Nineteen-Electron Radicals of the Type (η^6-C$_6$Me$_6$)Co(η^4-diolefin): Electrochemistry and ESR Results

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A series of 18e cationic complexes of the type [(HMB)Co(η^4-diolefin)]$^+$ (HMB = η^6-C$_6$Me$_6$), in which diolefin = 1,3-cyclohexadiene, 1,3-cycloheptadiene, norbornadiene, and 1,5-cyclooctadiene, have been electrochemically reduced in nonaqueous solvents. Each complex has a reversible one-electron reduction to a persistent 19e radical with a formal reduction potential between −1.7 and −1.9 V vs Fc/Fc$^+$. ESR results suggest that the electronic ground states of the radicals have 60−70% metal character. The fact that the singly occupied MOs (SOMOs) of the radicals are virtually identical with those of 19e [CpCo(diolefin)]$^-$ analogues suggests that the arene retains η^6 coordination in the 19e radicals.

Introduction

In comparison to the many examples of complexes of the type (η^5-C$_5$R$_5$)CoL$_2$,[1] rather few isoelectronic analogues of composition [(η^6-arene)CoL$_2$]$^+$ are known.[2] We showed earlier[2a] that complexes of the latter (with arene = hexamethylbenzene, HMB) were accessible through the action of L$_2$ = diolefin on the 20e symmetrical sandwich complex [(η^6-C$_6$Me$_6$)$_2$Co]$^+$ in polar media (eq 1). The synthetic strategy is analogous to that employed

$$[(C_6Me_6)_2Co]^+ + \text{diolefin} \rightarrow$$
$$[(C_6Me_6)Co(\eta^4-\text{diolefin})]^+ + C_6Me_6 \quad (1)$$
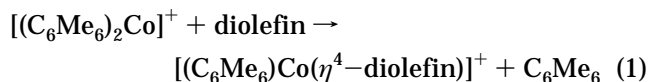
for the preparation of (η^6-arene)FeL$_2$ from 20e (η^6-arene)$_2$Fe.[3]

In this paper we describe aspects of the electron-transfer reactions of the 18e half-sandwich complexes [(HMB)Co(η^4-diolefin)]$^+$ (Chart 1; arene = hexamethylbenzene) as studied by electrochemistry. One-electron Nernstian reductions were observed by cyclic voltammetry (CV) and controlled-potential coulometry for the four complexes with diolefin = 1,3-cyclohexadiene (**1**), 1,3-cycloheptadiene (**2**), norbornadiene (**3**), and 1,5-cyclooctadiene (COD) (**4**). The resulting 19e neutral radicals were characterized by ESR spectroscopy and shown to have an electronic ground state similar to those of their [CpCoL$_2$]$^-$ analogues.

Experimental Section

Compounds. The 19e and 20e cobalt sandwich complexes [(HMB)$_2$Co]$^{2+}$ and [(HMB)$_2$Co]$^+$, respectively, were prepared

Chart 1

as their [PF$_6$]$^-$ salts by the Fischer method.[4] Commercially obtained polyolefins were passed down an alumina column before use. Electrochemical solvents and the supporting electrolyte ([NBu$_4$][PF$_6$]) were prepared as described earlier.[5] Other synthetic operations were performed using standard Schlenk procedures, employing dried and degassed solvents.

The four half-sandwich complexes described in this work were prepared in 80−90% purified yields by the reaction of excess diolefin with [(HMB)$_2$Co][PF$_6$] in propylene carbonate, followed by addition of diethyl ether, filtration, and recrystallization from dichloromethane/diethyl ether of the yellow to red salts, [(HMB)Co(η^4-polyolefin)][PF$_6$].[2a,6]

It was also possible to prepare the half-sandwich compounds without first isolating the 20e Co(I) Fischer complex. The 19e Co(II) complex [(HMB)$_2$Co]$^{2+}$ was dissolved in propylene carbonate along with an equimolar amount of cobaltocene and an excess of diolefin. Cobaltocene reduced the Co(II) complex to Co(I) and allowed the substitution of diolefin for one hexamethylbenzene in the sandwich complex. In the absence of cobaltocene, no reaction was observed between the Co(II) sandwich complex and the diolefin. While it obviates the need for separate preparation of [(HMB)$_2$Co]$^+$, this procedure was inferior because it gave precipitates contaminated with cobaltocenium ion.

