Carbodicarbenes

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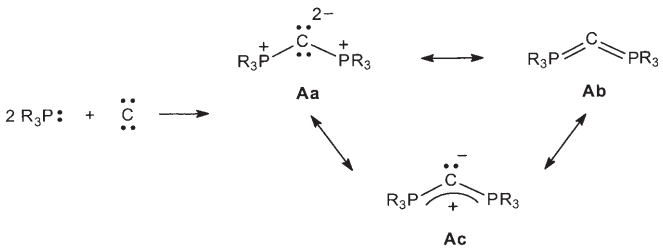
Carbodicarbenes: Divalent Carbon(0) Compounds

*Oliver Kaufhold and F. Ekkehardt Hahn**

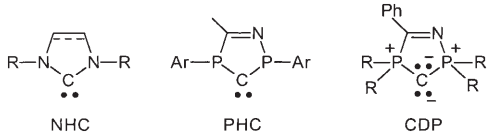
carbenes · carbodicarbenes · carbodiphosphoranes · divalent carbon

Is it possible to coordinate two donor ligands L to a carbon(0) atom, and what would be the properties of such a carbon atom? These questions have been of interest to chemists for many years. First answers to this question have been obtained with the synthesis[1] and structural characterization[2] of carbodiphosphoranes (CDPs) **A** using donor ligands of type $L = R_3P$.[3] Carbodiphosphoranes can be formulated as bisphosphine complexes of a naked carbon atom (**Aa**). Alternatively, a heterocumulene $R_3P{=}C{=}PR_3$ (**Ab**) resonance structure and the description as a carbenoid species (**Ac**) are possible. The bonding parameters and reactivity of the carbodiphosphoranes indicate that the electronic situation of these compounds is reasonably described by a polar structure with two electron lone pairs at the central carbon atom (**Aa**, Scheme 1).



Scheme 1. Resonance structures for carbodiphosphoranes.

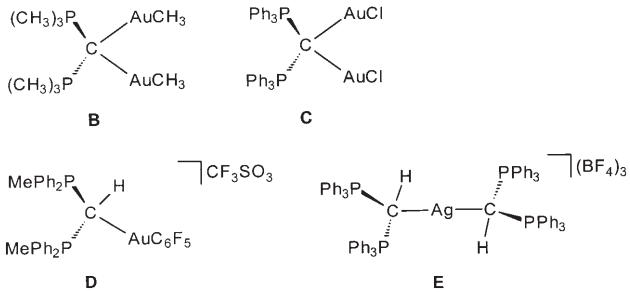
The related carbodiarsoranes[4] as well as a series of cyclic carbodiphosphoranes[2f,5] have also been described. Carbodiphosphoranes are all strong bases and nucleophiles. The high degree of charge excess at the ylidic carbon atom, which is not compensated by the phosphorus centers, makes them good donor ligands. The electronic situation found in carbodiphosphoranes differs however from that in diphosphino- or diaminocarbenes. A comparison of cyclic derivatives of these three types of donor ligands (Scheme 2) illustrates these differences. The carbene carbon atoms of N-heterocyclic



Scheme 2. Electronic situation in cyclic NHCs, PHCs, and CDPs.

carbenes (NHCs)[6] or P-heterocyclic carbenes (PHCs)[7] possess two joint electron pairs with the substituents in addition to a electron lone pair, whereas the P–C bonds in carbodiphosphoranes (CDPs) are best described as P→C donor–acceptor interactions.[8] Two fully occupied, nonbonding orbitals (HOMO und HOMO-1) remain at the central carbon atom, which can be described as free electron pairs with π and σ symmetry.[8a]

The electronic situation in carbodiphosphoranes possessing two electron pairs at the central carbon atom should enable the formation of 1:2 complexes with transition metals. The reaction of hexamethylcarbodiphosphorane with $[CH_3{-}Au{\leftarrow}P(CH_3)_3]$ does indeed lead to the 1:2 complex **B** with a tetrahedrally coordinated carbon atom (Scheme 3).[9] The



