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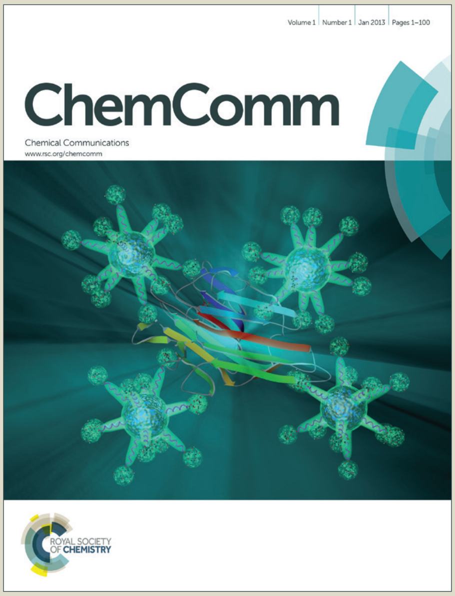

ROYAL SOCIETY OF CHEMISTRY

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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Novel zwitterionic complexes arising from the coordination of an ambiphilic phosphorus-aluminum ligand to gold

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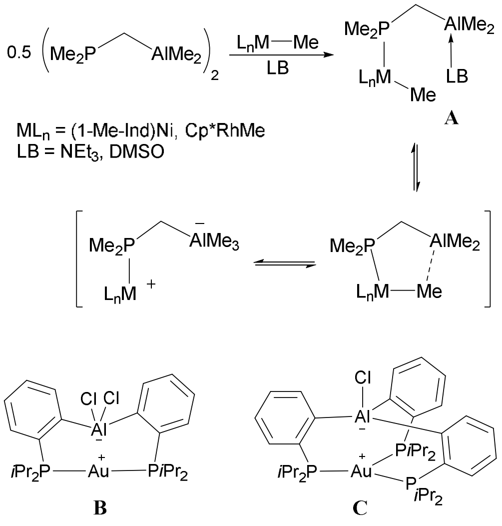
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Coordination of $Mes_2PC(=CHPh)AltBu_2$ to metal chlorides has been investigated. Bridging P→M–Cl→Al coordinations were observed with Rh and Pd fragments, while chloride abstraction systematically occurred with gold. The resulting zwitterionic complexes have been crystallographically characterized and the active participation of aluminum has been analyzed by DFT calculations.

Over the last few years, ambiphilic ligands have been shown to possess versatile coordination properties.[1] The introduction of Lewis acid moieties in the coordination sphere of transition metals has resulted in unusual bonding situations[2] as well as unique reactivity patterns.[3] Most studies in this area derive from phosphine–boranes (PB) but variations of the Lewis base (for *N*–based donors)[4] as well of the Lewis acid (for heavier group 14 and 15 elements)[5] have also been considered. Comparatively, the incorporation of heavier group 13 elements has been scarcely explored.[6,7,8] In particular, only a very few PAl complexes in which aluminum participates in coordination have been directly and unambiguously authenticated (Fig. 1).[6,7] Most significant are the contributions of Zargarian and Fontaine using the dimeric species $(Me_2PCH_2AlMe_2)_2$.[6] Complexes of type **A** have been characterized, and the ability of aluminum to interact and eventually abstract a methyl group at Ni or Rh has been supported. The coordination of *o*-phenylene bridged phosphorus-aluminum ligands to gold has also been investigated by some of us, and zwitterionic complexes **B-C** resulting from the dissociation of Au–Cl bonds were described.[7]

