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Trans Influence of Boryl Ligands and Comparison with C, Si, and Sn Ligands

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In this paper, the trans influence of boryl ligands, together with that of other ligands commonly believed to have a strong trans influence, has been investigated theoretically via density functional theory (DFT) calculations on a series of square-planar platinum(II) complexes of the form *trans*-[$\mathrm{PtL(Cl)(PMe_3)_2}$]. The following order of trans influence has been obtained: $-\mathrm{BMe_2} > -\mathrm{SiMe_3} > -\mathrm{BH_2} > -\mathrm{SnMe_3} \sim -\overline{\mathrm{BNHCH_2CH_2NH}} > -\mathrm{Bpin} > -\overline{\mathrm{BOCH_2CH_2O}} > -\overline{\mathrm{BOCH{=}CHO}} \sim -\mathrm{Bcat} \sim -\mathrm{BCl_2} \sim -\mathrm{BBr_2} \sim -\mathrm{SiH_3} > -\mathrm{CH_2CH_3} > -\mathrm{CH{=}CH_2} > -\mathrm{H} \sim -\mathrm{Me} > -\mathrm{C_6H_5} > -\mathrm{SiCl_3} > -\mathrm{SnCl_3} > -\mathrm{C{\equiv}CH}$. Natural bond order analyses have been used to understand how the substituents at the boron center affect the trans-influence properties of the boryl ligands. The major factor is the σ-donor strength of the boryl ligand. However, surprisingly, very strong π acceptors also *enhance* the trans influence.

Introduction

Transition-metal boryl complexes[1] have attracted considerable interest because of their role in catalyzed hydroboration and diboration reactions of unsaturated organics[2−4] as well as catalyzed borylation of C−H bonds in alkanes and arenes.[5] Over the past decade, there has been a healthy discussion[6−9] of the relative importance of the metal(d)-to-boryl(p_π) back-bonding interaction in the complexes. It is generally well accepted now that while there is some π component in the $\mathrm{M{-}BR_2}$ bond,[1] this is relatively weak even in $\mathrm{B(C_6F_5)_2}$ complexes.[10] Despite the controversy, it is well-known that the boryl ligands exhibit a very strong trans influence because of their strong σ-donating characteristics.[5u,11] However, several important questions remain, the answers to which should enhance our understanding of the structure and bonding in metal boryl complexes and aid in the design of new catalytic systems. How do boryl ligands compare with

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other strong trans-influence ligands, such as hydride, methyl, and silyl? What is the effect of boron substituents on the trans influence of the boryl ligands? What are the effects of substituents on C, Si, or Sn on the trans influence of alkyl, silyl, or stannyl ligands? In this paper, we focus on square-planar platinum(II) complexes in order to gain a deeper insight into the trans-influence properties of boryl ligands.

Computational Details

Molecular geometries of platinum boryl complexes were optimized at the Becke3LYP (B3LYP) level of density functional theory.[12] Frequency calculations at the same level of theory have also been performed to confirm that all stationary points were minima (no imaginary frequencies). The effective core potentials of Hay and Wadt with a double-ζ valence basis set (LanL2DZ)[13] were used to describe Pt, P, Si, Sn, and Cl atoms, while the standard 6-31G basis set was used for C, N, B, O, and H atoms. Polarization functions were added for Cl [ζ(d) = 0.514], B [ζ(d) = 0.6], Si [ζ(d) = 0.262], Sn [ζ(d) = 0.183], C [ζ(d) = 0.6], and P [ζ(d) = 0.34] that are directly bonded to the metal center.[14] All calculations were performed with the *GAUSSIAN98* software package.[15]

Results and Discussion

We carried out density functional theory (DFT) molecular orbital calculations on a series of square-planar chloroplatinum(II) complexes of the form *trans*-[PtL(Cl)(PMe_3)$_2$] to study the trans-influence properties of various types of ligands, L. These are also models for the known *trans*-[Pt(boryl)(Cl)(PR_3)$_2$] complexes.[8b,16]

