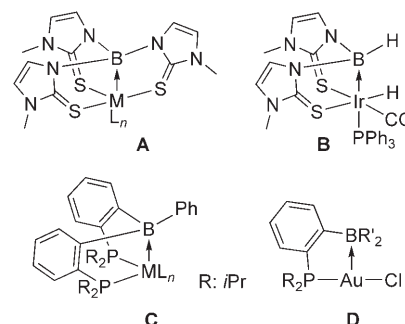


Transition-Metal Complexes Featuring Z-Type Ligands: Agreement or Discrepancy between Geometry and d^n Configuration?

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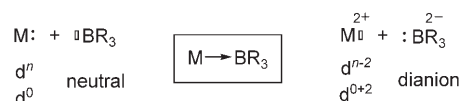
The seminal formalism ML_nX_x (M = transition metal, L = 2e-donor ligand, X = 1e-donor ligand) provides a unified description for transition-metal complexes. Besides the well-known L- and X-type ligands, the ability of Lewis acids to act as zero-electron donors/two-electron acceptors was recognized early on,^[1] and these ligands were referred to as Z-type ligands in $ML_nX_xZ_z$ complexes. Although such σ -acceptor ligands remain considerably less developed than their σ -donor counterparts, significant advances have been achieved over the last decade with Group 13 Lewis acids of the type ER_3 (E = B, Al).^[2–4] In particular, an increasing number and variety of transition-metal–borane complexes ($M \rightarrow BR_3$) have been unambiguously authenticated.^[5] Following the pioneering contribution of Hill et al.,^[6] metallaboratranes **A** have become general scaffolds for supporting $M \rightarrow BR_3$ interactions (M = Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt; Scheme 1).^[7] The related iridium complex **B** further expanded the variety of such interactions to complexes featuring only two methimazolyl buttresses.^[8] In addition, we have demonstrated that $M \rightarrow B$ interactions^[9] are readily accessible by coordination of preformed ambiphilic phosphanylborane ligands.^[17–19] The ensuing square-pyramidal complexes **C** exemplified the possibility for $M \rightarrow B$ interactions to exist in the absence of σ -donor ligands in the position *trans* to the Lewis acid^[17a] and substantiated the marked influence that the metal (M = Rh, Pt, Pd) may have on such interactions.^[17d]



Scheme 1. Structurally characterized complexes featuring $M \rightarrow BR_3$ interactions.

Furthermore, the T-shaped complexes **D** provided the first evidence for $M \rightarrow B$ interactions in 14-electron complexes supported by a single phosphane buttress.^[17b]

The increasing number and variety of complexes featuring dative $M \rightarrow B$ bonds have raised fundamental questions as to the very nature of such interactions. Accordingly, Hill^[20a] and Parkin^[20b] proposed two conflicting bonding situations to describe complexes featuring such Z-type ligands: 1) retention of the original d^n configuration of the metal center and a coordinated neutral BR_3 ligand, and 2) two-electron oxidation of the metal center resulting in a d^{n-2} configuration and a dianionic BR_3^{2-} ligand (Scheme 2). At first glance, these two



Scheme 2. The two limiting bonding situations for dative $M \rightarrow BR_3$ interactions proposed by Hill^[20a] and Parkin,^[20b] respectively.

descriptions may be considered as just different representations of dative $M \rightarrow B$ bonds, but they in fact reflect two extreme bonding situations that are intimately related to the extent of electron-density transfer from the metal atom to the boron center. In this context, we report herein a combined experimental and theoretical investigation of $[AuCl(diphosphanylborane)]$ complexes featuring short Au–B contacts. The observed square-planar coordination geometries of the tetracoordinate gold centers could be considered as indicating d^8 gold(III) configurations, but natural bond orbital (NBO) analyses and Mössbauer spectroscopic measurements unambiguously established that these complexes retain d^{10} gold(I) configurations. These results provide the first evidence that

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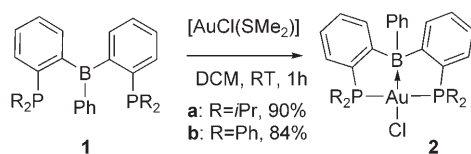
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[**] The CNRS, the UPS, and the ANR are acknowledged for financial support of this work. We also thank Dr. P. W. Dyer, Dr. K. Miqueu, and Dr. J. M. Sotiropoulos for helpful discussions.

