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Telluroformaldehyde, Tellurido, and Ditellurido Derivatives of Permethyltantalocene

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Summary: The telluroformaldehyde complex $Cp^*_2Ta(\eta^2\text{-}TeCH_2)H$ has been prepared by the PMe_3-catalyzed addition of Te to the $[Ta{=}CH_2]$ double bond in $Cp^*_2Ta(CH_2)H$. Of the two limiting resonance structures, i.e. metal–telluroformaldehyde versus metallatellurirane, the Te—C bond length of 2.21(2) Å suggests that the tantalum(V) metallatellurirane formalism may be the more appropriate description for the $[Ta(\eta^2\text{-}TeCH_2)]$ interaction. $Cp^*_2Ta(\eta^2\text{-}TeCH_2)H$ is converted to its more stable tellurido–methyl isomer $Cp^*_2Ta(Te)CH_3$ at 130 °C. The ditellurido and tellurido-hydrido complexes $Cp^*_2Ta(\eta^2\text{-}Te_2)H$ and $Cp^*_2Ta(Te)H$ have also been prepared.

The chemistry of tellurium is dominated by its propensity to form single bonds, in contrast to its lightest congener, oxygen, for which multiple bonding is common.[1–3] As such, complexes that exhibit multiple bonding to tellurium are of intrinsic interest, and we have recently described the synthesis of the first complex with a terminal metal–tellurium double bond, namely $W(PMe_3)_4(Te)_2$.[4] However, simple telluroaldehydes and telluroketones with carbon–tellurium double bonds have yet to be isolated and structurally characterized, even though such compounds have recently been generated and trapped *in situ* by dienes and other substrates.[5,6] In this paper we pursue our interest in multiple bonding of tellurium in relation to telluroformaldehyde ($CH_2{=}Te$) derivatives.[7] Here we report (i) the first X-ray structure determination of a mononuclear telluroformaldehyde complex, namely $Cp^*_2Ta(\eta^2\text{-}TeCH_2)H$ ($Cp^* = \eta^5\text{-}C_5Me_5$), and (ii) the rearrangement of $Cp^*_2Ta(\eta^2\text{-}TeCH_2)H$ to the more stable tellurido–methyl isomer, $Cp^*_2Ta(Te)CH_3$.

Telluroformaldehyde was first stabilized by coordination to transition-metal centers in 1983, with independent reports by Roper [$Os(\eta^2\text{-}TeCH_2)(PPh_3)_2(CO)_2$ and $Os(\eta^2\text{-}TeCH_2)(PPh_3)_2(NO)Cl$],[8,9] Werner [$CpRh(PMe_3)(\eta^2\text{-}TeCH_2)$],[10] and Herrmann [$\{CpMn(CO)_2\}_2(\mu\text{-}\eta^1{:}\eta^2\text{-}TeCH_2)$].[11] However, in the 10 years following these seminal discoveries, there have been relatively few advances, and the only other telluroformaldehyde complexes of which we are aware are $CpRh(PPr^i_3)(\eta^2\text{-}TeCH_2)$,[12] $Cp^*Rh(CO)(\eta^2\text{-}TeCH_2)$,[12] and $\{Cp^*Mn(CO)_2\}_2(\mu\text{-}\eta^1{:}\eta^2\text{-}TeCH_2)$.[13–15]

Bercaw has demonstrated that the permethyltantalocene moiety $[Cp^*_2Ta]$ provides an excellent framework for stabilizing formaldehyde and thioformaldehyde complexes. Specifically, the complexes $Cp^*_2Ta(\eta^2\text{-}OCH_2)H$ and $Cp^*_2Ta(\eta^2\text{-}SCH_2)H$ have been obtained by the reactions of $Cp^*_2Ta(CH_2)H$ and $Cp^*_2Ta(CCH_2)H$ with CH_3OH and CH_3SH, respectively.[16–18] Although it may be anticipated that the telluroformaldehyde analogue $Cp^*_2Ta(\eta^2\text{-}TeCH_2)H$ could be synthesized by the reaction of $Cp^*_2Ta(CH_2)H$ with CH_3TeH, the instability of the latter reagent limits the applicability of such an approach.[19] However, we have discovered that the telluroformaldehyde derivative $Cp^*_2Ta(\eta^2\text{-}TeCH_2)H$ may be readily prepared by the addition of tellurium to the $[Ta{=}CH_2]$ double bond of $Cp^*_2Ta(CH_2)H$ (Scheme 1).[20,21] Such a reaction is

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[2] For a general review on bonding involving the heavier main-group elements, see: Kutzelnigg, W. *Angew. Chem., Int. Ed. Engl.* **1984,** *23,* 272–295.