Trans Influence of Bcat and Bpin. Bcat and Bpin are among the most popular boryl ligands found in transition-metal boryl complexes as a result of their applicability to catalytic processes. Therefore, we first optimized the geometries of *trans*-[Pt(Bcat)(Cl)(PMe_3)$_2$] (**1**) and *trans*-[Pt(Bpin)(Cl)(PMe_3)$_2$] (**2**) to examine the strength of the trans influences of Bcat and Bpin. We also computed optimized structures of *trans*-[Pt(T)(Cl)(PMe_3)$_2$] [T = Me (**3**), H (**4**), and SiH_3 (**5**)] for comparison. It is commonly believed that alkyl, hydride, and silyl are among the strongest trans-influence ligands. The calculated structures for the two boryl complexes and for the three complexes used for comparison are shown in Figure 1. The dihedral angle between the plane of the Bcat ligand and the platinum square plane is calculated to be 51.5° for **1**, smaller than the experimentally reported value of 78.3° for *trans*-[Pt(Bcat)(Cl)(PPh_3)$_2$].[16a] The discrepancy could well be due to use of PMe_3 in the model complex instead of PPh_3. The orientation of the boryl ligands is expected to be closely related to the metal(d)-to-boryl(p) π-back-bonding interaction. As one will see later, the π-back-bonding interaction is certainly much less important than σ effects in determining the trans influence of the boryl ligands, yet it cannot be completely ignored. Therefore, the dihedral angles, which indicate the interplanar angles between the boron trigonal plane and the platinum square plane, are given in Figure 1.

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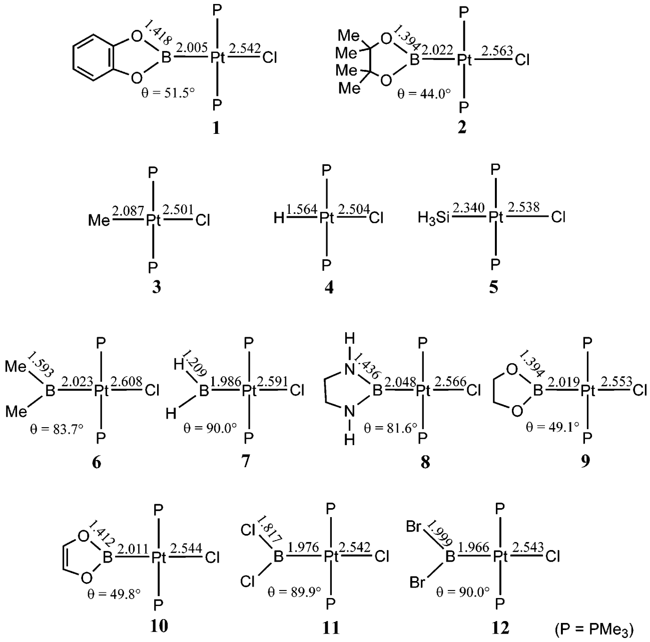

Figure 1. Calculated structures of various square-planar platinum(II) boryl complexes. For comparison, calculated structures of complexes **3**−**5** containing methyl, hydride, and silyl ligands are also given. The bond distances are given in angstroms. θ is the P−Pt−B−R dihedral angle, showing the orientation of the boryl ligand plane.

Trans influence is purely a thermodynamic phenomenon; i.e., ligands can influence the ground-state properties of groups to which they are trans such as the metal-to-ligand bond distance, the vibrational frequency or force constant, the NMR coupling constant, or a host of other parameters.[17] We know that state-of-the-art theoretical methods have the best performance in calculating molecular structures and that they give limited accuracy in calculating other physical properties, such as NMR parameters.[18] Therefore, we used calculated bond lengths as the most straightforward measure of the trans influence. As shown in Figure 1, the Pt−Cl bond lengths in the Bcat and Bpin complexes are longer than those in the other three complexes, indicating that the trans influence of the boryl ligands is certainly stronger than that of the other ligands, and we suggest that this is due to their strong σ-donating properties. Interestingly, and unexpectedly, although the Pt−Cl bond in complex **2** (2.563 Å) is longer than that in **1** (2.542 Å), the Pt−B bond in **2** (2.022 Å) is also longer than that in **1** (2.005 Å).

In general, a strong trans-influence ligand will weaken the bond between the metal and the trans ligand.[19] According to Pidcock et al.,[20] for a linear L−M−X fragment, the shorter the M−L bond, the higher the trans influence of the ligand L and the longer the M−X bond. To obtain a deeper insight into the trans influence of boryl ligands, we computed optimized structures of other platinum(II) boryl complexes.

