

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 $\text{Fe}(\text{TPP})\text{Cl}$ with ligand were determined at 25 °C by optical methods described previously.⁴

Acknowledgment. Financial support from the USPHS (GM 28222) and the NSF is gratefully acknowledged. R.Q. was the recipient of a Johnson and Johnson Fellowship in Chemistry. We also acknowledge the contributions of Angela Fotia and Irwin Green in the initial stages of this work and the assistance of Dr.

Catherine Franklin in obtaining some of the IR spectra. We also thank Professor B. M. Hoffman and Dr. M. A. Stanford for helpful discussions.

Registry No. tMU, 70346-51-9; cMU, 88181-49-1; $\text{Fe}(\text{TPP})-(\text{ImH})_2\text{SbF}_6$, 80939-25-9; $\text{Fe}(\text{TPP})(4\text{MeImH})_2\text{SbF}_6$, 80939-26-0; $\text{Fe}(\text{TPP})(4\text{PhImH})_2\text{SbF}_6$, 90388-44-6; $\text{Fe}(\text{TPP})(\text{tMU})_2\text{SbF}_6$, 90388-46-8; $\text{Fe}(\text{TPP})(\text{cMU})_2\text{SbF}_6$, 90457-44-6; $\text{Fe}(\text{TPP})(1\text{MeIm})_2\text{SbF}_6$, 90388-47-9; $\text{Fe}(\text{TPP})\text{Cl}$, 16456-81-8; $\text{Fe}(\text{TPP})(\text{SbF}_6)_2$, 79949-97-6; $\text{Fe}(\text{TPP})-(\text{ImH})_2\text{Cl}$, 25442-52-8; $\text{Fe}(\text{TPP})(\text{cMU})_2\text{Cl}$, 90457-45-7; $\text{Fe}(\text{TPP})-(\text{tMU})_2\text{Cl}$, 90388-48-0; urocanic acid, 104-98-3.

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

Michael J. Maroney and William C. Trogler*†

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. Received October 31, 1983

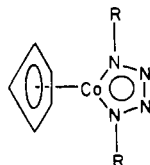
Abstract: The results of electrochemical and electronic and EPR spectroscopic studies on a series of novel 19-electron anionic complexes derived from reduction of neutral cyclopentadienylcobalt tetraazabutadienes— $\text{CpCo}(1,4\text{-R}_2\text{N}_4)$ ($\text{R} = \text{CH}_3$, C_6H_5 , C_6F_5 , 2,4- $\text{F}_2\text{C}_6\text{H}_3$, 2,6- $\text{Me}_2\text{C}_6\text{H}_3$; $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$)—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 ($g = 2.16\text{--}2.21$) at ambient temperatures characteristic of cobalt-centered radicals ($a_{\text{iso}} = 50\text{--}58$ 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 $\text{CpCo}[1,4-(\text{C}_6\text{H}_5)_2\text{N}_4]^-$ is interpreted in terms of the presence of different conformations of the aryl substituents for this compound.

Unsaturated metallacycles containing 1,4-disubstituted tetraazabutadienes¹⁻¹³ 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 $\text{CpNi}(1,4\text{-Ar}_2\text{N}_4)$ [$\text{Ar} = 4\text{-MeC}_6\text{H}_4$, $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$]. This neutral, 19-electron complex was isolated as a stable intermediate in the synthesis of $\text{Ni}(1,4\text{-Ar}_2\text{N}_4)_2$ from $\text{Ni}(\text{Cp})_2$.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, $\text{CpCo}(1,4\text{-R}_2\text{N}_4)$ ($\text{R} = \text{CH}_3$,

unique in the chemistry of metallacyclopentatetraazabutadienes 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



C_6H_5 , 2,6- $\text{Me}_2\text{C}_6\text{H}_3$, 2,4- $\text{F}_2\text{C}_6\text{H}_3$, 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 $(\eta^5\text{-C}_5\text{H}_5)\text{Co}$ derivatives. The results of these experiments are interpreted in the context of SCF- $X\alpha$ -DV calculations on $\text{CpCo}(1,4\text{-H}_2\text{N}_4)$ and its anion. The reversible redox activity of these compounds is

