The present work demonstrates that metallothiols can function similarly and in so doing reduce unsaturated organic substrates. This hydrogen transfer behavior is of likely relevance to the chemistry which occurs on metal sulfide catalysts under hydrogenation conditions.[17]

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Registry No. 1, 12245-02-2; 2, 79681-97-3; 3, 79681-99-5; 4a, 79682-00-1; 4b, 79682-01-2; 4c, 79682-02-3; 5, 78356-91-9; Cp_2WCl_2, 12184-26-8.

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Cyclopentadienylnickel Cyclooctadiene: A Stable Organometallic π Radical Containing a Nonconjugated Polyolefin

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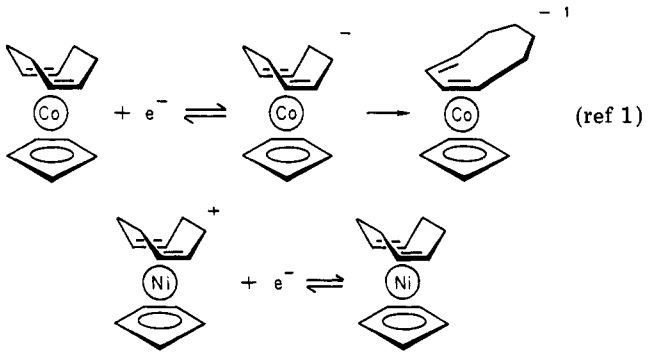
Summary: Reduction of cyclopentadienylnickel cyclooctadiene cation, $CpNiCod^+$, in which the polyolefin ring is bonded as a nonconjugated diene to the metal, has been accomplished electrochemically in weakly polar nonaqueous media. An $E°$ value of −0.46 V was found for the redox process in CH_2Cl_2/0.1 M Bu_4NPF_6. The reduction is chemically and electrochemically reversible and gives the neutral free radical, 19-electron CpNiCod, which is stable without decomposition for over 1 h at −10 °C in dichloromethane. Eventual decomposition occurs through disproportionation to nickelocene and bis(cyclooctadiene)nickel. The stability of the 1,5-diene Cod in the radical is in marked contrast to the behavior of the isoelectronic cobalt complex $CpCoCod^-$, in which isomerization of Cod to the 1,3-diene isomer has been observed. Differences in preferred isomeric form of the Cod ligand are discussed in terms of the probable electronic structures of the radicals.

We wish to report electrochemical data showing that the neutral organometallic π complex radical (η^5-cyclopentadienyl)nickel cyclooctadiene, CpNiCod, can be generated via facile one-electron reduction of the cationic precursor, $CpNiCod^+$. Furthermore, our data show that in the 19-electron radical the Cod ligand retains its 1,5-diene mode of coordination, whereas in the isoelectronic cobalt anion, $(CpCoCod)^-$, isomerization of the polyolefin from a η^4-1,5-diene to a η^4-1,3-diene had been observed (Scheme I)[1]

Reduction of $[CpNiCod]^+PF_6^{-2}$ in either dichloromethane or THF solutions containing 0.1 M Bu_4NPF_6 occurred in a diffusion-controlled one-electron step to yield