Trans Influence of Other Boryl Ligands. Calculated bond lengths (Å) for other square-planar platinum(II) boryl complexes are shown in Figure 1. On the basis of the Pt−Cl bond distances, we conclude that (1) all of the boryl ligands studied here have a stronger trans influence than hydride, alkyl, and SiH_3 ligands and (2) the decreasing order of the trans influence for the boryl ligands is $-BMe_2 > -BH_2 > -\overline{BNHCH_2CH_2NH} > -Bpin > -\overline{BOCH_2CH_2O} > -\overline{BOCH{=}CHO} > -Bcat \sim -BCl_2 \sim -BBr_2$. Examining the Pt−B distances, we found that they do not show a close correlation with the above order, although the unexpected trend, i.e., the shorter the Pt−B bond, the shorter the Pt−Cl bond, can be found among some complexes, e.g., between **6** and **7** and among **8**−**10**. For **6** and **7**, **6** has longer Pt−B and Pt−Cl bonds while **7** has shorter Pt−B and Pt−Cl bonds. From **8** to **9** and to **10**, the Pt−B and Pt−Cl bond distances decrease simultaneously.

It is generally accepted that both the σ- and π-bonding properties of a ligand affect the strength of its trans influence. It is important to recall that the trans *influence* is a ground-state (thermodynamic) property, in contrast to the trans *effect*, which is a transition-state (kinetic) effect. Increased σ-donating ability of a ligand enhances its trans influence. However, enhanced π-accepting ability of a ligand, situated trans to a π donor, such as chloride, is expected to reduce its trans influence because it reduces the d_π-electron density on the metal center, alleviating the repulsive interaction between the metal d_π electrons and the π electrons from the ligand trans to it. Let us first investigate how the π-bonding property of a boryl ligand affects the strength of its trans influence.

We calculated the electron population of the d_π orbitals on Pt on the basis of the natural bond order (NBO) analysis[21] for the boryl complexes **1**, **2**, and **6**−**10** and plotted the population against the Pt−Cl distances, shown in Figure 2a. We do not observe a reasonable correlation between the electron population of the d_π orbitals on Pt and the Pt−Cl distances. A greater electron population of the d_π orbitals on Pt does not translate into a longer Pt−Cl bond. In other words, the π-acceptor properties of the boryl ligands are not the major factor in determining the strength of their trans influence.

The question now is how the σ-bonding properties of the boryl ligands affect their trans influence. With the aid of an NBO analysis, we can calculate the percentage (Pt %) contribution of Pt to the Pt−B σ bonds in the boryl complexes. For a given complex, the greater the percentage (Pt %) contribution to the Pt−B σ bond, the greater the σ-donating ability of the boryl ligand because this represents transfer of the electron density from the boron donor to the platinum acceptor orbitals. Figure 2b shows a plot of Pt % vs the Pt−Cl distances for the boryl complexes studied. Generally, a good correlation between Pt % in the Pt−B σ bonds and the Pt−Cl distances is observed, suggesting that

