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Notes

Synthesis and Reactivity of New (Methoxy)methyl Complexes of Manganese(I) and Rhenium(I)

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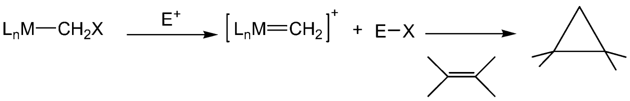
*Summary: The reactions of Na[M(CO)$_3$(bipy)] (M = Mn, Re) with ClCH$_2$OCH$_3$ afford the (methoxy)methyl complexes [M(CH$_2$OCH$_3$)(CO)$_3$(bipy)] (M = Mn, **1**; Re, **2**), characterized by IR and NMR spectroscopy and, in the case of **1**, also by X-ray diffraction. Highly electrophilic species, presumably cationic alkylideneoxonium complexes, although they were not detected, were prepared in situ by reaction of **1** and **2** with methyl triflate. These species react with neutral nucleophiles such as SMePh to generate the alkylidenesulfonium complexes [M(CH$_2$SPhMe)(CO)$_3$(bipy)]$^+$[OTf]$^-$ (M = Mn, **3**; Re, **4**) and with styrene to give phenylcyclopropane and the corresponding triflate complexes [M(OTf)(CO)$_3$(bipy)].*

Introduction

Although much less studied than heteroatom-stabilized Fischer carbenes, highly electrophilic, low oxidation state nonstabilized carbenes have been found to mediate several important organic transformations, such as olefin cyclopropanation.[1] One of the synthetic approaches to the nonstabilized carbenes is the reaction of an electrophile with α-substituted alkyl complexes L$_n$M-CH$_2$X (where X = OR, SR, halide, etc.) (eq 1).[2]



Recently we reported the synthesis and characterization of new (alkylthio)methyl complexes [M(CH$_2$SR)(CO)$_3$(bipy)] (M = Mn, Re),[3] which react with methyl triflate to afford stable cationic alkylidenesulfonium complexes [M(CH$_2$SRMe)(CO)$_3$(bipy)]$^+$[OTf]$^-$. The latter do not react with styrene at room temperature; however they cyclopropanate this olefin at 110 °C. In general, (alkoxy)methyl complexes can react with strong electrophiles to form highly electrophilic alkylideneoxonium species, which cannot be detected but can cyclopropanate olefins in much milder conditions than related alkylidenesulfonium complexes. Herein we report the synthesis and characterization of the new (methoxy)methyl complexes [M(CH$_2$OCH$_3$)(CO)$_3$(bipy)] (M= Mn, Re), their reactivity toward electrophiles, and their ability to cyclopropanate styrene in the presence of an electrophile. The organometallic fragments {M(CO)$_3$(bipy)} (M = Mn, Re) have been widely studied in coordination and organometallic chemistry and, in the particular case of M = Re, in the fields of photophysics,[4] CO$_2$[5] activation, and biological labeling;[6] however their use as auxiliaries for organic transformations remains less explored.[7]

Results and Discussion

A THF solution of Na[MnCO)$_3$(bipy)] (generated in situ by reaction of the bromo complex [MnBrCO)$_3$(bipy)] and sodium amalgam, see Experimental Section) was allowed to react with chloromethyl methyl ether, yielding the new compound [Mn(CH$_2$OCH$_3$)(CO)$_3$(bipy)] (**1**) (Scheme 1). The reaction was accompanied by a dramatic color change from deep blue-violet to red. The ν_{CO} IR bands of the crude solution of **1** showed the characteristic pattern for a *fac*-tricarbonyl moiety, with two intense bands at 1991 and 1889 (broad) cm^{-1}. These values are significantly shifted to lower frequencies with respect to the bromo precursor (2022, 1934, 1914 cm^{-1}), but they are only slightly different from the values found for the (methylthio)methyl complex [Mn(CH$_2$SCH$_3$)(CO)$_3$(bipy)] (1996, 1896 cm^{-1}). The higher electron-releasing ability of the (methoxy)methyl ligand [compared to the (methylthio)methyl group] accounts for the difference of 5 cm^{-1} in the values of the ν_{CO} IR of these compounds. Compound **1** was isolated as red crystals in a high yield and characterized in solution using NMR spectroscopy and in the solid state by X-ray diffraction studies. Its ^{1}H NMR spectrum showed the presence of four multiplets for the

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[6] See for instance: (a) Kutal, C.; Corbin, J.; Ferraudi, G. *Organometallics* **1987**, *6*, 553. (b) Scheiring, T.; Klein, A.; Kaim, W. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2569.

