volume data was analyzed graphically and the value of the pK_a was taken as the pH at the midpoint between the first and second end points. The estimated errors of reported pK_a values is ±0.02 pK_a units. Equilibrium constants for the reaction of Fe(TPP)Cl with ligand were determined at 25 °C by optical methods described previously.[4]

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Registry No. tMU, 70346-51-9; cMU, 88181-49-1; Fe(TPP)-$(ImH)_2SbF_6$, 80939-25-9; Fe(TPP)$(4MeImH)_2SbF_6$, 80939-26-0; Fe-(TPP)$(4PhImH)_2SbF_6$, 90388-44-6; Fe(TPP)$(tMU)_2SbF_6$, 90388-46-8; Fe(TPP)$(cMU)_2SbF_6$, 90457-44-6; Fe(TPP)$(1MeIm)_2SbF_6$, 90388-47-9; Fe(TPP)Cl, 16456-81-8; Fe(TPP)(SbF_6), 79949-97-6; Fe(TPP)-$(ImH)_2Cl$, 25442-52-8; Fe(TPP)$(cMU)_2Cl$, 90457-45-7; Fe(TPP)-$(tMU)_2Cl$, 90388-48-0; urocanic acid, 104-98-3.

Redox Chemistry of Cyclopentadienylcobalt Tetraazabutadienes. Characterization of 19-Electron Anionic Complexes

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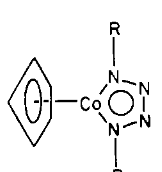
Abstract: The results of electrochemical and electronic and EPR spectroscopic studies on a series of novel 19-electron anionic complexes derived from reduction of neutral cyclopentadienylcobalt tetraazabutadienes—$CpCo(1,4\text{-}R_2N_4)$ (R = CH_3, C_6H_5, C_6F_5, 2,4-$F_2C_6H_3$, 2,6-$Me_2C_6H_3$; Cp = η^5-C_5H_5)—are reported. Investigation of the reduction process by cyclic voltammetry reveals a large dependence of the reduction potential on the nature of R. The reduction potentials are −1.53, −1.01, −0.71, −0.97, and −1.31 V, respectively, vs. the NHE in CH_3CN (0.1 M Bu_4NBF_4). Each anion displays an isotropic EPR spectrum (g = 2.16–2.21) at ambient temperatures characteristic of cobalt-centered radicals (a_{iso} = 50–58 G). The reduction of the neutral complexes has also been followed by electronic absorption spectroscopy, which reveals several isosbestic points in each case. All of the radical anion complexes exhibit a characteristic absorption ca. 1000 nm. Exposure of solutions containing the anion to air or O_2 results in essentially quantitative conversion of the anions to the corresponding neutral complexes. Observation of more than one Co-centered radical in the EPR spectrum of $CpCo[1,4\text{-}(C_6H_5)_2N_4]^-$ is interpreted in terms of the presence of different conformations of the aryl substituents for this compound.

Unsaturated metallacycles containing 1,4-disubstituted tetraazabutadienes[1-13] have attracted interest due to their novel bonding features. Attention has focused on the delocalization of π-electron density in the metallacycles and the role of the metal 3d orbitals in bonding. All of the compounds previously characterized are diamagnetic and obey the 18-electron rule,[14] with the exception of $CpNi(1,4\text{-}Ar_2N_4)$ [Ar = 4-MeC_6H_4, Cp = η^5-C_5H_5]. This neutral, 19-electron complex was isolated as a stable intermediate in the synthesis of $Ni(1,4\text{-}Ar_2N_4)_2$ from $Ni(Cp)_2$.[3] We report the results of electrochemical and optical and EPR spectroscopic studies of 19-electron anions derived from the reduction of the neutral compounds, $CpCo(1,4\text{-}R_2N_4)$ (R = CH_3,



C_6H_5, 2,6-$Me_2C_6H_3$, 2,4-$F_2C_6H_3$, C_6F_5). These complexes are the only 19-electron systems containing the cyclopentadienylcobalt moiety for which isotropic room-temperature EPR spectra are known. The chemical and electrochemical stability of the radical anions is also significantly greater than for other $(\eta^5\text{-}C_5H_5)Co$ derivatives. The results of these experiments are interpreted in the context of SCF–Xα–DV calculations on $CpCo(1,4\text{-}H_2N_4)$ and its anion. The reversible redox activity of these compounds is unique in the chemistry of metallacyclotetraazabutadienes and affords sensitive spectroscopic probes of the electronic structure of these compounds.

Experimental Section

Electronic absorption spectra were taken of ~1.0 mM solutions of complexes in THF (visible and UV regions) and of 5–10 mM solutions of the complexes in THF in the near-infrared region. The THF employed was freshly distilled from sodium benzophenone ketyl, and all manipulations were carried out under an atmosphere of prepurified nitrogen. The spectra were taken with a Schlenk tube that had been modified with

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two side arms, each connected to quartz spectral cells. Cells of 1-mm (UV-vis) and 1-cm (near IR) pathlength were employed in obtaining the spectra. Reductions of green to ochre-colored solutions of the neutral complexes were performed over Na/Hg amalgam in the Schlenk tube and decanted into the spectral cells. Reductions of 1 mM solutions were carried out until a constant spectrum was obtained. The color of the solutions of the anions ranged from orange to burgundy. The concentration of anion produced by reduction of 5–10 mM solutions for near-infrared experiments was accurately determined from the known extinction coefficients of absorptions in the visible region.

The chemical reversibility of the reductions was studied by exposing ~1.0 mM solutions of the anions to dry O_2 and comparing the resulting spectra with that of the corresponding neutral complex. All of the anions displayed 97–100% reversible oxidation by O_2 to the neutral complexes with the exception of $CpCo[1,4-(2,4-F_2C_6H_3)_2N_4]^-$, where the absorption at 467 nm in the neutral complex is shifted ~10 nm to lower wavelengths and *increases* slightly in intensity in the product obtained from reaction of the anion with O_2.

Electrochemical experiments were performed on solutions of the neutral complexes in 0.1 M solutions of Bu_4NBF_4 (Aldrich) in acetonitrile (distilled from CaH_2 under prepurified nitrogen) or dichloromethane (distilled from P_4O_{10} under prepurified nitrogen). Electrochemical measurements were made with a PAR Model 173 potentiostat/galvanostat, a Model 175 Universal programmer, a Model 179 digital coulometer, and a Model RE 0074 X-Y recorder. In all experiments the conventional three-electrode system was used. Cyclic voltammetry was performed on ~2 mM solutions of neutral complexes at a Pt-disk working electrode employing a Pt-wire auxillary electrode and a Ag|AgI|0.1 M Bu_4NI in CH_3CN reference electrode. The potential of the ferrocene/ferrocenium couple determined by this cell is +0.91 V in 0.1 M Bu_4NBF_4–acetonitrile solution and +0.99 V in 0.1 M Bu_4NBF_4–dichloromethane solution. The potentials reported were adjusted to the NHE reference electrode by using the potential of the ferrocene/ferrocenium couple in water (+0.400 V vs. NHE).[15] No IR compensation was employed. Alternatively, values of $E_{p_c} - E_{p_a}$ for the ferrocene/ferrocenium couple observed under experimental conditions are taken as representative of one-electron reversible redox processes.[15,16]

Constant potential coulometry was performed on ~1 mM solutions of complexes in 0.1 M Bu_4NBF_4–acetonitrile solution at a Pt-gauze working electrode using a Cu wire immersed in electrolyte solution as an auxillary electrode. The reference electrode described above was also employed. Potentials selected for coulometric measurements were at least 200 mV negative of a cathodic process and 200 mV positive of an anodic process.

