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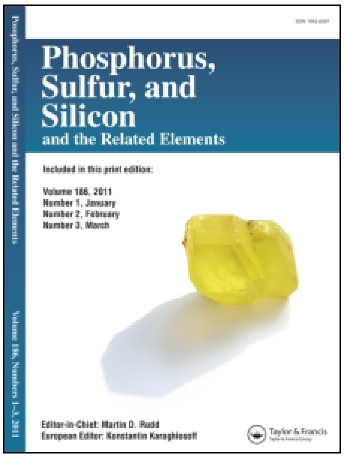

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Transition Metal Complexes Containing Phosphenium and Phosphite Ligands: Formation and Theoretical Approach

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Transition Metal Complexes Containing Phosphenium and Phosphite Ligands: Formation and Theoretical Approach

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*Treatments of Mo- and Mn-diphosphite complexes, cis-$Mo(CO)_4L_2$ (**1a**) and $CpMn(CO)L_2$ (**2a**) ($L = P(NMeCH_2)_2(OMe)$) with TMSOTf caused single OMe^- abstraction from the coordinated phosphite to give the corresponding cationic phosphenium phosphite complexes cis-$[Mo(CO)_4L\{P(NMeCH_2)_2\}]OTf$ (**1b**) and $[CpMn(CO)L\{P(NMeCH_2)_2\}]OTf$ (**2b**), respectively. DFT calculations for **1b** and $Cp(CO)_2Mo(SiMe_2)\{SiMe_2(OMe)\}$ (**3**) revealed that a non-bridging form is a local minimum and a bridging form is a transition state for **1b**, and both non-bridging and bridging forms are minima for **3**.*

Keywords DFT calculation; phosphenium ligand; phosphite ligand; transition metal complex

INTRODUCTION

Transition metal complexes containing phosphenium have attracted considerable attention because of double bond character between M and P.[1] Phosphenium is isolobal with a singlet carbene and silylene, and a phosphenium ligand shows electrophilicity. For a phosphenium phosphite complex, two structures (non-bridging and bridging forms) are conceivable. Several transition metal complexes with both phosphenium and phosphite ligands have been prepared and their X-ray and NMR data show their non-bridging forms.[2]But these complexes do not

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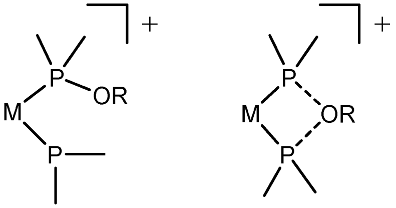
have a mirror symmetry even if it takes a bridging form. Here we report the syntheses of mirror symmetric Mo- and Mn-diphosphite complexes, *cis*-$Mo(CO)_4L_2$ (**1a**) and $CpMn(CO)L_2$ (**2a**), where L stands for $P(NMeCH_2)_2(OMe)$, and the conversion into phosphenium phosphite complexes. DFT calculations have also been reported. A part of this work was reported previously.[3]



phosphenium phosphite complex

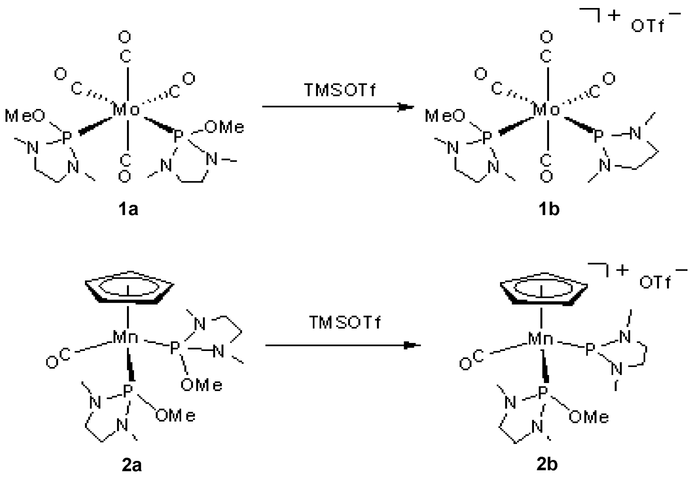
Preparation of Mo- and Mn-Diphosphite Complexes

Cis-$Mo(CO)_4L_2$ (**1a**) was obtained as a white powder in 83% yield from $Mo(CO)_4(nbd)$ (nbd = 2,5-norbornadiene) and 2 equiv of L. The reaction of $Mo(CO)_4(piperidine)_2$ with L also yielded **1a**, but $Mo(CO)_3L_3$ was a contaminant and its elimination was difficult. $CpMn(CO)L_2$ (**2a**) was prepared as a yellow power in 80% yield by the UV irradiation of a THF solution containing $CpMn(CO)_3$ and 2 equiv of L.

Conversion of Diphosphite Complexes into Phosphenium Phosphite Complexes

Treatments of **1a** and **2a** with an equimolar amount of $Me_3SiOSO_2CF_3$ (TMSOTf) yielded *cis*-$[Mo(CO)_4L\{P(NMeCH_2)_2\}]OTf$ (**1b**) and $[Cp(CO)MnL\{P(NMeCH_2)_2\}]OTf$ (**2b**), respectively (Scheme 1). Both reactions are very clean and the products (**1b** and **2b**) are stable in solution unless exposed to air. The reaction with excess TMSOTf did not yield a diphosphenium complex in both cases.

