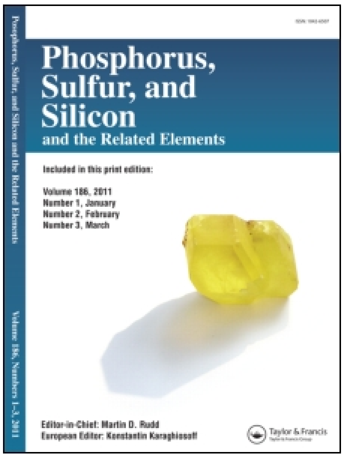

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Reactivity of Hydridomolybdenum Complex Having Diamino-Substituted Phosphite Ligand with $Me_3SiOSO_2CF_3$

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*The reaction of [Cp*Mo(H)(CO)$_2${P(NMeCH$_2$)$_2$(OMe)}] with TMSOTf (Me$_3$SiOSO$_2$CF$_3$) afforded [Cp*Mo(CO)$_2$(OTf){P(NMeCH$_2$)$_2$(OMe)}] (**2**), showing preferential hydrido abstraction rather than OMe abstraction at the phosphorus atom. [Cp*Mo(OTf)(CO)$_3$] reacted with P(NMeCH$_2$)$_2$(OMe) to afford cationic phosphite complexes [Cp*Mo(CO)$_{4\text{-}n}$ {P(NMeCH$_2$)$_2$(OMe)}$_n$][OTf] [n = 1, 2 (**6**)] but not to give **2**. Structures of **2** and **6** were determined by single crystal X-ray diffraction studies.*

Keywords Crystal structure; hydrido; Lewis acid; molybdenum; phosphite

INTRODUCTION

Cationic phosphenium complexes of transition metals described generally as $[L_nM\text{-}PR_2]^+$ have attracted considerable attention because they are phosphorus analogues to transition metal carbene complexes. It has been demonstrated that a transition metal complex bearing diamino-substituted phosphite, such as $P(NMeCH_2)_2(OR)$, is a good precursor of a phosphenium complex, because it readily reacts with a Lewis acid, such as $BF_3{\cdot}OEt_2$ or TMSOTf ($Me_3SiOSO_2CF_3$), resulting in abstraction of an OR group from the coordinating phosphite as an anion [Eq (1)].[1] A hydrido transition metal complex has also

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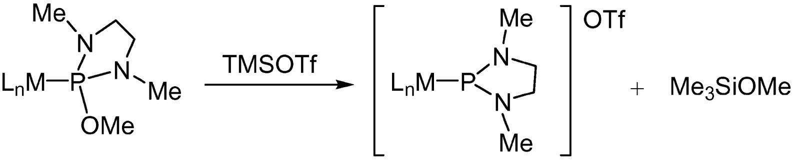
been reported to react with TMSOTf to undergo an H/OTf substitution reaction [Eq (2)].[2] These results stimulate us to examine a reaction of a transition metal complex bearing both $P(NMeCH_2)_2(OMe)$ and hydrido ligands with TMSOTf to elucidate whether OR abstraction from the phosphorus ligand takes place to give a cationic phosphenium complex or H/OTf substitution is preferred. Herein we report the reaction of $[Cp^*Mo(H)(CO)_2\{P(NMeCH_2)_2(OMe)\}]$ with TMSOTf where Cp^* stands for η^5-C_5Me_5.



(1)

