Applications of Low-valent Transition Metalates: Development of a Reactive Non-carbonyl Rhenium(I) Anion

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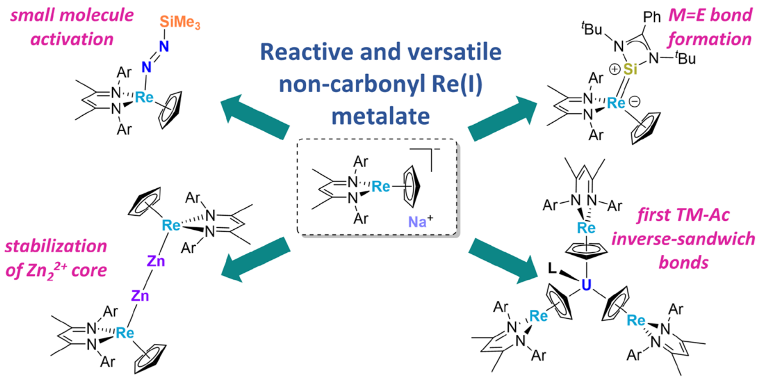
Conspectus



Low-valent transition metalates—anionic, electronic-rich organometallic complexes—comprise a class of highly reactive chemical reagents that find integral applications in organic synthesis, small molecule activation, stabilization of transient species, and M–E bond formation, among others. The inherent reactivity of such electron-rich metal centers has necessitated the widespread use of strong backbonding ligands, particularly carbonyls, to aid in the isolation and handling of metalate reagents, albeit sometimes at the expense of partially masking their full reactivity. However, recent synthetic explorations into transition metalate complexes devoid of archetypic back bonding ligands have led to the discovery of highly reactive metalates capable of performing a variety of novel chemical transformations.

Building off our group's long-standing interest in reactive organometallic species, a series of rational progressions in early-to-middle transition metal chemistry ultimately led to our isolation of a rhenium(I) β-diketiminate cyclopentadienide metalate that displays exceptional reactivity. We have found this Re(I) metalate to be capable of small molecule activation; notably, the complex reversibly binds dinitrogen in solution and can be utilized to trap N_2 for the synthesis of functionalized diazenido species. By employing isolobal analogues to N_2—CO and RNC—we were able to thoroughly monitor the mechanism of activation and conclude that the metalate's sodium counterion plays an integral role in promoting dinitrogen activation through a novel side-on interaction. The Re(I) metalate is also used in forming a variety of M–E bonds, including a series of uncommon rhenium-tetrylene (Si, Ge, Sn) complexes that display varying degrees of multiple bonding. These metal tetrylenes act to highlight deviations in chemical properties within the Group 14 elements. Our metalate's utility also applies to metal-metal bond formation, as demonstrated through the synthesis of a heterotetrametallic rhenium-zinc dimer. In this reaction, the Re(I) metalate performs a dual role as a reductant and metalloligand to stabilize a transient Zn_2^{2+} core fragment. Finally, the metalate displays unique reactivity with uranium(III) to yield the first transition metal–actinide inverse-sandwich bonds, in this case with three rhenium fragments bound through their Cp moieties surrounding the uranium center. Notably, throughout these endeavors we demonstrate that the metalate displays reactivity at multiple locations, including directly at the rhenium metal center, at a Cp carbon, through a Cp-sandwich mode, or through reversibly-bound dinitrogen.

Overall, the rhenium(I) metalate described herein demonstrates utility in diverse applications: small molecule activation, stabilization of reduced and/or unstable species, and formation of unconventional M–E/M–M bonds or heterometallic complexes. Moving forward, we suggest that the continued discovery of non-carbonyl, electron-rich transition metal anions featuring new or unconventional ligands should produce additional reactive organometallic species capable of stabilizing unique structural motifs and performing novel and unusual chemical transformations.

Key References

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- Lohrey, T. D.; Bergman, R. G.; Arnold, J. Controlling Dinitrogen Functionalization at Rhenium through Alkali Metal Ion Pairing. *Dalt. Trans.* **2019**, *48* (48), 17936–17944.[3] *Small molecule activation of dinitrogen, carbon monoxide, and isocyanides by a rhenium metalate is shown to have a strong dependence on side-on alkali metal ion pairing interactions.*
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Introduction

Low-valent transition metalates have a long and distinguished history within synthetic inorganic and organometallic chemistry. While early discoveries of reduced mono- and polyatomic metal anions were made beginning in the late 1890's via alkali metal reductions of metals and metalloids in liquid ammonia,[5] extensive research into metal carbonyl complexes in the mid 1900's led to isolation of the first monatomic, ion-separated transition metalates, including salts of $[Fe(CO)_4]^{2-}$.[6] These anionic, electron-rich metalate complexes are typically highly reactive—especially in terms of their basicity, nucleophilicity, and reducing nature—though this reactivity comes at the expense of their being difficult to handle and isolate. The latter point helps to explain why carbonyl ligands, with their excellent ability to accept electron density from metal *d*-orbitals through backbonding into their π*-orbitals, have found great utility in stabilizing metal anions. Such is the "Catch-22" of designing reactive, isolable low-valent metalates: carbonyl and other π-accepting ligands help stabilize electron-rich metal centers, but at the cost of making these complexes inherently less reactive.

There are a few notable, albeit not mutually exclusive, "classes" of low-valent metalates (Figure 1). Homoleptic metal carbonyl anions constitute the most prominent and exhaustively studied group of transition metalates. These species have been prepared for nearly all groups of the transition metals, typically via either alkali metal reduction, attack of a neutral complex with strong base, reductive carbonylation of metal halides, or ligand exchange of arenemetalates with CO.[6–9] Arenemetalates, often synthesized through reduction of metal halides with alkali metal arenes, are a fascinating class of complexes pioneered by Chatt and coworkers.[9] They have found utility as reagents for introducing "naked" atomic metal anions into reactions due to the high lability of arene ligands, though difficulties in synthesizing and characterizing these reactive species have limited the number of isolated examples.[10]

