

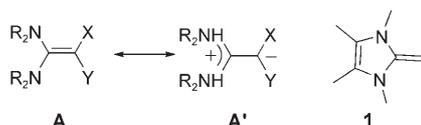
Ligand Design

Coordination Chemistry of Ene-1,1-diamines and a Prototype “Carbodicarbene”**

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Dedicated to Professor Andreas Pfaltz on the occasion of his 60th birthday

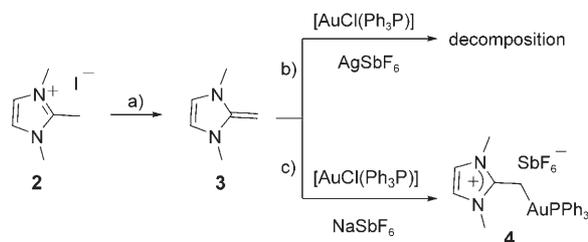
Ene-1,1-diamines (ketene amins, **A**) are a special class of olefins distinguished by a very electron rich and strongly polarized double bond.^[1] This dipolar character is caused by the significant contribution from the mesomeric extreme **A'** to their ground-state structure (Scheme 1), and becomes



Scheme 1. The two mesomeric extremes of a generic ene-1,1-diamine. Structure of the well investigated imidazoline derivative **1**.

particularly prominent if the nitrogen atoms are part of a heterocyclic ring able to accommodate positive charge. Likewise, coordination to a suitable (transition) metal template enhances the inherent ylide character of compounds such as **1**^[2,3] and its relatives. Surprisingly, however, few such metal complexes of ene-1,1-diamines have been reported,^[3,4] and no attempts have been made to generalize the underlying concept of charge separation. Outlined below are the results of our initial foray into this promising territory, with emphasis on the coordination chemistry of gold as a particularly “carbophilic” and catalytically relevant Lewis acid.^[5,6]

Although compound **1** has been investigated in some detail,^[2,3,7] the parent 1,3-dimethyl-2-methyleneimidazoline (**3**) itself has not been isolated in pure form. Gratifyingly, we found that this particular compound is readily obtained as an air-sensitive solid by deprotonation of imidazolium iodide **2** with KH in Et₂O (Scheme 2). However, first attempts at preparing the corresponding cationic gold complex through reaction of **3** with [AuCl(PPh₃)] and AgSbF₆ in THF were thwarted by the instantaneous formation of a black, intractable precipitate. On the assumption that the electron-rich



Scheme 2. Conditions and reagents: a) KH, Et₂O, 87%; b) [AuCl(PPh₃)], AgSbF₆, THF, decomp; c) [AuCl(PPh₃)], NaSbF₆, THF, 89%.

olefin might reduce one (or both) of the noble-metal components in the mixture, AgSbF₆ was replaced by NaSbF₆. This simple modification afforded the desired gold complex **4** in the form of colorless crystals with excellent yield. Its structure in the solid state confirms that the ligated olefin behaves very much like a “carbon ylide”, as evident from the end-on coordination to the metal center (Figure 1). The Au–C1 bond of 2.087(3) Å is even longer than the corresponding single bond in [AuPh(PPh₃)] (2.04 Å).^[8] Moreover, the heterocyclic ring shows all the structural attributes of an imidazolium cation.

