THEORETICAL STUDY OF METALLASILATRANES; BONDING NATURE AND PREDICTION OF NEW METALLASILATRANE

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Dedicated to Dr. Zdeněk Havlas on the occasion of his 60th birthday.

The new bond between Pt atom and hypervalent six-coordinate Si species in platinum-silatrane reported recently was theoretically investigated mainly with DFT method and in part with MP2 method. The DFT method with B3PW91 and M06 functionals reproduces well the Pt–Si, Pt–Cl and Si–N bond distances. Though the Si–Cl distance is overestimated by all functionals employed here when one d polarization function is added to each of Si and Cl, the M06-optimized Si–Cl distance is close to the experimental value when two d polarization functions are added to each of Si and Cl, suggesting that the functional and basis sets must be carefully employed in theoretical calculation of hypervalnet six-coordinate Si species. Population analysis clearly indicates that the Pt–Si bond is formed by the charge-transfer (CT) from the occupied d_σ orbital of Pt to the empty p orbital of Si, which enhances the CT from the S atoms and Cl ligand to the Pt center. Besides platinum- and palladium-silatranes, no metallasilatrane has been reported so far. Based on the knowledge of bonding nature, we presented theoretical prediction that iridium(I) can form a similar metallasilatrane. Actually, the DFT calculation indicates that iridium-silatrane has essentially the same equilibrium geometry and bonding nature as those of platinum-silatrane.

Keywords: Density functional calculations; Silicon; Transition metals; Hypervalent compounds.

The transition-metal complexes bearing hypervalent species is of considerable interests in modern inorganic and organic chemistry and also physical chemistry[1]. This is because new bonding features are expected between transition-metal element and hypervalent species unlike the usual coordinate bond. Such transition-metal complexes were first reported in pioneering works by Akiba, Yamamoto and their coworkers about 10 years ago[2–4].

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They synthesized groups 6[2], 8[3] and 9[4] transition-metal complexes interacting with five-coordinate Sb and P hypervalent species at the equatorial position. Also, the bonding interaction of the transition metal and hypervalent Si species was experimentally and theoretically suggested in the tungsten-silicon species, $Cp(CO)_2W[SiH_2(C{\equiv}CH)]$[5], in which the Si center interacts with the W center, two H and two C atoms. Recently, new type of compounds, metallasilatranes of platinum and palladium, have been experimentally reported[6] (see Fig. 1A for platinum-silatrane). In these compounds, the transition metal element interacts with six-coordinate Si

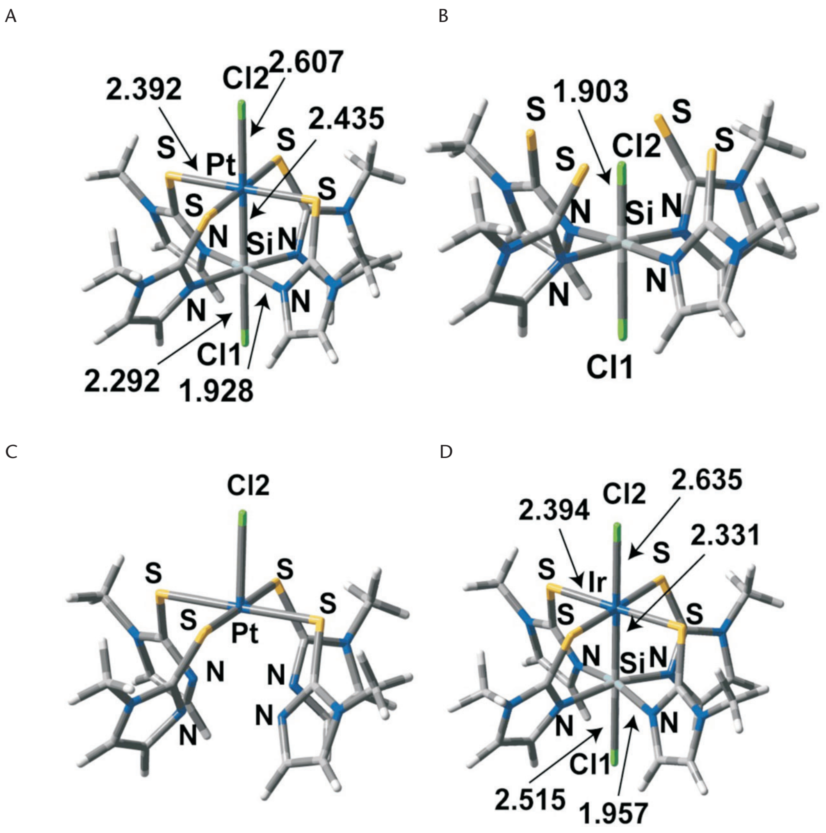

FIG. 1
Optmized geometries of platinum-silatrane (A), Cl-silatrane (B) and iridium-silatrane (D), and geometry of Pt-ClS_4 fragment (C; this geometry was taken to be the same as the optimized geometry of the corresponding moiety of platinum-silatrane). Bond lengths are given in Å

