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Communications

Silane-Catalyzed Reaction: *fac*−*mer* Isomerization of [Mo(CO)$_3$(phosphite)$_3$]

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Summary: Me$_3$SiX (X = Cl, Br, I) and related silane compounds catalyze fac−mer isomerization of [Mo(CO)$_3${P(OR)$_3$}$_3$] at room temperature. A hypervalent silicon structure has been shown to play a crucial role in the catalytic reaction.

Because of their unique, efficient, and selective reactivity, in addition to their ready availability and low toxicity, organosilicon compounds have been widely used, especially for organic syntheses.[1,2] Extensive studies over the past three decades have examined silicon compounds and have created many useful reactions, most of which involve conversion of a silicon compound into another silicon compound. In addition, several silicon-based catalysts have been developed: R$_3$SiOTf, R$_3$SiB(OTf)$_4$, R$_3$SiB(OTf)$_3$Cl, R$_3$SiN(SO$_2$F)$_2$, and R$_3$SiN(Tf)$_2$.[2] These catalysts can be described as containing R$_3$Si$^+$ and are considered Lewis acids. In contrast, no report describes silane (a neutral four-coordinate silicon compound) serving as a catalyst instead of a reagent. It has been speculated that a silane is not a catalyst any more than an alkane is. This is the first report of a silane-catalyzed reaction. Me$_3$SiX (X = Cl, Br, I) and related silane compounds catalyze *fac*−*mer* isomerization of [Mo(CO)$_3${P(OR)$_3$}$_3$] at room temperature.

Regarding M(CO)$_3$L$_3$ (M = Cr, Mo, W; L = phosphine, phosphite), principally two geometrical isomers exist: facial (*fac*) and meridional (*mer*) forms. The *fac* isomer is considered more stable electronically, as this isomer achieves stronger M to CO back-donation, but the *mer* isomer is favored from a steric point of view. The M(CO)$_3$L$_3$ complexes prepared to date from their transition-metal precursors and L have exclusively *fac* geometry. The *mer* isomers were obtained using isomerization of the *fac* isomers. Bond et al. reported *fac*−*mer* isomerization via a one-electron oxidation to produce the 17e cation species for M(CO)$_3$(η^3- Ph$_2$PCH$_2$CH$_2$P(Ph)CH$_2$CH$_2$PPh$_2$).[3] We reported the related isomerization for *fac*-[M(CO)$_3$(bpy){P(NMeCH$_2$)$_2$(OMe)}] (bpy = 2,2′-bipyridine, P(NMeCH$_2$)$_2$(OMe) = P(NMeCH$_2$CH$_2$NMe)(OMe)). The reaction of the *fac* isomer with BF$_3$·OEt$_2$ gives the cationic phosphenium complex *fac*-[Mo(bpy)(CO)$_3${P(NMeCH$_2$)$_2$}]$^+$, which then isomerizes to the *mer* form. It does so because the phosphenium ligand shows strong π acidity, leading to an electron-deficient metal center (not complete one-electron oxidation, but partial oxidation).[4] Thermal *fac*−*mer* isomerization has been reported by Rousche et al. for *fac*-[Mo(CO)$_3$(η^2-dppe){P(O^{i}Pr)$_3$}][5] and by Howell et al. for *fac*-[M(CO)$_3${P(OR)$_3$}$_3$].[6]

We examined the reaction of *fac*-[Mo(CO)$_3${P(OMe)$_3$}$_3$] (***fac*-1**) with 1 equiv of Me$_3$SiCl in CH$_2$Cl$_2$ at room temperature. The reaction was monitored by measuring the ^{31}P{^{1}H} NMR

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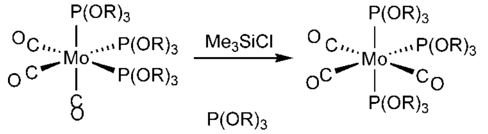
Table 1. Isomerization by Me_3SiCl in CH_2Cl_2 at Room Temperature



	$P(OR)_3$	
***fac*-1**	$P(OMe)_3$	***mer*-1**
***fac*-2**	$P(OEt)_3$	***mer*-2**
***fac*-3**	$P(OPh)_3$	***mer*-3**
***fac*-4**	$P(NMeCH_2)_2(OMe)$	***mer*-4**

entry	complex	amt of Me_3SiCl (equiv)	time (h)	*fac*:*mer*
1	***fac*-1**	1.0	3	1:3.4
2	***fac*-1**	0.5	5	1:3.4
3	***fac*-1**	0.1	8	1:3.4
4	***fac*-2**	1.0	2	1:2.2
5	***fac*-3**	1.0	72	1:1.3[a]
6	***fac*-4**	1.0	12	1:0.5