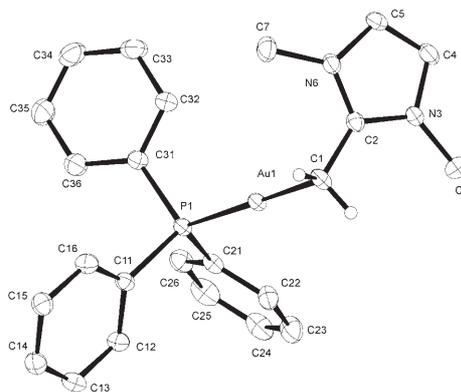


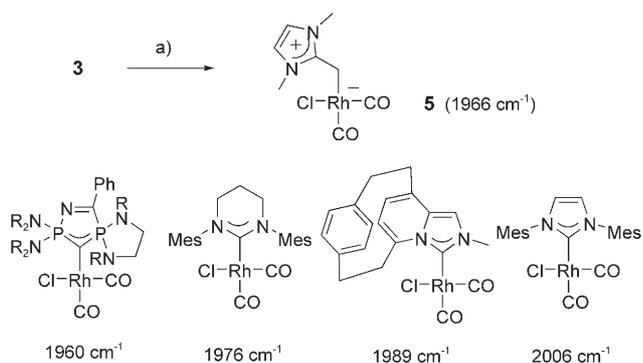
Figure 1. Structure of the complex cation of **4** in the solid state (the SbF₆[−] ion is removed for clarity).^[9]

Next, we prepared the corresponding rhodium complex **5**, as the IR stretching frequencies of the CO ligands in compounds of type [RhCl(CO)₂L] are commonly used to assess the electronic properties of a given ligand L (Scheme 3).^[10,11] According to this “rhodium scale”, even

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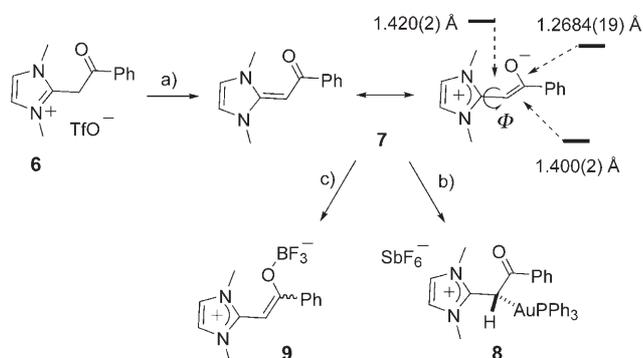
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Scheme 3. Preparation of the rhodium complex **5** and comparison of the donor capacity of its ene-1,1-diamine ligand with that of a cyclic “carbodiphosphorane” and three different NHCs. The wavenumbers ($\tilde{\nu}$, cm^{-1}) refer to the unsymmetrical stretching mode of the CO ligands. Conditions and reagents: a) $[\text{RhCl}(\text{CO})_2]_2$, Et_2O , RT, 59%. Mes = mesityl = 2,4,6-trimethylphenyl, R = *i*Pr.

the most simple 2-methylene-imidazoline **3**, outperforms the standard N-heterocyclic carbenes (NHC) in terms of donor capacity; these latter species are commonly employed wherever electron-rich metal templates are desirable in catalytic transformations.^[12,13] The donor property of **3** is similar to that of the much more elaborate cyclic carbodiphosphoranes recently introduced by Kato, Baceiredo, and co-workers (Scheme 3).^[14]

To probe the effect of functional groups, compound **7** bearing a ketone on the exocyclic double bond was targeted. Not only is this derivative easy to prepare by deprotonation of **6**^[15] (Scheme 4), but any appreciable degree of charge



Scheme 4. Conditions and reagents: a) KH, THF, RT, 79%; b) $[\text{AuCl}(\text{PPh}_3)]_2$, AgSbF_6 , THF, RT, 85%; c) $\text{BF}_3(\text{OEt}_2)$, Et_2O , RT, 92%.

separation should manifest itself in an enolate-like geometry of the carbonyl subunit. The structure of **7** in the solid state (Figure 2) nicely confirms this view, as the C4–C5 bond is shorter than the formal C4–C1 “double” bond, whereas the “carbonyl” bond length C5–O1 (1.2684(19) Å) clearly exceeds that of a regular enone (for example, 1.24 Å in chalcone).^[16] As expected for a Hückel aromatic system, the heterocyclic part is devoid of any significant bond alterations at the symmetry-related positions. Compound **7** is therefore

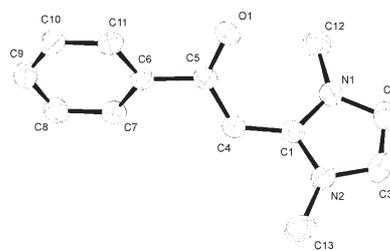


Figure 2. Structure of **7** in the solid state.^[9]

best described as a stable betaine. Likewise, the significant torsion angle $\Phi = 38.3^\circ$ is consistent with the notion that the dipolar resonance form is structure determining.

