Carbodicarbenes

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$C(NHC)_2$: Divalent Carbon(0) Compounds with N-Heterocyclic Carbene Ligands—Theoretical Evidence for a Class of Molecules with Promising Chemical Properties**

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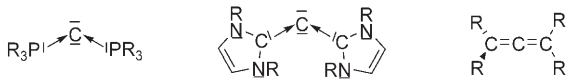
Interest in carbodiphosphoranes $C(PR_3)_2$ (Scheme 1) has recently been revitalized by experimental and theoretical studies which shed new light on the chemistry of this



Scheme 1. Schematic representation of carbodiphosphoranes (CDP), carbodicarbenes **1** ($C(NHC)_2$, NHC = N-heterocyclic carbene), and allenes (tetraaminoallenes (TAA) for R = NR_2) **2**.

neglected class of compounds. On the experimental side, the neutral donor–acceptor systems $(R_3P)_2C{\rightarrow}CO_2$ and $(R_3P)_2C{\rightarrow}CS_2$ and their adducts with $[Mo(CO)_4]$ could be isolated and the structures were fully characterized by X-ray structure analysis.[1] Another surprising finding was the isolation of the triply charged $[\{(Ph_3P)_2CH\}_2Ag]^{3+}$ ion, which exhibits two protonated carbodiphosphorane (CDP) moieties $[(Ph_3P)_2CH]^+$ that are bridged by a Ag^+ ion.[2] The spectrum of carbodiphosphoranes was significantly enlarged by the synthesis of the first five-membered cyclic CDP compounds that are stable at room temperature, which was recently reported by Baceiredo and co-workers.[3] On the theoretical site, a thorough bonding analysis of $C(PR_3)_2$ compounds showed that the C–PR_3 bonding arises from the donation of the phosphorus lone pair electrons into the vacant valence orbitals of the carbon atom, leaving the four valence electrons of C as two electron lone pairs, one with σ symmetry and one with π symmetry.[2] The electronic structure analysis explains the very strong Lewis base chemistry of the CDP compounds.

We have searched for other divalent carbon(0) compounds with the general formula $C(L)_2$ that have L→C donor–acceptor bonds. A straightforward choice for L was N-heterocyclic carbenes (NHCs), which are often compared with phosphanes as ligands in transition-metal chemistry.[4] Herein we report on the first theoretical investigation of carbodicarbenes[5] with the general formula $C(NHC)_2$ (**1**), in which NHC ligands are bound to the C atom. The calculations[6] predict that the experimentally unknown[7] $C(NHC)_2$ compounds should be synthetically accessible species with promising chemical properties.

Figure 1 shows the calculated geometries of the parent compound **1-H**, which bears hydrogen at the nitrogen atoms. The full set of geometrical data is given in Table S1 in the Supporting Information. The equilibrium geometry **1-H(a)** has an acute C-C-C angle of 125.8° and rather short C–C distances of 1.359 Å at the central carbon atom. The NHC planes are twisted, the torsion angle N1-C2-C2′-N1′ is 81.6°. The conformer **1-H(b),** in which the NHC moieties are orthogonal to each other (< (N1-C2-C2′-N1′) = 90°), is only 2.3 kcal mol^{-1} higher in energy than **1-H(a)**. The planar conformer **1-H(c)** is likewise only 3.3 kcal mol^{-1} less stable than **1-H(a)**. The central C–C bonds in **1-H(b)** are shorter than in **1-H(a)**, whereas those in **1-H(c)** are longer; however, the differences are not very large. The central C-C-C angle in the orthogonal conformer **1-H(b)** becomes more obtuse (142.7°) than in the equilibrium form. Further widening of the C-C-C angle yielding the linear structure **1-H(d)** requires only 3.7 kcal mol^{-1}. The latter structure corresponds to the equilibrium geometry of a tetraamino-substituted allene, which is discussed below. Note that the C–C distances in the allene structure **1-H(d)** (1.324 Å) are slightly shorter than in **1-H(a)**. These data indicate that twisting the NHC rings and widening the central C-C-C angle of **1-H(a)** costs little energy. The planar structure with a linear C-C-C arrangement **1-H(e)** is 11.7 kcal mol^{-1} less stable than **1-H(a)**. Ab initio calculations at the MP2 and CCSD(T) levels gave very similar values for the relative energies of **1-H(b)**–**1-H(e)**. They are given in Table S2 in the Supporting Information. The structure **1-H(c)** is a transition state ($i = 1$), whereas **1-H(b)** and **1-H(e)** are second-order saddle points ($i = 2$). Structure **1-H(d)** has two sets of degenerate imaginary modes ($i = 4$). Calculations of the intrinsic reaction coordinates[8] showed that **1-H(b)**–**1-H(e)** all relax to the energy minimum **1-H(a)**.

