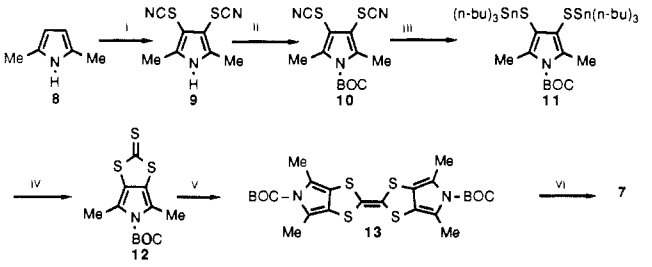
**Scheme I**



[a] (i) KSCN, $Br_2$, MeOH; (ii) $(BOC)_2O$, DMAP, $NEt_3$; (iii) 2 equiv of tributyltin hydride, $C_6H_6$; (iv) thiophosgene, $C_6H_6$; (v) hexabutylditin, $C_6H_6$, $h\nu$; (vi) 25% NaOMe.

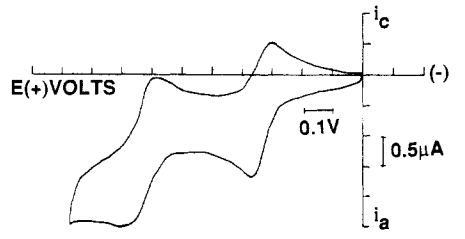



**Figure 1.** Cyclic voltammogram of $1.0 \times 10^{-4}$ M BP-TTF, **7**, in $CH_3CN$, using 0.1 M TBAHFP supporting electrolyte, Pt disk (working) and Pt wire (auxiliary) electrodes, versus an SCE reference electrode. Scan rate 0.050 V/s.

°C); when reacted with di-*tert*-butyldicarbonate [$(BOC)_2O$] it afforded the N-protected pyrrole **10** in 90% yield. Treatment of **10** with 2 equiv of tributyltin hydride[12] yielded **11** (60%). Compound **12**[13] was prepared in 35% yield by adding thiophosgene to a dilute benzene solution of **11**. The coupling reaction of **12**[14] was carried out by the photolysis method of Ueno[15] to give 15–20% of the product **13**. The *N*-*tert*-butoxycarbonyl substituent was removed rapidly under basic conditions to give the final product **7** nearly quantitatively.[16]

Figure 1 gives the cyclic voltammogram of **7**. We report in Table I measured solution oxidation potentials and relevant computed gas-phase ionization potentials. The computed ionization potential of BP-TTF is lower than that of TTF; this result is confirmed by lower solution oxidation potentials. It is clear that BP-TTF is an even better donor than TTF, illustrating the dramatic effect of the annelation by a highly electron-rich pyrrole ring. It should also be noted that facile chemical substitutions at the pyrrole N atoms make this donor particularly versatile. For example, we have already obtained the *N*-phenyl analogue **14** [bis(2,5-dimethyl-1-phenylpyrrolo-[3,4,*d*])tetrathiafulvalene][21] and find (Table I) that this donor has oxidation potentials (and calculated first ionization potential) very similar to those of **7**.

**Table I.** Half-Wave Solution Oxidation Potentials $E_{1/2}$ (Volts versus SCE),[a] Computed MNDO Vertical Ionization Potentials[b] $I_{MNDO}$ (eV), and Experimental Gas-Phase Ionization Energy[c] $I_{exp}$ (eV)

| compd | first $E_{1/2}$ | second $E_{1/2}$ | $I_{MNDO}$ | $I_{exp}$ |
|---|---|---|---|---|
| BP-TTF, **7** | 0.31 | 0.70 | 7.51 | |
| BPP-TTF, **14** | 0.39 | 0.74 | 7.46 | |
| TTF, **1** | 0.35 | 0.75 | 8.08 | 6.85[c] |
| ET, **3** | 0.54 | 0.96 | 8.08 | |
| DBTTF, **4** | 0.78[d] | 1.17[d] | 8.02 | |
| DTTTF, **5** | 0.75[e] | | 8.20 | |

[a] Reference 17. [b] Reference 18. [c] Reference 19. [d] Reference 4. [e] References 5 and 20.

Further studies to improve the yield, widen the scope of applicability, and grow ion-radical salts and charge-transfer complexes of **7** are in progress.