As a consequence, the corresponding gold adduct **8** can not only be viewed as an ylide complex, but is more accurately portrayed as a C-metalated noble-metal enolate.^[17] The C1–C6 and the C6–C7 bond lengths fall within the range for normal single bonds between sp^2 - and sp^3 -hybridized carbon atoms (1.478(3) and 1.495(3) Å, respectively), whereas the C7–O1 bond (1.232(2) Å) corresponds to a normal carbonyl group (Figure 3).^[16] Notably, the aurated carbon atom in **8** is tetrahedrally coordinated, and hence represents a chiral center.

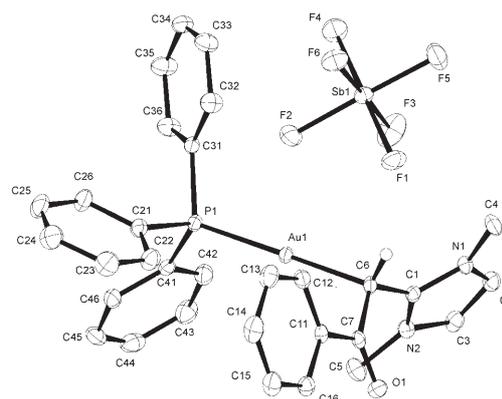


Figure 3. Structure of the gold enolate complex **8** in the solid state.^[9]

To further probe the enolate character, **7** was treated with $\text{BF}_3(\text{OEt}_2)$ in an attempt to address the oxygen terminus of the ambidentate nucleophile with a “hard” Lewis acid. Again, through X-ray analysis, the structure of the resulting O-metalated adduct **9** was unambiguously confirmed (Figure 4).

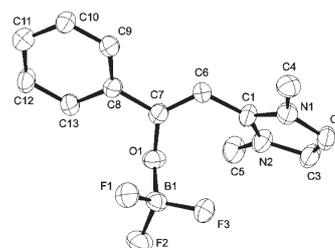
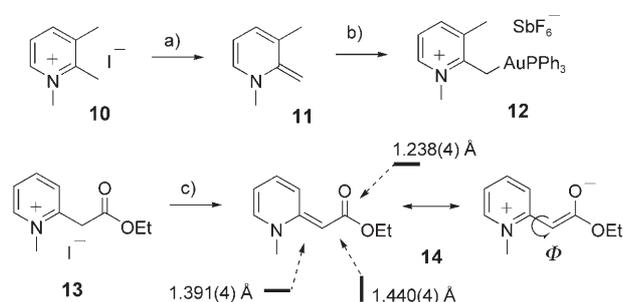


Figure 4. Structure of the boron adduct **9** in the solid state.^[9]

Next, we investigated whether the imidazolium unit could be replaced by other heterocyclic rings that are able to stabilize positive charge, namely *N*-alkyl pyridinium cations. The required *exo*-alkylidene derivatives **11** and **14**^[18] were prepared by the same, exceedingly simple route (Scheme 5).



Scheme 5. Conditions and reagents: a) KH, Et₂O, RT, 84%; b) [AuCl(PPh₃)], AgSbF₆, THF, RT, 68%; c) NaOH (1 M), THF, RT, 92%.

Whereas **11** is a pale orange liquid, **14** was obtained in multigram quantities as a bright yellow crystalline solid upon treatment of **13** with aqueous NaOH. However, its structure in the solid state (Figure 5) reveals that **14** is clearly less

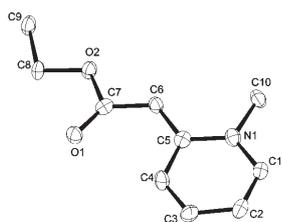


Figure 5. Structure of **14** in the solid state.^[9]

“enolate-like” than **7**, as evident from the pattern of alternating bond lengths and the very small torsion angle Φ of only 4.2° (Scheme 5). As a result, **14** does not form a stable gold complex under the chosen conditions, whereas the arguably more electron-rich parent compound **11** reacts smoothly to give **12**. This adduct again shows all the features of an ylide complex, in which the metal center is bound to the terminal carbon atom of the olefin; judging from the Au–C2 length, the contribution of the alternative η^2 -coordination mode must be marginal, if at all (Figure 6).