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[5] (a) Erker, G.; Hock, R. *Angew. Chem., Int. Ed. Engl.* **1989,** *28,* 179–180. (b) Segi, M.; Koyama, T.; Takata, Y.; Nakajima, T.; Suga, S. *J. Am. Chem. Soc.* **1989,** *111,* 8749–8751.

[6] Some examples of stable telluroesters and telluroamides have been reported, but these are stabilized by resonance structures of the types $Te^-{—}C{=}O^+R(R')$ and $Te^-{—}C{=}N^+R_2(R')$. See: (a) Minoura, M.; Kawashima, T.; Okazaki, R. *J. Am. Chem. Soc.* **1993,** *115,* 7019–7020 and references therein. (b) Kuhn, N.; Henkel, G.; Kratz, T. *Chem. Ber.* **1993,** *126,* 2047–2049.

[7] Telluroformaldehyde itself has been reported to exist as a cyclic trimer $(CH_2Te)_3$,[7a] while difluoromethyl telluroketone exists as a dimer, $(CF_2Te)_2$.[7b] (a) Williams, F. D.; Dunbar, F. X. *Chem. Commun.* **1968,** 459. (b) Boese, R.; Haas, A.; Limberg, C. *J. Chem. Soc., Dalton Trans.* **1993,** 2547–2556 and references therein.

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[14] The η^1-tellurobenzaldehyde complexes $(CO)_5W(\eta^1\text{-}Te{=}CHPh)$ and $[(CO)_5W]_2(\mu\text{-}\eta^1{:}\eta^2\text{-}Te{=}CHPh)$ have recently been reported: Fischer, H.; Früh, A.; Troll, C. *J. Organomet. Chem.* **1991,** *415,* 211–221.

[15] Some related complexes include the telluroketone and telluroketene derivatives $(CO)_5W(\eta^1\text{-}Te{=}CPh_2)$,[15a–c] $CpRh(\eta^2\text{-}Te{=}C{=}CHR)(PPr^i_3)$ (R = H, Me, Ph),[15d] and $(CO)_5M[\eta^1\text{-}Te{=}C\{N(Et)CH_2\}_2]$ (M = Cr, Mo, W):[15e] (a) Fischer, H.; Zeuner, S. *J. Organomet. Chem.* **1983,** *252,* C63–C65. (b) Fischer, H.; Gerbing, U. *J. Organomet. Chem.* **1986,** *299,* C7–C10. (c) Fischer, H.; Pashalidis, I. *J. Organomet. Chem.* **1988,** *348,* C1–C4. (d) Wolf, J.; Zolk, R.; Schubert, U.; Werner, H. *J. Organomet. Chem.* **1988,** *340,* 161–178. (e) Lappert, M. F.; Martin, T. R.; McLaughlin, G. M. *J. Chem. Soc., Chem. Commun.* **1980,** 635–637.

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[20] A mixture of $Cp^*_2Ta(CH_2)H$ (0.35 g, 0.75 mmol) and Te (0.19 g, 1.50 mmol) in toluene (30 mL) was treated with PMe_3 (*ca.* 0.5 mL) at −78 °C. The mixture was warmed to room temperature and stirred for 40 min. Hg (*ca.* 1 mL) was added, and the mixture was stirred for a further 30 min and filtered. The volatile components were removed *in vacuo,* and the product was washed with pentane at −78 °C, giving $Cp^*_2Ta(\eta^2\text{-}TeCH_2)H$ as a red-brown solid (0.36 g, 81%).

[21] All new compounds have been characterized analytically and spectroscopically (see the supplementary material).

