Platinum(II) Hydride Silanone Complexes and Cyclic Trimers of Silanone. A Theoretical Study of Their Geometries, Bonding Nature, and Stabilities

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Platinum(II) hydride silanone complexes $[PtH(dipe)(R_2SiO)]^+$ (R = H, F, CH_3, CF_3, or SiH_3; dipe = $H_2PCH_2CH_2PH_2$), their acetone and ethylene analogues, and cylic trimers of silanone, $(R_2SiO)_3$, were theoretically investigated with the DFT method. Unexpectedly, the platinum(II) hydride silanone complex does not involve a usual η^2-SiO coordinate bond with the platinum center but two bonding interactions, one between the O atom and the platinum center and the other between the Si atom and the hydride ligand. The former interaction mainly consists of electron donation from a silanone π orbital to a Pt d orbital, while the latter one consists of back-donation from the hydride 1s orbital to the silanone π^* orbital, as well as the electrostatic stabilization interaction between the Si atom and the hydride ligand. In the acetone analogue, on the other hand, only the O atom interacts with the platinum center, but the C atom does not interact with any part of $[PtH(dipe)]^+$. The Si═O bond lengthens by about 0.1 Å and the SiR_2 plane is bent back away from the platinum center by 20−30°, while the C═O and C═C bonds lengthen upon coordination of acetone and ethylene to a much lesser extent than does the Si═O bond. The binding energy of silanone with the platinum(II) hydride complex is much larger than those of ethylene and acetone, because the former complex involves an additional Si−H bonding interaction. The binding energy of the platinum(II) hydride silanone complex increases as the silanone π orbital rises in energy, which indicates that the donating interaction participates in the coordinate bond to a greater extent than does the back-donating interaction. Cyclic trimers of silanone are planar, in which the Si atom takes sp^3 hybridization. The silanone trimers are formed from silanone monomers with significantly large stabilization energy of 60−80 kcal/mol per molecule of silanone. Despite the considerably large binding energy of the platinum(II) hydride silanone complex, it easily converts to the di(μ-hydride)diplatinum(II) complex, $[Pt(\mu\text{-H})(dipe)]_2^{2+}$, with formation of a cyclic trimer of silanone because of the significantly large stabilization energies of silanone trimer and $[Pt(\mu\text{-H})(dipe)]_2^{2+}$. Hence, the platinum(II) hydride complex is not useful to isolate the transition-metal silanone adduct. Molybdenum(0) and zirconium(II) complexes, $Mo(dipe)_2(R_2SiO)_2$ (R = H or CH_3) and $Cp_2Zr(Me_2SiO)$, were also theoretically investigated. These complexes involve the usual η^2-SiO coordinate bond expectedly, in which the π-back-donating interaction is much stronger than the σ-donating interaction. Though the binding energy of silanone with $Mo(dipe)_2$ is as large as that with $[PtH(dipe)]^+$, coordination of silanone with Cp_2Zr yields a significantly large binding energy of about 90 kcal/mol. We wish to propose that Cp_2Zr is one of the useful complexes to isolate a transition-metal silanone adduct.

Introduction

As is well known, it is very difficult for the second- and third-row elements to form a multiple bond, unlike the first-row elements. In this regard, synthesis of the compound containing multiple-bonded silicon and germanium atoms is still one of the challenging subjects of research.[1] A good example is silanone, which contains an Si═O double bond. This compound was first detected by Eaborn and his collaborators.[2] Later, silanone was produced as a short-lived intermediate in an argon matrix[3] and in the gas phase.[4] A similar germanone was detected by Withnall and Andrews.[5] Also, chain and ring compounds of silanone have been reported experimen-

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tally.[6,7] However, all attempts to isolate silanone have failed, to our knowledge, whereas the compounds containing a Si═Si or Ge═Ge double bond have been successfully isolated.[1]

Recently, Milstein and his collaborators reported that a cyclic trimer of silanone was produced from silanol with a platinum(II) μ-hydride phosphine complex, [Pt(μ-H)(dmpe)]$_2$(OTf)$_2$ (dmpe = bis(dimethylphosphino)ethane).[8] They proposed that a platinum(II) hydride silanone complex was formed as a key intermediate in this reaction, but they could not detect the platinum(II) silanone complex. Similarly, an iridium silanone complex was proposed as an intermediate previously in the disproportionation reaction of silanol.[9] Considering that transition-metal complexes of η^2-silene and η^2-disilene have been successfully isolated, one reasonably expects that a transition-metal silanone complex can be isolated if an appropriate transition-metal element is selected.[9]

Many theoretical studies have been reported on silanone and its reactions.[1a,12−22] In those works, relative stabilities of silanone and hydroxysilylene were mainly investigated, and it was clearly concluded that not silanone (H_2SiO) but *trans*-hydroxysilylene (*trans*-HSi(OH)) was the absolute minimum.[15,16,19] However, no theoretical work has been reported on transition-metal complexes of silanone until recent works by Martin and his collaborators.[21] Considering the possibility that the Si═O double bond is stabilized by coordination with transition-metal elements,[5] it is of considerable importance to present theoretical knowledge of structure, bonding nature, and electron distribution of transition-metal silanone complexes. It is also interesting and worthwhile to make a comparison of the transition-metal silanone complex with ethylene and acetone analogues.

In this work, we carried out a theoretical study of platinum(II) hydride silanone complexes [PtH(dipe)(R_2SiO)]$^+$ (dipe = diphosphinoethane $H_2PCH_2CH_2PH_2$; R = H, CF_3, F, H, CH_3, or SiH_3), their ethylene and acetone analogues, and cyclic trimers of silanone, $(R_2SiO)_3$. [PtH(dipe)(R_2SiO)]$^+$ is adopted here for investigation because this complex is considered a reasonable model of the intermediate proposed by Milstein et al.[8] in the formation reaction of silanone trimer catalyzed by [Pt$_2$(μ-H)$_2$(dmpe)]$_2$(OTf)$_2$. Our purposes here are to present detailed study of geometries, bonding nature, and relative stabilities of [PtH(dipe)(R_2SiO)]$^+$ and $(R_2SiO)_3$ and to clarify characteristic features of the platinum(II) hydride silanone complex by comparing it with ethylene and acetone analogues. Molybdenum(0) and zirconium(II) complexes of silanone, Mo(dipe)$_2$(R_2SiO)$_2$ (R = H or CH_3) and Cp$_2$Zr(Me$_2$SiO), were also theoretically investigated here. Comparing the binding energies of the transition-metal silanone complex with the reaction energy of formation of silanone trimer, we wish to theoretically propose what transition-metal element is useful to isolate the silanone complex.

