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Reactions of *cis*- and *trans*-(η^5-C_5H_5)Mo(CO)$_2$[P(OPh)$_3$]CH_2OCH_3 with Electrophiles

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Reactions of *trans*- and *cis*-CpMo(CO)$_2$[P(OPh)$_3$]CH_2OCH_3 (**1a,b**) with a variety of protonic acids and with Me_3SiOTf have been examined. The composition of product mixtures has been shown to be dependent upon the strength of the electrophile and the presence of nucleophiles such as Br^- or PPh_3 or the methylene acceptor Ph_3SiH and is proposed to be governed by complex equilibria involving transient oxonium ions as well as methylidene cations. Neither type of transient intermediate can be observed in low-temperature reactions. Methoxymethylidene cations, *trans*- and *cis*-CpMo(CO)$_2$[P(OPh)$_3$](=$CHOCH_3$)$^+$, are generated in some low-temperature reactions with electrophiles. Independent synthesis of these has shown that they decompose in solution at room temperature to metallacycle **2**, CpMo(CO)$_2$[P(OPh)$_2$(*o*-$OC_6H_4CH_2$)], and CpMo(CO)$_3$[P(OPh)$_3$]$^+$. Reactions of *trans*- and *cis*-CpMo(CO)$_2$[P(OPh)$_3$]-$CH_2OC(O)CF_3$ (**6a,b**) with CF_3COOH indicate that metallacycle formation occurs directly from the cis isomer (**6b**) in an acid-catalyzed process. Thermolysis studies of **6a,b** indicate that trans to cis isomerization is facile and that **6b** is readily converted to **2**. Thermolysis of *trans*-CpMo(CO)$_2$[P(OPh)$_3$]CH_2Br (**10b**) yields **2** and its ring-opened derivative as major products. Metallacycle **2** has been characterized by X-ray crystallography: a = 14.457(3) Å, b = 10.729(2) Å, c = 15.611(3)Å, β = 103.65(2)°, Z = 4, d_c = 1.53 g cm^{-3}, space group $P2_1/n$, and R = 0.024.

Introduction

Reactions of transition metal alkoxymethyl complexes with electrophiles have long been used to generate cationic metal–methylidene complexes. The earliest report of this reaction was by Pettit and Jolly[1] who presented chemical evidence for the intermediacy of Fp(=CH_2)$^+$ [Fp = η^5-$C_5H_5Fe(CO)_2$] from reactions of the corresponding methoxymethyl complex with HBF_4. In the presence of alkenes or cycloalkenes, cyclopropanes were generated in addition to Fp(CO)$^+$ and $FpCH_3$. In the absence of a trapping agent, the products with $FpCH_3$ and Fp(ethylene)$^+$. Also, thermolysis of the corresponding chloromethyl complex in the presence of cyclohexene gave the cyclopropane (80%) and FpCl. Much later, Brookhart, Flood, and their co-workers[2] were able to generate CpFe(dppe)(=CH_2)$^+$ [Cp = η^5-C_5H_5; dppe = 1,2-bis(diphenylphosphinoethane)] and observe the labile complex at low temperature, thus supporting the earlier proposal.

Brookhart[3] later used trimethylsilyl triflate (Me_3SiOTf) to extract the methoxy group from a (methoxymethyl)-molybdenum complex. Also formed in the reaction were small amounts of the corresponding methyl complex and the methoxymethylidene cation; these were proposed to be formed by hydride transfer from unreacted starting complex to the methylidene cation. Disproportionation of the methylidene cation afforded the ethylene complex and a solvent- or triflate-coordinated product. Disproportionation was thought to occur via a dimetallacyclobutane in the manner established by Schrock and Sharp[4] for methylidenetantalum complexes. Davies and Maberly[5] later provided support for the proposed hydride transfer reaction by showing that CpFe(CO)(PPh_3)CH_3 and the analogous methoxymethylidene cation were formed from CpFe(CO)(PPh_3)CH_2OCH_3 when $^1/_3$ equiv of HBF_4 was used.

Guerchais and Lapinte[6] reported the low-temperature generation of methylidene cation complex from Cp*Fe-(CO)(PPh_3)CH_2OH (Cp* = η^5-C_5Me_5); the ^1H NMR spectrum showed the methylene protons at 16–17 ppm. More recently, Astruc, Cowley, and co-workers[7] generated the same methylidene cation from the corresponding methoxymethyl complex through reactions with Me_3SiOTf or CF_3COOH. Thermolysis of the methylidene cation from the related dicarbonyl complex gave the anion- or solvent-coordinated complex and lesser amounts of the carbonyl cation and the ethylene cation.

In summary, reactions between electrophiles and methoxymethyl complexes have given products of the types shown in eq 1 when no trapping agents were available. Not all product types are typically observed from a single substrate, however. The reactions have been formulated as proceeding via an intermediate methylidene cation complex. MCH_3 is formed from M=CH_2^+ and unreacted alkoxymethyl complex, thus M=$CHOCH_3^+$ must be formed as a tandem product, although it is sometimes not observable. Whether these products are observed or not depends on the facility of the reaction of the alkoxymethyl complex with the electrophile, the amount of electrophile

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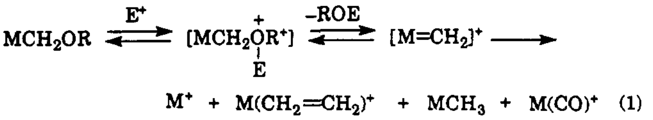


$$\mathrm{MCH_2OR} \overset{E^+}{\rightleftharpoons} [\mathrm{MCH_2}\overset{+}{\underset{E}{\mathrm{O}}}\mathrm{R^+}] \overset{-\mathrm{ROE}}{\rightleftharpoons} [\mathrm{M{=}CH_2}]^+ \longrightarrow$$

$$\mathrm{M^+ + M(CH_2{=}CH_2)^+ + MCH_3 + M(CO)^+} \quad (1)$$

M = metal and ancillary ligands

E = electrophile

R = H or alkyl

present, and the stability of the products. M(CO)$^+$ does not result directly from the methylidene cation, but it can result from CO scavenging by M$^+$ or as a consequence of disproportionation of other unstable species.

We have recently developed synthetic routes for several methoxymethyl complexes through reactions of the corresponding formyls with electrophiles.[8] In the course of this work, we have observed some interesting transformations of the complexes *trans*- and *cis*-CpMo(CO)$_2$[P(OPh)$_3$]CH$_2$OCH$_3$[9] (**1a** and **1b**, respectively), and related complexes, with electrophiles. These results are described below.

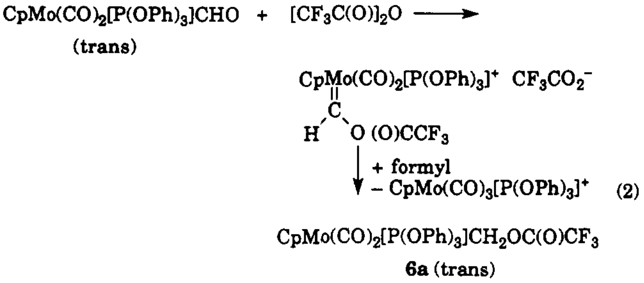
Results and Discussion

1. Synthesis and Characterization of Compounds. The methoxymethyl complexes, **1a,b**, were prepared as described previously.[9] Metallacycle 2, CpMo(CO)$_2$[P(OPh)$_2$(*o*-OC$_6$H$_4$CH$_2$)], can be synthesized in very good yield (83%) by reaction of **1a,b** with *p*-toluenesulfonic acid. The compound has been characterized by elemental analysis and IR and ^{1}H and ^{13}C NMR spectroscopy; the structure has been confirmed by X-ray crystallography (see below).

Compound **3a**, *cis*-CpMo(CO)$_2$[P(OPh)$_3$]OTf (OTf = OSO$_2$CF$_3$), was synthesized by metathesis of *cis*-CpMo(CO)$_2$[P(OPh)$_3$]I with silver triflate. The product is a red, crystalline solid; it has been characterized by elemental analysis and IR and ^{1}H and ^{13}C NMR spectroscopy. The presence of nonequivalent carbonyl resonances in the ^{13}C NMR spectrum clearly establishes **3a** as the cis isomer. A mixture of **3a** and the corresponding trans isomer, **3b**, can be prepared from reaction of methyl complexes **5a,b** (a 3:2 mixture of trans and cis isomers; see below) with triflic acid. Isomer **3b** was not separated from the mixture, but it was easily identified from ^{13}C NMR spectral data which show a single resonance for the terminal carbonyl groups in this isomer. The ratio of **3a**:**3b** was 1:1 in solution at room temperature. In the presence of 1 equiv of triflic acid, this ratio slowly changed over 1^1/$_2$ days to 5:3 **3a**:**3b**.

Metathesis of CpMo(CO)$_3$[P(OPh)$_3$]$^+$Br$^-$ (**11**; see below) with silver triflate afforded compound **4**, CpMo(CO)$_3$[P(OPh)$_3$]$^+$OTf$^-$; its spectral properties (IR, ^{1}H and ^{13}C NMR) are closely similar to those of CpMo(CO)$_3$[P(OPh)$_3$]$^+$BF$_4^-$.[10] A sample of **5a,b**, *trans*- and *cis*-CpMo(CO)$_2$[P(OPh)$_3$]CH$_3$ (3:2 trans:cis), was prepared as described previously.[11]

Synthesis of **6a**, *trans*-CpMo(CO)$_2$[P(OPh)$_3$]CH$_2$OC(O)CF$_3$, was accomplished by reaction of *trans*-CpMo(CO)$_2$[P(OPh)$_3$]CHO[10] with trifluoroacetic anhydride. Reactions of formyl complexes, at the formyl oxygen, with electrophiles are well-known, as is the ability of formyl complexes to transfer hydride to secondary methylidene cations.[12] Accordingly, the following sequence is suggested to rationalize the conversion of the formyl complex to **6a**:



$$\underset{(\mathrm{trans})}{\mathrm{CpMo(CO)_2[P(OPh)_3]CHO}} + \mathrm{[CF_3C(O)]_2O} \longrightarrow \mathrm{CpMo(CO)_2[P(OPh)_3]^+\ CF_3CO_2^-}\ (\mathrm{Mo{=}C(H)O(O)CCF_3}) \xrightarrow[-\ \mathrm{CpMo(CO)_3[P(OPh)_3]^+}]{+\ \mathrm{formyl}} \mathrm{CpMo(CO)_2[P(OPh)_3]CH_2OC(O)CF_3} \quad (2)$$

6a (trans)

The reaction must be done at low temperature in order to suppress formation of the cis isomer (**6b**) and metallacycle **2**. Compound **6a** was characterized by IR and NMR spectral data only since samples of the compound darken after a few hours at room temperature and could not be sent for analysis. The ^{13}C NMR spectrum shows a single terminal carbonyl absorption, as expected for the trans geometry. Cis isomer **6b** was generated during thermolysis of **6a**; it could not be separated from **6a** and has been characterized by spectral data only.

