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.

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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

Vincent Rotello, Jong-In Hong, and J. Rebek, Jr.*

Department of Chemistry
The Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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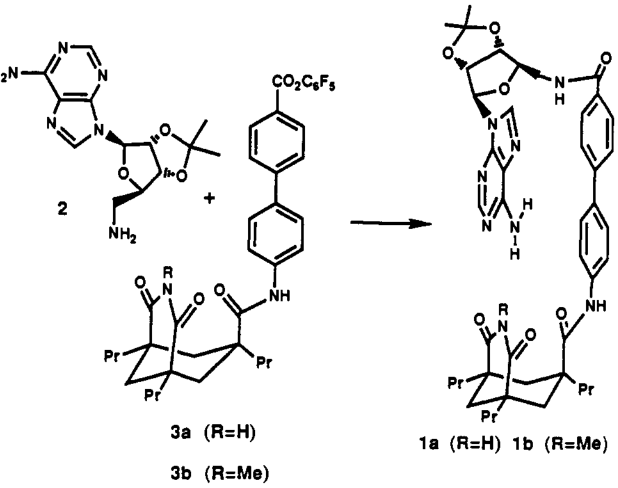
We recently introduced a synthetic molecule capable of self-replication and presented evidence of its autocatalytic nature.[1] While sigmoidal growth of the reaction product is the expected outcome of such systems,[2] evidence for this phenomena has been elusive and was only recently detected in nucleic 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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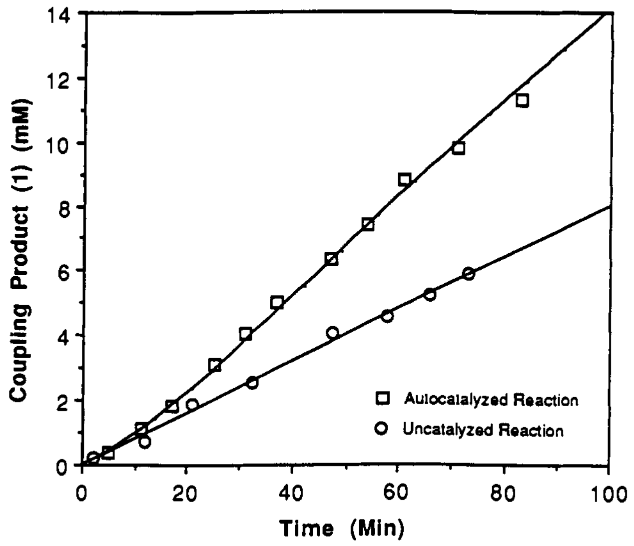


Figure 1. Plots of appearance of **1a** and **1b** vs time as determined by HPLC for a representative run. Initial concentrations of **2**, **3a**, and **3b** were 50 mM in $CHCl_3$ with 9 equiv of Et_3N added: (a) reaction of **2** and **3** and (b) reaction of **2** and **3b**. Boxes represent approximate uncertainty (±0.1 mmol). The lines drawn represent the best fit of the von Kiedrowski rate law expression.

Scheme II

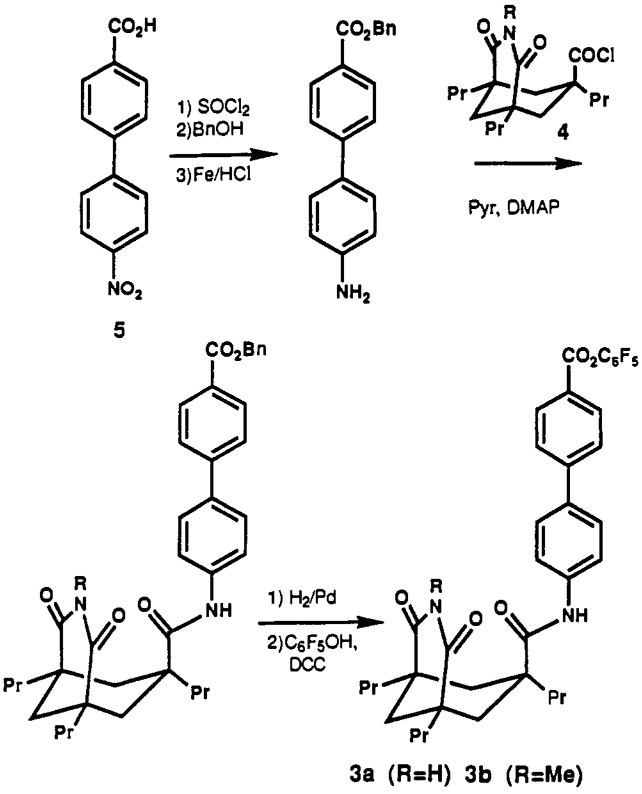
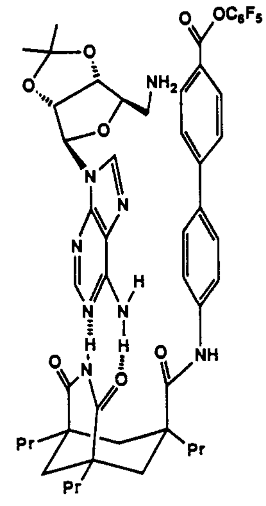
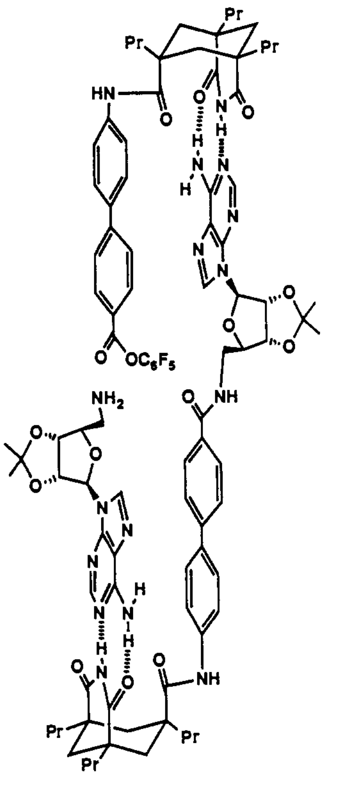


Figure 1 shows the appearance of **1** with time over 25% reaction for a typical run. Four complete data sets were obtained and all showed the appropriate curvature. The lines represent the best fit of the data to von Kiedrowski's's[3] square root law for autocatalysis. The coupling of *N*-methyl imide **3b**, which is incapable of base pairing, shows normal (linear) product growth with amine **2** but is slower than **3a**. Therefore, the mechanism involving bimolecular base paired species such as **7** is still operative. (This was the major pathway in molecules bearing shorter naphthyl or phenyl spacer surfaces.[1,2])

The sigmoidality of the autocatalyzed reaction curve is a consequence of the self-replicating pathway via termolecular complex **8**. Efficient autocatalysis results when template **1**, the product of the coupling reaction, is added to the reaction medium. For example, when 0.2 equiv of **1** is present at t_0, the rate enhancement observed is nearly 2-fold. NMR titrations of ester **3a** and 5′-acetyl-2′,3′-isopropylideneadenosine indicate a K_a for complex **7** of ~280 M^{-1}, and the estimated K_a for the termolecular species **8** is about 78 000 M^{-2}. Dimerization of the template was measured as ca. 80 000 M^{-1}. Thus the concentration of termolecular complex **8** at 25% completion is only 3%, yet its presence increases the rate of product formation 2-fold.



7



8

Simple derivatives of **2** show both reciprocity and mutation in competition experiments. The synthetic accessibility of these structures provides a tractable, modular system for the study of evolution at the molecular level.[9]

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