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# Synthesis, structural characterization, and coordination chemistry of imidazole-based alkylidene ketenes

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**Alkylidene ketenes typically display high intrinsic reactivity, impeding isolation on a preparative scale. Herein, we report the synthesis of alkylidene ketenes by reaction of imidazole-based diazoolefins with carbon monoxide. The good thermal stability of these heterocumulenes allows for a characterization by single crystal X-ray diffraction. N-Heterocyclic alkylidene ketenes can be used as C donor ligands for transition and main group metals, as evidenced by the isolation of complexes with AuCl, $RhCl(CO)_2$, $PdCl(C_3H_5)$ and $GaCl_3$.**

Alkylidene ketenes are heterocumulenes of the general formula $R_2C{=}C{=}C{=}O$ (Figure 1a).[1] The simplest member of this family, propadienone (R = H), was first detected in 1976.[2] Due to its high intrinsic reactivity, the experimental characterization of propadienone is challenging. Microwave[4] and infrared spectra[5] were recorded, the latter requiring matrix isolation techniques. By analyzing the spectroscopic data of $^{13}C$-labelled propadienone, it was inferred that the heavy atoms adopt a non-linear geometry,[4d] and this conclusion was corroborated by theoretical studies.[6]

Heavier analogues of propadienone with R = alkyl or aryl also display high intrinsic reactivity. Consequently, these alkylidene ketenes are typically prepared *in situ*, and their presence is evidenced by trapping experiments.[1,7]

An increased thermal stability can be achieved by connecting heteroatoms to C3. Wentrup and co-workers have synthesized amino-substituted alkylidene ketene **A** (Figure 1b) by flash vacuum pyrolysis of a Meldrum's acid derivative.[7k,8] The same method was employed by Pommelet *et al.* for the synthesis of the methoxy-substituted alkylidene ketene **B**.[9] Both compounds could be characterized by NMR spectroscopy, but structural data were not reported.

While our investigation was in its final stage, the group of Hansmann has reported the crystallographic analysis of alkylidene ketenes containing mesoionic triazole and imidazole heterocycles (**C**, Figure 1c).[10] Apart from a reaction with $CS_2$, reactivity studies were not reported. Below, we describe the synthesis and the characterization of N-heterocyclic alkylidene ketenes of type **D** (Figure 1d). Reactions with organic and inorganic compounds provide a first glance of the versatile chemistry of these heterocumulenes. Importantly, we demonstrate that alkylidene ketenes of type **D** can be used as C-donor ligands for transition and main group metal complexes.

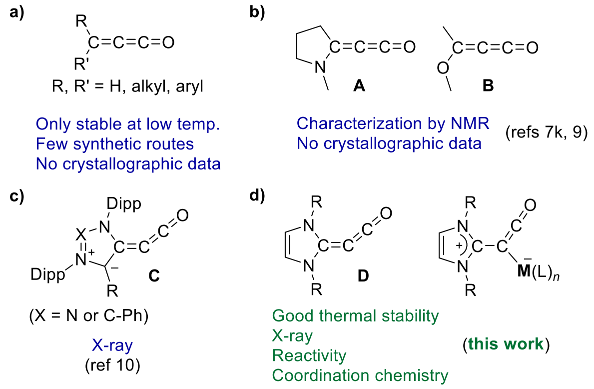

**Figure 1** Alkylidene ketenes typically display high intrinsic reactivity (a), and well-characterized compounds with terminal $C_3O$ groups are scarce (b, c; Dipp = 2,6-diisopropylphenyl). Imidazole-based alkylidene ketenes are described herein (d). The good thermal stability allows for a structural characterization, and for exploring the reactivity and coordination chemistry.