- (1) Miller, E. J.; Brill, T. B. *Inorg. Chem.* **1983**, *22*, 2392–2398.
- (2) Overbosch, P.; van Koten, G.; Overbeek, O. *J. Am. Chem. Soc.* **1980**, *102*, 2091–2093.
- (3) Overbosch, P.; van Koten, G.; Spek, A. L.; Roelofsen, G.; Duisenberg, A. J. M. *Inorg. Chem.* **1982**, *21*, 3908–3913.
- (4) Overbosch, P.; van Koten, G.; Grove, D. M.; Spek, A. L.; Duisenberg, A. J. M. *Inorg. Chem.* **1982**, *21*, 3253–3260.
- (5) Overbosch, P.; van Koten, G.; Overbeek, O. *Inorg. Chem.* **1982**, *21*, 2373–2378.
- (6) Overbosch, P.; van Koten, G.; Vrieze, K. *J. Chem. Soc., Dalton Trans.* **1982**, 1541–1547.
- (7) Overbosch, P.; van Koten, G.; Vrieze, K. *J. Organomet. Chem.* **1981**, *208*, C21–C24.
- (8) Gross, M. E.; Trogler, W. C.; Ibers, J. A. *Organometallics* **1982**, *1*, 732–739.
- (9) Chang, C.-Y.; Johnson, C. E.; Richmond, T. G.; Chen, Y.-T.; Trogler, W. C.; Basolo, F. *Inorg. Chem.* **1981**, *20*, 3167–3172.
- (10) Trogler, W. C.; Johnson, C. E.; Ellis, D. *Inorg. Chem.* **1981**, *20*, 980–986.
- (11) Johnson, C. E.; Trogler, W. C. *J. Am. Chem. Soc.* **1981**, *103*, 6352–6358.
- (12) Gross, M. E.; Trogler, W. C. *J. Organomet. Chem.* **1981**, *209*, 407–414.
- (13) Johnson, C. E.; Trogler, W. C. *Inorg. Chem.* **1982**, *21*, 427–429.
- (14) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; pp 17–19.

* Address correspondence to the Department of Chemistry, D-006, University of California, San Diego, La Jolla, CA 92093.

† Alfred P. Sloan Research Fellow, 1983–1985.

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_2O_{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 auxiliary 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 $E_{pc} - E_{pa}$ 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 auxiliary 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- $Me_2C_6H_3$, 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

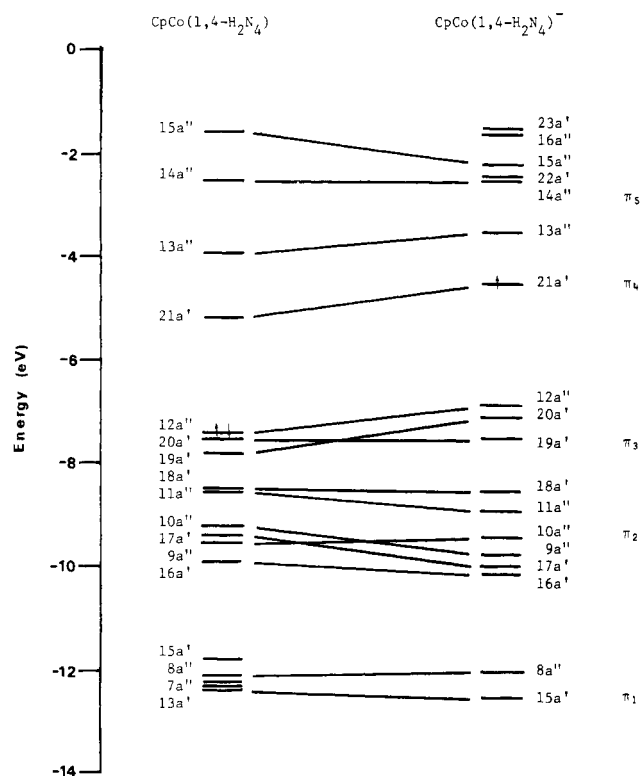


Figure 1. Molecular orbital energy level diagram for $CpCo(1,4-H_2N_4)^{0-}$. The energy levels of the anionic compound were adjusted by setting the energy level of the lowest valence orbital ($1a'$) equal to that of the neutral compound.

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.

Theoretical Studies. Calculations of the electronic structure of $CpCo(H_2N_4)$ and $CpCo(H_2N_4)^{-}$ employed the SCF- $X\alpha$ -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- $X\alpha$ -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.

(15) Gagné, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854–2855. Gagné, R. R.; Allison, J. L.; Gall, R. S.; Koval, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 7170–7178.

(16) Values of $E_{pc} - E_{pa}$ observed as a function of scan rates for the ferrocene/ferrocenium couple in 0.1 M Bu_4NBF_4 -acetonitrile solution were 99 mV at 1000 mV/s, 86 mV at 500 mV/s, 78 mV at 200 mV/s, and 72 mV at 100, 50, and 20 mV/s.

(17) Otsuka, S.; Nakamura, A. *Inorg. Chem.* **1968**, *7*, 2542–2544.

(18) Gross, M. E.; Johnson, C. E.; Maroney, M. J.; Trogler, W. C. *Inorg. Chem.*, in press.

(19) Delley, B.; Ellis, D. E. *J. Chem. Phys.* **1982**, *76*, 1949–1960.

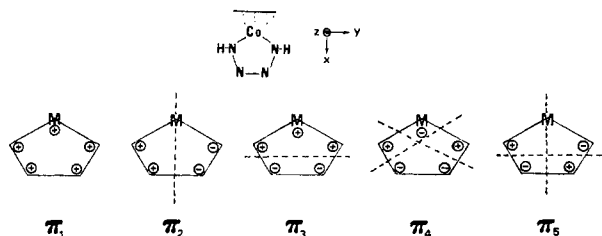
Table I. Valence Orbitals Calculated for $[\text{CpCo}(1,4\text{-H}_2\text{N}_4)]^{0-}$

orbital		energy, ev	% Co ^a		% N _α ^b		% N _β		% C	% H _N	% H _C
C _s	C _{2v}		total	3d	2p	2s	2p	2s			
CpCo(1,4-H ₂ N 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 _{x²-y²)}	3	0	1	1	5	2	1
18a'	a ₁	-8.454	67	61 (d _{z²)}	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 _{yz})	69 (π)	0	13 (π)	0	2	0	0
16a'	a ₁	-9.895	35	31 (d _{z²)}	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-H ₂ N 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 _{x²-y²)}	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 _{z²)}	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 _{z²)}	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-H₂N₄)⁻ 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:



These are identified for CpCo(1,4-H₂N₄)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-H₂N₄) corresponds to π₄. Although the d_{xz} orbital may participate in π bonding in the π₁, π₃, and π₄ orbitals, significant metal 3d character is found only in π₃ and π₄. The Co d_{yz} orbital has the

proper symmetry to participate in bonding to π₂ and π₃ in a δ fashion. However, only a small amount of Co d character is found in π₂, and none is found in π₃. 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-R₂N₄) 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-H₂N₄) with that observed for CpCo(1,4-Me₂N₄) in THF solution leads to the tentative assignments contained in Table III. The lowest energy transition of CpCo(1,4-Me₂N₄) is expected to be a combination of two transitions, one a d → π* transition and the other a metallacycle π → π* 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 π → π* transition. (This π → π* transition is now assigned to

Table II. Electronic Absorption Spectra of $[\text{CpCo}(1,4\text{-R}_2\text{N}_4)]^{0,-}$ (1700–220 nm)

R	solvent	neutral complex		anionic complex		isosbestic points, ^b nm	% reversibility ^c at λ (nm)
		λ_{max} , nm	(ϵ , $\text{M}^{-1} \text{cm}^{-1}$) ^a	λ_{max} , nm	(ϵ , $\text{M}^{-1} \text{cm}^{-1}$)		
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	(22 220)	310	sh		
2,6- $\text{Me}_2\text{C}_6\text{H}_3$	THF	634	(327)	1100	sh	585, 506, 401	100 (445)
		445	(5450)	1000	(58)		
		342	(3030)	526	(680)		
		280	sh	403	(2300)		
				335	sh		
	CH_3CN^d			255	sh		
				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	(20 900)	451	(2160)		
				345	(20 300)		
2,4- $\text{F}_2\text{C}_6\text{H}_3$	THF	658	(680)	1040	(165)	611, 524, 283	partly irreversible (see text)
		467	(7720)	539	(1890)		
		359	(4500)	330	sh		
		267	(21 600)	299	(17 100)		
		234	sh	260	(21 000)		
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	(13 500)		
$\text{CpCo}(\text{CO})_2$	THF	395	(378)	240	sh		
		339	(929)				
		293	(4910)				
		248	(10 000)				
		231	(9 940)				

^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 $\text{Bu}_4\text{NBF}_4\text{-CH}_3\text{CN}$ solution.

the lowest energy absorption at 623 nm). The third low-energy transition (338 nm) is assigned to a combination of two $d \rightarrow \text{Co-N } \sigma^*$ 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 $X\alpha$ 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 $\text{CpCo}[1,4\text{-(2,6-Me}_2\text{C}_6\text{H}_3)_2\text{N}_4]^-$ produced electrochemically in 0.1 M $\text{Bu}_4\text{NBF}_4\text{-acetonitrile}$ 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 $\text{CpCo}(1,4\text{-H}_2\text{N}_4)^-$ from the $X\alpha$ calculations and the electronic absorption spectrum of $\text{CpCo}(1,4\text{-Me}_2\text{N}_4)$ serve as guides for the assignment of the spectrum

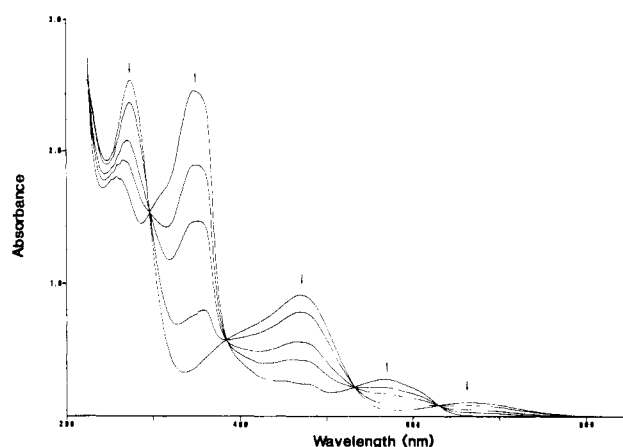


Figure 2. Electronic absorption spectral changes during the reduction of $\text{CpCo}[1,4\text{-(C}_6\text{H}_5)_2\text{N}_4]$ in THF (1.22 mM) over Na/Hg amalgam using a 1-mm cell.