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

basic principles usually dictating the geometry of transition-metal complexes may be challenged with Z-type ligands.

The diphosphanylborane **1a**^[17a,c] readily displaced the labile dimethyl sulfide ligand of [AuCl(SMe₂)] in dichloromethane (DCM) at room temperature (RT; Scheme 3). The



Scheme 3. Coordination of the ambiphilic diphosphanylborane ligands **1a,b** to AuCl.

resulting complex **2a** was isolated in 90 % yield as a white, air-stable powder. The ³¹P NMR spectrum of complex **2a** exhibited a single signal at $\delta = 73.2$ ppm, indicating symmetric coordination of the phosphorus atoms. In addition, the broad resonance observed at $\delta = 24.6$ ppm in the ¹¹B NMR spectrum of **2a** is very similar to that encountered for related rhodium complexes ($\delta = 19.4$ – 26.7 ppm), suggesting the presence of an Au→B interaction. The precise structure of **2a** was established by an X-ray diffraction study (Figure 1).^[21] The gold

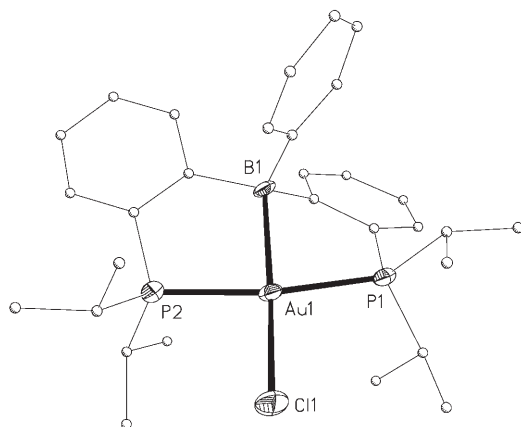


Figure 1. Molecular structure (thermal ellipsoids set at 50% probability) of complex **2a** in the solid state. Hydrogen atoms are omitted for clarity.

center is tetracoordinate and had a slightly distorted square-planar coordination geometry (sum of angles (ΣAu_a) = 362.2°). The two phosphane moieties span *trans* sites with a significantly bent P–Au–P arrangement (160.2°). The B–Au–Cl arrangement is closer to linear (168.7°). The Au–B distance ($2.309 \text{ \AA}$) is much shorter than those observed in related gold complexes with monophosphanylborane ligands (2.66 – $2.90 \text{ \AA}$),^[17b] but falls within the same range as those encountered in rhodium complexes with diphosphanylborane ligands (2.29 – $2.37 \text{ \AA}$).^[17a,d] The presence of a rather strong Au→B interaction^[22] is further supported by the noticeable pyramidalization of the boron environment ($\Sigma\text{B}_a = 341.2^\circ$). **2a** is the first example of a complex of an ambiphilic phosphanylbor-

ane ligand featuring a coligand in a position *trans* to the boron atom.

With regards to the bonding description of the M→B interactions, the square-planar geometry observed in **2a** may indicate a d^8 gold(III) configuration.^[23] Indeed, complexes of tetracoordinate d^{10} gold(I) adopt tetrahedral and not square-planar arrangements.^[24]

To probe substituent effects on M→B interactions, the isopropyl groups at the phosphorus atoms were replaced by phenyl moieties. The ligand **1b** and ensuing complex **2b** were prepared in a similar manner to **1a** and **2a**. X-ray diffraction analysis of **2b** revealed an overall geometry very similar to that of **2a**.^[21] Notably, the lower steric hindrance and electron-donating character of the PPh₂ groups does not affect the Au–P and Au–Cl distances, but results in a slightly elongated Au–B distance ($2.335 \text{ \AA}$) and a slightly less pronounced pyramidalization of the boron environment ($\Sigma\text{B}_a = 343.8^\circ$).