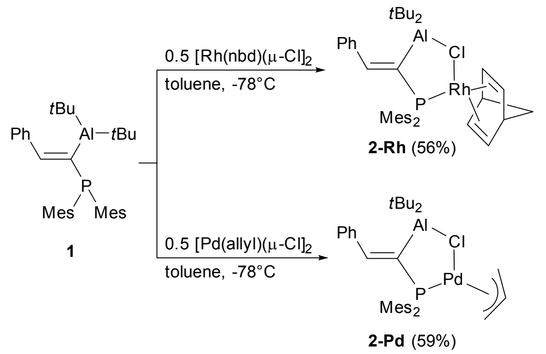
The unique properties of aluminum, in particular its more pronounced Lewis acid character compared to boron, makes phosphorus–aluminum ambiphilic ligands very appealing, but the relatively high sensitivity of the hitherto studied PAl (due to protonolysis or redistribution of Al-C bonds)[7a,9] represents a synthetic limitation. Thus, we became interested in exploring the coordination chemistry of the geminal PAl compound $Mes_2PC(=CHPh)AltBu_2$ **1** that has shown good stability and unique behaviour towards a range of small molecules.[10,11] Here, we report the synthesis and characterization of five new PAl complexes. The coordination of **1** is shown to be strongly influenced by the Lewis acid moiety. The role played by the aluminum center is discussed on the basis of X-ray diffraction analyses and DFT calculations.



ML_n = (1-Me-Ind)Ni, Cp*RhMe
LB = NEt_3, DMSO

Fig. 1 Known complexes deriving from phosphorus-aluminum ambiphilic ligands.

First, the coordination of **1** to Rh and Pd was investigated, using the chloride-bridged dimers $[Rh(nbd)(\mu–Cl)]_2$ (nbd = 2,5–norbornadiene) and $[Pd(allyl)(\mu–Cl)]_2$ as precursors (Scheme 1). The reactions proceed readily in toluene at low temperature. Complexes **2–Rh** / **2–Pd** were isolated in 56-59% yield after work-up. Coordination of the phosphine to Rh and Pd is clearly apparent from the low-field shift of the ^{31}P NMR resonance (from $\delta = -14.2$ ppm in **1**, to 27.5 ppm in **2–Rh**, and 11.5 ppm in **2–Pd**), and a diagnostic $^1J_{PRh}$ coupling constant (150.6 Hz) is observed for **2–Rh**.[12] In addition, mass spectrometry indicates the formation of monomeric complexes as the result of the cleavage of the chloride bridges. To assess the participation of aluminum in coordination, X-ray diffraction analyses were carried out (Fig. 2). Both complexes adopt monomeric square-planar structures with the PAl ligand engaged in bridging P→M–Cl→Al coordination. The environment around aluminum is pyramidalized (Σ(CAlC) ~ 351°) and the Al–Cl distance is relatively short [2.313(1) and 2.328(1) Å in **2–Rh** and **2–Pd**, respectively].[13]



Scheme 1 Bridging P→M–Cl→Al coordination of the phosphine-alane **1** with rhodium and palladium chlorides.

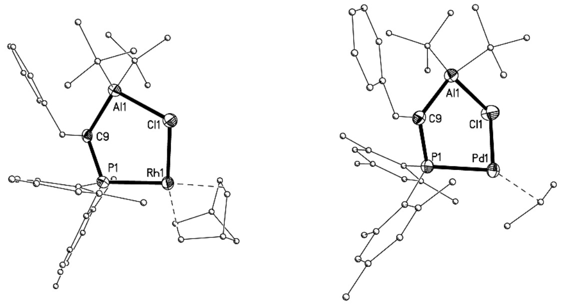


Fig. 2 Molecular views of complexes **2–Rh** (left) and **2–Pd** (right). **2**. The Mes, *t*Bu and Ph groups are simplified and the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows: **2–Rh**: P1–Rh, 2.341(1); Rh–Cl, 2.387(2); Al–Cl, 2.328(1); Al–C9, 2.033(5); C9–P, 1.841(4); P1–C9–Al, 118.18(2); C9–Al–Cl, 97.6(1); C9–Al–C1, 120.1(2); C1–Al–C5, 117.4(2); C5–Al–C9, 113.8(2). **2-Pd** : P1–Pd, 2.332(1); Pd–Cl, 2.390(1); Al–Cl, 2.313(1); Al–C9, 2.058(2); C9–P, 1.840(2); P1–C9–Al, 115.96 (8); C9–Al–Cl, 99.16(5); C9–Al–C1, 113.52(7); C1–Al–C5, 118.08(8); C5–Al–C9, 118.96(8).