We have recently reported the synthesis of the diazoolefins **1**–**3**.[11] These compounds can be obtained by reaction of N-heterocyclic olefins with $N_2O$,[12] and they represent rare examples of diazoolefins, which are stable at room temperature.[13] Earlier work by Brahms and Dailey had shown that the highly reactive diazoolefin $F_2C{=}CN_2$ can be converted photochemically into the alkylidene ketene $F_2C{=}C{=}C{=}O$ when irradiated in a dinitrogen matrix at 11 K in the presence of CO.[14]

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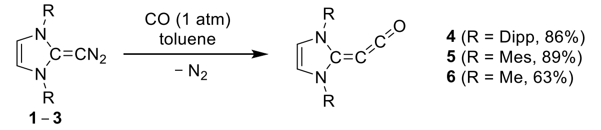
These studies prompted us to investigate the reaction of diazoolefins with CO. Upon addition of CO (1 atm) to a solution of **1** (R = 2,6-diisopropylphenyl = Dipp), **2** (R = 1,3,5-trimethylphenyl = Mes) or **3** (R = methyl = Me) in toluene, the alkylidene ketenes **4**–**6** could be isolated in yields between 63% and 89% (Scheme 1). The lower yield of **6** refers to a two-step procedure, in which the diazoolefin **3** is prepared *in situ* from the corresponding N-heterocyclic olefin and $N_2O$.



**Scheme 1** Synthesis of the alkylidene ketenes **4**–**6**.

Under oxygen- and moisture-free conditions, **4**–**6** are stable in solution at room temperature for weeks without showing any sign of decomposition. We were therefore able to characterize the alkylidene ketenes comprehensively, including crystallographic analysis, and to study some selected reactivity. The IR spectra of **4**–**6** show strong bands at 2106 $cm^{-1}$ (**4**), 2066 $cm^{-1}$ (**5**) and 2098 $cm^{-1}$ (**6**), respectively. These values are in the range found for other alkylidene ketenes.[5,7k,9,10] In the $^{13}C$ NMR spectra ($C_6D_6$), signals at 15.0 ppm (**4**), 12.0 ppm (**5**) and 9.4 ppm (**6**) are observed, which can be attributed to the central carbon atom of the $C_3O$ group. For comparison, the corresponding C atoms in the alkylidene ketenes **A** and **B** exhibit $^{13}C$ NMR shifts at 76.4 ppm ($CDCl_3$)[7k] and 68.6 ppm ($CD_2Cl_2$),[9] respectively. For the parent diazoolefins **1**–**3**, compounds with a strong ylidic character, the $^{13}C$ NMR signals of the central carbon atom ($\mathit{C}N_2$) are found at 35.1 ppm (**1**), 33.3 ppm (**2**) ($C_6D_6$), and 28.6 ppm (**3**) (THF-$d_8$).[11] A strongly shielded $^{13}C$ NMR signal is also found for triphenylphosphoranylideneketene ($Ph_3P{=}C{=}C{=}O$), known as 'Bestmann's ylide'.[15] Here, the C atom adjacent to the $Ph_3P$ group resonates at –9.7 ppm ($C_6D_6$).[16] The $^{13}C$ NMR signals of other divalent carbon(0) compounds[17] cover a broad range of shifts. The carbodiphosphorane $Ph_3P{=}C{=}PPh_3$, for example, shows a signal at 13.4 ppm,[18] whereas carbodicarbenes feature signals at around 110 ppm.[19]

Further information was obtained by spectroscopic analysis of isotope-labelled alkylidene ketenes $\mathbf{4}^{13C}$–$\mathbf{6}^{13C}$, which were prepared from **1**–**3** and $^{13}C$-enriched carbon monoxide. The IR spectra show an isotopic shift of the ketene band of –51 $cm^{-1}$ (**4**, $\nu$ = 2055 $cm^{-1}$), –50 $cm^{-1}$ (**5**, $\nu$ = 2007 $cm^{-1}$), and –53 $cm^{-1}$ (**6**, $\nu$ = 2045 $cm^{-1}$). Interestingly, the ketene band of $\mathbf{5}^{13C}$ is split into a doublet due to Fermi coupling, as it was already reported for other ketenes.[20] In the $^{13}C$ NMR spectra of $\mathbf{4}^{13C}$–$\mathbf{6}^{13C}$, the signal of the cumulene C atoms appears as a doublet. The coupling constants of $^1J_{C\text{–}C}$ = 143.2 Hz ($\mathbf{4}^{13C}$), $^1J_{C\text{–}C}$ = 143.7 Hz ($\mathbf{5}^{13C}$), and $^1J_{C\text{–}C}$ = 156.2 Hz ($\mathbf{6}^{13C}$) are within the expected range for C atoms with high s character.[21]

