Stable Ketenyl Anions via Ligand Exchange at an Anionic Carbon as Powerful Synthons

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Abstract: A (phosphino)diazomethyl anion salt **1** ([[P]−CN$_2$][K(18-C-6)(THF)]) ([P] = [(CH$_2$)(NDipp)]$_2$P; 18-C-6 = 18-crown-6) behaves as a (phosphino)carbyne anion-dinitrogen adduct ([P]−C$^-$←:N$_2$). Under an atmosphere of carbon monoxide (CO), **1** undergoes a facile N$_2$/CO ligand exchange reaction giving (phosphino)ketenyl anion salt [[P]−CCO][K(18-C-6)] **2**. Oxidation of **2** with elemental Se affords (selenophosphoryl)ketenyl anion salt ([P](Se)−CCO][K(18-C-6)]) **3**. These ketenyl anions feature a strongly bent geometry at the P-bound carbon and this carbon atom is highly nucleophilic. The electronic structure of **2** is examined by theoretical studies. Reactivity investigations demonstrate **2** as a versatile synthon for derivatives of ketene, enolate, acrylate and acrylimidate moieties.

Ketenes of the general formula R^{1}R^{2}C=C=O are widely used reagents in synthetic chemistry. Due to their polarized cumulated double bonds, ketenes are usually generated in situ as very reactive intermediates, which then ensue (cyclo)additions to provide access to carboxylic derivatives (i.e. acids, esters, anhydrides, amides), cyclobutenones, β-lactams and β-lactones.[1] Despite such utility, synthetic methods toward ketenes are limited and largely rely on transition metal (TM) reagents (e.g. metal carbenes).[2] The development of ketenyl anions/ynolates [RCCO]$^-$ (Figure 1a) represents an alternative available material leading to ketenes; however, these anions are generally unstable as well, generated at low temperatures (proposed as ynolates) and consumed as soon as they are produced in chemical syntheses.[3] Recently, low-temperature spectroscopic characterization of Me$_3$Si−C ≡ C−OK has been achieved.[4] Additionally, the group of Stephan spectroscopically characterized Ph$_2$P(S)C(Li(THF)$_2$)CO (**A**) at room temperature in a reaction mixture of dilithiomethandiide with CO and N$_2$O (Figure 1b).[5] During the preparation of this manuscript, Gessner showed an isolable ketenyl anion Ph$_2$P(S)C(K(18-C-6))CO (**B**) (18-C-6 = 18-crown-6) via an unprecedented phosphine/CO replacement reaction.[6] This breakthrough allowed the isolation of a series of ketene derivatives via facile ketenylations.
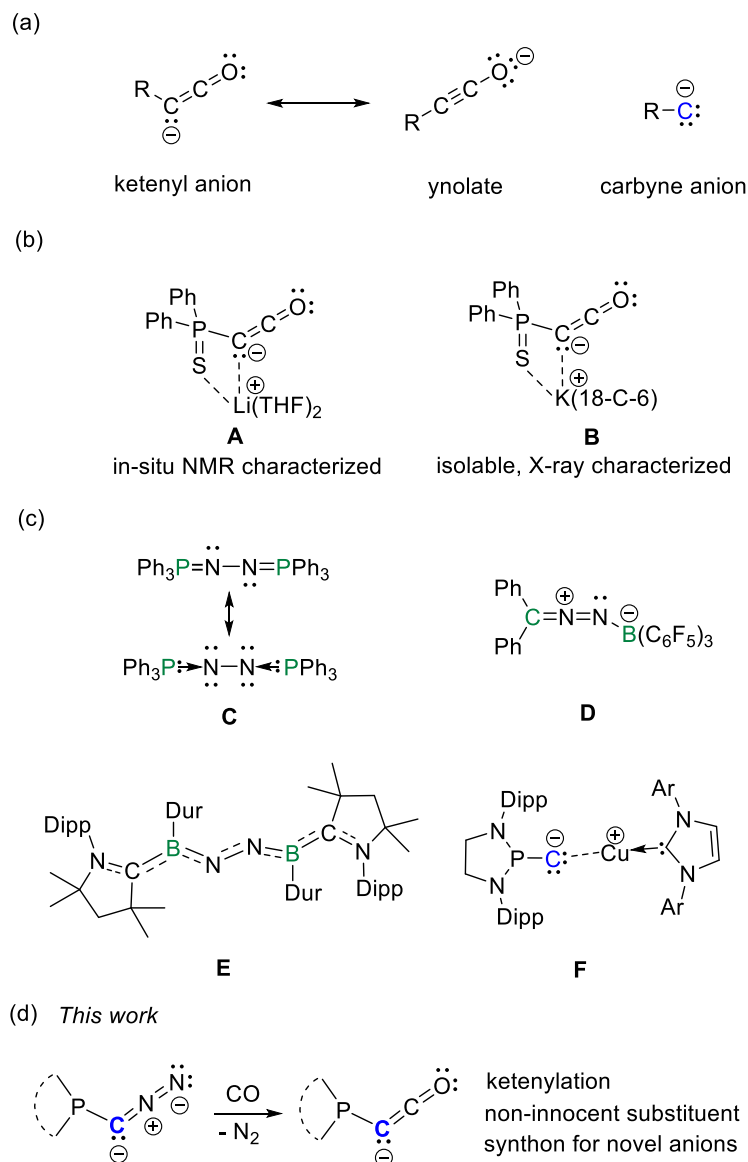
Figure 1. (a) Two major resonance structures of [RCCO]⁻ and representation of a carbyne anion. (b) Room-temperature-stable ketenyl anions **A** and **B**. (c) Main group element N_2 adducts **C-E** and an isolable carbyne anion complex **F**. (d) This work.