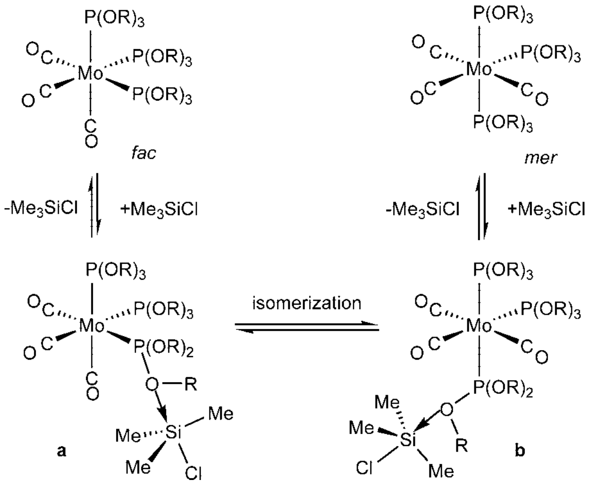
[a] The isomerization is very slow, and the equilibrium is not attained after 72 h. The final ratio obtained by using Me_3SiOTf is 1:30 (unpublished results).

spectrum. A triplet at 167.1 ppm (J_{PP} = 44.3 Hz) and a doublet at 175.3 ppm (J_{PP} = 41.7 Hz) attributable to ***mer*-1** appeared at the expense of an intensity of a singlet at 164.8 ppm because of ***fac*-1**. After 3 h, equilibrium between ***fac*-1** and ***mer*-1** was established with the ratio of 1:3.4.[7] Next, the reactions with 0.5 and 0.1 equiv of Me_3SiCl were examined. Table 1 (entries 1–3) shows that the final equilibrium position was found not to depend on the amount of Me_3SiCl used, although it takes a longer time to reach the equilibrium when the amount of Me_3SiCl is reduced. The equilibrium ratio resembles that obtained in thermolysis by Howell et al. (1:3). These results show that Me_3SiCl acts as a catalyst for *fac*−*mer* isomerization.

In our experiments dry CH_2Cl_2 distilled from CaH_2 was used. However, there is a possibility that adventitious HCl from Me_3SiCl hydrolysis could be responsible for the observed isomerization. Thus, the ^{29}Si NMR of Me_3SiCl in CH_2Cl_2 was measured. No signal other than a singlet attributable to Me_3SiCl was observed, indicating no silicon compound derived from Me_3SiCl hydrolysis exists (less than 5%, if any). We observed that the isomerization of ***fac*-1** is completed within 8 h in the presence of 10 mol % of Me_3SiCl. If 10% of the Me_3SiCl produces adventitious HCl, then the amount of HCl would be 1 mol % based on ***fac*-1** under the above conditions. The CH_2Cl_2 solution of ***fac*-1** containing 1 mol % of HCl was prepared and monitored by the ^{31}P NMR measurement, and no isomerization was observed after 10 h. These results clearly indicate that the *fac*−*mer* isomerization is catalyzed by Me_3SiCl but not by HCl.

The corresponding isomerization catalyzed by Me_3SiCl was observed for the triethyl phosphite complex ***fac*-2**, the triphenyl phosphite complex ***fac*-3**, and the diamino-substituted phosphite complex ***fac*-4**. In all cases, the ^{31}P NMR spectra of the reaction mixture suggested the formation of the corresponding *mer* isomers.[8] The isomerization of ***fac*-3** to ***mer*-3** was much slower (more than 72 h) than that of ***fac*-1** to ***mer*-1** (3 h), which might be attributed to a steric cause. The reaction of ***fac*-4** is noteworthy. We found that the reaction of ***fac*-4** with Me_3SiOTf abstracts one OMe as an anion from the phosphorus to give a cationic phosphenium complex, *fac*-$[Mo(CO)_3\{P(NMeCH_2)_2(OMe)\}_2\{P(NMeCH_2)_2\}]^+$.[9] In contrast, on the basis of ^{31}P NMR monitoring, the reaction of ***fac*-4** with Me_3SiCl generated no cationic phosphenium complex, which suggests that the pathway of the isomerization promoted by Me_3SiCl differs from that involving a cationic phosphenium complex produced by Me_3SiOTf.