Gold catalysis relies, to a large extent, on the propensity of this soft Lewis acid to enhance the electrophilicity of a bound alkene or alkyne. This property is thought to arise from “slippage” of the metal template along the axis of the π bond (Scheme 6).^[19] Complexes **4** and **12** described herein nicely manifest this putative $\eta^2 \rightarrow \eta^1$ deformation, and are hence of fundamental relevance for a better understanding of the structural basis of “ π acidity” as the characteristic trait of gold and related noble-metal catalysts.^[5,6]

The coordination chemistry becomes even more intriguing if two ene-1,1-diamine units are formally combined into the heterocumulene motif of a tetraaminoallene **B**. Although

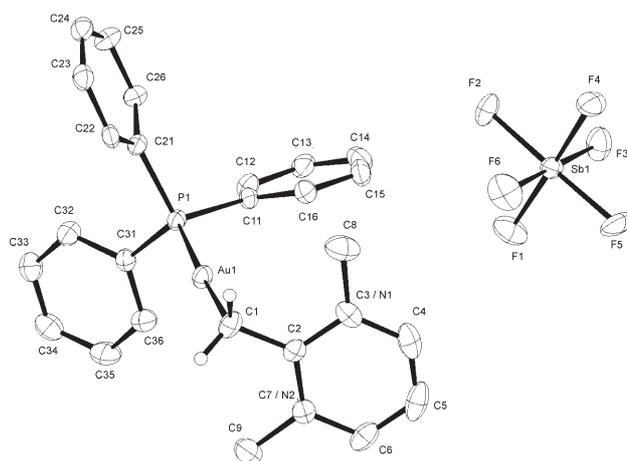
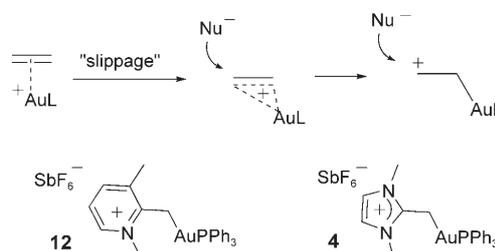
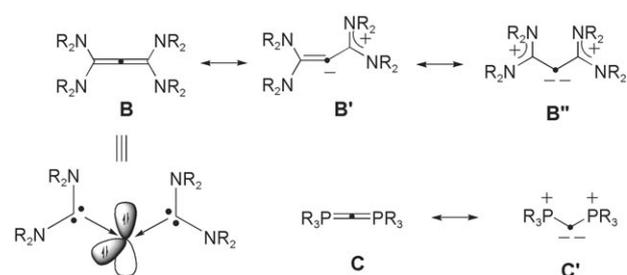


Figure 6. Structure of complex **12** in the solid state.^[9]



Scheme 6. Slippage mechanism responsible for the activation of π bonds by carbophilic Lewis acids and comparison with the structure of two representative ylide-type gold complexes escorted by a non-nucleophilic counterion. Nu[−] = nucleophile.

such compounds have been known for a long time,^[20] no transition-metal complex has ever been reported. A recent theoretical analysis of the bonding situation in tetraaminoallenes suggests that the mesomeric form **B''** makes a substantial contribution to their ground-state structure (Scheme 7).^[21]

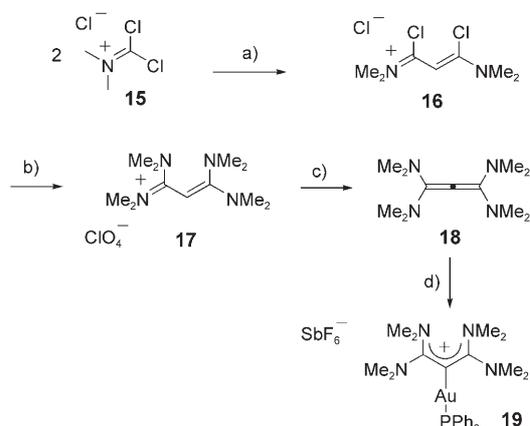


Scheme 7. Schematic representation of the bonding situation in tetraaminoallenes, to which the mesomeric extreme of a “carbodicarbene” makes a substantial contribution.