The articulation of the concept of "carbones" emerged in 2007 by Freaking from the perspective that an allene could be viewed as a carbon(0) atom supported by two ancillary ligands (L:→C←:L; L = N-heterocyclic carbene (NHC), phosphine, carbon monoxide).[7] Shortly afterward, a crystalline bent allene (Me₂-bimy:→C←:Me₂-bimy; Me₂-bimy = 1,3-di-methyl-benzimidazole-2-ylidene) was characterized by Bertrand,[8] while Robinson isolated a silicon complex (IDipp:→Si=Si←:IDipp; IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene).[9] These pioneering studies presented a strong analogy in the bonding scenario between TMs and main group elements and thus led to a paradigm shift in the area of main group chemistry.[10] In fact, the past few decades have continued to witness the emergence of a growing number of main group compounds that mimic the frontier orbitals of TMs and have the ability to react with small molecules in the same way, exemplified by heavier Group 14 dimetallynes and dimetallenes,[11] singlet carbenes and their analogs,[12] and

frustrated Lewis pairs (FLPs).[13]

Although ligands of N_2 and CO are pervasive in TM chemistry, the analogous chemistry based on main group elements has largely trailed behind.[10e, 14] In 2013, based on the "carbones" concept Freaking and Jones reinvestigated the bonding in $N_2(PPh_3)_2$ (**C**) and concluded that this compound is a donor-acceptor complex of dinitrogen ($Ph_3P: \rightarrow N_2 \leftarrow :PPh_3$) albeit it only releases N_2 above 215 °C (Figure 1c). Stephan demonstrated a diazomethane-borane adduct $Ph_2CN_2B(C_6F_5)_3$ (**D**) that serves as a model for FLP-N_2 chemistry.[15] It was not until 2017 that the borylene-N_2 adduct **E** was derived from a room-temperature activation of N_2 by the group of Braunschweig.[16] More recently, low-valent calcium compounds have exhibited the ability for N_2 complexation and reduction by the Harder[17] and Jones[18] groups. In a similar fashion, CO has been shown to form carbonyl complexes based on carbon,[19] boron,[20] phosphorus,[21] silicon[22] and alkaline earth metals.[23]

