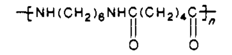
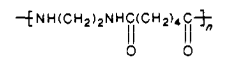
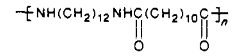
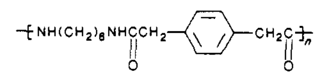
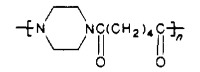
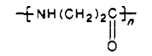
Table II. Polyamide Synthesis

polyamides[a]	mp, °C	M_n[b]	yield,[c] %
 $\left[NH(CH_2)_6NH\underset{\underset{O}{\|}}{C}(CH_2)_4\underset{\underset{O}{\|}}{C}\right]_n$	255	8900	98
 $\left[NH(CH_2)_2NH\underset{\underset{O}{\\|}}{C}(CH_2)_4\underset{\underset{O}{\|}}{C}\right]_n$	>300	3700	97
 $\left[NH(CH_2)_{12}NH\underset{\underset{O}{\|}}{C}(CH_2)_{10}\underset{\underset{O}{\|}}{C}\right]_n$	>300	3800	99
	>300	14000	93
	230	7200	73
 $\left[NH(CH_2)_2\underset{\underset{O}{\|}}{C}\right]_n$	175	1600	98

[a] The produci polyamide **9** in eq 3. Polymerization was carried out with 2 mmol of each monomer in the presence of 4 mmol of water and 3 mol % of $RuH_2(PPh_3)_4$ in DME at 160 °C for 24 h in a sealed tube under argon. The precipitated polymer was washed with $CHCl_3$ and dried in vacuo. [b] Molecular weight was determined by the titration of the terminal amino group with *p*-toluenesulfonic acid using Thimol-Blue. [c] The IR spectra and elemental analyses are consistent with the general polyamide structure.

prepared by the reaction of *trans*-cinnamonitrile with **5a** in 70% yield. Evidently, the acylation of primary amines proceeds chemoselectively in the presence of secondary amines. Direct selective acylation of polyamines, particularly spermidines and spermines, is of considerable importance, because their derivatives have potent antibiotic and antineoplustic properties.[6] However, the methods available are limited to a few, because of the higher nucleophilicity of secondary amines with most electrophilic reagents.[6]

The efficiency of our new process is highlighted by the synthesis of various, industrially important polyamides.[7] The ruthenium-catalyzed reaction of dinitriles **7** with diamines **8** in the presence of water gives polyamides **9** generally (eq 3).[8] As a model reaction

$$\underset{\mathbf{7}}{NCCH_2\text{-}X\text{-}CH_2CN} + \underset{\mathbf{8}}{RNH\text{-}Y\text{-}NHR} \xrightarrow[H_2O]{\text{Ru catalyst}} \underset{\mathbf{9}}{\text{-}(COCH_2\text{-}X\text{-}CH_2CONR\text{-}Y\text{-}NR)_n\text{-}} \quad (3)$$

the polycondensation of hexanedinitrile with 1,6-hexanediamine was investigated in the presence of water (2 equiv) and catalyst **1** (3 mol %) in DME at 160 °C for 24 h. The polyamide was obtained in 98% yield. The molecular weight ($\overline{M}_n$) was determined to be 8900 by titration of the terminal amino group.[9] The viscosity η in *m*-cresol was 0.7 dL g^{-1}, which corresponds to $\overline{M}_n$ 7900 and is consistent with the $\overline{M}_n$ value obtained above. Other representative examples of the polyamide synthesis are shown in Table II. Since various dinitriles have been prepared as the precursor of diamines,[10] the present reaction provides a wide-scope method for synthesis of polyamides without using diacids and diesters. Finally, aminonitriles undergo similar polycondensation efficiently. The ruthenium-catalyzed reaction of 3-aminopropionitrile gave nylon 3, $-(NH(CH_2)_2CO)_n-$ (mp 175 °C, $\overline{M}_n$ 1600), in 98% yield.

Work is in progress to investigate the interesting mechanism of the present reaction and to apply our method to other systems.

