previously shown experimentally to have a major role in the specificity of association with other heme proteins, indicating that cytochrome b_5 interacts with the electrode in an orientation similar to its association with other redox proteins, such as cytochrome *c*.[4]

In conclusion, although individual surface charges on a redox protein appear to have a relatively minor role in the determination of the reduction potential, it is apparent that the summed distribution pattern of surface charges can make a significant contribution. The excellent quantitative agreement between experimentally determined potential surfaces and the results of a simplified continuum dielectric model suggests that a protein interior can be approximated by a macroscopic dielectric constant in many instances. Our derived value for this parameter of between 2 and 4 is consistent with earlier estimates from fluorescence energy transfer[15] and the high-frequency dielectric of organic liquids[1f] and lower than that estimated for the hydrated pocket of myoglobin.[16]

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Supplementary Material Available: Figures of differential pulse and cyclic voltammograms and a description of electrochemical parameters and conditions used (3 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of $W(PMe_3)_4(Te)_2$: The First Transition-Metal Complex with a Terminal Tellurido Ligand

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In view of the current interest in both the bonding and reactivity of complexes that contain metal–ligand multiple bonds,[1,2] we are presently investigating synthetic methods for such complexes in which the ligands are derived from the heavier members of the main group elements. Furthermore, because of the increased tendency of the heavier elements to bridge two or more metal centers,[3-5] the synthesis of complexes that contain *terminal* metal–ligand multiple bonds is even more challenging. Here we report the synthesis and chracterization of *trans*-$W(PMe_3)_4(Te)_2$, a complex which, to our knowledge, contains the first *terminal* transition metal–tellurium double bond.

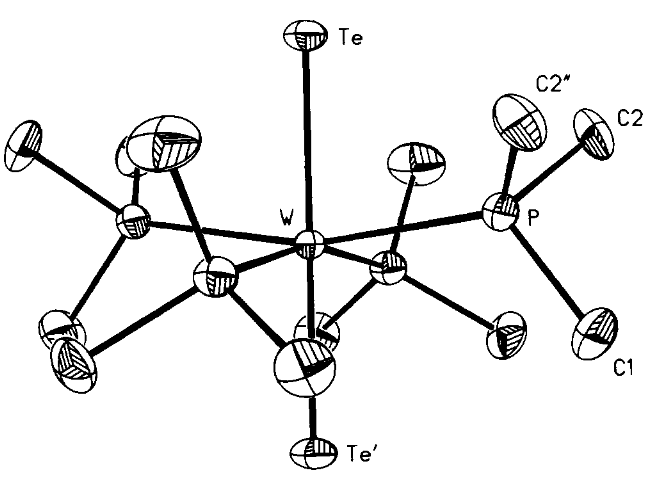
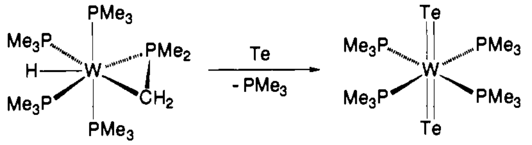


Figure 1. ORTEP drawing of *trans*-$W(PMe_3)_4(Te)_2$. Selected bond lengths (Å) and angles (deg): W–Te = 2.596 (1), W–P = 2.508 (2); Te–W–Te' = 180.0, Te–W–P = 82.1 (1), Te'–W–P = 97.9 (1), P–W–P* = 91.1 (1), 164.2 (1) (an asterisk indicates other phosphorus atoms).

