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Hajime Kameo, Yudai Tanaka, Yoshihiro Shimoyama, Daisuke Izumi, Hiroyuki Matsuzaka, et al..  
Square-Planar Anionic Pt(0) Complexes. *Angewandte Chemie International Edition*, 2023, 62 (20),  
10.1002/anie.202301509 . hal-04288599

**HAL Id: hal-04288599**

**<https://hal.science/hal-04288599>**

Submitted on 16 Nov 2023

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# Square-Planar Anionic Pt(0) Complexes

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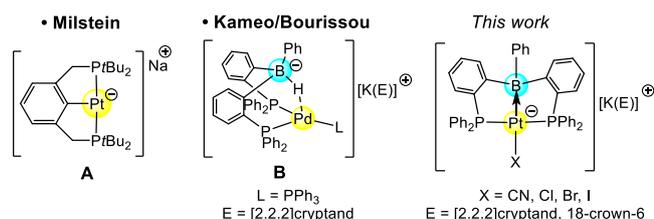
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## Abstract:

*A T-shaped Pt(0) complex with a diphosphine-borane (DPB) ligand was prepared. The Pt→B interaction enhances the electrophilicity of the metal and triggers the addition of Lewis bases to give the corresponding tetracoordinate complexes. For the first time, anionic Pt(0) complexes are isolated and structurally authenticated. X-ray diffraction analyses show the anionic complexes [(DPB)PtX]<sup>-</sup> (X = CN, Cl, Br, I) to be square-planar. The d<sup>10</sup> configuration and Pt(0) oxidation state of the metal were unambiguously established by X-ray photoelectron spectroscopy and DFT calculations. The coordination of Lewis acids as Z-type ligands is a powerful mean to stabilize elusive electron-rich metal complexes and achieve uncommon geometry.*

Anionic M(0) complexes (M = Group 10 metals) are important but elusive species. Following the pioneering work of Amatore and Jutand, they have been established and are now widely recognized as key intermediates in a number of catalytic cross-couplings such as the Heck, Stille, Suzuki and Buchwald-Hartwig reactions.<sup>[1,2]</sup> Nonetheless, the number and variety of such complexes to be characterized and/or isolated remain limited, and only anionic Ni(0) and Pd(0) species have been authenticated essentially.<sup>[3]</sup>

The literature about anionic Pt(0) complexes is extremely scarce, probably due to the higher Lewis basicity of Pt(0),<sup>[4]</sup> which makes the isolation of such electron-rich zerovalent complexes extremely challenging. The pioneering contribution by Reger and Ding dates back to 1994.<sup>[5]</sup> Deprotonation of the Pt(II) hydrido complex (Me<sub>2</sub>NCS<sub>2</sub>)Pt(PEt<sub>3</sub>)H at low temperature was reported to generate an anionic Pt(0) complex, which could only be characterized by <sup>31</sup>P NMR spectroscopy at -41°C. About 15 years later, Milstein *et al* took advantage of a sterically demanding PCP pincer ligand to isolate an anionic Pt(0) complex (Figure 1).<sup>[6]</sup> It was obtained by reduction of (PCP)Pt(II)X (X = Cl, BF<sub>4</sub>) precursors with sodium and proved stable at room temperature for days. The [(PCP)Pt][Na] complex **A** was characterized by multi-nuclear spectroscopy. No X-ray diffraction analysis could be performed, but a T-shaped structure was predicted by Density Functional Theory (DFT) calculations for the naked complex (without the Na<sup>+</sup> counter-cation).