Ligand exchange reactions are one of the most prototypical reactions in TM chemistry. It has been documented that exchanges of the L-type ligand at low-valent main group elements, including carbenes,[24] vinylidenes,[25] borylenes,[20d] aluminylenes[26] and phosphinidenes,[21c] are feasible. Diazirinyl or diazomethyl anions eliminate N_2 to generate extremely reactive carbyne anions upon collision-activated dissociation in the gas phase.[27] Note, in the reverse sense diazomethyl anions can be considered as carbyne anionic-N_2 adducts. Murai proposed the generation of $Me_3Si-C\equiv C-OLi$ at -78°C from the carbonylation of the lithium trimethylsilyldiazamethylide.[3c] While free carbyne anions ($R-C^-$) (Figure 1a) are not isolable in the condensed phase, we have very recently tamed a (phosphino)carbyne anion in the coordination sphere of copper, namely **F** (Figure 1c).[28] These results prompted us to probe whether diazomethyl anions ($R-CN_2^-$) behave as carbyne anion-N_2 adducts ($R-C^- \leftarrow :N_2$) and hence undergo L-type ligand exchange reactions. In the present work, we report the isolation of stable ketenyl anions via a N_2/CO ligand exchange at a carbyne anion (Figure 1d). The facile access to these species provides a powerful synthetic platform for ketene derivatives and enolate, acrylate, and acrylimidate anions.
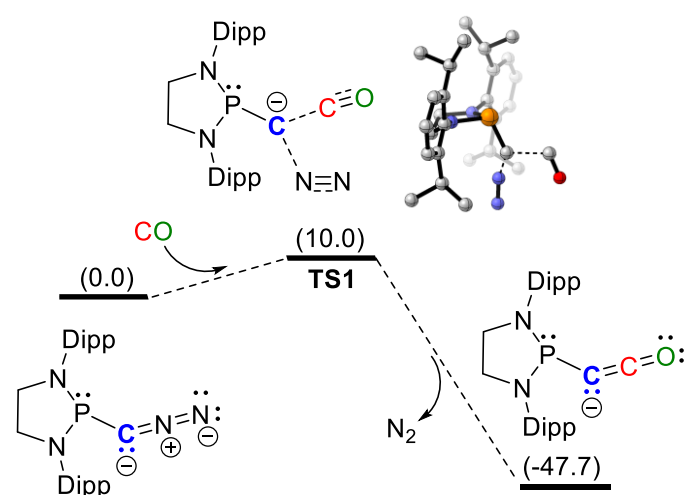

Figure 2. Free energy profile for the N_2/CO exchange reaction. Energies are given in kcal mol^{-1}.

Our computations on the model reaction of $[(CH_2)(NDipp)]_2P-CN_2^-$ with CO at the BP86/def2-SVP level of theory suggest a favorable associative N_2/CO exchange pathway (Figure 2), reminiscent of the N2/CO ligand exchange at a stable vinylidenes described by Hansmann.[25] This pathway involves a concerted transition state **TS1** (10.0 kcal mol^{-1}) of the ligand exchange at the

