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# Molecular Bis(chalcogenido) Titanates of Te, Se, and S

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**ABSTRACT:** A series of titanate cisoid bis(chalcogenidos) (Ch = Te, Se, and S) complexes supported by the $\beta$-diketiminate ligand BDI$^-$ = [ArNC(CH$_3$)]$_2$CH (Ar = 2,6-$^i$Pr$_2$C$_6$H$_3$) are readily assembled via treatment of the Ti$^{III}$ precursor (BDI)Ti(CH$_2$SiMe$_3$)$_2$ with 2.5 equiv of elemental "Ch" source and 1 equiv of reductant in the presence of crown-ether. In the absence of the electride, Te or S addition to (BDI)Ti(CH$_2$SiMe$_3$)$_2$ results instead in the isolation of a mononuclear tellurido-tellurolate [(BDI)Ti(=Te)-(TeCH$_2$SiMe$_3$)] and the bridging sulfido-thiolate complex [(BDI)Ti(SCH$_2$SiMe$_3$)($\mu$-S)]$_2$, respectively. In the case of Se, the rare selenido-perselenoate complex [(BDI)Ti(=Se)($\eta^2$-SeSeCH$_2$SiMe$_3$)] was isolated. In addition to crystallographically and spectroscopically characterizing all of the complexes, we demonstrate the latter species to be likely intermediates in the formation of [(BDI)Ti(Ch)$_2$]$^-$ via the addition of electride.



Transition metal bis(chalcogenidos) (TMBCs) are functionalities found in multifaceted areas of chemistry ranging from biological systems,[1] metal-catalyzed oxidations,[2] hydrodesulfurization,[3] and electronic and energy storage industries.[4] For the latter, TMBCs are considered the new generation of alkali-metal-free anodes for improved battery technology.[5] Specifically, attention has been shifted to early transition metal chalcogenidos composed of Ti (empirical formula of TiCh$_2$, Ch = Te, Se, and S) since these materials show promise as anodes for high-capacity and longer life-span rechargeable batteries that can operate with base metals such as Zn and under aqueous conditions.[6] Whereas TiTe$_2$ electrodes offer the prospect of high durability, the TiS$_2$ analogue provide higher voltage, higher energy density, and is generally considered a more environmentally friendly candidate.[7] Our research is aimed at developing a systematic approach to preparing well-defined models of TiCh$_2$ in the condensed phase, in the form of titanate complexes [(L)Ti-(=Ch)$_2$]$^-$ where L = PNP or BDI (PNP$^-$ = N[2-P$^i$Pr$_2$-4-methylphenyl]$_2$; BDI$^-$ = [ArNC(CH$_3$)]$_2$CH, Ar = 2,6-$^i$Pr$_2$C$_6$H$_3$), while expanding this motif to its lighter congeners such as an unknown bis(sulfido) titanate moiety. To date, our studies have been strictly limited to the chalcogen Te using various sources such as Te metal, Te/PR$_3$, or tellurolates.[8]

Since the late 20th century, a series of TMBCs has been reported. Parkin, Cotton, and Yoshida described the synthesis of a *trans*-M(Ch)$_2$(L)$_n$, where M = Mo, W; Ch = O, S, Se, Te; and L = P(CH$_3$)$_3$ ($n$ = 4), dppe (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$, $n$ = 2), and Me$_8$[16]-aneS$_4$ (Me$_8$[16]-aneS$_4$ = tetradentate thioether macrocycle, $n$ = 1) (Figure 1, left).[9] More recently, Chirik and co-workers reported on the synthesis and characterization of bis(chalcogenidos) of vanadium utilizing a reduced bis(imino)pyridine ligand framework (Figure 1) that can facilitate a four-electron redox profile via metal−ligand cooperativity.[10] In addition to the aforementioned reports, other studies outlining terminal tris-chalcogenidos of group 6 and 7,[11] along with terminal monochalcogenido for group 4 and 5, have also been reported.[12] However, mononuclear and terminal bis(chalcogenidos) for transition metals (TMs) earlier than group 5 remain far more under developed, especially when invoking 3d transition metals.[8a,b] Notably, a systematic approach to delivering two chalcogenide atoms for not only Te but also its lighter congeners Se and S is lackluster since S, in particular, has a greater tendency to catenate and/or bridge via the more nucleophilic sulfido group.[13]

