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N₂/CO Exchange at a Vinylidene Carbon Center: Stable Alkylidene Ketenes and Alkylidene Thioketenes from 1,2,3-Triazole Derived Diazoalkenes

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ABSTRACT: We present a new class of room-te	mperature stable
diazoalkenes featuring a 1,2,3-triazole backbone. Dinitrogen of the $R_{\rm sc} = c^{1/2}$ $R_{\rm sc} = c^{1/2}$ $R_{\rm sc} = c^{1/2}$	
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carbon monoxide. The latter alkylidene ketenes are typically considered as highly reactive compounds, traditionally only accessible by flash vacuum pyrolysis. We present a new and mild synthetic approach to the first structurally characterized alkylidene ketenes by a substitution reaction. Density functional theory calculations suggest the substitution with isocyanides to take place via a stepwise addition/ elimination mechanism. In the case of carbon monoxide, the reaction



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proceeds through an unusual concerted exchange at a vinylidene carbon center. The vinylidene ketenes react with carbon disulfide via a four-membered thiete intermediate to give vinylidene thioketenes under release of COS. We present spectroscopic as well as structural data for the complete isoelectronic series ($R_2C=C=X$; $X = N_2$, CO, CNR, CS) including ${}^1J({}^{13}C-{}^{13}C)$ data. As N_2 , CO, and isocyanides belong to the archetypical ligands in transition-metal chemistry, this process can be interpreted in analogy to coordination chemistry as a ligand exchange reaction at a vinylidene carbon center.

INTRODUCTION

The activation of carbon monoxide with main group elements is a vibrant area of research, exemplified by the recent characterization of carbonyl complexes based on silicon,^{1,2} boron,³⁻⁶ phosphorus,^{7,8} or alkaline earth metals.^{9,10} Carbonyl complexes of carbon, ketenes ($R_2C=C=O$) are well explored in organic chemistry and can even be generated by the combination of electrophilic carbenes with CO.11-14 In contrast to ketenes, the higher unsaturated homologues, alkylidene ketenes or more specifically vinylidene ketenes $(R_2C=C=C=O)$ are much less investigated, presumably a result of their challenging synthetic access and high reactivity.^{15,16} Carbon suboxide¹⁷ (I; Scheme 1A) is one of the few relatively stable compounds, which has received great interest and was suggested by Frenking and co-workers to be described as a carbon atom flanked by two neutral CO donor ligands (L \rightarrow C \leftarrow L; carbone).¹⁸ Following this analogy, the [CCO] fragment can be stabilized by a phosphine ligand leading to phosphoranylideneketenes (II).¹⁹⁻²² Besides phosphacumulene ylides, which are the only structurally characterized compounds containing the X=C=C=O fragment, alkylidene ketenes or cumulenones $(X = CR_2)$ are exceedingly rare. Typically, alkylidene ketenes are generated in the gas phase by flash vacuum pyrolysis (FVP) ($T > 500 \ ^{\circ}C$), trapped, and analyzed in matrixes at cryogenic temperatures (Scheme 1B).²³ Common precursors are Meldrum's acid derivates (III), which upon FVP eliminate acetone and CO_2 to

Scheme 1. (A) Carbon Suboxide (I) and Phosphoranylideneketene (II) are Rare Examples of Well-Characterized Cumulenones Containing the X=C=C=O Fragment and (B) Synthesis of Alkylidene Ketenes via FVP

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afford alkylidene ketenes (**IV**);^{24–27} the latter are prone to dimerize or subsequently decarbonylate to form highly reactive vinylidenes (**V**).^{28–30} Note, in the reverse sense, alkylidene ketenes can be considered as carbonylation products of elusive unsaturated carbenes ($R_2C=C$:), a rare reactivity observed for matrix isolated $F_2C=C$:.^{30,31} Interestingly, Wentrup and coworkers prepared alkylidene ketene **VI** via FVP (450 °C, 10⁻⁴ Torr) followed by trapping at low temperatures.³² As far as we know, **VI** is the only relatively stable alkylidene ketene, besides iminopropadienones (**VII**),³³ allowing even its room-temperature NMR characterization.