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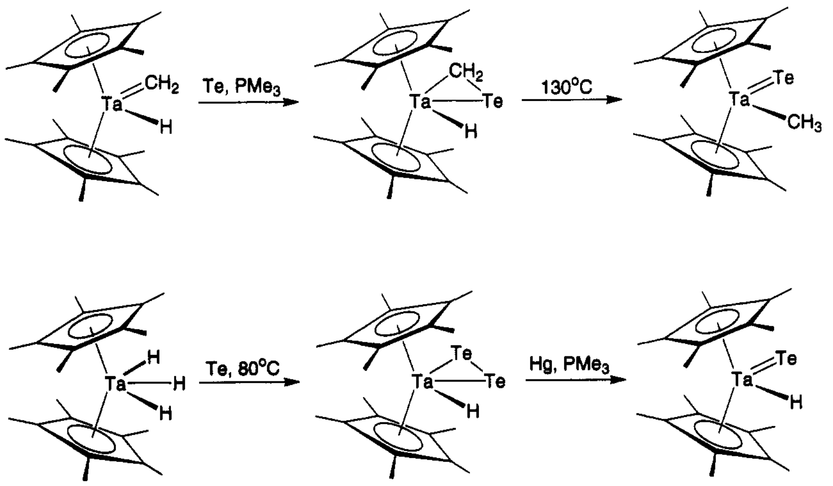
Scheme 1



particularly noteworthy, since the formaldehyde and thioformaldehyde complexes $Cp^*_2Ta(\eta^2\text{-}OCH_2)H$ and $Cp^*_2Ta(\eta^2\text{-}SCH_2)H$ are *not* readily prepared by such a method.[22] The reaction between $Cp^*_2Ta(CH_2)H$ and Te is achieved by the use of PMe_3 as a catalyst, so that the active tellurium transfer reagent is presumably Me_3PTe.[4] The telluroformaldehyde moiety in $Cp^*_2Ta(\eta^2\text{-}TeCH_2)H$ is characterized by ^1H, ^{13}C, and ^{125}Te NMR signals at δ 1.95 (d, $^3J_{H\text{-}H}$ = 1.1 Hz), δ 27.4 (t, $^1J_{C\text{-}H}$ = 143 Hz), and δ −80 ppm, respectively.

The molecular structure of $Cp^*_2Ta(\eta^2\text{-}TeCH_2)H$ has been determined by X-ray diffraction, as shown in Figure 1. A notable feature of this structure centers upon the orientation of the telluroformaldehyde ligand within the equatorial plane of the bent-sandwich moiety. Specifically, the tellurium atom is located in the central equatorial site, in contrast to the lateral location of the chalcogens in the formaldehyde and thioformaldehyde derivatives.[17,23,24] The larger size of the tellurium atom is presumably one of the factors that favors its central *versus* lateral location in $Cp^*_2Ta(\eta^2\text{-}TeCH_2)H$. The $[Ta(\eta^2\text{-}TeCH_2)]$ moiety is defined by the structural parameters d(Ta–Te) = 2.790(1) Å, d(Ta–C) = 2.27(1) Å, and d(Te–C) = 2.21(2) Å. In view of the limited structural data base available on compounds with multiple bonds to tellurium, it is difficult to comment definitively upon the relative importance of the tantalum(V) metallatellurirane and tantalum(III) telluroformaldehyde resonance forms. However, on the basis that single Te–C bond lengths are known to be in the range 2.025–2.298 Å in two-coordinate tellurium compounds,[25] a Te–C bond length of 2.21(2) Å in $Cp^*_2Ta(\eta^2\text{-}TeCH_2)H$ would suggest that the tantalum(V) metallatellurirane formalism may be the more appropriate description for the interaction in $Cp^*_2Ta(\eta^2\text{-}TeCH_2)H$. $Cp^*_2Ta(\eta^2\text{-}TeCH_2)H$ is quantitatively converted to the more stable red-brown tellurido–methyl isomer $Cp^*_2Ta(Te)CH_3$ in solution at 130 °C (Scheme 1).[21,26] Although the formation of a tellurido complex bears a close relation to the chemistry of $Cp^*_2Ta(\eta^2\text{-}ECH_2)H$ (E = O, S), it should be noted that, in contrast to oxo and sulfido derivatives, terminal tellurido complexes are particularly scarce and have only been synthesized recently.[4,27]