[7] For recent examples of our own work in this area see: (a) Hevia, E.; Pérez, J.; Riera, V.; Miguel, D. *Angew. Chem., Int. Ed.* **2002**, *20*, 3558. (b) Hevia, E.; Pérez, J.; Riera, V.; Miguel, D.; Campomanes, P.; Menéndez, M. I.; Sordo, T. L.; García-Granda, S. *J. Am. Chem. Soc.* **2003**, *125*, 3706.

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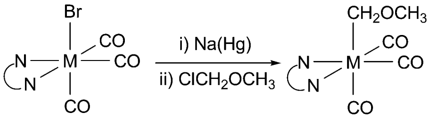
Scheme 1



	M
1	Mn
2	Re

bipyridine ligand, consistent with the presence of a mirror plane in the molecule. In addition, two resonances at 3.68 and 2.99 ppm were found for the methylene and methyl groups of the (methoxy)methyl ligand, respectively. These groups give rise to two signals in the ^{13}C NMR spectrum at 91.28 and 65.29, respectively. These values are considerably further downfield than the ones found for the related (alkylthio)methyl complex [1.27 (CH_2) and 1.82 (CH_3) ppm in the ^{1}H NMR spectrum, 32.36 (CH_2) and 24.29 (CH_3) ppm in the ^{13}C NMR spectrum],[3] showing the remarkable influence of the heteroatom present in the α-position to the CH_2 moiety. Following the same procedure, the rhenium congener [Re(CH_2OCH_3)(CO)$_3$(bipy)] (**2**) was prepared and spectroscopically characterized (see Experimental Section).

The chemical shifts of the resonances of the CH_3 moiety in complex **2** in the ^{1}H and ^{13}C NMR spectra (2.83 and 63.89 ppm, respectively) show little variation from the corresponding ones for complex **1** (2.99 and 65.29 ppm), whereas for the methylene group (which is directly bonded to the metal and, in consequence, will be more affected by the change of the transition metal from Mn to Re) there is a significant deviation in the chemical shifts (3.04 and 81.70 ppm for **2** versus 3.68 and 91.28 ppm for **1** in the ^{1}H and ^{13}C NMR spectra, respectively).

The structure of **1** was characterized by X-ray diffraction studies (Figure 1 and Table 1). Despite the fact that (methoxy)methyl complexes are well-known and important intermediates in synthesis, the number of elucidated crystal structures is still relatively scarce. On searching the Cambridge Structural Database,[8] only 13 complexes were found, and just one of these contains manganese.[9] The molecular structure of **1** shows a manganese atom in a distorted octahedral environment coordinated to three carbonyl ligands in a *fac* disposition, a chelating bipyridine, and a η^1(C) (methoxy)methyl ligand. The major deviation from an idealized octahedral geometry is imposed by the bite angle of the rigid bidentate ligand bipyridine [N1MnN2: 78.29(8)°]. The Mn−CO distance is significantly longer for the carbonyl ligand trans to the methoxy(methyl) ligand [1.835 (3) Å versus 1.790(3) and 1.785(3) Å for the other two Mn−CO distances], which indicates that the alkyl ligand has a stronger trans influence than the nitrogens of the bipy ligand. The large trans influence of the CH_2OCH_3 ligand has been previously reported.[10] The Mn−C distance [2.136(3) Å] is within the range for a single Mn−C bond found in other alkyl complexes of manganese tricarbonyl fragments such as the related (alkylthio)methyl [Mn(CH_2SPh)(CO)$_3$(bipy)] [2.125(4) Å][3] or the (methoxy)methyl [Mn(CH_2OCH_3)(CO)$_3$(dppp)] (dppp = 1,3-bis(diphenylphosphino)propane) [2.173(10) Å].[9]

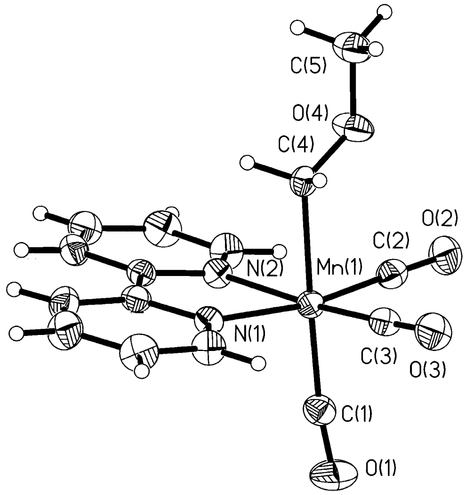


Figure 1. Molecular structure of **1** with 30% probability displacement ellipsoids.

