9822 *J. Am. Chem. Soc.* **1993,** *115,* 9822-9823

Isocyanide-Induced Coupling of Terminal Tellurido Ligands: The Synthesis and Structure of $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$

Daniel Rabinovich and Gerard Parkin*

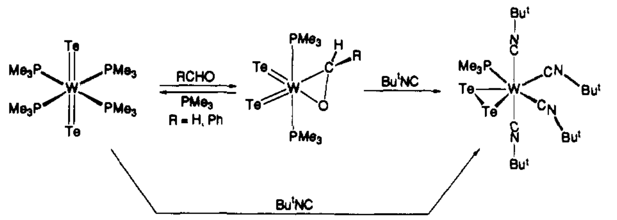
Department of Chemistry
Columbia University
New York, New York 10027

Received July 6, 1993

The chemistry of transition-metal selenido and tellurido complexes is noticeably underdeveloped compared with that of oxo and sulfido derivatives. However, selenido and tellurido complexes have recently been the objects of increased attention,[1-3] an interest that has been stimulated in part by applications to the electronics industry[3,4] and also by the discovery of selenium in biological systems.[5,6] Our specific interest in transition-metal tellurido complexes centers on the synthesis and reactivity of complexes with terminal M=Te and $M^-\equiv Te^+$ multiple bonds.[7] In this regard, we have recently reported the isolation of the first transition-metal complex containing a terminal tellurido ligand, namely *trans*-$W(PMe_3)_4(Te)_2$.[8] Subsequently, other terminal tellurido complexes have been prepared, including $(dmpe)_2M(TeR)_2(Te)$ [M = Zr, Hf; R = $Si(SiMe_3)_3$],[9] $Cp^*Nb(PMe_3)(NAr)(Te)$ ($Cp^* = \eta^5\text{-}C_5Me_5$; Ar = 2,6-$C_6H_3Pr^i_2$),[10] and $Cp^*_2Zr(Te)(NC_5H_5)$.[11] In this paper we report the unprecedented coupling of two terminal tellurido ligands giving a ditellurido moiety *via* a sequence that involves a reversible *trans*-to-*cis* rearrangement.

The trimethylphosphine ligands in *trans*-$W(PMe_3)_4(Te)_2$ are readily displaced by RCHO (R = H, C_6H_5) to give the dark red-brown diamagnetic η^2-aldehyde complexes $W(PMe_3)_2(Te)_2(\eta^2\text{-}OCHR)$ in 15–55% isolated yield (Scheme I).[12] Such reactivity is similar to that exhibited by the sulfido analogue *trans*-$W(PMe_3)_4(S)_2$.[13] The molecular structures of both aldehyde derivatives have been determined by X-ray diffraction.[14] Significantly, the tellurido ligands in $W(PMe_3)_2(Te)(\eta^2\text{-}OCHR)$ possess a *cis* disposition, in contrast to the *trans* arrangement observed in $W(PMe_3)_4(Te)_2$. As with the sulfido analogues, the *cis* arrangement of tellurido ligands in $W(PMe_3)_2(Te)_2(\eta^2\text{-}OCHR)$ is presumably dictated by the geometry that would allow maximum π-donation from Te to W (*i.e.*, $M{=}Te \leftrightarrow M^-{\equiv}Te^+$), resulting in an average bond order of 2.5 for each of the tellurido ligands.[15] Indeed, the W=Te bond lengths in $W(PMe_3)_2(Te)(\eta^2\text{-}OCHR)$ [2.531(1) Å (R = H); 2.534(1) and 2.524(1) Å (R = Ph)] are marginally shorter than those in $W(PMe_3)_4(Te)_2$ [2.596(1) Å],[8] with a formal bond order of 2.