We have recently reported that the bis(sulfido) complex *trans*-$W(PMe_3)_4(S)_2$ may be readily obtained by the reaction of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with H_2S, accompanied by elimination of dihydrogen.[6] Although the corresponding reaction with H_2Te may provide a route to the analogous (bis)tellurido complex *trans*-$W(PMe_3)_4(Te)_2$, the instability of H_2Te[7] limits the convenience of such a method. However, we have found that the reaction between $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ and elemental tellurium provides a straightforward synthesis of *trans*-$W(PMe_3)_4(Te)_2$. Thus, a solution of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ in pentane reacts smoothly with elemental tellurium at room temperature to give red-brown *trans*-$W(PMe_3)_4(Te)_2$ in good yield (eq 1).[8] The molecular structure of *trans*-$W(PMe_3)_4(Te)_2$ has been determined by X-ray diffraction, as shown in Figure 1.[9] Of particular significance, the W═Te bond length [2.596 (1) Å] is noticeably shorter than those observed for a variety of other complexes that contain W–Te single bonds, typically in the range 2.68–2.88 Å.[10] Furthermore, electronic considerations of the



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(8) A solution of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ (2.95 g, 5.23 mmol) in pentane (20 mL) was stirred with Te powder (1.20 g, 9.40 mmol) for 20 h at room temperature, resulting in the precipitation of *trans*-$W(PMe_3)_4(Te)_2$ as a red-brown solid. The mixture was filtered and the product extracted into benzene (ca. 30 mL) and filtered, and the solvent was removed under reduced pressure giving pure *trans*-$W(PMe_3)_4(Te)_2$ (1.37 g). The residue (0.89 g) is sufficiently pure for further reactions. Overall yield ca. 65%. Elemental analysis calculated for $W(PMe_3)_4(Te)_2$: C, 19.4, H. 4.9. Found: C, 19.4, H, 4.6. NMR data for *trans*-$W(PMe_3)_4(Te)_2$ (in C_6D_6): ^1H δ 1.91, virtual triplet, "J_{P-H}" = 2.8 Hz; $^{13}C\{^1H\}$ δ 33.6, multiplet, "J_{P-C}" = 15 Hz; $^{31}P\{^1H\}$ (relative to H_3PO_4) δ −51.2, s, $^1J_{W-P} = 238$ Hz (^{183}W, $I = ^1/_2$, 14.27%), $^2J_{P-Te} = 17$ Hz (^{125}Te, $I = ^1/_2$, 6.99%); $^{125}Te\{^1H\}$ (relative to Me_2Te) δ 958, quintet, $^2J_{P-Te} = 17$ Hz, $^1J_{Te-W} = 190$ Hz (^{183}W, $I = ^1/_2$, 14.27%). Note: the values of the coupling constants "J_{P-H}" and "J_{P-C}" of the second-order multiplets of the PMe_3 ligands refer to the separation between the lines and do not necessarily reflect the true coupling constants.
(9) Crystal data for *trans*-$W(PMe_3)_4(Te)_2$: tetragonal, $I\bar{4}2m$ (No. 121), $a = b = 9.717$ (1) Å, $c = 12.360$ (2) Å, $V = 1167.1$ (3) Å^3, $Z = 2$, $\rho_{calcd} = 2.12$ g cm^{-3}, μ(Mo Kα) = 80.3 cm^{-1}, λ(Mo Kα) = 0.71073 Å (graphite monochromator); 539 unique reflections with $3° < 2\theta < 60°$ were collected of which 499 reflections with $F > 6\sigma(F)$ were used in refinement; $R = 0.0202$, $R_w = 0.0292$, GOF = 1.136.

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18-electron nature of the tungsten center restrict the terminal tungsten–tellurium bond order in *trans*-$W(PMe_3)_4(Te)_2$ to two, with no significant lone-pair donation to tungsten (i.e. W═Te versus $W^-\equiv Te^+$). In this regard, the complexes $[(\eta^5\text{-}C_5Me_5)Mn(CO)_2]_2(\mu_2\text{-}Te)$[11] and $[(\eta^5\text{-}C_5H_5)Mn(CO)_2]_3(\mu_3\text{-}Te)$,[12] containing manganese–tellurium double bonds, have also been structurally characterized, but in these examples the tellurido ligands *bridge* two and three metal centers, respectively.

