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Stabilization of Anion Radicals by the Pentaphenylcyclopentadienyl Ligand. Evidence for Symmetrical Metal–C_5R_5 Bonding in $[(\eta\text{-}C_5Ph_5)M(CO)_2]^-$ (M = Co, Rh)

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Abstract: The pentaphenylcyclopentadienyl complexes $(\eta^5\text{-}C_5Ph_5)M(CO)_2$ (M = Co, Rh) were reduced by one electron to their corresponding radical anions. $E°$ potentials (vs. SCE) measured by cyclic voltammetry were −1.57 V for M = Co and −1.70 V for M = Rh in tetrahydrofuran solutions. Although the Rh anion was less stable than the Co anion, both radicals were studied by ESR spectroscopy. The half-filled molecular orbital shows a high degree of covalency, approximately half-localized in the metal d_{yz} orbital. The hyperfine tensor is nonaxial, apparently because of admixture of $(n + 1)$ p_y metal character into the half-filled orbital. The results are consistent with pseudo-C_{2v} symmetry of the radical anions, implying symmetric bonding of the metal to the cyclopentadienyl ring.

Carbonyl-rich 18-electron metal polyolefin compounds [e.g., $CpV(CO)_4$, $(arene)Cr(CO)_3$, $CpCo(CO)_2$, etc.] have been shown to be reducible either by electrochemical or chemical methods,[1-10] and the existence of a radical anion has almost always been demonstrated or implied. With the exception of certain anions in which the extra electron appears to be localized on the polyolefin moiety,[2,4,11,12] the resulting 19-electron complexes are usually quite unstable, reacting via various routes including loss of carbon monoxide[1,5,7,8] and partial decomplexation of the polyolefin,[1,3,9] both of which lead to 17-electron intermediates subject to further electron-transfer processes.[5,6,9]

In the case of the cobalt and rhodium complexes $CpM(CO)_2$ (M = Co, Rh), one-electron reduction results in polynuclear complexes of the type $[CpCo(\mu\text{-}CO)]_2^-$ or $[Cp_3Rh_3(CO)_2(\mu\text{-}CO)_2]^-$, the former being particularly important due to its rich reaction chemistry with electrophiles.[13] The radical anions $CpM(CO)_2^-$ (M = Co, Rh) are reactive enough to have eluded characterization by physical methods, except when produced in a frozen matrix (M = Co).[14] We set out to produce more stable analogues of the cobalt and rhodium radicals by reduction of the pentaphenylcyclopentadienyl complexes $(\eta^5\text{-}C_5Ph_5)M(CO)_2$.

Multiple functionalization of a Cp or arene ligand often results in dramatic kinetic stabilization of a complex[15b] and, depending on the desired oxidation state, may result in thermodynamic stabilization as well. This strategy has most often involved permethylation of C_5 or C_6 rings,[15a,16] which from the viewpoint of redox chemistry leads to thermodynamic stabilization of higher oxidation states.[16d,17] Recently, however, perphenylated cyclopentadienyl complexes have begun to receive attention[18-24] since the $(\eta^5\text{-}C_5Ph_5)$ ligand gives the desired kinetic stability of a π-complexed protecting group and acts as the complement to C_5Me_5 because of its ability to stabilize lower metal oxidation states through the electron-withdrawing properties of its aryl substituents.[20-22]

Our strategy of reducing $(\eta^5\text{-}C_5Ph_5)M(CO)_2$ follows closely that earlier employed[21] in production of the first paramagnetic Pd(I) π-complexes by one-electron reduction of their 18-electron Pd(II) $(\eta^5\text{-}C_5Ph_5)PdL_2^+$ precursors. With, for example, $L_2 = \eta^4\text{-}C_8H_{12}$, the 19-electron C_5Ph_5 complex had a lifetime ca. 10^4 times longer than the analogous C_5H_5 complex. Qualitatively similar results are reported in the present study of Co and Rh complexes. One objective of this work was to determine the electronic ground state of the radical anions $[(\eta^5\text{-}C_5Ph_5)M(CO)_2]^-$, which had been characterized as containing predominantly d_{yz}

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(1) Reduction of $(\eta^4\text{-}alkene)Fe(CO)_4$ to give $(\eta^2\text{-}alkene)Fe(CO)_3^-$: Krusic, P. J.; San Filippo, J., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 2645. This paper corrects an earlier paper in which the radical anion was thought to be that of the tetracarbonyl complex (Dessy, R. E.; Charkoudian, J. C.; Abeles, T. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1970**, *92*, 3947).

(2) $(\eta^4\text{-}C_8H_8)Fe(CO)_3^-$: (a) Dessy, R. E.; Stary, F. E.; King, R. B.; Waldrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 471. (b) El Murr, N.; Riveccie, M.; Laviron, E.; Deganello, G. *Tetrahedron Lett.* **1976**, 3339. (c) Tulyathan, B.; Geiger, W. E. *J. Electroanal. Chem.* **1980**, *109*, 325.

(3) $(\eta^4\text{-}C_8H_{12})Fe(CO)_3$ reduction giving $(\eta^2\text{-}C_8H_{12})Fe(CO)_3^-$: ref 1. The electrochemical reduction of the neutral complex is irreversible: N. Van Order, University of Vermont, unpublished data, 1982.

(4) $(\eta^4$-Benzylideneacetone$)Fe(CO)_3$ reduction to stable monoanion: El Murr, N.; Riveccie, M.; Dixneux, P. *Chem. Commun.* **1978**, 552.

(5) Reduction of $CpV(CO)_4$ to produce $CpV(CO)_3^{2-}$ ultimately forming $CpV(H)(CO)_3^-$ by reaction with water: El Murr, N.; Moise, C.; Riveccie, M.; Tirouflet, J. *Inorg. Chim. Acta* **1979**, *32*, 189.

(6) Reduction of $CpMn(CO)_3$ involves two electrons by coulometry but leads to isolation of a red solid which analyzes for $[Bu_4N][CpMn(CO)_3]$. This intriguing material eluded attempts at structural characterization: Würminghausen, T.; Sellman, D. *J. Organomet. Chem.* **1980**, *199*, 77. The reduction potential of the neutral complex had been reported earlier in ref 2a.