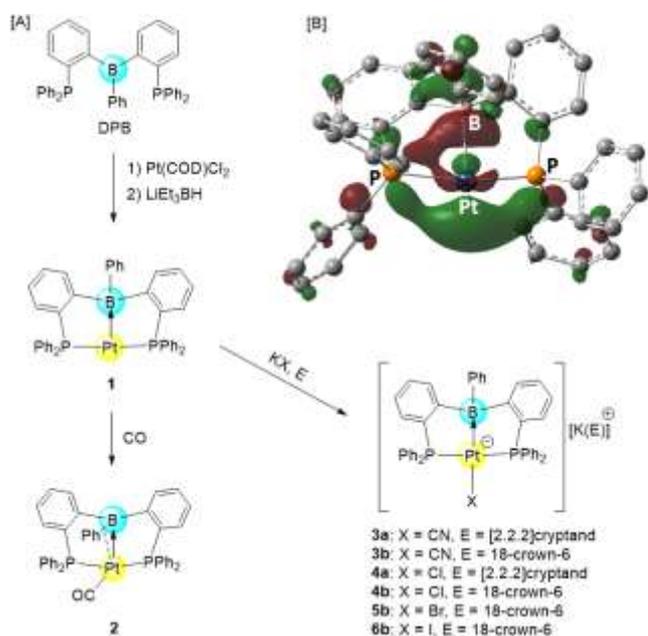


**Figure 1.** Isolable anionic Pt(0)<sup>[6]</sup> and Pd(0)<sup>[3d]</sup> complexes.

The coordination of Lewis acids as Z-type ligands has attracted considerable interest over the past 20 years from structural/bonding perspectives as well as reactivity/catalysis purposes.<sup>[7]</sup> Of note, we have recently demonstrated the ability of the diphosphine-borane ligand {(*o*-Ph<sub>2</sub>P)C<sub>6</sub>H<sub>4</sub>}BPh (DPB) to stabilize a monomeric anionic Pd(0) complex **B** featuring a Pd–H–B bridge (Figure 1).<sup>[3d]</sup> In the current work, we have explored the possibility to access anionic Pt(0) complexes with the DPB ligand. As reported hereafter, Pt→B interaction was found to enable the addition of Lewis bases to Pt(0), affording a straightforward and mild entry to the targeted complexes (Figure 1). Thorough analysis of their structure and bonding revealed a very uncommon combination of square-planar geometry and d<sup>10</sup> Pt(0) configuration.

Due to their electron-withdrawing character, Z-type ligands are well-suited to stabilize low-valent electron-rich complexes<sup>[8]</sup> and we surmised that a coordinatively unsaturated Pt→borane complex such as **1** could stand as a promising precursor for anionic Pt(0) complexes.<sup>[9]</sup> Complex **1** was synthesized in two steps, *ie* coordination of the diphosphine-borane DPB to Pt(II) using (COD)PtCl<sub>2</sub>, followed by reduction with LiHBEt<sub>3</sub> (Scheme 1A). Its structure was ascertained by multi-nuclear NMR spectroscopy and crystallography.<sup>[10]</sup> The Pt center is 3-coordinate and T-shaped (Figure 2): the two phosphines sit *trans* to each other [P–Pt–P 159.81(2)°] and the Pt–B bond distance is short at 2.216(3) Å.<sup>[11]</sup> The coordination of the borane moiety to Pt is expected to enhance its electrophilicity, as supported by DFT calculations. Indeed, the LUMO (Lowest Unoccupied Molecular Orbital) of

complex **1** shows major contributions from a 5d(Pt) orbital and a 2p(B) orbital (Scheme 1B) and it sits significantly lower in energy than that of the related bis-phosphine platinum(0) complex Pt(PPh<sub>3</sub>)<sub>2</sub> (0.12 versus 0.79 eV).