Electrolytic preparations of the half-sandwich complexes were also possible. Typically, the reactant solution contained 20 mg of [(HMB)$_2$Co][PF$_6$]$_2$ and 1 mL of COD in 250 mL of

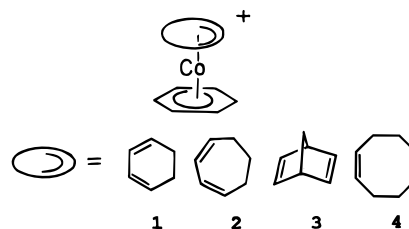† Present address: Eastman Kodak Co., Kodak Park, Rochester, NY.
⊗ Abstract published in *Advance ACS Abstracts,* April 1, 1996.
(1) Kemmitt, R. D. W.; Russell, D. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 5, p 244 ff.
(2) (a) Edwin, J.; Geiger, W. E. *Organometallics* **1984,** *3*, 1910. (b) L$_2$ = butadiene derivatives: Efraty, A.; Maitlis, P. *J. Am. Chem. Soc.* **1967,** *89*, 3744. Herberich, G.; Klein, W.; Kölle, U.; Spiliotis, D. *Chem. Ber.* **1992,** *125*, 1589.
(3) (a) Weber, S. R.; Brintzinger, H. H. *J. Organomet. Chem.* **1977,** *127*, 45. (b) Zenneck, U.; Suber, L.; Pritzkow, H.; Siebert, W. *Chem. Ber.* **1986,** *119*, 971.

(4) (a) Fischer, E. O.; Lindner, H. H. *J. Organomet. Chem.* **1964,** *2*, 222. (b) *J. Organomet. Chem.* **1964,** *1*, 307. (c) Crystal structure: Thompson, M. R.; Day, C. S.; Day, V. W.; Mink, R. I.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980,** *102*, 2979.
(5) Bowyer, W. J.; Geiger, W. E. *J. Am. Chem. Soc.* **1985,** *107*, 5657.
(6) Complexes **1** and **2** have not been previously reported. ^{1}H NMR data in CD$_2$Cl$_2$: **1**, δ 5.17 (q, 2 H), 3.17 (m, 2 H), 2.34 (s, 18 H), 1.44 (dd, 2 H), 0.68 (dd, 2 H); **2**, δ 4.87 (m, 2 H), 2.85 (m, 2 H), 2.27 (s, 18 H), 1.32 (m, 4 H), 1.05, (m, 1 H), 0.63 (m, 1 H). Anal. (Robertson Laboratories) Calcd for [**1**][PF$_6$]: C, 48.44; H, 5.87. Found: C, 48.29; H, 5.99. [**2**][PF$_6$]: C, 49.57; H, 6.13. Found: C, 49.37; H, 5.96.

propylene carbonate/0.1 M [NBu₄][PF₆]. The original CV's showed only the two waves of the Fischer sandwich complex at (vs Fc) +0.12 V (Co(II)/Co(I)) and −2.13 V (Co(I)/Co(0)). The applied potential of a Pt-basket working electrode was set to −0.6 V, sufficient to reduce the sandwich complex to its Co(I) state. As the electrolysis proceeded, periodic CV scans showed that the waves of the sandwich complex diminished and a new reversible wave grew in at $E_{1/2}$ = −1.70 V. The conversion was complete in ca. 75 min, and the reaction was essentially quantitative, judging from the CV wave heights of reactant and product. The wave at −1.70 V matches that of the isolated half-sandwich complex **4**.