A sample of **7**, *cis*-CpMo(CO)$_2$[P(OPh)$_3$](F-BF$_3$), was prepared by hydride abstraction as described previously.[13] Compound **8**, *cis*-CpMo(CO)$_2$[P(OPh)$_3$]OCOCF$_3$, was prepared from the corresponding hydride by treatment with trifluoroacetic anhydride. Its spectral properties are in agreement with those reported previously.[11]

Compound **9**, *cis*-CpMo(CO)$_2$[P(OPh)$_2$(*o*-OC$_6$H$_4$CH$_3$)]-OTf, was prepared by ring opening metallacycle **2** with triflic acid. It has been characterized by IR, ^{1}H and ^{13}C NMR, and elemental analysis. ^{13}C NMR spectral data for **9** support the cis formulation since two doublets are observed for the terminal carbonyls. Electrophile-promoted ring openings of related metallacycles have been reported previously.[14]

The characterization of **10a**, *trans*-CpMo(CO)$_2$[P(OPh)$_3$]CH$_2$Br, has been reported previously.[12g] At room temperature, **10a** establishes equilibrium with the cis isomer, **10b**; this compound was characterized by spectral data only (see thermolysis of **10a** in Experimental Section). The structure of compound **11**, CpMo(CO)$_3$[P(OPh)$_3$]$^+$Br$^-$, was confirmed by treating a sample of it with AgBF$_4$ and converting it to the known compound CpMo(CO)$_3$[P(OPh)$_3$]$^+$BF$_4^-$.[10] Compound **12**, *cis*-CpMo(CO)$_2$[P(OPh)$_3$]Br, was prepared by warming *trans*-CpMo(CO)$_2$[P(OPh)$_3$]CHO to convert it to the corresponding hydride (primarily the cis isomer);[10] the hydride was then treated with bromoform to convert it to **12**. Compound **12** has been characterized by elemental analysis and by spectral

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(13) (a) Sunkel, K.; Ernst, H.; Beck, W. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 474. (b) The ^{13}C NMR spectrum of compound **7** has not been reported previously: (CDCl$_3$) δ 247.19 (d, CO, J_{PC} = 40.3 Hz), 234.88 (s, CO), 150.52–120.03 (m, phenyl), 95.42 (s, Cp).

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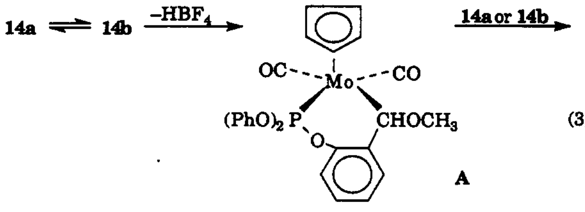
data. The ^{13}C NMR spectrum shows nonequivalent terminal carbonyls, indicating cis geometry.

Treatment of **2** with HBr gives the ring-opened compound **13**, *cis*-$CpMo(CO)_2[P(OPh)_2(o\text{-}OC_6H_4CH_3)]Br$. The compound was characterized by elemental analysis and spectral data; the ^{13}C NMR data support the cis formulation.

There have been two approaches taken previously to the synthesis of methoxymethylidene cations: methylation of formyl complexes[12e,15] and α-hydride abstraction from methoxymethyl complexes by the trityl cation.[16] We have tried both approaches, but only the trityl cation is effective in providing a product whose spectral properties are consistent with its formulation as $CpMo(CO)_2[P(OPh)_3](CH{=}OCH_3)^+BF_4^-$ (**14a,b**; the trans to cis ratio, **14a**:**14b**, is approximately 95:5). However, the low-temperature reaction between **1a,b** and the trityl cation provides **5a,b** and **14a,b** in approximately equal amounts, in addition to methyl trityl ether, indicating that the reaction actually proceeds by alkoxide abstraction.[3,16] The ^{13}C NMR spectrum of **14a** shows a low-field resonance at 328.46 ppm typical of the carbene carbon in other methoxymethylidene complexes,[6,12c,15] a doublet at 222.44 ppm for the equivalent terminal carbonyl ligands (indicating trans geometry), a singlet at 95.36 ppm for the Cp ring, and a singlet at 78.26 ppm for the methyl group. The proton spectrum shows one low-field resonance (12.96 ppm) which is assigned to the methylidene proton in **14a** and a much smaller one at 13.28 ppm for the analogous proton in **14b**. Compounds **14a,b** can be isolated, but the solid darkens upon standing at room temperature, precluding elemental analysis. Also, **14a,b** decompose upon standing in solution at room temperature to metallacycle **2** and $CpMo(CO)_3[P(OPh)_3]^+BF_4^-$ almost exclusively. The following sequence is suggested to rationalize the conversion of **14a,b** to these products:



Cyclization is proposed to result from electrophilic attack by the methylidene carbon in cis isomer **14b** on a phenyl ring of the phosphite ligand to yield a methoxy-substituted metallacycle (intermediate A). Removal of the methoxy group from A could occur through reaction with additional **14a** or **14b**. Nucleophilic dealkylation of methoxymethylidene cations is well-known;[15,17] the dealkylation product would be the corresponding formyl complex[10] which is capable of providing hydride to complete the formation of metallacycle **2** and would be converted to the observed cation complex. The proposed intermediate A in the sequence was not observed, but $HBF_4{\cdot}O(CH_3)_2$ was detected by ^{1}H NMR spectroscopy.

Table I. Summary of Crystallographic Data for $CpMo(CO)_2[P(OPh)_2(o\text{-}OC_6H_4CH_2)]$ (2)

formula	$C_{26}H_{21}MoO_5P$
fw	540.37
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	14.457(3)
b, Å	10.729(2)
c, Å	15.611(3)
β, deg	103.65(2)
vol, Å^3	2353.1
Z	4
D_c, g cm^{-3}	1.53
cryst dimens, mm	0.30 × 0.39 × 0.42
cryst descn	yellow plate
μ(Mo Kα), cm^{-1}	6.4
radiation (λ, Å)	Mo Kα (0.709 30)
diffractometer	CAD4
monochromator	graphite
temp, °C	23(1)
scan range	$0.8 + 0.340 \tan\theta$
scan speed, deg min^{-1}	1–3
max θ, deg	25
intensity decay, %	−1.0
no. of unique reflns collcd	4233
no. of reflns obsd ($I > 3\sigma(I)$)	3572
computing	SDP/VAX
weighting formula	$[\sigma(F)^2 + (0.005F)^2 + 0.5]^{-1}$
no. of variables	299
no. of observns	3572
max Δ/σ	0.02
GOF	1.01
ext coeff	$8(1) \times 10^{-8}$
resid ed, e Å^{-3}	0.26(4)
agreement factors	
R	0.024
R_w	0.026

Efforts have also been made to observe methylidene cations *cis*- or *trans*-$CpMo(CO)_2[P(OPh)_3]({=}CH_2)^+$ in low-temperature reactions of **1a,b** with trimethylsilyl triflate. We are unable to observe either of the isomeric cations under these conditions (see Experimental Section).

Reaction of **1a,b** with *p*-toluenesulfonic acid in the presence of 1 equiv of triphenylphosphine gives *trans*-$CpMo(CO)_2[P(OPh)_3](CH_2PPh_3)^+$ $(p\text{-}CH_3C_6H_4SO_3)^-$ (**15a**, 75% yield), the corresponding cis isomer (**15b**, 5%), metallacycle **2** (3%), and $CpMo(CO)_3[P(OPh)_3]^+(p\text{-}CH_3C_6H_4SO_3)^-$ (5%). The trans phosphonium salt has been characterized by X-ray crystallography;[18] the cis isomer was not isolated and was characterized by spectral data only.

2. X-ray Structure Determination of Metallacycle 2. Single-crystal X-ray data were obtained for the metallacycle under the conditions summarized in Table I. The unit cell was found to be monoclinic and the space group as $P2_1/n$. Refinement, described in the Experimental Section, included location of the hydrogen atoms from a difference Fourier map. An ORTEP representation of the metallacycle is shown in Figure 1. Bond distances and bond angles are compiled in Table II. The P–Mo–C1 angle (70.76°) is slightly smaller than those of P–Mo–C3 (78.95°), C1–Mo–C2 (75.2°), and C2–Mo–C3 (77.2°) while the Mo–C1 distance (2.348 Å) is much larger than Mo–C2 (1.960 Å) and Mo–C3 (1.957 Å). The differences in bond distances and bond angles may be due to the fact that C1

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(16) Competition between α-hydride abstraction and alkoxide abstraction has been noted previously; see: Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411.

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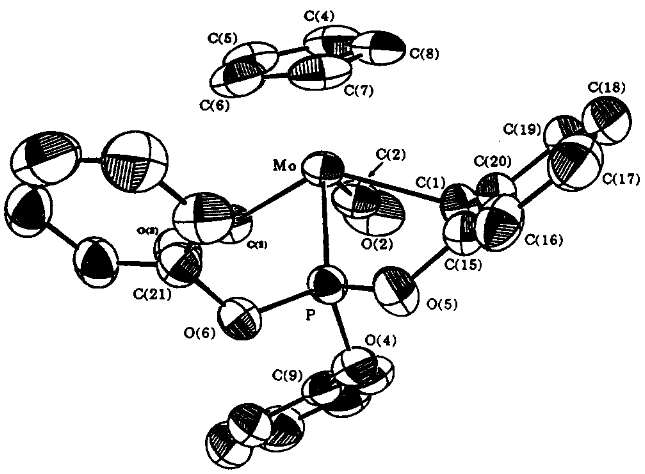


Figure 1. Molecular structure of 2, $\mathrm{CpMo(CO)_2[P(OPh)_2(\mathit{o}\text{-}OC_6H_4CH_2)]}$. Ellipsoids are drawn at the 50% probability level.

