric bulk of the additional phosphine ligand inhibits coordination by the triflate anion.<sup>74</sup> Finally, the stability of **4** compared to its iridium analogue could also be due to a greater propensity for rhenium to undergo metal–ligand multiple bonding.<sup>75</sup>

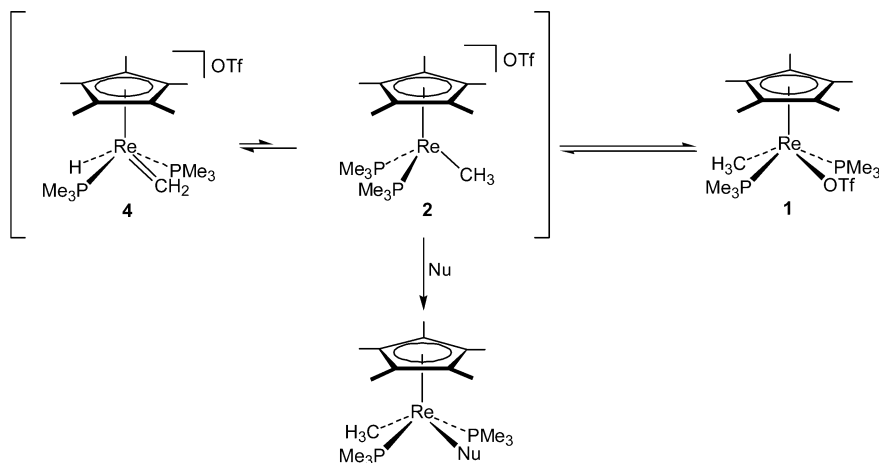
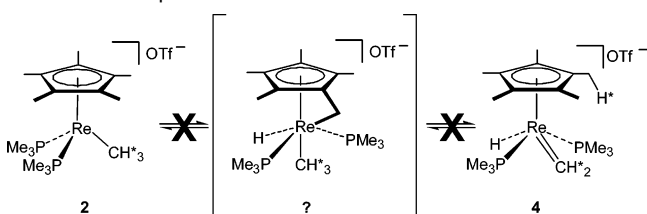
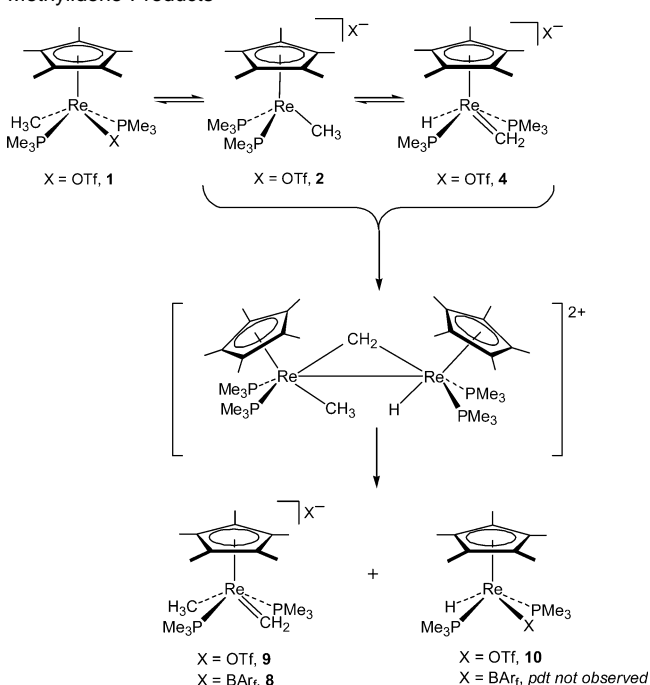
The results of the DFT calculations also support the proposed mechanism in Scheme 5. As discussed previously, formation of **2-calc** by elimination of CH<sub>4</sub> from **5-calc** was found to be exothermic ( $-16.3$  kcal/mol for the PH<sub>3</sub> complex species,  $-17.2$  kcal/mol for the CO ligated species). The subsequent formation of the *trans*-methylidene species **4** is calculated to be energetically favorable for the PH<sub>3</sub> and PMe<sub>3</sub> complexes (*trans-4-calc* and *trans-4-calc'*) but unfavorable for the carbonylated species **CO-trans-4-calc**. While the calculated thermochemistry is consistent with the experimental observations, we note the significant barriers that were calculated for the formation of either cis or trans forms of **4-calc'** from the methyl cation **2-calc'**.

The reactivity of the hydridorhenium methylidene compound **4** toward trimethylphosphine was initially surprising, as previous reports of methylidene reactivity led us to expect attack at the CH<sub>2</sub> carbon, leading to formation of an ylide complex.<sup>19,46,48,76,77</sup> In a closely related example, Radzewich and Heinekey observed that an ylide species was produced upon treatment of a cationic rhenocene methylidene with PMe<sub>3</sub>.<sup>22</sup> It is possible that in our system, **4** reacts directly with PMe<sub>3</sub> to form an ylide, which subsequently rearranges to form **6**. However, Green and co-workers have shown that such rearrangements proceed via reversible  $\alpha$ -migration equilibria (i.e., via species analogous to **4**).<sup>46–48</sup> Given this literature precedent and the reactivity of **4** with chloride ion, we propose that **4** and methylrhenium complex **2** exist in rapid equilibrium, and that the coordinatively unsaturated complex **2** is more effectively trapped (in a rate-determining step) by nucleophiles than is the hydridorhenium methylidene complex **4** (Scheme 6).

The hypothesis that methyl cation **2** and hydridorhenium methylidene complex **4** exist in equilibrium is supported both by the literature precedent mentioned above and by calculations. As described in the Results section, the Cp/PH<sub>3</sub> analogue of **4**

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**Scheme 6.** Proposed Reversible  $\alpha$ -Migration Equilibrium**Scheme 7.** Proposed Fulvalene Intermediate**Scheme 8.** Proposed Mechanism for Formation of Methylrhenium Methylidene Products

was calculated to be approximately 1.0 kcal/mol more stable than the corresponding analogue of **2**.

