Carbodicarbenes and Striking Redox Transitions of their Conjugate Acids: Influence of NHC versus CAAC as Donor Substituents

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Dedicated to the memory of the late Professor K. V. R. Chary

Abstract: Herein, a new type of carbodicarbene (CDC) comprising two different classes of carbenes is reported; NHC and CAAC as donor substituents and compare the molecular structure and coordination to Au(I)Cl to those of NHC-only and CAAC-only analogues. The conjugate acids of these three CDCs exhibit notable redox properties. Their reactions with [NO][SbF$_6$] were investigated. The reduction of the conjugate acid of CAAC-only based CDC with KC$_8$ results in the formation of hydrogen abstracted/eliminated products, which proceed through a neutral radical intermediate, detected by EPR spectroscopy. In contrast, the reduction of conjugate acids of NHC-only and NHC/CAAC based CDCs led to intermolecular reductive (reversible) carbon–carbon sigma bond formation. The resulting relatively elongated carbon–carbon sigma bonds were found to be readily oxidized. They were, thus, demonstrated to be potent reducing agents, underlining their potential utility as organic electron donors and n-dopants in organic semiconductor molecules.

Introduction

Since the pioneering report of hexaphenyl-carbodiphosphorane I[1] (Scheme 1) as divalent carbon(0) by Frenking et al.,[2] several compounds of this class II were reported employing different donors such as, *inter alia*, N-heterocyclic carbenes (NHC), silylenes, and sulfoxide.[3] Also, heteroleptic divalent carbon(0) compounds of type III are known with a combination of two different donors, such as phosphines and N-heterocyclic carbenes.[4] In recent times, after disclosing the synthesis, structural characterization, and coordination properties of NHC-based divalent carbon(0), also known as carbodicarbene **1a** by Bertrand and co-workers,[3, a)] this class of compounds IV has attracted considerable attention in the chemical sciences as evidenced by various quantum chemical calculations,[5] and their utilization as ligands for the development of main group

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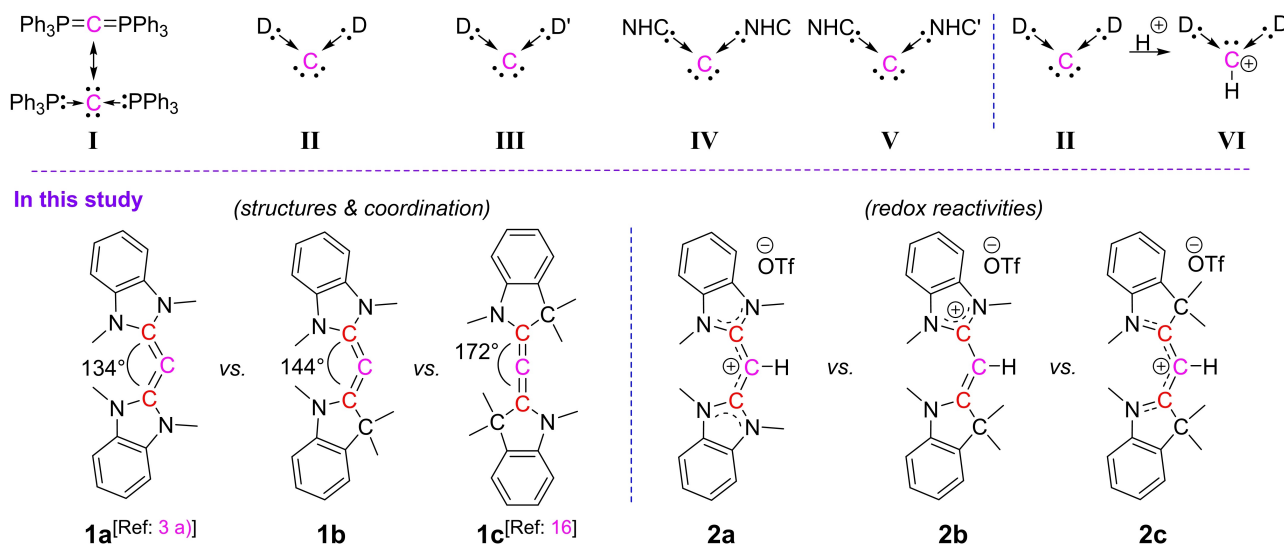
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Scheme 1. Chemical structures of **I–VI**, CDCs **1a/1b/1c** and their conjugate acids **2a/2b/2c** (D/D′ = donor, NHC/NHC′ = N-heterocyclic carbene).

chemistry (isolation of unprecedented classes of compounds),[6] in transition metal coordination chemistry,[7] as catalysts in organic transformations,[8] and even in actinide chemistry.[9] In recent years, Ong and co-workers have employed N-heterocyclic carbene-stabilized divalent carbon(0) compounds **IV** (Scheme 1), known as carbodicarbenes (CDC), as organocatalysts.[10] As a variation thereof, divalent carbon(0) compounds **V** stabilized by two different N-heterocyclic carbene donors were also developed.[11] Notably, however, there is no report available to date on the isolation of a divalent carbon(0) species bearing two different classes of carbenes.[12]

To expand the structure and reactivity scope of divalent carbon(0) compounds, two electronically different classes of carbenes[13] were considered as donors in this work, i.e., N-heterocyclic carbene (NHC)[14] and cyclic(alkyl)(amino)carbene (CAAC).[15]

Interestingly, the synthesis of cyclic(alkyl)(amino)carbene (CAAC)-based carbodicarbene **1c** as 1,3-diaminoallene was reported by Grahn et al.[16] well before CAACs were described as ligands.[15]

