Ambiphilic Ligands

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# Gold(I) Complexes of Phosphanyl Gallanes: From Interconverting to Separable Coordination Isomers**

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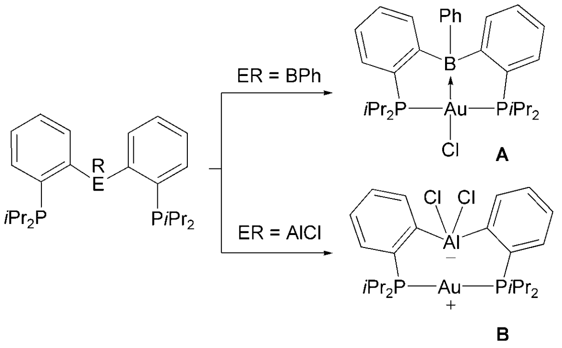
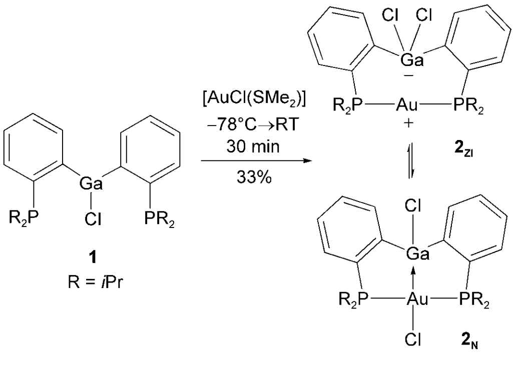
Over the last few years, several groups have been investigating the coordination chemistry of so-called ambiphilic donor–acceptor ligands.[1] The combination of phosphane and borane or alane moieties has allowed more insight to be gained into unusual metal–Lewis acid interactions[2–4] and the activation of M−X bonds through bridging coordination, leading ultimately to heterolytic cleavage.[4b,c,g,5] Representative examples are the neutral and zwitterionic gold(I) complexes **A**[4d] and **B**,[5e] derived from diphosphanyl borane (DPB) and diphosphanyl alane (DPA) ligands, respectively (Scheme 1).

The spectacular results obtained in recent years in the coordination chemistry of gallium[6–10] prompted us to study ambiphilic phosphanyl gallane ligands,[11] and herein we report on their unusual coordination properties. Upon coordination to the AuCl fragment, both neutral complexes of type **A** featuring an unprecedented gold–gallane interaction, and zwitterionic complexes of type **B**, have been characterized. Remarkably, the coexistence and interconversion of these coordination isomers can be directly monitored by NMR spectroscopy with diphosphanyl gallane (DPG), whereas the neutral and zwitterionic complexes derived from the corresponding triphosphanyl gallane (TPG) proved readily separable and were both structurally characterized.



*Scheme 1.* Neutral and zwitterionic gold(I) complexes derived from ambiphilic diphosphanyl borane and diphosphanyl alane ligands.

The DPG **1** was prepared by adding *o*-lithiated diisopropylphenylphosphine to $GaCl_3$ in toluene at room temperature. Treatment of **1** with $[AuCl(SMe_2)]$ in dichloromethane (DCM) afforded the desired complex **2** in 33% yield of isolated product (Scheme 2).[12] Colorless crystals suitable for X-ray diffraction analysis were obtained from a DCM/pentane solution at −30°C.[13] Complex **2** adopts the zwitterionic form $\mathbf{2_{ZI}}$ in the solid state (Figure 1). The gallium center is bound to the two chlorine atoms (Ga−Cl = 2.266 and 2.278 Å) and adopts a slightly distorted tetrahedral environment. As a result, the gold center is only two-coordinate (P-Au-P = 165°). The Au···Ga and shortest Au···Cl distances are 3.02 and 3.04 Å, respectively, indicating a complete transfer of the chloride from gold to gallium.



*Scheme 2.* Coordination of the diphosphanyl gallane ligand **1** to AuCl.

