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Cyanoketenate Anion | Hot Paper

# Synthesis and Reactivity of the [NCCCO]⁻ Cyanoketenate Anion

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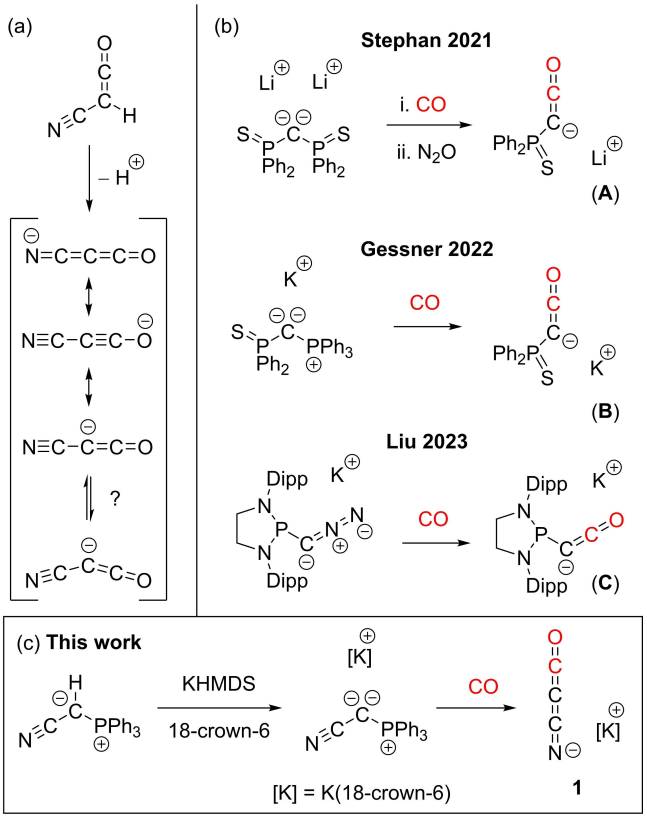
*Dedicated to the memory of Professor Ian Manners*

**Abstract:** Cyanoketene is a fundamental molecule that is actively being searched for in the interstellar medium. Its deprotonated form (cyanoketenate) is a heterocumulene that is isoelectronic to carbon suboxide whose structure has been the subject of debate. However, the investigation of cyanoketene and its derivatives is hampered by the lack of practical synthetic routes to these compounds. We report the first synthesis of the cyanoketenate anion in [K(18-crown-6)][NCCCO] (**1**) as a stable molecule on a multigram scale in excellent yields (>90 %). The structure of this molecule is probed crystallographically and computationally. We also explore the protonation of **1**, and its reaction with triphenylsilylchloride and carbon dioxide. In all cases, anionic dimers are formed. The cyanoketene could be synthesized and crystallographically characterized when stabilized by a N-heterocyclic carbene. The cyanoketenate is a very useful unsaturated building block containing N, C and O atoms that can now be explored with relative ease and will undoubtedly unlock more interesting reactivity.

The synthesis and investigation of the reactivity of molecules detected in interstellar environments are crucial for comprehending the formation of life-related molecules from simpler ones. Additionally, exploring their reactivity can offer valuable insights for the radio-astronomy detection of related compounds. (Hetero)cumulenes and nitrile-containing molecules have been widely identified in interstellar space. The quest for cyanoketene (NCCHCO, Scheme 1a) has garnered significant attention due to its simplicity and its incorporation of the four fundamental elements for life-related molecules.[1]

The deprotonated cyanoketenate [NCCCO]⁻ is isoelectronic with carbon suboxide (O=C=C=C=O), which has been widely studied as the structure and bonding situation in this molecule is ambiguous between a linear heterocumulene structure or a bent motif.[2] Despite numerous attempts by chemists to generate cyanoketene and the cyanoketenate anion using various techniques, the unusual connectivity and reactive nature of these molecules have posed challenges. Consequently, scientists have only succeeded in trapping




*Scheme 1.* (a) Cyanoketene, and resonance structures and geometries of cyanoketenate. (b) Prior literature on formation of anionic ketenates from CO. (c) This work on the synthesis of [NCCCO]⁻ cyanoketenate anion.

