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Geometrical isomerization of *fac*/*mer*-$Mo(CO)_3(phosphite)_3$ and *cis*/*trans*-$Mo(CO)_4(phosphite)_2$ catalyzed by $Me_3SiOSO_2CF_3$

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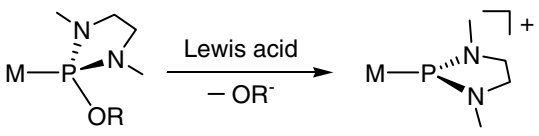
Abstract

Geometrical isomerization of *fac*-$Mo(CO)_3L_3$ ($L = P(OPh)_3$, $P(OMe)_3$, $P(OEt)_3$) to the *mer* form and that of *cis*-$Mo(CO)_4L_2$ ($L = P(OPh)_3$, $P(OMe)_3$, $PPh_2(OMe)$) to the *trans* form were observed in CH_2Cl_2 at room temperature in the presence of a catalytic amount of $Me_3SiOSO_2CF_3$ (TMSOTf). Crossover experiments suggest that a ligand dissociation is not involved in the isomerization. A catalytic cycle involving an interaction of the silicon atom in Me_3Si^+ with one oxygen in $P(OR)_3$ ligands has been proposed. The first isolation and the X-ray structure analysis were attained for *mer*-$Mo(CO)_3\{P(OPh)_3\}_3$ through the TSMOTf-assisted isomerization of *fac*-$Mo(CO)_3\{P(OPh)_3\}_3$.

Keywords: Geometrical isomerization; Catalysis; Mo complex; Phosphite

1. Introduction

Transition metal complexes with a phosphenium ligand ($^+PR_2$) have attracted considerable attention because a cationic phosphenium is isolobal with a singlet carbene, silylene, and the heavier congeners [1–5]. One of the best methods for preparation of cationic phosphenium complexes of transition metals is OR anion abstraction by a Lewis acid such as $BF_3 \cdot OEt_2$ or TMSOTf ($Me_3SiOSO_2CF_3$) from coordinating diamino-substituted phosphite $P(NMeCH_2)_2(OR)$ as shown in Eq. (1) [4,5]. This method is applicable for many types of transition



(1)

metal complexes; $M(bpy)(CO)_3\{P(NMeCH_2)_2(OR)\}$ [6–12], $M(dppe)(CO)_3\{P(NMeCH_2)_2(OR)\}$ [7], $M(bpy)(CO)_2\{P(NMeCH_2)_2(OR)\}_2$ [8,11,12], $M(CO)_3\{P(NMeCH_2)_2(OR)\}_3$ [13], $M(CO)_4\{P(NMeCH_2)_2(OR)\}_2$ [13], $CpM(CO)_2(ER_3)\{P(NMeCH_2)_2(OR)\}$ (M = Cr, Mo, W) [14–17], and $CpM(CO)(ER_3)\{P(NMeCH_2)_2(OR)\}$ (M = Fe, Ru) ($ER_3 = CH_3$, $SiMe_3$, $GeMe_3$, $SnMe_3$) [10,18–23]. Systematic researches for reactions of $Mo(bpy)(CO)_3\{PXY(OR)\}$ with $BF_3 \cdot OEt_2$ revealed the effect of the substituents (X, Y) on the stability of cationic phosphenium complexes; the stability increases with increasing the number of amino substituents on the phosphenium phosphorus [9]. TMSOTf has been demonstrated to be an appropriate Lewis acid for *fac*-$Mo(CO)_3\{P(NMeCH_2)_2(OR)\}_3$ and *cis*-$Mo(CO)_4\{P(NMeCH_2)_2(OR)\}_2$ [13].

During the course of investigation of suitability of a Lewis acid to yield a cationic phosphenium complex by OR anion abstraction, we obtained unexpected results in the reaction with TMSOTf of *fac*-$Mo(CO)_3\{P(OR)_3\}_3$ and *cis*-$Mo(CO)_4\{P(OR)_3\}_2$ having no amino-substituent on the coordinating phosphites; TMSOTf does not abstract an

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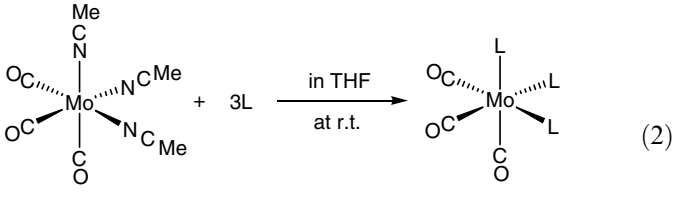
OR anion to give a cationic phosphenium complex, but promotes the geometrical isomerization of the complexes (*fac–mer* and *cis–trans* isomerization), and it works as a catalyst.

The $Mo(CO)_3L_3$ complexes (M = Cr, Mo, W; L = phosphine, phosphite) have been synthesized in the facial form from $M(CO)_3L'_3$ (L′ = weekly coordinating 2e-donor ligand) and L. The *mer* isomers were obtained by using isomerization of the corresponding *fac* isomers. Bond et al. reported that a one electron-oxidation promotes *fac–mer* isomerization for $M(CO)_3\{Ph_2PCH_2CH_2$-$P(Ph)CH_2CH_2P\ Ph_2$-$\kappa^3P\}$ [24]. We reported that the reaction of *fac*-$M(CO)_3(bpy)\{P(NMeCH_2)_2(OMe)\}$ with $BF_3 \cdot OEt_2$ yields a cationic phosphenium complex, *fac*-$[M(CO)_3(bpy)\{P(NMeCH_2)_2\}]^+$, which then isomerizes to the *mer* form [7–9]. The strong π-acidity of a phosphenium ligand causes an electron deficient metal center which may induce the *fac–mer* isomerization. Thermal *fac–mer* isomerization has been reported by Rousche et al. for *fac*-$Mo(CO)_3(\eta^2$-dppe$)\{P(O^iPr)_3\}$ [25] and by Howell et al. for *fac*-$M(CO)_3\{P(OR)_3\}_3$ [26]. We recently found that Me_3SiX (X = Cl, Br, I) promotes the *fac–mer* isomerization for *fac*-$Mo(CO)_3\{P(OR)_3\}_3$ [27].