carbyne anion, leading to a phosphinoketenyl anion [(CH$_2$)(NDipp)]$_2$P−CCO$^-$ (-47.7 kcal mol^{-1}). Experimentally, exposure of a THF solution of ([(CH$_2$)(NDipp)]$_2$P−CN$_2$][K(18-C-6)(THF)])[28] (**1**) (^{31}P NMR: 136.2 ppm) to excess dry CO at room temperature cleanly led to a new species **2** within minutes (Figure 3a), as characterized by a new singlet resonance at 98.7 ppm in the ^{31}P NMR spectrum. As well, we observed the intensity loss of the infrared ν(CN$_2$) absorption of **1** (1920 cm^{-1}) and the appearance of the infrared ν(CCO) absorption of **2** (2047 cm^{-1}). After workup, species **2** was obtained in 93% yield as a pale-yellow solid. The ^{13}C NMR doublet signals of the ketenyl of **2** resonate at 36.2 ($^1J_{P-C}$ = 58.5 Hz) and 145.8 ppm ($^2J_{P-C}$ = 24.6 Hz) for C(1) and C(2), respectively. The C(1) resonance is strongly high-frequency shifted compared to those observed for **A** (5.8 ppm) and **B** (2.4 ppm), while the C(2) signal is slightly high-frequency shifted (136.4 ppm for **A** and 142.7 ppm for **B**).[5-6]
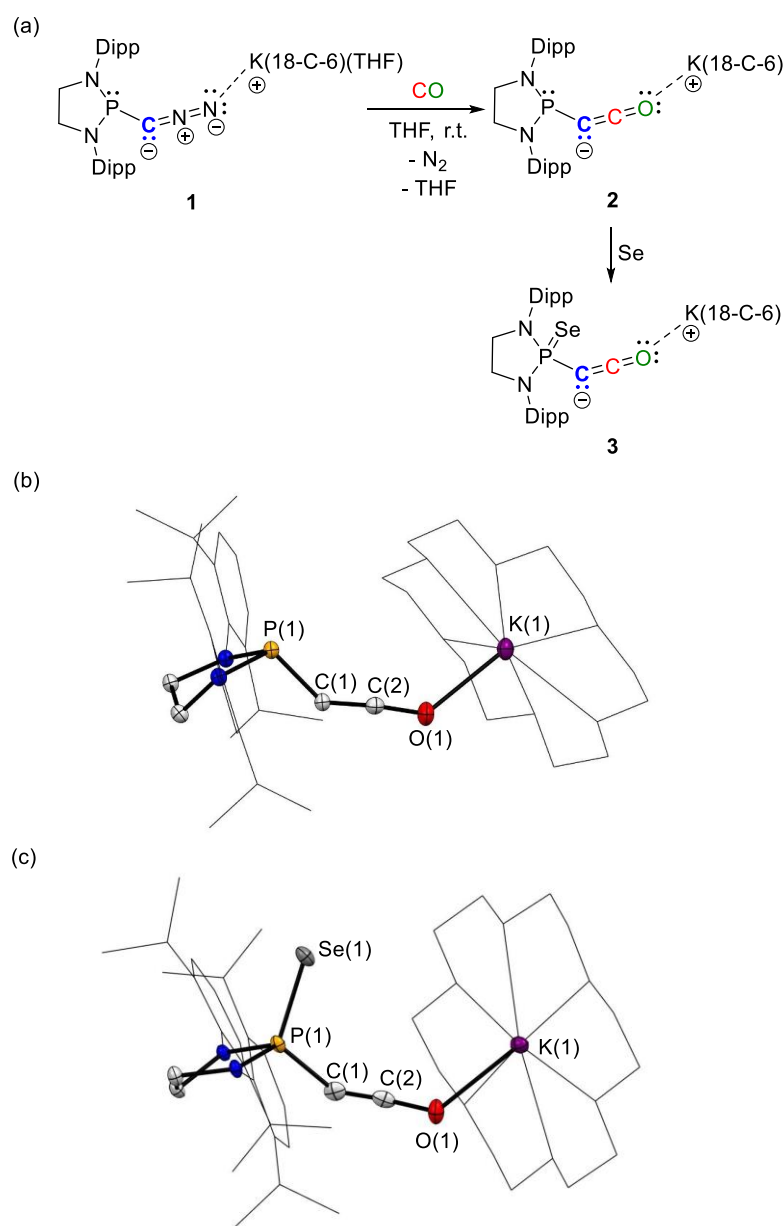

Figure 3. (a) Synthetic route toward **2** and **3**. (b) Solid-state structures of **2** (b) and **3** (c). Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set at the 40% probability level.

