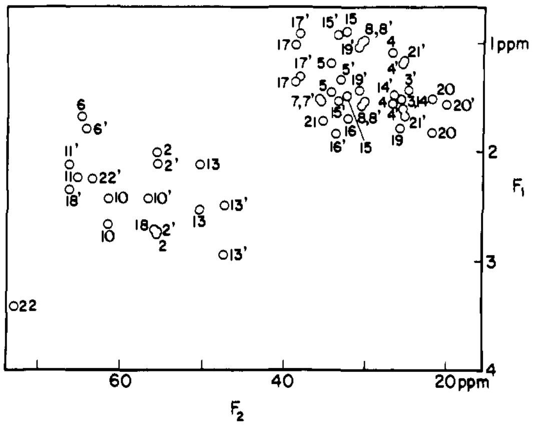

Figure 16. Map obtained by replotting the proton–carbon shift correlation results for ormosinine (III) from Figure 13, with primes denoting the ormosanine moeity. A detailed comparison with the map of Figure 10 indiates that ormosinine (III) is made up of panamine (I) and ormosanine (II).

the coupling constant H20–H21 that might indicate the configuration at the last stereochemical uncertainity, C21.

Discussion

The compounds investigated here provide illustration of two useful routes to structure elucidation and the assignment of proton and carbon-13 chemical shifts. Determination of the connectivity of the carbon skeleton[16] is a powerful but insensitive technique, requiring (at 50-MHz carbon-13 resonance) at least 0.5 M concentration but giving very detailed information about the molecular framework. The analysis of these double-quantum spectra is simple and largely unequivocal; however, in order to determine stereochemistry, it is usually necessary to turn to the proton spectrum (which is often only poorly resolved) by using proton–proton correlation spectroscopy. Proton–carbon shift correlation[24] is practicable at concentrations down to 10–20 mM on the instrument used, and with simpler spectra than those discussed here can often be used directly to assign proton and carbon-13 spectra. In very complex systems the measurement of the proton–proton correlation spectrum[28,30] not only allows the identification of individual proton resonances that would otherwise remain unresolvable but enables the structure of a molecule to be mapped out by correlations through C–H–H–C coupling relationships. Although much less direct than the double-quantum method, this route is navigable at much lower concentrations and, as seen above, can unravel very tangled spectra. It is, however, essential in such crowded spectra to ensure identical conditions for the two kinds of shift correlation experiment, since an error in registration of only a few hertz could prevent an unequivocal assignment being made.

Two-dimensional NMR is more difficult to use than conventional NMR, and the interpretation of the spectra is often as time-consuming as their measurement. Nevertheless the experiments described above can be implemented on most Fourier transform NMR spectrometers and are widely and generally applicable. When the conventional NMR spectra lie near the limits of resolving power for a particular instrument, the case for using two-dimensional NMR is a strong one.

Acknowledgment. This work was made possible by an equipment grant and a Research Studentship (T.A.F) from the Science and Engineering Research Council (U.K.) We are grateful to Dr. P. Naegeli, Givandan Research Company Ltd., Zurich, Switzerland, for samples of ormosanine, ormosinine, and panamine diperchlorate.

Registry No. Panamine, 2448-27-3; ormosanine, 5001-21-8; ormosinine, 14350-67-5.

Electrochemical Studies of the Reduction of Fluorenone Triphenylphosphazine. Formation of the Stable Dimeric Dianion, $(FlN_2)_2^{2-}$

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Abstract: The electrochemical reduction of fluorenone triphenylphosphazine (Fl=NN=PPh$_3$) in *N,N*-dimethylformamide–0.1 M $(n\text{-}Bu)_4NClO_4$ is initially a one-electron process which affords the corresponding anion radical. Fl=NN=PPh$_3^{-}\cdot$ is unstable on the cyclic voltammetric time scale, decomposing by nitrogen–phosphorus bond cleavage (k = 0.45 s^{-1} at T = 1 °C) to give PPh$_3$ and 9-diazofluorene anion radical ($FlN_2^{-}\cdot$). The latter species then reacts rapidly with either Fl=NN=PPh$_3$ or $FlN_2^{-}\cdot$ to give a stable dimeric dianion. The dianion, which was shown from chronoamperometric and coulometric gas-pressure studies to have the empirical formula $(FlN_2)_2^{2-}$, is oxidized in successive one-electron steps to $(FlN_2)_2$ which slowly loses N$_2$ on the cyclic voltammetric time scale to give fluorenone azine (Fl=NN=Fl). The structure of the dimeric species is considered to be the tetraazatriene Fl=NN=NN=Fl. No evidence was obtained for the formation of the carbene anion radical, $Fl^{-}\cdot$, via the loss of N$_2$ from $FlN_2^{-}\cdot$.

Introduction

Carbenes have been prepared from several classes of organic compounds, including diazoalkanes, diazirines, oxiranes, and phosphazines.[1] Certain diazoalkanes also appear to be well-suited for the preparation of carbene anion radicals ($R_2C^{-}\cdot$). For example, dissociative electron attachment to diazomethane[2] and diazocyclopentadiene[3] in the gas phase affords methylene ($H_2C^{-}\cdot$) and cyclopentadienylidene ($c\text{-}C_5H_4^{-}\cdot$) anion radicals, respectively.

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[1] (a) Jones, M., Jr.; Moss, R. A., Ed. "Carbenes"; Wiley-Interscience: New York, 1973, 1975; Vol. 1, 2. (b) Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971.

[2] Zittel, P. F.; Ellison, G. B.; O'Neil, S. V.; Lineberger, W. C.; Reinhardt, W. R. *J. Am. Chem. Soc.* **1976**, *98*, 3732.

[3] McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 6491.

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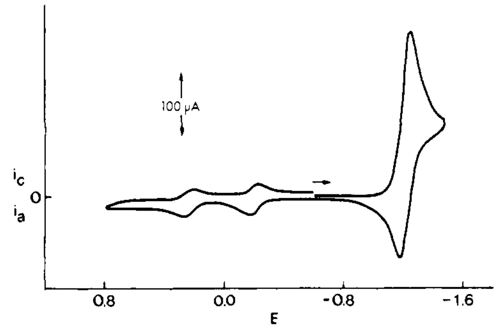

Figure 1. Cyclic voltammogram for the reduction of a 6.16 mM solution of Fl=NN=PPh$_3$ in DMF - 0.1 M (n-Bu)$_4$NClO$_4$ at a planar platinum electrode. The scan rate was 0.2 V s^{-1}; the temperature was 1 °C.