However, to date there is no report available of its solid-state molecular structure or coordination properties. In the meantime, there were various theoretical studies published of the CAAC-based carbodicarbenes and their protonated forms.[17]
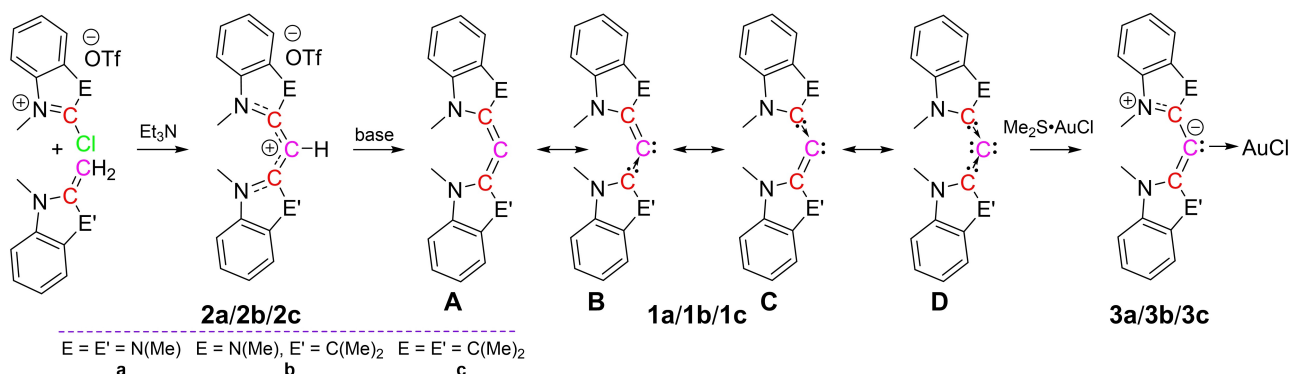
The respective protonated forms, i.e., conjugate acids of divalent carbon(0) compounds, **VI** (Scheme 1), have mostly been considered as either synthons for the synthesis of divalent carbon(0) compounds by deprotonation[18] or for further protonation (second protonation),[19] coordination to transition metals,[20] and *meta*-chloroperoxybenzoic acid oxidation.[21] Compounds of this class **VI** (Scheme 1) can also be considered as two donor-stabilized parent carbeniumylidenes.[22] The silicon and germanium analogues of carbeniumylidene, silyliumylidene[23] and germyliumylidene,[24] are known, including some utilization in various chemical reactions.[25]

Herein, we report the synthesis and coordination to Au(I)Cl of carbodicarbene **1b** bearing NHC and CAAC and a comparison with its NHC-only and CAAC-only analogues **1a/1c** along with the redox properties of their conjugate acids **2a/2b/2c**.

Results and Discussion

For the synthesis of carbodicarbenes **1a/1b/1c** we have considered their corresponding conjugate acids **2a/2b/2c** as synthons. Compounds **2a/2b/2c** were synthesized as per Scheme 2 employing benzannulated-NHC[26] and -CAAC[27] scaffolds in good yields.[28] Their ^{1}H/^{13}C{^{1}H} NMR spectra exhibit resonances at $\delta = 4.56/50.3$, $5.17/69.5$, and $5.51/77.6$ ppm, respectively, for their carbonic-hydrogen and carbonic-carbon atoms. The trend of chemical shifts is directly correlated to the relative acidity of the carbonic-proton.[29] Solid-state single crystal X-ray diffraction studies of **2a/2c** (Figure 1)[30] reveal the two distances between carbonic carbon (C1) and carbenic carbons (C2/C3) to be quite similar due to the symmetric nature of the donor substituents in both cases (**2a**: C1–C2 1.398(2) Å, C1–C3 1.390(2) Å and **2c**: C1–C2 1.384(4) Å, C1–C3 1.392(3) Å). In **2b** (Figure 1) the distance between the carbonic carbon (C1) and the NHC-carbenic carbon (C3) is 1.439(2), and longer than that of the carbonic carbon (C1) and the CAAC-carbenic carbon (C2) 1.347(2) (Table 1), which is in agreement with the natural resonance theory (NRT) calculations with the highest double bond character of 61.0% for C1–C2, indicating that the CAAC is a better σ-donor and π-acceptor than the NHC in **2b**.[13]

Subsequently, the deprotonation of **2a/2b/2c** led to the isolation of crystalline **1a/1b/1c** (Scheme 2; for **2a**: KHMDS, for **2b**: *n*BuLi or KHMDS, and for **2c**: NHC^{Dip2} or NHC^{Me4}).[28] The ^{13}C{^{1}H} NMR spectra exhibit resonances at $\delta = 110.2$, 140.5, and 158.5 ppm, respectively, for their respective carbonic-carbons. The solid-state single crystal X-ray diffraction studies of **1b/1c** (Figure 2)[30] reveal C2–C1–C3 bond angles of 144.4(3)° and

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Scheme 2. Synthesis of **1a/1b/1c**, **2a/2b/2c**, and **3a/3b/3c** (though for compounds **1a/1b/1c** we have drawn different possible resonance forms **A**, **B**, **C**, and **D**, however each has most contributing forms: for **1a**: **B/C** and **D**; for **1b**: **C** and **D**; and for **1c**: **A**).[31]
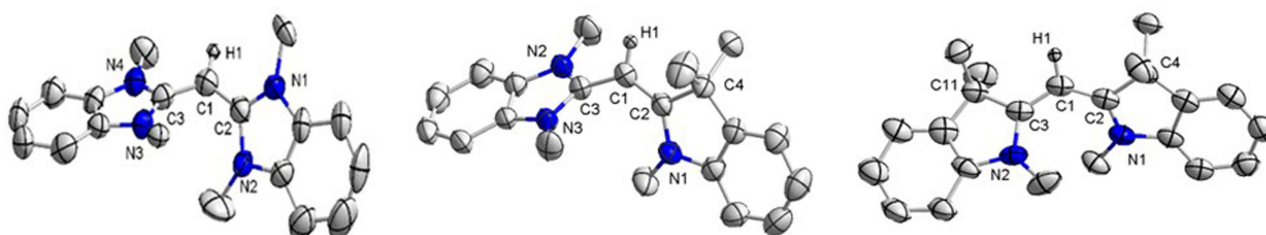

Figure 1. Molecular structures of **2a-BPh₄** (left), **2b-Cl** (middle), and **2c-Cl** (right) with thermal ellipsoids at 50% probability level. All hydrogen atoms except at C1, the co-crystallized solvent molecules and the counter anions are omitted for clarity. Selected bond lengths and angles are summarized in Table 1.

Table 1. Selected bond lengths (Å), bond angles (°), and angles between carbene scaffolds in **2a-BPh₄**, **2b-Cl**, **2c**, **2c-Cl**, **1a**, **1b**, **1c**, **3a**, **3b**, **3c**, **8a**, **8b**, **8c**, **9b**, *gauche*-**11a**, *gauche*-**11b**, and *anti*-**11b**.

