Communication

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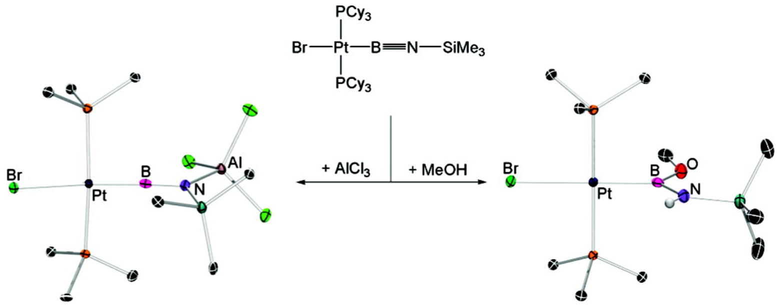

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Reactivity of a Platinum Iminoboryl Complex toward Lewis and Brønsted Acids

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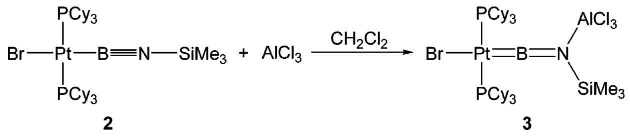
Recently, research in our laboratory focused on the interaction of bromoboranes with [Pt(PCy$_3$)$_2$] (**1**), leading to the isolation of a number of unusual platinum complexes, such as a cationic T-shaped platinum boryl species,[1a] a cationic base-stabilized borylene complex,[1a] and a cationic terminal borylene compound.[1b] Furthermore, we recently reported the straightforward formation and full characterization of the iminoboryl complex *trans*-[(PCy$_3$)$_2$Pt(B≡NSiMe$_3$)(Br)] (**2**), obtained upon B−Br bond oxidative addition of (Me$_3$Si)$_2$NBBr$_2$ to **1** and subsequent Me$_3$SiBr elimination at room temperature.[2] Iminoboranes, RB≡NR′, are highly reactive compounds by virtue of their polar, unsaturated nature. As a result, in the absence of sterically encumbering substituents on either side of the B≡N triple bond, these species are prone to cyclooligomerization or polymerization.[3] Differently from typical iminoboranes, **2** displays a remarkable stability against oligomerization. We, therefore, devoted our efforts to a detailed investigation of the reactivity of the metal-bonded iminoboryl ligand, not only in view of its structural novelty, but also in light of its isoelectronic relationship to the σ-bonded alkynyl group. The applications of metal alkynyl complexes in the areas of liquid crystalline materials and optoelectronic devices[4b] call for an assessment of the iminoboryl complexes' potential in analogous research areas, to evaluate possible innovative properties brought about by the presence of the −BN− moiety.[4a] Herein we report our first results of a reactivity study of complex **2**, namely the full characterization of the neutral platinum borylene complex *trans*-[(PCy$_3$)$_2$Pt{BN(SiMe$_3$)(AlCl$_3$)}(Br)] (**3**), obtained upon coordination of AlCl$_3$ to the imino-nitrogen of iminoboryl complex **2**, and of the alkoxy(amino)boryl species *trans*-[(PCy$_3$)$_2$Pt{B(OMe)(N(H)SiMe$_3$)}(Br)] (**8**), stemming from the addition of MeOH to the B≡N triple bond of **2**. These findings, most importantly, highlight the clean reactivity of the transition metal-bonded B≡NR linkage toward Lewis[5] and Brønsted acids and the remarkable stability of the Pt−B bond under these conditions, which represents a fundamental prerequisite for further functionalization.

Monitoring the reaction of **2** with AlCl$_3$ in CD$_2$Cl$_2$ by multinuclear NMR spectroscopy reveals the gradual consumption of **2** and the clean formation of a new compound, **3**. The signals at δ = 0.52 ppm for the SiMe$_3$ group in the ^{1}H NMR spectrum and at δ = 46 ppm in the ^{11}B{^{1}H} NMR spectrum of **3** appear considerably downfield shifted with respect to those of the starting material **2** (δ = 0.02 and 26 ppm, respectively).[2] This suggests removal of electron density from the boron atom upon product formation, with a $\Delta\delta$ comparable to that observed upon coordination of group 13 element trihalides to the amino(imino)boranes tmpB≡NR (tmp = 2,2,6,6-tetramethylpiperidino; R = *t*Bu, 2,6-*i*Pr$_2$C$_6$H$_3$).[5] While the new singlet resonance in the ^{31}P{^{1}H} NMR spectrum at δ = 31.2 ppm barely differs from that of **2** (δ = 31.1 ppm), it shows a smaller platinum−phosphorus coupling constant, $^1J_{\text{Pt-P}}$ = 2135 Hz, (cf. **2**: $^1J_{\text{Pt-P}}$ = 2389 Hz),[2] resembling rather the one exhibited by the cationic platinum borylene complex *trans*-[(PCy$_3$)$_2$Pt(BMes)(Br)][B(C$_6$F$_5$)$_4$] ($^1J_{\text{Pt-P}}$ = 2073 Hz).[1b]