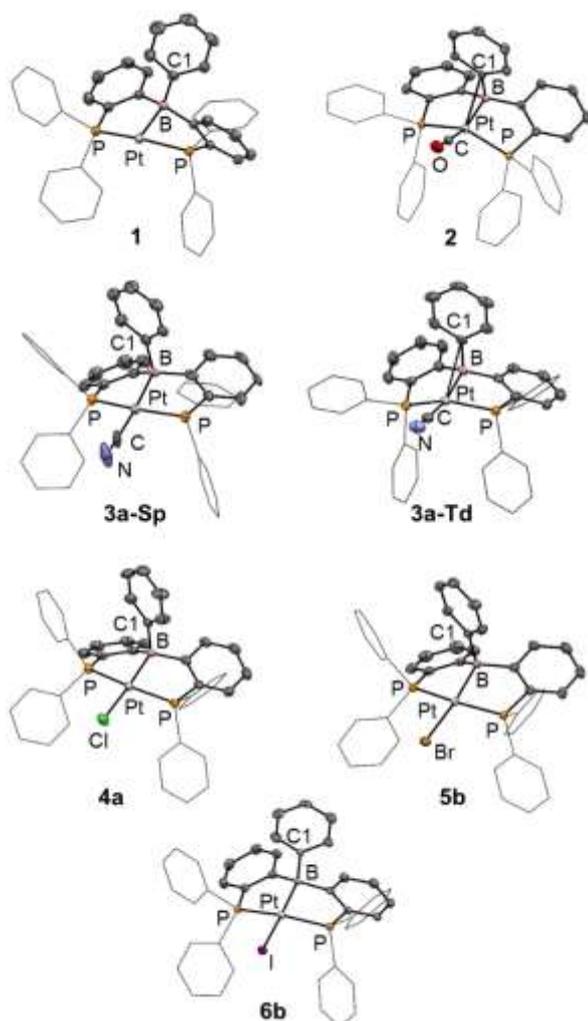
**Scheme 1.** [A] Synthesis of the T-shaped (DPB)Pt complex **1**, coordination of additional ligands to Pt giving the neutral complex **2** and the anionic Pt complexes **3-6**. [B] LUMO of **1** (isovalue = 0.4).

The coordinatively unsaturated nature of the Pt center in complex **1** was first probed by reacting it with CO to give complex **2**. Infra-red spectroscopy ( $\nu_{\text{CO}}$  1994.0 cm<sup>-1</sup>) and X-ray diffraction (Figure 2) substantiated the ligation of CO to Pt and revealed a noticeable change in the coordination of the DPB ligand. The BPh moiety is  $\eta^2$ -BC<sub>ipso</sub> bonded to the metal center (as apparent from the short Pt–B and Pt–C<sub>ipso</sub> distances, 2.285(4) and 2.474 Å, respectively)<sup>[12]</sup> while the P–Pt–P skeleton is strongly bent (126.38(4)<sup>o</sup>), resulting in tetrahedral geometry at Pt, as typically expected for a tetracoordinate d<sup>10</sup> complex. The facile addition of CO to complex **1** encouraged us to investigate then the formation of an anionic Pt(0) complex. To start with, we studied the addition of CN<sup>-</sup>, which is isoelectronic with CO, using KCN in the presence of [2.2.2]cryptand or 18-crown-6. Gratifyingly, the corresponding anionic Pt complexes [(DPB)PtCN][K(E)] (E = [2.2.2]cryptand (**3a**), 18-crown-6 (**3b**)) formed readily (80-84% isolated yields). Interestingly, X-ray diffraction analysis revealed the presence of two independent molecules in the asymmetric unit of **3a** (Figure 2). They are both tetracoordinate Pt cyanide complexes but they differ noticeably in geometry (Table 1). One, referred as **3a-Sp**, is square-planar ( $\Sigma(\text{Pt}) = 361.34(33)^\circ$ ) with the incoming CN ligand in *trans* position to the boron atom (B–Pt–CN: 173.6(3)<sup>o</sup>). The Pt–B distance (2.253(6) Å) is comparable to that found in **2**, but the C<sub>ipso</sub> carbon of the B–Ph moiety remains far from the Pt center (> 3 Å), indicating  $\eta^1$ -B not  $\eta^2$ -BC<sub>ipso</sub> coordination in this case. The other form of the complex, referred as **3a-Td**, significantly deviates from square-planar ( $\Sigma(\text{Pt}) = 367.99(32)^\circ$ ). The bent P–Pt–P fragment (144.09(5)<sup>o</sup>) and the short Pt–C<sub>ipso</sub> distance (2.845 Å) are reminiscent of the structure of **2**, although the  $\eta^2$ -BC<sub>ipso</sub> interaction with the Pt center is apparently weaker in **3a-Td** than in **2**. As such, the geometry of **3a-Td** falls in between the square-planar complex **3a-Sp** and the tetrahedral complex **2**. Of note, complex **3b** featuring a K(18-C-6)<sup>+</sup> counter-cation was also crystallographically characterized.<sup>[10]</sup> Only the square-planar form was authenticated in this case, with geometric features very similar to those of **3a-Sp**.