Given the proposed reversible  $\alpha$ -hydrogen migration equilibrium between **2** and **4**, we were surprised to observe no magnetization transfer between the methylidene protons and rhenium-bound hydride resonances in **4** in the EXSY experiment performed on this complex.<sup>9,10,50,72</sup> We considered the possibility that lack of magnetization transfer was due to proton exchange between the methylidene group of **4** and the Cp\* ligand of this complex via the formation of a fulvalene intermediate (Scheme 7).<sup>78</sup> To investigate this possibility, the deuterated compound **3-d<sub>6</sub>** was prepared and treated with HOTf at  $-78\text{ }^\circ\text{C}$  (eq 2). The resulting compound **4-d<sub>3</sub>** showed no scrambling of the labeled methylidene and deuteride resonances with the Cp\* ligand. These results indicate that a fulvalene intermediate is not involved in the exchange of **2** and **4**. Given this finding, lack of magnetization transfer between the methylidene and hydride protons of **4** can be explained if the equilibrium of **2** with **4** is rapid on the chemical time scale, but slow on the NMR time scale at the temperatures accessible to **4**.<sup>79</sup>

The formation of methylrhenium methylidene complexes in both the triflate (**9**) and BARf anion systems (**8**) can be understood in terms of the  $\alpha$ -hydrogen migration equilibrium described above. It is proposed that the carbene ligand of **4** acts as a nucleophilic trap for **2** (Scheme 8). Although the resulting dicationic intermediate may look somewhat unusual, dicationic bimetallic complexes are well known.<sup>80</sup> Ligand exchange between **4** and **2** via the resulting bridging carbene intermediate

results in formation of the observed methylrhenium methylidene complexes. Bimetallic complexes of bridging methylidene ligands are well preceded in the literature.<sup>50, 81–89</sup>

The mechanism depicted in Scheme 8 would also produce Cp\*(PMe<sub>3</sub>)<sub>2</sub>Re(H)OTf (**10**) stoichiometrically, and indeed, <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR resonances consistent with this complex were observed in the reaction mixtures containing triflate anion. The

(78) We thank a reviewer for suggesting this explanation for lack of magnetization transfer.

(79) This question would be best probed by a deuterium scrambling experiment. However, the nature of the synthesis of **4** (by hydride migration from an intact methyl group) makes it essentially impossible to obtain selectively deuterium-labeled compound.

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finding that the triflate methyl methylidene complex **9** was cleanly formed only under high concentration reaction conditions is consistent with this ligand redistribution mechanism, as such a mechanism may involve a second-order rate dependence on the concentration of rhenium starting material. (The fact that this reaction produces significant quantities of byproducts precluded its study by rigorous kinetic techniques.)

The difference in reactivity between the triflate and  $\text{BARf}$  systems is marked. While a rhenium hydride complex is observed in the presence of triflate (**10**), no such complex is observed when triflate is replaced with  $\text{BARf}$ . The triflate system is somewhat sensitive to concentration effects, while the  $\text{BARf}$  system forms the methylrhenium methylidene product over a wide range of concentrations. These observations can be understood in terms of the more coordinating nature of the triflate anion compared to that of  $\text{BARf}$ .<sup>90</sup> It is proposed that hydridorhenium methylidene complex **4** is in equilibrium not only with the coordinatively unsaturated methyl cation **2**, but also with a triflate-trapped complex, **1** (Scheme 6, above). Addition of  $\text{NaBARf}$  to this system causes precipitation of  $\text{NaOTf}$ , and prevents formation of **1**. This would be expected to increase the overall concentration of coordinatively unsaturated rhenium methyl complex **2**, and lead to more facile conversion of **4** and **2** to methyl methylidene complex **8** by the mechanism depicted in Scheme 8. The absence of any  $\text{BARf}$ -containing rhenium hydride complexes at room temperature is also consistent with the decreased coordination ability of the  $\text{BARf}$  anion. A coordinatively unsaturated rhenium hydride complex would likely be highly reactive, and potentially subject to rapid thermal decomposition.

As predicted by our calculations, no evidence for  $\alpha$ -hydrogen migration chemistry was observed in the dicarbonyl methylrhenium complex **12**. This observation could be due to any of the following three distinctive features of the carbonyl system. First, as predicted by calculations, a higher intrinsic barrier to  $\alpha$ -hydrogen migration may exist for conversion of the triflate-dissociated complex derived from **12** to its carbene analogue than exists for the migration from **2** to form **5** (both systems were calculated without an explicit counteranion). Second, also as predicted by calculations, the thermodynamics of the system involving **12** may favor the cationic methylrhenium species over the isomeric methylidene hydride. Finally, dissociation of triflate anion from **10** may be made more difficult than the analogous dissociation from **1** due to the relative electron deficiency of **10**. Without triflate dissociation,  $\alpha$ -hydrogen migration cannot occur.

## Conclusions

In the course of studies directed toward the synthesis of the methylrhenium cation **2**, novel cationic rhenium methylidene complexes were synthesized and characterized. The novel dimethylrhenium(III) complex  $\text{Cp}^*(\text{PMe}_3)_2\text{ReMe}_2$  (**3**) was prepared and fully characterized. Protonation of **3** with HOTf allowed for observation of the isomeric hydridorhenium(V) products **5a,b** at  $-85^\circ\text{C}$  by  $^1\text{H}$  NMR spectroscopy. Upon reductive elimination of methane, the hydridorhenium(III) methylidene complex  $[\text{Cp}^*(\text{PMe}_3)_2\text{Re}(\text{CH}_2)(\text{H})][\text{OTf}]$  (**4**) was observed and characterized by NMR spectroscopy at  $-60^\circ\text{C}$ .

Using density functional theory approaches, the reaction pathways involved in formation of the methylidene complexes **4** and their interconversion with methyl cation complexes **2** were examined for both phosphine and carbonyl complexes of  $\text{Re(III)}$ .

The formation of **4** represents a facile route into an interesting structural class, and this compound was found to undergo reactions with nucleophiles to form trapped methylrhenium(III) complexes. These and other observations led to the conclusion that the  $\alpha$ -hydrogen migration that forms **5** is reversible. Interestingly, treatment of **3** with HOTf in the presence of  $\text{NaBARf}$  yields a thermally stable methyl methylidene complex (**8**), presumably via a bridging carbene intermediate. The dicarbonyl methylrhenium triflate complex  $\text{Cp}^*(\text{CO})_2\text{Re}(\text{CH}_3)\text{OTf}$  (**12**) was prepared and, in accord with predictions from calculations, found to not form the analogous hydridorhenium methylidene complex. Our findings indicate that the level of electron density at the metal center has a marked influence on the proclivity of these complexes to undergo  $\alpha$ -migration reactions.

