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When Does Carbonylation of Carbenes Yield Ketenes? A Theoretical Study with Implications for Synthesis

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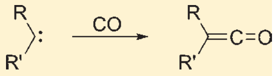
Supporting Information



ABSTRACT: Quantum-chemical calculations using DFT and ab initio methods have been carried out for 32 carbenes RR′C which comprise different classes of compounds and the associated ketenes $RR'C{=}C{=}O$. The calculated singlet−triplet gaps ΔE_{S-T} of the carbenes exhibit a very high correlation with the bond dissociation energies (BDEs) of the ketenes. An energy decomposition analysis of the $RR'C{-}CO$ bond using the triplet states of the carbene and CO as interacting fragments supports the assignment of ΔE_{S-T} as the dominant factor for the BDE but also shows that the specific interactions of the carbene may sometimes compensate for the S/T gap. The trend of the interaction energy ΔE_{int} values is mainly determined by the Pauli repulsion between the carbene and CO. The stability of amino-substituted ketenes strongly depends on the destabilizing conjugation between the nitrogen lone-pair orbital and the ketene double bonds. There is a ketene structure of the unsaturated N-heterocyclic carbene parent compound **NHC1** with CO as a local energy minimum on the potential-energy surface. However, the compound **NHC1−CO** is thermodynamically unstable toward dissociation. The saturated homologue **NHC2−CO** has only a very small bond dissociation energy of D_e = 3.2 kcal/mol. The [3]ferrocenophane-type compound **FeNHC−CO** has a BDE of D_e = 16.0 kcal/mol.

INTRODUCTION

Ketenes $RR'C{=}C{=}O$ are a versatile class of synthetically useful compounds which play an important role as reactive intermediates in organic chemistry.[1] The first ketene was reported in 1905 by Staudinger, who isolated diphenylketene $Ph_2C{=}C{=}O$ as a low-melting solid through dechlorination of chlorodiphenylacetylchloride $Ph_2(Cl)C{-}C(Cl){=}O$.[2] It was soon recognized that the stability of ketenes $RR'C{=}C{=}O$ strongly depends on the nature of the substituents. Many ketenes are highly reactive, and their existence in a condensed phase could only be proven by trapping them in low-temperature matrices or as products of specific addition reactions such as [2 + 2] cycloadditions. This holds in particular for ketenes with electronegative substituents like halogens or alkoxy groups OR.[3] Nitrogen-substituted ketenes, which are usually also quite unstable,[4] play a particular role because they are important precursors for the synthesis of penicillins.[5] Stable ketenes with nitrogen substituents could only be isolated by preventing strong conjugation between the nitrogen lone-pair electrons and the double bonds of the ketene moiety and by using bulky groups. For example, the phthalimidoketene $R^1R^2C{=}C{=}O$, where R^1 = phthalimid and R^2 = *tert*-butyl, is a solid which melts at 96 °C.[6]

$$RR'C + CO \rightarrow RR'C{=}C{=}O \qquad (1)$$

Ketenes may be synthesized by direct carbonylation of carbenes (reaction 1). Numerous ketenes $RR'C{=}C{=}O$ have been made by carbonylation of carbenes RR′C which were prepared in situ through photolysis of diazo compounds $RR'C{=}N_2$ as precursors.[7] The advent of stable carbenes in 1988 initiated by Bertrand,[8] who isolated phosphanylcarbenes $R_2P{-}C{-}SiR'_3$, and particularly the introduction of N-heterocyclic carbenes (NHCs) in synthetic chemistry by Arduengo in 1991[9] opened up new prospects for the synthesis of ketenes through carbonylation reactions of carbenes. Lyashchuk and Skrypnik[10] reported in 1994 that addition of CO to an NHC which carries adamantyl substituents at nitrogen yields a stable ketene (Scheme 1a). However, this result could not be reproduced by Dixon, Arduengo, Dobbs, and Khasnis,[11] who reported in a combined experimental/theoretical study that the carbonylation of the parent NHC gives only a weakly bonded van der Waals complex. This agrees with the experimental finding that NHCs which carry *tert*-butyl groups at nitrogen do not react with CO (Scheme 1b).[12]

The modification of the structure of NHCs toward carbenes which add CO, affording stable ketenes (reaction 1), has been a challenge for experimental chemists who used various strategies to overcome the destabilizing influence of the nitrogen substituents on the ketene moiety. Bertrand[13] reported in 2006 that cyclic and acylic alkylaminocarbenes readily add CO yielding ketenes which could be isolated and their structure determined through X-ray structure analysis (Scheme 1c and 1d). Very recently, two groups reported[14,15] that replacing the diamino by a diamido group in a six-membered N-heterocyclic carbene strongly enhances the electrophilicity of the carbene, which allows addition of CO and isolation of the respective ketene which could be characterized by X-ray structure analysis (Scheme 1e).[14]

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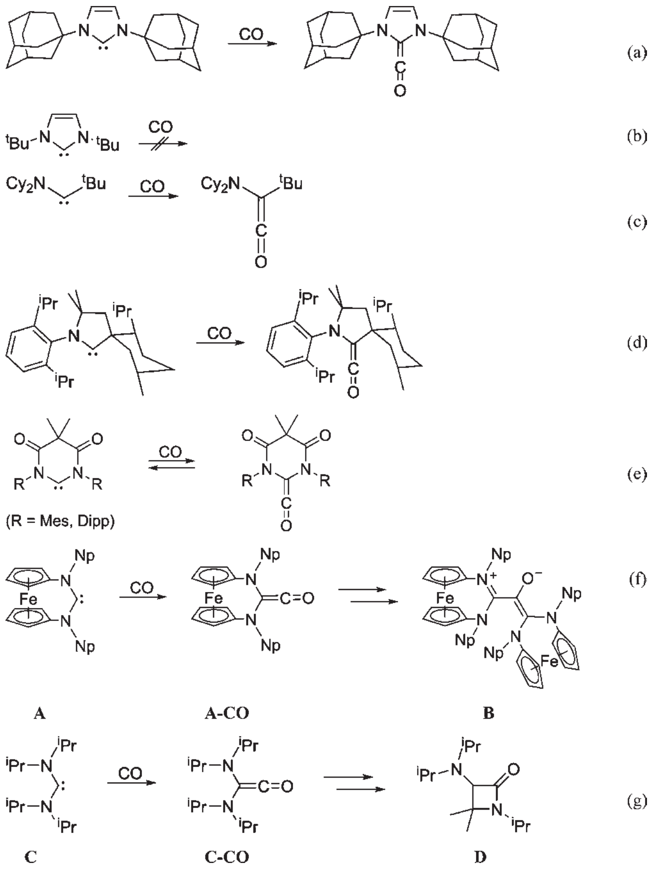
Scheme 1. Overview of Experimental Work on Carbonylation Reactions of Carbenes[a]



[a] (a) Ketene formation of an N-heterocyclic carbene which was reported in ref 10 but was questioned in ref 11. (b) CO does not react with NHC carrying *tert*-butyl groups (ref 12). (c) Acyclic alkylaminocarbene reacts with CO yielding a ketene (ref 13). (d) Cyclic alkylaminocarbene reacts with CO yielding a ketene (ref 13). (e) Diamidocarbene reacts with CO yielding a ketene (refs 14 and 15; R = Dipp and Mes). (f) [3]Ferrocenophane-type NHC reacts with CO yielding a ketene which reacts further with another [3]ferrocenophane-type NHC (ref 16). (g) Acyclic diaminocarbene reacts with CO yielding a ketene which reacts further yielding a lactam (ref 16).

The first experimental work which reports reproducible reactions where diaminocarbenes add CO yielding a ketene was recently published by Siemeling and co-workers.[16] The authors employed the [3]ferrocenophane-type NHC **A** (Scheme 1f), which had previously been synthesized and characterized through X-ray structure analysis by the same group.[17] The exploration of the chemical reactivity of this novel type of NHC revealed surprising features. The reaction of **A** with CO yields the ketene **A−CO**, which further reacts with another molecule **A** to afford the zwitterionic final product **B**, whose structure was determined by X-ray structure analysis. Although the ketene **A−CO** could not be isolated, its formation during the reaction course was strongly supported by quantum-chemical calculations, which showed that the reactions **A** + CO → **A−CO** and **A−CO** + **A** → **B** are exergonic processes which have very low activation barriers.[16] The authors also reported that the acylic diaminocarbene $[(i\text{-Pr})_2N]_2C$ (**C**) undergoes a facile reaction with CO affording the ketene **C−CO** which rearranges to the final product **D** (Scheme 1g). The reaction course **C** + CO → **C−CO** → **D** was supported by quantum-chemical calculations.[16]

The experimental findings concerning the carbonylation of carbenes raise the question about the reason for the different propensities of divalent carbon(II) compounds RR′C (carbenes)[18] to yield ketenes as reaction products. It has been suggested that the electrophilicity of a singlet carbene correlates with the singlet−triplet gap ΔE_{S-T}.[19] This model could be applied to the reaction of carbenes with CO because the bonding situation in ketenes RR′C=C=O implies that there is an electron-sharing double bond between RR′C and CO in the electronic triplet states. CO has a $X^1\Sigma^+$ singlet ground state and a first excited $a^3\Pi$ triplet state, which is 139.2 kcal/mol higher in energy.[20] If the excitation energy of the carbene from the singlet ground state to the triplet excited state is so high that the sum of the singlet−triplet excitation energies of CO and RR′C becomes higher than the bond dissociation energy (BDE) of the RR′C−CO bond, stable ketenes cannot be formed. We investigated this model for a large set of carbenes by correlating the calculated singlet−triplet gap ΔE_{S-T} of the divalent C^{II} compounds with the theoretically predicted BDEs of the ketenes.

In this paper we report the equilibrium geometries of 32 cyclic and acyclic carbenes RR′C in their lowest lying singlet and triplet state and the related ketenes RR′C=C=O. We give the theoretically predicted bond dissociation energies for breaking the carbon−carbon bond of the ketenes and discuss the correlation between the singlet−triplet gap of the carbenes and the BDE. We also present the results of an energy decomposition analysis (EDA) for the RR′C−CO bond of selected ketenes. An overview of the calculated carbenes is shown in Scheme 2.

METHODS

Geometry optimizations without symmetry constraints have been carried out at the BP86[21]/def2-TZVPP[22] level of theory for all molecules using the program package Gaussian03.[23] Stationary points were characterized as minima by calculating the Hessian matrix analytically at this level of theory.[24] The geometries of selected molecules were also optimized at B3LYP[25]/def2-TZVPP, M05-2X[26]/def2-TZVPP and MP2[27]/def2-TZVPP.