EPR spectra were obtained for ~1 mM solutions of the complexes obtained either synthetically or electrochemically as described above. Except where noted, isotropic spectra were obtained from fluid solutions at ambient temperatures, and anisotropic spectra were obtained from frozen solutions at 77 K. The spectra were recorded on a Varian E-4 X-band spectrometer. Field calibrations were performed by using Mn^{2+} in MgO (A = 86.9 G) and external DPPH (g = 2.0037). Microwave frequencies were measured with a Hewlett-Packard Model X532B frequency meter.

The complexes $CpCo(1,4-R_2N_4)$ (R = CH_3, C_6H_5, $2,6-Me_2C_6H_5$, $2,4-F_2C_6H_3$, and C_6F_5) were prepared from $CpCo(CO)_2$ (Strem Chemicals) and RN_3 by previously published procedures.[12,17] Similarly, $(CO)_3Fe(1,4-Me_2N_4)$ was prepared from $Fe_2(CO)_9$ and CH_3N_3.[13] Samples of the *N*-aryl-*o*-benzoquinone diimines $CpCo[HNC_6H_3MeN(C_6H_3Me_2)]$ and $CpCo[HNC_6H_4N(C_6H_5)]$ were obtained from photochemical reactions of $CpCo[1,4-(2,6-Me_2C_6H_3)_2N_4]$ and $CpCo[1,4-(C_6H_5)_2N_4]$, respectively, as previously described.[12,18] Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Dibenzo-18-crown-6-sodium Cyclopentadienyl(1,4-diphenyltetraazabutadiene)cobaltate $[C_{20}H_{24}O_6Na][CpCo(1,4-(C_6H_5)_2N_4)]$. The solvents employed were freshly distilled from sodium benzophenone ketyl under prepurified nitrogen and freeze–pump–thaw degassed prior to use. All manipulations were carried out in an atmosphere of prepurified nitrogen by use of standard Schlenkware techniques.

A solution of $CpCo[1,4-(C_6H_5)_2N_4]$ (100 mg, 0.30 mmol) in 25 mL of THF was stirred over Na/Hg amalgam for 1.5 h. The resulting burgundy-colored solution was decanted from the amalgam and filtered through a sintered glass frit. A solution of dibenzo-18-crown-6 (110 mg, 0.30 mmol) in 20 mL of THF was added. Pentane (40 mL) was layered over the THF solution and the flask was left undisturbed for 2 days. The solution was then decanted from the brick-red crystalline product. Upon drying under vacuum the crystals fracture, presumably due to loss of solvent of crystallization; yield 76 mg (38%). A small second crop of crystals was obtained by layering additional pentane over the mother liquor. Anal. Calcd for $C_{37}H_{39}O_6N_4CoNa$: C, 61.92; H, 5.48; N, 7.81; Na, 3.20; Co, 8.21. Found: C, 59.70; H, 5.62; N, 7.02; Na, 3.00; Co, 7.77.

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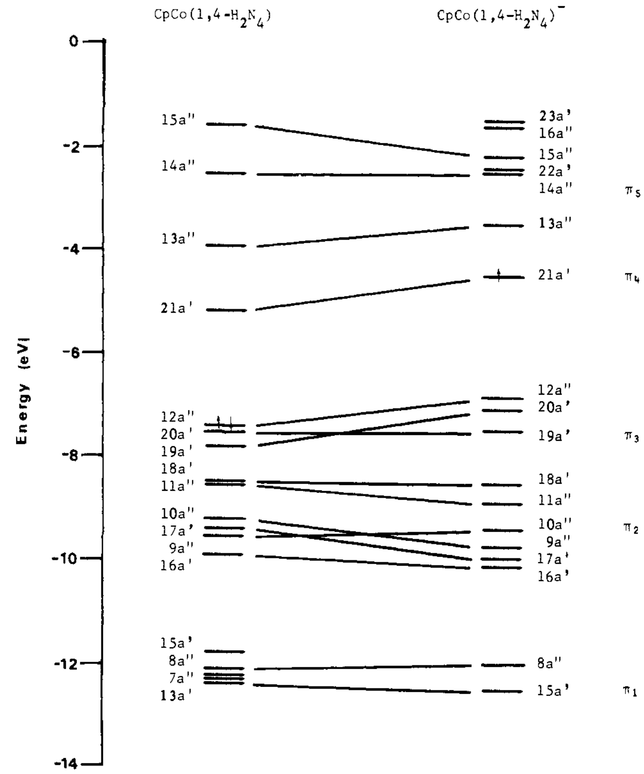

Figure 1. Molecular orbital energy level diagram for $CpCo(1,4-H_2N_4)^{0,-}$. The energy levels of the anionic compound were adjusted by setting the energy level of the lowest valence orbital (1a′) equal to that of the neutral compound.

Theoretical Studies. Calculations of the electronic structure of $CpCo(H_2N_4)$ and $CpCo(H_2N_4)^-$ employed the SCF–Xα–DV method at the l = 0 level for a least-squares potential.[19] Seven-fit functions were included in addition to the atomic radial densities. Exact HFS calculations were performed for the neutral atoms to generate numerical basis orbitals. Minimal basis sets were used for the light atoms, and Co 4s and 4p functions were added to augment its basis orbitals. Core 1s electrons on C and N and 1s, 2s, and 2p orbitals on cobalt were frozen in the molecular calculations. The geometric structure was idealized to mirror symmetry as described previously.[8] To simplify the calculations it was further assumed that the Cp carbons and hydrogens each belonged to a single potential type. The calculation for the radical anion was spin polarized to allow separate variational optimization of the spin-up and spin-down density.

The isotropic cobalt hyperfine (contact) splitting in the radical anion was estimated by taking the fractional orbital occupations for cobalt in the molecular calculation and using these to perform an atomic spin polarized hfs calculation. In this way core polarization could be accounted for with reasonable accuracy since the total s electron density at the nucleus was used to calculate the contact field.

Results and Discussion

Calculations. The results of the SCF–Xα–DV molecular orbital calculations on $CpCo(1,4-H_2N_4)^{0,-}$ are summarized in Table I and Figure 1. The occupation numbers of the Co 3d orbitals predicted for the neutral complex and the anion are 7.9 and 8.5, respectively. These values are most consistent with formal oxidation states of +I (d^8) and 0 (d^9) for the Co center in these molecules.