To address the bonding description of the Au→B interactions in more detail, DFT calculations were carried out on the actual complexes **2a,b**.^[25] As previously observed for related complexes of Group 9 and 10 transition metals, the B3PW91/SDD(Au,P),6-31G** (other atoms) level of theory was found to reproduce the experimental geometric features particularly well (Table 1). The corresponding frontier molec-

Table 1: Experimental and theoretical data for complexes **2a,b** and **2a*,b***, respectively. Selected bond lengths [$\text{\AA}$] and angles [$^\circ$].

	P–Au	Au–B	Au–Cl	$\Sigma_a\text{B}$	$\Sigma_a\text{Au}$	P–Au–P	B–Au–Cl
2a	2.313(2) 2.328(2)	2.309(8)	2.522(2)	341.2	362.2	160.2(1)	168.7(2)
2a*	2.35 2.37	2.32	2.56	340.1	362.5	158.0	170.8
2b	2.307(1) 2.329(1)	2.335(5)	2.524(1)	343.8	364.2	157.2 (1)	162.0(2)
2b*	2.34 2.36	2.35	2.56	343.5	362.9	158.2	168.8

ular orbitals reveal three-center B–Au–Cl interactions. These interactions involve the $d_{x^2-y^2}$ orbital of gold and the p_y orbitals of boron and chlorine, with bonding gold–boron and antibonding gold–chlorine interactions in the highest occupied molecular orbital (HOMO), and antibonding gold–boron and gold–chlorine interactions in the lowest unoccupied molecular orbital (LUMO; Figure 2). Parkin et al.

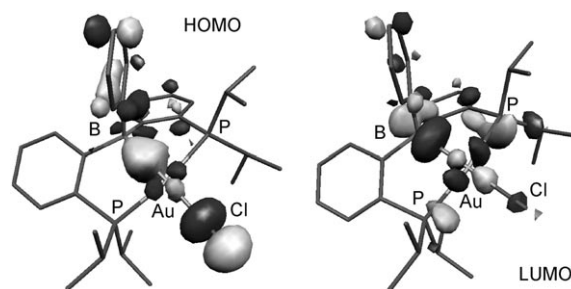


Figure 2. Frontier orbitals for complex **2a***. Hydrogen atoms are omitted for clarity.

reported similar three-center four-electron interactions for iridaboratranes and argued for a formal two-electron oxidation/ d^{n-2} configuration of the metal atom on the basis of its negligible contribution to the nonbonding B–Ir–Cl orbital.^[7g] Second-order perturbative NBO analyses of **2a,b*** also provided evidence for Au→B dative interactions, with NBO delocalization energies of about 55 kcal mol^{−1}. Notably, the coordination of the diphosphanylborane ligand induces only a moderate depletion of the NBO charge at boron (from +0.85 in the open form of the ligand **1a**^[17d] to +0.37 in the ensuing complex **2a**), which is accompanied by a slight increase of the charge at gold (from +0.30 in the model borane-free T-shaped complex [AuCl(PMe₃)₂] to +0.64 in **2a**). This result suggests that complexes **2a,b** would be more appropriately described as gold(I) than as gold(III) complexes, as initially proposed on the basis of geometric considerations. This hypothesis was further corroborated by the computed natural electron configuration^[26] of the metal center ([Xe]6s(0.70)5d(9.63)6d(0.01)7p(0.01) for **2a**), which deviates only marginally from the d^{10} configuration expected for a gold(I) center ([Xe]6s(0.88)5d(9.79)6p(0.03) computed for [AuCl(PMe₃)₂]).

To support such an unprecedented combination of a square-planar geometry with a d^{10} gold(I) configuration, further experimental evidence was necessary.¹⁹⁷Au Mössbauer spectroscopy, which has previously been used to determine the structure and bonding of a variety of inorganic gold compounds,^[27] was considered a particularly valuable probe. These measurements were performed on both complexes **2a,b** to avoid any ambiguity arising from substituent effects. The resulting spectra consist of well-resolved quadrupole doublets, with isomer shifts (ISs) of about 3.35 mm s^{−1} (relative to a ¹⁹⁶Pt/Pt source, corresponding to 4.57 mm s^{−1} relative to gold metal) and quadrupole splittings (QSs) of about 7.6 mm s^{−1} (Figure 3a). Although these values are hardly comparable with those observed for gold complexes featuring only σ -donor ligands, the well-known IS/QS rela-

tionship^[28] unambiguously positions complexes **2a,b** among gold(I) complexes (Figure 3b). These data, thus, definitely confirm that the square-planar complexes **2a,b** should be considered as complexes of d^{10} gold(I) rather than d^8 gold(III).