Slow evaporation of a concentrated dimethoxyethane solution of **2** at room temperature enabled the formation of single crystals, and the X-ray diffraction confirmed the formulation of **2** as [[(CH$_2$)(NDipp)]$_2$P−CCO][K(18-C-6)] (Figure 3b). The structural data for the PCCO unit are noteworthy, as they showed a distinctive bent geometry with the bond angle of P(1)–C(1)–C(2) at 138.6(1)° although K(1) is bound to the terminal O(1) atom rather than C(1). This angle is slightly acute relative to that of **B** (146.2(5)°) and deviates from straight angle by 33.8°, indicating that the ketenyl resonance form strongly contributes to the electronic structure of **2**. The angle of C(1)–C(2)–O(1) (174.9(1)°) is very comparable to that of **B** (174.5(11)°). According to the Pyykkö standard values,[29] the bond lengths of C(1)–C(2) (1.248(1) Å) and C(2)–O(1) (1.226(1) Å) lie between the corresponding double and triple bond, whereas the P(1)–C(1) bond length (1.739(1) Å) is found between the corresponding single and double bond. For comparison, the bond lengths of P(1)–C(1), C(1)–C(2) and C(2)–O(1) in **B** are 1.698(3), 1.178(8) and 1.226(1) Å, respectively.[6] It is notable that the [K(18-C-6)]$^+$ cation binds at C(1) in **B**, whereas in our case it is bound to O(1). This is attributed to the steric hindrance between two flanking Dipp substituents in the diazaphospholidinyl group and [K(18-C-6)]$^+$ as our calculations show the modeled [[(CH$_2$)(NDipp)]$_2$P−CCO][K(THF)$_2$] species energetically prefers the C(1)–K(THF)$_2$ isomer rather than the O(1)–K(THF)$_2$ by 1.8 kcal mol^{-1} (Figure S27).

We found that the phosphino group in **2** can be oxidized with elemental chalcogens. While an unidentified reaction mixture was detected upon reacting **2** with S$_8$, the analogous reaction with Se quantitatively gave **3** (^{31}P NMR: 30.1 ppm; ^{77}Se NMR: 40.3 ppm). An X-ray diffraction study revealed **3** to be a selenophosphoryl-ketenyl anion salt of [[(CH$_2$)(NDipp)]$_2$P(Se)−CCO][K(18-C-6)] with the CCO unit completely intact (Figure 2c). The solid-state structural parameters and ^{13}C NMR spectroscopic features are very close to those of **2**.
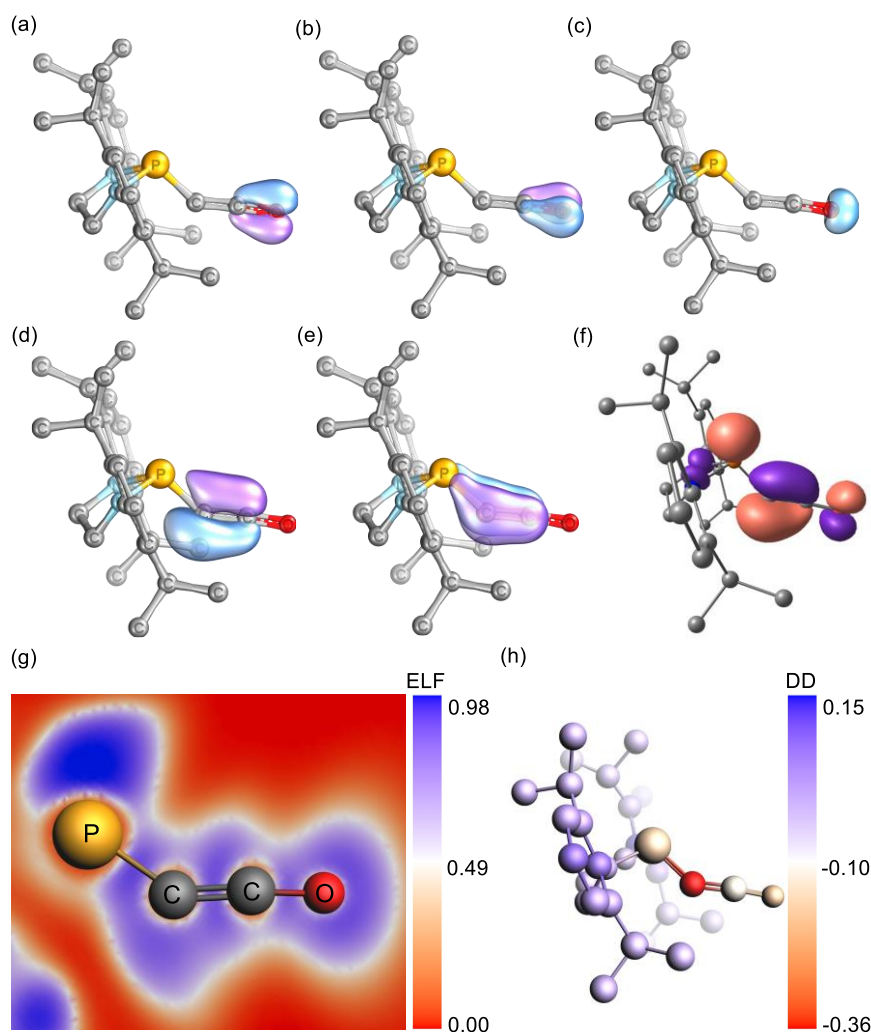
Figure 4. Depiction of selected IBOs and HOMO of the anion of **2**. (a-b) Polarized C(2)–O(1) π-bonding orbitals. (c) Lone-pair orbital at O(1). (d) Polarized C(1)–C(2) π-bonding orbital. (e) 3-center-2-electron π-bonding orbital over P(1)C(1)C(2) atoms. (f) HOMO. (g) ELF plot of the anion in the C(1)–C(2)–O(1) plane. (h) The condensed values of the dual descriptor that corresponds to the difference between FMO electron densities. Positive values correspond to atomic sites where electrophilicity is predominant, and negative values refer to atomic sites where nucleophilic tendencies dominate.