of $\text{CpCo}(1,4\text{-Me}_2\text{N}_4)^-$ (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 $[\text{CpCo}(\text{1,4-H}_2\text{N}_4)]^{0-}$ (0–4 eV)

transition	$E(\text{predicted}), \text{eV}$	C_{2v} selection rule	$E(\text{obsd}),^a \text{eV}$
$\text{CpCo}(\text{1,4-H}_2\text{N}_4)$			
$12a'' \rightarrow 21a'$	2.25	allowed	1.99
$20a' \rightarrow 21a'$	2.29	allowed	
$19a' \rightarrow 21a'$	2.68	allowed	2.90
$18a' \rightarrow 21a'$	3.29	allowed	
$11a'' \rightarrow 21a''$	3.36	forbidden	
$12a'' \rightarrow 13a''$	3.47	allowed	
$20a'' \rightarrow 13a''$	3.51	forbidden	3.67
$19a' \rightarrow 13a''$	3.90	allowed	
$10a'' \rightarrow 21a'$	4.04	forbidden	
$[\text{CpCo}(\text{1,4-H}_2\text{N}_4)]^-$			
$21a' \rightarrow 13a''$	1.23	forbidden	1.06 1.34
$21a' \rightarrow 14a''$	2.05	allowed	
$21a' \rightarrow 22a'$	2.11	allowed	
$21a' \rightarrow 15a'$	2.32	allowed	
$12a'' \rightarrow 21a'$	2.32	allowed	2.38
$20a' \rightarrow 21a'$	2.13 ^b	allowed	
$21a' \rightarrow 16a''$	2.87	forbidden	
$21a' \rightarrow 23a'$	3.00	allowed	
$19a' \rightarrow 21a'$	3.01	allowed	3.05
$12a'' \rightarrow 13a''$	3.34	allowed	
$20a' \rightarrow 13a''$	3.60	allowed	
$18a' \rightarrow 21a'$	4.00	allowed	4.00
$19a' \rightarrow 13a''$	4.03	forbidden	

^a Observed for $[\text{Cp}(\text{Co}(\text{1,4-Me}_2\text{N}_4))]^{0-}$ 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, $\text{CpCo}[\text{1,4-(2,6-Me}_2\text{C}_6\text{H}_3)]^-$.

Using the same strategy employed for the neutral compounds, the tentative assignment of the remaining transitions of $\text{CpCo}(\text{1,4-Me}_2\text{N}_4)^-$ is made. The absorptions at 520 nm are assigned to either or both of two $d \rightarrow \pi^*$ transitions. One of these transitions ($12a'' \rightarrow 21a'$) was involved in the 623-nm absorption of the neutral molecule and has increased slightly in energy. The other ($20a' \rightarrow 21a'$) 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 $\pi \rightarrow \pi^*$ transition involved in the 623-nm absorption in the neutral molecule. The absorption at 310 nm is assigned to the $d \rightarrow \pi^*$ transition assigned to the 420-nm absorption in $\text{CpCo}(\text{1,4-Me}_2\text{N}_4)$. The remaining feature at 250 nm (4.96 eV) probably involves the $10a'' \rightarrow 21a'$ metallacycle $\pi \rightarrow \pi^*$ 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 $\text{CpCo}[\text{1,4-(2,4-F}_2\text{C}_6\text{H}_3)_2\text{N}_4]^-$ 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 photo-oxidation 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}

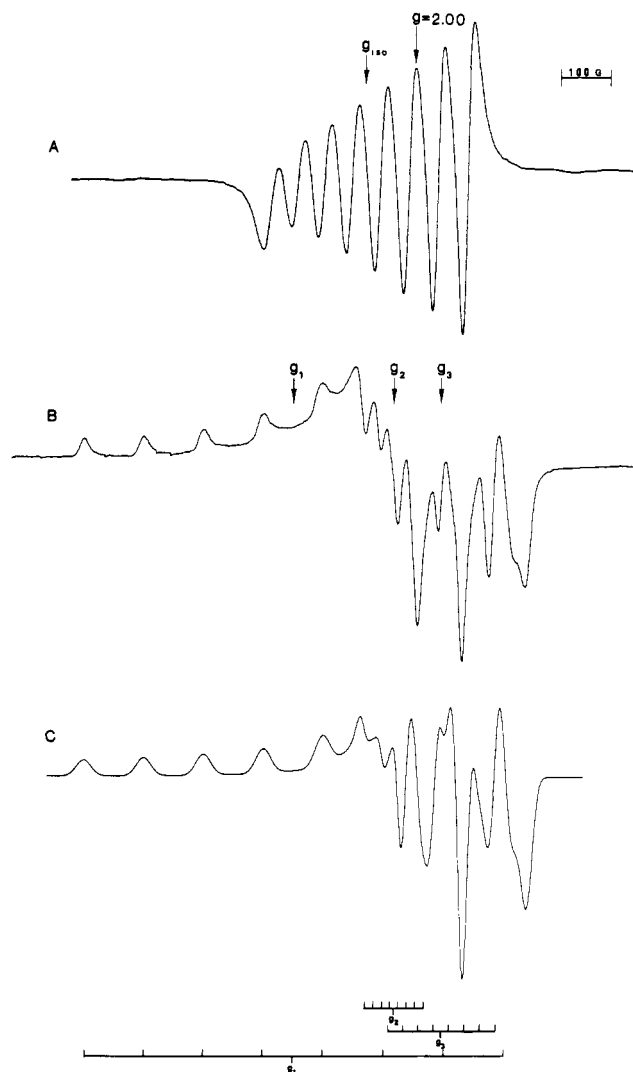


Figure 3. EPR spectra for $\text{CpCo}(\text{1,4-Me}_2\text{N}_4)^-$ in THF: (A) isotropic spectrum from fluid solution at ambient temperature; (B) anisotropic spectrum from a frozen solution at 77 K; (C) computer simulation, using Gaussian line shapes, of (B). Parameters: $g_1 = 2.161$, $g_2 = 2.022$, $g_3 = 1.967$; $A_1 = 121.9 \text{ G}$, $A_2 = 17.0 \text{ G}$, $A_3 = 31.0 \text{ G}$.