(7) Reduction of $CpCo(CO)_2$ electrochemically: ref 2a. By sodium amalgam: (a) Ilenda, C. S.; Schore, N. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1976**, *98*, 255. (b) Schore, N. E.; Ilenda, C. S.; Bergman, R. G. *Ibid.* **1976**, *98*, 256. (c) *Ibid.* **1977**, *99*, 1781.

(8) $CpRh(CO)_2$ reduction with Na/Hg: Jones, W. D.; White, M. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 6770 and references therein.

(9) $(\eta^6$-Arene$)Cr(CO)_3$ complexes reduce via two electrons, giving η^4-arene $Cr(CO)_3^{2-}$: Rieke, R. D.; Arney, J. S.; Rich, W. E.; Willeford, B. R., Jr.; Poliner, B. S. *J. Am. Chem. Soc.* **1975**, *97*, 5951 and references therein.

(10) $(\eta^6\cdot C_7H_6R)M(CO)_3^+$ (M = Cr, Mo, W) reductions produce dimers connected through the C_7 rings: (a) Munro, J. D.; Pauson, P. L. *J. Chem. Soc.* **1961**, 3484. (b) Lloyd, M. K.; McCleverty, J. A.; Conner, J. A.; Jones, E. M. *J. Chem. Soc., Dalton* **1973**, 1768. (c) Hoch, G.; Panter, R.; Ziegler, M. L. *Z. Naturforsch. B* **1975**, *31*, 294. (d) Green, M. L. H.; Pardy, R. B. A. *J. Organomet. Chem.* **1976**, *117*, C13. (e) Panter, R.; Ziegler, M. L. *Z. Allg. Chem.* **1979**, *453*, 14. (f) Armstead, J. A.; Cox, D. J.; David, R. *J. Organomet. Chem.* **1982**, *236*, 213.

(11) ESR of $(C_8H_8)Fe(CO)_3^-$: Albright, T. A.; Geiger, W. E.; Moraczweski, J.; Tulyathan, B. *J. Am. Chem. Soc.* **1981**, *103*, 4787.

(12) $(\eta^5\text{-}C_5H_4R)Mn(CO)_3$ or $(\eta^6\text{-}C_6H_5R)Cr(CO)_3$ complexes derivatized with ketonic groups: (a) Tirouflet, J.; Dabard, R.; Laviron, E. *Bull. Soc. Chim. Fr.* **1963**, 1655. (b) Gogan, N. J.; Chu, C.-K.; Gray, G. W. *J. Organomet. Chem.* **1973**, *51*, 323. (c) Ceccon, A.; Romainin, A.; Venzo, A. *Transition Met. Chem.* **1976**, *1*, 25. (d) Gogan, N. J.; Dickinson, I. L.; Doull, J.; Patterson, J. R. *J. Organometal. Chem.* **1981**, *212*, 71. (c) Ceccon, A.; Corvaja, C.; Giacommetti, G.; Venzo, A. *J. Chem. Soc., Perkin Trans. 2* **1978**, 283.

(13) Bergman, R. G. *Acc. Chem. Res.* **1980**, *13*, 113.

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

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metal contribution in the radical assigned to $CpCo(CO)_2^-$ produced by γ-irradiation of the neutral precursor in frozen acetone or methyltetrahydrofuran.[14] There appears to be no information on analogous d^9 Rh π-complexes, which have proven elusive.[25] The present results are consistent with a b_2 ground state (in pseudo-C_{2v} symmetry) for both the cobalt and rhodium radical anions, the dominant contribution coming from the metal d_{yz} orbital. In addition, the results suggest that the "allyl-ene" distortion of the Cp-metal bonding discovered in the neutral $(\eta^5\text{-}C_5R_5)M(CO)_2$ complexes (R = CH_3; M = Co,[26] Rh[27]) is relieved in the radical anions, a phenomenon explicable in terms of published MO schemes.[27-29]

Experimental Section

$(\eta^5\text{-}C_5Ph_5)M(CO)_2$ (M = Co, Rh) were prepared as previously described,[20] and electrochemical procedures were generally as noted earlier.[30] Potentials are referred to the aqueous saturated calomel electrode (SCE), and the supporting electrolyte was 0.1 M $(n\text{-}Bu)_4NPF_6$. Cyclic voltammetry experiments were peformed under a purge of dry nitrogen, and bulk coulometry, including electrochemical generation of the anion radicals, was performed inside a Vacuum Atmospheres drybox. A FTS Systems cryogenic cooler allowed temperature control of electrochemical solutions within the drybox with a precision of ±1 °. The preferred solvent both for electrochemical experiments and for chemical reductions was tetrahydrofuran (THF). Chemical reductions for ESR samples employed sodium naphthalenide (NaNap) as the reducing agent. Typically, 20–30 mg of $(\eta^5\text{-}C_5Ph_5)M(CO)_2$ in ca. 5 mL of THF was treated with a NaNap solution containing a slight molar excess of the reducing agent. The solutions were mixed in a high-vacuum cell at subambient temperatures, usually below 250 K. After mixing, the solutions were frozen in liquid nitrogen if glassy ESR spectra were to be obtained. The anion radical of the Co complex was stable enough to allow fluid solution ESR spectra to be obtained, but efforts to record solution ESR spectra of the rhodium complex were unsuccessful. ESR spectra were obtained with a modified Varian E-3 spectrometer and DPPH (g = 2.0036) was used as a calibrant.

Results and Discussion

Electrochemistry. $(\eta^5\text{-}C_5Ph_5)Co(CO)_2$ (**1**) displays a chemically reversible one-electron reduction to the corresponding anion radical, $(\mathbf{1})^-$, at $E°$ = −1.57 V. Polarograms are diffusion-controlled and have the shape expected of a Nernstein system, with $E_{3/4} - E_{1/4}$ = −57 mV.[31] Cyclic voltammograms at either a Pt bead or hanging mercury drop electrode confirm the diffusion-controlled nature of the reduction [$i_{pk} \propto$ scan rate $(v)^{1/2}$] and the chemical reversibility of the couple i_a/i_c = 1.0 ± 0.05 at 0.05 V/s < v < 0.50 V/s. Attempts were not made to minimize CV peak separations, ΔE_p, which were typically ca. 100 mV at v = 0.05 V/s, comparable to ferrocene under similar conditions. Thus, most of the increase over the Nernstian value of ΔE_p = 60 mV may be ascribed to electrolyte resistance effects. This does not seem to be the case for the rhodium complex, **2**, vide infra, which appears to obey true quasireversible charge transfer kinetics.

