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Abstract:

Anionic Pt(0) and Pd(0) complexes with unprecedented trigonal bipyramidal geometry have been prepared and thoroughly characterized by experimental and computational means. Coordination of a π-acceptor borane moiety supported by three phosphine buttresses enhances the electrophilicity of M(0) and triggers the binding of soft anions (X = Br, I, CN).

Anionic $[L_nM(0)X]^-$ complexes of the group 10 metals are considered as key species in various cross-coupling reactions.[1] Such ate complexes are however extremely challenging to study experimentally and only a few species have been isolated and unambiguously authenticated so far.[2,3] In this area, the use of ambiphilic ligands[4] has recently emerged as a powerful strategy for stabilizing such electron-rich complexes, the coordination of the σ-acceptor Z-type moiety enabling to withdraw electron-density from the metal.[3] Accordingly, we have recently leveraged a diphosphine-borane ligand to prepare and structurally characterize the first tetracoordinate anionic Pt(0) complexes (^{Ph}DPB)PtX$^-$ (Figure 1a).[3e] Soon after, Greb and co-workers extended the approach to a related Pd(0) complex using a bis(amidophenolato)silane as Z-type ligand (Figure 1b).[3f]

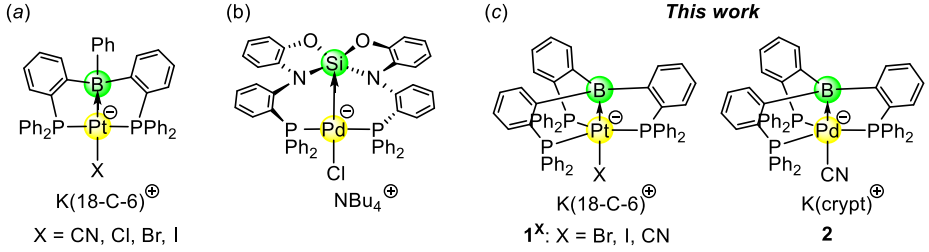


Figure 1. Isolable square-planar Pt(0) (a) / Pd(0) (b) anions and trigonal bipyramidal Pd(0) / Pt(0) anions (c).

Of note, these anionic tetracoordinate Pt(0) and Pd(0) complexes were found to adopt square-planar geometry contrasting with the nominal tetrahedral geometry of $M(0)L_4$ complexes and square-planar geometry of $M(II)L_2X_2$ complexes (Figure 2). Bonding analyses suggest that the non-classical square-planar geometry of the anionic $[M(0)L_2ZX]^-$ complexes results from the stabilization of an in-plane occupied d_{x2-y2} orbital *via* M→Z (Z = B, Si) dative interaction.

With the aim to further expand the variety of anionic Pt(0) and Pd(0) complexes, we became interested in pentacoordinate species deriving from triphosphine-boranes. Such tetradentate ligands ^{R}TPB (R = *i*-Pr, Ph) have proved versatile and powerful towards group 8-11 metals.[4,5] The ensuing cage complexes have been extensively studied, mainly neutral and cationic species, scarcely anionic M(0) ones.[6]

Here we report the synthesis and structurally characterization of anionic Pt(0) and Pd(0) complexes $\mathbf{1}^{X}$ and **2** (Figure 1c). The Z-type borane moiety enhances the electrophilicity of the metal center *via* M→B dative interaction and triggers the binding of soft anions to the metal. The $[M(0)L_3ZX]^-$ complexes adopt trigonal bipyramidal (TBP) structures. This geometry is typical for pentacoordinate Pt(II) and Pd(II) complexes, but very rare for Pt(0) and Pd(0), and it has only been observed in neutral species.[7] Hill and co-workers reported the first example in 2004 upon reaction of a trispyrazolyl borate with Pt.[7a]

