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Electron-Transfer-Induced Isomerizations of Co-, Ni-, and Pd-Cyclooctatetraene Complexes: The Role Played by the Ligand vs Metal Composition of the Redox Orbital[†]

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Abstract: The preparation and electrochemical reduction of a series of metal–cyclooctatetraene complexes is described. $(\eta^6\text{-}C_6Me_6)Co(1,3\text{-}C_8H_8)^+$ was prepared through the reaction of $(\eta^6\text{-}C_6Me_6)_2Co^+$ with C_8H_8. The nickel group complexes $(C_5R_5)Ni(C_8H_8)^+$, R = H, Me, were prepared by reaction of C_8H_8 with a 33e$^-$ dinuclear complex, respectively either $Cp_2Ni_2(\mu\text{-}C_2Ph_2)^+$ or $Cp^*{}_2Ni_2(\mu\text{-}CO)_2{}^+$. The Pd complex $(\eta^5\text{-}C_5Ph_5)Pd(C_8H_8)^+$ was formed in the reaction of C_8H_8 with $(C_5Ph_5)_2Pd_2(\mu\text{-}C_2Ph_2)^+$. The cyclooctatetraene ring adopted the chair-like 1,3-conformation in the Co complex and the tub-like (1,5-) conformation in the Ni and Pd complexes. One-electron reduction proceeded with retention of isomeric structure. The retention of the 1,5-conformation in the Ni and Pd complexes contrasts with formally isoelectronic $CpCo(C_8H_8)$, which undergoes rapid isomerization to the 1,3-isomer in the 19e$^-$ species. Electron spin resonance studies are able to rationalize the differences in rearrangement tendencies on the basis that the LUMOs of the Co complexes are largely ligand (C_8H_8)-based, whereas those of the Ni and Pd complexes are largely metal-based. The SOMO for the 19e$^-$ Co complexes is assigned as **4a**′, highly delocalized onto the cyclooctatetraene ring, with about 40% metal (d_{xy}) character for $CpCo(1,3\text{-}C_8H_8)^-$ and 50% metal character for $(C_6Me_6)Co(C_8H_8)$. The SOMO of the 19e$^-$ Ni and Pd complexes is assigned as $\mathbf{2b}_2$, about 70% metal (d_{yz}) in character.

Introduction

Molecular structures of organometallic complexes are generally influenced by electron-transfer (ET) reactions, and it is well accepted that substantial structural changes, including isomerizations, may occur as a consequence of reduction or oxidation.[1,2] Despite the obvious role of the redox orbital in ET reactions, few studies have probed the way in which variations in the makeup of this orbital affect structural rearrangements. This paper addresses ET-induced isomerizations of cyclooctatetraene complexes of Co, Ni, and Pd and shows that the degree of metal/ligand mixing in the redox orbital determines whether there is a change in the thermodynamically favored (tub or chair) isomer of the C_8H_8 ring in going from an 18e$^-$ to a 19e$^-$ complex.

The geometric preferences of *tetrahapto*-bonded C_8H_8 in 18e$^-$ complexes are interesting in their own right.[3] Two common coordination geometries have been identified in mononuclear complexes. Bonding through *nonadjacent* double bonds requires that C_8H_8 assumes a tube-like shape roughly equivalent to that of the free ligand.[4,5] We refer to this structure **1** as the 1,5-isomer. The other common geometry (1,3-isomer **2**) has a lawnchair-shaped cyclooctatetraene ring coordinated through *adjacent* double bonds.[6-8] The butadiene-like bonding of **2** is more prevalent with transition metals to the left of the Co subgroup,[9] whereas cyclooctadiene-like **1** is favored for metals to the right of Co.[10] Within the cobalt subgroup, approximately equal numbers of each isomer have been reported.[9f-h,10g-i]

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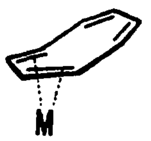

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In only one system, namely $(\eta^5\text{-}C_5R_5)Co(C_8H_8)$, R = H[11] or Me,[12] is the thermally equilibrated complex a measurable mixture of the two isomers, accounting for the attention these complexes have received.[11,12] There is a slight preference for the 1,5-isomer, the equilibrium constant K_{eq} {=[$CpCo(1,5\text{-}C_8H_8)$]/[CpCo(1,3-

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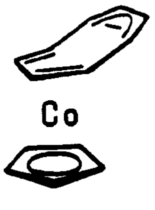
$C_8H_8)]\}$ being 3.3 at 298 K.[11] Combined photoelectron spectroscopy and MO treatments have not yielded a confident rationalization of these structural tendencies.[13]

One-electron reduction of $(C_5R_5)Co(1,5\text{-}C_8H_8)$ forms exclusively the 1,3-isomer (eq 1), presumably through a very short-lived

$$CpCo(1,5\text{-}C_8H_8) + e^- \rightleftharpoons CpCo(1,5\text{-}C_8H_8)^- \rightarrow CpCo(1,3\text{-}C_8H_8)^- \quad (1)$$

1,5-anionic intermediate.[11,12,14] A qualitative explanation of the structure change for $(C_5R_5)Co(C_8H_8)^{0/-}$ invoked a ligand-based (cyclooctatetraene) singly-occupied molecular orbital (SOMO) for the "19th" electron, conceptualized in the limiting electronic structure **3**:



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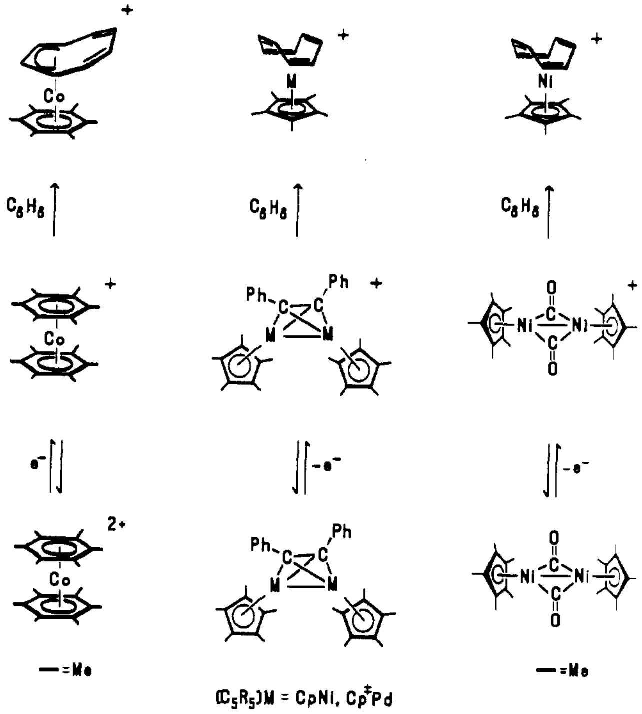
These observations are relevant to several areas of inquiry. Electrochemically induced isomerizations relate to questions of the redox control of metal–hydrocarbon structures and to hydrocarbon ring slippages.[15-17] The structural preferences of 17- and $19e^-$ species are still relatively unknown, in spite of increasing interest in the chemistry of such radicals.[18-22] The flexible C_8H_8 ligand is of particular interest in that it may undergo geometric changes similar to those of ordinary diolefins on high-energy surfaces such as heterogeneous metal catalysts.[23]

Scheme I



In the present work we sought answers to three questions. First, to what extent does **3** represent the real electronic structure of $CoCo(1,3\text{-}C_8H_8)$ and the isoelectronic radical $(C_6Me_6)Co(1,3\text{-}C_8H_8)$? Second, what are the preferred isomers of analogous $19e^-$ Ni group complexes, $CpM(C_8H_8)$, M = Ni, Pd? Third, can differences in structural preferences be rationalized knowing the composition of the redox orbital?

In part, the first question was prompted by the interesting IR data recently reported by Golovin and Weaver[24] which showed that the carbonyl bands for $(CO)_3Fe(C_8H_8)$ moved to ca. 100 cm^{-1} lower in energy when the complex was reduced by one electron. This magnitude of shift appeared more indicative of a *metal*-based SOMO than the cyclooctatetraene-based SOMO we had previously postulated.[25] For quantitation of the SOMO in these 19-electron complexes, we turned to ESR spectra of the Co complex, $CpCo(1,3\text{-}C_8H_8)^-$, in which the metal hyperfine splitting allows a reasonably quantitative estimate of the metal–ligand delocalization.[26] We conclude that for $CpCo(1,3\text{-}C_8H_8)^-$ the SOMO is about 40% metal in character. A slightly higher metal contribution is found for the SOMO of the new radical $(C_6Me_6)Co(C_8H_8)$.

The cationic complexes $LM(C_8H_8)^+$, LM = $(\eta^6\text{-}C_6Me_6)Co$, $(\eta^5\text{-}C_5R_5)Ni$ (R = H or Me), and $(\eta^5\text{-}C_5Ph_5)Pd$ are all reported for the first time. The Co complex appears to form *only* the 1,3-isomer in both the 18- and $19e^-$ complexes. The Ni and Pd complexes, although harder to characterize because of their high labilities, appear to retain the 1,5-isomeric structure ***even in their $19e^-$ forms***. This surprising result is rationalized through MO arguments suggesting an inversion of orbital ordering in going from $CpCo(C_8H_8)$ to $CpM(C_8H_8)^+$, M = Ni, Pd. Corroborative evidence is offered on the basis of ESR and electrochemical data.

Experimental Section

All compounds were prepared and handled under dry nitrogen using standard Schlenck procedures. Electrochemical procedures were as

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(26) The ESR spectrum of $CpCo(1,3\text{-}C_8H_8)^-$ published earlier in ref 25 did not allow measurement of all Co hyperfine components. The presently reported spectrum displayed better resolution.

previously described.[27] Potentials are referred to the ferrocene/ferrocenium couple,[28] for which potentials of +0.56 (THF), +0.48 (acetone), +0.46 (CH_2Cl_2), and +0.38 V (propylene carbonate) were obtained vs the SCE. The potentials in this paper may be converted to an SCE scale by addition of these values. Pt was the working electrode material in all cases, and the supporting electrolyte was 0.1 M $[Bu_4N][PF_6]$.

