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σ or π? Bonding interactions in a series of rhenium metallo-tetrylenes

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Salt metathesis reactions between a low-valent rhenium(I) complex, Na[Re(η⁵-Cp)(BDI)] (BDI = N,N’-bis(2,6-diisopropylphenyl)-3,5-dimethyl-β-diketiminate), and a series of amidinate-supported tetrylenes of the form EC[PhC(NtBu)₂] (E = Si, Ge, Sn) led to rhenium metallo-tetrylenes Re[EC(PhC(NtBu)₂)](η⁵-Cp)(BDI) (E = Si (1a), Ge (2), Sn (4)) with varying extents of Re–E multiple bonding. Whereas the rhenium-stannylene 4 adopts a σ-metallo-tetrylene arrangement featuring a Re–Sn single bond, the rhenium-silylene (1a) and -germylene (2) both engage in additional σ-interactions to form short Re–E multiple bonds. Temperature was found to play a crucial role in reactions between Na[Re(η⁵-Cp)(BDI)] and SiCl[PhC(NtBu)₂], as manipulation of reaction conditions led to isolation of an unusual rhenium-silane, [BDI]Re[μ-η⁵:η⁵-CpH]SiH[PhC(NtBu)₂] (1b) and a dinitrogen bridged rhenium-silylene, (η⁵-Cp)(BDI)[Re(μ-N₂)SiPhC(NtBu)₂] (1c), in addition to 1a. Finally, the reaction of Na[Re(η⁵-Cp)(BDI)] with GeCl₂-dioxane led to a rare μ-tetrelido complex, μ-Ge[Re(η⁵-Cp)(BDI)] (1d). Bonding interactions in these complexes are discussed through the lens of various spectroscopic, structural, and computational investigations.

Investigations have already led to the synthesis of a variety of transition metal tetrylenes1,12–23 and tetrylynes,24–28 most of which act as Fischer-type complexes.24 Two main synthetic pathways to transition metal-heavy group 14 multiple bonds incorporate divalent tetrylene precursors (Figure 1a): (1) salt metathesis of a halotetrylene with an anionic metal species to form a σ-metallo-tetrylene, followed by ligand dissociation at the metal (in this case to form the first reported metal–metal tetrylene).33 (b) Structures of the only previous work and recent report of a σ-metallo-tetrylene, reported by Filippou and coworkers33. (b) Structures of the metal tetrylyne and metal tetrylene reported by Filippou and coworkers33. (c) This work

Figure 1. (a) Two pathways to transition metal-heavy group 14 multiple bonding: (1) salt metathesis to form a σ-metallo-tetrylene, followed by ligand dissociation to form a metal-tetrylene,23 and (2) tetrylene ligand substitution to form a metal tetrylene, followed by halide migration to form a metal tetrylene. (b) Structure of the only previously reported amidinate-supported σ-metallo-tetrylene.33 (c) Structures of the rhenium-tetrylene complexes reported herein.

Introduction

The thoughtful design of transition metal–main group multiply-bonded systems has the potential to facilitate cooperative activations of small molecules and other catalytically relevant transformations.1 Multiple bonds between carbon and transition metals have been studied extensively, and many such systems play integral roles in organic synthesis and industrial catalysis.2–9 By studying the orbital interactions within these metal-carbon multiple bonds, including the factors that lead to Fischer- (electrophilic at carbon) versus Schrock- (nucleophilic at carbon) type carbenes and carbynes, researchers have been able to prepare complexes with desired modes of reactivity.

In contrast to metal-carbon multiple bonds, the breadth of molecular chemistry possible with heavier group 14 elements (e.g. Si, Ge, Sn) has yet to be fully realized. In comparison to carbon, these elements have large energy gaps between their s and p orbitals which disfavor s-p mixing.10,11 Accordingly, the study of the heavier analogues of transition metal carbenes and carbynes, known as tetrylenes or tetrylynes, could lead to the characterization of electronic properties and modes of reactivity substantially different from those of their carbon-containing relatives.