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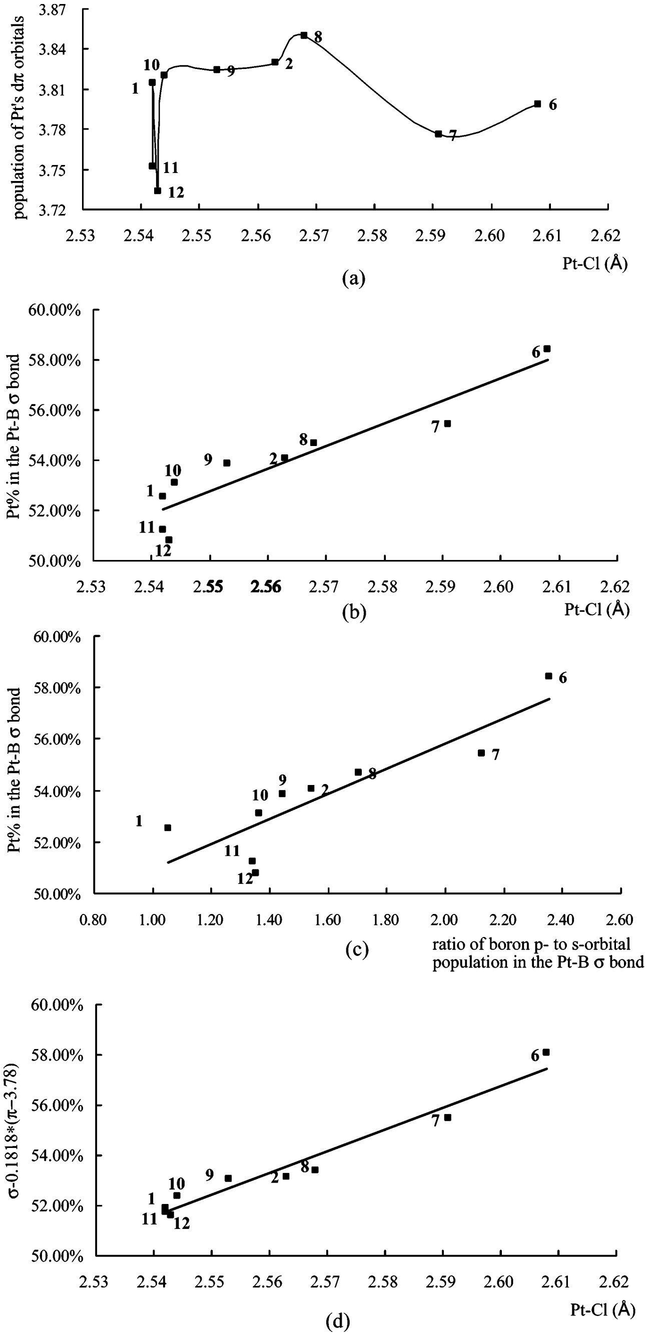
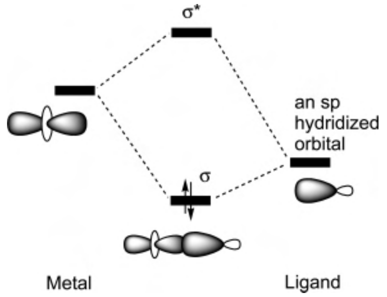


Figure 2. (a) Plot of the populations of Pt d_{π} orbitals (with respect to the Pt−Cl axis) vs the Pt−Cl distances. (b) Plot of the percentage contribution of Pt in the Pt−B σ bond against the Pt−Cl distances. (c) Plot of the percentage contribution of Pt vs the ratio of the boron p- to s-orbital population in the Pt−B σ bond. (d) Two-parameter fit considering Pt % in the Pt−B σ bond and the populations of Pt d_{π} orbitals, represented by σ and π, respectively.

the σ-donating properties of the boryl ligands play the primary role in determining the strength of their trans influence.

To understand how the substituents at B affect the Pt % contribution to the Pt−B σ bonds, we examined the ratios of the boron p- to s-orbital populations in the Pt−B σ bonds for the boryl complexes studied. A good correlation was observed between Pt % and the boron p/s population ratios in the Pt−B σ bonds (Figure 2c), with Pt % increasing with the p/s population ratio. Chart 1 illustrates a two-orbital interaction diagram between a metal d orbital and an sp-hybridized orbital from a ligand, which can help explain the good correlation. From the diagram, it is expected that the orbital energy of the ligand's sp-hybridized orbital increases with its p character because p orbitals are higher in energy than s orbitals. Therefore, the more p character that the ligand's sp-hybridized orbital has, the more covalent the interaction is between the metal and the ligand, giving rise to more contribution from the metal orbital in the metal−ligand σ bond. On the basis of the results shown in parts b and c of Figure 2, we conclude that the more boron p character in the hybrid used for Pt−B σ bonding, the greater the trans influence of the boryl ligand. This is a direct result of the fact that the more boron p character in the M−B bond, the more electron releasing the boryl ligand is. Conversely, the greater the boron s character in the Pt−B σ bond, the lower the trans influence even though the Pt−B bond is shorter because the most probable radius $r_{\max}$ of the boron s orbital is smaller than that of its p orbitals. This explains why we found that, in many cases, even when the Pt−B bond is shorter, the trans influence of the boryl ligand is actually weaker.

Chart 1



Bent's rule[22] states that more electronegative substituents "prefer" hybrid orbitals having less s character and more electropositive substituents "prefer" hybrid orbitals having more s character. Table 1 lists the boron s and p character in the Pt−B σ bond for the boryl complexes studied here together with the Pt−Cl bond distance. Interestingly, the s % character correlates well with the Pt−Cl distance that is used as a measure of the trans influence of the ligand trans to it. According to Bent's rule, we can understand that BMe_2 and BH_2 exert the strongest trans influence among the series of boryl ligands. Both Me and H substituents are relatively electropositive and "prefer" hybrid orbitals having more s character. Therefore, the boron center in each of the two boryl ligands uses a hybrid orbital having less s character to form the σ bond with Pt. The BMe_2 ligand exerts a stronger trans influence than the BH_2 ligand, reflecting the fact that Me is more electron-releasing than H.