The permethyltantalocene moiety has also proved to be capable of stabilizing a mononuclear ditellurido derivative, and yellow $Cp^*_2Ta(\eta^2\text{-}Te_2)H$ is readily obtained in *ca.* 70% yield by the direct reaction of $Cp^*_2TaH_3$ with elemental Te at 80 °C (Scheme 1).[21,28] The molecular structure of $Cp^*_2Ta(\eta^2\text{-}Te_2)H$ has been determined by X-ray diffraction,[29,30] and the two inequivalent tellurium sites are characterized by ^{125}Te NMR signals at δ −499 and −1088 ppm, with $^1J_{Te\text{-}Te}$ = 2180 Hz.

The ditellurido complex $Cp^*_2Ta(\eta^2\text{-}Te_2)H$ may be converted to the terminal tellurido–hydride derivative $Cp^*_2Ta(Te)H$ upon treatment with mercury in the presence of PMe_3 (Scheme 1).[21,31] The terminal tellurido ligand in $Cp^*_2Ta(Te)H$ is characterized by (i) a ^{125}Te NMR signal at δ 3085 ppm and (ii) a Ta═Te bond length of 2.588(2)

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(22) Thus, $Cp^*_2Ta(CH_2)H$ reacts with (i) elemental sulfur to give a mixture of, *inter alia*, $Cp^*_2Ta(\eta^2\text{-}SCH_2)H$ and $Cp^*_2Ta(S)CH_3$[22a] and (ii) O_2 to give a mixture of $Cp^*_2Ta(\eta^2\text{-}O_2)CH_3$ and $Cp^*_2Ta(O)CH_3$.[22b] (a) Shin, J. H.; Parkin, G. Unpublished results. (b) van Asselt, A.; Trimmer, M. S.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* 1988, *110*, 8254–8255.

(23) The chalcogen atoms in $Cp^*_2Ta(\eta^2\text{-}SCHCH_2Ph)H$ and $Cp^*_2Ta(\eta^2\text{-}OCH_2)H$ have been demonstrated by X-ray diffraction to be located in a lateral position. See ref 18 and: Burger, B. J. Ph.D. Thesis, California Institute of Technology, Pasadena, CA, 1987.

(24) However, it should be noted that the titanium and zirconium thioaldehyde complexes $Cp_2Ti(\eta^2\text{-}SCH_2)(PMe_3)$[24a] and $Cp_2Zr(\eta^2\text{-}SCHMe)(PMe_3)$[24b,c] have been shown to have sulfur located in the central equatorial position. (a) Park, J. W.; Henling, L. M.; Schaefer, W. P.; Grubbs, R. H. *Organometallics* **1990**, *9*, 1650–1656. (b) Buchwald, S. L.; Nielsen, R. B. *J. Am. Chem. Soc.* **1988**, *110*, 3171–3175. (c) Buchwald, S. L.; Nielsen, R. B.; Dewan, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 1590–1591.

(25) Cambridge Crystallographic Database. For example, the Te═C ↔ Te^-—C^+ bond length in $\{CMeNPr^i\}_2C{=}Te$ is 2.087(4) Å[6b] and the average Te—C bond length in $CH_2\{C(O)CH_2\}_2Te$ is 2.17 Å: Raston, C. L.; Secomb, R. J.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1976**, 2307–2310.

(26) ^1H NMR data (C_6D_6): δ 1.87 [s, 30 H, 2 Cp*], −1.83 [s, 3 H, Ta—CH_3]. ^{125}Te NMR data (C_6D_6): δ 2753.