Similar observations of ketenes (R₂C=CO) and alkylidene ketenes $(R_2C=C=CO)$ can be applied to diazoalkanes $(R_2C=N_2)$ and diazoalkenes $(R_2C=C=N_2)$. While the first class is well-studied,^{34,35} diazoalkenes are typically high-energy intermediates proposed in a series of reaction mechanisms such as the Seyferth-Gilbert homologation or the Colvin reaction.^{36,37} As a result of their tendency to rapidly eliminate dinitrogen, they are challenging to characterize, and their detection was so far limited to matrix isolation studies.^{30,31} However, by tuning the electronics, we recently were able to describe the synthesis of the first room temperature stable diazoalkene based on an imidazole heterocycle, enabling a new entry into vinylidene chemistry.³⁸ In this work, we present a new class of diazoalkenes and demonstrate a new mild synthetic strategy to access vinylidene ketenes by a N₂/CO exchange reaction.

RESULTS AND DISCUSSION

We started by investigating the reactivity of 1,2,3-triazole derived mesoionic N-heterocyclic olefin (mNHO) $1a^{39}$ with nitrous oxide (Scheme 2). Upon addition of 2–3 bar N₂O to

Scheme 2. Synthesis of 1,2,3-Triazole Derived Diazoalkenes 2 from mNHOs 1 with the Corresponding Lewis Structures



1a, the reaction turns over the course of 3-4 h from a homogeneous purple solution to a dark suspension. The desired diazoalkene 2a precipitates and can be isolated as an orange solid in 65% yield. The reaction can also be performed with the new mesoionic olefins 1b and 1c to afford 2b and 2c, respectively. 2a is stable in the solid-state and in solution under inert atmosphere, while differential scanning calorimetry (DSC) measurements indicate stability up to 180 °C (see SI). In analogy to the recently described synthesis of imidazole-based diazoalkenes, the mechanism most likely involves initial attack of the strong carbon donor onto the terminal N atom of nitrous oxide (I), followed by proton migration to II and dehydration (Scheme 2).^{40,41}

The transfer of N_2 from N_2O to form diazo species is typically a challenging process,⁴² with few literature precedents.^{43,44} Note, the analogy between the imidazole mNHO³⁹ and the 1,2,3-triazole mNHO-based reactions is not obvious, considering that the reaction of normal N-heterocyclic olefins (NHOs) with N₂O gives dimeric species of the type $R_2C =$ $CH(N=N)HC=CR_2$ and not the crucial diazoalkenes.⁴⁵ This change in selectivity highlights the unique reactivity of mesoionic N-heterocyclic olefins, since Tolman electronic parameters indicate the 1,2,3-triazole mNHOs to be only slightly stronger donors compared to normal N-heterocyclic olefins.^{39,46} Some differences between the two mNHO classes should be pointed out: The reaction rate is slower compared to the imidazole system. This finding is in line with the reduced nucleophilicity of the 1,2,3-triazole mNHOs³⁹ and the ratedetermining step being the initial addition. Furthermore, while the reaction of the imidazole system leads to a 1:1 stoichiometric water hydrolysis side product limiting the theoretical yield to 50%, in this case, only several minor hydrolysis products are detected and water can even be partially trapped by addition of molecular sieves.

The new diazoalkene class can be described through a series of zwitter-ionic Lewis structures $(2^{I}-2^{III})$ as well as dative descriptions such as a carbone (2^{IV}) . In the IR (ATR, solid) the diazo moiety shows up as a sharp signal at $\tilde{\nu} = 1953 - 1956$ cm^{-1} (2a-c), outside of the classical range for organic diazo compounds ($\tilde{\nu} \sim 2017-2180 \text{ cm}^{-1}$)³⁴ and at slightly larger wavenumbers compared to the only so far reported roomtemperature stable diazoalkene (1944 cm⁻¹).³⁸ While imidazole derived NHOs are more ylidically polarized, compared to 1,2,3-triazole mNHOs,³⁹ the polarization trend is also reflected in the IR of the diazoalkenes. The low IR absorption supports a C=N=N fragment disfavoring diazonium representations. The ¹³C NMR signal of the labeled =¹³C=N=N species appears at δ = 34.5–35.2 ppm (2a–c), being strongly high-field shifted, typical for diazo compounds. Natural abundance ¹⁵N NMR of 2a allows to detect all five nitrogen atoms, with the diazo N atoms being at δ (¹⁵N; rel. to NH₃): 288.7 ppm (N2) and 255.0 ppm (N1; Figure 1B).

