Ab-initio Calculations of T-shaped Phosphine-Platinum(II) Complexes

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Summary. The geometries and total energies of several T-shaped platinum(II) complexes of the type $(H_3P)PtXY$ ($X, Y = Cl$, CH_3, SiH_3, $Si(OH)_3$) were calculated by *ab-initio* methods. In the most stable isomer, the ligand with the smallest *trans* influence is *trans* to the PH_3 ligand. The *trans* influence increases in the order $Cl < CH_3 < SiH_3 < Si(OH)_3$.

Keywords. Silyl complexes; Alkyl complexes; *Trans* influence.

Introduction

In previous work, we have investigated the influence of hemilabile chelating ligands of the type Ph_2P-*X*-NR_2 ($P \cap N$) on the reactivity of Pt(II) complexes towards organosilanes, and found a remarkable reactivity enhancement compared to the corresponding bis(phosphine) complexes [1]. All mechanistic evidence gathered so far indicates that the originally four-coordinate platinum center becomes three-coordinate during the course of the reaction when the hemi-labile ligand opens. The three-coordinate, T-shaped complexes can thus be considered activated platinum(II) complexes. In this work we report on quantum chemical calculations, which were performed to study the influence of different ligands, including their respective *trans* influences, on the structure and the total energy of T-shaped complexes. Chlorine, methyl, silyl, and siloxy were the co-ligands under consideration. To get a reasonable model of the complexes for quantum chemical calculations, the coordinated phosphorous group on the platinum was replaced by a PH_3 group, the silyl group was modeled by a SiH_3 group, and the siloxy group by a $Si(OH)_3$ group.

Results and Discussion

In the first series, complexes $(H_3P)Pt(CH_3)Cl$, with chlorine either *trans* (**1**) or *cis* (**2**) to the PH_3 ligand, were calculated (Fig. 1) as well as the complexes
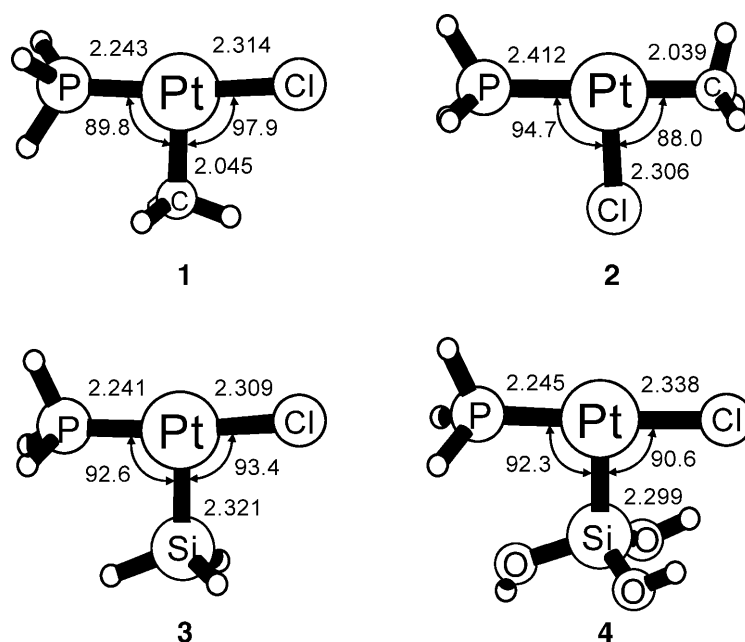
Fig. 1. Calculated geometry of structures **1**, **2**, **3**, and **4**. Unlabeled atoms are hydrogen atoms

Table 1. Calculated energies of compounds **1**, **2**, **3**, and **4**

Complex	Energy/Hartree
1	− 962.700959
2	− 962.664871
3	− 1214.141332
4	− 1440.027770

$(H_3P)Pt(SiH_3)Cl$ and $(H_3P)Pt[Si(OH)_3]Cl$ in which the methyl ligand of **1** was replaced by a SiH_3 or $Si(OH)_3$ ligand. Optimization of the SiH_3- or $Si(OH)_3$-substituted complexes with the chloride *cis* to the PH_3 ligand was not possible, since they relaxed during the optimization to the *trans* complexes **3** and **4**. This implies that a geometry where chlorine is in a *cis*-position to phosphorus is not stable at all for silyl-substituted derivatives.

The energies of the geometry-optimized complexes are summarized in Table 1. Complex **1**, where the CH_3 group is *cis* to the PH_3 ligand, is more stable by 94.5 kJ/mol compared to the corresponding *trans*-isomer **2**.