2. Results and discussion

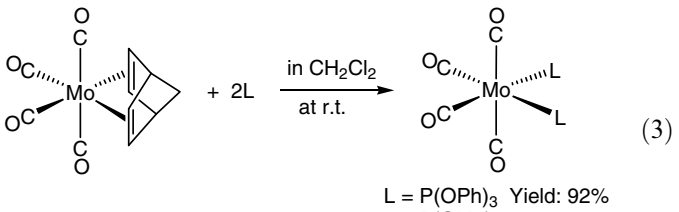
2.1. Preparation of fac-$Mo(CO)_3\{P(OR)_3\}_3$ and cis-$Mo(CO)_4\{P(OR)_3\}_2$

The *fac*-$Mo(CO)_3\{P(OR)_3\}_3$ complexes were obtained in good yield by modifying the literature methods [28]. $Mo(CO)_3(NCMe)_3$ was treated with $P(OR)_3$ in 1:3 molar ratio in THF at room temperature (Eq. (2)). A preparative method for *cis*-$Mo(CO)_4\{P(OR)_3\}_2$ was briefly described in the literature, where $Mo(CO)_4(NMe_2(CH_2)_3NMe_2)$ was used as an Mo source [29]. We modified the starting complex. $Mo(CO)_4(nbd)$ (nbd = norbornadiene) and $P(OR)_3$ were treated in 1:2 molar ratio in CH_2Cl_2 at room temperature to give *cis*-$Mo(CO)_4\{P(OR)_3\}_2$ in excellent yield (Eq. (3)).



L = $P(OPh)_3$ Yield: 82%
$P(OMe)_3$ 92%
$P(OEt)_3$ 92%

(2)



L = $P(OPh)_3$ Yield: 92%
$P(OMe)_3$ 96%
$PPh_2(OMe)$ 96%

(3)

2.2. Reaction of fac-$Mo(CO)_3L_3$ with TMSOTf

The *fac*-$Mo(CO)_3\{P(OPh)_3\}_3$ (***fac*-1**) was dissolved in CH_2Cl_2 and an equimolar amount of TMSOTf was added at room temperature and the reaction was monitored by the ^{31}P NMR measurement. A triplet at 148.2 ppm (t, $^2J_{PP} = 47.0$ Hz) and a doublet at 155.2 ppm (d, $^2J_{PP} = 47.0$ Hz) were newly observed at the expense of a singlet at 144.4 ppm attributed to ***fac*-1**. The new signals were reasonably assigned to ***mer*-1** based on their coupling pattern and the coupling constant. The isomerization reached at an equilibrium after 1.5 h and the ***fac*-1**:***mer*-1** ratio was 1: 30.

We confirmed that ***fac*-1** did not isomerize to ***mer*-1** in CH_2Cl_2 in the absence of TMSOTf at room temperature and even at the reflux temperature, showing that TMSOTf promotes its isomerization. Next question is whether TMSOTf works as a catalyst or not. The reactions of ***fac*-1** with 0.5 and 0.1 equivalent of TMSOTf revealed that the final equilibrium position did not depend on the amount of TMSOTf used although it took a longer time to reach the equilibrium when the amount of TMSOTf was reduced.

The ***mer*-1** could be isolated from the reaction mixture of ***fac*-1** and TMSOTf. After a treatment of ***fac*-1** with TMSOTf in CH_2Cl_2, a white powder which is a mixture of ***fac*-1** and ***mer*-1** (1:30) was washed with hexane/CH_2Cl_2/benzene (100/1/1) solution many times to obtain the pure complex formulated as ***mer*-1** $\cdot 0.5CH_2Cl_2 \cdot 0.5C_6H_6$ in 53% yield. Although several *mer*-$M(CO)_3L_3$ (M = Cr, Mo, W) type complexes have been reported, this is the first preparation and isolation of *mer*-$M(CO)_3\{P(OPh)_3\}_3$. The structure was confirmed by the X-ray analysis. The ORTEP drawing is depicted in Fig. 1 and the crystal data are summarized in Table 1. This X-ray structure is the first example among *mer*-$M(CO)_3$(tertiary phosphorus compound)$_3$ type complexes. The X-ray structure of ***fac*-1** was reported previously [29]. The structural comparison between *fac*- and *mer*-$Mo(CO)_3\{P(OPh)_3\}_3$ revealed some interesting points. The bond distance of Mo–C2 for ***mer*-1** (2.018 Å) is clearly shorter than those of Mo–C1 (2.041 Å) and Mo–C3 (2.041 Å). As C2O2 ligand is *trans* to $P(OPh)_3$, the CO ligand can get more π-back donation from the central metal than C1O1 and C3O3 ligands which are mutually *trans*. The mean Mo–C bond distance for ***fac*-1** (1.986 Å) is shorter than that for ***mer*-1** (2.033 Å), reasonably understood by greater π-back donation from the Mo to the CO ligands for ***fac*-1** because of the *trans* $P(OPh)_3$ ligand. Another interesting point is that the mean Mo–P bond distance for ***fac*-1** (2.435 Å) is longer than that for ***mer*-1** (2.417 Å). The difference may stem from the steric repulsion between $P(OPh)_3$ ligands in ***fac*-1**.