In conclusion, the square-planar gold(I) complexes **2a,b** with ambiphilic diphosphanylborane ligands provide a better understanding of the precise nature of M→BR₃ interactions. It is demonstrated that the coordination of σ -acceptor Z-type ligands to transition metals is not necessarily accompanied by formal two-electron oxidation. This type of coordination may eventual challenge the basic rules usually governing the geometry of transition-metal complexes. Further investigations in this area are currently in progress with lighter Group 11 elements, as well as triphosphanylborane ligands.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of dry argon, using standard Schlenk techniques.

2a: A solution of **1a** (600 mg, 1.26 mmol) in CH₂Cl₂ (5 mL) was added at room temperature to a suspension of [AuCl(SMe₂)] (371 mg, 1.26 mmol) in CH₂Cl₂ (5 mL). After stirring for 15 minutes, filtration of the reaction mixture over SiO₂ or Al₂O₃ and evaporation of the volatile components afforded **2a** as an air-stable solid (899 mg, 90% yield). Colorless crystals were obtained from a saturated pentane solution at room temperature. M.p. 183–185 °C; ³¹P NMR (202.5 MHz, CDCl₃, 23 °C): δ = 73.2 ppm; ¹B NMR (160.5 MHz, CDCl₃, 23 °C): δ = 24.6 ppm; MS (ESI⁺) m/z (%): 707.5 [M+H]⁺ (<1), 671.3 [M–Cl]⁺ (100); HRMS (ESI⁺) m/z calcd for [C₃₀H₄₁AuBP₂]⁺: 671.2442; found: 671.2451.

Received: August 2, 2007

Published online: October 8, 2007

Keywords: B,P ligands · donor–acceptor systems · electronic structure · gold · Mössbauer spectroscopy

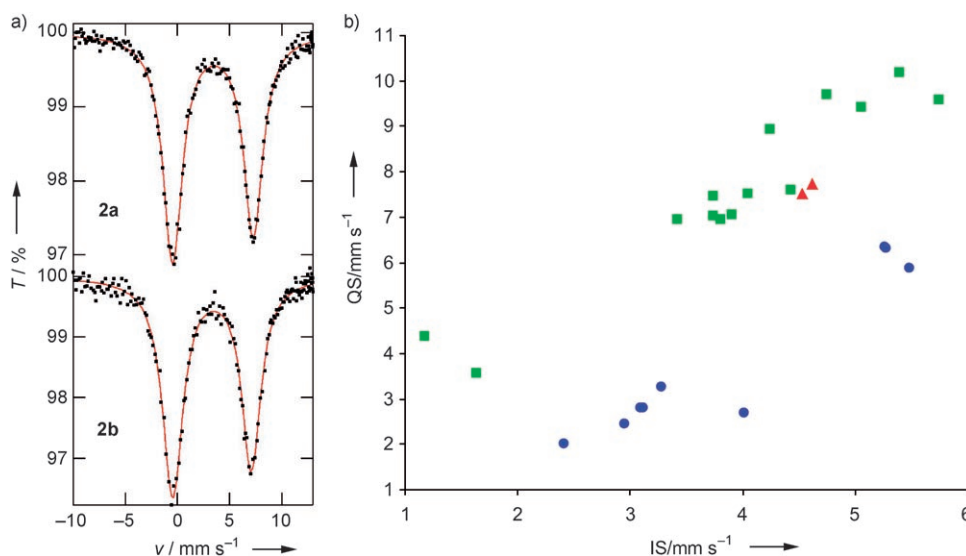


Figure 3. a) ¹⁹⁷Au Mössbauer spectra for complexes **2a,b** at 12 K. T = Relative transmission, v = Doppler velocity. b) QS/IS correlation for complexes **2a,b** (red triangles) and representative phosphane complexes of gold(I) (green squares) and gold(III) (blue circles). IS values are given relative to gold metal.

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