## Experimental Section

**General Procedures.** Unless otherwise noted, reactions and manipulations were performed at  $22^\circ\text{C}$  in an inert atmosphere ( $\text{N}_2$ ) glovebox, or using standard Schlenk and high-vacuum line techniques. Glassware was dried overnight at  $150^\circ\text{C}$  before use. All NMR spectra were obtained using Bruker AM-400, AMX-400, or DRX-500 MHz spectrometers. Except where noted, all NMR spectra were acquired at room temperature.  $^1\text{H}$  NMR spectra were referenced to residual protonated solvent, and chemical shifts are reported in parts per million downfield from tetramethylsilane.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were referenced to an external standard of 85%  $\text{H}_3\text{PO}_4$  and are reported in parts per million downfield from this resonance. Chemical shifts in  $^{19}\text{F}$  spectra are reported relative to external  $\text{CF}_3\text{Cl}$  at 0.00 ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were referenced to solvent. In cases where assignment of  $^{13}\text{C}\{^1\text{H}\}$  NMR resonances from the initial  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum was ambiguous, resonances were assigned using standard DEPT 45, 90, and/or 135 pulse sequences. Infrared (IR) spectra were recorded using samples prepared as KBr pellets, and spectral data are reported in wavenumbers ( $\text{cm}^{-1}$ ). Mass spectrometric (MS) analyses were obtained at the University of California, Berkeley, Mass Spectrometry Facility on VT ProSpec, ZAB2-EQ, or 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.

Sealed NMR tubes were prepared by attaching the NMR tube directly to a Kontes high-vacuum stopcock via a Cajon Ultra-Torr reducing union, and then flame-sealing on a vacuum line. Reactions with gases and low-boiling liquids involved condensation of a calculated pressure of gas from a bulb of known volume into the reaction vessel at  $-196^\circ\text{C}$ . Known-volume bulb vacuum transfers were accomplished with a digital MKS Baratron gauge attached to a high-vacuum line.

**Materials.** Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Celite (Aldrich), silica gel (Merck 60, 230–400), and alumina (Brockman I, Aldrich) were dried in vacuo at  $250^\circ\text{C}$  for 48 h. Toluene, pentane, hexanes, methylene chloride, and benzene (Fisher) were passed through a column of activated alumina (type A2, size  $12 \times 32$ , Purify Co.) prior to use. Diethyl ether and tetrahydrofuran (Fisher) were distilled from purple sodium/benzophenone ketyl under  $\text{N}_2$  prior to use. Deuterated solvents (Cambridge Isotope Laboratories) were purified by vacuum transfer from the appropriate drying agent ( $\text{Na}/\text{Ph}_2\text{CO}$  or  $\text{CaH}_2$ ) and stored over 3-Å molecular sieves prior to use. Trimethylphosphine (Aldrich) was vacuum-transferred from sodium metal prior to use.  $\text{Me}_3\text{SiCl}$  was distilled and stored over 4-Å molecular sieves prior to use.  $\text{PPNCl}$  was dissolved in benzene, placed over 4-Å

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molecular sieves, filtered, and pumped to dryness prior to use.  $\text{CCl}_4$  was dried over 4-Å molecular sieves prior to use. The compounds  $\text{Cp}^*\text{Re}(\text{CO})_3$ ,<sup>20</sup>  $\text{Cp}^*\text{Re}(\text{O})_3$ ,<sup>55</sup>  $\text{Cp}^*\text{ReCl}_4$ ,<sup>56</sup>  $\text{Cp}^*\text{Re}(\text{O})\text{Cl}_2$ ,<sup>53</sup>  $\text{Cp}^*(\text{PMe}_3)_2\text{ReCl}_2$ ,<sup>54</sup>  $\text{NaBARf}_4$ ,<sup>90</sup> and  $\text{H}(\text{OEt})_2\text{BARf}_4$ <sup>90</sup> were prepared according to published literature procedures.

**$\text{Cp}^*(\text{PMe}_3)_2\text{ReMe}_2$  (3), Method 1.**  $\text{Cp}^*(\text{PMe}_3)_2\text{ReCl}_2$  (126 mg, 0.231 mmol) was dissolved in diethyl ether (4 mL) in a sealable glass reaction vessel to give a dark red solution. Methylmagnesium chloride was added as a THF solution (0.18 mL, 3.0 M, 0.53 mmol) with stirring. The reaction vessel was sealed and heated to 70 °C for 12 h. After this time, the solution color was pale lemon yellow. After cooling to room temperature, solvent was removed under reduced pressure, and the yellow residue was extracted with pentane (3 × 5 mL). The combined pentane extracts were passed through a plug of silanized silica gel. Crystallization of the resulting orange solution gave dark orange crystals (68 mg, 60%). Anal. Calcd for  $\text{C}_{18}\text{H}_{39}\text{P}_2\text{Re}$ : C, 42.93; H, 7.80. Found: C, 43.22; H, 8.12.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 400 MHz):  $\delta$  1.48 (s, 15H,  $\text{C}_5(\text{CH}_3)_5$ ), 1.09 (virtual triplet, 18H,  $\text{P}(\text{CH}_3)_3$ ), 0.04 (t, 6H,  $^3J_{\text{HP}} = 12$  Hz,  $\text{Re-CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 125 MHz):  $\delta$  87.0 (t,  $^2J_{\text{CP}} = 3$  Hz,  $\text{C}_5(\text{CH}_3)_5$ ), 16.2 (six-line pattern,  $\text{P}(\text{CH}_3)_3$ ), 9.5 (s,  $\text{C}_5(\text{CH}_3)_5$ ), -26.6 (t,  $^2J_{\text{CP}} = 15$  Hz,  $\text{Re-CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 162 MHz):  $\delta$  -35.3 (s,  $\text{P}(\text{CH}_3)_3$ ). IR (KBr): 2972, 2909, 2817, 2070, 2001, 1426, 1371, 1293, 1274, 949  $\text{cm}^{-1}$ . MS (EI):  $m/z = 504$  ( $\text{M}^+$ ).