**Table 1.** Key geometric data for platinum complexes **1-6** (bond lengths in Å, bond angles in °) and atomic contributions to the NLMO accounting for the Pt→B interaction.

Complexes	$\Sigma(\text{Pt})^{[a]}$	Pt–B	Pt–C <sub>ipso</sub>	P–Pt–P	Pt–B–C <sub>ipso</sub>	NLMO(Pt/B) <sup>[b]</sup>
<b>1</b>	-	2.216(3)	3.072	159.81(2)	105.63(14)	79.9/18.2
<b>2</b>	376.68(23)	2.285(4)	2.474	126.38(4)	76.5(2)	72.0/23.6
<b>3a-Sp</b>	361.34(33)	2.253(6)	3.094	160.00(5)	103.7(3)	51.5/37.9
<b>3a-Td</b>	367.99(32)	2.240(6)	2.845	144.09(5)	92.9(3)	53.5/35.5
<b>3b</b>	361.73(32)	2.244(6)	3.080	158.01(4)	103.0(3)	-
<b>4a</b>	361.52(9)	2.219(2)	3.051	160.53(2)	103.80(15)	60.5/30.3
<b>5b</b>	361.68(13)	2.213(3)	3.028	160.26(3)	102.93(18)	61.4/32.5
<b>6b</b>	363.49(14)	2.216(3)	3.004	155.77(3)	100.9(2)	62.8/29.6

<sup>[a]</sup>Sum of the two P–Pt–B and two P–Pt–X angles (X = CO, CN, Cl, Br, I). <sup>[b]</sup>Calculations performed on the naked anionic complexes at the wB97XD/SDD(Pt,Br),6-311+G(d) (other atoms) level of theory.

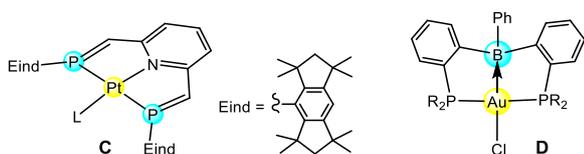


**Figure 2.** Molecular structures of the (DPB)Pt complexes **1-6** (thermal ellipsoids at 40% probability). For clarity, the [K(18-crown-6)]<sup>+</sup> / [K([2.2.2]-cryptand)]<sup>+</sup> cations and hydrogen atoms are omitted, and the Ph substituents (except those bonded to B) are simplified.

The formation and structure of the anionic (DPB)Pt(CN)<sup>−</sup> complexes **3a,b** prompted us to investigate then the addition of  $\pi$ -donor ligands to Pt. The potassium salts KCl, KBr and KI smoothly reacted with complex **1** in the presence of [2.2.2]cryptand or 18-crown-6 to afford the targeted complexes [(DPB)Pt(Cl)][K(E)] **4a,b** (E = [2.2.2]cryptand, 18-crown-6), [(DPB)Pt(Br)][K(18-crown-6)] **5b** and [(DPB)Pt(I)][K(18-crown-6)] **6b** (Scheme 1). **4a**, **5b** and **6b** were crystallographically characterized