The ***mer*-1** did not isomerize to ***fac*-1** in CH_2Cl_2 at room temperature, but it did by the addition of an equimolar amount or even a catalytic amount of TMSOTf. After several hours, the ***fac*-1**:***mer*-1** ratio was 1:30. The results mentioned above show that the equilibrium ratio is determined

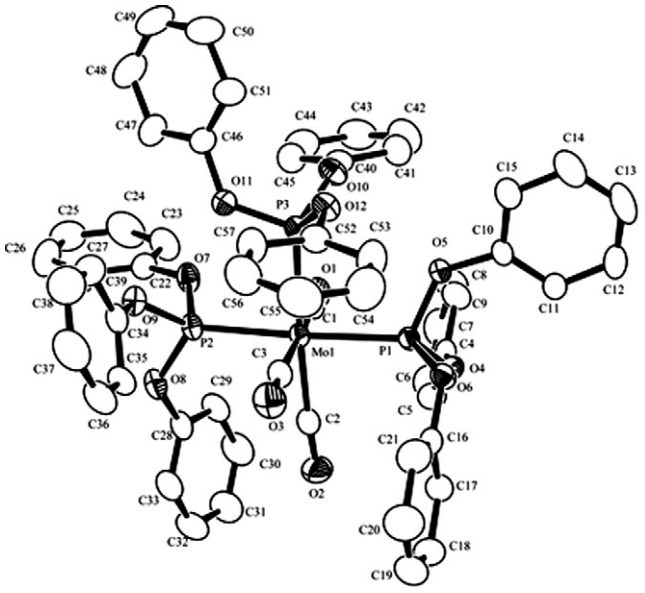


Fig. 1. ORTEP drawing of ***mer*-1** · $0.5CH_2Cl_2$ · $0.5C_6H_6$ (50% probability ellipsoids) showing the numbering system. All hydrogen atoms and the solvated CH_2Cl_2 and C_6H_6 molecules are omitted for clarity. Selected bond distances (Å) and bond angles (°): Mo1–P1, 2.3796(7); Mo1–P2, 2.4319(7); Mo1–P3, 2.4390(7); Mo1–C1, 2.041(3); Mo1–C2, 2.018(3); Mo1–C3, 2.041(3); P1–Mo1–P2, 174.24(2); P1–Mo1–P3, 89.76(2); P2–Mo1–P3, 89.57(2); P1–Mo1–C1, 91.21(8), P1–Mo–C2, 86.15(8); P1–Mo–C3, 91.51(8).

Table 1
Crystal data for ***mer*-1** · $0.5CH_2Cl_2$ · $0.5C_6H_6$

Empirical formula	$C_{60.50}H_{49}ClMoO_{12}P_3$
Formula weight	1192.30
Crystal system	Monoclinic
Crystal size (mm^3)	0.45 × 0.35 × 0.15
Temperature (°C)	−70.0
Space group	$P2_1/n$ (No. 14)
a (Å)	13.7319(5)
b (Å)	18.2658(7)
c (Å)	22.1401(9)
β (°)	95.744(2)
V ($Å^3$)	5525.4(4)
Z	4
μ (cm^{-1})	4.36
D_{calc} (g/cm^3)	1.433
Number of unique reflections	41908
Number of used reflections	12498
Number of variables	712
R	0.051
R_W	0.111
Goodness-of-Fit	1.06

thermodynamically and TMSOTf serves as a catalyst for the *fac–mer* isomerization.

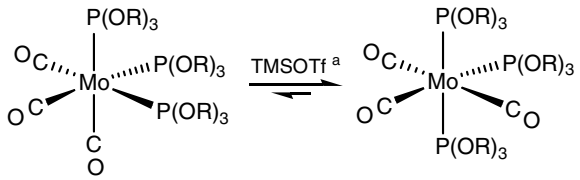
Reactions of *fac*-$Mo(CO)_3\{P(OMe)_3\}_3$ (***fac*-2**) and *fac*-$Mo(CO)_3\{P(OEt)_3\}_3$ (***fac*-3**) with TMSOTf were also examined in CH_2Cl_2 at room temperature. In the ^{31}P NMR spectra, a triplet at 166.9 ppm (t, $^2J_{PP} = 41.7$ Hz) and a doublet at 175.1 ppm (d, $^2J_{PP} = 41.7$ Hz) assignable to ***mer*-2** were observed in the reaction of ***fac*-2**, and a triplet at 162.7 ppm (t, $^2J_{PP} = 41.7$ Hz) and a doublet at 170.5 ppm (d, $^2J_{PP} = 41.7$ Hz) attributable to ***mer*-3** were observed in the reaction of ***fac*-3**. The equilibrium *fac–mer* ratios were independent of the amount of TMSOTf used, showing that TMSOTf serves as a catalyst. The results together with those for ***fac*-1** are shown in Table 2. The equilibrium *fac–mer* ratios are quite dependent on the kind of the phosphite ligand. It should be noted that these values are equal to those for the isomerization promoted by Me_3SiX (X = Cl, Br, I) [27], and the value for ***fac*-2** is similar to that reported by Howell [26]. Therefore, it can be said that the values are derived from the thermodynamic stability between the *fac* and *mer* isomers, not from the stability of the intermediates created from an Mo complex and a catalyst (presumably TMS^+, vide infra).

2.3. Isomerization mechanism

Regarding isomerization of $Mo(CO)_3\{P(OR)_3\}_3$ promoted by TMSOTf, two mechanisms are conceivable: mechanisms via a phosphenium complex and via a TMS^+ adduct.