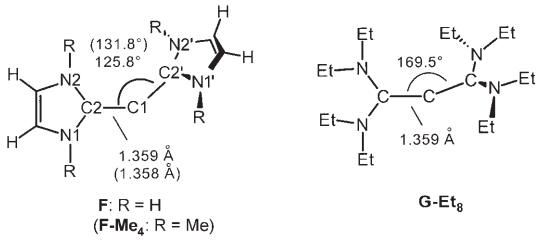
Scheme 3. Complexes with free (**B**, **C**) and singly protonated CDP ligands (**D**, **E**).

analogue 1:2 complex **C** of the Cl–Au complex fragment with $Ph_3P{-}C{-}PPh_3$[10] and a 1:1 complex **D** with a monoprotonated CDP[11] have also been described. Recently, the coordination of two singly C-protonated CDPs to a silver(I) cation with formation of the tricationic complex $[\{(Ph_3P)_2CH\}_2Ag]^{3+}$ **E** was achieved.[8a] The formation of this complex against the Coulomb repulsion again underlines the excellent donor properties of CDPs.

NHCs are often compared to phosphines, and have replaced these in various catalytically active metal complexes.[12a] Substitution of the phosphine substituents at the carbon

[*] Dipl.-Chem. O. Kaufhold, Prof. Dr. F. E. Hahn
Institut für Anorganische und Analytische Chemie
Westfälische Wilhelms-Universität Münster
Corrensstrasse 36, 48149 Münster (Germany)
Fax: (+49) 251-833-3108
E-mail: fehahn@uni-muenster.de
Homepage:
http://www.uni-muenster.de/Chemie.ac/hahn/welcome.html

atom of carbodiphosphoranes by NHCs leads to compounds with a carbon(0) atom that is formally stabilized by two NHC→C donor–acceptor bonds. Such carbodicarbenes (CDCs, Scheme 4) have been investigated by Tonner and Frenking using theoretical methods.[12b] These calculations indicate that CDCs should be experimentally accessible and should have interesting properties. The parent compound **F** (Scheme 4) was calculated to have an acute C–C–C angle of 125.8°, and the planes of the NHC ligands are oriented almost perpendicular to each other, with a torsion angle N1–C2–C2′–N1′ of 81.6° in the equilibrium geometry. The C–C distances involving the central carbon atom measure 1.359 Å, and are thus shorter than single bonds. Geometrical changes to this equilibrium structure require only little energy. The geometric parameters of the synthetically most interesting *N*-methyl substituted compound **F-Me$_4$** show only slight deviations in comparison to **F**. The shape of the HOMO und HOMO-1 orbitals in **F** is similar to those of the equivalent orbitals in carbodiphosphoranes, indicating that the bonding situation in CDCs is likewise best discribed as a NHC→C donor–acceptor interaction.



F: R = H
(**F-Me$_4$**: R = Me)

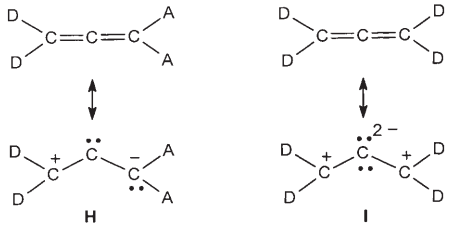
G-Et$_8$

Scheme 4. Calculated geometrical parameters for the carbodicarbene **F**, the N-methylated compound **F-Me$_4$** (in parentheses) and the tetraaminoallene $(Et_2N)_2C{=}C{=}C(NEt_2)_2$ **G-Et$_8$**.

The central moiety of the carbodicarbenes $N_2C{=}C{=}CN_2$ is the same as in tetraaminoallenes, of which several derivatives are experimentally known.[13] Calculations on the *N*-ethyl substituted compound **G-Et$_8$** (Scheme 4) result in an angle of 169.5° for the C–C–C unit, whereas the *N*-methyl analogue **G-Me$_8$** and the parent allene $H_2C{=}C{=}CH_2$ are linear.[12b] A subtle change in the amino substituents of tetraaminoallenes obviously induces a change of the bonding situation of the central C=C=C unit towards the situation found in the carbodicarbenes **F** and **F-Me$_4$**. In analogy to CDPs, tetraaminoallenes may also be singly or doubly protonated at the central carbon atom.[13d]