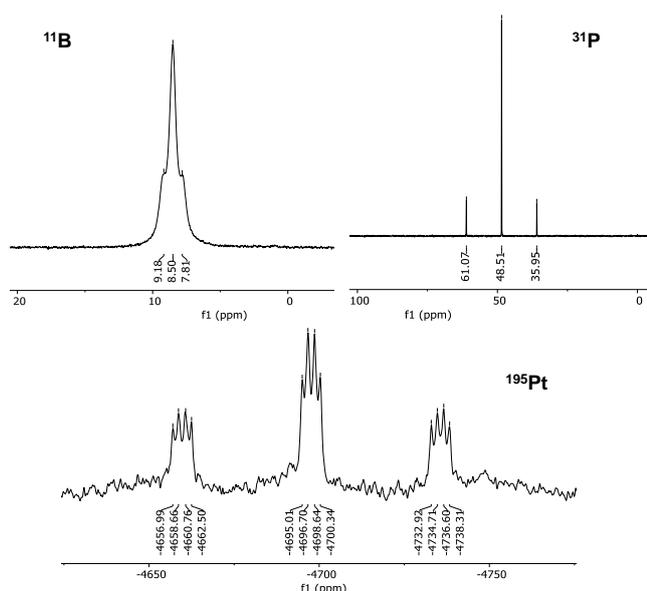
(Figure 2) and found to be tetracoordinate square-planar anionic Pt complexes ( $\sum(\text{Pt}) = 361.52(9)^\circ$  for **4a**,  $361.68(13)^\circ$  for **5b**,  $363.49(14)^\circ$  for **6b**) similar to **3a-Sp** and **3b**.

The square-planar geometry at Pt deserves special attention since tetracoordinate  $d^{10}$  complexes are normally tetrahedral. Using a PNP ligand, Ozawa *et al* recently prepared original pincer complexes **C** authenticated as square-planar Pt(0) complexes (Figure 3A).<sup>[13]</sup> Here, the strongly  $\pi$ -accepting phosphalkene sidearms withdraw electron density from Pt. The square-planar geometry was unambiguously established by X-ray diffraction. Based on DFT calculations, it was proposed to result from the interaction between a Pt center in  $d^9s^1$  configuration and a diradical (LX<sub>2</sub>-type) form of the PNP ligand. The genuine Pt(0) character has however not been inferred experimentally. Of note, the anionic [(DPB)Pt(X)]<sup>-</sup> complexes **3-6** are structurally very similar to the gold complexes (DPB)AuCl **D** (Figure 3),<sup>[14]</sup> whose  $d^{10}$  configuration and Au(I) oxidation state was supported by Mössbauer analyses.<sup>[15]</sup>



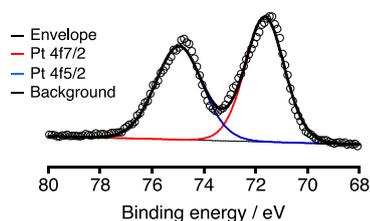
**Figure 3.** Ozawa's square-planar Pt(0) complexes **C** (L = PPh<sub>3</sub>, CO, DMAP)<sup>[13]</sup> and square-planar (DPB)Au(I) complexes **D** (R = Ph, *i*Pr).<sup>[14]</sup>