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tetrylene), and (2) dative ligand substitution/association at the metal by a tetrylene to form a metal tetrylene, which in certain cases undergoes halide migration to form a metal tetrylene (these complexes represent the first reported examples of rhenium germynes and germynes). For typical halotetrylene precursors (ERX or EX_2), these pathways are relatively straightforward, however we became interested in the use of a newer class of amidinate-supported halotetrylenes to form metal-heavy group 14 multiple bonds. While such tetrylenes have been found to bind to a vast number of metal centers through donation of the tetrylene-centered lone pair, there is only one reported example of salt metathesis between an amidinate-supported tetrylene and a transition metal species; reaction of a η^5-cyclopentadienyl dicarbonyl iron (Fp) salt with an amidinate-supported germylene resulted in an iron σ-metallotetrylene complex devoid of multiple bonding interactions (Figure 1b). Considering a highly nucleophilic rhenium(I) salt synthesized by our group has been shown to behave as a strong π-donor and participate in reactivity unseen in analogous Fp systems, we hypothesized that the use of such a metal complex might compel the formation of π-bonding interactions with amidinate-supported tetrylene reagents. Employing a π-donor strategy to form M-E multiple bonds should lead to novel amidinate-supported complexes, and the resulting increase in relative electron density at the group 14 atom may allow for a shift in reactivity from more traditional Fischer-type tetrylenes and tetrylenes.

Here we report reactions of Na[Re(η^5-Cp)(BDI)] (BDI = N,N'-bis(2,6-diisopropylphenyl)-3,5-dimethyl-β-diketiminate), with the chlorotetrylenes ECl(PhC(N'Bu)_2)] (E = Si, Ge, Sn), along with GeCl_2-dioxane, SnCl_2, and PbCl_2 (for an amidinate-free comparison), and our examinations of the unusual bonding motifs present in the subsequent product complexes, achieved through a variety of spectroscopic, structural, and computational investigations (Figure 1c).

Results and Discussion

Mixing of the chlorosilylene, SiCl(PhC(N'Bu)_2)], with Na[Re(η^5-Cp)(BDI)] in THF at ambient temperature for one hour led to the formation of two isomeric products that could be separated on the basis of their contrasting solubilities. Extraction of the crude reaction residue with pentane and subsequent crystallization enabled the isolation of a rhenium-silylene complex, Re(Si[PhC(N'Bu)_2])(η^5-Cp)(BDI) (1a) in 37% yield, whereas a rhenium-silane, (BDI)Re[μ-η^6:η^3-C_6H_4Ar](SiH[PhC(N'Bu)_2])] (1b), was extracted and crystallized from Et_2O in 15% yield (Scheme 1). Integrations from a ^1H NMR spectra of a crude mixture of 1a/1b products prior to any separation suggested the formation of 1a to 1b in a 65:35 ratio. We suggest that complex 1b is formed via migration of a hydrogen atom from the cyclopentadiene (Cp) ligand to the silicon center to give a bridging silane. The Si–H ^1H NMR resonance of bridging silane 1b manifests as a doublet at 5.74 ppm, suggesting weak, long-range coupling with the Cp proton resonance found at 4.70 ppm, which is confirmed by a cross peak in the ^1H–^1H COSY spectrum (Figure S4). The silane proton resonance also displays satellite peaks enabling determination of the large ^29Si–^1H coupling constant (^2J_Si,H = 238.1 Hz). A band at 2128 cm⁻¹ in the infrared spectrum of 1b, attributable to an Si–H stretch, further confirms our assignment of silane complex 1b (Figure S27). A ^29Si(^1H) resonance was observed for 1b at ~58.3 ppm, which is shifted upfield relative to the chlorosilylene starting material (δ = 14.6 ppm) and falls within an expected range for transition metal silyls. Unfortunately, attempts to locate a ^29Si(^1H) NMR signal for silylene 1a proved unsuccessful.