In the condensed phase, Ph$_2$C$^{-}\cdot$ has been prepared by the electrolytic reduction of Ph$_2$CN$_2$ in both dimethylformamide (DMF)[4] and acetonitrile.[5] In contrast to the gas phase, where the chemistry and thermochemical properties of c-C$_5$H$_4^{-}\cdot$ have been determined in flowing afterglow experiments,[3] the lifetime of electrogenerated Ph$_2$C$^{-}\cdot$ in DMF is too short to permit its direct study by electrochemical methods. Instead, the existence of Ph$_2$C$^{-}\cdot$ in the condensed phase has been inferred from the results of product studies, the effect of added proton donors, the coulometric n value, and the cyclic voltammetric and kinetic behavior of other, more stable reaction intermediates, e.g., Ph$_2$CH$^-$.

The reductive elimination of N$_2$ from 9-diazofluorene (FlN$_2$) was also attempted in an effort to prepare the 9-fluorenylidene anion radical (Fl$^{-}\cdot$), a species which is presumably a σ-radical π-anion in its ground-state electronic configuration.[6-8] Although the electrochemical reduction of FlN$_2$ proceeds by a chain process to give the azine (Fl=NN=Fl) as the principal product, the complexity of the cyclic voltammetric behavior and the presence of several unidentified electroactive intermediates preclude an unequivocal interpretation.[8] The study of the phosphazine Fl=NN=PPh$_3$ was, therefore, undertaken for two reasons: (1) to determine if the phosphazine would function as a carbene anion radical precursor, and (2) to obtain additional electrochemical information which might facilitate the interpretation of the results from the reduction of FlN$_2$.

Results

Cyclic Voltammetry. The cyclic voltammetric reduction of Fl=NN=PPh$_3$ in DMF was examined at a platinum electrode as a function of temperature (-51 °C $\leq T \leq 23$ °C), scan rate (0.05 V/s $\leq v \leq$ 100 V/s), supporting electrolyte (R$_4$NClO$_4$, where R = n-Bu, Et, Me), and switching potentials. If the negative-going sweep is switched at -1.50 V, only the cathodic wave ($E_{p,c} = -1.26$ V) that is assigned to the one-electron reduction of Fl=NN=PPh$_3$ to Fl=NN=PPh$_3^{-}\cdot$ is seen (Figure 1). Three anodic processes are observed for most combinations of scan rate and temperature on the reverse, positive-going sweep. The most negative of these ($E_{p,a} = -1.20$ V) corresponds to the reoxidation of any unreacted Fl=NN=PPh$_3^{-}\cdot$ that remains, while the two equal-size, anodic peaks near -0.18 and 0.26 V arise from the reversible oxidation of a product of the decomposition of Fl=NN=PPh$_3^{-}\cdot$. The relative magnitudes of the peak heights for the two reversible couples increase at the expense of the Fl=NN=PPh$_3^{-}\cdot$ anodic peak with either increasing temperature or decreasing scan rate. Since the ratio of the anodic peak height ($i_{p,a}$) for the oxidation of Fl=NN=PPh$_3^{-}\cdot$ to the cathodic peak height ($i_{p,c}$) for the reduction of Fl=NN=PPh$_3$ is a function of scan rate and temperature, but is independent of an 8-fold change in concentration of Fl=NN=PPh$_3$, reaction of Fl=NN=PPh$_3^{-}\cdot$ must occur by a first-order or a pseudo-first-order pathway.[10]

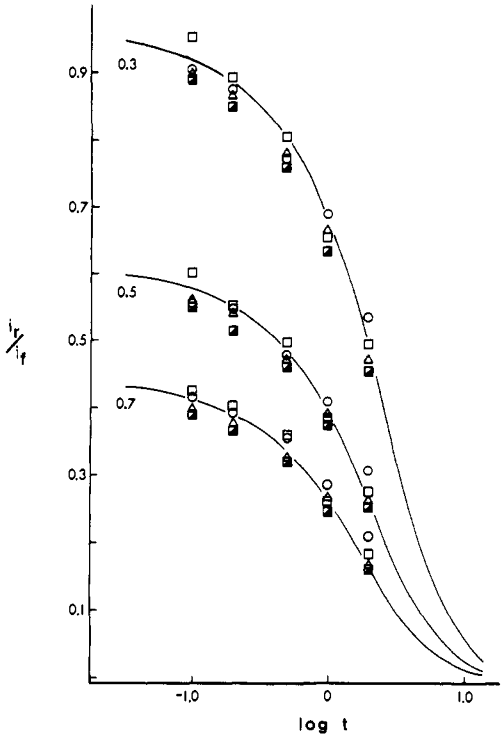

Figure 2. Double potential step chronoamperometric data for the reduction of Fl=NN=PPh$_3$ in DMF - 0.1 M (n-Bu)$_4$NClO$_4$ at a 0.196 cm^2 planar platinum electrode. The solid curves were obtained by digital simulation of eq 1 and 2 with the first-order rate constant k specified as 0.45 s^{-1}. The solid curves, from top to bottom, are for $(t-\tau)/\tau$ values of 0.3, 0.5, and 0.7. Concentrations of Fl=NN=PPh$_3$ were; (○) 0.77 mM, (□) 1.73 mM; (△) 3.09 mM; and (◘) 6.16 mM. The temperature was 1 °C.

Kinetic Studies of the Fl=NN=PPh$_3^{-}\cdot$ Reaction. The determination of the first-order or pseudo-first-order rate constant for the decomposition of Fl=NN=PPh$_3^{-}\cdot$ was made by double potential step chronoamperometry. In this technique the potential is first stepped from a value ($E_{\text{init}} = -0.80$ V) where no reduction of Fl=NN=PPh$_3$ occurs, to a value ($E_c = -1.50$ V) sufficiently negative such that the concentration of Fl=NN=PPh$_3$ at the electrode surface is zero. After reduction for a predetermined period of time, τ (0.01 s $\leq \tau \leq$ 5 s), the potential is stepped to $E_a = -0.80$ V for time $t - \tau$. This potential is sufficiently positive to effect oxidation of all unreacted Fl=NN=PPh$_3^{-}\cdot$ that diffuses back to the electrode surface, but is insufficiently positive to oxidize the decomposition product(s) derived from Fl=NN=PPh$_3^{-}\cdot$. Experimentally, ratios of the anodic current at various values of $t - \tau$ to the cathodic current at time τ are plotted as a function of log τ. These plots are shown in Figure 2 for several concentrations of Fl=NN=PPh$_3$ and for values of $(t-\tau)/\tau$ equal to 0.3, 0.5, and 0.7.