As shown in Fig. 1 the Pt–Cl and Pt–C bond lengths are similar, in contrast to the Pt–P bond which is lengthened from 2.243 Å in **1** to 2.412 Å in the less favorable **2**. This can be explained by the stronger *trans* influence of the CH_3 ligand compared to chloride which results in the longer Pt–P bond. Additionally, it can be seen from Fig. 1 that the Pt–P bond lengths in **1**, **3**, and **4** are nearly unchanged, indicating that the ligand in this *cis*-position has practically no influence on the length of the Pt–P bond.
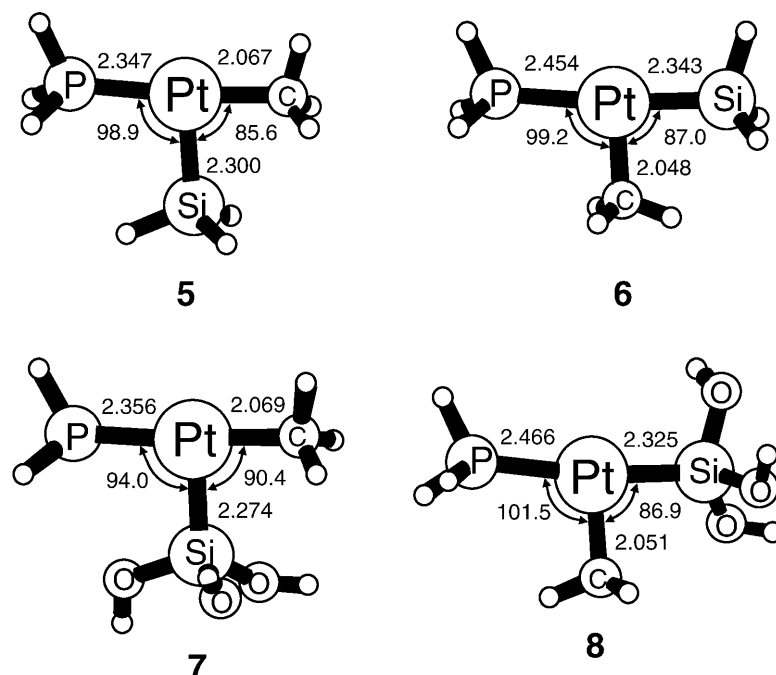
Fig. 2. Calculated geometry of structures **5**, **6**, **7**, and **8**. Unlabeled atoms are hydrogen atoms

These calculations were extended to the chlorine-free compounds $(H_3P)Pt(CH_3)(SiH_3)$ and $(H_3P)Pt(CH_3)[Si(OH)_3]$, to compare the *trans* influence of CH_3, SiH_3, and $Si(OH)_3$ in the T-shaped complexes. Figure 2 shows that the Pt–P bond length in the two $(H_3P)Pt(SiH_3)(CH_3)$ isomers **5** and **6** is 0.107 Å longer when the SiH_3 ligand is *trans* to the phosphorus atom (**6**) compared to the isomer with the SiH_3 ligand *cis* to phosphorus (**5**). The same is true for the two isomers of $(H_3P)Pt[Si(OH)_3](CH_3)$ where the Pt–P bond length is again longer by 0.110 Å when the silicon atom is *trans* to the phosphorus atom (**8**). Comparing the Pt–P bond length in **5** and **7** where the silicon atom is *cis* to phosphorus, there is a slight increase from 2.347 Å in **5** to 2.356 Å in **7**. Surprisingly, very little difference in the Pt–P bond length is observed when either a silyl or siloxy ligand is *trans* to phosphorus (2.454 Å and 2.466 Å in **6** and **8**).

Significant differences in the energy of the two isomers were also observed (Table 2). When the silicon atom is in a *cis*-position to the phosphorus atom the

Table 2. Calculated energies of structures **5**, **6**, **7**, **8**, **9**, and **10**

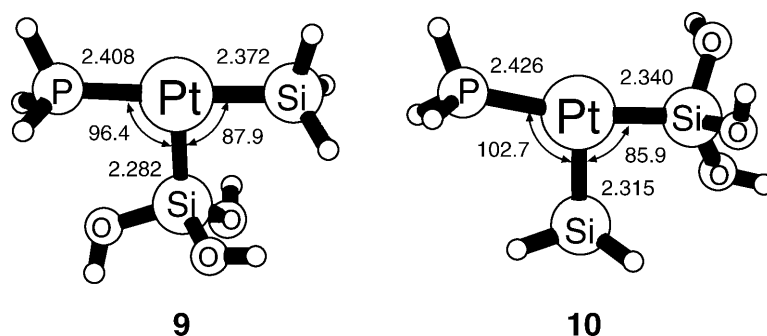| Complex	Energy/Hartree
5	− 793.751810
6	− 793.733614
7	− 1019.632664
8	− 1019.608922
9	− 1271.058587
10	− 1271.051671

Fig. 3. Calculated geometry of compounds **9** and **10**. Unlabeled atoms are hydrogen atoms

energy is 47.7 kJ/mol lower for the SiH_3-substituted complex (*i.e.*, for **5**), and 62.3 kJ/mol lower for the $Si(OH)_3$-substituted derivative (*i.e.*, for **7**) than the corresponding *trans*-isomer.