The most important bond lengths and angles of the synthetically more interesting N-methyl-substituted carbodicarbene **1-Me** in the different conformations **1-Me(a)**–**1-Me(e)** are given in parentheses in Figure 1. The methyl groups effectuate as expected more obtuse C-C-C bond angles particularly for the planar form **1-Me(c)**, which is 12.6 kcal mol^{-1} higher in energy than **1-Me(a)**. The relative energies and the geometrical variables of the conformers **1-Me(b)**, **1-**

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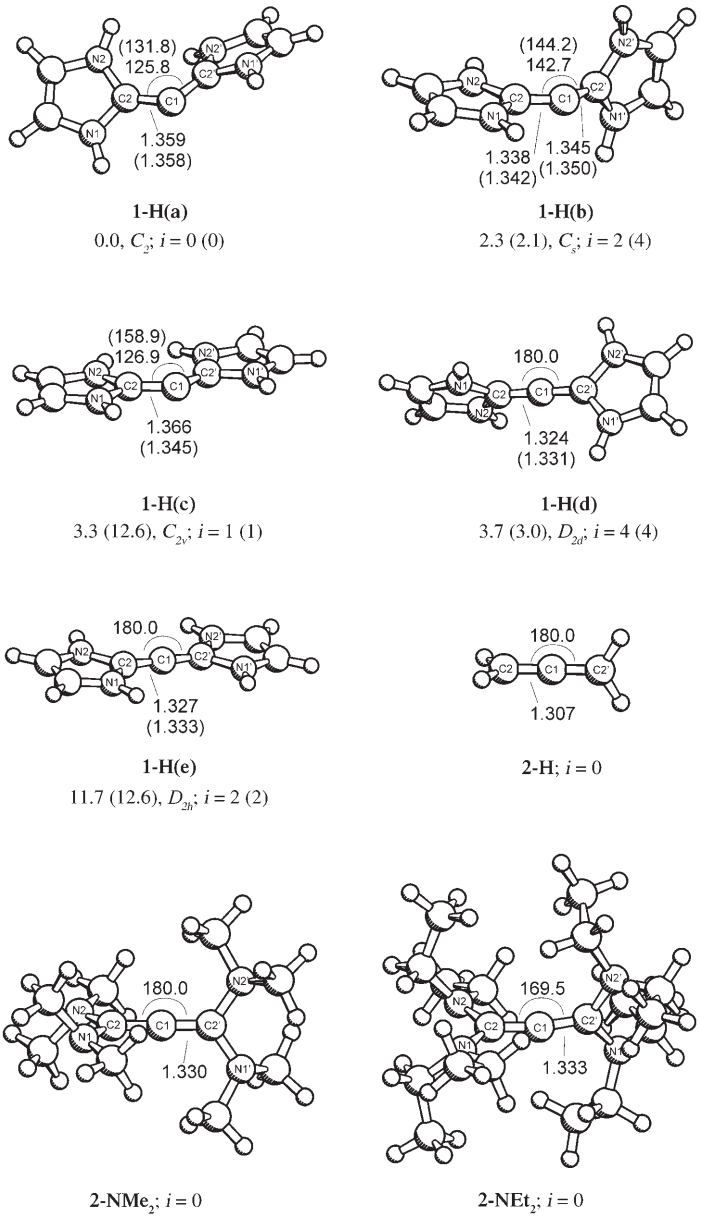

Figure 1. Optimized geometries and relative energies at the BP86/TZ2P level of theory for different conformations of $C(NHC)_2$ **1-H** and the optimized geometries of the parent allene **2-H**, and the TAAs **2-NMe$_2$** and **2-NEt$_2$**. Bond lengths are given in Å, angles in degrees. Number of imaginary frequencies *i*. The calculated values for **1-Me** are given in parentheses.

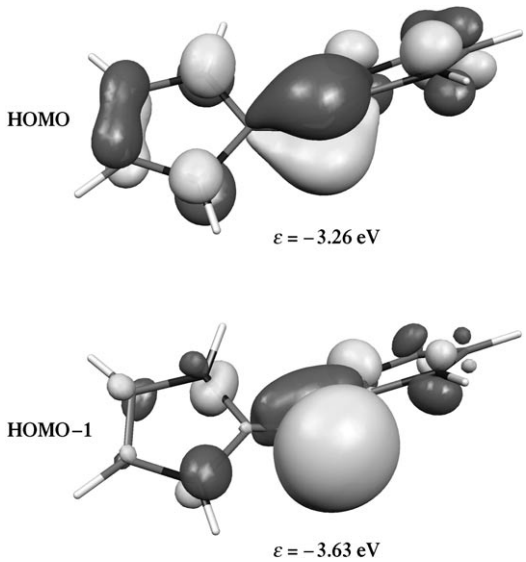

Figure 2. HOMO and HOMO−1 of **1-H(a)** and orbital energies ε at the BP86/TZ2P level of theory.