The energy decomposition analysis (EDA)[28] of the ketenes was performed with the program ADF2009.01b.[29] The calculations were carried out at BP86 using Slater-type orbitals with TZ2P quality[30] at the BP86/def2-TZVPP-optimized geometries.[31] The EDA focuses on the instantaneous interaction energy ΔE_{int} of a bond A−B between two fragments A and B in the particular electronic reference state and in the frozen geometry of AB. For the analysis of the RR′C−CO bond in the chosen ketenes we used the carbene and CO fragments in the lowest-lying triplet states. The interaction energy ΔE_{int} is divided into three components:

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb} \qquad (2)$$

The term ΔE_{elstat} corresponds to the quasiclassical electrostatic interaction between the unperturbed charge distributions of the prepared fragments and is usually attractive. The Pauli repulsion ΔE_{Pauli} comprises the destabilizing interactions between electrons of the same spin on either fragment. The orbital interaction ΔE_{orb} which can be used as a measure for the covalent bonding accounts for the stabilization which comes from the mixing of occupied and vacant orbitals and from polarization effects. To obtain the bond dissociation energy D_e (by definition with opposite sign than ΔE), the preparation energy ΔE_{prep}, which gives the relaxation of the fragments into their electronic and

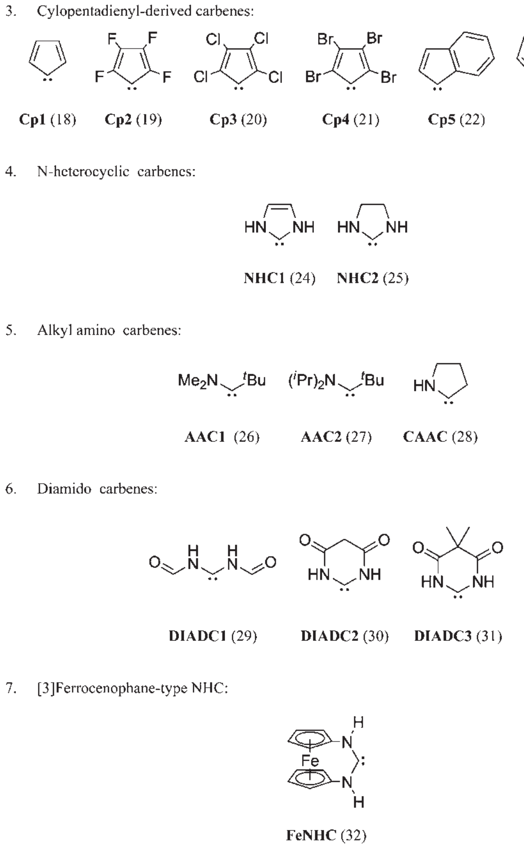
Scheme 2. Overview of the Carbenes Investigated in This Work

1. R_2C

   R = H (1), F (2), Cl (3), Br (4), I (5), Me (6), CO_2H (7), NH_2 (8), NMe_2 (9), OH (10), OMe (11)

2. RHC

   R = F (12), Cl (13), Br (14), I (15), Ph (16), 3-Py (17)



geometrical ground states, must be added to ΔE_{int}:

$$\Delta E(= -D_e) = \Delta E_{\text{int}} + \Delta E_{\text{prep}} \tag{3}$$

Further details about the EDA can be found in the literature.[32]

RESULTS

Below we present and discuss only the most important geometrical data of the molecules because the focus of the work is on the correlation of the singlet−triplet gap and the BDE of the ketenes. In particular, we give only a selected comparison of the calculated geometries with experimental values or with previous ab initio calculations, which shows that the theoretical values which are presented here are in good agreement with experiment and high-level ab initio values. The full set of geometrical data is given in the Supporting Information.

Acyclic Carbenes R_2C and Ketenes $R_2C{=}C{=}O$. Table 1 shows the most important bond lengths and bond angles of selected acyclic carbenes R_2C in the energetically lowest lying singlet and triplet states and the calculated singlet−triplet (S/T) energy differences ΔE_{S-T}. All carbenes have singlet ground states, except the parent methylene H_2C which has a $^3B_1$ ground state and Me_2C where the (^3A) triplet state is 0.3 kcal/mol lower in energy than the (^1A) singlet state. Note that the calculated S/T gaps do not include ZPE corrections. The calculated singlet−triplet energy differences are in agreement with experimental results. Gas-phase experiments have shown that H_2C has a $^3B_1$ ground state which is 9.0 kcal/mol lower in energy than the $^1A_1$ singlet state[33] while the $^1A_1$ singlet state of F_2C is 56.7 kcal/mol more stable than the $^3B_1$ triplet state.[34] The energy differences at BP86/def2-TZVPP with inclusion of ZPE corrections are 13.6 kcal/mol for H_2C in favor of the $^3B_1$ state and 52.8 kcal/mol for F_2C in favor of the $^1A_1$ state. Our DFT values for the S/T gap of the heavier dihalocarbenes concur with previous high-level ab initio calculations.[35]

The geometry optimizations of the CO adducts of the acyclic carbenes R_2C which are shown in Table 1 give stable ketenes as energy minima on the PES. The optimized structures of $R_2C{=}C{=}O$ have rather short carbon−carbon distances between 1.316

Table 1. Geometries and Energies of Carbenes R_2C and Ketenes $R_2C{=}C{=}O$ at BP86/def2-TZVPP[a]

	carbene R_2C												
	singlet			triplet				ketene $R_2C{=}C{=}O$					
R	state	d(R−C)	α(R−C−R)	state	d(R−C)	α(R−C−R)	ΔE_{S-T}	state	d(R−C)	α(R−C−R)	d(C−C)	D_e[b]	D_0[b]
H	$^1A_1$	1.123	100.6	$^3B_1$	1.086	135.4	−14.1	$^1A'$	1.087	120.6	1.316	106.6 (92.5)	100.6 (86.9)
F	$^1A_1$	1.321	104.5	$^3B_1$	1.329	119.9	52.8	$^1A'$	1.341	114.4	1.323	14.6	11.2
Cl	$^1A_1$	1.741	109.2	$^3B_1$	1.679	128.9	19.3	$^1A'$	1.730	120.9	1.324	42.5	38.8
Br	$^1A_1$	1.915	110.2	$^3B_1$	1.843	130.0	17.1	$^1A'$	1.892	122.3	1.320	46.3	42.8
I	$^1A_1$	2.124	112.3	$^3B_1$	2.039	132.7	12.1	$^1A'$	2.094	124.6	1.317	52.2	48.7
Me	^1A	1.468	122.6	^3A	1.464	134.8	−0.3	$^1A'$	1.514	119.5	1.319	77.8 (77.5)	72.2 (72.4)
CO_2H	^1A	1.408	128.0	^3A	1.439	134.5	4.7	^1A	1.448	122.6	1.343	78.8	74.7
NH_2	^1A	1.341	113.1	^3A	1.388	123.1	52.7	^1A	1.429	120.3	1.330	9.9	7.2
NMe_2	^1A	1.352	120.1	^3B	1.383	122.2	42.1	^1A	1.427	116.9	1.331	16.1	13.8
OH	$^1A_1$	1.338	104.4	^3B	1.355	124.5	55.6	^1A	1.384	120.0	1.328	9.4	7.3
OMe	$^1A'$	1.333	107.7	^3B	1.345	125.0	54.0	^1A	1.378	120.3	1.329	9.6	7.0

[a] Bond distances d(R−C) and d(C−C) in Angstroms and angles α(R−C−R) in degrees. Energy difference ΔE_{S-T} between the singlet and the triplet state of the carbene in kcal/mol. Bond dissociation energies of the ketene D_e yielding CO and R_2C in the singlet state in kcal/mol. Bond dissociation energies D_0 including zero-point vibrational correction in kcal/mol. Bond dissociation energies. [b] The values in parentheses give the BDE yielding singlet CO and the carbene in the triplet ground state.

Table 2. Geometries and Energies of Carbenes RHC and Ketenes RHC=C=O at BP86/def2-TZVPP[a]

	carbene RHC													
	singlet			triplet				ketene RHC=C=O						
R	state	d(R–C)	α(H–C–R)	state	d(R–C)	α(H–C–R)	ΔE_{S-T}	state	d(R–C)	d(C–C)	α(H–C–R)	β(H–C–C)	D_e[b]	D_0[b]
F	$^1A'$	1.323	101.7	$^3A''$	1.321	121.5	11.0	$^1A'$	1.366	1.326	117.4	122.2	61.4	56.7
Cl	$^1A'$	1.706	101.5	$^3A''$	1.659	126.8	3.5	$^1A'$	1.740	1.322	118.8	121.2	70.0	65.3
Br	$^1A'$	1.875	100.1	$^3A''$	1.810	126.9	3.8	$^1A'$	1.902	1.318	118.6	122.5	72.2	67.7
I	$^1A'$	2.076	99.5	$^3A''$	2.006	128.5	2.9	$^1A'$	2.099	1.315	118.8	123.0	75.1	70.5
Ph	^1A	1.439	106.4	^3A	1.389	136.0	−7.0	^1A	1.467	1.325	119.8	114.8	84.6 (77.6)	80.0 (73.2)
3-Py	^1A	1.433	107.1	$^3A''$	1.348	135.4	−8.4	^1A	1.464	1.326	119.6	115.4	85.6 (77.2)	81.0 (72.8)

[a] Bond distances d(R–C) and d(C–C) in Angstroms and angles α(H–C–R) and β(H–C–C) in degrees. Energy differences ΔE_{S-T} between the singlet and the triplet state of the carbene in kcal/mol. Bond dissociation energies of the ketene D_e yielding CO and R_2C in the singlet state in kcal/mol. Bond dissociation energies D_0 including zero-point vibrational correction in kcal/mol. [b] The values in parentheses give the BDE yielding singlet CO and the carbene in the triplet ground state.

and 1.343 Å (Table 1). The theoretically predicted BDEs for the R_2C–CO bond yielding the carbene and CO in the electronic singlet state span a wide range between D_e = 9.4 kcal/mol for R = OH and D_e = 106.6 kcal/mol for R = H. The latter value becomes only slightly lower with D_e = 92.5 kcal/mol when the triplet ground state of CH_2 is considered. Note that the R_2C–CO bond length does not correlate at all with the bond dissociation energy. It has been pointed out in numerous theoretical studies that neither the bond lengths nor the BDE are good indicators for the strength of a chemical bond, which is rather determined by the intrinsic interatomic interactions which can plausibly be interpreted in terms of orbital (covalent) bonding, electrostatic bonding, and Pauli repulsion.[36,37]

A comparison of the bond lengths of R_2C and $R_2C{=}C{=}O$ in the singlet states shows that the R–C distance in the ketene becomes clearly shorter in some cases such as for R = Cl, Br, I while for other substituents it becomes much longer as is the case for R = F, Me, CO_2H, NH_2, NMe_2, OH, OMe. Also, the bond angle R–C–R in the ketenes becomes sometimes wider like in the halogen-, amino-, and alkoxy-substituted systems, while it becomes more acute when R = Me, CO_2H. There is no correlation between the R–C bond alteration and the change in the R–C–R bond angle, which suggests a concerted interplay of different factors that affect the changes in the geometry. We did not further analyze this interesting finding because it is not the topic of the present study. However, we draw attention to the energy data in Table 1 which indicates that carbenes R_2C with R = F, NH_2, NMe_2, OH, OMe which have singlet ground states and a very high S/T gap yield ketenes which have rather small bond dissociation energies.

A particularly interesting system is the diaminocarbene $(Me_2N)_2C$ which is predicted to react with CO yielding the ketene $(Me_2N)_2C{=}C{=}O$. The latter molecule has a C–CO bond energy of D_e = 16.1 kcal/mol which becomes a little smaller when ZPE contributions are considered (D_0 = 13.8 kcal/mol, Table 1). The latter value should be large enough that the ketene $(Me_2N)_2C{=}C{=}O$ could be isolated. This is in agreement with the aforementioned experimental finding that the related diaminocarbene $[(i\text{-}Pr)_2N]_2C$ readily reacts with CO yielding the corresponding ketene which rearranges with a calculated low activation barrier to a β-lactam (Scheme 1g).[16]

Acyclic Carbenes RHC and Ketenes RHC=C=O. We calculated six monosubstituted carbenes RHC with R = F, Cl, Br, I, Ph, 3-Py (3-pyridinyl) and the associated ketenes, which are predicted to be stable molecules. Table 2 shows the most important theoretical data. The halogen-substituted carbenes have singlet electronic ground states and rather small singlet–triplet gaps $\Delta E_{S-T} \leq 11$ kcal/mol, which is in agreement with gas-phase experimental work[38] and with high-level ab initio calculations.[35] The calculations show that the aryl-substituted systems PhHC and 3-PyHC have triplet ground states, which concurs with experimental studies of phenylcarbene.[39] The ketenes RHC=C=O have rather large bond dissociation energies between D_e = 61.4 kcal/mol for R = F and D_e = 85.6 kcal/mol for R = 3-Py. The energy values in Table 2 indicate that the BDE increases when the S/T gap is small or even negative. In the ketenes, the R–C bond lengths are longer and the H–C–R bond angles are always wider than in the carbenes.