Cyclooctatetraene (Aldrich) was vacuum-distilled after drying over type 4A molecular sieve. Prepared by literature methods were $[(C_6Me_6)_2Co][PF_6]_2$,[29] $[(C_6Me_6)_2Co][PF_6]$,[29] $Cp_2Ni_2(\mu\text{-}C_2Ph_2)$,[30] $Cp^*{}_2Ni_2(\mu\text{-}CO)_2$,[31] $CpCo(C_8H_8)$,[9h] and $(C_5Ph_5)_2Pd_2(\mu\text{-}C_2Ph_2)$.[32] C,H analyses were done by the Robertson Analytical Laboratory of Madison, NJ. ^1H NMR spectra (Bruker 250 MHz) were referenced to Me_4Si. Low-temperature NMR experiments for $(C_6Me_6)Co(C_8H_8)^+$ employed a 1:1:1 mixture of freon 21 ($CHCl_2F$), freon 22 (CH_2ClF)(duPont), and CD_2Cl_2 as solvent. ESR spectra were obtained with a modified Varian E-4 spectrometer with the sample at 77 K.

$[(C_6Me_6)Co(1,3\text{-}C_8H_8)][PF_6]$. $[(C_6Me_6)_2Co][PF_6]$ (1.4 g, 2.8 mmol) and 1 mL of cyclooctatetraene were stirred together in a mixture of 25 mL of CH_2Cl_2 and 2 mL of propylene carbonate for 5 h. Aliquots of the mixture were monitored by cyclic voltammetry to follow the progress of the reaction. As the displacement of C_6Me_6 by C_8H_8 proceeded, the CV wave for the bisarene complex at ca. +0.1 V was replaced by that of the cyclooctatetraene complex at −1.35 V. CH_2Cl_2 was removed under vacuum. Addition of 100 mL of diethyl ether gave a black precipitate which was thrice recrystallized from CH_2Cl_2/ether. The vacuum-dried dark brown product yielded 1.06 g (80% yield). A 48% yield was obtained when the reaction medium was 1:10 acetone/CH_2Cl_2. Anal: C 49.91 (calc 51.07), H 5.53 (5.57). Repeated efforts to grow crystals suitable for X-ray analysis yielded only microcrystalline materials. ^1H NMR in CD_2Cl_2: δ 4.90 (s, C_8H_8), 1.70 (s, C_6Me_6), rel intensity 1:2.5. Chemical shifts of δ 5.1–5.5 have been reported for fluxional 1,3-C_8H_8 complexes of Co.[9f–h]

Generation of $CpNi(C_8H_8)^+$. Solutions containing this ion were generated by reaction of cyclooctatetraene with the radical cation $[Cp_2Ni_2(\mu\text{-}C_2Ph_2)]^+$. However, the desired complex was too unstable to be isolated. Two approaches were used. (a) $[Ag][PF_6]$ as oxidant: 0.25 g (0.59 mmol) of $Cp_2Ni_2(\mu\text{-}C_2Ph_2)$ in 50 mL of CH_2Cl_2 was reacted with 0.15 g of $[Ag][PF_6]$ for 0.25 h at 245 K, followed by addition of 1 mL of C_8H_8. After 0.25 h the mixture was cooled to 195 K, treated with cold ether, and filtered. This residue, which contained Ag, was partially soluble in cold (243 K) CH_2Cl_2, giving two reversible CV waves of approximately equal height with $E°$ values of −0.74 and −1.01 V. The former is attributed to the desired ion, but the latter is unidentified. Attempts to purify these residues led to decomposition and formation of Cp_2Ni. (b) Formation through anodic oxidation of $Cp_2Ni_2(\mu\text{-}C_2Ph_2)$: Electrolysis of 0.5 mM $Cp_2Ni_2(\mu\text{-}C_2Ph_2)$ in CH_2Cl_2 (243 K) at a Pt electrode in the presence of excess C_8H_8 produced almost exclusively a couple with a reversible CV wave at $E° = -0.74$ V. Little decomposition was noted over 1 h when the solution temperature was raised to ambient, but again attempts at isolation identified only nickelocene.

$[Cp^*Ni(C_8H_8)][PF_6]$. $Cp^*{}_2Ni_2(\mu\text{-}CO)_2$ (0.202 g, 0.45 mmol) and 0.5 mL of C_8H_8 were stirred in 15 mL of acetone with 0.28 g (0.84 mmol) of $[Cp_2Fe][PF_6]$ at 273 K for 1.5 h. After removal of solvent the residue was extracted with ether (3 × 50 mL) to remove ferrocene and $Cp^*{}_2Ni_2(\mu\text{-}CO)_2$, then dissolved in CH_2Cl_2, and filtered, giving a green solution which yielded green crystals when concentrated at 273 K: yield 0.148 g; ^1H NMR in $CDCl_3$ δ 1.43 (s, CH_3), 4.14 (s, C_8H_8), 5.90 (s, C_8H_8).

$[Cp^*Ni(C_8H_{12})][PF_6]$. A similar procedure to that just above, involving 0.319 g (0.72 mmol) of $Cp^*{}_2Ni_2(\mu\text{-}CO)_2$, 0.463 g (1.40 mmol) of $[Cp_2Fe][PF_6]$, and 1.0 mL of cyclooctadiene in 75 mL of CH_2Cl_2/10 mL of acetone for 2.25 h gave 0.35 g of green crystals of $[Cp^*Ni(C_8H_{12})][PF_6]$, the purity of which was established by reference to the literature ^1H NMR spectrum.[33]

$[(C_5Ph_5)Pd(C_8H_8)][PF_6]$. This complex was prepared by analogy to the literature method[34] for $(C_5Ph_5)Pd(diolefin)^+$ through the action of C_8H_8 on $(C_5Ph_5)_2Pd_2(\mu\text{-}C_2Ph_2)^+$. Recrystallization from CH_2Cl_2/hexane gave the desired complex as a green solid in 46% yield. Anal. for $[(C_5Ph_5)Pd(C_8H_8)][PF_6]\cdot 0.25\ CH_2Cl_2$ (NMR) C, 62.9 (calc 63.2), H, 3.8 (4.1); ^1H NMR in CD_2Cl_2 δ 5.73 (s, C_8H_8), 6.43 (s, C_8H_8), 7.09, 7.24, 7.27 (C_6H_5).

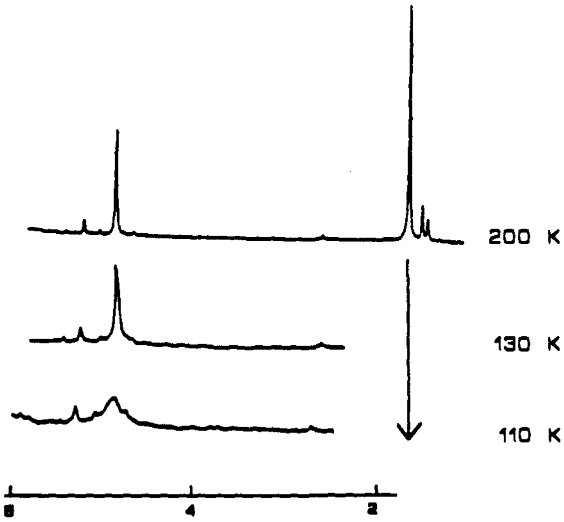

Figure 1. ^1H NMR spectrum of $(C_6Me_6)Co(C_8H_8)^+$ in 1:1:1 freon-21/freon-22/CD_2Cl_2 at temperature shown. The arene methyl resonance, omitted in reproduction of the two colder spectra for purpose of clarity, remained sharp.

Results and Discussion

Preparation and Reduction of Cationic Metal–Cyclooctatetraene Complexes of Co, Ni, and Pd. Relatively few cationic metal–cyclooctatetraene complexes have been reported, probably owing to the lack of suitable synthetic precursors. We used electrochemistry to put a precursor molecule in a substitutionally labile oxidation state, followed by attack with C_8H_8 to form the desired cationic 18-electron complex. In the case of $(C_6Me_6)Co(C_8H_8)^+$, the precursor complex was $(C_6Me_6)_2Co^+$, prepared by chemical or electrochemical reduction of the corresponding dication, $(C_6Me_6)_2Co^{2+}$. The bisarene monocation is reported to be a 20-electron complex with two hexahapto-bonded arene rings.[35,36] Substitution of an η^4-C_8H_8 for η^6-C_6Me_6 (eq 2) results in an 18-electron cation. This strategy was used earlier by Edwin to prepare a series of $(C_6Me_6)Co(\eta^4\text{-diolefin})^+$ complexes.[37]

$$(\eta^6\text{-}C_6Me_6)_2Co^+ + C_8H_8 \rightarrow (\eta^6\text{-}C_6Me_6)Co(\eta^4\text{-}C_8H_8)^+ + C_6Me_6 \quad (2)$$

The preparation of Ni and Pd complexes $(\eta^5\text{-}C_5R_5)M(\eta^4\text{-}C_8H_8)^+$, M = Ni, Pd, relied on one-electron oxidation of a dinuclear dicarbonyl- or acetylene-bridged (L) precursor complex followed by cleavage of the dinuclear monocation with C_8H_8, eq 3. This approach was used by Lane, Connelly, and co-workers

$$[(C_5R_5)_2M_2(\mu\text{-}L)]^+ + C_8H_8 \rightarrow [(C_5R_5)M(\eta^4\text{-}C_8H_8)]^+ + (C_5R_5)M... \quad (3)$$

for preparation of $(C_5Ph_5)Pd(\eta^4\text{-diolefin})^+$.[34] The synthetic routes for all new compounds are summarized in Scheme I.