To further elucidate the unique bonding situation of the ketenyl anion, density functional theory (DFT) calculations at the BP86/def2-SVP level of theory were performed for the anion of **2** (Figure 4). The optimized structure correlates favorably with those determined by single-crystal X-ray diffraction analyses (Table S8). According to natural bond orbital (NBO) computations, a considerable amount of charge separation is revealed by NBO charges of P(1) (1.04 a.u.), C(1) (-0.94 a.u.), C(2) (0.51 a.u.) and O(1) (-0.57 a.u.). The Wiberg bond indices (WBIs) of P(1)–C(1), C(1)–C(2) and C(2)–O(1) are 1.17, 2.06 and 1.72, respectively. Analyses of intrinsic bond orbitals (IBOs)[30] show that, in addition to the P(1)–C(1), C(1)–C(2) and C(2)–O(1) σ-bonds (Figure S26), the ketenyl anion contains four polarized π-bonds (Figures 4a, 4b, 4d, 4e) and a lone pair of electrons at O(1) (Figure 4c). The in-plane C(1)–C(2) π-bond is polarized toward C(1) (Figure 4d), which exhibits to some extent a lone pair at C(1). This bond also contributes to the HOMO of the anion

(Figure 4f), responsible for its nucleophilic behavior at C(1) (vide infra). Indeed, electron localization function (ELF)[31] calculations clearly reveal strong localized electron density at P(1), C(1) and O(1) (Figure 4g), suggestive of the presence of lone pairs around these atoms. We then computed the dual descriptor (DD)[32] from conceptual DFT calculations. This provides that the DD value of C(1) (- 0.36) is the most negative (Figure 4h), indicating its predominant nucleophilic behavior.
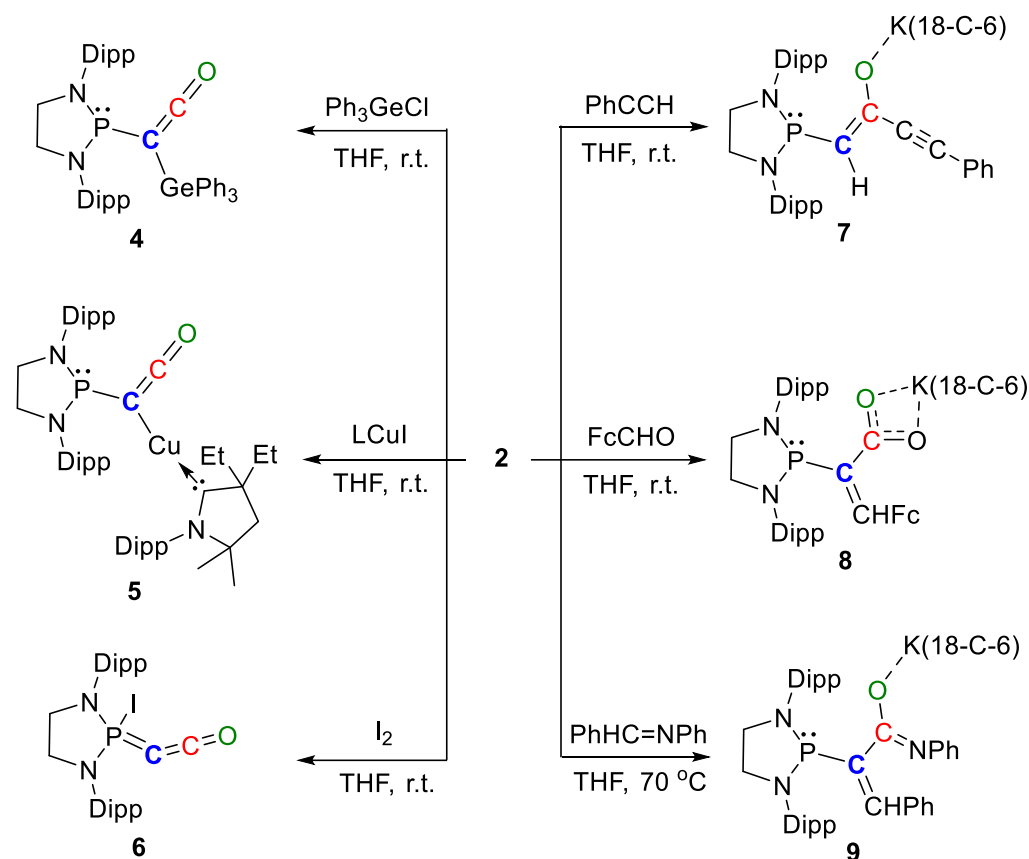