The assignment is based on the ${}^{15}N^{-13}C$ coupling constants derived from the labeled sample and supported by quantum chemical predictions (see SI). While N1 is in a usual ${}^{15}N$ NMR shift range for diazo compounds, N2 (288.7 ppm) is unusually high field shifted (N2 for diazoalkanes typically $\delta({}^{15}N) \sim 350-400$ ppm).^{34,38}

In the X-ray solid-state structures (Figure 1A), the C1–C2 bond lengths [2a: 1.401(2) Å; 2c: 1.399(1) Å] are positioned between a single and double bond similar to the C–C bond in benzene (1.398 Å).⁴⁷ The diazoalkenes are not linear but bent [2a: 121.6(1)°; 2c: 123.51(8)°]. Interestingly, in the solidstate, the C=N=N moiety is pointing down in the case of 2a and up for 2c, suggesting an unusual type of E/Z stereoisomers. Note, NMR data only show one isomer, suggesting a fast exchange on the NMR time scale (vide infra). The CN₂ moiety is in plane with the heterocycle [C3–C2–C1–N1; 2a: $-17.1(3)^\circ$; 2c: 178.1(1)°], supporting a partial double bond contribution. The N1–N2 [2a: 1.157(2) Å; 2c: 1.153(1) Å] bonds are shorter compared to the previously reported diazoalkene [1.184(7) Å],³⁸ however, still long compared to regular diazoalkanes [diazomethane: N–N 1.12 Å]⁴⁸ disfavoring N–N triple bond representations.



Figure 1. (A) X-ray solid-state structures of 2a and 2c. Thermal ellipsoids are shown with 50% probability. Selected bond lengths and angles in [Å] and [°]: (2a) C1–C2 1.401(2), C1–N1 1.274(2), N1–N2 1.157(2), C2–C1–N1 121.6(1), C1–N1–N2 169.1(1), C3–C2–C1–N1 –17.1(3); (2c): C1–C2 1.399(1), C1–N1 1.276(1), N1–N2 1.154(1), C2–C1–N1 123.51(8), C1–N1–N2 168.71(9), C3–C2–C1–N1 178.1(1). (B) Natural abundance ¹⁵N NMR spectrum (60 MHz, d_8 -THF, ref against liq. NH₃) of 2a.

Next, we investigated the reactivity of the diazoalkenes toward ambiphilic reagents such as 2,6-dimethylphenyl isocyanide (Scheme 3A). At room temperature, a clean substitution of dinitrogen takes place to give vinylidene ketenimine 3a.

¹³C labeling of **3a** allows to assign C_a : 48.4 ppm and C_{β} : 137.2 ppm (verified by INADEQUATE measurements). In the solid-state structure the C2-C1-C4 angle $[176.4(1)^{\circ}]$ is significantly widened, while the C1-C4 [1.233(2) Å] and C1-C2 bond lengths [1.365(2) Å] are short (Figure 2), supporting a resonance hybrid between a cumulenic structure (3a) and a zwitter-ion with a C–C triple bond (3a'). Previously, we speculated that such an exchange reaction most likely proceeds via a (3 + 2) cycloaddition leading to IntA (Scheme 3A) followed by a cycloreversion with N₂ liberation.³⁸ At first sight, a restriction to a cycloaddition mechanism appears to be a severe limitation for a more general concept. In order to probe if this approach is limited to isocyanides, we selected carbon monoxide as an ambiphilic, isoelectronic species. We were delighted to see that carbon monoxide (2-3 bar) reacted highly selectively (no side products) with diazoalkene 2a at room temperature in 3-4 h to give vinylidene ketene 4a as a yellow solid in 79% yield (Scheme 3B).

In order to prove the generality of this transformation, we also performed the reaction with 2b to give 4b (72%) and with the recently described diazoalkene 5 to give vinylidene ketene 6 (46%). Vinylidene ketenes 4/6 can be described through an array of Lewis resonance structures such as a cumulenone (4^{I}),

Scheme 3. Ligand Exchange Reactions of Diazoalkenes with (A) an Isocyanide and with $(B) CO^{a}$



^{*a*}Xyl: 2,6-Dimethylphenyl.