**Acknowledgment.** We are grateful to the National Science Foundation (Grant CHE-86-07458) for partial support of this work. We are also indebted to the Office of Naval Research (Grant N-00014-86-G-0215) for the purchase of the MicroVAX-II and to the Alabama Supercomputer Authority for computer time on the Cray X/MP-24.

## Monomeric Metaphosphate Formation during Radical-Based Dephosphorylation

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*Received June 9, 1988*

Radical-based dephosphorylation[1,2] via a phosphonyl radical **1a** (Scheme I) constitutes one formulation for the mechanism of carbon-to-phosphorus bond cleavage during microbial degradation of organophosphonates.[3] Chemical precedent for the biotic dephosphorylation follows from chemical and electrochemical oxidation of alkylphosphonic acids.[1a,b] Oxidative approaches have been restricted to analysis of the carbon fragments formed during C–P bond cleavage and provide little information relevant to reactive phosphorus-containing intermediate **2a**. This report describes a nonoxidative method for phosphonyl radical generation which has led to the first evidence for monomeric metaphosphate **2** formation[4,5,9] during radical-based dephosphorylation of orga-

(12) Ueno, Y.; Nozomi, M.; Okawara, M. *Chem. Lett.* **1982**, 1119.
(13) Mp 165 °C; *m/e* (rel intensity) 301 ($M^+$, 32), 245 (31), 201 (13), 57 (100); $^1H$ NMR $\delta$ ($CDCl_3$) 2.37 (6 H, s), 1.60 (9 H, s).
(14) Mp >280 °C; *m/e* (rel intensity) 538 ($M^+$, 14), 438 (39), 426 (93), 382 (76), 338 (100), 57 (41); $^1H$ NMR $\delta$ ($CDCl_3$) 2.35 (12 H, S), 1.58 (18 H, s).
(15) Ueno, Y.; Nakayama, A.; Okawara, M. *J. Am. Chem. Soc.* **1976**, *98*, 7440.
(16) Mp >300 °C; *m/e* (rel intensity) 338 ($M^+$, 100), 213 (53), 169 (14); $^1H$ NMR $\delta$ ($CDCl_3$) 2.17 (s).
(17) $E_{1/2}$ values are obtained as $E_{1/2}$ = oxidation peak −0.030 V in cyclic voltammograms measured in $CH_3CN$ solution (with 0.1 molar TBAHFP supporting electrolyte) with a BAS CV-27 cyclic voltammograph, platinum disk (working), platinum wire (auxiliary), and SCE (reference) electrodes. All waves are reversible.
(18) The MNDO vertical ionization potentials were obtained by using computer program MOPAC version 3.11 on a MicroVAX-II computer or computer program MOPAC 4.01 on a Cray X/MP-24 computer, with geometry optimization of each structure.
(19) Gleiter, R.; Schmidt, E.; Cowan, D. O.; Ferraris, J. P. *J. Electron Spectrosc.* **1973**, *2*, 207.
(20) Assuming that V versus SCE = 0.320 + volts versus [Ag]0.1 M $AgNO_3$]0.1 M $LiClO_4$], cf.: Larson, R. C.; Iwamoto, R. T.; Adams, R. N. *Anal. Chim. Acta* **1961**, *25*, 371.
(21) Compound **14** was synthesized from *N*-phenyl-2,5-dimethylpyrrole by the procedure described in Scheme I.

