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Journal Name

COMMUNICATION

Unsaturated Vicinal Frustrated Phosphane/Borane Lewis Pairs as Ligands in Gold(I) Chemistry

Atsushi Ueno, Kohei Watanabe, Constantin G. Daniliuc, Gerald Kehr and Gerhard Erker*[a]

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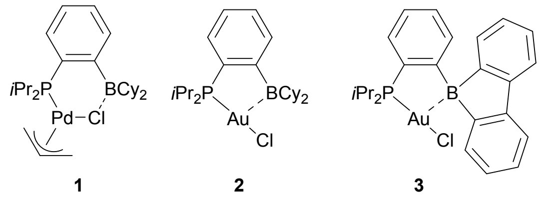
The P/B FLP 6, formed by 1,1-hydroboration of dimesitylphosphino(trimethylsilyl)acetylene with HB(C_6F_5)$_2$ forms the Au(I)X complexes 9a (X: Cl) and 10a (X: NTf$_2$), respectively. Both show marked Au···B interaction. The P/B FLP isomer 8, featuring the bulky SiMe$_3$ substituent at carbon adjacent to boron formes the gold complexes 9b and 10b, which both show weaker Au···B contacts. Complex 10a was employed in catalytic hydroamination of a series of alkynes with *p*-toluidine. The complexes 9 and 10 were characterized by X-ray diffraction.

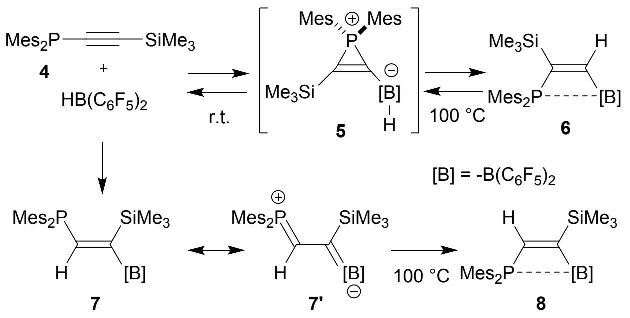
Frustrated Lewis pairs (FLPs) have seen a variety of applications, the most important of them probably being small molecule activation and their use in metal-free catalysis.[1] FLPs have also been used as ambiphilic ligands in transition metal chemistry. [2,3,4] Bourissou's complexes **1** to **3** are typical examples as is their further development to boratrane chemistry.[5]



Scheme 1 Previous work on transition metal complexes with amphiphilic ligands

In compound **1**, the chloride ligand is used for bridging between Pd and B, but in both the complexes **2** there is a Au···B contact (**2**: 2.90 Å, **3**: 2.66 Å) that is markedly below the sum of the Au/B van der Waals radii of ca. 3.9 Å.

We have recently described the formation of the pair of geminal P/B FLPs **6** and **8**.[6] Compound **6** was readily prepared by means of an unusual 1,1-hydroboration of dimesitylphosphino(trimethylsilyl)acetylene **4** with Piers' borane [HB(C_6F_5)$_2$][7] at ambient conditions. There is indirect evidence that this reaction might proceed through the respective phosphirenium borate zwitterion[8] intermediate **5** under the conditions of kinetic control. At 100 °C compound **6** rearranges to the thermodynamically favoured isomer **8**, probably via reversible formation of the **4**/HB(C_6F_5)$_2$ pair, which then undergoes the "normal" hydroboration reaction to give **7**. This might then in turn undergo rotation to the P/B FLP **8** under the prevailing forced conditions, potentially making use of the incipient participation of the mesomeric phospha-iminium/borata-alkene resonance structure of the system **7**/**7'** (see Scheme 2). Both the isomers **6** and **8** show weak internal P···B interactions.



Scheme 2 Plausible reaction pathway of the formation of compounds **6** and **8**

We have now used the pair of unsaturated P/B FLP isomers as ligands in gold(I) chemistry. The preparation of the respective complexes, their characterization and the use of some of them in catalytic alkyne hydroamination chemistry will be reported in this account.

