


 Cite this: *Chem. Commun.*, 2025, 61, 752

 Received 4th September 2024,
Accepted 1st December 2024

DOI: 10.1039/d4cc04562a

rsc.li/chemcomm

Synthesis of cerium ylidiide complexes and their reactivity with CO is demonstrated. In the case of the sulphur-tethered ylidiide, the ketenyl complex is formed with release of PPh₃, while Ph₃PCCO is formed along with a sulfinato ligand in the case of the tosyl-substituted ylidiide. Computational analysis shows that this diverging reactivity is due to the stability of the two isomers in the first step of each mechanism.

Metalated ylides, also known as ylidiides (Fig. 1), have emerged as an interesting class of reagents and ligands, with applications ranging from the generation of highly efficient phosphines for applications in transition metal catalysis to the stabilization of unusual bonding situations.^{1–3} In addition, ylidiides have demonstrated remarkable reactivity with small molecules, affording rare moieties and reagents.^{4,5} For example, exchange of the phosphine group in ylidiides with CO produces ketenyl anions, which can be further functionalized with other substrates to ketenes as well as other carbonyl-containing compounds. Ketenyl anions have often been proposed as intermediates and although there has been a resurgence in recent years,^{6–9} they remain a rare functional moiety,^{10–13} making their structural characterization crucial for gaining further insights into their reactivity patterns.

The selectivity of the PPh₃/CO exchange in ylidiides was found to depend on the nature of the alkali metal.¹⁴ This dependency was attributed to the different coordination chemistry of the metal cations in the decisive intermediates, but no intermediate structures could be identified. The metal dependency suggests that carbonylation in the coordinating sphere of other metals in the periodic table could offer an additional

Cerium(III) ylidiide complexes with divergent CO reactivity†

 Alexander J. Gremillion,^a Hemant Kumar,^a Iker Del Rosal,^b Steven P. Kelley,^{id a}
Laurent Maron,^{id *b} Viktoria H. Gessner,^{id *c} and Justin R. Walensky,^{id *a}

means for selectivity control and might provide further insights into the underlying mechanism. Given the similarities in bonding between the s-block metals and lanthanides, we turned our attention toward the rare earth metals.

Small molecule activation with organolanthanide complexes has been an active area of interest due to their ability to even transform relatively challenging molecules such as CO.¹⁵ While ketene-type ligands are known in f element chemistry, these are rare and have always been stabilized by a carboxylate group forming a ketene carboxylate.^{16–21} We selected cerium as first test system, as Ce(III) typically forms coloured compounds, often facilitating reaction monitoring. Additionally, due to its high oxophilicity, we speculated that it would result in further interactions with the carbonyl oxygen. Herein, we report the synthesis of two cerium(III) ylidiide complexes, [(C₅Me₅)₂Ce{C(PPh₃)(R)}], R = P(S)Ph₂, SO₂(4-CH₃C₆H₄), from the salt metathesis reactions of [(C₅Me₅)₂CeCl₂K(THF)] with the corresponding potassium ylidiides. These ylidiides react with CO to form, in the case of R = SPPH₂, a ketenyl anion with concomitant release of PPh₃, or a sulfinato complex with release of Bestmann's ylide, Ph₃P=C=C=O (Scheme 1).

Treatment of [(C₅Me₅)₂CeCl₂K(THF)₂] with [K{C(PPh₃)(R)}], yields the corresponding cerium(III) ylidiides, [(C₅Me₅)₂Ce{C(PPh₃)(R)}] (R = P(S)Ph₂, **1**; SO₂(4-CH₃C₆H₄), **2**), with a colour change from yellow to bright red/pink observed in both reactions. Both **1** and **2** can be isolated in good crystalline yields of 73% and 82%, respectively.

The solid-state structure of **1** and **2** were determined by X-ray crystallography (Fig. 2), each being monomeric and having pseudo-tetrahedral geometries with two (C₅Me₅)^{1–} ligands

^a Department of Chemistry, University of Missouri, Columbia, MO 65211, USA.

E-mail: walenskyj@missouri.edu

^b Université de Toulouse and CNRS, INSA, UPS, CNRS, UMR 5212, Toulouse 31077,

France. E-mail: Laurent.maron@irsamc.ups-tlse.fr

^c Faculty of Chemistry and Biochemistry, Ruhr-University Bochum, 44801 Bochum,

Germany. E-mail: viktorija.gessner@rub.de

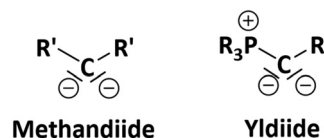
 † Electronic supplementary information (ESI) available. CCDC 2362374–2362377 and 2394687. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4cc04562a>


Fig. 1 ChemDraw showing methandiide versus ylidiide ligands.