(1) (a) Cordeiro, M. L.; Pompliano, D. L.; Frost, J. W. *J. Am. Chem. Soc.* **1986**, *108*, 332. (b) Frost, J. W.; Loo, S.; Cordeiro, M. L.; Li, D. *J. Am. Chem. Soc.* **1987**, *109*, 2166. (c) Avila, L. Z.; Loo, S. H.; Frost, J. W. *J. Am. Chem. Soc.* **1987**, *109*, 6758.
(2) (a) Wackett, L. P.; Shames, S. L.; Venditti, C. P.; Walsh, C. T. *J. Bacteriol.* **1987**, *169*, 710. (b) Shames, S. L.; Wackett, L. P.; LaBarge, M. S.; Kuczkowski, R. L.; Walsh, C. T. *Bioorg. Chem.* **1987**, *15*, 366.
(3) (a) Kishore, G. M.; Jacob, G. S. *J. Biol. Chem.* **1987**, *262*, 12164. (b) Tamari, M. *J. Gen. Appl. Microbiol.* **1977**, *23*, 49. (c) Alam, A. U.; Bishop, S. H. *Can. J. Microbiol.* **1969**, *15*, 1043. (d) Harkness, D. R. *J. Bacteriol.* **1966**, *92*, 623. (e) James, E. A., Jr.; Meyers, T. C.; Titchener, E. B. *Fed. Proc. (Abstr.)* **1965**, *24*, 440. (f) Zeleznick, L. D.; Meyers, T. C.; Titchener, E. B. *Biochim. Biophys. Acta* **1963**, *78*, 546. (g) Balthazor, T. M.; Hallas, L. E. *Appl. Environ. Microbiol.* **1986**, *51*, 432. (h) Daughton, C. G.; Cook, A. M.; Alexander, M. *J. Agric. Food Chem.* **1979**, *27*, 1375. (i) Cook, A. M.; Grossenbacher, J.; Huetter, R. *Experientia* **1983**, 1191. (j) Daughton, C. G.; Cook, A. M.; Alexander, M. *FEMS Microbiol. Lett.* **1979**, *5*, 91. (k) Cook, A. M.; Daughton, C. G.; Alexander, M. *Biochem. J.* **1979**, *184*, 453. (l) Cook, A. M.; Daughton, C. G.; Alexander, M. *Appl. Environ. Microbiol.* **1978**, *36*, 668. (m) Cook, A. M.; Daughton, C. G.; Alexander, M. *J. Bacteriol.* **1978**, *133*, 85.
(4) (a) Westheimer, F. H. *Chem. Rev.* **1981**, *81*, 313. (b) Knowles, J. R. *Ann. Rev. Biochem.* **1980**, *49*, 877.

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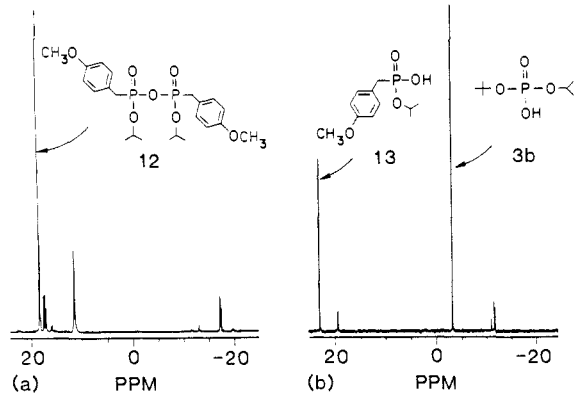
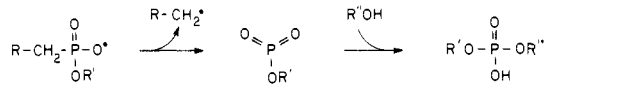



**Figure 1.** Partitioning of fragmentation crude reaction products: (a) $^{31}P$ NMR of the benzene layer and (b) $^{31}P$ NMR of the aqueous layer. Chemical shifts are relative to an external standard of 85% phosphoric acid.

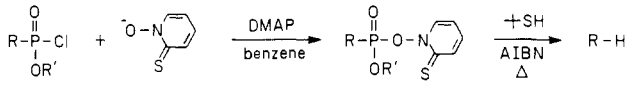
**Scheme I**



1a R' = H 2a R' = H 3a R' = H, R'' = H

1b R' = $(CH_3)_2CH$ 2b R' = $(CH_3)_2CH$ 3b R' = $(CH_3)_2CH$, R'' = $(CH_3)_3C$

**Scheme II**

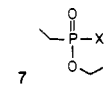
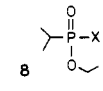
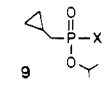
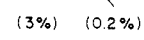
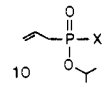
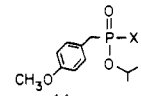
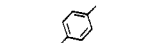
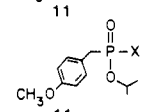
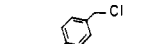


4 5 6

nophosphonates.