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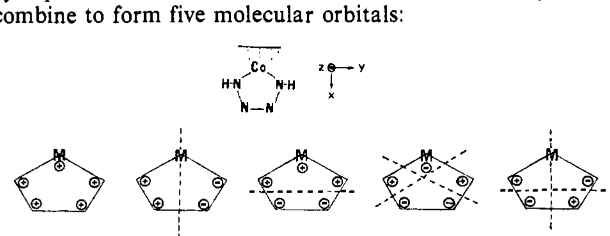
Table I. Valence Orbitals Calculated for $[CpCo(1,4\text{-}H_2N_4)]^{0,-}$

orbital			% Co[a]		% N_α[b]		% N_β				
C_s	C_{2v}	energy, ev	total	3d	2p	2s	2p	2s	% C	% H_N	% H_C
					$CpCo(1,4\text{-}H_2N_4)$						
15a″	a_2	−1.567	7	7	0	0	0	0	92	0	0
14a″	a_2	−2.511	2	2	29 (π)	0	68 (π)	0	1	0	0
13a″	b_1	−3.946	39	37 (d_{xy})	21	8	3	2	29	2	0
21a′	b_2	−5.166	35	35 (d_{xz})	29 (π)	0	11 (π)	0	26	0	0
12a″	a_2	−7.416	71	71 (d_{yz})	14 (π)	0	10 (π)	0	4	0	0
20a′	b_2	−7.452	17	16 (d_{xz})	37 (π)	0	21 (π)	0	25	0	0
19a′	a_1	−7.847	88	85 ($d_{x^2-y^2}$)	3	0	1	1	5	2	1
18a′	a_1	−8.454	67	61 (d_{z^2})	13	6	8	0	6	0	0
11a″	b_1	−8.535	1	0	16	0	23	16	44	1	0
10a″	b_1	−9.206	18	18 (d_{xy})	5	1	26	10	40	1	0
17a′	b_2	−9.430	34	33 (d_{xz})	2	0	5	1	58	0	1
9a″	a_2	−9.543	17	17 (d_{yx})	69 (π)	0	13 (π)	0	2	0	0
16a′	a_1	−9.895	35	31 (d_{z^2})	12	0	36	10	5	2	0
15a′	a_1	−11.784	3	0	2	1	4	0	89	0	0
8a″	b_1	−12.071	14	13 (d_{xy})	47	6	4	1	19	6	3
14a′	a_1	−12.141	0	0	0	0	1	0	78	0	21
7a″	b_1	−12.222	1	1	1	0	0	0	78	0	21
13a′	b_2	−12.262	0	0	24 (π)	0	66 (π)	0	7	0	2
					$[CpCo(1,4\text{-}H_2N_4)]^-$						
23a′	b_2	−1.537	50 ($4p_z$)	0	18 (π)	0	0	0	31	0	1
16a″	b_1	−1.661	49 ($4p_z$)	5	7	18	3	1	21	0	1
15a″	a_2	−2.210	11	11	13 (π)	0	26 (π)	0	49	0	0
22a′	a_1	−2.424	8	7	0	0	0	0	92	0	0
14a″	a_2	−2.484	1	1	18 (π)	0	41 (π)	0	40	0	0
13a″	b_1	−3.510	41	40 (d_{xy})	18	6	2	1	30	3	0
21a′	b_2	−4.532	45	45 (d_{xz})	26 (π)	0	7 (π)	0	21	0	0
12a″	a_2	−6.850	73	73 (d_{yz})	9 (π)	0	10 (π)	0	7	0	0
20a′	a_1	−7.105	89	86 ($d_{x^2-y^2}$)	1	0	2	1	4	2	1
19a′	b_2	−7.538	25	22 (d_{xz})	43 (π)	0	23 (π)	0	9	0	0
18a′	a_1	−8.531	71	63 (d_{z^2})	12	5	6	1	6	0	0
11a″	b_1	−8.859	5	5	22	1	40	22	9	1	0
10a″	a_2	−9.448	11	11 (d_{yz})	73 (π)	0	15 (π)	0	1	0	0
9a″	b_1	−9.749	8	7	4	0	6	1	79	1	0
17a′	b_2	−9.949	19	15 (d_{xz})	9	1	17	5	48	1	0
16a′	a_1	−10.140	31	27 (d_{z^2})	8	0	20	6	34	1	0
8a″	b_1	−12.024	18	17 (d_{xy})	52	8	6	2	5	9	0
15a′	b_2	−12.488	1	1	24 (π)	0	74 (π)	0	1	0	0

[a] The coordinate system for the Co orbitals is given in the text. [b] α denotes the N bound to cobalt and β those not bound.

The HOMO predicted for the neutral complex (12a″) is largely a Co d_{yz} orbital and differs slightly from the energy ordering of an earlier calculation.[8] The LUMO (21a′) for this complex is a metallacycle π^* orbital with ~35% Co d character. It is this orbital which accepts the additional electron, acquired upon reduction of the neutral complex, and becomes the HOMO of the anion. The metal character of this orbital is increased ~10% in the anion. The LUMO of $CpCo(1,4\text{-}H_2N_4)^-$ is predicted to be the 13a″ orbital which contains significant Co d character and is best described as a Co–N σ^* orbital.

The presence of a pair of electrons on the metal of π symmetry with respect to the tetraazadiene moiety allows this metallacycle to be viewed as a (4 + 2)-π-electron system in analogy with cyclopentadienide ion.[10] The atomic orbitals of π symmetry combine to form five molecular orbitals:



π_1 π_2 π_3 π_4 π_5

These are identified for $CpCo(1,4\text{-}H_2N_4)^{0,-}$ in Figure 1. Inspection of the molecular orbital energy level diagram (Figure 1) reveals that the acceptor orbital in the reduction of $CpCo(1,4\text{-}H_2N_4)$ corresponds to π_4. Although the d_{xz} orbital may participate in π bonding in the π_1, π_3, and π_4 orbitals, significant metal 3d character is found only in π_3 and π_4. The Co d_{yz} orbital has the proper symmetry to participate in bonding to π_2 and π_5 in a δ fashion. However, only a small amount of Co d character is found in π_2, and none is found in π_5. As one might expect on the basis of overlap, the δ interaction does not appear to be a significant factor.

Electronic Absorption Spectra. The neutral $CpCo(1,4\text{-}R_2N_4)$ complexes in THF display three low-energy maxima in the 700–300-nm region of the spectrum, near 650, 450, and 350 nm. these bands are essentially insensitive to solvent polarity and do not differ substantially from spectra reported in benzene, toluene, and methanol solvents.[8] In addition to the three low-energy bands, a band near 250 nm is observed, usually as a shoulder on an intense higher energy transition. The SCF–Xα–DV theoretical model provides some insight into the nature of these transitions. Several absorptions are predicted in the 2–4-eV energy range, all of which would be allowed for this low-symmetry molecule. If we make the assumption of C_{2v} pseudosymmetry, then some of the predicted transitions can be ruled out by symmetry selection rules. Other transitions between molecular orbitals localized on very different parts of the molecule (e.g., Cp and metallacycle π orbitals) are not expected to be very intense. The remaining allowed transitions are expected to contribute to the observed spectra. Comparing the spectra predicted for $CpCo(1,4\text{-}H_2N_4)$ with that observed for $CpCo(1,4\text{-}Me_2N_4)$ in THF solution leads to the tentative assignments contained in Table III. The lowest energy transition of $CpCo(1,4\text{-}Me_2N_4)$ is expected to be a combination of two transitions, one a d → π^* transition and the other a metallacycle $\pi \rightarrow \pi^*$ transition. The most intense visible absorption (428 nm) is assigned to a combination of two d → π^* transitions. This assignment differs from the earlier assignment of this band as a $\pi \rightarrow \pi^*$ transition. (This $\pi \rightarrow \pi^*$ transition is now assigned to

Table II. Electronic Absorption Spectra of $[CpCo(1,4-R_2N_4)]^{0,-}$ (1700–220 nm)