I. $(C_6Me_6)Co(\eta^4\text{-}C_8H_8)^+$. Cyclooctatetraene appeared to be unreactive toward the 19-electron dication $(C_6Me_6)_2Co^{2+}$. However, a reaction was readily apparent with CH_2Cl_2 solutions of the 20-electron monocation $(C_6Me_6)_2Co^+$ which contained a few percent of a polar solvent such as acetone or propylene carbonate. It did not matter whether $(C_6Me_6)_2Co^+$ was produced through electrolysis or through cobaltocene reduction of $(C_6Me_6)_2Co^{2+}$, and used in situ, or isolated according to the procedure of Fischer.[29] The desired half-sandwich cation $(C_6Me_6)Co(C_8H_8)^+$ was isolated as brown microcrystals which

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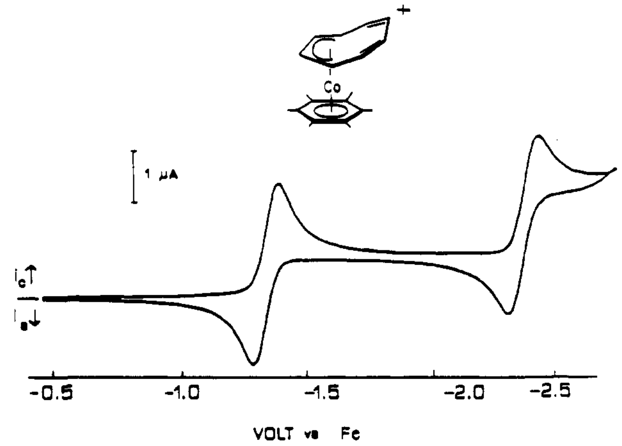

Figure 2. CV scan (v = 0.2 V s^{-1}) of 1.1 mM $(C_6Me_6)Co(C_8H_8)^+$ in CH_2Cl_2 at Pt electrode, T = 245 K.

gave stable solutions in several solvents.

^{1}H NMR spectroscopy of $(C_6Me_6)Co(C_8H_8)^+$ shows only one resonance that can be assigned to the cyclooctatetraene protons, δ = 4.9 ppm, down to the limiting temperature of the probe, ca. 100 K (Figure 1). 1,3-Bonded C_8H_8 ligands are typically fluxional with low activation barriers.[8,9f,g,38] On the other hand, 1,5-bonded C_8H_8 ligands display static spectra. Therefore the NMR data are taken as strong evidence that the cyclooctatetraene ligand' adopts the butadiene-like (1,3-isomer) bonding mode **2** in $(C_6Me_6)Co(C_8H_8)^+$. There is considerable line broadening evident in the C_8H_8 resonance at 110 K, an indication that freezing out of the fluxional behavior may occur at slightly lower temperatures. The static spectrum for the well-studied analogue $(CO)_3Fe(C_8H_8)$ is observed below ca. 120 K.[8]

Two cathodic waves and one anodic wave were observed in cyclic voltammetric (CV) scans of $(C_6Me_6)Co(C_8H_8)^+$ in CH_2Cl_2. Both reductions were one-electron reactions corresponding to formation of the 19- and 20-electron complexes as in eqs 4 and 5 (Table I).

$$(C_6Me_6)Co(C_8H_8)^+ + e^- \rightleftharpoons (C_6Me_6)Co(C_8H_8) \quad (4)$$

$$(C_6Me_6)Co(C_8H_8) + e^- \rightleftharpoons (C_6Me_6)Co(C_8H_8)^- \quad (5)$$

At ambient temperatures the first reduction is diffusion controlled, chemically reversible and Nernstian,[39,40] $E°_1$ = −1.35 V. The second reduction is chemically irreversible at ambient temperatures and slow CV sweep rates but reversible at reduced temperatures (Figure 2), $E°_2$ = −2.39 V (245 K). Similar results were obtained when the solvent was propylene carbonate. The oxidation of $(C_6Me_6)Co(C_8H_8)^+$ was irreversible in CH_2Cl_2 even at 243 K, E_p = +1.25 V with v = 0.20 V s^{-1}, several product waves being observed (E_{pc} = +0.85, +0.59, +0.50, and +0.43 V).[41] Seventeen-electron metal–cyclooctatetraene cations have been shown to be very short-lived and produce an interesting but diverse product distribution.[42]

Bulk coulometric reduction of $(C_6Me_6)Co(C_8H_8)^+$ in CH_2Cl_2 at 245 K (E_{appl} = −1.6 V) gave a smooth conversion to a deep red solution of the 19-electron complex (1.0 F passed).[43] RPE scans (Figure 3) suggested about 90% yield of $(C_6Me_6)Co(C_8H_8)$. A strong but poorly resolved ESR spectrum of this frozen solution (77 K) led us to repeat this experiment with 1:1 $CH_2Cl_2/C_2H_4Cl_2$, which forms a better glass matrix, whereupon the spectrum shown in Figure 4 was obtained (spectral simulation parameters in Table III).[44] Our interpretation of the spectrum (vide infra) is consistent with a high degree of delocalization in the SOMO of the radical. This delocalization aids in assigning the 19-electron complex as the 1,3-C_8H_8 isomer, since this structure favors mixing of the metal (mostly d_{xz}) orbital with the cyclooctatetraene ring. The electrochemical results support this assignment, since no change in $E°$ is observed between the 19-electron system and its 18-electron cationic precursor to which the 1,3-isomeric structure was assigned. The 1,3- and 1,5-isomers are known to differ in $E°$ values by ca. 200 mV in the $(C_5R_5)Co(C_8H_8)$ analogues.[11,12,14]

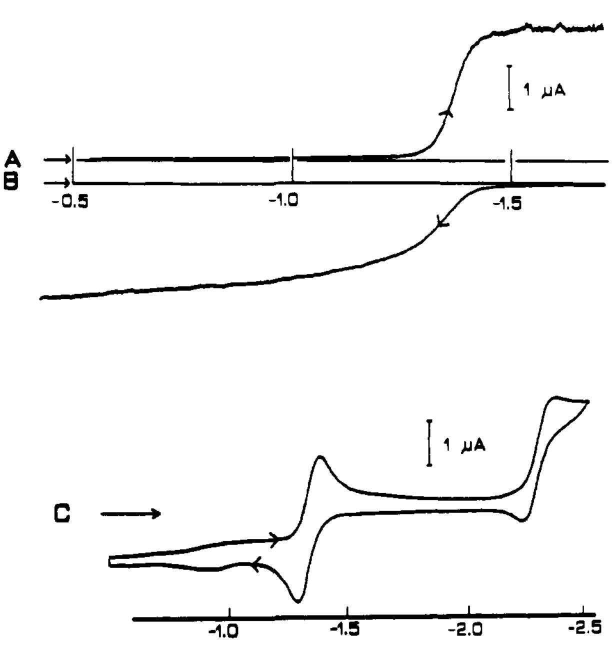

Figure 3. A, B: rotating Pt electrode voltammograms prior to (A) and after (B) coulometric reduction of 1.1 mM $(C_6Me_6)Co(C_8H_8)^+$ in CH_2Cl_2 at E_{appl} = −1.7 V; C: CV scan after coulometric reduction, with conditions same as those in Figure 2. Temperature was 245 K.

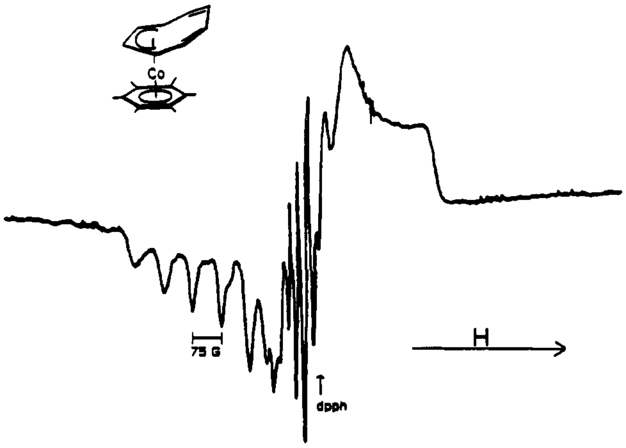

Figure 4. ESR spectrum of $(C_6Me_6)Co(C_8H_8)$ at 77 K produced by coulometric reduction of 1.0 mM $(C_6Me_6)Co(C_8H_8)^+$ in 1:1 $CH_2Cl_2/C_2H_4Cl_2$ at T = 245 K.

II. $Cp^*Ni(\eta^4\text{-}1,5\text{-}C_8H_8)^+$. The preparative strategy for this ion involved attack of cyclooctatetraene on the cation of the dinuclear complex $Cp^*_2Ni_2(\mu\text{-}CO)_2$. Feasibility was demonstrated through electrochemical experiments. $Cp^*_2Ni_2(\mu\text{-}CO)_2$ has a one-electron oxidation in CH_2Cl_2 (Table II, $E°$ = −0.36 V), and

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[40] CV peak currents proportional to square root of scan rate, ΔE_p values near those of ferrocene in CH_2Cl_2 (70 mV at v = 0.1 V/s) and propylene carbonate (64 mV); i_a/i_c = 1.0 at all v for $(C_6Me_6)Co(C_8H_8)^{+/0}$.

[41] The oxidation of $(C_6Me_6)Co(C_8H_8)^+$ produced an insulating film at Pt electrodes, so that rotating electrode voltammetry or controlled potential coulometry in CH_2Cl_2 resulted in passivated electrodes.

[42] Aggarwal, R. P.; Connelly, N. G.; Dunne, B. J.; Gilbert, M.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1991**, 1, and references therein.

[43] A smooth log i vs time plot was obtained for electrolysis at 243 K. At ambient temperatures, 1.3F/eq was passed, and the final yellow-green solution contained no electroactive products.