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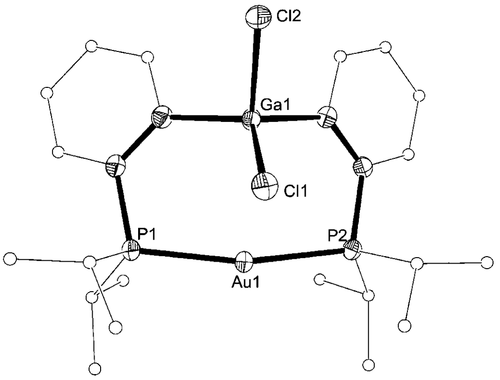


***Figure 1.*** View of complex $\mathbf{2_{ZI}}$ with ellipsoids set at 50% probability. Hydrogen atoms are omitted and isopropyl and phenyl groups are simplified for clarity.

Although the solid-state structure of the DPG complex **2** is very similar to that of the DPA complex **B**,[5e] spectroscopic analyses revealed a very different situation in solution. Indeed, on dissolution of crystals of **2** in chloroform, two species were observed by $^{31}$P NMR spectroscopy, with $\delta =$ 70 ppm (major) and 86 ppm (minor). The major compound was assigned to the zwitterionic form $\mathbf{2_{ZI}}$, which has a single signal at 71 ppm in the solid state. Dynamic interconversion of the two species in $CDCl_3$ was supported by the presence of cross peaks between the two resonance signals in the 2D $^{31}$P/$^{31}$P EXSY NMR spectrum.[12] The activation barrier for the exchange of the two forms was estimated to be circa $(15 \pm 1)$ kcal mol$^{-1}$ by variable-temperature and spin saturation transfer $^{1}$H NMR experiments.[12] Furthermore, the proportion of the zwitterionic form, as estimated from $^{31}$P and $^{1}$H NMR, was found to vary noticeably with the solvent polarity. From 68% in pure $CDCl_3$, it increases to 88% in the more polar $CD_2Cl_2$, and decreases to 52% in $CDCl_3/CCl_4$ 1:3 (Figure 2). All these data are consistent with the exchange in solution between the zwitterionic form $\mathbf{2_{ZI}}$ and the corresponding neutral form $\mathbf{2_N}$ in the slow regime of the NMR timescale.

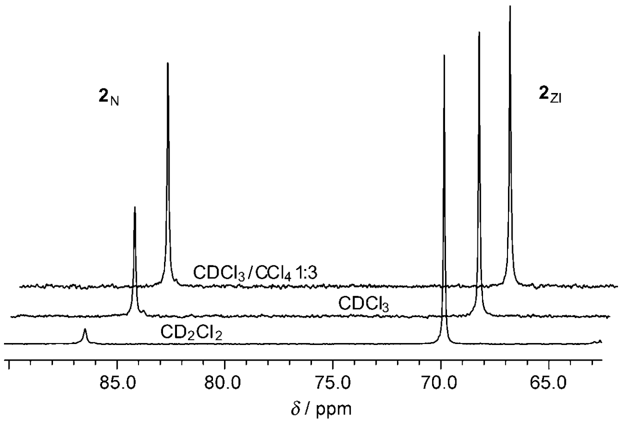
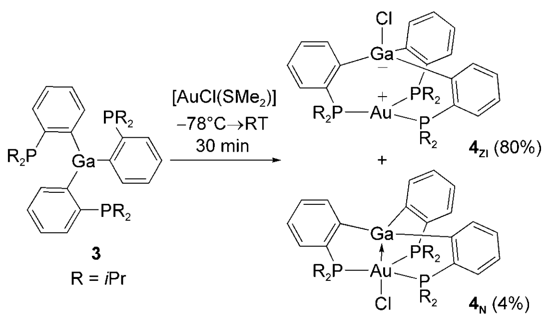