The molecular structures of **4**–**6** in the solid state are depicted in Figure 2. All compounds display a pronounced bond length alternation within the $C_3O$ group, with long C–$C_2O$ bonds of 1.376(3) Å (**4**), 1.375(2) Å (**5**), and 1.386(2) (**6**), and short C–CO bonds of 1.213(5) Å (**4**), 1.234(2) (**5**), and 1.239(2) (**6**), respectively.[22] The latter values are shorter than what is found for the central C=C bond of [3]cumulenes,[23] whereas the former values are longer than what is found for a typical C=C double bond (~ 1.3 Å).

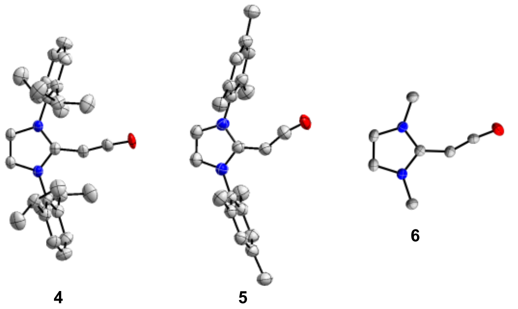


**Figure 2** Molecular structures of the alkylidene ketenes **4**–**6** in the solid state. Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°), **4**: C–$C_2O$ 1.376(3), C–CO 1.213(5), C–C–CO 160.1(12), C–C–O 175.5(3);[22] **5**: C–$C_2O$ 1.375(2), C–CO 1.234(2), C–C–CO 136.14(13), C–C–O 165.20(17); **6**: C–$C_2O$ 1.386(2), C–CO 1.239(2), C–C–CO 149.51(12), C–C–O 172.39(12).

Cumulene ketones were predicted to adopt a kinked geometry,[4d-e,6,24] and bent $C_3O$ groups are indeed found for crystalline **4**–**6**. An important difference between the structures is observed, with C–C–CO bent angles ranging from 136.14(13)° for compound **5** to 160.1(12)° for compound **4**. However, the energy potential for bending is shallow, and packing effects may thus play a role. A geometry optimization of **4** at BP86/def2-SVP level of theory gave a C–C–CO bent angle of 146.2°. A structure with a linear $C_3O$ group, which corresponds to a transition state connecting two bent structures, was only 8 kJ/mol higher in Gibbs free energy (electronic energy: 2 kJ/mol; enthalpy: 2 kJ/mol) exhibiting an imaginary frequency of the $C_3O$ bending vibration of –34 $cm^{-1}$.[25]

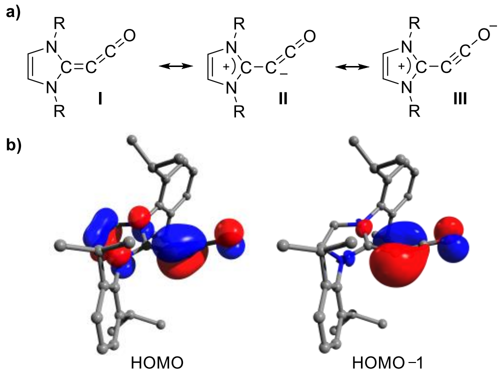
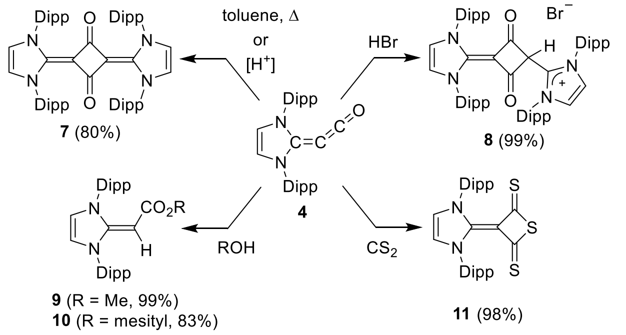


**Figure 3** a) Resonance structures to describe the electronic situation of **4**–**6.** b) Surface diagrams of the two highest lying occupied molecular orbitals of **4** (BP86/def2-SVP at an isodensity value of 0.05).