[44] There is ambiguity in the high field Co splitting because of the inhomogeneous broadening of the high field components. A value for a_3(Co) is given in Table III from simulations done under the assumption that the high field line width is about 20 G.

Table I. Formal Reduction Potentials for Some 18-Electron Metal–Cyclooctatetraene Complexes (in V), Referenced to Ferrocene$^{0/+}$ Couple[d]

complex	solvent	$E°$ (18/19e$^-$)	$E°$ (19/20e$^-$)	lifetime of 19e$^-$ species	ref
$(CO)_3Fe(1,3\text{-}C_8H_8)$	DMF	−1.69	−2.16	persistent	61
$CpCo(1,3\text{-}C_8H_8)$	THF	−2.38	−3.06	persistent	11
$CpCo(1,5\text{-}C_8H_8)$	THF	−2.51		$t_{1/2}$ < 1 ms	11, 14
$(C_6Me_6)Co(1,3\text{-}C_8H_8)^+$	CH_2Cl_2	−1.35	−2.39[a]	persistent	this work
$(C_6Me_6)Co(1,3\text{-}C_8H_8)^+$	PC[b]	−1.42	irrev	not studied	this work
$CpNi(1,5\text{-}C_8H_8)^+$	CH_2Cl_2	−0.74		$t_{1/2}$ ca. 2 s	this work
$Cp^*Ni(1,5\text{-}C_8H_8)^+$	CH_2Cl_2	−1.06	−1.72[c]	persistent	this work
$(C_5Ph_5)Pd(1,5\text{-}C_8H_8)^+$	CH_2Cl_2	−0.78		$t_{1/2}$ = 1.7 s	this work

[a] T = 245 K; irreversible at ambient temperatures and sweep rates below 1 V/s. [b] PC = propylene carbonate. [c] Solvent was THF for study of second reduction, which was irreversible in CH_2Cl_2. [d] Lifetimes of 19 electron species were measured by cyclic voltammetry using the method of Nicholson and assuming first-order decomposition of the radical, see: Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

Table II. Formal Potentials for Other Complexes Pertinent to This Study[a]

complex	$E°(0/+)$	comments
$CpNi(1,5\text{-}C_8H_{12})^+$	−0.92	1e$^-$ reduction (ref 48)
$Cp^*Ni(1,5\text{-}C_8H_{12})^+$	−1.28	Nernstian 1e$^-$ reduction to persistent radical
$Cp^*_2Ni_2(\mu\text{-}CO)_2$	−0.36	1e$^-$ oxidation to cation persistent at 245 K
$Cp_2Ni_2(\mu\text{-}C_2Ph_2)$	+0.07	1e$^-$ oxidation to persistent cation
$(C_5Ph_5)_2Pd_2(\mu\text{-}C_2Ph_2)$	+0.06	1e$^-$ oxidation to stable cation (ref 34)
$(C_5Ph_5)Pd(1,5\text{-}C_8H_{12})^+$	−0.93	Nernstian 1e$^-$ reduction (ref 52)

[a] Potentials (in Volt) Referenced to Ferrocene$^{0/+}$ Couple in CH_2Cl_2.

bulk anodic electrolysis at 245 K gave about a 70% conversion to deep purple $Cp^*_2Ni_2(\mu\text{-}CO)_2^+$ (eq 6). When excess cyclooctatetraene or cyclooctadiene was added to the electrolyzed solutions and the temperature was raised to ca. 280 K, the wave for $Cp^*_2Ni_2(\mu\text{-}CO)_2^{0/+}$ diminished and a new one grew in at $E°$ = −1.06 or −1.28 V, respectively, reaching full conversion after ca. 1 h.[45] Equation 7 describes this reaction. Mechanistic aspects of the oxidative cleavage of dinuclear complexes have been discussed.[34]

$$Cp^*_2Ni_2(\mu\text{-}CO)_2 \rightleftharpoons Cp^*_2Ni_2(\mu\text{-}CO)_2^+ + e^- \quad (6)$$

$$Cp^*_2Ni_2(\mu\text{-}CO)_2^+ + C_8H_n \rightarrow Cp^*Ni(C_8H_n)^+ \quad n = 8 \text{ or } 12 \quad (7)$$

Our choices of chemical oxidant, solvents, and reaction conditions for the preparations of $Cp^*Ni(C_8H_8)^+$ and $Cp^*Ni(C_8H_{12})^+$ were based on these electrochemical studies. A procedure based on ferrocenium as oxidant proved to be convenient and is described in the Experimental Section. The cyclooctadiene complex had been previously prepared through the action of C_8H_{12} on $Cp^*_2Ni_2(\mu\text{-}Cl)_2$, but the cyclooctatetraene complex had proven elusive.[33] The ^1H NMR spectrum establishes that the 1,5-isomer is formed exclusively in $Cp^*Ni(C_8H_8)^+$.

Reduction of both $Cp^*Ni(C_8H_8)^+$ and $Cp^*Ni(C_8H_{12})^+$ proceeded by uncomplicated one-electron processes in CH_2Cl_2 (Figure 5), the $E°$ value of the C_8H_8 complex being 220 mV positive of that of the C_8H_{12} complex (eq 8, Tables I and II). The cyclooctatetraene complex also exhibited a second reduction which was chemically irreversible in CH_2Cl_2 but reversible in THF ($E°$ = −1.72 V, eq 9, Table I).

$$Cp^*Ni(C_8H_n)^+ + e^- \rightleftharpoons Cp^*Ni(C_8H_n) \quad (8)$$

$$Cp^*Ni(C_8H_8) + e^- \rightleftharpoons Cp^*Ni(C_8H_8)^- \quad (9)$$

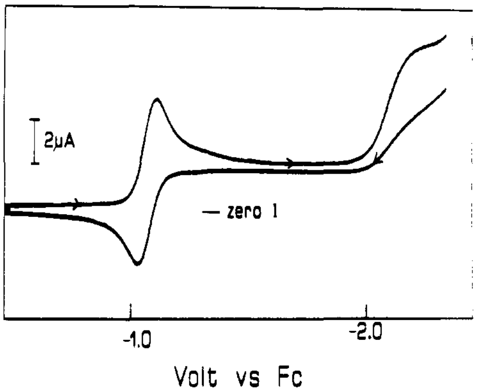

Figure 5. CV scan (v = 0.20 V s^{-1}) of 0.6 mM $Cp^*Ni(C_8H_8)^+$ in CH_2Cl_2 at Pt electrode, T = 273 K.

Electrolysis of $Cp^*Ni(C_8H_8)^+$ in CH_2Cl_2 at 245 K gave 1.15 F (two trials), verifying the one-electron first reduction. Comparison of RPE scans before and after electrolysis suggested about a 30% yield of the 19-electron species $Cp^*Ni(C_8H_8)$, in the dark solution. A similar result was obtained with THF as solvent. ESR spectra of the reduced solutions of $Cp^*Ni(C_8H_8)^+$ in THF showed two signals, a major one at $g_\parallel$ = 2.152, $g_\perp$ = 2.015, and a minor one with features at g = 2.057 and 2.027 (Table III).

None of the voltammetric data for $Cp^*Ni(C_8H_8)^{+/0}$ leads us to believe that the 19-electron complex undergoes isomerization to the 1,3-bonded complex. Based on analogies with the $C_5R_5Co(C_8H_8)$ complexes and supported by molecular orbital calculations,[25] the 1,3-isomer should have a reduction potential significantly more positive than that of the 1,5-isomer. Cathodic electrolysis of the cation $Cp^*Ni(C_8H_8)^+$ yielded no such product with a shifted $E°$ value.

III. $CpNi(\eta^4\text{-}C_8H_8)^+$. Attempts to prepare this cation had failed earlier.[46] Although we were also unable to isolate it, the following experiments are consistent with its in situ generation and characterization. The electrochemical properties of $CpNi(C_8H_8)^+$ are consistent with *1,5-coordination* of the C_8H_8 ligand.

The diphenylacetylene-bridged dinickel complex $Cp_2Ni_2(\mu\text{-}C_2Ph_2)$ undergoes a reversible one-electron oxidation, eq 10, Table II. If the electrode potential was held positive of this wave in a solution containing C_8H_8, scans to more negative potentials showed

$$Cp_2Ni_2(\mu\text{-}C_2Ph_2) \rightleftharpoons Cp_2Ni_2(\mu\text{-}C_2Ph_2)^+ + e^- \quad (10)$$

$$Cp_2Ni_2(\mu\text{-}C_2Ph_2)^+ + C_8H_8 \rightarrow CpNi(C_8H_8)^+ \quad (11)$$

Table III. ESR Spectral Parameters for Metal–Cyclooctatetraene Radicals

radical	g_x	g_y	g_z	$A_x(Co)$[a]	$A_y(Co)$[a]	$A_z(Co)$[a]
$CpCo(1,3\text{-}C_8H_8)^-$	2.172	2.022	1.927	(±)38.6	−45.8	−38.4
		g_{iso} = 2.040 at T = 220 K (fluid THF)				
$(C_6Me_6)Co(1,3\text{-}C_8H_8)$	2.155	2.047	1.890	(±)28	−78	−22.5
$(CO)_3Fe(C_8H_8)^-$	2.016	2.009	1.980	(ref 25; see also ref 65)		
$CpNi(1,5\text{-}C_8H_8)$	2.029	2.029	2.198			
$Cp^*Ni(1,5\text{-}C_8H_8)$	2.020	2.020	2.152			

[a] In units of 10^{-4} cm^{-1}.

