

Multiple Bonding of Titanium and Vanadium to the Heavier Chalcogens: Syntheses and Structures of the Terminal Selenido and Tellurido Complexes $[\eta^4\text{-Me}_8\text{taa}]M=E$ ($M = \text{Ti, V}$; $E = \text{Se, Te}$)

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Received April 2, 1997

Multiple bonding of the transition metals is under intense scrutiny.^{1,2} To date, however, most of these studies have been concerned with transition metal complexes exhibiting multiple bonds to the second-row groups 14–16 elements: carbon, nitrogen, and oxygen. By comparison, relatively few reports describe multiple bonding to the heavier congeners of these elements. We have a particular interest in multiple bonding of transition metals to the heavier chalcogens (especially tellurium),^{3,4} and, with this paper, we extend our investigations to titanium and vanadium. These studies include the first structural characterization of multiply bonded titanium and vanadium terminal tellurido complexes.

As with multiply bonded chalcogenido complexes of the transition metals in general, the vast majority of studies concerned with titanium and vanadium have centered on oxo and sulfido derivatives.⁵ Terminal tellurido complexes of these elements are particularly elusive. For example, Piers and Ziegler recently described several attempts to prepare the titanium tellurido complex $\text{Cp}^*_2\text{Ti}(\text{Te})(\text{NC}_5\text{H}_5)$;⁶ rather than yielding a terminal tellurido complex, however, only the bridging tellurido and ditellurido complexes $[\text{Cp}^*_2\text{Ti}]_2(\mu\text{-Te})$ and $\text{Cp}^*_2\text{Ti}(\eta^2\text{-Te}_2)$ were isolated. The inability to isolate the titanium tellurido complex $\text{Cp}^*_2\text{Ti}(\text{Te})(\text{NC}_5\text{H}_5)$ is especially significant in light of the fact that both the zirconium and hafnium tellurido analogues $\text{Cp}^*_2\text{M}(\text{Te})(\text{NC}_5\text{H}_5)$ ($M = \text{Zr, Hf}$)^{3a,b} and the titanium oxo and sulfido complexes, $\text{Cp}^*_2\text{Ti}(\text{O})(\text{NC}_5\text{H}_5)$ ⁷ and $\text{Cp}^*_2\text{Ti}(\text{S})(\text{NC}_5\text{H}_5)$,⁸ are known.⁹ The synthesis of a complex containing a multiply bonded $[\text{Ti}=\text{Te}]$ moiety, therefore, presented a challenge. Since macrocyclic ligands (e.g., porphyrin, phthalocyanine, and tetraazaannulene) have proven to be most effective for the isolation of terminal titanium oxo complexes,¹⁰ it was

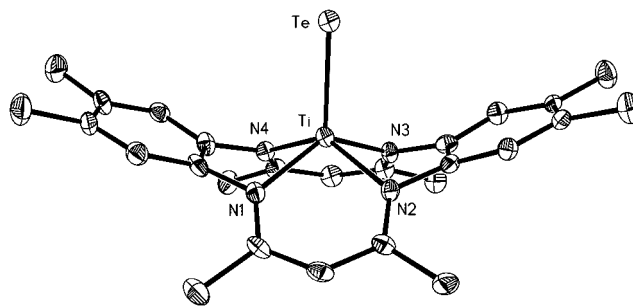


Figure 1. Molecular structure of $[\eta^4\text{-Me}_8\text{taa}]\text{Ti}=\text{Te}$.

rationalized that such a ligand system could likewise support a $[\text{Ti}=\text{Te}]$ moiety, in a manner similar to our previously reported use of the octamethylidibenzotetraaza[14]annulene dianion to stabilize the group 14 terminal tellurido counterpart $[\eta^4\text{-Me}_8\text{taa}]\text{GeTe}$.^{11–13}