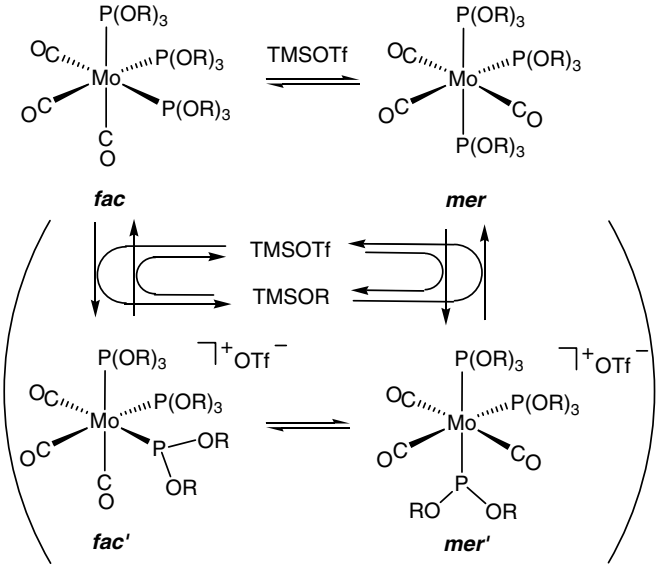
A mechanism via a phosphenium complex is shown in Scheme 1. As transition-metal complexes bearing a diamino-substituted phosphite have been reported to react with a Lewis acid to give cationic phosphenium complexes by OR^- abstraction as shown in Eq. (1), a similar OR^- abstraction may take place in the reaction of $Mo(CO)_3\{P(OR)_3\}_3$ with TMSOTf to produce a cationic phosphenium complex (***fac*′** in Scheme 1). Then, isomerization from ***fac*′** to ***mer*′** is expected to take place. The similar isomerization has been reported previously (Eq. (4)), where the driving force of the *fac–mer* isomerization is thought to be the gain of more π-back donation for the phosphenium ligand. The reaction of ***mer*′** with TMSOR formed would give *mer*-$Mo(CO)_3\{P(OR)_3\}_3$ with regeneration of TMSOTf. However, this catalytic cycle seems not plausible based on the following observations. (i) A complex having a phosphenium ligand was not detected in the reaction of $Mo(CO)_3\{P(OR)_3\}_3$ with TMSOTf. (ii) After the treatment

Table 2
Isomerization of $Mo(CO)_3\{P(OR)_3\}_3$ by TMSOTf in CH_2Cl_2 at room temperature

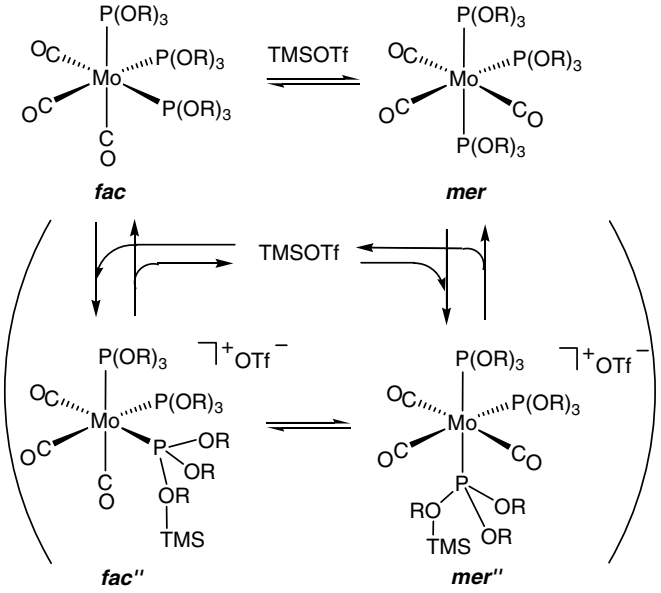


$P(OR)_3$			*fac*:*mer*[b]
$P(OPh)_3$	***fac*-1**	***mer*-1**	1:30
$P(OMe)_3$	***fac*-2**	***mer*-2**	1:3.4
$P(OEt)_3$	***fac*-3**	***mer*-3**	1:2.2

[a] 1.0, 0.5 and 0.1 equvalents based on the *fac* complex were used.
[b] *fac*:*mer* equilibrium ratio after completion of the isomerization.

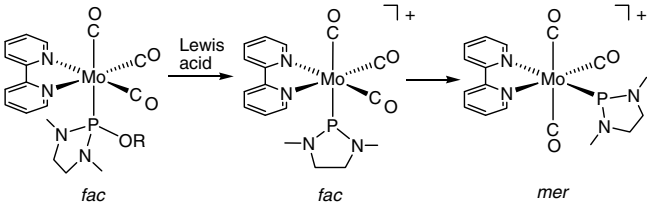


Scheme 1.



Scheme 2.

of ***fac*-1** with 1 equiv of TMSOTf in the presence of 1 equiv of TMSOMe in CH_2Cl_2, the ^{31}P NMR spectra of the reaction mixture were measured and ***fac*-1** and ***mer*-1** were detected but *fac*- and *mer*-$Mo(CO)_3\{P(OPh)_3\}_2\{P(OPh)_2(OMe)\}$ were not detected at all. This indicates that the reaction of ***mer′*** with TMSOR to give ***mer*** in Scheme 1 does not proceed.



