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Silver Halide Complexes of a Borane/Bis(Phosphine) Ligand

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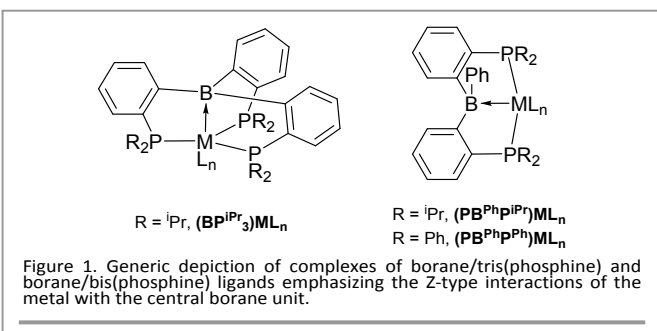
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Silver halide complexes of a borane/bis(phosphine) ligand have been prepared and characterized. With AgF, the borane abstracts fluoride, resulting in a zwitterionic complex. With AgCl, AgBr, and AgI, the halide stays coordinated to Ag, with little to no Ag-B interaction.

Incorporation of Z-type, Lewis-acidic sites into polydentate ligands has become one of the widely used tools to influence reactivity at the metal centers.¹⁻³ Ligands containing borane sites connected to flanking phosphine donors via an *ortho*-phenylene linkage have been especially prominent (Figure 1).^{1,2} Borane/bis(phosphine) PB^{Ph}P^{4,5} and borane/tris(phosphine) BP₃⁶ are closely related and have been used to analyze the fundamentals of the M-Z bonding^{5,7-10} and in applications such as hydrogenation¹¹ and dinitrogen reduction.¹² Our group recently became interested in PB^{Ph}P^{iPr} as a precursor to boryl/bis(phosphine) pincer complexes of Rh and Ir, which are obtained via insertion of the transition metal into the B-Ph bond.¹³⁻¹⁵ Tauchert et al. disclosed the related work with Pd.¹⁶⁻¹⁸

The binding of BP₃ was studied with Cu, Ag, and Au

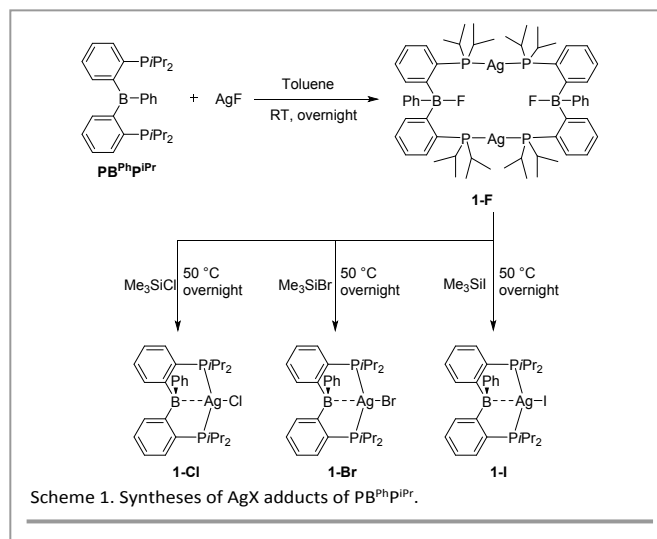


monochlorides.⁸ Bourissou and coworkers examined the CuCl

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adduct with PB^{Ph}P^{iPr}¹⁹ and AuCl adducts with both PB^{Ph}P^{iPr} and PB^{Ph}P^{Ph}.⁵ Building on Bourissou's work, Inagaki, Mukai and coworkers utilized cationic (PB^{Ph}P^{Ph})Au complexes for the catalysis of cyclization reactions.²⁰⁻²² The lack of studies of the complexes of silver with bis(phosphine)/borane ligands moved us to examine the nature of the complexes of PB^{Ph}P^{iPr} with silver monohalides, and specifically whether the borane moiety would show interactions with either the silver center or with the halide.