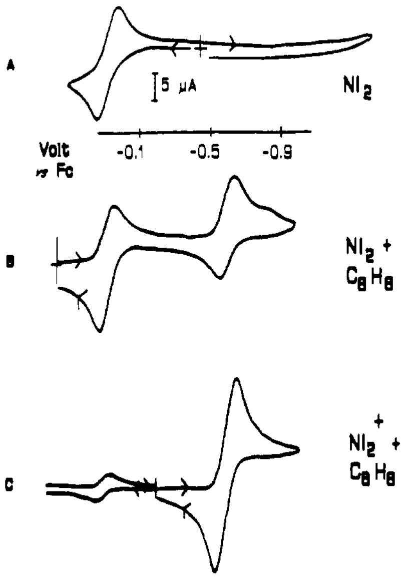

Figure 6. CV scans of A, 0.5 mM $Cp_2Ni_2(\mu\text{-}C_2Ph_2)$ in CH_2Cl_2; B, 0.5 mM $Cp_2Ni_2(\mu\text{-}C_2Ph_2)$ and 1 mL of C_8H_8 in CH_2Cl_2. Scan initiated after holding potential positive of $Cp_2Ni_2(\mu\text{-}C_2Ph_2)^{0/+}$ wave for 30 s. C, solution B [$Cp_2Ni_2(\mu\text{-}C_2Ph_2)$ plus C_8H_8] after electrolysis at $E_{appl} = +0.20$ V. The reversible wave at $E° = -0.74$ V is that of $CpNi(C_8H_8)^+$. Other conditions: Pt electrode, $v = 0.20$ V s^{-1}, $T = 243$ K.

a product wave at −0.74 V (Figure 6b). Bulk anodic electrolysis of $Cp_2Ni_2(\mu\text{-}C_2Ph_2)$ in the presence of C_8H_8 at 243 K gave a light green solution (2 F) and a single electroactive product, $E° = -0.74$ V (Figure 6c). At low temperatures the reduction of the new product is chemically reversible, but the reversibility decreases as the temperature is increased.[47]

This product wave is ascribed to $CpNi(1,5\text{-}C_8H_8)^+$ on the basis of both of the expected reaction chemistry (eq 11) and the potential of the observed wave. Concerning the latter, it is instructive to consider the differences in potentials between reductions of the C_8H_{12} and C_8H_8 complexes of both Cp*Ni and $(C_5Ph_5)Pd^+$. As seen in Table I the potential of the C_8H_8 complex is 220 mV positive of that of the C_8H_{12} complex in both cases. Since the potential of the couple $CpNi(C_8H_{12})^{+/0}$ is −0.92 V,[48] this analogy predicts a value of −0.70 V for $CpNi(C_8H_8)^{+/0}$, very close to the value measured for the electrolysis product (−0.74 V).

$CpNi(C_8H_8)^+$ produced in this way was electrolytically reduced at $E_{appl} = -1.0$ V, giving about a 30% yield of $CpNi(C_8H_8)$, the remainder going to Cp_2Ni [formed through the disproportionation of $CpNi(C_8H_8)$[50]] and a black insoluble material that may be $[Ni(C_8H_8)_x]_y$.[49] A solution sample withdrawn for ESR study gave an intense signal of axial symmetry with $g_\parallel = 2.198$, $g_\perp = 2.029$. These values compare closely with those measured for $CpNi(1,5\text{-}C_8H_{12})$, namely $g_\parallel = 2.182$ and $g_\perp = 2.051$.[48a] Both the voltammetric properties and the ESR values are therefore consistent with a *1,5-isomeric formulation* for $CpNi(C_8H_8)^m$ in both the 18e⁻ cations (m = 1+) and the 19e⁻ (m = 0) neutral complexes.

IV. $(C_5Ph_5)Pd(\eta^4\text{-}1,5\text{-}C_8H_8)^+$. ^{1}H NMR spectra of $(C_5Ph_5)Pd(C_8H_8)^+$ show that the cyclooctatetraene ring is bonded in the 1,5-configuration (δ 5.73 and 6.43 for C_8H_8 resonances). Reduction of this ion ($E° = -0.78$ V) gives a short-lived ($t_{1/2}$ = 1.7 s in CH_2Cl_2 at 298 K) 19-electron neutral complex. The reduction (eq 12) was chemically reversible at 228 K, but at

$$(C_5Ph_5)Pd(C_8H_8)^+ + e^- \rightleftharpoons (C_5Ph_5)Pd(C_8H_8) \qquad (12)$$

ambient temperatures a scan rate above 1 V s^{-1} is necessary to outrun the postelectrode reaction of $(C_5Ph_5)Pd(C_8H_8)$. A secondary product, which appears as an anodic wave at ca. 0 V in slow CV sweeps of $(C_5Ph_5)Pd(C_8H_8)^+$ (Figure 7a) was produced in high yield through coulometric reduction of $(C_5Ph_5)Pd(C_8H_8)^+$ in either THF or CH_2Cl_2. After completion of the reduction (1.0 F) at 243 K, CV scans of the brown product showed that a species with the same potential as that of the reactant cation $(C_5Ph_5)Pd(C_8H_8)^+$ is regenerated in its reoxidation (Figure 7b). Anodic bulk electrolysis of this brown solution gave a green product with a reduction peak potential matching that of $(C_5Ph_5)Pd(C_8H_8)^+$, but the spectra of reduced solutions of this new product differed from those produced from the cathodic electrolysis of $(C_5H_5)Pd(C_8H_8)^+$, arguing against the recycled product being the starting material.[50]

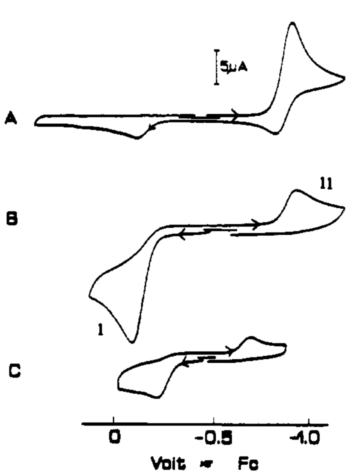

Figure 7. CV scans of A: 0.5 mM $(C_5Ph_5)Pd(C_8H_8)^+$ in CH_2Cl_2, v = 0.15 Vs^{-1}; B: solution A after coulometric reduction with $E_{appl} = -1.2$ V, v = 0.20 V s^{-1}; C: ca 0.2 mM isolated product (see text), v = 0.20 V s^{-1}. Other conditions: Pt electrode, T = 245 K.

The tan-brown reduction product of $(C_5Ph_5)Pd(C_8H_8)^+$ was extracted from the electrolysis solution with hexane and precipitated by addition of nitromethane. However, the isolated product had a different voltammetry than that of the original reduction product (Figure 7c), showing that the isolation procedure had altered the product. Further efforts did not result in its identification.[51] By analogy to the fates of Pd(I) polyolefin radicals such as $(C_5Ph_5)Pd(C_8H_{12})$ and (C_5Ph_5)Pd(dibenzocyclooctatetraene) it is likely that radical addition to the C_8H_8 ring is responsible for the high reactivity of $(C_5Ph_5)Pd(C_8H_8)$.[52] There is no indication of the formation of a $1,3\text{-}C_8H_8$ isomer in either the 18- or 19-electron complexes $(C_5Ph_5)Pd(C_8H_8)^{+,0}$. The $E°$ value of this complex is 150 mV positive of that of the analogous C_8H_{12} complex (Table II), similar to the shifts seen for C_8H_8 vs C_8H_{12} complexes of $(C_5R_5)Ni(\text{diolefin})^+$ (vide ante).

Table V summarizes the thermodynamically favored isomers for the most pertinent tetrahapto C_8H_8 complexes both from this study and those in earlier literature.

Metal–Ligand Covalency in $Co(1,3\text{-}C_8H_8)$ Radicals: ESR Results. The neutral radical $(C_6Me_6)Co(1,3\text{-}C_8H_8)$ is isoelectronic

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(45) The waves for the products $Cp^*Ni(C_8H_8)^+$ and $Cp^*Ni(C_8H_{12})^+$ were also seen in slow CV sweeps through the $Cp^*{}_2Ni_2(\mu\text{-}CO)_2$ oxidation in solutions containing excess C_8H_8 or C_8H_{12} at ambient temperatures.

(46) Salzer, A.; Court, T. L.; Werner, H. *J. Organomet. Chem.* **1973**, *54*, 325.

(47) At a CV sweep rate of 0.2 V s^{-1}, the following i_a/i_c values were measured for the reduction of $CpNi(C_8H_8)^+$ at various temperatures: 0.71 at 293 K; 0.78 at 253 K; 0.94 at 233 K.

(48) (a) Lane, G.; Geiger, W. E. *Organometallics* **1982**, *1*, 401. (b) Koelle, U.; Werner, H. *J. Organomet. Chem.* **1981**, *221*, 367. (c) Koelle, U.; Ting-Zhen, D.; Keller, H.; Ramakrishna, B. L.; Raabe, E.; Krueger, C.; Raabe, G.; Fleischhauer, J. *Chem. Ber.* **1990**, *123*, 227.

(49) (a) Wilke, G.; Bogdanovic, B.; Heimbach, P.; Kroner, M.; Muller, J. W. *Adv. Chem. Ser.* **1962**, *34*, 137. (b) Brauer, D. J.; Kruger, C. *J. Organomet. Chem.* **1976**, *122*, 265. (c) Lehmkuhl, H.; Leuchte, W.; Eisenbach, W. *Annalen* **1973**, 692.

(50) The product formed in the oxidation wave 1 (Figure 7b) had a reduction wave (11) with less chemical reversibility than did $(C_5Ph_5)Pd(C_8H_8)^+$. Oxidation and rereduction of this product gave solutions with different optical spectra than those produced in the cathodic electrolysis of $(C_5Ph_5)Pd(C_8H_8)^+$ (former, λ_{max} = 360 nm, latter, λ_{max} = 395 nm).

(51) The ^{1}H NMR spectrum suggested coordinated C_5Ph_5 and C_8H_8 groups (the latter through decoupling experiments), but there were also unaccounted-for-resonances. The field desorption mass spectrum indicated a molecular ion peak containing Pd at ca. 760 amu.