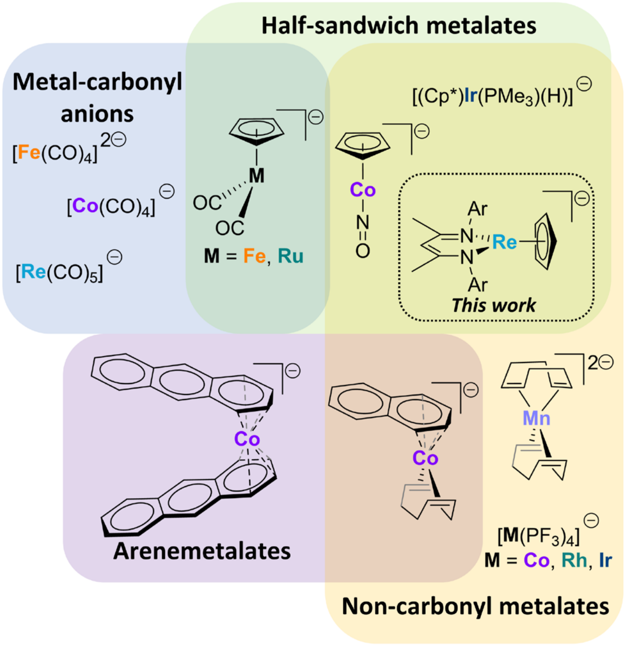
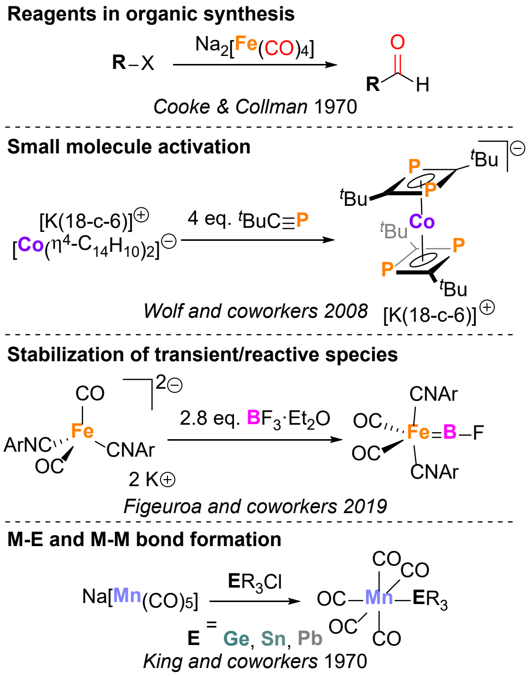


Figure 1. Illustrative examples of the main classes of low-valent transition metal anions.

In contrast, half-sandwich carbonyl metalates benefit from robust syntheses, reasonable stability, and generalizable reactivity. In fact, the iron-containing anion, $[(Cp)Fe(CO)_2]^-$ (commonly abbreviated as "Fp^-"), is found so readily throughout the chemical literature that Fp^- can be considered as the "standard model" for nucleophilic transition metal anions.[11] In addition to the countless homoleptic and half-sandwich carbonyl metalates, a number of analogous complexes featuring isolobal π-accepting ligands—including isocyanides, phosphines, and olefins—in place of one or all of the CO ligands have been reported. Despite their relative rarity in comparison with metal carbonyl anions, many of these non-carbonyl metalates are exceptionally reactive and thus are of synthetic interest. To that end, early work by our group involved the study of both an iridium hydridometalate, Li$[(Cp^*)Ir(PMe_3)(H)]$, formed via deprotonation of an iridium dihydride with lithium bases,[12–14] as well as the first low-valent nitrosyl metalate devoid of other backbonding ligands, namely Na[(Cp)Co(NO)].[15,16]

While the foundational reactivity of low-valent metalates includes their nucleophilicity, basicity, and reducing ability, these molecular metal anions have found diverse and essential applications throughout various fields of chemistry (Scheme 1). Metalates have been used extensively in organic synthesis, as highlighted by Collman's reagent, $Na_2[Fe(CO)_4]$; this iron carbonyl dianion is well-known for transforming alkyl halides into aldehydes via CO insertion into organic substrates, though it also finds use in syntheses of ketones, carboxylic acids, esters, and amides.[17] Additionally, the related nitrosyl-substituted "Hieber anion", $[Fe(CO)_3(NO)]^-$, finds use in catalytic transesterification and allylic substitution transformations.[18,19] The high reactivity of transition metalates has also been harnessed for the activation of small molecules. For instance, anionic metal-dinitrogen adducts have been used for protonation and silylation of dinitrogen to form ammonia and tris(trimethylsilyl)amine, respectively,[20–22] and C–CN bond activation has been achieved with rhodium metalates.[23] Activation of small molecule phosphorous reagents such as P_4,[24–26] phosphaalkynes (RC≡P),[27] and P–P bonds[28,29] has also been demonstrated. Each of these highlighted examples of small molecule activation is performed with non-carbonyl metalates.

Scheme 1. Low-valent metalates are employed in a variety of novel chemical processes.



Another fascinating function of low-valent metalates, especially those with bulky or non-traditional ligands, is their ability to enforce a strong coordination environment that stabilizes transient or reactive species. For example, Figueroa and coworkers harnessed the electron-rich nature of an iron dianion featuring bulky isocyanide ligands to coordinate boron monofluoride generated from BF_3 and observed the seminal example of π-backdonation to BF.[30] Chemists had long postulated that BF, an isoelectronic but much more reactive analogue to CO, would bind transition metals, but it had been too fleeting at room temperature to work with experimentally. Gratifyingly, the iron metalate enabled the generation, capture, and stabilization of this fragment. Finally, the nucleophilicity of transition metalates makes them prime reagents for the production of a huge variety of metal-element and metal-metal bonds. Some of the earliest endeavors with low-valent anions resulted in the formation of metal-Group 14 bonds, such as Wilkinson's generation of the first metal-silicon bond from reactions of Fp^- with Me_3SiCl[31,32] or King's efforts in preparing bonds between metalates and heavier Group 14 congeners.[33,34] Metalates have also been used extensively with organic electrophiles to form M–C bonds,[11,17] while also finding utility in M–B,[35] M–Group 13,[36] M–TM,[11,37] M–Ae,[38,39] M–Ln,[40,41] and M–Ac[42] bond formation, among others.

In general, low-valent metalates have been employed for a host of inorganic, organometallic, and organic transformations. While the bulk of reported syntheses and reactions of metalates have historically involved metal carbonyl anions, the more recent use of non-carbonyl, bulky, and versatile ligands has led to new metalates with unique reactivity patterns and that are capable of accessing unusual motifs. Thus, the synthesis and exploration of electron-rich, anionic transition metal complexes devoid of archetypic back bonding ligands often leads to the discovery of highly reactive metalates capable of performing a variety of desirable chemical transformations. In this account we present the extensive work we have performed in developing the chemistry of a highly reactive rhenium(I) β-diketiminate cyclopentadienide anion that has displayed exceptional and unprecedented reactivity.