The structural and the spectroscopy data suggest that the electronic situation of alkylidene ketenes **4**–**6** can be described by the three resonance structures depicted in Figure 3a. The relevance of form **III** is underlined by the short C–CO bond, which is in the range of C≡C triple bonds. The importance of the ylidic form **II**, on the other hand, is corroborated by the bent geometry of the $C_3O$ group. In line with this description, we find the largest coefficients for the HOMO and the HOMO–1 of **4** at the ylidic carbon atom (Figure 3b).

The methoxy-substituted alkylidene ketene **B** (Figure 1b) forms a dimer within a few hours at 28 °C. The alkylidene ketenes investigated herein show much higher thermal stability. No signs of degradation or dimerization at room temperature in solution (toluene or benzene) were observed after two weeks. Even at elevated temperatures, dimerization takes place only slowly, as evidenced from VT NMR experiments with **4** and **6** in toluene-$d_8$. Only at temperatures above 80 °C dimerization of **4** to **7** could be observed (Scheme 2). After 120 h at 120 °C, dimer formation was not complete, and a significant amount of **4** was still present (ratio **7** : **4** = 3.7 : 1). For **6**, no dimerization or degradation could be observed after heating for 3 h at 120 °C. Since alkylidene ketene **6** exhibits sterically non-demanding methyl wingtip groups, one can conclude that the thermal stability is due to electronic effects.

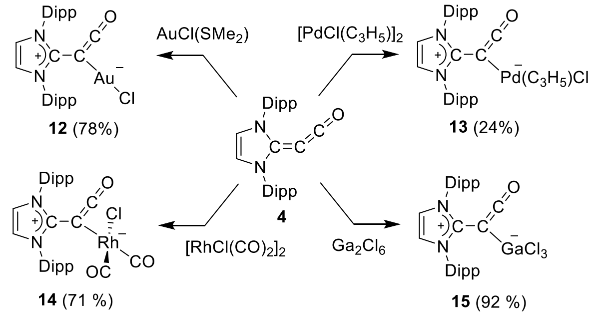
The formation of dimer **7** can be catalyzed by HCl (Scheme 2). In the presence of 5 mol% HCl (1 M in $Et_2O$), the conversion of **4** into **7** was complete within 24 h at room temperature. Larger amounts of acid lead to the formation of a protonated dimer, as exemplified by the HBr adduct **8**.



**Scheme 2** Dimerization and addition reactions of **4**.

In reactions with alcohols, **4** shows a ketene-like reactivity, giving esters in high yields (**9** and **10**). The dithio thietane **11** is formed in a reaction of **4** with excess $CS_2$, presumably via a thioketene intermediate.[7i,10] Attempts to isolate this intermediate were not successful (a reaction of **4** with one equivalent of $CS_2$ gave a mixture of products). In addition to a spectroscopy characterization, we were able to characterize the products **7**–**11** by single crystal X-ray diffraction, and details regarding the solid-state structures are provided in the electronic supplementary information (ESI).

To the best of our knowledge, the coordination chemistry of alkylidene ketenes is completely unexplored.[26] From reactions of **4** with AuCl($Me_2S$), [PdCl($C_3H_5$)]$_2$, [RhCl(CO)$_2$)]$_2$, or $Ga_2Cl_6$, we were able to isolate the complexes **12**–**15** in yields between 24% and 92% (Scheme 3). The complexes were characterized by NMR and IR spectroscopy, high-resolution mass spectrometry, and single crystal X-ray diffraction. In solution, under oxygen and moisture free conditions and in the absence of light, the Pd(II) complex **13** and the Rh(I) complex **14** were found to display limited stability even at lower temperatures (–40 °C). The Au(I) and Ga(III) complexes **12** and **15**, on the other hand, did not show any signs of decomposition over the course of several days in the absence of oxygen and moisture in solution at room temperature.