Me(d), and **1-Me(e)** are similar to the values of the parent species (Figure 1).

Figure 2 shows the two highest lying occupied molecular orbitals HOMO and HOMO−1 of **1-H(a)**. The HOMO−1 is clearly a σ-type[9] lone pair orbital, which is localized at the central carbon atom C1. The HOMO is a π-type[9] orbital that has also the largest coefficient at C1. The shape of the HOMO and HOMO−1 of the $C(NHC)_2$ compound **1-H(a)** resembles the two highest lying occupied orbitals of the carbodiphosphoranes $C(PR_3)_2$, but the π-type lone-pair orbital of the former is more delocalized than the HOMO of the latter because the π orbitals of the NHC ligands are in conjugation with the π-type carbon orbital. Nevertheless, the shape of the occupied frontier orbitals of **1-H(a)** indicates that the bonding situation in the $C(NHC)_2$ compounds may also be discussed in terms of NHC→C donor–acceptor interactions, as was suggested for the bonding in $C(PR_3)_2$.[2] We therefore calculated the first and second proton affinities (PA) of **1-H** and **1-Me** and compared them with the theoretically predicted values for the PA of carbodiphosphoranes (Table 1).

The theoretical values of the first PA of **1-H** (292.3 kcal mol^{-1}) and **1-Me** (294.3 kcal mol^{-1}), which refer to protonation of the σ-type orbitals HOMO−1, are very high. The compounds are thus predicted to be very basic and actually more basic than $C(PR_3)_2$ (R = H, Me, Ph). Even the second PA of the $C(NHC)_2$ compounds are predicted to be rather strong. Note that the second PA of **1-H** (155.3 kcal mol^{-1}) and **1-Me** (168.4 kcal mol^{-1}) differ much more from each other than the first PAs do. This is because the second PA comes from the π-type HOMO, which is more strongly influenced by the nature of the NHC ligands than the σ-type HOMO−1. A second effect is the better stabilization of two positive charges by molecules with larger substituents. A similar situation is found for the CDP compounds where the second PA of $C(PR_3)_2$ exhibits a larger change with different substituents R than the values of the first PA. The first and second PA of $C(NHC)_2$ are clearly larger than the calculated values for $C(CO)_2$—another compound which can be described with the formula $C(L)_2$[10] (Table 1). Nevertheless, the positive second PA for $C(CO)_2$ is remarkable because it indicates the synthetic accessibility for this unusual seven-atom dication $[C(CO)_2H_2]^{2+}$.

The central moiety of the carbodicarbenes **1**, N_2C-C-CN_2, is the same as in tetraaminoallenes (TAAs) $(R_2N)_2C{=}C{=}C(NR_2)_2$. The latter compounds are experimentally known and their reactivity and properties have been studied many

Table 1: First and second proton affinities in kcal mol^{-1} at the MP2/TZVPP//BP86/SVP level of theory. (Values at the BP86/TZVPP//BP86/SVP level of theory are given in parentheses).

Compound	1st PA	2nd PA
1-H(a)	292.3 (289.7)	155.3 (148.7)
1-Me(a)	294.3 (289.7)	168.4 (163.4)
2-H	182.4 (182.3)[a]	−5.2 (−2.8)
2-NMe$_2$	282.5 (284.0)	151.6 (152.0)
2-NEt$_2$	268.2(272.6)	175.8 (175.0)
C(PH$_3$)$_2$	255.7(252.8)	114.4 (113.4)
C(PMe$_3$)	278.4 (279.0)	156.2 (159.1)
C(PPh$_3$)$_2$	280.0(280.3)	185.6 (188.2)
C(CO)$_2$	182.5 (176.6)[b]	28.7 (18.2)

[a] Exptl.: 185.3 kcal mol^{-1}.[21] [b] Exptl.: 189.0 kcal mol^{-1}.[22]