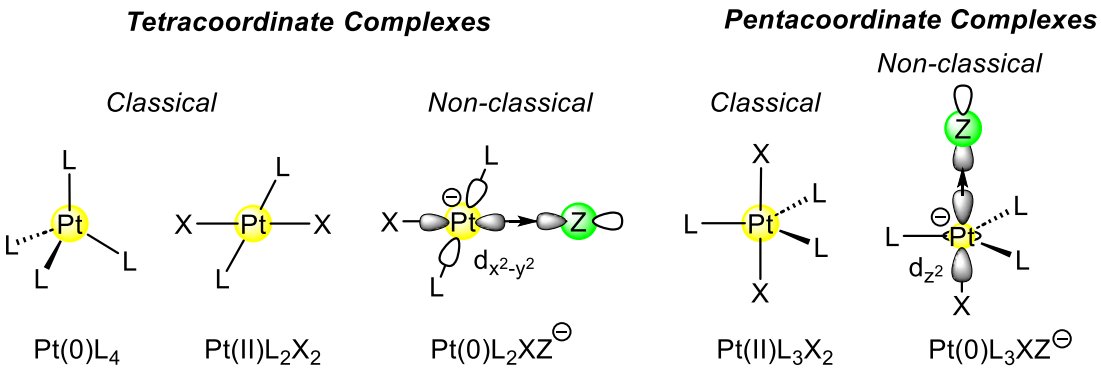
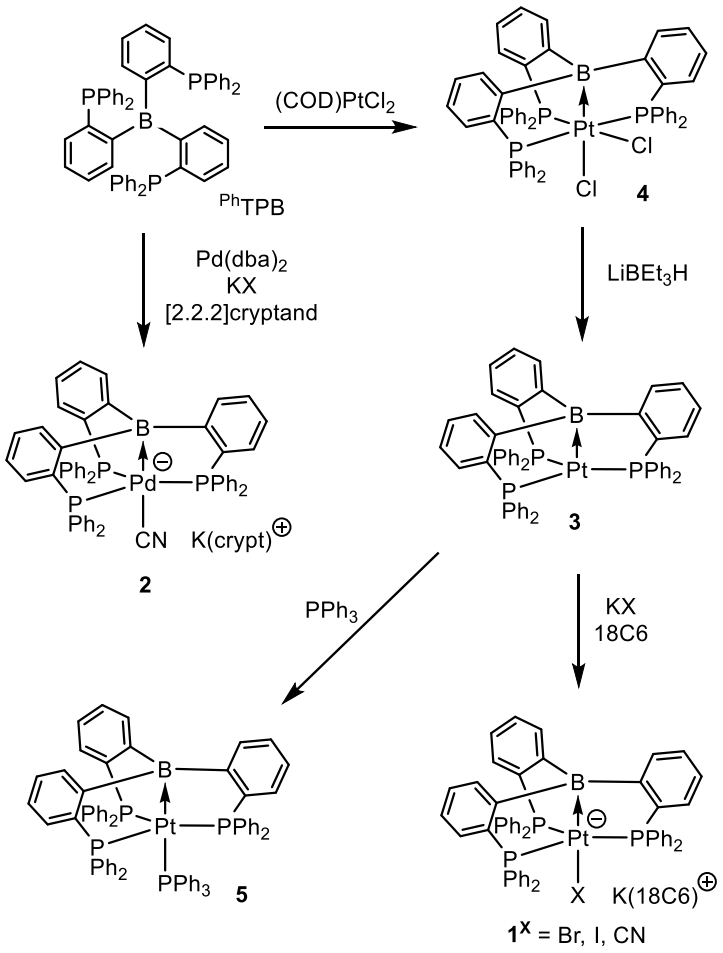


Figure 2. Classical / non-classical geometries for Pt(0) and Pt(II) complexes.