Interestingly, a reaction between these same starting materials in diethyl ether at ~−78 °C followed by a workup and crystalization from pentane allowed for the observation of a new dinitrogen-bridged silylene product, (η^5-Cp)(BDI)Re[μ-NN=Si][PhC(N'Bu)_2]) (1c), which forms in a 75:25 ratio to minor product silylene 1a based on ^1H NMR integrations of the crude product mixture. Despite multiple crystallization attempts, we were unable to isolate dinitrogen-bridged silylene 1c as a pure, bulk material, but infrared absorbance measurements of the product mixture revealed an N–N stretch at 1682 cm⁻¹, indicating significant weakening of the N–N bond relative to free N_2 (v_NN = 2359 cm⁻¹) (Figure S28). Formation of 1c, in which a molecule of dinitrogen from the reaction atmosphere has been incorporated into the complex, is not entirely unexpected given recent results from our group indicating that Na[Re(η^5-Cp)(BDI)] reversibly binds N_2 in solution. While we were able to observe dinitrogen-bridged silylene 1c via ^1H and ^29Si(^1H) NMR, IR, and X-ray diffraction (see below), further characterization was hampered by the instability of 1c at ambient temperature.

Solutions of dinitrogen-bridged silylene 1c in benzene-d_6 left at ambient temperature were monitored by ^1H NMR, which showed slow conversion of 1c to the bridging silane 1b (Scheme 1, Figure S8). Our attempts to convert pure samples of silylene 1a directly to 1b – either at elevated or ambient temperature in solution – were unsuccessful, instead leading to decomposition
of 1a. It is likely that even at ambient temperature, the dinitrogen-bridged 1c acts as a transient intermediate along the path to forming 1b; since binding of dinitrogen by Na[Re(η^5-Cp)(BDI)] is lower at ambient temperature (compared to at −78 °C), 1c is formed as a minor species relative to 1a and rearranges to the minor product, 1b. In contrast, binding of dinitrogen by Na[Re(η^5-Cp)(BDI)] is favored at −78 °C, leading to formation of the dinitrogen-bridged 1c as a major product since the cold workup impedes decomposition to 1b.

The solid-state structures of 1a-c were determined by single crystal X-ray diffraction (Figure 2). Complex 1a displays a short Re–Si bond of 2.2413(9) Å, which is the shortest Re–Si bond reported by 0.154(2) Å. Additionally, Re1–Si1–N3/N4 angles of 138.90(9)° and 151.4(1)° (sum of bond angles about Si: 359.4°) illustrate a roughly trigonal planar geometry about the silicon center (see Figures S20-22 for additional perspectives of 1a-c). This short, planar coordination of the amidinate-supported silylene to rhenium suggests the absence of a non-bonding silicon-centered lone pair (as is observed in the silylene starting material); these electrons are likely involved in bonding interactions with rhenium. The amidinate tert-butyl groups in silylene 1a are distinguishable in the ^1H NMR spectrum, indicating lack of free rotation about the Re–Si bond in solution, which corroborates the hypothesis of multiple bonding interactions that lock this orientation in place.

In contrast, we find a Re1–Si1 bond distance of 2.5299(8) Å in bridging silane 1b, consistent with a rhenium–silicon single bond. The silane hydrogen was located in the difference map, and refined isotropically. While we have previously observed which silicon is bonded to five atoms. Despite the nonplanar silicon, leading to an unusual bridged bonding arrangement in the SiCl[PhC(N^3-Bu)_3] starting material, indicating the silylene center in 1c preserves a non-bonding lone pair orbital.

We were intrigued by the unusual structural metrics displayed within these molecules, so we next turned to density functional theory (DFT) using the B3PW91 functional (see ESI for complete computational details) and natural bond orbital (NBO) analyses for each compound. In silylene 1a, we found two discrete bonding interactions that can be described through the use of qualitative frontier orbitals for the rhenium (as derived from a qualitative molecular orbital analysis of M(η^5-Cp)(L)_2 fragments, Figure 3a) and silicon (Figure 3b) fragments. The first interaction is of σ-donation interaction of roughly 60 kcal/mol. Natural charges in silylene 1a were calculated as −0.72 on Re and +1.36 on Si, suggesting polarization across this bond, with a calculated Wiberg Bond Index (WBI) of 1.64. These results are consistent with a strong, polarized double bond in silylene 1a, a bonding motif not previously observed between rhenium and silicon.