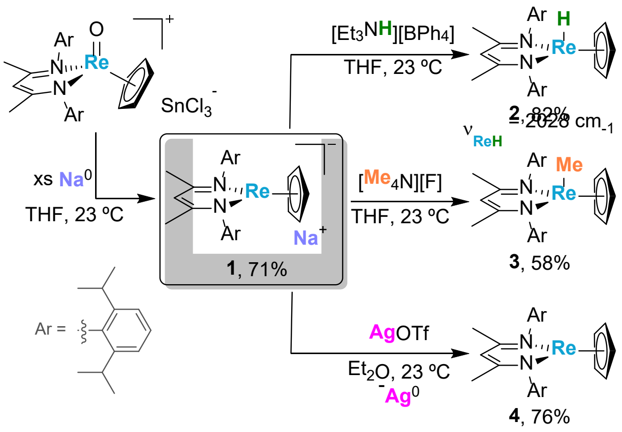
Synthesis of a Re(I) Metalate

This story begins over a decade ago, when we first became interested in the use of β-diketiminates (BDI)—a class of monoanionic, bidentate, robust, and tunable supporting ligands—to stabilize and study the reactivity of niobium(III) complexes.[43,44] Our group has long been interested in the design of highly reactive organometallic species capable of activating traditionally inert and/or industrially relevant substrates, and our work with low-valent Nb-BDI complexes was successful in this regard, highlighted by their ability to act as hydrodefluorination[45] and semihydrogenation catalysts,[46] along with other stoichiometric transformations.[44,47,48] We recognized the advantages of low-valent metal centers in performing productive chemistry due to their potential as powerful reductants. However, despite the success of these niobium systems, we repeatedly encountered limitations in the chemistry of low-valent Group 5 complexes due to unproductive non-innocence of the BDI ligand under certain conditions, particularly reductive cleavage of the ligand.[49] When confronted with this limitation, we envisioned two routes forward: either change the ancillary ligand or change the metal. Indeed, our efforts with new ancillary ligands led to a host of interesting Group 5 chemistry,[50–53] but of more relevance to this account was our decision to target rhenium-BDI systems. We hypothesized that the marginal increase in electronegativity from niobium to rhenium, as well as rhenium's ability to access a wide range of oxidation states,[54] might increase our chances of isolating reactive low-valent species (specifically because Re is less likely than Nb to cleave the BDI ligand to form a higher-valent product). Additionally, by increasing the *d*-electron count by an even pair of electrons from Nb to Re, we left open the potential to access similar two-electron transformations as the Nb system using the same set of ligands.[55] Despite encountering the occasional roadblock, our switch to rhenium ultimately led to the metalate of interest described below.

Our initial entry into rhenium-BDI chemistry involved installation of *N*,*N′*-bis(2,6-diisopropylphenyl)-β-diketiminate onto Re(V) oxo precursors. Frustratingly, our early work with this oxo rhenium(V)-BDI complex, $OReCl_2$(BDI), again demonstrated non-innocent reductive cleavage of the BDI ligand, similar to the niobium systems, upon lowering the valence at rhenium through oxygen atom transfer (OAT) to PEt_3.[56] However, we found that the addition of a π-acidic ligand, in this case an olefin, finally led to stable rhenium(III) oxo species;[57] the resulting complex could actually be further reduced to rhenium(I)-BDI isocyanide and carbonyl complexes,[58] again highlighting the utility of CO/RNC ligands in stabilizing low-valent metal centers.

The chemistry of this rhenium-oxo BDI system took a surprising turn after installation of a cyclopentadienide (Cp) ligand, leading to isolation of the rhenium(V) cation, [ORe(Cp)(BDI)][$SnCl_3^-$].[57] Remarkably, when attempts were made to reduce this complex using excess metallic sodium, we found that the Re(V) center could be reduced directly to Re(I) with concomitant loss of the oxo moiety to give the sodium metalate Na[(Cp)Re(BDI)] (**1**) in good yield (Scheme 2, Figure 2).[1] The resulting product is extremely air- and moisture-sensitive, requiring meticulous care in isolating and handling the material. Metalate **1** represents a rare example of a d^6 rhenium(I) complex without π-acceptor (e.g., carbonyl) ligands.[54]

Scheme 2. Synthesis of a low-valent rhenium(I) metalate via alkali metal reduction and its representative reactivity as a base, nucleophile, and reductant.



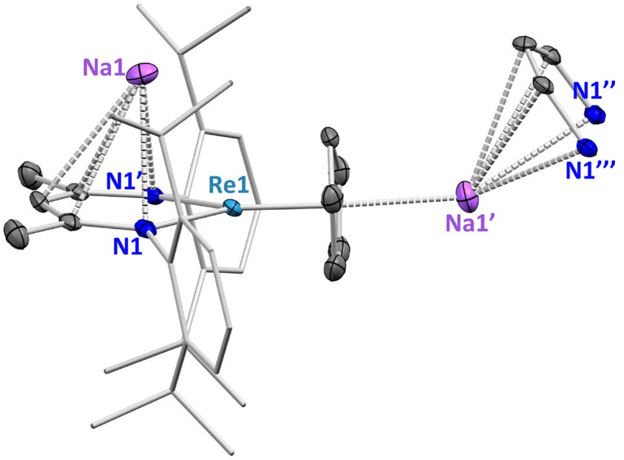


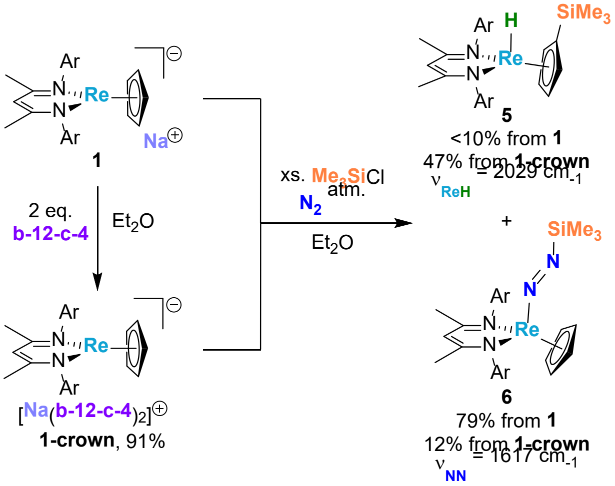
Figure 2. X-ray crystal structure of rhenium(I) metalate, **1**, extended to display the full coordination environment of the Na$^+$ counterion.

As for the general reactivity of **1**, we established early on that it can act as a base, nucleophile, or reductant. Protonation of **1** was optimized with [Et$_3$NH][BPh$_4$] to yield the rhenium(III)-hydride complex **2**, while reactions of **1** with tetraalkylammonium salts led to rhenium(III)-alkyl species, such as methyl complex **3**, via nucleophilic attack by **1** at the alkyl α-positions. Metalate **1** is also readily oxidized to form a rare acceptor-free[59], paramagnetic rhenium(II) species **4**, which has been the subject of several electronic structure and reactivity studies.[60–62] Our failed attempts to form direct M–M bonds through salt eliminations of **1** with several divalent first-row metal halides (Mn, Co, Cu) also highlights the reducing power of **1**; instead of M–M bond formation, we observe reduction of the metal halides and formation of either **4** or the rhenium(III)-halide species Re(X)(Cp)(BDI) (X = Cl, Br, I).[63] Ultimately, the reactive nature of **1** motivated us to explore the limits of its chemical reactivity; specifically, we were excited to determine how **1** could be used to activate typically inert species, stabilize unusual moieties, and form new or unusual M–E bonds.