In the extreme, tetraaminoallenes can be considered to consist of a formally zerovalent central carbon atom, which is endowed with two pairs of electrons and flanked by two strongly donating diamino-stabilized carbene entities (“carbodicarbene”). The lone pairs of electrons reside in an orbital

of π symmetry (highest occupied molecular orbital; HOMO), largely centered on the central carbon atom, and in an σ orbital (HOMO-1), thus potentially rendering tetraaminoallene derivatives neutral, yet very basic net four-electron donors.^[21] The analogy to the more abundant carbodiphosphoranes **C** and related cumulated ylides is clear.^[14,22–25] At first glance, one might mistake “carbodicarbenes” for singlet carbenes of the NHC type; note, however, that the latter are formally divalent carbon species, with a pair of electrons in a σ orbital as well as an orthogonal but empty π orbital.^[12] In striking contrast, the two respective orbitals of a “carbodicarbene” are both filled, containing a pair of electrons each.^[21]

Compound **18** is a representative example of this particular class of allene derivatives and was conveniently prepared from commercially available **15** by following a reported route (Scheme 8).^[20,26] Again, reaction with $[\text{AuCl}(\text{PPh}_3)]/\text{AgSbF}_6$



Scheme 8. Conditions and reagents: a) DMA, CH_2Cl_2 , reflux; b) 1. Me_2NH (neat); 2. sat. aq NaClO_4 , CH_2Cl_2 , 89% (over 2 steps); c) $n\text{BuLi}$, THF, RT, 76%; d) $[\text{AuCl}(\text{PPh}_3)]$, NaSbF_6 , THF, RT, 72%. DMA = *N,N*-dimethylacetamide.

failed to afford a stable complex, but we were pleased to see that the use of NaSbF_6 as a halide scavenger worked nicely to provide product **19** in 72% yield. Its remarkable structure in the solid state is depicted in Figure 7. The metalated carbon

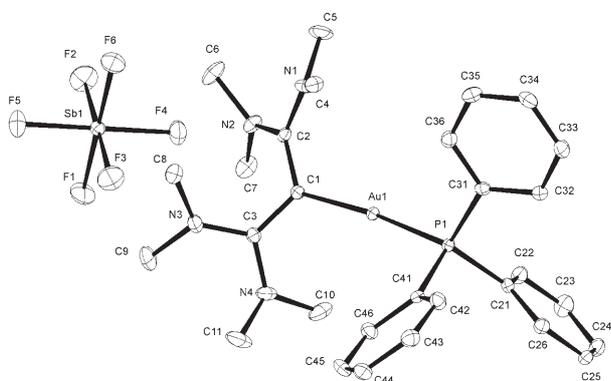
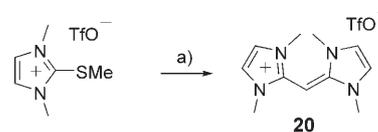


Figure 7. Structure of the gold “carbodicarbene” complex **19** in the solid state.^[9]

atom exhibits the expected trigonal planar coordination geometry, with the in-plane lone pair of electrons of the ligand binding to the gold template. Each of the lateral diamino-stabilized “carbene” moieties is also planar, but they are tilted relative to each other to relieve allylic strain.

Although complex **19** engages only one of the two lone pairs of electrons proposed to reside on the central carbon atom of the tetraaminoallene **18** in bonding to the transition-metal center, it remains to be seen if a dimetalation of this position can also be achieved.^[24] To this end, it will be interesting to extend this study to metals other than gold, which was chosen for our preliminary investigation because of its pronounced carbophilicity. Equally promising is the outlook in structural terms, as different types of cumulated ylides are known which might serve as ligands with unusual structural characteristics and donor properties; compound **20** is an obvious candidate amongst the many conceivable choices (Scheme 9).^[27] Investigations along these lines are



Scheme 9. Conditions and reagents: a) **3**, KH, THF, 72%.

being actively pursued by our research group and will be reported in due course.

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