The decomposition rate constant k (eq 2) was determined by fitting the experimental data for the several values of $(t-\tau)/\tau$ to the theoretical dimensionless working curves which were obtained when the diffusion, homogenous chemical reaction, and heterogenous electron transfer processes were digitally simulated[11]

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[4] McDonald, R. N.; Triebe, F. M.; January, J. R.; Borhani, K. J.; Hawley, M. D. *J. Am. Chem. Soc.* **1980**, *102*, 7867.

[5] Triebe, F. M.; Barnes, J. H.; Hawley, M. D.; McDonald, R. N. *Tetrahedron Lett.* **1981**, *22*, 5145.

[6] The electrochemical reduction of FlN$_2$ has been suggested to give Fl$^{-}\cdot$ as a reasonably long-lived intermediate.[7] More recent data from both this[8] and other laboratories[9] have shown that this suggestion is incorrect and that neither Fl$^{-}\cdot$ nor FlH$^-$ lies in the principal fluorenone azine product forming channel.

[7] McDonald, R. N.; Borhani, K. J.; Hawley, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 995.

[8] Triebe, F. M. Ph.D. Dissertation, Kansas State University, Manhattan, KS, 1981.

[9] (a) Parker, V. D.; Bethell, D. *Acta Chem. Scand. B* **1981**, 691. (b) Parker, V. D.; Bethell, D. *Acta Chem. Scand. B* **1980**, 617. (c) Bethell, D.; Galsworthy, P. J.; Handoo, K. L.; Parker, V. D. *J. Chem. Soc., Chem. Commun.* **1980**, 534.

[10] Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

[11] Feldberg, S. W. In "Electroanalytical Chemistry"; Bard, A. J., Ed.; Vol. 3, Marcel Dekker: New York, 1969; pp 199-296.

for the reactions given in eq 1 and 2. The best fits of the ex-

$$\mathrm{Fl{=}NN{=}PPh_3} + e^- \rightleftharpoons \mathrm{Fl{=}NN{=}PPh_3}^{-}\cdot \tag{1}$$

$$\mathrm{Fl{=}NN{=}PPh_3}^{-}\cdot \xrightarrow{k} \text{product(s)} \tag{2}$$

perimental data to the working curves were obtained for $k = 0.45$ s^{-1} when $T = 1$ °C. The absence of dependence of the rate constant on Fl=NN=PPh$_3$ concentration (8-fold variation) confirms the earlier cyclic voltammetric result that decomposition of Fl=NN=PPh$_3^{-}\cdot$ occurs by either a first-order or a pseudo-first-order pathway.

Chronoamperometric Studies Involving the Fl=NN=PPh$_3^{-}\cdot$ Decomposition Product(s). When the solution temperature is raised to 23 °C, the cathodic electrolysis time is 1 s or longer, and $(t - \tau)/\tau \geq 0.3$, decomposition of Fl=NN=PPh$_3^{-}\cdot$ to give the product which is electroactive at −0.18 and 0.26 V is essentially complete. Although the absence of significant unreacted Fl=NN=PPh$_3^{-}\cdot$ under these specific reaction conditions precludes kinetic studies of the decomposition of Fl=NN=PPh$_3^{-}\cdot$, the product(s) of the Fl=NN=PPh$_3^{-}\cdot$ reaction can now be studied by double potential step chronoamperometry, unhindered by unreacted Fl=NN=PPh$_3^{-}\cdot$. In this experiment, the anodic currents which arise from the oxidation of the Fl=NN=PPh$_3^{-}\cdot$ decomposition product(s) are measured as a function of both time and the anodic potential. Since the concentration of the Fl=NN=PPh$_3^{-}\cdot$ decomposition product(s) is a function of the original Fl=NN=PPh$_3$ concentration, it is a straightforward process to relate these currents to the relative number of electrons associated with each anodic step. In order to perform these measurements, the potential in the reverse, anodic step of the double potential step chronoamperometry experiment must be adjusted such that the oxidation of the decomposition product(s) from Fl=NN=PPh$_3^{-}\cdot$ is effected stepwise. Thus, when $E_a = 0.0$ V, only the anodic process at −0.18 V occurs; when the anodic potential in the reverse step is made 0.5 V, both steps in the oxidation of the decomposition product(s) occur at their maximum, diffusion-controlled rates. Analysis of the current–time curves showed unequivocally that the anodic processes at −0.18 and 0.26 V are equal in magnitude. In addition, when both anodic processes are made to occur, a total of one electron is removed for each electron that is used to reduce Fl=NN=PPh$_3$ originally. This result means that the oxidation product from the unidentified intermediate at the potential of its more positive anodic peak ($E_{p,a} = 0.26$ V) is electrically neutral. Furthermore, single potential step chronoamperometric experiments show that electroreduction of Fl=NN=PPh$_3$ at $E = -1.40$ V is a diffusion-controlled process. Since the reversible reduction of Fl=NN=Fl to Fl=NN=Fl$^{-}\cdot$ affords nearly the same chronoamperometric value of $it^{1/2}/cA$ under these solution conditions,[8] we conclude that the electroreduction of Fl=NN=PPh$_3$ at $E = -1.40$ V must also be an overall one-electron process. *The most plausible interpretation of the chronoamperometric and cyclic voltammetric data requires the unidentified intermediate to be a dimeric dianion.* A monomeric intermediate is specifically excluded because a two-step oxidation of a singly negatively charged anion or anion radical cannot afford a neutral species as the final oxidation product.