Small Molecule Activation: Reduction of N_2, CO, and RNC

Our first observation of dinitrogen activation by metalate **1** came about serendipitously when performing reactions with Me$_3$SiCl under an atmosphere of N_2 (i.e. our standard procedure for air-free synthetic conditions). During early attempts to silylate **1** using Me$_3$SiCl, we were surprised to observe the formation of two products: a rhenium(III)-hydride (**5**) formed via silylation of the Cp moiety accompanied by migration of a Cp hydrogen to the rhenium center, and a rhenium(III)-silyldiazenido (**6**) resulting from incorporation and subsequent silylation of dinitrogen from the reaction atmosphere (Scheme 3, Figure 3).[3] The silyldiazenido product exhibited a lengthened N–N bond distance (1.25(2) Å) and decreased N–N stretching frequency (1617 cm^{-1}) relative to free N_2 (1.098 Å and 2331 cm^{-1}, respectively),[64] consistent with a direduced diazenido fragment. We also observed the ratio of products (**5** and **6**) formed in this reaction to be temperature dependent, with lower temperatures favoring N_2 binding and thus silyldiazenido **6**. Intriguingly, we noted a marked decrease in the formation of diazenido **6** when sequestering the sodium cation from **1**: product ratios of diazenido **6** to hydride **5** went from ca. 8:1 when using **1** as a reagent to ca. 0.25:1 when using a crowned salt (**1-crown**). These results informed us that the Na$^+$ counterion helps promote dinitrogen binding at rhenium, though the specific role of the ion within the dinitrogen binding mechanism was unclear at this point. Unfortunately, efforts to isolate an N_2-bound species prior to silylation were unsuccessful, prompting us to explore other avenues for determining counterion influences.

Scheme 3. Relative product ratios of rhenium-hydride **5** to rhenium-diazenido **6** are affected by sequestration of the sodium counterion in **1**.



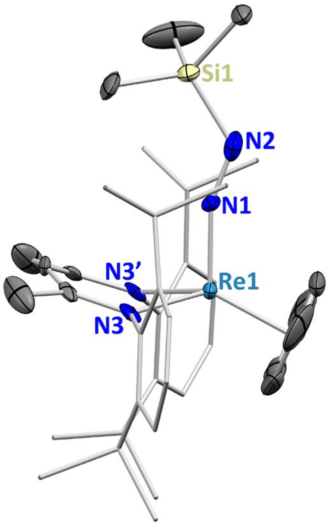
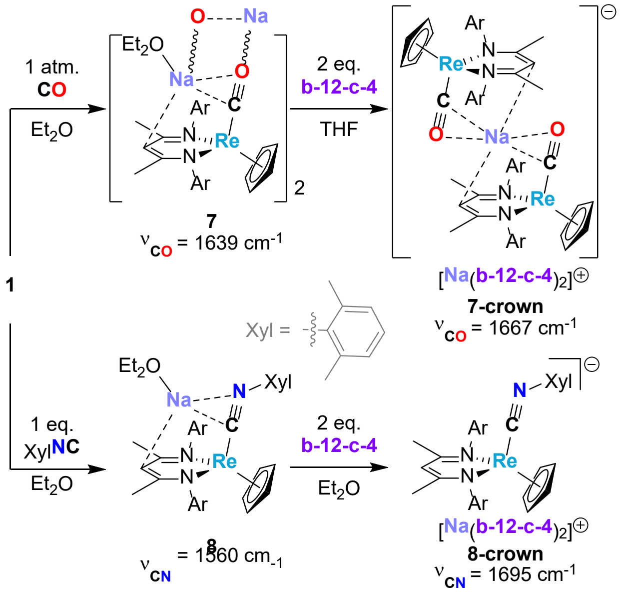


Figure 3. X-ray crystal structure of **6**.

We turned to isolobal analogues of N_2—CO and RNC—with the goal of crystallographically and spectroscopically monitoring side-on Na^+-CO/RNC interactions in this system. By adding CO or 2,6-xylylisocyanide (xylNC) to **1** we were able to synthesize CO and RNC adducts **7** and **8**, respectively (Scheme 4, Figure 4). We saw clear evidence of activation of both C–O and C–N bonds in these complexes, indicated by lengthened bond distances and redshifted stretching frequencies relative to their unbound counterparts. Critically, solid-state structures of **7** and **8** (which adopt equivalent coordination environments with the exception that **7** dimerizes) clearly showed the sodium counterion in a close side-on interaction with both atoms of the CO and CN units, as well as the backbone carbon of the BDI ligand. Adding benzo-12-crown-4 to **7** and **8** enabled us to isolate species where either partial (**7-crown**) or complete (**8-crown**) sequestration of Na^+ was achieved. In both cases, we observed shortening of the C–O and C–N bonds and blueshifts in their infrared spectra relative to their uncrowned analogues, with the magnitude of these changes more pronounced for **8-crown**. These distinct changes when removing the cation correspond with lowering the degree of activation of CO or CN and highlight the importance of side-on cation interactions in this system.

Scheme 4. Synthesis of CO and xylNC adducts **7** and **8**, and subsequent sequestration of the sodium counterions to form **7-crown** and **8-crown**, respectively.



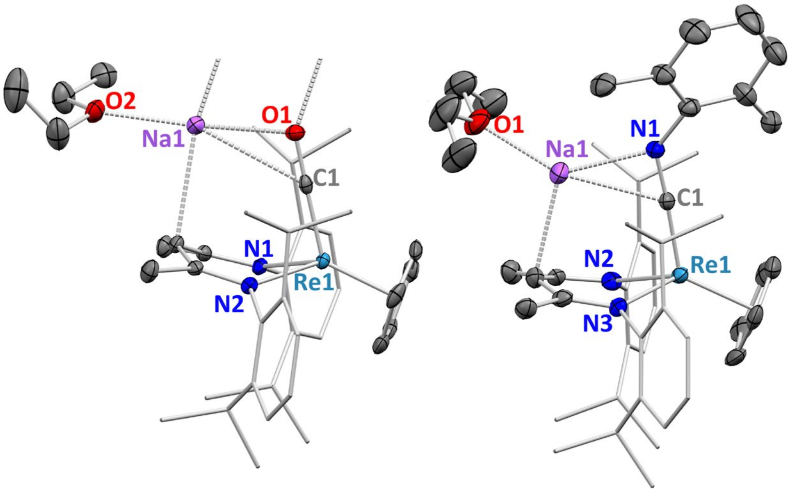


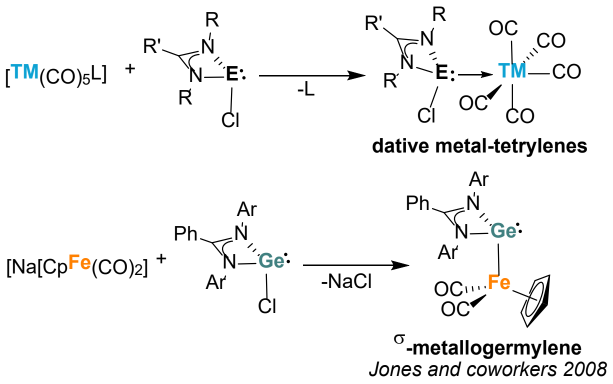
Figure 4. X-ray crystal structures of **7** and **8**.