Compounds	C1–C2	C1–C3	C2–N	C3–N	C1–E[a]	C2–C1–C3	N–C3-N/C/N–C2–C/N[b]
2a-BPh₄	1.398(2)	1.390(2)	1.359(2)/1.261(2)	1.369(2)/1.302(1)		125.9(2)	51.1(1)
2b-Cl	1.347(2)	1.439(2)	1.370(2)	1.335(2)/1.352(2)		128.9(2)	61.3(1)
2c-Cl	1.384(4)	1.392(4)	1.348(3)	1.346(3)		130.8(2)	52.2(2)
1a[3 a)]	1.343(1)	1.343(1)	1.400(2)/1.407(2)	1.400(2)/1.407(2)		134.8(1)	69.6(1)
1b	1.324(3)	1.338(3)	1.405(3)	1.400(3)/1.394(3)		144.4(3)	86.8(1)
1c	1.308(3)	1.308(3)	1.400(6)	1.402(2)		172.6(2)	87.8(1)
3a	1.394(5)	1.395(5)	1.361(5)/1.383(5)	1.390(5)/1.373(5)	2.031(4)	118.9(2)	64.6(2)
3b	1.373(7)	1.442(7)	1.409(6)	1.349(6)/1.355(6)	2.004(5)	119.2(5)	65.0(4)
3c	1.373(2)	1.404(2)	1.360(1)	1.359(2),	2.034(1)	122.8(1)	56.9(2)
8a	1.471(2)	1.458(6)	1.317(7)/1.347(7)	1.342(7)/1.324(8)	1.319(1)	119.9(4)	88.7(3)
8b	1.491(2)	1.489(5)	1.304(4)	1.335(5)/1.334(6)	1.296(5)	125.9(3)	84.1(1)
8c	1.496(4)	1.465(4)	1.304(3)	1.296(3)	1.297(3)	124.9(2)	88.4(4)
9b	1.406(5)	1.474(6)	1.331(5)	1.337(5)/1.341(5)	1.390(1)	117.7(2)	72.4(2)
gauche-**11a**	1.354(2)	1.493(2)	1.398(2)/1.392(2)	1.480(2)/1.473(2)		131.2(1)	73.6(2)
gauche-**11b**	1.343(2)/1.342(2)	1.499(2)/1.500(2)	1.386(2)/1.390(2)	1.464(2)/1.467(2); 1.477(2)/1.470(2)		134.5(1)/ 134.7(1)	87.0(1)/ 82.3(1)
anti-**11b**	1.347(2)	1.492(2)	1.409(2)	1.493(2)/1.488(2)		134.6(1)	81.2(1)

[a] E denotes the substituents at the carbonic carbon. [b] N–C3-N/C/N–C2–C/N defines the angle between the planes consisting of NHC/CAAC- and CAAC/NHC-scaffolds.

172.6(2)°, respectively, both larger than that of **1a** (134.8(1)°).[3a] This clearly reflects the influence of the donor substituents: NHC vs. CAAC. It is also mirrored in the angle formed between the planes of the two respective carbene scaffolds (**1a**: 69.6(1)°, **1b**: 86.8(1)°, and **1c**: 87.8(1)°). The C1–C2 and C1–C3 bond lengths in **1b** are 1.324(3) and 1.338(3) Å, and thereby shorter than those of the analogous bonds in **1a** (1.343(1) Å) but slightly longer than these bonds are in **1c** (1.308(3) Å).

DFT calculations suggest that **1a** and **1b** have σ-type (HOMO) and π-type (HOMO-1) nonbonding orbitals at C1 with interactions of the C2 and C3 atoms (Figure 3). However, no lone-pair orbitals or donor-acceptor interactions at the central carbon atom or lone-pair orbitals of terminal carbon atoms, respectively, were observed in NBO calculations which may go back to a somehow hidden character carbon(0) property. In case of **1c**, HOMO and HOMO-1 are both π-type, indicating

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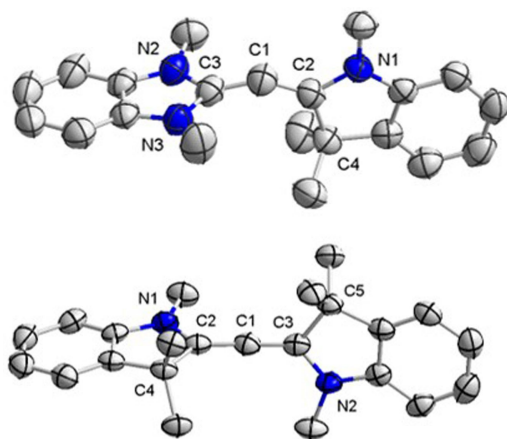**Europe**
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Figure 2. Molecular structures of **1b** (top) and **1c** (bottom) with thermal ellipsoids at 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths and angles are summarized in Table 1.

allene resonance for it. On the other hand, the frontier molecular orbitals (FMOs) analysis of **2a/2b/2c** show the HOMO is mostly situated on the respective carbonic carbon along with nitrogen centers, whereas the LUMO is mostly situated on the central C–C–C motif (Figure 3). The AIM (Atoms in Molecules) analysis[32] at the BCPs (bond critical points) of C1–C2 and

C1–C3 also suggests the highest electron densities with 0.341 for C1–C2 and C1–C3 for **1c**, whereas the lowest ones have been calculated for that of **1a** (0.325) (Table S20). This is in line with the Wiberg bond index values of C1–C2 and C1–C3 bonds of **1a** and **1c** with 1.603 and 1.766, respectively (Table S21). Additionally, the NRT[33] analysis at the BP86/def2-TZVP level of theory indicates that the lowest double bond content is found for the structure **1a** (74.6%) along with the highest lone pairs on the central carbon atom (Table S22). A similar trend is noticed in the calculations of the first and second proton affinities (PA1 and PA2) with the highest values of 294.1 kcal mol^{-1} and 173.4 kcal mol^{-1} for **1a**, respectively, which bear a considerable resemblance to those of reported NHC and NHC–CAAC coordinated carbodicarbene analogues.[34,35] Consequently, the contribution of the carbodicarbene resonance form **D** for **1a** is higher than for **1b** and **1c**.

