

Manganese(I) and Rhenium(I) Tricarbonyl (Alkylthio)methyl and Alkylidenesulfonium Complexes

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The reactions of $\text{Na}[\text{M}(\text{CO})_3(\text{bipy})]$ ($\text{M} = \text{Mn}, \text{Re}$) compounds with ClCH_2SR ($\text{R} = \text{Me}, \text{Ph}$) afford the (alkylthio)alkyl complexes $[\text{Mn}(\text{CH}_2\text{SMe})(\text{CO})_3(\text{bipy})]$ (**1a**), $[\text{Mn}(\text{CH}_2\text{SPh})(\text{CO})_3(\text{bipy})]$ (**1b**), $[\text{Re}(\text{CH}_2\text{SMe})(\text{CO})_3(\text{bipy})]$ (**2a**), and $[\text{Re}(\text{CH}_2\text{SMe})(\text{CO})_3(\text{bipy})]$ (**2b**). Methylation at sulfur of these compounds with methyl triflate affords the methylidenesulfonium cations $[\text{Mn}(\text{CH}_2\text{SMe}_2)(\text{CO})_3(\text{bipy})]^+$ (**5a**), $[\text{Mn}(\text{CH}_2\text{SMePh})(\text{CO})_3(\text{bipy})]^+$ (**5b**), $[\text{Re}(\text{CH}_2\text{SMe}_2)(\text{CO})_3(\text{bipy})]^+$ (**6a**), and $[\text{Re}(\text{CH}_2\text{SMePh})(\text{CO})_3(\text{bipy})]^+$ (**6b**) as their triflate salts. These new compounds were characterized by IR and NMR spectroscopy, and the crystal structures of **1b**, **2a**, **5b**, and **6b** have been determined by X-ray diffraction. The sulfonium complexes are unreactive toward PPh_3 and pyridine. The reactions of **5b** and **6b** with I^- , PPh_2^- , and SEt^- anions afford the (phenylthio)methyl complexes **1b** and **2b**, resulting from nucleophilic attack at the methyl group. **5b** and **6b** react with styrene to give phenylcyclopropane, free thioanisole, and the corresponding $[\text{M}(\text{OTf})(\text{CO})_3(\text{bipy})]$ complex.

Introduction

Two families of electrophilic d^6 complexes, namely, octahedral chromium and tungsten Fischer alkoxycarbene $[(\text{CO})_5\text{M}=\text{C}(\text{R})\text{OR}]^1$ and cationic iron complexes $[\text{Cp}(\text{CO})_2\text{Fe}=\text{C}(\text{R})\text{R}']^+$, are among the transition-metal compounds best studied regarding their ability to transfer carbene moieties to olefins. Due to the lack of heteroatom stabilization, the latter compounds show a higher electrophilicity at the carbene carbon and, as a result, cyclopropanate a broader range of olefins, and these reactions can be conducted at lower temperatures. Owing to their limited stability, these highly electrophilic species are often generated in situ. The corresponding sulfide–alkylidene adducts,³ i.e., salts of the cationic alkylidenesulfonium complexes $[\text{Cp}(\text{CO})_2\text{FeCH}_2\text{SR}_2]^+$, have been found to be stable yet active in olefin cyclopropanation.⁴ Reagents of this kind have been prepared with several other metal fragments.⁵ Most

pertinent to the work described here are the d^6 Re(I) sulfonium complexes $[\text{CpRe}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{SR}_2)]^+$, which were synthesized by addition of dialkyl sulfides to the highly electrophilic $[\text{CpRe}(\text{=CH}_2)(\text{NO})(\text{PPh}_3)]^+$ methylidene cation.⁶ This route exemplifies the reverse of the in situ generation of carbenes mentioned above. Normally, sulfonium complexes, whose carbene-transfer activity avoids the need for the difficult isolation of the highly electrophilic alkylidene complexes, are conveniently prepared by addition of electrophiles to the sulfur atom of (alkylthio)methyl complexes, in turn obtained by reaction of chloromethyl alkyl sulfides with suitable anionic complexes.⁷ However, such anions are not available for the derivatives of the $\{\text{CpRe}(\text{NO})(\text{PPh}_3)\}$ fragment.

Octahedral complexes of $\{\text{M}(\text{CO})_3(\text{bipy})\}$ ($\text{M} = \text{Mn}, \text{Re}$) fragments are robust and do not present steric hindrance to the access of reagents to the ligand occupying the remaining coordination position.⁸ Moreover, generation of $[\text{M}(\text{CO})_3(\text{bipy})]^-$ anions can be accomplished by the reduction of easily available, stable

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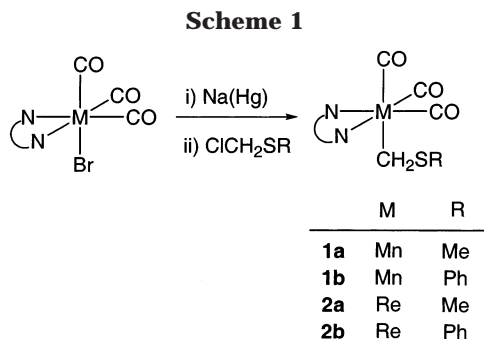
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[MX(CO)₃(bipy)] halo complexes on these manganese and rhenium systems.⁹ Here we report the employment of these anions to prepare isolable (alkylthio)methyl complexes, subsequent methylation of which with MeOTf affords cationic alkylidenesulfonium compounds. The reactivity of the latter toward nucleophiles and the structural characterization of several new compounds are also included.

Results and Discussion

A THF solution of the compound Na[Mn(CO)₃(bipy)],^{9a} generated in situ by reaction of [MnBr(CO)₃(bipy)] with sodium amalgam, was added to an equimolar amount of chloromethyl methyl sulfide. The disappearance of the intense blue color of the anion indicated an instantaneous reaction. The ν_{CO} IR bands of the crude solution showed the formation of the single *fac*-tricarbonyl species **1a**, with wavenumber values compatible with a neutral formulation (1998 and 1890 cm⁻¹ versus 1912, 1823, and 1782 cm⁻¹ for the anion). These values are shifted to lower frequencies with respect to the bromo complex precursor (2022, 1934, and 1914 cm⁻¹ in THF) and are closer to those of known [Mn(R)(CO)₃(bipy)] alkyls (1988 and 1889 cm⁻¹ in CH₂Cl₂ for R = CH₃).^{9a} This suggests a [Mn(CH₂SCH₃)(CO)₃(bipy)] composition, as depicted in Scheme 1. Pure **1a** could be isolated in good yield as a microcrystalline solid and was characterized on the basis of its spectroscopic and analytical data. The ¹H NMR spectrum includes a four-signal pattern for the bipy ligand, as expected for a molecule with a mirror plane, and singlets at 1.82 and 1.27 ppm assigned to the methyl and methylene groups of the (methylthio)methyl ligand, respectively. These groups occur as signals at 32.36 (CH₂) and 24.29 (CH₃) ppm in the ¹³C NMR spectrum. In this spectrum two of the carbonyl ligands appear as a single signal, and the bipy ligand gives rise to five signals, further indicating the presence of a molecular mirror plane.