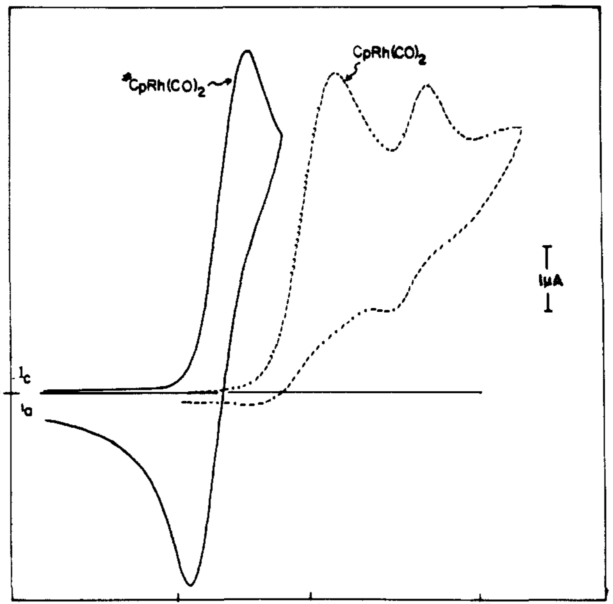

Figure 1. CV scans of $CpRh(CO)_2$ (dashed line) and **2** (solid line) under similar conditions: Pt electrode, scan rate 100 mV/s, T = 298 K, concentrations ca. 5 × 10^{-4} M.

Bulk coulometry confirmed the one-electron process and established that the anion displays reasonable long-term stability. Electrolysis at 273 K at a platinum gauze electrode proceeded smoothly to ca. 95% completion with consumption of 1.0 faraday of charge. After the current had dropped to ca. 5% of its initial value, a steady-state current was observed, presumably due to catalytic regeneration of neutral **1** from reaction of $(\mathbf{1})^-$ with adventitious O_2 or other trace oxidants. After electrolysis the original reduction wave at $E_{1/2}$ = −1.57 V had become an oxidation wave, with rotating platinum electrode (RPE) scans giving a plateau height of about 80% of the original wave. A small reversible wave was also present at $E°$ = −0.3 V after electrolysis, which we ascribe to the free ligand couple[32] $(C_5Ph_5)^{-/0}$, apparently arising from slow release of the pentaphenylcyclopentadienyl moiety from $(\mathbf{1})^-$. After the solution was allowed to sit for 2 h, neutral **1** was present in about 70% of its original concentration, with about a 30% yield of $C_5Ph_5^-$ also being detected.

The $E°$ potential of **1** is shifted 250 mV positive from that of its Cp analogue, $CpCo(CO)_2$, which we measure to be −1.82 V in THF.[33] This is expected on the basis of the electron-withdrawing properties of the phenyl substituents. The shift is approximately the same as that observed earlier for palladium π-complexes.[21]

Cylic voltammetry experiments were conducted in which excess PPh_3 was added to solutions of **1**. No effect was observed on the position, magnitude, or reversibility of the reduction wave. Thus,

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(15) (a) Maitlis, P. M. *Acc. Chem. Res.* **1978**, *11*, 301. (b) Maitlis, P. M. *Chem. Soc. Rev.* **1981**, *10*, 1. (c) Silverthorn, W. *Adv. Organomet. Chem.* **1975**, *13*, 48.

(16) (a) Wolszanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (b) Marks, T. J. *Science* **1982**, *217*, 989. (c) Wayda, A. L.; Evans, W. J. *Inorg. Chem.* **1980**, *19*, 2190. (d) Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882. (e) Carbomethoxy analogues: Bruce, M. I.; Wallis, R. C.; Williams, M. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 2183, and earlier references.

(17) (a) Smart, J. C.; Robbins, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 3936. (b) Koelle, U.; Khouzami, F. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 640.

(18) Heeg, M. J.; Janiak, C.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 4259.

(19) Powell, J.; Dowling, N. I. *Organometallics* **1983**, *2*, 1742.

(20) Connelly, N. G.; Raven, S. J. *J. Chem. Soc., Dalton Trans.* in press.

(21) Broadley, K.; Lane, G. A.; Connelly, N. G.; Geiger, W. E. *J. Am. Chem. Soc.* **1983**, *105*, 2486.

(22) Broadley, K.; Connelly, N. G.; Lane, G. A.; Geiger, W. E. *J. Chem. Soc., Dalton Trans.*, in press.

(23) Zhang, R.; Tsutsui, M.; Bergbreiter, D. E. *J. Organomet. Chem.* **1982**, *229*, 109.

(24) Slocum, D. W.; Johnson, S.; Matusz, M.; Duraj, S.; Amarik, J. L.; Simpson, K. M.; Owen, D. A. Abstracts of 186th Meeting of the American Chemical Society, 1983.

(25) There are reports of electrochemical reduction of Rh(I) π-complexes. $CpRh(\eta^4\text{-quinone})$ complexes reduce to radical anions, as shown by polarography [Gubin, S. P.; Khandkarova, V. S. *J. Organomet. Chem.* **1968**, *12*, 523] and cyclic voltammetry [Sueoka, N.; Geiger, W. E., unpublished data]. The related cyclopentadienone complexes $CpRh(\eta^4\text{-}C_5R_4O)$ (R = Ph or C_6F_5) are reduced to their radical anions electrochemically or by alkali metal, but instability of the radicals precluded recording of ESR spectra [van Willigen, H.; Geiger, W. E.; Rausch, M. D. *Inorg. Chem.* **1977**, *16*, 581].

(26) Byers, L. R.; Dahl, L. F. *Inorg. Chem.* **1980**, *19*, 277. See also: Olson, W. L.; Nagaki, D. A.; Dahl, L. F. *Organometallics* **1986**, *5*, 630.

(27) Lichtenberger, D. L.; Calabro, D. C.; Kellogg, G. E. *Organometallics* **1984**, *3*, 1623.

(28) Hoffman, P. *Angew Chem., Int. Ed. Engl.* **1977**, *16*, 536.

