Heterobimetallic Cooperativity in the Reduction of Methyl Isocyanide by $(C_5H_5)_2W(SH)_2$

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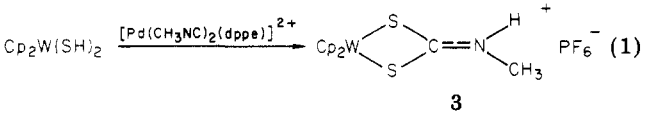
Summary: The metallodithiol $(C_5H_5)_2W(SH)_2$ reacts with $[Pd(CH_3NC)_2(Ph_2PCH_2CH_2PPh_2)](PF_6)_2$ to form the *N*-methyldithiocarbamate $[(C_5H_5)_2WS_2CN(H)CH_3]PF_6$ (**3**) via a novel hydrogen-transfer reaction. An independent synthesis of **3** and $(C_5H_5)_2W$ derivatives of other sulfur ligands is also reported.

Metallothiols are a class of compounds characterized by the presence of the M–SH functional group. As such, soluble mononuclear metallothiols can be considered to be the simplest analogues of surface and cluster polymetallothiols which are of likely relevance to certain biological and industrial catalysts.[1] $Cp_2W(SH)_2$, **1** (Cp = $^5\eta$-C_5H_5), is a metallo*di*thiol which was first reported by Green[2] but is otherwise a neglected chemical entity. Since it shows enhanced nucleophilicity relative to other similar compounds, e.g., $Cp_2Ti(SH)_2$,[3,4] it was selected for the study described herein.

With the objective of assessing the ability of metallothiols for hydrogen atom transfer to small molecules, we examined the reactivity of **1** toward methyl isocyanide. Although **1** does not react directly with methyl isocyanide, we have found an interesting reaction with its transition-metal derivative $[Pd(CH_3NC)_2(dppe)](PF_6)_2$,[5] **2** (dppe = 1,2-bis(diphenylphosphino)ethane). Thus, reaction of equimolar quantities of **1** and **2** in acetonitrile under an atmosphere of N_2 at 25 °C resulted in a rapid color change from deep red to yellow. After 2 h the reaction mixture was evaporated to dryness and the residue was extracted with dichloromethane leaving the *N*-methyldithiocarbamate complex **3** as an orange solid which was recrystallized from acetonitrile (90%) (eq 1). Analytical[7]

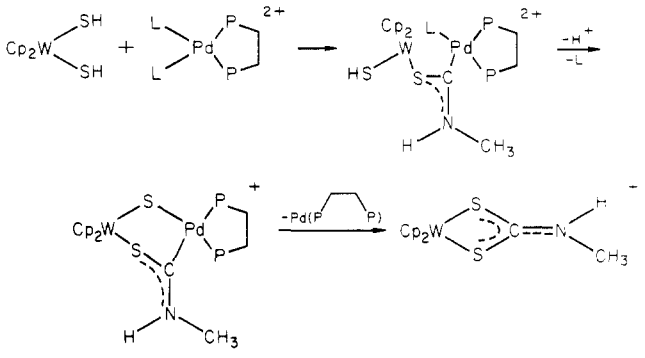


(1)

3

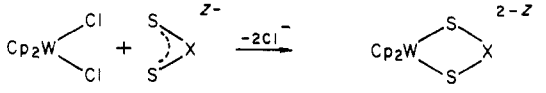
and spectroscopic data for **3** were consistent with our formulation, the most important observations being the IR absorptions (Nujol mull) at 3380 cm^{-1} (ν_{N-H}) and 1549 cm^{-1} ($\nu_{C=N}$), the D_2O-collapsible *N*-methyl doublet at 2.8 ppm in the ^1H NMR (CD_3CN solution), and a molecular ion (m/e = 420) in the field desorption mass spectrum. Final confirmation of the identity of **3** follows from the preparation of a spectroscopically identical compound from