$$L_nM{-}H \xrightarrow{TMSOTf} L_nM{-}OTf + Me_3SiH \qquad (2)$$

RESULTS AND DISCUSSION

The reaction of $[Cp^*Mo(H)(CO)_2\{P(NMeCH_2)_2(OMe)\}]$ (**1**)[3] with TMSOTf in a 1:2 molar ratio at room temperature was carried out. After workup, the brown powder **2** was obtained (crude yield, 72%). Considerable difficulty was encountered in our attempts to obtain sufficient elemental analysis data and detailed NMR data of **2** due to the high reactivity. Fortunately, the molecular structure of **2** could be obtained by X-ray crystallography (Figure 1). Suitable single-crystals of **2** were obtained by solvent diffusion at $-20°C$ over a few days from a CH_2Cl_2 layer containing the reaction mixture and an overlayer of hexane. The crystal data and the selected bond lengths and angles are listed in Tables I and II. Complex **2** is described as $[Cp^*Mo(OTf)(CO)_2\{P(NMeCH_2)_2(OMe)\}]$. The central molybdenum has a Cp^* ligand in an η^5-fashion, an OTf ligand, the phosphite ligand, and two carbonyl ligands with a *cis* configuration. The X-ray analysis revealed that preferential H/OTf substitution on Mo takes place, and the OMe group on the phosphite remains intact [Eq (3)]. The Mo-O distance of **2** [2.233(5) Å] is slightly longer than that of the previously reported Mo–OTf complex [2.212(2) Å],[4] and considerably longer than those of acetylacetonato molybdenum complexes (2.138 and 2.194 Å).[5] The Mo-C bond distance in terms of the CO ligand *trans* to the phosphite [1.979(6) Å] is longer than that *trans* to OTf [1.957(7) Å]. The

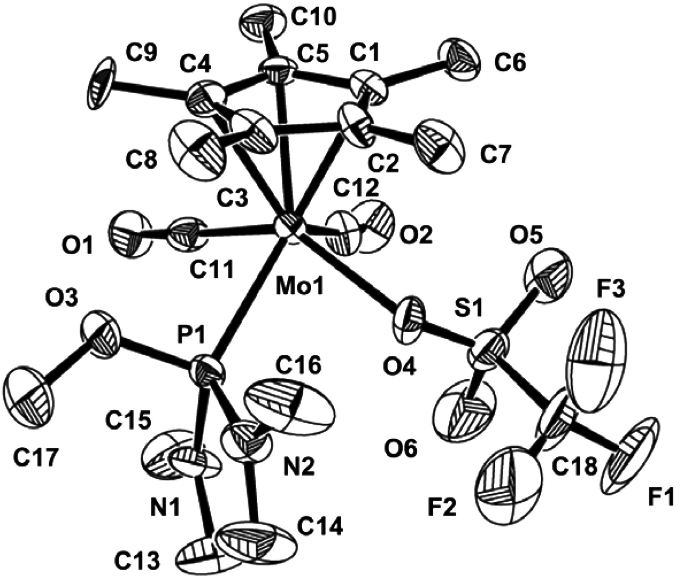
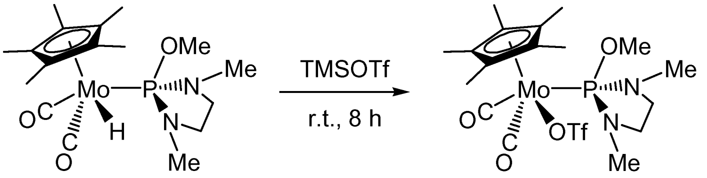


FIGURE 1 An ORTEP drawing of **2** at the 50% ellipsoidal level. The hydrogen atoms are omitted for simplicity.

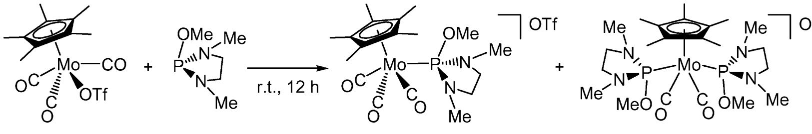
Mo–P distance [2.494(1) Å] is about 0.1 Å longer than that of **1** [2.372(1) Å].[3]



(3)

1 **2**: 72%

Next, we planned to prepare **2** by another synthetic route such as the displacement of one of CO ligands in [Cp*Mo(OTf)$(CO)_3$] (**3**)[4] by the diamino-substituted phosphite, $P(NMeCH_2)_2(OMe)$ (**4**).[6] The reaction of **3** with **4** yielded a dingy yellow solid. Recrystallization from CH_2Cl_2/hexane afforded yellow crystals. The $^{31}P\{^1H\}$ NMR spectrum showed two signals at δ 139.3 and 155.9 in ca. 20:1 peak area ratio. The ^1H, ^{13}C, and ^{19}F NMR spectra and the elemental analysis suggested that the major species is a cationic phosphite complex [Cp*$Mo(CO)_3\{P(NMeCH_2)_2(OMe)\}$][OTf] (**5**) [Eq (4)]. Therefore, in the reaction of **3** with **4**, the OTf ligand but not the CO ligand is selectively replaced by the added phosphite.