In contrast, the Re–Si bond in bridging silane 1b was modeled by a single σ-bonding interaction (Figure S32).
Corresponding natural charges of −0.72 on Re and +1.48 on Si were found, along with a much smaller WBI of 0.69, relative to that of silylene 1a. Calculations of dinitrogen-bridged silylene 1c revealed significant backbonding interactions from rhenium d-orbitals into dinitrogen π* orbitals, consistent with the observed redshift of the N–N stretching frequency (Figure S33). In addition, a pure non-bonding lone pair orbital was located on silicon (HOMO–4), as predicted based on the crystal structure.

We next sought to translate the abovementioned reactivity and bonding to the synthesis of heavier tetrylene derivates, especially given that germylene and stannylene derivatives are commonly less reactive than their silicon counterparts and are typically less inclined to be involved in multiple bonding interactions.11,43 Reaction of Na[Re(η⁵-Cp)(BDI)] with GeCl₂·dioxane at −78 °C led to the formation of a germanium-bridged dirhenium complex, Ge[Re(η⁵-Cp)(BDI)]₂ (3), in 61 % yield (Scheme 2). Solution NMR spectra of germanium-bridged complex 3 revealed effective C₂ symmetry (see Newman projection in Figure 5b). This observation rules out syn- and anti-periplanar conformations of 3 in solution at ambient temperature and suggests free rotation about the Re–Ge–Re bond.

Neither performing this reaction at ambient temperature nor attempts at thermal conversion of germylene 2 led to an isolable product.

We were also curious as to the importance of amidinate stabilization in tetrylene complexes 1a and 2 and sought, instead, to form rhenium-tetrylene multiple bonds using readily available divalent tetrylene halide salts. Accordingly, we treated Na[Re(η⁵-Cp)(BDI)] with GeCl₂·dioxane at −78 °C, which led to the isolation of dark purple needles of a germanium-bridged dirhenium complex, Ge[Re(η⁵-Cp)(BDI)]₂ (3), in 61 % yield (Scheme 2).

Figure 3. (a) Qualitative frontier molecular orbitals of the [Re(η⁵-Cp)(BDI)]⁻ fragment.42 (b) Qualitative frontier molecular orbitals of a planar [PhC(N(tBu))₂]+(E = Si, Ge) fragment. (c) Renderings of select calculated molecular orbitals of silylene 1a including a σ-bonding orbital (HOMO–14), n-bonding orbital (HOMO–2), and π-symmetry dative interaction from rhenium towards silicon (HOMO–1).
axis is restricted, either by steric restraints or by bonding orbital restrictions.

The solid-state structure of rhenium-germylene 2 closely resembles that of rhenium-silylene 1a, with a short Re–Ge distance of 2.3322(4) Å and distorted trigonal planar geometry about the germanium atom, as evidenced by Re1–Ge1–N3/N4 angles of 139.76(8) and 151.49(8)° (Figure 4; sum of bond angles about Ge: 356.2°). This geometry is in stark contrast to the iron σ-metallogermylene discussed earlier (Figure 1b), which was synthesized via a similar salt metathesis reaction; in that case, the amidinate-supported germylene was bound in a bent fashion to accommodate a germylene-centered lone pair. In addition, there are several other reported σ-metallogermylenes synthesized from salt metathesis reactions between transition metals (M = Cr, Mo, W) and chlorogermylenes without amidinate stabilization, and they consistently adopt both bent geometries and long M–Ge bond distances. The only exception is a case where ligand dissociation at the metal center facilitates metal-germylyne formation, as in the formation of (η⁵-Cp)(CO)₂Mo≡Ge(C₆H₃-2,6-Mes₂)) (see above, Figure 1a).²⁶