Scheme I



Cp = C_5H_5; L = CH_3NC; P P = $Ph_2PCH_2CH_2PPh_2$

Cp_2WCl_2[8] and methylammonium *N*-methyldithiocarbamate[9] (eq 2). This synthetic method appears to be



(2)

3, X = C–N(H)CH_3, Z = 1
4a, X = C–N$(CH_3)_2$, Z = 1
b, X = C–N$(C_2H_5)_2$, Z = 1
c, X = C–N(H)(C_6H_5), Z = 1
5, X = MoS_2, Z = 2

a general one, and we have utilized it to prepare other, related derivatives such as **4a–c**[10] and the tetrathiomolybdate **5**.[11] These complexes were characterized by elemental analyses, IR, and when soluble, ^1H NMR.

A reasonable mechanism for the formation of **3** can be proposed on the basis of the precedents in monometallic chemistry. Addition of the WS–H unit to a coordinated isocyanide would form the heterobimetallic carbene[13] (Scheme I), via a reaction analogous to that previously observed between organic thiols and $[Pd(CH_3NC)_4](PF_6)_2$.[6] Deprotonation of the remaining metallothiol group followed by displacement of the unreacted isocyanide ligands affords a cyclic intermediate which, upon reductive elimination of palladium(0) as Pd(dppe),[14] gives the dithiocarbamate **3**.

The reactivity of coordinated isocyanide toward RSH, where R = H[15,16] and alkyl,[6] has been reported previously.

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(3) Köpf, H.; Schmidt, M. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 953. McCall, J. M.; Shaver, A. *J. Organomet. Chem.* **1980**, *193*, C37.
(4) Ruffing, C. J.; Rauchfuss, T. B., unpublished results.
(5) $[Pd(CH_3NC)_2(dppe)](PF_6)_2$ was synthesized from equimolar quantities of $[Pd(CH_3NC)_4](PF_6)_2$[6] and dppe in acetonitrile and was recrystallized from CH_2Cl_2/Et_2O. Anal. Calcd for $C_{30}H_{30}F_{12}N_2P_4Pd$: C, 40.89; H, 3.41; P, 14.54. Found: C, 40.68; H, 3.38; P, 14.22. IR (Nujol mull): 2260 cm^{-1} (ν_{CN}). ^1H NMR (CD_3CN): 7.5 (m, 10 H), 3.25 (s, 3 H), 3.20 (m, 2 H).
(6) Miller, J. S.; Balch, A. L. *Inorg. Chem.* **1972**, *11*, 2069.
(7) Anal. Calcd for $C_{12}H_{14}F_6WS_2NP$: C, 25.49; H, 2.47; N, 2.47. Found: C, 25.66; H, 2.52; N, 2.53. Melting point: 260 °C dec.
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(9) Methylammonium *N*-methyldithiocarbamate was synthesized in a manner analogous to that for $NH_4S_2CNH_2$. Fackler, J. P.; Coucouvanis, D. *Inorg. Chem.* **1967**, *6*, 2047.
(10) In a typical preparation, a suspension of 0.15 mmol each of Cp_2WCl_2 and 1,1-dithio ligand in 10 mL of absolute ethanol was heated under reflux for 2 h. Addition of an ethanolic solution of 0.6 mmol of NH_4PF_6 precipitated an orange solid. The suspension was then evaporated to dryness and washed with CH_2Cl_2. Addition of Et_2O to the CH_2Cl_2 extract afforded orange microcrystalline solids in 60–80% yield. Compounds **4a–c** gave satisfactory elemental analyses and were spectroscopically analogous to **3**.
(11) Compound **5** was synthesized by refluxing 0.15 mmol each of Cp_2WCl_2 and NH_4MoS_4 in 10 mL of absolute ethanol. After 2 h the product was filtered from the reaction mixture and air-dried. The IR spectrum (Nujol mull) of compound **5** shows absorptions characteristic of terminal (502, 488 cm^{-1}) and bridging (446 cm^{-1}) Mo–S vibrations of chelating MoS_4^{2-}.[12] Anal. Calcd for $C_{10}H_{10}WS_4Mo$: C, 22.30; H, 1.85; S, 23.79. Found: C, 22.21; H, 1.92; S, 23.90.
(12) Coucouvanis, D.; Simhon, E. D.; Baenziger, N. C. *J. Am. Chem. Soc.* **1980**, *102*, 6646.
(13) The intermediacy of carbenes has been invoked in the heterobimetallic reduction of carbon monoxide: Marsella, J. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 5596.
(14) The palladium product(s) of this reaction have been isolated but identified only to the extent that it contains the fragment Pd^{II}dppe-(MeNC)PF_6. Anal. Found: C, 46.35; H, 3.69; N, 1.89; Cl, 3.15. IR (Nujol mull): 2220 (ν_{NC}), 1050 (dppe Pd), 850 cm^{-1} (ν_{PF}). FDMS: ions observed at m/e = 398 ($dppe^+$), 504 ($Pd(dppe)^+$), 545 ($Pd(dppe)(MeNC)^+$), and 569.
(15) Treichel, P. M.; Knebel, W. J. *Inorg. Chem.* **1972**, *11*, 1285.