Figure 2. X-ray solid-state structures of 3a (left) and 4a (right). Thermal ellipsoids are shown with 50% probability. Selected bond lengths and angles in [Å] and [°]: 3a: C1-C2 1.365(2), C2-C3 1.414(2), C1-C4 1.233(2), C4-N1 1.262(2), C2-C1-C4 176.4(1), C1-C4-N1 170.8(1), C4-N1-C5 129.9(1); 4a: C1-C2 1.387(2), C2-C3 1.404(2), C1-C4 1.237(2), C4-O1 1.201(2), C2-C1-C4 146.0(2), C1-C4-O1 171.5(2). In the case of 4a, a solvent molecule of THF is omitted for clarity.

a zwitter-ionic ketene (4^{II}), a zwitter-ionic alkoxy alkyne (4^{III}), and a zwitter-ionic oxonium ion (4^{IV}) as well as by additional dative descriptions $(4^{V}-4^{VI})$ (Scheme 3B). In the IR, the = C=C=O moiety appears as a strong signal at 2096-2099 cm^{-1} (4a; 4b) and 2085 cm^{-1} (6) similar to Wentrup's stable ketene $(2080 \text{ cm}^{-1})^{32}$ and matrix isolated methyleneketenes (typically ~ 2100 cm⁻¹).⁴⁹ The IR band is at lower wavenumbers than in free CO (2143 cm⁻¹), indicating π backbonding into the CO fragment. ¹³C-labeled 4a allows to unambiguously assign the ¹³C NMR signals (C_{α}): 13.9 ppm (4a) $[C_{\alpha}: 12.7 \text{ ppm (6)}]$ and $C_{\beta}: 149.2 \text{ ppm (4a)} [C_{\beta}: 144.5]$ ppm (6)]. The strong high field shift from 34.5 ppm (C_a : 2a) to 13.9 ppm (C_{α} : 4a) suggests a significant negative charge at C_{α} . At first sight, this appears rather counterintuitive since CO should be a superior π -acceptor than N₂, but it follows the same trend observed for diazomethane $H_2C=N_2$ (23.1 ppm) and ketene H₂C=CO (2.5 ppm).⁵⁰ Note, the ¹³C chemical shift is quite different to Wentrup's alkylidene ketene VI

(Scheme 1B) [76 ppm (C_{α}) and 161 ppm (C_{β})],³² resembling more carbon suboxide [¹³C: -14.6 (C_a) and 129.7 ppm (C_b)], which was interpreted to show considerable oxonium character.⁵¹ The strong shielding effect is in agreement with high electron density at $C_{\alpha\nu}$ favoring resonance structure $4a^{II}$ rather than an alkyne (4a^{III}). However, it should be pointed out that the interpretation of ¹³C NMR shifts solely based on the diamagnetic contributions to shielding (electron density arguments) might be problematic since paramagnetic contributions might play a role. In case of 4a and 4b (see SI), we were able to obtain single crystals suitable for X-ray diffraction (Figure 2). Strikingly, the C2–C1–C4 angle $[146.0(2)^{\circ} (4a);$ $147.5(1)^{\circ}$ (4b)] is significantly widened compared to 2a $[121.6(1)^{\circ}]$, but still far away from linearity. Interestingly, in 1985, Brown and co-workers proposed by microwave spectroscopy the parent propadienone $(H_2C=C=CO)$ to feature a zigzag structure with two angles of 144.5° (C=C=C) and 169.4° (C=C=O),⁵² but so far, no X-ray data on any alkylidene ketene were reported. The here described solid-state structures confirm the zigzag microwave data. Furthermore, the C1-C2 [1.387(2) Å 4a; 1.378(1) Å 4b] and C1-C4 [1.237(2) Å 4a; 1.236(2) Å 4b] bond lengths are in the range of cumulenic bond distances. In order to gain more experimental insight into the electronic structure, we determined the ${}^{1}J({}^{13}C-{}^{13}C)$ coupling constants for the isoelectronic series 2a, 3a, and 4a based on the ${}^{13}C(C_{\alpha})$ labeled compounds. The ${}^{1}J({}^{13}C-{}^{13}C)$ coupling constants for C_{α} - C_{γ} follow the trend: 60 Hz (2a), 107 Hz (4a), and 120 Hz (3a), while the ${}^{1}J({}^{13}C-{}^{13}C)$ coupling constants for $C_{\alpha}-C_{\beta}$ are 154 Hz (4a) and 177 Hz (3a). It has been established that the magnitude of the ${}^{1}J({}^{13}C-{}^{13}C)$ coupling is primarily determined by the hybridization of the two carbon atoms involved.⁵³ The absolute values for ${}^{1}J(\text{sp}^2-\text{sp}^2)$ coupling constants of ca. 60–70 Hz⁵³ agree with **1a** and **2a** to feature a central (C_{α}) sp² carbon atom. Interestingly, the increase in ${}^{1}J({}^{13}C-{}^{13}C)$ for 4a (107 Hz) and 3a (120 Hz) can be correlated with an increase in s-character in the order C=C= $N_2 < C = C = O < C = C NR$, in agreement with the trend in bending angles. Note, coupling constants for ${}^{1}J(sp^{2}-sp)$ such as in $H_2C = C = CH_2$ are typically around 100 Hz.⁵³ The large $C_{\alpha}-C_{\beta}$ coupling constants of 154 Hz (4a) and 177 Hz (3a) support the high s-orbital contribution (sp hybridized) in a typical range for alkynes (ca. 170–190 Hz).⁵³ Note, while the hybridization of the two carbon atoms involved can be estimated, the bond order is not necessarily a triple bond [for comparison: $HC \equiv CH^{-1}J({}^{13}C - {}^{13}C) = 171$ Hz; $HC \equiv C - C \equiv CH^{-1}J({}^{13}C - {}^{13}C) = 154$ Hz].⁵³