Complex **4** was isolated from the electrolysis solution by addition of 90 mL of diethyl ether, filtration, dissolution of the solid residue in 3 mL of acetone, and reprecipitation with ether.

Physical Methods. Full descriptions of the electrochemical procedures and methodologies have appeared elsewhere.[5] Although the saturated calomel electrode was the operational reference electrode, all potentials reported in this paper have been referenced to the ferrocene/ferrocenium couple, as recommended by IUPAC.[7] ESR data were obtained on frozen solutions at temperatures between 77 and 150 K on a modified Varian E-4 spectrometer. Simulations of ESR spectra were run using a program described by Rieger.[8]

Results and Discussion

Electrochemistry. Each Co(I) diolefin complex undergoes one oxidation and one reduction in the potential range +1.5 to −2.5 V vs Fc. In all cases, the oxidation wave was irreversible; since it originated presumably from formation and decomposition of a dicationic 17e Co(II) species, the anodic process was not studied in detail. A second reduction process detected for complex **1** was irreversible in DMF and THF (E_{pk} = −2.7 to −2.8 V at v = 0.2 V/s). Experimental emphasis was given to the reversible Co(I)/Co(0) couple observed for these complexes, which will now be discussed.

The voltammetric behaviors of complexes **1−4** are essentially interchangeable with regard to the reduction of the 18e Co(I) monocations. Each complex displays an electrochemically and chemically reversible one-electron couple, the product of which is the 19e neutral radical (HMB)Co(η⁴-diolefin) (eq 2). The cyclohexadiene complex **1** serves as a model for discussion.

$$[(HMB)Co(\eta^4\text{-diolefin})]^+ + e^- \rightarrow$$
$$(HMB)Co(\eta^4\text{-diolefin}) \quad (2)$$
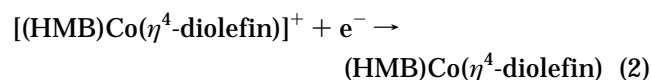
The reduction of **1** was studied in several nonaqueous solvents, including dichloromethane, THF, DMF, and propylene carbonate (PC). CV traces similar to those in Figure 1 were observed in each case. Over the scan rate (v) regime of 75 to 500 mV/s, the cathodic peak currents were exactly proportional to the square root of the scan rate; the anodic to cathodic current ratio was 1.02 ± 0.03, and the difference in cathodic and anodic peak potentials was virtually identical with that of ferrocene measured under the same conditions (e.g., for propylene carbonate solutions, 60 mV when v = 80 mV/s, 80 mV when v = 400 mV/s). These parameters and responses are diagnostic of essentially Nernstian chemically reversible one-electron couples.

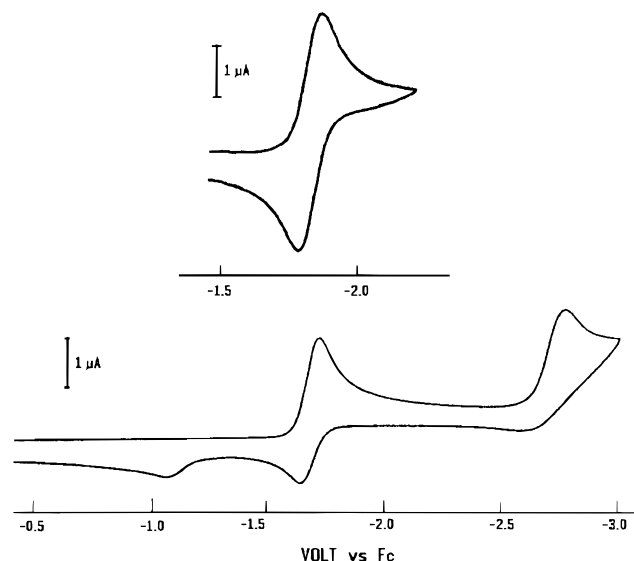The potentials of the 18e/19e couples are collected in Table 1 along with those of isoelectronic CpCo complexes

(7) Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1984**, *56*, 461.
(8) DeGray, J. A.; Rieger, P. H. *Bull. Magn. Reson.* **1987**, *8*, 95.