(29) Albright, T. A.; Hoffman, R. *Chem. Ber.* **1978**, *111*, 1578.

(30) Moraczweski, J.; Geiger, W. E. *J. Am. Chem. Soc.* **1981**, *103*, 4779. Geiger, W. E.; Rieger, P. H.; Tulyathan, B.; Rausch, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 7000.

(31) This is the Tomes criterion for reversibility [Tomes, J. *Collect. Czech. Chem. Commun.* **1937**, *9*, 12, 81, 150].

(32) This wave at $E°$ = −0.3 V had been observed earlier in the reduction of $(C_5Ph_5)Pd$ complexes (ref 21 and 22).

(33) This reduction had been previously reported in glyme in ref 2a ($E°$ = −1.75 ± 0.1 V when converted to SCE reference electrode) and as −1.83 V (ref 7a, converted to SCE) and −1.80 V (J. Moraczewski, unpublished data, University of Vermont, 1980) in CH_3CN.

on the CV time scale (ca. 10 s in these experiments) neither **1** nor $(\mathbf{1})^-$ react with PPh_3. Under similar conditions multinuclear cobalt compounds undergo electrocatalytic substitution of PR_3 for CO.[34] Rupture of a Co–Co bond, generating an intermediate with a coordinatively unsaturated metal, ha been postulated[34a] to account for the facile phosphine substitution in radical anions such as $Co_2(CO)_6(\mu\text{-}C_2R_2)^-$. A similar mechanism is obviously not possible for a mononuclear radical anion like $(\mathbf{1})^-$. However, an unsaturated metal could be generated by loss of CO from $(\mathbf{1})^-$ (or by η^5–η^3 slippage of the *Cp ligand). Although carbonyl ligands are generally held more strongly in *isoelectronic* complexes containing increasingly negative charge,[35] there is ample precedent for loss of CO after addition of electrons to complexes.[1,5,36-38] Indeed, the 17-electron intermediate generated by carbonyl loss may then add phosphine.[1,5,38] Since phosphine substitution does not occur for $(\mathbf{1})^-$, the carbonyl ligands must be strongly held in the 19-electron cobalt complex.

In their study of the preparation of the dimer $[Cp_2Co_2(\mu\text{-}CO)_2]^-$ from alkali metal reduction of $CpCo(CO)_2$, Schore et al. postulated the intermediacy of the radical anion $CpCo(CO)_2^-$ and considered that carbonyl loss from the mononuclear anion might provide a route to the dinuclear complex.[7b] However, they later rejected that possibility when it was found that metal reduction of $CpCo(CO)_2$ in the presence of PR_3 resulted in formation of $NaCo(CO)_{3-x}(PR_3)_x$ ($x = 0, 1$) rather than $CpCo(CO)PR_3$. This showed that $CpCo(CO)_2^-$ is prone to loss of Cp^- rather than CO and suggested that the dinuclear anion is formed by CO expulsion *after* formation of an intermediate dimetallic anion.[7c] The present study of the fate of the analogous but more stable $(\mathbf{1})^-$ lends support to the latter mechanism,[7c] since loss of $(C_5Ph_5)^-$, rather than CO, is observed for $(\mathbf{1})^-$.

1 demonstrated an irreversible oxidation wave of apparent 2-electron height at $E_p = +1.17$ V ($v = 0.1$ V/s), which was not studied in detail. By contrast, the monosubstituted complexes $(\eta\text{-}C_5Ph_5)Co(CO)[P(OR)_3]$ (R = Me or Ph) undergo fully reversible one-electron oxidation to the corresponding monocation.[20]

The rhodium complex **2** also displays a one-electron reduction (Figure 1) at $E° = -1.71$ V by CV. Polarography and normal pulse polarography show well-shaped voltammograms with $E_{1/2} = -1.72$ V and $E_{3/4} - E_{1/4} = -58$ mV. CV studies showed that reduction of the Rh complex was less reversible, both in the Nernstian sense and with regards to anion stability, than the Co complex. ΔE_p values at a Pt electrode at $v = 0.02$ V/s were 95–100 mV under conditions (minimizing *iR* loss)[39] which gave $\Delta E_p = 67$ mV for ferrocene. At $v = 0.10$ V/s, ΔE_p was 155 mV for **2** and only 71 mV for the reversible standard, Cp_2Fe. Hence, quasireversible heterogeneous electron-transfer kinetics are indicated for **2** at a Pt electrode.

Perhaps more importantly, the reduction of **2** was not completely chemically reversible at very slow sweep rates, and $v > 0.1$ V/s was necessary to achieve $i_a/i_c = 1.0$. We estimate the lifetime of $(\mathbf{2})^-$ to be roughly 10 s at room temperature. Solutions of $(\mathbf{2})^-$ produced by bulk electrolysis ($n = 1.0\ e^-$) required temperatures below 240 K to avoid appreciable decomposition of the radical. Even then, solutions of purple $(\mathbf{2})^-$ became brown on standing at 230 K.

Nevertheless, $(\mathbf{2})^-$ is extremely stable compared to its Cp analogue, $[CpRh(CO)_2]^-$, which is not even detectable in CV scans of the reduction of $CpRh(CO)_2$ (Figure 1). The reduction wave of the C_5H_5 complex is about 300 mV negative of the C_5Ph_5 derivative.