(4)

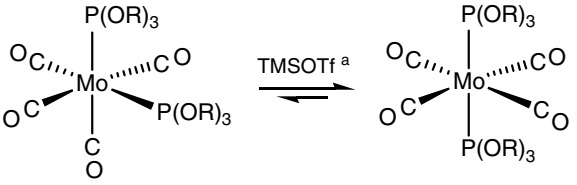
The other isomerization mechanism is shown in Scheme 2. The silicon atom in TMS^+ interacts with one oxygen in $P(OR)_3$ ligands to form ***fac″***, but does not abstract the OR group as an anion. The interaction weakens the coordination of the $P(OR)_3(TMS)$ ligand toward the central metal and makes the ligand bulky, thereby decreasing the isomerization energy barrier to give its *mer* isomer (***mer″***). Dissociation of TMS^+ from ***mer″*** gives *mer*-$Mo(CO)_3\{P(OR)_3\}_3$ with regeneration of TMSOTf. The similar isomerization mechanism has been proposed for the isomerization of $Mo(CO)_3\{P(OR)_3\}_3$ promoted by Me_3SiX (X = Cl, Br, I) [27].

There is a possibility that dissociation of one of the phosphites in $Mo(CO)_3\{P(OR)_3\}_3$ induces the isomerization and TMSOTf promotes the dissociation. To check the possibility, a crossover experiment was conducted. Both ***fac*-2** and ***fac*-3** were dissolved in CH_2Cl_2, TMSOTf was added, and the products were estimated from the ^{31}P NMR spectra of the resulting CH_2Cl_2 solution. Signals assignable to ***mer*-2** and ***mer*-3**, in addition to ***fac*-2** and ***fac*-3** were observed, but those due to phosphite exchange products such as *fac*- or *mer*-$Mo(CO)_3\{P(OMe)_3\}_2\{P(OEt)_3\}$ and OR exchange products such as *fac*- or *mer*-$Mo(CO)_3\{P(OMe)_3\}_2\{P(OMe)_2(OEt)\}$ were not detected. These results strongly suggest that neither phosphite dissociation nor OR^- abstraction shown in Scheme 1 is involved in the *fac–mer* isomerization. Therefore, we proposed the isomerization mechanism shown in Scheme 2, though the intermediates have not been observed.

2.4. Reaction of *cis*-$Mo(CO)_4$ L_2 with TMSOTf

In addition to the isomerization of *fac*-$Mo(CO)_3\{P(OR)_3\}_3$ promoted by TMSOTf, the isomerization of *cis*-$Mo(CO)_4\{P(OR)_3\}_2$ was also investigated. The results were shown in Table 3. The *cis–trans* isomerization occurred in the presence of TMSOTf and did not in the absence of TMSOTf for ***cis*-5**, and ***cis*-6**, and TMSOTf worked as a catalyst. The ^{31}P NMR signals of ***trans*-5** and ***trans*-6** were observed at 173.4 and 155.1 ppm, respectively. In contrast, ***cis*-4** did not isomerize to ***trans*-4** even in the presence of TMSOTf. For the *cis–trans* isomerization, the reaction pathway similar to that for the *fac–mer* isomerization of $Mo(CO)_3\{P(OR)_3\}_3$ shown in Scheme 2 is proposed. Interaction of TMS^+ with an oxygen in the $P(OR)_3$ ligands may initiate the *cis–trans* isomerization. The basicity of the phosphite oxygen in *cis*-$Mo(CO)_4\{P(OR)_3\}_2$ is considered to be less than that in *fac*-$Mo(CO)_3\{P(OR)_3\}_3$ because the former complex has more CO ligands in number being a strong π-accepter ligand. Among ***cis*-4**, ***cis*-5**, and ***cis*-6**, ***cis*-4** has least oxygen basicity because of the sub-

Table 3
Isomerization of $Mo(CO)_4\{P(OR)_3\}_2$ by TMSOTf in CH_2Cl_2 at room temperature



$P(OR)_3$			*cis*:*trans*[b]
$P(OPh)_3$	***cis*-4**	***trans*-4**	no reaction
$P(OMe)_3$	***cis*-5**	***trans*-5**	1:0.9
$PPh_2(OMe)$	***cis*-6**	***trans*-6**	1:2.3

[a] 1.0, 0.5 and 0.1 equvalents based on the *cis* complex were used.
[b] *cis*:*trans* equilibrium ratio after completion of the isomerization.

stituents (Ph vs. Me). Therefore, ***cis*-4** may not have enough basicity on the oxygen to form an interaction with TMS^+.

2.5. Reaction of *fac*-$Mo(CO)_3L_3$ and *cis*-$Mo(CO)_4L_2$ with $BF_3 \cdot OEt_2$

TMSOTf and $BF_3 \cdot OEt_2$ are effective Lewis acids to obtain a cationic phosphenium complex by an OR anion abstraction from a diamino-substituted phosphite ligand in a transition metal complex. In contrast, TMSOTf does not abstract an OR anion from a $P(OR)_3$ ligand of *fac*-$Mo(CO)_3\{P(OR)_3\}_3$ and *cis*-$Mo(CO)_4\{P(OR)_3\}_2$, but promotes the *fac–mer* and *cis–trans* isomerization. Therefore, reactions of *fac*-$Mo(CO)_3\{P(OMe)_3\}_3$ (***fac*-2**) and *cis*-$Mo(CO)_4\{P(OMe)_3\}_2$ (***cis*-5**) with $BF_3 \cdot OEt_2$ were examined and it was found that $BF_3 \cdot OEt_2$ causes some complicated reactions in addition to isomerization.

The ^{31}P NMR spectrum of the reaction mixture of ***fac*-2** and an equimolar amount of $BF_3 \cdot OEt_2$ in CH_2Cl_2 showed several unidentified signals in addition to signals assignable to ***mer*-2**. These signals increased in intensity with time but the singlet due to the starting complex (***fac*-2**) still remained after several hours.