The calculated trend of the BDEs for the C–CO bond of the acyclic ketenes $R_2C{=}C{=}O$ and $RHC{=}C{=}O$ yielding the singlet state of the carbenes is in excellent agreement with previous high-level ab initio calculations. The D_e value of H_2C–CO at CCSD(T)/6-31G(d) (BP86/def2-TZVPP values are given in parentheses) is predicted to be 43.8 kcal/mol (45.2 kcal/mol) higher than for FHC–CO, which in turn has a BDE that is 47.3 kcal/mol (46.8 kcal/mol) higher than for F_2C–CO.[47b] The calculated difference between the BDE of H_2C–CO and F_2C–CO is 91.1 kcal/mol (92.0 kcal/mol).

Cyclopentadienyl-Derived Carbenes and Ketenes. Cyclopentadienyl-derived carbenes and their reactions with CO have been the subject of several experimental and theoretical studies.[40] The parent compound cyclopentadienylidene (**Cp1**) has a triplet ground state and reacts readily with CO in low-temperature matrices yielding cyclopentadienylketene.[40a−40e] The tetrachloro- and tetrabromo-substituted systems **Cp3** and **Cp4** and the benzoannelated cyclopentadienylidenes **Cp5** and **Cp6** also give the corresponding ketenes upon reaction with CO in low-temperature matrices, but the electronic ground states of **Cp3**–**Cp6** have not been established.[40f,40g] There are no theoretical studies of **Cp3**–**Cp6** known to us. Tetrafluoroyclopentadienylidene **Cp2** has been the subject of neither experimental nor theoretical work until now.

Table 3 shows the most important calculated results for **Cp1**–**Cp6**. The cyclopentadienylidenes **Cp1**, **Cp3**, **Cp4**, and **Cp5** are predicted to have triplet ground states, while the calculations suggest that **Cp2** and **Cp6** have singlet ground states which are,

Table 3. Geometries and Energies of Cyclopentadienyl-Derived Carbenes and Ketenes (Scheme 2) at BP86/def2-TZVPP[a]

	carbene							ketene					
	singlet			triplet									
	state	d(C1−C2)	α(C2−C1−C5)	state	d(C1−C2)	α(C2−C1−C5)	ΔE_{S-T}	state	d(C1−C2)	α(C2−C1−C5)	d(C=CO)	D_e	D_0[b]
Cp1	^{1}A	1.427	119.5	$^3B_1$	1.428	113.3	−5.6	$^1A_1$	1.462	108.1	1.334	88.7 (83.1)	83.8 (78.5)
Cp2	^{1}A	1.357	103.5	^{3}B	1.404	104.5	0.8	^{1}A′	1.466	106.6	1.332	71.9	68.3
Cp3	^{1}A	1.465	112.5	^{3}B	1.417	113.2	−2.2	$^1A_1$	1.460	107.5	1.337	81.1 (78.9)	76.9 (74.0)
Cp4	^{1}A	1.459	113.2	^{3}B	1.414	113.6	−2.7	$^1A_1$	1.458	107.5	1.339	80.8 (78.1)	76.7 (73.4)
Cp5	^{1}A	1.455	109.7	^{3}A″	1.437	112.5	−8.9	^{1}A′	1.471	107.5	1.331	85.5 (76.6)	81.0 (72.6)
Cp6	^{1}A′	1.459	101.6	^{3}A	1.420	112.4	2.8	^{1}A	1.473	107.6	1.329	72.5	71.7

[a] Bond distances d(C1−C2) in Angstroms and angles α(C2−C1−C5) in degrees. Energy differences ΔE_{S-T} between the singlet and the triplet state of the carbene in kcal/mol. Bond dissociation energies of the ketene D_e yielding CO and R_2C in the singlet state in kcal/mol. Bond dissociation energies D_0 including zero-point vibrational correction in kcal/mol. [b] The values in parentheses give the BDE yielding singlet CO and the carbene in the triplet ground state.

however, only slightly lower in energy than the lowest lying triplet state. The calculated triplet ground state for **Cp1** concurs with experimental findings.[40a−40e] The singlet−triplet gap which is calculated here (5.6 kcal/mol) is in very good agreement with previous values which come from DFT (4.3 kcal/mol)[40a] and ab initio calculations (6.3 kcal/mol).[40e]

The equilibrium geometries of **Cp1**−**Cp6** in the singlet and triplet states exhibit unusual features which deserve to be briefly discussed. Figure 1 shows that the singlet cyclopentadienylidene **Cp1(S)** has a nonplanar geometry with an envelope-shaped five-membered ring. Previous ab initio calculations by Collins et al.[40c] gave a C_{2v} structure for **Cp1(S)**, but this result may be questioned. The authors reported that the wave function which was calculated at the Hartree−Fock level was constrained to C_{2v} symmetry. The geometry optimization of the $^1A_2$ state gave a structure which had large imaginary frequencies for the asymmetric deformation. The authors assigned this to an artifact of the single-determinant wave function, and they write that the true equilibrium geometry of **Cp1(S)** probably has C_{2v} symmetry. The same result was found for the $^3A_2$ triplet state **Cp1(T)**, which was calculated with C_{2v} symmetry constraint. The optimized structure has also imaginary frequencies for the asymmetric deformation, which were considered as artifacts. Our DFT calculations suggest that **Cp1(T)** indeed has a C_{2v} equilibrium geometry, but **Cp1(S)** has a nonplanar geometry (Figure 1).

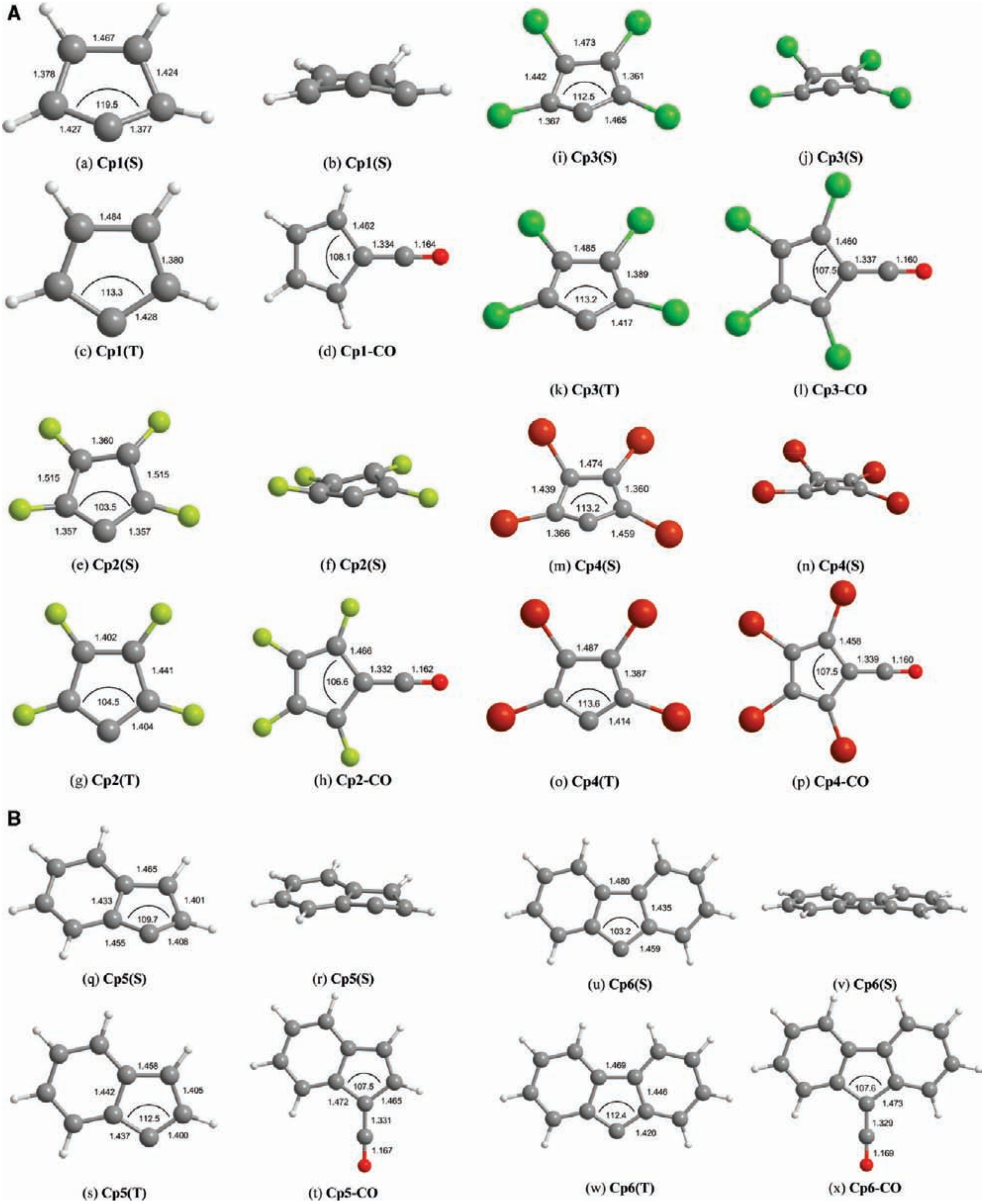
The optimized geometry of the tetrafluorocyclopentadienylidene **Cp2(S)** also has a nonplanar geometry, but the C−C distances in the ring exhibit the pattern of a C_{2v} structure with two long bonds (1.515 Å) and three rather short bonds (1.357−1.360 Å). The C−C bond lengths in **Cp1(S)** vary between 1.377 and 1.467 Å. Note that the C−C bonds of the dicoordinated carbon atom in **Cp2(S)** have the same length of 1.357 Å, while they are widely different in **Cp1(S)** with values of 1.377 and 1.427 Å. The triplet structure of **Cp2(T)** and the other halogen-substituted cyclopentadienylidenes **Cp3(T)** and **Cp4(T)** have C_{2v} symmetry. The singlet species **Cp3(S)** and **Cp4(S)** possess nonplanar puckered geometries where all five C−C bonds have different values (Figure 1). The equilibrium geometries of the benzoannelated cyclopentadienylidenes in the singlet state **Cp5(S)** and **Cp6(S)** possess slightly nonplanar geometries, while the triplet state structures **Cp5(T)** and **Cp6(T)** are planar.

The geometry optimizations of the CO adducts of the cyclopentadienylidenes **Cp1**−**Cp6** all give ketenes which have rather short C−CO bonds and quite large BDEs for dissociation into CO and singlet carbene between D_e = 88.7 kcal/mol (**Cp1**) and 71.9 kcal/mol (**Cp1**). The latter values become slightly smaller for dissociation into the triplet ground states of **Cp1**, **Cp3**, **Cp4**, and **Cp5**, but the BDEs are still rather large. It is interesting to note that the parent carbene **Cp1** has the highest BDE of all cyclopentadienylidenes **Cp1**−**Cp6**. We want to point out that the two systems **Cp2** and **Cp6**, which are calculated with a singlet ground state, clearly have the lowest BDEs.