*N*-Hydroxypyridine-2-thione adduct fragmentation chemistry[6] is translated (Scheme II) to organophosphonates by 4-(dimethylamino)pyridine (DMAP)-catalyzed condensation of monoesterified organophosphonochloridates **4** with deprotonated *N*-hydroxypyridine-2-thione **5**. The benzene solution of 2-thionopyridine-*N*-hydroxamic organophosphonate (adduct **6**) is then reacted with *tert*-butyl mercaptan, tributyltin hydride, or carbon tetrachloride at reflux with azobisisobutyronitrile (AIBN) initiation. While formation of ethane (Table I) from ethylphosphonate **7** adduct is similar to the carbon fragments formed during microbial and chemical oxidative dephosphorylation of alkylphosphonic acids, one difference is the absence of ethene as a product. Formation of 1-butene during fragmentation of cyclopropylmethylphosphonate **9** adduct indicates the intermediacy of a carbon-centered radical.[7]

**Table I**[a]

| phosphonate | chain propagator/ radical quencher | product (% yield) |
|---|---|---|
|  7 |  |  (0.4%) |
|  8 |  |  (3%) |
|  9 |  |  (3%) (0.2%) |
|  10 |  |  (20%) |
|  11 | $Bu_3SnH$ |  (28%) |
|  11 | $CCl_4$ |  (27%) |

[a] Products were analyzed by gas chromatography. Volatiles (adducts **7**, **8**, **9**, and **10** fragmentation) were characterized according to ref 1a and 1b. The reaction solutions resulting from adduct **11** fragmentation were filtered through Florisil prior to separation on an OV 101 column.

After addition of *tert*-butyl alcohol (0.3 M) to *p*-methoxybenzylphosphonate **11** adduct fragmentation, products are partitioned between aqueous and organic layers. The $^{31}P$ resonance which dominates the organic layer corresponds to *p*-methoxybenzylpyrophosphonate (**12**, Figure 1a). Formation of pyrophosphonate **12** (52% yield) largely accounts for the modest production of *p*-methoxytoluene (28% yield). Further information follows from isolation of isopropyl *tert*-butyl phosphate[8] (**3b**, Figure 1b) from the aqueous layer. Decomposition of the phosphonyl radical (**1b**, Scheme I) generated from *p*-methoxybenzylphosphonate **11** adduct would lead to the formation of the isopropyl ester (**2b**, Scheme I) of monomeric metaphosphate. Isopropyl *tert*-butyl phosphate (**3b**, Scheme I) is the expected product of isopropyl metaphosphate interception by *tert*-butyl alcohol.[9] Isolation of this phosphate diester indicates a 38% trapping efficiency[10] and establishes the intermediacy of monomeric metaphosphate during fragmentation of 2-thionopyridine-*N*-hydroxamic organophosphonates. Monoester **13** (Figure 1b) likely results from hydrolysis of pyrophosphonate **12** or *p*-methoxybenzylphosphonate **11** adduct.

The opening of a new entry route into the monomeric metaphosphate reaction manifold is likely only one of several mechanistic and synthetic dividends to follow from nonoxidative

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(6) (a) Barton, D. H. R.; Bridon, D.; Zard, S. Z. *Heterocycles* **1987**, *25*, 449. (b) Crich, D. *Aldrich. Acta* **1987**, *20*, 35. (c) Barton, D. H. R.; Bridon, D.; Zard, S. Z. *Tetrahedron Lett.* **1986**, *27*, 4309. (d) Barton, D. H. R.; Crich, D.; Kretzschmar, G. *J. Chem. Soc., Perkin* Trans. *1* **1986**, 39. (e) Barton, D. H. R.; Crich, D.; Motherwell, W. B. *Tetrahedron* **1985**, *41*, 3901. (f) Barton, D. H. R.; Crich, D.; Motherwell, W. B. *Tetrahedron Lett.* **1983**, *24*, 4979. (g) Newcomb, M.; Park, S.; Kaplan, J.; Marquardt, D. J. *Tetrahedron Lett.* **1985**, *26*, 5651. (h) Newcomb, M.; Deeb, T. M. *J. Am. Chem. Soc.* **1987**, *109*, 3163. (i) Beckwith, A. L. J.; Hay, B. P. *J. Am. Chem. Soc.* **1988**, *110*, 4415.

(7) (a) Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7024. (b) Kochi, J. K.; Krusic, P. J.; Eaton, D. R. *J. Am. Chem. Soc.* **1969**, *91*, 1877. (c) Wilt, J. W. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, Chapter 8.