(52) Lane, G. A.; Geiger, W. E.; Connelly, N. G. *J. Am. Chem. Soc.* **1987**, *109*, 402.

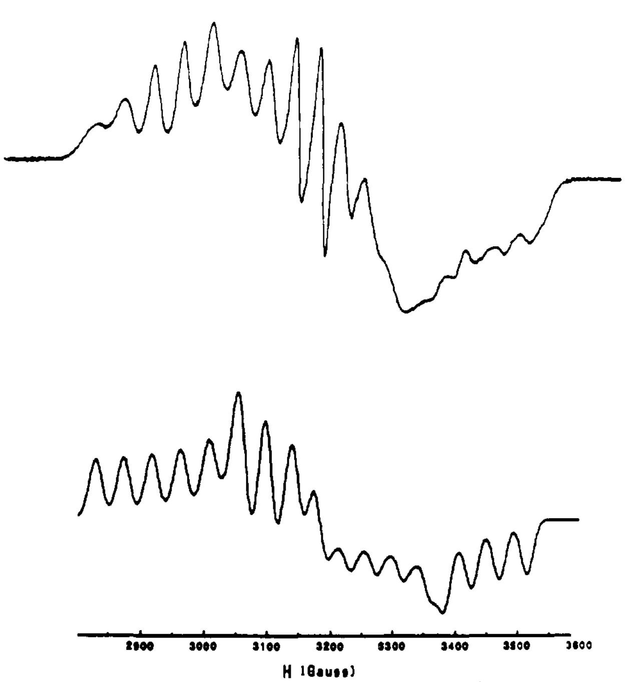


Figure 8. Experimental (top) and simulated (bottom) ESR spectra of $CpCo(1,3\text{-}C_8H_8)^-$. EXPT: Frozen THF solution at 77 K after bulk coulometric reduction of $CpCo(C_8H_8)$. SIMULATION parameters: given in Table III.

with the radical anion $CpCo(1,3\text{-}C_8H_8)^-$. The presence of the Co nucleus in these complexes makes it feasible to characterize the SOMO using the g-tensor and the ^{59}Co (100%, $I = 7/2$) hyperfine tensor.

The frozen-solution ESR spectrum of $CpCo(1,3\text{-}C_8H_8)^-$ was reported earlier along with a qualitative interpretation.[25] In order to obtain a better estimate of the degree of mixing of metal and ligand orbitals in the 19-electron anion, we first acquired a better-resolved spectrum. Bulk cathodic electrolysis of 1 mM $CpCo(C_8H_8)$ in THF at 243 K at −2.5 V gave a high yield of $CpCo(1,3\text{-}C_8H_8)^-$, as shown by RPE and CV scans after the electrolysis current had dropped near the background value. The rapidly frozen brown solution displayed a strong and clean signal (Figure 8a) showing approximately half of the 24 features anticipated for a rhombic Co hyperfine tensor. The spectrum was analyzed using a least-squares fitting procedure[53] to give the parameters listed in Table III. The interpretation, which was similar to that reported earlier,[25] was supported by computer simulation of the spectrum.

Two of the three g-tensor components are well resolved in the ESR spectrum of $(C_6Me_6)Co(C_8H_8)$ (Figure 4) and the corresponding parameters were easily obtained.[39] The unusual width and shape of the high field feature is due to unresolved Co hyperfine coupling. Computer simulations resulted in an estimate of the unresolved splitting, A_z, in Table III.[53]

According to the extended Huckel MO calculations of Albright[25] the SOMO for $CpCo(1,3\text{-}C_8H_8)^-$ or $(C_6Me_6)Co(1,3\text{-}C_8H_8)$ is expected to be **4a′**, concentrated most heavily on the uncoordinated portion of the cyclooctatetraene ring with some metal d_{xz} character (see drawing **4** and Figure 9b), eq 13, where the sum is over the cycloocatetraene orbitals:

$$|\text{SOMO}\rangle = a|xz\rangle + \sum_i b_i|z_i\rangle \tag{13}$$

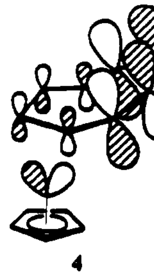
Neglecting spin-orbit coupling for the carbon orbitals, the g-tensor components are given by eq 14[54]

$$\Delta g_x = 2\zeta\sum_k \frac{a^2(c_{xy,k})^2}{E_0 - E_k} \tag{14a}$$

$$\Delta g_y = 2\zeta\sum_k \frac{a^2(c_{x^2-y^2,k})^2 + 3a^2(c_{z^2,k})^2}{E_0 - E_k} \tag{14b}$$

$$\Delta g_z = 2\zeta\sum_k \frac{a^2(c_{yz,k})^2}{E_0 - E_k} \tag{14c}$$

where ζ is the metal spin-orbit coupling parameter, E_0 is the energy of the SOMO, and for example, $c_{xy,k}$ is the LCAO coefficient of d_{xy} in the kth MO with energy E_k.



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The EHMO scheme (see Figure 9b) suggests that the lowest empty MO for these radicals is **3a″** with d_{yz} character, the highest doubly occupied MO is **3a′** with d_{xz} character, and at lower comparable energies are **1a″**, **1a′**, **2a′**, and **2a″** (with d_{xy}, $d_{x^2-y^2}$, d_{z^2}, and d_{yz} character, respectively). Thus eq 14 predicts $\Delta g_z < 0$ and $\Delta g_y \approx 4\Delta g_x$, providing the basis for the assignments of Table III.

The isotropic hyperfine coupling is given by

$$\langle A\rangle = A_s + \frac{1}{3}P(\Delta g_x + \Delta g_y + \Delta g_z) \tag{15}$$

where A_s is the Fermi-contact contribution and $P = 282 \times 10^{-4}$ cm^{-1} is the dipolar coupling parameter for cobalt.[55] The 3d spin density, $\rho^d = a^2$, can be computed from[54]

$$A_y - \langle A\rangle = P\left[-\frac{4}{7}a^2 + \frac{2}{3}\Delta g_y - \frac{5}{42}(\Delta g_x + \Delta g_z)\right] \tag{16}$$

The departure of the hyperfine tensor from axial symmetry is expected to be[54]

$$A_x - A_z = \frac{17}{14}P(\Delta g_x - \Delta g_z) + \frac{6}{7}P\zeta a^2\sum_k \frac{(c_{x^2-y^2,k})^2 - (c_{z^2,k})^2}{E_0 - E_k} \tag{17}$$

In the case of $CpCo(1,3\text{-}C_8H_{12})^-$ (note: the polyolefin is cycloocta*diene* in this instance), the observed isotropic cobalt coupling is nearly exactly the average of the three principal values of the hyperfine tensor;[25,54] thus the three components must have the same sign. In this case, admixture of Co 4s character into the **a″** SOMO is symmetry forbidden and the Fermi contact coupling must arise entirely from spin polarization; A_s is therefore expected to be negative.

The situation is more complicated for $CpCo(1,3\text{-}C_8H_8)^-$ and $(C_6Me_6)Co(1,3\text{-}C_8H_8)$ since (i) resolved isotropic spectra were not obtained so that the relative signs of the A_i components are indeterminate,[53] and (ii) the expected **a′** symmetry permits 4s admixture. Since polarization is expected to dominate, A_s is still expected to be negative, eliminating four of the eight possible choices of signs of the hyperfine components. The departure from axial symmetry computed from eq 17 (neglecting the second term), $A_x - A_s = 32$ and 54×10^{-4} cm^{-1}, suggests that $A_x > 0$, $A_s < 0$, further reducing the sign ambiguities;[56] the resulting hyperfine

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(53) The value of A_3(Co) could not be obtained by calculation from A_1(Co), A_2(Co), and A_{iso}(Co) since the latter is apparently less than the line width of the radical in fluid media. $CpCo(C_8H_8)^-$ displayed a broad (100 G peak-to-peak) line with $g = 2.040$ at 220 K in THF. For the fitting procedure of the glassy spectrum, see: DeGray, J. A.; Reiger, P. H. *Bull. Magn. Reson.* **1987**, *8*, 95.

(54) Reiger, P. H. in ref 19, Chapter 8.

(55) Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1978**, *30*, 577.

(56) If we do not use the criterion of eq 17 to establish the signs of the hyperfine components, we have four possibilities: $A_x > 0$, A_z, $A_y < 0$ gives the results shown in Table IV; A_x, A_y, $A_z < 0$ leads to negative ρ^s; $A_x < 0$, A_y, $A_z > 0$ leads to negative ρ^d; with A_x, $A_z > 0$, $A_y < 0$, we obtain $\rho^d = 0.56$ and 0.57, $\rho^s = 0.04$ and 0.03 for $CpCo(1,3\text{-}C_8H_8)^-$ and $(C_6Me_6)Co(C_8H_8)$, respectively, but with $A_x - A_z = 0$ and -6×10^{-4} cm^{-1}.