Coulometry and Product Studies. The addition of one electron per molecule of Fl=NN=PPh$_3$ ($E_{\text{applied}} \geq -1.40$ V) typically resulted in the consumption of 75% of the starting material (Table I). In addition to the presence of unreacted Fl=NN=PPh$_3$, cyclic voltammetric examination of the electrolyzed solution (Figure 3b) shows the presence of the reversible couples at −0.18 and 0.26 V which are attributed to the intermediate dimeric dianion, and a small peak at 0.50 V which is due to the irreversible oxidation of Fl=NNH$^-$.[12] The relative magnitudes of the cyclic voltammetric anodic peaks at 0.26 and 0.50 V are kinetically controlled, with the magnitude of the Fl=NNH$^-$ peak ($E_{p,a} = 0.50$ V) growing at the expense of the former peak as the scan rate is increased. This behavior is attributed to the electrocatalytic process which is described by eq 3–5. The homogenous electron

$$\text{dimer}^{2-} \underset{e^-}{\overset{-e^-}{\rightleftharpoons}} \text{dimer}^{-}\cdot \underset{e^-}{\overset{-e^-}{\rightleftharpoons}} \text{dimer} \tag{3}$$

$$\text{dimer} + \mathrm{Fl{=}NNH}^- \overset{K<1}{\rightleftharpoons} \text{dimer}^{-}\cdot + \mathrm{Fl{=}NNH}\cdot \tag{4}$$

$$\mathrm{Fl{=}NNH}\cdot + \mathrm{Fl{=}NNH}^- \xrightarrow{\text{fast}} \mathrm{FlN_2}^{-}\cdot + \mathrm{FlNNH_2} \tag{5}$$

transfer reaction in eq 4, although thermodynamically unfavorable ($\Delta E_{p,a} = -0.24$ V), is facilitated by the rapid transfer of a proton or hydrogen atom between Fl=NNH$\cdot$ and Fl=NNH$^-$ (eq 5).

The electrochemical oxidation of the dimeric dianion to its neutral form causes fluorenone azine (Fl=NN=Fl) to be formed slowly. The formation of Fl=NN=Fl is evidenced by the appearance on the second, negative-going scan of a cathodic wave at −0.64 V for the reversible reduction of Fl=NN=Fl$^{-}\cdot$ to Fl=NN=Fl^{2-} (Figure 3). The anodic and cathodic peaks associated with the reversible reduction of Fl=NN=Fl to Fl=NN=Fl$^{-}\cdot$ ($E_{p,c} = -0.24$ V) are less discernible because of their overlap with the more negative redox process of the unidentified dimeric species.

The product distribution is dependent upon the method which is used to treat the electrolyzed solution. If all anionic species are oxidized (entries 1 and 2, Table I), the principal fluorene-containing product that is found by both HPLC and cyclic voltammetry is Fl=NN=Fl. As demonstrated in Figure 3c, Fl=NN=Fl is reduced stepwise and reversibly to Fl=NN=Fl^{2-} at $E_{p,c,1} = -0.24$ V and $E_{p,c,2} = -0.64$ V. The small cathodic peak which is just observable near −1.0 V is due to the reduction of Fl=NNH$_2$ and/or Fl=NH.[12,13] Reduction of both Fl=NNH$_2$ and Fl=NH will occur at the potential that is used to reduce Fl=NN=PPh$_3$ in the initial cathodic step; both species afford FlHNH$_2$ as their final reduction product. The only phosphorus-containing reduction product found was PPh$_3$. Although PPh$_3$ is not electroactive in the limited potential range $-1.5 \text{ V} \leq E \leq 0.8$ V, it can be reduced irreversibly to unknown products at significantly more negative potentials ($E_{p,c} = -1.92$ V).

If the partially electrolyzed solution of Fl=NN=PPh$_3$ is treated instead with either glacial acetic acid (entry 3, Table I) or 1,1,1,3,3,3-hexafluoro-2-propanol (entry 4, Table I), the principal fluorene-containing products are Fl=NNH$_2$ and Fl=NN=Fl. Since cyclic voltammetric examination of the electrolyzed solution before acidification shows the dimeric dianion to be the predominant reduction product, protonation of the dimeric dianion must ultimately afford Fl=NNH$_2$ and Fl=NN=Fl.

Treatment of the electrolytically generated dimeric dianion with 9-diazofluorene (FlN$_2$) resulted in the rapid transformation of both the dimeric dianion and FlN$_2$ into a reduced form of Fl=NN=Fl (entry 5, Table I). Subsequent oxidation of the resulting solution at a potential ($E_{\text{applied}} = 0.0$ V) which is sufficiently positive to oxidize Fl=NN=Fl$^{-}\cdot$ ($E_{p,a} = -0.18$ V), but insufficiently positive to oxidize Fl=NNH$^-$ ($E_{p,a} = 0.5$ V), afforded Fl=NN=Fl as the major fluorene-containing product.

Gas-Pressure Studies and Intermediate Product Studies. The formation of one molecule of Fl=NN=Fl from two molecules of Fl=NN=PPh$_3$ requires the loss of one molecule of N$_2$ and two molecules of PPh$_3$. To determine if N$_2$ is lost prior or subsequent to the formation of the dimeric dianion, differential gas-pressure studies were performed as a function of the number of coulombs consumed. As shown in Figure 4, the head-gas pressure in the working electrode compartment, measured with an oil manometer, increases slowly during the electroreduction of Fl=NN=PPh$_3$, but rises rapidly when the anionic reduction products of Fl=NN=PPh$_3$ are oxidized. In order to relate these pressure data to the volume of N$_2$ produced during the electrolysis, a control experiment was performed on PhN$_3$. This species has been shown in separate experiments in our laboratory to undergo an overall two-electron, two-proton process when controlled-potential electrolytic reduction is effected in the presence of a proton

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[12] Triebe, F. M.; Hawley, M. D. *J. Electroanal. Chem.* **1981**, *125*, 421.

[13] Barnes, J. H.; Triebe, F. M.; Hawley, M. D. *J. Electroanal. Chem.*, in press.

Table I. Coulometric Data and Product Distribution Studies for the Controlled Potential Electrolytic Reduction[a] of Fl=NN=PPh$_3$

						products, % yield							
entry no.	concn, mM	E_{red}, V	E_{ox}, V	n_{red}	n_{total}	Fl=NN=Fl	Fl=NNH$_2$	Fl=NH	FlH$_2$	FlHNH$_2$	Fl=O	Fl=NN=PPh$_3$	PPh$_3$
1	2.23	−1.30	0.35	1.01	0.39	55	7	2.6	6		2.3	20	81
2	4.61	−1.40	0.80	1.15	0.58	66	12	1.5	1.2		0.5	13	92
3[b]	4.87	−1.30	--	1.0	1.00	29	38	0.6	3.2		0.8	28	70
4[c]	4.07	−1.35	--	1.0	1.00	17	41	1.4	1.3	3.6	0.2	26	72
5[d]	3.51	−1.30	0.00	1.0	0.59	47	6	0.5	1.5		0.2	34	60

[a] Controlled potential electrolysis was effected in DMF-0.1 M (n-Bu)$_4$NClO$_4$ at a platinum electrode. [b] The reduced solution was acidified with acetic acid. [c] The reduced solution was acidified with 1,1,1,3,3,3-hexafluoro-2-propanol. [d] After partial reduction, FlN$_2$ (4.36 mM) was added to the electrolyzed solution. The anionic products were subsequently oxidized electrochemically.