species, interestingly. The Si center is considered to take +IV oxidation state and the metal moiety participates in the M–Si bond as one ligand of the Si center. Such Pt–Si bond was discussed in terms of the dative bond from the metal center to the Si(IV) center[6]. Also, DFT study was reported recently on this type of platinum-metallasilatrane[7], in which the Si NMR chemical shift and the bonding nature were discussed in comparison with other usual Si species.

As mentioned above, one can expect new and interesting features in the bonding interaction between transition-metal element and hypervalent species. Actually, there are many important issues to be theoretically investigated; e.g., it is of considerable interest to clarify the electronic structure of the Pt center as well as the Si one, to show what influences the Si center induces on the Pt one, to present theoretical prediction of new metallasilatrane of transition-metal element, and to make comparison between these matallasilatranes and transition-metal complexes with five-coordinate Sb and P species. Also, it is important to know what computational method is useful for theoretical study of this type of new compound.

As the first step of comprehensive theoretical study, we wish to present our preliminary report about the theoretical study of metallasilatrane of platinum(II) and iridium(I). Our main purposes here are to show what computational method can be applied to this type of compound, to present theoretical understanding of the electronic structure of the Pt moiety, and to present theoretical prediction of new metallasilatrane[8].

COMPUTATIONAL DETAILS

The DFT method was mainly employed with B3PW91 [9], LC-BLYP [10,11], M06 [12] and M06-2X [12]. Core electrons of transition-metal elements were replaced with effective core potentials of LANL2DZ [13] and their valence electrons were represented with (541/541/111/1) basis sets[13–15]. We name this basis set HW-Dz for brevity, hereafter. In some calculations, we employed cc-pVDZ-pp [16] for Pt to examine the basis set effects. For other atoms, we employed 6-31G(d) [17], 6-311G(d) and 6-311G(2d) basis sets[18], where one diffuse function was added to Cl because this atom is anion-like.

The geometry optimization was carried out by the DFT method with the above-mentioned functionals. MP2 calculations were also carried out to examine several important geometrical parameters. These calculations were carried out with Gaussian 09 [16] and GAMESS-US [17] program packages.

RESULTS AND DISCUSSION

Geometry of Platinum-Silatrane

The characteristic features of the geometry will be mentioned first. As shown in Fig. 1A, the Si center takes a six-coordinate structure in which the Si center coordinates with four N atoms, one Cl1 ligand and one Pt center (see Fig. 1A for Cl1 and Cl2). These geometrical features indicate that the Si center is understood to take six-coordinate hypervalency. Also, the Pt center takes a six-coordinate structure, in which four S atoms, one Cl2 ligand and one Si center coordinate with the Pt center. This six-coordinate structure is interesting because the Pt center takes +II oxidation state bearing d^8 electron configuration in this compound, as will be discussed below in detail; remember that the d^8 metal tends to form a four-coordinate planar complex. In this regard, the Pt–Si and Pt–Cl2 bonds must be examined carefully in theoretical study of platinum-silatrane as well as the Si–Cl1 and Si–N bonds. We mainly checked these bond distances in the geometry optimization.

We investigated first the basis sets effect on the geometry, as shown in Table I. The use of cc-pVDZ-pp instead of HW-Dz for Pt little changes the Pt–Si and Pt–S distances. The use of cc-pVDZ-pp moderately decreases the Pt–Cl distance by 0.018 Å, which leads to larger deviation from the experimental value; note that the Pt–Cl distance is underestimated by these calculations. This means that HW-Dz is useful to calculate this type of compound. The use of 6-311G(d) instead of 6-31G(d) for other atoms also little changes the bond distances.