Scheme 1. Proposed *fac*−*mer* Isomerization Mechanism Catalyzed by Me_3SiCl



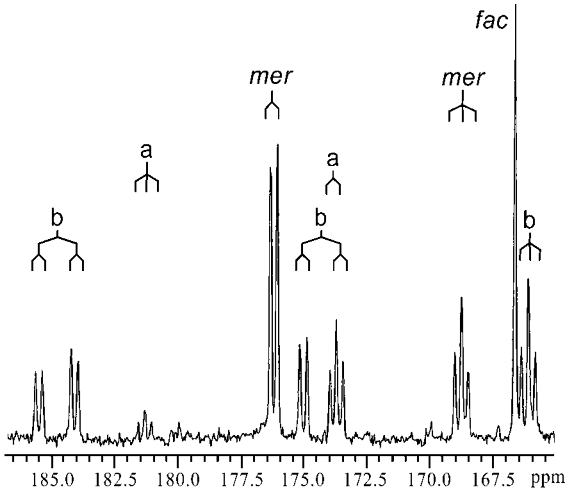


Figure 1. ^{31}P NMR spectrum of a Me_3SiCl solution at room temperature in which ***fac*-1** is dissolved.

Scheme 1 presents a plausible mechanism for the *fac*−*mer* isomerization promoted by Me_3SiCl. The silicon atom in Me_3SiCl interacts with one oxygen in $P(OR)_3$ ligands to form a Si hypervalent structure (**a**). The interaction weakens the coordination of $P(OR)_3 \cdot Me_3SiCl$ toward the central metal and makes the ligand bulky, thereby decreasing the isomerization energy barrier to give its *mer* isomer (**b**). The following dissociation of the Me_3SiCl gives the *mer* isomer, reproducing free Me_3SiCl.

The ^{31}P and ^{29}Si NMR measurements of a CH_2Cl_2 solution containing ***fac*-1** and Me_3SiCl showed no signals assignable to either **a** or **b** in Scheme 1. To obtain some evidence of **a** and **b**, we dissolved ***fac*-1** in Me_3SiCl and measured the ^{31}P and ^{29}Si NMR spectra of the solution. The ^{31}P NMR is shown in Figure 1. In addition to a singlet at 166.7 ppm attributable to ***fac*-1** and a doublet at 176.2 ppm and a triplet at 168.8 with J_{PP} =

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[7] In the absence of Me_3SiCl no *fac*−*mer* isomerization occurred at room temperature in CH_2Cl_2.

[8] ^{31}P{^{1}H} NMR (161.7 MHz, CH_2Cl_2, 25 °C, reference 85% H_3PO_4; δ, ppm): ***fac*-1**, 164.8 (s); ***mer*-1**, 167.1 (t, J_{PP} = 44.3 Hz, *cis*-PP), 175.3 (d, J_{PP} = 41.7 Hz, *trans*-PP); ***fac*-2**, 145.4 (s); ***mer*-2**, 148.8 (t, J_{PP} = 52.1 Hz, *cis*-PP), 155.7 (d, J_{PP} = 52.1 Hz, *trans*-PP); ***fac*-3**, 146.1 (s); ***mer*-3**, 143.9 (d, J_{PP} = 46.9 Hz, *cis*-PP), 180.9 (t, J_{PP} = 46.9 Hz, *trans*-PP).