The combination of $^{125}Te\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopies provides further characterization of *trans*-$W(PMe_3)_4(Te)_2$. Specifically, the $^{125}Te\{^1H\}$ resonance observed at δ 958 ppm exhibits coupling to both tungsten ($^1J_{Te-W}$ = 190 Hz; ^{183}W, $I = {}^1/_2$, 14.27%) and the four phosphorus nuclei of the PMe_3 ligands ($^2J_{Te-P}$ = 17 Hz). Furthermore, the $^{31}P\{^1H\}$ NMR resonance at δ −51.2 also exhibits coupling to both tungsten ($^1J_{P-W}$ = 238 Hz; ^{183}W, $I = {}^1/_2$, 14.27%) and tellurium ($^2J_{P-Te}$ = 17 Hz; ^{125}Te, $I = {}^1/_2$, 6.99%). Significantly, the ratio of the intensities of the tungsten to tellurium satellites [1.0 (1):1] compares favorably with that predicted for a molecule of composition $W(PMe_3)_4(Te)_2$ [1.02:1],[13] and thus provides further evidence for the presence of *two* tellurido ligands.

Our studies suggest that the mechanism for the formation of *trans*-$W(PMe_3)_4(Te)_2$ involves tellurium atom transfer via Me_3PTe, in which PMe_3 acts as a solid-solution phase transfer catalyst. Evidence that Me_3PTe is a catalytically active species in the formation of *trans*-$W(PMe_3)_4(Te)_2$ is provided by the observation that the reaction is instantaneous when Me_3PTe, generated in situ, is used as the reagent.[14] Further support for this suggestion is provided by the reports that (i) tertiary phosphines react with elemental tellurium to give phosphine tellurides R_3PTe[15] and (ii) R_3PTe act as tellurium atom transfer reagents for the synthesis of other tellurium complexes.[16] Moreover, in some cases stable adducts of phosphine tellurides with transition metals have also been isolated, e.g. $W(CO)_5(TePBu^t_3)$.[17]

In summary, *trans*-$W(PMe_3)_4(Te)_2$, the first example of a complex that contains a terminal transition metal–tellurium double bond, has been synthesized by the reaction of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with tellurium and characterized by X-ray diffraction and NMR techniques.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. G.P. is the recipient of an A. P. Sloan Research Fellowship (1991–1993) and a Camille and Henry Dreyfus Teacher-Scholar Award (1991–1996). We thank Dr. C. Turner for assistance with the NMR studies and are very grateful for helpful comments from the reviewers.

Supplementary Material Available: Tables of crystal and intensity collection data, atomic coordinates, bond distances and angles, and anisotropic displacement parameters and an ORTEP drawing for $W(PMe_3)_4(Te)_2$ (5 pages); listing of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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(10) For example, $[W(O)(\eta^2\text{-}Te_4)_2]^{2-}$ (2.68 Å average),[10a] $[W(CO)_4(\eta^2\text{-}Te_4)]^{2-}$ (2.819 (1) and 2.856 (1) Å),[10b] $[W(CO)_4(\eta^3\text{-}Te_3)]^{2+}$ (2.81 Å average),[10c] $[(CO)_5W]_3(\mu\text{-}TeTe)$ (2.739 (2) and 2.881 (3) Å),[10d] and $[\{(\eta^5\text{-}C_5Me_5)W(CO)_2\}_2(\mu\text{-}H_2Te_2)]^{2+}$ (2.75 Å average).[10e] (a) Flomer, W. A.; Kolis, J. W. *Inorg. Chem.* **1989**, *28*, 2513–2517. (b) Flomer, W. A.; O'Neal, S. C.; Jeter, D.; Cordes, A. W.; Kolis, J. W. *Inorg. Chem.* **1988**, *27*, 969–971. (c) Faggiani, R.; Gillespie, R. J.; Campana, C.; Kolis, J. W. *J. Chem. Soc., Chem. Commun.* **1987**, 485–486. (d) Scheidsteger, O.; Huttner, G.; Dehnicke, K.; Pebler, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 428. (e) Endrich, K.; Guggolz, E.; Serhadle, O.; Ziegler, M. L.; Korswagen, R. P. *J. Organomet. Chem.* **1988**, *349*, 323–351.