The reaction of Na[Mn(CO)₃(bipy)] with chloromethyl phenyl sulfide yielded [Mn(CH₂SPh)(CO)₃(bipy)] (**1b**) in an analogous manner. As expected for the substitution of methyl by the less electron-releasing phenyl group, the IR ν_{CO} bands occur at frequencies slightly higher than those of **1a**. In addition to its spectroscopic and analytical characterization (see Experimental Section), the structure of **1b** was determined by X-ray diffraction (see Figure 1a and Table 1). The molecule of this complex consists of a manganese atom in an ap-

Table 1. Selected Bond Distances and Angles for Complexes 1b and 2a

	1b	2a
M(1)–C(4)	2.125(4)	2.276(6)
M(1)–C(1)	1.820(4)	1.943(7)
M(1)–C(2)	1.772(5)	1.906(7)
M(1)–C(3)	1.780(4)	1.902(7)
M(1)–N(1)	2.045(4)	2.184(5)
M(1)–N(2)	2.039(3)	2.187(7)
C(4)–S(1)	1.763(4)	1.759(6)
S(1)–C(5)	1.764(4)	1.797(5)
C(1)–O(1)	1.124(4)	1.160(8)
C(2)–O(2)	1.152(5)	1.171(8)
C(3)–O(3)	1.162(5)	1.182(8)
C(1)–M(1)–C(4)	176.47(19)	177.4(2)
C(2)–M(1)–C(4)	86.98(19)	91.6(2)
C(3)–M(1)–C(4)	93.95(19)	94.1(2)
N(1)–M(1)–C(4)	83.76(14)	83.1(2)
N(2)–M(1)–C(4)	85.30(15)	82.6(2)
C(3)–M(1)–C(1)	89.0(2)	87.6(3)
C(3)–M(1)–C(2)	89.0(2)	89.4(3)
C(2)–M(1)–C(1)	91.2(2)	90.5(3)
C(3)–M(1)–N(1)	173.91(18)	97.8(2)
C(2)–M(1)–N(1)	96.51(19)	171.3(2)
C(1)–M(1)–N(1)	93.45(17)	94.7(2)
C(3)–M(1)–N(2)	96.11(19)	171.5(2)
C(2)–M(1)–N(2)	171.02(2)	98.5(2)
C(1)–M(1)–N(2)	96.26(16)	95.5(2)
N(1)–M(1)–N(2)	78.12(16)	74.11(18)
S(1)–C(4)–M(1)	114.5(2)	110.9(3)
C(4)–S(1)–C(5)	106.9(2)	104.5(3)

proximately octahedral environment formed by three mutually facial carbonyls, the two nitrogens of a 2,2'-bipyridine chelate, and a monodentate, C-bound (phenylthio)methyl ligand. By similar procedures, the rhenium complexes [Re(CH₂SMe)(CO)₃(bipy)] (**2a**) and [Re(CH₂SPh)(CO)₃(bipy)] (**2b**) were synthesized and characterized (see Experimental Section). The structure of **2a** was determined by single-crystal X-ray diffraction (Figure 1b and Table 1). The geometry of the molecule is, with regard to the metal environment, like that described for the manganese complex **1b**, the major deviation from idealized octahedral geometry being for both compounds the acute N–M–N angles (<79°) imposed by the natural bite angle of the rigid chelate. In both structures, the M–CO distance is significantly longer for the carbonyl group trans to the (alkylthio)methyl ligand, revealing that the latter exerts a trans influence larger than the bipy nitrogens. Unfortunately, despite the abundance of complexes containing *fac*-{M(CO)₃(N–N)} (M = Mn, Re) fragments whose structures have been determined by means of X-ray diffraction, the only simple alkyl derivative within this family is [Re(CH₃)(CO)₃(ⁱPr-DAB)] (ⁱPr-DAB = 1,4-diisopropyl-1,4-diaza-1,3-butadiene), for which the disorder affecting the methyl group precludes any meaningful comparison.¹⁰ The M–CH₂SR distances in **1b** (2.125(4) Å) and **2a** (2.276(6) Å) do not show significant differences from M–C(alkyl) distances found for other octahedral alkyl carbonyl complexes of these metals. For instance, a Mn–CH₃ distance of 2.14(2) Å was found for the complex [Mn(CH₃)(P(OMe)₃)(CO)₂(ⁱPr-DAB)].¹¹

In an attempt to synthesize cationic sulfonium complexes, [Re(CH₂SPh)(CO)₃(bipy)] (**2b**) was allowed to react with an equimolar amount of triflic acid in CH₂-

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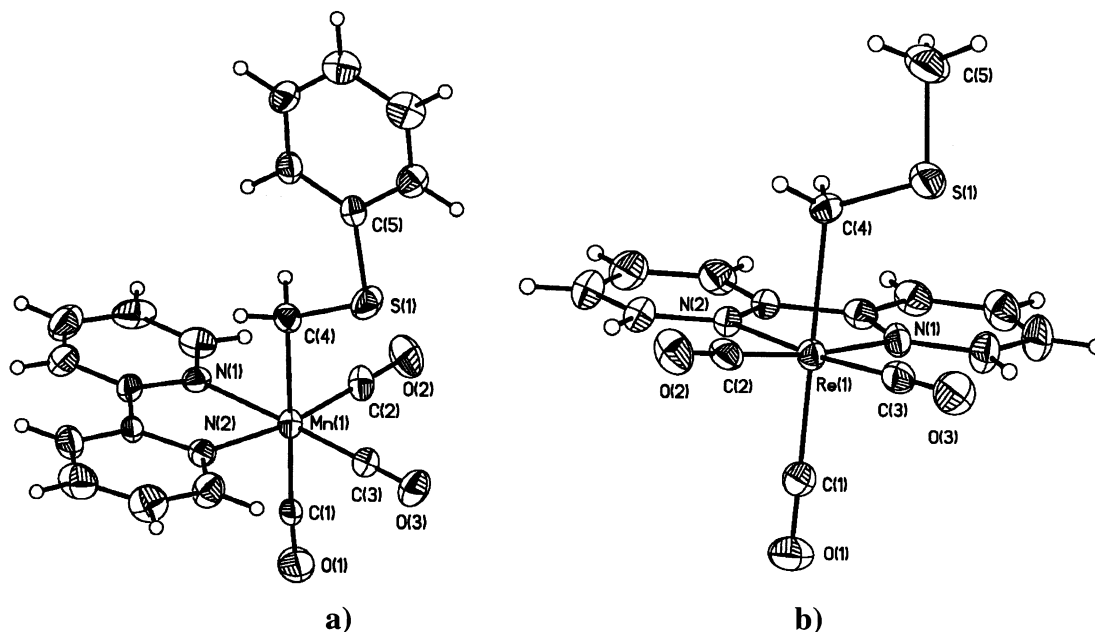
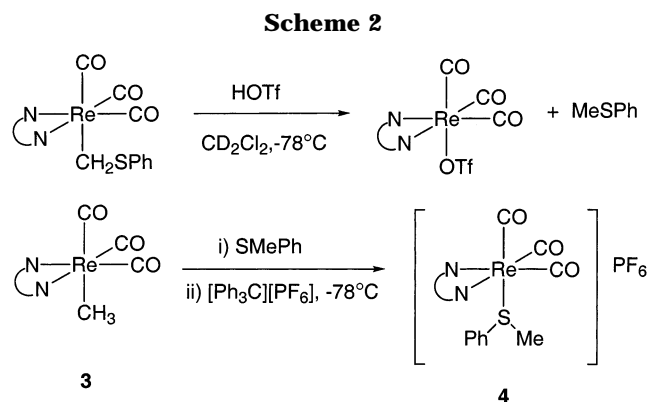


Figure 1. Thermal ellipsoid (30%) plots of **1b** (a) and **2a** (b).

