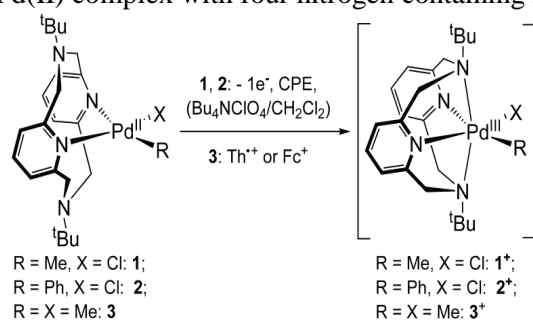


## 2P-104

### Comparative Theoretical Study of Reactivities of Pd (II), Pd (III), and Pd(IV) Complexes towards C-C and Si-Si bond reductive elimination reactions

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**[Introduction]** The activation of small molecules by transition metals is of fundamental importance in recent organometallic chemistry. One of the typical examples is C-H bond activation reaction of alkanes and aromatics. This reaction is difficult by conventional organic reagents in general. However, the activation of C-H bond has been achieved by many transition metal complexes. During the past few decades, palladium (Pd) has gained much attention as a one of the most versatile and efficient transition metal catalysts for wide range of C-C coupling and C-H functionalization. Though Pd(0) and Pd(II) chemistries have been extensively studied, much less is known about the Pd(III) complex until the recent studies by Ritter et al.<sup>1</sup> and Sanford et al.<sup>2</sup> They reported that the dinuclear Pd(III) complexes play important role as a key intermediate in the oxidative functionalization of C-H bond. Though several such dinuclear Pd(III) complexes have been structurally characterized, no mononuclear Pd(III) complex has been known till the recent report by Khusnutdinova et al.<sup>3</sup> These authors succeeded in the synthesis of mononuclear organometallic Pd(III) complexes starting from Pd(II) complex with four nitrogen containing ligands shown in Scheme 1.



**Scheme 1: Synthesis of Pd(III) Complexes**

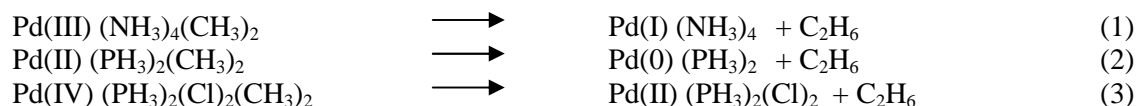
In this work, we wish to report theoretical investigation on the electronic structure of one of the Pd(III) complexes (3<sup>+</sup>, where R=X=Me) mentioned in Scheme 1, in comparison to the Pd(II) and Pd(IV) complexes. As the first step toward understanding the reactivity of Pd(III) complex, the C-C and Si-Si reductive elimination reactions are investigated. The reactivities of these Pd-complexes for such reactions are discussed with the electronic structures of these complexes.

**[Computational Details]** Geometry optimization was carried out with B3PW91 functional. Two kinds of basis set system (BS-I and BS-II) were employed. For H, C, N, P, and Cl, 6-31G\* were used in BS-I and cc-pVTZ basis sets were used in BS-II. The (311111/22111/411) basis set for Pd-atom was used in both BS-I and BS-II, where its core electrons were replaced by Stuttgart-Dresden-Born (SDD) ECP. To test the suitability for DFT functionals, calculations of model systems were carried out at various levels of theory. The reaction energies and population were calculated with basis set III (BS-III), where (311111/22111/411/11) basis sets was used for Pd atom with SDD ECP and cc-pVTZ basis sets for H, C, N, P, and Cl atoms.

### [Results and Discussion]

First, we investigated the electronic structure of the Pd(III) complex. In this complex, the d<sub>z</sub><sup>2</sup> orbital is SOMO. In the other possible electron configuration, the dx<sup>2</sup>-y<sup>2</sup> is SOMO. However, the latter electron configuration is much less stable than the former by 53.05 kcal/mol in the DFT calculation of the real complex and 17.85 kcal/mol in the calculations of model complex. Considering this result, we investigated the former electron configuration hereafter.

To find out suitable DFT functional, model reactions 1 to 3 shown below were considered.



The reaction energies and activation barrier in these reactions were computed with various DFT functionals and were compared with CCSD(T) values. Only B3PW91 and M06L functionals reproduce the trend in the reactivities obtained at CCSD(T) level. Here, we used B3PW91 and M06L functionals for studying the reactivity in the real Pd-complexes shown in reaction 7 to 9.