In order to investigate further the different *trans* influence of the silyl and siloxy ligands, the complexes $(H_3P)Pt[Si(OH)_3](SiH_3)$ (**9**) and $(H_3P)Pt(SiH_3)[Si(OH)_3]$ (**10**) were also calculated (Fig. 3).

The Pt–P bond is 2.408 Å when the SiH_3 group is *trans* to the PH_3 ligand and 2.426 Å when it is *cis*. This implies that the $Si(OH)_3$ ligand has a larger *trans* influence than the SiH_3 ligand. The energy difference is 18.0 kJ/mol between the more stable complex **9** and the corresponding isomer **10**.

Conclusions

The Pt–P bond lengths of the complexes shown in Figs. 1–3 suggest the following order of the considered ligands with regard to their *trans* influence: $Cl < CH_3 < SiH_3 < Si(OH)_3$. Inspection of Tables 1 and 2 shows that the complexes in which the ligand with a lower *trans* influence is *trans* to the PH_3 ligand are thermodynamically more stable than the corresponding *cis* isomers. Given a four-coordinate *bis*-phosphine platinum(II) complex, *cis*-$(R_3P)_2PtXY$, the phosphine ligand in *trans* position to the ligand with the larger *trans* influence is more easily eliminated, which means that this Pt–P bond is weaker than the other Pt–P bond. As a result, the energy required to form the three-coordinate complex is lower when the phosphine *trans* to the ligand with the higher *trans* influence is eliminated. Since the loss of a ligand is always endothermic, the more easily formed three-coordinate platinum complex is the energetically more stable complex. Therefore, comparison of the calculated energies of the relevant complexes also results in an ordering of the ligands with respect to their respective *trans* influences.

Another consequence of the calculated differences is that in the square planar complexes $(P \cap N)PtXY$ the ligand (*X* or *Y*) with the stronger *trans* influence is *trans* to the nitrogen atom of the chelating ligand. This was found earlier spectroscopically for $(P \cap N)Pt(CH_3)[Si(OMe)_3]$, where the $Si(OMe)_3$ ligand is *trans* to nitrogen [2], or for $(P \cap N)Pt(ER_3)Cl$ where $ER_3 = Me$ [3] or $SiMe_2Ph$ [4] is *trans* to N.

Computational Details

The geometry optimizations of the equilibrium geometries and transition structures were performed using the B3LYP version of DFT, which is comprised of *Becke*'s

hybrid three-parameter exchange functional [5] and the correlation functional of *Lee*, *Yang*, and *Parr* [6]. For the calculations the 6-311G ++(d) basis set was used on all atoms. The relativistic effective core potential and basis set of *Preuss* and coworkers [7] which is available in the Gaussian98 software package as SDD basis set was used for platinum. Vibrational mode analyses were carried out to confirm that on potential energy surfaces optimized geometries correspond to a local minimum that has no imaginary frequency mode or a saddle point that has only one imaginary mode. Corrections of zero-point vibrational energies were taken into account in stationary structures obtained. All of the calculations were carried out with the Gaussian98 package of electronic structure programs [8].

Acknowledgment

References

[1] Review: Schubert U, Pfeiffer J, Stöhr F, Sturmayr D, Thompson S (2002) J Organomet Chem **646**: 53

[2] Pfeiffer J, Schubert U (1999) Organometallics **18**: 3245

[3] Stöhr F, Sturmayr D, Kickelbick G, Schubert U (2002) Eur J Inorg Chem 2305

[4] Stöhr F, Sturmayr D, Schubert U (2002) J Chem Soc Chem Comm 2222

[5] Becke AD (1993) J Chem Phys **98**: 5648

[6] Lee C, Yang W, Parr RG (1988) Phys Rev B **785**: 37

[7] Andrae D, Haeussermann U, Dolg M, Stoll H, Preuss H (1990) Theor Chim Acta **123**: 123

[8] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA (1998) Gaussian 98 Gaussian, Pittsburgh, PA