R	solvent	neutral complex λ_{max}, nm	(ϵ, M^{-1} cm^{-1})[a]	anionic complex λ_{max}, nm	(ϵ, M^{-1} cm^{-1})	isosbestic points,[b] nm	% reversibility[c] at λ (nm)
CH_3	THF	623	(246)	1175	sh	579, 495, 381, 243	99 (428)
		428	(7650)	926	(57)		
		338	(1860)	520	sh		
		252	sh	407	(2080)		
		230	(22220)	310	sh		
				250	(16700)		
2,6-$Me_2C_6H_3$	THF	634	(327)	1100	sh	585, 506, 401	100 (445)
		445	(5450)	1000	(58)		
		342	(3030)	526	(680)		
		280	sh	403	(2300)		
				335	sh		
				255	sh		
	CH_3CN[d]			530	sh		
				412	(2630)		
				350	sh		
				260	sh		
C_6H_5	THF	669	(860)	1012	(189)	630, 533, 384, 293, 221	98 (471)
		471	(7520)	569	(2300)		
		390	sh	474	sh		
		270	(20900)	451	(2160)		
				345	(20300)		
				255	(14900)		
2,4-$F_2C_6H_3$	THF	658	(680)	1040	(165)	611, 524, 283	partly irreversible (see text)
		467	(7720)	539	(1890)		
		359	(4500)	330	sh		
		267	(21600)	299	(17100)		
		234	sh	260	(21000)		
C_6F_5	THF	656	(523)	1084	(146)	598, 521, 403, 282, 255, 240	97 (467)
		467	(6740)	986	sh		
		342	(3520)	533	(1720)		
		255	sh	328	(9320)		
				292	(13500)		
				240	sh		
$CpCo(CO)_2$	THF	395	(378)				
		339	(929)				
		293	(4910)				
		248	(10000)				
		231	(9940)				

[a] sh = shoulder. [b] Isosbestic points observed during the reduction of the neutral complexes over Na/Hg amalgam. [c] % reversibility = [(100%)(absorbance for anion + O_2) − (absorbance before reduction)]/(absorbance before reduction). [d] Produced by electrolysis in 0.1 M Bu_4NBF_4–CH_3CN solution.

the lowest energy absorption at 623 nm). The third low-energy transition (338 nm) is assigned to a combination of two d $\rightarrow$ Co–N σ^* transitions.

The number of allowed transitions predicted at higher energies makes the assignment of the shoulders at 252 nm (4.92 eV) impossible from the calculations alone. However, it is likely that this shoulder is at least in part a metallacycle $\pi \rightarrow \pi^*$ transition (20a′ $\rightarrow$ 14a″) predicted at 4.94 eV. The assignments suggested are the most consistent ones in the framework of the Xα calculation. They should only be taken as rough guide because of the large number of possible transitions.

Stirring THF solutions of the neutral complexes over Na/Hg amalgam leads to the formation of the corresponding anions. The reductions are accompanied by a color change from green to red and exhibit several isosbestic points in the absorption spectra (see Figure 2 and Table II). The electronic absorption spectra of the anions (Table II) display a broad, weak, low-energy absorption in the near infrared (sometimes a shoulder is also present) and four additional maxima. These maxima occur in the 570–520-, 330–450-, 280–350, and 240–260-nm regions of the spectra. The spectrum obtained for $CpCo[1,4-(2,6-Me_2C_6H_3)_2N_4]^-$ produced electrochemically in 0.1 M Bu_4NBF_4–acetonitrile solution is essentially unchanged from that observed in THF and demonstrates the insensitivity of the four bands in the UV–visible portion of the spectra of this compound to solvent polarity. Although similar absorptions are observed for the anions and the neutral compounds, the transitions involved are not in general the same. The electronic absorption spectrum predicted for $CpCo(1,4-H_2N_4)^-$ from the Xα calculations and the electronic absorption spectrum of $CpCo(1,4-Me_2N_4)$ serve as guides for the assignment of the spectrum

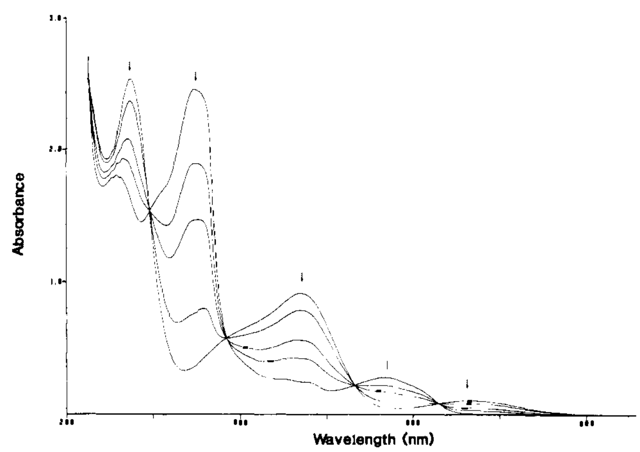


Figure 2. Electronic absorption spectral changes during the reduction of $CpCo[1,4-(C_6H_5)_2N_4]$ in THF (1.22 mM) over Na/Hg amalgam using a 1-mm cell.

of $CpCo(1,4-Me_2N_4)^-$ (see Table III). The near-infrared maximum (926 nm) is assigned to the 21a′ $\rightarrow$ 13a″ transition. This transition is symmetry forbidden, consistent with the low intensity observed. The energy predicted for this transition (1.22 eV) agrees well with the energy of the observed absorption (1.34 eV) and provides support for the reliability of the theoretical model. In actuality it was the prediction of a low-energy optical transition in the anion radical that prompted us to examine the near-IR spectra region. The alternative assignment of the near-IR tran-

Table III. Electronic Transitions Predicted for $[CpCo(1,4\text{-}H_2N_4)]^{0,-}$ (0–4 eV)

transition	E(predicted), eV	C_{2v} selection rule	E(obsd),[a] eV
	$CpCo(1,4\text{-}H_2N_4)$		
12a″ → 21a′	2.25	allowed	1.99
20a′ → 21a′	2.29	allowed	
19a′ → 21a′	2.68	allowed	2.90
18a′ → 21a′	3.29	allowed	
11a″ → 21a″	3.36	forbidden	
12a″ → 13a″	3.47	allowed	
20a″ → 13a″	3.51	forbidden	3.67
19a′ → 13a″	3.90	allowed	
10a″ → 21a′	4.04	forbidden	
	$[CpCo(1,4\text{-}H_2N_4)]^-$		
21a′ → 13a″	1.23	forbidden	1.06
			1.34
21a′ → 14a″	2.05	allowed	
21a′ → 22a′	2.11	allowed	
21a′ → 15a′	2.32	allowed	
12a″ → 21a′	2.32	allowed	2.38
20a′ → 21a′	2.13[b]	allowed	
21a′ → 16a″	2.87	forbidden	
21a′ → 23a′	3.00	allowed	
19a′ → 21a′	3.01	allowed	3.05
12a″ → 13a″	3.34	allowed	
20a′ → 13a″	3.60	allowed	
18a′ → 21a′	4.00	allowed	4.00
19a′ → 13a″	4.03	forbidden	

[a]Observed for $[Cp(Co(1,4\text{-}Me_2N_4)]^{0,-}$ in THF. [b]Calculated by using transition-state approximation.

sition to a dimer, perhaps derived from metal–metal bond formation between two 19-electron complexes, was rejected because of the persistence of the transition in the sterically blocked compound, $CpCo[1,4\text{-}(2,6\text{-}Me_2C_6H_3)]^-$.