Previously, we documented the synthesis and reactivity of the first 3d transition metal bis(tellurido), (PNP)V(=Te)$_2$ (PNP$^-$ = N[2-P$^i$Pr$_2$-4-methylphenyl]$_2$, Figure 1), from (PNP)-V(CH$_2$$^t$Bu)$_2$[14] and Te.[8a] More recently, the bis(telluride) titanate, [CoCp*$_2$][(L)Ti(=Te)$_2$] (L = PNP or BDI) was also reported.[8b] Unfortunately, complex [CoCp*$_2$][(BDI)Ti-(=Te)$_2$] is always accompanied with formation of the ditelluride, [CoCp*$_2$][(BDI)Ti(=Te)(Te$_2$)], due to the presence of residual Te metal in the mixture and its propensity to react with the four-coordinate fragment [(BDI)Ti(Te)$_2$]$^-$ (Figure 1, right). More recently, we found that formation of the bis(tellurido) functionality could be extended systematically to group 5 TM via the use of a tellurolate reagent "LiTeCH$_2$SiMe$_3$".[8c] Since TMBCs are quite scant with 3d metals and given our breakthrough with vanadium[8a] and titanium,[8b] we inquired if low-coordinate bis(tellurido) motifs could be extended to the other chalcogens that would provide us access to this rare motif without the deleterious catenated products. To establish an appropriate synthetic route to the TMBCs, we focused on a ligand scaffold that was more resistant to oxidation but which allowed the coordination

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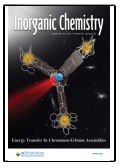


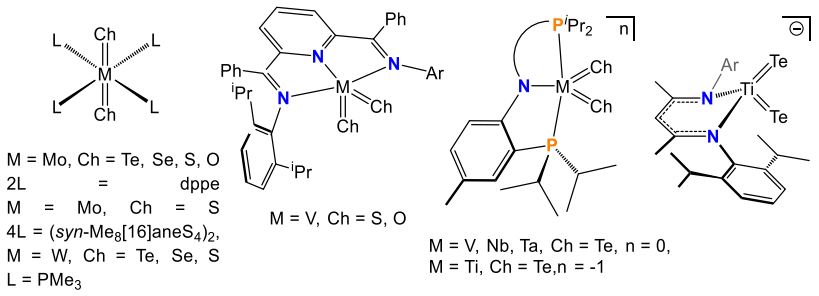
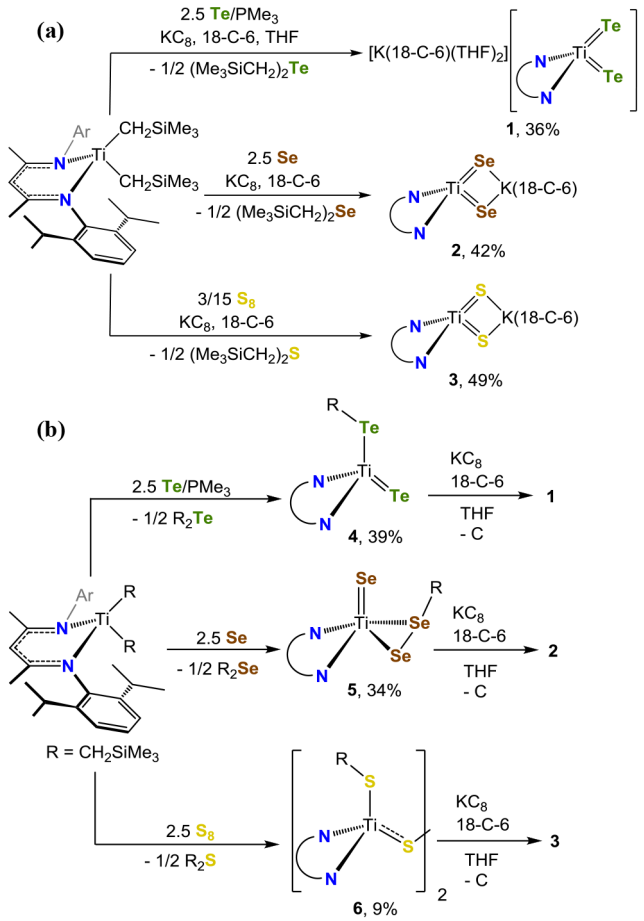



