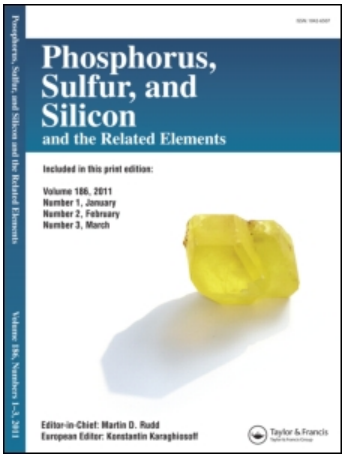


## Phosphorus, Sulfur, and Silicon and the Related Elements

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# Organometallic Derivatives of Dithiadiazoles

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# ORGANOMETALLIC DERIVATIVES OF DITHIADIAZOLES

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Abstract Electrochemical studies of 1,2,3,5-dithiadiazole complexes with iron carbonyl and nickel cyclopentadienide are reported. These are consistent with paramagnetism only in the latter. The former are in fact complexes of the dithiadiazole imine. Initial investigation of routes to ferrocene-linked dithiadiazoles are described. Electrochemistry of cyanoferrocene and ferrocene-1H-tetrazole is reported.



## INTRODUCTION

1,2,3,5-Dithiadiazoles can exist in three stable oxidation states, 6π cation, 7π neutral radicals and 8π anions.[1] They have exciting applications in the design of new molecular metals.[2] Organometallic derivatives of these inorganic ring systems offer the potential of mediating the redox states of the rings with tremendous potential for the development of their materials science properties. We were therefore very interested in the reports that complexes of the rings with both iron carbonyl[3] and nickel cyclopentadienide[4] can be prepared, and that they retain the unpaired electron. In this work we describe the results of our electrochemical studies on these complexes and the preparation of several analogues with superior properties for NMR experiments. We also describe initial attempts at covalently linking a dithiadiazole to a ferrocene ring. The electrochemical properties of cyanoferrocene and ferrocene-1H-tetrazole are reported.

## DITHIADIAZOLE CLUSTERS

We have studied $[Fe_2(CO)_6(S_2N_2CC_6H_4X)]$ **1a** X=H, **1b** X=$OCH_3$, **1c** X=$CF_3$ and $[Ni_2Cp_2(S_2N_2CPh)]$ **2** by cyclic voltammetry. The complexes underwent irreversible oxidation at +1.2, +1.0, +1.3 and +1.9 V *vs* SCE, respectively. Only **2** also underwent a reversible oxidation at +0.45 V. All four clusters could be reduced reversibly at -1.70, -1.69, -1.57 and -0.79 V, respectively. Thus the

behaviour of the nickel cluster is quite different from that of the iron clusters, and is the only one which is reminiscent of dithiadiazole free radicals in being stable in three oxidation states, cation, radical and anion.[1]

The electrochemical behaviour of these complexes was corroborated by solution studies. **2** has a strong ESR signal in $CH_2Cl_2$ solution, whereas **1** do not. The NMR spectrum of **1** contain relatively broad peaks integrating for 1H which are washed out on the addition of a little $D_2O$ to the sample tube (Figure 1). Also they have peaks in the IR at 3376-3381 $cm^{-1}$ ($CHCl_3$ solution). Both these data are consistent with the presence of hydrogen attached to N. We therefore reformulate **1** as complexes of the dithiadiazole imines $[Fe_2(CO)_6(S_2\{NH\}NCC_6H_4X)]$ which are neutral and diamagnetic. **2** has a broad, featureless NMR spectrum and has no peaks in the N-H region in the IR, and therefore appears to be correctly formulated.



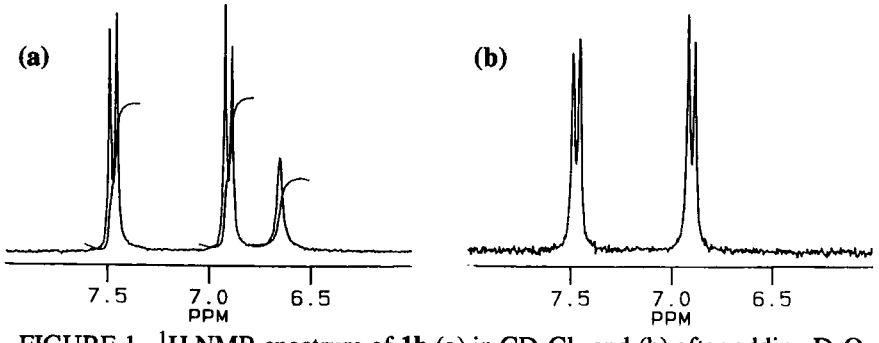


FIGURE 1 $^1H$ NMR spectrum of **1b** (a) in $CD_2Cl_2$ and (b) after adding $D_2O$

## FERROCENE DERIVATIVES

In order to prepare dithiadiazoles covalently linked to ferrocene, we have attempted to prepare the silylated amidines $C_5H_5FeC_5H_4C\{=NSiMe_3\}N(SiMe_3)_2$ from cyanoferrocene, **3**. These reactions have been unsuccessful so far. In order to assess the electrophilicity of the nitrile carbon of **3**, we have prepared the corresponding tetrazole, **4**, using the azide nucleophile. Cyclic voltammetry indicates that **3** undergoes reversible oxidation at +0.86 V, and that **4** undergoes reversible oxidation at +0.70 V and irreversible reduction at -1.18 V.

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