Using the same strategy employed for the neutral compounds, the tentative assignment of the remaining transitions of $CpCo(1,4\text{-}Me_2N_4)^-$ is made. The absorptions at 520 nm are assigned to either or both of two d → π* transitions. One of these transitions (12a″ → 21a′) was involved in the 623-nm absorption of the neutral molecule and has increased slightly in energy. The other (20a′ → 21a′) was involved in the 428-nm absorption in the neutral molecule and decreased slightly in energy. The absorption at 407 nm is assigned to the π → π* transition involved in the 623-nm absorption in the neutral molecule. The absorption at 310 nm is assigned to the d → π* transition assigned to the 420-nm absorption in $CpCo(1,4\text{-}Me_2N_4)$. The remaining feature at 250 nm (4.96 eV) probably involves the 10a″ → 21a′ metallacycle π → π* transition predicted at 4.92 eV.

Upon exposure to O_2, the red color of the anions instantly reverts to the green to ochre color of the corresponding neutral compounds. In all cases the spectrum of the neutral compound is obtained. The reversibility of the reduction was quantified by the intensity of the maximum observed near 450 nm upon oxidation of the anions by O_2 (see Table II). Only in the case of $CpCo[1,4\text{-}(2,4\text{-}F_2C_6H_3)_2N_4]^-$ did the spectrum obtained after reaction with O_2 differ slightly from that expected for the neutral compound, indicating some irreversibility in the redox process. All of the other complexes exhibited nearly quantitative reversibility. We also found that UV irradiation of the anions in the presence of an electron acceptor such as chlorobenzene led to rapid photooxidation back to the neutral complex.

EPR Spectra

The parameters from the EPR spectra of the anions are similar (Table IV) to those of other Co(I) centered radicals[20-23]

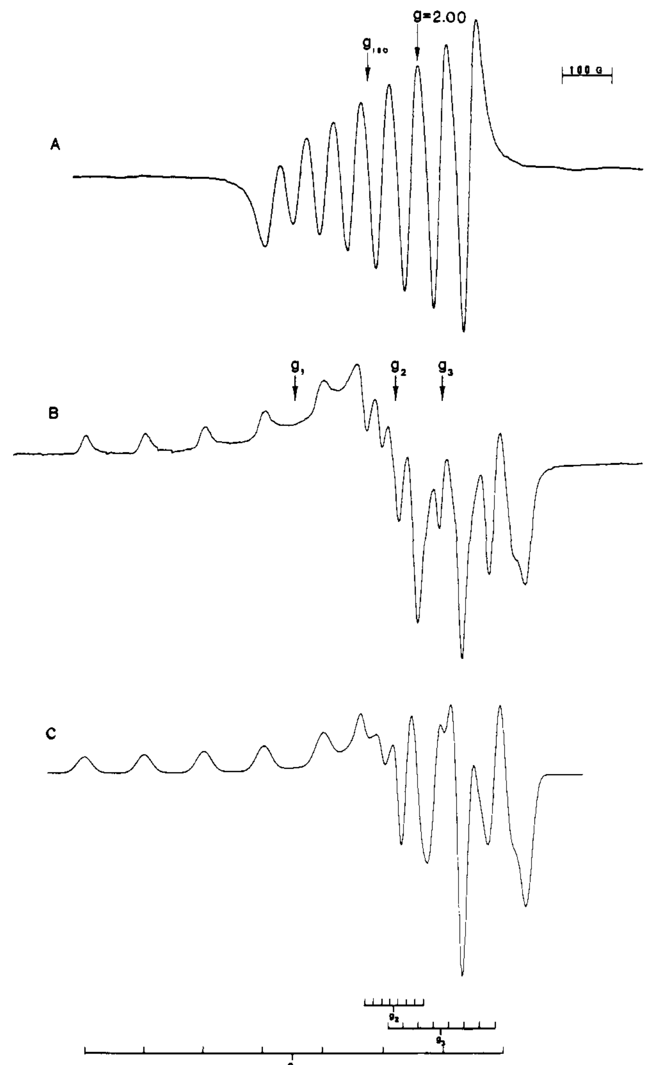


Figure 3. EPR spectra for $CpCo(1,4\text{-}Me_2N_4)^-$ in THF: (A) isotropic spectrum from fluid solution at ambient temperature; (B) anisotropic spectrum from a frozen solution at 77 K; (C) computer simulation, using Gaussian line shapes, of (B). Parameters: g_1 = 2.161, g_2 = 2.022, g_3 = 1.967; A_1 = 121.9 G, A_2 = 17.0 G, A_3 = 31.0 G.

[$(CpCoCOT)^-$ is a ligand-centered radical][21] with the unpaired electron in a 3d orbital other than d_{z^2} [$Co(CO)_4^-$ contains the unpaired spin in a d_{z^2} orbital].[23] Isotropic spectra were obtained for each anion from fluid solutions at ambient temperatures. These solutions are stable indefinitely in the absence of air, but immediate loss of the EPR signal is observed upon exposure to air. The isotropic spectrum of $CpCo(1,4\text{-}Me_2N_4)^-$ (Figure 3) is representative of all the isotropic spectra except that the line-width anisotropy is much more pronounced in the 1,4-diaryl substituted compounds. In every case, eight lines attributable to hyperfine interaction with ^{59}Co ($I = ^7/_2$) are observed. The anisotropic glass spectra (see Figures 3 and 4) are best described as rhombic where the eight ^{59}Co hyperfine lines associated with each of the three g values overlap to a large extent. Powder samples of $[C_{28}H_{24}O_6Na][CpCo(1,4\text{-}(C_6H_5)_2N_4)]$ display a rhombic spectrum with g_1 = 2.22, g_2 = 2.06, and g_3 = 1.98. Further, a simulation[24] of the anisotropic spectrum of $CpCo(1,4\text{-}Me_2N_4)^-$ (Figure 3) was only possible assuming a rhombic set of parameters (see Table IV and Figure 3). The simulation also dictates that all three hyperfine coupling constants have the same sign. That this is the

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(21) Albright, T. A.; Geiger, W. E., Jr.; Moraczewski, J.; Tulyathan, B. *J. Am. Chem. Soc.* **1981**, *103*, 4787–4794.
(22) van Willigen, H.; Geiger, W. E., Jr.; Rausch, M. D. *Inorg. Chem.* **1977**, *16*, 581–584.
(23) Hanlan, L. A.; Huber, H.; Kundig, E. P.; McGarvey, B. R.; Ozin, G. A. *J. Am. Chem. Soc.* **1975**, *97*, 7054–7068.
(24) Spectral simulation was achieved by using SIM 14 (obtained from Professor B. M. Hoffman, Chemistry Department, Northwestern University), and is limited to two line widths (g_1, g_2 = g_3).