Cl₂. The instantaneous formation of the triflate complex [Re(OTf)(CO)₃(bipy)] (IR ν_{CO} : 2035, 1935, and 1914 cm⁻¹)¹² revealed that the metal–alkyl bond, instead of the sulfur atom, was the site of the attack of the strong acid. This was confirmed by the observation of 1 equiv of thioanisole (aromatic multiplet at 7.25 ppm and singlet at 2.47 ppm), in addition to the signals of the triflate complex, when the reaction was carried out in CD₂Cl₂ in an NMR tube. We have found a related result in earlier work; thus, in an attempt to obtain the cationic methylidene complex [Re(=CH₂)(CO)₃(bipy)]⁺, we reacted equimolar amounts of [Re(CH₃)(CO)₃(bipy)] (**3**)¹³ and [Ph₃C][PF₆]. The resulting solution showed an IR spectrum consistent with the formulation [Re(L)(CO)₃(bipy)]⁺ (2038 and 1934 cm⁻¹),¹⁴ but no signal attributable to a methylidene complex could be detected in the NMR.¹⁵ We reasoned that if an unstable methylidene complex was being formed, it could be trapped as the more stable methylidenesulfonium derivative (see above) by generating the electrophilic complex in the presence of a dialkyl sulfide. However, the reaction of the methyl complex, the trityl salt, and thioanisole led to [Re(SMePh)(CO)₃(bipy)]PF₆ (**4**) (see Scheme 2) as the only organometallic species spectroscopically observed, indicating abstraction by the trityl cation of the entire methyl group instead of the hydride. The fact that thioanisole is coordinated in compound **4**, while the triflate complex [Re(OTf)(CO)₃(bipy)] and free thioani-



sole are obtained from the reaction of **2b** with HOTf, results from the lower coordinating ability of the hexafluorophosphate anion compared with triflate.

Next, methylation of **1a** was attempted. Methyl iodide failed to react (see below). Thus, the stronger methylating agent methyl triflate was used, and an instantaneous reaction led to the single product **5a**, as indicated by the IR and ¹H NMR monitoring. The IR ν_{CO} bands of **5a** still feature the pattern typical of a *fac*-tricarbonyl moiety but occur at wavenumbers some 20 cm⁻¹ higher than the neutral (alkylthio)methyl complex precursor. While this shift has the sign expected for a conversion of a neutral complex into a cationic one, its magnitude is rather small. In fact, the ν_{CO} IR bands of **5a** are very close to those of the neutral complex [MnBr(CO)₃(bipy)] (see above). The ¹H NMR spectrum of **5a** includes a two-hydrogen singlet at 1.18 ppm attributed to the methylene group, and a six-hydrogen singlet at 2.71 ppm, corresponding to two equivalent methyl groups. These data are consistent with a [Mn(CH₂SMe₂)(CO)₃(bipy)]-OTf formulation for **5a**, as depicted in Scheme 3. The IR ν_{CO} bands at frequencies relatively low for a cationic complex (see above) can be, thus, taken as indicative of a strong donor character for the sulfur ylide ligand.

Complex [Mn(CH₂SPh)(CO)₃(bipy)] (**1b**) underwent a similar methylation to yield the compound [Mn(CH₂-

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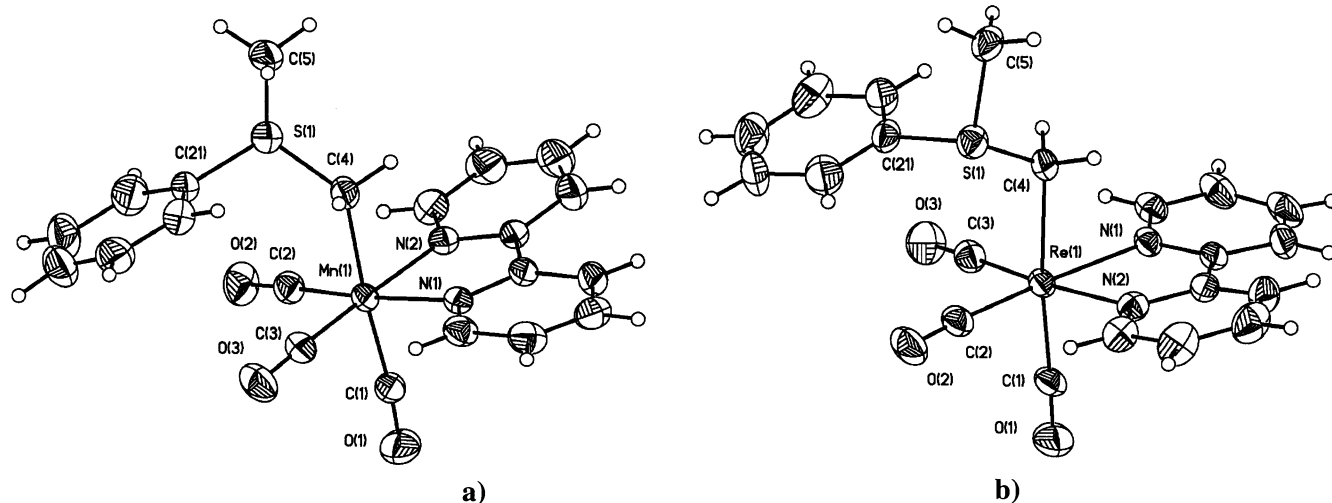
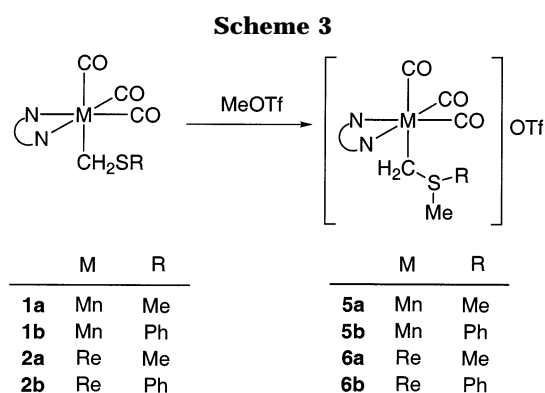


Figure 2. Thermal ellipsoid (30%) plots of **5b** (a) and **6b** (b).



