

Communications

Silane-Catalyzed Reaction: *fac*–*mer* Isomerization of [Mo(CO)₃(phosphite)₃]

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Summary: Me_3SiX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and related silane compounds catalyze *fac*–*mer* isomerization of $[\text{Mo}(\text{CO})_3\{\text{P}(\text{OR})_3\}_3]$ 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_3SiOTf , $\text{R}_3\text{SiB}(\text{OTf})_4$, $\text{R}_3\text{SiB}(\text{OTf})_3\text{Cl}$, $\text{R}_3\text{SiN}(\text{SO}_2\text{F})_2$, and $\text{R}_3\text{SiN}(\text{Tf})_2$.² These catalysts can be described as containing R_3Si^+ 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_3SiX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and related silane compounds catalyze *fac*–*mer* isomerization of $[\text{Mo}(\text{CO})_3\{\text{P}(\text{OR})_3\}_3]$ at room temperature.

Regarding $\text{M}(\text{CO})_3\text{L}_3$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{L} = \text{phosphine}, \text{phosphite}$), 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 $\text{M}(\text{CO})_3\text{L}_3$ 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 $\text{M}(\text{CO})_3(\eta^3\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{P}(\text{Ph})\text{CH}_2\text{CH}_2\text{PPh}_2)$.³ We reported the related isomerization for *fac*– $[\text{M}(\text{CO})_3(\text{bpy})\{\text{P}(\text{NMeCH}_2)_2(\text{OMe})\}]$ ($\text{bpy} = 2,2'$ -bipyridine, $\text{P}(\text{NMeCH}_2)_2(\text{OMe}) = \text{P}(\text{NMeCH}_2\text{CH}_2\text{NMe})(\text{OMe})$). The reaction of the *fac* isomer with $\text{BF}_3 \cdot \text{OEt}_2$ gives the cationic phosphonium complex *fac*– $[\text{Mo}(\text{bpy})(\text{CO})_3\{\text{P}(\text{NMeCH}_2)_2\}]^+$, which then isomerizes to the *mer* form. It does so because the phosphonium 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*– $[\text{Mo}(\text{CO})_3(\eta^2\text{-dppe})\{\text{P}(\text{O}^i\text{Pr})_3\}]$ ⁵ and by Howell et al. for *fac*– $[\text{M}(\text{CO})_3\{\text{P}(\text{OR})_3\}_3]$.⁶

We examined the reaction of *fac*– $[\text{Mo}(\text{CO})_3\{\text{P}(\text{OMe})_3\}_3]$ (**1**) with 1 equiv of Me_3SiCl in CH_2Cl_2 at room temperature. The reaction was monitored by measuring the $^{31}\text{P}\{^1\text{H}\}$ NMR

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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 $J_{\text{PP}} = 41.7$ Hz can be assigned to **a**. The triplet is assignable to $\text{P}(\text{OMe})_3 \cdot \text{Me}_3\text{SiCl}$ because of the molecular symmetry. The remaining three signals at 184.8 ppm (dd, $J_{\text{PP}} = 41.7$ and 229.3 Hz), 174.3 ppm (dd, $J_{\text{PP}} = 44.3$ and 229.3 Hz), and 166.2 ppm (t, $J_{\text{PP}} = 44.3$ Hz) can be reasonably assigned respectively to $\text{P}(\text{OMe})_3 \cdot \text{Me}_3\text{SiCl}$ and trans and cis $\text{P}(\text{OMe})_3$ in $\text{P}(\text{OMe})_3 \cdot \text{Me}_3\text{SiCl}$ 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*- $[\text{Mo}(\text{CO})_3(\text{phosphine})_3]$ (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*- $[\text{Mo}(\text{CO})_3\{\text{P}(\text{OMe})_3\}_2\{\text{P}(\text{OEt})_3\}]$ nor OR exchange products such as *fac*- and *mer*- $[\text{Mo}(\text{CO})_3\{\text{P}(\text{OMe})_3\}_2\{\text{P}(\text{OMe})_2(\text{OEt})\}]$. 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*- $[\text{Mo}(\text{CO})_3(\text{phosphite})_3]$; the activity of other silanes was examined for **fac-1**. Me_2SiCl_2 , MeSiCl_3 , and

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

entry	R_3SiX	time (h)	<i>fac:mer</i>
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	$(\text{EtO})_3\text{SiCl}$	25	1:3.4

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

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 $\text{Me}_n\text{SiCl}_{4-n}$ ($n = 0-4$) 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 $(\text{EtO})_3\text{SiCl}$ (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.

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 $[\text{Mo}(\text{CO})_3(\text{phosphite})_3]$. 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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