Figure 5. (a) Reactivity of **2** toward Ph₃GeCl, LCuI, I₂, PhC≡CH, FcCHO, and PhHC=NPh (L = cyclic (alkyl)(amino)carbene).

Next we unveiled species **2** as a powerful ketenylating reagent. Electrophiles including Ph₃GeCl and LCuI (L = cyclic (alkyl)(amino)carbene) were readily ketenylated to give a germanyl-substituted ketene **4** (³¹P NMR: 122.7 ppm) and a Cu-substituted ketene **5** (³¹P NMR: 103.7 ppm) (Figure 5), concurrent with the elimination of KCl and KI, respectively. Infrared spectroscopic studies of showed that ν(CCO) stretching frequencies of **4** (2055 cm⁻¹) and **5** (2011 cm⁻¹) are smaller in comparison to those of Ph₂CCO (2105 cm⁻¹)[33] and (ⁱPr₂N)(ᵗBu)CCO (2066 cm⁻¹).[19b] Furthermore, the structures of **4** and **5** in the solid state was determined by single crystal X-ray crystallography (Figures 6a and 6b). This analysis represents the first example of a crystallographically characterized germanyl-substituted ketene structure.[34] Even more remarkable is that Cu-substituted ketenes were hitherto unknown species. The facile access to **4** and **5** showcases the exciting ability of the ketenyl anion for constructing ketenes with previously uncharted substituents.

Interestingly, the reaction of **2** with I₂ gave rise to phosphoranylideneketene **6** within 5 min (³¹P