Registry No. 1, 19529-00-1; **2**, 1699-40-7; **3**, 105-60-2; **4**, 931-20-4; **6a**, 82414-35-5; **6b**, 95245-15-1; **6c**, 41590-65-2; $H_2N(CH_2)_5CN$, 2432-74-8; $H_3CNH(CH_2)_4CN$, 6066-89-3; $H_3C(CH_2)_5NH(CH_2)_4CN$, 104807-50-3; CH_3CN, 75-05-8; **5a**, 124-20-9; **5b**, 56-18-8; $C_6H_5CH_2CN$, 140-29-4; *trans*-$C_6H_5CH{=}CHCN$, 1885-38-7; $H_3CCONHC_4H_9$, 1119-49-9; $H_3CCON(CH_3)CH_2C_6H_5$, 29823-47-0; $H_3COCH_2CONHC_4H_9$, 53848-63-8; 3-(benzyloxy)-4-methoxybenzenecarbonitrile, 1699-39-4; [3-methoxy-4-(benzyloxy)-β-phenethyl]amine, 22231-61-4; *N*-hexylpiperidone, 89013-13-8; 1-(*N*-piperidino)ethanone, 618-42-8; 1,4-dipyrrolidinyl-1,4-dioxobutane, 63958-62-3; $(H_2N(CH_2)_6NH_2)(NC(CH_2)_4CN)$(copolymer), 51937-09-8; $(H_2N(CH_2)_6NH_2)(NC(CH_2)_4CN)$(copolymer, SRU), 3213-17-2; $(H_2N(CH_2)_2NH_2)(NC(CH_2)_4CN)$(copolymer), 70087-99-9; $(H_2N(CH_2)_2NH_2)(NC(CH_2)_4CN)$(copolymer, SRU), 26951-61-1; $(H_2N(CH_2)_{12}NH_2)(NC(CH_2)_{10}CN)$(copolymer), 104807-51-4; $(H_2N(CH_2)_{12}NH_2)(NC(CH_2)_{10}CN)$(copolymer, SRU), 36348-71-7; $(H_2N(CH_2)_6NH_2)(NCCH_2C_6H_4$-*p*-$CH_2CN)$(copolymer), 104807-52-5; $(H_2N(CH_2)_6NH_2)(NCCH_2C_6H_4$-*p*-$CH_2CN)$(copolymer, SRU), 52236-37-0; (1,6-hexanedinitrile)(1,4-piperazine)(copolymer), 104807-53-6; (1,6-hexanedinitrile)(1,4-piperazine)(copolymer, SRU), 26967-89-5; poly(3-aminopropionitrile)(homopolymer), 28157-83-7; poly(3-aminopropionitrile)(SRU), 104807-54-7.

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[6] (a) Chantrapromma, K.; Ganem, B. *Tetrahedron Lett.* **1981**, *22*, 23. (b) Husson, A.; Besselievre, R.; Husson, H.-P. *Ibid.* **1983**, *24*, 1031. (c) Kunieda, T.; Higuchi, T.; Abe, Y.; Hirobe, M. *Tetrahedron* **1983**, *39*, 3253. (d) Nagao, Y.; Seno, K.; Kawabata, K.; Miyasaka, T.; Takao, S.; Fujita, E. *Chem. Pharm. Bull.* **1984**, *32*, 2687. (e) Acher, F.; Wakselman, M. *J. Org. Chem.* **1984**, *49*, 4133. (f) Joshua, A. V.; Scott, J. R. *Tetrahedron Lett.* **1984**, *25*, 5725.

[7] (a) Schule, E. C. In *Encyclopedia of Polymer Science and Technology*; Bikales, N. M., Ed.; Interscience: New York, 1969; Vol. 10, p 347. (b) Sweeny, W.; Zimmerman, J. *Idem.* p 597.

[8] Reported polyamide synthesis from nitriles and amines, see: (a) Greene, J. L.; Loza, R. US patent 4380623; *Chem. Abstr.* **1983**, *99*, 23111v.

[9] Schaefgen, J. R.; Flory, P. J. *J. Am. Chem. Soc.* **1948**, *70*, 2709.

