A Zwitterionic Gold(I) Complex from an Ambiphilic Diphosphino−Alane Ligand

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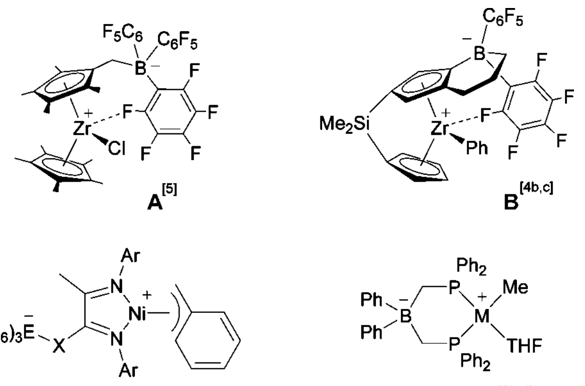
*Summary: The diphosphino−alane ligand $ClAl[C_6H_4(o\text{-}P\text{-}i\text{-}Pr_2)]_2$ (**1**) has been prepared and reacted with $[AuCl(SMe_2)]$. X-ray analyses and DFT calculations substantiate the preference of the ensuing complex **2** for a zwitterionic structure, resulting from internal chloride abstraction by aluminum over a neutral form featuring an Au→Al interaction.*

Charge-neutral zwitterionic complexes have attracted considerable interest in catalysis over the past few years, especially those combining an electrophilic cationic metal center with anionic ligands. Representative examples concern the polymerization and copolymerization of alkenes, as well as their hydrogenation and functionalization (via hydroformylation, hydroboration, diboration, hydroacylation, and hydrosilylation reactions. . .).[1] The zwitterionic complexes containing an anionic borate ligand, and to a lesser extent an aluminate variant, are clearly at the forefront of this area. Selected examples **A**−**D** are given in Scheme 1. From a synthetic viewpoint, two main strategies have been developed to access such borate or aluminate zwitterionic complexes: (i) the reaction of coordinated ligands with highly electrophilic boranes or alanes, as pioneered by Erker and Piers,[2–6] and (ii) the coordination of borate-containing ligands to cationic metal fragments.[7–9] The coordination of ambiphilic ligands that combine donor sites (typically phosphines or pyridines) and Lewis acids (such as boranes or alanes) with transition metals featuring an X coligand (X being

Scheme 1. Representative Borate- and Aluminate-Containing Zwitterionic Complexes A−D



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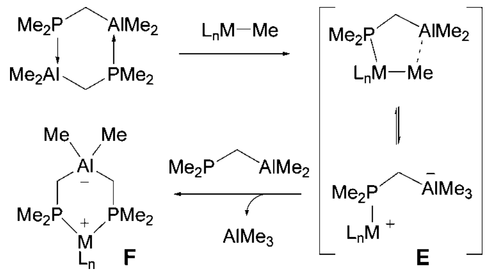
10.1021/om800101s CCC: \$40.75

Scheme 2. Internal M−Me Activation Proposed upon Coordination of $Me_2PCH_2AlMe_2$ and Subsequent Rearrangement into Zwitterionic Complexes F[a]



[a] ML_n = (1-Me-Ind)Ni, Cp*RhMe.

a halogen, hydrogen atom, or alkyl group) may also open access to such zwitterionic complexes as the result of X abstraction from the metal by the Lewis acid site of the ambiphilic ligand.

This type of internal activation of a Ni−Me bond has been proposed by Fontaine and Zargarian to account for the spectacular rate enhancement observed in the dehydrogenative oligomerization of $PhSiH_3$ with the [IndNiMe]/$Me_2PCH_2AlMe_2$ combination (Scheme 2).[10a] A related Rh−Me heterolytic cleavage has also been supported for the Cp^*RhMe_2/$Me_2PCH_2AlMe_2$ system.[10b] In both cases, the key zwitterionic intermediates **E** could not be isolated or characterized,[10] and only the zwitterionic complexes **F** resulting from the reaction of a second equivalent of $Me_2PCH_2AlMe_2$ were authenticated.

Our interest in M→Lewis acid interactions[11] and bridging coordinations of M−X bonds[11b,12] supported by ambiphilic ligands[13] prompted us to compare the behavior of boron and aluminum. Here we report evidence for an internal ionization process upon coordination of a diphosphino−alane to the AuCl fragment. The ensuing zwitterionic complex has been structurally characterized, and the influence of the Lewis acid on the outcome of the coordination (internal ionization vs M→Lewis acid interaction) has been analyzed through DFT calculations.

