Inorg. Chem. **2002**, *41*, 136–139

Inorganic Chemistry

Note

Electrochemistry of Cycloaddition Products of Olefins with Nickel Dithiolenes: A Reinvestigation of the Reduction of the 1:1 Adduct between $Ni(S_2C_2(CF_3)_2)_2$ and Norbornadiene

William E. Geiger*

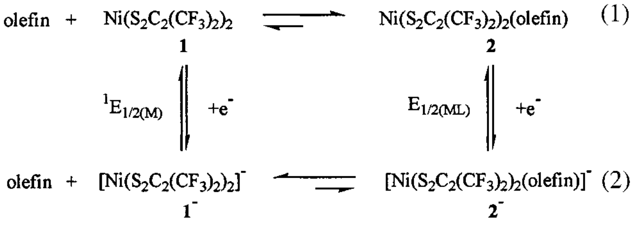
Department of Chemistry, University of Vermont, Burlington, Vermont 05405

Received September 12, 2001

Introduction

The electron-transfer-induced (ET-induced) reversible uptake and cleavage of olefins and diolefins by transition-metal dithiolene complexes has potential relevance for the isolation of olefins through a "redox switch mechanism".[1,2] The required olefin-addition reactions in different metal oxidation states (eqs 1 and 2) are represented in Scheme 1, using $Ni(S_2C_2(CF_3)_2)_2$, **1**, as the metal dithiolene complex.[1] The feasibility of this method depends in part on the relative kinetic and thermodynamic characteristics of the two ET reactions, of which one (at ${}^1E_{1/2(M)}$) involves the olefin-free metal complex, and the other (at $E_{1/2(ML)}$) involves the olefin adduct. In this scheme, the reductive cleavage reaction goes ideally through a one-electron intermediate $\mathbf{2}^-$, after which the monoanion $\mathbf{1}^-$, produced by loss of olefin (eq 2), may be reoxidized back to the neutral complex **1**.

Scheme 1



A complication to Scheme 1 may arise if the olefin-free monoanion undergoes a further reduction (e.g., $\mathbf{1}^- \rightarrow \mathbf{1}^{2-}$, ${}^2E_{1/2(M)}$) at the potential ($E_{1/2(ML)}$) at which it is formed. As will be shown in this paper, this situation may prove to be common for olefin adducts of nickel-group dithiolenes. Specifically, the reductions of three different olefin or diolefin adducts of $Ni(S_2C_2(CF_3)_2)_2$ are shown to proceed by an ECE mechanism (eqs 3–5) with an overall two-electron stoichiometry, rather than by the reversible one-electron process reported earlier for the norbornadiene adduct of **1**.[3]

$$\underset{\mathbf{2}}{Ni(S_2C_2(CF_3)_2)_2\,(olefin)} + e^- \xrightleftharpoons{E_{1/2(ML)}} \underset{\mathbf{2^-}}{[Ni(S_2C_2(CF_3)_2)_2(olefin)]^-} \tag{3}$$

$$\underset{\mathbf{2^-}}{Ni(S_2C_2(CF_3)_2)_2\,(olefin)^-} \xrightarrow{\text{fast}} \underset{\mathbf{1^-}}{[Ni(S_2C_2(CF_3)_2)_2]^-} + \text{olefin} \tag{4}$$

$$\underset{\mathbf{1^-}}{[Ni(S_2C_2(CF_3)_2)_2]^-} + e^- \xrightleftharpoons{{}^2E_{1/2\,(M)}} \underset{\mathbf{1^{2-}}}{[Ni(S_2C_2(CF_3)_2)_2]^{2-}} \tag{5}$$

We find no evidence for the oxidation of compounds of structure **2** in scans of up to +1.3 V vs ferrocene.