On the other hand, the effects of functional on the geometry are significantly large. The Pt–Si bond, which is an important geometrical parameter here, is underestimated by the LC-BLYP and M06-2X, while it is well reproduced by the B3PW91 and M06. The Pt–Cl2 bond, which is also an important geometrical parameter here, is considerably underestimated by B3PW91, LC-BLYP and M06-2X, but it is reproduced well by the M06 functional. The Pt–Si bond is reproduced well by the B3PW91 and M06. The S–N bond is expected to be optimized well because this is not a coordinate bond but a usual covalent bond. The B3PW91, however, provides somewhat longer Si–N bond, while the M06 provides moderately longer Si–N bond and the LC-BLYP and M06-2X functionals reproduce well this bond distance. Unexpectedly, considerably longer Si–Cl2 bond than the experimental value is presented by all functionals employed here when one d polarization function was added to each of Si and Cl, though this bond does

TABLE I
Several important geometrical parameters optimized with various basis sets and functionals[a]

	Basic sets			Optimized distance				
	Pt	Si	Cl	Pt–Si	Pt–Cl	Pt–S	Si–N	Si–Cl
B3PW91	HW-Dz	6-31G(d)	6-31G+(d)	2.431	2.561	2.358	1.951	2.325
		6-311G(d)	6-311G+(d)	2.426	2.576	2.363	1.942	2.337
		6-311G(2d)	6-311G+(2d)	2.422	2.578	2.362	1.941	2.307
LC-BLYP	HW-Dz	6-311G(d)	6-311G+(d)	2.405	2.538	2.339	1.910	2.319
	ccPVDZ-pp	6-311G(d)	6-311G+(d)	2.404	2.520	2.335	1.913	2.324
M062X	HW-Dz	6-311G(d)	6-311G+(d)	2.393	2.608	2.358	1.917	2.329
M06	HW-Dz	6-311G(d)	6-311G+(d)	2.432	2.592	2.388	1.932	2.318
	HW-Dz	6-311G(2d)	6-311G+(2d)	2.435	2.607	2.392	1.928	2.292
MP2[b]	HW-Dz	6-31G(d)	6-31G+(d)	–	2.565	–	–	2.345
Exp.[c]				2.457	2.629		1.903	2.218

[a] Bond lengths are given in Å. [b] The Pt–Cl and Si–Cl bonds were manually changed and the minima were found by curve fitting of potential energy curve. [c] Ref. 3.

not contain transition-metal element. Because the hypervalent bond is understood to contain strong electrostatic interaction (ionic interaction), it is likely that the long-range correction of the Hartree–Fock exchange term provides the good bond distance. However, the LC-BLYP presents a considerably longer Si–Cl1 distance, too. We examined this Si–Cl1 bond distance with the MP2 method, as shown in Table I. However, the Si–Cl1 bond is calculated to be longer than the experimental value, too. Though we could not employ basis sets of triple-zeta quality in MP2 calculations due to the limit of computational facility, it is concluded that the MP2 method overestimates this bond distance because the basis sets of double-zeta quality tend to provide shorter distance. Finally, we employed 6-311G(2d) for Si and Cl, where one diffuse function was also added to Cl. DFT(M06) calculation with these basis sets provides the best Si–Cl1 bond distance here; though it is still moderately longer than the experimental value, the deviation of 0.074 Å is not very large, considering that this is hypervalent bond. This result clearly shows that two d polarization functions should be added to each of Si and Cl to present correct description of hypervalent six-coordinate Si–Cl1 bond.

Hereafter, we will employ the M06 functional, where the HW-Dz and 6-311G(d) basis sets were employed for Pt and other atoms, respectively, except for Cl and Si for which 6-311G(2d) basis sets were used with one diffuse function added to Cl.

Electron Distribution and Bonding Nature

NPA and NBO populations of platinum-silatrane are shown in Table II, in comparison with those of Cl-silatrane and the Pt-ClS$_4$ fragment; note that substitution of Pt–Cl2 moiety for Cl2 in platinum-silatrane leads to the formation of Cl-silatrane, as shown in Fig. 1B, and removing the Si–Cl1 moiety from platinum-silatrane leads to the formation of the Pt-ClS$_4$ fragment, as shown in Fig. 1C.

The electron distribution of the Pt-ClS$_4$ fragment is discussed first. The $d_{x^2-y^2}$ orbital population is 1.362 e and the d_{z^2} orbital population is 1.927 Å, as shown in Table II. These results indicate that only the $d_{x^2-y^2}$ orbital participates in the coordinate bonds with the S atoms and the d_{z^2} orbital little participates in the coordinate bond. Hence, it is concluded that the Pt center takes +II oxidation state bearing d^8 electron configuration. Total d orbital population is 9.019 e, which is much larger than 8.0 e. However, this is not unreasonable because the $d_{x^2-y^2}$ orbital receives electron population from four S ligands through the charge-transfer (CT) interaction.

