vinyltrimethylsilane **33** (65%) and aromatized product **34** (7%). When employing the conditions of method 2 (R^2Li = MeLi) to 2-cyclohexen-1-one (**35**), we also isolated the corresponding vinyltrimethylsilane **36** as the major product (36%). The desired allyltrimethylsilane **38** was obtained in 15% yield; other minor products included aromatic silane **37** (15%) and trimethylsilyl ether **39** (5%).

In conclusion, use of the counterattack method facilitated the preparation of allyltrimethylsilanes. Treatment of the readily available starting material, allyl alcohols, enals, enones, aldehydes, or ketones with organolithium reagents gave allyl alkoxides. The alkoxides then reacted with $Me_3SiSiMe_3$ to afford trimethylsilyl ethers and Me_3Si^-. In situ a substitution reaction occurred between these two species to produce allyltrimethylsilanes in good yields. In these one-flask reactions, $Me_3SiSiMe_3$ behaved as a counterattack reagent.

Acknowledgment. Hwu is grateful for financial support provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society; the American Heart Association, the Maryland Affiliate, Inc.; the American Cancer Society Institutional Research Grant IN-11Z; and the Biomedical Research Support Grant S07 RR7041 awarded by the National Institutes of Health. A grant from the National Institutes of Health for supporting the purchase of a VG 70-S mass spectrometer is also acknowledged. Lin and Liaw thank the National Science Council of the Republic of China for a research grant.

Electronic Properties and Redox Conduction of Ferrocene-Substituted High Polymeric Phosphazenes

Reginaldo A. Saraceno, Geoffrey H. Riding,
Harry R. Allcock,* and Andrew G. Ewing*

Department of Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802

Received June 29, 1988
Revised Manuscript Received September 2, 1988

We have recently reported on the electronic properties of phosphazene substituents which affect thermodynamic shifts in the oxidation peak potential of ferrocene.[1] Examination of the electrochemistry of ferrocene bonded to phosphazenes provides a direct probe of the electronic and bonding structure of this important class of molecules. In this paper we present the first thermodynamic and kinetic data obtained for the electrochemical oxidation and reduction of ferrocene-substituted polyphosphazenes $[N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe]_n$ (I), $[N_3P_3(OCH_2CF_3)_5(\eta\text{-}C_5H_4)Fe(\eta\text{-}C_5H_5)]_n$ (II), and $[N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe]_n$ (III).

Cyclic voltammetry and chronoamperometry at platinum disk electrodes (radius = 1.9 mm) coated with evaporatively deposited (from DMF) polymers were used to study electron transfer and cross exchange processes. Voltammograms for a surface immobilized film of I in dichloromethane are shown in Figure 1A. Voltammetry of I in acetonitrile solutions results in irreproducible electrochemistry and deterioration of the polymer film apparently due to a chemical reaction of oxidized I with acetonitrile. Electrochemistry in dichloromethane is reproducible and can be used to ascertain the thermodynamic properties of this polymer. The surface coverage of the polymer (Γ) was obtained by integrating the area under the oxidation wave.[2]

The large difference between oxidation and reduction peak potentials (ΔE_p) and asymmetrical peak shapes are typical of the voltammetry obtained with platinum electrodes modified with polymer films of I. The separation between voltammetric peaks ranges from a low of 0.26 V at a 10 mV/s scan rate to a high of 1.24 V at a 200 mV/s scan rate. Plots of $(i_p)_{anod}$ versus square root of scan rate ($v^{1/2}$) were linear (correlation coefficient = 0.9965, n = 5) for values between the scan rate limits examined.