NHCs and CO Adducts. A particularly interesting class of divalent carbon(II) compounds are the NHCs and related compounds, whose reactivity has been the topic of intensive investigations.[41] The synthesis of a stable ketene which is derived from the adamantly substituted NHC (Scheme 1a)[10] could not be reproduced and was challenged by Dixon et al.[11] The latter authors also carried out DFT calculations of the CO adduct of parent NHC (**NHC1**) using BP86 in conjunction with a DZP quality basis set. They did not find an energy minimum structure of a ketene-type adduct. A geometry optimization of a planar geometry with enforced C_{2v} symmetry gave a ketene-type structure with a short C−CO bond (1.337 Å) which possesses, however, three imaginary frequencies. Following the imaginary mode which corresponds to the out-of-plane motion of the carbonyl carbon atom, Dixon et al. found a weakly bonded complex where the CO molecule is above the NHC ring with a rather long C−CO distance of 3.64 Å. The geometry of the NHC moiety is essentially the same as that of free **NHC1**. The **NHC1**−**CO** complex which was found is only 0.3 kcal/mol more stable than the separated fragments, and it is 18.8 kcal/mol lower in energy than the ketene-type structure.[11]

We also calculated the parent unsaturated **NHC1** as well as the saturated molecule **NHC2** and their CO adducts. The results for the former system differ significantly from the data which were reported by Dixon et al.[11] Therefore, we present the calculated results for these two compounds in more detail.

Figure 2 shows the optimized geometries of **NHC1** and **NHC2** at four different levels of theory. The inclusion of several levels of theory was provoked by the unexpected results for the CO adducts **NHC1**−**CO** and **NHC2**−**CO**, which are also shown in Figure 2. Contrary to the findings which were reported by Dixon et al.,[11] we could locate a ketene structure **NHC1**−**COa** as a minimum on the potential-energy surface. A calculation where we took the planar C_{2v} structure with a short C−CO distance of **NHC1**−**CO** as the starting point for a geometry optimization without symmetry constraints gave eventually a



(a) **Cp1(S)** (b) **Cp1(S)** (i) **Cp3(S)** (j) **Cp3(S)**

(c) **Cp1(T)** (d) **Cp1-CO** (k) **Cp3(T)** (l) **Cp3-CO**

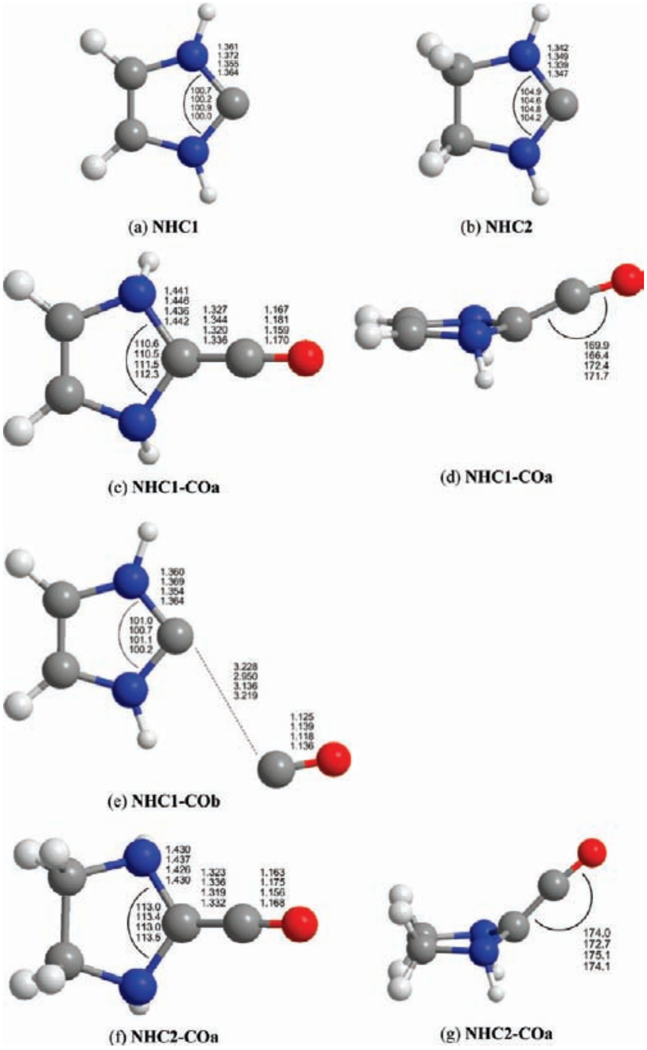
(e) **Cp2(S)** (f) **Cp2(S)** (m) **Cp4(S)** (n) **Cp4(S)**

(g) **Cp2(T)** (h) **Cp2-CO** (o) **Cp4(T)** (p) **Cp4-CO**

(q) **Cp5(S)** (r) **Cp5(S)** (u) **Cp6(S)** (v) **Cp6(S)**

(s) **Cp5(T)** (t) **Cp5-CO** (w) **Cp6(T)** (x) **Cp6-CO**

Figure 1. Optimized geometries of (a) **Cp1(S)** (top view), (b) **Cp1(S)** (side view), (c) **Cp1(T)** (top view), (d) **Cp1−CO**, (e) **Cp2(S)** (top view), (f) **Cp2(S)** (side view), (g) **Cp2(T)** (top view), (h) **Cp2−CO**, (i) **Cp3(S)** (top view), (j) **Cp3(S)** (side view), (k) **Cp3(T)** (top view), (l) **Cp3−CO**, (m) **Cp4(S)** (top view), (n) **Cp4(S)** (side view), (o) **Cp4(T)** (top view), (p) **Cp4−CO**, (q) **Cp5(S)** (top view), (r) **Cp5(S)** (side view), (s) **Cp5(T)** (top view), (t) **Cp5−CO**, (u) **Cp6(S)** (top view), (v) **Cp6(S)** (side view), (w) **Cp6(T)** (top view), and (x) **Cp6−CO**. Calculated bond lengths in Angstroms and bond angles in degrees at BP86/def2-TZVPP.



(a) **NHC1** (b) **NHC2**

(c) **NHC1-COa** (d) **NHC1-COa**

(e) **NHC1-COb**

(f) **NHC2-COa** (g) **NHC2-COa**

Figure 2. Optimized geometries of (a) **NHC1**, (b) **NHC2**, (c) **NHC1−COa** (top view), (d) **NHC1−COa** (side view), (e) **NHC1−COb**, (f) **NHC2−COa** (top view), and (g) **NHC2−COa** (side view). Calculated bond lengths in Angstroms and bond angles in degrees at four levels of theory from top to bottom: B3LYP/def2-TZVPP, BP86/def2-TZVPP, M05-2x/def2-TZVPP, and MP2/def2-TZVPP.

structure where the nitrogen atoms have a strongly pyramidal coordination but the C−CO distance remains very short. Figure 2 shows that the calculated C−CO bond length of **NHC1−COa** is predicted to be between 1.320 (M05-2X/def2-TZVPP) and 1.344 Å (BP86/def2-TZVPP). Calculation of the vibrational frequencies shows that **NHC1−COa** is a genuine minimum on the PES. Since the ketene structure is found to be an energy minimum using ab initio (MP2/def2-TZVPP) calculations as well as three different DFT methods, we think that the surprising finding of the ketene structure **NHC1−COa** is not an artifact of the theoretical methods. Note that the C═C═O bonds are slightly bent out of the ring plane toward the other side of the hydrogen atoms at nitrogen (Figure 2d). It is also interesting that the C═C═O moiety is not linear but has a bond angle of ∼170°. The hydrogen atoms at nitrogen are strongly tilted to the opposite side of the five-membered ring as the C═C═O moiety, which indicates that the conjugation between the nitrogen lone-pair electrons and the former double bond is diminished. The dihedral angle H−N−C−CO in **NHC1−COa** is 86.2° (BP86/def2-TZVPP).

We searched for a weakly bonded van-der-Waals complex of **NHC1−CO**. Structure **NHC1−COb** was finally located as an energy minimum form which however looks very different from the vdW complex that was reported by Dixon et al.[11] Figure 2e shows that **NHC1−COb** has a planar (C_s) structure where the CO molecule is far away from the carbene carbon atom. The calculated C−CO distances are between 3.228 (B3LYP/def2-TZVPP) and 2.950 Å (BP86/def2-TZVPP), which is even longer than the distance which was reported for the vdW complex by Dixon et al.[11] The main difference between the latter species and **NHC1−COb** is the location of CO. We could not locate a weakly bonded vdW complex as the energy minimum form where the CO moiety is above the carbene carbon atom like the one which was reported by Dixon et al. The calculated energies show that the weakly bonded complex **NHC1−COb** is between 15.8 (BP86/def2-TZVPP) and 25.3 kcal/mol (MP2/def2-TZVPP) lower in energy than the ketene structure **NHC1−COa**. Thus, the latter structure is only a local minimum on the PES. The dissociation of CO from **NHC1−COa** is calculated to be exothermic between D_0 = −15.0 kcal/mol (BP86/def2-TZVPP) and −27.7 kcal/mol (B3LYP/def2-TZVPP). It is therefore unlikely that **NHC1−COa** can be observed experimentally. Thus, although the calculated structures **NHC1−COa** and **NHC1−COb** which we found as products of the addition of CO to **NHC1** are different from the results which were given by Dixon et al.,[11] our results agree with their conclusion that the synthesis of a stable ketene by reacting *N*-adamantyl-substituted NHC with CO that was published by Lyashchuk and Skrypnik[10] is questionable.

Figure 2f and 2g shows also the optimized geometry of the ketene structure **NHC2−COa** which was found as an energy minimum for the CO adduct of the saturated **NHC2**. The structural features of **NHC2−COa** are similar to the equilibrium geometry of **NHC1−COa**. The nitrogen atoms have a pyramidal environment, and the slightly bent C═C═O moiety is tilted to the opposite side of the ring plane as the N−H groups. The dihedral angle H−N−C−CO in **NHC2−COa** (114.8° at BP86/def2-TZVPP) is somewhat larger than in **NHC1−COa**. Unlike **NHC1−COb**, we could not locate an energy minimum structure for a weakly bonded complex **NHC2−COb**. Geometry optimizations using different starting structures of **NHC2−CO** all lead to the ketene form **NHC2−COa**. This may be explained with the relative energy of the complex **NHC2−COa** and the fragments **NHC2** and **CO**. The latter complex is 3.2 kcal/mol (BP86/def2-TZVPP) lower in energy than **NHC2** + **CO**. Unlike the ketene form of the unsaturated complex **NHC1−COa**, the saturated homologue **NHC1−CO** is stable toward dissociation, although the BDE is very small. Nevertheless, the calculated results for **NHC2−COa** suggest that suitable alteration of the electronic structure may yield NHCs which give stable ketene adducts.

Table 4 summarizes the most important energies and geometrical data for **NHC1** and **NHC2** and the related ketenes **NHC1−CO** and **NHC2−COa**. The NHCs have very large S/T gaps which agree with the very small or even negative BDEs. Table 4 also shows the calculated results for alkyl amino carbenes, diamino carbenes, and ferrocene-based carbene, together with the associated ketenes which are discussed below.