In this system, it is likely that negative charge density is localized on the CO and RNC moieties as a result of π-donation from the electron-rich rhenium center, and the sodium counterion aids in stabilizing and enhancing this donation, likely through a "push-pull" type mechanism.[65] Given electronic parallels between CO, RNC, and N_2, we presume a similar mechanism occurs during dinitrogen functionalization by **1**. As such, this study showcased the importance of side-on cation influence in binding and activating small molecules such as dinitrogen. Literature examples of side-on alkali-cation interactions with dinitrogen are uncommon and, given that these results imply such interactions increase activation of π-acids, we suggest that rational optimization of side-on interactions could be a fruitful design strategy for future dinitrogen activation systems. To summarize, metalate **1** has been shown to behave as a strong π-donor capable of reversibly binding and subsequently functionalizing N_2, and lessons learned from our investigations with this metalate will play an important role in the design of both molecular and heterogenous systems capable of activating industrially relevant small molecules such as dinitrogen.

Synthetic Access to Uncommon Metal-Tetrylenes

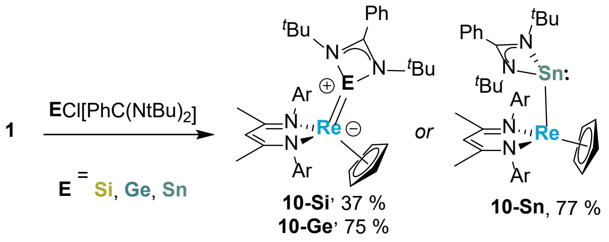
We have found that the potent π-donation ability of **1** can be applied not only to activate small molecules, but also to enforce strong bonding with certain main group elements. We sought to harness the π-donor capability of **1** to access rhenium-heavy Group 14 element (i.e., Si, Ge, Sn) multiply-bonded complexes, thus producing reactive heavy element analogues to transition metal carbenes, otherwise known as "tetrylenes". In particular, amidinate-supported tetrylenes had previously been shown to coordinate transition metals through a tetrylene-centered lone pair in dative donor-acceptor interactions (Scheme 5),[66] while metal-substituted amidinatotetrylenes, such as σ-metallotetrylenes, are extremely rare.[67] However, in the realm of non-amidinate-supported tetrylenes, low-valent metalates comparable to **1** have been employed to synthesize transition metal–Group 14 multiply-bonded species, such as the first metal-tetrylyne (metal-Group 14 triple bond) complex synthesized from $[(Cp)Mo(CO)_3]^-$.[68] As such, we envisioned a scenario in which strongly electron-donating **1** could enforce additional π-interactions with amidinatotetrylenes to produce electronically unique, and potentially reactive, metal-tetrylene species.

Scheme 5. Illustrative examples of amidinate-supported tetrylenes in the formation of M–E (E = Si, Ge, Sn) bonds.



In salt elimination reactions between **1** and chlorotetrylenes ECl[PhC(N^{t}Bu)$_2$] (E = Si, Ge, Sn), we were able to isolate metal-tetrylene products **10-E** in moderate to high yields (Scheme 6). However, we immediately noticed a marked difference between the silicon and germanium products **10-Si** and **10-Ge** relative to the tin species **10-Sn**. Proton nuclear magnetic resonance (NMR) spectra revealed **10-Sn** to exhibit free rotation about the Re–Sn bond, whereas **10-Si**/**10-Ge** did not, and solid-state structures of **10-Si** and **10-Ge** demonstrated near-planar amidinate geometries, compared to the bent geometry of **10-Sn** (Figure 5). Further, the Re–Si (2.2413(9) Å, the shortest reported Re–Si bond by 0.154(2) Å[69]) and Re–Ge (2.3322(4) Å) bonds were very short, whereas the Re–Sn bond (2.7562(5) Å) was comparable to reported Re–Sn single bonds. As a result, we concluded that **10-Sn** was best described as a σ-metallotetrylene, whereas **10-Si** and **10-Ge** display multiple bonding interactions between rhenium and the tetrylene atom.

Scheme 6. Reactions of metalate **1** with amidinate-supported chlorotetrylenes lead to complexes **10-E** (E = Si, Ge, Sn).



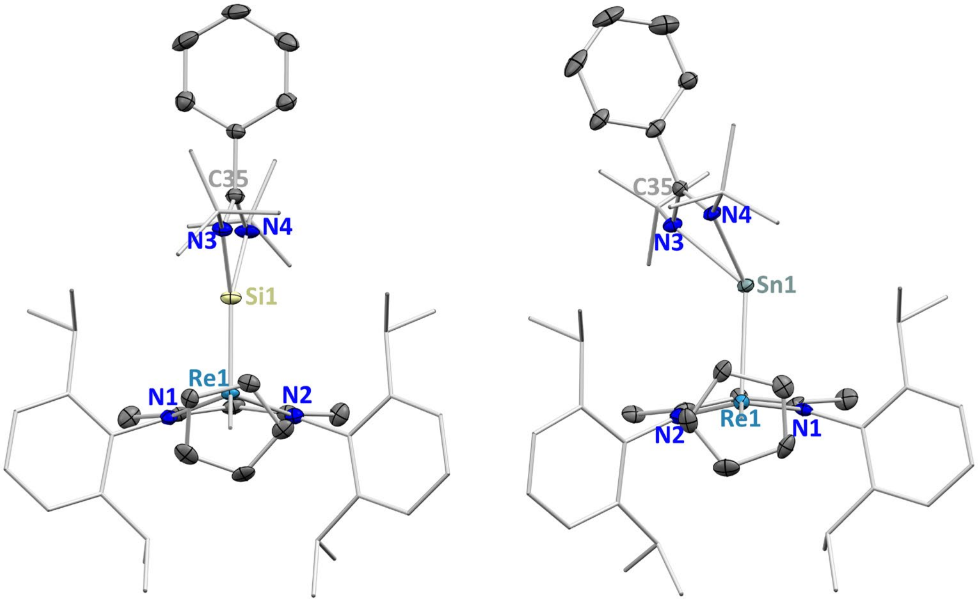
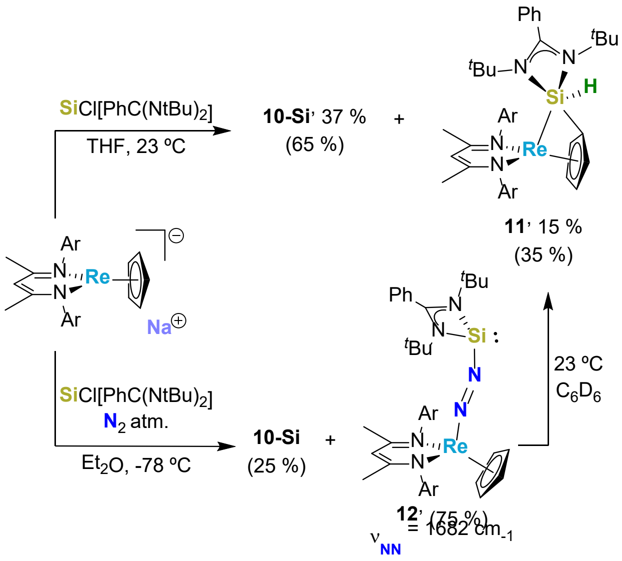