$[(\text{CpCoCOT})^- \text{ is a ligand-centered radical}]^{21}$ with the unpaired electron in a 3d orbital other than d_{z^2} [$\text{Co}(\text{CO})_4^-$ 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 $\text{CpCo}(\text{1,4-Me}_2\text{N}_4)^-$ (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 $[\text{C}_{28}\text{H}_{24}\text{O}_6\text{Na}][\text{CpCo}(\text{1,4-(C}_6\text{H}_5)_2\text{N}_4)]$ display a rhombic spectrum with $g_1 = 2.22$, $g_2 = 2.06$, and $g_3 = 1.98$. Further, a simulation²⁴ of the anisotropic spectrum of $\text{CpCo}(\text{1,4-Me}_2\text{N}_4)^-$ (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

(20) Symons, M. C. R.; Bratt, S. W. *J. Chem. Soc., Dalton Trans.* **1979**, 1739–1743.

(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 $\text{CpCo}(1,4\text{-R}_2\text{N}_4)^-$ 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
$\text{CpCo}(1,4\text{-Me}_2\text{N}_4)^-$	THF	2.055	57.9	2.161	2.022 ^b	1.967 ^b	121.9	17 ^b	30 ^b	this work
$\text{CpCo}[1,4\text{-(2,6-Me}_2\text{C}_6\text{H}_3)_2\text{N}_4]^-$	THF	2.061	56.3	2.178		ca. 2.0	119		ca. 46	this work
	CH_3CN^c	2.065	56.1							this work
$\text{CpCo}[1,4\text{-(C}_6\text{H}_5)_2\text{N}_4]^-$	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
$\text{CpCo}[1,4\text{-(2,4-F}_2\text{C}_6\text{H}_3)_2\text{N}_4]^-$	THF	2.070	51.6	2.204		ca. 2.0	111		ca. 44	this work
$\text{CpCo}[1,4\text{-(C}_6\text{F}_5)_2\text{N}_4]^-$	THF	2.066	51.7	2.214		ca. 2.0	111		ca. 46	this work
$\text{CpCo}(\text{CO})_2^-$	MTHF ^f			2.005		2.004	172		45	20
$\text{CpCo}(1,5\text{-COD})^-$	DMF (163 K)			2.165		ca. 2.0	158		ca. 50	21
$\text{CpCo}(1,3\text{-COD})^-$	THF (153 K)			2.189		ca. 2.0	140		ca. 42	21
$\text{CpCo}(1,3\text{-COT})^-$	THF (153 K)			2.196	2.002		1.946	46	41	21
$\text{CpCo}(\text{tpc})$	MTHF (100 K)			2.103	2.025		1.906	144	41	22
$\text{Co}(\text{CO})_4^-$	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 $\text{CpCo}(\text{H}_2\text{N}_4)^-$ is 80 G on the basis of SCF-X α -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_0^3 , 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-X α -DV calculations on the model complex $\text{CpCo}(1,4\text{-H}_2\text{N}_4)^-$, which predict that the analogous orbital is ~45% Co. This value compares with 56% Co 3d character calculated for $\text{CpCo}(\text{CO})_2^-$ and is further evidence¹⁰ 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 $\text{CpCo}[1,4\text{-(C}_6\text{H}_5)_2\text{N}_4]^-$ 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 exception of $\text{CpCo}[1,4\text{-(C}_6\text{H}_5)_2\text{N}_4]^-$ which has a g_1 value comparable with that of $\text{CpCo}[1,4\text{-(C}_6\text{F}_5)_2\text{N}_4]^-$. The crystal structure of $\text{CpCo}[1,4\text{-(C}_6\text{F}_5)_2\text{N}_4]$ 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