3 **4** **5**: 81% **6**: < 3% (4)

The yellow crystals obtained by recrystallization from CH_2Cl_2/hexane consisted of two types of crystals due to **5** and **6**. As crystals of **6** were suitable for X-ray analysis, the structure was characterized by X-ray analysis. The ORTEP drawing (Figure 2) shows that **6** is described as *trans*-[Cp*Mo(CO)$_2${P(NMeCH$_2$)$_2$(OMe)}$_2$][OTf]. The crystal data and the selected bond lengths and angles are listed in Tables I and III. Complex **6** has a typical four-legged piano-stool configuration: the molybdenum has two terminal CO ligands, two phosphite ligands, and a Cp* ligand bonded in an η^5-fashion. Two phosphite ligands are

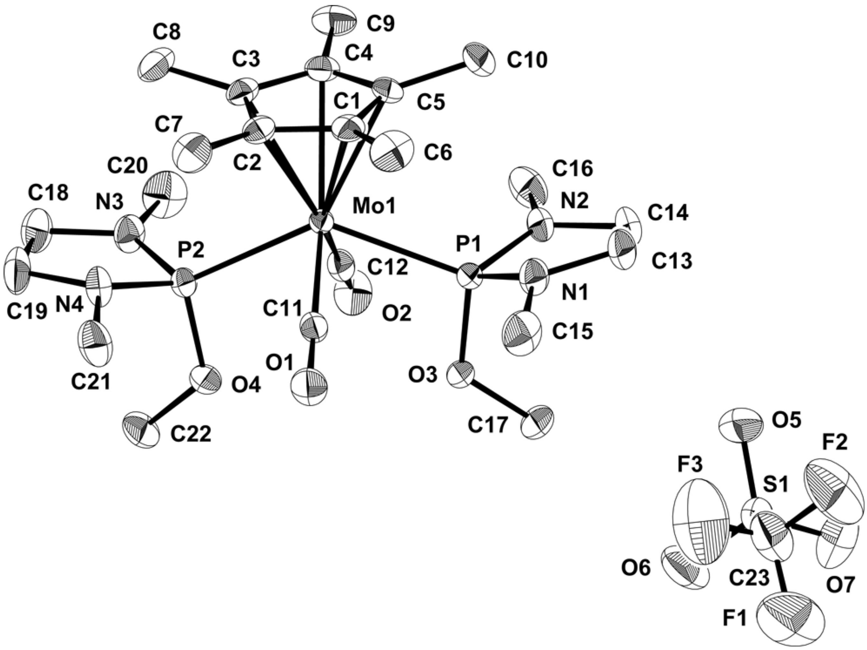


FIGURE 2 An ORTEP drawing of **6** at the 50% ellipsoidal level. The hydrogen atoms are omitted for simplicity.

TABLE I Crystal Data and Experimental Parameters Used for the Intensity Data Collection of 2 and 6: Procedure and Final Results of the Structure Determination