Figure 5. X-ray crystal structures of **10-Si** and **10-Sn**, highlighting the variation in coordination geometry between the planar silylene/germylene species versus the bent σ-metallostannylene.

Density functional theory calculations helped pinpoint the relevant orbitals involved in bonding in complexes **10-E**. In **10-Si**/**10-Ge**, overlap of an *s*/p_z-hybridized silicon lone pair with a hybridized rhenium orbital constituted a bond of σ-symmetry, and we also found a π-symmetry interaction comprised of a silicon p_x orbital with a rhenium orbital of primarily *d*-character. In contrast, calculations on **10-Sn** clearly showed a single bonding interaction (of σ-symmetry) and the existence of a non-bonding tin-centered lone pair orbital. Rhenium tetrylenes **10-Si** and **10-Ge** constitute unusual examples of multiple bonding between three-coordinate amidinatotetrylenes and a transition metal. They also represent a departure from the established σ-metallotetrylene coordination seen previously with Fp^- and in **10-Sn**, which highlights both the π-donating ability of **1** relative to Fp^-, as well as deviation in chemical properties among heavier Group 14 elements.

In addition, the reactivity of metalate **1** led to discovery of a number of other highly unusual rhenium–Group 14 complexes. In our initial preparation of tetrylene **10-Si**, we discovered that room temperature reactions produced a rhenium silane byproduct, **11**, that displays an unprecedented bonding arrangement in which silicon is bridged between a metal center and a carbon atom on an η^1:η^5-cyclopentadienide ligand (that is also bound to the same metal center) (Scheme 7). However, analogous reactions at low temperatures resulted in a different major product, in this case a diazene-functionalized silylene, **12**, again showcasing the N_2-binding abilities of **1**. Curiously, diazenido **12** slowly decomposed in solution to silane **11**. These species further demonstrate the synthetic utility of metalate **1** and highlight its ability to react at multiple sites on the complex: at the metal center, through a Cp carbon, or through reversibly-bound dinitrogen.

Scheme 7. Modification of reaction conditions leads to different product distributions, including bridging silane **11** and diazenido **12**. Yields in parentheses refer to product ratios determined by proton NMR. Adapted from ref. 4 with permission from the Royal Society of Chemistry.

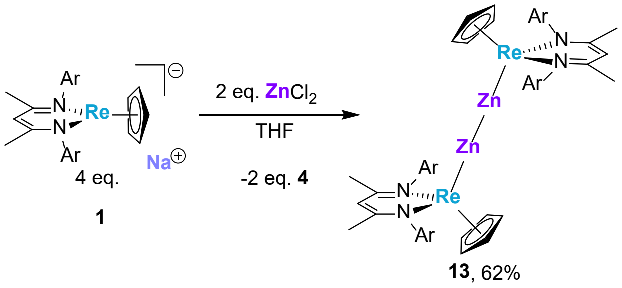


A Metalate as Both a Reductant and Metalloligand

Thus far, we have seen metalate **1** reduce inert species and stabilize novel tetrylene moieties, and given its reducing and stabilizing properties, **1** appeared a prime candidate for reductive formation and subsequent stabilization of metal-metal bonded species. Metal-metal bonds are attractive both in terms of their fundamental electronic structure, such as pushing the limits of M–M bond order, and for their potential applications, such as cooperative catalysis.[70] We attempted to use **1** as a synthon in salt elimination reactions with metal halides and discovered its remarkable ability to synchronously act as both a reductant and stabilizing metalloligand in a single reaction with zinc dichloride.

In a reaction of **1** (4 equiv.) with $ZnCl_2$ (2 equiv.), we observed the formation of $[ZnRe(Cp)(BDI)]_2$ (**13**, Scheme 8). The concurrent generation of the rhenium(II) species **4** suggests that 2 equiv. of **1** act as a one-electron reductant to reduce Zn(II) to Zn(I). The crystal structure of **13** revealed a linear tetrametallic bonding arrangement (Figure 6) comprised of a Zn_2^{2+} core encapsulated in a Re(I)–Zn(I)–Zn(I)–Re(I) array, notably the first example of zinc(I) coordinated solely by other metal centers.

Scheme 8. Synthesis of heterotetrametallic complex **13**.



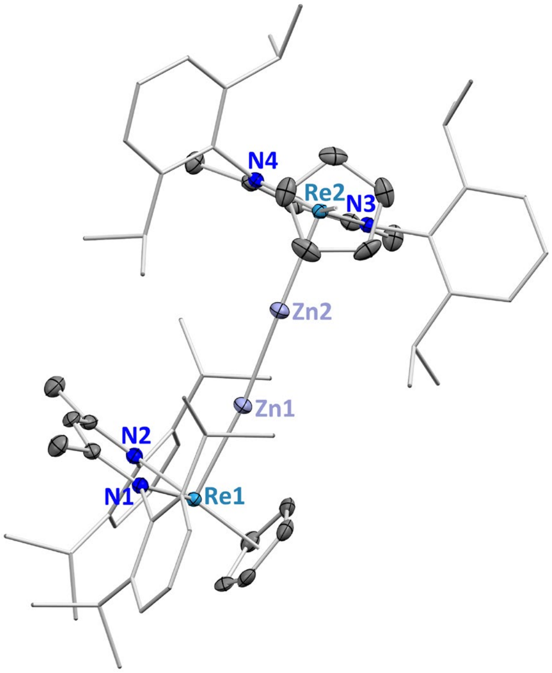


Figure 6. X-ray crystal structure of **13**.