For **1b**, the ^{31}P NMR spectrum showed two broad resonances at about 285 and 140 ppm at room temperature, but the spectrum at −60°C exhibited two doublets at 285.01 and 139.42 ppm with $J_{PP} = 42.5$ Hz. This shows that **1b** is a phosphenium phosphite complex with a non-bridging form. The value of the coupling constant indicates a *cis* configuration. The broadening at room temperature may be the symptom of slow OMe group migration from the phosphite P to the phosphenium P. For **2b**,



SCHEME 1

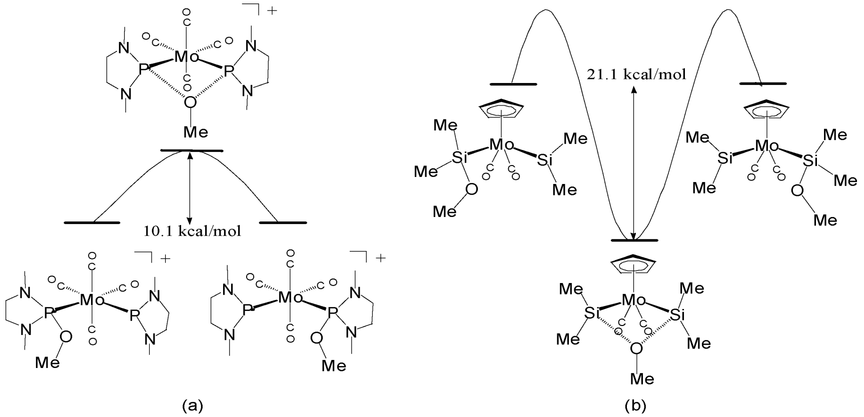
the ^{31}P NMR spectrum showed two broad resonances at about 312 and 183 ppm at room temperature, but the spectrum at −60°C exhibited two doublets at 311.2 and 183.1 ppm with $J_{PP} = 120.0$ Hz. This shows **2b** is a phosphenium phosphite complex with a non-bridging form.

DFT Calculation for 1b and 3

The comparison of phosphenium complexes with silylene complexes is particularly interesting because P and Si are situated in the same third row of the periodic table. A silylene alkoxysilyl complex corresponds to a phosphenium phosphite complex. All of silylene alkoxysilyl complexes reported to date adopt bridging forms.[4] In order to get a clue why a phosphenium phosphite complex prefers a non-bridging form and a silylene alkoxysilyl complex prefers a bridging form, we conducted DFT calculations for **1b** and $CpMo(CO)_2(SiMe_2)\{SiMe_2(OMe)\}$ (**3**) (Scheme 2).

For **1b**, DFT calculations revealed that only the non-bridging structure was a local minimum (LM) and the bridging structure was a transition state (TS). The energy difference was estimated to be 10.1 kcal/mol. In contrast, for silylene alkoxysilyl complex **3**, both bridging and non-bridging structures were found to have minima. The energy minimum in a bridging form was lower by 21.1 kcal/mol than that in a non-bridging form.

Comparison of the bond distances and angles in E-Mo-E-OMe (E = P, Si) portion for the non-bridging form with those for the bridging form has been done to elucidate why a non-bridging form is favorable for



SCHEME 2 Energy diagram of **1b** (a) and **3** (b).

phosphenium phosphite complexes, whereas a bridging form is favorable for silylene alkoxysilyl complexes. The P—O bond distance elongates on going from the non-bridging to the bridging forms from 1.645 to 1.939 Å by 0.294 Å for **1b**. The SiO distance in **3** elongates from 1.698 to 1.854 Å only by 0.156 Å. The lengthening is about a half of that for **1b**. The P-Mo-P angle reduces on going from the non-bridging to the bridging forms from 98.2 to 75.6° by 22.6° for **1b**. The Si-Mo-Si angle in **3** also reduces from 71.7 to 64.9°, but only by 6.8°. These changes mean that the cyclization forming the bridge requires larger geometrical change for a phosphenium phosphite complex than for a silylene alkoxysilyl complex, which is probably responsible for the bridging form being a TS for the phosphenium phosphite complex. With a bridging form, the Si-Mo-Si angle in **3** (64.9°) is considerably smaller than the P-Mo-P angle in **1b** (75.6°). The smaller angle of **3** may be attributed to its four-legged piano stool geometry, but silylene alkoxysilyl complexes with three-legged piano stool geometries also have relatively small Si-Mo-Si angles (72.6° for Cp*(CO)Fe($SiMe_2$){SiMe(OMe)}(OMe) and 70.7° for Cp(CO)Ru{$SiMe_2$}$_2$(OMe)). Therefore, we can say that a silylene alkoxysilyl complex has flexibility in terms of an Si-Mo-Si angle, which renders a bridging form an energy minimum for the silylene alkoxysilyl complex.

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