A high proton affinity was calculated for carbodicarbenes of type **F**, which are consequently strong bases and good nucleophiles. The modification of the NHC moiety in CDCs appears unproblematic, and thus should lead, in analogy to the CDPs, to a series of interesting divalent $(NHC)_2C^0$ ligands for transition metals, provided that synthetic procedures for the generation of such molecules and their complexes can be developed. Preparative methods for the generation of carbodicarbenes or carbene-substituted ylides, have been found recently by Bertrand et al.[14] and Fürstner et al.,[15] respectively.

The synthetic strategy by Bertrand et al. is based on the observation that C=C=C allenes are always linear, with a perpendicularly arranged pair of substituents,[16] whereas their analogues with heavier elements of Group 14 have nonlinear structures (Si=Si=Si 136.5°,[17] Ge=Ge=Ge 122.6°[18]). This difference is believed to arise from the weakness of the π bonds in the silicon or germanium derivatives.[19] Bertrand et al. thus concluded that weakening of the π bonds in C=C=C allenes should also lead to nonlinear structures. It is known that polarization of C–C π bonds leads to their weakening. Such a polarization can be achieved by a "push–pull" (**H**) or "push–push" substitution pattern (**I**) at the allene (Scheme 5).



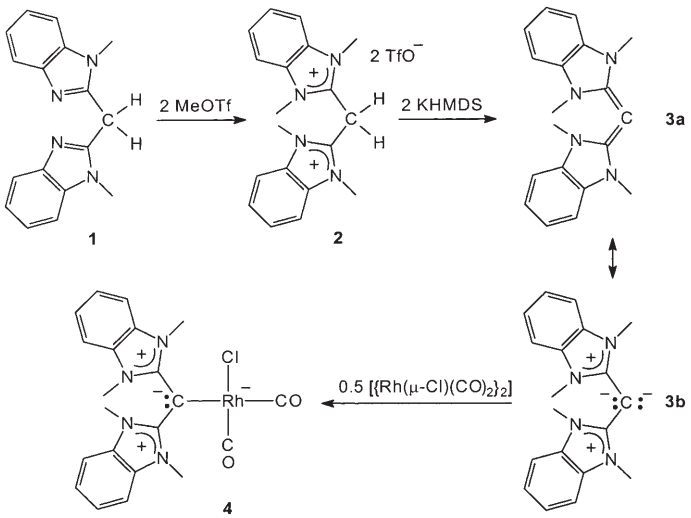
H **I**

Scheme 5. Resonance structures for push–pull (**H**) and push–push (**I**) substituted allenes. D = donor group, A = acceptor group.

Push–pull-polarized allenes of type **H** show partial carbene character at the central allene carbon atom, and therefore a tendency for dimerization.[20] In contrast, push–push-substituted allenes **I** can be considered to contain a dicarbanionic central carbon atom that is coordinated by two formal positively charged donor groups. This situation corresponds to the electronic structure that has been proposed for CDPs (Scheme 1).

Bertrand et al. selected benzimidazolin-2-ylidene[21] as CD_2 donor group for bent allenes, and the deprotonation of the conjugated acid of the allene as the synthetic strategy. Compound **1** is easily N-alkylated to give **2** (Scheme 6). Double deprotonation results in the push–push-substituted allene **3**. The ^{13}C NMR spectrum of **3** shows chemical shifts for the allene carbon atoms [$\delta = 110.5$ ppm ($C_{central}$), 144.8 ppm ($C_{terminal}$)] that differ substantially from those reported for nonpolarized allenes [$\delta = 185$–215 ppm ($C_{central}$), 60–130 ppm ($C_{terminal}$)], but which are in agreement with the values measured for tetrakis(dimethylamino)allene **G-Me$_8$** [$\delta = 136$ ppm ($C_{central}$), 162 ppm ($C_{terminal}$)]. These observations suggest that the π system in **3** is strongly polarized, but they are no indication for a nonlinear molecular structure. The X-ray structure analysis shows that the C=C bond lengths in **3** (1.343(2) Å) are only slightly longer than those in nonpolarized allenes.[22] The N–C–N planes of the benzimidazoline units are twisted by 69° relative to one another. The allene framework is indeed nonlinear, with a C–C–C angle of 134.8(2)°. Obviously, the allene π system in **3** is highly distorted and the central carbon atom is not sp hybridized. The electronic situation in this compound is best described by resonance structure **3b**, with two free electron pairs at the central carbon atom (Scheme 6).