Alkyl Amino Carbenes and Ketenes. Isolation of acyclic[42,43] and cyclic[44] alkyl amino carbenes (AACs) by Bertrand and coworkers opened the door to a new facet of carbene chemistry

Table 4. Geometries and Energies of Amino and Amido Carbenes and Ketenes (Scheme 2) at BP86/def2-TZVPP[a]

	carbene							ketene					
	singlet			triplet									
no.[b]	state	d(N−C)	α(N−C−R)	state	d(N−C)	α(N−C−R)	ΔE_{S-T}	state	d(N−C)	α(N−C−R)	d(C═CO)	D_e	D_0
NHC1	$^1A'$	1.372	100.2	^3A	1.405	108.5	82.8	^1A	1.446	110.5	1.344	−13.8	−15.0
NHC2	^1A	1.349	104.6	^3A	1.400	115.9	69.0	$^1A'$	1.437	113.4	1.336	3.2	0.2
AAC1	^1A	1.312	120.6	^3A	1.374	127.0	28.1	^1A	1.447	121.0	1.329	37.7	34.7
AAC2	^1A	1.304	128.5	^3A	1.368	131.4	22.4	^1A	1.437	134.8	1.333	39.3	36.3
CAAC	^1A	1.312	101.7	^3A	1.388	114.9	48.8	^1A	1.449	112.7	1.323	25.9	22.7
DIADC1	^1A	1.349	112.6	^3A	1.369	126.3	45.4	^1A	1.418	123.4	1.339	19.7	16.9
DIADC2	$^1A'$	1.364	112.8	$^3A'$	1.356	119.9	46.6	$^1A'$	1.418	117.3	1.344	17.2	15.0
DIADC3	$^1A'$	1.362	112.3	$^3A'$	1.356	119.2	46.6	$^1A'$	1.413	116.4	1.344	15.8	13.8
FeNHC	^1A	1.359	117.7	^3A	1.396	122.8	54.2	^1A	1.433	124.5	1.335	16.0	13.6

[a] Bond distances d(N−C) and d(C═CO) in Angstroms and angles α(N−C-R) in degrees. Energy differences ΔE_{S-T} between the singlet and the triplet state of the carbene in kcal/mol. Bond dissociation energies of the ketene D_e yielding CO and R_2C in the singlet state in kcal/mol. Bond dissociation energies D_0 including zero-point vibrational correction in kcal/mol. [b] See Scheme 2 for notation.

because the reactivity of the compounds was found to be clearly different from diamino carbenes.[45] In 2006, Bertrand[43] reported that, in marked contrast to NHCs, AACs readily react with CO to afford stable alkyl amino ketenes which could be isolated and structurally characterized by X-ray structure analysis (Scheme 1c and 1d). We therefore calculated the acyclic carbenes **AAC1** and **AAC2** and the cyclic system **CAAC** as well as the related ketenes **AAC1−CO**, **AAC2−CO**, and **CAAC−CO**. The optimized geometries of the six compounds and the most important bond lengths and angles are shown in Figure 3.

A comparison of the calculated interatomic distances and angles with the experimental values of substituted analogues of **AAC2**, **AAC2−CO**, **CAAC**, and **CAAC−CO** shows a good agreement between the theoretical and the observed data. Note that **CAAC** possesses a planar amino group, while **CAAC−CO** exhibits a strongly pyramidal environment surrounding the nitrogen atom. The bond dissociation energies for breaking the C−CO bonds of the acyclic systems **AAC1−CO** (37.7 kcal/mol) and **AAC2−CO** (39.3 kcal/mol) are larger than for the cyclic compound **CAAC−CO** (25.9 kcal/mol), and they are significantly stronger than for **NHC1−CO** and **NHC2−COa**. The theoretically predicted larger bond energies for the alkyl amino systems compared with the ketenes derived from NHCs concur with the significantly smaller singlet−triplet gaps of the former systems (Table 4). They also agree with the finding that substituted alkyl amino carbenes afford stable ketenes,[43] while ketenes which are derived from NHCs could not be isolated except for the ferrocene-based system which is discussed below.[16]

Diamido Carbenes and Ketenes. The reluctance of imidazole-derived NHCs to bind CO affording stable ketenes has been a challenge for chemists who thought about a modification of the electronic structure of diaminocarbenes which makes them amenable for CO addition. A successful approach was recently reported by Bielawski,[14] who synthesized a cyclic diamido carbene (DIADC) which readily reacts with CO yielding a stable ketene which could be isolated and structurally characterized by X-ray structure analysis (Scheme 1e). The authors argued that the DIADC is more electrophilic than Arduengo type NHCs because the donation of the nitrogen electron lone-pair to the carbene center in the former compound is weaker due to conjugation with the carbonyl group.

We calculated the acylic diamido carbene **DIADC1** and the cyclic analogues **DIADC2** and **DIADC3**, which are model compounds for the experimental compound that was reported by Bielawski.[14] Figure 4 shows the optimized geometries and the most important bond lengths and angles of the three diamido carbenes and the related ketenes **DIADC1−CO**, **DIADC2−CO**, and **DIADC3−CO**. The figure of the latter ketene shows also the experimental values for the bond lengths and angles of the real compound which are in good agreement with the data for the model system. Note that the amido substituents in planar **DIADC1** are in π conjugation with the carbene carbon atom, which leads to rather short N−C−N bonds (1.349 Å). By contrast, the amido groups in the ketene **DIADC1−CO** are rotated by ~90° out of the molecular plane, and they are orthogonal to the $N_2C{=}C{=}O$ fragment. This effectively eliminates the π conjugation between the amido groups and the ketene moiety, which explains why the N−C−N bonds become significantly longer (1.418 Å). A similar effect can be observed for the optimized geometries of the cyclic diamido carbenes **DIADC2** and **DIADC3**, which have a planar HN−C−NH fragment, while the N−H and C−CO bonds in the ketenes **DIADC2−CO** and **DIADC3−CO** are rotated in opposite directions out of the six-membered ring. The calculated torsion angle H−N−C═CO is 70.6° in **DIADC2−CO** and 58.0° in **DIADC3−CO**. The BDEs of the three diamido ketenes are between D_e = 19.7 kcal/mol (**DIADC1−CO**) and 15.8 kcal/mol (**DIADC3−CO**), which is less than the BDEs of the alkyl amino ketenes **AAC1−CO**, **AAC2−CO**, and **CAAC−CO**. The weaker C−CO bonds of the former ketenes compared with the values for the latter ketenes correlate with the singlet−triplet gap of the diamido carbenes, which are larger than those of the acylic alkyl amino carbenes, but not with the ΔE_{S-T} value for **CAAC** (Table 4).

[3]Ferrocenophane-Type NHC and CO Adduct. We optimized the geometry of the [3]ferrocenophane-type NHC **FeNHC** (Figure 5), which is a model for the experimental compound that possesses bulky neopentyl groups at nitrogen.[17] The calculated structure of **FeNHC** is in very good agreement with the results of the X-ray structure analysis. Figure 5 also shows the optimized geometry of the related ketene **FeNHC−CO**, which has a rather short C−CO bond of 1.335 Å. The N−C−N bonds in the ketene (1.433 Å) are significantly longer than in the parent carbene (1.354 Å).

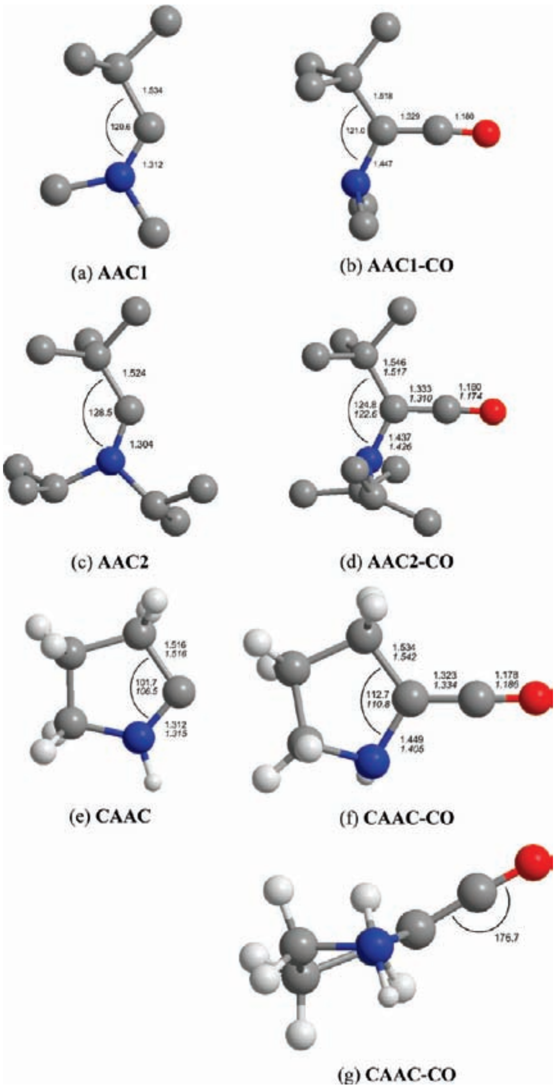


Figure 3. Optimized geometries of (a) **AAC1**, (b) **AAC1−CO**, (c) **AAC2**, (d) **AAC2−CO**, (e) **CAAC**, (f) **CAAC−CO** (top view), and (g) **CAAC−CO** (side view). In (a−d), hydrogen atoms have been omitted for clarity. Calculated bond lengths in Angstroms and bond angles in degrees at BP86/def2-TZVPP. Experimental values for substituted homologues are shown in italics (ref 43).

The C=C=O moiety is strongly tilted out of the N−C−N plane, and so are the hydrogen atoms at nitrogen, which are tilted toward the other side of the plane. The torsion angle H−N−C−CO is 109.7°, which means that the nitrogen lone pair is not in conjugation with the C=C=O π bond. This becomes obvious from Figure 5c.

Table 4 shows that the theoretically predicted bond energy of **FeNHC−CO** is D_e = 16.0 kcal/mol (D_0 = 13.6 kcal/mol), which is nearly the same as the BDE of the acyclic diaminoketene $(Me_2N)_2C-CO$ (D_e = 16.1 kcal/mol; D_0 = 13.8 kcal/mol). The formation of the ketene structure **FeNHC−CO** with bulky neopentyl groups at nitrogen has been inferred from the calculated reaction profile for the reaction of the carbene with CO where the ketene reacts further with a second carbene yielding the final product.[16] The S/T gap of the former parent carbene **FeNHC** is 54.2 kcal/mol, which is somewhat larger than the S/T gap of $(Me_2N)_2C$ (42.1 kcal/mol). The comparison of the S/T gaps with the BDEs shows that the R_2C-CO bond strength in ketenes is also influenced by other factors than the singlet−triplet gap of the carbene R_2C. This is discussed below.