To address the coordination properties[36] of **1a/1b/1c**, we carried out 1:1 reactions[37] with Me$_2$S·AuCl, which afforded the crystalline gold(I)chloride complexes **3a/3b/3c**, respectively (Scheme 2).[28] Solid-state single crystal X-ray diffraction studies of **3a/3b/3c** (Figure 4)[30] reveal the three-coordinated carbonic carbon to adopt trigonal planar geometry. Upon η^1-coordinating to the Au(I)-center the carbonic scaffold (C2–C1–C3) became more bent than in the free carbones (**1a/3a**: 134.8(1)° to 118.9(2)°, **1b/3b**: 144.4(3)° to 119.2(5)°, and **1c/3c**: 172.6(2)° to 122.8(1)°). Concomitantly, distances between the carbonic
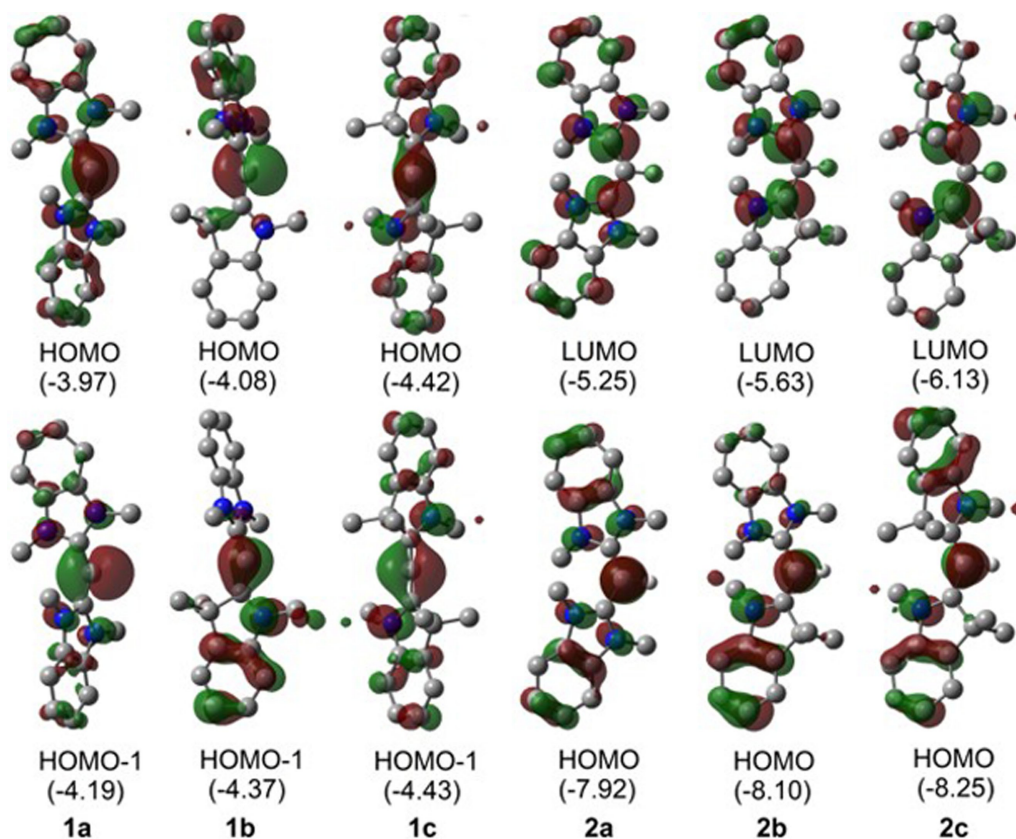

Figure 3. Selected frontier molecular orbitals and their energies (eV) of the optimized geometries of **1a/1b/1c** and **2a/2b/2c** (isovalue = 0.04). Hydrogen atoms are omitted for clarity except for the central C-H of **2a/2b/2c**.
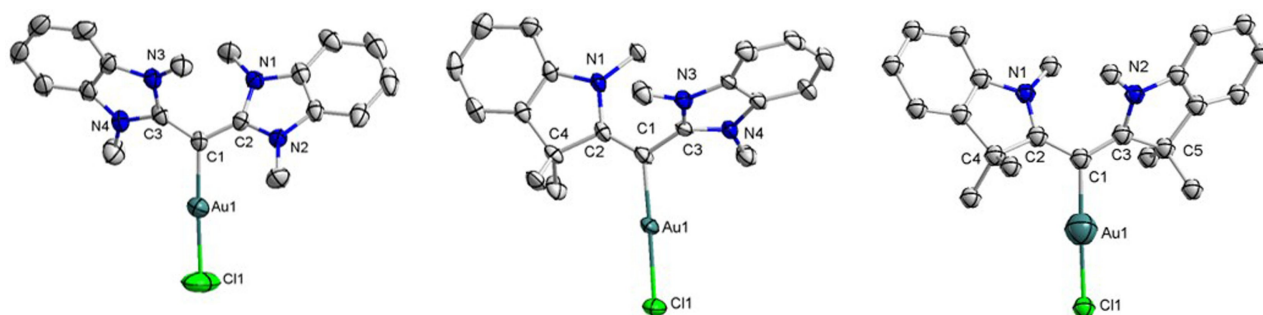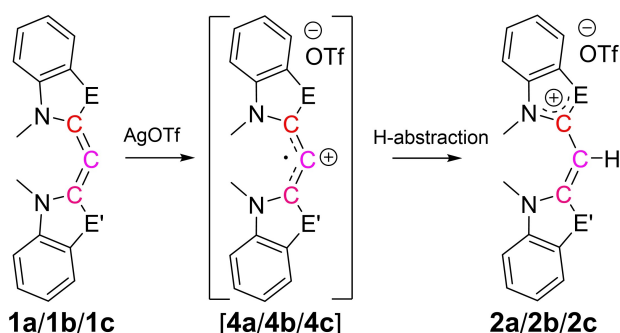
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Figure 4. Molecular structures of **3a** (left), **3b** (middle), and **3c** (right) with thermal ellipsoids at 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths and angles are summarized in Table 1.

carbon (C1) and carbenic carbons (C2/C3) become elongated upon coordination (for **3a**: 1.394(5)/1.395(5) Å, for **3b**: 1.373(7)/1.442(7) Å, and for **3c**: 1.371(2)/1.404(2) Å). The C−Au bond distances are 2.031(4), 2.004(5), and 2.034(1) Å, respectively, which are larger than that of the NHC^{Dip2} coordinated Au(I)Cl complex (1.942 Å).[38]