[10] (a) Kan, P. T. In *Condensation Monomers*; Still, J. K., Campbell, T. W., Eds.; Wiley-Interscience; New York, 1972; p. 155. (b) Michael addition, see: O'Sullivan, D. A. *Chem. Eng. News* **1986**, March 3, p 21. (c) Hydrocyanation of olefins and dienes, see: Parshall, G. W. *Homogeneous Catalysis*, Wiley: New York, 1980; p 219. Tolman, C. A.; McKinney, R. J.; Seidel, W. C.; Druliner, J. D.; Stevens, W. R. *Adv. Catal.* **1985**, *33*, 1. (d) Electrolytic coupling of acrylonitrile, see: Daly, D. E. CHEMTECH **1980**, 302.

Electrocatalytic Four-Electron Reduction of Dioxygen by Iridium Porphyrins Adsorbed on Graphite

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The electrocatalytic reduction of dioxygen by macrocyclic transition-metal complexes adsorbed on electrodes has been studied extensively in conjunction with the search for an inexpensive cathode material for oxygen fuel cells.[1] We and other laboratories have shown that dicobalt cofacial porphyrin dimers can catalyze dioxygen reduction to water without producing significant amounts of hydrogen peroxide.[2] To our knowledge, however, no monomeric macrocyclic metal complex has been reported to catalyze the direct four-electron reduction of dioxygen in acidic solution.[3,4] In a survey of electrocatalytic oxygen reduction by various metalloporphyrins adsorbed on activated carbon, iridium complexes were reported to be the most active catalysts.[5] Since the reduction

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[1] (a) Schiffrin, D. J. *Electrochemistry* **1983**, *8*, 126. (b) Yeager, B. *Electrochim. Acta* **1984**, *29*, 1527. (c) van Veen, J. A. R.; van Baar, J. F. *Rev. Inorg. Chem.* **1982**, *4*, 293.

[2] (a) Collman, J. P.; Denisevich, P.; Konai, Y.; Marocco, M.; Koval, C.; Anson, F. C. *J. Am. Chem. Soc.* **1980**, *102*, 6027. (b) Durand, R. R., Bencosme, C. S.; Collman, J. P.; Anson, F. C. *J. Am. Chem. Soc.* **1983**, *105*, 2710. (c) Liu, H. Y.; Weaver, M. J.; Wang, C.-B.; Chang, C. K. *J. Electroanal. Chem.* **1983**, *145*, 439. (d) Chang, C. K.; Liu, H. Y.; Abdalmuhdi, I. *J. Am. Chem. Soc.* **1984**, *106*, 2725.

[3] Planar dicobalt macrocycles catalyze O_2 reduction to H_2O in alkaline solution. Reference 1b and: van der Putten, A.; Elzing, A.; Visscher, W.; Barendrecht, E. *J. Chem. Soc., Chem. Commun.* **1986**, 477.

[4] (a) Iron phthalocyanines are reported to catalyze four-electron O_2 reduction in basic solution: Kozawa, K.; Zilionis, V. E.; Brodd, R. J. *J. Electrochem. Soc.* **1970**, *117*, 1470. (b) Iron porphyrins catalyze overall four-electron reduction of O_2 which proceeds through a H_2O_2 intermediate: Shigehara, K.; Anson, F. C. *J. Phys. Chem.* **1982**, *86*, 2776. (c) Polymer-bound iron tetrakis(*o*-aminophenyl)porphyrin (TAPP) and electropolymerized CoTAPP catalyze overall four-electron reduction by dismutation of intermediate H_2O_2: Bettelheim, A.; Chan, R. J. H.; Kuwana, T. *J. Electroanal. Chem.* **1980**, *110*, 93. Bettelheim, A.; White, B. A.; Murray, R. W., unpublished results.

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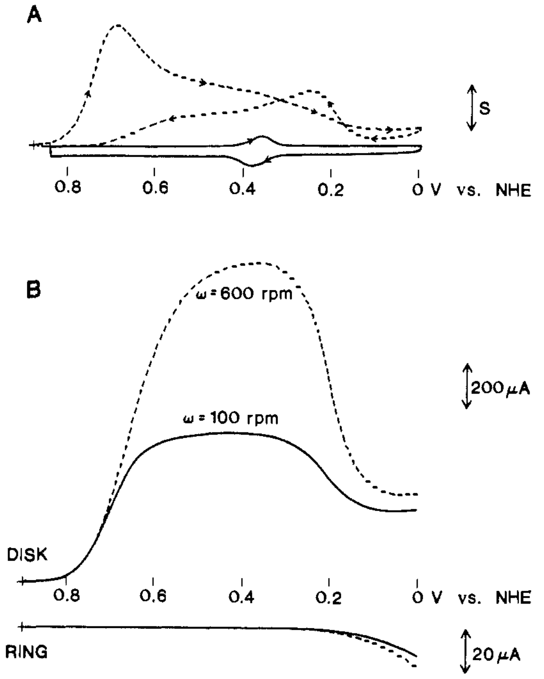