Stirring AgF with PB^{Ph}P^{iPr} in a 1:1 ratio in toluene overnight resulted in the formation of **1-F**, which was isolated in 89% yield upon workup (Scheme 1). The other AgX complexes were prepared by treatment of pure **1-F** with 2-20 equiv. of the corresponding Me₃SiX reagent (Scheme 1). These reactions resulted in the formation of Me₃SiF (¹H NMR: 0.020 ppm) and new complexes **1-Cl**/**1-Br**/**1-I**. We were able to isolate a 68% yield of an analytically pure solid of the iodo complex **1-I**. The bromide and chloride analogs **1-Cl** and **1-Br** were the dominant products as indicated by NMR spectroscopy, but persistently contained ca. 2-3% of an impurity that we were not able to identify or completely remove.²³

The NMR spectra of the **1-Cl/1-Br/1-I** complexes were very similar to each other and starkly different from the spectra of **1-F**, which presented an especially complex pattern in the ^{31}P NMR spectrum. This pattern was analyzed as arising from a pair of inequivalent ^{31}P nuclei attached to each Ag atom. The two ^{31}P nuclei at the same Ag are coupled to each other, in addition to each being coupled (with its own coupling constants) to one ^{19}F nucleus and one silver nucleus. Since silver is composed of two $S = \frac{1}{2}$ isotopes (^{107}Ag and ^{109}Ag) in a ca. 52:48 ratio, each type of the ^{31}P nucleus gives rise to a concentric, overlapping pair of ddd resonances.²⁴ The ^{19}F NMR resonance of **1-F** is relatively broad, consistent with fluorine being attached to a quadrupolar boron nucleus. In addition, **1-F** displayed an ^{11}B NMR resonance at 7.7 ppm, indicating an sp^3 -hybridized, four-coordinate boron. On the other hand, **1-Cl/1-Br/1-I** gave rise to a ^{11}B NMR resonance in the 61-64 ppm range, contained equivalent phosphines and time-averaged C_s symmetry overall in its NMR spectra. The magnitude of the $J_{\text{Ag-P}}$ values in **1-Cl/1-Br/1-I** was about 20% smaller than in **1-F**.

Taken together, these spectroscopic data suggested that the boron of $\text{PB}^{\text{Ph}}\text{P}^{\text{Pr}}$ abstracted the fluoride from AgF , but the heavier halides in the complexes **1-Cl/1-Br/1-I** remained bound to silver.