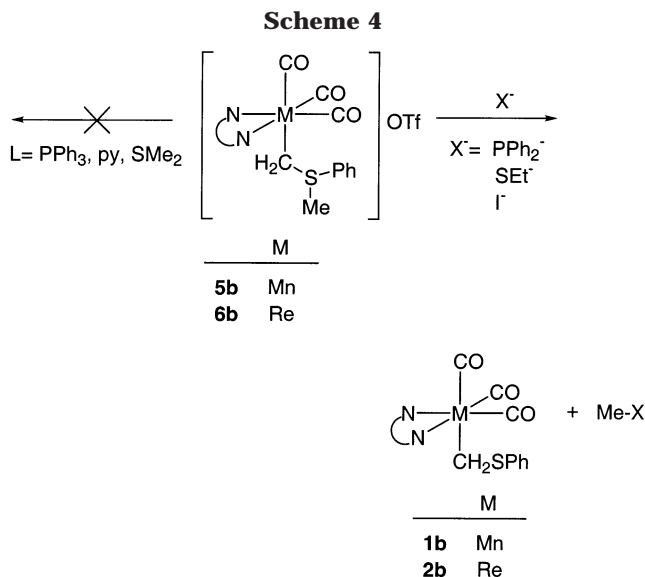
$\text{SMePh}(\text{CO})_3(\text{bipy})\text{OTf}$ (**5b**), and parallel results were encountered with the rhenium complexes **2a** and **2b**, which afford the sulfonium salts $[\text{Re}(\text{CH}_2\text{SMe}_2)(\text{CO})_3(\text{bipy})\text{OTf}]^+$ (**6a**) and $[\text{Re}(\text{CH}_2\text{SMePh})(\text{CO})_3(\text{bipy})\text{OTf}]^+$ (**6b**), respectively (see Scheme 3). As expected, diastereotopic methylene hydrogens are observed for the methylphenylsulfonium complexes **5b** and **6b**, in which the sulfur atoms are stereocenters. Accordingly, asymmetric bipy patterns are observed in the ^1H NMR spectra of these compounds. Low solubility precluded the acquisition of significant ^{13}C NMR spectra for complexes **5a** and **6a**, whereas for their more soluble methylphenylsulfonium counterparts, whose ^{13}C NMR data could be obtained, the methylene singlets occur at chemical shift values (34.30 ppm for **5b** and 25.79 ppm for **6b**) close to those found for the neutral precursors **1b** (23.57 ppm) and **2b** (26.39 ppm). Ten signals for the bipy carbons and three carbonyl signals are seen in the ^{13}C NMR for each of the chiral complexes **5b** and **6b**.

The structures of **5b** and **6b** were determined by X-ray diffraction, and the results are shown in parts a and b, respectively, of Figure 2 and in Table 2. These results confirm that the new complexes consist of a triflate anion (not shown in Figure 2) and a $[\text{M}(\text{CH}_2\text{SMePh})(\text{CO})_3(\text{bipy})]^+$ cation ($\text{M} = \text{Mn}$, **5b**; $\text{M} = \text{Re}$, **6b**), resulting from the methylation at sulfur of the (alkylthio)methyl precursor. For the first time, the structures of neutral (alkylthio)alkyl complexes and those of the corresponding cationic alkylidenesulfonium complexes are available. A comparison between the neutral and cationic complex for each metal reveals, as the most

Table 2. Selected Bond Distances and Angles for Complexes **5b** and **6b**

	5b	6b
M(1)–C(4)	2.122(6)	2.243(6)
M(1)–C(1)	1.804(6)	1.921(7)
M(1)–C(2)	1.792(6)	1.919(7)
M(1)–C(3)	1.803(7)	1.912(8)
M(1)–N(1)	2.055(5)	2.187(5)
M(1)–N(2)	2.040(5)	2.173(5)
C(4)–S(1)	1.755(6)	1.744(7)
S(1)–C(5)	1.806(7)	1.787(7)
S(1)–C(21)	1.787(6)	1.786(7)
C(1)–O(1)	1.130(7)	1.140(7)
C(2)–O(2)	1.148(7)	1.145(8)
C(3)–O(3)	1.143(8)	1.152(8)
C(1)–M(1)–C(4)	173.9(3)	173.6(3)
C(2)–M(1)–C(4)	96.1(3)	96.9(3)
C(3)–M(1)–C(4)	92.4(3)	94.4(3)
N(1)–M(1)–C(4)	82.3(2)	81.2(2)
N(2)–M(1)–C(4)	86.7(2)	83.7(2)
C(3)–M(1)–C(1)	87.4(3)	87.0(3)
C(3)–M(1)–C(2)	88.7(3)	88.3(3)
C(2)–M(1)–C(1)	90.0(3)	89.4(3)
C(3)–M(1)–N(1)	97.0(2)	99.6(2)
C(2)–M(1)–N(1)	174.2(2)	172.0(2)
C(1)–M(1)–N(1)	91.7(2)	92.4(2)
C(3)–M(1)–N(2)	175.9(2)	174.1(2)
C(2)–M(1)–N(2)	95.5(2)	97.6(3)
C(1)–M(1)–N(2)	93.0(2)	94.2(2)
N(1)–M(1)–N(2)	78.90(19)	74.6(2)
S(1)–C(4)–M(1)	118.3(3)	116.8(3)
C(21)–S(1)–C(5)	101.1(3)	102.0(3)
C(4)–S(1)–C(21)	105.7(3)	105.8(3)
C(4)–S(1)–C(5)	105.6(4)	105.8(3)

salient feature, virtually identical M–CH₂ distances. This is somewhat unexpected; thus, some shortening of the M–C bond would be anticipated to occur upon methylation, given that the methylidenesulfonium complex can be considered the adduct of a dialkyl sulfide and a methyldene complex and, therefore, should have some incipient carbene character.^{4c} In the structure of both cationic complexes, the three M–CO distances are virtually identical; thus, in contrast with alkylthioalkyl groups (see above), the alkylidenesulfonium ligand has a trans influence indistinguishable from that of the bipyridyl chelate. The geometries around the sulfur atoms of **5b** and **6b** are pyramidal, and the sums of the three C–S–C angles, 312.4 and 313.6°, respectively, and the C–S distances are similar to the values previously found for other alkylidenesulfonium complexes.^{4c}



We have explored the reactivity of the new sulfonium complexes toward nucleophiles. No reaction was observed with either triphenylphosphine or pyridine (3 equiv, THF as solvent, 24 h, room temperature).¹⁶ Furthermore, the complexes $[\text{M}(\text{CH}_2\text{SMePh})(\text{CO})_3(\text{bipy})]\text{OTf}$ ($\text{M} = \text{Mn}$, **5b**; $\text{M} = \text{Re}$, **6b**) did not react with dimethyl sulfide under the same conditions. These results contrast with those found for other sulfonium complexes. Thus, $[\text{CpRe}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{SMe}_2)]^+$ reversibly loses dimethyl sulfide (to give the methyldene complex $[\text{CpRe}(\text{=CH}_2)(\text{NO})(\text{PPh}_3)]^+$), which can also be displaced by neutral nucleophiles such as PPh_3 and pyridine.⁶ On the other hand, the complex $[\text{Cp}(\text{CO})_2\text{Fe}(\text{CH}_2\text{SMe}_2)]^+$ exchanged dimethyl sulfide with other dialkyl sulfides, yielding new alkylidenesulfonium complexes.^{4e} The geometry of our $[\text{M}(\text{CH}_2\text{S}(\text{Me})\text{R})(\text{CO})_3(\text{bipy})]^+$ complexes is octahedral, and, considering that the alkylidenesulfonium group occupies an axial position, the planar ring of the bipy chelate and the two carbonyl groups lie in an equatorial plane. Therefore, the above-mentioned lack of reactivity toward neutral nucleophiles cannot be due to steric hindrance. Most likely, then, the low electrophilicity at the metal and methylene carbon results from the presence of the strongly donating bipyridine ligand.