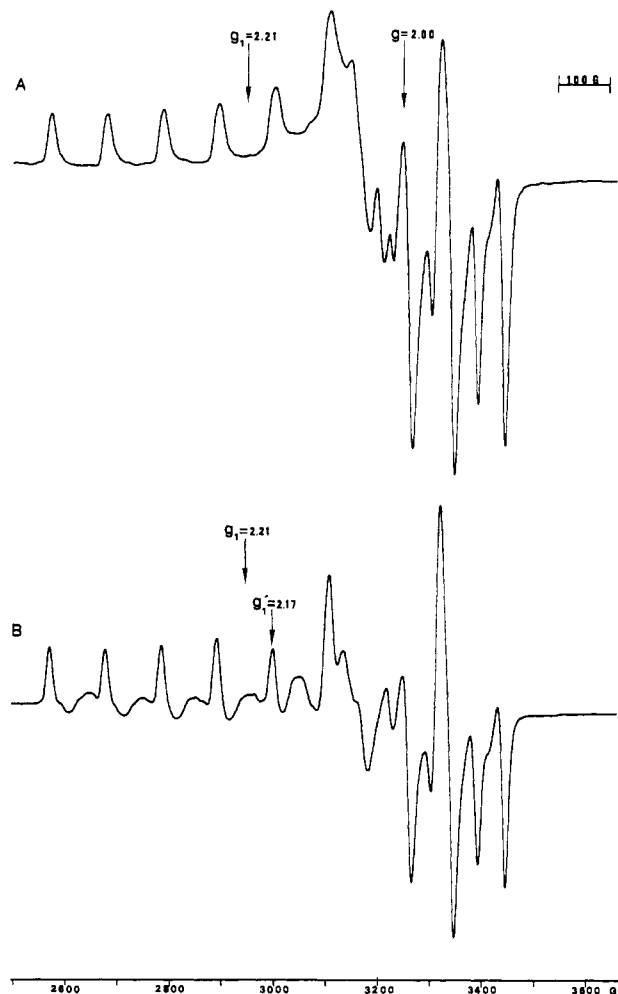


Figure 4. Anisotropic EPR spectra for $\text{CpCo}[1,4\text{-(C}_6\text{H}_5)_2\text{N}_4]^-$ in a frozen THF solution at -165°C : (A) frozen slowly; (B) frozen by plunging into liquid N_2 , then warming to -165°C .

fluorine substituents and is presumed to be the case for the other ortho-substituted xyl 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 $\text{CpCo}[1,4\text{-(C}_6\text{H}_5)_2\text{N}_4]^-$ are assigned to conjugated phenyl substituents that are slightly more energetically favored than nonconjugated phenyl substituents. These are observed to the exclusion of the non-conjugated 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.

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

when $g_1 \approx 2.0$. % d character = $2G/2B^\circ$. ⁵⁹Co - $2B^\circ = -152.3$ G. Froese, C. J. *Chem. Phys.* 1966, 45, 1417.

(26) Drago, R. S. "Physical Methods in Chemistry"; Saunders: Philadelphia, 1977.

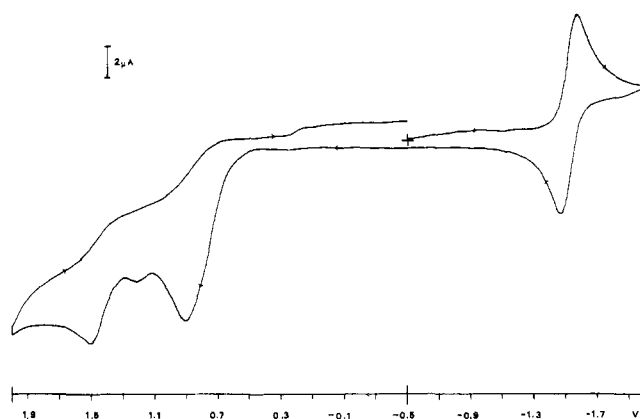
Table V. Electrochemical Data for the Most Negative Redox Process of CpCo(1,4-R₂N₄) Complexes and Related Compounds

compd	solvent ^a	scan rate, mV/s	E ^{o',b} V	E _{pc} - E _{pa} ^c , mV	I _{pa} /I _{pc}	compd	solvent ^a	scan rate, mV/s	E ^{o',b} V	E _{pc} - E _{pa} ^c , mV	I _{pa} /I _{pc}
CpCo(1,4-Me ₂ N ₄)	CH ₃ CN	1000	-1.52	215	0.9	CpCo[1,4-(C ₆ F ₅) ₂ N ₄]	CH ₃ CN	1000	-0.70	150	0.8
		500	-1.52	178	0.9			500	-0.71	120	0.7
		200	-1.53	116	0.9			200	-0.70	95	0.8
		100	-1.53	98	1.0			100	-0.71	86	0.8
		50	-1.54	84	1.0			50	-0.71	80	0.8
		20	-1.54	81	1.0			20	-0.71	80	0.8
	CH ₂ Cl ₂	1000	-1.58	202	0.9	CpCo(CO) ₂	CH ₃ CN	1000	-1.99	404	0.6
		500	-1.57	163	0.9			500	-1.97	372	0.7
		200	-1.57	134	0.9			200	-1.94	307	0.7
		100	-1.57	116	1.0			100	-1.91	253	0.6
CpCo[1,4-(2,6-Me ₂ C ₆ H ₃)N ₄]	CH ₃ CN	1000	-1.32	104	1.1			50	-1.87	201	0.6
		500	-1.31	90	1.0	Fe(CO) ₃ (1,4-Me ₂ N ₄)	CH ₃ CN	1000	-1.20	133	0.6
		200	-1.31	78	1.0			500	-1.20	105	0.6
		100	-1.31	73	1.1			200	-1.20	83	0.6
		50	-1.31	67	1.1			100	-1.20	71	0.6
		20	-1.31	65	1.1			50	-1.20	67	0.7
	CH ₂ Cl ₂	1000	-1.42	175	0.7			20	-1.20	72	0.8
		500	-1.42	152	0.7	CpCo(HNC ₆ H ₃ -MeNC ₆ H ₃ Me ₂)	CH ₃ CN	1000	-1.35	168	0.9
		200	-1.41	120	0.7			500	-1.35	158	1.0
		100	-1.40	104	0.8			200	-1.35	145	1.1
		50	-1.40	96	0.8			100	-1.36	140	1.0
CpCo[1,4-(C ₆ H ₅) ₂ N ₄]	CH ₃ CN	1000	-1.01	96	0.9			50	-1.36	140	1.0
		500	-1.01	91	1.0	CpCo(HNC ₆ H ₄ -NC ₆ H ₅)	CH ₃ CN	1000	-1.30	110	0.9
		200	-1.01	88	1.0			500	-1.31	97	1.0
		100	-1.00	83	1.0			200	-1.31	76	0.9
		50	-1.01	90	0.9			100	-1.31	72	1.0
CpCo[1,4-(2,4-F ₂ C ₆ H ₃) ₂ N ₄]	CH ₃ CN	1000	-0.98	113	0.9			50	-1.31	67	1.0
		500	-0.97	86	0.9			20	-1.31	60	0.9
		200	-0.97	78	1.0		CH ₂ Cl ₂	1000	-1.37	129	0.6
		100	-0.97	77	1.0			500	-1.37	120	0.8
		50	-0.97	77	1.0			200	-1.37	100	0.8
		20	-0.97	77	1.0			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 Bu₄NBF₄. ^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-(2,6-Me₂C₆H₃)₂N₄]⁻, an observation that adds support to the assignments.