Computational Details

Geometries of platinum(II) hydride silanone complexes, [PtH(dipe)(R_2SiO)]$^+$, molybdenum(0) silanone complexes, Mo(dipe)$_2$(R_2SiO)$_2$, zirconium(II) silanone complex, (Cp)$_2$Zr(MeSiO), and silanone trimers, $(R_2SiO)_3$, were optimized with the DFT method, where the B3LYP functional[23,24] was adopted for the exchange−correlation term. Core electrons of Pt (up to 4f), Mo (up to 3p), Zr (up to 3p), Si (up to 2p), and P (up to 2p) were replaced with effective core potentials (ECPs),[25,26] and their valence electrons were represented with such split valence type basis sets as the (311/311/21) set[25] for Pt, (311/311/211) sets[25] for Mo and Zr, and (21/21/1) sets[22,27] for Si and P. For C, O, and F atoms, MIDI-3 basis sets[28] were used, where a d-polarization function was added to C and O atoms that directly interacted with the metal center. The usual (31) set was employed for the H atom,[29] where a p-polarization function was added to the hydride ligand. This basis set system is called BAS-I here.

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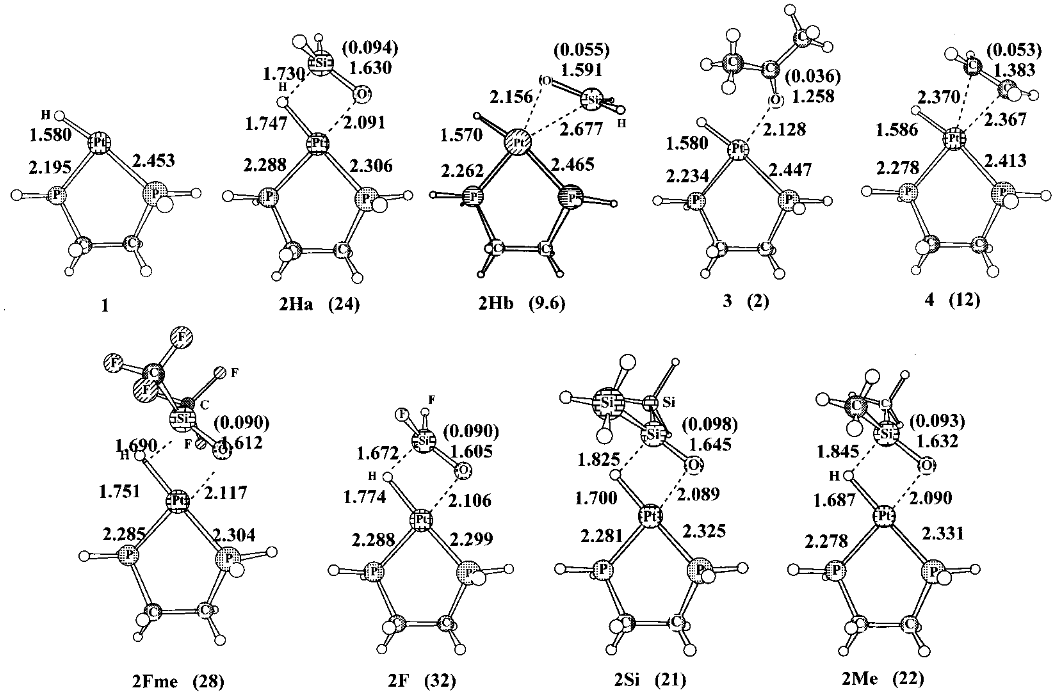

Figure 1. DFT/BAS-I optimized geometries (bond distances in Å and bond angles in deg) of $[PtH(dipe)]^+$, $[PtH(dipe)(R_2SiO)]^+$, $[PtH(dipe)(C_2H_4)]^+$, and $[PtH(dipe)(Me_2CO)]^+$ (R = CF_3, CH_3, SiH_3, F, or H; dipe = $H_2PCH_2CH_2PH_2$).

The binding energy of silanone with the platinum center was calculated with the DFT, MP4(SDQ), and CCSD(T) methods, where a better basis set system (BAS-II) was adopted. In CCSD(T) calculation, the contribution of triple excitations was evaluated noniteratively with the CCSD wave function.[30] In BAS-II, we adopted a (541/541/111) basis set[31] for Pt and (541/541/211) basis sets[31] for Mo and Zr with the same ECPs as those of BAS-I. For C, O, F, and Si, Huzinage−Dunning basis sets[29] were employed, where a d-polarization function[29] was added to C, O, and Si atoms that were involved in C═C, C═O, and Si═O bonds. For H, the (31) set[29] was used, where a p-polarization function was added to the hydride ligand. The same basis set and ECPs as those of BAS-I were used for P. In $(H_2SiO)_3$ and $(Me_2SiO)_3$, cc-pvdz and cc-pvtz basis sets were used to examine the basis set effects. Also, the simplest silanone (H_2SiO) and its cyclic trimer were investigated with the G2 method.[34] The Gaussian 98 program package[35] was used for all these calculations.

Results and Discussion

First, we will discuss the geometry, bonding nature, and electron distribution of $[PtH(dipe)(R_2SiO)]^+$ and $(R_2SiO)_3$, then inspect if one can isolate the platinum(II) hydride silanone complex, and finally investigate silanone complexes of Mo(0) and Zr(II) to present useful ideas how to isolate transition-metal silanone complexes.

Optimized Geometries of $[PtH(dipe)(R_2SiO)]^+$, 2. The geometry of **2** was optimized with the DFT/BAS-I method and compared with the geometries of ethylene and acetone analogues in Figure 1. Interestingly, two minima were observed in $[PtH(dipe)(H_2SiO)]^+$, **2H**. In both structures, the O atom of silanone interacts with the platinum center, while the Si atom of silanone takes a position near the hydride ligand in one structure, **2Ha**, but takes a position distant from the hydride ligand in the other one, **2Hb**. In **2Ha**, the Pt−O distance is shorter than that in **2Hb**. The Si−H(hydride) distance (1.672 Å) of **2Ha** is not very much longer than the usual Si−H covalent bond. Consistent with this Si−H distance, the SiR_2 plane is considerably bent back away from the platinum center by 25°. These features suggest that **2Ha** contains a considerably strong back-bonding interaction between the Si atom of silanone and the hydride ligand in addition to the Pt−O interaction. The strong Si−H back-donating interaction is not surprising because Si p_π and hydride 1s orbitals mainly contribute to the silanone π^* orbital and the frontier orbital ϕ_{HOMO-2}[36] of $[PtH(dipe)]^+$, respectively, as shown in Figure 2. In **2Hb**, on the other hand, the SiH_2 plane is bent back away from the platinum center by 10° to a much lesser extent than that in **2Ha**, which indicates that the back-donating interaction is much weaker in **2Hb** than that in **2Ha**. This result shows that the platinum(II) d orbital contributes much less to the back-donating interaction than does the hydride ligand in **2Ha**. Also, an electrostatic stabilization interaction is formed between the positively charged Si atom and the negatively charged hydride ligand. It is noted here that