Figure 1. (Top) CV scan of 0.66 mM **1** in CH₂Cl₂/C₂H₄Cl₂ (Pt electrode, ambient temperature, v = 0.20 V/s). (Bottom) CV scan including the second reduction of **1** in DMF (Pt electrode, concentration 0.70 mM, ambient temperature, v = 0.20 V/s).

**Table 1. Formal Potentials of
[(C₆Me₆)Co(diolefin)]⁺ Complexes and Relevant
Analogues (Potentials vs Ferrocene⁰/⁺)**

diolefin, complex	solvent	$E_{1/2}$ (V) of 0/+ couple	E_{pk} of +/2+ wave
[(C₆Me₆)Co(diolefin)] Complexes			
1,3-C₆H₈, **1**	CH₂Cl₂	−1.83	+0.90
	THF	−1.73	
	DMF	−1.68	
	PC	−1.78	
1,3-C₇H₁₀, **2**	CH₂Cl₂	−1.74	+0.76
	PC	−1.62	
norbornadiene, **3**	CH₂Cl₂	−1.93	+0.86
	PC	−1.86	
1,5-C₈H₁₂, **4**	CH₂Cl₂	−1.71	+0.58
	PC	−1.68	
Other Relevant Co(I)/Co(0) Couples			
[(C₆Me₆)Co(1,3-C₈H₈)]⁺		−1.35[a]	
CpCo(1,3-C₈H₈)		−2.38[b]	
CpCo(1,5-C₈H₁₂)		ca. −3.0[b,c]	
CpCo(1,3-C₄H₂Ph₄)		−2.82[d]	
CpCo(1,3-C₇H₁₀)		−3.04[e]	

[a] Reference 12. [b] 0/1− couple.[13a] [c] Solvent dependent. [d] 0/1− couple.[13b] [e] 0/1− couple.[13c]

for comparison. A spread of ca. 200 mV is found for the four Co(I) arene complexes, with Co(I)/Co(0) couples falling in the range of −1.7 to −1.9 V vs Fc. These potentials are about 1 V more positive than those needed to reduce the analogous CpCo(η⁴-diolefin) complexes, reflecting no doubt the greater electron-withdrawing ability of the arene compared to the cyclopentadienyl anion.

The one-electron nature of the redox couple was confirmed by bulk coulometry at a Pt-basket electrode. Coulometric measurements were complicated only by a tendency of the 19e product to spontaneously reoxidize to the 18e cation on standing in solution. At least 90% conversion to each of the four 19e neutral radicals was achieved, however, with passage of 1 faraday of charge. In the course of the electrolyses, solutions turned from the red-orange of the Co(I) species to yellow, the apparent color of the 19e Co(0) species. CV and RPE
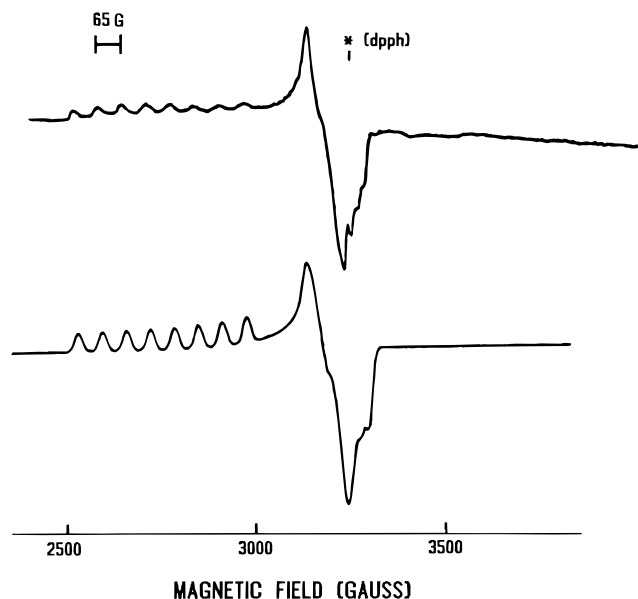
Figure 2. Experimental (top) and theoretical (bottom) ESR spectra of $(HMB)Co(C_6H_8)$ in a frozen glass. The experimental spectrum was obtained from a cathodically electrolyzed sample of **1** (0.66 mM in $CH_2Cl_2/C_2H_4Cl_2$) frozen at $T = 77$ K. The calculated spectrum was based on the values from Table 2, using a single line width of 10.5 G.