Electrochemistry. Employing cyclic voltammetry, all of the CpCo(1,4-R₂N₄) 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_{pa}/i_{pc}) ≈ 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-Me₂N₄), CpCo[1,4-(C₆H₅)₂N₄], and CpCo[1,4-(2,6-Me₂C₆H₃)₂N₄]. 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 CH₂Cl₂ 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-R₂N₄)⁻ 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 voltammogram of CpCo(1,4-Me₂N₄) in 0.1 M Bu₄NBF₄-acetonitrile solution. Potentials vs. NHE.

is provided by the reduction of (CO)₃Fe(1,4-Me₂N₄) which displays a redox process at comparable potentials to the cobalt tetraazabutadiene complexes but with i_{pa}/i_{pc} considerably less than 1.

Reduction potentials of the CpCo(1,4-R₂N₄) 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-

(27) Illenda, C. S.; Schore, N. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1976**, *98*, 255-256. Schore, N. E.; Illenda, C. S.; Bergman, R. G. *Ibid.* **1976**, *98*, 256-258; **1977**, *99*, 1781-1787.

(28) Walker, F. A.; Beroiz, D.; Kadish, K. M. *J. Am. Chem. Soc.* **1976**, *98*, 3784-3789.

(29) Strecker, J. A.; Pillsbury, D. G.; Busch, D. H. *Inorg. Chem.* **1980**, *19*, 3148-3159.

Table VI. Electrochemical Data for Other Redox Processes Observed for $\text{CpCo}(1,4\text{-R}_2\text{N}_4)$ and Related Compounds^a

compd	solvent	E_{pc}, V	E_{pa}, V
$\text{CpCo}(1,4\text{-Me}_2\text{N}_4)$	CH_3CN		+1.59 +0.89 +1.02
$\text{CpCo}[1,4\text{-(2,6-Me}_2\text{C}_6\text{H}_3)_2\text{N}_4]$	CH_2Cl_2		+1.36
$\text{CpCo}[1,4\text{-(C}_6\text{H}_5)_2\text{N}_4]$	CH_3CN		+0.92 +0.79 +1.24
$\text{CpCo}[1,4\text{-(2,4-F}_2\text{C}_6\text{H}_3)_2\text{N}_4]$	CH_3CN		+0.49
$\text{CpCo}(\text{CO})_2$	CH_3CN	+0.16	
$(\text{CO})_3\text{Fe}(1,4\text{-Me}_2\text{N}_4)$	CH_3CN		+1.24
$\text{CpCo}(\text{HNC}_6\text{H}_3\text{MeNC}_6\text{H}_3\text{Me}_2)$	CH_3CN		+0.40
		+0.31 +0.07	
$\text{CpCo}(\text{HNC}_6\text{H}_4\text{NC}_6\text{H}_5)$	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_{pa} 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 $\text{CpCo}(1,4\text{-Me}_2\text{N}_4)$) solvent dependent. The solvent dependence suggests that CH_3CN may coordinate to Co in the oxidized species. Attempts to prepare oxidized forms of $\text{CpCo}(1,4\text{-Me}_2\text{N}_4)$ and $\text{CpCo}[1,4\text{-(2,6-Me}_2\text{C}_6\text{H}_3)_2\text{N}_4]$ 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 behavior³¹ of other CpCoL_n compounds.