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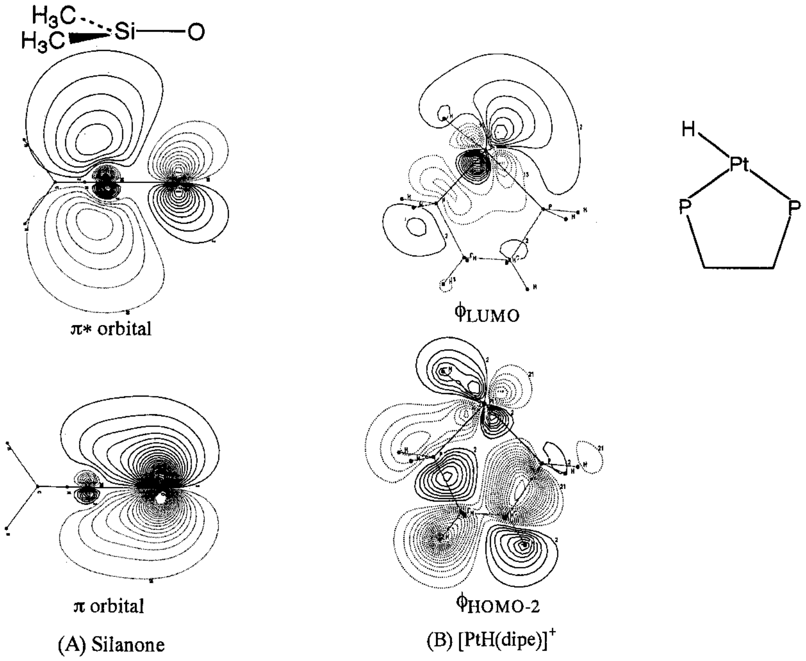

π* orbital

ϕ_{LUMO}

π orbital

ϕ_{HOMO-2}

(A) Silanone

(B) $[PtH(dipe)]^+$

Figure 2. Contour maps[a] of π and π* orbitals of silanone, and the LUMO (ϕ_{LUMO}) and the third HOMO (ϕ_{HOMO-2}) of $[PtH(dipe)]^+$ (dipe = $H_2PCH_2CH_2PH_2$). (a) Hartree–Fock orbital; contour values are 0.0 to ±0.25 with an interval of 0.025.

Table 1. Atomic Charge[a] and π and π* Orbital Energies[b] of Ethylene, Acetone, and Various Silanone

			R_2SiO				
	C_2H_4	$(CH_3)_2CO$	R = CF_3	R = F	R = H	R = SiH_3	R = CH_3
			Atomic Charge				
Si (or C)	−0.390	0.403	1.421	1.666	1.055	0.685	1.377
O		−0.378	−0.699	−0.783	−0.804	−0.773	−0.818
			Orbital Energy (eV)				
π	−10.0	−13.2	−14.1	−13.7	−12.1	−11.8	−11.6
π*	4.13	4.29	−0.36	2.20	1.27	0.67	2.61

[a] NBO charge.[39] [b] Hartree–Fock orbital energy.

not the HOMO (nonbonding p orbital of the O atom) but the π orbital of silanone interacts with the platinum center, whereas the former orbital is at a slightly higher energy than the latter one; for instance, π and nonbonding p orbitals are at −12.1 and −11.9 eV, respectively, in H_2SiO, and at −13.2 and −11.2 eV, respectively, in acetone. The interaction of the silanone π orbital with the platinum center is necessarily formed, as follows: To achieve the good overlap between the silanone π* orbital and the hydride 1s orbital, not the nonbonding p orbital but the π orbital needs to overlap with the platinum(II) d_σ orbital, since the nonbonding p orbital is perpendicular to the silanone π* orbital. Because **2Ha** contains the Si–H bonding interaction in addition to the Pt–O bonding interaction, **2Ha** is more stable than **2Hb** by 19.4 kcal/mol (DFT/BAS-II). We examined the different structure of **2H** in which the Si=O bond is perpendicular to the molecular plane. However, the geometry optimization led to **2Ha**.

Hence, we optimized geometries of the other silanone complexes, $[PtH(dipe)(R_2SiO)]^+$ (**2Me** for R = Me, **2Si** for R = SiH_3, **2Fme** for R = CF_3, and **2F** for R = F), in which the Si atom takes a position near the hydride ligand like **2Ha**. The Pt–O distance is not different so much among them, while the Si–H distance considerably depends on the substituent on the Si atom, and it becomes longer in the order **2F** < **2Fme** < **2Ha** < **2Si** < **2Me**. This increasing order seems to be related with the electron-releasing ability of the substituent, as discussed below in more detail. The other important geometrical features are observed in **2**, as follows: The Si=O bond in **2** is longer than that of free silanone by about 0.1 Å, and the SiR_2 plane is bent back away from the platinum center by 20–30°.

Comparison of **2** with acetone and ethylene analogues $[PtH(dipe)(Me_2CO)]^+$, **3**, and $[PtH(dipe)(C_2H_4)]^+$, **4**, is interesting. In **3**, the O atom interacts with the platinum center, while the C atom does not interact with any part of $[PtH(dipe)]^+$ unlike that in **2Me.** The C=O bond is not on the molecular plane so as to avoid the steric repulsion between methyl groups and the phosphine ligand. This feature is easily interpreted in terms of the absence of back-donating interaction. As shown in Table 1, the π* orbital of acetone is at a high energy, and thereby, acetone cannot form efficiently the back-donating interaction with the hydride ligand. Thus, the π* orbital does not need to overlap with the hydride 1s orbital, unlike that in **2Me**, and not the π orbital but the nonbonding p orbital on the O atom (HOMO) interacts with the platinum center (see **3** in Figure 1). As a result, the orientation of acetone is completely different from that of silanone in **2**. In the ethylene analogue **4**, the C=C bond is on the molecular plane, unlike that of the well-known Zeise's salt, in which the C=C bond is perpendicular to the molecular plane.[37] This is probably because the steric repulsion between ethylene and the hydride ligand is smaller in **4** than that between ethylene and Cl ligands in Zeise's salt.[38] Also in **3** and **4**, the C=O and C=C bonds lengthen by 0.040 and 0.043 Å upon coordination of acetone and ethylene, respectively, to a much lesser extent than does the Si=O bond. These results suggest that the Si=O bond more strongly interacts with the platinum(II) hydride complex than do the C=C and C=O bonds.

The Pt−P and Pt−H distances also change upon coordination of silanone. For instance, the Pt−P distance trans to silanone, acetone, or ethylene becomes longer in the order **1** ≪ **3** < **2** ≈ **4**, indicating that the trans-influence strengthens in the order acetone < silanone ≈ ethylene. The strong trans-influence of ethylene results from its π orbital at a high energy (Table 1). Though the silanone π orbital (−11.6 to −14.1 eV; HF/BAS-II) is at a lower energy than the O lone pair orbital of acetone (−11.2 eV; HF/BAS-II), the trans-influence of silanone is stronger than that of acetone. This is probably because the Si−H bonding interaction shortens the Pt−O distance to enhance the Pt−O bonding interaction; actually, the Pt−O distance of **2Ha** is shorter than that of **2Hb** (vide supra). Also, it is noted that the Pt−H distance lengthens greatly upon coordination of silanone. This significant lengthening of the Pt−H bond is consistent with the above discussion that not only electrostatic interaction but also charge-transfer interaction is formed between the silanone π^* and hydride 1s orbitals. Though the Pt−P bond trans to the hydride ligand is very long (2.453 Å) in **1**, it considerably shortens upon coordination of silanone. This result is easily interpreted in terms that the trans-influence of the hydride ligand is much weaker in **2** than that in **1** because the Pt−H bond of **2** is considerably lengthened by silanone coordination. In **3** and **4**, on the other hand, the Pt−H bond lengthens little and the Pt−P bond trans to the hydride ligand does not shorten very much. This is because the hydride ligand does not form any bonding interaction with acetone and ethylene.

