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Chiral heterobimetallic complexes of carbodiphosphoranes and phosphinidene–carbene adducts[†]

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Heterobimetallic complexes derived from carbodiphosphoranes or phosphinidene–carbene adducts are reported, in which the central atom accepts two lone-pairs from two different donor ligands and – at the same time – donates two lone-pairs to two different metal centers. Therefore these complexes are carbogenic yet captodative chiral entities.

Although the strong Lewis basicity and unusual coordination properties of carbodiphosphoranes were recognized early on,¹ it was not until the recent computational studies of Frenking and co-workers that the chemical nature of such compounds was fully appreciated.² These investigations suggested that carbodiphosphoranes cannot be adequately described as heterocumulenes; rather, they are thought to consist of two phosphine ligands coordinated to a central carbon atom, which keeps its own valence electrons in the form of two orthogonal lone pairs and hence gains formally zero-valent character. It was not least because of this provocative interpretation of stable carbogenic compounds as captodative entities that the chemistry of carbodiphosphoranes and structurally related compounds has flourished. Moreover, it was suggested that the same bonding situation is found in carbodicarbenes,³ in "heteroleptic" C^0 moieties stabilized by one phosphane and one carbene ligand,⁴ as well as in related species in which the central carbon atom is formally replaced by isolobal BR,⁵ N⁺,⁶ or P⁺⁷ units.

Three possible coordination modes can be conceived for carbodiphosphoranes based on the rationale outlined above: (i) the central carbon atom can donate only two electrons and hence behave as a traditional σ -donor ligand as shown in the generic structure **A**;⁸ (ii) both electron pairs of the central carbon serve to bind an electrophile each; if the latter are metal fragments, geminally dimetallated complexes **B** will ensue;^{4a,9} (iii) finally, it is possible that all four available electrons are involved in simultaneous σ - and π -donation to the same Lewis acid center as shown





in C (Scheme 1).¹⁰ All three situations have already been experimentally confirmed. What has not been realized so far, however, is the possibility of employing **A**-type compounds as starting materials for a second metallation step using a *different* Lewis acid. Despite the plausible interest in the resulting heterobimetallic species **D** from a structural point of view (they may offer a new platform for the study of metal-metal interactions) and in the area of cooperative bimetallic catalysis, we are unaware of any precedent for such a molecular architecture. Outlined below are the first examples of coordination compounds of this type, which also demonstrate that zerovalent carbon centers can be rendered chiral when surrounded by two different internal phosphine donors and two different metal acceptor sites.

To this end, carbodiphosphorane **3** was chosen as a suitable starting material. While the strongly donating triphenylphosphine and 2-(pyridyl)diphenylphosphine ligands impose C⁰ character onto its central atom, the pyridyl substituent might assist in the coordination of a second Lewis acid by chelation. Compound **3** was readily attained as a yellow solid upon reaction of bromomethyl triphenylphosphonium bromide **1** with (2-pyridyl)PPh₂ and subsequent deprotonation of the resulting diphosphonium salt **2** with NaNH₂ in liquid NH₃. The carbodiphosphorane nature of **3** is evident from the high-field ¹³C NMR signal at $\delta = 11.8$ ppm (dd, ${}^{1}J_{C-P} = 122, 119$ Hz), which is a characteristic trait of all known compounds comprising a R₃P \rightarrow C \leftarrow PR₃ entity. The structure in the solid state is also informative, as it shows that the putative P–C–P "hetero-cumulene"

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Scheme 2 Synthesis and molecular structure of 3 in the solid state (hydrogen atoms and solvent molecules have been removed for clarity; ellipsoids at 50% probability).¹¹ Reagents and conditions: (a) 1, 1 equiv.; PPh₂(2-pyridyl), 1 equiv., (PhO)₃PO, 120 °C, 12 h, 24%; (b) NaNH₂/NH₃, -35 °C, 7 h, 88%.

axis is in fact significantly bent away from linearity ($\Theta = 133.25(10)^{\circ}$; Scheme 2).

In line with our expectations, compound 3 reacted smoothly with $[Ph_3PAuCl]$ in the presence of $NaSbF_6$ to give the monoaurated species 4 (Scheme 3). Despite its cationic character, this complex was able to intercept either CuCl or $[(Me_2S)AuCl]$ with formation of the corresponding dimetallated complexes 5 and 6, respectively, in remarkably good yields.

The comparison of the structures of **5** and **6** is highly informative. In the solid state, the Cu atom of **5** is tightly bound to the central carbon of the ligand; actually, the Cu(1)–C(1) bond length of 1.981(5) Å is only slightly longer than the one found in closely related mono-metallated carbodiphosphorane–Cu complexes



Scheme 3 Synthesis of **4–6** and molecular structures of **5** and **6** in the solid state (hydrogen atoms, anions and solvent molecules have been removed for clarity; ellipsoids at 50% probability).¹¹ *Reagents and conditions*: (a) [Ph₃PAuCI], NaSbF₆, THF, 0 °C, 1 h, 97%; (b) CuCl, CH₂Cl₂, 0 °C, 12 h, 95%; (c) [(Me₂S)AuCI], CH₂Cl₂, 0 °C, 2 h, 85%.