We next studied the reactivity of **5b** and **6b** toward anionic nucleophiles. The reactions of **5b** with potassium diphenylphosphide (generated in situ by reaction of diphenylphosphine with $\text{K}[\text{N}(\text{SiMe}_3)_2]$), potassium ethanethiolate (from EtSH and $\text{K}[\text{N}(\text{SiMe}_3)_2]$), or tetraethylammonium iodide afforded the complex $[\text{Mn}(\text{CH}_2\text{SPh})(\text{CO})_3(\text{bipy})]$ (**1b**) as the single organometallic product (see Scheme 4). Parallel results were found when these reactions were carried out with the rhenium complex **6b**. Thus, anions attack the methyl carbon of **5b** and **6b**, cleaving the $\text{S}-\text{CH}_3$ bond, in contrast with the sulfide elimination observed for $[\text{CpRe}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{SMe}_2)]$ complexes⁶ or with attack at the metal with $\text{P}-\text{C}$ cleavage, as found for $[\text{CpNi}(\text{L})(\text{CH}_2\text{SMe}_2)]^+$ ($\text{L} = \text{P}(\text{OMe})_3$).^{5a} When the reaction of Et_4NI with **6b** was carried out in CD_2Cl_2 in an NMR tube, free methyl

(16) No reaction was observed between **5b** and PPh_3 in toluene at 110°C over 1 h, conditions chosen to establish a comparison with the reaction with styrene, discussed in the text.

iodide (2.16 ppm) was observed in the ^1H NMR spectrum of the resulting solution. This reactivity of the sulfonium cation toward iodide anion explains the lack of reactivity shown by $[\text{Mn}(\text{CH}_2\text{SCH}_3)(\text{CO})_3(\text{bipy})]$ (**1a**) toward methyl iodide (see above), since the expected products for this reaction would be the sulfonium cation and iodide, which have now been shown to react to generate the reagents of the unobserved reaction. Therefore, the strength of our sulfonium complexes as methylating agents is intermediate between methyl iodide and methyl triflate.¹⁷ Likewise, MePPh_2 (-26.33 ppm in ^{31}P NMR) was observed as the product in the reaction of **5b** with KPPh_2 .

We wanted to study the reactivity of the cationic sulfonium complexes toward olefins and chose styrene as an olefin for which cyclopropanation experiments have been described.¹⁸ Since methylphenylsulfonium complexes have been reported to be more reactive than their dimethyl counterparts,^{4e} we studied the reactivity of compounds **5b** and **6b** toward styrene. No reaction was observed upon mixing the reagents in CH_2Cl_2 , THF, or toluene and allowing the mixtures to stand at room temperature for several hours. Heating equimolar amounts of **5b** and styrene in THF at 65°C led to conversion of the sulfonium complex to $[\text{Mn}(\text{OTf})(\text{CO})_3(\text{bipy})]$ over a period of 5 h (IR monitoring). The nature of the manganese product, which could be isolated by in vacuo evaporation of volatiles followed by washing with hexane, was ascertained by ^1H and ^{19}F NMR. To minimize the reaction time, we then employed toluene as solvent. Thus, the reactions of complexes **5b** and **6b** with styrene in toluene at 110°C took 20 min and 1 h, respectively (IR monitoring of the conversion to the triflate complex). To make possible a ^1H NMR analysis of the mixtures obtained as products, the reactions were repeated using deuterated toluene as solvent, and the resulting solutions, once filtered, were found to consist of mixtures of the corresponding triflate complex, phenylcyclopropane, unreacted styrene, and thioanisole (see Scheme 5).

The complexes $[\text{M}(\text{OTf})(\text{CO})_3(\text{bipy})]$ ($\text{M} = \text{Mn}$, Re) are only slightly soluble in toluene at room temperature; as a result, significant precipitation occurred as they form and upon subsequent cooling at room temperature and are thus separated as solids in the filtration. This solid accounted for 80–90% of the manganese or rhenium complex used as precursor.¹⁹ The presence of thioanisole indicates that, under the reaction conditions used, the $\text{S}-\text{CH}_2$ bond is cleaved, the CH_2 unit is transferred from the metal fragment to the olefin, and the triflate ion, initially present as counterion of the cationic sulfonium complex, coordinates the metal, recycling the metal fragment (since the treatment of the triflate complexes with Na/Hg affords the $\text{Na}[\text{M}(\text{CO})_3(\text{bipy})]$ salts). The typical ratio of cyclopropane to unreacted styrene obtained either with $[\text{Mn}(\text{CH}_2\text{SMePh})-$

(17) For an example of the employment of organic sulfur ylides as alkylating agents, see: Matsuyama, H.; Nakamura, T.; Iyeda, M. *J. Org. Chem.* **2000**, *65*, 4796.

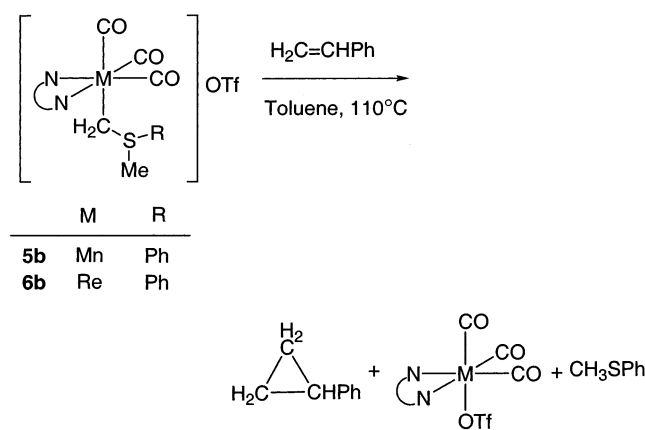
(18) See for instance: (a) Brookhart, M.; Nelson, G. O. *J. Am. Chem. Soc.* **1977**, *99*, 6097. (b) Kegley, S. E.; Brookhart, M.; Husk, G. R. *Organometallics* **1982**, *1*, 760. (c) Kuo, G.-H.; Helquist, P.; Kerber, R. C. *Organometallics* **1984**, *3*, 806.

(19) When the mixture obtained from the reaction of styrene and either **5b** or **6b** is extracted with CH_2Cl_2 and washed with hexane, the triflate complexes $[\text{Mn}(\text{OTf})(\text{CO})_3(\text{bipy})]$ and $[\text{Re}(\text{OTf})(\text{CO})_3(\text{bipy})]$, respectively, are obtained in nearly quantitative yield.

