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The lithium effect in ketenyl anion chemistry†

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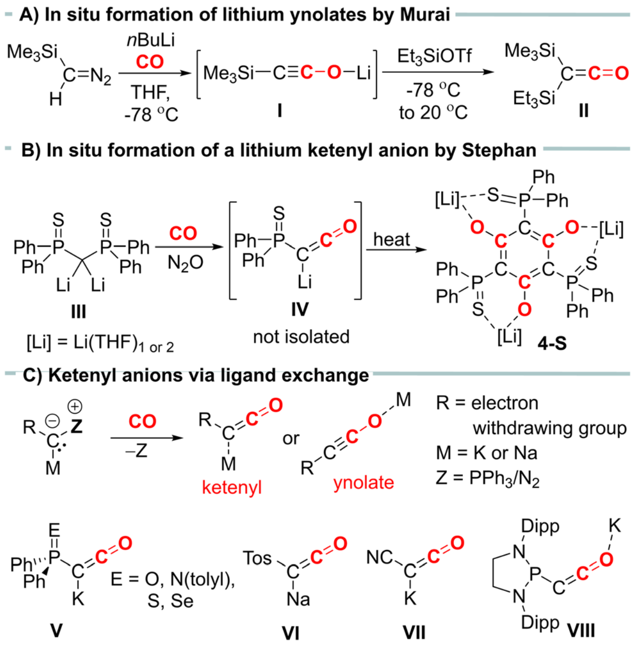
Ketenyl lithium compounds of type [RC(Li)CO] (with R = $Ph_2P(E)$, E = O, S, Se) were found to exhibit lower thermal stabilities than their potassium analogues due to the stronger coordination of the oxygen of the ketene moiety to the harder metal cation, resulting in a more pronounced ynolate character. Using additional ligands allows manipulation of the O–Li interaction, thereby influencing the stability and reactivity of the ketenyl anions.

Ketenes are important intermediates in synthetic organic chemistry, offering access to a variety of carbonyl containing compounds.[1] In general, ketenes are highly reactive species due to their polarized cumulated double bond.[2] Therefore, they are often generated *in situ* and directly converted to the desired products. Over the years, several synthetic methods to ketenes have been developed, including the Wolff rearrangement of diazoketones,[3] photolytic or pyrolytic reactions of suitable precursors,[4] or the carbonylation of carbenes or metal carbenes.[5] However, many of these methods have drawbacks, such as requiring harsh conditions or unstable starting materials, resulting in low yields and poor selectivity, or having limitations regarding substrate scope.

Ketenyl anions, $[RC{=}C{=}O]^-$, offer an alternative entry into ketene chemistry. In the past, these anions were synthesized by carbonylation of diazomethanides (*e.g.* **I**, Fig. 1A) and used without isolation.[6,7] Recently, we developed a novel synthetic route to ketenyl anions through a mild PPh_3/CO exchange at the ylidic carbon center in α-metalated ylides.[8,9] This method enabled the first isolation and structure elucidation of a ketenyl anion, revealing an intermediate bonding situation in the anion between the ketenyl and ynolate form (Fig. 1C). Using this synthetic pathway, we isolated the complete series of phosphinoyl-substituted ketenyl anions **V**,[10] the tosyl-ketenyl anion (**VI**),[11] and the cyano-substituted ketenyl anion (**VII**).[12] Furthermore, the Liu group reported the isolation of ketenyl anion **IIX** using the N_2/CO exchange in diazomethanides.[13]

Remarkably, all isolated ketenyl anions reported to date have had either sodium or potassium as counter cation. No lithium salt has been isolated yet.[14] In 2021, Stephan and coworkers reported the formation of $Li[Ph_2P(S)CCO]$ (**IV**) from the reaction of dilithiomethandiide **III** with CO and N_2O (Fig. 1B),[15] but in contrast to its potassium analogue **V**, it was unstable and cyclotrimerized to compound **4-S**. Thus, we became interested in understanding the effect of lithium on the stability of ketenyl anions. We recently demonstrated that changes in the electronegativity of the substituents at carbon affect the relative preference of the ynolate *versus*


A) In situ formation of lithium ynolates by Murai

B) In situ formation of a lithium ketenyl anion by Stephan

C) Ketenyl anions via ligand exchange

Fig. 1 (A) *In situ* formation of a lithium ynolate by carbonylation of metalated a diazomethane. (B) Formation of ketenyl anion from the reaction of a dilithiomethandiide with CO and N_2O or (C) *via* PPh_3/CO exchange and examples of isolated ketenyl anions.