As triphosphine-borane, we chose the ^{Ph}TPB ligand[4,5] whose phosphine arms are moderately σ-donating and sterically encumbering. Access to the targeted anionic Pt(0) complexes was envisioned by coordinating anions to the neutral precursor [(^{Ph}TPB)Pt] (**3**). The dichloro Pt(II) complex [(DPB)PtCl$_2$] (**4**) was first synthesized by reacting ^{Ph}TPB with (COD)PtCl$_2$ (Scheme 1).[8] X-ray diffraction (XRD) analysis confirmed the structure of **4** (Figure 3a) with octahedral geometry, short Pt–B distance [2.270(3) Å, comparable to the sum of the covalent radii 2.20 Å][9] and noticeably elongated Pt–Cl bond *trans* to the borane ligand [2.6820(7) Å *versus* 2.3829(7) Å for the other Pt–Cl bond].[4,10] The desired 16-electron Pt(0) complex **3** was then obtained by reduction of **4** with Li[BEt$_3$H]. It adopts trigonal pyramidal geometry (Figure 3b) with the borane moiety in apical position, and slightly shorter Pt–B distance (2.252(5) Å) than **4**.[8] It is worth nothing that DFT calculations suggest the presence of an accessible coordination site at Pt. The LUMO of **3** is mainly distributed over Pt *trans* to the borane ligand with significant 6p-orbital contribution[11] (Figure S8). It is lowered in energy by 0.75 eV when compared to that of the related boron-free trigonal Pt(0) complex Pt(PPh$_3$)$_3$ and by 0.19 eV with respect to [(^{iPr}TPB)Pt].[8] Consistently, some previous works have shown that the coordination of Lewis acids to low-valent metals may promote the *trans*-binding of L-type ligands.[12]



Scheme 1. Synthesis of the triphosphine-borane Pt and Pd complexes $\mathbf{1}^{X}$-**5**. See Figure S15 for pictures showing the colors of solutions of complexes $\mathbf{1}^{X}$-**5**.[8]

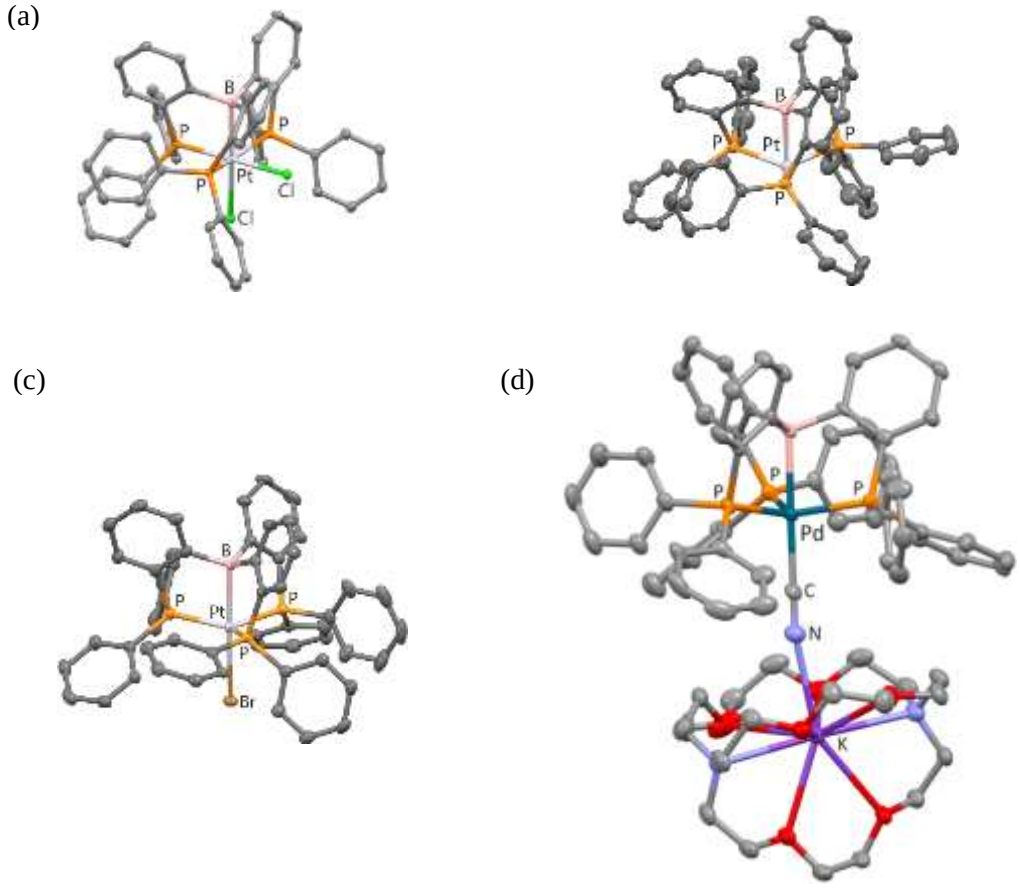


Figure 3. Molecular structures of the Pt and Pd complexes **4** (a), **3** (b), $\mathbf{1^{Br}}$. (c) and **2** (d). Thermal ellipsoids are shown at 40% probability. For clarity, the $[K(18\text{-}C\text{-}6)]^+$ cation and hydrogen atoms are omitted.

