Ambiphilic Ligands

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Metallaboratranes Derived from a Triphosphanyl–Borane: Intrinsic C_3 Symmetry Supported by a Z-Type Ligand**

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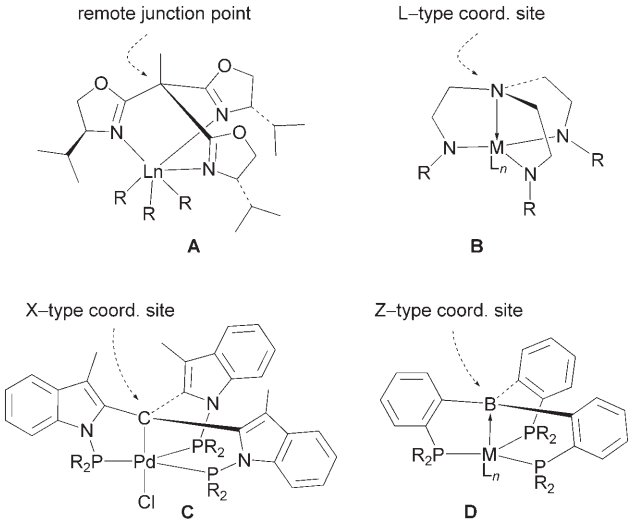
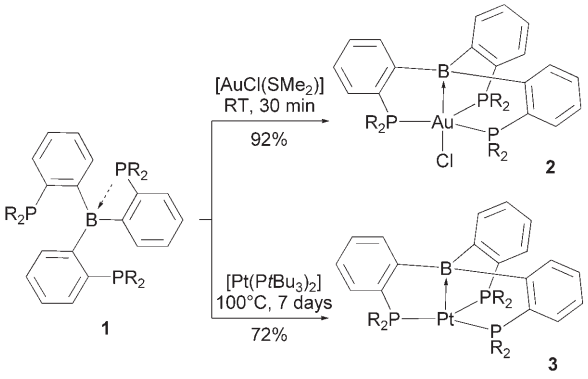
Following the pioneering contributions of Knowles, Kagan, and Noyori, C_1 and C_2 chiral ligands have played a prominent role in asymmetric catalysis with transition-metal complexes.[1] Over the last few years, increasing attention has been devoted to C_3-symmetric derivatives,[2] and spectacular achievements have been reported using facially coordinating tripodal ligands assembled around a remote junction point (which does not enter the coordination sphere), an L-type coordination site, or an X-type coordination site.[3] The trisoxazoline,[4] trisamido,[5] and triphosphane[6] complexes **A**–**C** are archetypal examples of these three different situations (Scheme 1). Our interest in ambiphilic ligands[7] that combine donor and acceptor moieties prompted us to investigate the ability of σ-acceptor (Z-type)[8] coordination sites to also support such a three-fold geometry.[9,10] Accordingly, an L_3Z tetradentate triphosphanyl–borane (TPB) ligand is reported herein to afford gold and platinum metallaboratranes **D** featuring dative M→B interactions and exhibiting C_3 symmetry.[11–14] Such helical geometry has been shown to result from the tendency of the PCCBM metallacycles to adopt envelope conformations, and its configurational stability has been estimated spectroscopically.



Scheme 1. Representative examples for the four types of tripodal ligands that can support C_3 symmetry in the ensuing complexes.

The formation of unusual complexes[7b,f] by coordination of mono- and diphosphanyl–borane ligands to the AuCl fragment prompted us to investigate the reaction of the related TPB ligand **1**[15] towards [AuCl(SMe$_2$)] (Scheme 2). The coordination proceeds rapidly and cleanly at room temperature, affording complex **2** after standard workup. The unique signal observed at $\delta = 47.6$ ppm in the ^{31}P NMR spectrum is consistent with symmetric coordination of the three phosphorus atoms, while the low-field ^{11}B NMR chemical shift ($\delta = 27.7$ ppm) suggests the presence of a dative Au→B interaction.[16]



Scheme 2. Coordination of the triphosphanyl–borane ligand **1** to AuCl and Pt; R = *i*Pr.

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

An X-ray diffraction analysis revealed a metallaboratrane structure organized around a pentacoordinate L_3ZXAu center[17] (Figure 1).[19] To our knowledge, pentacoordination without aurophilic interactions has not been evidenced so far

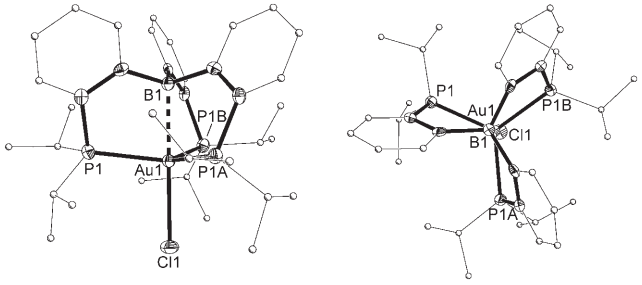

Figure 1. Molecular views of complex **2**, including a top view along the B-Au-Cl C_3 axis (right). Hydrogen atoms and solvate molecules are omitted for clarity.