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them in low-temperature matrices or detecting them through mass spectrometry, achieved by subjecting precursors to heat and irradiation.[3] Therefore, a synthetically approachable methodology for the generation of cyanoketene and cyanoketenate is highly desired.

The utilization of carbon monoxide as a C1 feedstock dates back to 1834 when Liebig demonstrated the reductive homologation of CO with molten potassium.[4] Several industrial processes exploit the functionalization of CO on very large scales, such as the Fischer–Tropsch and Oxo processes for the conversion of synthesis gas (syngas, a mixture of CO and $H_2$) into hydrocarbons and aldehydes;[5] and the Monsanto and Cativa processes that convert methanol into acetic acid with CO using rhodium and iridium catalysts, respectively.[6] Although this field of chemistry was once dominated by transition metal-catalyzed reactions, there has been growing interest in the functionalization of CO using main-group compounds.[7] In our own recent work, we have explored the activation of CO with alkali metal salts of reactive nucleophiles. Potassium di-*tert*-butylphosphide and benzyl potassium both react with CO to yield intermediates with carbene character.[8] Lithium dicyclohexylamide enabled transition metal-free Fischer–Tropsch chemistry,[9] and various alkali metal silylamides could readily convert CO into cyanide ($CN^-$) and isocyanides (RNC).[10]

Most pertinently to the current work, we showed that a dilithiomethane derivative featuring two phosphine sulfide substituents could react with CO, and this intermediate was oxidized with $N_2O$ to afford an anionic ketenate (**A**, Scheme 1b).[11] This ketenate could be heated to promote cyclo-trimerization and the formation of a hexa-functionalized benzene. The Gessner group subsequently developed an elegant synthesis of anionic ketenates by reacting CO with an alkali metal ylid derivative (**B**), and demonstrated that this ketenate moiety could be transferred to a range of electrophiles.[12] This process was explored in more detail to enable selectivity control of the ketenate formation.[13] The Liu group also developed a synthesis of a (phosphino)ketenate by reaction of the corresponding (phosphino)diazomethyl anion and CO (**C**).[14] In the present study, we explore the functionalization of CO targeting the first large-scale synthesis of the fundamental $[NCCCO]^-$ anion as the $[K(18\text{-crown-}6)]^+$ salt (Scheme 1c). We probe its solid-state and electronic structure, explore its reactivity with respect to electrophiles, and synthesize the parent cyanoketene stabilized by a carbene.

Freshly prepared potassium bis(trimethylsilyl)amide (K-$[N(SiMes_3)_2]$, KHMDS) was added to a cloudy suspension of (triphenylphosphoranylidene)acetonitrile to generate the anionic ylid that was first prepared as the sodium salt by Bestmann and Schmidt in 1987.[15] Addition of 18-crown-6 and CO to this mixture, by analogy with the pioneering work from the Gessner group,[12–13] led to loss of triphenylphosphine (detected by $^{31}P$ NMR spectroscopy) and clean formation of the target compound [K(18-crown-6)][NCCCO] (**1**) after purification in an isolated yield of 93%. The $^{13}C$ NMR spectrum of **1** shows highly distinctive resonances at 120.1, 115.9 and −13.2 ppm that correspond to the C3, C1 and C2 carbon atoms, respectively. This latter resonance with a negative chemical shift corresponds to the central carbon in the $[NCCCO]^-$ anion, and is significantly upfield shifted from the analogous signals in the aforementioned phosphorus-bound ketenate species (**A**, **B**, **C**, Scheme 1b) that resonate at 5.8, 2.4 and 36.2 ppm, respectively.[11–12,14] The IR spectrum of **1** showed absorption bands at 2242, 2176, 2120, and 1462 $cm^{-1}$; comparison with the computed vibrational modes reveals that these symmetric and asymmetric stretching modes are highly coupled across the NCCCO moiety and not localized on any one particular bond.