The short, planar rhenium–germanium bonding arrangement in germylene 2 is indicative of multiple bonding interactions between these atoms, and again suggests the absence of a localized non-bonding lone pair on germanium. For reference, the few structurally reported Re–Ge single bonds range from 2.5446(3)–2.6383(4) Å, while Gladysz and coworkers found a slightly shorter Re–Ge distance of 2.4738(6) Å due to the ionicity of a triflate group on germanium, which in effect led to double bond character of the rhenium–germanium bond. Additional comparative insight into the rhenium-germanium bond distances of both germylene 2 and germanium-bridged complex 3 can be made with the rhenium germylene (Re=GeR₂: 2.3253(4)–2.3422(4) Å) and germylyne (Re≡Ge: 2.2609(3)–2.2772(2) Å) complexes synthesized by Filippou and coworkers (Figure 1a).²⁹

Germanium-bridged complex 3 adopts a gauche conformation in the solid state (dihedral angle of 71.3° between the Cp centroids), consistent with its solution state C₂ symmetry.
(Figure 5a). Additionally, the Re–Ge distances were measured at 2.4395(5) Å and 2.4367(5) Å, with a slightly bent Re1–Ge1–Re2 angle of 163.18(2)°. This represents a rare example of μ2-tetrelido coordination involving a heavy group 14 atom bridged between two transition metal centers, with the most prevalent analogous system based on a structurally similar [Mn(η5-C5R5)(CO)2]2 fragment bridged by germanium, tin, and lead.54–60 More recently, however, the first bridging silicon centers have also been reported within different transition metal systems.61,62

We also investigated the electronic structures of germylene 2 and germanium-bridged complex 3 computationally. Natural bond orbital analysis of rhenium-germylene 2 revealed a nearly identical bonding scheme to rhenium-silylene 1a. Two covalent bonding interactions were identified, with an α-symmetry orbital containing slightly more germanium character than the analogous silicon contribution in 1a and a π-type orbital with more rhenium character (Table S5). Again, second-order perturbation analysis suggests a 76.5 kcal/mol donation from μ2-Ge[Mn(η5-C5R5)(CO)]2 (due to the difference between anionic BDI versus neutral CO ligands). The slightly bent geometry precludes a cylindrically symmetric π-system; thus, rotation about the Re–Ge–Re axis, which may be a result of germanium-bridged complex 3 containing two fewer valence electrons relative to μ2-Ge[Mn(η5-C5R5)(CO)]2, is orbitally non-degenerate and leads to an energetic barrier that prevents facile rotation about the Re–Ge–Re axis. It is also possible, however, that the barrier to rotation is sterically determined. For example, another bridged dirhenium complex reported by our group, [ZnRe(η5-Cp)(BDI)]2, also did not freely rotate in solution about the Re–Zn–Zn–Re axis.35 The lack of rotation in this example was almost certainly due to steric constraints, as the compound was devoid of any Re–Zn π-bonding, and as such we cannot rule out similar steric factors in 3.

Continuing to descend the group 14 column, we found that reactions between Na[Re(η5-Cp)(BDI)] and both SnCl2 and PbCl2 were unsuccessful in producing any isolable Re–E (E = Sn, Pb) bonded products. Instead, we noted the formation of Re(η5-Cp)(BDI), a common byproduct in reactions with this rhenium(I) starting material upon one-electron oxidation, suggesting that, in contrast to GeCl2, both SnCl2 and PbCl2 are reduced by Na[Re(η5-Cp)(BDI)]. However, use of an amidinate-supported stannylene led to the desired reactivity. Addition of Na[Re(η5-Cp)(BDI)] to SnCl[PhC(NBu)2] in Et2O at –78 ºC led to a dark purple solution. Following a cold workup and crystallization from pentane at ambient temperature for two hours, we obtained the α-metallostanllene, Re[SnC(PhC(NBu)2)](η5-Cp)(BDI) (4), in 77% yield (Scheme 3). Longer crystallization times or slower reaction workups with ambient temperature