Table IV. EPR Data for $CpCo(1,4\text{-}R_2N_4)^-$ Complexes and Related Compounds[a]

compd	solvent	g_{iso}	a_{iso}	g_1	g_2		g_3	A_1, G	A_2, G		A_3, G	ref
$CpCo(1,4\text{-}Me_2N_4)^-$	THF	2.055	57.9	2.161	2.022[b]		1.967[b]	121.9	17[b]		30[b]	this work
$CpCo[1,4\text{-}(2,6\text{-}Me_2C_6H_3)_2N_4]^-$	THF	2.061	56.3	2.178		ca. 2.0		119		ca. 46		this work
	CH_3CN[c]	2.065	56.1									this work
$CpCo[1,4\text{-}(C_6H_5)_2N_4]^-$	THF[d]	2.078	50.2	2.211		ca. 2.0		109		ca. 50		this work
	THF[e]			2.21				109				this work
				2.17				102				this work
	CH_3CN[c]	2.076	50.5									this work
$CpCo[1,4\text{-}(2.4\text{-}F_2C_6H_3)_2N_4]^-$	THF	2.070	51.6	2.204		ca. 2.0		111		ca. 44		this work
$CpCo[1,4\text{-}(C_6F_5)_2N_4]^-$	THF	2.066	51.7	2.214		ca. 2.0		111		ca. 46		this work
$CpCo(CO)_2^-$	MTHF[f]			2.005		2.004		172		45		20
$CpCo(1,5\text{-}COD)^-$	DMF (163 K)			2.165		ca. 2.0		158		ca. 50		21
$CpCo(1,3\text{-}COD)^-$	THF (153 K)			2.189		ca. 2.0		140		ca. 42		21
$CpCo(1,3\text{-}COT)^-$	THF (153 K)			2.196	2.002		1.946	46	41		41	21
CpCo(tpc)	MTHF (100 K)			2.103	2.025		1.906	144	41		57	22
$Co(CO)_4^-$	CO matrix (6 K)			2.007		2.128		58		55		23

[a] Isotropic spectral data obtained at ambient temperature; anisotropic data collected at 77 K unless otherwise noted. [b] From spectral simulation. [c] Generated electrochemically in 0.1 M Bu_4NBF_4. [d] Frozen slowly. [e] Frozen rapidly. [f] MTHF = 2-methyltetrahydrofuran.

case is confirmed by the average of the three hyperfine coupling constants (56.7 G), which is close to a_{iso} obtained from the EPR spectrum of a fluid solution (57.9 G). The calculated Fermi contact hyperfine splitting for $CpCo(H_2N_4)^-$ is 80 G on the basis of SCF–Xα–DV theory. Most of the splitting can be attributed to core polarization. The excess spin density in the cobalt 1s, 2s, 3s, and 4s orbitals was calculated to be −0.012, −0.288, +0.128, and −0.042 e^2/a_o^3, respectively. Quantitatively the agreement between theory and experiment is good when one considers the small population (−0.008 e) of the valence 4s orbital responsible for the core polarization and contact splitting. For example, the contact hyperfine splitting for atomic cobalt is 1273 G.[26] The orbital containing the unpaired spin in the anions is calculated from the EPR data given in Table IV to be ~60% Co 3d.[25] This is also in reasonable agreement with the results of the SCF–Xα–DV calculations on the model complex $CpCo(1,4\text{-}H_2N_4)^-$, which predict that the analogous orbital is ~45% Co. This value compares with 56% Co 3d character calculated for $CpCo(CO)_2^-$ and is further evidence[10] that the π-acceptor ability of the tetraazabutadiene ligand is comparable to two CO ligands. The anisotropy in the g values ($g_1 > g_2$, g_3) indicates that the 3d character of the orbital containing the unpaired spin is not d_{z^2} and is consistent with the prediction that this orbital contains Co d_{xz} character.

When frozen THF samples of $CpCo[1,4\text{-}(C_6H_5)_2N_4]^-$ were prepared by plunging the quartz tubes containing the samples into liquid nitrogen, the EPR spectrum of more than one Co(I) species is observed (Figure 4). We performed a variable-temperature study and showed that only one Co(I) spectrum was obtained from solutions that were cooled slowly. This may indicate the presence of different conformations of the 1,4-aryl substituents which freeze out during rapid cooling; however, a ring-opened form (azido nitrene) such as that suggested by Overbosch et al.[6] cannot be ruled out. The g_1 values show a smooth increase as the electron-withdrawing character of the 1,4-substituent is increased, with the expection of $CpCo[1,4\text{-}(C_6H_5)_2N_4]^-$ which has a g_1 value comparable with that of $CpCo[1,4\text{-}(C_6F_5)_2N_4]^-$. The crystal structure of $CpCo[1,4\text{-}(C_6F_5)_2N_4]$ reveals that the perfluorophenyl rings are roughly perpendicular to the metallacycle,[8] preventing significant π delocalization onto the aryl substituents. This configuration may arise from steric restraints imposed by the ortho

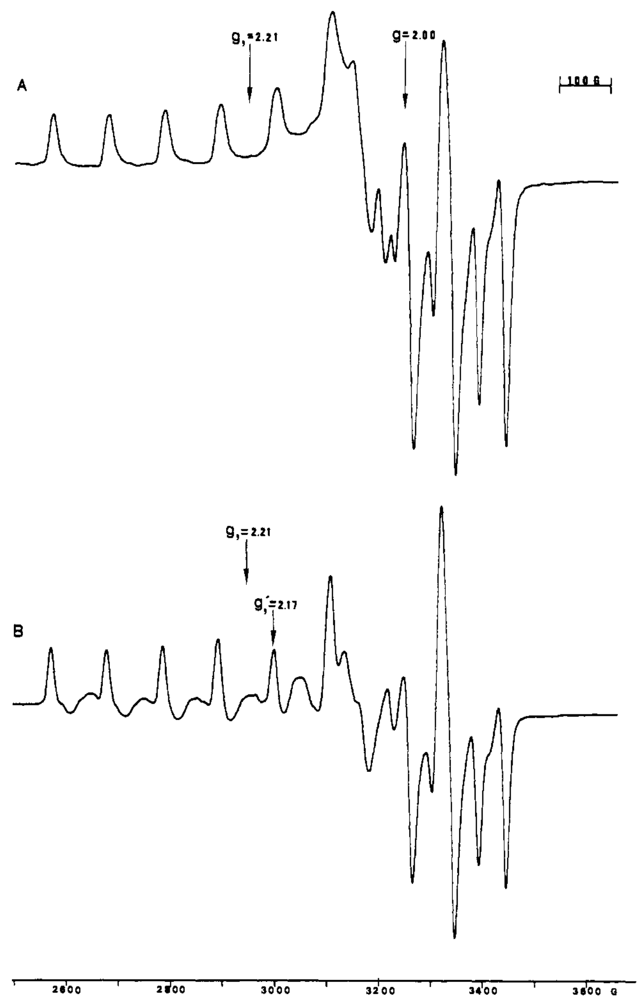

Figure 4. Anisotropic EPR spectra for $CpCo[1,4\text{-}(C_6H_5)_2N_4]^-$ in a frozen THF solution at −165 °C: (A) frozen slowly; (B) frozen by plunging into liquid N_2, then warming to −165 °C.

fluorine substituents and is presumed to be the case for the other ortho-substituted xylyl derivative. If the unsubstituted aryl rings in the phenyl complex were allowed to be coplanar with the metallacycle, the delocalization that might be achieved would increase the electron-withdrawing character of the ligand and would be reflected in an abnormally large value of g_1. On this basis, the features associated with g_1 = 2.211 for $CpCo[1,4\text{-}(C_6H_5)_2N_4]^-$ are assigned to conjugated phenyl substituents that are slightly more energetically favored than nonconjugated phenyl substituents. These are observed to the exclusion of the nonconjugated form(s) when the sample is cooled very slowly. the

(25) Using an axial approximation and equations described in: Goodman, B. A.; Raynor, J. B. *Adv. Inorg. Chem. Radiochem.* **1970**, *13*, 135–362.

$$2B = \frac{A_\parallel - a_{iso}}{1 - \frac{7}{4}\Delta g_\parallel - \frac{3}{4}\Delta g_\perp} \simeq \frac{A_\parallel - a_{iso}}{1 - \frac{7}{4}\Delta g_\parallel}$$

when $g_\perp \simeq 2.0$. % d character = $2G/2B°$. $^{59}Co - 2B° = -152.3$ G. Froese, C. *J. Chem. Phys.* **1966**, *45*, 1417.