Single crystals of **1** suitable for single crystal X-ray diffraction were grown by slow diffusion of either pentane or diethyl ether into an acetonitrile solution of **1** at −20 °C and confirmed the target structure (Figure 1a).[16] The solid-state structure shows one-dimensional coordination polymers of $[K(18\text{-crown-}6)]^+$ cations capping each end of the $[NCCCO]^-$ anion (Figure 1b). **1** crystallizes in the monoclinic space group $P2_1/c$, and the central carbon C2 sits on an inversion centre, so only half an equivalent of **1** makes up the asymmetric unit. This feature enforces linearity on the C1–C2-C3 moiety although the thermal ellipsoids for the NCCCO moiety suggest that the linearity may be an artifact of crystal packing. We note that similar deviation from linearity was also suggested for the isoelectronic carbon suboxide, where irregular thermal ellipsoids for the OCCCO unit were also seen.[2a] The end-for-end disorder precludes a detailed discussion of the bond metrics, and thus the structure of **1** has been further probed using computational methods.

DFT calculations performed at the M06-2X–D3-(benzene)/Def2-TZVP//M06-2X–D3/Def2-SVPP level of theory were used to probe the structure of **1** further (see Supporting Information for full details). The optimized structure of the free anion was shown to have a linear geometry (Figure 2a). This is in agreement with observations for the isoelectronic system of carbon suboxide, in which only high levels of computational theory could replicate the non-linear structure that was observed in the solid state.[2a,17] Inclusion of the K counterion in the calculations result in a

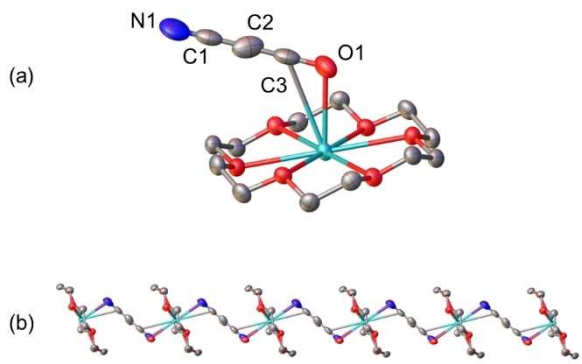



***Figure 1.*** (a) Crystal structure of **1**. (b) Structure of the extended polymeric network. Thermal ellipsoids at 50%, hydrogen atoms omitted for clarity. Atom colours: C (grey), O (red), N (blue), K (cyan). Structures generated through -x,-y,-z symmetry element.[16]

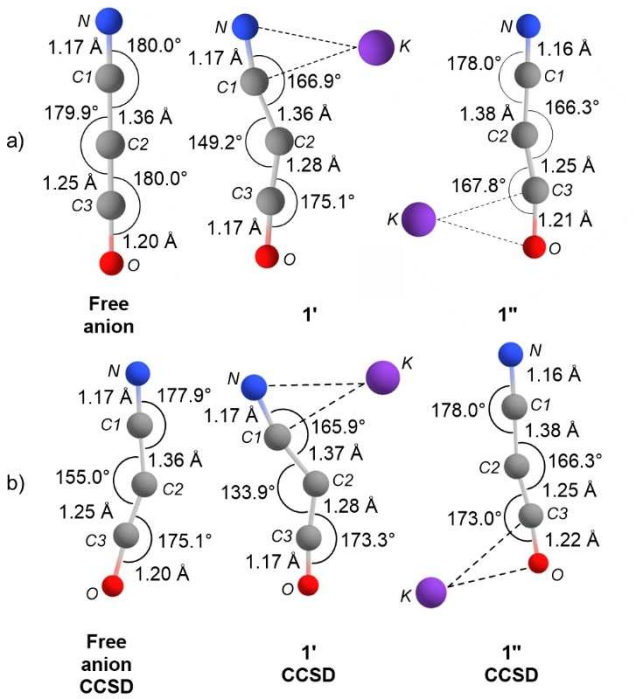
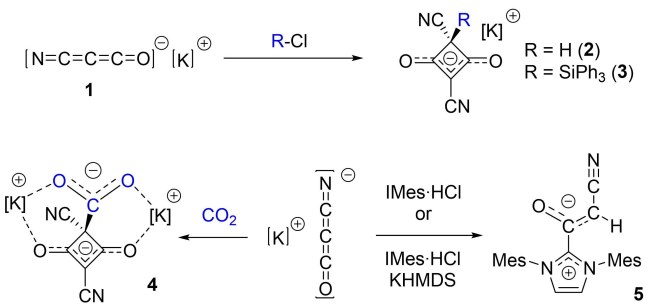