The trifluoromethyldithiolato–nickel complex $Ni(S_2C_2(CF_3)_2)_2$, **1**, has been shown to have attractive properties for the capture of olefins from industrially important gases and liquids.[1] To our knowledge, the only electrochemical data reported for an isolated Ni–dithiolene olefin adduct is that assigned to the norbornadiene complex $Ni(S_2C_2(CF_3)_2)_2(C_7H_8)$, **3**, which was reported[3] to possess two reversible one-electron processes: an oxidation at $E_{1/2} = 0.37$ V vs Fc[4] and a reduction at $E_{1/2} = -0.60$ V vs Fc. The reduction of **3** was stated to occur at roughly the same potential as that of the reversible $\mathbf{1}^-/\mathbf{1}^{2-}$ redox process of the olefin-free complex (${}^2E_{1/2(M)}$ in the present terminology).[3] Overlapping potentials for the reductions of an adduct and its olefin-free nickel complex anion were also invoked to rationalize the absence of a separate wave for the adduct between $Ni(S_2C_2(CN)_2)_2$ (**4**) and 1-hexene that is produced when the anion $[Ni(S_2C_2(CN)_2)_2]^-$ is oxidized in the presence of an excess of the olefin.[1] Since the thermodynamic potentials of the couples, as well as their chemical and electrochemical

---

* E-mail: wgeiger@zoo.uvm.edu.

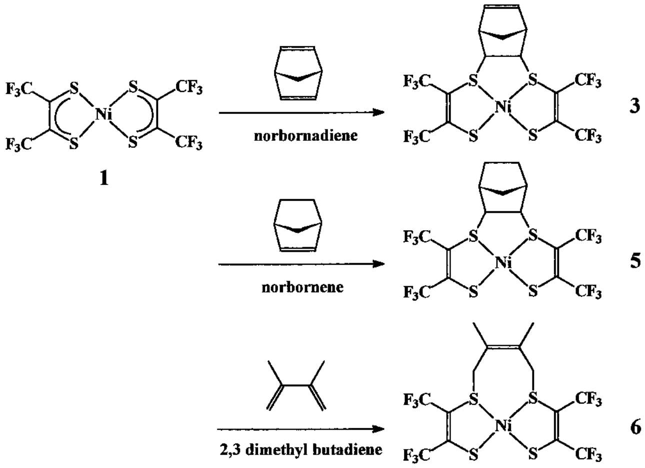
(1) Wang, K.; Stiefel, E. I. *Science* **2001**, *291*, 106.

(2) Goodman, J. T.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1999**, *121*, 5017.

(3) Wing, R. M.; Tustin, G. C.; Okamura, W. H. *J. Am. Chem. Soc.* **1970**, *92*, 1935.

(4) The potentials in ref 3 were given vs the saturated calomel electrode (SCE). They are converted to the ferrocene/ferrocenium reference potential as described in the Experimental Section.

10.1021/ic010968b CCC: $22.00



reversibilities, impact directly on the applicability of a switch mechanism, we decided to reinvestigate the electrochemistry of adduct **3**. Our skepticism arose in part from the reported *reversibility* of the reduction, which would imply that the olefin is not readily cleaved from the monoanion $\mathbf{3}^-$. In fact, as we show here, the previously reported electrochemical behavior of **3** arises from a minor amount of the olefin-free anion, $\mathbf{1}^-$, produced during the reaction of **1** with norbornadiene. The correct reduction potential of **3** is $\sim$700 mV negative of the previously reported value. Furthermore, the reduction of **3** is highly *irreversible*, leading to rapid loss of norbornadiene and production of the *dianion* $[Ni(S_2C_2(CF_3)_2)_2]^{2-}$ through the ECE process of eqs 3−5.

Experimental Section

Although solid samples of **3** did not appear to be air sensitive, solutions of this compound degraded slowly when exposed to air. All preparative and electrochemical experiments were conducted, therefore, under an atmosphere of either argon or dinitrogen using Schlenk-type conditions. Solvents were dried and distilled from CaH_2 or potassium. Spectroscopy experiments were conducted with the following spectrometers: Bruker ESP 300E for ESR spectra, ATI-Mattson FTIR for IR spectra, and OLIS-modified Cary-14 for UV−vis−NIR spectra.