At the end of this paragraph, it should be emphasized that **2** is considered a reasonable model of the transition state in the insertion reaction of the Si=O bond into the platinum(II)−hydride bond, because of the rather short Si−H distance. Thus, the synthesis of **2** is considerably interesting.

Binding Energy and Electron Distribution of Platinum(II) Hydride Silanone Complexes. The binding energies of **2Me** and **4** were calculated with various computational methods, as shown in Table 2. Their binding energies moderately fluctuate around MP2 and MP3 levels, but converge to 57 and 45 kcal/mol, respectively, upon going to MP4(SDQ) and CCSD(T) methods. Though the DFT method provides a slightly smaller binding energy than the MP4(SDQ) and CCSD(T) methods by 3−5 kcal/mol, the difference in binding energy between **2Me** and **4** is almost the same in DFT and CCSD(T) calculations. Hence, the relative stabilities would be reliably discussed with DFT-calculated binding energies.

Table 2. Binding Energy (kcal/mol) of Silanone and Ethylene with the Platinum Center in PtH(dipe)(Me$_2$SiO), 2Me, and PtH(dipe)(C$_2$H$_4$), 4

	2Me	**4**
DFT	54.9	39.7
MP2	59.1	50.9
MP3	57.7	42.2
MP4(DQ)	56.7	44.2
MP4(SDQ)	57.4	45.7
CCSD	57.0	42.4
CCSD(T)	58.7	44.6

As apparently shown in Table 3, coordination of silanone yields a much larger binding energy than those of ethylene and acetone by about 10 kcal/mol. This larger binding energy of **2** is interpreted in terms of the Si−H bonding interaction, as follows: Complex **2Hb** does not contain the Si−H bonding interaction, in which the binding energy is much smaller than that of **2Ha** by about 19 kcal/mol. Since the difference in binding energy between **2Ha** and **2Hb** is considered to result from the Si−H bonding interaction, the stabilization energy by this interaction is evaluated to be about 19 kcal/mol. The stabilization energy by the Pt−O interaction is estimated to be 27−35 kcal/mol by subtracting the Si−H stabilization energy (19 kcal/mol) from the binding energy of **2**. The above estimated Pt−O interaction is weaker than the binding energies of **3** and **4**. From these results, it is reasonably concluded that the larger binding energy of **2** arises from the Si−H bonding interaction.

The binding energy of **2** increases in the order **2Fme** < **2F** < **2Ha** < **2Si** < **2Me**, as shown in Table 3, where **2Hb** is excluded from the discussion since it does not involve the Si−H bonding interaction unlike the other complexes. Silanone coordination induces electron population changes, as shown in Table 3, where natural bond orbital population analysis is adopted.[39] Apparently, Pt atomic population slightly decreases but electron population of silanone slightly increases upon silanone coordination except for **2Me**. Pt atomic population depends little on the substituent, but the electron population of silanone decreases in the order **2Fme** > **2F** > **2Ha** > **2Si** > **2Me**, which agrees with the increasing order of the binding energy. Though the increasing order of binding energy does not correlate with both decreasing order of silanone π^* orbital energy and increasing order of Si atomic charge, the binding energy increases as the silanone π orbital lowers in energy (see Table 1). These results lead us to a conclusion that electron donation from silanone to the platinum center plays an important role in **2**, and the Si−H bonding interaction contributes to the stabilization of **2** in addition.

Of course, we do not intend here to neglect contributions of the back-donating interaction. Certainly, the electron population of silanone increases upon silanone coordination with the platinum center. Also, the contribution of the back-donating interaction is clearly

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(36) HOMO of **2** mainly consists of Pt d$_{z^2}$ orbital in which the hydride 1s orbital somewhat participates (see Supporting Information). Thus, not the HOMO but the $\phi_{\mathrm{HOMO}-2}$ (the third HOMO) is considered a frontier orbital for coordination of silanone, since both Pt d and hydride 1s orbitals can participate in this orbital.

(37) Love, R. A.; Koetzle, T. F.; Williams, G. J. B.; Andrews, L. C.; Bau, R. *Inorg. Chem.* **1975**, *14*, 2653.

(38) (a) The reason that ethylene is perpendicular to the molecular plane in Zeise's salt was interpreted in terms of the steric repulsion between ethylene and Cl ligands.[38b] (b) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801.

(39) Reed, A. E.; Curtis, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 849, and references therein.

Table 3. Binding Energy (BE; kcal/mol)[a] and Electron Populations of Various Platinum(II) Hydride Silanone Complexes, $[PtH(dipe)(R_2SiO)]^+$

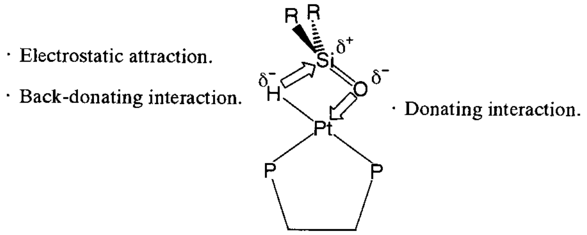
			R_2SiO					
	C_2H_4	Me_2CO	R = CF_3	R = F	R = H(a)[b]	R = H(b)[b]	R = SiH_3	R = CH_3
BE	39.6	39.8	46.8	51.7	51.7	32.3	52.9	54.9
			Population Changes by Silanone Coordination[c]					
Pt	0.055	−0.001	−0.085	−0.077	−0.079	0.023	−0.076	−0.075
d	0.018	−0.056	−0.084	−0.103	−0.090	−0.056	−0.077	−0.086
H	0.027	−0.037	0.112	0.186	0.120	−0.075	0.089	0.115
dipe	0.081	0.143	−0.171	−0.165	−0.066	−0.112	−0.019	−0.006
L[d]	0.108	0.178	0.144	0.056	0.026	−0.061	0.006	−0.033
Si	−0.068	0.069	0.174	0.061	0.145	0.055	0.221	0.085
O	0.388	−0.056	0.049	0.005	0.019	0.0	0.042	−0.007

[a] DFT/BAS-II calculation. [b] See **2Ha** and **2Hb** in Figure 1. [c] A positive value represents an increase in electron population, and vice versa. [d] L = C_2H_4, Me_2CO, or R_2SiO.