The reaction of ***cis*-5** with an equimolar amount of $BF_3 \cdot OEt_2$ in CH_2Cl_2 at room temperature was followed by the ^{31}P NMR measurement. After 4 h, in addition to a strong singlet due to ***cis*-5**, a doublet of doublet at 164.5 ppm (d, $^1J_{PF} = 1157.1$, and $^2J_{PP} = 46.9$ Hz) and a doublet at 163.4 ppm (d, $^2J_{PP} = 46.9$ Hz) were observed. The large coupling constant (1157.1 Hz) suggests the existence of a P–F bond and the small coupling constant (46.9 Hz) indicates that two phosphorus ligands are *cis* to each other. Therefore, the formation of *cis*-$Mo(CO)_4\{P(OMe)_3\}\{P(OMe)_2F\}$ was proposed. The similar OR/F substitution reaction has been reported [6,9,11]. The ^{31}P NMR spectrum after 24 h, signals due to *cis*-$Mo(CO)_4\{P(OMe)_3\}\{P(OMe)_2F\}$ increased in intensity and a new singlet at 173.4 ppm attributable to ***trans*-5** was observed. In addition, several unidentified signals were observed. Therefore, it was found in the reaction of ***cis*-5** with $BF_3 \cdot OEt_2$, relatively fast OMe/F substitution reaction and relatively slow *cis* to *trans* isomerization and some unidentified reactions take place.

3. Experimental

3.1. General remarks

All reactions were carried out under an atmosphere of dry nitrogen by using Schlenk tube techniques. CH_2Cl_2 was distilled from CaH_2, and hexane and THF were distilled from sodium metal. These were stored under nitrogen atmosphere. $Mo(CO)_3(NCMe)_3$ [30] and $Mo(CO)_4$(nbd) [31] were prepared according to the literature methods. *Fac*-$Mo(CO)_3(L)_3$ and *cis*-$Mo(CO)_4(L)_2$ (L = phosphite) were prepared by the modification of the published procedures [28,29]. IR spectra were recorded on a Perkin–Elmer Spectrum One spectrometer. A JEOL JNM-AL400 spectrometer was used to obtain ^1H, ^{13}C, and ^{31}P NMR spectra. ^1H and ^{13}C NMR data were referenced to Me_4Si. ^{31}P NMR data were referenced to 85% H_3PO_4.

3.2. Preparation of *fac*-$Mo(CO)_3\{P(OPh)_3\}_3$ (***fac*-1**)

A THF solution (20 mL) containing $Mo(CO)_3(NCMe)_3$ (0.52 g, 1.72 mmol) and $P(OPh)_3$ (1.36 mL, 5.19 mmol) was stirred for 4 h at room temperature. After volatile materials were removed under reduced pressure, the resulting precipitate was washed with hexane a few times and dried in vacuo to give a white powder of ***fac*-1** (1.57 g, 1.41 mmol, 82%). ^1H NMR (δ, in $CDCl_3$): 6.98–7.18 (m, Ph). $^{13}C\{^1H\}$ NMR (δ, in $CDCl_3$): 121.9 (s, *p*-Ph), 124.3 (s, *m*-Ph), 129.4 (s, *o*-Ph), 152.1 (s, *ipso*-Ph), 212.2 (m, CO). $^{31}P\{^1H\}$ NMR (δ, in $CDCl_3$): 145.0 (s). IR (cm^{-1}, in $CHCl_3$): ν (CO) 1917, 1992.

3.3. Preparation of *fac*-$Mo(CO)_3\{P(OMe)_3\}_3$ (***fac*-2**)

A THF solution (20 mL) containing $Mo(CO)_3(NCMe)_3$ (0.55 g, 1.81 mmol) and $P(OMe)_3$ (0.65 mL, 5.51 mmol) was stirred for 4 h at room temperature. After volatile materials were removed under reduced pressure, the resulting precipitate was washed with hexane a few times and dried in vacuo to give a white powder of ***fac*-2** (0.92 g, 1.67 mmol, 92%). ^1H NMR (δ, in $CDCl_3$): 3.61 (d, $^3J_{PH} = 10.8$ Hz, OCH_3). $^{13}C\{^1H\}$ NMR (δ, in $CDCl_3$): 51.4 (m, OCH_3), 215.9 (m, CO). $^{31}P\{^1H\}$ NMR (δ, in $CDCl_3$): 168.0 (s). IR (cm^{-1}, in $CDCl_3$): ν (CO) 1880, 1967.

3.4. Preparation of *fac*-$Mo(CO)_3\{P(OEt)_3\}_3$ (***fac*-3**)

A THF solution (20 mL) containing $Mo(CO)_3(NCMe)_3$ (0.39 g, 1.30 mmol) and $P(OEt)_3$ (0.67 mL, 3.90 mmol) was stirred for 4 h at room temperature. After volatile materials were removed under reduced pressure, the resulting precipitate was washed with hexane a few times at −78 °C and

dried in vacuo to give a white powder of ***fac*-3** (0.61 g, 1.2 mmol, 92%). ^{1}H NMR (δ, in $CDCl_3$): 1.22 (m, 3H, OCH_2CH_3), 3.96 (m, 2H, OCH_2CH_3). $^{13}C\{^1H\}$ NMR (δ, in $CDCl_3$): 16.4 (m, OCH_2CH_3), 59.7 (s, OCH_2CH_3), 216.4 (m, CO). $^{31}P\{^1H\}$ NMR (δ, in $CDCl_3$): 161.2 (s). IR (cm^{-1}, in $CHCl_3$): ν (CO) 1860, 1963.