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41.7 Hz attributable to ***mer*-1**, five signals were observed clearly. Among them, a triplet at 181.3 ppm and a doublet at 173.9 ppm with $J_{PP} = 41.7$ Hz can be assigned to **a**. The triplet is assignable to $P(OMe)_3 \cdot Me_3SiCl$ because of the molecular symmetry. The remaining three signals at 184.8 ppm (dd, $J_{PP} = 41.7$ and 229.3 Hz), 174.3 ppm (dd, $J_{PP} = 44.3$ and 229.3 Hz), and 166.2 ppm (t, $J_{PP} = 44.3$ Hz) can be reasonably assigned respectively to $P(OMe)_3 \cdot Me_3SiCl$ and trans and cis $P(OMe)_3$ in $P(OMe)_3 \cdot Me_3SiCl$ in **b**. The ^{29}Si NMR showed two singlets at 6.62 and 6.53 ppm in addition to a strong singlet at 29.8 ppm attributable to the solvent Me_3SiCl. Coordination of nitrogen or oxygen to silicon to form a pentacoordinate bond has been shown to produce a strong shielding effect of the silicon chemical shift.[10] Kummer et al. reported the ^{29}Si NMR chemical shift at 11.1 ppm in CD_2Cl_2 for an Si hypervalent compound with Cl and N in apical positions and two Me groups and one CH_2 group in equatorial positions.[11] The ^{13}C NMR of the Me_3SiCl solution containing ***fac*-1** was also measured. Two lumps consisting of several signals were observed at 213.9−214.1 and 218.0−218.2 ppm. These signals are attributable to terminal carbonyl ligands, indicating that Me_3SiCl does not have an interaction with an oxygen atom in the terminal carbonyl ligand. Therefore, our observations suggest the formation of hypervalent Si compounds.

No *fac*−*mer* isomerization was confirmed in reactions between Me_3SiCl and *fac*-[Mo(CO)$_3$(phosphine)$_3$] (phosphine = PEt_3, $Bu^n{}_3$) having no OR group on a coordinating phosphorus, suggesting that a phosphite oxygen plays a crucial role in *fac*−*mer* isomerization.

To elucidate whether *fac*−*mer* isomerization involves a phosphite dissociation process or not, a crossover experiment was performed. Addition of Me_3SiCl to a CH_2Cl_2 solution containing both ***fac*-1** and ***fac*-2** yielded ***mer*-1** and ***mer*-2** but formed neither phosphite exchange products such as *fac*- and *mer*-[Mo(CO)$_3${P(OMe)$_3$}$_2${P(OEt)$_3$}] nor OR exchange products such as *fac*- and *mer*-[Mo(CO)$_3${P(OMe)$_3$}$_2${P(OMe)$_2$(OEt)}]. These results show intramolecular isomerization, which is consistent with the mechanism shown in Scheme 1.

The results showed that Me_3SiCl can promote *fac*−*mer* isomerization for *fac*-[Mo(CO)$_3$(phosphite)$_3$]; the activity of other silanes was examined for ***fac*-1**. Me_2SiCl_2, $MeSiCl_3$, and $SiCl_4$ promoted the isomerization, but some byproducts were also formed. In contrast, $SiMe_4$, with no chloride substituent, did not promote isomerization at all. Therefore, among the Me_nSiCl_{4-n} (n = 0–4) series, Me_3SiCl is the best promoter, which might stem from its superior hypervalent arrangement: two electronegative substituents (Cl and O from phosphite) in apical positions and three electron -releasing groups (three Me groups) in equatorial positions. Table 2 shows the R_3SiX activity. Bromosilane and iodosilane (entries 2 and 3) show activity better than that of chlorosilane. Ph_3SiCl (entry 4) does not promote isomerization, presumably because of the bulky substituents. Slow isomerization was observed in the reaction with $(EtO)_3SiCl$ (entry 5), which might be attributable to the weak electron-releasing ability of an OEt group compared to that of the Me group. A similar *fac*−*mer* ratio was obtained for entries 1−3 and 5, meaning that the ratio is determined thermodynamically and is unaffected by the added silane.

Table 2. Isomerization of *fac*-1 Promoted by R_3SiX[a]

entry	R_3SiX	time (h)	*fac*:*mer*
1	Me_3SiCl	3	1:3.4
2	Me_3SiBr	<0.1	1:3.6
3	Me_3SiI	<0.1	1:3.7
4	Ph_3SiCl	25	no reacn
5	$(EtO)_3SiCl$	25	1:3.4

[a] ***fac*-1** was treated with 1 equiv of R_3SiX in CH_2Cl_2 at room temperature.

In conclusion, this paper describes, for the first time, a halosilane-catalyzed reaction. The results showed that an interaction of silane with one phosphite oxygen to form a hypervalent silicon structure reduces the *fac*−*mer* isomerization energy barrier of [Mo(CO)$_3$(phosphite)$_3$]. The hypervalent silicon species was detectable spectroscopically. This finding is believed to be a starting point for exploring the potential catalytic activity of halosilanes.

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Supporting Information Available: Detailed experimental procedures and the characterization of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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