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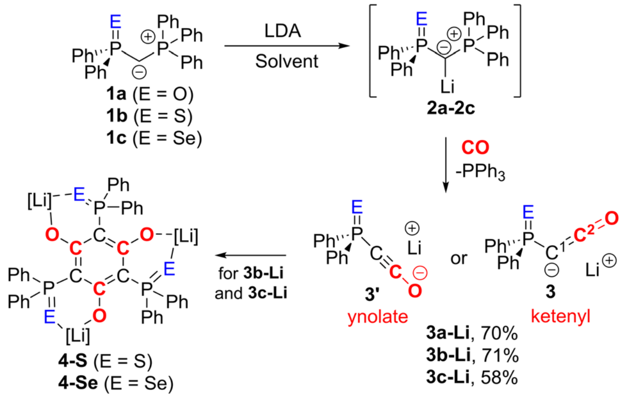

Scheme 1 Synthesis of yldiide **2**, ketenyl anion **3** and their decomposition products **4**. Solvent = toluene (for E = O), toluene/THF mixture (E = S, Se).

the ketenyl form.[10] Therefore, we hypothesized that a similar shift can be induced by the metal cation depending on the strength and site (C *versus* O) of the cation–anion interaction.

We began our investigations with the preparation of lithium yldiides **2** with different phosphinoyl moieties P═E (E = O, S, Se), the potassium analogues of which we have recently reported.[10] Lithium diisopropylamide (LDA) was found to be a suitable base to selectively generate the α-metalated ylides **2** (Scheme 1).[15] Due to their reactivity, yldiides **2** were not isolated but used as *in situ* prepared reagents. The formation of **2** was confirmed in each case by $^{31}P\{^1H\}$ NMR spectroscopy, which showed a significant high-field shift of the signal compared to the parent ylides **1** (see ESI†).[16] For **2b** and **2c**, few crystals suitable for X-ray diffraction (XRD) analysis were obtained by the slow diffusion of hexane into toluene/THF solutions, further confirming the successful metalation.

In the crystal, the metalated ylides **2b** and **2c** form centrosymmetric dimers, with the lithium cations being coordinated by the S and Se atom, respectively, the ylidic carbon atom, and an additional THF molecule (see Fig. 2 for **2b**, the ESI† for **2c**). In **2b**, the P–C distances (1.671(2) and 1.651(2) Å) are significantly shorter than in the ylide precursor (1.729(1) and 1.696(1) Å) due to increased electrostatic interactions within the P–C–P linkage upon metalation. A similar trend has been observed for the corresponding potassium compound with 18-crown-6.[17]

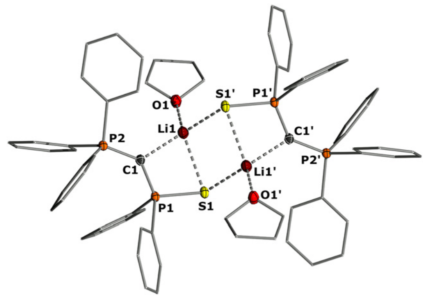

Fig. 2 Crystal structure of **2b** (ellipsoids at the 50% probability level, hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: P1–C1 1.671(2), P2–C1 1.651(2), P1–S1 2.030(1), C1–Li1 2.128(3), S1–Li1 2.558(3), P1–C1–P2 135.9(1).