Scheme 1 Synthesis of cerium metallated ylide complexes **1** and **2** (top) and divergent reactivity with CO (bottom).

and a bidentate ylide coordinated through the ylidic carbon and either sulphur (in **1**) or oxygen (in **2**). Organocerium(III) compounds with Ce–C (σ bonds) are relatively rare,^{22–32} and the Ce–C (ylidic) bond lengths in **1** and **2** are long at 2.623(2) and 2.597(3) Å, respectively. These distances can be compared to Ce(III)–C (alkyl) complexes such as the 2.50(2)–2.54(2) Å in $[\text{Ce}(\text{Bu}_4)][\text{Li}(\text{THF})_4]$,³³ 2.600(2)–2.614(2) Å in $\text{Ce}(\text{CH}_2\text{Ph})_3(\text{THF})_3$, 2.577(4) Å or 2.584(4) Å in $[(\text{C}_5^t\text{Bu}_3\text{H}_2)_2\text{Ce}(\text{CH}_2\text{Ph})]$ (two molecules in the asymmetric unit),³⁴ and 2.535(5) Å in $[(\text{C}_5\text{Me}_5)_2\text{Ce}\{\text{C}(\text{H})\text{-(SiMe}_3)_2\}]$. A few Ce(III)–C(aryl) bonds have been reported at distances of 2.5574(17) Å and 2.563(3) Å in $[(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Ce}(\kappa^2\text{-ortho-oxazoline})]$ and $[\text{Li}(\text{DME})_3][(\text{C}_5\text{Me}_5)_2\text{Ce}(\text{biphenyl})]$,²² respectively. The Ce–S distance in **1** is 2.8775(6) Å, much longer than cerium(III)–thiolate distances in $[\text{Ce}(\text{SMes}^*)_3]$, $\text{Mes}^* = 2,4,6\text{-}^t\text{Bu}_3\text{C}_6\text{H}_2$, which range from 2.703(4)–2.744(4) Å,³⁵ but similar to the 2.8567(17)–3.0381(19) Å in $[\text{Ce}(\text{THF})_3(\text{SC}_6\text{F}_5)_3]_2$,³⁶ but this is also a dimer in the solid-state so Ce–S distances are expectedly longer.

The ^1H NMR and UV-vis spectra of **1** and **2** show similar features as expected given the similar coordination environment. In **1**, two ^{31}P NMR resonances are observed at –25.4 and –96.6 ppm, while the ^{31}P NMR signal for **2** is seen at 2.86 ppm. Unfortunately, similar to other Ce(III) complexes,³⁰ we also could not observe the ylidic carbon in the ^{13}C NMR spectrum.

With **1** and **2** in hand, treatment with 1 atm CO was conducted with each. Both reactions require approx. 12 hours for completion at room temperature. In the case of **1**, the

growth of a signal corresponding to PPh_3 (–5.31 ppm, Fig. S18, ESI[†]) in the ^{31}P NMR spectrum as well as another resonance at 21 ppm for the Ce complex was observed. The solid-state structure of **1** with CO revealed a ketenyl product, $[(\text{C}_5\text{Me}_5)_2\text{Ce}\{\text{C}(\text{CO})\{\text{P}(\text{S})\text{Ph}_2\}\}]_2$ (**3**) which forms a dimer in the solid-state (Fig. 2) in 70% crystalline yield. Further, the infrared spectrum of **3** showed a characteristic C=C=O stretching vibration at 2088 cm^{-1} .³⁷ The Ce–C(ketenyl) distance in **3** is 2.851(6) Å, which is longer than the sum of the covalent radii of 2.77 Å, presumably due to the dimeric structure in the solid-state. Therefore, these Ce–C bonds in **1**, **2**, and **3** are some of the longest reported. The Ce–S1 distance of 2.988(6) Å and Ce–O1 distance of 2.531(4) Å are in the expected range for a dimer. The C1–C2 distance of 1.241(6) Å is longer than the one observed in the potassium ketenyl (1.178(8) Å), while the C1–O1 distance of 1.206(5) Å is slightly shorter (*cf.* 1.248(8) Å).⁵