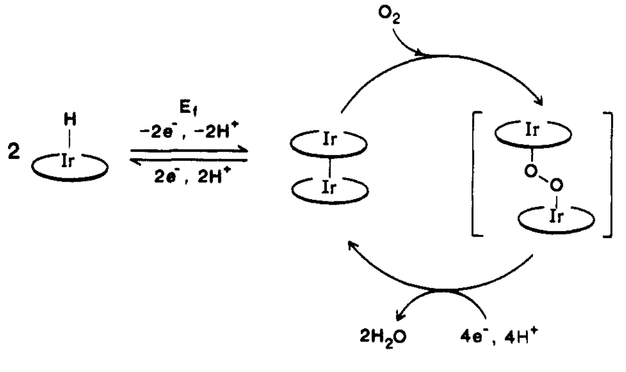
Figure 1. (a) Cyclic voltammogram of Ir(OEP)H adsorbed on graphite under N_2 (solid line) and O_2 (dashed line). (B) Rotating-ring–disk voltammogram of Ir(OEP)H in O_2-saturated solution.

Table I. Electrochemical Data for Reduction of Oxygen Catalyzed by Ir(OEP)H and Dicobalt Cofacial Porphyrin Dimers Adsorbed on Graphite Electrodes

catalyst	E_f,[a] V vs. NHE	$E_{1/2}$,[b] V vs. NHE	n[c]	electrolytes	ref
Co_2FTF4	0.82, 0.48	0.72	3.9	0.5 M TFA	2a
Co_2DPB	0.88, 0.58	0.70	3.7–3.8	0.5 M TFA	2d
IrOEPH	0.38	0.72	3.9	0.1 M TFA	*e*
	0.09	0.31	3.6	pH 7 buffer	*e*
	−0.22	0.03	3.3	0.1 M NaOH	*e*
Pt/C[d]		0.79	4.0	0.1 M TFA	*e*

[a] Formal potential of the adsorbed porphyrin evaluated from cyclic voltammetric peak potentials under N_2. [b] Half-wave potential for O_2 reduction at the rotating-disk electrode (rotation rate = 100 rpm). [c] Number of electrons consumed (determined from the slope of a Koutecky–Levich plot). [d] Reference 18. [e] This work.

Scheme I



product and the reaction pathway had not been elucidated in that work, we were prompted to study the electrocatalytic activity of iridium porphyrins toward dioxygen reduction. Here we report the first observation of a *direct four-electron* reduction of dioxygen catalyzed by Ir(OEP)H[6,7] adsorbed on graphite in acidic electrolyte solution.

The cyclic voltammogram of Ir(OEP)H adsorbed on a graphite electrode[8] in deaerated 0.1 M trifluoroacetic acid (TFA) exhibits a quasi-reversible surface-confined redox couple[9] (Figure 1A, solid curve). The catalytic reduction of dioxygen by this system is demonstrated by the cyclic voltammogram (Figure 1A, dashed curve) and rotating-ring–disk voltammograms[10] (Figure 1B) obtained in the oxygen-saturated solution. As shown in Figure 1B, the cathodic disk current starts flowing at a potential much more positive (ca. 460 mV) than the formal redox potential (E_f) of the catalyst in the absence of O_2. After reaching a plateau, the current decreases rapidly when the potential becomes more negative than E_f. This unusual current–potential behavior is reproduced with gradually decreasing maximum currents in subsequent scans.