Once the selective formation of the metalated ylides **2** was confirmed, we examined their reactivity towards CO and selected **2c** as first test system. Its reaction with CO in toluene/THF solution led to the selective formation of PPh_3, indicated by a signal at −5.26 ppm in the $^{31}P\{^1H\}$ NMR spectrum, and another species characterized by a signal at 5.57 ppm, which we assigned to the targeted lithium ketenyl **3c-Li**. **3c-Li** could be isolated as a colourless solid in 58% yield. The lithium ketenyl is further characterized by a doublet at 5.9 ppm with $^1J_{PC}$ coupling constant of 184.9 Hz for the C1 carbon atom and another doublet at 139.8 ppm with $^2J_{PC}$ coupling constant of 45.0 Hz for the C2 carbon atom in $^{13}C\{^1H\}$ NMR spectrum (Table 1). The larger J_{PC} coupling constants of the C1 and C2 carbon atom compared to those in the potassium analogue **3c-K** (164.0 and 39.0 Hz) indicate a larger P–C–C angle and the preference for the ynolate form in **3c-Li** relative to **3c-K.**[18]

Interestingly, lithium ketenyl **3c-Li** was found to be unstable in solution. At room temperature, a THF solution converted to a new compound within a few days. This compound was identified as the hexa-substituted benzene derivative **4-Se**, formed by trimerization of the ketenyl anion (see ESI†). This trimerization is consistent with the observation made by the Stephan group (Fig. 1B) but contrasts the stability of the potassium analogue of **IV**, which showed no analogous trimerization reaction at room temperature.[15]

Given the lower stability of the lithium salt **3c-Li** relative to its potassium salt **3c-K**, we next evaluated whether this was a general trend. To this end, the lithium ketenyls **3a-Li** and **3b-Li** were isolated as colourless solids in high yields of over 70% after stirring of the metalated ylide in toluene/THF solution under 1 atm. of CO overnight (Scheme 1). Like the selenide, **3a-Li** and **3b-Li** show two characteristic doublets in the $^{13}C\{^1H\}$ NMR spectrum for the C1 and C2 carbon atom, with $^1J_{PC}$ and $^2J_{PC}$ coupling constants larger than those observed for the corresponding potassium compounds (Table 1). Thus, the oxide and the sulfide confirm the trend observed for the selenide, further suggesting that the lithium compounds exhibit a more pronounced ynolate character. Nonetheless, **3b-Li** was found to be surprisingly stable in THF solution at room temperature, but it began to trimerize to **4-S** when heated to 70 °C. Full conversion was observed after 7 days (Fig. 3). The phosphine oxide **3a-Li** demonstrated even greater stability. After heating a THF solution of **3a-Li** at 70 °C for 2 weeks, no noticeable changes were observed in the $^{31}P\{^1H\}$ NMR spectrum. These observations suggest that increased ynolate character generally decreases the stability of the lithium compounds, but this trend varies with different substituents. According to the J_{PC} coupling constants, the ynolate

Table 1 NMR spectroscopic data of the lithium salts of the ketenyl anions compared with their potassium salts. NMR Shifts are given in ppm and coupling constants in Hz

	3a-Li	3a-K	3b-Li	3b-K	3c-Li	3c-K
$\delta(P)$	12.3	13.2	21.6	22.5	5.6	6.2
$\delta(C1)$	2.3	3.1	6.7	2.4	5.9	2.5
$^1J_{PC}$	218.3	210.0	193.8	175.0	184.9	164.0
$\delta(C2)$	141.9	140.8	138.3	142.7	139.8	143.9
$^2J_{PC}$	48.8	47.5	46.0	40.7	45.0	39.0

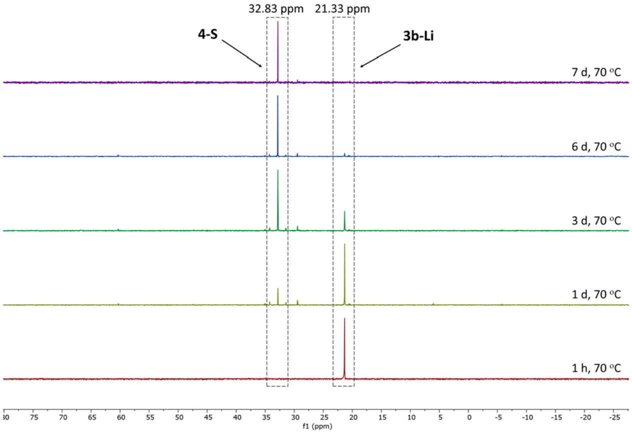

Fig. 3 Monitoring of the conversion of **3b-Li** into **4-S** by ^{31}P{^{1}H} NMR spectroscopy in THF-d$_8$ at 70 °C.

character increases from the phosphine selenide to the oxide, yet the stability increases in the same order. We assumed that this contradictory trend is due to lithium binding to both the ketenyl and the phosphinoyl moiety. The strength of the E–Li interaction increases with the hardness of the donor (O > S > Se), leading to a greater electron density shift towards the Group 16 element. Thus, the J_{PC} coupling constant increases due to a stronger C–P(E) bond, rather than an increased ynolate character.