demonstrated by the geometrical features of the SiR_2 plane, which is considerably bent back away from the platinum center, and the Si═O bond is considerably lengthened by silanone coordination (vide supra). Contour maps of molecular orbitals provide some evidence of the presence of a back-donating interaction, which will be discussed below. However, the π^* orbital energy does not correlate with the Si−H distance, which is considered a measure of the strength of the back-donation from the hydride 1s orbital to the silanone π^* orbital, as follows: The Si−H distance becomes shorter in the order **2Me** > **2Si** > **2H** > **2Fme** > **2F**, while the π^* orbital lowers in energy in the order R = CH_3 > F > H > SiH_3 > CF_3. One reason is the steric repulsion, and the other is the electrostatic interaction. For instance, $(CF_3)_2SiO$ has the π^* orbital at the lowest energy, but the Si−H distance of **2Fme** is longer than that of **2F**. This is easily interpreted in terms that CF_3 is more bulky than F and the Si atom is less positively charged in $(CF_3)_2SiO$ than that in F_2SiO (see Table 1). Also, the Si−H distance of **2Si** is much longer than that of **2Ha** (see above), while $(SiH_3)_2SiO$ has the π^* orbital at a lower energy than that of H_2SiO. Again, this is because the SiH_3 group is more bulky than the H atom and the Si atom is less positively charged in $(SiH_3)_2SiO$ than that in H_2SiO. Thus, the strength of the Si−H interaction does not correlate to the π^* orbital energy.

It is noted that the H atomic population increases upon coordination of silanone, interestingly. This does not seem consistent with the presence of the back-donating interaction between the hydride ligand and the silanone π^* orbital. However, this result is easily interpreted in terms that not only the back-donation but also the polarization of the Pt−H bond is induced by the approach of the positively charged Si atom. This polarization increases the H atomic population and decreases the Pt atomic population. Actually, the H atomic population increases in the order **2Si** < **2Fme** ≈ **2Me** ≈ **2H** < **2F**, which roughly correlates to the increasing order of the positive charge of Si.

Scheme 1



Interaction of Silanone with a Platinum(II) Hydride Complex. Summarizing the above discussion, it is reasonably concluded that the platinum(II) hydride silanone complex is constructed by the four-centered interaction shown in Scheme 1. Since this four-centered interaction is completely different from the usual η^2-SiO coordinate bond, we investigate here in detail the orbital interactions involved in **2**. One important interaction is the electron donation from the silanone π orbital to the platinum(II) d orbital, and the other is the back-donation from the hydride 1s orbital to the silanone π^* orbital. Certainly, hydride 1s and Pt d_σ orbitals largely contribute to the ϕ_{HOMO-2}[36] and ϕ_{LUMO} of $[PtH(dipe)]^+$, **1**, respectively, as shown in Figure 2. These ϕ_{HOMO-2} and ϕ_{LUMO} orbitals are considered to participate in the Si−H back-donating interaction and the Pt−O donating interaction, respectively. Since the silanone π orbital mainly consists of the O p_π orbital (see also Figure 2), this π orbital is expected to overlap well with the ϕ_{LUMO} of **1**. Also, the silanone π^* orbital is expected to overlap well with the ϕ_{HOMO-2} of **1**, since the Si p_π orbital component is much greater than the O p_π orbital component in the silanone π^* orbital. To ascertain these orbital interactions, we investigated molecular orbitals of **2Me**. However, all occupied orbitals do not show clear features of the above-mentioned bonding interactions. Contour maps of two important molecular orbitals are given as examples in Figure 3B,C. Apparently, the HOMO (ψ_{HOMO} in Figure 3B) of **2Me** mainly consists of O p_π and hydride 1s orbitals. This HOMO does not result from simple overlap of the silanone π orbital with the LUMO (ϕ_{LUMO}) of **1**, since the Si p orbital almost disappears in ψ_{HOMO} (remember that the Si p orbital somewhat contributes to the silanone π orbital, as shown in Figure 2). This orbital picture of ψ_{HOMO} is interpreted in terms of the orbital mixings of π and π^* orbitals of silanone with the ϕ_{HOMO-2} and ϕ_{LUMO} of **1**, as follows: The silanone π orbital overlaps with the ϕ_{LUMO} of **1** in a bonding way and with the ϕ_{HOMO-2} in an antibonding way, because the silanone π orbital is at a higher energy than the ϕ_{HOMO-2} but at a lower energy than the ϕ_{LUMO}. Into this orbital interaction, the silanone π^* orbital mixes in a bonding way with the ϕ_{HOMO-2} of **1**, since the π^* orbital is at a higher energy than the ϕ_{HOMO-2} of **1**. As shown in Figure 3A,D, this mixing of silanone π^* orbital decreases the Si p orbital component and increases the O p orbital component. As a result, the ψ_{HOMO} mainly

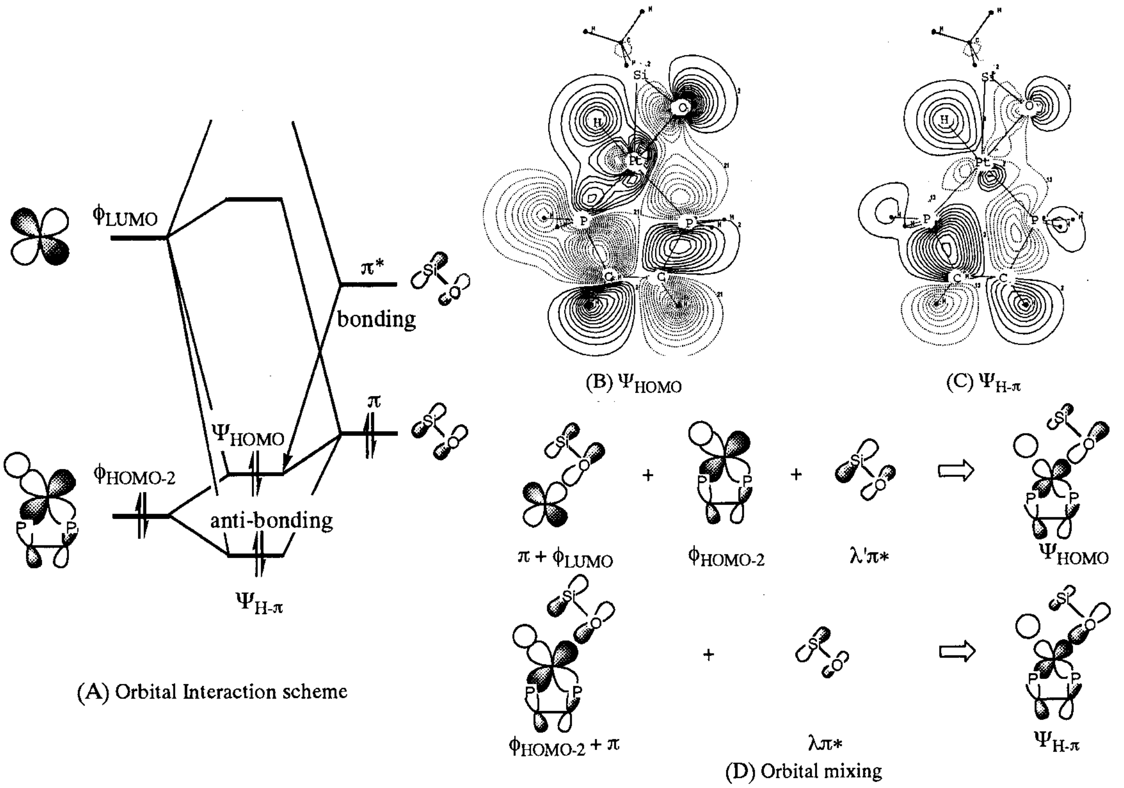
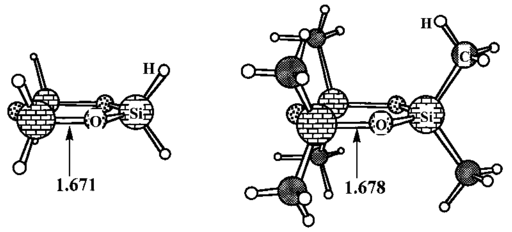