Scheme I



Scheme II

$CpNiCod^+ + e^- \rightleftharpoons CpNiCod$

$CpNiCod \longrightarrow {}^1/_2Cp_2Ni + {}^1/_2Cod_2Ni$

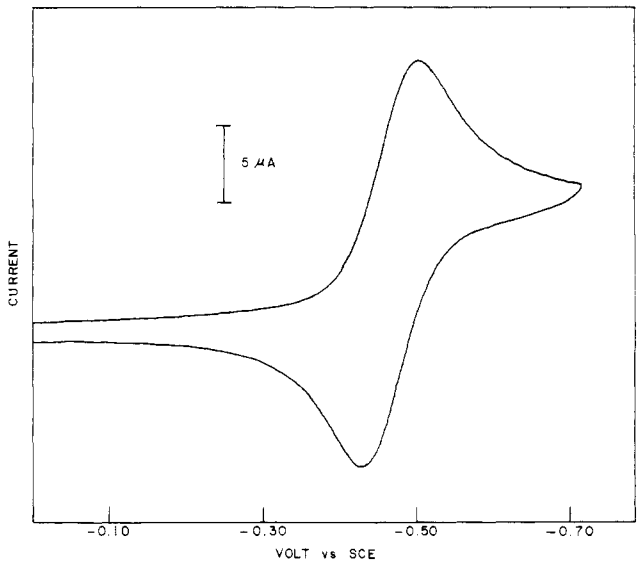


Figure 1. Cyclic voltammogram of 1.0×10^{-3} M $CpNiCod^+PF_6^-$ in CH_2Cl_2 at a platinum bead electrode in CH_2Cl_2/0.1 M Bu_4NPF_6 (scan rate = 100 mV/s).

the neutral radical. Direct current polarography gave an $E_{1/2}$ of −0.49 V[3] in CH_2Cl_2. The slope of the plot[4] of applied potential vs. log $[i/(i_d - i)]$ was −53 mV in CH_2Cl_2, consistent with the reduction being a reversible one-electron process. This was confirmed through cyclic voltammetry (CV) measurements[5] at either a platinum microelectrode or a hanging mercury drop electrode ($E°$ = −0.46 V in CH_2Cl_2). At scan rates as low as 100 mV/S, the ratio of the anodic to cathodic currents was unity, implying a very stable one-electron reduction product (Figure 1). Peak potential separations were also consistent the process being electrochemically reversible.[6]

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(3) Potentials are reported vs. the aqueous saturated calomel electrode.
(4) i is the current at any point on the rising portion of the polarographic wave, and i_d is the diffusion limited current measured on the plateau of the wave. A slope of −59 mV/n, where n is the number of electrons transferred, is calculated for reversible electron-transfer processes.
(5) Procedures for the electrochemical experiments were as described in ref 1. Spectrograde dichloromethane was distilled from calcium hydride before use. Anhydrous tetrahydrofuran (Aldrich) was distilled from lithium aluminum hydride. Since the nickel cation is an air-stable compound, all of the voltammetric measurements except those associated with bulk electrolytic reductions were carried out by using inert atmosphere purging techniques. Bulk coulometry and handling of solutions of electrolysis products were accomplished inside a Vacuum Atmosphere drybox.

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Room temperature controlled potential electrolysis measurements at a platinum basket resulted in a change from green to yellow and consumption of one-electron (n = 0.95 e^-). Voltammograms taken immediately after electrolysis showed mainly the reversible couple for $CpNiCod^{0/+}$ at –0.46 V, but a small reverisible wave was also present at –0.02 V, together with another minor wave (irreversible) at +1.04 V. As time went on, the wave due to CpNiCod diminished and the others grew in. By matching these waves with potentials measured independently for the pure compounds, we have identified the wave at –0.02 V as arising from the oxidation of nickelocene and the wave at +1.04 V as being due to bis(cyclooctadiene)nickel. Therefore, there is good evidence that the ultimate fate of the 19-electron radical is disproportionation into compounds containing metals with 20 valence electrons (Cp_2Ni) and 18 valence electrons (Cod_2Ni) (Scheme II). The reaction appears to be quantitative.

Electrolysis at subambient temperatures slowed down the disproportionation reaction and allowed production of stable solutions of the radical. Thus, electrolysis at –10 °C in CH_2Cl_2 gave only the wave for the neutral radical. By voltammetry at the rotating platinum electrode it was shown that the original reduction wave at –0.46 V had been quantitatively replaced by an oxidation wave at the identical potential. Solutions at this temperature were stable for at least 1 h after electrolysis before any wave for Cp_2Ni was noticed.

The stability of this radical is noteworthy. It is a very rare example of a neutral π-complex radical containing a nonconjugated polyolefin ligand. Previous examples of stable metal π radicals have been generally restricted to "sandwich"-type compounds like Cp_2Co,[7] $CpFe(C_6R_6)$,[8] $(C_6R_6)_2V$,[9] $CpV(C_7H_7)$,[10] $CpCr(C_6H_6)$,[11] and $CpTi(\eta^8$-cyclooctatetraene).[12] The present example suggests that metal–olefin compounds without extensively delocalized orbitals may in certain cases be isolable in free radical form.