Compounds. The neutral complex $Ni(S_2C_2(CF_3)_2)_2$ (**1**) and its monoanion, $[NBu_4]$**1**, had been prepared earlier by the literature method.[5] Samples were checked for purity by optical spectroscopy,[6] cyclic and steady-state voltammetries,[6b,7,8] bulk coulometry, and ESR spectroscopy.[6b,8]

The norbornadiene adduct **3** was prepared by the method of Wing et al.[3] by reacting approximately 170 mg of **1** in 20 mL hexane with 1 mL of distilled norbornadiene (Aldrich), giving an average yield of 150 mg of an off-green solid, which was recrystallized from CH_2Cl_2/hexane, mp 204−205.5 °C (lit. mp 205−206 °C). Anal. Measd: C, 30.00; H, 1.38. Calcd: C, 29.87; H, 1.34. IR spectra recorded in KBr were identical to the literature spectrum.[3] Fluid solution ESR spectra of the sample in dichloromethane gave a single line having a 9-gauss width, $g_{iso} = 2.064$. Since **3** is expected to be diamagnetic,[9] the ESR signal is attributed to contamination of the sample by the paramagnetic anion $\mathbf{1}^-$.[6b]

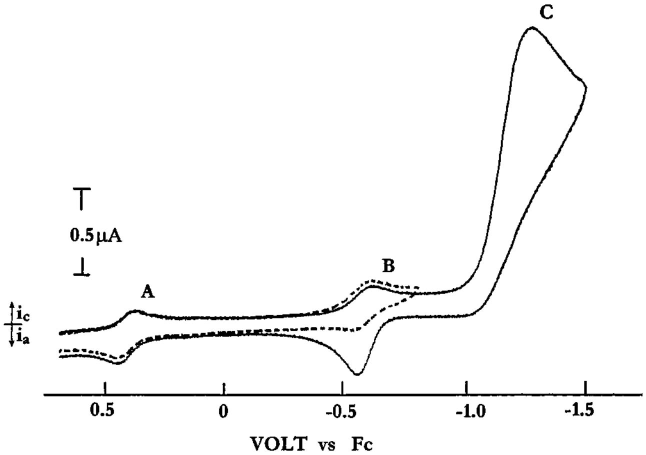


Figure 1. Cyclic voltammograms over two potential regimes of sample of **3** tainted with $\mathbf{1}^-$. Waves A and B arise from the oxidation and reduction, respectively, of $\mathbf{1}^-$, with C being the reduction of **3**. Conditions: ca. 3×10^{-4} M analyte in CH_2Cl_2/0.1 M $[NBu_4][PF_6]$, scan rate 0.5 V/s, 250 μm Pt disk, ambient temperature.

Electrochemistry. Experiments were conducted at ambient temperatures using a PARC model 273 potentiostat operated with M270 software. The solvent/supporting electrolyte mixture was CH_2Cl_2/0.1 M $[NBu_4][PF_6]$. Pt or glassy carbon working electrodes were polished with successively finer alumina slurries down to 1 μm. Most CV scans were recorded using a homemade Pt disk of 250 μm diameter. Quasi-steady-state scans (i.e., linear scan voltammograms, LSV) were obtained using unstirred solutions at slow scan rates of 1−3 mV/s. Bulk electrolyses were carried out with a Pt basket working electrode separated from the auxiliary compartment by two fine-porosity frits. The experimental reference electrode was an aqueous SCE separated from the solution by an agar bridge and a fine frit. Potentials reported in this paper are referenced to the ferrocene/ferrocenium potential[10] by addition of −0.46 V to the experimental (SCE) value. CV scan rates over the range 0.05−1 V/s were routinely employed as described elsewhere[11] to address diagnostic questions having to do with mass transfer and with chemical and electrochemical reversibility.

Results and Discussion

A sample of the 1:1 adduct **3** prepared by the literature method[3] displays three voltammetric waves in CH_2Cl_2/0.1 M $[NBu_4][PF_6]$ (Figure 1). Linear scan voltammograms (LSV scans)[12] of the two minor waves indicate that wave A ($E_{1/2} = 0.37$ V vs Fc) is an oxidation, and wave B ($E_{1/2} = -0.62$ V vs Fc) is a reduction. After converting from SCE to

---

(5) Davison, A.; Holm, R. H. In *Inorganic Syntheses*; Muetterties, E. L., Ed.; McGraw-Hill: New York, 1967; Vol. X, pp 17−20.