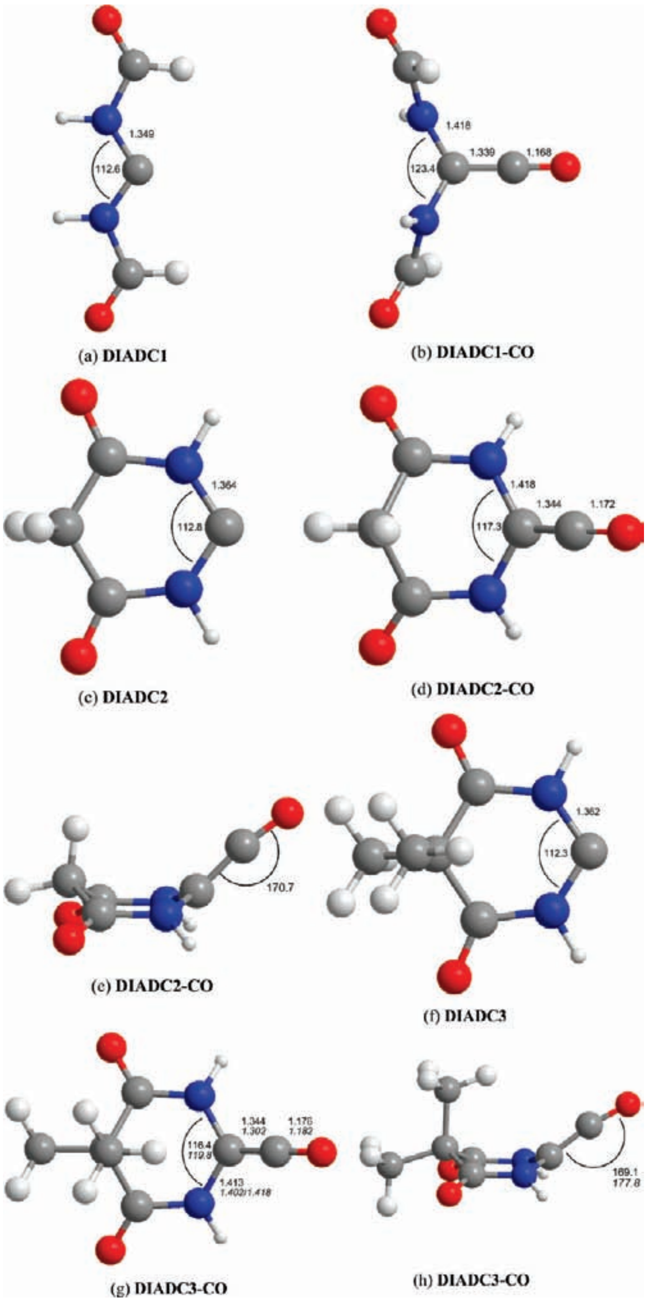
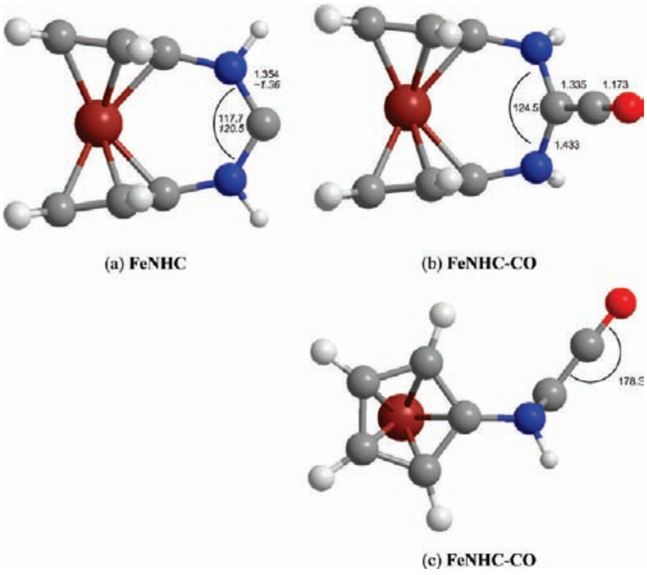


Figure 4. Optimized geometries of (a) **DIADC1**, (b) **DIADC1−CO**, (c) **DIADC2**, (d) **DIADC2−CO** (top view), (e) **DIADC2−CO** (side view), (f) **DIADC3**, (g) **DIADC3−CO** (top view), and (h) **DIADC3−CO** (side view). Calculated bond lengths in Angstroms and bond angles in degrees at BP86/def2-TZVPP. Experimental values for a substituted homologue of **DIADC3−CO** are shown in italics (ref 14).

■ DISCUSSION

The theoretical results presented in Tables 1−4 show that the investigated ketenes span a wide range of bond dissociation energies for breaking the RR′C−CO bond yielding a singlet carbene and CO. The calculated D_e values are between 106.6



(a) **FeNHC**

(b) **FeNHC-CO**

(c) **FeNHC-CO**

Figure 5. Optimized geometries of (a) **FeNHC**, (b) **FeNHC—CO** (top view), and (c) **FeNHC—CO** (side view). Calculated bond lengths in Angstroms and bond angles in degrees at BP86/def2-TZVPP. Experimental values for a substituted homologue of **FeNHC** are shown in italics (ref 17b).

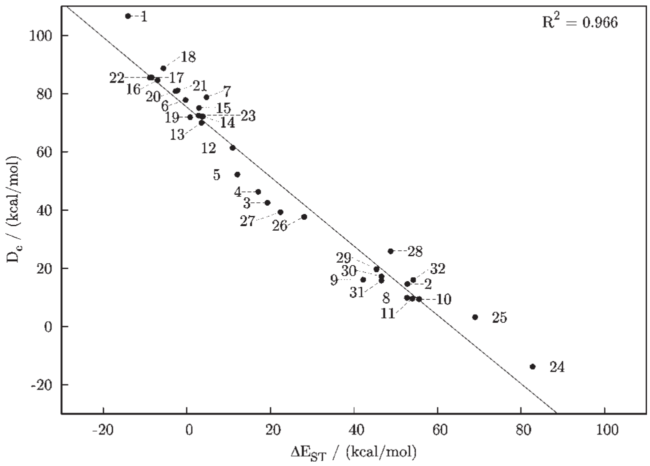


Figure 6. Correlation between the calculated singlet—triplet gap of the carbenes 1—32 and the BDE of the respective ketene at BP86/def2-TZVPP. For the numbering of the carbenes see Scheme 2.

kcal/mol for H_2C—CO and −13.8 kcal/mol for **NHC1—CO**. Figure 6 shows the correlation diagram between the singlet—triplet gaps of the carbenes and the BDEs of the respective ketenes. The correlation between the calculated values for ΔE_{S-T} and D_e is remarkably good considering the fact that the carbenes comprise very different types of compounds. The correlation coefficient of 0.966 suggests that the dominant factor determining the strength of the chemical bond RR′C—CO in a ketene is the singlet—triplet gap of the carbene RR′C.

A closer examination of the entries in Figure 6 reveals that factors other than the singlet—triplet gap also influence the RR′C—CO bond strength in the ketenes. This should be expected because the carbenes in the triplet states have different electronic structures, and thus, they have different interactions with (triplet) CO. It is actually surprising that the latter factor apparently is less important than the S/T gap of the carbene. In order to analyze the RR′C—CO bond in the ketene in more detail, we carried out EDA calculations of selected ketenes using the carbene RR′C and CO in the triplet states as interacting fragments. The results are shown in Table 5.

The calculated data of the EDA give detailed insights into the nature of the RR′C—CO bonds. The BDE of H_2C—CO (D_e = 106.6 kcal/mol) is 92.0 kcal/mol higher than the BDE of F_2C—CO (D_e = 14.6 kcal/mol). The difference between the singlet—triplet gaps of H_2C (ΔE_{S-T} = −14.1 kcal/mol) and F_2C (ΔE_{S-T} = 52.8 kcal/mol) is only 66.9 kcal/mol, but the interaction energy between the triplet fragments in H_2C—CO (ΔE_{int} = −232.3 kcal/mol) is 25.6 kcal/mol higher than F_2C—CO (ΔE_{int} = −206.7 kcal/mol). The sum of the $\Delta\Delta E_{S-T}$ and $\Delta\Delta E_{int}$ values is 92.5 kcal/mol, which comes close to the BDE. Note that the larger interaction energy in the former ketene comes mainly from the weaker Pauli repulsion (ΔE_{Pauli} = 231.3 kcal/mol), which is 16.6 kcal/mol smaller than in the latter ketene (ΔE_{Pauli} = 247.9 kcal/mol).

The significantly weaker F_2C—CO bond compared with H_2C—CO is in agreement with experimental observations[46] and with earlier ab initio calculations.[47] Difluoroketene has been observed in gas-phase reactions via neutralization—reionization mass spectrometry which showed that F_2CCO is a metastable species in the microsecond time frame with respect to CO loss.[46b] It has also been prepared in low-temperature matrix experiments through reaction of difluorovinylidene $F_2C{=}C$ with CO_2.[46a] The resulting difluoroketene could become characterized via IR spectroscopy in combination with isotope labeling and DFT calculations at the B3LYP/6-311G(d,p) level which predict a BDE for the F_2C—CO bond of 5.7 kcal/mol. More recent ab initio calculations at CCSD(T)/6-31G(df,p) suggest that the dissociation of F_2CCO yielding F_2C and CO is nearly thermoneutral.[47b]

Figure 6 shows that the correlation of the D_e values of $(NMe_2)_2C$—CO (9), **DIADC1—CO** (29), and **CAAC—CO** (28) with ΔE_{S-T} is in the opposite direction of the overall correlation of the BDE with the singlet—triplet gap. Table 5 gives the respective numbers, which indicate that $(NMe_2)_2C$—CO has the smallest ΔE_{S-T} value of 42.1 kcal/mol and the smallest BDE with D_e = 16.1 kcal/mol, while **CAAC—CO** possesses the largest ΔE_{S-T} value (48.8 kcal/mol) and also the largest BDE (D_e = 25.9 kcal/mol) in the series. The EDA results show that the trend of the interaction energies ΔE_{int} of the three ketenes compensates for the trend of the ΔE_{S-T} values. The largest interaction energy is calculated for **CAAC—CO** (ΔE_{int} = −216.1 kcal/mol), while the smallest value is computed for $(NMe_2)_2C$—CO (ΔE_{int} = −197.9 kcal/mol). We want to point out that the trend of the attractive interaction energy is *not* the same as the trend of the attractive terms ΔE_{orb} and ΔE_{elstat}. **CAAC—CO** has the largest overall attraction (ΔE_{int} = −216.1 kcal/mol) of the three ketenes, although the orbital interactions (ΔE_{orb} = −338.9 kcal/mol) and the electrostatic attraction (ΔE_{elstat} = −188.7 kcal/mol) are weaker than in $(NMe_2)_2C$—CO and **DIADC1—CO** (Table 5). The strongest overall attraction in the former ketene is a result of the Pauli repulsion (ΔE_{Pauli} = 311.5 kcal/mol), which is clearly weaker than in the latter two species.

The EDA results for the cyclopentadienylketenes **Cp1—CO** and **Cp2—CO** suggest that the relaxation energy of the carbene fragments may also have a large effect on the BDE and thus on the correlation between the D_e values and ΔE_{S-T}. Table 5 shows that **Cp1—CO** has a significantly larger BDE (D_e = 88.7 kcal/mol) than **Cp2—CO** (D_e = 71.9 kcal/mol), but the carbene—CO

Table 5. Results of the Energy Decomposition Analysis of the RR′C−CO Bond of Selected Ketenes at BP86/TZ2P[a]

ketene	No[b]	D_e[c]	ΔE_{S-T}[d]	ΔE_{int}	ΔE_{Pauli}	ΔE_{elstat}[e]	ΔE_{orb}[e]
H_2C-CO	1	106.6	−14.1	−232.3	231.3	−152.9 (32.9%)	−310.9 (67.1%)
F_2C-CO	2	14.6	52.8	−206.7	247.9	−142.2 (31.3%)	−312.4 (68.7%)
$(NMe_2)_2C-CO$	9	16.1	42.1	−197.9	361.2	−215.1 (38.5%)	−343.9 (61.5%)
Cp1−CO	18	88.7	−5.6	−224.9	273.4	−166.8 (33.5%)	−331.4 (66.5%)
Cp2−CO	19	71.9	0.8	−223.5	242.2	−144.5 (31.0%)	−321.1 (69.0%)
NHC1−CO	24	−13.8	82.8	−210.9	302.9	−193.2 (37.6%)	−320.6 (62.4%)
NHC2−CO	25	3.2	69.0	−215.4	309.4	−182.2 (34.7%)	−342.6 (65.3%)
CAAC−CO	28	25.9	48.8	−216.1	311.5	−188.7 (35.8%)	−338.9 (64.2%)
DIADC1−CO	29	19.7	45.4	−209.9	327.0	−191.7 (35.7%)	−345.2 (64.3%)
FeNHC−CO	32	16.0	54.2	−212.5	362.3	−211.2 (36.7%)	−363.6 (63.3%)

[a] The interacting fragments are the carbene and CO in the lowest lying electronic triplet state. All energy values in kcal/mol. [b] See Scheme 2 for the numbering. [c] Bond dissociation energies yielding the carbene and CO in the electronic singlet state. [d] Singlet−triplet gaps were calculated at the BP86/def2-TZVPP level of theory. [e] The numbers in parentheses give the percentage contributions to the total attractive interaction ΔE_{int}.

interaction energy in the former ketene (ΔE_{int} = −224.9 kcal/mol) is about the same as in the latter compound (ΔE_{int} = −223.5 kcal/mol). The difference between the singlet−triplet gaps of **Cp1−CO** (ΔE_{S-T} = −5.6 kcal/mol) and **Cp2−CO** (ΔE_{S-T} = 0.8 kcal/mol) is 6.4 kcal/mol, which means that the relaxation of the fragments contributes ~11 kcal/mol to the difference between the BDEs.