We found that **1a/1b/1c** are prone to be oxidized;[39] the reaction with AgOTf led to the formation of **2a/2b/2c** along with metallic silver (Scheme 3).[28] It is proposed that the reaction proceeds through the formation of the transient radical-cation [**4a/4b/4c**] followed by hydrogen abstraction. In case of **1b**, the abstraction of the hydrogen from THF molecules

was confirmed by employing [D$_8$]THF as solvent and subsequently recording the ^{2}H NMR spectrum. The spin density plot of [**4a/4b/4c**] clearly shows considerable spin population over the central carbon atom and some delocalization through the NHC/CAAC units (Figure S125). The transient formations of [**4a/4b/4c**] are along the line of previously reported oxidations of allenes under the formation of transient radical-cations (1-electron oxidation) and triplet carbenes (2-electron oxidation).[40] The radical-cations of carbodicarbenes are stabilized within the coordination sphere of transition metal complexes.[41]

Subsequently, we focused on cyclic voltammogram (CV) studies of **2a/2b/2c** in CH$_3$CN/0.1 M [Bu$_4$N][PF$_6$] against Fc/Fc$^+$ as a reference (Figure 5).[28] Compound **2a** exhibits a reversible oxidation wave at $E_{1/2} = +0.63$ V and an irreversible reduction at $E_{pc} = -2.49$ V. Whereas **2b** shows an irreversible reduction at $E_{pc} = -2.23$ V and an irreversible oxidation at $E_{pa} = +1.05$ V. The oxidation wave appears at the onset of the decomposition range of the solvent/conducting electrolyte mixture.[42] Moreover, compounds **2a** and **2b** exhibit follow up oxidation waves at $E_{pa} = -1.18$ V and -1.04 V, respectively, after the respective reduction wave. On the other hand, **2c** exhibits a reversible reduction at $E_{1/2} = -1.68$ V and no oxidation wave within the solvent permissible range was observed.[43]

Subsequently, the reaction of **2a** with [NO][SbF$_6$] ($E_{1/2} = +0.87$ V vs. Fc/Fc$^+$ in MeCN)[44] in MeCN leads to the isolation of
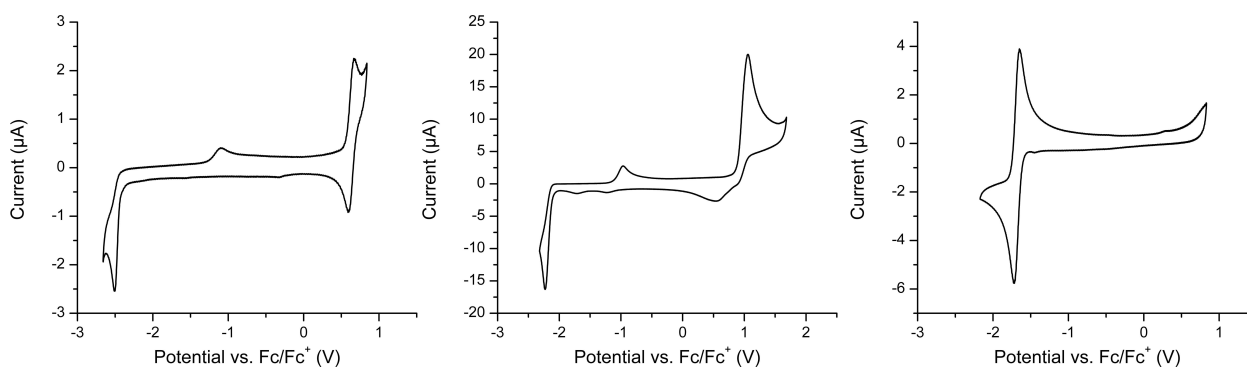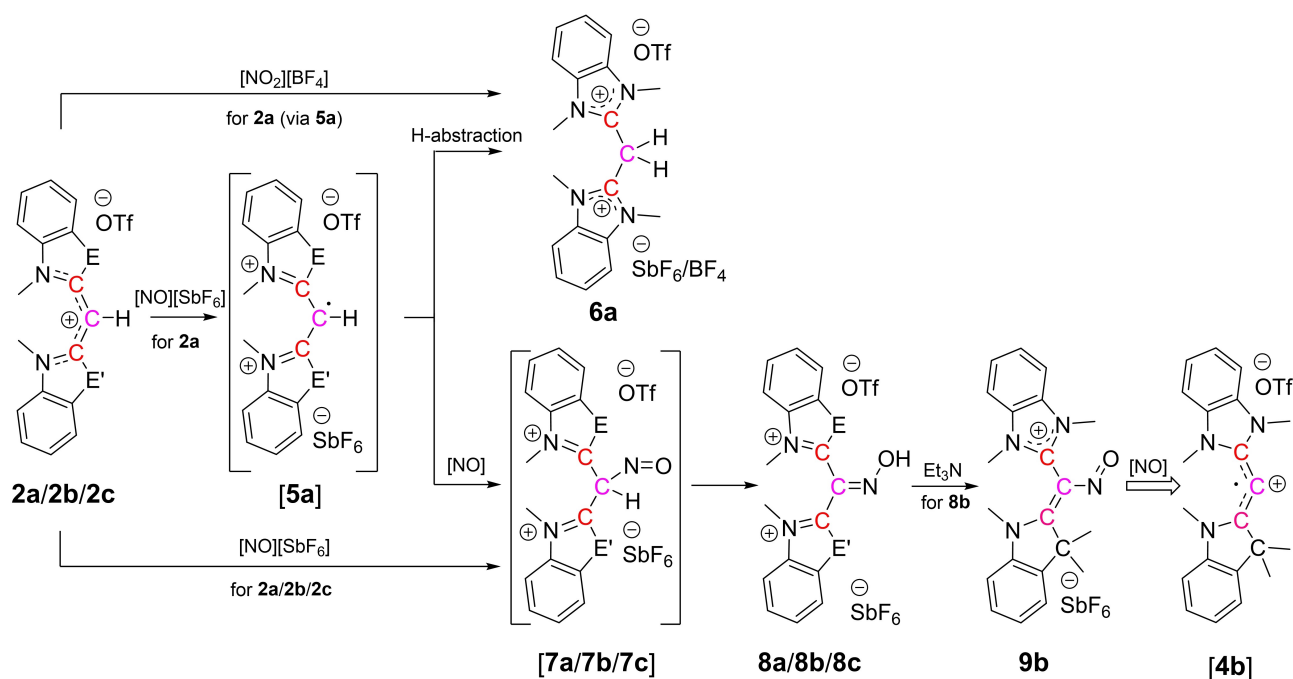

Scheme 3. Oxidations of **1a/1b/1c**.