Table 3. Crystal Data and Refinement Details for Complexes 1b, 2a, 5b, and 6b

	1b	2a	5b	6b
formula	C ₂₀ H ₁₅ MnN ₂ O ₃ S ^{-1/4} CH ₂ Cl ₂	C ₁₅ H ₁₃ N ₂ O ₃ ReS	C ₂₂ H ₁₈ F ₃ MnN ₂ O ₆ S ₂	C ₂₂ H ₁₈ F ₃ N ₂ O ₆ ReS ₂
fw	439.57	487.53	582.44	713.70
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 1	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> , Å	13.6409(19)	6.925(4)	28.751(2)	28.484(3)
<i>b</i> , Å	16.735(2)	8.634(5)	12.3958(10)	12.5962(11)
<i>c</i> , Å	17.352(2)	15.094(8)	15.3655(13)	15.3112(14)
α, deg	90	78.728(8)	90	90
β, deg	99.517(2)	81.920(9)	114.397(2)	113.469(2)
γ, deg	90	70.037(8)	90	90
<i>V</i> , Å ³	3906.6(9)	829.3(8)	4980.9(7)	5039.0(8)
<i>Z</i>	8	2	8	8
<i>T</i> , K	298(2)	298(2)	293(2)	298(2)
<i>D</i> _c , g cm ⁻³	1.495	1.953	1.553	1.882
<i>F</i> (000)	17960	464	2368	2768
λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73	0.710 73
cryst size, mm	0.06 × 0.07 × 0.23	0.16 × 0.14 × 0.04	0.10 × 0.24 × 0.30	0.08 × 0.14 × 0.16
μ, mm ⁻¹	0.875	7.464	0.761	5.051
scan range, deg	1.70 ≤ θ ≤ 23.35	1.38 ≤ θ ≤ 23.64	1.56 ≤ θ ≤ 23.28	1.56 ≤ θ ≤ 23.27
no. of rflns measd	24 517	5187	15 561	11 092
no. of indep rflns	5639	2412	3586	3613
no. of data/restraints/params	5639/0/511	2412/0/200	3586/0/326	3613/0/327
goodness of fit on <i>F</i> ²	1.016	1.001	1.015	1.007
R1/wR2 (<i>I</i> > 2σ(<i>I</i>))	0.0461/0.0560	0.0248/0.0647	0.0794/0.2434	0.0305/0.0785
R1/wR2 (all data)	0.1068/0.0632	0.0278/0.0659	0.0893/0.2578	0.0392/0.0812

Scheme 5



(CO)₃(bipy)]OTf (**5b**) or with [Re(CH₂SMePh)(CO)₃(bipy)]OTf (**6b**) as cyclopropanating reagent was 1:1. Since the triflate complex [M(OTf)(CO)₃(bipy)] (M = Mn, Re) is obtained in high yield as the product (with respect to **5b** or **6b**), but a conversion of only about 50%²⁰ is found for the cyclopropanation of styrene, it must be assumed that the transient carbenoid species has more pathways for evolution than olefin cyclopropanation. Decomposition of some of the carbene complex in stoichiometric cyclopropanation reactions has been previously noted,² and accordingly, excesses of these complexes or the substituted sulfonium salts in their reactions with olefins are commonly used.^{4e} A plausible decomposition product for our sulfonium compounds would be ethylene, resulting from the formal coupling of two methylene moieties;²¹ however, we have been unable to detect it in our reaction mixtures, likely due to its low solubility at the temperature at which the

(20) The yield of phenylcyclopropane, evaluated by ¹H NMR integration using ferrocene as internal standard, was found to be 44(±5)% with compound [Mn(CH₂SMePh)(CO)₃(bipy)]OTf (**5b**).

(21) For instance, the olefins resulting from formal carbene coupling are formed as byproducts in metal-catalyzed cyclopropanations using diazo compounds as the primary carbene source: Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911.

reactions were conducted. Similar cyclopropanation experiments conducted with [Mn(CH₂SMePh)(CO)₃(bipy)]BF₄ (**7**; prepared by reaction of **1b** with trimethyloxonium tetrafluoroborate) afforded a mixture of phenylcyclopropane, unreacted styrene, and thioanisole in a ratio indistinguishable (¹H NMR integration) from that obtained using compound **5b**, along with an unidentified metal species.²² Thus, in contrast with the results obtained by Helquist, cyclopropanation of styrene with the cationic complexes reported here shows no appreciable dependence of the nature of the counterion.^{4c}

Experimental Section

General procedures were given elsewhere.⁸

Crystal Structure Determination for Compounds 1b, 2a, 5b, and 6b. A suitable crystal was attached to a glass fiber and transferred to a Bruker AXS SMART 1000 diffractometer with graphite-monochromatized Mo Kα X-radiation and a CCD area detector. A hemisphere of the reciprocal space was collected up to 2θ = 48.6°. Raw frame data were integrated with the SAINT²³ program. The structure was solved by direct methods with SHELXTL.²⁴ A semiempirical absorption correction was applied with the program SADABS.²⁵ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms with a common thermal parameter. All calculations and graphics were made with SHELXTL. Crystal and refinement data are presented in Table 3.

[Mn(CH₂SMe)(CO)₃(bipy)] (1a). An oven-dried Schlenk flask was charged with [MnBr(CO)₃(bipy)] (0.300 g, 0.800 mmol) and a PTFE-coated stirbar. The flask was subjected to three vacuum–nitrogen cycles. Under a strong stream of nitrogen, THF (25 mL) was added. After the mixture was

(22) This compound showed IR ν_{CO} bands at 2041 and 1938 cm⁻¹ in CH₂Cl₂ and was only slightly soluble in CH₂Cl₂, THF, or toluene. These wavenumber values are consistent with a cationic formulation, but we have been unable to further characterize this species.

(23) SAINT+: SAX area detector integration program, version 6.02; Bruker AXS, Inc., Madison, WI, 1999.

(24) Sheldrick, G. M. SHELXTL, An integrated system for solving, refining, and displaying crystal structures from diffraction data, version 5.1; Bruker AXS, Inc., Madison, WI, 1998.

(25) Sheldrick, G. M. SADABS, Empirical Absorption Correction Program; University of Göttingen, Göttingen, Germany, 1997.

stirred to ensure complete dissolution, the flask was open under nitrogen, and 15 g of 0.5% sodium amalgam was added to the orange solution. Three new vacuum–nitrogen cycles were applied, and a vigorous magnetic stirring was maintained for 2 h at room temperature. Although a deep blue-violet color developed in about 15 min, IR monitoring showed that the longer time was necessary for the reaction to reach completion. The anion showed IR ν_{CO} bands at 1912, 1823, and 1782 cm^{-1} . After it was allowed to settle, the solution was transferred onto a solution of $\text{ClCH}_2\text{SCH}_3$ (67 μL , 0.800 mmol) in THF (10 mL), previously cooled to -78°C , using a cannula tipped with filter paper. The color of the solution changed to red. The solution was filtered through Florisil. The solvent was removed under vacuum to afford complex **1a** as an orange solid. Yield: 0.199 g, 70%. IR (THF, cm^{-1}): 1996, 1896. ^1H NMR (CD_2Cl_2): δ 9.05, 8.09, 7.90, and 7.38 (m, 2H each, bipy), 1.82 (s, 3H, CH_3), 1.27 (s, 2H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 227.04 (2CO), 213.33 (CO), 154.53, 153.10, 136.92, 125.33, 122.12 (bipy), 32.36 (CH_2), 24.29 (CH_3). Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{MnN}_2\text{O}_3\text{S}$: C, 50.69; H, 3.67; N, 7.86. Found: C, 50.45; H, 3.62; N, 7.78.