Figure 3. Contour maps of important molecular orbitals that significantly contribute to the coordinate bond of silanone in $[PtH(dipe)(Me_2SiO)]^+$ (dipe = $H_2PCH_2CH_2PH_2$); Hartree–Fock orbital; contour values are 0.0 to ±0.25 with an interval of 0.025.

involves hydride 1s and O p orbitals (Figure 3B). In other words, the ψ_{HOMO} mainly consists of both the Si–H back-donating interaction and the Pt–O donating one. Of course, the molecular orbital including all the bonding interactions exists at a lower energy, as shown in Figure 3C.

Formation of the Cyclic Trimer of Silanone. It was experimentally reported that a cyclic trimer of silanone is formed as a final product of the reaction of silanol with $[Pt_2(\mu\text{-}H)_2(dmpe)_2]^{2+}$.[8] Since one of our important purposes is to investigate whether a transition-metal silanone complex can be isolated or not, it is worthwhile to estimate relative stabilities of the silanone trimer and the platinum(II) hydride silanone complex **2**. Geometries of the silanone trimers are shown in Figure 4, and the binding energies are listed in Table 4. Interestingly, the silanone trimer is planar. Of course, the frequency calculation shows that this planar structure is at a minimum.[40] Both RSiR and SiOSi angles are about 110°, indicating that the Si atom takes sp^3 hybridization.

The stabilization energy by formation of the silanone trimer from the corresponding silanone monomer was calculated with various computational methods in the cases of $(H_2SiO)_3$ and $(Me_2SiO)_3$, as shown in Table 4(A). In both compounds, the stabilization energy moderately fluctuates around MP2 and MP3 levels but little upon going from MP4(SDQ) to CCSD(T). In $(H_2SiO)_3$, the DFT/BAS-II method yields almost the same stabilization energy as that of the G2 calculation, while MP4(SDQ)/BAS-II and CCSD(T)/BAS-II methods give a slightly larger stabilization energy than does the G2 calculation. The stabilization energies calculated with the MP4(SDQ) and CCSD(T) methods somewhat fluctuate upon going to cc-pvdz and cc-pvtz from BAS-II, whereas the stabilization energy by the DFT method fluctuates much less. From these results, it should be concluded that MP4(SDQ) and CCSD(T) methods need a basis set of high quality for these molecules and even cc-pvtz is not sufficient. On the other hand, the quality of BAS-II, cc-pvdz, and cc-pvtz seems sufficient for the DFT calculations of these molecules. Considering these results, we present our discussion here, based on the DFT/BAS-II method.



	$(H_2SiO)_3$	$[(CH_3)_2SiO]_3$
∠OSiO	131	132
∠SiOSi	109	108
∠RSiR	111	112

Figure 4. DFT/BAS-I optimized geometries (bond distances in Å and bond angles in deg) of cyclic trimers of silanone $(R_2SiO)_3$ (R = H or CH_3).

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[40] We tried to optimize the chairlike and boatlike structure of a silanone trimer like cyclohexane, but we failed it. All the careful optimizations led to the planar structure.

Table 4. Binding Energy[a] (BE; kcal/mol) and Electron Populations of Cyclic Trimers $(R_2SiO)_3$ of Silanone

(A) Binding Energy of Silanone Trimer[a] Calculated with Various Computational Methods

	$(H_2SiO)_3$			$(Me_2SiO)_3$		
	BAS-II	cc-pvdz	cc-pvtz	BAS-II	cc-pvdz	cc-pvtz
MP2	69.9	67.5	72.1	70.0	67.1	
MP3	74.5	72.4	77.3	74.2	71.5	
MP4(DQ)	72.5	67.7	75.2	72.3	69.6	
MP4(SDQ)	70.3	67.7	74.6	70.5	67.4	
CCSD	71.4	68.9		71.5		
CCSD(T)	70.0	67.0		70.5		
DFT	69.0	66.8	68.4	66.0	64.1	65.1
G2(0K)		69.1				
G2MP2(0K)		68.3				

(B) Binding Energy (BE; kcal/mol) and Population Changes[b]

R	CF_3	F	H	SiH_3	CH_3
BE	75.9	79.6	69.0	61.8	66.0
Si	−0.235	−0.226	−0.224	−0.228	−0.234
O	0.243	0.202	0.220	0.243	0.195

[a] The stabilization energy of a molecule of silanone. [b] DFT/BAS-II calculation.

The stabilization energy in the formation of silanone trimer increases in the order $R = SiH_3 < CH_3 < H < CF_3 < F$. This increasing order does not correlate with the HOMO−LUMO energy gap but roughly correlates with the Si atomic charge, which suggests that the electron-withdrawing substituent is favorable for the formation of the silanone trimer. This is not surprising because the polarized bond would become strong due to the electrostatic interaction.

Then, we estimated the reaction energy of eq 1 with the DFT method, where we added fluoride anion (F^-) to **1** and **2** since the formation energy of the dinuclear complex of platinum is calculated to be abnormally small in the absence of counteranion when the monomeric platinum complex is positively charged.[41] The reaction of eq 1 is significantly exothermic,[42] and the

$$[PtH(dipe)(silanone)]F \rightarrow (1/2)[Pt_2(\mu\text{-}H)_2(dipe)_2]F_2 + 1/3\ (R_2SiO)_3 \quad (1)$$

exothermicity increases in the order $R = SiH_3$ (41.6) < CH_3 (46.0) < H (46.5) < CF_3 (47.5) < F (48.3), where the exothermicity is in parentheses (kcal/mol; DFT/BAS-II). This means that the platinum(II) hydride silanone complex easily converts to $[Pt_2(\mu\text{-}H)_2(dipe)_2]^{2+}$ concomitantly with formation of silanone trimer. Thus, it is clearly concluded that one cannot isolate the platinum(II) hydride silanone complex. The most important reason of this exothermicity is that significantly large stabilization energy is provided by formation of the silanone trimer from three molecules of silanone, as shown in Table 4. The second reason is that formation of $[Pt(\mu\text{-}H)(dipe)]_2F_2$ yields a stabilization energy of about 25 kcal/mol. These results mean that the silanone trimer is easily formed from **2**, and it is reasonably concluded that $[Pt(H)(dipe)]^+$ is not useful for isolation of the platinum(II) hydride silanone complex.