Thus, despite the steric bulk imparted by the *t*Bu substituents at Al, **1** behaves as a chelating ambiphilic ligand upon coordination to Rh and Pd chlorides. Similar bridging coordinations were observed in complexes deriving from the phosphine-borane *i*Pr_2P-*o*-C_6H_4-BCy_2 (Cy: cyclohexyl).[14] But in that case, steric factors were found to strongly influence the participation of the Lewis acid, no Cl→B interaction being observed when mesityl groups were introduced at boron (Chart 1). The higher Lewis acidity and chloride affinity of Al relative to B,[7a] certainly play a major role in the bridged structures adopted by **2–Rh** and **2–Pd**. In turn, this is also reflected in the structural features of the complexes: Al interacts more tightly with the chloride than B (the respective distances exceed the sum of covalent radii by only 4% for Al, but 15% for B) and the M–Cl bonds are slightly longer in the PAl *vs* PB complexes (2.39 *vs* 2.35 Å).

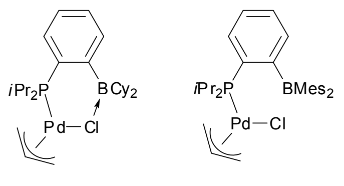
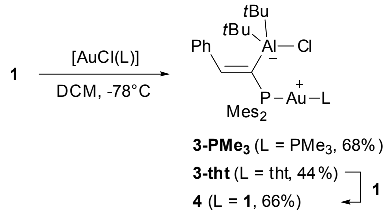


Chart 1

Next, coordination of **1** to gold(I) chlorides was investigated. The way ambiphilic ligands coordinate strongly depends on the geometry of the metal fragments, and the PAl ligand was expected to behave differently with such dicoordinate linear fragments. Treatment of **1** with [AuCl(PMe_3)] in dichloromethane at −78°C cleanly afforded the new complex **3–PMe₃** in 68% isolated yield (Scheme 2). Coordination of the phosphorus atom of **1** was indicated by the corresponding doublet observed at δ 30.5 ppm ($^2J_{PP}$ = 330.6 Hz) in the ^{31}P NMR spectrum.[15] X-ray diffraction analysis (Fig. 3, left) confirmed that the two phosphines are coordinated to gold in a quasi-linear arrangement (PAuP = 176.37(2)°). The chloride has been transferred from gold to aluminum. The Au–Cl distance exceeds 3.2 Å ruling out any Au–Cl→Al bridging interaction. Conversely, the AlCl distance in **3–PMe₃** (2.241(1) Å) is shorter than in the bridged complexes **2–Rh** and **2–Pd**,[16] and the pyramidalization of the environment around aluminum is more pronounced [Σ(CAlC) = 346°]. The formation of **3–PMe₃** substantiates the ability of PAl ligands to form zwitterionic complexes by internal abstraction of chlorides and its structure is reminiscent to that of complex **B**.[7a]



Scheme 2 Chloride abstraction upon coordination of **1** to gold.