In order to gain additional insight into the electronic structures of the isoelectronic series $[R_2C=C=X; X = N_2]$ CO, CNR], we performed quantum chemical calculations on the simplified systems (for the full systems, see SI) (Figure 3A). The structural data (BP86/def2TZVPP) are in very good agreement with the data obtained from the solid-state structures. Natural charges at C_{α} : -0.29e (2) < -0.55e (4) agree with the ¹³C NMR data $\delta \sim 35$ ppm (2) and ~ 13 ppm (4). Interestingly, the frontier molecular orbitals of the three systems are fairly similar (Figure 3B). The LUMO is centered on the heterocyclic ring, while HOMO and HOMO-1 are primarily centered on the CNN, CCO, CCN fragments (three center 4-electron bond). The HOMO is in plane with the heterocycle, while the HOMO-1 is perpendicularly oriented in agreement with theoretical predictions by Frenking and coworkers on related systems.⁵⁴ In order to computationally



Figure 3. (A) Computational comparison (BP86/def2TZVPP) of the isoelectronic series $R_2C=C=X$ (X = $N_2 2^5$; CO 4⁵; CNMe 3⁵). (B) Frontier molecular orbitals (BP86/def2TZVPP) shown with an isovalue of 60%.

confirm the differences in bending, we performed for the series 2^{s} , 3^{s} , and 4^{s} a relaxed potential energy surface scan for the bending angle C-C-X (Figure 4; for the full system see the



Figure 4. Relaxed potential energy surface scan (BP86/def2TZVPP) for $R_2C==C==X$ (X = N_2 2^S; CO 4^S; CNMe 3^S) as a function of the bending angle (CCN, CCC). The energy at the minimum was referenced to zero to allow comparison.

SI). In agreement with the increasing ${}^{1}J({}^{13}C-{}^{13}C)$ coupling constants in the series 2a < 4a < 3a, a higher s-orbital contribution would expect minima shifted toward larger bending angles (also observed by X-ray diffraction).

Interestingly, bending **2a** into a linear C=C=N=N species proceeds with a barrier of ca. 10 kcal/mol. This relatively low value renders the isolation of potential E/Zisomers to be unlikely. In case of vinylidene ketene **4a** and vinylidene ketenimine **3a**, the minima are shifted to ca. 150° [exp. 146.0(2)° (**4a**)] and ca. 175° [exp. 176.4(1)° (**3a**)]. In both cases, the bending potential is very shallow with an energy difference of <1 kcal/mol between 140° and 180°, indicating the CCX entity to be flexible in solution. This observation is reminiscent to the shallow bending potential of carbon suboxide⁵⁵ and carbones in general.¹⁸

Besides the electronic structure, we were interested in the reaction mechanism for this unusual substitution reaction at a sp²-carbon center. Even though singlet^{11–14} and triplet^{56,57} carbones are known to activate CO, a dissociative mechanism via a free vinylidene (S_N1 type) seems highly unlikely. Computational analysis (BP86/def2TZVPP) revealed the substitution to be strongly exergonic [$\Delta G = -50.6$ kcal/mol (CO); $\Delta G = -55.7$ kcal/mol (isocyanide)]. Optimizations of the full system indicated a single transition state II ($\Delta G^{\ddagger} = 18.9$ kcal/mol) which connects 2 and 4 in an intrinsic reaction coordinate (IRC) calculation via a shoulder III (Figure 5).