(27) Other examples of terminal tellurido complexes include $W(PMe_3)_2(Te)_2(\eta^2\text{-}OCHR)$,[27a] $(dmpe)_2M(TeR)_2(Te)$ (M = Zr, Hf; R = $Si(SiMe_3)_3$),[27b] $Cp^*Nb(PMe_3)(NAr)(Te)$ (Ar = 2,6-$C_6H_3Pr^i_2$),[27c] $[\{(Me_3Si)NCH_2CH_2\}_3N]TaTe$,[27d] and $[\{(Me_3Si)NCH_2CH_2\}_3N]VTe$:[27e] (a) Rabinovich, D.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 9822–9823. (b) Christou, V.; Arnold, J. *J. Am. Chem. Soc.* **1992**, *114*, 6240–6242. (c) Siemeling, U.; Gibson, V. C. *J. Chem. Soc., Chem. Commun.* **1992**, 1670–1671. (d) Christou, V.; Arnold, J. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1450–1452. (e) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1994**, *33*, 1448–1457.

(28) A mixture of $Cp^*_2TaH_3$ (1.0 g, 2.20 mmol) and Te (0.62 g, 4.84 mmol) in toluene (40 mL) was heated at 80 °C for 3 days. The mixture was filtered, and the volatile components were removed *in vacuo*. The product was washed with pentane at −78 °C, giving $Cp^*_2Ta(\eta^2\text{-}Te_2)H$ as a yellow solid (1.1 g, 71%).

(29) $Cp^*_2Ta(\eta^2\text{-}Te_2)H$ resides on a crystallographic 2-fold axis which bisects the Ta—Te and Ta—Te′ bonds. Since the complex itself does not possess a molecular C_2 axis, the structure is necessarily disordered.

(30) Mononuclear ditellurido derivatives $M[\eta^2\text{-}Te_2]$ are also rare, and the only structurally characterized examples of which we are aware are $W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)$[27a] and $L_3Ni(\eta^2\text{-}Te_2)$ (L_3 = η^3-$PhP(CH_2CH_2PPh_2)_2$, η^3-$MeC(CH_2PPh_2)_3$): Di Vaira, M.; Peruzzini, M.; Stoppioni, P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 916–917.

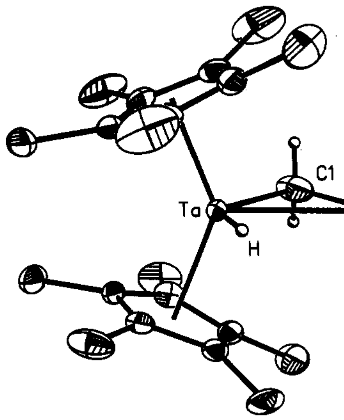

Figure 1. Molecular structure of Cp*$_2$Ta(η^2-TeCH$_2$)H.

Å, which is similar to that in [{Me$_3$Si)NCH$_2$CH$_2$}$_3$N]TaTe (2.568(1) Å)[27d] but substantially shorter than the Ta—Te single-bond lengths in both Cp*$_2$Ta(η^2-TeCH$_2$)H (2.790(1) Å) and Cp*$_2$Ta(η^2-Te$_2$)H (2.855(1) Å).

In summary, Cp*$_2$Ta(η^2-TeCH$_2$)H, the first telluroformaldehyde complex of tantalum, has been prepared by the addition of Te to the [Ta=CH$_2$] double bond of Cp*$_2$Ta(CH$_2$)H. Although stable at room temperature, the telluroformaldehyde complex Cp*$_2$Ta(η^2-TeCH$_2$)H is readily converted to its tellurido-methyl isomer Cp*$_2$Ta(Te)CH$_3$ at 130 °C.

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Supplementary Material Available: Tables of analytical and spectroscopic data for all new complexes and crystallographic data for Cp*$_2$Ta(η^2-TeCH$_2$)H, Cp*$_2$Ta(η^2-Te$_2$)H, and Cp*$_2$Ta(Te)H, including tables of crystal and intensity collection data, positional and thermal parameters, and bond distances and angles and figures giving additional views of the structures (26 pages). Ordering information is given on any current masthead page.

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(31) A mixture of Cp*$_2$Ta(η^2-Te$_2$)H (0.5 g, 0.71 mmol) and Hg (1 mL) in toluene (30 mL) was treated with PMe$_3$ (*ca.* 0.5 mL) at −78 °C. The mixture was stirred at room temperature for 1 day and filtered. The volatile components were removed *in vacuo*, and the product was washed with pentane at −78 °C, giving Cp*$_2$Ta(Te)H as a yellow-green solid (0.37 g, 90%).