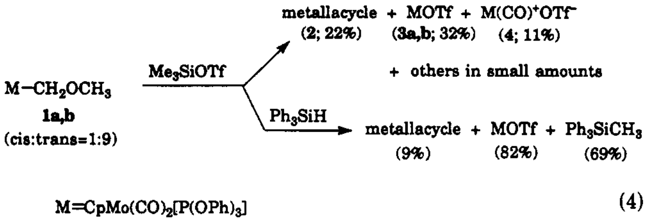
Table II. Selected Bond Distances (Å) and Angles (deg) for Compound 2[a]

Bond Distances			
Mo–P	2.3590(7)	O5–C15	1.392(3)
Mo–C1	2.348(3)	O6–C21	1.408(4)
Mo–C2	1.960(3)	C1–C20	1.486(3)
Mo–C3	1.957(3)	C4–C5	1.393(5)
Mo–C4	2.357(3)	C4–C8	1.389(5)
Mo–C5	2.317(3)	C5–C6	1.418(4)
Mo–C6	2.320(3)	C6–C7	1.410(5)
Mo–C7	2.346(3)	C7–C8	1.401(4)
Mo–C8	2.370(3)	C15–C16	1.378(3)
P–O4	1.611(2)	C15–C20	1.381(3)
P–O5	1.605(2)	C16–C17	1.393(5)
P–O6	1.610(2)	C17–C18	1.373(4)
O2–C2	1.143(3)	C18–C19	1.378(4)
O3–C3	1.150(3)	C19–C20	1.399(5)
O4–C9	1.411(3)		
Bond Angles			
P–Mo–C1	70.76(7)	C4–C8–C7	108.8(4)
P–Mo–C2	105.87(8)	C3–Mo–C8	146.4(1)
P–Mo–C3	78.95(8)	C4–Mo–C5	34.7(1)
P–Mo–C4	155.71(8)	C4–Mo–C6	58.3(2)
P–Mo–C5	140.79(8)	C4–Mo–C7	57.7(2)
P–Mo–C6	107.10(7)	C4–Mo–C8	34.2(1)
P–Mo–C7	98.82(7)	C5–Mo–C6	35.6(1)
P–Mo–C8	122.49(8)	C5–Mo–C7	58.5(2)
C1–Mo–C2	75.2(2)	C5–Mo–C8	57.5(1)
C1–Mo–C3	130.9(2)	C6–Mo–C7	35.2(1)
C1–Mo–C4	103.8(1)	C6–Mo–C8	57.9(1)
C1–Mo–C5	137.8(2)	C7–Mo–C8	34.6(2)
C1–Mo–C6	132.4(2)	Mo–P–O4	122.45(6)
C1–Mo–C7	97.3(2)	Mo–P–O5	118.39(7)
C1–Mo–C8	82.7(2)	Mo–P–O6	119.81(7)
C2–Mo–C3	77.2(1)	O4–P–O5	94.6(1)
C2–Mo–C4	95.0(2)	O4–P–O6	96.63(9)
C2–Mo–C5	107.7(2)	O5–P–O6	99.52(9)
C2–Mo–C6	142.8(1)	P–O4–C9	123.5(2)
C2–Mo–C7	149.7(1)	P–O5–C15	123.8(2)
C2–Mo–C8	115.3(1)	P–O6–C21	121.2(2)
C3–Mo–C4	118.5(1)	Mo–C1–C20	111.6(2)
C3–Mo–C5	89.4(1)	Mo–C2–O2	177.6(3)
C3–Mo–C6	92.7(1)	Mo–C3–O3	177.1(2)
C3–Mo–C7	125.4(1)	Mo–C4–C5	71.1(2)
C5–C4–C8	108.2(3)	Mo–C4–C8	73.4(2)
Mo–C5–C4	74.2(2)	O5–C15–C16	115.8(2)
Mo–C5–C6	72.3(2)	O5–C15–C20	120.7(3)
C4–C5–C6	108.2(3)	C16–C15–C20	123.6(3)
Mo–C6–C5	72.1(2)	C15–C16–C17	118.3(3)
Mo–C6–C7	73.4(2)	C16–C17–C18	119.8(3)
C5–C6–C7	107.2(3)	C17–C18–C19	120.6(3)
Mo–C7–C6	71.4(2)	C18–C19–C20	121.4(3)
Mo–C7–C8	73.7(2)	C1–C20–C15	121.7(2)
C6–C7–C8	107.7(3)	C1–C20–C19	122.0(2)
Mo–C8–C4	72.5(2)	C15–C20–C19	116.3(2)
Mo–C8–C7	71.8(2)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

is a part of the metallacycle ring. Positional parameters are listed in Table III.

3. Reactions of 1a,b and 6a,b with Electrophiles. As noted above, Me_3SiOTf has proved to be an effective reagent for extracting the methoxy group from methoxymethyl complexes. Also, Lapinte[6] and Astruc[7] have shown that Ph_3SiH is a good acceptor for a methylidene ligand transferred from a metal complex. The equations below indicate the main products of reactions of the molybdenum complexes 1a,b with 1 equiv of Me_3SiOTf in the presence and in the absence of Ph_3SiH. In addition to the expected products, both reactions give significant amounts of metallacycle 2.



(4)

The formation of this product can be rationalized in terms of electrophilic attack, followed by proton loss, on the ortho position of a phenyl group of the phosphite ligand by an intermediate cis methylidene cation; however, an alternate pathway is possible, as discussed below. The trans to cis ratio in the mixture of 1a,b is 9:1, and although isomerization is not evident during the reactions, clearly trans to cis isomerization is required to provide the metallacycle. The triflate anion is an efficient scavenger of the $CpMo(CO)_2[P(OPh)_3]$ fragment; an 82% yield of triflates 3a,b is obtained in the reaction involving the silane. The effectiveness of Me_3SiOTf in cleaving the methoxy group is evidenced by the absence of methyl complexes 5a,b in either product mixture, although small amounts of these may have been destroyed by triflic acid generated when the metallacycle was formed (see discussion involving reactions of 1a,b with protonic acids below). No evidence of 14a,b (the usual companion to the methyl complex) was seen in the product mixture either, although its decomposition products (2 and 4) are observed in the absence of Ph_3SiH. Also not seen, at least as a major product, is the ethylene cation complex, $CpMo(CO)_2[P(OPh)_3](C_2H_4)^+OTf^-$, an expected disproportionation product of the intermediate methylidene complex. When only $^1/_2$ equiv of Me_3SiOTf was used with 1a,b, the yield of metallacycle 2 *increased* to 30%. Methyl complexes 5a,b were also significant components of the product mixture (14%). No evidence for 14a,b was obtained, but the enhancement of 2 and the presence of 4 (18%) probably reflect the intermediacy of these compounds. When $^1/_2$ equiv of Me_3SiOTf together with 1 equiv of Ph_3SiH was used with 1a,b, the yield of metallacycle dropped to 20%, the yield of methyl complexes 5a,b dropped to 2%, and the yield of triflates 3a,b increased to 71%. Note, also, that the yield of Ph_3SiCH_3 differs very little in the two trapping experiments (69% versus 61%) even though there is $^1/_2$ equiv less of Me_3SiOTf in the second experiment.

Table III. Positional Parameters and Their Estimated Standard Deviations for Compound 2[a]

atom	*x*	*y*	*z*	*B* (Å^2)
Mo	0.32070(1)	0.16539(2)	0.56057(1)	3.262(4)
P	0.28661(4)	0.35969(6)	0.48940(4)	3.22(1)
O2	0.5189(2)	0.1903(2)	0.6899(2)	6.82(6)
O3	0.2772(2)	0.3220(2)	0.7137(1)	5.83(5)
O4	0.3581(1)	0.4767(2)	0.5113(1)	4.14(4)
O5	0.2769(1)	0.3662(2)	0.3849(1)	4.38(4)
O6	0.1915(1)	0.4340(2)	0.4953(1)	3.94(4)
C1	0.4260(2)	0.1992(3)	0.4691(2)	4.07(6)
C2	0.4460(2)	0.1839(3)	0.6418(2)	4.56(6)
C3	0.2928(2)	0.2668(3)	0.6556(2)	4.06(6)
C4	0.3161(2)	−0.0534(3)	0.5728(2)	5.54(8)
C5	0.2450(2)	−0.0019(3)	0.6085(2)	5.27(7)
C6	0.1779(2)	0.0577(3)	0.5398(2)	5.13(7)
C7	0.2102(2)	0.0425(3)	0.4619(2)	5.31(7)
C8	0.2949(2)	−0.0264(3)	0.4833(2)	5.62(8)
C9	0.4025(2)	0.5145(2)	0.5977(2)	3.97(5)
C10	0.4952(2)	0.4805(3)	0.6306(2)	4.63(6)
C11	0.5419(2)	0.5191(3)	0.7144(2)	5.98(8)
C12	0.4966(3)	0.5917(4)	0.7626(2)	7.09(9)
C13	0.4043(3)	0.6286(3)	0.7285(2)	7.09(8)
C14	0.3547(2)	0.5901(3)	0.6444(2)	5.85(8)
C15	0.3041(2)	0.2702(3)	0.3361(2)	3.79(5)
C16	0.2557(2)	0.2639(3)	0.2489(2)	4.91(7)
C17	0.2809(2)	0.1709(3)	0.1964(2)	5.88(7)
C18	0.3528(2)	0.0893(3)	0.2320(2)	5.91(7)
C19	0.3997(2)	0.0977(3)	0.3196(2)	4.99(6)
C20	0.3767(2)	0.1899(2)	0.3744(2)	3.84(5)
C21	0.1046(2)	0.3714(2)	0.4886(2)	3.92(5)
C22	0.0611(2)	0.3102(3)	0.4129(2)	5.22(7)
C23	−0.0256(3)	0.2537(4)	0.4083(3)	7.0(1)
C24	−0.0681(2)	0.2605(4)	0.4786(3)	7.5(1)
C25	−0.0238(2)	0.3228(3)	0.5536(2)	6.30(8)
C26	0.0643(2)	0.3794(3)	0.5601(2)	4.85(6)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter.

However, a proton is liberated when the metallacycle is formed, effectively increasing the amount of electrophile available.

An alternative method for generating methylidene cation complexes is to treat a methoxymethyl complex with a strong protonic acid.[16] The results of reactions between **1a,b** and various protonic acids are summarized in the Experimental Section. There is a relatively wide variation in the distribution of products. Also, overall product yields are generally lower in these reactions as compared with those involving Me_3SiOTf because of degradative reactions. In all cases, metallacycle **2** is a significant product; its yield is highest when the weakest acid (trifluoroacetic, TFA) is employed and lowest when an acid with a strongly nucleophilic anion (HBr) is used. The trifluoroacetate anion is capable of trapping the methylidene cations, but **6a,b** are not stable under the conditions of the experiments at 0 °C (see discussion below). The reaction of **1a,b** with HBr is relatively clean and gives a 79% yield of bromomethyl compounds **10a,b**; (primarily trans isomer **10a**) and metallacycle **2** (8%) only; again some degradation also occurs. The absence of disproportionation products, MBr (**12**) and $M(CO)^+Br^-$ (**11**) suggests that the methylidene cation complex is not generated in this reaction. Use of *p*-toluenesulfonic acid (monohydrate) with **1a,b** provides the best synthetic route to the metallacycle (83% yield; see Experimental Section). However, when the reaction of **1a,b** with *p*-toluenesulfonic acid was done in the presence of 1 equiv of triphenylphosphine, the phosphonium ylides **15a,b** (15:1 trans:cis based on NMR spectral data) were the predominant products (total yield 80%).