Examining the order of trans influence for the boryl ligands studied, we see that the boryl ligand having N substituents has a greater trans influence than those having O substituents. The results reflect the electronegativity order of N < O; i.e.,

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Table 1. Boron s and p Character in the Pt−B σ Bond Together with the Pt−Cl Bond Distance

trans-[PtL(Cl)(PMe$_3$)$_2$]	L	Pt−Cl (Å)	s %	p %
6	$-\mathrm{BMe_2}$	2.608	12.4	29.1
7	$-\mathrm{BH_2}$	2.591	14.2	30.3
8	$-\mathrm{BNHCH_2CH_2NH}$	2.566	16.8	28.5
2	−Bpin	2.563	18.4	27.6
9	$-\mathrm{BOCH_2CH_2O}$	2.553	18.9	27.2
10	$-\mathrm{BOCH{=}CHO}$	2.544	19.8	27.0
12	$-\mathrm{BBr_2}$	2.543	20.9	28.3
11	$-\mathrm{BCl_2}$	2.542	20.8	27.9
1	−Bcat	2.542	23.1	24.3

boryl ligands having more electronegative substituents have a weaker trans influence.

Among the four boryl ligands having O substituents, Bpin and its ethylene glycolato analogue, $\mathrm{BOCH_2CH_2O}$, have stronger trans influences than Bcat and its analogue, $\mathrm{BOCH{=}CHO}$. Because of the geometrical requirement resulting from the presence of sp^2 carbons and the aromatic ring capable of removing electron density from the oxygens, the B−O σ bonds are relatively weaker in Bcat and its analogue than those in Bpin and its analogue.[1g] The B−O bond distances differ by 0.02 Å between the two types of ligands. Because of the weaker B−O bonding interactions, the B center in Bcat or its analogue uses hybrid orbitals having more p character to form σ bonds with O and a hybrid orbital having more s character to form the σ bond with Pt, evidenced by the shorter Pt−B bonds in **1** and **10** when compared with those in **2** and **9**. Therefore, the hybrid orbital in Bcat or its analogue used to form the σ bond with the metal center is less electron-releasing, leading to the observation that Bcat and its analogue have a weaker trans influence than Bpin and its analogue.

Interestingly, the trans influence of the BX$_2$ (X = Cl and Br) ligands is comparable to that of Bcat, although Cl and Br are less electronegative than O. At first glance, Bent's rule appears applicable only to those boryl ligands having substituents in which the boron-bonded atoms lie in the second period. The B−X bonds are much longer than the B−C, B−N, and B−O bonds. We would expect that the orbitals of X overlap better with the p orbitals than with the s orbitals of boron. This is why the trans influence of the halide-substituted boryl ligands is the weakest in the series. However, we note that for compounds **7**, **11**, and **12**, for which strong π back-bonding is expected and for which the dihedral angles of 90° maximize the π bonding, we find a stronger trans influence than would be expected from Pt % values (Figure 2b). While this is unexpected, the most reasonable explanation is that the π bonding leads to exceptionally short Pt−B separations, which, in turn, lead to stronger σ donation than that expected on the basis of the p/s ratio in the σ bond (Figure 2c). Therefore, a two-parameter fit was explored with a small and *negative* coefficient for the π-bonding component. As can be seen in Figure 2d, this leads to an excellent fit, with the coefficient for the π component being −0.18 compared with that of the σ coefficient. Thus, we can conclude that the σ effect is approximately 5−6 times more important than the π effect and that the π effect is in the opposite sense to what would have been anticipated.