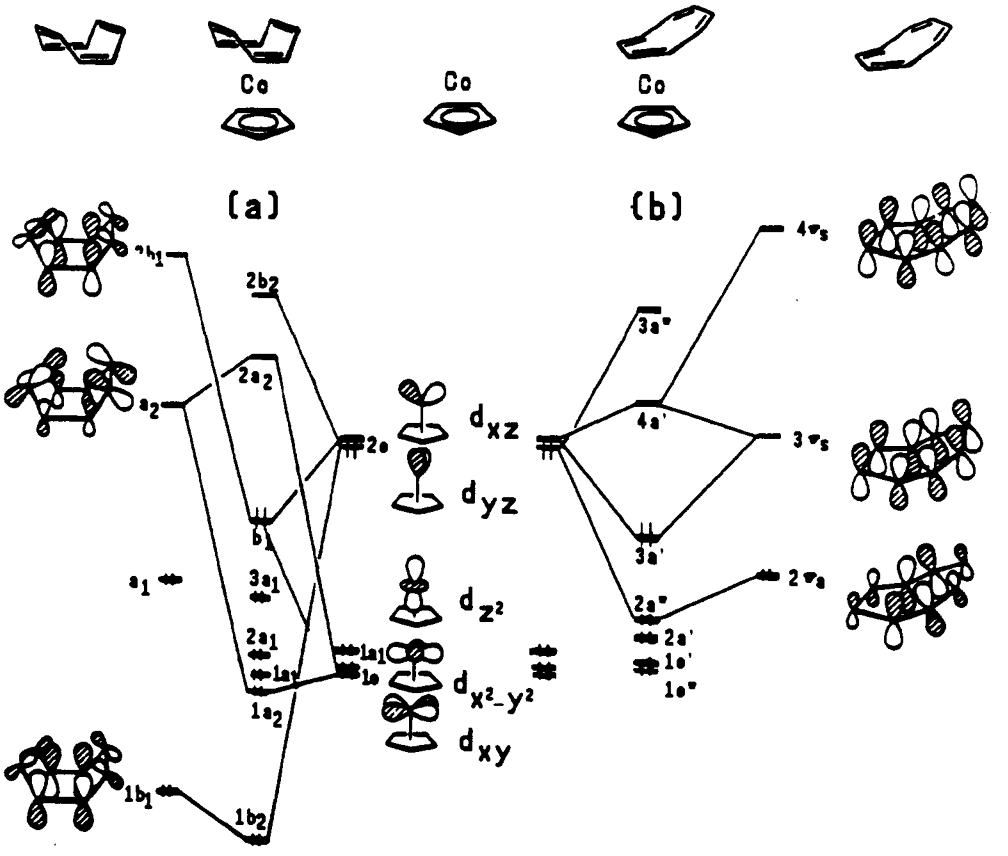

Figure 9. MO diagrams for CpCo(1,5-C_8H_8) [column (a)] and CpCo(1,3-C_8H_8) [column (b)] adapted from ref 25. The orbital occupancy shown is for 18e⁻ species. In the isoelectronic Ni, Pd complexes the $2b_2$ lies below the $2a_2$ [column (a)].

Table IV. Spin Densities Derived from ESR Parameters

radical	$A_x{}^a$	$\langle A\rangle^a$	$A_s{}^a$	ρ^d	ρ^s
CpCo(1,3-C_8H_8)⁻	+38.6	−15.3	−26.1	0.40	−0.010
	−38.6	−40.9	−51.7	0.24	0.013
(C_6Me_6)Co(C_8H_8)	+28	−28	−36	0.50	0.001
	−28	−43	−51	0.41	0.015

[a] In units of 10^{-4} cm⁻¹.

components are given in Table III. The 3d spin densities, 0.40 for CpCo(1,3-C_8H_8)⁻ and 0.50 for (C_6Me_6)Co(C_8H_8), are considerably smaller than that of the related anion lacking a noncomplexed π system, CpCo(1,5-C_8H_{12})⁻, $\rho^d = 0.74$.[54]

The Fermi contact coupling is expected to have contributions from spin polarization of innershell s electrons and from direct contribution of 4s spin density (eq 18)

$$A_s = Q_d\rho^d + Q_s\rho^s \tag{18}$$

where $Q_d = -131 \times 10^{-4}$ cm⁻¹ and $Q_s = 1984 \times 10^{-4}$ cm⁻¹.[54,55] Thus $Q_d\rho^d$ is expected to be larger in magnitude than A_s. The 4s spin densities computed from eq 18 are given in Table IV.

The axial or nearly axial ESR spectra of the nickel radicals, (C_5R_5)Ni(1,5-C_8H_8), are incompatible with the $2a_2$ SOMO of the Co analogue (Figure 9a). Recalling that the metal contribution to this orbital is d_{xy} in the pseudo-C_{2v} symmetry of the complexes, an axial g-tensor would require that d_{xz} and d_{yz} be essentially degenerate in all their relevant contributions to the MOs. Such a requirement is clearly inconsistent with Figure 9a, in which the $b_1(d_{xz})$ and $1b_2(d_{yz})$ MOs are at very different energies.

A second candidate for the SOMO of the Ni group radicals is the $2b_2$ orbital, which is predominantly metal-based (d_{yz}) in character. Its position now *below* $2a_2$ is readily rationalized on the basis of the higher formal charge for Ni(2+) compared to Co(1+): the energies of all metal orbitals are expected to be lower in Ni complexes than in isoelectronic Co analogues; in the present case, this results in substantially reduced participation of ligand orbitals in the frontier MOs.

Table V. Thermodynamically Favored Isomers for Some η^4-Cyclooctatetraene Complexes of the Co and Ni Groups and Other Selected Complexes

1,5-isomer, **1**	1,3-isomer, **2**
A. 18e⁻ Complexes	
(C_5R_5)Co(C_8H_8), R = H, Me	(C_6Me_6)Co(C_8H_8)⁺
(C_5R_5)Rh(C_8H_8), R = H, Me	(triphos)Co(C_8H_8)⁺
(C_5R_5)Ir(C_8H_8), R = H, Me	(PMe_3)$_3$Co(C_8H_8)⁺
(C_5R_5)Ni(C_8H_8)⁺, R = H, Me	(CO)$_3$Fe(C_8H_8)
(C_5Ph_5)Pd(C_8H_8)⁺	(CO)$_3$Ru(C_8H_8)
(η^4-quinone)Ni(C_8H_8)	(C_6R_6)Ru(C_8H_8)
(η^4-C_4R_4)Ni(C_8H_8)	
B. 19e⁻ Complexes	
(C_5R_5)Ni(C_8H_8), R = H, Me	(C_5R_5)Co(C_8H_8)⁻, R = H, Me
(C_5Ph_5)Pd(C_8H_8)	(C_6Me_6)Co(C_8H_8)
	(CO)$_3$Fe(C_8H_8)⁻

For a $2b_2$ SOMO, g_z is expected to be significantly greater than g_e, owing to mixing with b_1 (d_{xz}), while g_x and g_y are expected to be only slightly larger than g_e, and possibly nearly equal,[57] since the remainder of the d-orbital set lies at much lower energies.

Confirmation of these arguments comes through consideration of the spectrum of the related 19e⁻ radical CpNi(C_8H_{12}). The SOMO for this system is almost certainly d_{yz}, the predicted[25] and observed ground state for d⁹ π-complexes of simple diolefins.[58] The g values of this radical, $g_\parallel = 2.182$, $g_\perp = 2.025$,[48a] are very similar to those of the Ni cyclooctatetraene complexes. This assures that the ordering of the relevant d-containing MOs must be essentially the same in the three complexes, CpNi(C_8H_{12}), CpNi(C_8H_8), and Cp*Ni(C_8H_8).

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(57) A nearly axially symmetric spectrum with a $2b_2$ SOMO in C_{2v} symmetry requires that $1/\Delta E_{xy} \approx [1/\Delta E_{x^2-y^2} + 3/\Delta E_{z^2}]$.[56] Since the $2a_1$, $1a_1$, and $1a_2$ orbitals are all distant in energy from the SOMO, all three contributions to the values of g_x and g_y will be small, making their (near) accidental degeneracy more likely.

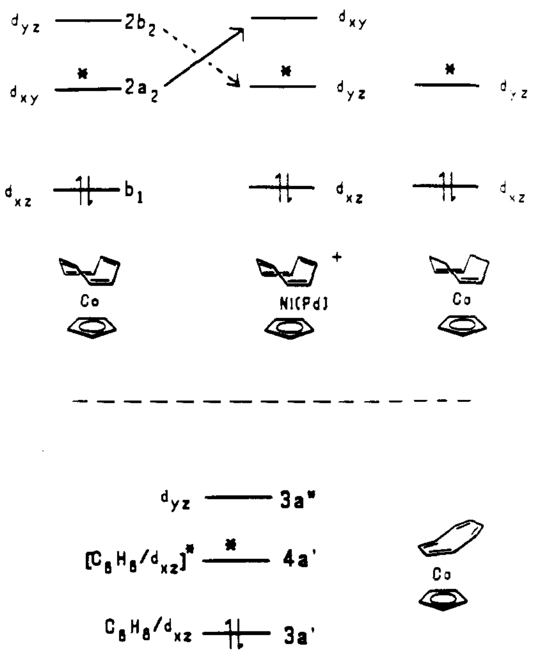

Figure 10. Sequence of energy levels proposed for pertinent orbitals of 18e⁻ 1,5-polyolefin compounds (top) and $CpCo(1,3\text{-}C_8H_8)$ (bottom). The redox orbital (LUMO of the 18e⁻ complex) is designated by an asterisk.

Role of Redox Orbital in ET-Induced Isomerizations. A relatively complete and consistent picture emerges for the isomeric preferences and electronic ground states of 19-electron cyclooctatetraene complexes of the later transition metals (Table V and Figure 10). Iron and cobalt radicals are found exclusively (to date) in the chair (1,3-) conformation. Nickel and palladium radicals prefer the tub (1,5-) conformation. ESR data on the Co complexes confirm earlier EHMO calculations[25] which predicted a **4a**′ SOMO containing some d_{xz} but predominantly C_8H_8 in character. The estimate of fractional metal character is 0.30 from the EHMO calculations and 0.40 from ESR results (**4** gives a pictoral representation of this orbital). When the metal fragment is changed from $CpCo^-$ to $(C_6Me_6)Co$, the same **4a**′ electronic ground state is found. There is somewhat greater metal character in the SOMO of the latter complex, 0.50 from the ESR results.