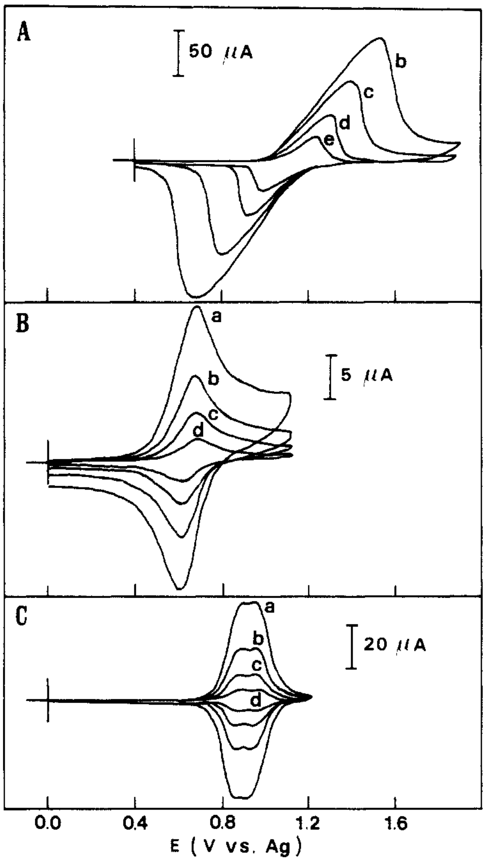

Figure 1. Cyclic voltammograms of evaporatively deposited polyphosphazenes I (A), II (B), and III (C), on Pt electrodes, in 0.1 M tetrahexylammonium perchlorate/dichloromethane (A) or 0.1 M tetraethylammonium perchlorate/acetonitrile (B and C). Scan rates: 0.2 (a), 0.1 (b), 0.05 (c), 0.02 (d), 0.01 (e) V/s. Surface coverage $\Gamma = 4.9 \times 10^{-8}$ mol/cm^2 (A), 1.6×10^{-9} mol/cm^2 (B), and 4.8×10^{-9} mol/cm^2 (C).

Table I. Charge Transport Rates of Ferrocene-Substituted Polyphosphazenes[a]

compd	$(D_{ct}^{1/2}C)_{anod}$[b,c] (10^{-8} mol/cm^2)	$(D_{ct}^{1/2}C)_{cath}$[c] (10^{-8} mol/cm^2)
I[d]	1.41 (±0.15)	1.52 (±0.24)
II	1.96 (±0.18)	1.81 (±0.44)
III	3.20 (±0.20)[e]	6.19 (±1.65)
III	7.49 (±0.71)[f]	

[a] The preanalysis potential was held at either 0.0 or 1.0 V for II and 1.3 V for III for at least 60 s prior to the application of the forward (oxidation) or reverse (reduction) potential step, respectively, to assure a homogeneous film oxidation state and to eliminate effects from insufficient film oxidation or reduction as an initial condition. [b] n = 18 for all averages except I (n = 5) and $(D_{ct}^{1/2}C)_{anod}$ for II (n = 21). [c] Values in parentheses represent the 95% confidence interval. [d] Values for this polymer calculated with the Randles–Sevcik equation. [e] Values obtained between 10 and 25 ms. [f] Values obtained between 25 and 50 ms.

The linear relationship between $(i_p)_{anod}$ and $v^{1/2}$ indicates that charge transfer is similar to a semi-infinite linear diffusion process as described by the Randles–Sevcik equation.[3] Rates for charge transport ($D_{ct}^{1/2}C$) for I are listed in Table I. The large variation of peak potentials with scan rate suggests that the polymer film undergoes a chemical reaction following the oxidation of ferrocene. This result is similar to the voltammetry observed for its low molecular weight analogue $N_3P_3F_4(\eta\text{-}C_5H_4)_2Fe$.[1] The oxidized and chemically rearranged phosphazenyl ferrocene is reduced at

---

(1) Saraceno, R. A.; Riding, G. H.; Allcock, H. R.; Ewing, A. G. *J. Am. Chem. Soc.* **1988**, *110*, 980–982.

(2) Murray, R. W. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1984; Vol. 13.

(3) Randles-Sevcik equation: $i_p = (2.69 \times 10^5)n^{3/2}AD^{1/2}Cv^{1/2}$, ref 9, p 218.