**Crystallographic Study of  $\text{Cp}^*(\text{PMe}_3)_2\text{ReMe}_2$  (3).** Data were collected and interpreted using a SMART CCD area detector with graphite-monochromated Mo  $\text{K}\alpha$  radiation. Hydrogen atoms were included but not refined. Random errors and thermal motion erased any sign of localization in the  $\text{Cp}^*$  rings. The rhenium-bound methyl groups were found to be trans-disposed to one another in this piano-stool complex. Important bond distances and angles are included in Figure 1. Crystallographic data follow: space group  $Pbca$ ,  $a = 17.4197(4)$  Å,  $b = 14.6308(3)$  Å,  $c = 32.8142(3)$  Å,  $V = 8363.2(2)$  Å<sup>3</sup>,  $Z = 16$ ,  $D_{\text{calc}} = 1.600$  g/cm<sup>3</sup>,  $\mu(\text{Mo K}\alpha) = 59.62$  cm<sup>-1</sup>, number of unique reflections = 8398,  $R = 2.4\%$ .

**$\text{Cp}^*(\text{PMe}_3)_2\text{ReMe}_2$  (3), Method 2.**  $\text{Cp}^*\text{ReO}_3$  (95 mg, 0.26 mmol) was dissolved in a 50/50 mixture of hexane and toluene (15 mL), forming a dark yellow solution. This solution was cooled to -78 °C in a dry ice/2-propanol bath, and  $\text{Me}_3\text{Al}$  (54  $\mu\text{L}$ , 0.57 mmol) was added dropwise, resulting in a color change to dark red. A solution of  $\text{PMe}_3$  in hexane/toluene (0.085 M, 10 mL) was immediately transferred into this solution via cannula, resulting in a color change to yellow/orange. This solution was stirred at -78 °C for 5 h, and then warmed to room temperature, where it was stirred for 2 h. After this time, the volatile materials were removed under reduced pressure, and the residue was dissolved in pentane and passed through a plug of silanized silica gel. Removal of volatile materials under reduced pressure gave an orange oil identical by  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy to  $\text{Cp}^*(\text{PMe}_3)_2\text{ReMe}_2$  prepared by method 1 (30 mg, 23%).

**$\text{Cp}^*(\text{PMe}_3)_2\text{Re}(\text{CD}_3)_2$  (3-d<sub>6</sub>).**  $\text{Cp}^*(\text{PMe}_3)_2\text{ReCl}_2$  (150 mg, 0.275 mmol) was dissolved in diethyl ether (5 mL) in a sealable glass reaction vessel to give a dark red solution. Methylmagnesium iodide-d<sub>3</sub> was added as an ether solution (0.63 mL, 1.0 M, 0.63 mmol) with stirring. The reaction vessel was sealed and heated to 75 °C for 18 h. After this time, the solution color was pale lemon yellow. After cooling to room temperature, solvent was removed under reduced pressure, and the yellow residue was extracted with pentane (3 × 5 mL). The combined pentane extracts were passed through a plug of silanized silica gel. Crystallization of the resulting orange solution gave dark orange crystals (118 mg, 85%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 400 MHz):  $\delta$  1.57 (s, 15H,  $\text{C}_5(\text{CH}_3)_5$ ), 1.17 (virtual triplet, 18H,  $\text{P}(\text{CH}_3)_3$ ).  $^2\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 76.8 MHz):  $\delta$  -0.04 (s,  $\text{Re-CD}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 162 MHz):  $\delta$  -35.0 (s,  $\text{P}(\text{CH}_3)_3$ ).

**Observation of  $[\text{Cp}^*(\text{PMe}_3)_2\text{Re}(\text{H})(\text{CH}_3)_2][\text{OTf}]$  (5a,b) at Low Temperature in Solution.**  $\text{Cp}^*(\text{PMe}_3)_2\text{ReMe}_2$  (24 mg, 0.047 mmol) was dissolved in  $\text{CD}_2\text{Cl}_2$  (0.5 mL) in an NMR tube fitted with a Cajon adaptor. The tube was frozen in liquid nitrogen (-196 °C). Against a

positive pressure of nitrogen, HOTf was added as a  $\text{CD}_2\text{Cl}_2$  solution (50  $\mu\text{L}$ , 1.02 M, 0.051 mmol). The tube was flame-sealed and stored frozen until the NMR probe was cooled to -85 °C. At this time, the tube was briefly thawed to -130 °C in a pentane/liquid nitrogen bath and quickly transferred into the cooled probe. The reaction mixture was characterized by  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopies at -85 °C. Although the presence of a mixture of compounds (including unreacted dimethylrhenium compound **3** and one broad, probably paramagnetic species) was observed, the resonances assigned to the protonation products **5a** and **5b** are listed below.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 500 MHz, -85 °C):  $\delta$  1.43–2.41 (m,  $\text{P}(\text{CH}_3)_3 + \text{C}_5(\text{CH}_3)_5$ , **5a** + **5b** + **3**), 1.02 (br s, 6H,  $\text{Re-CH}_3$ , **5a**), -0.15 (br t, 6H,  $\text{Re-CH}_3$ , **5b**), -7.88 (t, 1H,  $^2J_{\text{HP}} = 48$  Hz,  $\text{Re-H}$ , **5a**), -10.45 (dd, 1H,  $^2J_{\text{HP}} = 43$ , 18 Hz,  $\text{Re-H}$ , **5a**).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 203 MHz, -85 °C):  $\delta$  -32.3 (s,  $\text{P}(\text{CH}_3)_3$ , **5a**), -38.9 (d,  $^2J_{\text{PP}} = 20$  Hz,  $\text{P}(\text{CH}_3)_3$ , **5b**), -52.2 (d,  $^2J_{\text{PP}} = 20$  Hz,  $\text{P}(\text{CH}_3)_3$ , **5b**).