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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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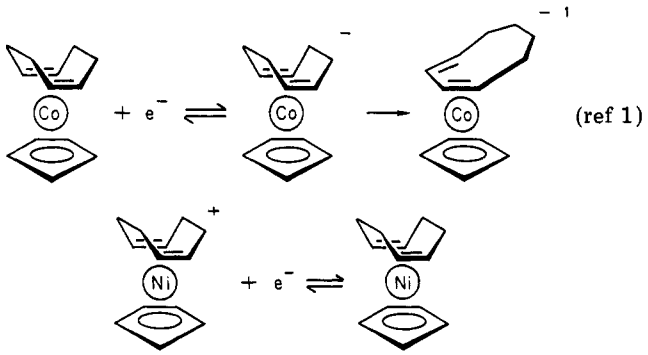
Summary: Reduction of cyclopentadienylnickel cyclooctadiene cation, $CpNiCod^+$, in which the polyolefin ring is bonded as a nonconjugated diene to the metal, has been accomplished electrochemically in weakly polar nonaqueous media. An $E°$ value of −0.46 V was found for the redox process in CH_2Cl_2/0.1 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

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

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

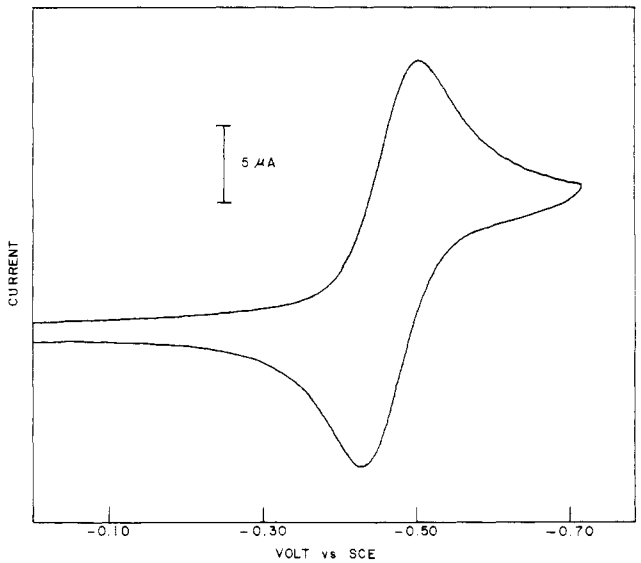


Figure 1. Cyclic voltammogram of 1.0×10^{-3} M $CpNiCod^+PF_6^-$ in CH_2Cl_2 at a platinum bead electrode in CH_2Cl_2/0.1 M Bu_4NPF_6 (scan rate = 100 mV/s).

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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