(8) $^1H$ NMR ($D_2O$, TSP = $\delta$ 0.0) $\delta$ 1.28 (d, $J$ = 12.8 Hz, 6 H), 1.42 (s, 9 H), 4.42 (m, 1 H); $^{13}C$ NMR ($D_2O$, $CH_3CN$ = $\delta$ 3.69) $\delta$ 26.0, 32.1, 72.8 (d, $J$ = 6.1 Hz), 81.7 (d, $J$ = 6.8 Hz); $^{31}P$ NMR ($D_2O$, external 85% $H_3PO_4$) $\delta$ −3.33.

(9) (a) Friedman, J. M.; Knowles, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 6126. (b) Freeman, S.; Friedman, J. M.; Knowles, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3166. (c) Ramirez, F.; Maracek, J. F. *Tetrahedron* **1979**, *35*, 1581. (d) Ramirez, F.; Maracek, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 1460. (e) Ramirez, F.; Maracek, J. F. *Tetrahedron* **1980**, *36*, 3151. (f) Ramirez, F.; Maracek, J. F. *Pure Appl. Chem.* **1980**, *52*, 1021. (g) Ramirez, F.; Maracek, J. F.; Yemal, S. S. *J. Am. Chem. Soc.* **1982**, *104*, 1345.

(10) trapping efficiency = moles diester **3b**/moles metaphosphate **2b** = moles diester **3b**/moles *p*-methoxytoluene.

phosphonyl radical generation. Microbes might also exploit some variant of this chemistry. Formation and subsequent homolytic fragmentation of organophosphonate adduct would circumvent the high oxidation potentials associated with direct, oxidative generation of phosphonyl radicals.[1b] The relevance of such a mechanism will depend on ongoing characterization of the genes and intermediate metabolites associated with organophosphonate biodegradation.[11]

**Acknowledgment.** Research was supported by National Institutes of Health (GM36558). We are indebted to Professor D. P. Curran for helpful discussion.

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## The Selective Hydrogenation of Benzene to Cyclohexene on Pentaammineosmium(II)

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*Received July 11, 1988*

Heterogeneous catalytic hydrogenation of aromatic molecules has been reported with a number of Group VIII metals including Ni, Pt, Rh, and Ru.[1] Though cyclic olefins are undoubtedly intermediates in this process, their rapid hydrogenation usually precludes their isolation in high yield. Partial selectivity toward cyclohexene has been achieved with modified ruthenium surfaces,[2] but this is accompanied by a dramatic decline in catalytic activity. Homogeneous reduction to cyclohexene has also been accomplished on various metal centers to which the arene is $\eta^6$ coordinated.[3] In these cases, however, reducing agents more potent than hydrogen are required.

Recently we reported the synthesis of a novel class of pentaammineosmium(II) compounds in which an arene is coordinated $\eta^2$ to the metal center.[4] Relative to others reported,[5] these complexes offer unusual kinetic stability, allowing their convenient manipulation and study at room temperature. Both theoretical calculations[6] and crystallographic data[7] indicate that the $\eta^2$ mode of ligation disrupts the aromaticity of the arene. Thus, the benzene complex $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)]^{2+}$ has been shown to be activated toward olefinic reactivity.[8] These considerations led us to investigate the hydrogenation of the complexes $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)](OTf)_2$ (**1**) and $[\{Os(NH_3)_5\}_2(\eta^2\text{:}\eta^2\text{-}\mu\text{-}C_6H_6)](OTf)_4$ (**2**) under mild conditions.