In contrast to **1**, the carbonylation of **2** does not result in the formation of PPh_3 but in a compound characterized by a signal at 2.86 ppm in the ^{31}P NMR spectrum. X-ray crystallography of crystals obtained from the reaction mixture revealed the formation of complex $[(\text{C}_5\text{Me}_5)_2\text{Ce}(\mu\text{:}\kappa^1\text{-O}_2\text{S-4-MeC}_6\text{H}_4)]_2$ (**4**) with a bridging sulfinato ligand (Fig. S24, ESI[†]). This is consistent with the ^{31}P NMR chemical shift at 2.86 ppm which is assigned to Bestmann's ylide, $\text{Ph}_3\text{P}=\text{C}=\text{C}=\text{O}$.³⁸ Similar reactivity has been observed with the lithium ylide producing mostly Ph_3PCCO , while the Na and K form yielded the ketenyl anion as the major product.⁸ In nearly all carbonylation reactions of the alkali metal ylides, both the phosphaketanyl, Ph_3PCCO , and ketenyl moieties were observed, while we only observed formation of **4** in the case of Ce, which we could isolate in a 65% yield. We note that the UV-vis spectra for **4** does not display a band around 540 nm which is observed in both **1** and **2**, which suggests that this absorption is due to the ylide ligand.

To gain insights into the reaction of complexes **1** and **2** with CO density functional theory (DFT) calculations (B3PW91) calculations were carried out. For clarity, structures of all computed intermediates and transition states along with the charges and WBI are available in the ESI[†] (Fig. S25 and S26). In the case of the complex **2** (Fig. 3, left), the formation of a ketenyl complex (not experimentally observed) was also considered for



Fig. 2 Molecular structure of **1** (left), **2** (middle), and **3** (right) shown at the 50% probability level. The hydrogen atoms have been omitted for clarity.



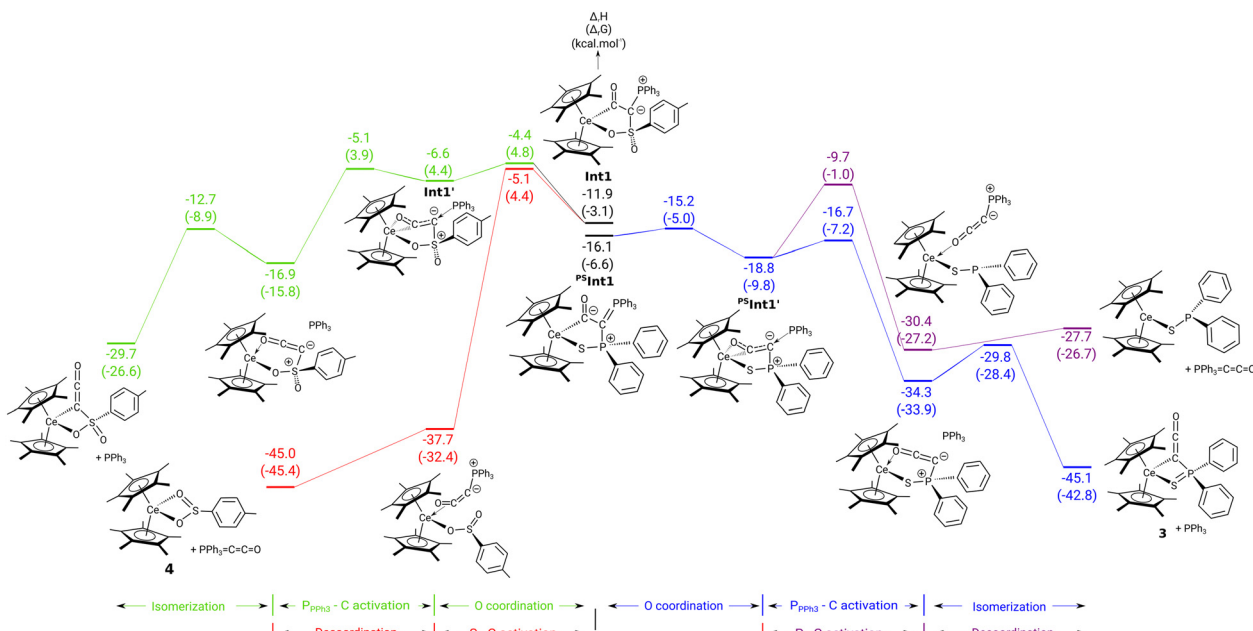


Fig. 3 Computed enthalpy (kcal mol^{-1}) profile for the transformation of complex **1** to **3** (right) and **2** to **4** (left) upon CO addition.