scans after completion of the electrolyses always gave byproduct waves smaller than 10% of the original wave heights. The Co(I)/Co(0) couple was judged to be largely uncomplicated, even on an electrolytic time scale.

Electron Spin Resonance Spectroscopy of 19e Complexes. Samples containing the 19e Co(0) samples were taken from electrolysis solutions for the purpose of ESR measurements. The electrolysis medium of choice was a 1:1 mixture of dichloromethane and 1,2-dichloroethane, which gives ESR-quality glasses, and in which the Co(0) complexes were stable. High-quality frozen-solution spectra were obtained in all cases, but repeated attempts to record fluid-solution spectra failed. It is most likely that the fluid-solution spectra are broadened beyond recognition by the rapid relaxation and rather large g-value anisotropies of the radicals.

Spectra of the cyclohexadiene complex $(HMB)Co(C_6H_8)$ and the cyclooctadiene complex $(HMB)Co(COD)$ are shown in Figures 2 and 3, respectively, along with the results of spectral simulations. All four radicals have nearly axial **g**-tensors with two g values much closer to the free spin value (Table 2). The largest cobalt hyperfine splitting (hfs) in each case accompanied the highest **g** component, as seen previously for other Co-(0) π-radicals.[9,10] The two smaller splittings could not be determined with great accuracy, owing to the large amount of overlap of lines in the centers of the spectra. We could with reasonable certainty, however, specify that errors of no more than 10×10^{-4} cm^{-1} are likely for the two smaller Co splittings, and on that basis we assign error limits to the covalency parameters in Table 3.

(9) (a) van Willigen, H.; Geiger, W. E.; Rausch, M. D. *Inorg. Chem.* **1977**, *16*, 581. (b) Connelly, N. G.; Geiger, W. E.; Lane, G. A.; Raven, S. J.; Rieger, P. H. *J. Am. Chem. Soc.* **1986**, *108*, 6219.
(10) The actual symmetry of the radicals cannot be higher than C_s, but the electronic structures of analogues have been adequately treated by assignment of C_{2v} symmetry.[11,12]
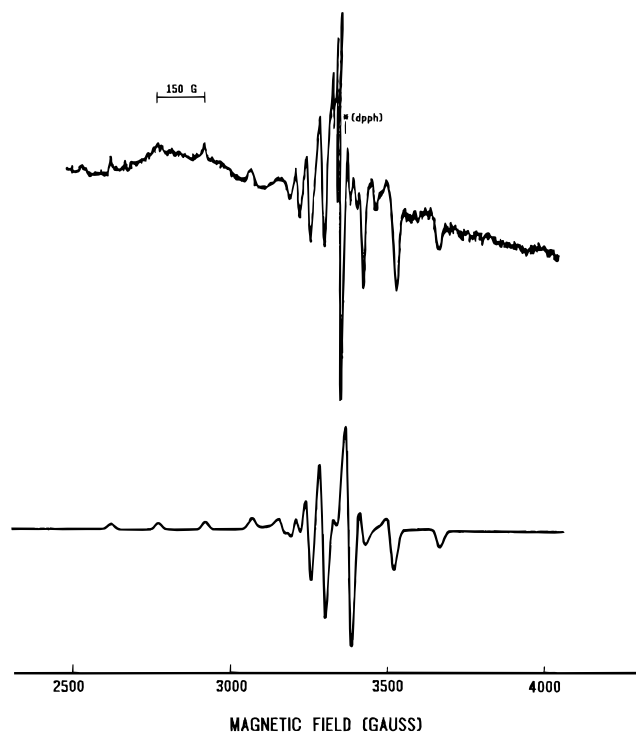

Figure 3. Experimental (top) and theoretical (bottom) ESR spectra of $(HMB)Co(COD)$. The conditions same as those of Figure 2, except that the concentration of **4** was 0.52 mM prior to electrolysis.