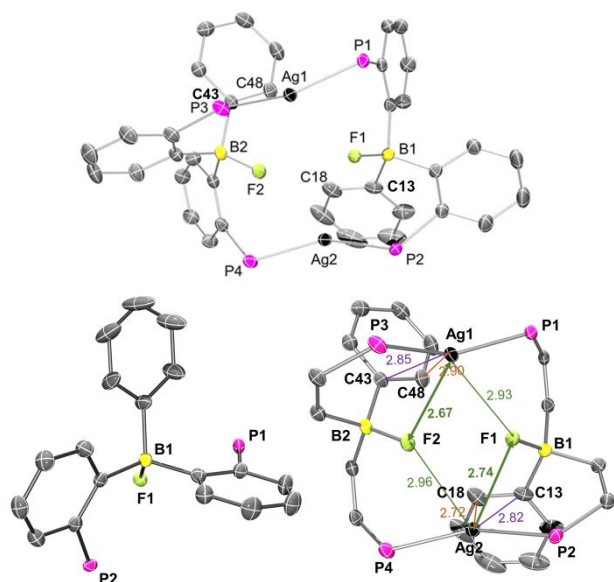


Figure 2. Top: POV-Ray rendition of the ORTEP drawing (50% thermal ellipsoids) of **1-F** showing selected atom labelling. Hydrogen atoms, isopropyl groups, and the cocrystallized molecule of toluene are omitted for clarity. Bottom left: a view of the conformation the $\text{PB}^{\text{Ph}}\text{P}$ ligand adopts in **1-F** intended to highlight the inequivalence of the two P sites in the same $\text{PB}^{\text{Ph}}\text{P}$ unit in **1-F**. Bottom right: POV-Ray rendition of the ORTEP drawing (50% thermal ellipsoids) of truncated **1-F** showing selected atom labelling and selected interatomic distances rounded to 0.01 Å. Selected bond distances (Å) and angles ($^\circ$): Ag1-P1, 2.4342(6); Ag1-P3, 2.4425(8); Ag2-P2, 2.4323(8); Ag2-P4, 2.4255(7); Ag1-F1, 2.928(1); Ag1-F2, 2.667(1); Ag2-F1, 2.735(1); Ag2-F2, 2.960(1); Ag1-C48, 2.901(2); Ag1-C43, 2.850(2); Ag2-C18, 2.720(2); Ag2-C13, 2.820(2); F1-B1, 1.464(2); F2-B2, 1.463(2);

The X-ray diffraction studies on **1-F** (Figure 2) and **1-I** (Figure 3) corroborated this conclusion. **1-F** was found to be a dimeric molecule where each of the newly formed fluoroborate/bis(phosphine) ligands bridges two silver centers. Although the solid-state structure does not possess a crystallographic 2-fold axis of symmetry, it can be viewed as

nearing the C_2 symmetry it displays in solution on the NMR time scale. The two phosphorus atoms in each PBP ligand (and the two phosphorus atoms attached to each silver) are made different by virtue of the conformation the ligand adopts. For example, although the two phosphorus atoms are separated by similar distances from the fluoride in the same ligand, one is positioned much farther from the B-Ph group than the other. The bottom left view in Figure 2 emphasizes this difference. The geometry about Ag deviates from linearity (P-Ag-P angles of ca. 151 - 153°), with the Ag atom being drawn slightly into the center of the dimer, towards the borate moieties. After the Ag-P bonds, the next four closest non-hydrogen contacts are with

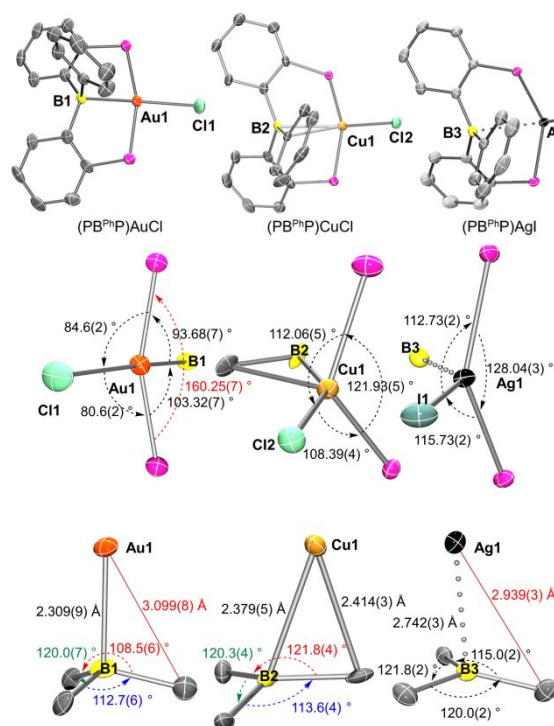


Figure 3. POV-Ray rendition of the ORTEP drawing (50% thermal ellipsoids) of **1-I**, $(\text{PB}^{\text{Ph}}\text{P})\text{AuCl}$ and $(\text{PB}^{\text{Ph}}\text{P})\text{CuCl}$. Top: Front view showing selected atom labelling and M-B Distance. Hydrogen atoms and isopropyl groups are omitted for clarity. Middle: Truncated molecules with metal center and atoms around metal. Bottom: Truncated molecules with boron center and atoms around boron.

the two fluorides (Ag-F distances in the 2.66-2.96 Å range) and the $C_{\text{ipso}}/C_{\text{ortho}}$ carbons of the B-Ph group (Ag-C distances in the ca. 2.7-2.9 Å range). These distances are quite long (cf. Ag-P bond distances of ca. 2.42-2.44 Å), but the geometry clearly points to the presence of an interaction between the cationic Ag centers and the anionic fluoroborate centers in this zwitterionic molecule. Each Ag atom shows close contact with only one Ph group, again underlining the pairwise inequivalence of the P atoms in **1-F**. It is interesting that NMR spectra of **1-F** show lack of fluxionality, indicating the persistence of this inequivalence on the NMR timescale.