**Figure 1.** Examples of bis(chalcogenido) complexes.

number to remain relatively low. As a result, we excluded the use of PNP and turned our attention to the *N*-based chelate BDI.

Treatment of $[(BDI)Ti(CH_2SiMe_3)_2]$[15] with 2.5 equiv of Te solubilized with $P(CH_3)_3$, followed by reduction with $KC_8$ and 18-crown-6 (18-C-6) in THF resulted in the isolation of the $Ti^{IV}$ complex $[K(18\text{-}C\text{-}6)(THF)_2][(BDI)Ti(=Te)_2]$ (**1**) in 36% yield (Scheme 1a), following workup of the reaction mixture. Multinuclear NMR spectroscopic studies revealed a single product corresponding to **1** without evidence of formation of the ditelluride-tellurido anion $[(BDI)Ti(=Te)(Te_2)]$ impurity produced via the original report using $Te^0$/$P(CH_3)_3$ and reductant $[CoCp^*_2]$ (vide supra, Figure 1).[8b] Single-crystal X-ray diffraction studies (scXRD), obtained from a saturated THF solution at −35 °C, confirm the formation of a four-coordinate monomeric $Ti^{IV}$ complex containing two terminal tellurido ligands fashioned in a *cisoid* configuration about the metal center (Figure 2, left). The structure of **1** reveals Ti−Te bond distances of 2.5271(5) and 2.5002(5) Å, comparable to those recently reported by our group for the discrete salts ($[CoCp^*_2][(PNP)Ti(=Te)_2]$: 2.5185(6) Å; $[CoCp^*_2][(BDI)Ti(=Te)_2]$: 2.5188(7), 2.4890(7) Å).[8b] Additionally, the solid-state structure of **1** shows no close contact pairing of the tellurido ligands and sequestered potassium $[K(18\text{-}C\text{-}6)(THF)_2]^+$.

**Scheme 1. (a) Synthesis of the Bis(chalcogenido) from the Bis(alkyl)titanium Precursor to Form Complexes 1, 2, 3; (b) Synthesis of Complexes 4, 5, and 6 and Subsequent Conversion to the Corresponding Bis(chalcogenido) Complexes 1−3**




Using our successful approach to preparing **1** directly from precursor $[(BDI)Ti(CH_2SiMe_3)_2]$ with Te and electride,[16] we decided to extend our strategy to Se and S. Accordingly, treatment of $[(BDI)Ti(CH_2SiMe_3)_2]$ with 2.5 equivalents of $Se^0$ powder, followed by $KC_8$ and 18-C-6, resulted in the formation of the bis(selenido) titanate complex $[(BDI)Ti(=Se)_2\{K(18\text{-}C\text{-}6)\}]$ (**2**) (Scheme 1a) in 42% yield. Conveniently, $PMe_3$ was not needed as a phase-transfer catalyst for elemental Se. Multinuclear NMR spectroscopy performed on **2** revealed a $C_{2v}$ symmetric complex (Figure S3) although no resonances were observed via $^{77}Se\{^1H\}$ NMR spectroscopy. Single crystals of **2** could be obtained by DME/$Et_2O$ vapor diffusion at −35 °C, which revealed a four-coordinate $Ti^{IV}$ ate-complex supported by two *cis*-terminal selenido ligands which are symmetrically related about a 2-fold axis (Figure 2, center). The Ti = Se bond lengths in **2**, reported in Table 1, are 2.302(4) and 2.294(4) Å, with a Se−Ti−Se angle of 115.59(2)°. Unlike **1**, the *cisoid* selenido ligands chelate to a potassium center with Se−K distances of 3.551(5) and 3.347(5) Å (Table 1).