Figure 5. IRC calculations conducted on TS-II (BP86/def2TZVPP).

Transition-state II can be rationalized by an attack of a carbon centered lone pair of 2 (HOMO/HOMO-1) into the antibonding lowest unoccupied molecular orbital (LUMO) of carbon monoxide. Note, this polarization is the opposite to a regular S_N2 reaction as well as the opposite to the activation of CO (HOMO) with carbenes (LUMO).^{11–14} The activation is supported by reports of carbanion-mediated carbonylation reactions such as the addition of organolithium compounds to CO to give highly reactive acyllithium intermediates.⁵⁸⁻⁶¹ While typically such acyl anions are trapped by an electrophile, in this case, the adjacent diazonium moiety allows for synchronous elimination.⁶² In order to support the unusual mechanism, we calculated the potential energy surface for the substitution reaction based on the small system 2^{s} as a function of the C-C and C-N bond distances for CO and an isocyanide (Figure 6). The data agree with the IRC calculation of the full system with a single transition state (TS-II^S) and no acyl intermediate being involved. The direct downhill transformation on a temporarily flat potential surface (area around III⁵) leads to a strongly exergonic dinitrogen liberation (Figure 6A). This reaction mechanism might be classified as two-step (addition/elimination) no intermediate transformation, even though no bifurcation scenario is involved.⁶³ Note, the elementary step involves the concerted bond cleavage of a C=N multiple bond to form a new C=C multiple bond. The conclusions derived from the energy surface of the small system agree with the optimizations of the full systems.

Interestingly, we also compared the potential energy surface for the reaction with an isocyanide (Figure 6B). While the first transition state [TS-IV^S] is structurally and energetically similar to (TS-II^S; Figure 6C) and can also be rationalized by a nucleophilic activation of the isocyanide, it leads to an initial intermediate, the (3 + 2) cycloaddition product Int-V^S. A second transition state (TS-VI^S) connects the cyclic intermediate Int-V^S with the strongly exergonic substitution



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Figure 6. Relaxed potential energy surfaces (electronic energy) for the exchange of N_2 by CO (A) and N_2 by an isocyanide (B) as a function of the C–N and C–C bond distances at the BP86/def2TZVPP level of theory. The dotted lines indicate the energetically lowest energy path (IRC) from starting material to product. Optimized transition states and intermediates of the isocyanide reaction (C).

product 3^S. Optimizations of the full system are in excellent agreement with the potential energy surface of the small system, featuring an activation energy of $\Delta G^{\ddagger} = 21.6$ kcal/mol (TS-IV) on the reaction path to the (3 + 2) cycloaddition product Int-V ($\Delta G = -5.8$ kcal/mol) in an overall strongly exergonic reaction ($\Delta G = -55.7$ kcal/mol; for the optimized structures see the SI).

Finally, we were curious if it is possible to transfer the vinylidene ketene into its sulfur derivative, thereby extending the isoelectronic series $R_2C==C=X$ to X=S. Some cumulenes, such as $[P==C==O]^-$, are known to give the corresponding thio derivatives $[P==C==S]^-$ by addition of CS₂ under release of COS.⁶⁴ In analogy, we attempted the synthesis of the thio analog of 4 (Scheme 4).

Upon addition of 1 equiv of carbon disulfide to 4a, an instant color change from dark brown to orange was observed. Monitoring the reaction by *in situ* NMR spectroscopy indicated the immediate formation of a new species, which rearranged into another compound (see SI). Low-temperature $(-20 \ ^{\circ}C)$ NMR spectroscopy allowed the clean characterization of the intermediate, the unknown 2-oxo-2H-thiete-4-thiolate heterocycle 7b. Additionally, we also obtained single crystals at $-25 \ ^{\circ}C$ and could establish the solid-state structure

Scheme 4. Reaction of Vinylidene Ketenes 4 with CS_2 to Give Vinylidene Thioketenes 8 via a Four-Membered Intermediate (7)



of the reactive thiete heterocycle 7b (Figure 7). Interestingly, a thiete heterocycle was proposed as an unstable intermediate by



Figure 7. X-ray solid-state structures of 7b and 8b. Thermal ellipsoids are shown with 50% probability. Selected bond lengths and angles in [Å] and [°]: 7b: C1–C2 1.437(2), C2–C3 1.398(2), C1–C4 1.443(2), C1–C5 1.411(2), C4–S1 1.875(2), C4–O1 1.198 (2), C5–S1 1.814(2), C5–S2 1.633(2), N3–C2–C1–C4 36.3; 8b: C1–C2 1.379(3), C2–C3 1.409(3), C1–C4 1.227(3), C4–S1 1.616(2), C2–C1–C4 166.4(2), C1–C4–S1 179.4(2). In the case of 7b, two molecules of CH_2Cl_2 are omitted for clarity.