(6) (a) Geiger, W. E.; Maki, A. H. *J. Phys. Chem.* **1971**, *75*, 2387. (b) Davison, A.; Edelstein, N.; Maki, A. H.; Holm, R. H. *Inorg. Chem.* **1963**, *2*, 1227.

(7) Geiger, W. E.; Mines, T. E.; Senftleber, F. C. *Inorg. Chem.* **1975**, *14*, 2141.

(8) Geiger, W. E. *J. Phys. Chem.* **1973**, *77*, 1862.

(9) The ^1H NMR spectra of our samples of **3** in CD_2Cl_2 were complex and irreproducible, most likely owing to the presence of paramagnetic $\mathbf{1}^-$ and/or a cationic derivative of norbornadiene. ^{19}F spectra, on the other hand, are strongly suggestive of two isomeric forms of the 1:1 adduct **3** (Hughes, R. P., and LeSuer, R. J., personal communications).

(10) Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1984**, *56*, 461.

(11) Geiger, W. E. In *Laboratory Techniques in Electroanalytical Chemistry*, 2nd ed.; Kissinger, P. T., Heineman, W. R., Eds.; Marcel Dekker, Inc.: New York, 1996; Chapter 23.

(12) When conducted at very slow sweep rates, LSV scans may approximate steady-state conditions and be used effectively to monitor the ratio of the oxidized and reduced forms of a redox couple present in the bulk of solution. See: Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*, 2nd ed.; John Wiley and Sons: New York, 2001; pp 29−34.

Table 1. Potentials (V vs Fc/Fc$^+$) for the Reduction of Nickel Dithiolene Adducts in CH_2Cl_2/0.1 M $[NBu_4][PF_6]$

compound	no.	0/1−	1−/2−
$Ni[S_4C_4(CF_3)_4]$	**1**	0.37[a]	−0.62[a]
$Ni[S_4C_4(CF_3)_4]$(norbornadiene)	**3**	−1.32 (irrev)[b]	
$Ni[S_4C_4(CF_3)_4]$(norbornene)	**5**	−1.32 (irrev)[b]	
$Ni[S_4C_4(CF_3)_4]$(2,3-dimethylbutadiene)	**6**	−1.21 (irrev)[b]	

[a] Fully reversible (Nernstian) processes. [b] E_{pc} at $\nu = 0.5$ V/s; overall two-electron wave (see text).

ferrocene$^{0/+}$ potentials (see Experimental Section), the two minor waves match those previously described as arising from the adduct **3**.[3] By cyclic voltammetry, both waves A and B are shown to be chemically and electrochemically reversible. These features are also identical to those reported in the literature[6−8] and remeasured in our laboratory for authentic samples of **1** (reversible reductions at 0.37 and −0.62 V) and $[NBu_4]$**1** (reversible oxidation at 0.37 V, reversible reduction at −0.62 V). All pertinent electrochemical potentials used in this paper are summarized in Table 1. Clearly, the monoanion **1**$^-$, present as an impurity in samples of **3**, is responsible for the earlier misassignment of the electrochemical properties of the latter.

The major electrochemical feature of this sample is the cathodic peak at $E_{pc} = -1.32$ V[13] (wave C). This wave has the shape and scan rate dependence[11,12] of a highly irreversible, diffusion-controlled, cathodic process. Its width at half-height, δE_{pc},[14] is 125 mV, consistent with an irreversible ET process having a charge-transfer coefficient (α) of approximately 0.38. The electrochemical irreversibility of this couple suggests a follow-up reaction for **3**$^-$, presumed to be the loss of norbornadiene (eq 6), which is very rapid, and perhaps concomitant with electron transfer.