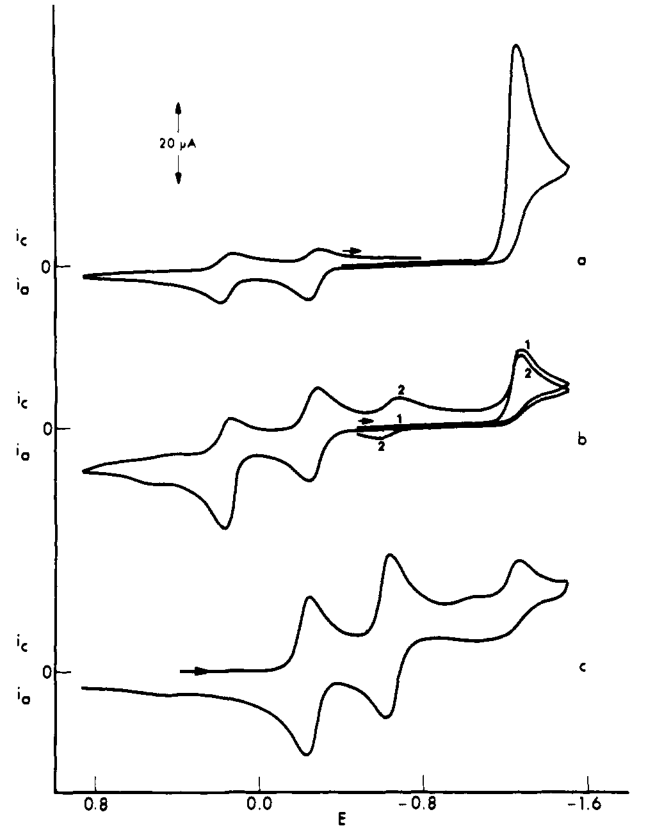

Figure 3. Cyclic voltammograms of a 4.61 mM solution of Fl=NN=PPh$_3$ in DMF - 0.1 M (n-Bu)$_4$NClO$_4$ at a spherical platinum electrode: (a) v = 0.2 V s^{-1}, T = 25 °C; (b) same as (a) except the solution has been reduced at −1.40 V to n = 1.0 e$^-$; (c) same as (b) except that the solution has been oxidized at 0.50 V to n_{net} = 0.6 e$^-$. The number 2 represents the second cycle.

donor.[14] This electroreduction affords N$_2$ and aniline quantitatively in equimolar amounts.

$$PhN_3 + 2H^+ + 2e^- \rightarrow PhNH_2 + N_2 \qquad (6)$$

A variation of approximately 1 mm of oil in the manometer was observed during the course of a non-gas producing electrolysis. If the gas-pressure data are also corrected for the cyclic voltammetrically determined yield of 72% for the intermediate dimeric dianion formed in the reduction of Fl=NN=PPh$_3$, an absolute slope of 0.9 ± 0.2 mm of oil/C is obtained for the oxidation of the dimeric dianion Figure 4a). This slope is in reasonable agreement with the slope of 0.79 ± 0.05 mm of oil/C obtained for the two-electron reduction of PhN$_3$ (eq 6) to give PhNH$_2$ and N$_2$ (Figure 4b). These data demonstrate that (1) the loss of N$_2$ occurs subsequent to both the rate-determining step in the decomposition of Fl=NN=PPh$_3^{-}\cdot$ and the formation of the dimeric dianion intermediate, and (2) one molecule of N$_2$ is evolved from

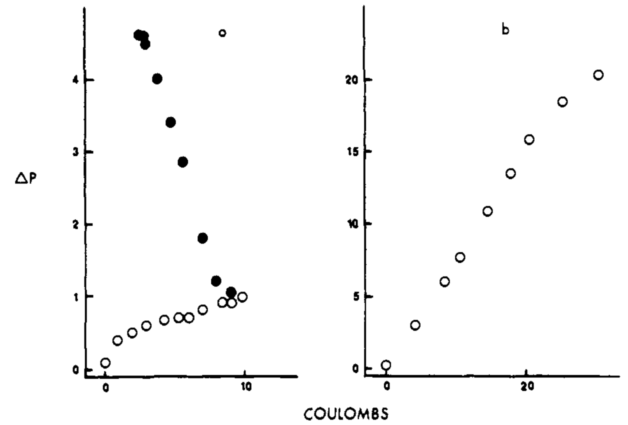

Figure 4. Gas pressure data. (a) The electrolysis of a 3.27 mM solution of Fl=NN=PPh$_3$ in DMF - 0.1 M (n-Bu)$_4$NClO$_4$. After the addition of approximately one electron per molecule of Fl=NN=PPh$_3$ at E = −1.40 V (○), the Fl=NN=PPh$_3^{-}\cdot$ decomposition products were oxidized at E = 0.50 V (●). (b) The reduction at −1.80 V of a 6.44 mM solution of PhN$_3$ in the presence of 98.2 mM diethyl malonate in DMF - 0.1 M (n-Bu)$_4$NClO$_4$. The pressure change in the working electrode compartment was monitored with an oil manometer (see Experimental Section).

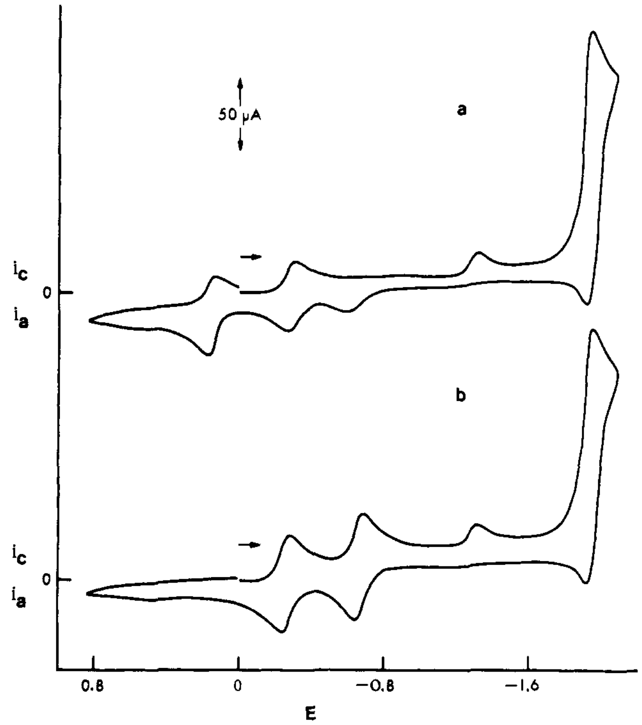

Figure 5. Cyclic voltammograms of a 3.31 mM solution of Fl=NN=PPh$_3$ in DMF - 0.1 M (n-Bu)$_4$NClO$_4$ at a spherical platinum electrode: (a) v = 0.2 V s^{-1}, T = 25 °C, and reduced at −1.40 V to n = 1.15 e$^-$; (b) same as (a) except that the solution has been oxidized at 0.50 V to n_{net} = 0.59 e$^-$.