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(13) The relative intensities of the tungsten and tellurium satellites is directly related to the natural abundance of the spin active nuclei, statistically adjusted for consideration of the molecular composition. Thus, for $W(PMe_3)_4(Te)_2$, the predicted relative intensity of the tungsten-to-tellurium satellites in the $^{31}P\{^1H\}$ NMR spectrum is [14.27%:(2 × 6.99%)], i.e. 1.02:1.

(14) Me_3PTe was generated in situ (due to its instability) by addition of PMe_3 to a suspension of Te in benzene, prior to the addition of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$. Also see ref 15.

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(16) Some examples include $[(\eta^5\text{-}C_5Me_5)_2Yb]_2(\mu\text{-}Te)$,[16a] $[(\eta^5\text{-}C_5H_4Me)_3U]_2(\mu\text{-}Te)$,[16b] $Mn(CO)_3(PEt_3)_2TeCH_2Ph$,[16c] and $[(PEt_3)_2(CO)_3Mn]_2(\mu\text{-}Te_2)$.[16d] (a) Berg, D. J.; Burns, C. J.; Andersen, R. A.; Zalkin, A. *Organometallics* **1989**, *8*, 1865–1870. (b) Brennan, J. G.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1986**, *25*, 1761–1765. (c) McGregor, K.; Deacon, G. B.; Dickson, R. S.; Fallon, G. D.; Rowe, R. S.; West, B. O. *J. Chem. Soc., Chem. Commun.* **1990**, 1293–1294. (d) Steigerwald, M. L.; Rice, C. E. *J. Am. Chem. Soc.* **1988**, *110*, 4228–4231.

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Sigmoidal Growth in a Self-Replicating System

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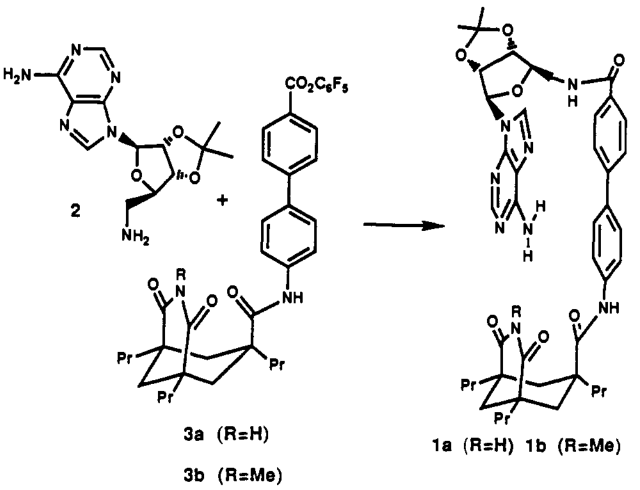
We recently introduced a synthetic molecule capable of self-replication and presented evidence of its autocatalytic nature.[1] While sigmoidal growth of the reaction product is the expected outcome of such systems,[2] evidence for this phenomena has been elusive and was only recently detected in nucleic acid chemistry.[3] Here we show that such behavior can also be observed with synthetic replicators.

Adenine–imide conjugate **1** (Scheme I), possesses self-complementarity, the key feature of replicating molecules that act as templates for their reproduction.[3,4] Compound **1** was prepared by acylation of the 5′-aminoadenosine derivative **2**[5] with the biphenyl ester **3** in $CHCl_3$. Ester **3** was prepared as shown in Scheme II from imide acid chloride **4**[6] and the biphenyl carboxylic acid **5**.[7,8]

Scheme I



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