Scheme I



The aldehyde ligands in $W(PMe_3)_2(Te)_2(\eta^2\text{-}OCHR)$ are labile, and addition of excess PMe_3 regenerates $W(PMe_3)_4(Te)_2$ *via* a *cis*-to-*trans* rearrangement of the tellurido ligands. Displacement of the aldehyde ligands by Bu^tNC is also possible; however, the isolated product is not the result of the *cis*-to-*trans* rearrangement that may have been anticipated by comparison with the sulfido system, for which the isolated product is *trans-trans-trans*-$W(PMe_3)_2(CNBu^t)_2(S)_2$.[13] In marked contrast, the addition of Bu^tNC to $W(PMe_3)_2(Te)_2(\eta^2\text{-}OCHR)$ induces the unprecedented coupling of the *cis* tellurido ligands, resulting in the formation of the dark green-brown η^2-ditelluride derivative $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$ (Scheme I).[12] We also note that the tellurido ligands in *trans*-$W(PMe_3)_4(Te)_2$ may be coupled to give $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$ by the direct addition of Bu^tNC in *ca.* 80% isolated yield. Although the coupling of CR, CO, and CNR ligands has been studied extensively,[16-18] the coupling of other multiply bonded ligands at a single metal center is substantially less well-documented.[7,19]

The molecular structure of $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$ has been determined by X-ray diffraction, as shown in Figure 1. Mononuclear complexes containing $\eta^2\text{-}Te_2$ ligands are rare, and the only structurally characterized examples of which we are aware are the nickel derivatives $L_3Ni(\eta^2\text{-}Te_2)$ [$L_3 = \eta^3\text{-}PhP(CH_2CH_2PPh_2)_2$, $\eta^3\text{-}MeC(CH_2PPh_2)_3$].[20,21] The Te–Te bond length in $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$ [2.680(2) Å] is intermediate between those of Te_2 in the gas phase [2.59(2) Å][22] and elemental Te_x in the solid state [2.835(2) Å][23] and is also similar to those in $L_3Ni(\eta^2\text{-}Te_2)$ [2.665(2) and 2.668(1) Å].[20,24] It is also

---

(1) Roof, L. C.; Kolis, J. W. *Chem. Rev.* **1993**, *93*, 1037–1080.

(2) (a) Ansari, M. A.; Ibers, J. A. *Coord. Chem. Rev.* **1990**, *100*, 223–266. (b) Kanatzidis, M. G. *Comments Inorg. Chem.* **1990**, *10*, 161–195. (c) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 56–76. (d) Compton, N. A.; Errington, R. J.; Norman, N. C. *Adv. Organomet. Chem.* **1990**, *31*, 91–182. (e) Kolis, J. W. *Coord. Chem. Rev.* **1990**, *105*, 195–219.

(3) Siemeling, U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 67–68.

(4) (a) O'Brien P. *Chemtronics* **1991**, *5*, 61–69. (b) Pain, G. N.; Christiansz, G. I.; Dickson, R. S.; Deacon, G. B.; West, B. O.; McGregor, K.; Rowe, R. S. *Polyhedron* **1990**, *92*, 921–929. (c) Steigerwald, M. L. *Mater. Res. Soc. Symp. Proc.* **1989**, *131*, 37–43.

(5) (a) Stadtman, T. C. *Annu. Rev. Biochem.* **1990**, *59*, 111–127. (b) Soda, K.; Tanaka, H.; Esaki, N. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Ed.; Wiley: New York, 1987; Vol. 2, Chapter 7, pp 349–365.

(6) Biochemical aspects of tellurium derivatives are also under investigation. See: Sadeh, T. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Ed.; Wiley: New York, 1987; Vol. 2, Chapter 8, pp 367–376.

(7) For a review of metal–ligand multiple bonds, see: Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.

(8) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1991**, *113*, 9421–9422.

(9) Christou, V.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 6240–6242.

(10) Siemeling, U.; Gibson, V. C. *J. Chem. Soc., Chem. Commun.* **1992**, 1670–1671.

(11) Howard, W. A.; Parkin, G., submitted for publication.

(12) All new complexes have been characterized analytically and spectroscopically (see supplementary material).

(13) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1991**, *113*, 5904–5905.

(14) Consideration of the C–O bond lengths within the aldehyde ligands [1.363(22) Å (R = H); 1.395(11) Å (R = Ph)] suggests that the complexes are best described as W(VI) metallaoxirane derivatives rather than W(IV) aldehyde adducts. Typical single (C—O) and double (C=O) bond lengths are 1.41 and 1.20 Å, respectively. March, J. *Advanced Organic Chemistry*; Wiley: New York, 1985; p 19.

(15) (a) Mingos, D. M. P. *J. Organomet. Chem.* **1979**, *179*, C29–C33. (b) Brower, D. C.; Templeton, J. L.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1987**, *109*, 5203–5208. (c) Lin, Z.; Hall, M. B. *Coord. Chem. Rev.* **1993**, *123*, 149–167.