3.5. Preparation of cis-$Mo(CO)_4\{P(OPh)_3\}_2$ (*cis*-4)

A CH_2Cl_2 solution (10 mL) containing $Mo(CO)_4$(nbd) (0.81 g, 2.46 mmol) and $P(OPh)_3$ (0.83 mL, 4.92 mmol) was stirred for 4 h at room temperature. After volatile materials were removed under reduced pressure, the resulting precipitate was washed with hexane a few times at −78 °C and dried in vacuo to give a white powder of ***cis*-4** (1.87 g, 2.68 mmol, 92%). ^{1}H NMR (δ , in $CDCl_3$): 7.18–7.36 (m, Ph). $^{13}C\{^1H\}$ NMR (δ, in $CDCl_3$): 121.6 (s, *p*-Ph), 124.9 (s, *m*-Ph), 129.8 (s, *o*-Ph), 151.4 (t, $^2J_{PC} = 4.2$ Hz, *ipso*-Ph), 205.5 (t, $^2J_{PC} = 13.3$ Hz, *cis*-CO), 209.5 (t, $^2J_{PC} = 17.4$ Hz, *trans*-CO). $^{31}P\{^1H\}$ NMR (δ, in $CDCl_3$): 151.4 (s). IR (cm^{-1}, in $CHCl_3$): ν (CO) 1940, 2046.

3.6. Preparation of cis-$Mo(CO)_4\{P(OMe)_3\}_2$ (*cis*-5)

A CH_2Cl_2 solution (10 mL) containing $Mo(CO)_4$(nbd) (0.73 g, 2.21 mmol) and $P(OMe)_3$ (0.52 mL, 4.42 mmol) was stirred for 4 h at room temperature. After volatile materials were removed under reduced pressure, the resulting precipitate was washed with hexane a few times at −78 °C and dried in vacuo to give a orange sticky powder of ***cis*-5** (0.97 g, 2.13 mmol, 96%). ^{1}H NMR (δ, in $CDCl_3$): 3.62 (s, OCH_3). $^{13}C\{^1H\}$ NMR (δ, in $CDCl_3$): 51.4 (s, OCH_3), 207.9 (t, $^2J_{PC} = 14.1$ Hz, *cis*-CO), 212.1 (t, $^2J_{PC} = 13.3$ Hz, *trans*-CO). $^{31}P\{^1H\}$ NMR (δ, in $CDCl_3$): 165.6 (s). IR (cm^{-1}, in $CHCl_3$): ν (CO) 2036, 1921.

3.7. Preparation of cis-$Mo(CO)_4\{PPh_2(OMe)\}_2$ (*cis*-6)

A CH_2Cl_2 solution (10 mL) containing $Mo(CO)_4$(nbd) (0.63 g, 1.91 mmol) and $PPh_2(OMe)$ (0.76 mL, 3.82 mmol) was stirred for 3 h at room temperature. After volatile materials were removed under reduced pressure, the resulting precipitate was washed with hexane a few times at −78 °C and dried in vacuo to give a white powder of ***cis*-6** (1.17 g, 1.82 mmol, 96%). ^{1}H NMR (δ, in $CDCl_3$): 3.27 (s, 3 H, OCH_3), 7.40–7.53 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR (δ, in $CDCl_3$): 53.6 (s, OCH_3), 128.1 (s, *p*-Ph), 130.1 (s, *m*-Ph), 131.2 (t, $^2J_{PC} = 6.6$ Hz, *o*-Ph), 139.0 (t, $^2J_{PC} = 15.8$ Hz, *ipso*-Ph), 209.5 (t, $^2J_{PC} = 10.3$ Hz, *cis*-CO), 214.6 (t, $^2J_{PC} = 9.5$ Hz, *trans*-CO). $^{31}P\{^1H\}$ NMR (δ, in $CDCl_3$): 144.9 (s). IR (cm^{-1}, in $CHCl_3$): ν (CO) 2026, 1912.

3.8. Isolation of mer-$Mo(CO)_3\{P(OPh)_3\}_3$ (*mer*-1)

A solution of ***fac*-1** (2.31 g, 2.08 mmol) and TMSOTf (0.38 mL, 2.08 mmol) in CH_2Cl_2 (20 mL) was stirred for 1.5 h at room temperature. After volatile materials were removed under reduced pressure, the resulting precipitate was washed with hexane (3 mL, 5 times) at −78 °C and dried in vacuo to give a white powder of a mixture of ***fac*-1** and ***mer*-1** (1:30). To obtain pure ***mer*-1**, the powder was washed with hexane/CH_2Cl_2 = 100/1 solution (5 mL, 20 times) at room temperature, and the powder was dried in vacuo (1.22 g, 1.10 mmol, 53%). ^{1}H NMR (δ, in $CDCl_3$): 6.83–7.25 (m, Ph). $^{13}C\{^1H\}$ NMR (δ, in $CDCl_3$): 121.6 (s, *p*-Ph), 124.2 (s, *m*-Ph), 129.4 (s, *o*-Ph), 151.9 (s, *ipso*-Ph), 208.0 (m, CO), 213.0 (m, CO). $^{31}P\{^1H\}$ NMR (δ, in $CDCl_3$): 148.6 (t, $^2J_{PP} = 46.9$ Hz, equatorial-P), 155.4 (d, $^2J_{PP} = 46.9$ Hz, apical-P). IR (cm^{-1}, in $CHCl_3$): ν (CO) 1931, 1813.