The structure of **1-I** is best described as approximately trigonal planar about the Ag center, with ostensibly little if any interaction between Ag and B. The angles in the P2AgI plane are within the 112 - 128° range, adding up to ca. 356.5° . Likewise, the sum of the C-B-C angles about the boron center is ca. 357° .

The Ag-B distance of ca. 2.74 Å is ca. 0.2 Å longer than the Ag-B distance in (BP₃)AgCl.⁸

Interestingly, the very weak interaction between Ag and the borane moiety in PB^{Ph}P is in contrast to the analogous (PB^{Ph}PiPr)AuCl⁵ and (PB^{Ph}PiPr)CuCl¹⁹ complexes (Figure 3). For Au, a meaningful Au→B bond was established, which results in a near-square-planar environment about Au with a short Au-B bond distance of 2.309(9) Å. For Cu, the solid-state structure contained four independent molecules with a varying degree of interaction between Cu and the B-C_{Ph} bond, with closest approach of the B and C to Cu in one of them of ca. 2.4 Å. The P₂CuCl fragment in these structures is definitively pyramidalized, with the Cu atom displaced from the P₂Cl plane towards the B-C bond. Qualitatively, it is possible to conclude that the order of the strength of interaction of the borane moiety in PB^{Ph}PiPr with MHal follows the order of Au > Cu > Ag, even if different structural modes are observed. With the BP₃ ligand, the metallatrane cage enforces the same structural motif for all three coinage metal-monochloride complexes, but the strength of interaction was also determined to be in the Au > Cu > Ag order.⁸

In summary, we have determined that the PB^{Ph}PiPr ligand readily binds to silver monohalides. The binding proceeds with abstraction of fluoride, but the heavier halides remain bound to silver. These latter complexes contain a borane moiety in the same molecule as the silver center, but the spectroscopic and structural evidence points to a very weak interaction between B and Ag at best. The weakness of this interaction contrasts with the observations in the analogous AuCl and CuCl complexes reported by Bourissou et al. earlier,^{5,19} but the Au > Cu > Ag trend for the strength of interaction with a Z-type borane among the coinage metals appears to be general.

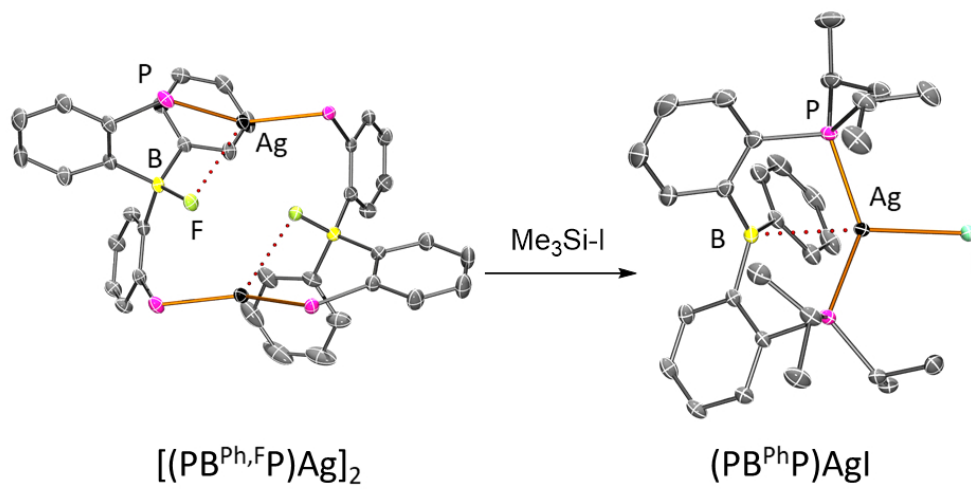
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Notes and references

- ¹ A. Amgoune, D. Bourissou, *Chem. Commun. (Camb.)* 2011, **47**, 859-871.
- ² H. Kameo, H. Nakazawa, *Chemistry – An Asian Journal* 2013, **8**, 1720-1734.