(16) Carnahan, E. M.; Protasiewicz, J. D.; Lippard, S. J. *Acc. Chem. Res.* **1993**, *26*, 90–97.

(17) Mayr, A.; Bastos, C. M. *Prog. Inorg. Chem.* **1992**, *40*, 1–98.

(18) Hoffmann, R.; Wilker, C. N.; Lippard, S. J.; Templeton, J. L.; Brower, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 146–147.

(19) For example, an η^2-peroxo intermediate $[Mn(O)_2(\eta^2\text{-}O_2)]^-$ has been postulated (but not spectroscopically characterized) for the photoinduced decomposition of $[Mn(O)_4]^-$,[19a] and $[Mo(O)_2(S)_2]^{2-}$ decomposes to the dinuclear complex $[(\eta^2\text{-}S_2)(O)Mo(\mu\text{-}S)_2Mo(O)(\eta^2\text{-}S_2)]^{2-}$ that contains two η^2-disulfido ligands.[19b] (a) Lee, D. G.; Moylan, C. R.; Hayashi, T.; Brauman, J. I. *J. Am. Chem. Soc.* **1987**, *109*, 3003–3010. (b) Rittner, W.; Müller, A.; Neumann, A.; Bäther, W.; Sharma, R. C. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 530–531.

(20) Di Vaira, M.; Peruzzini, M.; Stoppioni, P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 916–917.

(21) The Te_2 ligand is, however, known to coordinate in a variety of other coordination modes. See, for example, ref 1 and (a) Ansari, M. A.; Bollinger, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 3838–3839. (b) Schreiner, B.; Dehnicke, K.; Fenske, D. *Z. Anorg. Allg. Chem.* **1993**, *619*, 1127–1131. (c) Bachman, R. E.; Whitmire, K. H. *Organometallics* **1993**, *12*, 1988–1992.

(22) Maxwell, L. R.; Mosley, V. M. *Phys. Rev.* **1940**, *57*, 21–23.

(23) Cherin, P.; Unger, P. *Acta Crystallogr.* **1967**, *23*, 670–671.

0002-7863/93/1515-9822$04.00/0

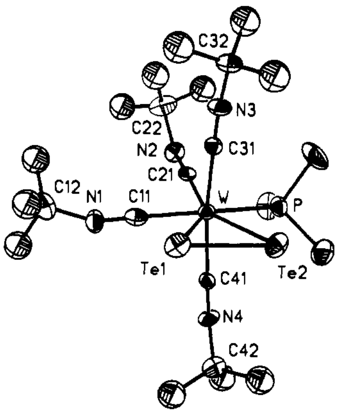


Figure 1. Molecular structure of $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$.

noteworthy that the W–Te bond lengths in $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$ [2.868(2) and 2.877(2) Å] are substantially longer than the corresponding multiple bonds in *trans*-$W(PMe_3)_4(Te)_2$ and $W(PMe_3)_2(Te)_2(\eta^2\text{-}OCHR)$ [2.524(1)–2.596(1) Å].[25]

Examination of the coordination modes of the Bu^tNC ligands in $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$ offers some insight into the origin of the different reaction pathways, *i.e.*, *cis*-to-*trans* rearrangement *versus* coupling of the tellurido ligands. Thus, $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$ exhibits two types of Bu^tNC ligands, namely (i) two mutually *trans* Bu^tNC ligands that possess effectively linear geometries at nitrogen with C–N–Bu^t bond angles of 167(2)° and (ii) two mutually *cis* Bu^tNC ligands that are markedly bent at nitrogen, with C–N–Bu^t bond angles of 138(1)° and 146(2)°. Although not as common as linear coordination, bent coordination of isocyanides is precedented.[26] The occurrence of a bent isocyanide ligand is indicative of extensive π-back-bonding and is therefore associated with a resonance form of the type $M{=}C{=}\ddot{N}{-}R$, in contrast to $M^-{-}C{\equiv}N^+{-}R$ for linear coordination. Therefore, as a consequence of the strong π-acceptor character, which reduces electron density at the tungsten center and thereby stabilizes the lower valence state, the Bu^tNC ligands would be expected to promote the reductive coupling[27] of the two tellurido ligands.[28] In contrast, the strong σ-donor PMe_3 ligands (with little π-acceptor character) stabilize higher valence states and so would be expected to inhibit the reductive coupling of the two tellurido ligands.