for gold(I) complexes and only scarcely for gold(III) complexes.[20] The gold atom deviates by only 0.301 Å from the equatorial plane defined by the three phosphorus atoms. The B–Au bond length (2.318(8) Å) and the pyramidalization around the boron atom (ΣB_α 339.3°) are similar to those observed in the related diphosphanyl–borane (DPB) complexes,[7f] and are diagnostic for a dative Au→B interaction. The Au–Cl bond (2.607(2) Å) is slightly longer than in the related DPB complex.[7f,21] Notably, complex **2** was found to display C_3 symmetry (rhombohedral crystals, space group $R\bar{3}$), with all of the PCCBAu metallacycles adopting an envelope conformation oriented in the same direction. The resulting helicity, quantified by the P-Au-B-C torsion angle (referred to as θ)[22] is found to be almost as large in **2** (27.0°) as in **C** (ca. 33.1°). The helical geometry of **2** most probably results from the presence of sp^3-hybridized P and B atoms, and from the steric congestion between the phosphorus substituents of neighboring phosphanyl arms. In marked contrast, the related metallaboratranes featuring tris(methimazolyl)borane (Tm) ligands [23] typically exhibit planar five-membered (SCNBM) metallacycles in the solid state, so that the trigonal bipyramidal $[(Tm)Co(PPh_3)]^+$, [(Tm)NiCl], and $[(Tm)Pd(PMe_3)]$ complexes[24] display approximately C_{3v} symmetry.

To confirm the propensity of the TPB ligand to form C_3-symmetric metallaboratranes, the corresponding $[L_3ZPt]$ complex **3** was prepared. Thermolysis of $[Pt(PtBu_3)_2]$ with 1.1 equiv of **1** (toluene, 7 days, 100 °C) led to the formation of **3**, which was isolated in 72% yield upon workup. The presence of a single resonance ($\delta = 79.4$ ppm, $^1J_{P,Pt} = 3578$ Hz) in the ^{31}P NMR spectrum of **3** is consistent with the symmetric coordination of the TPB ligand. Red crystals of **3** suitable for an X-ray diffraction analysis were grown from a toluene/pentane mixture (Figure 2).[19] The platinum center was found to adopt a trigonal-pyramidal geometry with only a marginal deviation from the basal plane formed by the three phosphorus atoms (0.171 Å). Although the coordination environment about the Pt center in **3** is likely largely imposed by the cage structure of the TPB ligand, it is worth noting that the related

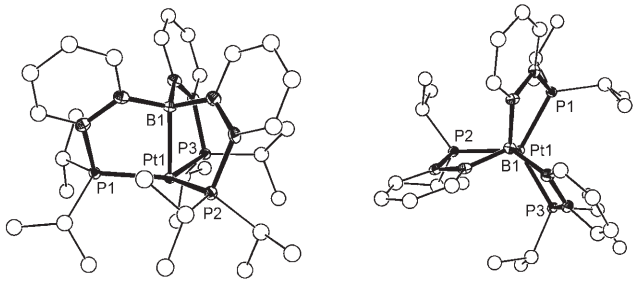

Figure 2. Molecular views of complex **3**,including a top view along the B-Pt C_3 axis (right). Hydrogen atoms and solvate molecules are omitted for clarity.

$[L_3PtZ]$ complex $[(Ph_3P)_3Pt{\rightarrow}(SO_2)]$ adopts a geometry that is intermediate between tetrahedral (typical for $[L_4Pt]$) and trigonal-pyramidal.[25] Despite the slightly larger size of Pt vs. Au, the axial Pt–B bond in **3** (2.224(4) Å) is significantly shorter than the Au–B bond in **2**, presumably owing to the higher basicity of Pt^0 vs. Au^I.[26] The notion of a stronger M→B interaction in **3** is reinforced by the more upfield ^{11}B NMR chemical shift demonstrated by **3** ($\delta = 18.2$ ppm).[7e] Complex **3** crystallizes in the *Cc* space group, but its geometry only slightly deviates from C_3 symmetry with values of the torsion angle θ of 24.2, 24.3, and 24.4°.

DFT calculations were carried out on the actual complexes to further probe the tendency of the TPB complexes to adopt C_3 rather than C_{3v} symmetry.[27] The geometry of **2** and **3** were very well reproduced at the B3PW91/SDD(Au, Pt, P, Cl),6-31G**(other atoms) level of theory (Table 1). Despite considerable efforts, no minimum could be located on the potential-energy hypersurfaces for the corresponding C_{3v} structures, thus confirming the propensity of the PCCBM metallacycles to adopt envelope conformations.