Indeed, the titanium tellurido complex $[\eta^4\text{-Me}_8\text{taa}]\text{Ti}=\text{Te}$ is readily synthesized by the reaction of $[\eta^4\text{-Me}_8\text{taa}]\text{TiCl}_2$ ¹⁴ with $(\text{Bu}^i\text{Me}_2\text{Si})_2\text{Te}$ ^{15,16} (Scheme 1). The molecular structure of $[\eta^4\text{-Me}_8\text{taa}]\text{Ti}=\text{Te}$ has been determined by X-ray diffraction,¹⁷ as illustrated in Figure 1, thereby providing evidence for the monomeric nature of the complex and the presence of a terminal tellurido ligand. Of most relevance, the $\text{Ti}=\text{Te}$ bond length of 2.484(2) Å in $[\eta^4\text{-Me}_8\text{taa}]\text{Ti}=\text{Te}$ is significantly shorter than all other $\text{Ti}-\text{Te}$ interactions that have been reported, clearly attesting to the multiply bonded nature of the interaction. Specifically, $\text{Ti}-\text{Te}$ single bonds are known to span the range 2.62–2.91 Å, with a mean of 2.78 Å.¹⁸

As would be expected, the multiply bonded $[\text{Ti}=\text{Te}]$ moiety is reactive and $[\eta^4\text{-Me}_8\text{taa}]\text{Ti}=\text{Te}$ is readily converted to the oxo derivative $[\eta^4\text{-Me}_8\text{taa}]\text{Ti}=\text{O}$ ^{12d} upon treatment with either

(10) For a brief review, see: McAuliffe, C. A.; Barratt, D. S. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Chapter 31.

(11) Kuchta, M. C.; Parkin, G. *J. Chem. Soc., Chem. Commun.* **1994**, 1351–1352.

(12) In this regard, tetraaza[14]annulene dianions have also been used to support oxo and sulfido complexes of titanium and vanadium, e.g., $[\eta^4\text{-Me}_8\text{taa}]\text{ME}$ ($M = \text{Ti, V}$; $E = \text{O, S}$) and $[\eta^4\text{-Me}_8\text{taa}]\text{TiO}$.^{12d} (a) Goedken, V. L.; Ladd, J. A. *J. Chem. Soc., Chem. Commun.* **1982**, 142–144. (b) Yang, C.-H.; Ladd, J. A.; Goedken, V. L. *J. Coord. Chem.* **1988**, 19, 235–251. (c) Housmekerides, C. E.; Pilato, R. S.; Geoffroy, G. L.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1991**, 563–566. (d) Housmekerides, C. E.; Ramage, D. L.; Kretz, C. M.; Shontz, J. T.; Pilato, R. S.; Geoffroy, G. L.; Rheingold, A. L.; Haggerty, B. S. *Inorg. Chem.* **1992**, 31, 4453–4468. (e) Goedken, V. L.; Ladd, J. A. *J. Chem. Soc., Chem. Commun.* **1981**, 910–911. (f) Yang, C.-H.; Ladd, J. A.; Goedken, V. L. *J. Coord. Chem.* **1988**, 18, 317–334. (g) Lee, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1989**, 145–149. (h) Cotton, F. A.; Czuchajowska, J.; Feng, X. *Inorg. Chem.* **1991**, 30, 349–353. (i) Schumann, H. *Polyhedron* **1996**, 15, 845–850. (j) Davies, D. L.; Grist, A. *J. Inorg. Chim. Acta* **1994**, 216, 217–221. (k) Schumann, H. *Z. Naturforsch.* **1995**, 50B, 1494–1504. (l) Sakata, K.; Kuroda, M.; Yanagida, S.; Hashimoto, M. *Inorg. Chim. Acta* **1989**, 156, 107–112. (m) Sakata, K.; Hashimoto, M.; Tagami, N.; Murakami, Y. *Bull. Chem. Soc. Jpn.* **1980**, 53, 2262–2270. (n) Sakata, K.; Yamaura, F.; Hashimoto, M. *Synth. React. Inorg. Met.-Org. Chem.* **1990**, 20, 1043–1057.

(13) For other terminal tellurido complexes of Ge, see: (a) Tokitoh, N.; Matsumoto, T.; Okazaki, R. *J. Am. Chem. Soc.* **1997**, 119, 2337–2338. (b) Ossig, G.; Meller, A.; Brönneke, C.; Müller, O.; Schäfer, M.; Herbst-Irmer, R. *Organometallics* **1997**, 16, 2116–2120.