Table 1. Key geometric data for the triphosphine-borane Pt and Pd complexes $\mathbf{1^X}$**-5** (bond lengths in Å, bond angles in °).

Complex	M–B	M–X	B–M–X	∑(PMP)
4	2.270(3)	2.3829(7) 2.6820(7)	92.92(9) 168.36(9)	353.24(5)
3	2.252(5)	–	–	355.42(6)
$\mathbf{1^{Br}}$	2.257(4)	2.7037(4)	177.39(11)	356.16(5)
$\mathbf{1^{I}}$	2.243(5)	2.8565(4)	176.85(14)	355.04(7)
$\mathbf{1^{CN}}$	2.297(3)	2.101(3)	178.75(10)	351.19(4)
5	2.334(11)	2.422(3)	176.2(3)	348.21(11)
2	2.301(6)	2.123(6)	176.5(2)	351.74(9)

The accessibility of the vacant site at Pt was confirmed by reacting **3** with PPh_3, affording the corresponding PPh_3 complex **5** (the XRD structure is shown in Figure S7).[8] Then, the synthesis of the corresponding chloro platinate complex was attempted by treating **3** with KCl in the presence of 18-crown-6 or [2.2.2]cryptand as for the corresponding diphosphine-borane Pt complex. However, no reaction occurred at ambient temperature and heating led to an intractable mixture.[13] This is contrast with the previous observation that [(^{Ph}DPB)Pt] readily reacted with KCl under similar conditions to afford the anionic Pt(0) complex [(^{Ph}DPB)PtCl][K(18-crown-6)].[3e] Thus, a third phosphine buttress to Pt prevents Cl^- binding, which is probably due to the metal center being more electron-rich and sterically hindered in **3** than in [(^{Ph}DPB)Pt].[3e] Next, the addition of softer Br^- was investigated by employing KBr instead of KCl. Gratifyingly, the anionic bromo complex $\mathbf{1^{Br}}$ was thereby obtained. However, Pt–Br binding proved labile. Complex $\mathbf{1^{Br}}$ gradually decomposed in the absence of KBr and 18-crown-6 to afford an intractable

mixture including some neutral complex **3**. Fortunately, single crystals suitable for XRD analysis (Figure 3c) could nevertheless be obtained by slow diffusion of *n*-hexane into a THF solution of **3**, KBr and 18-crown-6.[8] Accordingly, complex $\mathbf{1^{Br}}$ adopts trigonal bipyramidal geometry with the B and Br atoms in apical positions (Br–Pt–B 177.39(11)°), and the three P atoms in the equatorial plane ($\sum$(PPtP) = 356.16(5)°). The iodo analogue $\mathbf{1^{I}}$ was then prepared similarly. It proved much more stable, no sign of decomposition being observed over a week in acetone solution in this case.[14] The nature of the halide has thus a strong impact. The softer it is, the more accessible and stable is the anionic [Ph(TPB)PtX]$^-$ complex.[15] To complete the series, another soft anion, CN^-, was employed. The corresponding anionic cyanide complex $\mathbf{1^{CN}}$ was obtained by reacting **3** with KCN in the presence of 18-crown-6. It proved also stable and could be isolated in pure form.[16] The molecular structures of $\mathbf{1^{I}}$ and $\mathbf{1^{CN}}$ were confirmed by XRD analyses (Figures S1-2).[8] The CN ligand in $\mathbf{1^{CN}}$ is coordinated to the K atom. Its IR stretching (2100 cm^{-1}) is comparable to that of [(DPB)Pt(CN)]$^-$ (2089-2091 cm^{-1})[3e] whose X-ray diffraction analysis showed the absence of CN–K binding. Excepted the Pt–X bond length, no significant geometric difference was observed in the series $\mathbf{1^{Br}}$, $\mathbf{1^{I}}$ and $\mathbf{1^{CN}}$ (Table 1). In particular, the Pt–B distance varies very little with the X co-ligand (2.243-2.297 Å). The distances are also comparable to those of **3** (2.252(5) Å) and **4** (2.270(3) Å), suggesting that significant Pt→B interactions exist even in these neutral Pt systems. On the other hand, it is in all cases shorter than that found in the isoelectronic neutral Au(I) complex [(^{iPr}TPB)AuCl][17] (2.318(8) Å) despite the same covalent radii of the two metals (1.36 Å).[9]