Reactions between metal alkyl complexes and strong protonic acids such as HBF_4 and HOTf have provided a general synthetic route to metal complexes with weakly coordinated ligands.[19] HBF_4·etherate reacts with methyl complexes **5a,b** to give **7** only slowly under our reaction conditions. Alternatively, triflic acid reacts rapidly with **5a,b** to give triflates **3a,b**; furthermore, **5a,b** are not observed as products from **1a,b** when a full equivalent of HOTf is employed. The weaker trifluoroacetic acid does not react with **5a,b** under the experimental conditions used.

In summary, reactions between **1a,b** and electrophiles yield metallacycle **2** as a significant product even when the trapping agent (Ph_3SiH) or a strong nucleophile (Br^- or PPh_3) is present. Higher yields of metallacycle are produced from the weaker electrophiles (ones which are least likely to be effective in cleaving the C–O bond and generating the methylidene cation complexes). The effect of added Ph_3SiH on the reaction with trifluoroacetic acid is dramatic, lowering the metallacycle yield from 71% to 20%.

Perhaps the most revealing aspects of the studies with electrophiles come from observations on the (trifluoroacetoxy)methyl complexes **6a,b**. A sample of the trans isomer (**6a**) was obtained by low-temperature crystallization; its ^1H NMR spectrum was recorded at −10 °C, and then the sample tube was slowly warmed to 20 °C in the probe during a few minutes. After this, the mixture consisted solely of a 4:1 mixture of trans to cis isomers. The tube was again cooled to 0 °C in the NMR spectrometer, and the spectrum revealed the same 4:1 distribution of isomers. Trifluoroacetic acid (2.7 equiv) was added quickly, and the tube was returned to the 0 °C probe. After this, the sample consisted solely of a 3.4:1 mixture of trans isomer and metallacycle **2**. The probe temperature was increased to 10 °C and, after a short time, the spectrum showed a 2.3:1 mixture of trans isomer and metallacycle. Finally, at 20 °C, the spectrum showed a trans to metallacycle ratio of 1:9; again, no cis isomer was present. This sequence of experiments shows clearly that trans to cis isomerization is facile at room temperature, that the metallacycle was formed at the expense of the cis isomer, **6b**, and that acid promotes the rapid conversion of **6b**, exclusively, to metallacycle **2**. Covalent trifluoroacetate **8** was not a product, suggesting that a methylidene cation was not generated from either **6a** or **6b**. A second experiment, with an internal standard, gave similar results; only metallacycle **2** (88%) and **8** (6%) were present at the end of the reaction. Simple thermolysis of **6a** (see section 4 below) occurred after prolonged standing at room temperature and afforded metallacycle **2** and a small amount of **8** (15:1, respectively).

The observations on **6a,b**, together with the results of experiments involving methylating and protonating agents in combination with **1a,b**, suggest that metallacycle formation does not require the intermediacy of the methylidene cation but can be augmented by its presence. These conclusions do require that other types of reactive intermediates be present during the early stages of the electrophile-induced transformations. We suggest that these are oxonium ions and that the pathways by which products are formed in reactions of **1a,b** or **6a,b** are better represented by the complex series of equations in Scheme I. We have no direct evidence for equilibrium of trans

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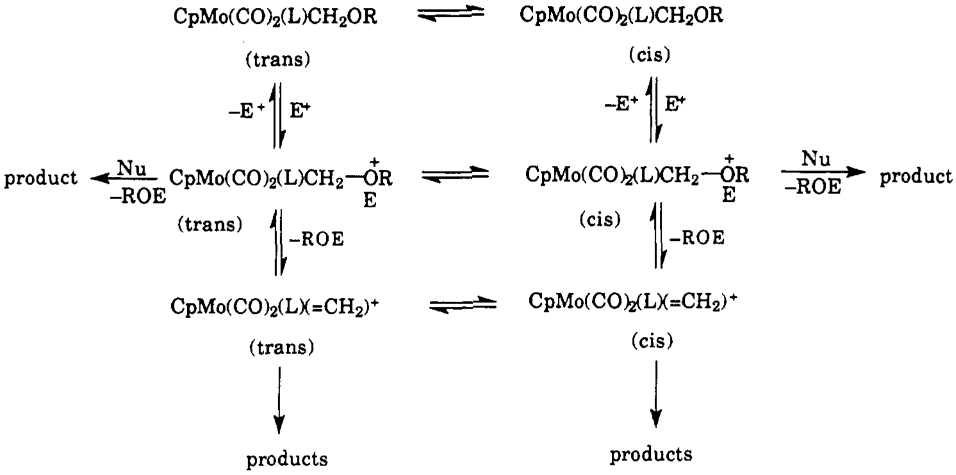
[19] Beck, W. *Inorg. Synth.* **1990**, *28*, 1 and references cited therein.

Scheme I. Intermediates in the Reactions of 1a,b and 6a,b with Electrophiles



L=P(OPh)$_3$

and cis methylidene cations, but the observed conversion of methoxymethylidene cations **14a,b** (primarily the trans isomer) to metallacycle **2** requires that equilibrium between these two be established and suggests that it would be established with isomeric methylidene cations also.

The expected effect of Ph_3SiH in reactions of **1a,b** or **6a,b** with electrophiles would be to shift the equilibria involving oxonium ions and methylidene cations toward the latter because the trapping reaction is irreversible. In the absence of the silane, internal nucleophilic displacement could compete effectively, particularly when a weak electrophile is present. It is significant that reactions of **1a,b** with triflic acid and trimethylsilyl triflate yield the cis triflate, **3a**, in high predominance over the corresponding trans isomer, **3b**. Compound **3b** does not isomerize rapidly to **3a** at room temperature, even in the presence of triflic acid. Thus we conclude that reactions of cis oxonium ions generated from **1b** are the more reactive under these conditions. However, the availability of a strong external nucleophile (Br^-, PPh_3) can shift the equilibrium mixture of oxonium ions toward the trans isomer because of the easier steric access to the methylene carbon in oxonium ions derived from **1a**. Note that reaction of **1a,b** with *p*-toluenesulfonic acid alone gives an 83% yield of the metallacycle, but a similar reaction conducted with 1 equiv of PPh_3 gives the trans phosphonium ion **15a**, preferentially, in high yield (75%).

The presence of intermediate oxonium ions in reactions of alkoxymethyl complexes has been mentioned only rarely,[20] probably because they have been thought to dissociate too rapidly to have influence on the types of products formed. However, alkylation of thiomethoxymethyl complexes has frequently afforded stable sulfonium salts.[20] The subsequent reactions of many of these with olefins provide an excellent synthetic route to cyclopropanes in the manner of their methoxymethyl counterparts.[21]

The results obtained from **1a,b** in combination with electrophiles contrast sharply with results obtained by others on phosphine- and/or pentamethylcyclopentadienyl-substituted alkoxymethyl systems. The latter systems may be more reactive toward C–O bond breaking in the alkoxyl ligand, and the methylidene complex is certainly better stabilized, in some cases allowing its observation. When the ancillary ligands do not provide stabilization of a potential methylidene ligand, the chemistry of other reactive intermediates may predominate.

4. Thermolysis of Bromomethyl and (Trifluoroacetoxy)methyl Complexes. Another method previously used to generate methylidene cations is through thermal decomposition reactions of halomethyl complexes.[1] Thermolysis of bromomethyl complexes **10a,b** (2:1 trans to cis after 1 h at room temperature) requires slightly more than 20 h total time at room temperature. After this, the product mixture consisted of metallacycle **2** (21%), covalent bromide **12** (11%), and an additional bromide (**13**, 53%) which is known to result from ring opening of the metallacycle by HBr.

An analogous reaction was conducted with 1 equiv of Ph_3SiH present during thermolysis. After the same reaction time, the product mixture was analyzed as before. The mixture consisted of metallacycle **2** (15%), its ring-opened derivative **13** (27%), bromide **12** (50%), and Ph_3SiCH_3 (38%).

For comparison, we have done thermolyses of the trifluoroacetoxymethyl complex **6a** in the same manner. After 11 h at room temperature, **6a** afforded a product mixture containing metallacycle **2** as the major product (88%) and trifluoroacetate **8** as the minor product (6%). In the presence of Ph_3SiH, **6a** gave metallacycle **2** (46%), trifluoroacetate **8** (37%), and Ph_3SiCH_3 (34%) after 26 h.

The results of these experiments also strongly support a reaction pathway involving competition between intramolecular nucleophilic displacement of the leaving group bound to the methylene ligand (and formation of **2**) and ionization resulting in a methylidene cation (followed by cyclization to **2** and/or disproportionation in the absence of Ph_3SiH). The small amounts of **12** and **8** that are formed in the absence of the silane suggest that metallacycle formation, by internal displacement, is preferred.

Experimental Section

General Data. All reactions were conducted under an atmosphere of prepurified nitrogen gas, unless otherwise indi-

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(20) Oxonium ions have been suggested as transient intermediates in related reactions; see Salsini, L.; Pasquali, M.; Leoni, P.; Braga, D.; Sabatino, P. *Gazz. Chim. Ital.* **1990**, 120, 465.

(21) (a) Kremer, K. A. M.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 1862. (b) O'Connor, E. J.; Helquist, P. *J. Am. Chem. Soc.* **1982**, *104*, 1869. (c) Davidson, J. G.; Barefield, E. K.; Van Derveer, D. G. *Organometallics* **1985**, *4*, 1178.

cated. Reagent grade dichloromethane, methanol, acetone, and anhydrous ether were used as received. Hexane and pentane were dried over sulfuric acid and then fractionally distilled. Trifluoroacetic acid (TFA), trifluoroacetic anhydride (TFAA), *p*-toluenesulfonic acid monohydrate (HOTs·H_2O), tetrafluoroboric acid etherate (HBF_4·Et_2O, 85%), hydrobromic acid (48% in water), triflic acid (HOTf), triphenylsilane (Ph_3SiH), 1,4-dimethoxybenzene (used as the internal standard for quantitative analysis of NMR spectral data), trimethylsilyl triflate (Me_3SiOTf), silver triflate (AgOTf), CD_2Cl_2, and $CDCl_3$ were purchased from Aldrich and used directly; HBr gas was purchased from Curtin-Matheson and was used directly. Compounds **1a,b**,[9] **5a,b**,[11] and **7**[13] were prepared as described previously, as was *trans*-$CpMo(CO)_2[P(OPh)_3]CHO$.[10]

Infrared spectra were obtained using a Perkin-Elmer 599B spectrophotometer and are calibrated against polystyrene film. ^1H and ^{13}C NMR spectra were obtained on Brüker AMX-500 and Varian XL-300 spectrometers. The chemical shifts are expressed in parts per million relative to tetramethylsilane (TMS). Melting points were obtained using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, and Midwest Microlab, Indianapolis, IN.

