

On the Electrochemical Preparation of the Neutral Complexes $M[S_4C_4(CN)_4]$, $M(mnt)_2$, $M = Ni, Pd, Pt$

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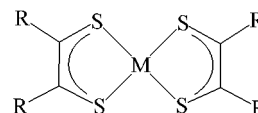
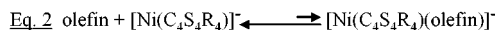
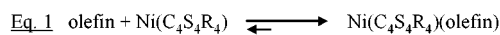
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This communication reports on the electrolytic generation of neutral $M(mnt)_2$ complexes **1–3**, $M = Ni, Pd, Pt$, where *mnt* is the maleonitriledithiolate ligand. We are prompted in part by the recent report of Wang and Stiefel, who describe a redox-dependent approach to the separation and purification of olefins using nickel dithiolene complexes.¹ Their method takes advantage of differences in the thermodynamics and kinetics of metal complex–olefin adduct equilibria for two different oxidation states of the complex in order to first trap (eq 1 of Scheme 1) and then release (eq 2) the olefin in a type of electrochemical square scheme.² Success was reported¹ for two Ni dithiolene complexes with the electron-withdrawing groups $R = CF_3$ (**4**) and $R = CN$ (**1**). The former is quite stable and easily isolable after preparation from $Ni(CO)_4$ ³ or by electrosynthetic oxidation⁴ of the monoanion **4**[−]. In previous studies, only the short-term existence (over a few seconds) of soluble *mnt* analogues **1–3** has been indicated, based on cyclic voltammetry (CV) scans.^{1,3–5,7} We now show that the entire set of complexes **1–3** can be electrochemically generated and used for reactions, including those with olefins, on a synthetic time scale.

The Ni-group monoanions of this series, $[M(mnt)_2]^-$, are well-known and easily prepared.⁶ Although the Ni complex **1** is detected by CV in the oxidation of **1**[−] in CH_2Cl_2 ($E_{1/2}^{0/1-} = 0.71$ V vs Fc), it resists longer term observation, even at low temperatures, in IR spectroelectrochemical experiments.^{7,8} Bulk anodic electrolysis of 3–5 mM **1**[−] gave a poorly soluble dark brown oligomer.⁴ We now find that if this electrolysis (Pt electrode, $E_{app} = 1.0$ V vs Fc) is carried out at lower concentrations (≤ 1 mM), the neutral complex **1** is formed in a direct one-electron process (0.96 F/equiv measured). The blue solution of **1** ($\lambda_{max} = 802$ nm, $\epsilon \approx 1.7 \times 10^4$ M^{−1} cm^{−1}) was shown by steady-state voltammetry to contain only the neutral (oxidized) complex. After about 30 min, rereduction of the solution at $E_{app} = 0.2$ V quantitatively regenerated **1**[−] in a cathodic one-electron process. Two back-and-forth electrolyses were repeated without evidence of decomposition over a 2 h time period.

Although the second-row complex $Pd(mnt)_2$ (**2**, $E_{1/2}^{0/1-} = 0.70$ V vs Fc)⁹ may be generated by oxidation of **2**[−], the electrochemical behavior of this complex is not as straightforward as that of

Scheme 1. Electrochemical Square Scheme



- 1** M = Ni, R = CN
- 2** M = Pd, R = CN
- 3** M = Pt, R = CN
- 4** M = Ni, R = CF₃

the Ni and Pt (vide infra) systems. In the Pd case, voltammetric scans and bulk electrolyses are highly dependent on both temperature and the concentration of **2**. If the anodic electrolysis ($E_{app} = 1.0$ V) is conducted at relatively high concentrations (e.g., several millimoles/liter) or at lower temperatures (e.g., 245 K), a black precipitate forms, leaving a virtually clear solution. With a concentration of less than 0.5 mM, a deep purple solution of **2** is formed. This concentration effect is also noted in CV scans, in which the **2**[−]/**2** oxidation wave is well behaved and reversible at lower concentrations (e.g., 0.3 mM) but poorly defined at higher concentrations (Figure 1).¹⁰ Furthermore, the chemical reversibility of the **2**[−]/**2** oxidation is strongly dependent on temperature. At 273 K, the CV response is irreversible whereas a chemically reversible response is observed at ambient temperatures. These observations appear to account for earlier descriptions of the oxidation of **2**[−] as “ill-defined”³ or as unable to generate solutions having detectable $\nu(CN)$ IR spectra.⁷ Although steady-state scans after bulk electrolyses confirm the quantitative interconversions of **2**, **2**[−], and **2**^{2−}, coulometric variations have been noted in these experiments, most likely arising from oligomerization of **2**. Details of these effects are under investigation.

The simplest electrochemical behavior in this series is found for **3**, formed in the reversible one-electron oxidation of **3**[−] (Figure 2, $E_{1/2}^{0/1-} = 0.59$ V vs Fc). Exhaustive anodic oxidation (1.01 F/equiv measured) of green **3**[−] (room temperature with concentrations of 0.3–1.0 mM) gave a stable solution of purple **3** having a major visible absorption band at $\lambda_{max} = 740$ nm ($\epsilon \approx 9 \times 10^3$ M^{−1} cm^{−1}).¹¹ Changing the electrolysis potentials between E_{app}

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(9) The $E_{1/2}$ values are given for solutions using 0.1 M $[NBu_4][PF_6]$ as supporting electrolyte. The value measured for **2** was 0.65 V vs Fc when 0.075 M $[NBu_4][B(C_6F_5)_4]$ was the supporting electrolyte (see Figure 1).