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Table V. Electrochemical Data for the Most Negative Redox Process of $CpCo(1,4\text{-}R_2N_4)$ Complexes and Related Compounds

compd	solvent[a]	scan rate, mV/s	$E^{\circ\prime}$,[b] V	$E_{p_c} - E_{p_a}$,[c] mV	I_{p_a}/I_{p_c}
$CpCo(1,4\text{-}Me_2N_4)$	CH_3CN	1000	−1.52	215	0.9
		500	−1.52	178	0.9
		200	−1.53	116	0.9
		100	−1.53	98	1.0
		50	−1.54	84	1.0
		20	−1.54	81	1.0
	CH_2Cl_2	1000	−1.58	202	0.9
		500	−1.57	163	0.9
		200	−1.57	134	0.9
		100	−1.57	116	1.0
		50	−1.57	100	1.0
		20	−1.57	100	1.1
$CpCo[1,4\text{-}(2,6\text{-}Me_2C_6H_3)N_4]$	CH_3CN	1000	−1.32	104	1.1
		500	−1.31	90	1.0
		200	−1.31	78	1.0
		100	−1.31	73	1.1
		50	−1.31	67	1.1
		20	−1.31	65	1.1
	CH_2Cl_2	1000	−1.42	175	0.7
		500	−1.42	152	0.7
		200	−1.41	120	0.7
		100	−1.40	104	0.8
		50	−1.40	96	0.8
$CpCo[1,4\text{-}(C_6H_5)_2N_4]$	CH_3CN	1000	−1.01	96	0.9
		500	−1.01	91	1.0
		200	−1.01	88	1.0
		100	−1.00	83	1.0
		50	−1.01	90	0.9
$CpCo[1,4\text{-}(2,4\text{-}F_2C_6H_3)_2N_4]$	CH_3CN	1000	−0.98	113	0.9
		500	−0.97	86	0.9
		200	−0.97	78	1.0
		100	−0.97	77	1.0
		50	−0.97	77	1.0
		20	−0.97	77	1.0
$CpCo[1,4\text{-}(C_6F_5)_2N_4]$	CH_3CN	1000	−0.70	150	0.8
		500	−0.71	120	0.7
		200	−0.70	95	0.8
		100	−0.71	86	0.8
		50	−0.71	80	0.8
		20	−0.71	80	0.8
$CpCo(CO)_2$	CH_3CN	1000	−1.99	404	0.6
		500	−1.97	372	0.7
		200	−1.94	307	0.7
		100	−1.91	253	0.6
		50	−1.87	201	0.6
		20	−1.86	133	0.6
$Fe(CO)_3(1,4\text{-}Me_2N_4)$	CH_3CN	1000	−1.20	105	0.6
		500	−1.20	83	0.6
		200	−1.20	71	0.6
		100	−1.20	67	0.7
		50	−1.20	67	0.7
		20	−1.20	72	0.8
$CpCo(HNC_6H_3\text{-}MeNC_6H_3Me_2)$	CH_3CN	1000	−1.35	168	0.9
		500	−1.35	158	1.0
		200	−1.35	145	1.1
		100	−1.36	140	1.0
		50	−1.36	140	1.0
$CpCo(HNC_6H_4\text{-}NC_6H_5)$	CH_3CN	1000	−1.30	110	0.9
		500	−1.31	97	1.0
		200	−1.31	76	0.9
		100	−1.31	72	1.0
		50	−1.31	67	1.0
		20	−1.31	60	0.9
	CH_2Cl_2	1000	−1.37	129	0.6
		500	−1.37	120	0.8
		200	−1.37	100	0.8
		100	−1.37	90	0.9
		50	−1.37	70	1.0
		20	−1.37	70	1.0

[a] All solutions 0.1 M in Bu_4NBF_4. [b] vs. NHE. [c] Without IR compensation.

features associated with $g_1' = 2.17$ are assigned to conformations with nonconjugated phenyls. This value of g_1' is similar to that found for g_1 of $CpCo[1,4\text{-}(2,6\text{-}Me_2(C_6H_3)_2N_4)]^-$, an observation that adds support to the assignments.

Electrochemistry. Employing cyclic voltammetry, all of the $CpCo(1,4\text{-}R_2N_4)$ complexes display quasi-reversible reductions at potentials ranging from −0.7 to −1.5 V vs. NHE in acetonitrile (Figure 5, Table V). These potentials suggested to us that the reductions could be achieved synthetically employing alkali metals and that proved to be feasible (vide supra). Although the electrochemical reductions display some scan rate dependence (Table V), each of the compounds exhibit current ratios $(i_{p_a}/i_{p_c}) \cong 1$, indicative of a chemically reversible process. That this redox process involves the transfer of one electron was confirmed by constant potential coulometric studies on acetonitrile solutions of $CpCo(1,4\text{-}Me_2N_4)$, $CpCo[1,4\text{-}(C_6H_5)_2N_4]$, and $CpCo[1,4\text{-}(2,6\text{-}MeC_6H_3)_2N_4)]$. Solutions of these complexes may be reduced and subsequently reoxidized several times with the transfer of one (±0.1) electron in each redox process. The reduction potential shows essentially no solvent dependence, as evidenced by data collected in CH_2Cl_2 electrolyte solution, thereby ruling out coordination of solvent to cobalt in either the anion or neutral species. The quasi-reversible nature of this reduction contrasts with that of the parent compound, $CpCo(CO)_2$, which displays an irreversible reduction at more negative potentials than our system. The stability of the $CpCo(1,4\text{-}R_2N_4)^-$ anions compared with $CpCo(CO)_2^-$ is probably due to the fact that cyclopentadienylcobalt tetraazabutadienes cannot lose one ligand and dimerize as $CpCo(CO)_2^-$ is known to do.[27] Support for this hypothesis

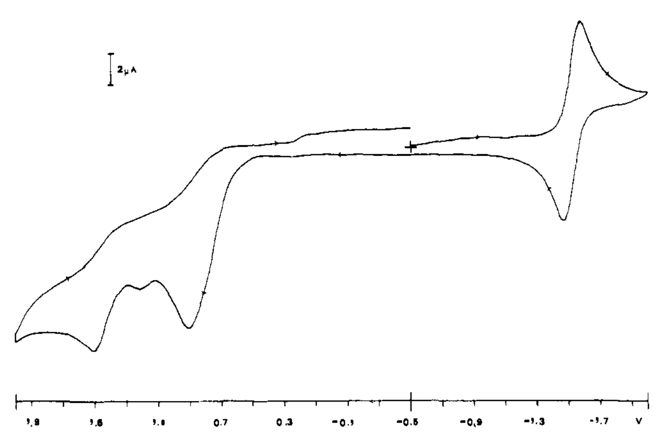

Figure 5. Cyclic voltammagram of $CpCo(1,4\text{-}Me_2N_4)$ in 0.1 M Bu_4NBF_4–acetonitrile solution. Potentials vs. NHE.

is provided by the reduction of $(CO)_3Fe(1,4\text{-}Me_2N_4)$ which displays a redox process at comparable potentials to the cobalt tetraazabutadiene complexes but with i_{p_a}/i_{p_c} considerably less than 1.