Synthesis of $\overline{CpMo(CO)_2[P(OPh)_2][o\text{-}OC_6H_4CH_2]}$ (2). *p*-Toluenesulfonic acid monohydrate (0.12 g, 0.65 mmol) was dissolved in 20 mL of a 1:10 methanol/CH_2Cl_2 mixture. To the solution was added 0.19 g (0.32 mmol) of **1a,b** and the mixture stirred for 5 h. The solvent was removed on a rotary evaporator, and the residue was extracted with 3 × 10 mL of hexane. The combined extracts were filtered through Celite and concentrated to about 10 mL. After chilling to −30 °C for a few hours, a yellow-orange solid precipitated which was collected and dried under vacuum for several hours. The ^1H NMR spectrum ($CDCl_3$) indicated the presence of the methyl complexes **5a,b** and metallacycle **2** in a ratio of approximately 1:14. The mixture was separated on a Florisil column, eluting first with hexane, 1:20 CH_2Cl_2/hexane, and finally CH_2Cl_2. The first fractions, as indicated by IR spectroscopy, contained the methyl complexes. The later fractions, which contained the metallacycle, were combined, evaporated to near dryness, and then treated with a few drops of ether followed by dilution with 10 mL of hexane. Chilling to −30 °C for several hours gave 0.15 g (83%) of compound **2**, mp 95.5–97 °C.

Anal. Calcd for $C_{26}H_{21}O_5MoP$: C, 57.76; H, 3.92. Found: C, 57.59; H, 3.96. IR, ν_{CO} (hexane): 1967 (vs), 1900 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.47 (s, Cp), 2.58 (dd, CH_2, J_{HH} = 12.3 Hz, J_{PH} = 6.2 Hz), 2.40 (dd, CH_2, J_{HH} = 12.2 Hz, J_{PH} = 19.5 Hz). ^{13}C NMR ($CDCl_3$): δ 246.53 (d, CO, J_{PC} = 39.4 Hz), 232.19 (s, CO), 152.02 (d, ipso, J_{PC} = 4.1 Hz), 151.14 (d, ipso, J_{PC} = 8.2 Hz), 140.78 (d, CH_2C, J_{PC} = 11.6 Hz), 129.50 (s, meta), 129.34 (s, meta) [125.82 (s), 125.18 (s)], 125.01 (s, para), 124.90 (s, para), 122.12 (d, ortho, J_{PC} = 4.2 Hz), 118.46 (d, J_{PC} = 4.4 Hz), 92.22 (s, Cp), −1.22 (d, CH_2, J_{PC} = 25.6 Hz).

X-ray Crystal Structure of $\overline{CpMo(CO)_2[P(OPh)_2][o\text{-}OC_6H_4CH_2]}$ (2). A suitable crystal was grown from hexane and ether. Data were collected on an Enraf-Nonius CAD4 diffractometer as outlined in Table I. Of the 4233 unique reflections collected, 3572 had $I > 3\sigma(I)$. The molybdenum position was obtained from a three-dimensional Patterson map. Several cycles of Fourier synthesis and least squares refinement yielded positions of all non-hydrogen atoms. The positions of the metallacyclic hydrogens were located from a difference Fourier map and included in these positions. All non-hydrogen atoms were refined with anisotropic thermal parameters while the hydrogen atom positions and thermal parameters were kept constant. A final *R* index of 0.024 with R_w = 0.026 was obtained for 299 variables.

Synthesis of *cis*-$CpMo(CO)_2[P(OPh)_3]OTf$ (3a). *cis*-$CpMo(CO)_2[P(OPh)_3]I$[11,22] (0.5 g, 0.76 mmol) was dissolved in 30 mL of CH_2Cl_2. AgOTf (0.22 g, 0.84 mmol) was then added in portions during about 30 min and the progress of the reaction followed by IR spectroscopy. After 90 min, the sample was filtered and the filtrate was evaporated to near dryness; addition of pentane (10 mL) afforded a dark red precipitate. The product was recrystallized from CH_2Cl_2 and pentane to give 0.36 g (69%) of **3a** as a red crystalline solid, mp 104–111 °C dec.

Anal. Calcd for $C_{26}H_{20}F_3MoO_8P_2S$: C, 46.17; H, 2.98; P, 4.58. Found: C, 46.39; H, 3.10; P, 4.61. IR, ν_{CO} (CH_2Cl_2): 1995 (s), 1920 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.34 (m, Ph), 5.27 (s, Cp). ^{13}C NMR ($CDCl_3$): δ 249.34 (d, CO, J_{PC} = 41.3 Hz), 236.49 (d, CO, J_{PC} = 3.1 Hz), 150.50 (d, ipso, J_{PC} = 6.8 Hz), 130.00 (s, meta), 125.79 (d, para, J_{PC} = 1.2 Hz), 121.43 (d, ortho, J_{PC} = 4.6 Hz), 118.34 (q, CF_3, J_{CF} = 318.6 Hz), 94.61 (s, Cp).

Synthesis of *cis*- and *trans*-$CpMo(CO)_2[P(OPh)_3]OTf$ (3a,b). Solid $CpMo(CO)_2[P(OPh)_3]CH_3$ (**5a,b**; 0.01 g, 0.18 mmol) and the standard were mixed in a 5-mm NMR tube and dissolved in $CDCl_3$. The tube was cooled to −78 °C prior to adding triflic acid (16 μL, 0.18 mmol) via microsyringe. A spectrum taken at −60 °C indicated the formation of two products; one at δ 5.21 (31%) and another at δ 5.15 (23%). A ^{13}C NMR spectrum at the same temperature indicated that these are *trans*- and *cis*-$CpMo(CO)_2[P(OPh)_3]OTf$ (**3b** and **3a**, respectively), as evidenced by the presence of three doublets in the terminal carbonyl region: trans, δ 251.02 (J_{PC} = 37.8 Hz); cis, 248.50 (J_{PC} = 40.3 Hz), 241.08 (J_{PC} = 3.8 Hz). Unreacted **5a** (24%) and **5b** (17%) remained also. As the sample was allowed to warm to room temperature over a 2-h period, a slight downfield shift of the resonances of the two products were noted (δ 5.30 and 5.27) as well as a change in the isomer distribution, 1:1 (34%:34%). Unreacted **5a** and **5b** (15% and 9%) were still observed along with small amounts of unidentified peaks. Addition of 1 equiv of triflic acid and allowing the sample to stand at room temperature for about 1.5 days showed a **3a**:**3b** ratio of about 5:3 (53% to 34%); the starting methyl complexes had completely disappeared.

Synthesis of $CpMo(CO)_3[P(OPh)_3]^+OTf^-$ (4). A 0.11-g sample (0.17 mmol) of $CpMo(CO)_3[P(OPh)_3]^+Br^-$ (**11**; see below) was dissolved in 5 mL of CH_2Cl_2. The resulting yellow solution was treated with 0.045 g (0.18 mmol) of AgOTf. The mixture turned cloudy after 10 min of stirring. After another 20 min, the sample was filtered through Celite and the filtrate was concentrated on a rotary evaporator. The sample was diluted with hexane until cloudy, and as a yellow oily material formed, ether was then added and the mixture swirled for several minutes. During this time, crystals had formed and the sample was then cooled to −30 °C for a few hours to effect complete crystallization. The crystals were collected by filtration and dried in air to give 0.09 g (74% yield) of the cation. IR, ν_{CO} (CH_2Cl_2): 2070 (vs), 2010 (s, sh), 1985 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.34 (m, Ph), 5.63 (s, Cp). ^{13}C NMR ($CDCl_3$): δ [222.24 (d, CO, J_{PC} = 40.9 Hz), 221.00 (d, CO, J_{PC} = 3.4 Hz), ratio = 2:1], 149.65 (d, ipso, J_{PC} = 9.9 Hz), 130.72 (s, meta), 127.12 (s, para), 120.81 (d, ortho, J_{PC} = 4.7 Hz), 120.62 (q, CF_3, J_{CF} = 321.2 Hz), 94.40 (s, Cp). The spectral properties of the product are similar to those of $CpMo(CO)_3P(OPh)_3{}^+BF_4{}^-$.[10]

Synthesis of *trans*- and *cis*-$CpMo(CO)_2[P(OPh)_3]CH_2OCOCF_3$ (6a,b). Trifluoroacetic anhydride (0.20 mL, 1.44 mmol) was added to 10 mL of CH_2Cl_2 and the solution chilled to −40 °C. *trans*-$CpMo(CO)_2[P(OPh)_3]CHO$[10] (0.40 g, 0.72 mmol) was added in portions (1 min) and the bath removed. After 5 min, the mixture was evaporated to dryness under vacuum and the residue was extracted with 2 × 15 mL of an ether/hexane mixture (1:5). The combined extracts were filtered through Celite, concentrated to 10 mL, and then chilled to −30 °C for a few hours, affording *trans*-$CpMo(CO)_2[P(OPh)_3]CH_2OCOCF_3$ (**6a**; 0.16 g, 68%) as a beige crystalline solid The solid darkens at room temperature after a few hours. IR, ν_{CO} (hexane): 1970 (s), 1897 (vs), 1770 (w) cm^{-1}. ^1H NMR ($CDCl_3$, −20 °C): δ 7.32 (m,

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[22] Haines, R. J.; Nyholm, R. S.; Stiddard, M. H. B. *J. Chem. Soc. A* 1967, 94.

Ph), 5.52 (d, CH_2, J_{PH} = 3.5 Hz), 4.71 (s, Cp). ^{13}C NMR ($CDCl_3$, −20 °C): δ 232.46 (d, CO, J_{PC} = 35.3 Hz), 158.42 (q, C=O, $^2J_{C-F}$ = 40.3 Hz), 150.63 (d, ipso, J_{PC} = 7.6 Hz), 129.80 (s, meta), 125.37 (s, para), 121.48 (d, ortho, J_{PC} = 3.8 Hz), 114.17 (q, CF_3, J_{CF} = 287.2 Hz), 91.46 (s, Cp), 61.15 (d, CH_2, J_{PC} = 12.8 Hz).