***Figure 2.*** Optimised structures for **1**, without counterion (**free anion**), with the $K^+$ coordinated through the C–N bond (**1′**) and with the $K^+$ coordinated through the C–O bond (**1″**) optimised using a) DFT and b) CCSD methods. See Supporting Information for full details.

contraction of the bond angles around the carbon atoms. Due to the polymeric network observed in the solid state, structures with the K bound through the C–N bond (**1'**) and the C–O bond (**1"**) separately were optimized (Figure 2). **1"** is marginally higher in energy than **1'**, but within the error of the computational method ($\Delta E = +1.1$ kcal/mol), in accord with the observation of the polymeric network. In both cases the coordination of the K ion results in a considerable contraction of the central C1–C2–C3 angle to 149.2° (**1'**) and 166.3° (**1"**), and of the angle around the carbon atom involved in K coordination to 166.9° (N–C1–C2 in **1'**) and 167.8° (C2–C3–O in **1"**). This produces a W-shaped geometry, reminiscent of that observed with carbon suboxide, again highlighting the similarity between these isoelectronic species.[2a,b] These deviations from linearity are more pronounced than those observed in the solid-state structure; however, interactions with the cation and packing forces in the solid state are thought to override the small barriers between these two computed bonding geometries. The calculations were repeated using higher level coupled cluster methods (CCSD; see Supporting Information for details). Interestingly the free anion shows a more pronounced bent structure using CCSD, as the C1–C2–C3 bond angle contracts to 155.0° (Figure 2b). The analogous angle is also contracted in **1'_CCSD**, although not in **1"_CCSD**. Despite these significant geometric changes in terms of angles, the bond lengths and Wiberg bond indices between the structures calculated using DFT and CCSD methods are incredibly similar (see Supporting Information for details).

The electronic structure of **1** was explored using NBO analysis performed at the M06-2X/Def2-TZVP level of theory (see Supporting Information for full details). In all the calculated structures the NPA charges alternate across the structure in the format $N^{\delta-}$–$C^{\delta+}$–$C^{\delta-}$–$C^{\delta+}$–$O^{\delta-}$. In the free anion the most negative charge is calculated to reside on the oxygen atom, but this value is close to that of the central carbon atom. Inclusion of the K counterion changes this, as the NPA charges in **1'** for C2 and O are −0.80 and −0.54, respectively, and in **1"** they are −0.61 and −0.71, respectively. As these two structures represent the two extremes of the K coordination, an average of these charges could represent the experimental observations that would occur due to the polymeric framework. The average NPA charges on C2 and O are therefore −0.71 and −0.63, respectively, which suggests that C2 could be the site of nucleophilic reactivity in **1**.

The stability of this unusual unsaturated molecule Is undoubtedly due to its negative charge, which confers stability with respect to dimerization or oligomerization by nature of electrostatic repulsion. This draws parallels with other fundamental unsaturated main-group molecules such as $[PCO]^-$, where the reactive P–C multiple bond is stabilized with respect to dimerization by the same electrostatic repulsion.[18] Compound **1** is stable under inert conditions and can be obtained on a multigram scale in excellent yield. This prompted us to probe various aspects of its reactivity. Our first target was the parent cyanoketene. Diffusion of HCl gas into a benzene suspension of **1** at 10 °C resulted in formation of a cloudy yellow suspension, and after work-up the product was obtained as **2** (Scheme 2). This species was confirmed by single crystal X-ray diffraction to be a dimer (Figure 3a) comprising a four-membered core presumed to form from a head-to-tail [2+2] cycloaddition reaction of the parent cyanoketene and another equivalent of **1**. In the corresponding reaction of **1** with a more sterically demanding electrophile, $Ph_3SiCl$, the product (**3**) also contained a mono-anionic four-membered core (Figure 3b). Compound **2** and **3** represent mono-anionic derivatives of 1,3-butadione species. Notably, the [K(18-crown-6)] cation displayed varying binding patterns with different CN groups in **2** and **3**, likely influenced by a combination of steric and crystal packing effects. X-ray single crystal studies revealed a double bond character of the four carbonyl C=O bonds within the central 1,3-