Figure 5. Cyclic voltammograms of **2a** (left), **2b** (middle), and **2c** (right) in CH$_3$CN/0.1 M [Bu$_4$N][PF$_6$] at 100 mV/sec scan rate (measurements for **2a/2c** started in the reductive direction whereas for **2b** started in oxidative direction).

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an almost 1:1 mixture of the compounds **6a** and **8a** (Scheme 4).[28] On the other hand, the reactions of **2b** and **2c** with [NO][SbF$_6$] only yield dicationic oximes **8b** and **8c** (Scheme 4).[28] We assume that the formation of **6a** and **8a** proceeds through the initial formation of radical-dication [**5a**] followed by H-abstraction and [NO] trapping[45] plus subsequent tautomerization,[46] respectively. The formation of **8a** can also be envisioned through the electrophilic addition of [NO][SbF$_6$] to **2a**.[47] Such electrophilic addition has occurred in the cases of **2b** and **2c** since their oxidation potentials are more positive than that of [NO][SbF$_6$]. Notably, the reaction of **2a** with [NO$_2$][BF$_4$] ($E_{1/2} = 0.91$ V vs. Fc/Fc$^+$ in MeCN)[44 b), 48] exclusively leads to the formation of **6a** (Scheme 4). Attempts to detect the radical intermediate [**5a**] by monitoring the reaction of **2a** with [NO][SbF$_6$] / [NO$_2$][BF$_4$] at $-30\,°C$ in acetonitrile by EPR spectroscopy failed, indicating a particularly short-lived character of this radical intermediate.[49] However, the transient formation of radical dication [**5a**] is in accordance with the CV and DPV study of **2a** (Figure S95 and Figure S97).

The solid-state molecular structure analyses of dicationic oximes **8a**/**8b**/**8c** (Figure 6) reveal the C−N bond distances of the oxime moiety to be 1.319(1), 1.296(5), and 1.297(3) Å, respectively, which are in the range for a typical C−N double bond.[50] To further showcase the functionalization of dicationic oximes, we performed a deprotonation reaction of **8b** using Et$_3$N which leads to the formation of **9b** (Scheme 4),[28] that can be considered as [NO] trapped product of **4b**, the radical cation of carbone **1b**. However, the reaction of **1b** with [NO][SbF$_6$] led to an intractable mixture of products, and it was impossible to find any indication for the formation of **9b**. Overall, the formation of **9b** from **1b** can be outlined with an initial protonation to **2b**, then electrophilic addition of [NO][SbF$_6$] to **8b**, and finally deprotonation to the target molecule **9b**. For this reaction sequence, the protonation and deprotonation events are essential and thereby similar to protection-deprotection strategies towards target molecules, which are well known in synthetic organic chemistry.[51] This leads for the first time to the incorporation of [NO] at the central carbon of a

Scheme 4. Reactions of **2a**/**2b**/**2c** with [NO][SbF$_6$], reaction of **2a** with [NO$_2$][BF$_4$], and reaction of **8b** with Et$_3$N.
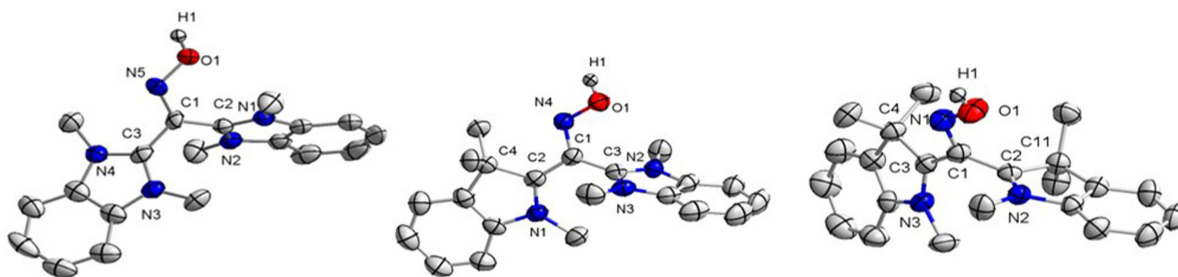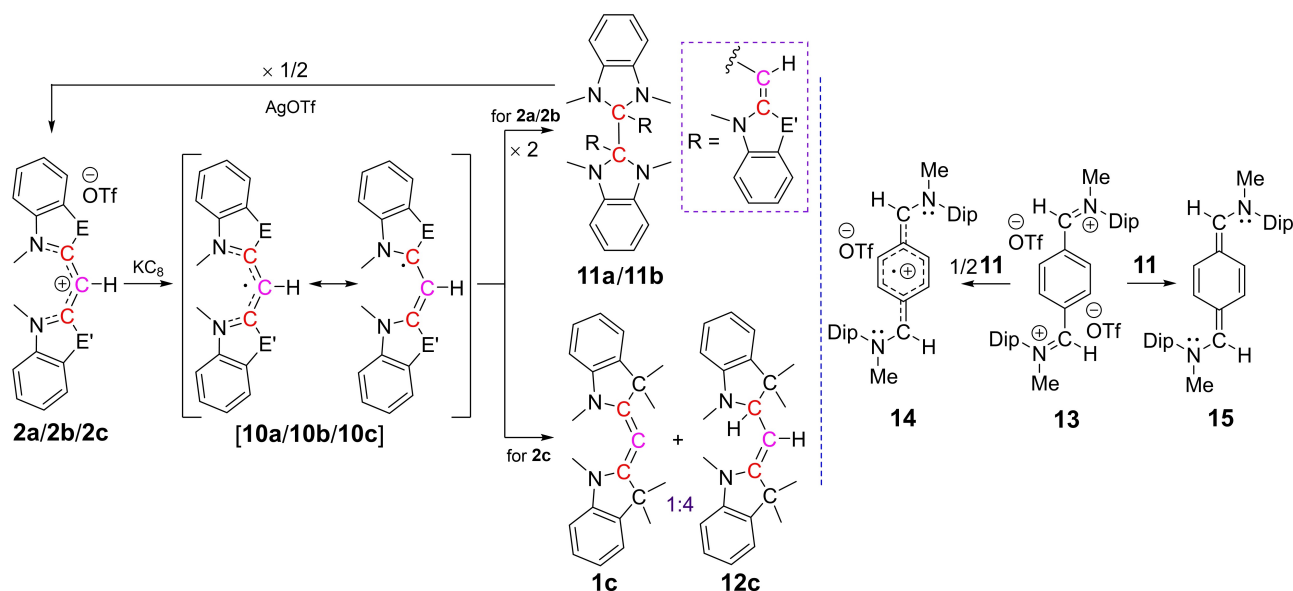

Figure 6. Molecular structures of **8a** (left), **8b** (middle), and **8c** (right) with thermal ellipsoids at 50 % probability level. All H atoms except for the H atom of the OH group are omitted for clarity. Selected bond lengths and angles are summarized in Table 1.