0002-7863/88/1510-7254$01.50/0 © 1988 American Chemical Society

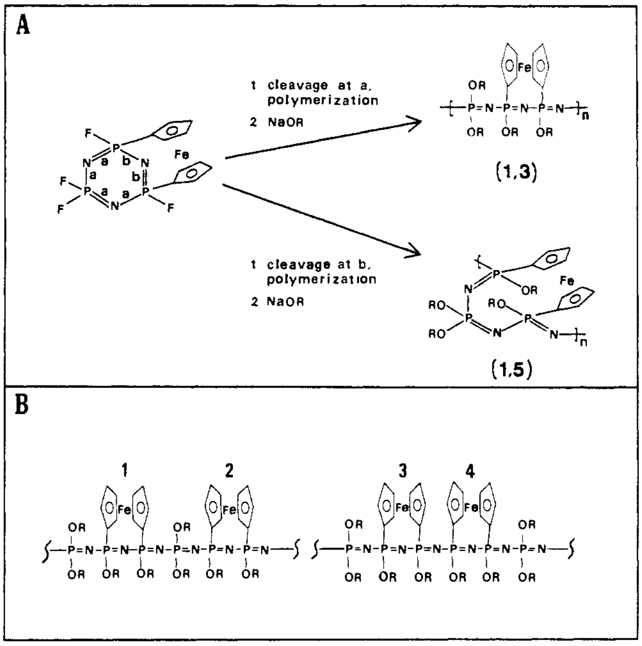

Figure 2. (A) Polymerization schemes for polyphosphazene III; OR = OCH_2CF_3. (B) Arrangements of ferrocene units on the polyphosphazene backbone.

potentials more than 1 V negative of oxidation. The nature of this reaction is still not understood.[4] However, the oxidized polymer undergoes a quantitative reduction upon scan reversal, whereas the oxidized trimer does not at similar scan rates.

Cyclic voltammetry obtained with polymer II (Figure 1B) is typical of that obtained from surface immobilized ferrocenyl compounds.[5,6] The peak potentials for oxidation and reduction remain unchanged over a range of moderate scan rates, and the voltammetric waves are symmetrical. The expected linear relationship[2] between $(i_p)_{anod}$ and v is observed for this polymer (correlation coefficient = 0.998, $n = 4$).

Figure 1C shows cyclic voltammetry of polymer III. As with II, the peak potentials for oxidation and reduction do not vary with changing scan rate, and plots of $(i_p)_{anod}$ versus v are linear (correlation coefficient = 0.9994, $n = 5$). The most striking and unique feature of the voltammetry of this polymer is the presence of two closely associated surface waves. This suggests the presence of two different types of ferrocene electron-transfer sites within the polymer. We have previously shown that different structural configurations and different amounts and types of substituents on the phosphazene affect the electrochemistry of ferrocene-substituted phosphazenes.[1] The voltammetric behavior of III might be rationalized by the presence of different microstructures of the polymer produced by different, competing polymerization routes.

Polymerization routes via cleavage of the cyclic trimer at two different sites forming a 1,3- and 1,5-type polymer can be envisioned (Figure 2A). While the oxidation peak potentials of these two different polymer types are nearly identical with those of the analogous 1,3- and 1,5- cyclic tetramers,[1] no spectroscopic (^{19}F and ^{31}P NMR) evidence for the 1,5-polymerization route has been found.[7] A more likely possibility is that the polymerization route forms a 1,3-polymer, but the ring-opened trimers link up in a head-to-tail as well as a head-to-head arrangement (Figure 2B). Here, a ferrocene unit in an arrangement as ferrocene 1 would have a slightly greater oxidation potential than ferrocene 4 because it is surrounded by more trifluoroethoxy groups.[1] A random arrangement of these two different ferrocene groups would result in a 1:1 ratio of these species.