$$\mathbf{3} + e^- \rightarrow \mathbf{1}^- + \text{norbornadiene} \qquad (6)$$

To see if the monoanion **1**$^-$ was produced during the workup of samples of **3**, in situ experiments were conducted in which solutions were electrochemically monitored during adduct formation. When excess (20 mM) norbornadiene was allowed to react with neutral **1** (0.5 mM) in CH_2Cl_2 in an electrochemical cell under argon, the solution adopted a greenish-yellow color and waves A−C appeared in virtually the same ratios as seen for solutions made from isolated samples of **3**. LSV scans confirmed that **1**$^-$ was present at about a 5−10% level. This estimate of the quantity of **1**$^-$ was obtained by standard addition methods and by quantitative ESR measurements on the in situ solutions, which showed the expected single line at room temperature, $g_{iso} = 2.064$.[15]

Turning now to the reductive electrochemistry of adduct **3** ($E_{pc} = -1.32$ V), the rapid loss of olefin from putative **3**$^-$ is readily observed by CV scans which originate at a rest potential negative of wave C (ca. −1.5 V). As shown in Figure 2, this results in striking increases in waves A and B compared to the small currents present from the minor amount of **1**$^-$ in the bulk of solution. Because the reduction of **3** (eq 3) is negative of the reduction of **1**$^-$ (eq 5), any **1**$^-$ formed in the initial reduction of **3** must be reduced at the CV starting potential to **1**$^{2-}$, which is then oxidized twice on the positive-going scan, first to **1**$^-$ (∼−0.6 V) and then to **1** (∼0.4 V).[16] The overall *two-electron* (ECE) nature of the reduction of **3** at $E_{appl} < -1.4$ V (successively, eqs 3 and 5) was confirmed by exhaustive electrolysis, which produced a solution having **1**$^{2-}$ as the only electroactive species, $n_{app} = 1.96$ e$^-$.

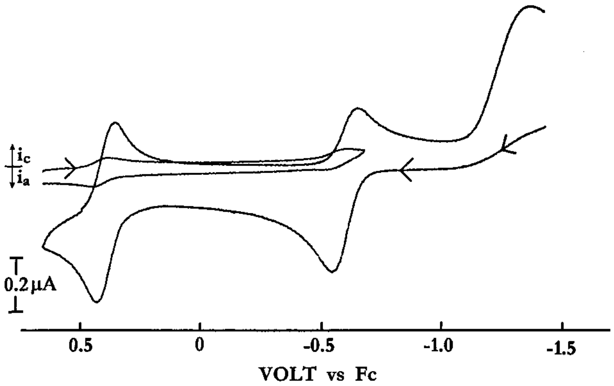


Figure 2. Cyclic voltammograms over two potential regimes and different scan directions for sample of **3** tainted with **1**$^-$. The small negative-going scan shows the two waves for **1/1**$^-$ and **1**$^-$/**1**$^{2-}$ (waves A and B in Figure 1). The more dominant positive-going scan, which originates at the rest potential of −1.5 V, demonstrates that the dianion **1**$^{2-}$ is formed in the reduction of **3**. Conditions same as in Figure 1 except that the scan rates are 1.0 V/s and the concentration of **3** is nominally 4×10^{-4} M.

It is not yet clear to us why the anion **1**$^-$ is produced in the reaction of **1** with norbornadiene, nor what cation is present in the sample.[17] Although the value of 0.38 V vs Fc for the$^1E_{1/2}$ value of **1** establishes that the neutral Ni complex is a strong oxidizing agent,[18] the much more positive E_{pa} for the oxidation of norbornadiene in nonaqueous media (1.1 V vs Fc)[19] diminishes the chances that the diolefin is undergoing electron transfer with **1** that is competitive with adduct formation.[20] The monoolefin norbornene, C_7H_{10}, which is comparatively even more difficult to oxidize (∼1.5 V vs Fc),[19] also forms a 1:1 adduct, **5**, with **1**.[3] In our hands, this reaction also gives rise to the monoanion **1**$^-$. Thus, when in situ generation of **5** was carried out under conditions similar to those described above for **3**, the same pair of minor waves from **1**$^-$ was seen, along with a major irreversible reduction wave for the green adduct, **5**, at $E_{pc} = -1.32$ V. By comparison of the appropriate peak currents, the fractional yield of **5** was only about half of that observed for **3**,

---

(13) The quoted value of E_{pc} is given for a scan rate, ν, of 0.5 V/s.