The molecular parameters of **3** are in good agreement with the values calculated by Tonner and Frenking for

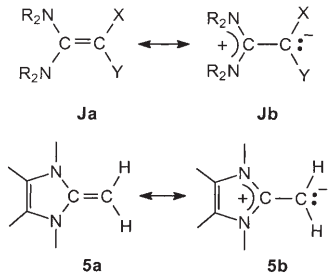


Scheme 6. Synthesis of the polarized allene **3** and of the rhodium complex **4**.

carbodicarbenes (Scheme 4).[12b] According to the calculations, these strongly basic carbon(0) compounds are good ligands for transition metals, which in contrast to normal allenes (η^2 coordination of one double bond[23]) should function as η^1-ligands by coordination of the formally dianionic central carbon atom. Indeed, the reaction of **3** with $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ gives complex **4** with the allene ligand bound to the metal in the η^1 mode. The carbonyl stretching vibrations in complexes of type $[RhCl(CO)_2L]$ have been used to assess the electronic properties of a ligand L.[24] The values measured for complex **4** demonstrate that the η^1-allene ligand **3**, formally possessing two electron lone pairs at the central carbon atom, is a stronger σ donor and weaker π acceptor than N-heterocyclic or acyclic diaminocarbenes, which possess only one electron lone pair at the carbene carbon atom.

Fürstner et al. investigated polarized double bonds in ene-1,1-diamines **J** (ketene aminals).[15] These electron-rich olefins also contain strongly polarized double bonds (Scheme 7) in which the resonance structure **Jb** significantly contributes to the ground state. Incorporation of the nitrogen atoms into a heterocyclic ring, as found in **5**, helps to stabilize a positive charge in particular, and allows the olefinic carbon atom to serve as an anionic ylidic donor (resonance structure **5b**).

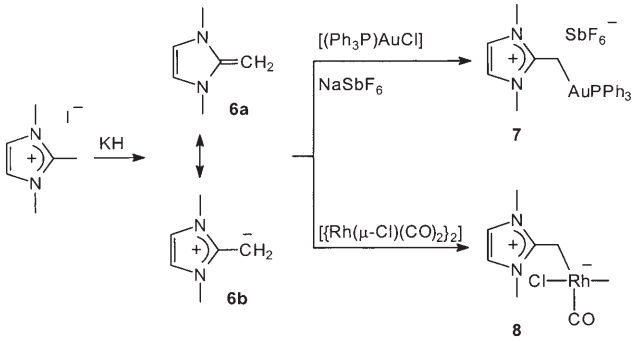
Kuhn et al. have studied compound **5**[25a–c] and numerous other imidazolin-2-ylidene adducts with main group ele-



Scheme 7. Resonance structures of ene-1,2-diamine **J** and 2-methyleneimidazoline **5**.