Table 1: Experimental and theoretical data for complexes **2** and **3**. Selected bond lengths [Å], boron pyramidalization [°], and torsion angles [°].

Complex	P-M_{av}[a]	M-B	M/P_3[b]	ΣB_α	P-C-C-B	θ[c]
2 (X-ray)	2.425(1)	2.318(8)	0.301	339.3	5.0	27.0
2 (DFT)	2.48	2.32	0.33	338.6	2.8	28.6
3 (X-ray)	2.296(2)	2.224(4)	0.171	337.2	7.5	24.3
3 (DFT)	2.38	2.25	0.20	338.4	2.1	27.0

[a] Mean value for the three P–M bonds. [b] Deviation of the metal center from the equatorial plane defined by the three phosphorus atoms. [c] Degree of helicity deduced from the mean value of the P-M-B-C torsion angles.

Furthermore, the NMR data provided interesting information on the symmetry of metallaboratranes **2** and **3** in solution. Two signals attributable to the *exo*/*endo* $CH(CH_3)_2$ moieties were observed in both the ^1H and ^{13}C NMR spectra of **2**. For the platinum complex **3**, the two $CH(CH_3)_2$ environments were distinguishable by ^{13}C NMR, but a single resonance was observed in the ^1H NMR spectrum. Variable-temperature experiments (from −80 to +70 °C) revealed

coalescence phenomena, and the inversion barriers of the three-bladed propellers were thereby estimated to be 14.5–15 kcal mol^{-1}.[27]

Lastly, the UV spectrum of the Pt^0 complex **3** was simulated by time-dependent DFT calculations to gain more insight into its unusual red color. Two absorptions, associated with allowed HOMO→LUMO and HOMO−1→LUMO transitions, were predicted at 528 and 519 nm, respectively. These values match very well with the experimental λ_{max} value (541 nm in toluene). The Z-type ligand, which has a major contribution in the LUMO (Figure 3), is found to play a crucial role in the optical properties of **3**, and no such transitions in the visible region were predicted for the related borane-free complex $[Pt(PiPr_2Ph)_3]$.[27]

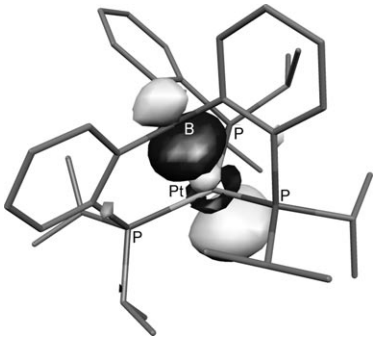

Figure 3. LUMO calculated for complex **3**.

In conclusion, the coordination of the triphosphanyl–borane ligand **1** to AuCl and Pt was found to give metallaboratranes featuring axial dative M→B interactions and exhibiting C_3 symmetry. These results demonstrate the propensity of Z-type ligands to support chiral three-bladed propeller geometry around transition-metal centers. In addition, complexes **2** and **3** deriving from the achiral TPB ligand extend the family of *intrinsically* C_3-symmetric complexes. Current efforts are aimed at determining the influence of the metal fragments and ligand structure on the geometry and configurational stability of the resulting cage complexes. Further investigations are also in progress to probe the mechanism of inversion of such helical complexes.[28]

Experimental Section

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

2: A solution of TPB **1** (148 mg, 0.25 mmol) in CH_2Cl_2 (10 mL) was added to a suspension of $[(Me_2S)AuCl]$ (74 mg, 0.25 mmol) in CH_2Cl_2 (5 mL) at room temperature. After subsequent stirring for 30 min, volatile components were removed and the residue was extracted with diethyl ether (4 × 10 mL). Colorless crystals of **2** (179 mg, 92 %) were obtained from a saturated diethyl ether solution at 4 °C; m.p. 192.8–193.0 °C (decomp); ^{31}P NMR (202.5 MHz, 296 K, [D$_8$]THF): $\delta = 47.6$ ppm; ^{11}B NMR (160.5 MHz, 298 K, [D$_8$]THF): $\delta = 27.7$ ppm. HRMS (ESI, positive mode) calcd for $C_{36}H_{54}AuBP_3$: 787.3197; found: 787.3157.

3: TPB **1** (55 mg, 0.094 mmol) was added to a solution of $[Pt(PtBu_3)_2]$ (51.5 mg, 0.086 mmol) in toluene (5 mL). After subsequent stirring for 7 days at 100 °C, the volatile components were removed in vacuo and the residue was washed with cold *n*-pentane (3 × 2 mL). Red powder of **3** (48 mg, 72 %) was obtained from a saturated toluene solution at −35 °C. ^{31}P NMR (161.8 MHz, 296 K, [D$_6$]benzene): $\delta = 79.4$ ppm ($^1J_{P,Pt} = 3578$ Hz); ^{11}B NMR (160.5 MHz, 298 K, [D$_6$]benzene): $\delta = 18.2$ ppm.

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