(14) $[\eta^4\text{-Me}_8\text{taa}]\text{MCl}_2$ and $[\eta^4\text{-Me}_8\text{taa}]\text{M}=\text{O}$ ($M = \text{Ti, V}$) are obtained analogously to their $[\eta^4\text{-Me}_8\text{taa}]\text{MCl}_2$ and $[\eta^4\text{-Me}_8\text{taa}]\text{M}=\text{O}$ counterparts. See ref 12 and the Supporting Information.

(15) Detty, M. R.; Seidler, M. D. *J. Org. Chem.* **1982**, 47, 1354–1356.

(16) The synthesis of bridging chalcogenido complexes via metathesis of $\text{M}-\text{Cl}$ (including $\text{Ti}-\text{Cl}$ and $\text{V}-\text{Cl}$) bonds with $(\text{Me}_2\text{Si})_2\text{E}$ ($E = \text{S, Se, Te}$) is well precedented. See, for examples: (a) Maué, P. G.; Fenske, D. *Z. Naturforsch.* **1988**, 43B, 1213–1218. (b) Fenske, D.; Grissinger, A. *Z. Naturforsch.* **1990**, 45B, 1309–1313. (c) Fenske, D.; Grissinger, A.; Loos, M.; Magull, J. *Z. Anorg. Allg. Chem.* **1991**, 598/599, 121–128. (d) Fenske, D.; Ohmer, J.; Hachgenei, J.; Merzweiler, K. *Angew. Chem., Int. Ed. Engl.* **1988**, 27, 1277–1296.

(17) $[\eta^4\text{-Me}_8\text{taa}]\text{Ti}=\text{Te}\cdot 1.5(\text{C}_6\text{H}_6)$ is monoclinic $P2_1/c$ (no. 14), $a = 9.848(3)$ Å, $b = 24.290(8)$ Å, $c = 14.416(4)$ Å, $\beta = 94.15(2)^\circ$, $V = 3439(2)$ Å³, $Z = 4$.

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(3) For example, studies on the groups 4–6 transition metals include the following: (a) Howard, W. A.; Trnka, T. M.; Waters, M.; Parkin, G. *J. Organomet. Chem.* **1997**, 528, 95–121. (b) Howard, W. A.; Parkin, G. *J. Organomet. Chem.* **1994**, 472, C1–C4. (c) Shin, J. H.; Parkin, G. *Organometallics* **1994**, 13, 2147–2149. (d) Shin, J. H.; Parkin, G. *Organometallics* **1995**, 14, 1104–1106. (e) Rabinovich, D.; Parkin, G. *Inorg. Chem.* **1995**, 34, 6341–6361. (f) Murphy, V. J.; Parkin, G. *J. Am. Chem. Soc.* **1995**, 117, 3522–3528.

(4) For other examples of structurally-characterized terminal tellurido complexes, see: (a) Christou, V.; Arnold, J. *Angew. Chem., Int. Ed. Engl.* **1993**, 32, 1450–1452. (b) Gerlach, C. P.; Christou, V.; Arnold, J. *Inorg. Chem.* **1996**, 35, 2758–2766. (c) Gardner, D. R.; Fettingler, J. C.; Eichorn, B. W. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 1859–1860.

(5) (a) Trnka, T. M.; Parkin, G. *Polyhedron* **1997**, 16, 1031–1045. (b) Parkin, G. *Prog. Inorg. Chem.*, in press.

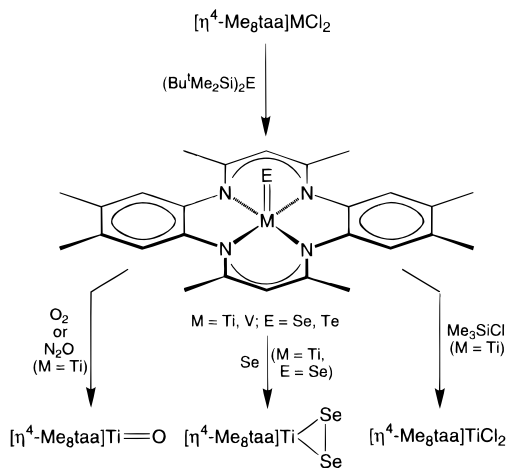
(6) (a) Fischer, J. M.; Piers, W. E.; MacGillivray, L. R.; Zaworotko, M. J. *Inorg. Chem.* **1995**, 34, 2499–2500. (b) Fischer, J. M.; Piers, W. E.; Ziegler, T.; MacGillivray, L. R.; Zaworotko, M. J. *Chem. Eur. J.* **1996**, 2, 1221–1229.