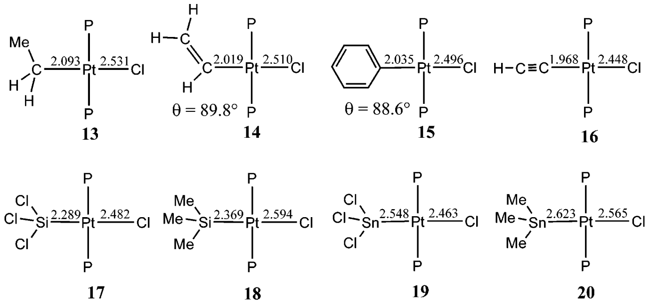

Figure 3. Calculated structures for various square-planar platinum(II) complexes having donor ligands derived from the carbon group atoms. The bond distances are given in angstroms. θ is the P−Pt−C−C dihedral angle, showing the orientation of the vinyl and phenyl ligand planes.

Trans Influence of $-\mathrm{CH_2CH_3}$, $-\mathrm{CH{=}CH_2}$, $-\mathrm{C_6H_5}$, and $-\mathrm{C{\equiv}CH}$. Figure 3 shows the optimized structures calculated for the *trans*-Pt(R)Cl(PMe$_3$)$_2$ complexes (**13**−**16**). The trans influence decreases in the order of $-\mathrm{CH_2CH_3} > -\mathrm{CH{=}CH_2} > -\mathrm{C_6H_5} > -\mathrm{C{\equiv}CH}$. Interestingly, we also see the unexpected trend that the shorter the Pt−C bond, the shorter the Pt−Cl bond is. The Muirs[23] explained this unexpected trend by their "metal-to-ligand π-back-bonding" model. They suggested that the trans influence of the carbon-donor ligands depended mainly on the extent of M−C π back-bonding, which reduces the d$_\pi$-electron density on the metal center, alleviating the repulsive interaction between the metal d$_\pi$ electrons and the π electrons from the ligand trans to the one in question. According to the Muirs,[23] the $-\mathrm{CH_2CH_3}$ ligand would be expected to have the strongest trans influence because it does not have low-lying π* orbitals, while the $-\mathrm{C{\equiv}CH}$ ligand is expected to be the weakest trans-influence ligand among the four carbon-donor ligands because it has two available π* orbitals. In fact, many studies[24] show that acetylide ligands are poor π acceptors and appear to be modest π donors, inconsistent with the argument of the Muirs.

A reasonable, although not perfect, correlation between the d$_\pi$-orbital populations and the Pt−Cl distances is illustrated in Figure 4a, suggesting that the π model may be justified for the four carbon-donor ligands studied here. However, we note that the variation in the population of the Pt d$_\pi$ orbitals in the series **13**−**16** is very small, so π bonding must also be rather weak. Can the σ model also explain the trans-influence order of the four carbon-donor ligands as it does for the boryl ligands? To answer this question, we plotted both the percentage (Pt %) contribution of Pt to the Pt−C σ bonds against the Pt−Cl distances, shown in Figure

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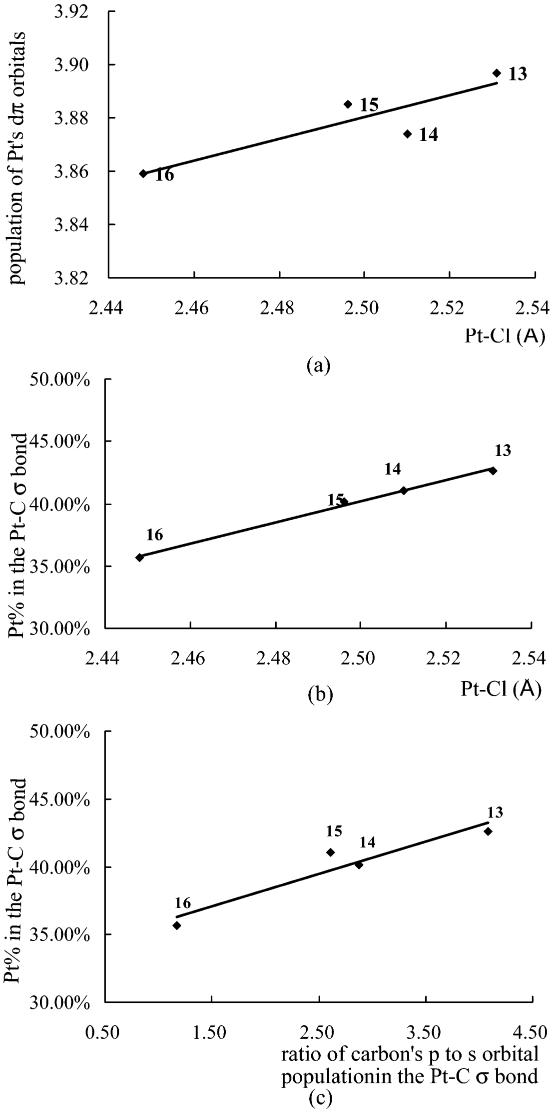

(a)

(b)

(c)

Figure 4. (a) Plot of the populations of Pt d_π orbitals (with respect to the Pt−Cl axis) vs the Pt−Cl distances. (b) Plot of the percentage contribution of Pt in the Pt−C σ bond against the Pt−Cl distances. (c) Plot of the percentage contribution of Pt against the ratio of carbon p- to s-orbital population in the Pt−C σ bond.