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carbodicarbene.[52] The solid-state molecular structure analysis of **9b** finds the C1-N4 bond length at 1.390(1) Å (Figure S123), which is slightly shorter than that of a formally related [NO] adduct of an NHC-derived radical cation (1.412 Å).[53]

The reduction of **2a/2b** with KC$_8$ in THF, on the other hand, leads to the formation of exclusively **11a/11b** (Scheme 5 – left).[28] This observation implies a dimerization of the proposed initially formed transient radical [**10a/10b**] (Figure S125). However, with EPR spectroscopy, even at the reaction temperature of −30 °C, it was impossible to detect the putative radical intermediate. In solution, compounds **11a/11b** exist in their two rotational isomers. In the case of **11a**, the obtained crystal structure shows the *gauche*-isomer, whereas *gauche*- and *anti*-isomers were obtained for **11b** from two different solvents (Figure 7). The *gauche*-**11b** has 2.4 kcal mol^{-1} lower energy than the *anti*-form. The central intermolecular newly formed C−C single sigma bond distances for *gauche*-**11a**, *gauche*-**11b** and *anti*-**11b** are

1.623(2) 1.622(2) and 1.639(3) Å, respectively. These bond lengths are significantly longer than those of standard C(sp^3)−C(sp^3) single bonds (ca. 1.54 Å).[54] The HOMO orbitals of *gauche*-**11a**, *gauche*-**11b**, and *anti*-**11b** show delocalization mostly at the newly formed central C−C σ-bonds and their geminal cyclic-diamino substituents and two NHC units, whereas those of HOMO-2 are delocalized over the C−C double bond and two CAAC units (Figure S126).

In contrast to **2a** and **2b**, the 1:1 reaction of **2c** with KC$_8$ in THF first led to the appearance of a red-color which persisted at room temperature for about 30 minutes and then slowly changed to a colorless solution (Scheme 5 - left).[28] The ^{1}H NMR of the crude reaction mixture indicates the formation of **1c**, a hydrogen eliminated product[55] along with **12c**, a hydrogen abstracted product[56] in about a 1:4 ratio. We propose the reaction proceeds through the initial formation of radical [**10c**], which has limited stability.[57] Convincing evidence for [**10c**] presence was obtained from

Scheme 5. Reductions of **2a/2b/2c** with KC$_8$, oxidations of **11a/11b** with AgOTf (left) and utilization of **11a/11b** as reducing reagents (right).
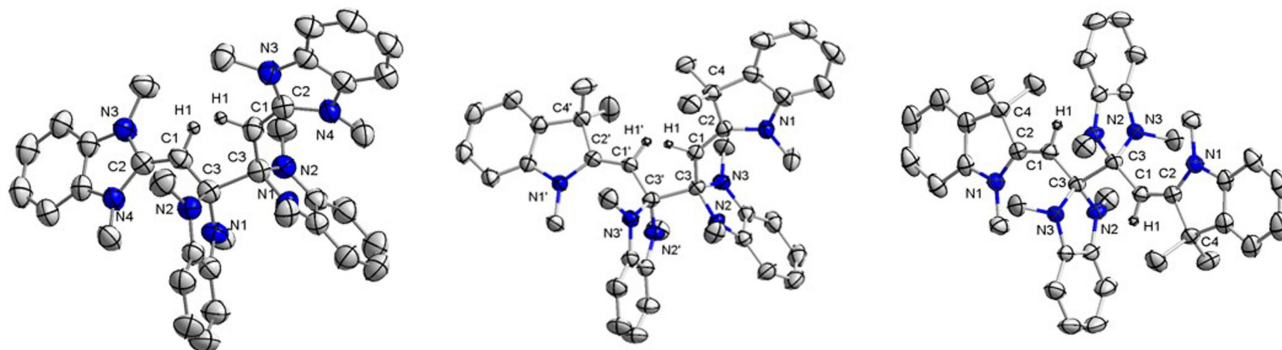

Figure 7. Molecular structures of *gauche*-**11a** (left), *gauche*-**11b** (middle) and *anti*-**11b** (right) with thermal ellipsoids at 50% probability level. All H atoms except at C1 and C1′ and co-crystallized toluene (*gauche*-**11a**), MeCN (*gauche*-**11b**) and C$_6$D$_6$ (*anti*-**11b**) are omitted for clarity. Selected bond lengths and angles are summarized in Table 1.

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EPR spectroscopy (Figure 8). The EPR spectrum shows a large proton hyperfine coupling ($A(^1H) = 12.8$ G) to the single proton at the central carbon atom and weak couplings to the two nitrogen atoms ($A(^{14}N) = 1.9$ G) of the carbene moieties, indicating a spin distribution mainly along the NCCCN linkage. A similar EPR response, with a dominant proton doublet signal, was observed in radical cations of benzimidazole derivatives.[58] Compound **10c** can be considered as donor-stabilized carbyne.[59] Theoretical calculations at the BP86/Def2TZVP level of theory suggest that the doublet electronic state is more stable than the quartet state by 66.37 kcal mol^{-1} of electronic energy. Notably, the first synthesis of hexaphenylcarbodiphosphorane **I** was reported as being realized through the reduction of its conjugate acid (methylidebis-(triphenylphosphonium)bromide), using potassium metal in diglyme.[1 a)]