Isolation of Transition-Metal Silanone Complexes. Since silanone eliminates from **2** to afford the silanone trimer in the reaction reported by Milstein et al.,[8] one can expect that a coordinatively unsaturated complex traps silanone eliminated from **2** to yield a transition-metal silanone complex. Since the stabilization energy of the silanone trimer is estimated to be 60−80 kcal/mol per molecule of silanone, the binding energy of silanone with the transition-metal complex should be larger than 60−80 kcal/mol. Martin and his collaborators theoretically investigated various transition-metal silanone complexes, such as $M(PH_3)_2(R_2SiO)$, $M(PR'_3)(CO)(R_2SiO)$, $M(PMe_3)_2(R_2SiO)$, $M(dhpe)(R_2SiO)$, $M(dmpe)(R_2SiO)$, $M(dhpp)(R_2SiO)$ (M = Pd or Pt; R = H, F, Me, ${}^iPr$, CF_3, or MeO; R′ = H or Me; dhpe = 1,2-bis(dihydrophosphino)ethane; dmpe = 1,2-bis(dimethylphosphino)ethane; dhpp = 1,2-bis(dihydrophosphino)propane), $M'Cl(PR'_3)_2(R_2SiO)$, $M'H(PR'_3)_2(R_2SiO)$, $M'(CO)(PR'_3)_2(R_2SiO)$, $[M'(PR'_3)_3(R_2SiO)]^+$, $M'Cl(dhpe)(R_2SiO)$, and $M'Cl(dhpp)(R_2SiO)$ (M′ = Rh or Ir).[21] According to their calculations, Pt(dmpe) and Pd(dmpe) form H_2SiO complexes with binding energies of about 59 and 44 kcal/mol, respectively, which are larger than those of $M(PH_3)_2(R_2SiO)$, $M(PR'_3)(CO)(R_2SiO)$, and $M(PMe_3)_2(R_2SiO)$. However, these binding energies are still smaller than 60−80 kcal/mol, indicating that these Pd(0) and Pt(0) complexes would not be useful for isolation of the transition-metal silanone complex. On the other hand, some iridium(I) complexes exhibit a considerably large binding energy; for instance, 75.8 kcal/mol for *trans*-$IrCl(PH_3)_2[(CF_3)_2SiO]$ and 62.2 kcal/mol for *trans*-$Ir(CO)(PH_3)_2({}^iPr_2SiO)$. Since these binding energies are as large as the stabilization energy by formation of a silanone trimer, these iridium(I) complexes should be applied to the isolation of iridium(I) silanone adducts.

Besides many transition-metal silanone complexes discussed above, a molybdenum(0) phosphine silanone complex is expected to be stable, since molybdenum(0) phosphine carbon dioxide complexes were isolated[43] despite the weak coordinate bond of carbon dioxide. Also, zirconium(II) is considered to be a strong Lewis

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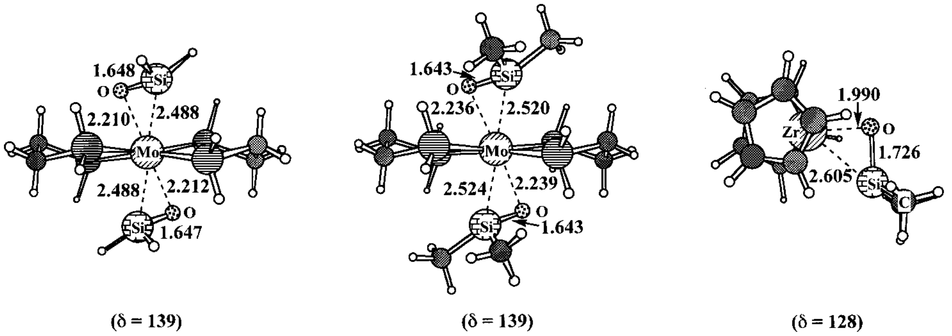
(41) Sugimoto, M.; Horiuchi, F.; Sakaki, S. *Chem. Phys. Lett.* **1997**, *274*, 543.

(42) The exothermicity is overestimated by a few kcal/mol, since the binding energy of silanone with **1** would be underestimated by 2−3 kcal/mol.

(43) For instance: (a) Alvarez, R.; Carmona, E.; Poveda, M. L.; Sanchez-Dolgado, R. *J. Am. Chem. Soc.* **1984**, *106*, 2731. (b) Alvarez, R.; Carmona, E.; Martin, J. M.; Poveda, M. L.; Gutierrez-Puebla, E.; Monge, A. *J. Am. Chem. Soc.* **1986**, *108*, 2286. (c) Carmona, E.; Hughes, A. K.; Munez, M. A.; O'Hare, D. M.; Perez, P. J.; Poveda, M. L. *J. Am. Chem. Soc.* **1991**, *113*, 9210. (d) Jegat, C.; Fovassin, M.; Mascetti, J. *Inorg. Chem.* **1991**, *30*, 1521.



5H **5Me** **6Me**

Figure 5. DFT/BAS-I optimized geometries (bond distances in Å and bond angles in deg) of $Mo(dipe)_2(R_2SiO)_2$ (R = H or CH_3; dipe = $H_2PCH_2CH_2PH_2$) and $Cp_2Zr[(CH_3)_2SiO]$. In parentheses are the dihedral angle between the SiO bond and the SiR_2 plane.

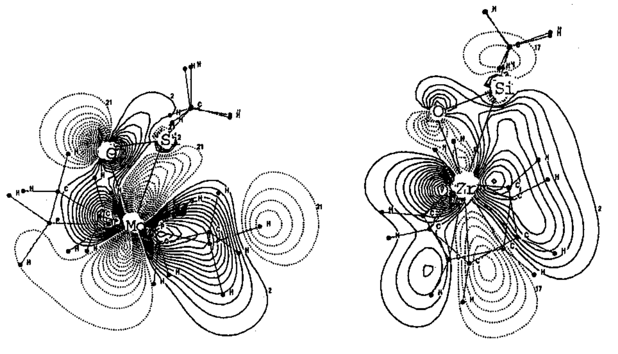
Table 5. Binding Energy (BE; kcal/mol) and Electron Distribution of $Mo(dipe)_2(R_2SiO)_2$ (R = H or Me) and $Cp_2Zr(Me_2SiO)$[a]

	$Mo(dipe)_2(R_2SiO)_2$	$Mo(dipe)_2(R_2SiO)_2$	$Cp_2Zr(Me_2SiO$
BE	62.0	50.7	89.0
	Changes in Electron Population[b]		
M	0.256	0.291	0.008
d	0.148	0.203	−0.125
R_2SiO	0.308	0.260	0.604
Si	0.346	0.242	0.593
O	0.002	−0.015	0.018

[a] DFT/BAS-II calculation. [b] A positive value represents an increase in electron population, and vice versa.

base. Hence, we theoretically investigated molybdenum(0) phosphine silanone and di(cyclopentadienyl)zirconium(II) silanone complexes. Their optimized geometries are shown in Figure 5, and the binding energies are listed in Table 5. The binding energies of molybdenum(0) complexes are moderate: 62.0 kcal/mol for $Mo(dipe)_2(H_2SiO)_2$, **5H**, and 50.7 kcal/mol for $Mo(dipe)_2(Me_2SiO)_2$, **5Me**.[44] However, the binding energy of $Cp_2Zr(Me_2SiO)$, **6**, is substantially large (89.0 kcal/mol). From these binding energies, we wish to predict that Cp_2Zr(silanone) is one of the best candidates for isolation of the stable transition-metal silanone adduct.