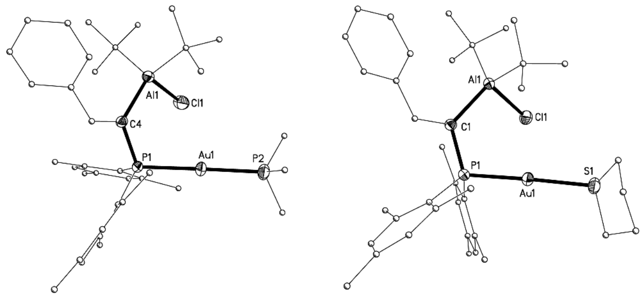


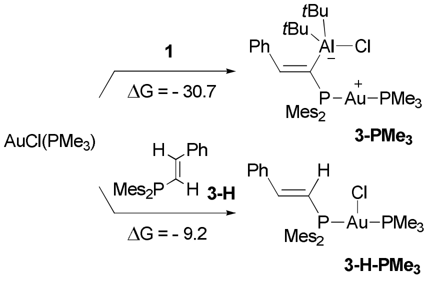
Fig. 3 Molecular views of complexes **3–PMe₃** (left) and **3–tht** (right). The Mes, *t*Bu and Ph groups are simplified and the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows: **3–PMe₃**: P1–Au, 2.334(1); Au–P2, 2.585(1); P1–C4, 1.839(2); C4–Al, 2.067(3); Al–Cl, 2.241(1); P1–Au–P2, 176.37(2); P1–C4–Al, 118.4(1); C4–Al–Cl, 101.41(8); C12–Al–C4, 111.9(1); C4–Al–C16, 117.8(1); C12–Al–C16, 1146.5(1). **3–tht**: P1–Au, 2.301(1); Au–S, 2.329(1); P1– C1, 1.837(2); Al1–C1, 2.071(2); Al1–Cl, 2.276(1); P1–Au–S, 173.39(2); P1–C1–Al, 121.8(1); C1–Al–Cl, 99.46(6); C13–Al–C9, 114.49(9); C9–Al–C1, 117.88(9); C1–Al–C13, 114.09(9).

At this point, we became interested in reacting **1** with [AuCl(tht)] (tht: tetrahydrothiophene). By doing so, we aimed to assess to which extent the abstraction of Cl by Al is favored, as the labile tht co–ligand at Au typically favors ligand displacement allowing the formation of the corresponding linear neutral complex [AuCl(L)]. The reaction followed a different course and the zwitterionic complex **3–tht** was selectively obtained. The tht co-ligand remains coordinated to gold, as clearly apparent by ^1H NMR spectroscopy (respective signals are found at δ 2.28 and

3.40 ppm). Crystallographic analysis unambiguously confirmed the structure of **3–tht** (Fig. 3, right) and its geometric features are very similar to those of **3–PMe$_3$**. The Au–Cl distance again exceeds 3.2 Å. Phosphines are known to readily displace tht from gold. The fact that dissociation of the Au–Cl bond is favored with **1** indicates that the Lewis acid moiety plays a major role and actually drives the coordination to an unexpected zwitterionic structure.[17,18]

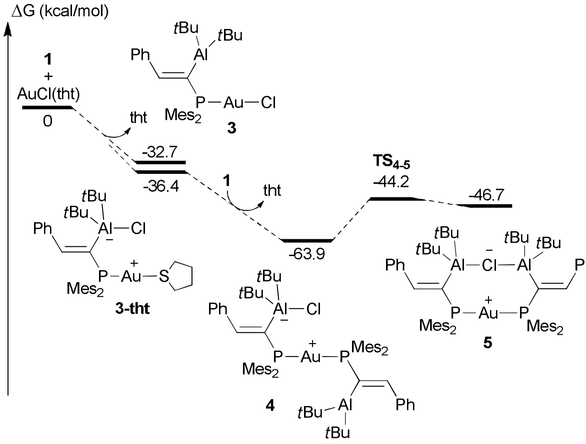
Complex **3–tht** was then treated with a second equivalent of PAl ligand so as to introduce a second aluminum center in the coordination sphere of gold, this time by classical tht displacement. The ensuing complex **4** proved extremely sensitive to hydrolysis[19] and crystals suitable for X–ray diffraction analysis could not be obtained. But its structure was supported by NMR spectroscopy and further corroborated by DFT calculations (*vide infra*). The ^{31}P NMR spectrum of **4** shows a broad signal at $\delta \sim$ 31.6 ppm at room temperature, suggesting some fluxional behavior. Cooling down the solution to –60°C resulted in the appearance of a well–resolved AB system (δ 25.2 and 36.1 ppm, $^2J_{PP}$ = 309.0 Hz) indicating an unsymmetrical zwitterionic structure with two PAl ligands coordinated to gold and chloride siting at one of the Al center. At higher temperature, the chloride apparently shifts from one aluminum to the other, resulting on average in a symmetrical Al–Cl–Al bridged species.[20] The activation barrier associated with this dynamic phenomenon (12.2 ± 1 kcal/mol at 30°C) was estimated by variable-temperature measurements.[21]