Table 1. Selected Bond Distances and Angles for 1

Mn(1)−C(4)	2.136(3)	Mn(1)−N(1)	2.042(2)
Mn(1)−C(1)	1.835(3)	Mn(1)−N(2)	2.047(2)
Mn(1)−C(2)	1.790(3)	C(4)−O(4)	1.387(3)
Mn(1)−C(3)	1.785(3)	O(4)−C(5)	1.413(3)
C(1)−Mn(1)−C(4)	178.28(10)	C(2)−Mn(1)−N(1)	170.70(10)
C(2)−Mn(1)−C(4)	88.69(10)	C(1)−Mn(1)−N(1)	97.03(10)
C(3)−Mn(1)−C(4)	86.91(11)	C(3)−Mn(1)−N(2)	172.07(10)
N(1)−Mn(1)−C(4)	84.15(9)	C(2)−Mn(1)−N(2)	95.41(10)
N(2)−Mn(1)−C(4)	86.62(9)	C(1)−Mn(1)−N(2)	94.85(10)
C(3)−Mn(1)−C(1)	91.70(12)	N(1)−Mn(1)−N(2)	78.29(8)
C(3)−Mn(1)−C(2)	89.03(12)	O(4)−C(4)−Mn(1)	113.93(3)
C(2)−Mn(1)−C(1)	90.27(12)	C(4)−O(4)−C(5)	113.1(2)
C(3)−Mn(1)−N(1)	96.48(10)		

In a first attempt to prepare cationic oxonium or methylene complexes following the methodology previously employed for the iron compounds [(CO)$_2$CpFe(CH_2XR)],[1] compounds **1** and **2** were treated with a stoichiometric amount of triflic acid in CH_2Cl_2. The triflate compounds [M(OTf)(CO)$_3$(bipy)] were formed instantaneously, as shown by the IR ν_{CO} bands of the solutions, which shifted almost 30 cm^{-1} in each case to higher frequencies. When these reactions were carried out in a NMR tube in CD_2Cl_2 solution, the ^{1}H NMR spectra revealed not only the signals of the triflate complexes but also a singlet at 3.25 ppm assignable to Me_2O, showing that the metal−alkyl bond, and not the oxygen atom, has been the site of electrophilic attack. This is an interesting result, as previous examples found in the literature show that for other related complexes, such as [Cp($Ph_2PCH_2CH_2PPh_2$)Fe(CH_2OCH_3)][11] or [(CO)$_5$W{CH(OMe)OPh}],[12] the protonation occurs at the oxygen atom.[1] This difference can, in part, be due to the high reactivity that the metal−carbon bonds in these manganese and rhenium compounds present toward acids. For instance, they react with much weaker acids than HOTf such as phenols or thiols.

We next studied the reactivity of **1** and **2** toward the strong methylating agent MeOTf. The ^{1}H NMR spectra of the solutions in CD_2Cl_2 showed once again the formation of the triflate compounds and Me_2O. This result implies that this time the electrophilic attack has occurred on the oxygen atom, facilitating the O−C bond cleavage. No (methyl)ethyl ether (the expected product of an electrophilic attack to the M−C bond) was

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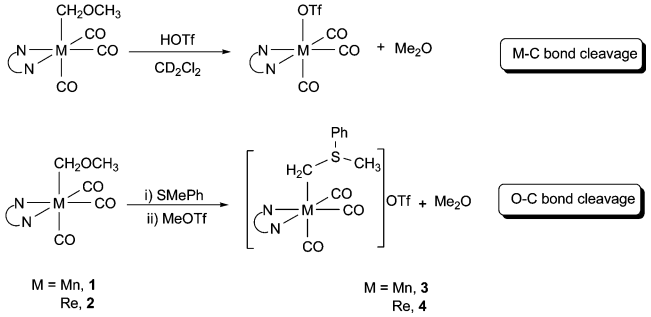
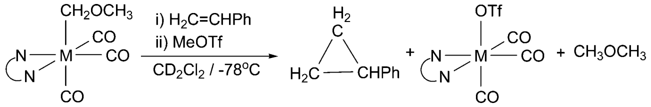
Scheme 2



Scheme 3



detected. The fact that the only organometallic products observed in the ^1H NMR spectra are the triflate compounds can be due to the instability, at least at room temperature, of the alkylidene-oxonium compounds, which preclude their observation by NMR techniques.