When going from the Pt-ClS_4 fragment to platinum-silatrane, the Pt–Si bond is formed. In this process, the Pt atomic population considerably decreases, as shown in Table II. This decrease in the Pt atomic population arises from the considerably large decrease in the Pt d_{z^2} orbital population; the d_{z^2} orbital population decreases to 1.640 e from about 2.0 e when going from the Pt-ClS_4 fragment to platinum-silatrane. This decrease in population clearly indicates that the CT occurs from the Pt d_{z^2} orbital to the Si center. The same CT interaction was proposed in the experimental work[6]. Also, this CT was clearly disclosed by the NBO and energy decomposition analyses in the recent theoretical work[7]; this analysis indicates that the or-

TABLE II
Electron populations[a] of metallasilatranes and important species

	Si–ClN_4 fragment[b]	Pt–ClS_4 fragment[c]	Pt-silatrane	Ir-silatrane	Cl-silatrane[d]
Pt or Ir					
s	–	0.493	0.641	0.561	–
p	–	0.730	1.110	1.035	–
d	–	9.019	8.942	8.490	–
$d_{x2\text{-}y2}$	–	1.170	1.362	1.158	–
d_{z2}	–	1.927	1.640	1.462	–
Cl2		17.782	17.536	17.582	17.253
Si					
s	0.755	–	0.767	0.797	0.726
p	1.069	–	1.294	1.234	1.323
p_z	0.470	–	0.596	0.598	0.526
S	16.278	16.088	15.851	15.886	16.352
N	7.779	7.465	7.719	7.710	7.736
Cl1	17.552	–	17.505	17.638	17.585

[a] NBO population analysis was employed. [b] This is the Si species formed by removing the Pt–Cl2 moiety from platinum-silatrane. [c] This is the Pt species formed from platinum-silatrane by removing the Si–Cl1 moiety (see Fig. 1C). [d] This Cl-silatrane is formed from platinum-silatrane by substituting the Pt–Cl2 moiety for Cl2. Its geometry was not fully optimized, where only the Si–Cl2 bond was optimized with other geometrical parameters fixed (see Fig. 1B).

bital relaxation induces energy stabilization of 60 kcal/mol to which the CT from the metal d_{z^2} to the Si center mainly contributes.

We will discuss here the formal oxidation state of the Pt center. The d_{z^2} orbital population of 1.640 e is considerably larger than the $d_{x^2-y^2}$ orbital population. If the Pt center took +IV oxidation state, the Pt d_{z^2} orbital was empty in a formal sense and hence the considerably strong CT must occur from the Cl2 ligand and the Si center to the Pt center to present such large Pt d_{z^2} orbital population. But, the Cl2 ligand possesses 17.505 e in platinum-silatrane, suggesting that the Cl2 ligand donates about 0.5 e to the Pt center at the most, which is about one-third of the Pt d_{z^2} orbital population. This means that the considerably large CT must occur from the Si center to the Pt center. However, the Si center is considered to take +IV oxidation state in a formal sense, indicating that such large CT from the Si center to the Pt center is unlikely. Thus, it is concluded that the Pt center takes +II oxidation state and the strong CT occurs from the d_{z^2} orbital of Pt to the Si center. In other words, the Si species acts as a σ-electron withdrawing ligand. The similar interaction was reported for the interaction between transition-metal and η^1-C coordinated CO_2 species by previous theoretical studies[21]. It is of considerable interest that essentially the same bonding nature is found in platinum-silatrane and very different η^1-C coordinated CO_2 complexes. Because of this CT from the Pt d_{z^2} orbital to the Si center, the Cl2 anion stronger coordinates with the Pt center in platinum-silatrane than in the Pt-ClS_4 fragment because the d_{z^2} orbital is a perfect doubly-occupied orbital in the Pt-ClS_4 fragment but not in platinum-silatrane. Actually, the S and Cl2 atomic populations considerably decrease, as shown in Table II, when going from the Pt-ClS_4 fragment to platinum-silatrane. These results clearly indicate that the CT from the Pt d_{z^2} to the Si p_z enhances the CTs from the S atoms and the Cl2 ligand to the Pt center.