In summary, the η^2-aldehyde ligands in $W(PMe_3)_2(Te)_2(\eta^2\text{-}OCHR)$ may be substituted by either PMe_3 or Bu^tNC ligands. Substitution by the strong σ-donor PMe_3 ligand results in the formation of *trans*-$W(PMe_3)_4(Te)_2$, whereas substitution by the strong π-acceptor Bu^tNC ligand promotes the reductive coupling of the *cis* tellurido ligands with the formation of the ditellurido complex $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$. It is anticipated that an understanding of the factors that influence the interconversion of $[M](Te)_2$ and $[M](\eta^2\text{-}Te_2)$ moieties will also have implications for the coupling and cleavage of ligands in other systems, such as the interconversion of $[M](O)_2$ and $[M](\eta^2\text{-}O_2)$ groups.

Acknowledgment. We thank the U.S. Department of Energy, Office of Basic Energy Sciences (No. DE-FG02-93ER14339), and the donors of the Petroleum Research Fund, administered by the ACS, for partial support of this research. G.P. is the recipient of an A. P. Sloan Research Fellowship (1991–1993), a Camille and Henry Dreyfus Teacher-Scholar Award (1991–1996), and a Presidential Faculty Fellowship Award (1992–1997).

Supplementary Material Available: Tables of analytical and spectroscopic data for all new complexes and crystallographic data for $W(PMe_3)_2(Te)_2(\eta^2\text{-}OCHR)$ (R = H, Ph) and $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$ (25 pages); observed and calculated structure factors (39 pages). Ordering information is given on any current masthead page.

---

(24) Further comparisons of Te–Te bond lengths may be made with binary tellurides (*ca.* 2.81 Å),[24a] Ph_2Te_2 [2.712(2) Å],[24b] and $(p\text{-tolyl})_2Te_2$ [2.697(3) Å].[24c] (a) Böttcher, P. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 759–772. (b) Llabres, G.; Dideberg, O.; Dupont, L. *Acta Crystallogr.* **1972**, *B28*, 2438–2444. (c) Spirlet, M. R.; Van Den Bossche, G.; Dideberg, O.; Dupont, L. *Acta Crystallogr.* **1979**, *B35*, 1727–1729.

(25) W–Te single bonds have been reported in the range 2.64–2.88 Å. See footnote 10 in ref 8 and (a) Mar, A.; Jobic, S.; Ibers, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 8963–8971. (b) Gorzellik, M.; Bock, H.; Gang, L.; Nuber, B.; Ziegler, M. L. *J. Organomet. Chem.* **1991**, *412*, 95–120. (c) Roof, L. C.; Pennington, W. T.; Kolis, J. W. *Inorg. Chem.* **1992**, *31*, 2056–2064.

(26) For some recent examples of complexes that contain bent isocyanide ligands see: (a) Carnahan, E. M.; Rardin, R. L.; Bott, S. G.; Lippard, S. J. *Inorg. Chem.* **1992**, *31*, 5193–5201 and references therein. (b) Jones, W. D.; Foster, G. P.; Putinas, J. M. *Inorg. Chem.* **1987**, *26*, 2120–2127 and references therein.

(27) By analogy to the widely-accepted terms "reductive elimination" and "oxidative addition", we use the term "reductive coupling" (and its microscopic reverse, "oxidative cleavage") to indicate changes in formal oxidation state at the metal center and not at the ligands. According to this criterion, the coupling of dative ligands (*e.g.*, C_2H_4, CO, CNR) would be regarded as "oxidative coupling", a term that has been previously defined in this way. See: Elschenbroich, C.; Salzer, A. *Organometallics: A Concise Introduction*, 2nd. ed.; VCH Publishers: New York, 1992; pp 412–414.

(28) Theoretical calculations on the coupling of methylene groups indicate that the barrier would be lowered by incorporation of acceptor ligands on the metal. See: Wilker, C. N.; Hoffmann, R.; Eisenstein, O. *Nouv. J. Chim.* **1983**, *7*, 535–544.