The NMR sample was then warmed to 20 °C; after 20 min, analysis showed the presence of a second compound whose NMR spectral properties are consistent with its formulation as the cis isomer **6b**. ^{1}H NMR ($CDCl_3$, 20 °C): δ 7.32 (m, Ph) [5.75 (dd) and 5.59 (dd), CH_2], 4.89 (s, Cp). ^{13}C NMR ($CDCl_3$, 20 °C): δ 245.78 (d, CO, J_{PC} = 36.5 Hz), 232.30 (s, CO), 158.44 (q, C=O, $^2J_{C-F}$ = 39.3 Hz), 150.85 (d, ipso, J_{CF} = 7.6 Hz), 129.78 (s, meta), 125.28 (s, para), 121.49 (d, ortho, J_{PC} = 5.0 Hz), 114.98 (q, CF_3, J_{CF} = 286.8 Hz), 91.40 (s, Cp), 62.25 (d, CH_2, J_{PC} = 30.4 Hz). The trans:cis ratio was about 4:1.

Isolation of CpMo(CO)$_3$[P(OPh)$_3$]$^+$OCOCF$_3$$^-$. The hexane-insoluble portion from the procedure above was triturated with 30 mL of a 1:2 ether/hexane mixture. The extract was concentrated to 10 mL and chilled to −30 °C for a few hours to give a yellow crystalline solid (0.19 g, 80% yield). IR, ν_{CO} (CH_2Cl_2): 2073 (s), 2015 (m, sh), 1987 (vs, br), cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.34 (m, Ph), 5.61 (s, Cp). ^{13}C NMR ($CDCl_3$): δ 222.21 (d, CO, J_{PC} = 41.6 Hz), 220.99 (d, CO, J_{PC} = 3.8 Hz), 160.27 (q, C=O, $^2J_{C-F}$ = 37.8 Hz), 149.71 (d, ipso, J_{PC} = 10.1 Hz), 130.75 (s, meta), 127.23 (s, para), 120.74 (d, ortho, J_{PC} = 3.8 Hz), 116.04 (q, CF_3, J_{CF} = 290.9 Hz), 94.21 (s, Cp). The spectral properties of this compound are similar to those of the corresponding fluoroborate salt.

Synthesis of *cis*-CpMo(CO)$_2$[P(OPh)$_3$]OCOCF$_3$ (8). CpMo(CO)$_2$P(OPh)$_3$CHO[10] (0.440 g, 0.79 mmol) was dissolved in 10 mL of CH_2Cl_2. After 15 min of stirring, the yellow solution had turned pale pink; an IR spectrum showed the disappearance of the formyl complex and formation of the hydride, *cis*-CpMo(CO)$_2$P(OPh)$_3$H, as expected.[10] The solution was cooled to 0 °C, and to it was added dropwise 1.10 mL (7.80 mmol) of TFAA, causing the solution to turn pale red. The ice bath was then removed and the sample stirred for 15 min, after which it was evaporated to dryness on a rotary evaporator. The residue was extracted with ether, and the extract was filtered through Celite. The filtrate was diluted with hexane until cloudy and then cooled to 0 °C overnight; deep red crystals precipitated which were collected and dried to give 0.30 g [59% yield based on CpMo(CO)$_2$P(OPh)$_3$CHO] of the product; it melted at 119–121 °C [lit.[11] 115–117 °C]. IR, ν_{CO} (CH_2Cl_2): 1993, 1918, 1704, 1682 cm^{-1} [lit.[11] (CH_2Cl_2): 1996, 1925, 1705, 1692 cm^{-1}]. ^{1}H NMR ($CDCl_3$: δ 7.29 (m, Ph), 5.12 (s, Cp) [lit.[11] ($CDCl_3$): δ 7.26 (m, Ph), 5.09 (s, Cp)]. ^{13}C NMR ($CDCl_3$): δ 251.52 (d, CO, J_{PC} = 40.9 Hz), 235.63 (d, CO, J_{PC} = 3.3 Hz), 163.08 (dq, C=O, J_{CF} = 36.5 Hz, J_{PC} = 5.0 Hz), 150.78 (d, ipso, J_{PC} = 6.4 Hz), 129.81 (s, meta), 125.49 (s, para), 121.34 (d, ortho, J_{PC} = 4.6 Hz), 114.73 (q, CF_3, J_{CF} = 292.2 Hz), 94.05 (s, Cp).

Synthesis of *cis*-CpMo(CO)$_2$[P(OPh)$_2$(*o*-OC$_6$H$_4$CH$_3$)]OTf (9). HOTf (30 μL, 0.34 mmol) was added to 5 mL of CH_2Cl_2 via microsyringe, and the mixture was cooled to −30 °C. Metallacycle **2**, 0.11 g (0.20 mmol) dissolved in 5 mL of CH_2Cl_2, was then added dropwise, producing an orange mixture; the cold bath was removed. The mixture was stirred for 40 min, during which time the color turned pale red then dark red. The sample was evaporated to dryness, and the residue was extracted with ether. The extract was filtered, concentrated on a rotary evaporator, and diluted with hexane until slightly cloudy. Cooling to −30 °C for several hours yielded burgundy crystals which were collected and dried under vacuum (0.07 g, 50% yield). The solid melted at 102–103 °C dec.

Anal. Calcd for $C_{27}H_{22}F_3MoO_8PS$: C, 46.97; H, 3.21. Found: C, 46.85; H, 3.23. IR, ν_{CO} (CH_2Cl_2): 1993 (vs), 1918 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.33 (m, Ph), 5.33 (s, Cp), 2.28 (s, CH_3). ^{13}C NMR ($CDCl_3$): δ 249.38 (d, CO, J_{PC} = 41.6 Hz), 236.70 (s, CO) [OPh: 150.46 (d, ipso, J_{PC} = 7.6 Hz), 150.30 (d, ipso, J_{PC} = 5.0 Hz), 129.93 (s, meta), 129.91 (s, meta), 125.80 (s, para), 125.75 (s, para), 121.56 (d, ortho, J_{PC} = 5.0 Hz), 121.51 (d, ortho, J_{PC} = 5.0 Hz)] [*o*-OC$_6$H$_4$-: 149.80 (d, J_{PC} = 10.1 Hz), 131.89 (s), 129.81 (s), 127.14 (s), 125.31 (s), 120.12 (d, J_{PC} = 5.0 Hz)], 118.30 (q, CF_3, J_{CF} = 318.6 Hz), 94.70 (s, Cp), 16.49 (s, CH_3).

Synthesis of *trans*-CpMo(CO)$_2$[P(OPh)$_3$]CH$_2$Br (10a) and CpMo(CO)$_3$P(OPh)$_3$$^+Br^-$ (11). PhCH$_2$N(Et)$_3$Br (1.00 g, 3.68 mmol) was added to 35 mL of CH_2Cl_2, and the mixture was cooled to 0 °C. HBr (48% in water, 0.98 mL, 8.66 mmol) was added which was followed by 0.97 g (1.74 mmol) of solid *trans*-CpMo(CO)$_2$[P(OPh)$_3$]CHO. The progress of the reaction was monitored by IR spectroscopy; the formyl complex had disappeared after 10 min. The mixture was allowed to warm to room temperature (10 min), and the solvent was evaporated to dryness under vacuum. The residue was dried for 1 h, after which it was extracted with 2 × 30 mL of ether. The combined extracts were filtered through a layer of $MgSO_4$ over Celite, and the filtrate was concentrated to about 5 mL. Hexane (30 mL) was added, and the mixture was chilled to −30 °C for a few hours giving yellow crystals. These were collected and vacuum dried to give compound **10a** (0.40 g, 74%), mp 79.5–81.5 °C.

Anal. Calcd for $C_{26}H_{22}BrMoOP$: C, 50.26; H, 3.57; Br, 12.86. Found: C, 50.34; H, 3.69; Br, 13.03. IR, ν_{CO} (Nujol mull): 1955 (s), 1867 (vs, br) cm^{-1}. ^{1}H NMR (CD_2Cl_2, −10 °C): δ 7.35 (m, Ph), 4.81 (s, Cp), 4.01 (d, CH_2, 4.3 Hz). ^{13}C NMR (CD_2Cl_2, −10 °C): δ 232.93 (d, CO, J_{PC} = 35.9 Hz), 151.04 (d, ipso, J_{PC} = 7.9 Hz), 130.07 (s, meta), 125.59 (s, para), 121.68 (d, ortho, J_{PC} = 4.6 Hz), 93.66 (s, Cp), 25.08 (d, CH_2, J_{PC} = 14.1 Hz).

Compound **11** was obtained from the ether-insoluble residue as a yellow oily material (74% crude yield) and could not be crystallized. IR, ν_{CO} (CH_2Cl_2): 2067 (s), 1998 (s, sh), 1983 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.23 (m, Ph), 5.68 (s, Cp). ^{13}C NMR ($CDCl_3$): δ 221.53 (d, CO, J_{PC} = 40.4 Hz), 220.46 (d, CO, J_{PC} = 1.9 Hz), 148.49 (d, ipso, J_{PC} = 9.4 Hz), 129.94 (s, meta), 126.18 (s, para), 120.04 (d, ortho, J_{PC} = 3.5 Hz), 95.22 (s, Cp). Cation **11** was treated with $AgBF_4$ in CH_2Cl_2; the IR spectrum of the product was identical to that of CpMo(CO)$_3$P(OPh)$_3$$^+BF_4$$^-$.[10]

Synthesis of *cis*-CpMo(CO)$_2$[P(OPh)$_3$]Br (12). *trans*-CpMo(CO)$_2$P(OPh)$_3$CHO[10] (1.20 g, 2.16 mmol) was dissolved in 20 mL of CH_2Cl_2. After 15 min of stirring, the yellow solution had turned pale pink; an IR spectrum showed the disappearance of the formyl complex and appearance of *cis*-CpMo(CO)$_2$[P(OPh)$_3$]H.[10] Bromoform (3 mL) was then added, causing a color change to pale red within 5 min. After 15 min, the sample was concentrated to 5 mL on a rotary evaporator, diluted with pentane until cloudy and cooled to 0 °C for a few hours. The red-gold crystalline solid that came out was collected and dried to give 1.10 g (85% yield) of the product.

Anal. Calcd for $C_{25}H_{20}BrMoO_5P$: C, 49.45; H, 3.32. Found: C, 49.43; H, 3.55. IR, ν_{CO} (CH_2Cl_2): 1983 (vs), 1908 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.36 (m, Ph), 5.01 (s, Cp). ^{13}C NMR ($CDCl_3$): δ 248.13 (d, CO, J_{PC} = 40.7 Hz), 232.16 (d, CO, J_{PC} = 4.0 Hz), 151.02 (d, ipso, J_{PC} = 7.0 Hz), 129.64 (s, meta), 125.29 (s, para), 121.86 (d, ortho, J_{PC} = 4.5 Hz), 93.38 (s, Cp).