**Characterization of  $[\text{Cp}^*(\text{PMe}_3)_2\text{Re}(\text{CH}_2)(\text{H})][\text{OTf}]$  (4) at Low Temperature in Solution.**  $\text{Cp}^*(\text{PMe}_3)_2\text{ReMe}_2$  (26 mg, 0.052 mmol) was dissolved in  $\text{CD}_2\text{Cl}_2$  (0.5 mL) in an NMR tube fitted with a Cajon adaptor. The tube was cooled to -78 °C in a dry ice/2-propanol bath. Against a positive pressure of nitrogen, HOTf was added as a  $\text{CD}_2\text{Cl}_2$  solution (134  $\mu\text{L}$ , 0.39 M, 0.052 mmol). The tube was flame-sealed and stored at -78 °C until the NMR probe was cooled to -60 °C. The pale brown solution of  $[\text{Cp}^*(\text{PMe}_3)_2\text{Re}(\text{CH}_2)(\text{H})][\text{OTf}]$  (**4**) was characterized by NMR spectroscopy at this temperature. A yield of 99% was calculated on the basis of internal standard (hexamethylbenzene).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz, -60 °C):  $\delta$  14.51 (br s, 2H,  $\text{Re-CH}_2$ ), 2.04 (s, 15H,  $\text{C}_5(\text{CH}_3)_5$ ), 1.50 (d, 18H,  $\text{P}(\text{CH}_3)_3$ ), -7.11 (tt, 1H,  $^3J_{\text{HH}} = 8$  Hz,  $^2J_{\text{HP}} = 56$  Hz,  $\text{Re-H}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 125 MHz, -60 °C):  $\delta$  229.5 (s,  $\text{Re-CH}_2$ ), 104.6 (s,  $\text{C}_5(\text{CH}_3)_5$ ), 24.6 (m,  $\text{P}(\text{CH}_3)_3$ ), 11.3 (s,  $\text{C}_5(\text{CH}_3)_5$ ). The  $\text{CF}_3$  carbon of the triflate anion was not observed in the  $^{13}\text{C}\{^1\text{H}\}$  spectrum.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 162 MHz, -60 °C):  $\delta$  -28.1 (s,  $\text{P}(\text{CH}_3)_3$ ).  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 377 MHz, -60 °C):  $\delta$  -78.9 ( $\text{OSO}_2\text{CF}_3$ ).

**Characterization of  $[\text{Cp}^*(\text{PMe}_3)_2\text{Re}(\text{CD}_2)(\text{D})][\text{OTf}]$  (4-d<sub>3</sub>) at Low Temperature in Solution.**  $\text{Cp}^*(\text{PMe}_3)_2\text{Re}(\text{CD}_3)_2$  (25 mg, 0.049 mmol) was dissolved in  $\text{CD}_2\text{Cl}_2$  (0.5 mL) in an NMR tube fitted with a Cajon adaptor. The tube was cooled to -78 °C in a dry ice/2-propanol bath. Against a positive pressure of nitrogen, HOTf was added as a  $\text{CD}_2\text{Cl}_2$  solution (275  $\mu\text{L}$ , 0.18 M, 0.049 mmol). The tube was flame-sealed and stored at -78 °C until the NMR probe was cooled to -60 °C. The pale brown solution of  $[\text{Cp}^*(\text{PMe}_3)_2\text{Re}(\text{CD}_2)(\text{D})][\text{OTf}]$  (**4-d<sub>3</sub>**) was characterized by NMR spectroscopy at this temperature.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 500 MHz, -60 °C):  $\delta$  2.03 (s, 15H,  $\text{C}_5(\text{CH}_3)_5$ ), 1.49 (d, 18H,  $\text{P}(\text{CH}_3)_3$ ).  $^2\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 76.8 MHz, -60 °C):  $\delta$  14.50 (s,  $\text{Re-CD}_2$ ), 7.01 (t,  $\text{Re-D}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 162 MHz):  $\delta$  -28.4 (s,  $\text{P}(\text{CH}_3)_3$ ).

**Characterization of  $[\text{Cp}^*(\text{PMe}_3)_3\text{ReCH}_3][\text{OTf}]$  (6) at Low Temperature in Solution.**  $\text{Cp}^*(\text{PMe}_3)_2\text{ReMe}_2$  (16 mg, 0.031 mmol) was dissolved in  $\text{CD}_2\text{Cl}_2$  (0.5 mL) in an NMR tube fitted with a Cajon adaptor. The tube was cooled to -78 °C in a dry ice/2-propanol bath. Against a positive pressure of nitrogen, HOTf was added as a  $\text{CD}_2\text{Cl}_2$  solution (28  $\mu\text{L}$ , 1.1 M, 0.031 mmol). The tube was degassed by three freeze-pump-thaw cycles, and  $\text{PMe}_3$  (88 Torr, 6.6 mL known-volume bulb, 0.031 mmol) was added by vacuum transfer. The tube was sealed and stored at -78 °C until the NMR probe was cooled to -40 °C. The dark yellow solution of  $[\text{Cp}^*(\text{PMe}_3)_3\text{ReCH}_3][\text{OTf}]$  (**6**) was characterized by NMR spectroscopy at this temperature. A yield of 67% was calculated on the basis of internal standard (hexamethylbenzene). Compound **6** rapidly decomposed to multiple products upon warming to room temperature.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz, -40 °C):  $\delta$  1.81 (m, 9H,  $\text{P}(\text{CH}_3)_3$ ), 1.69 (s, 15H,  $\text{C}_5(\text{CH}_3)_5$ ), 1.42 (virtual triplet, 18H,  $\text{P}(\text{CH}_3)_3$ ), 0.43 (td, 3H,  $^3J_{\text{HP}} = 10$ , 2 Hz,  $\text{Re-CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 125 MHz, -40 °C):  $\delta$  94.6 (s,  $\text{C}_5(\text{CH}_3)_5$ ), 20.7 (t,  $J = 16$  Hz,  $\text{P}(\text{CH}_3)_3$ ), 16.0 (d,  $J = 36$  Hz,  $\text{P}(\text{CH}_3)_3$ ), 10.7 (s,  $\text{C}_5(\text{CH}_3)_5$ ), -31.2 (m,  $\text{Re-CH}_3$ ). The  $\text{CF}_3$  carbon of the triflate anion was not observed in the

$^{13}\text{C}\{^1\text{H}\}$  spectrum.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 162 MHz,  $-40^\circ\text{C}$ ):  $\delta$   $-44.1$  (d,  $J_{\text{PP}} = 32$  Hz,  $P(\text{CH}_3)_3$ ),  $-49.7$  (t,  $J_{\text{PP}} = 32$  Hz,  $P(\text{CH}_3)_3$ ).