Of note, all the anionic complexes $\mathbf{1^{X}}$ exhibit a well-resolved ^{31}P NMR signal at δ ~ 30 ppm with ^{195}Pt satellite peaks.[8] The corresponding $^1J_{Pt\text{-}P}$ coupling constants (3666-3879 Hz) largely exceed those of referential Pt(II) complexes (2634.5 Hz for *trans*-$(Ph_3P)_2PtCl_2$[18a]). They actually fall in the lower range of those reported for neutral and anionic Pt(0) complexes (3829 Hz for $Pt(PPh_3)_4$, 4438 Hz for $Pt(PPh_3)_3$,[18b] 3874Hz for [(PCP)Pt][Na], 4068-4296 Hz for [(DPB)Pt(X)] [K(18C6)][4e]).

The preparation of a related anionic Pd(0) complex was then pursued. Attempts to access the neutral precursor [(^{Ph}TPB)Pd] analogous to **3** failed. The slightly larger size of Pd *versus* Pt (covalent radii of 1.39 *versus* 1.36 Å)[9] may make kinetic stabilization by the Ph groups at P less effective. We thus turned to *in situ* reactions between ^{Ph}TPB, Pd(0) precursors and anions. Gratifyingly, complex **2**, the Pd analog of $\mathbf{1^{CN}}$, could be obtained thereby using $Pd(dba)_2$, KCN and [2.2.2]cryptand. XRD analysis revealed close structural analogy between the two complexes (Fig. 3d).[8]

The bonding situation in complexes $\mathbf{1^{X}}$ and **2** was then analysed to confirm they retain M(0) character despite the M→B interaction.[5] Assigning the electronic configuration of metals engaged in M→Z interactions is not trivial and it is often based on theoretical data. Intrinsic Bond Orbital (IBO) analyses showed the presence of five doubly-occupied d(M)-centered orbitals in all cases (Figures S10-13).[8] In molecular orbital analyses, the d(z^2)-symmetry orbital shows in-phase combination with the 2p(z) orbital at boron, in line with M→B interaction (Figure 4). It is found as the HOMO–2 ($\mathbf{1^{Br}}$, $\mathbf{1^{CN}}$, and **2**) or HOMO–4 ($\mathbf{1^{I}}$). The corresponding Natural Localized Molecular Orbital (NLMO) is mainly centered on the metal (57-75%), while boron contributes to only 22-32 % (Table S8). The d^{10} electronic configuration of the Pt complexes $\mathbf{1^{X}}$ was further corroborated by X-ray photoelectron spectroscopy (XPS),[8] an experimental technique enabling direct analysis of the metal electronic structure. Accordingly, the bonding energy of the Pt $4f_{7/2}$ orbital found for the anionic Pt complexes $\mathbf{1^{X}}$ (71.5 eV for $\mathbf{1^{Br}}$, 71.3 eV for $\mathbf{1^{I}}$, 71.9 eV for $\mathbf{1^{CN}}$) was very similar to that of the neutral precursor [(PhTPB)Pt] (**3**) (71.8 eV) and referential Pt(0) complexes (71.6 eV for $Pt(PPh_3)_4$ and $Pt(PPh_3)_3$,[19] 71.5-71.7 eV for [(DPB)PtX][K(18-C-6)][4e]). For comparison, a much higher value was found for the octahedral Pt(II) complex **4** (73.6 eV), in line with referential Pt(II) complexes (73.3 eV for *cis*-$(Ph_3P)_2PtCl_2$[19a] and 72.8eV for $(Et_3P)_2Pt(H)(Cl)$[19b]).