(7) Smith, M. R., III; Matsunaga, P. T.; Andersen, R. A. *J. Am. Chem. Soc.* **1993**, 115, 7049–7050.

(8) Sweeney, Z. K.; Polse, J. L.; Andersen, R. A.; Bergman, R. G.; Kubinec, M. G. *J. Am. Chem. Soc.* **1997**, 119, 4543–4544.

(9) One of the principal factors responsible for the difficulty in synthesizing $\text{Cp}^*_2\text{Ti}(\text{Te})(\text{NC}_5\text{H}_5)$ is a particularly weak $[\text{Ti}=\text{Te}]$ interaction. For example, Piers and Ziegler^{6b} have calculated the following $\text{M}=\text{E}$ bond energies: $\text{Cp}^*_2\text{Ti}=\text{O}$ (143.2 kcal mol⁻¹); $\text{Cp}^*_2\text{Ti}=\text{Te}$ (61.8 kcal mol⁻¹); $\text{Cp}^*_2\text{Zr}=\text{Te}$ (88.0 kcal mol⁻¹).

Scheme 1



O_2 or N_2O at room temperature (Scheme 1). Furthermore, $[\eta^4\text{-Me}_8\text{taa}]\text{Ti}=\text{Te}$ reacts with excess Me_3SiCl at room temperature to regenerate $[\eta^4\text{-Me}_8\text{taa}]\text{TiCl}_2$ (Scheme 1).¹⁹

The methodology used to synthesize $[\eta^4\text{-Me}_8\text{taa}]\text{Ti}=\text{Te}$ is also applicable to its vanadium counterpart $[\eta^4\text{-Me}_8\text{taa}]\text{V}=\text{Te}$ (Scheme 1). Unlike Schrock's $[\eta^4\text{-N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_3]\text{V}=\text{Te}$,²⁰ which is the only other example of a terminal vanadium tellurido complex, $[\eta^4\text{-Me}_8\text{taa}]\text{V}=\text{Te}$ is sufficiently stable to permit characterization by X-ray diffraction.²¹ Consistent with the presence of a multiple bond, the $\text{V}=\text{Te}$ bond lengths in the two crystallographically independent molecules [2.433(1) and 2.435(1) Å] are shorter than those in the bridging vanadium tellurido complex $[\text{V}(\text{CO})_3(\text{dppe})]_2(\mu_2\text{-Te})$ [2.514(3) and 2.522(3) Å].^{22,23}

In addition to the terminal tellurido complexes $[\eta^4\text{-Me}_8\text{taa}]\text{M}=\text{Te}$ ($\text{M} = \text{Ti, V}$), both the titanium and vanadium selenido analogues have been synthesized *via* reactions of $[\eta^4\text{-Me}_8\text{taa}]\text{MCl}_2$ with $(\text{Bu}^i\text{Me}_2\text{Si})_2\text{Se}$.²⁴ Notably, these complexes are also obtained by the reactions of the oxo derivatives $[\eta^4\text{-}$

(18) Structurally characterized complexes with $\text{Ti}-\text{Te}$ bonds include $[(\text{Cp}^{\text{Me}})_2\text{Ti}(\mu\text{-Te})_2]$, 2.791(3)–2.799(3) Å;^{18a} $(\text{Cp}^{\text{Me}})_5\text{Ti}_2(\mu\text{-Te})_6$, 2.622(2)–2.858(2) Å;^{18a} $[\text{Cp}^{\text{Me}}_2\text{Ti}(\mu\text{-Te})_2]$, 2.697(3)–2.705(3) Å;⁶ $\text{Cp}^{\text{Me}}_2\text{Ti}(\eta^2\text{-Te}_2)$, 2.808(3) Å;⁶ $\text{CpMe}_2\text{Ti}[\text{TeSi}(\text{SiMe}_3)_3]_2$, 2.788(1) Å;^{18b} and $\text{Cp}_2\text{Ti}[\text{TeSi}(\text{SiMe}_3)_3](\text{PMe}_3)$, 2.879(3)–2.912(3) Å.^{18b} (a) Fenske, D.; Grissinger, A. *Z. Naturforsch.* **1990**, *45B*, 1309–1313. (b) Christou, V.; Wuller, S. P.; Arnold, J. *J. Am. Chem. Soc.* **1993**, *115*, 10545–10552.