(10) Double potential step chronocoulometry measurements confirm anodic adsorption at higher concentrations.

(11) Unpublished UV–vis spectroelectrochemistry, Craig Jones, University of Vermont, 1995.

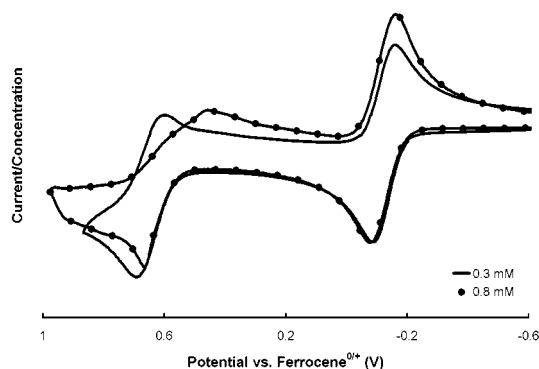


Figure 1. CV scans of $[\text{NBu}_4]_2[\text{Pd}(\text{mnt})_2]$ in $\text{CH}_2\text{Cl}_2/0.075 \text{ M } [\text{NBu}_4][\text{B}(\text{C}_6\text{F}_5)_4]$ using a 2 mm diameter Pt electrode, scan rate 0.2 V/s, at two different concentrations of Pd complex: (a) solid line, 0.3 mM; (b) dotted line, 0.8 mM. The current is normalized to the concentration. The first oxidation wave ($E_{1/2} = -0.09 \text{ V vs Fc}$) is due to the couple $2^{2-}/2^-$. The anodic peak current for the second oxidation wave was about $0.75 \mu\text{A}$ for scan a and $2.0 \mu\text{A}$ for scan b. Analogous results were obtained when 0.1 M $[\text{NBu}_4][\text{PF}_6]$ was used as supporting electrolyte.

= 0.9 and 0.4 V allowed quantitative switching between 3^- and **3**. Since the neutral compound **3** is expected to be a strong¹² oxidant, it was allowed to react with an organic compound known to form a stable radical cation. Thus, addition of equimolar phenothiazine ($E_{1/2}^{0/1+} = 0.25 \text{ V vs Fc}$) to a solution of **3** immediately turned the solution brown, and optical spectroscopy indicated formation of 3^- and the phenothiazine cation radical ($\lambda_{\text{max}} = 520 \text{ nm}^{13}$).

Whereas previous literature suggested that the simple neutral complexes **1–3** are stable, at best, on a CV time scale,^{1,3–5,7} the present results show that all three of the blue to purple complexes are accessible on a synthetic time scale under appropriate bulk electrolysis conditions. The Ni and Pd complexes are prone to formation of dark (likely dimeric or oligomeric) solids which quantitatively regenerate the monoanion $[\text{M}(\text{mnt})_2]^-$ when dissolved in weakly basic solvents such as acetone.

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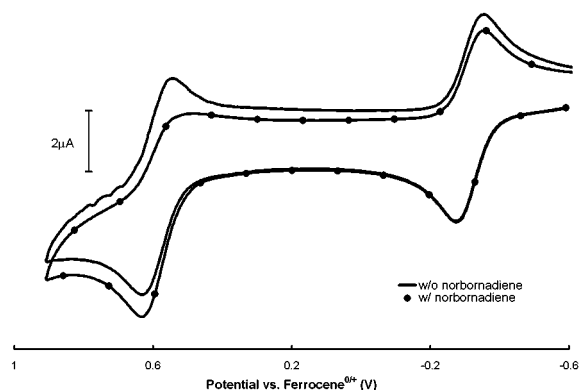


Figure 2. CV scan of 0.5 mM $[\text{NBu}_4]_2[\text{Pt}(\text{mnt})_2]$ in $\text{CH}_2\text{Cl}_2/0.1 \text{ M } [\text{NBu}_4][\text{PF}_6]$ at a Pt disk electrode, scan rate 0.2 V/s. The dotted line indicates the behavior after addition of excess norbornadiene. The first oxidation wave ($E_{1/2} = -0.28 \text{ V vs Fc}$) is due to the couple $3^{2-}/3^-$.

Cyclic voltammetry (Figure 2) and bulk electrolysis experiments establish that rapid reactions occur when any of the anions 1^- , 2^- , or 3^- is oxidized in the presence of norbornadiene, a diolefin which is particularly disposed toward cycloaddition processes with Ni-group dithiolene complexes.¹⁴ Several products are formed with reduction potentials in the range -0.6 to -1.7 V vs Fc . The bulk reductions of these products regenerate, at least in part, the dianion of the original complex (e.g., 2^{2-}). Detailed studies of these processes are in progress. It is hoped that the present results on the bulk electrochemical generation of neutral $\text{M}(\text{mnt})_2$ complexes will aid those interested in probing the possible extension of the metal–olefin electrochemical switch method¹ to reactions which involve other metal dithiolene complexes.

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