We reacted each of the P/B FLPs **6** and **8** with ca. one molar equivalent of Me$_2$SAuCl. The compounds were allowed to react during 18 h at r.t. in dichloromethane. Workup then

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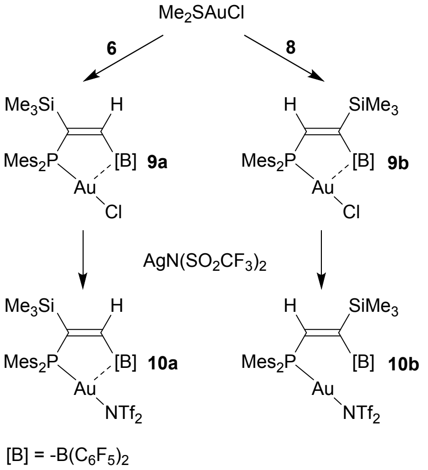
gave the adducts **9a** and **9b** (see Scheme 3) as yellow solids both in >75% yield. The FLP/gold complexes were characterized by C,H elemental analysis, by spectroscopy and by X-ray diffraction (see below and Table 1). We then reacted each of these compounds with one molar equivalent of $AgNTf_2$. After removal of a precipitate of AgCl, the solvent was removed *in vacuo* and the residue was suspended in pentane. The respective anion exchange products **10a** and **10b** (see Scheme 3) were collected by filtration and obtained in >80% yield.



Scheme 3 Preparation of gold(I) complexes with P/B ligands

Table 1 Selected structural and spectroscopic data of the complexes **9** and **10**

Cmpd.	**9a**	**9b**	**10a**	**10b**
[Au]-X	Cl	Cl	NTf_2	NTf_2
X-ray data[a]				
C1-C2	1.356(18)	1.341(7)	1.339(9)	1.328(4)
P1-C1	1.801(14)	1.827(5)	1.824(7)	1.828(3)
B1-C2	1.550(20)	1.548(7)	1.582(10)	1.553(4)
P1-Au1	2.273(3)	2.245(1)	2.272(2)	2.235(1)
Au1-X	2.290(4)	2.288(1)	2.160(6)	2.114(2)
Au1-B1	2.347(17)	2.973	2.712(8)	3.607
P1-Au1-X	173.7(2)	176.8(1)	169.7(2)	172.2(1)
$\Sigma B1^{CCC}$	345.6(11)	358.3(4)	354.6(6)	359.4(3)
C2-C1-P1-Au1	22.5(10)	-32.3(4)	-31.2(5)	-51.5(3)
NMR data[b]				
$\delta^{31}P$	43.9	19.8	32.9	5.2
$\Delta\delta^{31}P(^{10/11}B)$[c]	-15.8	-47.5	-76.7	-
$\delta^{11}B$	34.2	54.8	51.0	59.6
$\Delta\delta^{19}F_{m,p}$[d]	11.2	15.3	14.0	16.0

[a] bond length in Å, angles in deg. [b] chemical shifts, δ scale, in d_2-dichloromethane, 299 K, for **10a** at 273 K. [c] isotope-induced chemical shift in ppb was calculated by using $\Delta\delta^{31}P(^{10/11}B) = \delta^{31}P(^{11}B) - \delta^{31}P(^{10}B)$ [ref.9]. [d] in ppm.

The quartet of the gold complexes **9** and **10** was characterized by C,H respectively C,H,N elemental analysis, by spectroscopy and by X-ray diffraction. We noted a gradual change of essential structural and spectroscopic features on going from **9a** through **10a** and **9b** all the way to compound **10b** (see Table 1). Complex **9a** shows a five-membered core formed by binding of the Au-Cl unit to the phosphorus atom of the P/B FLP **6.** The gold atom in complex **9a** shows a marked interaction with the boron atom B1 (see Fig. 1).

Compound **10a** has the Au-NTf_2 moiety bonded to the FLP phosphane ligand in a close to linear arrangement as well. The P1-Au bond length is the same as in **9a**, but the Au1-B1 distance is markedly longer (Δd≈0.37 Å) (the structure of **10a** is depicted in the Supporting Information).

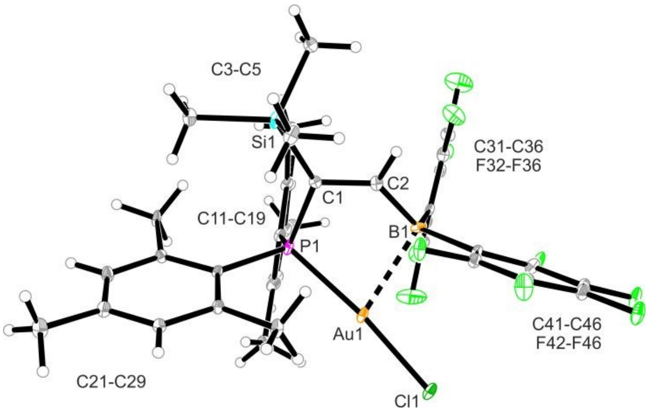


Fig. 1 Molecular structure of the P/B FLP gold complex **9a**

Compound **9b** has the Au-Cl unit close to linearly attached at the phosphane Lewis base of the FLP. Most of the characteristic structural data of compound **9b** are similar to those of **10a**, although the Au1···B1 distance is slightly longer (Δd≈0.26 Å, see Table 1). Both the complexes **9b** and **10a** show envelope type conformations of their FLP/Au frameworks with angles between the PC_2B and PAuB planes around ca. 30°. (the structure of complex **9b** is depicted in the Supporting Information).