Following the successful recipe for the more nucleophilic bis(selenido) motif in **2**, an analogous titanium product was obtained by using elemental sulfur. Adding 2.5 equiv of $S_8$ to a stirring THF solution of $[(BDI)Ti(CH_2SiMe_3)_2]$, followed by addition of $KC_8$/18-C-6 at 25 °C and subsequent recrystallization at −35 °C yielded the *cisoid* bis(sulfido) $Ti^{IV}$ complex $[(BDI)Ti(=S)_2\{K(18\text{-}C\text{-}6)\}]$ (**3**) in 49% isolated yield, identified by a combination of multinuclear NMR spectroscopy (Figures S14 and S15) and scXRD (Figure 2, right). Resonances in $^1H$ NMR spectroscopy reveal a $C_{2v}$ symmetric complex, and the structure of **3** shows short Ti=S bond lengths of 2.1713(17) and 2.1520(18) Å, joining a handful of Ti=S moieties having been crystallographically characterized.[12b,c,h,m,17,18] Akin to **2**, the bis(sulfido) ligands chelate a potassium center with S−K bond lengths of 3.547(2) and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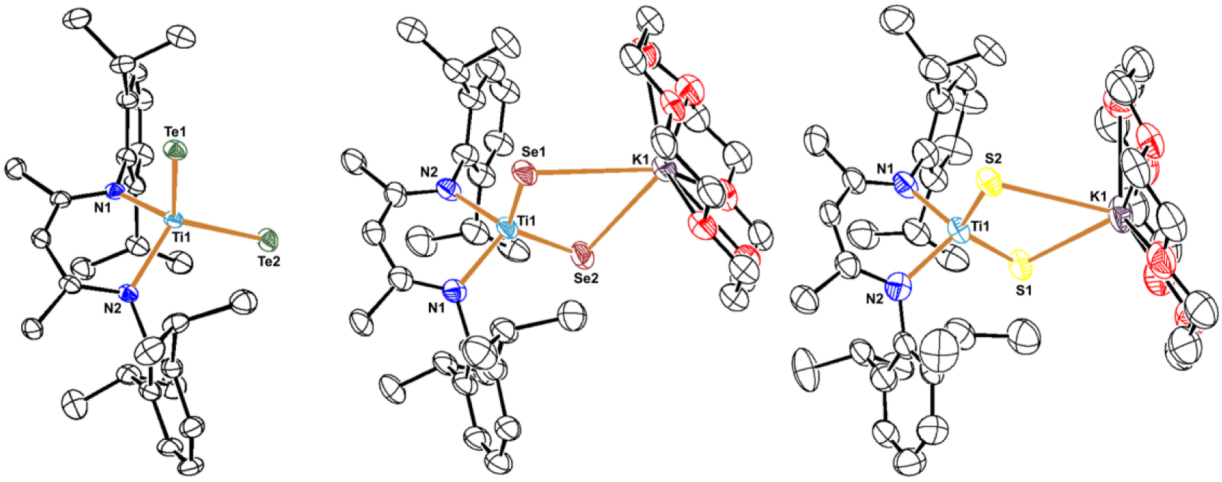


**Figure 2.** Solid-state structures of **1** (left), **2** (center), and **3** (right) with thermal ellipsoids at 50% probability. H atoms, residual solvent, and counterion $[K(18\text{-C-}6)(THF)_2]^+$ are omitted for clarity (for complex **1**).