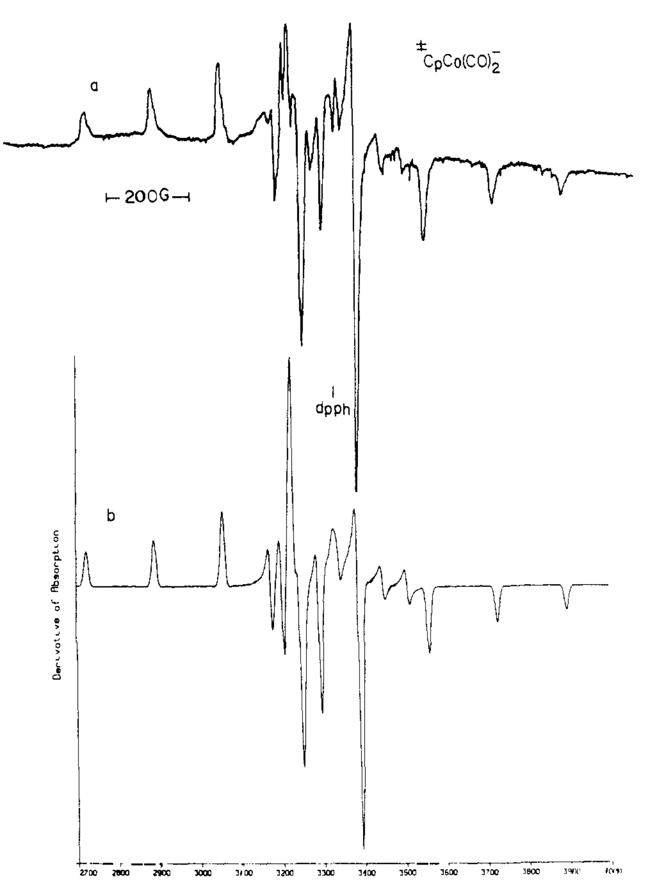

Figure 2. (a) Experimental X-band ESR spectrum of ${}^*CpCo(CO)_2^-$ in frozen THF, $T = 77$ K, modulation amplitude 3 G. (b) Calculated spectrum using the parameters in Table II and a Gaussian line width of 5 G.

Table I. Standard Reduction Potentials[a] for $(\eta\text{-}C_5R_5)M(CO)_2$ (R = Ph or H; M = Co or Ph)

complex	$E°$ (vs. SCE), V
$(\eta\text{-}C_5Ph_5)Co(CO)_2$	−1.57
$(\eta\text{-}C_5H_5)Co(CO)_2$	−1.82[b]
$(\eta\text{-}C_5Ph_5)Rh(CO)_2$	−1.71
$(\eta\text{-}C_5H_5)Rh(CO)_2$	ca. −2.0[c]

[a] In THF/0.1 M Bu_4NPF_6 at 298 K, Pt electrode. [b] See ref 33 for values in other solvents. [c] Reduction is chemically irreversible, thus $E°$ is unknown. However, if charge transfer kinetics are rapid and resistive errors are assumed small, the cathodic peak potential (−2.05 V) will be ca. 30 mV negative of the $E°$ value.

The oxidative electrochemistry of **2** and of its Lewis base derivatives have been discussed elsewhere.[20]

Electron Spin Resonance. The anion radicals $[(C_5Ph_5)M(CO)_2]^-$ (M = Co, Rh) were generated for ESR studies with low-temperature controlled-potential coulometry (ca. 275 K for M = Co, 255 K for M = Rh) in THF, and the solutions were transferred to ESR sample tubes under nitrogen. These samples were rapidly immersed in liquid nitrogen for analysis of their frozen solution spectra. Melting the samples and refreezing them resulted in loss of the paramagnetic signal for M = Rh, but the Co anion was more stable and fluid solution spectra were also obtained for $(\mathbf{1})^-$. No secondary radicals were observed in these experiments, and spectra obtained following reduction of **1** or **2** by 1 equiv of sodium naphthalenide were identical with those seen after electrochemical reduction.

The ESR spectrum of $(\mathbf{1})^-$ in THF solution shows the eight hyperfine lines expected from coupling to a ${}^{59}Co$ nucleus ($I = {}^7/_2$): $\langle g \rangle = 2.018$, $\langle A \rangle = 77.4\ G = 72.9 \times 10^{-4}\ cm^{-1}$. The spectrum of the same solution, frozen at liquid nitrogen temperature, is shown in Figure 2a. This spectrum is virtually identical with that reported by Symons and Bratt[14] for $CpCo(CO)_2^-$, formed by γ-radiolysis of a 2-methyltetrahydrofuran glass containing the

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[34] (a) Arewgoda, C. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J.; Visco, S. *J. Am. Chem. Soc.* **1982**, *104*, 5633. (b) Bezems, G. J.; Rieger, P. H.; Visco S. *J. Chem. Soc., Chem. Commun.* **1981**, 265.

[35] For studies on $Ni(CO)_4$, $Co(CO)_4^-$, and $Fe(CO)_4^{2-}$ see: Hieber, W.; Wollmann, K. *Chem. Ber.* **1962**, *95*, 1552.

[36] Chen, Y.-S.; Ellis, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1689.

[37] Pickett, C. J.; Pletcher, D. *J. Chem. Soc., Dalton Trans.* **1976**, 749.

[38] Grobe, J.; Zimmermann, H. *Z. Naturforsch.* **1978**, *36b*, 301.

[39] Lower concentrations of **2** (ca. 3×10^{-4} M) and a luggin reference probe were used to minimize resistive losses. For a discussion of the usee of a luggin probe, see: Sawyer, D. T.; Roberts, J. *Experimental Electrochemistry for Chemists*; J. Wiley and Sons: New York, 1974, pp 118ff.

Table II. ESR Parameters[a] for $[(C_5Ph_5)M(CO)_2]^-$

species	g_1	g_2	g_3	A_1	A_2	A_3	$\langle g \rangle$	$\langle A \rangle$
(**1**)$^-$, M = Co	2.018	1.995	2.041	(−)157.9	(−)44.1	(−)16.8	2.018	(−)72.9
(**2**)$^-$, M = Rh	2.005	1.945	2.019	(+) 26.5	(+)14.8	(+) 7.5	1.990[b]	(+)16.3

[a] Hyperfine couplings in units of 10^{-4} cm^{-1} [b] Average of frozen solution parameters.