Finally, to address the oxidation[60] of **11a/11b**, they were studied by cyclic voltammetry in THF/0.1 M [Bu$_4$N][PF$_6$] (Figures S106-S112). The voltammograms show oxidation waves at $E_{pa} = -1.17$ and -0.91 V vs. Fc/Fc$^+$, respectively. This confirms that the reducing power of **11a/11b** is stronger than those of the dimers of 2-substituted (cyclohexyl/4-(dimethylamino)/ferrocenyl/ ruthenocenyl) N,N'-dimethylbenzimidazoline radicals (for cyclohexyl: $E_{pa} = -0.64$ V, for 4-(dimethylamino): $E_{pa} = -0.75$ V, for ferrocenyl: $E_{pa} = -0.89$ V, and for ruthenocenyl: $E_{pa} = -0.59$ V vs. Fc/Fc$^+$ in THF/0.1 M [Bu$_4$N][PF$_6$]).[61]

Accordingly, the oxidation of **11a/11b** with AgOTf in THF produced **2a/2b** (Scheme 5 - left).[28] As a proof of principle, in a follow-up experiment compounds **11a/11b** were utilized as a two-electron source for reducing the p-phenylene bridged bis-iminium cation **13**[62] (Scheme 5 - right).[28] The 1:2 reaction of **11a/11b** and **13** leads to radical cation **14**, whereas a 1:1
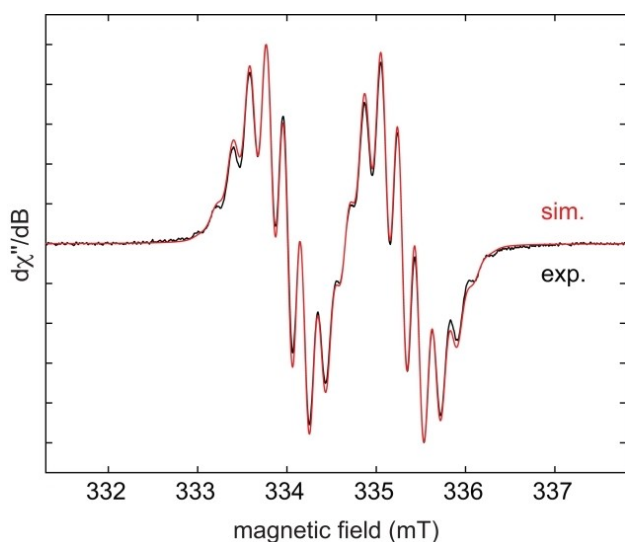
reaction leads to α,α'-diamino-p-quinodimethane **15**. These compounds therefore express organic electron donor (OED) reactivity[63] involving the oxidation of a C(sp^3)–C(sp^3) single σ-bond. Notably, organic electron donors (OEDs), in contrast, are commonly electron-rich alkenes (with π-bonds).[64]

Conclusion

The striking influence of NHCs versus CAACs as donor substituents on the properties of three varied carbodicarbenes (NHC/NHC, NHC/CAAC, and CAAC/CAAC), is conveyed. Their respective protonated forms (conjugate acids) can be considered as donor-stabilized parent carbeniumylidene. The stronger σ-donor and π-acceptor properties of CAACs compared to NHCs are clearly reflected in their structural properties. The η^1-coordination mode of these three carbodicarbenes was revealed upon reactions with Au(I)Cl. The electrochemical study of these conjugate acids show the NHC- and CAAC-donor substituent(s) to control the oxidation as well as reduction properties. In the cyclic voltammograms the NHC/NHC-carbodicarbene exhibits reversible oxidation (along with irreversible reduction) whereas CAAC/CAAC-carbodicarbene exhibits reversible reduction and no oxidation wave in the employed solvent window. The NHC/CAAC-carbodicarbene exhibits both oxidation and reduction in an irreversible manner. The reaction of these conjugate acids with [NO][SbF$_6$] led to the isolation of dicationic oxime derivatives. In the case of the NHC/CAAC-system, the dicationic oxime derivative leads to nitroso-substituted carbeniumylidene under deprotonation. The reactions of NHC/NHC- and NHC/CAAC-carbodicarbenes with KC$_8$ led to the intermolecular reductive (reversible) carbon–carbon bond formation through the carbenic carbon center of the NHC-scaffold (dimerization of transient vinyl substituted benzimidazoline radicals). Interestingly, the resulting carbon–carbon single bond can be oxidized and consequently utilized as a two-electron source, pointing to its potential for various applications, including a role as an n-dopant within organic semiconductor molecules.[65] In contrast, the reaction of CAAC/CAAC-carbodicarbene with KC$_8$ leads to the hydrogen abstracted/eliminated products, which proceed through a neutral allyl radical intermediate, evidenced by EPR spectroscopy. More broadly, our synthetic route for all these newly synthesized compounds is completely modular and can be tuned through substituents to obtain derivatives with properties optimized for the respective targeted application.

Figure 8. Experimental (black) and simulated (red) continuous-wave (CW) X-band EPR spectra of **10c** in THF at room temperature. The best-fit simulation parameters are $g_{iso} = 2.0030$, $A(^{14}N, 2N) = 5.3$ MHz (1.9 G), $A(^1H, 1H) = 35.9$ MHz (12.8 G), and $A(^1H, 6H) = 5.0$ MHz (1.8 G).

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Conflict of Interest

We are working to file a patent related to the compounds of **11a** and **11b**.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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[28] See the Supporting Information for the experimental details, analytical data, NMR spectra, UV/Vis spectra, X-ray crystallographic details, and the quantum chemical calculation details.

[29] Please see the Supporting Information (Page S38-S43) for the detailed study of relative acidity of **2a/2b/2c** and its comparison with the conjugate acids of two commonly used N-heterocyclic carbenes.

[30] Deposition Number(s) 2122849 (**1b**), 2162645 (**1c**), 2179792 (**2a-BPh₄**), 2122848 (**2b-Cl**), 2162643 (**2c**), 2162644 (**2c-Cl**), 2179793 (**3a**), 2122850 (**3b**), 2162646 (**3c**), 2162649 (**6a-(BF₄)₂**), 2162648 (**8a**), 2122853 (**8b**), 2128781 (**8b-(SbF₆)₂**), 2162647 (**8c-(SbF₆)₂**), 2122854 (**9b**), 2162650 (*gauche*-**11a**), 2122855 (*anti*-**11b**), and 2122856 (*gauche*-**11b**) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

[31] Although we have collectively referred to compounds **1a/1b/1c** as carbodicarbenes, the most contributing resonances form, which is either a carbodicarbene/carbone(0), a donor-stabilized vinylidene, or an allene, depends on the end-cap substituents.

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