Empirical formula	$C_{18}H_{29}N_2F_3O_6PSMo$ (**2**)	$C_{23}H_{41}N_4F_3O_7P_2SMo$ (**6**)
Formula weight	584.40	732.54
T (K)	203(2)	200(2)
Crystal system	orthorhombic	Monoclinic
Space group	Aba2	$P2_1/n$
a (Å)	28.014(5)	13.2675(8)
b (Å)	14.049(3)	8.5731(5)
c (Å)	12.300(3)	27.8535(17)
β (°)		95.444(3)
Volume (Å^3)	4840(1)	3153.9(3)
Z	2	4
ρ_{calcd} (mg m^{-3})	1.604	1.543
μ (cm^{-1})	7.52	6.47
F(000)	2384	1512
Crystal size (mm^3)	0.27 × 0.27 × 0.44	0.25 × 0.20 × 0.03
Reflections collected	18058	23973
Independent reflections (R(int))	5218 (0.032)	7156 (0.044)
R ($I > 2\sigma(I)$)	0.050	0.056
wR2	0.123	0.098
Goodness of fit	1.20	1.00

situated mutually in a *trans* position presumably for the steric reason. The Mo1–P1, Mo–P2, Mo–C11, and Mo–C12 distances [2.4648(10), 2.4670(10), 1.962(4), 1.990(4) Å] are similar to those of previously reported complexes.[7] It is considered that **6** is synthesized by the displacement of the labile triflate in **3** by the phosphite ligand to give **5**, followed by CO/phosphite substitution reaction. Although each of OTf^-/phosphite and CO/phosphite substitution reaction are well kwon, the example containing both of these reactions is quite rare.[8]

TABLE II Selected Bond Lengths (Å) and Bond Angles (°) for 2

Mo(1)–C(1)	2.325(5)	C(11)–O(1)	1.150(9)
Mo(1)–C(2)	2.427(4)	C(12)–O(2)	1.162(8)
Mo(1)–C(3)	2.412(6)	P(1)–O(3)	1.624(6)
Mo(1)–C(4)	2.309(7)	P(1)–N(1)	1.662(6)
Mo(1)–C(5)	2.274(6)	P(1)–N(2)	1.652(7)
Mo(1)–C(11)	1.957(7)	O(4)–S(1)	1.486(5)
Mo(1)–C(12)	1.979(6)		
Mo(1)–P(1)	2.494(1)	C(11)–Mo(1)–C(12)	74.6(3)
Mo(1)–O(4)	2.233(5)	P(1)–Mo(1)–O(4)	76.9(1)

TABLE III Selected Bond Lengths (Å) and Bond Angles (°) for 6

Mo(1)–C(1)	2.337(4)	C(11)–O(1)	1.157(5)
Mo(1)–C(2)	2.331(4)	C(12)–O(2)	1.147(4)
Mo(1)–C(3)	2.381(4)	P(1)–O(3)	1.609(3)
Mo(1)–C(4)	2.395(4)	P(2)–O(4)	1.615(3)
Mo(1)–C(5)	2.374(4)		
Mo(1)–C(11)	1.962(4)	P(1)–Mo(1)–C(11)	77.64(11)
Mo(1)–C(12)	1.990(4)	P(1)–Mo(1)–C(12)	72.79(11)
Mo(1)–P(1)	2.4648(10)	P(2)–Mo(1)–C(11)	77.91(11)
Mo(1)–P(2)	2.4670(10)	P(2)–Mo(1)–C(12)	73.48(11)

EXPERIMENTAL

All reactions were carried out under an atmosphere of dry nitrogen by using standard Schlenk tube techniques. Dichloromethane was distilled from P_2O_5, and hexane and benzene were distilled from sodium metal. They were stored under nitrogen atmosphere. [Cp*Mo(H)(CO)$_2${P(NMeCH$_2$)$_2$(OMe)}],[3] [Cp*Mo(OTf)(CO)$_3$],[5] and P(NMeCH$_2$)$_2$(OMe)[6] were synthesized according to the reported procedures. NMR spectra (^{1}H, ^{13}C, ^{19}F, ^{31}P) were measured on JEOL JNM-AL400 spectrometer at 25°C. ^{1}H and ^{13}C NMR data were referred to residual peaks of solvent as an internal standard. Peak positions of the ^{19}F and ^{31}P NMR spectra were referenced to external CCl_3F and 85% H_3PO_4, respectively.