(1.906(2)–1.948(5) Å).¹² Compound 5 also displays an additional example of weak metallophilic interaction between Cu and Au (Cu(1)–Au(1) bond distance 2.8483(10) Å).¹³ Finally, the Cu atom also coordinates with the nitrogen of the pyridyl substituent. Although the Cu(1)–N(1) bond distance in 5 (2.267(6) Å) is longer than those in regular Cu(i)–pyridine complexes, it is clearly within the sum of the van der Waals radii of the partners.¹⁴

In complex **6**, the Au(2) atom introduced in the second auration step binds tighter to C(1) than Au(1) (Au(2)–C(1) and Au(1)–C(1) bond lengths are 2.080(9) and 2.127(8) Å, respectively). This is somewhat counterintuitive, given the fact that Au(2) belongs to a neutral AuCl fragment, whereas the Au(1) centre is, *a priori*, positively charged.^{15,16} We tentatively ascribe the weaker interaction with the Au(1) centre to the *trans*-effect of the PPh₃ ligand. The Au(1)–Au(2) distance in **6** is 3.1274(6) Å and in contrast to complex **5**, featuring a distinctive Cu–N bond, the pyridine nitrogen atom in **6** interacts with neither of the neighbouring gold atoms.

To the best of our knowledge, complexes **5** and **6** are the first examples of heterodimetallated C^0 compounds. In both cases, the central C(1) atom carries four chemically different substituents and hence constitutes a chiral center. In assessing this situation, one should bear in mind that the nature of the four bonds engaging C(1) is captodative and, therefore, fundamentally different from the bonding situation in ordinary (chiral) organic molecules.

Unfortunately, all our attempts to coordinate non-linear metal fragments to 4 failed, presumably because of the congestion about the C^0 atom caused by the phosphine ligands. Therefore, we next focused our attention on phosphinidenes, a series of compounds in which the central carbon from carbodiphosphoranes has been formally replaced by an isolobal [PR]-fragment (Scheme 4). It is expected that the longer metal phosphorus bonds should facilitate the coordination of a wider variety of metal fragments.¹⁷

Due to the experience of our group with cyclopropenylidenes, these excellent two electron donors were employed as ancillary ligands to stabilize the central PR group.¹⁸ An appropriate phosphinidene–carbene adduct **8** was obtained by reaction of 1-chloro-2,3-bis(di-isopropylamino) cyclopropenium tetrafluoroborate **7** with 2,4,6-tris(isopropyl)phenylphosphine followed by deprotonation with KHMDS (for details, see the ESI†).¹⁹

When compound **8** was allowed to react with two equivalents of $[(Me_2S)AuCl]$, the bis-aurated complex **9** was isolated in good yield. Its formation clearly parallels the chemistry of carbodiphosphoranes and bears witness to the availability of two electron lone pairs at the P^I center. If **8** is first reacted with only one equivalent of $[RhCl(cod)]_2$ followed by addition of half equivalent of $[(Me_2S)AuCl]$ to the reaction mixture, the heterodimetallic species **10** could be obtained (Scheme 5). The structure of **10** in the solid state was elucidated using X-ray diffraction, which showed that the AuCl and the RhCl(cod) moieties both coordinate to the phosphorus atom. It seems, however, that there is no interaction between the two metals,



Scheme 4 Isolobal relationship between carbodiphosphoranes and phosphinidenes.



Scheme 5 Synthesis and molecular structure in the solid state of **9** and **10** (hydrogen atoms and solvent molecules have been removed for clarity; ellipsoids at 50% probability).¹¹ *Reagents and conditions*: (a) [(Me₂S)AuCI], 2 equiv., toluene, $-78 \degree C \rightarrow rt$, 16 h, 83%; (b) [RhCl(cod)]₂, 0.5 equiv., toluene, $-78 \degree C \rightarrow rt$, 1 h; then [(Me₂S)AuCI], 1 equiv., $-78 \degree C \rightarrow rt$, 16 h, 54%; cod = 1,5-cyclooctadiene.

since the Rh(i)-Au(i) distance is 3.891(5) Å. Similar to compounds 5 and 6, complex 10 is a chiral entity comprising a quaternary phosphorous atom surrounded by two different donor ligands and two different acceptor sites.²⁰

In summary, we report herein the syntheses and structures of various heterodimetallic complexes of carbodiphosphoranes and phosphinidene–carbene adducts, in which the central atom of these ligands donates electron density to two different metal centers that are forced into close proximity; as a result, these complexes are centrally chiral. Plausible applications of these unusual chemical entities in polymetallic catalysis as well as attempts to control their absolute configuration are currently under investigation.

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