***Figure 2.*** $^{31}$P NMR spectra of complex **2** in different solvent combinations at 25 °C.

To gain some insight into the structure of $\mathbf{2_N}$ and to further confirm its possible interconversion with $\mathbf{2_{ZI}}$, DFT calculations were carried out at the B3PW91/SDD(Au,P,Ga,Cl),6-31G**(C,H) level of theory, both in the gas phase and in $CDCl_3$ solution (C-PCM model).[12] The optimized structure of the zwitterionic form $\mathbf{2_{ZI}}$ is in excellent agreement with that determined crystallographically. Another minimum was located for the corresponding neutral square planar complex $\mathbf{2_N}$. The short Au···Ga distance (2.59 Å) and noticeable pyramidalization of the gallium environment ($\Sigma Ga_\alpha = 345°$) in $\mathbf{2_N}$ are diagnostic of a Au→Ga interaction. This result is further corroborated by NBO analysis, in which a dative Au→Ga interaction ($\Delta E_{int} = 33$ kcal mol$^{-1}$) is found at the second-order perturbation level. In marked contrast with that observed for the related DPB and DPA complexes **A** and **B**,[14] the zwitterionic and neutral forms of complex **2** are essentially isoenergetic ($\Delta G = 0.3$ kcal mol$^{-1}$ in the gas phase, and 1.0 kcal mol$^{-1}$ in $CDCl_3$ solution), supporting the hypothesis of their coexistence. Furthermore, the dipole moment predicted for $\mathbf{2_{ZI}}$ is about twice that computed for $\mathbf{2_N}$ ($\mu = 10.7$ vs. 5.2 D in the gas phase), which is in agreement with the decrease of the $\mathbf{2_{ZI}}/\mathbf{2_N}$ ratio when the polarity of the solvent decreases.

The interconversion of the neutral and zwitterionic forms is associated with the transfer of the chloride between the metal and the Lewis acid site of the ambiphilic ligand. To slow down or even prevent this process, we then envisioned the preparation of cage complexes with reduced flexibility by introducing a third phosphanyl buttress at gallium. Addition of $GaCl_3$ to three equivalents of the *o*-lithiated diisopropylphenylphosphine afforded the TPG **3**, which was subsequently reacted with $[AuCl(SMe_2)]$ in DCM (Scheme 3).[12] The ensuing complex **4** once again coexists in solution between the zwitterionic and neutral forms. But in the case of compound **4**, the two coordination isomers proved separable, as complex $\mathbf{4_N}$ (4% yield of isolated product), but not $\mathbf{4_{ZI}}$ (80% yield of isolated product), is soluble in pentane. The two coordination isomers of complex **4** lie close in energy ($\Delta G = 4.1$ kcal mol$^{-1}$ in the gas phase).[12] However, in marked contrast with the related DPG complex **2**, no sign of interconversion between the zwitterionic and neutral forms of the TPG complex **4** was detected over days when solutions of pure $\mathbf{4_{ZI}}$ or $\mathbf{4_N}$ were monitored by NMR spectroscopy at room temperature, even at 50 °C.



***Scheme 3.*** Coordination of the triphosphanyl gallane ligand **3** to AuCl.

The structures of both complexes were unambiguously confirmed by X-ray analyses (Figure 3).[13] In **4**$_{\mathrm{ZI}}$, the gold center is surrounded by the three phosphorus atoms organized in a trigonal planar environment (sum of P-Au-P bond angles = 359°). In the neutral complex **4**$_{\mathrm{N}}$, the gold center is pentacoordinate and adopts a quasi ideal trigonal bipyramidal geometry.[15] The AuGa distance in **4**$_{\mathrm{ZI}}$ (2.969 Å) is very similar to that observed in **2**$_{\mathrm{ZI}}$, and is much shorter in **4**$_{\mathrm{N}}$ (2.578 Å), and fits well with the sum of covalent radii (2.48–2.58 Å).[16] The presence of a Au→Ga interaction in **4**$_{\mathrm{N}}$ is further supported by the inward pyramidalization of the gallium environment (sum of C-Ga-C bond angles = 347°). In **4**$_{\mathrm{ZI}}$, the gallium center also adopts a pseudo-tetrahedral environment, but points opposite to the gold center (outward pyramidalization, ΣC-Ga-C = 356°). According to NBO analysis, the magnitude of the Au→Ga interaction in **4**$_{\mathrm{N}}$ ($\Delta E_{\mathrm{int}} =$ 25 kcal mol$^{-1}$) is comparable to that predicted for **2**$_{\mathrm{N}}$. A few adducts between transition metals (Mo, Fe, Co, Ru, Rh, Pt) and trihalogallanes have been structurally characterized,[17] but to the best of our knowledge, complex **4**$_{\mathrm{N}}$ is the first example of such a M→GaR$_3$ interaction with a Group 11 element.[18,19] Similar to metal boratranes derived from the corresponding triphosphanyl borane,[4f,h] the two complexes **4**$_{\mathrm{ZI}}$ and **4**$_{\mathrm{N}}$ display approximately $C_3$ symmetry in the solid state, with average P-Au-Ga-C$_{\mathrm{ipso}}$ torsion angles $\theta$[20] of 27° and 19°, respectively.