The coordination of **1** to Au was then studied by DFT calculations using the B97D functional, the SDD(f) basis set for Au, and 6-31G** for all other atoms.[21] First, the importance of aluminum in the coordination of **1** to [AuCl(PMe$_3$)] was investigated. It was found that Cl abstraction by Al is quite exergonic, with a free energy gain of 30.7 kcal/mol for the formation of **3–PMe$_3$** from its constituents. Using the Al–free ligand (Mes)$_2$P(CH=CHPh) (**3-H**)[10d] instead, the coordination energy is reduced considerably (by 21.5 kcal/mol) to a modest ΔG = –9.2 kcal/mol for the formation of **3-H–PMe$_3$** (Scheme 3).



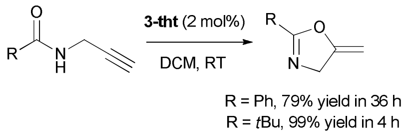
Scheme 3 Influence of Al upon coordination of **1** to AuCl(PMe$_3$).

Then, the coordination of **1** to [AuCl(tht)] was examined (Scheme 4). In agreement with experimental observations, formation of the zwitterionic complex **3-tht** is exergonic by 36.4 kcal/mol, and it is favored thermodynamically over tht displacement ($\Delta\Delta G$ = 3.7 kcal/mol). Addition of a second PAl ligand to **3-tht** does induce ligand exchange and gives the unsymmetrical complex **4** (ΔG = –27.5 kcal/mol; Al–Cl 2.284 Å). The gold center is surrounded by two PAl ligands (PAuP = 164.1°). The chloride sits at one of the aluminum centers, which is pyramidalized [Σ(CAlC) = 343°], while the other Al atom remains planar [Σ(CAlC) = 359°] and points in the opposite direction. The fluxional behaviour of **4** was explored computationally. The shift of Cl from one aluminum center to the other indeed proceeds *via* the symmetrical Al–Cl–Al bridged species **5** (Al–Cl 2.445 Å; $\Delta\Delta G$ = 17.2 kcal/mol) and involves a barrier of 19.7 kcal/mol at 30°C (**TS$_{4-5}$**).



Scheme 4 Thermochemistry of the coordination of **1** to AuCl(tht).

In conclusion, Mes$_2$PC(=CHPh)Al*t*Bu$_2$ proved to be a robust and versatile ligand for transition metals. Bridging P→M–Cl→Al coordinations were observed with Rh and Pd fragments, while chloride abstraction systematically occurred with gold. The fact that **1** reacts with ClAu(tht) *via* Au–Cl dissociation instead of tht displacement is particularly noteworthy and represents a rare example of Lewis acid-controlled coordination. The Al center drives the reaction to the formation of zwitterionic complexes, and thereby, ambiphilic ligands may offer an alternative to silver salts for the activation of gold(I) precatalysts. To test this hypothesis, complex **3-tht** was evaluated in the cycloisomerization of propargylamides (Scheme 5).[17a,22] The reactions were performed at room temperature using 2 mol% of **3-tht**. Cyclization proceeds readily and the corresponding alkylidene oxazolines were formed cleanly within hours.[21] Complex **3-tht** shows similar catalytic activity than the reference complex (Ph$_3$P)AuNTf$_2$ prepared from (Ph$_3$P)AuCl and AgNTf$_2$.



Scheme 5 Cyclization of propargylamides catalyzed by **3-tht**.

This work was supported financially by the Centre National de la Recherche Scientifique (CNRS), the Université Paul Sabatier (UPS), the Deutsche Forschungsgemeinschaft, the European Union (Marie Curie ITN SusPhos, Grant Agreement No. 317404), the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (NWO/CW) by a VIDI grant (J.C.S.), and the PHC Van Gogh program (PROJECT N° 31616SK).

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details and characterization data, including crystallographic data for **2**-**4**; computational studies. See DOI: 10.1039/b000000x/

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