![Scheme 3. Synthesis of α-metallostanllene 4. Gradual decomposition of 4 is observed in toluene-d8 solution above ca. 0 ºC to form Re(η5-Cp)(BDI)66 and an unknown amidinate product.](image)
silylene indicating significant deviation from the planarity observed in distance in σ-metallostannylene at –63°C in the spectrometer (Figures S16–S18). Initial spectra at –63°C show that the two amidinate tert-butyl groups are distinguishable as separate singlets, suggesting restricted rotation about the Re–Sn bond. However, these singlets coalesce around –3°C, as the relatively small energetic barrier to rotation is overcome. Around this same temperature, however, signals attributable to decomposition products appear, and upon warming to 17°C, resonances for both Re(η⁵-Cp)(BDI) and an unknown amidinate byproduct are observed. Unfortunately, attempts to observe a ¹¹¹Sn(¹H) resonance for σ-metallostannylene 4 were unsuccessful.

Contrary to the planar tetrylene geometries observed for silylene 1a and germylene 2, σ-metallostannylene 4 adopts a bent coordination geometry at the tin center in the solid state (Figure 7). In this case, the Re–Sn bond distances for the two molecules of σ-metallostannylene 4 in the asymmetric unit were found to be 2.7532(5) and 2.7562(5) Å, which are more than 0.4 Å longer than that of the Re–Ge bond in germylene 2. The Re–Sn distance in σ-metallostannylene 4 falls in line with reported Re–Sn single bonds, with the additional feature that this is the first example of rhenium bound to a formally Sn(II) center. The Re–Sn–N3/N4 angles range from 124.35(9)° to 129.58(9)°, indicating significant deviation from the planarity observed in silylene 1a and germylene 2, likely due to the accommodation of a tin-based lone pair. While the bent geometry in 4 is slightly more planar relative to the few previously reported σ-metallostannylene complexes,⁴⁵,⁴⁶,⁵⁰,⁶⁶–⁷¹ the geometry is generally more consistent with a σ-metallotetrylene structure than with rhenium-silylene and -germylene complexes 1a and 2.

Computational investigations of σ-metallostannylene 4 corroborated the presence of a Re–Sn single bond with a non-bonding lone pair orbital on tin (Figure 8). The natural bonding orbital of 4 exhibits σ-symmetry and is polarized towards rhenium, with a WBI of 0.9 and natural charges of –0.43 on Re and 1.18 on Sn. The lone pair of tin in 4 therefore does not interact significantly with rhenium-based orbitals, as is the case in silylene 1a and germylene 2, leading to the observed σ-metallostannylene structure in 4. It may be the case that the more diffuse orbitals of tin and decreased mixing of its s and p atomic orbitals, relative to silicon and germanium, leads to less favorable orbital overlap with rhenium d-orbitals and precludes the necessary orbital mixing required for the trigonal planar bonding geometry seen in silylene 1a and germylene 2. This type of geometric distortion upon moving to a heavier group 14 analogue is consistent with trends seen previously between heavy main group elements.¹¹

Conclusions
We have demonstrated that salt metathesis reactions between a series of amidinate-supported tetrylenes, ECl[PhC(N(t₂-Bu))₂] (E = Si, Ge, Sn), and the sodium salt of a bulky rhenium(I) cyclopentadienide β-diketiminate leads to rhenium metallotetrylenes with unusual bonding arrangements. While the silicon and germanium analogues engage in short, polarized multiple bonds with rhenium through incorporation of the tetrylene-based lone pair in bonding along with backdonation from rhenium d-orbitals to tetrylene p-orbitals, the heavier stannylene compound retains its non-bonding lone pair orbital in a bent geometry, consistent with established disparities in the bonding of heavier main group elements. In addition, we found that manipulation of reaction conditions, especially temperature, leads to multiple products in the case of reactions with SiCl[PhC(N(t₂-Bu))₂]. We isolated a complex with a very unusual silane bridge between rhenium and a Cp ligand and observed a diazene-functionalized silylene via dinitrogen activation. Finally, we accessed a rare example of a μ₂-tetrrelido complex featuring a naked germanium atom bridged between two rhenium centers that had a slightly bent geometry relative...
to those of related complexes. Investigations into potential reactivity across this array of polarized M–E bonds is ongoing and will be the subject of future reports.

Conflicts of interest

There are no conflicts to declare.

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Notes and references