**Characterization of  $\text{Cp}^*(\text{PMe}_3)_2\text{ReMeCl}$  (**7**) at Low Temperature in Solution.**  $\text{Cp}^*(\text{PMe}_3)_2\text{ReMe}_2$  (5.9 mg, 0.012 mmol) and  $\text{PPNCl}$  (6.7 mg, 0.012 mmol) were dissolved in  $\text{CD}_2\text{Cl}_2$  in an NMR tube fitted with a Cajon adaptor. The tube was cooled to  $-78^\circ\text{C}$  in a dry ice/2-propanol bath. Against a positive pressure of nitrogen,  $\text{HOTf}$  was added as a  $\text{CD}_2\text{Cl}_2$  solution (16  $\mu\text{L}$ , 0.73 M, 0.012 mmol). The tube was sealed and stored at  $-78^\circ\text{C}$  until the NMR probe was cooled to  $-40^\circ\text{C}$ . The orange solution of  $\text{Cp}^*(\text{PMe}_3)_2\text{ReMeCl}$  (**7**) was characterized by NMR spectroscopy at this temperature. A yield of 93% for **7** was calculated on the basis of internal standard (hexamethylbenzene). Upon warming to room temperature, the resonances for **7** became broad, presumably due to the presence of  $\text{PPNOTf}$  in the reaction mixture. Attempts to isolate **7** directly from this reaction mixture were unsuccessful, although it was prepared independently, as described below.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz,  $-40^\circ\text{C}$ ):  $\delta$  7.45 (m, 30H,  $\text{PPNOTf}$ , PhH) 1.46 (s, 15H,  $\text{C}_5(\text{CH}_3)_5$ ), 1.20 (d, 18H,  $P(\text{CH}_3)_3$ ),  $-0.05$  (t, 3H,  $^3J_{\text{HP}} = 12$  Hz,  $\text{Re-CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 125 MHz,  $-40^\circ\text{C}$ ):  $\delta$  133.71 (s,  $\text{PPNOTf } \text{C}_6\text{H}_5$ ), 132.05 (m,  $\text{PPNOTf}, \text{C}_6\text{H}_5$ ), 129.48 (m,  $\text{PPNOTf } \text{C}_6\text{H}_5$ ), 89.59 (s,  $\text{C}_5(\text{CH}_3)_5$ ), 16.47 (six-line pattern,  $P(\text{CH}_3)_3$ ), 9.63 (s,  $\text{C}_5(\text{CH}_3)_5$ ),  $-27.3$  (s,  $\text{Re-CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 162 MHz,  $-40^\circ\text{C}$ ):  $\delta$  23.2 (s,  $\text{PPNOTf}$ ),  $-31.7$  (s,  $P(\text{CH}_3)_3$ ).

**Independent Synthesis of  $\text{Cp}^*(\text{PMe}_3)_2\text{ReMeCl}$  (**7**).** In the glovebox,  $\text{Cp}^*(\text{PMe}_3)_2\text{ReMe}_2$  (280 mg, 0.56 mmol) was dissolved in THF (20 mL) to give a yellow solution, which was transferred to a sealable glass reaction vessel. Using a vacuum line, the vessel was charged with gaseous HCl (20.4 mTorr, 505.7 mL known-volume bulb, 0.56 mmol) by condensation, resulting in a color change to dark orange. After 1 h at room temperature, the volatile materials were removed from the reaction in vacuo, leaving the methylrhenium chloride **7** as a spectroscopically pure dark orange powder (273 mg, 0.52 mmol, 93%). A concentrated pentane solution of complex **7** was cooled to  $-30^\circ\text{C}$ , yielding analytically pure dark orange crystals (212 mg, 0.41 mmol, 73%). Anal. Calcd for  $\text{C}_{17}\text{H}_{36}\text{ClP}_2\text{Re}$ : C, 38.96; H, 6.92. Found: C, 38.66; H, 6.61.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 500 MHz):  $\delta$  1.45 (s, 15H,  $\text{C}_5(\text{CH}_3)_5$ ), 1.21 (virtual triplet, 18H,  $P(\text{CH}_3)_3$ ), 0.14 (t, 3H,  $^3J_{\text{HP}} = 14$  Hz,  $\text{Re-CH}_3$ ).  $^1\text{H}$  NMR chemical shifts in  $\text{CD}_2\text{Cl}_2$  match those reported above for synthesis of **7** by method 1.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 125 MHz):  $\delta$  90.55 (t,  $^2J_{\text{CP}} = 4$  Hz,  $\text{C}_5(\text{CH}_3)_5$ ), 17.42 (six-line pattern,  $P(\text{CH}_3)_3$ ), 10.24 (s,  $\text{C}_5(\text{CH}_3)_5$ ),  $-26.3$  (t,  $^2J_{\text{CP}} = 19$  Hz,  $\text{Re-CH}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 162 MHz):  $\delta$   $-32.2$  (s,  $P(\text{CH}_3)_3$ ). IR (KBr): 1427, 1371, 1293, 1272, 1025, 956, 942, 845.

**$[\text{Cp}^*(\text{PMe}_3)_2\text{Re}(\text{CH}_2)(\text{CH}_3)][\text{BARf}]$  (**8**).**  $\text{Cp}^*(\text{PMe}_3)_2\text{ReMe}_2$  (61 mg, 0.12 mmol) and  $\text{NaBARf}$  (161 mg, 0.182 mmol) were dissolved in  $\text{CH}_2\text{Cl}_2$  (7 mL) in a Schlenk flask. This yellow solution was cooled to  $-78^\circ\text{C}$  in a dry ice/2-propanol bath.  $\text{HOTf}$  was added as a  $\text{CH}_2\text{Cl}_2$  solution (0.8 mL, 0.15 M, 0.12 mmol) via syringe. The color of the reaction mixture became dark orange-brown, and the solution was stirred at  $-78^\circ\text{C}$  for 2 h. It was then warmed to  $-40^\circ\text{C}$  in a dry ice/acetonitrile bath, stirred at this temperature for 2 h, and warmed to room temperature. The dark brown solution was filtered through Celite, and volatile materials were removed from the filtrate under reduced pressure. Crystallization of the resultant brown powder from methylene chloride layered with pentane at  $-30^\circ\text{C}$  gave dark orange crystals (69 mg, 42%). Anal. Calcd for  $\text{C}_{50}\text{H}_{50}\text{P}_2\text{ReBF}_2$ : C, 43.97; H, 3.69. Found: C, 43.64; H, 3.51.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 400 MHz,  $-40^\circ\text{C}$ ):  $\delta$  14.39 (t, 2H,  $^3J_{\text{HP}} = 20$  Hz,  $\text{Re-CH}_2$ ), 7.72 (s, 8H,  $\text{BARf}$ ), 7.56 (s, 4H,  $\text{BARf}$ ), 1.85 (s, 15H,  $\text{C}_5(\text{CH}_3)_5$ ), 1.26 (d, 18H,  $P(\text{CH}_3)_3$ ), 0.30 (t, 3H,  $^3J_{\text{HP}} = 18$  Hz,  $\text{Re-CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 125 MHz):  $\delta$  162.2 (q,  $J_{\text{CF}} = 270$  Hz,  $\text{BAR-CF}_3$ ), 134.7 (s,  $\text{BAR-C}_{\text{ortho}}$ ), 128.8 (q,  $J_{\text{CF}} = 50$  Hz,  $\text{BAR-C}$ ), 117.42 (br s,  $\text{BAR-C}_{\text{para}}$ ), 106.0 (s,  $\text{C}_5(\text{CH}_3)_5$ ), 19.5 (virtual triplet,  $P(\text{CH}_3)_3$ ), 10.0 (s,  $\text{C}_5(\text{CH}_3)_5$ ). The methyl and methylene carbon resonances could not be observed in  $^{13}\text{C}\{^1\text{H}\}$  or DEPT135 spectra at room temperature. This is presumably due to fluxional broadening.