Table 2. ESR Parameters of 19e Co(0) Radicals in Frozen Glasses of 1:1 CH_2Cl_2: 1,2-$C_2H_4Cl_2$[a]

radical	g_1	g_2	g_3	$A(Co)_1$	$A(Co)_2$	$A(Co)_3$
Compounds Studied in This Work						
$(HMB)Co(C_6H_8)$	2.364	2.044	2.026	70	ca. 5	20
$(HMB)Co(C_7H_{10})$	2.398	2.088	2.068	74	ca. 5	17
$(HMB)Co(NBD)$[b]	2.132	2.043	2.010	148	ca. 10	ca. 10
$(HMB)Co(COD)$[b]	2.122	2.027	2.022	148	33	33
Relevant Analogues[11]						
$[CpCo(1,5-COD)]^-$	2.171	2.027	1.985	159	37	46
$[CpCo(1,3-COD)]^-$	2.151	2.027	1.997	139	36	38

[a] Hyperfine splittings are in units of 10^{-4} cm^{-1}; parameters are determined from a best fit of the simulated spectra. [b] Abbreviations: NBD = norbornadiene, COD = cyclooctadiene.

Table 3. Covalency Parameters, a^2, for Co(0) Radicals with Nominal d_{yz} Ground States, Computed from Eq 3 and Data in Table 2

radical	covalency factor	ref
$(HMB)Co(1,3-C_6H_8)$	0.65 ± 0.03	this work
$(HMB)Co(1,3-C_7H_{10})$	0.69 ± 0.03	this work
$(HMB)Co(NBD)$	0.71 ± 0.02	this work
$(HMB)Co(COD)$	0.61 ± 0.02	this work
$[CpCo(1,5-COD)]^-$	0.68	11
$[CpCo(1,3-COD)]^-$	0.59	11

The electronic ground state for Co(0) polyolefin radicals is expected to be of B_2 type if pseudo-C_{2v} molecular symmetry is assumed.[10-12] The primary contribution to this orbital is the metal d_{yz}. The ESR parameters reported for **1**−**4** are entirely consistent with this ground state, with one g value considerably greater than 2, the other two close to 2 and to each other, and the largest

(11) Rieger, P. H. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: Amsterdam, 1990; pp 290−294.
(12) Geiger, W. E.; Rieger, P. H.; Corbato, C.; Edwin, J.; Fonseca, E.; Lane, G. A.; Mevs, J. M. *J. Am. Chem. Soc.* **1993**, *115*, 2314.

metal hyperfine splitting along the high-g component, which is almost certainly g_x.[11,12]

A qualitative look at the major Co hfs (A_x) for radicals **1**−**4** (Table 2) reveals an appreciable spread in values, from 70 to 148 ($\times 10^{-4}$ cm^{-1}), which might be taken to indicate appreciable differences in metal spin densities in the half-filled orbitals of the four radicals. That this is *not* the case is shown by consideration of the entire set of ESR parameters, rather than just the A_x value.

Rieger has shown[11] that the metal contribution (i.e., the covalency factor) to the SOMO of Co(0) polyolefins with a B$_2$ ground state may be computed through eq 3, in which a^2 is the metal covalency factor, $\langle A \rangle$ is the isotropic hfs, $P = 282 \times 10^{-4}$ cm^{-1}, and $\Delta g_i = g_i - g_e$.

$$A_x - \langle A \rangle = P[-^4/_7 a^2 + ^2/_3 \Delta g_x - ^5/_{42}(\Delta g_y + \Delta g_z)] \quad (3)$$

We assume that all Co hfs values have the same sign. Although we cannot confirm this experimentally, owing to lack of observation of isotropic spectra, there is ample precedent for this assumption.[9,11,12] Otherwise, the largest error comes in the values of A_2 (A_y), the smallest of the three Co splittings; usually only estimated from our data owing to incomplete spectral resolution, these values are used to compute $\langle A \rangle$ ($=^1/_3(A_x + A_y + A_z)$). Since the uncertainties in A_2 (A_y) are rather small in the absolute sense, they do not lead to inordinately large imprecision in the covalency factors computed from eq 3, which are listed in Table 3.