[Mn(CH₂SPh)(CO)₃(bipy)] (1b). Following the procedure described for **1a**, the reaction of $[\text{MnBr}(\text{CO})_3(\text{bipy})]$ (0.300 g, 0.800 mmol) with sodium amalgam (15 g, 0.5%), followed by the reaction with ClCH_2SPh (107 μL , 0.800 mmol) afforded **1b** as an orange solid. Slow diffusion of hexanes into a solution of **1b** in THF at room temperature afforded orange crystals, one of which was used for X-ray analysis. Yield: 0.241 g, 72%. IR (THF, cm^{-1}): 1999, 1901. ^1H NMR (CD_2Cl_2): δ 9.11, 8.13, 7.93, and 7.43 (m, 2H each, bipy), 7.03 (m, 5H, Ph), 1.27 (s, 2H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 226.31 (2CO), 223.14 (CO), 154.63, 153.24 (bipy), 147.88 (Ph), 137.28, 128.23 (bipy), 125.59 (Ph), 124.74 (bipy), 123.00, 122.35 (Ph), 23.57 (CH_2). Anal. Calcd for $\text{C}_{20}\text{H}_{15}\text{MnN}_2\text{O}_3\text{S}$: C, 57.42; H, 3.61; N, 6.69. Found: C, 57.37; H, 3.78; N, 6.56.

[Re(CH₂SMe)(CO)₃(bipy)] (2a). A solution of $[\text{ReBr}(\text{CO})_3(\text{bipy})]$ (0.300 g, 0.592 mmol) in THF (25 mL) was kept vigorously stirred with 15 g of 0.5% sodium amalgam for 24 h at room temperature. Given the long reaction time, a flask provided with a PTFE Young stopcock (rather than a greased glass stopcock) was used. The resulting blue-violet solution was transferred with a cannula tipped with filter paper to a solution of $\text{ClCH}_2\text{SCH}_3$ (50 μL , 0.593 mmol) in THF (10 mL), previously cooled to -78°C . The color of the solution changed to orange. Subsequent workup as described for **1a,b** afforded **2a** as an orange solid. Slow diffusion of hexanes into a solution of **2a** in CH_2Cl_2 at -20°C afforded orange crystals, one of which was used for X-ray analysis. Yield: 0.179 g, 62%. IR (THF, cm^{-1}): 1998, 1890. ^1H NMR (CD_2Cl_2): δ 9.04, 8.22, 8.07, 7.99 (m, 2H each, bipy), 1.76 (s, 3H, CH_3), 1.03 (s, 2H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 202.44 (2CO), 192.53 (CO), 155.36, 153.28, 134.12, 126.84, 123.27 (bipy), 25.86 (CH_3), 23.25 (CH_2). Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_3\text{ReS}$: C, 36.95; H, 2.68; N, 5.74. Found: C, 36.87; H, 2.62; N, 5.68.

[Re(CH₂SPh)(CO)₃(bipy)] (2b). Following the procedure described for **2a**, complex **2b** was obtained by reaction of $[\text{ReBr}(\text{CO})_3(\text{bipy})]$ (0.300 g, 0.592 mmol) with sodium amalgam (0.5%), followed by the reaction with ClCH_2SPh (80 μL , 0.592 mmol). Yield: 0.101 g, 65%. IR (THF, cm^{-1}): 2001, 1891. ^1H NMR (CD_2Cl_2): δ 9.08, 8.20, 8.07, 7.50 (m, 2H each, bipy), 6.90 (m, 5H, Ph), 1.22 (s, 2H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 201.79 (2CO), 192.74 (CO), 155.41, 153.44 (bipy), 149.44 (Ph), 138.44, 128.20 (bipy), 127.03 (Ph), 124.30 (bipy), 123.42, 122.86 (Ph), 26.39 (CH_2). Anal. Calcd for $\text{C}_{20}\text{H}_{15}\text{N}_2\text{O}_3\text{ReS}$: C, 43.70; H, 2.75; N, 5.09. Found: C, 43.64; H, 2.70; N, 5.01.

[Re(CH₃)(CO)₃(bipy)] (3). Complex **3** was prepared as described in ref 13 by reaction of $[\text{ReBr}(\text{CO})_3(\text{bipy})]$ (0.100 g, 0.198 mmol) with methylmagnesium chloride (66 μL of a 3.0 M solution in Et_2O , 0.198 mmol) in THF (20 mL). The color of the solution changed from yellow to orange. The solution was filtered through silica, and the solvent was removed under vacuum, affording an orange solid. IR (THF, cm^{-1}): 1991,

1883, 1878. ^1H NMR (CD_2Cl_2): δ 9.09, 8.25, 8.02, 7.46 (m, 2H each, bipy), -0.91 (s, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 204.58 (2CO), 192.81 (CO), 155.01, 152.85, 137.57, 126.63, 123.38 (bipy), -0.35 (CH_3).

[Re(SPhMe)(CO)₃(bipy)]PF₆ (4). SPhMe (12 μL , 0.104 mmol) was added to a solution of $[\text{Re}(\text{CH}_3)(\text{CO})_3(\text{bipy})]$ (0.046 g, 0.104 mmol) in CH_2Cl_2 (10 mL) and the solution was cooled at -78°C . A solution of $[\text{CPh}_3][\text{PF}_6]$ (0.040 g, 0.104 mmol) in CH_2Cl_2 (10 mL), previously cooled to -78°C , was added. The color of the solution changed from orange to yellow. Volatiles were removed under vacuum, and the solid residue was washed with diethyl ether (2×5 mL). The solid was redissolved in CH_2Cl_2 (5 mL). Slow diffusion of hexanes at room temperature into this solution afforded **4** as yellow crystals. Yield: 0.072 g, 87%. IR (CH_2Cl_2): 2042, 1951, 1936. ^1H NMR (CD_2Cl_2): δ 8.81 (m, 2H, bipy), 8.25 (m, 4H, bipy), 7.63 (m, 2H, bipy), 7.32 (m, 1H, Ph), 7.15 (m, 3H, Ph), 6.67 (m, 2H, Ph), 2.99 (s, 3H, CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 197.26 (2CO), 194.64 (CO), 155.60, 153.62, 141.43 (bipy), 130.52 (Ph), 130.38 (bipy), 129.01, 128.36, 127.01 (Ph), 124.99 (bipy), 23.74 (CH_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -143.07 (m (711.48), PF_6). Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{F}_6\text{N}_2\text{O}_3\text{PSRe}$: C, 34.53; H, 2.31; N, 4.02. Found: C, 34.57; H, 2.19; N, 4.11.

[Mn(CH₂SMe₂)(CO)₃(bipy)]OTf (5a). MeOTf (32 μL , 0.280 mmol) was added to a solution of **1a** (0.100 g, 0.280 mmol) in CH_2Cl_2 (20 mL) at -78°C . The solution was allowed to reach room temperature and stirred for 15 min. The solvent was removed under vacuum to afford complex **5a** as a yellow solid. Yield: 0.134 g, 92%. IR (CH_2Cl_2 , cm^{-1}): 2019, 1930, 1906. ^1H NMR (CD_2Cl_2): δ 9.03, 8.35, 8.11, and 7.58 (m, 2H each, bipy), 2.71 (s, 6H, CH_3), 1.18 (s, 2H, CH_2). ^{19}F NMR (CD_2Cl_2): δ -77.81 . Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{F}_3\text{MnN}_2\text{O}_6\text{S}_2$: C, 39.23; H, 3.09; N, 5.38. Found: C, 39.37; H, 3.12; N, 5.40.