4b, and the percentage (Pt %) contributions against the carbon p/s population ratios, shown in Figure 4c. Good correlations are found in both cases, suggesting that the σ model developed for the boryl ligands is also applicable to the carbon-donor ligands. In the ethyl complex, *trans*-Pt(CH_2CH_3)Cl(PMe_3)$_2$ (**13**), the Pt-bonded carbon is formally sp^3-hybridized, while in the acetylide complex, *trans*-Pt(C≡CH)Cl(PMe_3)$_2$ (**16**), the Pt-bonded carbon is formally sp-hybridized. In **13**, the Pt-bonded carbon uses a hybrid orbital having more p and less s character for Pt−C bonding. As a result, the hybrid orbital used is more electron-releasing and exerts a greater trans influence. Again, the more p and less s character in the Pt−C bond, the longer the bond, so the ethyl complex has the longest Pt−C bond but the strongest trans influence among the four complexes with carbon-donor ligands.

Trans Influence of $SiCl_3$, $SiMe_3$, $SnCl_3$, and $SnMe_3$. Because compounds containing Pt−Si or Pt−Sn bonds are frequently found as intermediates in transition-metal-mediated organic synthesis,[25] the trans influence of $SiCl_3$, $SiMe_3$, $SnCl_3$, and $SnMe_3$ was also investigated. Figure 3 shows the optimized structures calculated for complexes **17**−**20**. On the basis of the Pt−Cl distances, we find the following order of the trans influence: $SiMe_3 > SnMe_3 > SiCl_3 > SnCl_3$. The Me subsitituents have a profound effect on the trans influence of the ligands. Sn and Si have similar electronegativities and electron affinities.[26] The Pt−Si bond distances are much shorter (by ca. 0.25 Å) than the Pt−Sn ones. Therefore, $SiCl_3$ (or $SiMe_3$) exerts a stronger trans influence than $SnCl_3$ (or $SnMe_3$).

Conclusion

The trans influence of boryl ligands, together with other ligands commonly believed to have a strong trans influence, has been investigated, theoretically, via DFT calculations on a series of square-planar platiumn(II) complexes. The following order of trans influence has been obtained: $-BMe_2 > -SiMe_3 > -BH_2 > -SnMe_3 \sim -\overline{BNHCH_2CH_2NH} > -Bpin > -\overline{BOCH_2CH_2O} > -\overline{BOCH{=}CHO} \sim -Bcat \sim -BCl_2 \sim -BBr_2 \sim -SiH_3 > -CH_2CH_3 > -CH{=}CH_2 > -H \sim -Me > -C_6H_5 > -SiCl_3 > -SnCl_3 > -C{\equiv}CH$.

The boryl ligands are among the strongest trans-influence ligands. On the basis of NBO analyses, a σ model emphasizing the Pt−B σ-bonding interaction for the platinum boryl complexes has been proposed to explain the order of the trans influence of the boryl ligands. A boryl ligand having a greater σ-donating ability uses a hybrid orbital having more p character to form the σ bond with Pt. Substituents on the boryl ligands tune the hybrid used for the Pt−B σ bonding and therefore affect the ligand's trans influence.

Our NBO analyses show that the σ model is also applicable to carbon-donor ligands, such as $-CH_2CH_3$, $-CH{=}CH_2$, $-C_6H_5$, and $-C{\equiv}CH$. The previously proposed π model,[23] which emphasizes the Pt−C π-back-bonding interaction, would only explain the order of the trans influence if one assumes that the acetylide ligand is a good π acceptor, which is known not to be the case. Indeed, for the series of four hydrocarbon ligands above, the σ model suffices without the need for significant π correction.

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Supporting Information Available: Cartesian coordinates for all of the calculated structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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