To gain structural insights into the ketenyl lithium compounds, we attempted to obtain single crystals for XRD analysis. Suitable crystals of **3a-Li** were grown by slow diffusion of hexane into a saturated toluene/THF solution (Fig. 4, top). In the solid state, **3a-Li** forms a polymeric structure with a Li_2O_2 four-membered ring as central structural motif.[19] The lithium ions are each coordinated by the phosphinoyl moiety of two molecules of **3a**, the ketenyl oxygen of two neighboring molecules and an additional THF molecule. No contact to the ketenyl C1 carbon atom is observed. The C1–C2 bond in the ketene moiety is slightly shorter (~1.230 Å) and C–O bond (~1.214 Å) is slightly longer than in the potassium salt **3a-K** with [2,2,2]-cryptand (1.240 Å for C1–C2 and 1.212 Å for C2–O), indicating a stronger contribution of the ynolate form **3′** in the lithium salt as suggested by the J_{PC} coupling constants.[10] Accordingly, the P–C–C angle (~160.5°) in **3a-Li** is also larger than in the potassium salt (148.9°), almost approaching linearity.

Since we could not obtain suitable crystals for the THF complexes of **3b-Li** and **3c-Li**, we isolated the lithium salts **3** with PMDETA (*N*,*N*,*N′*,*N″N″*-pentamethyldiethylenetriamine)[20] as additional ligand to gain further information about the coordination chemistry of the lithium ketenyls.[21] We hypothesized that the coordination of PMDETA would weaken the O–Li interaction and thereby increase stability. Stirring of the α-metalated ylides **2** with 1 eq. of PMDETA in toluene/THF solvent under an atmosphere of CO led to the precipitation of the corresponding complexes **3-Li**(PMDETA), which were isolated as colourless solids in moderate to good yields (see the ESI†). In contrast to the THF complexes, all PMDETA complexes turned out to be stable and did not trimerize to the corresponding benzene derivatives **4**, demonstrating the advantageous influence of the ligand on stability. Single crystals of **3c-Li**(PMDETA) were obtained by slow diffusion of hexane into a toluene/THF solution at −30 °C. In the solid-state, **3c-Li**(PMDETA) forms a centrosymmetric dimer with the lithium cations coordinated by PMDETA and the oxygen of the ketenyl moiety (Fig. 4, bottom). The C–C and C–O bond lengths in the ketene moiety (1.243(8) and 1.222(7) Å) slightly change towards the values of the free anion (1.244(5) and 1.207(4) Å),[10] indicating that the additional ligand weakens the O–Li interaction, thereby increasing the ketenyl character in C–C–O moiety and enhancing its stability.