However, when the same methodology was employed in the presence of 1 molar equiv of thioanisole, the alkylidenesulfonium species $[M(CH_2SPhMe)(CO)_3(bipy)]^+[OTf]^-$ (M = Mn, **3**; Re, **4**)[3] were obtained (Scheme 2). This can be rationalized in terms of the initial formation of highly electrophilic alkylideneoxonium complexes that then would react with a weak nucleophile such as PhSMe to afford the more stable alkylidenesulfonium complexes **3** and **4** along with dimethyl ether. This result is particularly noteworthy since it contrasts with the ones previously found for the complexes **3** and **4**, which were found to be inert toward neutral nucleophiles such as pyridine, dimethyl sulfide, or PPh_3,[3] and illustrates the higher electrophilic character of the alkylideneoxonium complexes. On the other hand, Barefield has shown that the reactions of $[Cp(CO)_2Fe(CH_2SPh_2)]BF_4$ with nucleophiles occur in two steps. First the cation $[Cp(CO)_2Fe(CH_2SPh_2)]^+$ undergoes reversible dissociative loss of SPh_2 to afford the relevant methylene complex $[Cp(CO)_2Fe({=}CH_2)]^+$ followed by the capture of this reactive species with the relevant nucleophile.[13] If a similar two-step mechanism was involved in the reactions of these rhenium and manganese alkylidenoxonium and alkylidenesulfonium compounds with nucleophiles, then their different reactivity toward neutral nucleophiles could be explained in terms of the diference in the relative rates of the two steps.

We investigated the ability of **1** and **2** to function as cyclopropanation reagents by studying their reaction with methyl triflate in the presence of styrene.[14] The mixture of the reagents was carried out at low temperature (−78 °C) in order to minimize possible side reactions or partial degradation of the reactive cationic intermediates, in deuterated dichloromethane, and monitored by ^1H NMR spectroscopy. After allowing the samples to reach room temperature, the spectra showed the conversion of the (methoxy)methyl compounds **1** and **2** to the triflate complexes $[M(OTf)(CO)_3(bipy)]$ (M = Mn, Re), as well as a mixture of phenylcyclopropane, unreacted styrene, and dimethyl ether (Scheme 3). At this point it is noteworthy that the treatment of the triflate complexes with sodium amalgam affords the $Na[M(CO)_3(bipy)]$ salts, recycling the metal fragments. The triflate complexes are obtained in almost quantitative yields; however, the conversion of styrene to phenylcyclopropane is only about 45−50%.[15] This can be explained by considering that the transient carbenoid species can evolve through different pathways.[16] A variety of side reactions related to decomposition of intermediate carbene species are known, and generally an excess of the organometallic complex is employed.[1] One possible decomposition route would be the coupling of two CH_2 moieties to form ethylene and an unsaturated organometallic fragment, which would be trapped by the triflate anion. The cyclopropane conversions are thus similar to the ones obtained using alkylidenesulfonium complexes $[M(CH_2SPhMe)(CO)_3(bipy)]^+[OTf]^-$ (M = Mn, **3**; Re, **4**);[3] however for the latter temperatures above 100 °C were required, whereas employing complexes **1** and **2** as precursors, the in situ-generated alkylideneoxonium complexes successfully cyclopropanate styrene under much milder conditions.

Table 2. Crystal Data and Refinement Details for 1

formula	$C_{15}H_{13}mnN_2O_4$
fw (g·mol^{-1})	340.21
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	6.9674(7)
b (Å)	8.5023(8)
c (Å)	14.1923(13)
α (deg)	74.046(2)
β (deg)	81.882(2)
γ (deg)	69.172(2)
V (Å^3)	3372.5(6)
Z	2
F(000)	348
D_c (g·cm^{-3})	1.497
cryst size (mm)	0.12 × 0.19 × 0.29
μ (Mo Kα, mm^{-1})	0.893
temperature (K)	298(2)
λ(Mo Kα) (Å)	0.71073
scan range (deg)	$1.49 \leq \theta \leq 23.28$
no. of data/restraints/params	2149/0/200
R1/wR2 ($I > 2\sigma(I)$)	0.034/0.0962
R1/wR2 (all data)	0.0359/0.0977

Experimental Section

General procedures were given elsewhere.[17]

Crystal Structure Determination for Compound 1. 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 $2\theta = 48.6°$. Raw frame data were integrated with the SAINT program.[18] The structure was solved by direct methods with SHELXTL.[19] A semiempirical absorption correction was applied with the program SADABS.[20]

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(13) McCarten, P.; Barefield, E. K. *Organometallics* **1998**, *17*, 4645.

(14) See for instance: O'Connor, E. J.; Brandt, S.; Helquist, P. *J. Am. Chem. Soc.* **1987**, *109*, 3739.