The surprising preference for the 1,5-conformation in 19e⁻ nickel complexes can be understood in terms of alteration of their electronic ground state compared to the Co (and, presumably, Fe) analogues. The lowering of the (mostly metal d_{yz}) $2b_2$ below the $2a_2$ gives the Ni radicals a SOMO like those of d⁹ $CpML_2$ complexes with simple diolefins, e.g., $CpCo(1,5\text{-}C_8H_{12})^-$,[54] $CpCo(\eta^4\text{-diene})^-$,[58] $CpNi(1,5\text{-}C_8H_{12})$,[48a] and $(C_5Ph_5)Pd$(dibenzo-1,5-cyclooctatetraene).[59] The amount of Ni character in the SOMO of $(C_5R_5)Ni(1,5\text{-}C_8H_8)$ is likely to be 0.7 or higher, based on analogy with the aforementioned radicals.

Perhaps most important to our understanding of the electron-transfer-induced isomerizations of this family of complexes, *occupancy of the $2a_2$ (d_{xy}, but mostly C_8H_8) orbital appears to be key to facilitating the tub- to chair-isomerization.* In Co complexes, this orbital lies *below* the $2b_2$ (d_{yz}) and is the SOMO of $CpCo(1,5\text{-}C_8H_8)^-$. In the M = Ni, Pd complexes, it lies *above* the $2b_2$ (d_{yz}) and is not involved in the reduction of $CpM(1,5\text{-}C_8H_8)^+$. This situation is summarized in Figure 10, and provides a rationalization for the striking differences between the Co and Ni group complexes in terms of tendencies to undergo ET-induced isomerizations.

In terms of 18-electron complexes, the structural assignments of the newly prepared cations $LM(C_8H_8)^+$: LM = $(C_6Me_6)Co^+$ to the 1,3-isomer **2** and LM = CpNi, Cp*Ni, and $(C_5Ph_5)Pd$ to the 1,5-isomer **1**, adds to empirical knowledge of the bonding preferences of $\eta^4\text{-}C_8H_8$ complexes. However, if there is a simple underlying determining factor in these preferences, it eludes the present authors. If the lowering of the metal d-orbital set is important in favoring the tub isomer, as expected for the more compact Ni(II) compared with Co(I), one might expect that the chair isomer **2** would be more highly favored for LM = CpRh than for LM = CpCo. Such does not appear to be the case, for thermally equilibrated samples of $(C_5R_5)Rh(C_8H_8)$ are reported to contain only the tub isomer **1**,[10i,60] whereas $(C_5R_5)Co(C_8H_8)$ exist as mixtures of both isomers.[11,12]

It is likely that the relative energies of the tub- and chair-bound isomers are determined by a delicate balance dependent on the comparative energies of the cyclooctatetraene orbitals and those of the LM fragment as well as the overlap possible between those orbitals. The cobalt complexes $(C_5R_5)Co(C_8H_8)$ are still the only ones known in which this energetic balance can be tipped in favor of either isomer depending on the electron count of the complex.

Finally we comment briefly on the reduction of the complex $(CO)_3Fe(C_8H_8)$. This complex remains as the 1,3-isomer in the process $(CO)_3Fe(C_8H_8)^{0/1-}$.[61] EHMO calculations suggested a LUMO identical to that of $CpCo(1,3\text{-}C_8H_8)$, with about 2/3 ligand (cyclooctatetraene) character.[25] Yet, the large decrease in ν_{CO} upon one-electron reduction brings the LUMO makeup into question.[24] These results may be reconciled on the basis that the changes in backbonding which lead to shifts in CO frequency are sensitive to the *charge density* (rather than *spin density*) on the metal (summed over *all* orbitals), whereas the makeup of the LUMO only addresses the contribution from *one* orbital.

Summary

The ESR results on the two formally 19-electron cobalt complexes, $CpCo(C_8H_8)^-$ and $(C_6Me_6)Co(C_8H_8)$, give quantitative support to the theoretical model[25] which ascribed the electron-transfer-induced isomerization of $CpCo(1,5\text{-}C_8H_8)$ to $CpCo(1,3\text{-}C_8H_8)^-$ to the presence of a cyclooctatetraene-based LUMO in the neutral complexes. It is found that the SOMO in the 19e⁻ Co complexes of the 1,3-isomer is delocalized over the C_8H_8 ring (major portion) and the metal (d_{xz}, minor portion). This is reminiscent of the redox orbitals of "noninnocent" metal dithiolenes[62] or cobaltacycles,[63] rather than those of systems with nonmixing metal and ligand orbitals, such as metal–bipyridyl complexes.[64]

Given the demonstrated strong preference for the 1,3-isomer in the Co complexes, we anticipated that analogous 19e⁻ complexes of the Ni group would also undergo electron-transfer-induced isomerizations in reductions of $CpM(1,5\text{-}C_8H_8)^+$, M = Ni, Pd, by one electron. Such is not the case. Instead, the 1,5-isomeric structure appears to be retained.

It is the nature of the redox orbital that seems to account for the difference in behavior in this series of isobal metal cyclooctatetraene radicals. When the LUMO of the 18e⁻ complex is predominantly ligand polyolefin-based, ET-induced isomerizations are more likely. Addition of 1e⁻ to the $2a_2$ LUMO of $CpCo(1,5\text{-}C_8H_8)$ leads to formation of the 1,3-isomer apparently owing to the greater ability of the latter to delocalize the extra electron onto the metal through overlap of the cyclooctatetraene orbital with the metal d_{xz}. The $2a_2$ orbital is destabilized in the Ni group complexes compared to the d_{yz} ($2b_2$) orbital. In this situation,

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J. Am. Chem. Soc. **1993**, *115*, 2323–2334 2323

one-electron reduction is essentially metal-based and results in a more traditional 19e⁻d⁹ complex lacking a high degree of delocalization onto the cyclooctatetraene ring, just as is obtained, for example, with simple metal–diolefin compounds.[65]

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Note Added in Proof. Koelle et al., in ref 48c, have recently interpreted the ESR spectra of $CpNi(C_8H_{12})$ in a $CpCo(C_8H_{12})$ matrix in terms of a metal d_{xz} ground state, with the d_{yz} level lying just below.

(65) Leading references to d^9 π-hydrocarbon complexes may be found in refs 25, 54, 58, and 59. Note that the possibility of electron-transfer-induced isomerization of a metal–cycloocta*diene* bond is raised in refs 11b, 25, and in Baghdadi, J.; Bailey, N. A.; Dowding, A. S.; White, C. *J. Chem. Soc., Chem. Commun.* **1992**, 170.

Synthesis, Structure, and Spectroscopic Properties of Chiral Rhenium Aromatic Aldehyde Complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}CHAr)]^+X^-$: Equilibria between π and σ Aldehyde Binding Modes

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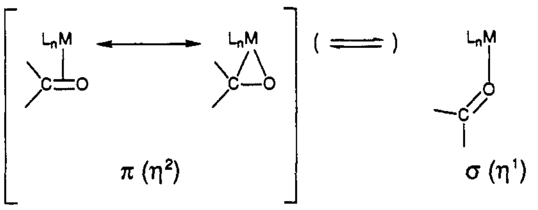
Abstract: Reactions of $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ and ArCHO (Ar = **a**, C_6F_5; **b**, 4-$C_6H_4CF_3$; **c**, 3-$C_6H_4CF_3$; **d**, 3-$C_6H_4OCH_3$; **e**, 2-$C_6H_4OCH_3$; **f**, 4-C_6H_4Cl; **g**, 4-C_6H_4F; **h**, 1-naphthyl; **i**, C_6H_5; **j**, 3,4,5-$C_6H_2(OCH_3)_3$; **k**, 4-$C_6H_4C_6H_5$; **l**, 4-$C_6H_4CH_3$; **m**, 2,4-$C_6H_3(OCH_3)_2$; **n**, 3,4-$C_6H_3(OCH_3)_2$; **o**, 4-$C_6H_4OCH_3$) give aromatic aldehyde complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O{=}CHAr)]^+BF_4^-$ (**4a–o**$^+BF_4^-$, 80–97%). IR analyses (CH_2Cl_2, 26 °C) show **4a–o**$^+BF_4^-$ to be >96:<4 to 15:85 mixtures of π/σ isomers (ν_{NO} 1745–1733/1701–1692 cm^{-1}). Electron withdrawing substituents (which enhance aldehyde π acidity and lower σ basicity) favor the π binding mode. Electron donating substituents have an opposite effect. The π/σ ratios increase in more polar solvents and at lower temperatures. Van't Hoff plots give ΔH (**4i,l,o**$^+BF_4^-$; $\pi \rightarrow \sigma$) of 3.6, 2.8, and 1.8 kcal/mol and ΔS of 9.2, 9.5, and 9.1 eu. IR features unique to both binding modes, and visible absorptions characteristic of σ isomers, are identified. Complex **4o**$^+PF_6^-$ crystallizes as a σ isomer, with a conjugated Ar/C=O linkage, a lengthened C=O bond (1.271 (8) Å), and a 0° N–Re–O–C torsion angle. This Re–O conformation maximizes overlap of the d orbital HOMO of the rhenium fragment with C=O π* orbital lobes on oxygen. The CPMAS ^{13}C NMR spectrum of **4m**$^+BF_4^-$ exhibits a HC=O resonance at 196.2 ppm, consistent with a σ binding mode.

Metal complexes of organic carbonyl compounds play critical roles in a variety of important processes: enzymatic transformations of carboxylic acid derivatives, aldehydes, and ketones;[1,2] biological ion transport;[3] homogeneously and heterogeneously catalyzed reactions of industrial feedstocks;[4] and numerous preparative catalytic transformations.[5] As such, the study of binding between metal fragments and organic carbonyl compounds is of considerable fundamental importance. Notably, diverse types of isomerism can occur. Of these, the most basic is *linkage* or π/σ (η^2/η^1) isomerism,[6] as illustrated in eq i.



(i)

A B C

Many π and σ transition-metal aldehyde and ketone complexes have been isolated.[7-9] Surprisingly, however, few quantitative studies of π/σ equilibria have been undertaken.[9,10] Such efforts

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