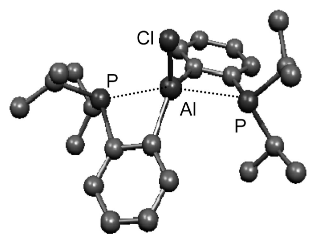
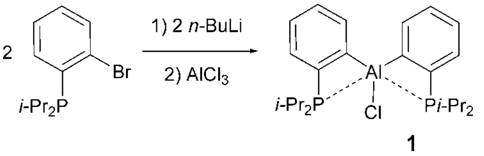
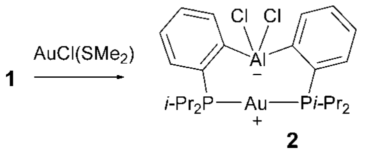


Figure 1. Optimized ground-state structure of the diphosphino−alane ligand **1** (at the B3PW91/6-31G** level of theory).

Scheme 3. Synthesis of the Diphosphino−Alane Ligand 1



Scheme 4. Synthesis of the Zwitterionic Complex 2 by Internal Ionization of the Au—Cl Bond



The diphosphino−alane (DPA) ligand **1** was prepared by bromine−lithium−aluminum exchange starting from (*o*-bromophenyl)diisopropylphosphine and $AlCl_3$ (Scheme 3). Compound **1** exhibits a single resonance at +24 ppm by ^{31}P NMR spectroscopy. By comparison with the chemical shifts observed for the diphosphino− and triphosphino−boranes ($\delta(^{31}P)$ ∼+25 ppm for a phosphorus atom engaged in a P→B interaction and $\delta(^{31}P)$ ∼0 ppm for a phosphorus atom free of P→B interaction),[14] this value suggests the existence of a degree of P→Al interaction. The broad signal observed at +102.5 ppm in the ^{27}Al NMR spectrum corroborates this hypothesis.[15] So far, the extreme sensitivity of **1** has precluded its structural characterization, but DFT calculations[16] support a pentacoordinate environment around the aluminum center as the result of weak, slightly dissymmetric contacts with both phosphorus atoms (P$\cdots$Al = 2.66 and 2.78 Å) (Figure 1). A similar situation has been reported by Müller et al. in the solid-state structure of $Al[C_6H_4(o\text{-}CH_2PPh_2)]_3$ (2.68 and 2.78 Å).[17] The alternative structures of **1** featuring one or no intramolecular P→Al interaction were predicted to be about 10 and 28 kcal/mol higher in energy, respectively.[16] The excellent agreement between the experimental and computed ^{27}Al chemical shifts (GIAO method, +106.6 ppm) further supports the structure proposed for **1**.[16,18]

Treatment of the DPA ligand **1** with [AuCl(SMe_2)] in dichloromethane (DCM) readily afforded the corresponding complex **2** (Scheme 4). The expected empirical formulation of **2** as (DPA)AuCl was confirmed by elemental analysis, and the

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(15) $\delta(^{27}Al)$ 96 ppm has been reported for the related compound $Al(C_6H_4\text{-}o\text{-}CH_2NMe_2)_2Cl$ featuring a pentacoordinate aluminum center, as the result of two intramolecular N→Al contacts: Müller, J.; Englert, U. *Chem. Ber.* **1995**, *128*, 493.

(16) See the Supporting Information for details.

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(18) ^{27}Al chemical shifts of 128.4 and 171.3 ppm were predicted for the alternative forms of the DPA ligand featuring one and no intramolecular P→Al interaction, respectively.

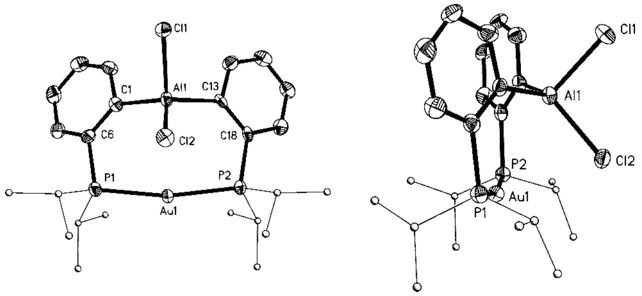
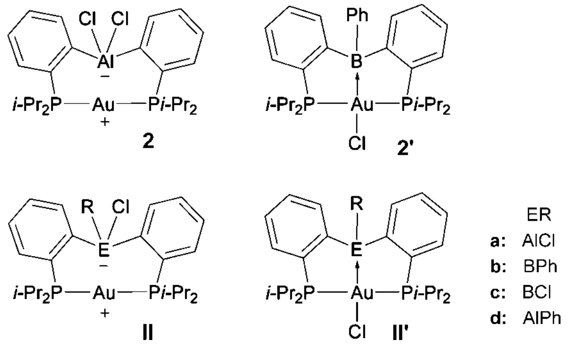


Figure 2. Molecular top and side views of complex **2**. The isopropyl groups are simplified, and the hydrogen atoms are omitted for clarity.