years ago.[11] Figure 1 shows the optimized geometries of the parent allene $H_2C{=}C{=}CH_2$ (**2-H**) and the substituted homologues $(R_2N)_2C{=}C{=}C(NR_2)_2$ with R = methyl (**2-NMe$_2$**) and R = ethyl (**2-NEt$_2$**). Contrary to the $C(NHC)_2$ compounds **1**, the central carbon atoms of **2-H** and **2-NMe$_2$** have a linear arrangement, whereas the geometry optimization of the ethyl-substituted homologue **2-NEt$_2$** gives a C-C-C bond angle of 169.5°. We optimized the geometries of **2-H**, **2-NMe$_2$**, and **2-NEt$_2$**, in which the C-C-C bond angle was kept frozen at 125.8°, which is the equilibrium bond angle of **1-H(a)**. The calculations predict that the bent structure of **2-H** is 25.4 kcal mol^{-1} higher in energy than the energy minimum. The energy differences for **2-NMe$_2$** (8.7 kcal mol^{-1}) and **2-NEt$_2$** (8.8 kcal mol^{-1}) are much less. The smaller energy differences for the bent structures of **2-NMe$_2$** and **2-NEt$_2$** suggest that the amino substituents have a strong effect on the chemical bonds of the C=C=C allene moiety toward a bonding situation that is exhibited by the carbodicarbenes **1**. The latter conclusion is supported by the experimentally observed reactivity of TAAs. For example, compound **2-NMe$_2$** reacts with weak Lewis bases CO_2 and CS_2 to yield complexes in which the central carbon atom of **2-NMe$_2$** binds through a donor–acceptor bond in $[(NMe_2)_2C]_2C{\rightarrow}CX_2$ (X = O, S).[11a] The latter complexes exhibit the same bonding motif as the CDP complexes $(Ph_3P)_2C{\rightarrow}CX_2$.[1] It has also been observed that TAAs can bind two protons at the central carbon atom yielding the crystallographically characterized dication $[\{(NHR)_2C\}_2CH_2]^{2+}$ (R = *tert*-butyl).[11d] This is again a striking analogy to CDP compounds for which the dication $[(Ph_3P)_2CH_2]^{2+}$ has been synthesized and characterized by X-ray structure analysis.[12]

Tetraaminoallenes are very strong nucleophiles and very strong bases, which was explained by an analogy to tetraaminoethylenes and diaminoacetylenes.[11c] The comparison is misleading, because the nucleophilicity and basicity of the TAAs comes from the particular electronic structure of the bent geometries which are exhibited in the protonated form and in donor–acceptor complexes.[11] It seems that the latent carbon(0) chemistry of TAAs, which comes to the fore in these reactions, has not been recognized. A recent review on the chemistry of allenes mentions the work by Gompper et al. and states that: "…this chemistry has not been developed further during the last three decades".[13]

Table 1 gives the calculated first and second PA of **2-H**, **2-NMe$_2$**, and **2-NEt$_2$**. The first PA of **2-H** is much less than that of the CDP and $C(NHC)_2$ compounds, whereas the second PA is even negative. The calculations predict that the TAAs **2-NMe$_2$** and **2-NEt$_2$** have a much higher first PA than **2-H**. The values of the first and the second PA of **2-NMe$_2$** and **2-NEt$_2$** are comparable to the values calculated for the CDP and $C(NHC)_2$ compounds. Since the linear or quasi-linear TAAs are proven to exhibit a similar chemical reactivity as CDPs[11] it can safely be predicted that the carbodicarbenes **1** will be even stronger nucleophiles. Because $C(NHC)_2$ compounds can be electronically modified in many ways through variation of the NHC ligands they offer interesting perspectives for synthetic chemistry. In particular, we think that carbodicarbenes are promising ligands for transition-metal compounds. Since complexes with NHC ligands are useful catalysts for many important chemical reactions,[4] it might be worthwhile to explore the use of $C(NHC)_2$ complexes as well, provided that inventive chemists find a way for synthesizing them. Theory indicates that there is no thermodynamic barrier for the synthesis. The calculations suggest that reaction (1) is exergonic by 19.8 kcal mol^{-1}.

$$(Ph_3P)_2C + 2\,NHC(Me) \rightarrow \mathbf{1\text{-}Me} + 2\,PPh_3 \qquad \Delta G = -19.8\ \text{kcal mol}^{-1} \qquad (1)$$

The theoretical results of this work present a challenge for experimental chemists.

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[5] A more precise denotation for **1** is carbodiimidazol-2-ylidene. We prefer the name carbodicarbene because it is more generic. Note that compounds **1** are not carbenes! A carbene is a divalent carbon(II) compound, whereas **1** and carbodiphosphoranes are divalent carbon(0) compounds.
[6] Geometry optimizations without symmetry constraints were carried out using the Gaussian03 optimizer[14] together with TurboMole5[15] energies and gradients at the BP86[16]/def-SVP[17b] level of theory. For the phenyl rings of the PPh_3 groups a minimal basis set was used (benzene BS) except for the α-C atom. Stationary points were characterized as minima by calculating the Hessian matrix analytically at this level. Thermodynamic corrections were taken from these calculations. The standard state for all thermodynamic data was $T = 298.15$ K and $p = 1$ atm. Single-point energies were calculated for some molecules with the MP2 method,[18] applying the frozen core

approximation for non-valence shell electrons and BP86 using the def2-TZVPP[17a] basis set. For both methods the resolution-of-identity method was applied.[19] Smaller molecules were reoptimized with the program package ADF[20] by using the BP86/TZ2P level of theory described in more detail in an earlier publication.[1] For the sake of analysis some conformers were optimized under the given symmetry constraints.

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