Conclusions

The EPR spectroscopic data for the $\text{CpCo}(1,4\text{-R}_2\text{N}_4)^-$ complexes establish the similarity between these systems and $\text{CpCo}(\text{CO})_2^-$ and $\text{CpCo}(\text{COD})^-$. This agrees with our view⁸⁻¹² of the tetraazabutadiene as a neutral π -acid ligand but is at odds with a suggestion³ that the $1,4\text{-R}_2\text{N}_4$ moiety be regarded as a dianion in these compounds. In this context it should be noted that a recent NQR study¹ 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 $\text{CpCo}(1,4\text{-R}_2\text{N}_4)^-$ (ca. 60% cobalt), the conformational equilibria in the 1,4-diphenyl derivative, and the discrete variational $X\alpha$ 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 found¹ 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 noted¹⁰ that the similarity between the average C-O stretching frequency in $\text{Fe}(\text{CO})_3(1,4\text{-Me}_2\text{N}_4)$ and $\text{Fe}(\text{CO})_5$ suggests that a tetraazabutadiene group compares to two CO ligands in electron-withdrawing power. The present observation that $\text{CpCo}(1,4\text{-Me}_2\text{N}_4)$ reduces at a less negative potential (-1.53 V) than $\text{CpCo}(\text{CO})_2$ (-1.94 V) supports this view. By comparison $\text{CpCo}(\text{PR}_3)_2$ and $\text{CpCo}[\text{P}(\text{OR})_2]_2$ complexes have not been reported to reduce to stable anion radicals; however, they can be oxidized³¹ 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 $\text{Mo}(\text{CO})_4(\text{DAB})$ (DAB = diazabutadiene) can be reduced to 19-electron complexes. EPR spectra³² suggest the odd electron is ligand centered in this instance. If one compares the CO stretching frequencies for $\text{Fe}(\text{CO})_3(1,4\text{-Me}_2\text{N}_4)$ [2070, 2000 cm^{-1}]¹¹ and $\text{Fe}(\text{CO})_3[\text{N}(\text{C}_6\text{H}_5)\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)\text{N}(\text{C}_6\text{H}_5)]$ (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.

Acknowledgment. This material is based upon work supported by the Air Force Office of Scientific Research under Grant No. AFOSR-84-0021. We thank Professor James Ibers for the use of electrochemical equipment and Michael Lilga for helpful discussions. Professor Brian Hoffman generously provided us access to EPR instrumentation and gave us expert advice. We also acknowledge Professor D. E. Ellis and Dr. Frank Kutzler for helpful discussions concerning the $X\alpha$ calculations.

Registry No. $\text{CpCo}(1,4\text{-H}_2\text{N}_4)$, 80738-20-1; $\text{CpCo}(1,4\text{-H}_2\text{N}_4)^-$, 90460-30-3; $\text{CpCo}(1,4\text{-Me}_2\text{N}_4)$, 80738-16-5; $\text{CpCo}(1,4\text{-Me}_2\text{N}_4)^-$, 90460-31-4; $\text{CpCo}[1,4\text{-(2,6-Me}_2\text{C}_6\text{H}_3)_2\text{N}_4]$, 90460-32-5; $\text{CpCo}[1,4\text{-(2,6-Me}_2\text{C}_6\text{H}_3)_2\text{N}_4]^+$, 90460-33-6; $\text{CpCo}[1,4\text{-(C}_6\text{H}_5)_2\text{N}_4]$, 76418-81-0; $\text{CpCo}[1,4\text{-(C}_6\text{H}_5)_2\text{N}_4]^+$, 90460-34-7; $\text{CpCo}[1,4\text{-(2,4-F}_2\text{C}_6\text{H}_3)_2\text{N}_4]$, 80738-18-7; $\text{CpCo}[1,4\text{-(2,4-F}_2\text{C}_6\text{H}_3)_2\text{N}_4]^+$, 90481-24-6; $\text{CpCo}[1,4\text{-(C}_6\text{F}_5)_2\text{N}_4]$, 76418-82-1; $\text{CpCo}[1,4\text{-(C}_6\text{F}_5)_2\text{N}_4]^+$, 90460-35-8; $\text{CpCo}[1,4\text{-(CpCo}(\text{CO})_2)_2\text{N}_4]$, 90460-36-9; $\text{Fe}(\text{CO})_3(1,4\text{-Me}_2\text{N}_4)$, 38668-89-2; $\text{CpCo}(\text{HNC}_6\text{H}_3\text{MeNC}_6\text{H}_3\text{Me}_2)$, 90460-37-0; $\text{CpCo}(\text{HNC}_6\text{H}_4\text{NC}_6\text{H}_5)$, 12133-03-8.

(30) Bond, A. M.; Lawrence, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 2010-2021.

(31) McKinney, R. J. *Inorg. Chem.* **1982**, *21*, 2051-2056.

(32) tom Dieck, H.; Renk, I. W. *Chem. Ber.* **1971**, *104*, 110-130; **1972**, *105*, 1419-1430. Franz, K. D.; tom Dieck, H.; Krynitz, U.; Renk, I. W. *J. Organomet. Chem.* **1974**, *64*, 361-366. Franz, K. D.; tom Dieck, H.; Ostojka Starzewski, K. S.; Hohmann, F. *Tetrahedron* **1975**, *31*, 1465-1469.

(33) Shi, Q.-Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *Organometallics* **1982**, *1*, 1033-1037.