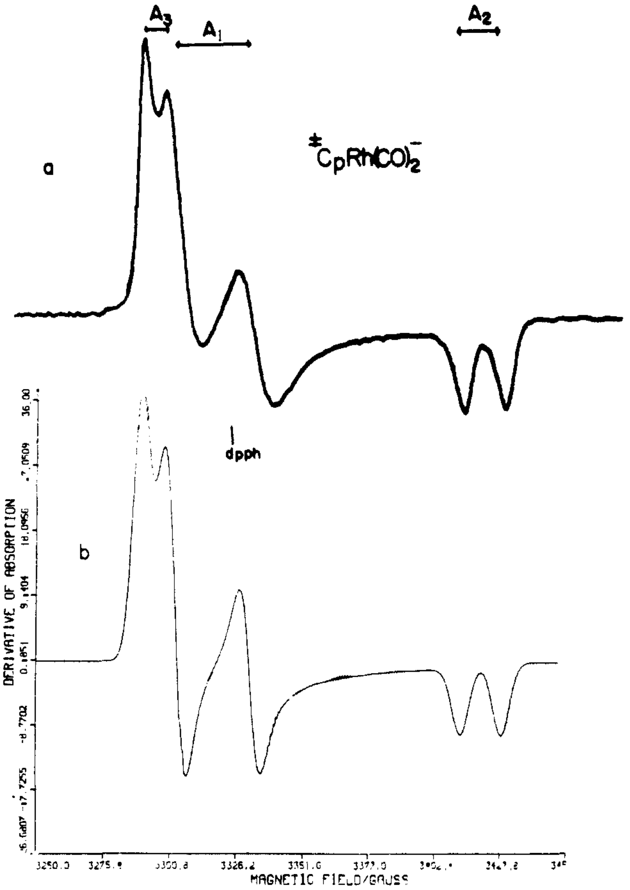

Figure 3. (a) Experimental X-band ESR spectrum of $^*CpRh(CO)_2^-$ in frozen THF, T = 77 K, modulation amplitude 2 G. (b) Calculated spectrum using the parameters in Table II and a Gaussian line width of 3.2 G.

neutral parent molecule. Symons and Bratt interpreted their spectrum in terms of axial g and hyperfine tensors ($g_\parallel$ = 2.005, $g_\perp$ = 2.004, $a_\parallel$ = 172 G, $a_\perp$ = 45 G), but the spectrum shown in Figure 2a is clearly not axial. There are too many lines in the g = 2 region, structure which was obscured by an impurity resonance in the spectrum reported by Symons. Furthermore, an axial interpretation gives parameters which do not average to the observed $\langle g \rangle$ and $\langle A \rangle$ values. A computer simulation using Symons' parameters gives a good account of the positions of the resolved features in the published spectrum, but the perpendicular features in the simulation have considerably larger amplitudes than the corresponding features in the experimental spectrum.

About 14 features of the spectrum shown in Figure 2a can be assigned with confidence to minimum, most probable, or maximum resonant fields corresponding to various nuclear spin quantum numbers. A least-squares fit of these field positions to a second-order solution to the spin Hamiltonian[40] gave the parameters listed in Table II; a computer simulation based on these parameters is shown in Figure 2b. The averages of the g and hyperfine tensor components are in essentially perfect agreement with the isotropic parameters, and thus the hyperfine tensor components, A_x, A_y, A_z, must have the same sign as $\langle A \rangle$. Since the eight features corresponding to the largest hyperfine tensor component are equally spaced (within small second-order corrections), we can be confident that at least this component shares its principal axis with the g tensor. The detailed match of the experimental and simulated spectra is only fair in the central region. The discrepancies are probably due to quadrupolar effects which become important for those orientations for which the effective hyperfine coupling is small. Nonetheless, the overall fit is very good, and we can proceed to an interpretation of the parameters with some confidence.

The frozen solution spectrum of (**2**)$^-$, shown in Figure 3a, is relatively straightforward. Six features are expected corresponding to the three components of the g and hyperfine tensors and the two ^{103}Rh ($I = {}^1/_2$) spin states. Five features are actually observed, but the second feature from the low-field end of the spectrum appears to be the superposition of the minimum field feature of the $m_I = -{}^1/_2$ resonance with the central feature of the $m_I = +{}^1/_2$ resonance. Computer simulation (Figure 3b) confirms this assignment; the parameters are given in Table II.

Discussion

Interpretation of ESR Parameters. We begin by assuming that the singly occupied molecular orbital (SOMO) in (**1**)$^-$ and (**2**)$^-$ is mainly metal nd_{yz} in character, as predicted by molecular orbital theory calculations.[27-29] With this assumption, we expect the g and hyperfine tensor components to be given by

$$g_x = g_e + 2\lambda_d a^2 \left[\frac{1}{\Delta E_{x^2-y^2}} + \frac{3}{\Delta E_{z^2}} \right] \tag{1a}$$

$$g_y = g_e + \frac{2\lambda_d a^2}{\Delta E_{xy}} \tag{1b}$$

$$g_z = g_e + \frac{2\lambda_d a^2}{\Delta E_{xz}} \tag{1c}$$

$$A_x = A_s + a^2 P_d \left[-\frac{4}{7} + 2\lambda_d \frac{1}{\Delta E_{x^2-y^2}} + \frac{3}{\Delta E_{z^2}} + \frac{3\lambda_d}{7} \frac{1}{\Delta E_{xy}} + \frac{1}{\Delta E_{xz}} \right] \tag{2a}$$

$$A_y = A_s + a^2 P_d \left[\frac{2}{7} + \frac{2\lambda_d}{\Delta E_{xy}} - \frac{3\lambda_d}{7} \frac{1}{\Delta E_{xz}} - \frac{1}{\Delta E_{x^2-y^2}} + \frac{1}{\Delta E_{z^2}} \right] \tag{2b}$$

$$A_z = A_s + a^2 P_d \left[\frac{2}{7} + \frac{2\lambda_d}{\Delta E_{xz}} - \frac{3\lambda_d}{7} \frac{1}{\Delta E_{xy}} + \frac{1}{\Delta E_{x^2-y^2}} - \frac{1}{\Delta E_{z^2}} \right] \tag{2c}$$

where a is the LCAO coefficient of d_{yz} in the SOMO, λ_d is the spin–orbit coupling parameter for nd electrons, g_e is the free electron g value, A_s is the isotropic Fermi contact contribution to the hyperfine coupling, and

$$P_d = g_e g_N \mu_B \mu_N \langle r^{-3} \rangle_{nd} \tag{3}$$

We take P_d = 282 × 10^{-4} cm^{-1} for Co and −40.4 × 10^{-4} cm^{-1} for Rh.[41] The ΔE's are given by

$$\frac{1}{\Delta E_i} = \sum_{k \neq 0} \frac{c_{ik}^2}{E_0 - E_k} \tag{4}$$

where c_{ik} is the LCAO coefficient of atomic orbital i in molecular orbit k and $E_0 - E_k$ is the energy difference between the SOMO and molecular orbital k.