To investigate how much the Pt–Si bond formation influences the electronic structure of the Si center, we constructed the Si-ClN_4 fragment by removing the Pt-Cl2 moiety from platinum-silatrane without any other geometry change; the geometry of the Si-ClN_4 fragment is not presented here to save page space. When going from the Si-ClN_4 fragment to platinum-silatrane, the Pt–Si and four Pt–S bonds are formed. Consistent with the considerable decrease in Pt d_{z^2} orbital population when going from the Pt-ClS_4 fragment to platinum-silatrane, the p_z orbital population of the Si center considerably increases by 0.126 e when going from the Si-ClN_4 fragment to platinum-silatrane, as shown in Table II. Also, the S atomic population considerably decreases when going from the Si-ClN_4 fragment to platinum-silatrane. This decrease in the S atomic population results from the formation of Pt–S coordinate bonds in platinum-silatrane. Summarizing above results, the electron re-distribution of platinum-silatrane is understood in terms of the CT from the d_{z^2} orbital of the Pt center to the p_z orbital of the Si center and the CTs from the S atoms and the Cl ligand to the Pt center.

It is also of considerable interest to compare the platinum-silatrane with non-transition-metal-silatrane. We calculated Cl-silatrane as a model of non-transition-metal-silatrane, in which the Pt-Cl2 moiety is substituted for one Cl2, as shown in Fig. 1B. In Cl-silatrane, only the Si–Cl2 distance was optimized to be 1.903 Å without any other geometry change. The p_z orbital population of the Si center is somewhat smaller in the Cl-silatrane than in the platinum-silatrane, indicating that the Pt-Cl2 moiety forms stronger CT interaction with the Si center than does the Cl anion.

Theoretical Prediction of New Metallasilatrane of Ir(I)

As discussed above, the presence of doubly occupied d_σ orbital is crucial to form this type of metallasilatrane. Because Ir(I) takes d^8 electron configuration like Pt(II), one can expect that Ir(I) can form a metallasilatrane. Actually, the optimized geometry of iridium-silatrane is essentially the same as that of platinum-silatrane, as shown in Fig. 1D. However, several interesting differences are found between them, as follows: The Ir–Si distance is considerably shorter than the Pt–Si distance, suggesting that the Ir analogue is more stable than platinum-silatrane. The Si–Cl1 distance of the iridium-silatrane is, on the other hand, much longer than that of platinum-silatrane and the Ir–Cl2 distance is somewhat longer than the Pt–Cl2 distance. These results suggest that the strong Ir–Si bond leads to elongations of the Ir–Cl2 and Si–Cl1 bonds. The other geometrical parameters such as the M–S and Si–N bond distances are little different between platinum- and iridium-silatranes.

Consistent with the geometrical features, the Ir atomic population is considerably smaller than the Pt atomic population, which results from the smaller d_{z^2} orbital population of the Ir center than that of the Pt center. The Cl1 atomic population is larger than that in platinum-silatrane. However, the Si atomic and its p_z orbital populations are similar to those of platinum-silatrane. These results indicate that the Ir center forms stronger CT with the Si center than does the Pt center, which induces the weakening of the Ir–Cl2 bond and accumulation of negative charge on the Cl1 atom without significant change of the Si p_z orbital population.

In general, the d orbital energy becomes lower when going from the left-hand side to the right-hand side in periodic table. Thus, the d orbital of the

Ir(I) exists at higher energy than that of the Pt(II), which is favorable for the CT interaction from the Ir center to the Si center. It is likely to expect that group 9 transition-metal elements bearing doubly occupied d_σ orbital can be utilized for formation of stable metallasilatrane because their d orbitals exist at higher energy than that of Pt.

CONCLUSIONS

Platinum-silatrane which contains a new bond between transition-metal and hypervalent six-coordinate Si species was theoretically investigated mainly with DFT method. Though LC-BLYP and M06-2X functionals do not reproduce well the experimental geometry, the B3PW91 and M06 functionals provide good Pt–Si, Pt–Cl2 and Si–N distances, except for the Si–Cl1 distance. The hypervalent Si–Cl1 bond distance was represented well by the use of M06 with the addition of two d polarization functions to each of Si and Cl atoms. The Pt–Si bond is formed by the charge transfer from the doubly-occupied d_{z^2} orbital of Pt to the empty p_z orbital of Si, which enhances the CTs from the S atom and the Cl2 ligand to the Pt center. The knowledge of this bonding nature suggests us that a transition-metal element bearing doubly-occupied d_σ orbital can form metallasilatrane. We examined if the Ir(I) bearing d^8 electron configuration can form a similar metallasilatrane and found that iridium-silatrane is in equilibrium geometry and its geometry and bonding nature resemble well those of platinum-silatrane. Theoretical calculation suggests that the Ir–Si bond is stronger than that of the platinum analogue.

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