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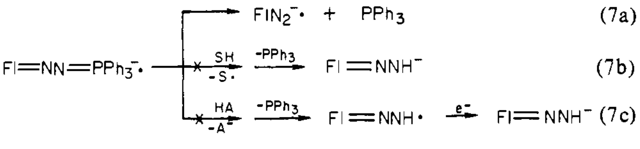
[14] McDonald, R. N.; Herbranson, D. E.; Hawley, M. D., unpublished results.

each dimeric dianion that is oxidized to its electrically neutral form.

In an attempt to determine when formation of PPh_3 occurs, an electrolyzed solution of $Fl{=}NN{=}PPh_3$ was examined for PPh_3 content prior and subsequent to the reoxidation of all anionic $Fl{=}NN{=}PPh_3$ reduction products. Cyclic voltammetric examination of the PPh_3 cathodic peak at −1.92 V shows that PPh_3 is present in a reduced solution of $Fl{=}NN{=}PPh_3$ (Figure 5a) and that oxidation of the anionic intermediate does not affect the magnitude of the PPh_3 cathodic peak (Figure 5b). This result requires that PPh_3 is formed either prior to or concomitantly with the formation of the dimeric dianion.

Discussion

$Fl{=}NN{=}PPh_3^{-}\cdot$ Decomposition. The electrochemical kinetic data do not permit the identification of the bond(s) broken or formed in the rate determining step of the $Fl{=}NN{=}PPh_3^{-}\cdot$ decomposition. However, since the kinetic studies have established that the rate law for decomposition of $Fl{=}NN{=}PPh_3^{-}\cdot$ is either first order or pseudo first order, and that PPh_3 is produced either prior to or concomitantly with the formation of the dimeric dianion, the most plausible reaction channels include nitrogen–phosphorus bond cleavage of $Fl{=}NN{=}PPh_3$ to give $FlN_2^{-}\cdot$ and PPh_3 (eq 7a)

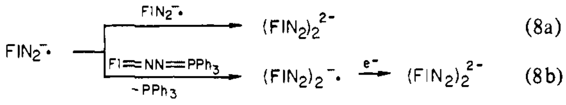


and either H-atom abstraction by or protonation of $Fl{=}NN{=}PPh_3^{-}\cdot$. The H-atom or H^+ donor is assumed to be a component of the solvent–electrolyte system. The cyclic voltammetric observation that $Fl{=}NNH^-$ is a minor product in the electroreduction of $Fl{=}NN{=}PPh_3$ suggests eq 7b and 7c as specific possibilities for the latter two reactions.

However, neither $Fl{=}NNH^-$, which was prepared by the action of Me_4NOH on $Fl{=}NNH_2$, nor $Fl{=}NNH\cdot$, which was prepared by oxidizing $Fl{=}NNH^-$ electrochemically, was found in separate cyclic voltammetric experiments to react with $Fl{=}NN{=}PPh_3$ to give the unidentified dimeric intermediate. Moreover, the product distribution rules out H-atom abstraction, in general, as being the predominant reaction pathway. If H-atom abstraction were to occur, hydrogen must be incorporated into the final reduction products. Although small amounts of $Fl{=}NNH_2$, $Fl{=}NH$, and FlH_2 are found in electrolyzed solutions of $Fl{=}NN{=}PPh_3$ (entries 1 and 2, Table I), the combined yields of these three products (<20% based on $Fl{=}NN{=}PPh_3$ consumed) is insufficient for H-atom abstraction to be the principal decomposition channel for $Fl{=}NN{=}PPh_3^{-}\cdot$.

Proton abstraction as the primary reaction pathway for the decomposition of $Fl{=}NN{=}PPh_3^{-}\cdot$ may also be ruled out for similar reasons. If the $Fl{=}NN{=}PPh_3^{-}\cdot$ reaction products were formed by pathways involving protonation and did not subsequently transfer their protons to either $Fl{=}NN{=}PPh_3^{-}\cdot$ or the conjugate base of the H^+ donor, the protons must be incorporated into the final products ($Fl{=}NNH_2$, $Fl{=}NH$, and FlH_2). Again, this is inconsistent with the observed product distribution. Another possibility, that a relatively long-lived intermediate ($t_{1/2} > 1$ s) is formed which eventually serves as a proton donor for $Fl{=}NN{=}PPh_3^{-}\cdot$, is inconsistent with all of the electrochemical results. There is no electroactive intermediate which is interposed between the decomposition of $Fl{=}NN{=}PPh_3^{-}\cdot$ and the formation of $(FlN_2)_2^{2-}$ that is observed by either cyclic voltammetry (Figure 1) or double potential step chronoamperometry.

The most plausible pathway which remains for the decomposition of $Fl{=}NN{=}PPh_3^{-}\cdot$ involves nitrogen–phosphorus bond cleavage (eq 7a). This mode of reaction is supported by the observation that the dimeric dianion is also a short-lived intermediate in the electrochemically induced transformation of FlN_2 into $Fl{=}NN{=}Fl$.[8,9] Thus, all results suggest that the intermediate dimeric dianion is formed either by dimerization of $FlN_2^{-}\cdot$ (eq 8a) or by the attack of $FlN_2^{-}\cdot$ on unreduced $Fl{=}NN{=}PPh_3$ (eq 8b).