single resonance observed at δ 70.4 ppm in the ^{31}P NMR spectrum of **2** (vs 73.2 ppm for the related diphosphino−borane (DPB) complex **2′**)[11c] agreed with the symmetric coordination of the two phosphorus atoms. However, the poor solubility of **2** in organic solvents, except DCM, contrasted with those of the DPA ligand **1** and of the (DPB)AuCl complex **2′**, which were both soluble in pentane. In order to gain more insight into the precise structure of **2**, an X-ray diffraction study was carried out (Figure 2, Table 1).[19] This revealed a zwitterionic structure resulting from the transfer of the chloride from gold to aluminum. As a consequence, the metal center only interacts with the two phosphorus atoms (P−Au−P = 165.2°). The two Al−Cl bond lengths are identical (2.21 Å) and are in the range typical for a dichloroaluminate, while the shortest Au−Cl distance amounts to 3.04 Å, ruling out any significant bridging Al−Cl→Au interaction.[20]

Table 1. Experimental Data for Complexes 2 and 2′ and Theoretical Data[a] for Complexes IIa−d and II′a−d: Selected Bond Lengths (Å), Bond Angles (deg), and Relative Energies (kcal/mol)



complex		P−Au	Au···E	Au···Cl	E···Cl	P−Au−P	Δ*E*
2	X-ray	2.303 2.304	3.048	3.042[b]	2.208 2.208	165.2	
2′[11c]	X-ray	2.313 2.328	2.309	2.522	4.807	160.2	
IIa	DFT	2.374 2.374	3.178	3.101[b]	2.196 2.225	166.7	0
II′a	DFT	2.391 2.393	2.539	2.535	2.184 6.067	161.7	+7.8
IIb	DFT	2.328 2.322	3.339	2.884	1.996	155.3	0
II′b	DFT	2.352 2.367	2.323	2.564	4.884	161.9	−14.3
IIc	DFT	2.330 2.323	3.288	2.916[b]	1.934 1.921	155.2	0
II′c	DFT	2.354 2.376	2.256	2.537	1.902 4.737	154.9	−9.1
IId	DFT	2.369 2.369	3.300	3.057	2.256	166.7	0
II′d	DFT	2.385 2.385	2.581	2.563	5.137	163.1	+4.8

[a] At the B3PW91/SDD (Au), 6-31G** (other atoms) level of theory. [b] Shortest distance.

In order to gain more insight into the influence of the Lewis acid moiety on the contrasting structures adopted by the (DPA) and (DPB)AuCl complexes **2** and **2′**, DFT calculations were carried out. The B3PW91/SDD (Au), 6-31G** (other atoms) level of theory reproduced very well the experimental geometric features of **2** and was used throughout this study (Table 1). In addition to the zwitterionic structure **IIa**, another local minimum was located for the corresponding neutral form **II′a** about 8 kcal/mol higher in energy. The short Au−Al distance (2.54 Å) and noticeable pyramidalization of the aluminum environment ($\sum \mathrm{Al}_\alpha$ = 344°) in **II′a** are diagnostic of an Au→Al interaction.[21] In line with the experimental observations,[11c] the opposite situation was predicted for the related DPB complex, the neutral form **II′b** being in this case favored by about 14 kcal/mol over the zwitterionic structure **IIb**. Similar trends were obtained when the phenyl substituent at boron was replaced by a chlorine atom (the neutral form **II′c** is about 9 kcal/mol more stable than the zwitterionic structure **IIc**) and when the chlorine atom at aluminum was replaced by a phenyl group (**IId** is about 5 kcal/mol more stable than **II′d**). These data demonstrate the prominent role of aluminum in favoring the zwitterionic structure. Second-order perturbation NBO analyses[16] confirmed the presence of Au→E donor−acceptor interactions[22,23] within all of the neutral complexes **II′a−d**. Notably, the corresponding

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(19) Crystal data: $C_{24}H_{36}AlAuCl_2P_2$, M_r = 681.31, monoclinic, space group $P2_{1/c}$, a = 13.1769(6) Å, b = 11.8237(5) Å, c = 18.8682(9) Å, α = 90°, β = 108.7250(10)°, γ = 90°, V = 2784.1(2) Å^3, Z = 4, crystal size 0.05 × 0.05 × 0.02 mm^3, 21 620 reflections collected (4093 independent, R_{int} = 0.0757), 279 parameters, R1 ($I > 2\sigma(I)$) = 0.0300, wR2 (all data) = 0.0630, largest difference peak and hole: 1.059 and −0.695 e Å^{-3}.

(20) According to a Cambridge Database search, Cl−M distances within Al−Cl−TM (TM = transition metal) bridged complexes range from 2.35 to 2.86 Å.