Given the novelty of this bonding arrangement, calculations were performed to identify the relevant orbitals involved. The Zn–Zn bond was determined to consist of a covalent interaction of 4*s* orbitals on each Zn atom (Figure 7, HOMO-10). In contrast, the Re–Zn interactions were of dative character, resulting from donation of electron density from filled rhenium 5*d* orbitals towards empty zinc 4*p* orbitals (HOMO-5). As for the frontier orbitals of **13**, calculations revealed these orbitals to be of primarily rhenium 5*d* character, devoid of meaningful contributions from zinc. In addition, by examining calculated charge densities on the metal atoms, we were able to confirm the assignment of anionic Re(I) centers flanking a positively charged Zn(I)–Zn(I) core.

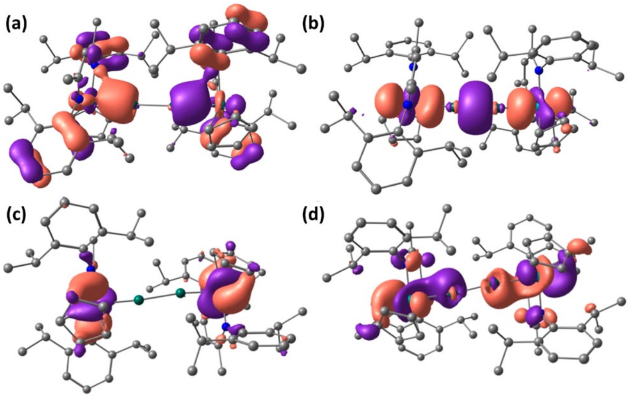
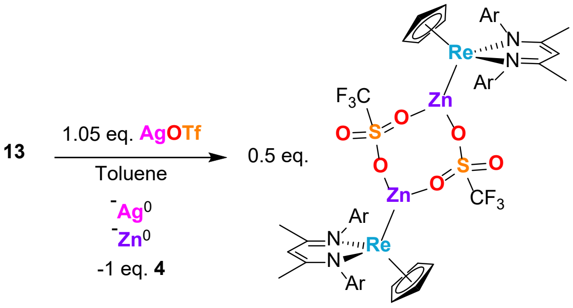


Figure 7. Renderings of select calculated molecular orbitals of **13**: (a) Re–Zn bonding orbital (HOMO-5), (b) Zn–Zn bonding orbital (HOMO-10), (c) HOMO, and (d) LUMO. Adapted from ref. 1. Copyright 2019 American Chemical Society.

We subsequently subjected heterotetrametallic complex **13** to oxidation and observed redox reactivity at the rhenium centers. When AgOTf was added, we observed formation of the triflate-bridged dimer **14** along with another significant quantity of rhenium(II) complex **4** (Scheme 9). Especially given that the HOMO/LUMO of **13** are rhenium-centered, we propose that oxidation occurs at Re(I) to produce **4** first, then disproportionation of the Zn–Zn bond occurs followed by incorporation of triflate moieties, ultimately leading to formation of Re(I)–Zn(II) complex **14**.

Scheme 9. Oxidation of **13** to form triflate-bridged **14**.



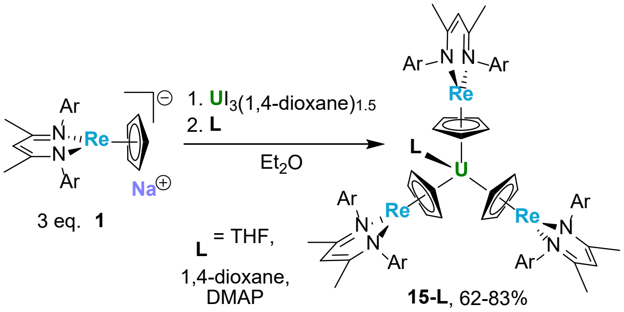
14, 54%

The ability of **1** to stabilize a highly reactive Zn_2^{2+} core via donation into Zn 4p orbitals further emphasizes the strong donor capabilities of our metalate. The result is reminiscent of prior applications of low-valent metalates in stabilizing reactive or unstable chemical fragments, such as the trapping of BF discussed above. In this case, however, metalate **1** both generates the reactive species by acting as an electron donor and additionally behaves as a metalloligand for the stabilization of the transient species. In both cases, these examples of low-valent metalates as stabilizers or trapping agents of reactive chemical fragments are useful for extracting fundamental details on electronic structure, bonding, and reactivity of otherwise inaccessible moieties.

A First in Transition Metal-Actinide Heterobimetallics

Given the utility of metalate **1** in forming a variety of M–E and M–M bonds and our group's interest in organoactinide chemistry, we were curious if **1** could be used as a synthon for accessing Re–Ac bonds. We began by attempting reactions of metalate **1** with uranium(III) reagents, hoping to avoid reduction of uranium (we assumed **1** would readily reduce uranium(IV) species to uranium(III)). However, instead of isolating a product containing Re–U bonds, we observed formation of triple inverse-sandwich complexes **15-L** (L = THF, 1,4-dioxane, DMAP) (Scheme 10). The geometry of this striking complex was determined crystallographically, confirming the presence of three $[(Cp)Re(BDI)]^-$ moieties coordinated via η^5-Cp interactions to uranium (Figure 8). Not only was this the first example of an actinide-transition metal inverse-sandwich complex, but it also represented direct assembly of an inverse-sandwich species via salt elimination, whereas previous actinide sandwich complexes had typically been accessed via reductions of arene solvents.

Scheme 10. Synthesis of triple inverse-sandwich species **15-L**.



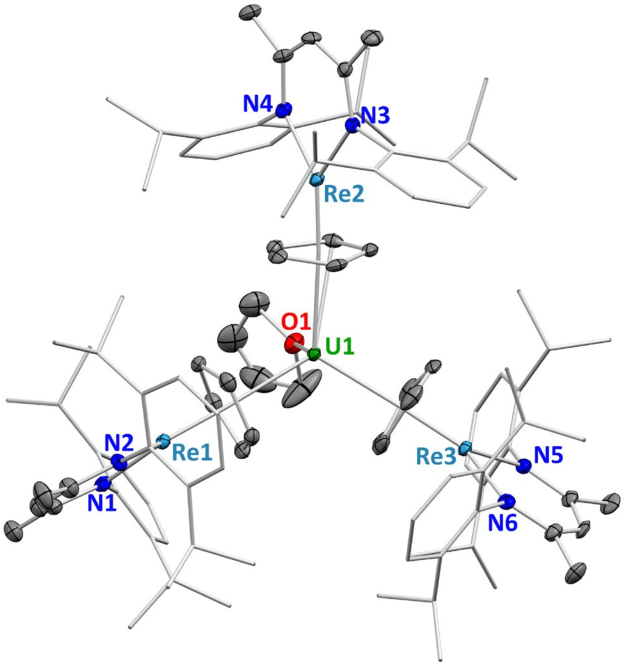


Figure 8. X-ray crystal structure of **15-THF**.