(15) The yields of phenylcyclopropane have been evaluated by ^1H NMR integration using ferrocene as an internal standard, and they have been found to be 42(±5)% with compound **1** and 47%(±5)% with compound **2**. Similar yields of phenylcyclopropane were observed when the experiment was repeated with increasing amounts of styrene.

(16) However, no spectroscopic evidence of the relevant methylene complex was found even when the reaction was carried out at low temperature and monitored by ^1H NMR.

(17) Hevia E.; Pérez, J.; Riera, V.; Miguel, D. *Organometallics* **2002**, *21*, 1966.

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

(19) 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.

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

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 2.

Synthesis of [Mn(CH_2OCH_3)$(CO)_3$(bipy)] (1). To an orange solution of [MnBr$(CO)_3$(bipy)] (0.30 g, 0.80 mmol) in THF (30 mL) was added 15.00 g of 0.5% sodium amalgam, and the mixture was vigorously stirred for 2 h. Although a deep purple color developed after 15 min, IR monitoring showed that longer reaction times are required to convert all the starting material into an anionic species, for which IR ν_{CO} bands appear at 1912, 1823, and 1782 cm^{-1}. The reaction mixture was allowed to settle, and the solution was transferred onto a solution of $ClCH_2OCH_3$ (60 μL, 0.80 mmol) in THF (10 mL) previously cooled at −78 °C using a cannula tipped with filter paper. The color of the solution changed instantaneously from deep violet to deep red. The solution was filtered through Florisil. The solvent was removed under vacuum, affording complex **1** as a red solid. Slow diffusion of hexane at room temperature into a solution of **1** in THF afforded red crystals, one of which was employed for X-ray analysis. Yield: 0.21 g, 77%. IR(THF, cm^{-1}): 1991, 1889. ^1H NMR(CD_2Cl_2): 9.07, 8.09, 7.87, 7.36 (m, 2H each, bipy), 3.68 (s, 2H, CH_2), 2.99 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 228.34 (2CO), 212.97 (CO), 154.24, 152.88, 136.33, 124.95, 122.04 (bipy), 91.28 (CH_2), 62.59 (CH_3). Anal. Calcd for $C_{15}H_{13}MnN_2O_4$: C, 52.95; H, 3.85; N, 8.23. Found: C, 52.87; H, 3.77; N, 8.35.

Synthesis of [Re(CH_2OCH_3)$(CO)_3$(bipy)] (2). To a yellow solution of [ReBr$(CO)_3$(bipy)] (0.30 g, 0.59 mmol) in THF (30 mL) was added 15.00 g of 0.5% sodium amalgam, and the mixture was allowed to stir at room temperature for 24 h. Given the long reaction times required, a flask provided with a Young stopcock (rather than a greased glass stopcock) was employed to minimize partial decomposition due to traces of oxygen. The resulting dark blue-violet solution was transferred via cannula onto another flask containing a solution of $ClCH_2OCH_3$ (45 μL, 0.52 mmol) in THF (10 mL) previously cooled at −78 °C. The color of the solution changed to orange. Similar workup as described for **1** affords compound **2** as an orange microcrystalline solid. Yield: 0.20 g, 77%. IR (THF, cm^{-1}): 1994, 1885. ^1H NMR (CD_2Cl_2): 9.05, 8.19, 7.99, 7.46 (m, 2H each, bipy), 3.04 (s, 2H, CH_2), 2.83 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 203.81 (2CO), 193.96 (CO), 155.41, 153.10, 137.83, 126.56, 123.10 (bipy), 81.70 (CH_2), 63.89 (CH_3). Anal. Calcd for $C_{15}H_{13}N_2O_4Re$: C, 38.21; H, 2.77; N, 5.94. Found: C, 38.32; H, 2.71; N, 5.85.

Cyclopropanation of Styrene. [M(CH_2OCH_3)$(CO)_3$(bipy)] (0.03 mmol) was dissolved in CD_2Cl_2 (0.5 mL), and a stoichiometric amount of styrene (3.5 μL, 0.03 mmol) was added. The solution was cooled at −78 °C, and MeOTf (3.4 μL, 0.03 mmol) was then introduced. The mixture was allowed to reach room temperature. A ^1H NMR spectrum recorded 4 h later showed the presence of [M(OTf)$(CO)_3$(bipy)], Me_2O, unreacted styrene, and phenylcyclopropane [7.22 (m, 5H, Ph), 1.78 (m, 1H), 0.93 (m, 2H), 0.72 (m, 2H)].

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Supporting Information Available: X-ray crystallographic data for compound **1** in CIF format. This material is available free of charge via the Internet at http://pubs.ac.org.

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