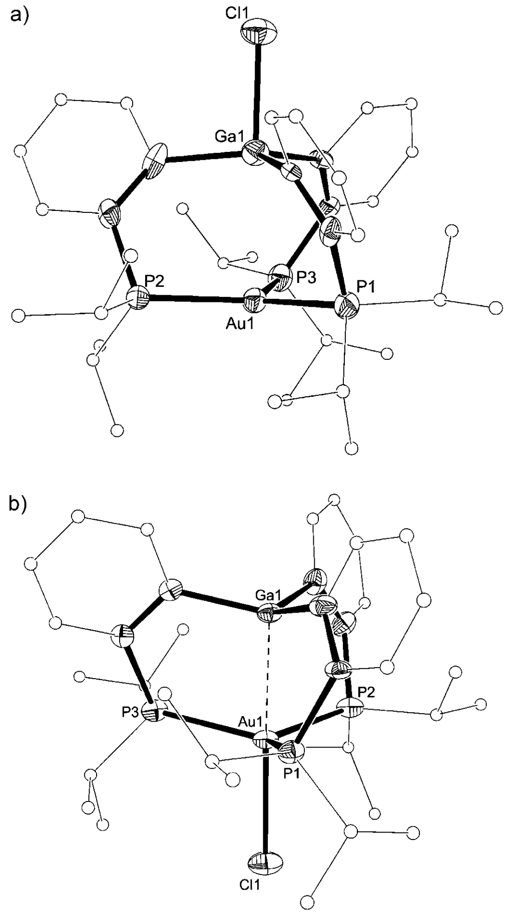


***Figure 3.*** Views of the two coordination isomers **4**$_{\mathrm{ZI}}$ (a) and **4**$_{\mathrm{N}}$ (b) with ellipsoids set at 50% probability. Hydrogen atoms and solvate molecules are omitted and isopropyl and phenyl groups are simplified for clarity.

Over the last few years, the four conceivable coordination modes of ambiphilic ligands have been exemplified experimentally and authenticated crystallographically. To further increase the versatility of such bifunctional ligands, dynamic systems susceptible to interconvert between different forms are particularly desirable. But to date, only indirect evidence for such an exchange process has been reported.[5b,c,f] Herein we reported the direct observation by NMR spectroscopy of the neutral and zwitterionic forms of the (DPG)AuCl complex **2**, including their mutual interconversion in solution. The presence of a third phosphanyl buttress at gallium was found to inhibit the transfer of the chloride between the metal and Lewis acid centers, so that the two coordination isomers are then separable and could be both structurally characterized. Dynamic systems derived from ambiphilic ligands offer new possibilities to finely tune the reactivity of complexes, and thereby open interesting perspectives in catalysis.

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[12] See the Supporting Information for details.

[13] CCDC 719580 (**2**$_{\mathbf{ZI}}$), CCDC 719581 (**4**$_{\mathbf{ZI}}$), and CCDC 719582 (**4**$_{\mathbf{N}}$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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