comparison. For the formation of both complexes, the reaction of **2** begins in the same way that is the CO insertion into the Ce–C bond. This readily occurs with a low activation barrier ($4.6 \text{ kcal mol}^{-1}$) in line with a facile $[2\sigma+2\pi]$ metathesis reaction. Following the intrinsic reaction coordinate, it yields a thermodynamically stable ketenyl type intermediate ($-11.9 \text{ kcal mol}^{-1}$). This intermediate possesses two isomers, shown in the middle of Fig. 3. In these isomers, the ketenyl moiety binds to the metal through the C1 carbon atom (**Int1**) or through both the C1 carbon and oxygen atom (**Int1'**). Although kinetically facile (barrier of $7.5 \text{ kcal mol}^{-1}$), the O-bonded isomer **Int1'** is less stable than the non-bonded one **Int1** by $5.3 \text{ kcal mol}^{-1}$. Interestingly, the two competing reactions start from the most stable intermediate **Int1** (blue and black in Fig. 3, left). As can be seen, the two pathways (S–C versus P–C bond breaking) are in kinetic competition (barrier difference of $0.7 \text{ kcal mol}^{-1}$ favouring the formation of the sulfinato complex **4**). However, there is a clear thermodynamic preference for the formation of **4**, which confirms its exclusive formation in the experiment. The similar barriers for the two reactions are explained by the Wiberg bond indexes (WBI) in the **Int1** that are similar for the P–C and S–C bonds (0.98–0.99).

The situation is different for the reaction of **1** with CO (Fig. 3, right). In this case, the CO-bonded isomer of the ketenyl intermediate (**PSInt1'**) is energetically favoured (-18.8 vs. $-16.1 \text{ kcal mol}^{-1}$) with a low activation barrier of isomerization ($0.9 \text{ kcal mol}^{-1}$). As observed for **2**, the two competing reactions (P–C vs. S–C activation) start from the most stable isomer **PSInt1'**. In case of the thiophosphinoyl system, the P–C bond breaking pathway (black lines in Fig. 3) is predicted to be both kinetically and thermodynamically favoured over the S–C bond cleavage (blue lines on Fig. 3, right). This can be attributed to the already strong P–C bond

activation in the O-bonded intermediate **PSInt1'** reflected by a low WBI(P–C) of only 0.59 similar to the one found in the transition state. P–C cleavage finally yields the ketenyl complex **3**.

The difference of reactivity between **1** and **2** is therefore attributed to the difference of stability of the two isomers after CO insertion. In the case of **1**, the presence of the weak sulphur donor atom makes the O-bonded isomer the most stable, while the stronger oxygen donor in **2** inverts the situation, making the C-bonded isomer more stable.

In summary, we have isolated Ce(III) complexes with two different ylide ligands, each exhibiting long cerium–carbon bonds. These distances are reminiscent of sterically crowded complexes with f elements, indicating no double bond character. Both complexes display divergent reactivity when treated with CO, one forming a rare ketenyl complex along with PPh_3 , while the other one eliminates the ylide moiety, forming Ph_3PCCO and a cerium sulfinato complex. Calculations reveal that this diverging reactivity is due to two competing coordination modes in the intermediate ketene complex, which depend on the binding strength of the second donor (sulfonyl or thiophosphinoyl). The stronger coordination of the sulfonyl group prevents the binding *via* the oxygen of the ketene moiety and thus results in the elimination of Ph_3PCCO . These findings explain why both the alkali metal ylides previously reported and the cerium complexes presented here show divergent reactivity with CO. This adds to the limited organocerium(III) chemistry, which we are continuing to investigate with these unusual metalated ylide ligands.

This project was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy – EXC-2033-390677874-RESOLV. J. R. W. gratefully acknowledge the Alexander von Humboldt Foundation for the



award of a research fellowship and the U.S. Department of Energy, Office of Basic Energy Sciences, Heavy Element Program under Award DE-SC0021273. L. M. is a senior member of the Institut Universitaire de France and acknowledge the HPCs CALcul en Midi-Pyrénées (CALMIP-EOS-grant 1415).

Data availability

The dataset supporting this article have been uploaded as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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