In an attempt to distinquish between these possibilities, electroreduction of an equimolar mixture of FlN_2 and $Fl{=}NN{=}PPh_3$ was effected at a potential ($E = -0.60$ V) such that only FlN_2 was reduced. The chain reaction[8] that ensued afforded the dimeric species as a transient intermediate and caused all FlN_2 to be transformed into $Fl{=}NN{=}Fl$, but did not affect the concentration of $Fl{=}NN{=}PPh_3$. Unfortunately, this result is not conclusive, since it is consistent with either the dimerization of $FlN_2^{-}\cdot$ or the more facile reaction of $FlN_2^{-}\cdot$ with FlN_2 than with $Fl{=}NN{=}PPh_3$. A distinction between these possibilities cannot be made without additional kinetic information which would be difficult, if not impossible, to obtain by present methods.

Finally, $Fl{=}NNH^-$ was observed in a minor amount when a nearly exhaustively reduced solution of $Fl{=}NN{=}PPh_3$ was examined by cyclic voltammetry. Since $Fl{=}NNH^-$ is not observed as a product during the initial stages of $Fl{=}NN{=}PPh_3$ coulometric reduction, we favor the pathway described be eq 9 for its

$$FlN_2^{-}\cdot + HA + e^- \rightarrow Fl{=}NNH^- + A^- \qquad (9)$$

formation. The proportion of $FlN_2^{-}\cdot$ which may react by this channel would be expected to increase as the concentrations of $Fl{=}NN{=}PPh_3$ and $FlN_2^{-}\cdot$ are decreased by the electrolysis of $Fl{=}NN{=}PPh_3$. Because this formation of $Fl{=}NNH^-$ from $Fl{=}NN{=}PPh_3$ is an overall two-electron process, this pathway could account, at least in part, for nonintegral n values (>1) which are obtained for the coulometric reduction of $Fl{=}NN{=}PPh_3$ (entries 1 and 2, Table I).

Structure of the Proposed Dimeric Intermediate. The one-electron, diffusion-controlled reduction of $Fl{=}NN{=}PPh_3$ to its anion radical was demonstrated by single potential step chronoamperometry. Because double potential step chronoamperometry showed that (1) the long-lived intermediate which was formed from the decomposition of $Fl{=}NN{=}PPh_3^{-}\cdot$ was oxidized in successive steps at −0.18 and 0.26 V, and (2) each step in the oxidation of the intermediate involved the removal of one-half electron per molecule of $Fl{=}NN{=}PPh_3$ reduced, we concluded that the intermediate species must be a dimeric dianion. Cyclic voltammetric studies of the dimeric dianion solution, both prior and subsequent to its oxidation, also showed that the dimeric dianion did not contain the PPh_3 moeity, while differential gas-pressure and product studies demonstrated that one molecule each of $Fl{=}NN{=}Fl$ and N_2 ultimately arose from the two-electron oxidation of each dimeric dianion. Since the gas-pressure data indicated that no nitrogen was evolved in either the reduction of $Fl{=}NN{=}PPh_3$, or the steps leading to the formation of the dimeric dianion, the empirical formula of the dimeric dianion must be $(FlN_2)_2^{2-}$.

The redox behavior of $(FlN_2)_2^{2-}$ provides some information concerning its structure. First, the stepwise, nearly reversible oxidation of $(FlN_2)_2^{2-}$ requires that this molecular species contain two conjugated fluorenylidene centers. Unconjugated fluorenylidene centers are ruled out, since the oxidation of all fluorene centers would then be expected to occur irreversibly in essentially a single anodic step. Second, a comparison of the redox behavior of $(FlN_2)_2^{2-}$ with those of $Fl{=}NN{=}Fl^{2-}$[7,8] and bifluorenylidene dianion, $Fl{=}Fl^{2-}$,[8] reveals numerous similarities, including stepwise reversible oxidations which are separated by approximately 0.4 V. Since the oxidation of both $Fl{=}NN{=}Fl^{2-}$ and $Fl{=}Fl^{2-}$ also occur approximately 0.4 V more readily than that of $(FlN_2)_2^{2-}$, it seems reasonable that the tetraazadiene moiety, $-N{=}NN{=}N-$, serves as the link between the two negatively charged fluorenylidene centers.[15] The tetraazatriene dianion, $Fl{=}NN{=}NN{=}Fl^{2-}$, is therefore suggested as the structure of $(FlN_2)_2^{2-}$.

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(15) The presence of the diazo function facilitates reduction; for example, the potentials for the cathodic peaks for the reduction of 4,4′-dinitroazobenzene and 4,4′-dinitrobibenzyl to their corresponding anion radicals are 0.22 and −0.47 V, respectively.

The pathway by which $(\mathrm{FlN_2})_2$ is transformed into Fl=NN=Fl and $\mathrm{N_2}$ is unknown. Although it should be feasible to determine which pair of nitrogen atoms is lost from Fl=NN=NN=Fl with suitable $^{15}\mathrm{N}$-labeling studies, the result/cost ratio does not justify such experiments at this time.

Relationship of This Work to Studies of Reduction of $\mathrm{FlN_2}$. $\mathrm{FlN_2}$ was shown above to oxidize $(\mathrm{FlN_2})_2{}^{2-}$, affording a reduced form of Fl=NN=Fl as the principal product (entry 5, Table I). Since the electrochemical reduction of $\mathrm{FlN_2}$ ($E_{\mathrm{p,c}} = -0.60$ V)[8] occurs with greater difficulty than the reduction of $(\mathrm{FlN_2})_2{}^{-\cdot}$ to $(\mathrm{FlN_2})_2{}^{2-}$ ($E_{\mathrm{p,c}} = -0.24$ V), extensive electron transfer in the reaction described by eq 10 is feasible only if one or both of the products is removed rapidly by a succeeding chemical reaction. In this system, the follow-up reaction appears to involve either dimerization of $\mathrm{FlN_2}^{-\cdot}$ (eq 12) or the coupling of $\mathrm{FlN_2}^{-\cdot}$ with unreacted $\mathrm{FlN_2}$ (eq 13). Both reactions should ultimately regenerate $(\mathrm{FlN_2})_2{}^{2-}$.

$$(\mathrm{FlN_2})_2{}^{2-} + 2\mathrm{FlN_2} \overset{K<1}{\rightleftharpoons} (\mathrm{FlN_2})_2 + 2\mathrm{FlN}^{-\cdot} \qquad (10)$$

$$(\mathrm{FlN_2})_2 \xrightarrow{\text{slow}} \mathrm{Fl{=}NN{=}Fl} + \mathrm{N_2} \qquad (11)$$

$$\mathrm{FlN_2}^{-\cdot} + \mathrm{FlN_2}^{-\cdot} \xrightarrow{\text{fast}} (\mathrm{FlN_2})_2{}^{2-} \qquad (12)$$

or

$$\mathrm{FlN_2}^{-\cdot} + \mathrm{FlN_2} \xrightarrow{\text{fast}} (\mathrm{FlN_2})_2{}^{-\cdot} \xrightarrow{e^-} (\mathrm{FlN_2})_2{}^{2-} \qquad (13)$$

The two nearly reversible couples at −0.18 and 0.26 V are observed in both the Fl=NN=$\mathrm{PPh_3}$ and the $\mathrm{FlN_2}$ systems.[8,9] While these processes are suggested here to arise from the stepwise oxidation of Fl=NN=NN=Fl^{2-}, Parker and Bethell[9a] have proposed instead that the dimeric dianion is due to *cis*-Fl=NN=Fl^{2-}. We reject their proposal because of our determination that evolution of nitrogen follows the oxidation of the dimeric dianion, rather than preceding or accompanying its formation.