Synthesis of *cis*-CpMo(CO)$_2$[P(OPh)$_2$(*o*-OC$_6$H$_4$CH$_3$)]Br (13). HBr gas was bubbled into 15 mL of CH_2Cl_2 for about 15 s, and the mixture was cooled to −30 °C. Metallacycle **2** (0.27 g, 0.50 mmol) was added, causing an immediate color change from yellow to pale red; the cold bath was then removed. The reaction was complete, as indicated by an IR spectrum, after 10 min of stirring. The mixture was evaporated to dryness and dried further for a few hours under vacuum. The residue was extracted with a 1:10 CH_2Cl_2/hexane mixture (20 mL), and the extracts were filtered through Celite. The filtrate was concentrated to about 5 mL and then cooled to 0 °C overnight. The reddish-brown crystals that came out were collected and dried to give 0.27 g (87% yield) of the product; it melted at 106–107.5 °C.

Anal. Calcd for $C_{26}H_{22}BrMoO_5P$: C, 50.26; H, 3.57. Found: C, 50.42; H, 3.59. IR, ν_{CO} (CH_2Cl_2): 1980 (s), 1908 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.38 (m, Ph), 5.06 (s, Cp), 2.33 (s, CH_3). ^{13}C NMR ($CDCl_3$): δ 248.41 (d, CO, J_{PC} = 40.3 Hz), 232.31 (d, CO, J_{PC} = 5.0 Hz) [OPh: 150.84 (d, ipso, J_{PC} = 6.3 Hz), 150.63 (d, ipso, J_{PC} = 5.0 Hz), 129.52 (s, meta), 129.48 (s, meta), 125.34 (s, para), 125.28 (s, para), 122.18 (d, ortho, J_{PC} = 5.0 Hz), 122.06 (d, ortho, J_{PC} = 5.0 Hz)] [*o*-OC$_6$H$_4$-: 150.52 (d, J_{PC} = 11.3 Hz), 131.64

(s), 129.63 (d, J_{PC} = 5.0 Hz), 126.84 (s), 124.63 (s), 120.14 (d, J_{PC} = 3.8 Hz)], 93.40 (s, Cp), 16.92 (s, CH_3).

Synthesis of $CpMo(CO)_2[P(OPh)_3]({=}CHOCH_3)^+BF_4^-$ (14a,b). A. In a glovebox under argon, Ph_3CBF_4 (0.13 g, 0.39 mmol) was added to 8 mL of cold (−60 °C) CH_2Cl_2. Solid $CpMo(CO)_2[P(OPh)_3]CH_2OCH_3$ (**1a,b**) (0.40 g, 0.70 mmol) was then added in portions during about 1 min, and after $^1/_2$ h, the sample was diluted with cold ether; the resulting milky mixture was allowed to stand for several minutes. The pale yellow powder that precipitated was collected to give 0.15 g (65%) of the product. Trans isomer: IR, ν_{CO} (Nujol mull) 2018 (s), 1935 (s br) cm^{-1}; ^1H NMR (CD_2Cl_2, −30 °C) δ 12.96 (s, ═CHO), 7.38 (m, Ph), 5.29 (s, Cp), 4.60 (s, OCH_3); ^{13}C NMR (CD_2Cl_2, −30 °C) δ 328.46 (s, ═CHO), 222.44 (d, CO, J_{PC} = 39.2 Hz), 149.59 (d, ipso, J_{PC} = 8.7 Hz), 130.48 (s, meta), 126.79 (s, para), 121.21 (d, ortho, J_{PC} = 4.1 Hz), 95.36 (s, Cp), 78.26 (s, OCH_3). A small peak at δ 13.28 was also observed in the proton spectrum and was attributed to the cis isomer; its amount (1:24 cis-to-trans) was very small.

B. A 5-mm NMR tube was charged with solid $CpMo(CO)_2[P(OPh)_3]CH_2OCH_3$ (**1a,b**) (0.05 g, 0.09 mmol), Ph_3CBF_4 (0.03 g, 0.09 mmol), and the standard. The tube was then cooled to −78 °C prior to adding cold CD_2Cl_2. The ^1H NMR spectrum taken at −70 °C showed an 88% yield of $CpMo(CO)_2[P(OPh)_3]({=}CHOCH_3)^+BF_4^-$ (only the trans isomer, **14a**, was observed), a 90% yield of **5a,b** (86% **a**, 4% **b**), and small amounts of unidentified compounds. Also obtained was a 94% yield of $Ph_3C{-}OCH_3$[23] identified by comparison with an authentic sample.

Thermolysis of $CpMo(CO)_2[P(OPh)_3]({=}CHOCH_3)^+BF_4^-$ (14a,b). In the glovebox, a cold (−60 °C) CD_2Cl_2 solution of **14a,b** (0.026 g, 0.04 mmol) was transferred into a 5-mm NMR tube charged with the internal standard. The ^1H NMR spectrum taken at −30 °C showed *cis*- and *trans*-$CpMo(CO)_2[P(OPh)_3]({=}CHOCH_3)^+BF_4^-$ at about 1:20, respectively, a small amount of $CpMo(CO)_3[P(OPh)_3]^+BF_4^-$ (7%) and very small amounts of unidentified compounds. After 30 min at room temperature, the sample did not show any significant change in its composition. After standing at room temperature for 24 h, the sample showed metallacycle **2** at 36% yield and $CpMo(CO)_3[P(OPh)_3]^+BF_4^-$ at 50% yield with unconverted **14a,b** (3%) and small amounts of several unidentified compounds. A peak at δ 3.72 compares favorably with that of an authentic sample of HBF_4·(dimethyl ether) taken in the same solvent.

Synthesis of $CpMo(CO)_2[P(OPh)_3](CH_2PPh_3)^+OTs^-$ (15a,b). Compounds **1a,b** (0.05 g, 0.09 mmol) and PPh_3 (0.025 g, 0.10 mmol) were dissolved in 5 mL of CH_2Cl_2, and the solution was cooled to 0 °C. $HOTs{\cdot}H_2O$ (0.017 g, 0.09 mmol) was then added, and the mixture was stirred for 30 min. The sample was dried over $MgSO_4$, filtered, and evaporated to dryness. The residue was then dissolved in $CDCl_3$ (with added standard) and the ^1H NMR spectrum taken. The results showed a 75% yield of *trans*-$CpMo(CO)_2[P(OPh)_3](CH_2PPh_3)^+OTs^-$ (**15a**), 5% of **15b**, 3% of metallacycle **2**, 5% of the carbonyl cation, $CpMo(CO)_3[P(OPh)_3]^+OTs^-$, and small amounts of unidentified compounds. **15a,b** was recrystallized from CH_2Cl_2/pentane. IR, ν_{CO} (CH_2Cl_2): 1964 (m, br), 1883 (vs, br) cm^{-1}. ^1H NMR ($CDCl_3$): **15a** δ 7.42 (m, Ph), 5.00 (d, Cp, 1.5 Hz), 2.31 (d, CH_2, 15.2 Hz), 2.28 (s, CH_3); **15b** δ 7.42 (m, Ph), 4.65 (s, Cp), CH_2 and CH_3 are not visible; the ratio of **15a**:**15b** is 20:1. ^{13}C NMR ($CDCl_3$): **15a** δ 236.21 (dd, CO, J_{PC} = 39.0 Hz, J_{PC} = 5.1 Hz) [$P(OPh)_3$: 150.57 (d, ipso, J_{PC} = 9.6 Hz), 129.88 (s, meta), 125.64 (s, para), 121.24 (d, ortho, J_{PC} = 4.1 Hz)] [PPh_3: 124.23 (d, ipso, J_{PC} = 84.3 Hz), 129.37 (d, meta, J_{PC} = 11.8 Hz), 133.14 (d, para, J_{PC} = 2.7 Hz), 133.36 (d, ortho, J_{PC} = 9.5 Hz)], 92.95 (s, Cp), 21.23 (s, CH_3), −22.70 (dd, CH_2, J_{PC} = 37.0 Hz, J_{PC} = 7.8 Hz); **15b** 92.52 (s, Cp), other signals are not observable.

The carbonyl cation, $CpMo(CO)_3[P(OPh)_3]^+OTs^-$ was obtained as a dark yellow oil-like material. IR, ν_{CO} (CH_2Cl_2): 2071 (s), 2010 (m, sh), 1984 (vs, br) cm^{-1} [these spectral data are closely similar to those for the known $CpMo(CO)_3[P(OPh)_3]^+BF_4^-$ [10]]. ^1H NMR ($CDCl_3$): δ 7.38 (m, Ph), 5.61 (s, Cp), 2.29 (s, CH_3). ^{13}C NMR ($CDCl_3$): δ 222.45 (d, CO, J_{PC} = 40.8 Hz), 220.97 (d, CO, J_{PC} = 3.1 Hz), 94.45 (s, Cp), 21.22 (s, CH_3), phenyl carbons are not distinct.

Attempted Synthesis of $CpMo(CO)_2[P(OPh)_3]({=}CH_2)^+OTf^-$. A 15-mg sample of **1a,b** was dissolved in CD_2Cl_2 in an NMR tube. The tube was flushed with nitrogen, capped with a septum, and then frozen in liquid nitrogen. Me_3SiOTf (5 μL) was then injected into the tube followed by 0.1 mL of CD_2Cl_2 to wash down the sides of the tube. A ^1H NMR spectrum was recorded at −80 °C and showed that some reaction had already taken place. Resonances for **5a,b**, **14a**, and metallacycle **2** were identified in addition to those for unreacted **1a,b**. Peaks attributable to HOTf and **14a** were the only low-field resonances which could be observed. The tube was warmed to −60 °C and the spectrum recorded again; resonances for the same products were enhanced (**5a,b** and **14a** had increased by about the same amount), and there were no low-field resonances which could be attributed to the methylidene cation.

Reaction of 6a with TFA. A. A 0.03-g sample (0.046 mmol) of **6a** was dissolved in cold (<−10 °C) $CDCl_3$ in an NMR tube. The ^1H NMR spectrum of the solution was taken at 0 °C (probe temperature), showing that the trans isomer (δ 4.90, s, Cp) was the only compound in the solution. After the solution was warmed to 10 °C for 15 min, the cis isomer (**6b**) began to appear. After another 15 min at 20 °C, the amount of the cis isomer had increased. The trans:cis isomer distribution was 4:1 at this point. When the solution was cooled back down to 0 °C, no significant change was observed. Also, there was no evidence for the metallacycle during the course of the experiment. The sample was then cooled to −10 °C prior to the next experiment.