***Scheme 2.*** Reactivity of **1** to afford products **2–5**. Abbreviations in text.

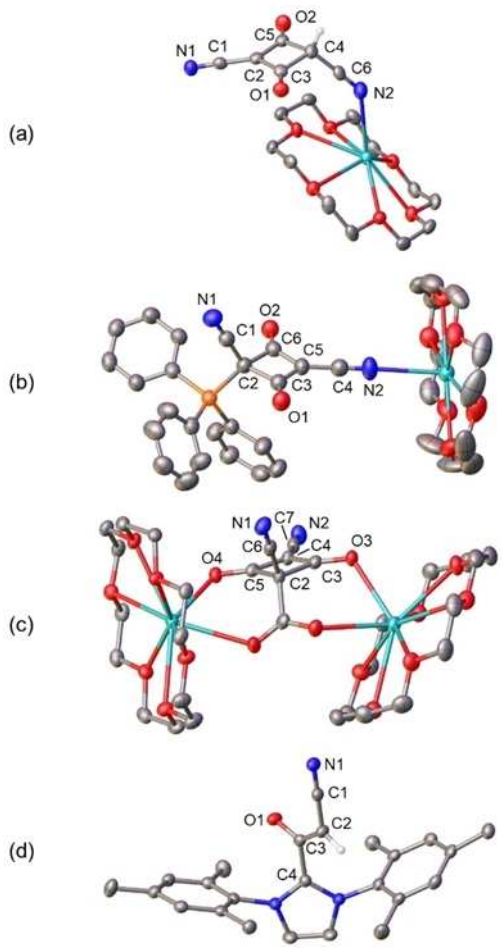



***Figure 3.*** Crystal structures of (a) **2**; (b) **3**; (c) **4** and (d) **5**. Thermal ellipsoids at 50%, most hydrogen atoms are omitted for clarity. Atom colours: C (grey), O (red), N (blue), K (cyan), Si (orange), H (white). Selected bond metrics can be found in the SI.[16]

butadione cores of **2** and **3**, with average bond lengths of approximately 1.21 Å. The C–C distances within the fragment were determined to be around 1.42 Å between the $sp^2$-hybridized carbons, indicative of an intermediate bond length between single and double bonds, suggesting a delocalization of the negative charge. In comparison, single-bonded C–C distances were observed between the tetravalent $sp^3$-hybridized carbon atoms and the carbonyl carbon atoms, ranging from 1.57 to 1.58 Å. These bond lengths are comparable to those reported by Gessner for analogous mono-anionic tosyl-substituted trimethylsilyl cyclobutadione species.[13]

Interestingly, a similar dimeric product was obtained in the reaction of **1** with $CO_2$ at 10 °C. The resulting pale yellow cloudy suspension afforded the product **4** in a 76% isolated yield (Figure 3c). This species contains two $[K(18\text{-crown-}6)]^+$ cations and a dianionic component, where the two negative charges are delocalized in OCCCO moiety across the four-membered core (as in **2** and **3**), and the carboxylate fragment, respectively. Analysis of the crystal structure revealed a single C–C bond length of 1.563(4) Å between C2 and the carboxylate group. The two C–O distances in the carboxylate group were found to be 1.250(3) and 1.241(3) Å, respectively, indicative of charge delocalization. In contrast, the C3–O3 and C5–O4 distances in the central cyclobutadione fragment were measured to be 1.220(3) and 1.224(3) Å, respectively. Carbon atom C4 formed bonds with two $sp^2$-hybridized carbonyl carbons, C3 and C5, at approximately 1.42 Å, suggesting effective delocalization of the second negative charge within the C3–C4-C5 linkage. Notably, the Gessner group observed complementary reactivity when reacting **1** with $CO_2$ in a more polar solvent (dichloromethane), yielding a six-membered $C_5O$ heterocycle instead.[19] This transformation likely occurs through the cleavage of the carboxylate C–O bond followed by intramolecular rearrangement, possibly facilitated by the enhanced solubility and polarity of the solvent.