**Table 1. Selected Bond Lengths and Angles for Complexes 1−3**

| Complex | **1**(Te) | **2**(Se) | **3**(S) |
|---|---|---|---|
| Ti=Ch (Å) | 2.5271(5) | 2.302(4) | 2.1713(17) |
| | 2.5002(5) | 2.294(4) | 2.1520(18) |
| Ch−Ti−Ch (°) | 116.79(2) | 115.49(14) | 115.20(7) |
| Ch−K (Å) | n/a | 3.359(5) | 3.126(2) |
| | | 3.581(5) | 3.547(2) |

3.126(2) Å, and having a similar S−Ti−S angle of 115.20(7)° (Figure 2, Table 1).

Arnold, McDonald, and Piers have demonstrated the formation of metal chalcogenides of group 3, 4, and 5 via dialkyl- or disilylchalcogenide ($R_2Ch$; where Ch = Te, Se, S) elimination.[19−21] To the best of our knowledge, the formation of metal bis(chalcogenidos) through $R_2Ch$ elimination remains unknown. To gain insight into the mechanism of formation of **1**−**3**, we explored different conditions in the hopes of isolating intermediates in these reactions. Thus, we explored the reactivity of 2.5 equiv of Ch (Ch = Te, Se, S) to $[(BDI)Ti(CH_2SiMe_3)_2]$ in the absence of reductant and crown-ether.

To a suspension of $[(BDI)Ti(CH_2SiMe_3)_2]$ and Te powder was added 2 drops of $P(CH_3)_3$, which afforded a dark-red crystalline material, identified to be $[(BDI)Ti(=Te)(TeCH_2SiMe_3)]$ (**4**), in 39% yield (Scheme 1b). Multinuclear NMR spectroscopy of **4** reveals a diamagnetic, $C_s$ symmetric complex (Figure S7) along with a highly upfield tellurolate $^{125}Te\{^1H\}$ NMR resonance of 112 ppm (Figure S10), when compared to other reported chemical shifts of Ti tellurolate complexes ($^{125}Te\{^1H\}$, $C_6D_6$; 810, 783, 709, 659 ppm).[22] A scXRD study of **4** confirms a monomeric four-coordinate $Ti^{IV}$ complex featuring a terminal tellurido and tellurolate ligand (Figure 3, left). The tellurido, Ti−Te1 bond length of 2.4526(7) Å in **4** is the shortest bond length reported to date when compared to other examples {*cf.* $[(\eta^4\text{-Me}_8\text{taa})Ti(=Te)]$: Ti−Te = 2.484(2) Å ($\eta^4\text{-Me}_8\text{taa}^{2-}$ = octamethyldibenzotetraaza[14]annulene); $[CoCp^*_2][(PNP)Ti(=Te)_2]$: Ti−Te = 2.5185(6) Å; $([CoCp^*_2][(BDI)Ti(=Te)_2]$: Ti−Te = 2.5188(7), 2.4890(7) Å}.[8b,12b] Interestingly, the Ti1−Te2 bond of 2.6465(8) Å for the tellurolate is also comparatively shorter than in previously characterized titanium tellurolate complexes {*cf.* $(\mu,\eta^5{:}\eta^5\text{-Pn}^{\dagger})_2[Ti(TePh)]_2$, Ti−Te = 2.6866(7) Å ($Pn^{\dagger-}$ = 1,4-$\{Si^iPr_3\}_2C_8H_4$); $[Cp_2Ti\{TeSi(SiMe_3)_3\}_2]$, Ti−Te = 2.788(1) Å; $[Cp_2Ti\{Te(SiMe_3)_3\}$-