Birum and Matthews in the chemistry of phosphorus ylides, but so far not characterized.⁶⁵ In a closed J-Young NMR tube, 7b releases quickly (~ 1 h) at room-temperature COS (13 C NMR 153.8 ppm; CD_2Cl_2) until an equilibrium (~3:1 7b:8b) is reached, indicating a reversibility in the presence of COS. Note, it is important to remove excess of CS₂ since 8b remains reactive. Upon removing COS under reduced pressure, the vinylidene thioketene can be obtained as a single species. Vinylidene thioketenes are rare compounds which have been derived from thiophosgene⁶⁶⁻⁶⁸ or by FVP.⁶⁹ In the ATR-IR, 8 features an intense band at 2035-2036 cm⁻¹ (8a; 8b). ¹³C labeling of 8a allows to assign C_{α} : 51.2 ppm and C_{β} : 140.4 ppm with ${}^{1}J({}^{13}C_{\alpha} - {}^{13}C_{\beta}) = 172$ Hz and ${}^{1}J({}^{13}C_{\alpha} - {}^{13}C_{\gamma}) = 122$ Hz. The NMR parameters are similar to the data obtained for vinylidene ketenimine 3a, supporting a significant triple-bond contribution. Additionally, we were able to obtain single crystals of 8b suitable for X-ray diffraction (Figure 7). Upon O/S exchange, the C-C-C bond angle widens from 147.5(1)° (O; 4b) to 166.4(2)° (S; 8b), while the C1-C4 distance shortens [1.236(2) Å (O; 4b); 1.227(3) Å (S; 8b)]. These data agree with a lower tendency of sulfur to form C=S double bonds and favor an alkyne representation 8' similar to the structural data for vinylidene ketenimine 3a.

CONCLUSION

In summary, we report a new stable diazoalkene class based on the dinitrogen transfer from N₂O to a 1,2,3-triazole derived mNHO. As such mNHOs are easily accessible and structurally variable, this finding opens up a simple synthetic access to a structurally rich class of diazoalkenes. We show that the exchange reaction of N₂ with ambiphilic compounds is not limited to isocyanides, but can also be performed at room temperature with CO. Computations suggest the mechanism proceeds through a nucleophilic activation of CO via a concerted mechanism under release of dinitrogen. The new type of substitution offers a mild and atom-economic synthetic approach to alkylidene ketenes. We present the first structural data of vinylidene ketenes, confirming their proposed structure to feature a zigzag conformation, and give an experimental comparison between the complete isoelectronic series $R_2C =$ C = X (X = N₂, CO, CNR, CS) including ¹J(¹³C-¹³C) data. The vinylidene thioketenes can be accessed by reaction of alkylidene ketenes with CS₂. We verified the mechanism takes place via a structural characterized four-membered thiete intermediate. Even though the spectral data of the new compounds indicate cumulenic character, it remains to be evaluated if the new substitution approach might also add additional insights into carbone chemistry. Previously, carbonbased ylidic compounds have been interpreted as coordination compounds.^{18,70} Considering that N₂, CO, and isocyanides belong to the archetypical ligands in transition-metal chemistry, the here described concept of ligand exchange might add a new dimension in the understanding of carbonbased "coordination" complexes, thereby mimicking transitionmetal reactivity. Importantly, the substitution with other small molecules should be applicable since no restriction to a cycloaddition mechanism is required. We believe the exchange of entities at a vinylidene carbon center opens a new atomeconomic synthetic approach to access novel unsaturated compounds, which we are currently further investigating.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c06906.

Experimental procedures, characterization data, and computational details (PDF)

Accession Codes

CCDC 2094184–2094190 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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All authors performed the experimental work. M.M.H. performed the calculations and wrote the manuscript. All authors have given approval to the final version of the manuscript.

Notes

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