NMR: -45.4 ppm) (Figure 5). The pathway is likely via the migration of an iodine atom from the transient iodine-substituted ketene. Similar to the bent structure of $R_3P=C=C=O$ (R = Ph, Cy),[35] C(1) of **6** adopts a bent geometry with the bond angle of P(1)–C(1)–C(2) of 130.0(1)° (Figure 6b). This indicates the non-innocent behavior of the phosphino group during the ketenylation, paving a new way to accessing phosphacummulene ylides.
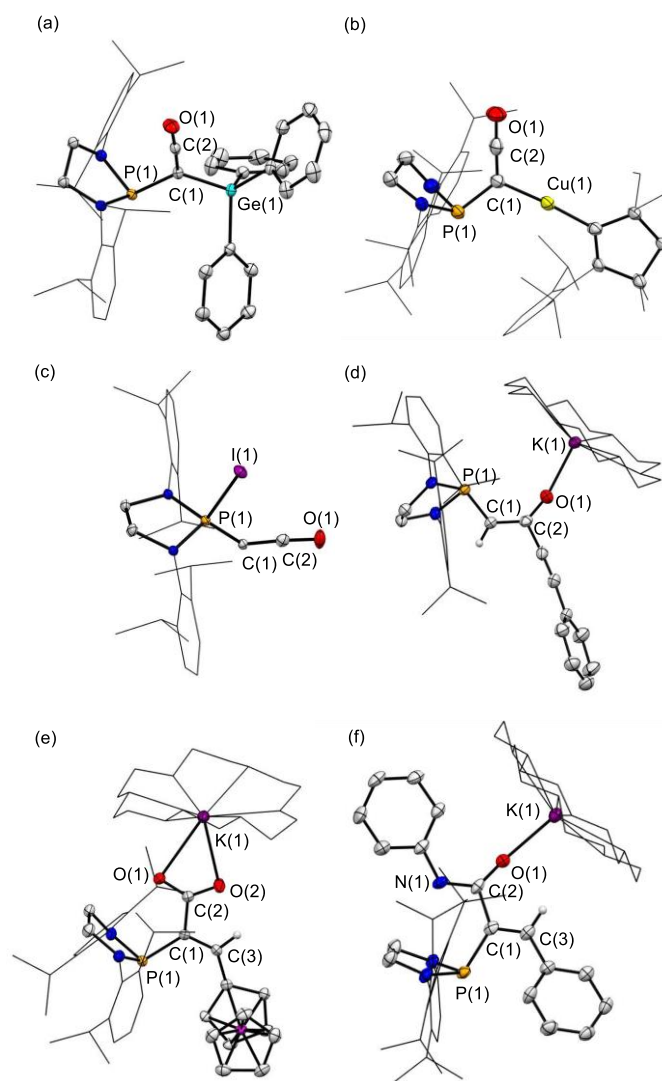

Figure 6. Solid-state structures of **4** (a), **5** (b), **6** (c), **7** (d), **8** (e) and **9** (f). Hydrogen atoms except C(1)–H of **7** and C(3)–H of **8** and **9** are omitted for clarity. Thermal ellipsoids are set at the 40% probability level.

We further investigated the likelihood of transforming the ketenyl anion to other functional groups. Stirring a room temperature THF solution of **2** with phenylacetylene led to consumption of the starting material within 5 min and formation of a new compound **7** (^{31}P NMR: 95.0 ppm; 78% yield), as indicated by the ^{31}P NMR spectroscopy. In the ^{1}H NMR spectrum of **7**, we observed a singlet in the alkene region at 5.52 ppm integrating for one proton. X-ray diffraction authenticated **7** to be a phenylethynylenolate salt (Figure 6c), generated via an apparent addition of phenylacetylene to the C(1)–C(2) unit of **2**. Next we treated **2** with FcCHO (Fc = ferrocenyl) at room temperature and the

reaction proceeded rapidly to give **8** (^{31}P NMR: 96.5 ppm) in 65 % yield. In the solid state, **8** was characterized to be a ferrocenylacrylate salt (Figure 6d). Remarkably, the aldehyde C=O double bond was completely cleaved during the transformation, concurrent with creation of a C=C and a C–O bond. In a similar vein, the reaction of **2** with PhCH=NPh at 70 °C ended up with the scission of the imine C=N double bond affording an acrylimidate salt **9** (^{31}P NMR: 99.2 ppm) in 64% yield (Figure 6e).

We have successfully isolated ketenyl anion salts **2** and **3** at ambient conditions through a synthetic method involving N$_2$/CO exchange at a phosphinocarbyne anion. These ketenyl anions featuring a highly bent PCCO unit exhibit high nucleophilic behavior at C(1), which allows facile ketenylation reactions with electrophiles. Significantly, this ketenyl anion's ability as a synthon for derivatives of enolate, acrylate and acrylimidate moieties was demonstrated. The utilization of diazomethyl anions as transfer reagents of carbyne anions for unusual main group compounds is under active investigation in our lab.

Notes
The authors declare no competing financial interest.

Keywords: Ketene; Ketenyl Anion; Ligand Exchange; Main Group Element; Carbyne Anion

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