Electronic Structure of the Radical. CpNiCod is also of interest because it is isoelectronic with $CpCoCod^-$, in which the cyclooctadiene ligand prefers the 1,3-diene mode of coordination.[1] Electron spin resonance measurements and molecular orbital calculations agree that the half-occupied orbital in the cobalt anion is predominantly metal in character.[13] Because ^{61}Ni is present in low natural abundance (1.2%), no hyperfine splitting is observed from ESR spectra of solutions of CpNiCod, but frozen solution spectra in dichloromethane (163 K) are indicative that, qualitatively, reduction of the cation has again involved a metal-based orbital. An axially symmetric **g** tensor was observed, with $g_{\parallel}$ = 2.182 and $g_{\perp}$ = 2.025. The fact that the unique g value is at low-field is consistent with findings for other d^9 metal π complexes[13,14] and inconsistent with a ligand-based orbital (because of large g value anisotropy) or a d^7 metal configuration. The latter is ruled out because in that case, the unique g value is expected to be the high-field component.[8] Thus, the ESR is consistent with CpNiCod being a formal Ni(I), with appreciable spin density on the metal.

Bonding Mode of the Cod Ligand. In spite of the isoelectronic nature of $CpCoCod^-$ and CpNiCod, the cyclooctadiene ligand prefers the nonconjugated (1,5-diene) mode of coordination in the nickel complex. The electrochemical data clearly supports this conclusion, since changes in the ligand coordination mode would give an electrolysis product with a different $E°$ potential. In the analogous CpCo(diene) complexes, the differences in reduction potentials varied from ca. 200 mV (diene = cyclooctatetraene) to almost 1 V (diene = Cod) when alterations from 1,5 to 1,3 bonding occurred.[1]

The question arises as to why the ligand isomerizes from the nonconjugated to the conjugated form in the cobalt anion but remains as the 1,5 diene in the nickel complex. The obvious difference between the two isoelectronic compounds is the negative charge on the cobalt species, suggesting that delocalization of the excess charge into the Cod ring in $CpCoCod^-$ may be an important factor in dictating the isomerization of the polyolefin ligand to the conjugated isomer.

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Registry No. $CpNiCod^+ PF_6^-$, 42088-01-7; CpNiCod, 80010-11-3.

(6) ΔE_p values of ca. 70 mV were found for 5×10^{-4} M $CpNiCod^+$ in CH_2Cl_2/0.1 M Bu_4NPF_6, virtually identical with those of ferrocene under identical experimental conditions. The increase from the theoretical value of 60 mV is undoubtedly due to uncompensated iR loss common to these weakly polar nonaqueous electrolytes.

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(15) Notes Added in Proof: Dr. Ulrich Koelle and co-workers have recently prepared the title compound (*J. Organomet. Chem.*, in press). We thank Dr. Koelle for informing us of this prior to publication of his data. A series of related $CpNiL_2$ compounds (L = phosphines or other Lewis bases) has also been reported recently by Barefield and co-workers (*J. Am. Chem. Soc.*, **1981**, *103*, 6219).

Umpolung with Rhodium Iminoacyls. The Use of Metal Oxidation State To Control the Nucleophilicity or Electrophilicity of Acyl Carbons

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Summary: Rhodium(III) iminoacyl hydrides are reduced with dimethylcadmium to give rhodium(I) iminoacyl compounds. These show acyl anion-like reactivity. The same functional group can exhibit acyl anion or acyl cation reactivity depending upon the oxidation state of the attached transition metal.

Hydroacylation, the addition of an aldehyde's C–H bond across an olefin to give a ketone, can be achieved with stable acylrhodium(III) hydrides, or their derivatives, (iminoacyl)rhodium(III) hydrides, and unhindered olefins.[1] However, this methodology cannot be used to append several classes of carbon groups to aldehydes. Methyl groups cannot be appended, since this requires insertion of methylene between the aldehyde C–H bond. Similarly,

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