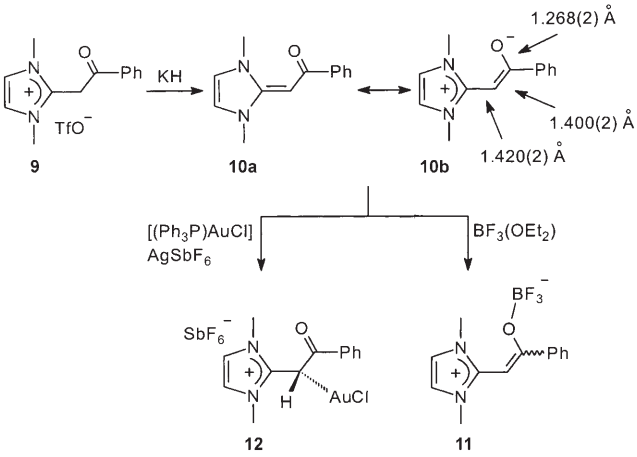
ments.[25d] They mention for the first time that compound **5** can act as a ylidic olefin towards transition metals.[25a] Fürstner et al. isolated 1,3-dimethyl-2-methyleneimidazoline **6** by deprotonation of the imidazolium salt (Scheme 8). The polarized olefin **6** reacts with $[(Ph_3P)AuCl]$ with formation of complex **7**. The structure analysis of **7** shows that the metalated olefin behaves like a carbon ylide, and that the N-heterocyclic ring displays the structural parameters of an imidazolium cation.[6b] Reaction of **6** with $[\{Rh(\mu\text{-}Cl)(CO)_2\}_2]$ yields the rhodium ylide complex **8** (Scheme 8). The ylide ligand in **8** acts as a very strong σ donor with a donor strength comparable to the cyclic carbodiphosphoranes (Scheme 2).[5b]

In a subsequent experiment, starting from **9**, the olefin **10** was functionalized with a ketone at the exocyclic double bond to give compound **10**. The resulting push–pull ylide should show a charge separation which should lead to an enolate-type geometry for the carbonyl group.



Scheme 8. Synthesis of the ylide complexes **7** and **8** from polarized olefin **6**.

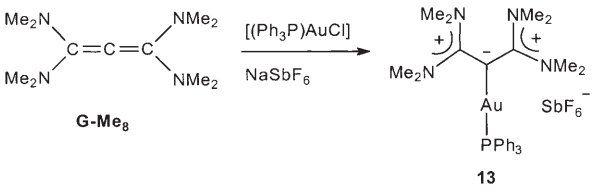
Indeed, the molecular structure of **10** (Scheme 9) shows an elongated N_2C–C bond and a shortened C–C(O) bond in addition to a significantly elongated C–O bond. Therefore, the electronic situation in **10** is best described by resonance structure **10b**. Compound **10** can be metalated at the oxygen atom with hard electrophiles to give, for example, the BF_3



Scheme 9. Reactions of the ketone-functionalized olefin **10**.

adduct **11**, whereas reaction with [(Ph_3P)AuCl] gives the gold ylide **12**, which can be regarded as a "gilded" *C*-metalated enolate (Scheme 9). The imidazole unit in **6** can be substituted by other heterocyclic rings, such as *N*-alkyl pyridine. The only requirement for the heterocycle is its ability to stabilize a positive charge in the subsequent formation of the ylide.

Fürstner et al. also studied the properties of tetraaminoallenes as ligands. Although these compounds have been known for a long time,[13a] they have never been utilized as ligands for transition metals. Quantum chemical calculations by Tonner and Frenking showed that the *N*-ethyl substituted derivative **G-Et$_8$** (Scheme 4) is slightly bent (C–C–C 169.5°) and can be regarded as carbodicarbene, whereas the *N*-methyl derivative **G-Me$_8$** exhibits a linear molecular structure.[12b] As **G-Me$_8$** can be protonated at the central carbon atom,[13a] an attempt was made to react it with transition metal Lewis acids. The reaction of **G-Me$_8$** with [(Ph_3P)AuCl]/$NaSbF_6$ does not lead to a gold complex with a η^2-bound olefin ligand but does indeed proceed with formation of **13** containing an a η^1-coordinated tetraaminoallene ligand (Scheme 10).



Scheme 10. Synthesis of complex **13** with the η^1-coordinated tetraaminoallene **G-Me$_8$**.

The utilization of carbodicarbenes as four-electron donors, in analogy to the carbodiphosphoranes (Scheme 3), has not yet been demonstrated. Whether the double metalation is possible or not will be shown by future experiments. However, at this point, carbodicarbenes constitute a very interesting new class of η^1-carbon ligands with a distinctive σ-donor behavior. This behavior makes the electron-rich carbodicarbenes and related ligands interesting substitutes for NHCs in catalytically active complexes.[26] It can be expected that additional theoretical[27] and experimental investigation will lead to a better understanding of the properties and reactivity of ligands with donor-stabilized carbon(0) atoms in the future.

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