(19) The ability of Me_3SiCl to regenerate $[\eta^4\text{-Me}_8\text{taa}]\text{TiCl}_2$, and thereby effect the reverse of the reaction between $(\text{Bu}^i\text{Me}_2\text{Si})_2\text{E}$ and $[\eta^4\text{-Me}_8\text{taa}]\text{TiCl}_2$, is presumably the result of the instability of $(\text{Me}_3\text{Si})_2\text{E}$ compared to $(\text{Bu}^i\text{Me}_2\text{Si})_2\text{E}$. For example, $(\text{Me}_3\text{Si})_2\text{Te}$ experiences serious decomposition even in the dark under Ar at -20°C . See ref 15.

(20) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1994**, *33*, 1448–1457.

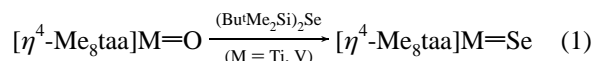
(21) $[\eta^4\text{-Me}_8\text{taa}]\text{V}=\text{Te}(\text{C}_6\text{H}_5\text{Me})$ is monoclinic $P2_1/c$ (no. 14), $a = 9.175(1)$ Å, $b = 25.923(5)$ Å, $c = 26.243(5)$ Å, $\beta = 93.96(1)^\circ$, $V = 6227(2)$ Å³, $Z = 4$.

(22) (a) Albrecht, N.; Hübener, P.; Behrens, U.; Weiss, E. *Chem. Ber.* **1985**, *118*, 4059–4067. (b) Schiemann, J.; Hübener, P.; Weiss, E. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 980–981.

(23) Other complexes for which $\text{V}-\text{Te}$ bond lengths have been determined include $[\text{TeSi}(\text{SiMe}_3)_3]_4$, $d(\text{V}-\text{Te}) = 2.550(3)$ – $2.570(3)$ Å;^{23a} $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{VTe}[\text{Si}(\text{SiMe}_3)_3]$, $d(\text{V}-\text{Te}) = 2.675(9)$ Å;^{23b} and $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{VTeSiPh}_3$, $d(\text{V}-\text{Te}) = 2.675(2)$ Å.^{23b} (a) Gerlach, C. P.; Wuller, S. P.; Arnold, J. *J. Chem. Soc., Chem. Commun.* **1996**, 2565–2566. (b) Gerlach, C. P.; Arnold, J. *Inorg. Chem.* **1996**, *35*, 5770–5780.

(24) $(\text{Bu}^i\text{Me}_2\text{Si})_2\text{Se}$ is prepared analogously to $(\text{Bu}^i\text{Me}_2\text{Si})_2\text{Te}$. See ref 12.

$[\eta^4\text{-Me}_8\text{taa}]\text{Ti}=\text{O}^{12d}$ and $[\eta^4\text{-Me}_8\text{taa}]\text{V}=\text{O}^{14}$ with $(\text{Bu}^i\text{Me}_2\text{Si})_2\text{Se}$ (eq 1). The structures of the selenido complexes $[\eta^4\text{-Me}_8\text{taa}]\text{M}=\text{O}$



$\text{Ti}=\text{Se}^{25}$ and $[\eta^4\text{-Me}_8\text{taa}]\text{V}=\text{Se}^{26}$ have been determined by X-ray diffraction and are characterized by $\text{Ti}=\text{Se}$ and $\text{V}=\text{Se}$ bond lengths of 2.269(2) and 2.210(2) Å, respectively, values that are substantially shorter than their corresponding $\text{M}-\text{E}$ single bond lengths.^{27,28} As with their tellurido counterparts, terminal selenido complexes of titanium²⁹ and vanadium^{20,23b,30–32} are rare, with only the latter having been structurally characterized by X-ray diffraction, *e.g.*, $[(\text{Me}_3\text{Si})_2\text{N}]_2[(\text{Me}_3\text{Si})_3\text{SiSe}]\text{V}=\text{Se}$ [2.1754(9) Å]^{23b} and $[\text{Et}_4\text{N}]_2[(\eta^2\text{-SCH}_2\text{CH}_2\text{S})_2\text{V}=\text{Se}]$ [2.196(3) Å].^{32,33}

With regard to reactivity, the titanium selenido complex behaves similarly to the tellurido derivative $[\eta^4\text{-Me}_8\text{taa}]\text{Ti}=\text{Te}$ upon treatment with O_2 , N_2O , and Me_3SiCl (Scheme 1); in addition, it also reacts with elemental selenium to give the diselenido complex $[\eta^4\text{-Me}_8\text{taa}]\text{Ti}(\eta^2\text{-Se}_2)^{34}$ (Scheme 1).