3.9. X-ray crystal structure determination of *mer*-1

Crystals of ***mer*-1** suitable for an X-ray diffraction study were obtained through crystallization from CH_2Cl_2/hexane/benzene for a few days. The single crystal was mounted in a glass capillary. Data for ***mer*-1** were collected at −70 °C on Rigaku/MSC Mercury CCD area-detector diffractometer equipped with monochromated Mo Kα radiation. Calculations for ***mer*-1** were performed with the teXsan crystallographic software package of Molecular Structure Corporation. H atoms were refined using a riding model, with C–H = 0.95 Å, and fixed individual displacement parameters [U_{iso} (H) = U_{eq}(C)]. The crystal was formulated as ***mer*-1** · $0.5CH_2Cl_2$ · $0.5C_6H_6$. The CH_2Cl_2 molecule was disordered in two positions with 50:50 probability in the unit cell.

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Appendix A. Supplementary material

X-ray crystallographic data in CIF format for ***mer*-1**. This material is available free of charge via the Internet at http://pubs.acs.org. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.02.024.

References

[1] A.H. Cowley, R.A. Kemp, Chem. Rev. 85 (1985) 367.
[2] (a) M. Sanchez, M.R. Mazieres, L. Lamande, R. Wolf, in: M. Regitz, O.J. Scherer (Eds.), Multiple Bonds and Low Coordination in Phosphorus Chemistry, Thieme, New York, 1990 (Chapter D1);
(b) A. Schmidpeter, in: M. Regitz, O.J. Scherer (Eds.), Multiple Bonds and Low Coordination in Phosphorus Chemistry, Thieme, New York, 1990 (Chapter D2).
[3] D. Gudat, Coord. Chem. Rev. 163 (1997) 71.

[4] H. Nakazawa, J. Organomet. Chem. 611 (2000) 349.
[5] H. Nakazawa, Adv. Organomet. Chem. 50 (2004) 107.
[6] H. Nakazawa, M. Ohta, K. Miyoshi, H. Yoneda, Organometallics 8 (1989) 638.
[7] H. Nakazawa, Y. Yamaguchi, K. Miyoshi, J. Organomet. Chem. 465 (1994) 193.
[8] H. Nakazawa, Y. Yamaguchi, T. Mizuta, K. Miyoshi, Organometallics 14 (1995) 4137.
[9] Y. Yamaguchi, H. Nakazawa, T. Itoh, K. Miyoshi, Bull. Chem. Soc. Jpn. 69 (1996) 983.
[10] H. Nakazawa, Y. Yamaguchi, K. Miyoshi, Phosphorus Sulfur Silicon Relat. Elem. 109 (1996) 129.
[11] H. Nakazawa, Y. Yamaguchi, K. Miyoshi, A. Nagasawa, Organometallics 15 (1996) 2517.
[12] K. Takano, H. Tsumura, H. Nakazawa, M. Kurakata, T. Hirano, Organometallics 19 (2000) 3323.
[13] H. Nakazawa, Y. Miyoshi, T. Katayama, T. Mizuta, K. Miyoshi, N. Tsuchida, A. Ono, K. Takano, Organometallics 25 (2006) 5913.
[14] H. Nakazawa, M. Kishishita, S. Yoshinaga, Y. Yamaguchi, T. Mizuta, K. Miyoshi, J. Organomet. Chem. 529 (1997) 423.
[15] H. Nakazawa, M. Kishishita, K. Miyoshi, Phosphorus Sulfur Silicon Relat. Elem. 144 (1999) 45.
[16] H. Nakazawa, M. Kishishita, T. Ishiyama, T. Mizuta, K. Miyoshi, J. Organomet. Chem. 617–618 (2001) 453.
[17] H. Nakazawa, Y. Yamashita, K. Miyoshi, Phosphorus Sulfur, Silicon Relat. Elem. 177 (2002) 1533.
[18] H. Nakazawa, Y. Yamaguchi, T. Mizuta, S. Ichimura, K. Miyoshi, Organometallics 14 (1995) 4635.
[19] H. Nakazawa, Y. Yamaguchi, K. Miyoshi, Organometallics 15 (1996) 1337.
[20] H. Nakazawa, Y. Yamaguchi, K. Kawamura, K. Miyoshi, Organometallics 16 (1997) 4626.
[21] K. Kawamura, H. Nakazawa, K. Miyoshi, Organometallics 18 (1999) 1517.
[22] K. Kawamura, H. Nakazawa, K. Miyoshi, Organometallics 18 (1999) 4785.
[23] H. Nakazawa, M. Kishishita, T. Nakamoto, N. Makanura, T. Ishiyama, K. Miyoshi, Chem. Lett. (2000) 230.
[24] A.M. Bond, R. Colton, S.W. Feldberg, P.J. Mahon, T. Whyte, Organometallics 10 (1991) 3320.
[25] J.-C. Rousche, G.R. Dobson, Inorg. Chim. Acta 28 (1978) L139.
[26] J.A.S. Howell, P.C. Yates, N.F. Ashford, D.T. Dixon, R. Warren, J. Chem. Soc., Dalton Trans. 20 (1996) 3959.
[27] K. Fukumoto, H. Nakazawa, Organometallics 26 (2007) 6505.
[28] E.C. Alyea, G. Ferguson, S.-Q. Song, Acta Crystallogr. C 51 (1995) 2238.
[29] G.R. Dobson, A.J. Rettenmaier, Inorg. Chim. Acta 6 (1972) 507.
[30] D.P. Tate, W.R. Knipple, J.M. Augl, Inorg. Chem. 1 (1962) 433.
[31] M.A. Bennett, L. Pratt, G. Wilkinson, J. Chem. Soc. (1961) 2037.