Chronoamperometry was used to evaluate the rate of electron transport through films of II and III (Table I). The behavior of II is nearly identical for oxidation versus reduction of the ferrocene sites, and the values for $D_{ct}^{1/2}C$ are similar to the values reported for plasma polymerized films of vinylferrocene in acetonitrile.[6]

Chronoamperometric data for the oxidation step of III (0.0 V to 1.3 V) do not show the characteristic Cottrell $t^{-1/2}$ dependence[8] for the decay current, whereas the reduction step (1.3 V to 0.0 V) is well behaved. Two current domains are apparent for the oxidation step: $t < 25$ and $t > 25$ ms. Plots of i versus $t^{-1/2}$ yield two nonparallel linear regions (correlation coefficient > 0.990). A comparison of values for $D_{ct}^{1/2}C$ (Table I) shows that the initial oxidation process is significantly slower than either the second oxidation domain or subsequent reduction step.

These trifluoroethoxy-substituted polymers permit a unique comparison of the rate of charge diffusion in ferrocene-containing polymer films with ferrocene both in a freely moving (II) and bound (III) configuration. All values of $D_{ct}^{1/2}C$ for III are larger than those for II. This is interesting since the pendent ferrocene polymer (II) would be expected to display greater mobility and, hence, a greater through-space electron cross exchange rate. The greater rate of charge transport observed with the rigid bridged ferrocene polymer might indicate a mechanism which involves both electron cross exchange and "metallic-like" conduction in the partially oxidized III which results in larger $D_{ct}^{1/2}C$ values for this structure.

Acknowledgment. This work was supported by the National Science Foundation under Grant No. BNS-8705777 (A.G.E.) and the U.S. Army Research Office (H.R.A). A.G.E. is a recipient of an N.S.F. Presidential Young Investigator Award (CHE-8657193).

---

(4) Saraceno, R. A.; Riding, G. H.; Ewing, A. G., submitted to *J. Electroanal. Chem.*

(5) Nowak, R. J.; Schultz, F. A.; Umana, M.; Lam, R.; Murray, R. W. *Anal. Chem.* **1980**, *52*, 315-321.

(6) Daum, P.; Murray, R. W. *J. Phys. Chem.* **1981**, *85*, 389-396.

(7) Allcock, H. R.; Lavin, K. D.; Riding, G. H. *Macromolecules* **1985**, *18*, 1340-1345.

(8) Cottrell equation: $i = nFAD^{1/2}C\pi^{-1/2}t^{-1/2}$, ref 9, p 143.

(9) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; J. Wiley and Sons: New York, 1980.

A Catalytic Reductive Cyclization of 1,6-Diynes

Barry M. Trost* and Donna C. Lee

Departments of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706
Stanford University, Stanford, California 94305

Received April 4, 1988

Intramolecular carbametalations are proving to be a useful strategy for ring construction.[1] The cyclization of diynes to generate dialkylidenecycloalkanes according to eq 1, path a, using stoichiometric amounts of low valent titanium and/or zirconium complexes represents a particularly intriguing reaction because of the utility of the 1,3-dienes in subsequent cycloadditions.[2,3] In this communication, we wish to report a general catalytic approach (eq 1, path b) for the preparation of 1,2-dialkylidenecyclopentanes from diynes and its extension to multiple ring construction.

The strategy and perceived complications are outlined in eq 2, based upon a novel catalyst presumed to be a hydridopalladium carboxylate.[5] Success requires (1) regioselective hydropalladation

---

* Address correspondence to this author at Stanford University.

(1) For a review, see: Negishi, E. *Acc. Chem. Res.* **1987**, *20*, 65.

(2) Nugent, W. A.; Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788. Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829.

(3) For Co-mediated cyclooligomerization of acetylenes in organic synthesis, see: Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539.

(4) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1985**, *107*, 1781. Trost, B. M.; Chung, J. Y. L. *J. Am. Chem. Soc.* **1985**, *107*, 4586. Trost, B. M.; Lautens, M. *Tetrahedron Lett.* **1985**, *26*, 4887.

0002-7863/88/1510-7255$01.50/0