(14) $\delta E_p = \langle E_p - E_{p/2} \rangle$.

(15) Literature value for **1**$^-$: $g_{iso} = 2.061$ (ref 6b).

(16) The oxidation of **1**$^-$ to **1** at $E_{1/2} = 0.37$ V is chemically reversible under the conditions of Figure 2 because the reaction of norbornadiene with $Ni(S_2C_2(CF_3)_2)_2$ is slow compared to the time scale of the CV scan.

(17) Carbonium ions and their derivatives are among the cationic possibilities. For early references to this type of chemistry, see: McManus, S. P.; Pittman, C. U., Jr. In *Organic Reactive Intermediates*; McManus, S. P., Ed.; Academic Press: New York, 1973; Chapter 6.

(18) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.

(19) Gassman, P. G.; Yamaguchi, R.; Koser, G. F. *J. Org. Chem.* **1978**, *43*, 4392.

(20) It is well-known that a simple comparison of two E_p or $E_{1/2}$ potentials is inadequate to predict electron-transfer reactivity if at least one of the ET processes is irreversible. See discussion in ref 18.

consistent with the significantly lower isolated yield of the former as described earlier.[3] Since the reaction of **1** with 2,3-dimethylbutadiene has been shown to give the 1:1 adduct $Ni(S_2C_2(CF_3)_2)_2(C_6H_{12})$ (**6**),[21] we also performed an in situ experiment between these two reagents in an electrochemical cell. Interestingly, no detectable quantity of the anion $\mathbf{1}^-$ was formed. Rather, any unreacted nickel dithiolene complex remained in the neutral state, **1**. After about 20 min, the reaction was virtually complete and the light green solution displayed the expected irreversible cathodic wave of the adduct, in this case at $E_{pc} = -1.21$ V. Two prominent oxidation waves for anodic processes of the olefin-free dianion $\mathbf{1}^{2-}$ were found if a CV scan was initiated at ca. −1.4 V, showing that reduction of adduct **6** leads, again, to rapid cleavage of the diolefin and an overall ECE cathodic process.

Summary

Electrochemical reductions of the 1:1 adducts between $Ni(S_2C_2(CF_3)_2)_2$ (**1**) and three different olefinic donors have E_{pc} values that are approximately 1.6−1.7 V negative of ${}^1E_{1/2(M)}$ and 0.6−0.7 V negative of ${}^2E_{1/2(M)}$ for this metal dithiolene complex. The latter values are about 0.7 V negative of the potential previously assigned to the reduction of **3**.[3]. The present data are much more consistent with the product peaks observed when neutral $M(S_2C_2(CN)_2)_2$ molecules (M = Ni, Pd, Pt) are allowed to react with norbornadiene. [22] The cathodic reactions of these adducts are highly irreversible owing to rapid loss of the olefin. Since $E_{pc(ML)} \ll {}^2E_{1/2(M)}$, the reduction of the adduct proceeds by a net two-electron ECE mechanism through eqs 3−5. This finding has implications for the proposed metal−olefin electrochemical switching process,[1] not only in the electron stoichiometry of the method, but also in practical considerations which must take into account the chemical and physical properties (e.g., stabilities and solubilities) of the metal dithiolene anions involved in the procedure.

Acknowledgment. This work was supported by the National Science Foundation (CHE 00-92702). I wish to thank Robert J. LeSuer (University of Vermont) for obtaining ^{19}F NMR spectra of **3** and Prof. R. Hughes (Dartmouth College) for helpful discussions of their significance.

IC010968B

---

(21) Herman, A.; Wing, R. M. *J. Organomet. Chem.* **1973**, *63*, 441.

(22) Geiger, W. E.; Barriere, F.; LeSuer, R. J.; Trupia, S. *Inorg. Chem.* **2001**, *40*, 2472.