Reduction potentials of the $CpCo(1,4\text{-}R_2N_4)$ complexes display a marked dependence on the nature of the 1,4-substituents (Table V) and span a potential range of 800 mV. The trend is for more electron-withdrawing substituents to lower the reduction potential and is consistent with previous observations of substituent effects.[22,28-30] It is intriguing that reductions of the related cy-

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Table VI. Electrochemical Data for Other Redox Processes Observed for $CpCo(1,4\text{-}R_2N_4)$ and Related Compounds[a]

compd	solvent	E_{p_c}, V	E_{p_a}, V
$CpCo(1,4\text{-}Me_2N_4)$	CH_3CN		+1.59
			+0.89
	CH_2Cl_2		+1.02
$CpCo[1,4\text{-}(2,6\text{-}Me_2C_6H_3)_2N_4]$	CH_3CN		+1.36
$CpCo[1,4\text{-}(C_6H_5)_2N_4]$			+0.92
			+0.79
$CpCo[1,4\text{-}(2,4\text{-}F_2C_6H_3)_2N_4]$	CH_3CN		+1.24
$CpCo(CO)_2$	CH_3CN		+0.49
		+0.16	
$(CO)_3Fe(1,4\text{-}Me_2N_4)$	CH_3CN		+1.24
$CpCo(HNC_6H_3MeNC_6H_3Me_2)$	CH_3CN		+0.40
		+0.31	
		+0.07	
$CpCo(HNC_6H_4NC_6H_5)$	CH_3CN		+0.36
		+0.28	
		+0.04	
	CH_2Cl_2		+0.52
		+0.36	
		+0.07	

[a] Data taken from +1.4 to −2.5 V scans at 200 mv/s. All processes are irreversible. The magnitude vs. NHE of I_{p_a} for many of the anodic processes suggest that more than one electron is involved.

clopentadienylcobalt *N*-aryl-*o*-benzoquinone diimines do not show a large substituent effect (Table V). The nature of the tetraazabutadiene ligand plays an unusually large role in determining the reduction potential of these complexes consistent with highly covalent metal–nitrogen interactions.

In addition to the reductions, several irreversible oxidations are observed (see Figure 5 and Table VI). These processes show peak currents indicative of oxidation involving more than one electron and are (at least in the case of $CpCo(1,4\text{-}Me_2N_4)$) solvent dependent. The solvent dependence suggests that CH_3CN may coordinate to Co in the oxidized species. Attempts to prepare oxidized forms of $CpCo(1,4\text{-}Me_2N_4)$ and $CpCo[1,4\text{-}(2,6\text{-}Me_2C_6H_3)_2N_4]$ by using $AgBF_4$, AgCN, or even $NOBF_4$ met with failure. In all cases the neutral complex is stable (for days) in the presence of these oxidants, in contrast to the behavior[31] of other $CpCoL_n$ compounds.

Conclusions

The EPR spectroscopic data for the $CpCo(1,4\text{-}R_2N_4)^-$ complexes establish the similarity between these systems and $CpCo(CO)_2^-$ and $CpCo(COD)^-$. This agrees with our view[8-12] of the tetrazabutadiene as a neutral π-acid ligand but is at odds with a suggestion[3] that the $1,4\text{-}R_2N_4$ moiety be regarded as a dianion in these compounds. In this context it should be noted that a recent NQR study[1] of neutral cyclopentadienylcobalt complexes favors the formal view of the tetraazabutadiene ligand as a neutral species. The dramatic substituent effects observed for the reduction potentials of the neutral complexes, the delocalized character of the odd electron in $CpCo(1,4\text{-}R_2N_4)^-$ (ca. 60% cobalt), the conformational equilibria in the 1,4-diphenyl derivative, and the discrete variational Xα calculations are consistent with the odd electron occupying a delocalized metallacycle π^* orbital in the radical anion complexes. It is interesting to contrast these observations with the lack of substituent effects found[1] in the NQR spectra of neutral cyclopentadienylcobalt tetraazabutadienes. That study did not evidence π-delocalization in the metallacycle. Two explanations of this contradiction are possible: (1) there is little π bonding in the ground state of the neutral complexes; (2) NQR is overly sensitive to σ bonding and may not be a good probe of π bonding which (although relatively small compared to the σ system) is *chemically* significant. It has been noted[10] that the similarity between the average C–O stretching frequency in $Fe(CO)_3(1,4\text{-}Me_2N_4)$ and $Fe(CO)_5$ suggests that a tetraazabutadiene group compares to two CO ligands in electron-withdrawing power. The present observation that $CpCo(1,4\text{-}Me_2N_4)$ reduces at a less negative potential (−1.53 V) than $CpCo(CO)_2$ (−1.94 V) supports this view. By comparison $CpCo(PR_3)_2$ and $CpCo[P(OR)]_2$ complexes have not been reported to reduce to stable anion radicals; however, they can be oxidized[31] to stable cation radicals.

Although it would be of interest to compare tetraazabutadiene complexes with diazabutadienes, there are few analogous systems available to evaluate. A wide variety of interesting diazabutadiene complexes have been prepared by tom Dieck and co-workers.[32] Complexes such as $Mo(CO)_4(DAB)$ (DAB = diazabutadiene) can be reduced to 19-electron complexes. EPR spectra[32] suggest the odd electron is ligand centered in this instance. If one compares the CO stretching frequencies for $Fe(CO)_3(1,4\text{-}Me_2N_4)$ [2070, 2000 cm^{-1}][11] and $Fe(CO)_3[N(C_6H_5)C(CH_3)C(CH_3)N(C_6H_5)]$ (2035, 1965 cm^{-1}),[33] it seems clear that tetraazabutadiene ligands are superior π-acceptor groups. In the present study (Table V) it was found that cyclopentadienylcobalt *N*-aryl-*o*-benzoquinone diimines (which contain especially good electron-withdrawing diazabutadienes) do not reduce as readily as the parent tetraazabutadiene complexes. All of this evidence suggests that tetraazabutadiene ligands have few peers in their ability to stabilize electron-rich organometallic complexes.

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Registry No. $CpCo(1,4\text{-}H_2N_4)$, 80738-20-1; $CpCo(1,4\text{-}H_2N_4)^-$, 90460-30-3; $CpCo(1,4\text{-}Me_2N_4)$, 80738-16-5; $CpCo(1,4\text{-}Me_2N_4)^-$, 90460-31-4; $CpCo[1,4\text{-}(2,6\text{-}MeC_6H_3)_2N_4]$, 90460-32-5; $CpCo[1,4\text{-}(2,6\text{-}MeC_6H_3)_2N_4]^-$, 90460-33-6; $CpCo[1,4\text{-}(C_6H_5)_2N_4]$, 76418-81-0; $CpCo[1,4\text{-}(C_6H_5)_2N_4]^-$, 90460-34-7; $CpCo[1,4\text{-}(2,4\text{-}F_2C_6H_3)_2N_4]$, 80738-18-7; $CpCo[1,4\text{-}(2,4\text{-}F_2C_6H_3)_2N_4]^-$, 90481-24-6; $CpCo[1,4\text{-}(C_6F_5)_2N_4]$, 76418-82-1; $CpCo[1,4\text{-}(C_6F_5)_2N_4]^-$, 90460-35-8; $CpCo[1,4\text{-}(CpCo(CO)_2)_2N_4]$, 90460-36-9; $Fe(CO)_3(1,4\text{-}Me_2N_4)$, 38668-89-2; $CpCo(HNC_6H_3MeNC_6H_3Me_2)$, 90460-37-0; $CpCo(HNC_6H_4NC_6H_5)$, 12133-03-8.

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