The EDA results for the NHC-derived ketenes **NHC1−CO** and **NHC2−CO** underscore the crucial influence of the S/T gap of the carbene on the C−CO bond strength. The intrinsic interaction energies ΔE_{int} between the fragments carbene and CO in **NHC1−CO** (ΔE_{int} = −210.9 kcal/mol) and **NHC2−CO** (ΔE_{int} = −215.4 kcal/mol), which have very low or even negative BDEs, have a similar strength as in H_2C-CO (ΔE_{int} = −232.3 kcal/mol) and F_2C-CO (ΔE_{int} = −206.7 kcal/mol), but the BDE of the latter compounds is much higher (Table 5). The BDE of **NHC2−CO** (D_e = 3.2 kcal/mol) is 17.7 kcal/mol higher than that of **NHC1−CO** (D_e = −210.9 kcal/mol), which comes mainly from the difference of 13.8 kcal/mol between the singlet−triplet gaps of **NHC1−CO** (ΔE_{S-T} = 82.8 kcal/mol) and **NHC2−CO** (ΔE_{S-T} = 69.0 kcal/mol), while the difference between the interaction energies is only $\Delta\Delta E_{int}$ = 4.5 kcal/mol.

We finally also analyzed the C−CO bond in the [3]ferrocenophane-type ketene with the EDA method. Table 5 shows that the BDE of **FeNHC−CO** (D_e = 16.0 kcal/mol) is nearly the same as the BDE of $(NMe_2)_2C-CO$ (D_e = 16.1 kcal/mol), although the S/T gap of the former compound (ΔE_{S-T} = 54.2 kcal/mol) is clearly larger than that of the latter molecule (ΔE_{S-T} = 42.1 kcal/mol). The difference of 12.1 kcal/mol between the S/T gaps is compensated by the intrinsic interaction energies, which is 14.6 kcal/mol stronger in **FeNHC−CO** (ΔE_{int} = −212.5 kcal/mol) than in $(NMe_2)_2C-CO$ (ΔE_{int} = −197.9 kcal/mol). This demonstrates that the strength of the carbene−CO interaction energy in the ketene may sometimes override the trend in the bond strength which is suggested by the singlet−triplet gaps. Note that the ΔE_{S-T} values which are given in Table 5 span a range of 96.9 kcal/mol between the largest (82.8 kcal/mol) and the smallest (−14.1 kcal/mol), while the ΔE_{int} values cover a range of only 48.9 kcal/mol.

SUMMARY AND OUTLOOK

The results of this paper can be summarized as follows. The calculated singlet−triplet gap of the 32 carbenes RR′C exhibits a very good correlation with the bond dissociation energy of the associated ketenes RR′C=C=O. An energy decomposition analysis of the RR′C−CO bond using the triplet states of the carbene and CO as interacting fragments supports the assignment of ΔE_{S-T} as the dominant factor for the BDE, but it also shows that the specific interactions of the carbene may sometimes compensate the S/T gap. The trend of the interaction energies ΔE_{int} is mainly determined by the Pauli repulsion between the carbene and CO. The stability of amino-substituted ketenes strongly depends on the destabilizing conjugation between the nitrogen lone-pair orbital and the ketene double bonds. There is a ketene structure of the unsaturated **NHC1** parent compound with CO as a local energy minimum on the potential-energy surface. However, the compound **NHC1−CO** is thermodynamically unstable toward dissociation. The saturated homologue **NHC2−CO** has only a very small dissociation energy of D_e = 3.2 kcal/mol. The [3]ferrocenophane-type compound **FeNHC−CO** has a BDE of D_e = 16.0 kcal/mol. It has been suggested that reaction of a bulky derivative of **FeNHC** with CO yields a ketene structure **FeNHC−CO** which reacts further and could not directly be observed.[16]

The search for carbenes which add CO yielding stable ketenes should focus on species which have a sufficiently low S/T gap. A similar conclusion has recently been made in a combined experimental/theoretical study of the reactivity of isocyanides to NHCs by Hudnall et al.[14c] The results of the present paper may be used as a guideline to how this can be achieved. For example, the finding that the Arduengo-type NHCs do yield (albeit energetically unstable) ketene-type structures **NHC1−CO** and **NHC1−CO** indicates which structural modification of NHCs are required to achieve such goal. The optimized structures **NHC1−CO** and **NHC1−CO** exhibit strongly pyramidal coordinated nitrogen atoms. Any skeletal or ligand variation which supports a pyramidal coordination at nitrogen should enhance the chances for the synthesis of an NHC-ketene. We draw attention to a recent paper by us where we calculated the activation barriers and reaction energies for addition of single and multiple bonds to P-heterocyclic carbenes (PHCs).[48] The reactions are predicted to be kinetically and thermodynamically much more favorable than for addition to NHCs. This was explained in terms of the significantly smaller S/T gaps of the PHCs than those of NHCs which comes from the intrinsic influence of P versus N and from the fact that the equilibrium geometries of the PHCs have strongly pyramidal coordinated P atoms. The nonplanar surrounding at phosphorus weakens the charge donation from the lone-pair orbital at P to the formally empty p(π) AO at the carbene carbon atom. The latter effect lowers the stability of the PHCs, which is the reason that until today only one PHC has been synthesized.[49] It is a challenge for experiment to design heterocyclic carbenes where the S/T gap becomes small enough to make stable ketenes viable while they are still large enough that the carbenes can be isolated.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Cartesian coordinates (in Angstroms) and total energies of all compounds discussed in the text; complete ref 23. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Tidwell, T. T. *Ketenes*, 2nd ed.; Wiley: New York, 2006. (b) Tidwell, T. T. *Angew. Chem., Int. Ed.* **2005**, *44*, 5778.

(2) Staudinger, H. *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 1735.

(3) (a) Staudinger, H.; Kupfer, O. *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 1638. (b) Maier, G.; Rohr, C. *Liebigs Ann.* **1996**, 307. (c) Stevens, H. C.; Reich, D. A.; Brandt, D. R.; Fountain, K. R.; Gaughan, E. J. *J. Am. Chem. Soc.* **1965**, *87*, 5257. (d) Brady, W. T.; Liddell, H. G.; Vaughn, W. L. *J. Org. Chem.* **1966**, *31*, 626. (e) Ghosez, L.; Montaigne, R.; Mollet, P. *Tetrahedron Lett.* **1966**, 135.

(4) (a) Sheehan, J. C.; Ryan, J. J. *J. Am. Chem. Soc.* **1951**, *73*, 1204. (b) Sheehan, J. C.; Ryan, J. J. *J. Am. Chem. Soc.* **1951**, *73*, 4367. (c) Sheehan, J. C.; Corey, E. J. *Org. React.* **1957**, *9*, 388.(d) Palomo, C.; Aizpurua, J. M. *Science of Synthesis (Houben-Weyl)*; Bellus, D., Danheiser, R., Eds.; Thieme: Stuttgart, 2006; Vol. 23.6. (e) Reichen, W. *Chem. Rev.* **1978**, *78*, 569.

(5) (a) Sheehan, J. C.; Buhle, E. L.; Corey, E. J.; Laubach, G. D.; Ryan, J. J. *J. Am. Chem. Soc.* **1950**, *72*, 3829. (b) Sheehan, J. C.; Corey, E. J. *J. Am. Chem. Soc.* **1951**, *73*, 4756.(c) Sheehan, J. C. *The Enchanted Ring*; MIT Press: Cambridge, 1982.

(6) Winter, S.; Pracejus, H. *Chem. Ber.* **1966**, *99*, 151.

(7) (a) Visser, P.; Zuhse, R.; Wong, M. W.; Wentrup, C. *J. Am. Chem. Soc.* **1996**, *118*, 1259. (b) Ammann, J. R.; Subramanian, R.; Sheridan, R. S. *J. Am. Chem. Soc.* **1992**, *114*, 7592. (c) Hayes, R. A.; Hess, T. C.; McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1983**, *105*, 7786. (d) Sander, W.; Müller, W.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 572. (e) Sander, W.; Hübert, R.; Kraka, E.; Gräfenstein, J.; Cremer, D. *Chem.—Eur. J.* **2000**, *6*, 4567. (f) Sander, W. W. *J. Org. Chem.* **1988**, *53*, 121. (g) Qiao, G. G.; Wong, C.; Wentrup, M. W. *J. Org. Chem.* **1996**, *61*, 8125. (h) Mal'tsev, A. K.; Zuev, P. S.; Nefedov, O. M. *Russ. Chem. Bull.* **1985**, *34*, 876.

(8) Igau, A.; Grutzmacher, H.; Baceiredo, A.; Bertrand, G. *J. Am. Chem. Soc.* **1988**, *110*, 6463.

(9) Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361.

(10) Lyashchuk, S. N.; Skrypnik, Y. G. *Tetrahedron Lett.* **1994**, *35*, 5271.

(11) Dixon, D. A.; Arduengo, A. J; Dobbs, K. D.; Khasnis, D. V. *Tetrahedron Lett.* **1995**, *36*, 645.

(12) Denk, M. K.; Rodezno, J. M.; Gupta, S.; Lough, A. J. *J. Organomet. Chem.* **2001**, *617*−*618*, 242.

(13) Frey, G. D.; Lavallo, V.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *Science* **2007**, *316*, 439.

(14) (a) Hudnall, T. W.; Bielawski, C. W. *J. Am. Chem. Soc.* **2009**, *131*, 16039. (b) Rosen, E. L.; Varnado, C. D., Jr.; Tennyson, A. G.; Khramov, D. M.; Kamplain, J. W.; Sung, D. H.; Cresswell, P. T.; Lynch, V. M.; Bielawski, C. W. *Organometallics* **2009**, *28*, 6695. (c) Hudnall, T. W.; Moorhead, E. J.; Gusev, D. G.; Bielawski, C. W. *J. Org. Chem.* **2010**, *75*, 2763. (d) Hudnall, T. W.; Moerdyk, J. P.; Bielawski, C. W. *Chem. Commun.* **2010**, *46*, 4288. (e) Hudnall, T. W.; Tennyson, A. G.; Bielawski, C. W. *Organometallics* **2010**, *29*, 4569.

(15) César, V.; Lugan, N.; Lavigne, G. *Eur. J. Inorg. Chem.* **2010**, 361.

(16) Siemeling, U.; Färber, C.; Bruhn, C.; Leibold, M.; Selent, D.; Baumann, W.; von Hopffgarten, M.; Goedecke, C.; Frenking, G. *Chem. Sci.* **2010**, *1*, 697.