Geometries, Electron Distribution, and Bonding Nature of $Mo(dipe)_2(R_2SiO)_2$ (R = H or Me) and $Cp_2Zr(Me_2SiO)$. Here, we will discuss the geometries and bonding nature of $Mo(dipe)_2(H_2SiO)_2$, **5H**, $Mo(dipe)_2(Me_2SiO)_2$, **5Me**, and $Cp_2Zr(Me_2SiO)$, **6**. It should be noted that the SiR_2 plane is significantly bent back away from the metal center and the Si−O bond considerably lengthens in these complexes. Since the Si−O distances of **5** and **6** are similar to those (1.68 Å; DFT/BAS-I) of SiH_3OH and $SiHMe_2OH$, the Si−O bonds of **5** and **6** are characterized to be a single bond. The electron population of silanone increases very much upon coordination with these metals, as shown in Table 5; in particular, it significantly increases by 0.6*e* in **6**. All these results clearly show that the π-back-donating interaction significantly contributes to the coordinate bond of silanone. The next important feature is that the O atomic population changes little, while the Si atomic population substantially increases. This feature is easily understood in terms that the donating interaction from the silanone π orbital to the metal d orbital also contributes to the coordinate bond, as follows: Since the O p_π orbital component is much larger than the Si p_π orbital component in the silanone π orbital, the donating interaction decreases the O atomic population to a greater extent than the Si atomic population, which compensates the electron accumulation on the O atom by the back-donating interaction.



(A) $Mo(dipe)_2[(CH_3)_2SiO]$ (B) $Cp_2Zr[(CH_3)_2SiO]$

Figure 6. Contour maps of important molecular orbitals that significantly contribute to the coordinate bond of silanone in $Mo(dipe)_2[(CH_3)_2SiO]_2$ (dipe = $H_2PCH_2CH_2PH_2$) and $Cp_2Zr[(CH_3)_2SiO]$; Hartree−Fock orbital; contour values are 0.0 to ±0.25 with an interval of 0.025.

We investigated contour maps of several important orbitals, as shown in Figure 6. In these complexes, the typical π-back-donating interaction is observed between silanone and the metal center. In particular, **6** seems to possess a Zr−Si single bond. This is because the substantially strong π-back-donating interaction is formed between the silanone π^* and Zr d_π orbitals, unlike **2**. The significant difference in back-donating interaction between these complexes and **2** would come from the fact that molybdenum(0) and zirconium(II) have occupied d orbitals at a much higher energy than does platinum(II).

Summarizing these results, we wish to present a proposal that a strongly electron-donating transition-metal complex is considered a good candidate for a stable transition-metal silanone complex because it can form a strong back-donating interaction with silanone.

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(44) $Mo(dipe)_2(R_2SiO)$ (R = H or Me), in which one molecule of silanone coordinates with the molybdenum(0) center, was also theoretically investigated. However, the binding energy of silanone is smaller than that of $Mo(dipe)_2(R_2SiO)_2$.

Conclusions

In this work, platinum(II) hydride silanone complexes $[PtH(dipe)(R_2SiO)]^+$, **2** (R = H, F, CH_3, CF_3, or SiH_3; dipe = diphosphinoethane), molybdenum(0) di(silanone) complexes $Mo(dipe)_2(R_2SiO)_2$, **5** (R = H or CH_3), di(cyclopentadienyl)zirconium(II) silanone complex $Cp_2Zr(Me_2SiO)$, **6**, and cyclic trimers of silanone $(R_2SiO)_3$ were theoretically investigated with the DFT method, where the reliability of the DFT method was examined by comparing the DFT-calculated binding energy with those of MP4(SDQ), CCSD(T), and G2 methods. In **2**, the O atom of silanone interacts with the platinum center through the donating interaction and the Si atom of silanone interacts with the hydride ligand through the back-donating interaction and the electrostatic one. This coordinate bond is completely different from the usual η^2-SiO coordinate bond. Because of the presence of additional Si−H stabilization interaction, **2** is more stable than the ethylene and acetone analogues and its geometry is much different from that of the acetone analogue.

In $[PtH(dipe)(R_2SiO)]^+$ **2**, the binding energy increases in the order R = CF_3 < F < H < SiH_3 < CH_3. This increasing order roughly agrees with the increasing orders of the silanone π orbital energy and the positive charge on the Si atom. This result clearly suggests that the donating interaction between silanone π and platinum(II) d orbitals mainly contributes to the binding energy.

Complex **2** easily converts to the di(μ-hydride)diplatinum(II) complex $[Pt(\mu\text{-}H)(dipe)]_2^{2+}$ and the silanone trimer with a considerably large exothermicity. This means that the platinum(II) hydride complex is not useful to isolate a platinum(II) silanone complex. Since the formation of the silanone trimer from silanone monomers yields a stabilization energy of 60−80 kcal/mol per molecule of silanone, the binding energy of a transition-metal silanone complex should be larger than 60−80 kcal/mol. Previous theoretical calculations[21] reported that the iridium(I) complex provided a considerably large binding energy; for instance 75.8 kcal/mol for *trans*-$IrCl(PH_3)_2[(CF_3)_2SiO]$ and 62.2 kcal/mol for *trans*-$Ir(CO)(PH_3)_2(^iPr_2SiO)$ (DFT(B3LYP)).[21] We also investigated molybdenum(0) phosphine silanone and di(cyclopentadienyl)zirconium(II) silanone complexes. Though the former complex provides a moderately large binding energy, the latter one yields a significantly large binding energy of 89 kcal/mol. We wish to propose here that the di(cyclopentadienyl)zirconium(II) silanone complex is a good candidate for a stable transition-metal silanone complex.

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Supporting Information Available: HOMO of $[PtH(dipe)]^+$, **1**, and optimized geometries of $(R_2SiO)_3$ (R = F, CF_3, or SiH_3) and $Mo(dipe)_2(R_2SiO)$ (R = H or CH_3). This material is available free of charge via the Internet at http://pubs.acs.org.

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