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[40] Rieger, P. H. *J. Magn. Reson.* **1982**, *50*, 485.

[41] Morton, J. S.; Preston, K. F. *J. Magn. Reson.* **1978**, *30*, 577.

Table III. Spin–Orbit Coupling Terms for Possible Hyperfine Component Assignments Assuming nd Interactions Only

	assignment (1, 2, 3)	$\gamma/\Delta E_{xz}$	$\lambda/\Delta E_{xy}$	$\lambda/\Delta E_{x^2-y^2}$	$\lambda/\Delta E_{z^2}$
M = Co	x, y, z	0.036	−0.006	−0.063	0.026
	x, z, y	−0.006	0.036	0.070	−0.018
M = Rh	x, y, z	0.019	−0.063	−0.171	−0.058
	x, z, y	−0.063	0.019	0.172	−0.056

If the symmetry of radicals is at least as high as C_s, then admixture of $(n + 1)$s character in the SOMO is forbidden and the isotropic coupling $\langle A\rangle$ must be due to spin polarization (plus a small contribution from spin–orbit coupling (see eq 2), and therefore negative for ^{59}Co and positive for ^{103}Rh. Equation 2 suggests that A_x will have the same sign as $\langle A\rangle$ and thus should be larger in magnitude than A_y or A_z. Thus, we assign the largest magnitude hyperfine coupling (see Table I) to A_x. Equations 1 and 2 can be combined to give

$$A_x - \langle A\rangle = P_d[-{}^4\!/_7a^2 + {}^2\!/_3\Delta g_x - {}^5\!/_{42}(\Delta g_y + \Delta g_z)] \quad (5)$$

where $\Delta g_i = g_i - g_e$ and $\langle A\rangle = 1/3(A_x + A_y + A_z)$. Equation 5 can be used, together with the appropriate values of P_d and the Δg_i, to compute $a^2 = 0.54$ for the cobalt radical and 0.45 for the rhodium analogue.

If the isotropic coupling is due to spin polarization (which is proportional to the d-electron spin density, a^2) and spin–orbit coupling, we can write

$$\langle A\rangle = A_s + {}^1\!/_3P_d(\Delta g_x + \Delta g_y + \Delta g_z) \quad (6)$$

where $A_s = Q_d{}^Ma^2$. The spin polarization coupling constant for cobalt 3d electrons, $Q_d{}^{Co} = -131 \times 10^{-4}$ cm^{-1}, has been estimated empirically.[42] With this parameter, eq 6 gives $\langle A^{Co}\rangle = -66 \times 10^{-4}$ cm^{-1}, in satisfactory agreement with the experimental value. Muniz, Vugman, and Danon[43] have estimated $Q_d{}^{Rh} = +32 \times 10^{-4}$ cm^{-1} so that eq 6 predicts $\langle A^{Rh}\rangle = +15 \times 10^{-4}$ cm^{-1}, in good agreement with the average of the three hyperfine components, 16.3×10^{-4} cm^{-1}.

The departure of the hyperfine tensors from axial symmetry is presumably due to unequal spin–orbit contributions to A_y and A_z. Subtracting eq 2b and 2c, this symmetry can be expressed by

$$A_y - A_z = P_d\left[\frac{17}{14}(\Delta g_y - \Delta g_z) + \frac{6a^2\lambda_d}{7}\left(\frac{1}{\Delta E_{x^2-y^2}} - \frac{1}{\Delta E_{z^2}}\right)\right] \quad (7)$$

Unfortunately, the last term in eq 7 cannot be evaluated in terms of the g-tensor components. However, we can use eq 1a and 7 to estimate the energy difference denominators, $\lambda_d/\Delta E_{x^2-y^2}$ and $\lambda_d/\Delta E_{z^2}$. These, together with $\lambda_d/\Delta E_{xy}$ and $\lambda_d/\Delta E_{xz}$ obtained from eq 1b and 1c, are given in Table III for the two possible assignments of the y- and z-components.

Notice that a negative sign for $\lambda_d/\Delta E_i$ implies a dominant contribution to the sum of eq 4 from a higher energy empty molecular orbital. Thus, the results given in Table III suggest that there are low-lying empty molecular orbitals with significant d_{xy} and $d_{x^2-y^2}$ character or with d_{xz} and $d_z{}^2$ character. This conclusion is not supported by the MO theory calculations which suggest that the SOMO is the highest energy MO with significant d character.

A clue to this apparent discrepancy is given by Albright and Hoffman,[29] who point out that the antibonding nature of the $2b_1(d_{xz})$ orbital in CpCo(CO)$_2$ is somewhat reduced by admixture of $4p_x$ character. Their extended Hückel calculations also show an empty orbital of a_1 symmetry and $4p_z$ character just above the $b_2(d_{yz})$ orbital (the SOMO in the present case). If we allow for admixture of $(n + 1)p_y$ character into the SOMO (allowed under C_{2v} symmetry), then the situation is substantially altered. If the metal contribution is written

$$\psi_{SOMO} = a|d_{yz}\rangle + b|p_y\rangle \quad (8)$$

we obtain the following additional terms for the g and hyperfine tensor components:

$$g_x(p_y) = \frac{2\lambda_pb^2}{\Delta E_z} \quad (9a)$$

$$g_y(p_y) = 0 \quad (9b)$$

$$g_z(p_y) = \frac{2\lambda_pb^2}{\Delta E_x} \quad (9c)$$

$$A_x(p_y) = b^2P_p\left[-\frac{2}{5} + \frac{2\lambda_p}{\Delta E_z} + \frac{3\lambda_p}{5\Delta E_x}\right] \quad (10a)$$

$$A_y(p_y) = b^2P_p\left[\frac{4}{5} - \frac{3\lambda_p}{5\Delta E_x} - \frac{3\lambda_p}{5\Delta E_z}\right] \quad (10b)$$

$$A_z(p_y) = b^2P_p\left[-\frac{2}{5} + \frac{2\lambda_p}{\Delta E_x} + \frac{3\lambda_p}{5\Delta E_z}\right] \quad (10c)$$

where

$$P_p = g_eg_N\mu_B\mu_N\langle r^{-3}\rangle_{(n+1)p} \quad (11)$$

Since the MOs with p_x or p_z character which couple via spin–orbit interaction will mostly be empty, eq 9a and 9c will give negative contributions to g_x and g_z, suggesting that the proper assignment of tensor axes 2 and 3 is to z and y, respectively. The effect is apparently considerably larger for Rh than for Co as might be expected.