(17) (a) Siemeling, U.; Färber, C.; Leibold, M.; Bruhn., C; Mücke, P.; Winter, R. F.; Sarkar, B.; von Hopffgarten, M.; Frenking, G. *Eur. J. Inorg. Chem.* **2009**, 4607. (b) Siemeling, U.; Färber, C.; Bruhn, C. *Chem. Commun.* **2009**, 98. (c) An analogous compound with less bulky substituents at nitrogen which was found to be too unstable for isolation has been described, see: Khramov, D. M.; Rosen, V. E. L.; Lynch, M.; Bielawski, C. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 2267.

(18) We distinguish between divalent carbon(II) compounds (carbenes) R_2C and divalent carbon(0) compounds (carbones) CL_2. The latter species have a divalent carbon atom which retains its four valence electrons of two lone pairs and where the carbon−ligand bonding takes place via donor−acceptor interactions $L \rightarrow C \leftarrow L$ with a strong σ donor such as PR_3 (carbodiphosphorane) or NHC (carbodicarbene). Carbones CL_2 are σ donors and π donors, while carbenes CR_2 are σ donors and π acceptors. Recent theoretical and experimental studies of carbones have been reported, see: (a) Tonner, R.; Öxler, F.; Neumüller, B.; Petz, W.; Frenking, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 8038. (b) Tonner, R.; Frenking, G. *Angew. Chem., Int. Ed.* **2007**, *46*, 8695–8898. (c) Tonner, R.; Frenking, G. *Chem.—Eur. J.* **2008**, *14*, 3260. (d) Tonner, R.; Frenking, G. *Chem.—Eur. J.* **2008**, *14*, 3273. (e) Deshmukh, M. M.; Gadre, S. R.; Tonner, R.; Frenking, G. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2298. (f) Kaufhold, O.; Hahn, F. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 4057. (g) Dyker, C. A.; Bertrand, G. *Nat. Chem.* **2009**, *1*, 265. (h) Frenking, G.; Tonner, R. *Pure Appl. Chem.* **2009**, *81*, 597. (i) Jablonski, M.; Palusiak, M. *Phys. Chem. Chem. Phys.* **2009**, *11*, 5711. (j) Fürstner, A.; Alcarazo, M.; Goddard, R.; Lehmann, C. W. *Angew. Chem., Int. Ed.* **2008**, *47*, 3210. (k) Alcarazo, M.; Lehmann, C. W.; Anoop, A.; Thiel, W.; Fürstner, A. *Nat. Chem.* **2009**, *1*, 295. (l) Patel, D. S.; Bharatam, P. V. *Curr. Sci.* **2010**, *99*, 425.

(19) Bach, R. D.; Su, M.-D.; Aldabbagh, E.; Andrés, J. L.; Schlegel, H. B. *J. Am. Chem. Soc.* **1993**, *115*, 10237.

(20) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules*; Van Nostrand-Reinhold: New York, 1979.

(21) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(22) Schaefer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.

(23) Frisch, M. J. et al. *Gaussian 03*, Revision E.01; Gaussian, Inc.: Wallingford, CT, 2004.

(24) Deglmann, P.; Furche, F.; Ahlrichs, R. *Chem. Phys. Lett.* **2002**, *362*, 511.

(25) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. *Phys. Rev. B* **1988**, *37*, 785Y.

(26) Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Theory Comput.* **2006**, *2*, 364.

(27) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9S*, 229.

(28) (a) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1755. (b) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1558. (c) Morokuma, K. *J. Chem. Phys.* **1971**, *55*, 1236.

(29) (a) http://www.scm.com. (b) Te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; Van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931.

(30) Van Lenthe, E.; Baerends, E. J. *J. Comput. Chem.* **2003**, *24*, 1142. The ($n-1$)s^2 and the ($n-1$)p^6 core electrons of the main-group elements and the (1s2s2p)^{10} core electrons of iron were treated by the frozen core approximation: Baerends, E. J.; Ellis, D. E.; Ros, P. *J. Chem. Phys.* **1973**, 41. An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular densities and represent the Coulomb and exchange potentials accurately in each SCF cycle, see: Krijn, J.; Baerends, E. J. *Fit Functions in the HFS-Method, Internal Report* (in Dutch); Vrije Universiteit Amsterdam: Amsterdam, The Netherlands, 1984. Scalar relativistic effects have been considered using the zero-order regular approximation (ZORA): Chang, C.; Pelissier, M.; Durand, P. *Phys. Scr.* **1986**, *34*, 394. Heully, J.-L.; Lindgren, I.; Lindroth, E.; Lundquist, S.; Martensson-Pendrill, A.-M. *J. Phys. B* **1986**, *19*, 2799. van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1993**, *99*, 4597. van Lenthe, E.; van Leeuwen, R.; Baerends, E. J.; Snijders, J. G. *Int. J. Quantum Chem.* **1996**, *57*, 281. van Lenthe, J. G.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1996**, *105*, 6505.

(31) Previous calculations in our group showed that the differences between the geometries and relative energies which are calculated at BP86/def2-TZVPP (Gauss functions) and BP86/TZVPP (Slater functions) are negligibly small.[26] They can be neglected for the present purpose.

(32) Bickelhaupt, F. M.; Baerends, E. J. *Reviews in Computational Chemistry*; Wiley-VCH, Inc.: New York, 2000; Vol. 15, pp 1.

(33) (a) McKellar, A. R. W.; Bunker, P. R.; Sears, T. J.; Evenson, K. M.; Saykally, R. J.; Langhoff, S. R. *J. Chem. Phys.* **1983**, *79*, 5251. (b) Leopold, D. G.; Murray, K. K.; Lineberger, W. C. *J. Chem. Phys.* **1984**, *81*, 1048. (c) Leopold, D. G.; Murray, K. K.; Miller, A. E. S.; Lineberger, W. C. *J. Chem. Phys.* **1985**, *83*, 4849. (d) Buenker, P. R.; Sears, T. J. *J. Chem. Phys.* **1985**, *83*, 4866.

(34) (a) Koda, S. *Chem. Phys. Lett.* **1978**, *55*, 353. (b) Koda, S. *Chem. Phys. Lett.* **1986**, *66*, 383.

(35) Gobbi, A.; Frenking, G. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 3153.

(36) (a) Frenking, G.; Wichmann, K.; Fröhlich, N.; Loschen, C.; Lein, M.; Frunzke, J.; Rayón, V. M. *Coord. Chem. Rev.* **2003**, *238*−*239*, 55.(b) Lein, M.;. Frenking, G. In *Theory and Applications of Computational Chemistry: The First 40 Years*; Dykstra, C. E., Frenking, G., Kim, K. S., Scuseria, G. E., Eds.; Elsevier: Amsterdam, 2005; p 367. (c) Frenking, G.; Wichmann, K; Fröhlich, N.; Loschen, C.; Lein, M.; Frunzke, J.; Rayón, V. M. *Coord. Chem. Rev.* **2003**, *238*−*239*, 55. (d) Kovács, A.; Esterhuysen, C.; Frenking, G. *Chem.—Eur. J.* **2005**, *11*, 1813. (e) Esterhuysen, C.; Frenking, G. *Theor. Chem. Acc.* **2004**, *111*, 381. (f) Krapp, A.; Bickelhaupt, F. M.; Frenking, G. *Chem.—Eur. J.* **2006**, *12*, 9196.

(37) (a) Pandey, K. K.; Patidar, P.; Aldridge, S. *J. Phys. Chem. A* **2010**, *114*, 12099. (b) Fernandez, I.; Bickelhaupt, F. M.; Cossio, F. P. *Chem.—Eur. J.* **2009**, *15*, 13022. (c) Dickinson, A. A.; Willock, D. J.; Calder, R. J.; Aldridge, S. *Organometallics* **2002**, *21*, 1146. (c) Cavigliasso, G.; Kaltsoyannis, N. *Inorg. Chem.* **2007**, *46*, 3557. (d) Kan, Y. *J. Mol. Struct.: THEOCHEM* **2007**, *805*, 127.

(38) Murray, K. K.; Leopold, D. G.; Miller, T. M.; Lineberger, W. C. *J. Chem. Phys.* **1988**, *89*, 5442.

(39) (a) Chapman, O. L.; McMahon, R. J.; West, P. R. *J. Am. Chem. Soc.* **1984**, *106*, 7973. (b) McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1987**, *109*, 683. (c) Haider, K. W.; Platz, M. S.; Despres, A.; Migirdicyan, E. *Chem. Phys. Lett.* **1989**, *164*, 443.

(40) (a) Maier, G. J.; Endres, P. R. *J. Mol. Struct.* **2000**, *556*, 179. (b) Zgierski, M. Z.; Zerbetto, F. *J. Chem. Phys.* **1993**, *99*, 3721. (c) Collins, C. L.; Davy, R. D.; Schaefer, H. F., III *Chem. Phys. Lett.* **1990**, *259*, 171. (d) Baird, M. S.; Dunkin, I. R.; Hacker, N.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 5190. (e) Baird, M. S.; Dunkin, I. R.; Poliakoff, M. *J. Chem. Soc., Chem. Commun.* **1974**, 904. (f) Bell, G. A.; Dunkin, I. R. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 725. (g) Dunkin, I. *Spectrochim. Acta, Part A: Mol. Spectrosc.* **1993**, *49*, 1179.

(41) Recent reviews:(a) Arduengo, A. J., III *Acc. Chem. Res.* **1999**, *32*, 913; (b) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39; (c) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290; (d) In *N-Heterocyclic Carbenes in Synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, Germany, 2006. (e) In *N-Heterocyclic Carbenes in Transition Metal Catalysis*; Glorius, F., Ed.; Springer: Berlin, 2007. (f) Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239; (g) Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247; (h) Díez-González, S.; Nolan, S. P. *Coord. Chem. Rev.* **2007**, *251*, 874; (i) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem.* **2007**, *119*, 2824; *Angew. Chem., Int. Ed.* **2007**, *46*, 2768. (j) Hahn, F. E.; Jahnke, M. C. *Angew. Chem., Int. Ed.* **2008**, *47*, 3122. (k) Würtz, S.; Glorius, F. *Acc. Chem. Res.* **2008**, *41*, 1523. (l) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612. (m) Wolf, R.; Uhl, W. *Angew. Chem., Int. Ed.* **2009**, *48*, 6774. (n) Dröge, T.; Glorius, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 6940.

(42) Lavallo, V.; Mafhouz, J.; Canac, Y.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *J. Am. Chem. Soc.* **2004**, *126*, 8670.

(43) Lavallo, V.; Canac, Y.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 3488.

(44) Lavallo, V.; Canac, Y.; Prasang, C.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 5705.

(45) Tidwell, T. T. *Angew. Chem., Int. Ed.* **2006**, *45*, 5580.

(46) (a) Kötting, C.; Sander, W.; Senzlober, M.; Bürger, H. *Chem.—Eur. J.* **1998**, *4*, 1611. (b) Dawson, D. F.; Holmes, J. L. *J. Phys. Chem. A* **1999**, *103*, 5217.

(47) (a) Boldyrev, A. I.; Schleyer, P.v.R.; Higgins, D.; Thomson, C.; Kramarenko, S. S. *J. Comput. Chem.* **1992**, *13*, 1066. (b) Lewars, E. *J. Mol. Struct.: THEOCHEM* **2002**, *579*, 155.

(48) Rullich, M.; Tonner, R.; Frenking, G. *New J. Chem.* **2010**, *34*, 1760.

(49) Martin, D.; Baceiredo, A.; Gornitzka, H.; Schoeller, W. W.; Bertrand, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 1700.