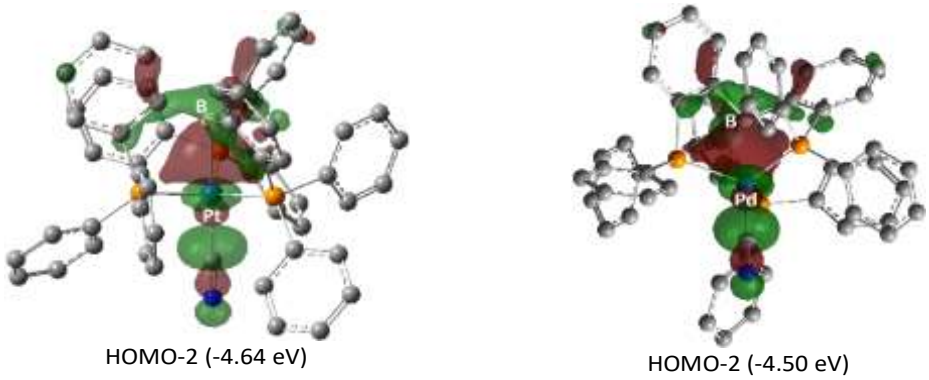


Figure 4. Molecular orbitals accounting for the M→B interactions in the anionic Pt(0) complex $\mathbf{1^{CN}}$ (a) and Pd(0) complex **2** (b).

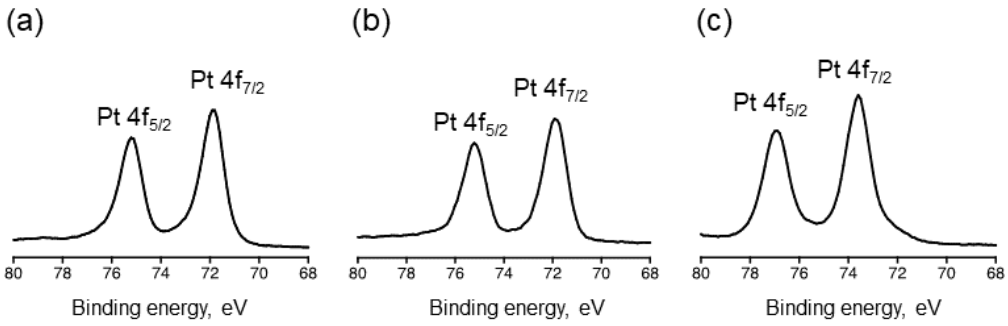


Figure 5. XPS spectra: neutral and anionic Pt(0) complexes **3** (a) and $\mathbf{1}^{CN}$ (b) as well as neutral Pt(II) complex **4** (c).

In conclusion, anionic Pt(0) and Pd(0) complexes adopting trigonal bipyramidal geometry were prepared and structurally authenticated for the first time. The neutral triphosphine-borane complex [(^{Ph}TPB)Pt] (**3**) proved to be a prime precursor. The σ accepting properties of the apical borane ligand enhances the electrophilicity of the Pt(0) center. Direct binding of soft anions is possible and provides straightforward access to anionic Pt(0) complexes [Ph(TPB)PtX]$^-$ complex $\mathbf{1}^{X}$ (X = Br, I, CN). The analogous anionic Pd(0) complex [(^{Ph}TPB)Pd(CN)]$^-$ complex **2** was prepared by direct complexation of $Pd(dba)_2$ with the triphosphine-borane ligand ^{Ph}TPB ligand in the presence of KCN. The d^{10} electronic configuration and M(0) oxidation state of the metal have been unequivocally ascertained by NMR spectroscopy, DFT calculations and XPS analyses. Future work will aim to apply further Z-type ligands to study low-valent metal complexes, in particular highly reduced species which may be stabilized thanks to M→Z interactions.

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