Scheme 1. Synthesis of **3**



Colorless crystals of **3** could be obtained by slow evaporation of a dichloromethane/hexane solution. A single-crystal X-ray diffraction study showed coordination of AlCl$_3$ to the nitrogen atom of the iminoboryl ligand, giving rise to the first example of a neutral platinum borylene complex *trans*-[(PCy$_3$)$_2$Pt{BN(SiMe$_3$)(AlCl$_3$)}(Br)] (**3**) (Scheme 1).

The molecular structure of **3** with relevant bond lengths and angles is shown in Figure 1. Compound **3** crystallizes in the orthorhombic space group *Pbca* and displays a slightly distorted square-planar geometry around the platinum center. The borylene ligand is oriented almost perpendicular to the PtP$_2$Br-fragment and reveals a stronger deviation from linearity (Pt1−B1−N1 170.38(18)°) than that observed within the group 6 aminoborylene complexes [(CO)$_5$M{BN(SiMe$_3$)$_2$}] (M = Cr: **4**, 177.4(4)°.[6b] Mo: **5**, 177.81(11)°.[6d] W: **6**, 177.4(4)°),[6a] or in the vanadium derivative [(η^5-C$_5$H$_5$)(CO)$_3$V{BN(SiMe$_3$)$_2$}] (**7**, 177.9(4)°).[6c] The decreased B−N bond order, caused by coordination of AlCl$_3$, leads to an elongated B1−N1 distance (**3**, 133.0(3) pm, cf. **2**, 126.0(4) pm)[2] that is very similar to those observed in the Cr and Mo complexes (**4**, 135.3(6) pm;[6b] **5**, 135.5(2) pm),[6d] statistically identical to that of the W complex **6** (133.8(8) pm),[6a] but moderately shorter than that of the vanadium derivative **7** (137.8(7) pm).[6c] The drain of electron density from the B≡N triple bond causes an electron deficiency at the boron center, leading to a distinctly shortened Pt1−B1 distance (190.4(3) pm) with respect to that of the iminoboryl precursor **2** (196.0(3) pm).[2] This is, however, moderately longer

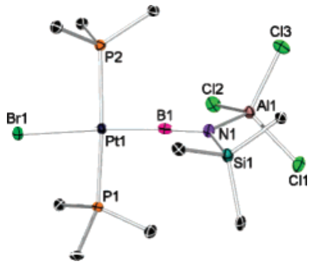


Figure 1. Molecular structure of **3**. Thermal ellipsoids are displayed at the 50% probability level. Hydrogen atoms and cyclohexyl groups are omitted for clarity. Bond lengths (pm) and angles (deg): Pt1−B1 190.4(3), Pt1−Br1 252.80(2), B1−N1 133.0(3), N1−Al1 187.77(19), Al1−Cl1 213.41(8), Al1−Cl2 213.42(9), Al1−Cl3 214.44(9); Pt1−B1−N1 170.38(18), Cl1−Al1−Cl2 112.01(4), Cl1−Al1−Cl3 107.83(4), Cl2−Al1−Cl3 107.70(4).

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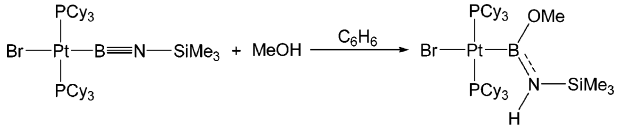
Scheme 2. Synthesis of **8**