Reaction of [Cp*MoH(CO)$_2${P(NMeCH$_2$)$_2$(OMe)}] with TMSOTf

A CH_2Cl_2 solution (5 mL) containing [Cp*Mo(H)(CO)$_2${P(NMeCH$_2$)$_2$ (OMe)}] (234 mg, 0.54 mmol) and TMSOTf (195 μL, 1.08 mmol) was stirred at room temperature. After 8 h, volatile materials were removed under reduced pressure. Addition of 5 mL of hexane to the dark red materials at −78°C led to the formation of a brown solid, which was washed with 2 mL of hexane at −78°C, collected by filtration, and dried in vacuo to give a brown powder of [Cp*Mo(OTf)(CO)$_2${P(NMeCH$_2$)$_2$(OMe)}] **2** (228 mg, 0.39 mmol, 72%). Complex **2**, crystallized from CH_2Cl_2/hexane at −20°C for a few days, afforded dark red crystals suitable for X-ray analysis.

Reaction of [Cp*Mo(OTf)(CO)$_3$] with P(NMeCH$_2$)$_2$(OMe)

A benzene solution (30 mL) containing Cp*Mo(OTf)(CO)$_3$ (760 mg, 1.64 mmol) and P(NMeCH$_2$)$_2$(OMe) (484 mg, 3.27 mmol) was stirred at room temperature. After 12 h, volatile materials were removed under reduced pressure, and the resulting residue was washed with a hexane (20 mL × 4 times), collected by filtration, and dried in vacuo to give a dingy yellow solid. Recrystallization from CH_2Cl_2/hexane afforded yellow crystals (854 mg) as the mixture of $[Cp^*Mo(CO)_3\{P(NMeCH_2)_2(OMe)\}][OTf]$ **5** (81% yield) and $[Cp^*Mo(CO)_2\{P(NMeCH_2)_2(OMe)\}_2][OTf]$ **6** (< 3% yield) in the ratio about 40:1 (determined by ^{31}P NMR). Crystals of **6** suitable for X-ray analysis were obtained from the yellow crystals. NMR spectroscopic analysis for **5**: ^1H NMR (400 MHz, CD_2Cl_2): $\delta = 2.05$ (s, 15H, C_5Me_5), 2.82 (d, $J_{PH} = 11.6$ Hz, 6H, NMe), 3.38–3.50 (br, 2H, CH_2), 3.45 (d, $J_{PH} = 12.8$ Hz, 3H, OMe), 3.57–3.67 (br, 2H, CH_2). $^{13}C\{^1H\}$ NMR (100.4 MHz, CD_2Cl_2): $\delta = 11.0$ (s, $C_5\mathit{Me}_5$), 33.4 (d, $J_{PC} = 9.9$ Hz, NMe), 52.8 (s, CH_2), 109.1 (s, C_5Me_5), 121.2 (q, $J_{FC} = 320.5$ Hz, CF_3), 227.3 (d, $J_{PC} = 38.1$ Hz, CO), 230.6 (s, CO). A signal of OMe group is overlapping with the signal of solvent. $^{19}F\{^1H\}$ NMR (376.4 MHz, CD_2Cl_2): $\delta = -84.18$ (s). $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_2Cl_2): $\delta = 139.3$ (s). Anal. Calc. for $C_{19}H_{28}N_2O_7F_3P_2SMo$: C, 37.26; H, 4.61; N, 4.57%. Found: C, 37.21; H, 4.72; N, 4.66%.

X-Ray Diffraction

X-ray intensity data were collected at −70°C for **2** and at −73°C for **6** on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo-Kα radiation. Calculations for **2** were performed with the teXsan crystallographic software package of Molecular Structure Corporation. Calculations for **6** were performed with the CrystalClear software package (Molecular Structure Corporation). The structures were solved by direct methods SIR92[9] for **2** and SIR97[10] for **6** and expanded using Fourier techniques. The structures were refined by full matrix least-squares technique using the program SHELXL-97.[11] The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in fixed positions. Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 268039 for **2** and CCDC 671894 for **6**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Tel.; +44 1223 336408; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

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