Most importantly, O_2 is reduced in a four-electron process to H_2O. Virtually no hydrogen peroxide is detected at the ring electrode until the disk potential reaches 0.25 V vs. NHE. Neither is added H_2O_2 reduced by this catalyst in the absence of O_2. The Koutecky–Levich plot[12] of (limiting current)$^{-1}$ vs. (rotation rate)$^{-1/2}$ confirms the four-electron reduction of dioxygen: the slope closely matches the theoretical four-electron line. The relatively small value of the Koutecky–Levich intercept indicates exceptionally fast kinetics. While a direct four-electron reduction pathway is followed almost exclusively in acidic solution, a two-electron pathway makes a small contribution in neutral or basic solution (Table I). The electrocatalytic activity of Ir(OEP)H is equal or superior to that of the best dicobalt cofacial porphyrins in terms of potential, rate, pH range, and four-electron selectivity (Table I). This is unprecedented for a monomeric macrocycle.

We also have examined the catalytic activity of several other iridium porphyrins. Interestingly, Ir(TTP)H[6,13] on graphite does *not* show a surface redox couple in the absence of oxygen nor significant catalytic activity for O_2 reduction. Both $[Ir(OEP)]_2$[14] and Ir(OEP)I[7] exhibit almost the same catalytic activity as Ir(OEP)H, but Ir(OEP)I requires conditioning at a reducing potential (<−0.1 V at pH 1) to become an active catalyst. When Ir(OEP)H solution in benzene is exposed to air or oxygen, a red precipitate is formed slowly. This diamagnetic product[16] has been formulated as Ir(OEP)O_2H. The hydroperoxo complex, like Ir(OEP)I, is not an active catalyst until it is reduced at a negative potential.

We suggest a plausible mechanism for O_2 reduction in Scheme I. We believe that the active catalyst on the surface is $[Ir(OEP)]_2$

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(5) van Veen, J. A. R.; van Baar, J. F.; Kroese, C. J.; Coolegem, J. G. F.; DeWit, N.; Colin, H. A. *Ber. Bunsenges. Phys. Chem.* **1981**, *85*, 693.

(6) Abbreviations: OEP = 2,3,7,8,12,13,17,18-octaethylporphyrin dianion; TTP = 5,10,15,20-tetra-*p*-tolylporphyrin dianion.

(7) Ogoshi, H.; Setsune, J.-I.; Yoshida, Z.-I. *J. Organomet. Chem.* **1978**, *159*, 317.

(8) For cyclic and rotating disk voltammetry edge-plane pyrolytic graphite electrodes (area 0.37 cm^2) were polished with no. 400 SiC paper, sonicated for 10 s, and coated with the catalyst by dipping in a fresh ca. (1-3) × 10^{-5} M benzene solution in an inert atmosphere box for 5 min. The typical coverage was estimated to be 2 × 10^{-9} mol cm^{-2}.

(9) The amount of charge passed during the redox process corresponds to one electron per Ir(OEP)H molecule applied to the graphite electrode (at monolayer or submonolayer coverage). The redox potential changes linearly with pH (−56 mV per pH unit), indicating that the same number of protons as electrons is involved.

(10) Platinum ring and pyrolytic graphite disk electrode (area = 0.46 cm^2) were used (ring collection efficiency = 0.12 at 100 rpm). After the platinum ring was pretreated[11] to obtain maximum efficiency in detecting H_2O_2, the graphite electrode was coated as described above.[8]

(11) Gileadi, E.; Kirowa-Eisner, E.; Penciner, J. *Interfacial Electrochemistry*; Addison-Wesley: Reading: MA, 1975; p 311.

(12) Koutecky, J.; Levich, V. G. *Zh. Fiz. Khim.* **1958**, *32*, 1565.

(13) Ir(TTP)H was synthesized in an analogous way to Ir(OEP)H.[7] ^1H NMR (C_6D_6) δ 8.43 (s, 8 H, H_β), 8.01 (d, J = 7.8 Hz, 4 H, H_o), 7.94 (d, J = 7.8 Hz, 4 H, $H_{o'}$) 7.54 (d, 4 H, H_m), 7.52 (d, 4 H, $H_{m'}$), 2.49 (s, 12 H, Me), −51.36 (s, 1 H, Ir H); UV/vis (benzene) λ_{max} 390 (sh), 408 (Soret), 506 nm; IR (KBr) 2320 cm^{-1} (ν_{Ir-H}).