2 **8**

than that of the cationic borylene complex *trans*-[$(PCy_3)_2Pt(BMes)(Br)][B(C_6F_5)_4]$, (185.9(3) pm) which is, to our knowledge, the shortest Pt−B distance ever reported.[1b] However, comparison with the base-stabilized borylene complex *trans*-[$(PCy_3)_2Pt\{B(Fc)(NC_5H_4\text{-}4\text{-}Me)\}][BAr^f_4]$ (Fc = ferrocenyl, 201.4(5) pm)[1a] shows the Pt1−B1 bond in complex **3** to be rather short. Furthermore, the shorter Pt1−Br1 bond length of compound **3** (252.80(2) pm, cf. **2**, 255.16(4) pm),[2] indicates a weaker trans influence of the newly formed borylene ligand with respect to the iminoboryl group. The N1−Al1 distance of 187.77(19) pm is slightly shorter than the ones of the $AlCl_3$ adduct with 4-(dimethylamino)pyridine (190.0(5) and 190.2(8) pm).[7a] In **3** the Cl−Al−Cl angles average 109.2° and the Al−Cl distance increases from 206.8(4) pm in $AlCl_3$[7b] to an average of 213.8 pm in **3**. These structural changes around the aluminum atom are more pronounced than those observed within the above-mentioned adduct (111.6°, 211.4 pm),[7a] providing an indication of the remarkably strong Lewis basicity of the iminoboryl moiety of complex **2**.

To explore further the chemical stability of the Pt−B linkage in **2**, its reactions with protic reagents were investigated. Treating a clear solution of **2** in C_6H_6 with a stoichiometric amount of MeOH leads to slow precipitation of a new compound. Addition of hexane and slow evaporation of the solvent mixture leads to isolation of an analytically pure sample. Multinuclear NMR data are consistent with the formation of *trans*-[$(PCy_3)_2Pt\{B(OMe)(N(H)SiMe_3)\}(Br)$] (**8**) obtained *via* 1,2-dipolar addition of MeOH to the B≡N triple bond (Scheme 2).

The resonance at $\delta = 30$ ppm in the $^{11}B\{^1H\}$ NMR spectrum of **8** is slightly downfield shifted with respect to that of **2**, while the signal at $\delta = 25.4$ ppm in the $^{31}P\{^1H\}$ spectrum features a platinum−phosphorus coupling constant ($^1J_{Pt-P} = 2923$ Hz) that is typical for boryl complexes of this type.[8] A single-crystal suitable for an X-ray diffraction study could be obtained by recrystallization of **8** from benzene/hexane. The molecular structure of **8** and relevant bond lengths and angles are displayed in Figure 2.

The structural parameters of **8** are not exceptional and are in full agreement with those of previously reported platinum boryl complexes of the type *trans*-[$(PCy_3)_2Pt(BXX')(Br)$].[8] Exceptional is, however, the stability of the Pt−B linkage, particularly toward protic reagents, which allows for the clean reactivity of **2** under these conditions. Indeed, **8** is also formed cleanly upon addition of excess MeOH, and NMR spectra of a solution of **8** in CD_2Cl_2 show no signs of decomposition over weeks in the presence of air or water. On the contrary, all attempts to synthesize the Pd analogue of **8** failed. Addition of methanol to a solution of *trans*-[$(PCy_3)_2Pd(B{\equiv}NSiMe_3)(Br)$] (**9**)[2] effects the cleavage of the Pd−B bond, instead. Therefore, the outstanding stability of the Pt−B bond can be attributed to electronic rather than steric reasons and distinguishes the Pt−B from most other TM−B bonds, which are cleaved under these conditions.[9] Notable, but rare, exceptions are the osmium complex [$Os(BCl_2)Cl(CO)(PPh_3)_2$] that reacts with water, alcohols and amines yielding the corresponding substituted boryl compounds,[10] and the chloroborylene species [$(\mu\text{-BCl})\{(\eta^5\text{-}C_5H_4Me)Mn(CO)_2\}_2$] which can be converted to the corresponding alkoxo- and hydroxoborylene complexes by treatment with alcohol and water, respectively.[11]

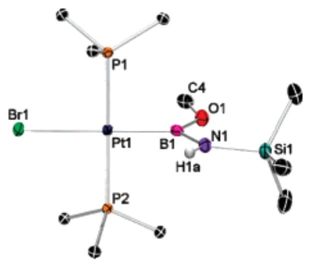


Figure 2. Molecular structure of **8**. The thermal ellipsoids are displayed at the 50% probability level. Hydrogen atoms, apart from the N1−H1a, and cyclohexyl groups are omitted for clarity. Bond lengths (pm) and angles (deg): Pt1−B1 205.3(2), Pt1−Br1 263.51(2), B1−N1 143.2(3), B1−O1 138.4(2); Si1−N1−B1−O1 2.7(2), N1−B1−O1−C4 175.97(17), N1−B1−Pt1−P2 87.65(15).

We have thus demonstrated that the platinum iminoboryl complex **2** displays not only increased stability against oligomerization than simple iminoboranes, but also clean reactivity toward Lewis and Brønsted acids, thus expanding the scope and versatility of the possible applications of transition-metal iminoboryl complexes.

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Supporting Information Available: Details of the synthesis, characterization, and crystallographic data of compounds **3** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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