- ³ J. S. Jones, F. P. Gabbaï, *Acc. Chem. Res.* 2016, **49**, 857-867.
- ⁴ S. Bontemps, H. Gornitzka, G. Bouhadir, K. Miqueu, D. Bourissou, *Angew. Chem., Int. Ed.* 2006, **45**, 1611-1614.
- ⁵ M. Sircoglou, S. Bontemps, M. Mercy, N. Saffon, M. Takahashi, G. Bouhadir, L. Maron, D. Bourissou, *Angew. Chem., Int. Ed.* 2007, **46**, 8583-8586.
- ⁶ S. Bontemps, G. Bouhadir, P. W. Dyer, K. Miqueu, D. Bourissou, *Inorg. Chem.* 2007, **46**, 5149-5151.
- ⁷ S. Bontemps, G. Bouhadir, W. Gu, M. Mercy, C.-H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov, D. Bourissou, *Angew. Chem., Int. Ed.* 2008, **47**, 1481-1484.
- ⁸ M. Sircoglou, S. Bontemps, G. Bouhadir, N. Saffon, K. Miqueu, W. Gu, M. Mercy, C.-H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov, D. Bourissou, *J. Am. Chem. Soc.* 2008, **130**, 16729-16738.
- ⁹ M.-E. Moret, J. C. Peters, *Angew. Chem., Int. Ed.* 2011, **50**, 2063-2067.
- ¹⁰ M.-E. Moret, L. Zhang, J. C. Peters, *J. Am. Chem. Soc.* 2013, **135**, 3792-3795.
- ¹¹ W. H. Harman, J. C. Peters, *J. Am. Chem. Soc.* 2012, **134**, 5080-5082.
- ¹² J. S. Anderson, J. Rittle, J. C. Peters, *Nature* 2013, **501**, 84.
- ¹³ W.-C. Shih, W. Gu, M. C. MacInnis, S. D. Timpa, N. Bhuvanesh, J. Zhou, O. V. Ozerov, *J. Am. Chem. Soc.* 2016, **138**, 2086-2089.
- ¹⁴ W.-C. Shih, O. V. Ozerov, *J. Am. Chem. Soc.* 2017, **139**, 17297-17300.
- ¹⁵ W.-C. Shih, W. Gu, M. C. MacInnis, D. E. Herbert, O. V. Ozerov, *Organometallics* 2017, **36**, 1718-1726.
- ¹⁶ P. Steinhoff, M. E. Tauchert, *Beilstein J. Org. Chem.* 2016, **12**, 1573-1576.
- ¹⁷ T. Schindler, M. Lux, M. Peters, L. T. Scharf, H. Osseili, L. Maron, M. E. Tauchert, *Organometallics* 2015, **34**, 1978-1984.
- ¹⁸ D. Schuhknecht, F. Ritter, M. E. Tauchert, *Chem. Commun. (Camb.)* 2016, **52**, 11823-11826.
- ¹⁹ M. Sircoglou, S. Bontemps, M. Mercy, K. Miqueu, S. Ladeira, N. Saffon, L. Maron, G. Bouhadir, D. Bourissou, *Inorg. Chem.* 2010, **49**, 3983-3990.
- ²⁰ F. Inagaki, C. Matsumoto, Y. Okada, N. Maruyama, C. Mukai, *Angew. Chem., Int. Ed.* 2015, **54**, 818-822.
- ²¹ F. Inagaki, K. Nakazawa, K. Maeda, T. Koseki, C. Mukai, *Organometallics* 2017, **36**, 3005-3008.
- ²² F. Inagaki, K. Maeda, K. Nakazawa, C. Mukai, *Eur. J. Org. Chem.* 2018, **2018**, 2972-2976.
- ²³ We cannot rule out that these impurities are isomers of **1-Cl** or **1-Br**, but they do not appear to possess the structure of **1-F**.
- ²⁴ See the full details in the ESI, Figure S2.



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