(14) $[Ir(OEP)]_2$ was prepared by photolysis of Ir(OEP)H in toluene.[15] The compound used in this experiment contains ca. 10% of unreacted Ir(OEP)H.

(15) (a) Collman, J. P.; Leidner, C. R.; Garner, J. M.; Johnson, K., unpublished results. (b) Del Rossi, K. J.; Wayland, B. B., unpublished results.

(16) Oxygen uptake during the formation of this compound was measured to be 0.85 mol per Ir(OEP)H. ^1H NMR (THF-d_8) δ 9.92 (s, 4 H, meso), 4.09 (m, 16 H, CH_2), 1.93 (t, 24 H, CH_3); IR (KBr) 3596 (ν_{OH}), 3584 ($\nu_{^{18}OH}$) cm^{-1}; UV/vis (THF) λ_{max} 391 (Soret), 502, 533 nm; MS (SIM) 759, 757 [$(M + H)^-$]; Triphenyl phosphine slowly reacts with this compound to form triphenylphosphine oxide.

formed from the precatalyst Ir(OEP)H by electrochemical oxidation at the beginning of the cathodic scan.[17] As the potential becomes more negative than E_f, the catalytic activity is diminished upon formation of Ir(OEP)H, which reacts with O_2 relatively slowly to form Ir(OEP)O_2H, which is not an intermediate in the fast four-electron catalytic cycle. Rapid oxidative dimerization of Ir(OEP)H to a very effective catalyst, $[Ir(OEP)]_2$, is therefore the key to the remarkable activity of this system.[19] This work is currently being expanded to include diiridium cofacial porphyrins. Further studies to elucidate the mechanistic details are also in progress.

Acknowledgment. We thank C. R. Leidner for the synthesis of $[Ir(OEP)]_2$ and assistance in data analysis and M. G. Finn, F. C. Anson, R. W. Murray, N. S. Lewis, and G. T. Yee for helpful discussions. We acknowledge the Bio-Organic, Biomedical Mass Spectrometry Resource, supported by the NIH Division of Research Resources Grant RR01614, and the National Science Foundation (Grant FSVCHE83-18512) for support.

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[17] The following cyclic voltammetric data is consistent with the reversible electrochemical interconversion of Ir(OEP)H and $[Ir(OEP)]_2$.[20] (a) Both Ir(OEP)H and $[Ir(OEP)]_2$ on graphite exhibit the same redox wave under N_2. (b) One electron per Ir(OEP)H is passed in the redox process;[9] however, the full width at half-maximum peak height (fwhm) is considerably narrower (~57 mV) that would be expected for a simple one-electron transfer, suggesting the presence of some other phenomenon, including a dimerization reaction. For the case of electron transfer followed by a dimerization reaction, the expected fwhm is a complicated function of the rate of dimerization and scan rate.[21] When the dimerization rate is much faster than the scan rate, the fwhm is calculated to be 47 mV for a one-electron process, close to the observed value.

[18] Wan, G. X.; Shigehara, K.; Tsuchida, E.; Anson, F. C. *J. Electroanal. Chem.* **1984**, *179*, 239.

[19] We believe that the inability of adsorbed Ir(TTP)H to show a surface redox wave and to catalyze the reduction of oxygen results from an inhibition of the rapid oxidative dimerization reaction, either by a different surface morphology or an intrinsic steric barrier to dimerization.

[20] It should be noted that the interconversion of Ir(OEP)H and $[Ir(OEP)]_2$ has not been demonstrated in solution. Cyclic voltammetry of Ir(OEP)H (0.2 M Bu_4NPF_6 in CH_2Cl_2 at a Pt electrode with Ag wire pseudoreference, $FeCp_2^{0/+}$ = 0.33 V) showed the following features: (1) irreversible reduction at ~-1.8 V; (2) one irreversible oxidation at 1.4 V and one reversible wave at 1.7 V; (3) a chemically and electrochemically irreversible oxidation at ~0.6 V. Features 1 and 2 are presumably ligand-centered processes. The nature of the oxidation at 0.6 V is not yet established.

[21] Laviron, E. *Electrochim. Acta* **1971**, *16*, 409.