Conclusions

The electrochemical reduction of Fl=NN=$\mathrm{PPh_3}$ has resulted in the preparation of the previously unknown tetraazatriene, Fl=NN=NN=Fl. This species has been shown to lose nitrogen slowly on the cyclic voltammetric time scale to give Fl=NN=Fl, while stepwise electroreduction of Fl=NN=NN=Fl has been shown to afford first the corresponding anion radical and then the stable dianion, Fl=NN=NN=Fl^{2-}. This dianion is also a transient intermediate which is observed in the electrochemically induced chain reaction that transforms $\mathrm{FlN_2}$ into Fl=NN=Fl.[8,9]

The generation of the carbene anion radical $\mathrm{Fl}^{-\cdot}$ from the electroreduction of Fl=NN=$\mathrm{PPh_3}$ was *not* realized. We had hoped that electrogenerated Fl=NN=$\mathrm{PPh_3}^{-\cdot}$ might undergo successive cleavage of the nitrogen–phosphorus and the nitrogen–carbon bonds to give $\mathrm{Fl}^{-\cdot}$.[6] Although the first step in the reaction of Fl=NN=$\mathrm{PPh_3}^{-\cdot}$ did proceed in the desired manner, the rate of the subsequent reaction of $\mathrm{FlN_2}^{-\cdot}$ with either $\mathrm{FlN_2}^{-\cdot}$ or Fl=NN=$\mathrm{PPh_3}$ greatly exceeds the rate of $\mathrm{N_2}$ loss from $\mathrm{FlN_2}^{-\cdot}$.

Experimental Section

Instrumentation. Cyclic voltammetric and chronoamperometric experiments were performed with three-electrode potentiostats which incorporate circuits for electronic correaction of ohmic potential loss between the reference and working electrodes.[16] Control of the potentiostat and the acquisition and processing of the chronoamperometric data were performed with a laboratory digital computer (ADAC model 2000, LSI 11/2). The three-electrode potentiostat which was used for the exhaustive, controlled-potential electrolysis has been described.[17]

Chromatography. The products of the electrolyzed solutions were separated by HPLC using a 6.35 mm diameter by 25 cm length stainless steel column packed with LiChrosorb RP-8, 10 μm mean particle size. The lower molecular weight compounds were separated with methanol-water (65:35) as the eluting solvent. The higher molecular weight compounds were also separated with methanol-water (80:20). Both solvent mixtures were used at a flow rate of 1.0 mL min^{-1}. The HPLC system utilized was a Beckman Scientific Model 332 with a Model 420 controller. The wavelength was 254 nm. Calibration curves for standards of all products were constructed daily.

Chemicals. *N*,*N*-Dimethylformamide (Burdick and Jackson, HPLC grade) was purified by passage through a column of alumina (80–200 mesh, Brockman activity 1, activated at 600 °C overnight) and was collected over a mixture of Davison 4A molecular sieves and activated alumina. This procedure was carried out in a dry, nitrogen-filled glove bag.

Fluorenone triphenylphosphazine,[18] fluorenone azine,[19] fluorenone hydrazone,[20] and fluorenone imine[21] were synthesized according to known procedures. All other compounds were commercially available. Recrystallizations of all compounds were performed until sharp melting points were obtained. Purities were verified by HPLC.

Cells, Electrodes, and Electrolysis Procedures. All electrochemical experiments were performed on an all-glass vacuum line. The solvent was transferred into the cell by trap-to-trap distillation. Traces of oxygen, if present, were removed by several freeze–pump–thaw cycles. Helium was used to bring the cell up to atmospheric pressure. A positive pressure of helium was maintained when the reference electrode and compounds were transferred into the cell. A slush bath of ice–water was used to maintain the cell at 1 °C for all chronoamperometric experiments. An isopropyl alcohol bath was maintained at the desired temperature with liquid nitrogen as the refrigerant for low-temperature studies.

Chronoamperometric experiments were performed with a planar platinum electrode which had an area of 0.196 cm^2. All potentials are listed with respect to a cadmium amalgam which is in contact with a dimethylformamide solution that is saturated with both cadmium chloride and sodium chloride (type A-III).[22] Dual reference electrodes were used in all cyclic voltammetric and chronomaperometric experiments.[23] The second reference electrode, which was a platinum wire in series with a 0.1 μF capacitor, was placed in parallel with the cadmium electrode.

Nitrogen evolution studies were performed under vacuum. Pressure changes in the electrolysis cell were constantly monitored with a manometer filled with Apiezon B oil. Before electrolysis the manometer and cell were evacuated separately. When both the manometer and cell were fully evacuated, the system was isolated from the vacuum pump at which time the manometer and cell were opened to each other. The stopcock at the top of the manometer was closed prior to the electrolysis such that the pressure of the cell before electrolysis was used as a reference. Periodic measurements of the oil level differences (in millimeters) were taken during the electrolysis and recorded vs. the number of coulombs passed. The cell was immersed in a constant-temperature bath maintained at 30 °C.

The cells used in all electrolyses were of an all-glass cylindrical design utilizing standard-taper ground glass joints for the attachment of the various electrodes. The working electrodes were small platinum spheres sealed in glass for cyclic voltammetric experiments and platinum gauze cylinders for preparative scale electrolyses. The reference and auxiliary electrodes were modified for work under vacuum. A Teflon stopcock was placed in the top of the auxiliary electrode such that any gases evolved during the electrolysis at the auxiliary electrode would not increase the pressure of the cell. The reference electrode used was a silver wire in contact with a DMF solution saturated with (n-Bu)$_4$NCl.

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