**Scheme 3** Synthesis of the complexes **12**–**15**.

In all four complexes, the metal is bound to the central carbon atom of the $C_3O$ group. Upon coordination, the C–$C_2O$ bond and the C–CO bond increases in length when compared to the free alkylidene ketene **4** (for details, see ESI, Table S1). Furthermore, the $C_3O$ group of coordinated **4** is strongly bent, with C–C–CO angles between 119.80(16)° (**15**) and 126.17(19)° (**14**). These structural data suggest that metalation increases the ylidic character of **4**.[27] The $^{13}C$ NMR data support this conclusion, as the signals of the central C atom are shifted to higher fields in the complexes.

The IR spectrum of the Rh(I) complex **14** shows three strong bands at 2067, 2052, and 1991 $cm^{-1}$. The band at 2052 $cm^{-1}$ can be attributed to the ketene stretching, and the other two correspond to stretchings of the CO ligands (the assignment was verified by preparing complex **14** with $^{13}C$ labelled alkylidene ketene $\mathbf{4}^{13C}$). The CO bands can be used to evaluate the donor capabilities of ligand **4**.[28] With an average CO stretching frequency of $\nu(CO)_{av} = 2029\ cm^{-1}$, the alkylidene ketene is a slightly weaker donor than the parent diazoolefin ($\nu(CO)_{av} = 2024\ cm^{-1}$)[11] but stronger than common five-membered N-heterocyclic carbenes (NHCs, $\nu(CO)_{av} = 2035–2046\ cm^{-1}$).[29] We note that the donor properties of Bestmann's ylide were so far only investigated on the DFT level of theory, predicting an average CO stretching of $\nu(CO)_{av} = 2041\ cm^{-1}$.[30] The pyramidalization of $GaCl_3$ in complexes with Lewis bases, expressed by the sum of the Cl-Ga-Cl angles ($\Sigma_{ClGaCl}$), was suggested as a measure for the σ-donating properties of a ligand.[31] Good σ-donors cause a stronger pyramidalization and thus a smaller $\Sigma_{ClGaCl}$. For complex **15**, a value of $\Sigma_{ClGaCl} = 326.6°$ was determined. This value is slightly larger than what was reported for the N-heterocyclic carbene IDipp (324.2°),[33] suggesting that **4** is a weaker σ-donor than IDipp. The better *overall* donor properties of **4** when compared to NHCs, as revealed by IR-spectroscopic analysis of **14**, can be explained by the fact that alkylidene ketenes are σ-donors *and* π-donors, whereas NHCs are π-acidic.[28,29]

To conclude: we have described the synthesis and the characterization of the N-heterocyclic alkylidene ketenes **4**–**6**. The $C_3O$ groups in **4**–**6** are bent, as it was found for NHC-derived cumulenes and allenes such as diazoolefins[11,13a] and carbodicarbenes.[19,34] Another noteworthy structural feature of

**4**–**6** are the very short C–CO bonds.[23] Reactivity studies show that **4** displays a ketene-like character. Furthermore, we were able to demonstrate that **4** can act as a C-donor ligand for metal complexes. Coordination to metals accentuates the ylidic character of **4**, resulting in a strongly bent $C_3O$ group with enlarged C–C bond distances. Charge-neutral, ylidic C-donor ligands are increasingly being used in the context of organometallic synthesis and catalysis,[35] and similar applications can be envisioned for N-heterocyclic alkylidene ketenes.

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## Conflicts of interest

There are no conflicts to declare.

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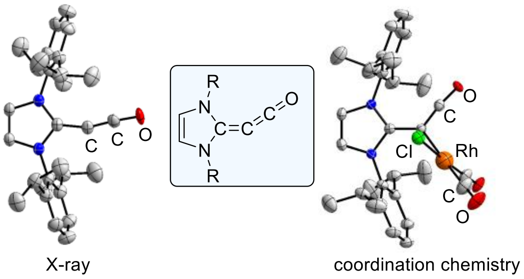
**Graphic for the TOC:**



Alkylidene ketenes are obtained in reactions of N-heterocyclic diazoolefins with CO. The heterocumulenes can act as C-donor ligands for metal complexes.