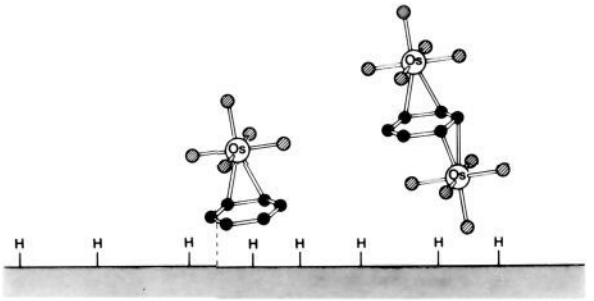


**Figure 1.** Steric interference in the catalytic hydrogenation of $\eta^2$-coordinated benzene complexes.

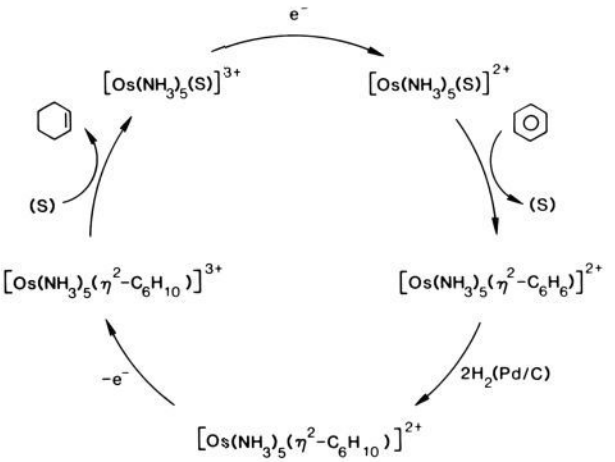


**Figure 2.** A cycle for the selective hydrogenation of benzene to cyclohexene.

Under 1 atm of hydrogen at 30 °C, $Pd^0$ on carbon (Pd/C) is ineffective as a catalyst for the hydrogenation of benzene.[9] However, when a MeOH solution of **1** is subjected to these conditions, the cyclohexene complex $[Os(NH_3)_5(\eta^2\text{-}C_6H_{10})](OTf)_2$ (**3**) is produced in quantitative yield.[10] $^1H$ NMR, cyclic voltammetric, and microanalytical data[11] confirm that complex **3** is obtained as a pure solid. Further support for the proposed identity of **3** is gained from the direct reaction of pentaammineosmium(II) with cyclohexene in which an identical product is obtained.[12] When the hydrogenation is repeated under similar conditions without the addition of the $Pd^0$ catalyst, the formation of **3** is not detected.

A proton NMR spectrum of **3** features five inequivalent resonances (3.40, 2.68, 1.52, 1.40, 1.12 ppm) corresponding to the ring protons, of which the olefinic signal occurs the furthest downfield (cf., the ethylene resonance for the complex $[Os(NH_3)_5(\eta^2\text{-}C_2H_4)](OTf)_2$ occurs at 3.22 ppm).[13] When the reduction of **1** is repeated using $D_2$ and $CD_3OD$, NMR data for **3**-$d_4$ reveal a dramatic loss of intensity at 2.68 and 1.52 ppm indicating that the dominant isomer is a product of cis hydro-

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(8) Though pentaammineruthenium(II) fails to form a complex with benzene analogous to **1**, the binuclear complex $[Os(NH_3)_5Ru(NH_3)_5(\eta^2\text{:}\eta^2\text{-}\mu\text{-}C_6H_6)](OTf)_4$ is readily prepared. See: Harman, W. D.; Taube H. *J. Am. Chem. Soc.*, accepted for publication.

(9) Control reaction run in $CD_3OD$ for 7 h at 50 psi.

(10) Synthesis of **3**. All reactions are carried out under rigorously anaerobic conditions. 28 mg of 5% Pd on C is suspended in 5 mL of degassed methanol and stirred under 1 atm of $H_2$ for 15 min. (The ratio of Os to Pd is 20:1). **1** (85 mg) is added to the slurry, and the mixture is stirred under $H_2$ for 15 h. The solution is filtered to remove the catalyst and then added slowly to 50 mL of $Et_2O$ upon which a light yellow precipitate is formed. Final yield: 89%.

(11) Characterization of **3**: Anal. Calcd for $C_8H_{25}OsS_2F_6O_6N_5$: C, 14.66; H, 3.84; N, 10.70. Found: C, 14.10; H, 3.76; N, 10.78. $^1H$ NMR (acetone-$d_6$, ppm vs TMS) 3.40 (m, 2 H), 2.68 (m, 2 H), 1.52 (m, 2 H), 1.40 (m, 2 H), 1.12 (m, 2 H), 2.88 (b, 12 H), 3.95 (b, 3 H); cyclic voltammetry (100 mV/s; $CH_3CN$; 1.0 M TBAH; $E_\lambda$ = 1.40 V; −1.40 V): $E_{1/2}$ = 0.55 V, NHE.

(12) Complex **3** can be generated from cyclohexene directly utilizing synthetic procedures previously described. See ref 18.

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