Given their unusual square-planar geometry, particular attention was given to the electronic structure of complexes **3-6** with the aim to assess the configuration and oxidation state of Pt. We first referred to spectroscopic data (See Figure 4 for representative <sup>11</sup>B, <sup>31</sup>P, <sup>195</sup>Pt NMR spectra associated with complex **3b**). The large <sup>1</sup>J<sub>Pt-P</sub> coupling constants (4068.5 Hz for **3b**, 4295.6 Hz for **4b**, 4293.5 Hz for **5b**, 4288.9 Hz for **6b**, as readily determined from the <sup>195</sup>Pt satellite peaks in the <sup>31</sup>P NMR spectra) fall in the typical range for referential Pt(0) complexes (3829 Hz for Pt(PPh<sub>3</sub>)<sub>4</sub>, 4438 Hz for Pt(PPh<sub>3</sub>)<sub>3</sub><sup>[16a]</sup>) and close to that found by Milstein *et al* for the anionic Pt(0) complex [(PCP)Pt][Na] **A** (3874 Hz), while referential Pt(II) complexes display much lower values (2634.5 Hz for *trans*-(Ph<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub><sup>[16b]</sup>).<sup>[17]</sup> All the anionic (DPB)Pt complexes were also characterized by <sup>195</sup>Pt NMR spectroscopy, showing low-field resonances ( $\delta$  -4698 ppm for **3b**, -4638 ppm for **4b**, -4733 ppm for **5b** and -4840 ppm for **6b**) as the [(PCP)Pt][Na] complex **A** ( $\delta$  -4034 ppm)<sup>[6]</sup> and (TPB)Pt ( $\delta$  -3623 ppm).<sup>[9b]</sup> It is also worth noting that <sup>1</sup>J<sub>B-Pt</sub> couplings were eventually observable and measurable in the <sup>195</sup>Pt{<sup>1</sup>H} and/or <sup>11</sup>B{<sup>1</sup>H} NMR spectra.<sup>[18]</sup> The coupling constant was found to increase substantially from the cyanide complex **3** (180 Hz) to the chloro, bromo and iodo complexes **4**, **5** and **6** (> 280 Hz),<sup>[10]</sup> in line with the  $\pi$ -accepting (CN) /  $\pi$ -donating (Cl, Br, I) nature of the X co-ligand and its weakening/strengthening impact on the Pt→B interaction in *trans* position.



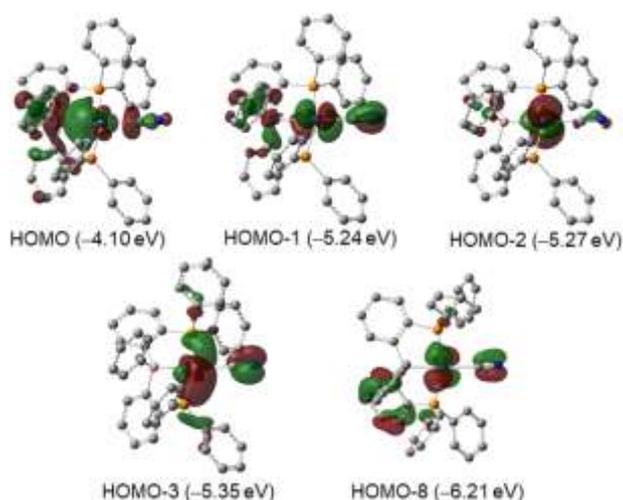
**Figure 4.**  $^1\text{H}$ -Decoupled heteronuclear NMR spectra for the anionic  $(\text{DPB})\text{Pt}(\text{CN})^-$  complex **3b**.<sup>[10]</sup>

The  $(\text{DPB})\text{Pt}$  complexes were also characterized by X-ray photoelectron spectroscopy (XPS) to further probe the oxidation state of Pt (Figure 5).<sup>[10]</sup> Accordingly, all the anionic complexes **3-6** display bonding energies of the Pt  $4f_{7/2}$  orbital (71.7 eV for **3b**, 71.7 eV for **4b**, 71.6 eV for **5b**, 71.5 eV for **6b**) very close to referential Pt(0) complexes (71.6 eV for  $\text{Pt}(\text{PPh}_3)_4$  and  $\text{Pt}(\text{PPh}_3)_3$ ) but very distinct from referential Pt(II) complexes (72.7 eV for  $(\text{Et}_3\text{P})_2\text{PtPh}_2$  and 72.8 eV for  $(\text{Et}_3\text{P})_2\text{Pt}(\text{H})(\text{Cl})$ <sup>[19]</sup>), definitely confirming the  $d^{10}$  configuration and Pt(0) oxidation state of the metal.