In summary, the macrocyclic octamethylidibenzotetraaza[14]-annulene dianion has proved to be an effective ligand for supporting terminal selenido and tellurido complexes of both vanadium and titanium. Furthermore, although sufficiently stable to permit isolation, the $\text{M}=\text{E}$ bonds in these complexes are reactive, as illustrated by conversions to $[\eta^4\text{-Me}_8\text{taa}]\text{Ti}=\text{O}$, $[\eta^4\text{-Me}_8\text{taa}]\text{TiCl}_2$, and $[\eta^4\text{-Me}_8\text{taa}]\text{Ti}(\eta^2\text{-Se}_2)$.

Acknowledgment. We thank the U.S. Department of Energy, Office of Basic Energy Sciences (Grant #DE-FG02-93ER14339) for support of this research. G.P. is the recipient of a Presidential Faculty Fellowship Award (1992–1997).

Supporting Information Available: Tables of analytical, spectroscopic, and crystallographic data and preparative details for $[\eta^4\text{-Me}_8\text{taa}]\text{ME}$ ($\text{M} = \text{Ti, V}$; $\text{E} = \text{Se, Te}$) (43 pages). See any current masthead page for ordering and Internet access instructions.

JA971043R

(25) $[\eta^4\text{-Me}_8\text{taa}]\text{Ti}=\text{Se} \cdot 1.5(\text{C}_6\text{H}_6)$ is monoclinic $P2_1/c$ (no. 14), $a = 9.662(3)$ Å, $b = 24.112(8)$ Å, $c = 14.309(4)$ Å, $\beta = 93.47(2)^\circ$, $V = 3327(2)$ Å³, $Z = 4$.

(26) $[\eta^4\text{-Me}_8\text{taa}]\text{V}=\text{Se} \cdot 1.5(\text{C}_6\text{H}_6)$ is monoclinic $P2_1/c$ (no. 14), $a = 9.577(1)$ Å, $b = 24.369(3)$ Å, $c = 14.167(2)$ Å, $\beta = 92.20(1)^\circ$, $V = 3304(2)$ Å³, $Z = 4$.

(27) For reference, $\text{Ti}-\text{Se}$ single bond lengths are observed in the range 2.37–2.76 Å, with a mean of 2.54 Å, while $\text{V}-\text{Se}$ single bond lengths are observed in the range 2.30–2.60 Å, with a mean of 2.47 Å. See: Cambridge Structural Database, Version 5.12, October 1996.

(28) The $\text{Ti}=\text{Se}$ and $\text{V}=\text{Se}$ bond lengths are *ca.* 0.22 Å shorter than their corresponding $\text{M}=\text{Te}$ bond lengths, a difference that is consistent with the difference in double bond covalent radii of Se (1.07 Å) and Te (1.27 Å). See: Pauling, L. *The Nature of The Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 224.

(29) The only terminal titanium selenido complex of which we are aware is (TTP)TiSe. See: Woo, L. K.; Hays, J. A.; Young, V. G., Jr.; Day, C. L.; Caron, C.; D'Souza, F.; Kadish, K. M. *Inorg. Chem.* **1993**, *32*, 4186–4192.

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(31) Ruppia, K. B. P.; Desmangles, N.; Gambarotta, S.; Yap, G.; Rheingold, A. L. *Inorg. Chem.* **1997**, *36*, 1194–1197.

(32) Nicholson, J. R.; Huffman, J. C.; Ho, D. M.; Christou, G. *Inorg. Chem.* **1987**, *26*, 3030–3034.

(33) (OEP)V=Se [2.19(2) Å] has been structurally-characterized by EXAFS. See ref 30a.

(34) Kisko, J. L.; Kuchta, M. C.; Parkin, G. Unpublished results.