$^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 162 MHz):  $\delta$   $-35.4$  (s,  $P(\text{CH}_3)_3$ ).  $^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 377 MHz):  $\delta$   $-60.9$  (s, 3,5- $(\text{CF}_3)_2\text{C}_6\text{H}_3$ ). IR (KBr): 2966, 2920, 2072, 2014, 1969, 1611, 1360, 1274, 1139, 947  $\text{cm}^{-1}$ .

#### Crystallographic Study of $[\text{Cp}^*(\text{PMe}_3)_2\text{Re}(\text{CH}_2)(\text{CH}_3)][\text{BARf}]$ (**8**).

Data were collected using a SMART CCD area detector with graphite-monochromated Mo  $K\alpha$  radiation. Hydrogen atoms were included but not refined, except for the hydrogens on C(11), which were located in the difference electron density map and refined with fixed thermal parameters. Random errors and thermal motion erased any sign of localization in the  $\text{Cp}^*$  rings. The  $\text{Re-C}$  bond distance for the  $\text{CH}_2$  ligand (2.06 Å) is significantly shorter than for the methyl ligand (2.25 Å). Important bond distances and angles are included in Figure 2. Crystallographic data follow: space group  $P\bar{1}$ ,  $a = 12.2338(3)$  Å,  $b = 12.9077(3)$  Å,  $c = 12.1496(4)$  Å,  $\alpha = 102.179(1)^\circ$ ,  $\beta = 93.149(1)^\circ$ ,  $\gamma = 96.009(1)^\circ$ ,  $V = 2777.35(11)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}} = 1.633$  g/cm<sup>3</sup>,  $\mu(\text{Mo } K\alpha) = 62.94$  cm<sup>-1</sup>, number of unique reflections = 7968,  $R = 3.7\%$ .

**$[\text{Cp}^*(\text{PMe}_3)_2\text{Re}(\text{CH}_2)(\text{CH}_3)][\text{BARf}]$  (**8**), Method 2.**  $\text{Cp}^*(\text{PMe}_3)_2\text{ReMe}_2$  (8.7 mg, 0.017 mmol) and  $[(\text{OEt})_2\text{H}][\text{BARf}]$  (17.5 mg, 0.017 mmol) were placed in an NMR tube fitted with a Cajon adaptor, and  $\text{CD}_2\text{Cl}_2$  (roughly 0.5 mL) was added by vacuum transfer. The tube was sealed and warmed to room temperature. The crude reaction mixture displayed resonances identical to those assigned to  $[\text{Cp}^*(\text{PMe}_3)_2\text{Re}(\text{CH}_2)(\text{CH}_3)][\text{BARf}]$  (**8**) prepared by method 1 in the  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra.

**Observation of Triflate Products **9** and **10**.**  $\text{Cp}^*(\text{PMe}_3)_2\text{ReMe}_2$  (21 mg, 0.042 mmol) was dissolved in  $\text{CD}_2\text{Cl}_2$  (0.5 mL) in an NMR tube fitted with a Cajon adaptor. The tube was cooled to  $-78^\circ\text{C}$  in a dry ice/2-propanol bath. Against a positive pressure of nitrogen,  $\text{HOTf}$  was added as a  $\text{CD}_2\text{Cl}_2$  solution (50  $\mu\text{L}$ , 0.84 M, 0.042 mmol). The tube was flame-sealed and stored at  $-78^\circ\text{C}$  until the NMR probe was cooled to  $-60^\circ\text{C}$ . The pale brown solution was characterized by  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopies at this temperature, and found to contain only  $[\text{Cp}^*(\text{PMe}_3)_2\text{Re}(\text{CH}_2)(\text{H})][\text{OTf}]$  (**4**). The tube was then warmed to room temperature. After 18 h, its contents were characterized again by  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopies. The triflate compounds **9** and **10** were identified in the reaction mixture (which was otherwise very clean) on the basis of these spectroscopic data. All attempts to separate compounds **9** and **10** from each other were unsuccessful. The resonances belonging to the triflate methylrhenium methyldiene compound **9** were assigned on the basis of their close similarity to those observed for the isolated methylrhenium methyldiene compound **8**. The remaining resonances in the reaction mixture were assigned to the hydridorhenium triflate compound **10**.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 500 MHz):  $\delta$  14.43 (t, 2H,  $^3J_{\text{HP}} = 20$  Hz,  $\text{Re-CH}_2$ , **9**), 1.88 (s, 15H,  $\text{C}_5(\text{CH}_3)_5$ , **10**), 1.83 1.88 (s, 15H,  $\text{C}_5(\text{CH}_3)_5$ , **9**), 1.52 (d, 18H,  $P(\text{CH}_3)_3$ , **10**), 1.28 (d, 18H,  $P(\text{CH}_3)_3$ , **9**), 0.30 (t, 3H,  $^3J_{\text{HP}} = 18$  Hz,  $\text{Re-CH}_3$ , **9**),  $-8.72$  (t, 1H,  $^2J_{\text{HP}} = 55$  Hz,  $\text{Re-H}$ , **10**).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 162 MHz):  $\delta$   $-34.2$  (s,  $P(\text{CH}_3)_3$ , **9**),  $-38.8$  (s,  $P(\text{CH}_3)_3$ , **10**).