[Mn(CH₂SMePh)(CO)₃(bipy)]OTf (5b). Following the procedure described for **5a**, complex **1b** (0.100 g, 0.239 mmol) reacted with MeOTf (27 μL , 0.239 mmol) to afford **5b** as a yellow solid. Slow diffusion of hexanes into a solution of **5b** in THF at room temperature afforded yellow crystals, one of which was used for X-ray analysis. Yield: 0.130 g, 94%. IR (CH_2Cl_2 , cm^{-1}): 2019, 1931, 1909. ^1H NMR (CD_2Cl_2): δ 8.98, 8.75 (m, 1H each, bipy), 8.36, 8.10 (m, 2H each, bipy), 7.65–7.33 (m, 7H, 2H, bipy, and 5H, Ph), 2.89 (s, 3H, CH_3), 1.74, 1.70, 1.44, 1.40 (AB, 2H, CH_2). ^{19}F NMR (CD_2Cl_2): δ -77.89 . $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 224.69 (CO), 222.77 (CO), 214.86 (CO), 156.31, 154.54, 154.27, 140.72, 140.59 (bipy), 135.33, 132.93, 132.47, 130.39 (Ph), 128.63, 128.41, 125.51, 125.48 (bipy), 121.92 (q(322.15), CF_3SO_3), 37.28 (CH_3), 34.30 (CH_2). Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{F}_3\text{MnN}_2\text{O}_6\text{S}_2$: C, 45.36; H, 3.11; N, 4.80. Found: C, 45.41; H, 3.26; N, 4.69.

[Re(CH₂SMe₂)(CO)₃(bipy)]OTf (6a). MeOTf (23 μL , 0.205 mmol) was added to a solution of **2a** (0.100 g, 0.205 mmol) in CH_2Cl_2 (20 mL) at -78°C . The solution was allowed to reach room temperature and then stirred for 15 min. The solvent was removed under vacuum to afford **6a** as a yellow solid. Yield: 0.118 g, 89%. IR (CH_2Cl_2 , cm^{-1}): 2017, 1916, 1898. ^1H NMR (CD_2Cl_2): δ 8.97, 8.44, 8.19, 7.61 (m, 2H each, bipy), 2.69 (s, 6H, CH_3), 1.28 (s, 2H, CH_2). ^{19}F NMR (CD_2Cl_2): δ -78.71 . Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{F}_3\text{N}_2\text{O}_6\text{ReS}_2$: C, 33.33; H, 2.47; N, 4.29. Found: C, 33.27; H, 2.54; N, 4.33.

[Re(CH₂SMePh)(CO)₃(bipy)]OTf (6b). Following the procedure described for **6a**, the reaction of **2b** (0.100 g, 0.182 mmol) with MeOTf (20 μL , 0.182 mmol) afforded **6b** as a yellow solid. Slow diffusion of hexanes into a solution of **6b** in THF at room temperature afforded yellow crystals, one of which was used for X-ray analysis. Yield: 0.109 g, 92%. IR (CH_2Cl_2 , cm^{-1}): 2017, 1915, 1900. ^1H NMR (CD_2Cl_2): δ 8.95, 8.68 (m, 1H each, bipy), 8.51, 8.18 (m, 2H each, bipy), 7.67–7.22 (m, 7H, 2H, bipy, and 5H, Ph), 2.88 (s, 3H, CH_3), 1.77, 1.73, 1.52, 1.48 (AB, 2H, CH_2). ^{19}F NMR (CD_2Cl_2): δ -78.72 . $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 199.14 (CO), 198.74 (CO), 190.64 (CO), 155.58, 153.15, 152.84, 140.25, 140.09 (bipy), 133.93, 132.02,

131.09, 128.99 (Ph), 128.22, 127.99, 125.16, 125.18 (bipy), 121.33 (q (321.07), CF₃SO₃), 35.99 (CH₃), 25.79 (CH₂). Anal. Calcd for C₂₂H₁₈F₃N₂O₆ReS₂: C, 37.02; H, 2.54; N, 3.92. Found: C, 37.11; H, 2.34; N, 3.79.

Reaction of [M(CH₂SMePh)(CO)₃(bipy)]OTf (5b) with KPPPh₂. To a solution of **5b** (0.050 g, 0.085 mmol) in THF (10 mL) cooled to -78 °C was added a solution of KPPPh₂ (prepared by reaction of HPPPh₂ (15 μL, 0.085 mmol) with K[N(SiMe₃)₂] (0.170 mL of a 0.5 M solution in toluene, 0.085 mmol)) in THF. The mixture was stirred for 20 min.²⁶ Volatiles were removed under vacuum, and the solid residue was extracted with CH₂-Cl₂ (2 × 10 mL). The solvent was evaporated, and the solid was redissolved in THF (10 mL). Slow diffusion of hexanes (15 mL) into this solution in THF at room temperature afforded orange crystals of **1b**.

Cyclopropanation of Styrene. [M(CH₂SMePh)(CO)₃(bipy)]-OTf (0.100 mmol) was dissolved in *d*₈-toluene (1 mL), and styrene (11 μL, 0.100 mmol) was added. The mixture was heated at 110 °C for 20 min for M = Mn or 1 h for M = Re. An ¹H NMR spectrum was recorded and showed the presence of [M(OTf)(CO)₃(bipy)],²⁷ SPhMe, unreacted styrene, and phenylcyclopropane (7.22 (m, 5H, Ph), 1.78 (m, 1H), 0.93 (m, 2H), 0.72 (m, 2H)). For the cyclopropanation with compound **5b**, 10 μL of a 1 M solution of ferrocene in CH₂Cl₂ (0.010 mmol)

(26) A ³¹P NMR spectrum of the crude reaction mixture showed the presence of free PMePPPh₂ (-26.33 ppm in THF using an internal capillary tube containing D₂O).

(27) Hevia, E.; Pérez, J.; Riera, L.; Riera, V.; Miguel, D. *Organometallics* **2002**, *21*, 1750.

was added to the mixture of the reagents. Integration of [Fe-(η⁵-Cp₂)] (4.05 ppm) and the styrene signal at 5.07 ppm confirmed the 10:1 ratio of the olefin and the standard. After completion of the reaction, the integration of the phenylcyclopropane signal at 0.72 ppm against that of ferrocene indicated a 44% yield of the cyclopropane.

[Mn(CH₂SMePh)(CO)₃(bipy)]BF₄ (7). Me₃OBF₄ (0.035 g, 0.239 mmol) was added to a solution of **1b** (0.100 g, 0.239 mmol) in THF (20 mL). Workup similar to that described for **5b** afforded **7** as a yellow solid. Yield: 0.113 g, 89%. IR (CH₂-Cl₂, cm⁻¹): 2018, 1930, 1909. ¹H NMR (CD₂Cl₂): δ 8.99, 8.78 (m, 1H each, bipy), 8.34, 8.10 (m, 2H each, bipy), 7.64–7.38 (m, 7H, 2H bipy and 5H Ph), 2.90 (s, 3H, CH₃), 1.73, 1.71, 1.44, 1.41 (AB, 2H, CH₂). Anal. Calcd for C₂₂H₁₈BF₄MnN₂O₃S: C, 49.65; H, 3.40; N, 5.26. Found: C, 49.59; H, 3.34; N, 5.20.

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Supporting Information Available: Tables giving positional and thermal parameters and bond distances and bond angles for **1b**, **2a**, **5b**, and **6b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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