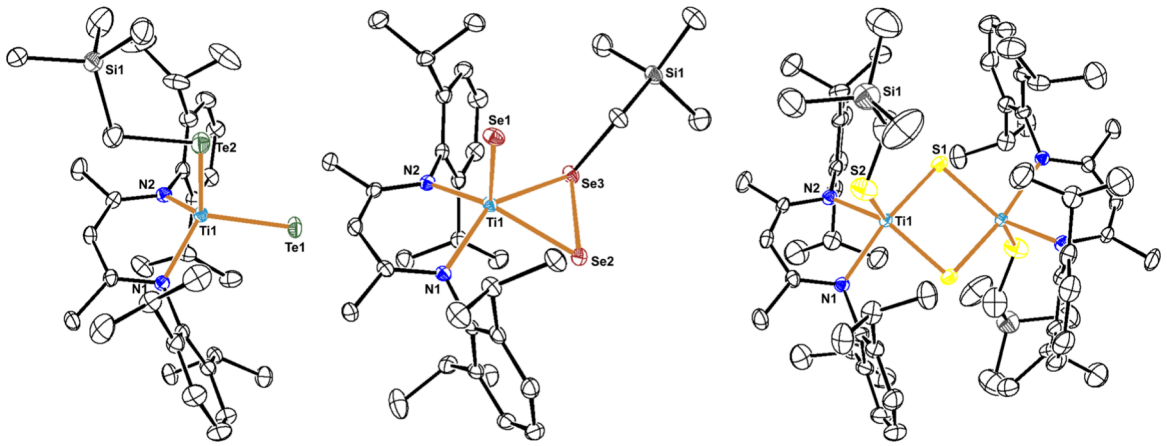


**Figure 3.** Crystal structures of **4** (left), **5** (center), and **6** (right) with thermal ellipsoids at 50% probability. H atoms and residual solvent have been omitted for clarity.



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$(P(CH_3)_3)]$, Ti−Te = 2.8955(30) Å; and $[Cp_2Ti(TeSnPh_3)]$, Ti−Te = 2.8681 (18) Å}[22,23] but longer than the sum of their double-bond covalent radii (2.45 Å).[24]

To our surprise, exploring similar conditions with $[(BDI)Ti(CH_2SiMe_3)_2]$ with 2.5 equiv of Se in the absence of reductant yielded a different outcome. This reaction furnished dark red crystals of $[(BDI)Ti(=Se)(\eta^2\text{-}SeSeCH_2SiMe_3)]$ (**5**) 34% yield (Scheme 1b), suitible for scXRD (Figure 3, center). The solid-state structure of **5** reveals a mononuclear five-coordinate $Ti^{IV}$ complex that features a terminal selenido ligand and an unprecedented $\eta^2$-perselenoate ligand (Figure 3). The Ti=Se motif in **5** (Ti=Se, 2.2452(4) Å) is comparable to the few other three known crystallographically characterized examples {*cf.* $[(\eta^4\text{-}Me_8taa)Ti(=Se)]$, Ti−Se = 2.269(2) Å ($\eta^4$-$Me_8taa^{2-}$ = octamethyldibenzotetraaza[14]annulene); $[(\kappa^3\text{-}Tp)(\kappa^2\text{-}Tp)Ti(=Se)]$, Ti−Se = 2.255(1) Å ($Tp^{1-}$ = hydrotris(pyrazol-1-yl)borate); and ($^{Ket}$Guan)($Im^{Dipp}$N)Ti(=Se), Ti−Se = 2.258(7) Å ($^{Ket}$guan$^-$ = $[(^tBu_2C{=}N)C(NDipp)_2]$, $Im^{Dipp}N^-$ = 1,3-bis(Dipp)imidazoline-2-iminato, Dipp = 2,6-diisopropylphenyl)}.[12b,m] The $\eta^2$-perselenoate[25] ligand of **5** displays Ti−Se bond lengths of 2.4970(4) and 2.6930(4) Å in addition to a Se−Se bond length of 2.3360(3) Å, typical for Se-Se single bond.[25,26] Despite not being able to spectroscopically identify the Ti=Se and Ti($\eta^2$-$SeSeCH_2SiMe_3$) motifs, a resonance at 325 ppm via $^{77}Se\{^1H\}$ NMR was observed for the $(Me_3SiCH_2)_2Se$ side-product.[27]