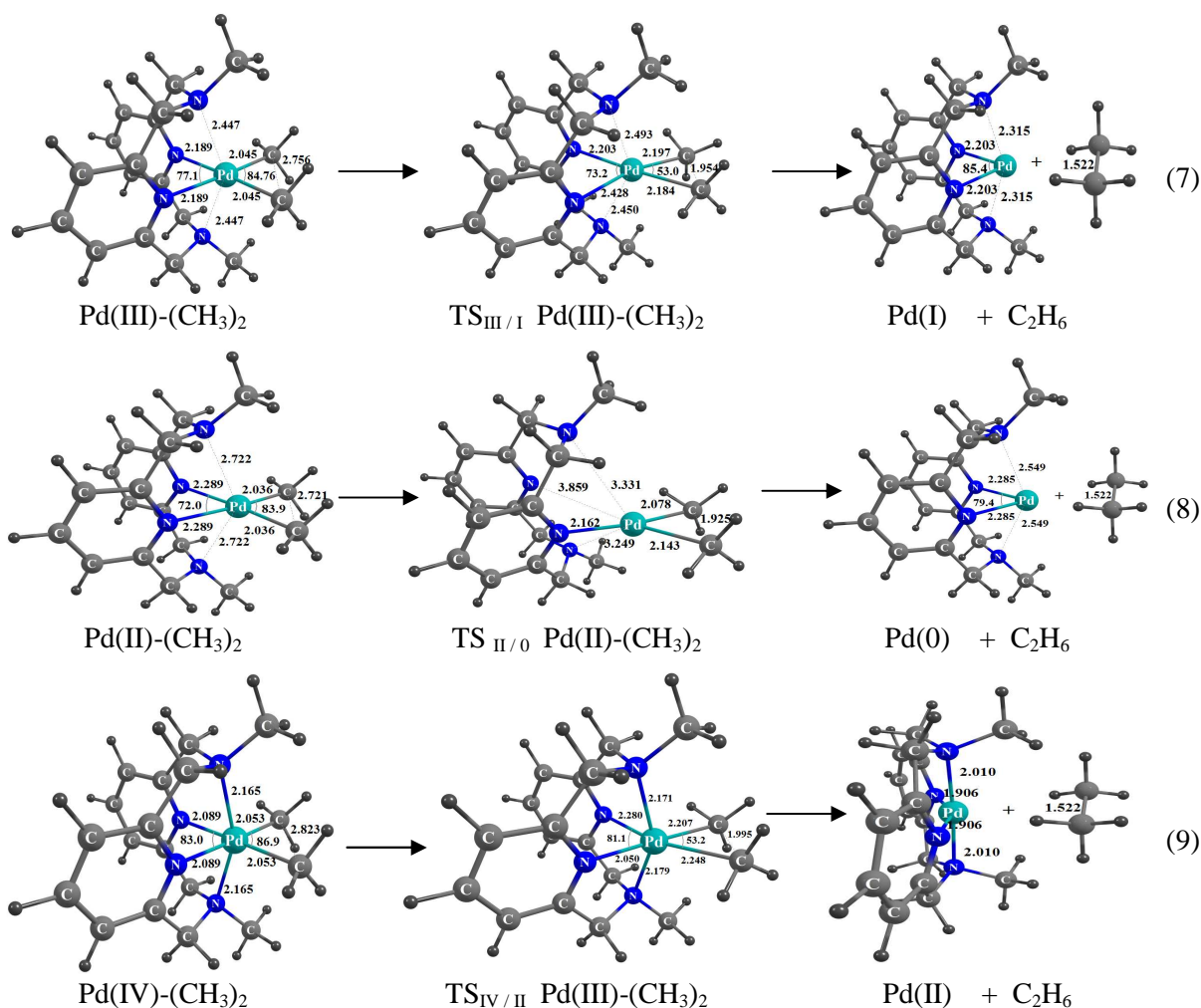


Table 1: Reaction energies, activation barrier, Pd-CH<sub>3</sub> and Pd-SiH<sub>3</sub> bond energies for reaction 7 to 12

Level of theory	Pd(III) → Pd(I) (7)			Pd(II) → Pd(0) (8)			Pd(IV) → Pd(II) (9)		
	E <sub>a</sub>	ΔE	Pd-CH <sub>3</sub> BE	E <sub>a</sub>	ΔE	Pd-CH <sub>3</sub> BE	E <sub>a</sub>	ΔE	Pd-CH <sub>3</sub> BE
B3PW91	28.5	-7.0	43.3	41.1	5.6	49.7	33.4	-10.4	41.7
Level of theory	Pd(III) → Pd(I) (10)			Pd(II) → Pd(0) (11)			Pd(IV) → Pd(II) (12)		
	E <sub>a</sub>	ΔE	Pd-SiH <sub>3</sub> BE	E	ΔE	Pd-SiH <sub>3</sub> BE	E <sub>a</sub>	ΔE	Pd-SiH <sub>3</sub> BE
B3PW91	16.6	28.5	51.1	21.8	56.5	65.1	23.1	20.7	47.2

As can be seen in Table 1, the reductive elimination of C-C bond from the Pd(III) and Pd(IV) complexes is exothermic, whereas that for Pd(II) is slightly endothermic. The activation barrier increases in the order Pd(III) < Pd(IV) < Pd(II) and the exothermicity decreases in the order Pd(IV) > Pd(III) > Pd(II). The exothermicity and small activation barrier suggest that the C-C bond elimination reactions would occur easily from Pd(IV) and Pd(III) centers. Interestingly, the reactivity of Pd(III) is close to that of Pd(IV). The Pd-CH<sub>3</sub> bond energies are correlated to reaction energies of above reactions, as expected. For instance, smaller Pd-CH<sub>3</sub> bond energy in the Pd(IV) complex is in agreement with the relatively large exothermicity of the reaction 9.

## [References]

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