The observed dimerization of the parent cyanoketene suggests that this species is amphoteric. Noting that strong donors such as N-heterocyclic carbenes (NHCs) have been exploited to stabilize and isolate a wide range of highly reactive main-group compounds,[20] we probed the corresponding reactivity of **1**. To this end, **1** was treated with 1,3-bis(2,4,6-trimethylphenyl) imidazolium chloride (IMes·HCl), which acted as a proton source and also generated the free NHC 1,3-bis-(2,4,6-trimethylphenyl) imidazol-2-ylidene (IMes) that could trap the cyanoketene in situ and generate the carbene-stabilized cyanoketene (**5**) in a 46% yield. The yield could be improved by employing KHMDS as a base and proton-shuttle. In this case, the reaction is thought to proceed via initial deprotonation of IMes·HCl to afford IMes and $HN(SiMe_3)_2$. NHC attack of the electrophilic carbonyl position of **1** increases the basicity of C2 of the ketenate, enabling deprotonation of $HN(SiMe_3)_2$. The enhancement of the Brønsted basicity of the anion by the NHC is clear as **1** is formed in the presence of $HN(SiMe_3)_2$ and does not effect deprotonation on its own.

The formulation of **5** as an IMes carbene adduct with cyanoketene was confirmed through an X-ray diffraction experiment. Orange crystals suitable for X-ray diffraction were grown by slow diffusion of $Et_2O$ into an acetonitrile solution of **5** (Figure 3d).[16] In the imidazolium-2-enolate, the C4–C3 bond length was determined to be 1.512(2) Å, while the C3–O1, C3–C2, and C2–C1 distances were found to be 1.2552(19), 1.381(2), and 1.410(2) Å, respectively. Notably, C2 and C3 were observed to be planar, with the sums of surrounding bond angles totaling 360°. These observations are indicative of charge delocalization from IMes to the cyanoketene C(O)–C–C fragment. In this arrangement, the oxygen atom and nitrile group are positioned in a *cis*-orientation on the C=C double bond. These structural parameters closely resemble those observed in the SIMes adduct with diphenyl ketene, as reported by Delaude in their mechanistic study of the NHC-catalyzed Staudinger reaction involving diphenyl ketene and imines.[21] This work shows that the σ-donating NHC enables the interception of the parent cyanoketene and precludes dimerization.

In conclusion the cyanoketenate anion, $[NCCCO]^-$ has been synthesized and characterized. The compound can be

isolated as the [K(18-crown-6)]$^+$ salt **1** on a multigram scale in over 90% yield from commercially available reagents. Reactions of **1** with the electrophiles HCl, $Ph_3SiCl$ or $CO_2$ give related structures in which the cyanoketenate fragment dimerizes to give a four-membered ring (products **2**, **3** and **4**, respectively). Additionally, the parent cyanoketene is stabilized by reaction of **1** with the nucleophilic NHC IMes (**5**) allowing the inception of the parent cyanoketene. Work is ongoing in our laboratories to explore the reactivity of the fundamental cyanoketenate anion as a building block to more complex molecular architectures.

## Supporting Information

The data that support the findings of this study are available in the supplementary material of this article and the computational data are available at https://doi.org/10.25500/eData.bham.00001076. The authors have cited additional references within the Supporting Information.[22]

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article and the computational data are available at https://doi.org/10.25500/eData.bham.00001076.

**Keywords:** cumulenes · cyanoketene · carbon monoxide · small-molecule activation · N-heterocyclic carbene

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## Cyanoketenate Anion

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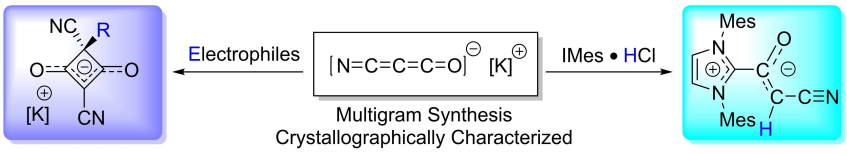
Synthesis and Reactivity of the $[NCCCO]^-$ Cyanoketenate Anion




We report the synthesis of the fundamental cyanoketenate anion from the functionalization of CO with simple reagents in >90% yields on a multigram scale. The reactivity with electrophiles is explored, which lead to dimeric products. The neutral cyanoketene, which is actively being sought in the interstellar medium, could also be isolated stabilized by a carbene.