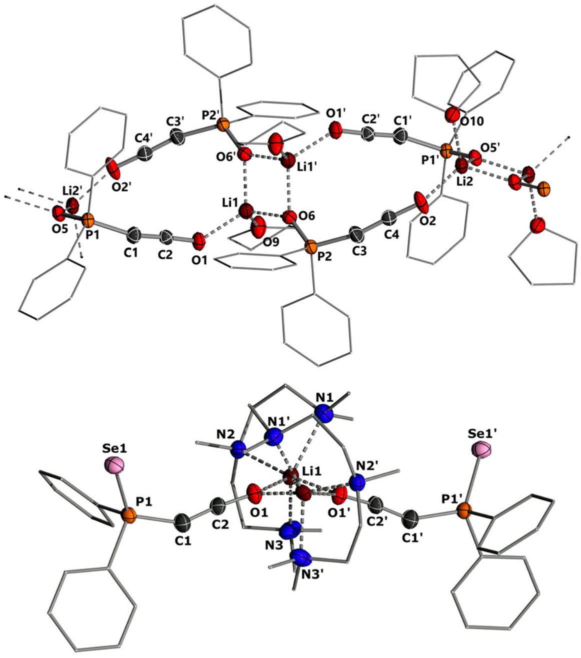

Fig. 4 Crystal structure of (top) **3a-Li** and (bottom) **3c-Li(PMDETA)**. Ellipsoids are drawn at the 50% probability level. Important bond lengths [Å] and angles [°]: 3a-Li: P1–C1 1.677(4), C1–C2 1.230(6), C2–O1 1.216(5), P1–O1 1.510(3), P1–C1–C2 161.9(4), C1–C2–O1 176.7(5), P2–C3 1.673(4), C3–C4 1.231(6), C4–O2 1.206(5), P2–O6 1.509(3), P2–C3–C4 162.4(4), C1–C2–O1 176.7(5). 3c-Li(PMDETA): P1–Se1 2.132(1), P1–C1 1.698(6), C1–C2 1.243(8), C2–O1 1.222(7), O1–Li1 2.069(10), P1–C1–C2 147.8(5), C1–C2–O1 173.9(6).

Given that the structural changes are minimal, we aimed to further confirm that the strength of the lithium–oxygen interaction affects the bonding situation by examining the IR vibration of the C═C═O group. Generally, the IR stretch of ketenyl anions falls between those of ketenes and alkynyl ethers,[22] with the vibration of ketenes (*e.g.*, 2080 cm^{-1} for $(SiR_3)(PhCH_2CH_2)C{=}C{=}O$) appearing distinctly red-shifted compared to those of alkynyl ethers (*e.g.*, 2280 cm^{-1} for $PhCH_2CH_2\text{–}C{\equiv}C\text{–}OSiMe_3$).[23,24] Thus, the C═C═O stretch is highly diagnostic for determining the ketenyl and ynolate character. IR measurements of anions **3-Li**, with and without PMDETA, were performed in the solid state as well as in THF solution to exclude solid-state effects (Table 2). In solid state, the lithium ketenyls without PMDETA exhibit stretching frequencies higher than 2125 cm^{-1}. In contrast, their potassium analogues show frequencies lower than 2100 cm^{-1}, thus corroborating with a more pronounced ynolate character of the lithium ketenyls. In addition, the value for the phosphine oxide **3a-Li** is lower than

Table 2 IR stretching frequencies of the ketenyl moiety in the lithium ketenyl complexes **3** with and without PMDETA (in cm^{-1})

	Solid state		THF solution	
	Ligand-free	+PMDETA	Ligand-free	+PMDETA
3a-Li	2129.83	2109.72	2093.91	2093.92
3b-Li	2142.03	2103.26	2126.31	2125.52
3c-Li	2138.44	2098.23	2124.80	2124.08

those of the sulfide (**3b-Li**) and selenide (**3c-Li**), corroborating with its higher stability. The stretching frequencies of **3-Li** with PMDETA are lower than those without it, corroborating with a shift towards increased ketenyl character and the enhanced stability of the ketenyl anions in presence of the additional ligand. In THF solution, the frequencies were found to be independent of the presence or absence of the PMDETA ligand, likely due to decreased cation–anion interactions in the coordinating THF solvent.

In conclusion, we have isolated lithium salts of phosphinoyl-substituted ketenyl anions through carbonylation of lithium yldiides through elimination of PPh_3. These lithium ketenyl anions are less thermally stable towards trimerization than their potassium analogues. NMR and IR spectroscopy as well as crystallographic studies showed that this lower stability is accompanied by lithium's preferential coordination by the oxygen atom of the ketene moiety. This coordination favours the ynolate character, indicated by larger coupling constants, blue-shifted C–C–O vibrations, and shorter C–C bonds. The bonding situation can be further influenced by using an additional ligand like PMDETA, weakening the Li–O interaction. These findings highlight the flexibility of the bonding situation in ketenyl anions, which can be regulated through ion-pairing. These effects decisively impact the stability of the anions and can be utilized for reactivity control essential for future applications.

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Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts of interest.

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