The same sample was withdrawn from the probe, and to it were added 2.7 equiv of TFA via a microsyringe. The ^1H NMR spectrum was taken at 0 °C which showed complete disappearance of the cis isomer and formation of metallacycle **2**; the metallacycle to trans isomer ratio at this point was 1:3.4. After 15 min at 10 °C, the amount of the metallacycle increased, making the metallacycle to trans isomer ratio 1:2.3. Another another 15 min at 20 °C, the ratio was 9:1. No cis isomer (**6b**) was observed during the latter course of the experiment.

B. A 0.04-g sample (0.061 mmol) of **6a** was dissolved in cold (<−10 °C) $CDCl_3$ in an NMR tube with 1,4-dimethoxybenzene as the internal standard. The ^1H NMR spectrum of the solution was taken at 0 °C, showing the presence of trans isomer **6a** (86%), a very small amount of the cis isomer **6b** (<1%), and the metallacycle **2** (12%). The solution was warmed (in the probe) to 10 °C for 15 min; the cis isomer increased to 4%, the trans isomer decreased to 83%, and the metallacycle increased slightly to 13%. Further warming to 20 °C for another 15 min showed the cis isomer at 15%, the trans isomer at 71%, and the metallacycle at 13%. The solution was then cooled to −10 °C for 30 min; the spectrum showed only slight changes: cis, 17%; trans, 70%; metallacycle, 13%.

The sample was withdrawn from the probe, and to it was added 2.7 equiv of TFA via a microsyringe. The proton spectrum was again taken, at 0 °C, showing almost complete disappearance of the cis isomer (<2%), a slight decrease in the trans isomer (65%), and an increase in the metallacycle (30%). After 15 min at 10 °C, only **6a** (52%) and **2** (43%) were present along with a very small amount of **8** (~2%); at 20 °C for another 15 min, **6a** had decreased further (27%) while the metallacycle continued to increase (64%); **8** was present at 4%. After standing at 20 °C for 40 min, the metallacycle was the major product (88%) and **8** was the minor product (6%). Small amounts of unidentified compounds were also observed (<3%).

Thermolysis of *trans*-$CpMo(CO)_2[P(OPh)_3]CH_2OC(O)CF_3$ (6a). $CpMo(CO)_2[P(OPh)_3]CH_2OC(O)CF_3$ (0.05 g, 0.08 mmol) was dissolved in cold $CDCl_3$ (<−10 °C) in an NMR tube and its ^1H NMR spectrum taken at −10 °C; only the trans isomer (**6a**) was present in the solution. The temperature was raised to 20 °C, and immediately, the ^1H NMR spectrum indicated the

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[23] Rutherford, K. G.; Mamer, O. A.; Prokipcak, J. M.; Jobin, R. A. *Can. J. Chem.* **1966**, *44*, 2337.

presence of the cis isomer (**6b**); after 1 h at this temperature, the trans-to-cis ratio had become 2.3:1. The sample was taken out of the probe and allowed to stand at room temperature while the progress of the conversion was monitored. After a total of 11 h, the ^{1}H NMR spectrum indicated the complete disappearance of the starting material. An internal standard (1,4-dimethoxybenzene) was added to the solution, and the yields of the products in the mixture were calculated: metallacycle **2** (88%) and trifluoroacetate **8** (6%).

In the presence of 1 equiv of Ph_3SiH (0.02 g, 0.08 mmol), the same reaction took 26 h to complete. The product mixture consisted of metallacycle **2** (46%), trifluoroacetate **8** (37%), and Ph_3SiCH_3 (34%), as indicated by the ^{1}H NMR spectrum (using 1,4-dimethoxybenzene as the internal standard).

Thermolysis of *trans*-CpMo(CO)$_2$[P(OPh)$_3$]CH$_2$Br (10a). A. A 0.10-g sample (0.16 mmol) of **10a** was dissolved in CD_2Cl_2 in an NMR tube. The ^{1}H NMR spectrum of the sample was taken after 1 h, showing a 2:1 trans-to-cis isomer ratio (**10a**:**10b**) [the cis isomer showed the following ^{1}H resonances: δ 5.00 (s, Cp), 4.21 (dd), and 4.11 (dd), CH_2. Also, its ^{13}C NMR spectrum showed the following resonances: δ 247.69 (d, CO, J_{PC} = 36.6 Hz), 233.37 (s, CO), 151.20 (d, ipso, J_{PC} = 8.0 Hz), 130.06 (s, meta), 125.50 (s, para), 121.70 (d, ortho, J_{PC} = 4.7 Hz), 93.65 (s, Cp), 24.51 (d, CH_2, J_{PC} = 30.2 Hz)]. The tube was then left standing for 20.5 h; the internal standard was added, and the ^{1}H NMR spectrum was again taken, this time showing the metallacycle **2** (21%), **12** (11%), and **13** (53%).

B. Following the same procedure as above, another 0.10 g of **10a** was dissolved in CD_2Cl_2 in the presence of 1 equiv (0.04 g, 0.16 mmol) of Ph_3SiH. After 1 h at room temperature, its ^{1}H NMR spectrum also showed a 2:1 trans to cis isomer ratio; no reaction with the silane was observed. The sample was allowed to stand 20.5 h, after which its ^{1}H NMR spectrum was taken with added internal standard. The result showed the formation of metallacycle **2** (15%), **12** (50%), **13** (27%), and Ph_3SiCH_3 (38%).

Reactions of *trans*- and *cis*-CpMo(CO)$_2$[P(OPh)$_3$]CH$_2$OCH$_3$ (1a,b) with Electrophiles. A. With 1.0 equiv of Electrophile. General Procedure. Compounds **1a,b** (0.05 g, 0.09 mmol) were dissolved in 5 mL of CH_2Cl_2 and the resulting yellow solution was cooled to −72 °C. The electrophile (0.09 mmol) was then added via a microsyringe, causing a rapid color change from yellow to pale red (slower for Me_3SiOTf). The mixture was allowed to warm to room temperature gradually (3 h) and then filtered through Celite layered with $MgSO_4$. The filtrate was evaporated to dryness on a rotary evaporator and dried under vacuum for several hours. The residue was dissolved in $CDCl_3$ and its ^{1}H NMR spectrum taken (with the internal standard). The results are indicated below; product yields are shown in parentheses. Experiment 4 below involves Ph_3SiH also; 1 equiv of the silane (0.023 g, 0.009 mmol) was added to the reaction mixture before cooling to −72 °C.

(1) *HBF_4·(etherate)*: metallacycle **2** (23%), methyl complexes **5a,b** (15%), compound **7** (17%), and $CpMo(CO)_3[P(OPh)_3]^+BF_4^-$ (13%). Unidentified compounds whose cyclopentadienyl signals appeared at δ 5.46 (5%) and δ 5.30 (2%) were also observed.

(2) *Triflic acid*: metallacycle **2** (18%), triflate **3a** (35%), triflate **3b** (4%), cation **4** (14%), and triflate **9** (3%).

(3) *Me_3SiOTf*: metallacycle **2** (22%), triflate **3a** (22%), triflate **3b** (10%), cation **4** (18%), and triflate **9** (4%).

(4) *Me_3SiOTf/Ph_3SiH*: metallacycle **2** (9%), triflate **3a** (78%), triflate **3b** (4%), and Ph_3SiMe (69%).

B. With 0.5 equiv of Electrophile. General Procedure. The electrophile, 0.045 mmol in 5 mL of CH_2Cl_2, was cooled to −72 °C. A sample of **1a,b** (0.05 g, 0.09 mmol), dissolved in 1 mL of CH_2Cl_2 and cooled to −72 °C, was then added. The resulting pale yellow mixture was stirred for 10 min at this temperature. The bath was then removed and the stirring was continued for another 20 min. The sample, which had turned dark yellow, was filtered through Celite layered with $MgSO_4$. The filtrate was evaporated to dryness on a rotary evaporator and dried under vacuum for several hours. The residue was dissolved in $CDCl_3$ and its ^{1}H NMR spectrum taken (with the internal standard). The results are indicated below; product yields are shown in parentheses. In experiment 4, 1 equiv (0.023 g, 0.09 mmol) of Ph_3SiH was added to the reaction mixture before cooling to −72 °C.

(1) *HBF_4·(etherate)*: metallacycle **2** (38%), methyl complexes **5a,b** (21%), compound **7** (5%), and $CpMo(CO)_3[P(OPh)_3]^+BF_4^-$ (7%).

(2) *HOTf*: metallacycle **2** (29%), methyl complexes **5a,b** (21%), triflate **3a** (8%), and triflate **4** (11%).

(3) *Me_3SiOTf*: metallacycle **2** (30%), methyl complexes **5a,b** (14%), triflate **3a** (10%), and triflate **4** (18%).

(4) *Me_3SiOTf/Ph_3SiH*: metallacycle **2** (20%), methyl complexes **5a,b** (2%), triflate **3a** (66%), triflate **3b** (5%), and Ph_3SiMe (61%).

C. With Excess Electrophile. General Procedure. Complexes **1a,b** (0.05 g 0.09 mmol) were dissolved in 5 mL of CH_2Cl_2, and the resulting yellow solution was cooled to 0 °C. The electrophile (0.24 mmol) was then added via a microsyringe and the bath removed. After stirring for 30 min, the mixture was filtered through Celite layered with $MgSO_4$ and the filtrate was evaporated to dryness on a rotary evaporator. The residue was dried under vacuum for several hours and was then dissolved in $CDCl_3$ and its ^{1}H NMR spectrum taken (with 1,4-dimethoxybenzene as an internal standard). The results are indicated below; product yields are shown in parentheses. In experiment 3, 1 equiv (0.023 g, 0.09 mmol) of Ph_3SiH was added before cooling to 0 °C.

(1) *TFA*: metallacycle **2** (71%), trifluoroacetate **8** (7%), and (trifluoroacetoxy)methyl complexes **6a,b** (7%).

(2) *TFA (5.4 equiv)*: metallacycle **2** (77%) and trifluoroacetate **8** (12).

(3) *TFA/Ph_3SiH (2.7:1)*: metallacycle **2** (20%), trifluoroacetate **8** (70%), and Ph_3SiMe (62%).

(4) *Aqueous HBr*: metallacycle **2** (8%) and bromomethyl complexes **10a** (52%) and **10b** (27%).

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Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom parameters, bond distances, bond angles, and torsional angles for **2** (10 pages). Ordering information is given on any current masthead page.

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