These calculations show that the metal contribution to the SOMO is 60−70% for the series of four (hmb)-Co(diolefin) radicals, despite the rather large (doubling) of A_x(Co) through the series. Equation 3 provides a rationalization of this observation, for it shows that the computed metal contribution is sensitive to not only the metal hfs but also the g-value anisotropy. The two radicals (**1** and **2**) which have smaller Co hfs values have significantly larger values of g_x. Included for comparison in Table 3 are other radicals of relevance. The isoelectronic anion [CpCo(1,5-COD)]$^-$ fits into the general category of ca. $^2/_3$ metal contribution to the SOMO. For comparison, two cyclooctatetraene derivatives in these series, namely (HMB)Co(C$_8$H$_8$)[12] and [CpCo(1,3-C$_8$H$_8$)]$^-$,[12,13a] have SOMOs which are considerably more ligand-based, with metal covalency factors of ca. 0.4. The

two C$_8$H$_8$-containing radicals also differ in their ground states (A′), and the metal contribution is d$_{xy}$.

Conclusions

Eighteen-electron half-sandwich complexes of the type [(HMB)Co(η^4-diolefin)]$^+$ are readily formed by the displacement of an arene from the 20e complex [(HMB)$_2$Co]$^+$ in polar media, followed by η^4 coordination of a diolefin. The half-sandwich Co(I) complexes are reduced at moderate potentials in nonaqueous solvents to persistent 19e Co(0) complexes. The SOMO of the 19e complexes is of B$_2$ type, having the greatest contribution from the metal d$_{yz}$ orbital. Despite the fact that the major Co hyperfine splitting varies by a factor of 2 in the series **1**−**4**, calculations reveal very little difference in the amount of metal character in the SOMO.

Although the reduction potentials of the cationic complexes **1**−**4** are ca. 1 V more positive than those of their neutral analogues, CpCo(η^4-diolefin),[13] the ESR results on the two 19e families, namely (HMB)Co-(diolefin) and [CpCo(diolefin)]$^-$, show that the redox orbitals involved are of very similar composition, each having about $^2/_3$ metal d$_{yz}$ character. This effectively eliminates the possibility that the arene ligand in **1**−**4** has undergone slip-fold distortion[14] to a η^4 bonding mode, since different ESR characteristics might reasonably be expected for 17e cobalt−polyolefin radicals.[15] Evidence suggests, therefore, that the title radicals are genuine 19e complexes.[16]

(13) (a) Moraczewski, J.; Geiger, W. E. *J. Am. Chem. Soc.* **1981**, *103*, 4779. (b) Kelly, R. S.; Geiger, W. E. *Organometallics* **1987**, *6*, 1432. (c) Geiger, W. E.; Gennett, T.; Lane, G. A.; Salzer, A.; Rheingold, A. L. *Organometallics* **1986**, *5*, 1352.

(14) For leading references see: Pierce, D. T.; Geiger, W. E. *J. Am. Chem. Soc.* **1992**, *114*, 6063.

(15) To the best of our knowledge, no ESR data have been reported for Co(0) 17e systems. The closest example of which we are aware is that of a 17e cyclopentadienyl cobaltafluorenyl anion: Donovan, B. T.; Geiger, W. E. *J. Am. Chem. Soc.* **1988**, *110*, 2335.

(16) Geiger, W. E. *Acc. Chem. Res.* **1995**, *28*, 351.