One of the salient features of **15-THF** in the solid-state was shortening of the Re–Cp(centroid) distance by ca. 0.06 Å relative to the starting metalate **1**. Calculations reproduced this bond shortening and provided insight into the electronic structure. The Cp bonding molecular orbitals are quite delocalized, with contributions from both uranium- and rhenium-based orbitals (Figure 9; SOMO-5, SOMO-4, SOMO-3), while the spin density was localized to the paramagnetic uranium(III) center. As for the shortening of the Re–Cp bonds relative to **1**, calculations suggested that this may be due to diminished Coulombic repulsion in **15-L**; to form U–Cp bonds, electron density is shifted away from the rhenium(I) centers and through the Cp moieties towards the electropositive uranium atom. As a result, electron-electron repulsions in the Re–Cp interatomic region are decreased, thereby shortening the Re–Cp bond.

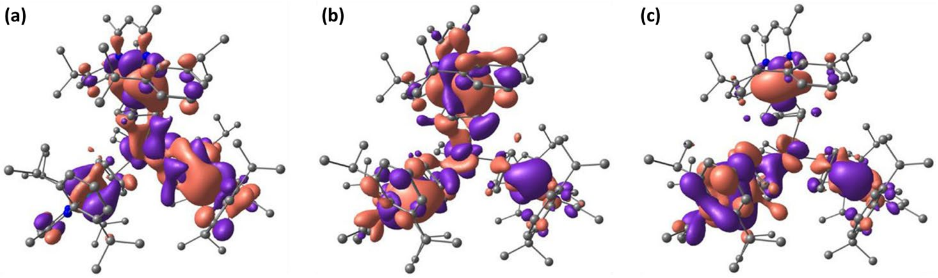


Figure 9. Renderings of select calculated molecular orbitals of **15-THF** showing both rhenium and uranium contributions to the Cp bonding molecular orbitals: (a) SOMO−5, (b) SOMO−4, and (c) SOMO−3. Adapted from ref. 2. Copyright 2019 American Chemical Society.

Regarding assignment of the uranium oxidation state, electron paramagnetic resonance (EPR) measurements confirmed the formal classification of U(III). Attempted oxidations of **15-L** led only to the observation of rhenium(II) species **4**, suggesting that, similar to rhenium-zinc species **13**, oxidation is more facile at the rhenium(I) centers than at the uranium center. Additionally, reactions of **1** (3 equiv.) with UCl_4 led to formation of **15-L** and **4**, further evidence that oxidation to Re(II) occurs before oxidation of U(III) to U(IV).

Overall, the nucleophilic reactivity of metalate **1** at the Cp ring to form inverse-sandwich complexes stands in contrast to some previous examples of metalates reacting with *f*-block elements, wherein M–M bonds are formed between lanthanides and Fe, Mn, and Re,[40,41] and between uranium and Re (though the "metalate" employed here is generated in situ and not isolated).[42] Additionally, the metalate Fp^- reacts with dysprosium through its carbonyl ligands, leading to an isocarbonyl-bridged dysprosium single-molecule magnet.[71] Thus, the formation of a novel triple inverse-sandwich motif between metalate **1** and uranium highlights the potential for discovering interesting electronic structures when combining transition metals with *f*-block elements in molecular complexes, whether through bridging ligands or direct interactions. It also emphasizes the unique ability of low-valent metalate **1** to form a diverse array of novel chemical bonds: we can now add inverse-sandwich coordination to the ever-growing list of binding modes that can be accessed using this rhenium metalate, along with direct bonding at Re, substitution at a Cp carbon to form a rhenium hydride, and bonding through a distal diazenido nitrogen.

Conclusions and Outlook

In this account, we have presented the discovery, extensive reactivity, and chemical behavior of a low-valent non-carbonyl transition metalate. While literature examples exist of different low-valent metalates being individually employed for distinct chemical applications, the rhenium(I) metalate described herein is singularly suitable for diverse applications: small molecule activation, stabilization of reduced and/or unstable species, and formation of unconventional M–E/M–M bonds or heterometallic complexes. Additionally, the ligand scaffold used in preparing metalate **1** not only lacks archetypal π-backbonding ligands such as carbonyls, but also presents multiple locations of nucleophilic reactivity. We have presented examples of **1** reacting directly at the rhenium metal center, at a Cp carbon, through a Cp-sandwich mode, or through reversibly-bound dinitrogen. While **1** has already demonstrated a thorough range of reactivity, we continue to explore the reactivity of this rhenium metalate, in particular its ability to form heterometallic complexes concurrent with dinitrogen activation and for accessing reactive rhenium-main group element bonds.

Finally, our adventures with this low-valent rhenium metalate have also elucidated several suggestions for future research in organometallic synthesis. In particular, we would like to stress that the continued discovery of non-carbonyl, electron-rich transition metal anions featuring new or unconventional ligands should produce additional reactive organometallic species capable of stabilizing unique structural motifs and performing novel and unusual chemical transformations. While carbonyls have historically found extensive use in this area, fresh approaches to ligand design—whether that be the use of sterically demanding substituents, inclusion of redox-active or non-innocent moieties, or the innovative incorporation of main-group elements—should continue to provide significantly greater steric and electronic control of metalates relative to their carbonyl congeners. Consequently, the already useful class of transition metalates will find new and original applications in organic, organometallic, and inorganic reaction chemistry. Finally, we firmly believe that continued interest in fundamentally reactive organometallic species is crucial; we support the approach of designing reactive metal species (such as electron-rich metalates), with or without a rigorously defined target reaction, and subsequently following the chemistry where it leads to determine the full scope of possible reactivity. In many cases, it is likely that lessons learned in these endeavors, such as key interactions in the coordination sphere of metal anions or the significance of counterions, will help inform the design of larger scale and/or industrially-relevant systems.

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Notes

The authors declare no competing financial interest.

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Erik T. Ouellette is a Ph.D. candidate in the College of Chemistry at the University of California, Berkeley, and previously received his B.A. in chemistry from the College of the Holy Cross. His current research interests include the synthesis of reactive rhenium-group 14 bonds, heterobimetallic dinitrogen activation, and transition metal–*f*-block bonding.

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Robert G. Bergman is Professor Emeritus and Professor of the Graduate School, recalled for research and part-time teaching in the College of Chemistry at the University of California, Berkeley. His current research is collaborative, focusing on synthetic and mechanistic studies of stoichiometric and catalytic reactions involving early metal complexes and supramolecular systems.

John Arnold is a Professor of Chemistry and Undergraduate Dean in the College of Chemistry at UC Berkeley. He is a graduate of the University of Salford (Applied Chemistry, 1982) and the University of California, San Diego (Ph.D. 1986). He carried out postdoctoral work with Professor Sir Geoffrey Wilkinson at Imperial College, London from 1987-88, before a short stint as a Royal Society University Research Fellow (1988-89). He began his independent career at UC Berkeley as an Assistant Professor in 1989.

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