**Figure 5.** XPS spectra for the anionic  $(\text{DPB})\text{Pt}(\text{CN})^-$  complex **3b**.

The description of complexes **3-6** as anionic Pt(0) complexes is further supported computationally by the inspection of their molecular orbitals (MOs). The presence of five doubly-occupied  $5d(\text{Pt})$ -centered orbitals (see Figure 6 for complex **3-Sp**) confirms the  $d^{10}$  configuration. One MO shows bonding interaction between the in-plane  $5d_{x^2-y^2}(\text{Pt})$  orbital and a  $2p(\text{B})$ -based orbital. It accounts for the  $\text{Pt} \rightarrow \text{B}$  interaction and stands as the HOMO (Highest Occupied Molecular Orbital). Consistently, the Natural Localized Molecular Orbital (NLMO) accounting for the  $\text{Pt} \rightarrow \text{B}$  interaction has major contribution from Pt (51-61%, versus 30-38% for B) (Table 1).<sup>[20]</sup> Note that the DFT calculations nicely reproduce the tendency of the DPB Pt(0) complexes to adopt square-planar geometry. This was the only form found as energy minimum for the chloro, bromo and iodo complexes **4-6**. For the cyanide and carbonyl complexes, both a square-planar and a tetrahedral structure were located on the potential energy surface. In line with experimental observations, the two forms are very close in energy for the  $(\text{DPB})\text{Pt}(\text{CN})^-$  complex **3** ( $\Delta G$  0.1 kcal/mol),<sup>[21]</sup> while the tetrahedral form is slightly more stable for the neutral carbonyl complex **2** (by 2.3 kcal/mol in Gibbs free energy). The  $\pi$ -accepting CO/ $\text{CN}^-$  ligands withdraw electron-density from Pt and make the BPh moiety to shift from  $\sigma^1\text{-B}$  to  $\sigma^2\text{-BC}_{\text{ipso}}$  coordination.



**Figure 6.** Doubly-occupied 5d(Pt)-centered molecular orbitals of **3-Sp** (wB97XD/SDD(Pt,Br),6-311+G(d) (other atoms)).

In conclusion, the T-shaped complex **1** whose electrophilicity is enhanced by Z-type coordination of the borane moiety, was found to readily react with potassium salts KX (X = CN, Cl, Br, I) in the presence of [2.2.2]cryptand or 18-crown-6 to afford **3-6**, the first anionic Pt(0) complexes to be structurally characterized. X-Ray photoelectron spectroscopy (XPS) unequivocally authenticated **3-6** as  $d^{10}$  Pt(0) complexes. X-Ray diffraction analyses and DFT calculations showed that the cyanide complex **3** may adopt both square-planar and tetrahedral geometries, the two forms being actually very close in energy. With  $\pi$ -donating ligands such as Cl, Br and I, only the square-planar form is observed, with bonding Pt $\rightarrow$ B interaction between the in-plane  $5d_{x^2-y^2}$ (Pt) orbital and a  $2p$ (B) orbital. Future studies will aim to further explore and exploit the ability of ambiphilic ligands to stabilize elusive low-valent metal complexes and to impart unusual electronic/geometric structures.

## Acknowledgements

This work was supported by JSPS KAKENHI Grant Numbers JP21H01953, JP21K18987, JP21K05088 from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. H.K. acknowledges the financial support from the Iketani Science and Technology Foundation. The Centre National de la Recherche Scientifique (CNRS) and the Agence Nationale de la Recherche (ANR-22-CE07-0001) are acknowledged for financial support of this work. H.K. thanks the Université Paul Sabatier (UPS) for a visiting research professorship.

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