**cis- $\text{Cp}^*(\text{CO})_2\text{Re}(\text{CH}_3)_2$  (**11**).**<sup>63</sup>  $\text{Cp}^*(\text{CO})_2\text{ReCl}_2$  (156 mg, 0.35 mmol) was dissolved in toluene (20 mL) in the glovebox. The resulting orange solution was cooled to  $-30^\circ\text{C}$ , and dimethylzinc (384  $\mu\text{L}$ , 2.0 M, 0.77 mmol) was added by syringe. After 5.5 h of stirring at room temperature, the solution had turned golden yellow, and an off-white precipitate had formed. At this time the reaction mixture was filtered through a plug of neutral  $\text{Al}(\text{III})$ , which was then washed with THF (2  $\times$  7 mL). The volatile materials were removed from the combined filtrate and washed in vacuo, leaving **11** as a spectroscopically and analytically pure light orange microcrystalline solid (82 mg, 57%). The spectroscopic and analytical data for **11** are consistent with the previously reported values for this compound, and are listed below. Anal. Calcd for  $\text{C}_{14}\text{H}_{21}\text{O}_2\text{Re}$ : C, 41.26; H, 5.19. Found: C, 41.10; H, 5.17.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 500 MHz):  $\delta$  1.34 (s, 15H,  $\text{C}_5(\text{CH}_3)_5$ ), 0.76 (s, 6H,  $\text{Re-CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 125 MHz):  $\delta$  97.68 (s,  $\text{C}_5(\text{CH}_3)_5$ ),

9.02 (s,  $C_5(CH_3)_3$ ),  $-27.88$  (s, Re- $CH_3$ ). The carbonyl carbon resonance was not observed. IR ( $CH_2Cl_2$ ): 1985, 1903.

**$Cp^*(CO)_2Re(CH_3)OTf$  (**12**).**  $Cp^*(CO)_2Re(CH_3)_2$  (34.4 mg, 0.083 mmol) was dissolved in benzene (5 mL) in the glovebox, forming a yellow solution. HOTf (12.4 mg, 0.083 mmol) was added as a benzene solution (1 mL), and the resulting golden orange reaction was immediately frozen at  $-30$  °C. Once frozen, the solvent was removed by lyophilization in vacuo, leaving an analytically pure tan solid (43 mg, 97%). When redissolved, this compound undergoes slow conversion to **13** ( $t_{1/2}$  roughly 1 h at 23 °C). As a result,  $^1H$  and  $^{13}C\{^1H\}$  spectra of **12** contained small quantities of **13**. Anal. Calcd for  $C_{14}H_{18}F_3O_5ReS$ : C, 31.05; H, 3.35. Found: C, 31.23; H, 3.43.  $^1H$  NMR ( $C_6D_6$ , 500 MHz):  $\delta$  1.14 (s, 15H,  $C_5(CH_3)_5$ ), 0.39 (s, 3H, Re- $CH_3$ ).  $^{13}C\{^1H\}$  NMR ( $C_6D_6$ , 125 MHz):  $\delta$  103.00 (s,  $C_5(CH_3)_3$ ), 8.96 (s,  $C_5(CH_3)_3$ ),  $-19.41$  (s, Re- $CH_3$ ). The carbonyl carbon resonance was not observed.  $^{19}F\{^1H\}$  NMR ( $C_6D_6$ , 377 MHz):  $\delta$   $-76.7$  ( $OSO_2CF_3$ ). IR ( $CH_2Cl_2$ ): 2038, 1961. IR (KBr): 2014, 1936.

**$Cp^*(CO)Re(OTf)-\eta^2-(COCH_3)$  (**13**).** A solution of  $Cp^*(CO)_2Re(CH_3)OTf$  (31 mg, 0.057 mmol) in  $C_6D_6$  (0.5 mL) was prepared and allowed to stand at room temperature for 18 h. After that time, a small amount of black precipitate had formed. After spectroscopic analysis, the reaction was filtered and the solvent was removed in vacuo to give an orange solid (18 mg, 58%). Anal. Calcd for  $C_{14}H_{18}F_3O_5ReS$ : C, 31.05; H, 3.35. Found: C, 30.81; H, 3.20.  $^1H$  NMR ( $C_6D_6$ , 500 MHz):  $\delta$  1.25 (s, 15H,  $C_5(CH_3)_5$ ), 1.20 (s, 3H, Re $COCH_3$ ).  $^{13}C\{^1H\}$  NMR ( $C_6D_6$ , 125 MHz):  $\delta$  210.24(s, CO), 204.61 (s, CO), 104.37 (s,  $C_5(CH_3)_3$ ), 22.25 (s, Re( $COCH_3$ )), 9.55 (s,  $C_5(CH_3)_3$ ).  $^{19}F\{^1H\}$  NMR ( $C_6D_6$ , 377 MHz):  $\delta$   $-77.3$  ( $OSO_2CF_3$ ). IR (KBr): 1904, 1385, 1336, and minor peaks corresponding to **12**.

**Computational Details.** The calculations used the Gaussian98 suite of electronic structure codes.<sup>91</sup> The electronic ground state and geometry optimization were determined within the B3LYP functional,<sup>92</sup> followed by an explicit calculation of the vibrational frequencies at the minimum and the zero-point energy corrections. Relativistic effects were included via the use of the LANL2 relativistic effective core potential (RECP) for the transition metal.<sup>93</sup> This RECP is the small-core potential developed from an atomic Hartree–Fock (HF) calculation, but we have found that HF-derived small-core RECPs can usually be transferred to

DFT calculations without concern.<sup>94</sup> However, as a general rule, we uncontract the associated basis sets (originally fit to HF pseudo-orbitals) because they sometimes need the added variational flexibility to adjust to the DFT potential.<sup>95</sup> The uncontracted basis set has two p-functions with very similar exponents; only one of these was retained. An f polarization function ( $\alpha = 0.6$ ) on the metal center (determined from preliminary energy optimizations) completes the set. All ligand species were described with the 6-31G\* basis. Solvent effects were not explicitly considered in these calculations.

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**Supporting Information Available:** X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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