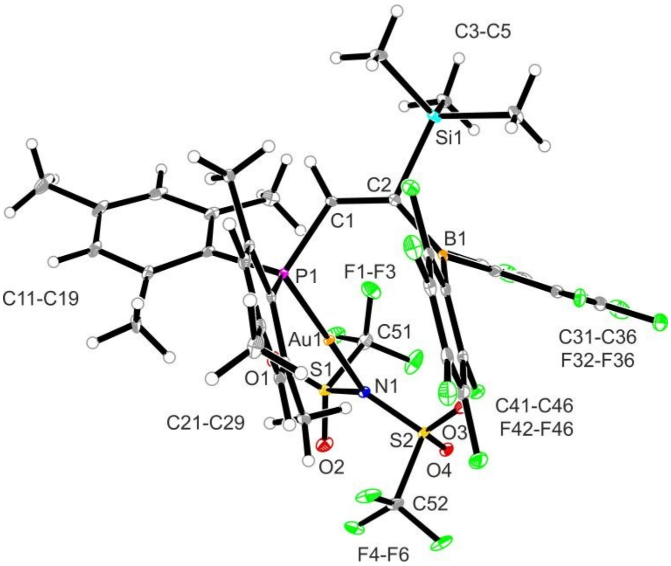


Fig. 2 A view of the molecular structure of complex **10b**

Complex **10b** shows only a marginal interaction of the phosphane moiety with the boron atom B1 of the Lewis acid function (see Fig.2). Consequently, the overall structure of the

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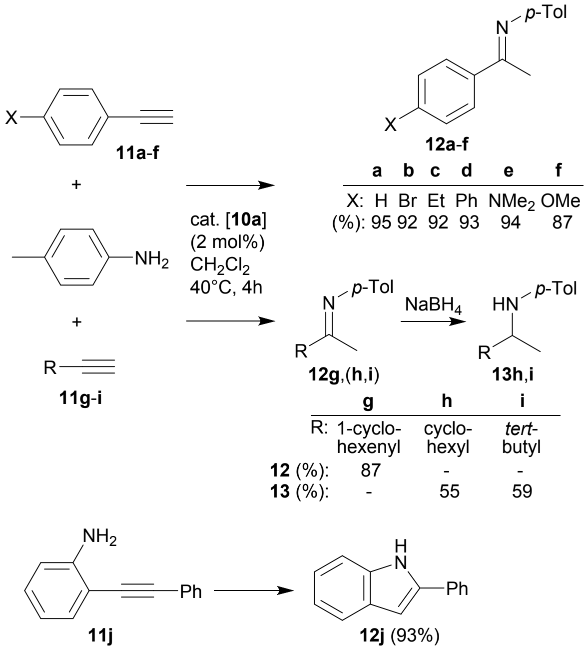
core of **10b** differs markedly from that of its relatives **9a**,**b** and **10a**: we find the P1-Au1 vector at the adjacent P1-C2 vector rotated almost into a conformational gauche position to the C1=C2 backbone. The coordination geometry at boron in complex **10b** is trigonal planar, similar as in the complexes **9b** and **10a**; only complex **9a** shows a markedly pyramidalized geometry at boron (see Table 1).

Complex **10b** shows a ^{31}P NMR signal at ca. δ 5 with a $^{2}J_{PH}$ = 26 Hz coupling constant. This is a chemical shift difference of ca -27 ppm relative to its isomer **10a** (see Table 1, $^{3}J_{PH}$ = 93 Hz). The Au-Cl complex **9a** shows a characteristically high $^{3}J_{PH}$ coupling constant of 98 Hz. Complex **10b** shows a ^{11}B NMR resonance in the typical area of a planar-tricoordinate boron atom in this substituent situation and a typically large $\Delta\delta^{19}F_{m,p}$ chemical shift difference. This is in accord with the presence of an almost free non-interacting borane moiety in **10b** in solution similar as it was found in the solid state by X-ray diffraction. The ^{11}B NMR resonances of the complexes **9b** and **10a** are shifted to slightly smaller values (by ca. 10 to 20%) and their respective $\Delta\delta^{19}F_{m,p}$ chemical shift differences are smaller than in **10b**, both effects probably indicating some Au···B interaction in these complexes in solution. The ^{11}B NMR signal of the Au-Cl complex **9a** is shifted to smaller δ-values by ca. 25 ppm relative to **10b** ($\Delta\delta^{19}F_{m,p}$ reduced by ca 5 ppm) which points to some marked metal-boron interaction in this complex in solution in accord with the X-ray diffraction result. We also note that the complexes **9a,b** and **10a** show a marked ^{31}P NMR chemical shift difference between the $^{10/11}$B isotopologues. The FLP starting materials **6** and **8** do not show this feature. Therefore, this might possibly serve as an additional indication of some P-metal-B interaction in these gold complexes[9] (see Table 1).