In the case of sulfur, addition of 2.5 equiv of its elemental form to a stirring THF solution of $[(BDI)Ti(CH_2SiMe_3)_2]$ and subsequent work up afforded dark red crystals in low yield (9%) from a pentane solution (Scheme 1b). A scXRD study of a single crystal confirms the formation of a dinuclear complex having bridging sulfido and terminal thiolate ligands, $[(BDI)Ti(SCH_2SiMe_3)(\mu\text{-}S)]_2$ (**6**) (Figure 3, right). We speculate that complex **6** forms as a result of the more nucleophilic nature of the sulfido ligand when compared to the tellurido counterpart in **4**. Specifically, the scXRD study of **6** features a highly distorted five-coordinate dimeric ($\tau_5$ = 0.56) $Ti^{IV}$ complex with bridging Ti−S bond lengths of 2.2723(11) and 2.3385(10) Å and thiolate bond of 2.3011(15) Å, within the expected range for similar and previously reported examples.[28,29] It was found that dissolving crystalline complex **6** in $C_6D_6$ over several minutes resulted in immediate decomposition via the formation BDI-H[30] when the mixture is assayed by $^1$H NMR spectroscopy. Gratifyingly, immediate collection of the $^1$H NMR spectrum of the reaction mixture, without workup, allows for the assignment of the $C_s$ symmetric product, **6**, some free BDI-H, and $(Me_3SiCH_2)_2S$.[31] Unfortunately, attempts to spectroscopically identify complex **6** in its pure form via NMR spectroscopy have been unsuccessful.

With complexes **4**−**6** in hand, addition of 1 equiv of $KC_8$ and 18-C-6 allowed for the isolation of the corresponding bis(chalcogenidos) **1**−**3** in near quantitative yields (Scheme 1b) via extrusion of a presumed $Me_3SiCH_2\cdot$ radical.[32,33] While this method may shed light on the possible intermediates involved in the reaction toward the bis(chalcogenidos), the one-pot synthesis from the bis(alkyl) titanium is a far more facile and higher-yielding route. Additionally, the byproducts formed in the one-pot reaction can be easily washed away with pentane, leaving the desired product in pure form.

In summary, we have established a synthetic route to bis(chalcogenidos) of titanium where Ch = Te, Se, S in the form of either the discrete salts or the ate complexes having the anion $[(BDI)Ti(Ch)_2]^-$. As the chalcogenido becomes more nucleophilic, the K(crown-ether)$^+$ coordinates as in the case of the bis(selenido) and bis(sulfido) ate-products. Although the mechanism to formation of these bis(chalcogenido) complexes of titanium is not straightforward, we speculate such a process is bimolecular in nature and likely involves low-valent Ti species. Using a chalcogen source, a bis(alkyl) titanium precursor followed by reduction, allows for a facile entry into these discrete, molecular analogues of $TiCh_2$.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.4c03060.

Synthetic procedures and NMR, IR, UV−vis, and X-ray crystallographic data (PDF)

### Accession Codes

CCDC 2333370−2333375 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.


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### Notes

The authors declare no competing financial interest.

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## ■ ABBREVIATIONS

CoCp*, decamethylcobaltocene; THF, tetrahydrofuran; Te, elemental tellurium; Se, elemental selenium; $S_8$, elemental sulfur; dipp, 2,6-$^{i}Pr_2C_6H_3$; $PNP^-$, N[2-P$^{i}Pr_2$-4-methylphenyl)$_2$; $BDI^-$, $[ArNC(CH_3)]_2CH$, (Ar = 2,6-$^{i}Pr_2C_6H_3$); scXRD, single-crystal X-ray diffraction studies

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