(21) A few transition-metal→alane interactions have been structurally authenticated: (a) Burlitch, J. M.; Leonowicz, M. E.; Petersen, R. B.; Hugues, R. E. *Inorg. Chem.* **1979**, *18*, 1097. (b) Golden, J. T.; Peterson, T. H.; Holland, P. L.; Bergman, R. G.; Andersen, R. A. *J. Am. Chem. Soc.* **1998**, *120*, 223. (c) Buchin, B.; Gemel, C.; Kempter, A.; Cadenbach, T.; Fischer, R. A. *Inorg. Chim. Acta* **2006**, *359*, 4833. (d) Braunschweig, H.; Gruss, K.; Radacki, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 7782.

(22) Transition-metal→borane interactions were first structurally authenticated within metallaboratranes: (a) Hill, A. F.; Owen, G. R.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2759. (b) Foreman, M. R. St.-J.; Hill, A. F.; White, A. J. P.; Williams, D. J. *Organometallics* **2004**, *23*, 913. (c) Crossley, I. R.; Hill, A. F. *Organometallics* **2004**, *23*, 5656. (d) Mihalcik, D. J.; White, J. L.; Tanski, J. M.; Zakharov, L. N.; Yap, G. P. A.; Incarvito, C. D.; Rheingold, A. L.; Rabinovitch, D. *Dalton Trans.* **2004**, 1626. (e) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2005**, *24*, 1062. (f) Crossley, I. R.; Foreman, M. R. St.-J.; Hill, A. F.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2005**, 221. (g) Landry, V. K.; Melnick, J. G.; Buccella, D.; Pang, K.; Ulichny, J. C.; Parkin, G. *Inorg. Chem.* **2006**, *45*, 2588. (h) Senda, S.; Ohki, Y.; Hirayama, T.; Toda, D.; Chen, J.-L.; Matsumoto, T.; Kawaguchi, H.; Tatsumi, K. *Inorg. Chem.* **2006**, *45*, 9914. (i) Blagg, R. J.; Charmant, J. P. H.; Connelly, N. G.; Haddow, M. F.; Orpen, A. G. *Chem. Commun.* **2006**, 2350. (j) Pang, K.; Quan, S. M.; Parkin, G. *Chem. Commun.* **2006**, 5015. (k) Figueroa, J. S.; Melnick, J. G.; Parkin, G. *Inorg. Chem.* **2006**, *45*, 7056. (l) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2007**, *26*, 3891. (m) Crossley, I. R.; Hill, A. F. *Dalton Trans.* **2008**, 201. (n) Crossley, I. R.; Hill, A. F.; Willis, A. C. *Organometallics* **2008**, *27*, 312. (o) Crossley, I. R.; Foreman, M. R. St.-J.; Hill, A. F.; Owen, G. R.; White, A. J. P.; Williams, D. J.; Willis, A. C. *Organometallics* **2008**, *27*, 381. (p) Pang, K.; Tanski, J. M.; Parkin, G. *Chem. Commun.* **2008**, 1008.

(23) For recent discussions on the bonding description of complexes featuring Z-type BR$_3$ ligands, see ref 11c and: (a) Hill, A. F. *Organometallics* **2006**, *25*, 4741. (b) Parkin, G. *Organometallics* **2006**, *25*, 4744.

NBO delocalization energies are about 3 times larger for the DPB complexes than for their DPA counterparts. Both the relative weakness of the Au→Al vs the Au→B interactions and the higher affinity of the chloride anion for alanes vs boranes seem to favor the formation of the zwitterionic structure by internal ionization.[24]

In conclusion, the zwitterionic complex **2** provides spectroscopic and structural evidence for M−X bond ionization upon coordination of an ambiphilic ligand. Future research will seek to further compare the behavior of diphosphino−alane and −borane complexes and to vary the nature of the metal and coligand in order to gain a better understanding of the factors controlling the internal activation of M−X bonds. Future applications of ambiphilic ligands in catalysis should greatly benefit from such investigations.

Note Added after Submission. The reaction of the phosphino−borane ligands $Ph_2PCH_2CH_2BR_2$ ($BR_2 = BCy_2$, BBN) with $(dmpe)NiMe_2$, affording zwitterionic Ni(II) complexes, via abstraction of one of the methyl groups and coordination of the phosphine moiety to the resulting cationic metal center, has been independently reported by Tilley and co-workers.[25]

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Supporting Information Available: Text, figures, tables, and CIF files giving experimental and computational details, synthetic and characterization details for **1** and **2**, X-ray crystallographic data for **2**, and Cartesian coordinates for the optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) The affinity of the chloride anion for alanes and boranes was estimated computationally from the reactions ($Ph_2ECl + Cl^- \rightarrow Ph_2ECl_2^-$): $\Delta E = -65.2$ (E = Al) and -35.9 kcal/mol (E = B).

(25) Fischbach, A.; Bazinet, P. R.; Waterman, R.; Tilley, T. D. *Organometallics* **2008**, *27*, 1135.