Intra- and intermolecular hydroamination reactions have attracted quite some attention. Most these reactions are metal-catalysed, with early examples concentrating on f-element and the group 4 metal derived catalysts.[10,11] More recent examples have used a great variety of metal catalysts throughout the periodic table.[12] Even $B(C_6F_5)_3$ induced hydroamination reactions were reported.[13] Since cationic Au^+ catalysts have come into focus for this reaction in the recent years[14] we have employed some of the here described FLPAuX examples for the hydroamination of a small series of alkynes with the primary amine *p*-toluidine (see Scheme 3). We carried out the reaction of phenylacetylene **11a** with *p*-toluidine at 40 °C in dichloromethane catalyzed by the $FLPAuNTf_2$ complex **10a** (2 mol%) which we generated *in situ* by treatment of the FLPAuCl complex **9a** with $AgNTf_2$. Workup after 4 h reaction time furnished the ketimine product **12a** in ca. 90% yield. A control experiment that was carried with removal of AgCl prior to the actual catalytic reaction gave a similar result. We compared the relative rates of this hydroamination reactions between the *in situ* generated FLP $FLPAuNTf_2$ species **10a** and **10b** and found the reaction involving the **10a** system markedly faster (see the ESI for details). Therefore, we employed the **10a** derived catalyst for the additional experiments. Catalytic hydroamination of the aryl alkynes **11b**-**f** with *p*-toluidine went smoothly at 40 °C and we isolated the resulting imines **12b**-**f** in yields around ca. 90% as colorless oils. Hydroamination of the conjugated enyne **11g** proceeded equally well under the optimized conditions and we isolated the respective conjugated imine product in close to 90% as well. Cyclohexylethyne (**11h**) and *t*-butylacetylene (**11i**) gave slightly lower yields of ~50% under our conditions. The internal alkyne *o*-aminotolane underwent intramolecular hydroamination[15] with the **10a** derived catalyst system to give the indole product **12j** which we isolated in 93% yield (Scheme 4, see the ESI for the characterization of the hydroamination products).



Scheme 4 Catalytic alkyne hydroamination reaction

The rigid FLPs **6** and **8** turned out to be very suitable ligands for the preparation of gold(I) complexes. The X-ray crystal structure analyses and NMR spectroscopy indicated a κP,B chelate structure of the Au(I)-Cl complex **9a**. The Au···B interaction in the here described complexes shows a marked steric response: placement of the bulky $-SiMe_3$ group at the α-position to boron markedly diminished the strength of the gold-boron contact. In this sense, the $FLPAuNTf_2$ complex **10a** seems to represent the best compromise between electronic metal-main group element interaction and repulsive features. This complex showing the $SiMe_3$ group at the α-carbon atom of the bridge adjacent to phosphorus and in a remote position to boron is characterized by only a slightly enlarged Au···B distance relative to **9a**, but already shows some indication of residual Lewis acid properties at boron. Consequently, the system **10a** provided the basics for the most active alkyne hydroamination catalyst in the series. It is likely that the active $FLPAu(I)^+$ cation is generated by Tf_2N-anion dissociation under the actual reaction conditions. We assume that the marked interaction of the metal centre with the strong boron Lewis acid may serve to enhance the electrophilic properties of the incipient gold(I) cation, so that it shows enhanced alkyne hydroamination reactivities. It seems to be promising

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to investigate such borane Lewis acid effect more closely in e.g. gold(I) catalysis and to consider using FLP ligands in catalysis more frequently.

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Conflicts of interest

There are no conflicts to declare

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TOC: The unsaturated vicinal P/B FLP obtained from the unusual 1,1-hydroboration of dimesitylphosphino(trimethylsilyl)acetylene with Piers' borane serves as an ambiphilic ligand in gold(I) chemistry.