Sigmatropic [1,3]-Hydrogen Migration in a 1-Silapropene

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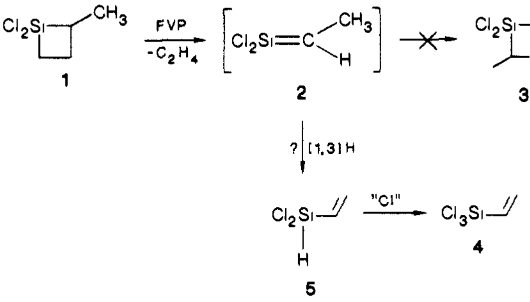
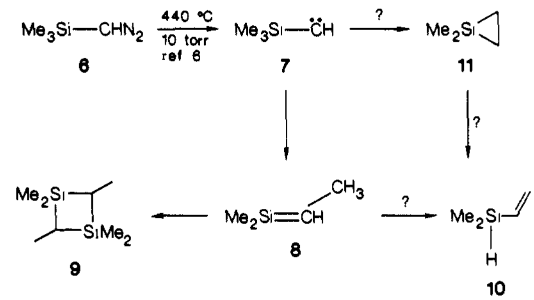
Suprafacial sigmatropic [1,3] shifts are symmetry-forbidden unless there is accompanying inversion of the migrating group, while the symmetry-allowed antarafacial [1,3] shift is rendered extremely awkward at best by geometric constraints.[1] Thus, although there are rare examples of the [1,3]-sigamtropic shifts of carbon,[2] to our knowledge the [1,3]-sigmatropic migration of hydrogen has not been observed. MINDO/CI calculations by Dewar[3] predict an activation energy of 49.2 kcal/mol for the 1,3-allylic hydrogen shift in propene.

In view of the above, it was with considerable surprise that we observed in the flash vacuum pyrolysis (FVP) of 1,1-dichloro-2-methyl-1-silacyclobutane (**1**) none of the expected dimer **3** of silene **2** and a 46% yield of vinyltrichlorosilane (**4**).[4] As silacyclobutane pyrolysis is a standard route to the silicon-carbon double bond,[5] it was difficult to ignore the possibility that **4** arose from a rearrangement of the anticipated 1,1-dichloro-1-silapropene (**2**). If, indeed, silene **2** rearranged via a [1,3]-hydrogen shift, the product would be dichlorovinylsilane **5** and not the trichloro species **5**. However, the facile H/Cl redistribution on silicons makes it possible that we might not actually observe **5** from this reaction mixture.[6]



The question of [1,3]-hydrogen migration in 2-methylsilenes has arisen before. In 1975 Shechter[7] reported that trimethylsilyldiazomethane (**6**) thermally produced carbene **7** which isomerized to 1,1,2-trimethylsilene (**8**) as evidenced by the formation of its head-to-tail dimer **9** in ca. 40% yield. Of considerable interest was the concomitant formation of dimethylvinylsilane (**10**) albeit in quite low yield (3-4%). It was recognized that the vinylsilane could either arise from rearrangement of **8** or from isomerization of 1,1-dimethylsilacyclopropane (**11**), derived directly from carbene **7**. Indeed, this latter process had literature precedent in the proposal of Skell[8] that reaction of $Me_3SiCHCl_3$ with Na-K vapor at 260 °C produced **10** via silirane **11**.



The obvious experiment for distinction between **8** and **11** as progenitors of **10** is deuterium labeling of the carbenic carbon of **7**. This experiment was conducted by Shechter but, unfortunately, insufficient **10-D** was produced for the crucial determination of the position(s) of deuterium substitution. The only clue was the formation of 2,5-dideuterio-3,3,4,4-tetramethyl-3,4-disilahex-1-ene (**12**) which was reasonably assumed to arise from insertion of **8-D** into the Si-H bond of **10-2D** and thus to deductively establish the position of the deuterium in **10-D**. Unfortunately, that interpretation now suffers from the absence of precedent for such an insertion reaction,[9] our inability to produce the formation of **12** under our conditions of FVP (vide infra), and an alternative mechanistic possibility for the formation of **12** (Scheme I). We note that **12** could have been produced by head-to-head dimer-

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