This explanation rests on the assumption that the parameters λ_p and P_p are not very much smaller than λ_d and P_d. The spin–orbit coupling parameters for the $3d^84p$ configuration of cobalt have been estimated recently by Roth,[44] who employed a least-squares fit of extensive spectral data to the theoretical framework, obtaining $\lambda_d = 451$ cm^{-1}, $\lambda_p = 141$ cm^{-1}. If we assume that the relevant configuration for our purposes would more correctly be $3d^{9-\epsilon}4p^{\epsilon}$, then both parameters are probably somewhat overestimated, for the $(3d^9)$ ^2P terms $\lambda_d = 390$ cm^{-1}.[45] Comparable estimates for the $4d^85p$ configuration of rhodium are not available. Dunn gives $\lambda_d = 940$ cm^{-1}, based on the spin–orbit splitting of the $(4d^9)$ ^2P term. We can estimate $\lambda_p = 503$ cm^{-1} by interpolating between spectral data for the $(4d^05p^1)$ ^2P and $(4d^{10}5p^1)$ ^2P configurations.[46] In any case, the spin–orbit coupling parameter λ_p is almost certainly large enough, both for Co and for Rh, to significantly affect the g-tensor anisotropy if there is significant $(n + 1)p_y$ participation in the SOMO.

Kawamura and co-workers[47] have recently reported the analysis of the ESR spectrum of $Re_2(\mu\text{-}H)_2(CO)_8^-$. These authors were led to the conclusion that the SOMO of this radical anion was of b_{1g} symmetry with Re $5d_{xy}$ and $6p_y$ character. Although no theoretical estimate of P_p was available, the authors concluded that this parameter was comparable in magnitude with P_d. Indeed, we expect the following trend: $P_{3d} \gg P_{4p}, P_{4d} > P_{5p}, P_{5d} \sim P_{6p}$, given the $\langle r^{-3}\rangle$ dependence of the dipolar parameters. p-Orbital admixture is expected to be more important for the heavier metals as well so that the hyperfine tensor for $(C_5Ph_5)Co(CO)_2^-$ is probably largely determined by the 3d character of the SOMO. This is no doubt less true for the rhodium analogue.

Early in our analysis, we were tempted to ascribe the nonaxial hyperfine tensor to distortion of the cyclopentadienyl ring in

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[42] Peake, B. M.; Rieger, P. H.; Robinson, B. H.; Simpson, J. *J. Am. Chem. Soc.* **1980**, *102*, 156.

[43] Muniz, R. P. A.; Vugman, N. V.; Danon, J. *J. Chem. Phys.* **1971**, *54*, 1284.

[44] Roth, C. *J. Res. NBS* **1981**, *86*, 1331.

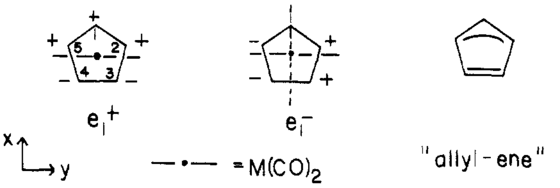
[45] Dunn, T. M. *Trans. Faraday Soc.* **1961**, *57*, 1441.

[46] Moore, C. E. *Atomic Energy Levels; NSB Circular* 467, Volume 3, Washington, D.C., 1958. A similar interpolation between $(3d^04p^1)^2$P and $(3d^{10}4p^1)^2$P gives $\lambda_p = 174$ cm^{-1} for cobalt.

[47] Sowa, T.; Kawamura, T.; Tamabe, T.; Yonezawa, T. *J. Am. Chem. Soc.* **1985**, *107*, 6471.

$(C_5Ph_5)M(CO)_2^-$. Crystal structures of $(C_5Me_5)Co(CO)_2$ and $(C_5Me_5)Rh(CO)_2$ show a significant departure of the rings from regular pentagons and reduction of molecular symmetry from pseudo-C_{2v} to C_s.[26,27] There are several reasons why this effect, if present in the radical anions, is unrelated to the ESR results. The plane of symmetry shown in the crystal structure is the *xz*-plane, bisecting the OC–M–CO angle. With this symmetry element, only d_{xy} can mix with d_{yz}. On MO theory grounds, it is difficult to see how such mixing could lead to lower energy. More significantly, however, d_{yz}–d_{xy} hybrids retain an axial dipolar hyperfine tensor, regardless of the degree of mixing, but the *x*- and *z*-axes are no longer principal axes of the resulting tensor. Since we are confident that the experimental g_x and A_x axes are coincident for **(1)**$^-$, this is good evidence against d_{yz}–d_{xy} mixing. From the most conservative viewpoint, there is reason to suspect Cp ring distortion to be less pronounced in the radical anions than in the neutral parents.

Lichtenberger et al.[27] argue that the loss of ring symmetry is due to the antibonding effect of the $2b_1(d_{xz})$ orbital. This effect may be visualized qualitatively in the following way. The highest energy ligand (Cp) orbitals taking part in the M–Cp bonding are the e_1^+ and e_1^- orbitals depicted below: In the e_1^+ orbital, which interacts with M d_{xz} to form the HOMO in neutral $CpM(CO)_2$, the node is parallel to the OC–M–CO vector. The e_1^-, with a node perpendicular to the OC–M–CO vector, is of correct symmetry to interact with M d_{yz}, which is empty in the neutral 18-electron complex. To the extent that the e_1^-, d_{yz} interaction mixes into the ground state, electron withdrawal takes place from e_1^-, decreasing its contribution to the M–Cp bonding and leading to lengthening of the C_2–C_3 and C_4–C_5 bonds. This suggests the limiting "allyl-ene" structure shown, in which the "single" bonds average 1.447 Å.[27] It would be expected that partial population of the $2b_2(d_{yz})$ orbital in the 19-electron anion would attenuate this antibonding interaction, weakening the metal–Cp bonds, of course, but reducing the distortion of the ring.



Conclusions

1. The pentaphenylcyclopentadienyl ligand stabilizes the 19-electron anion radicals $(\eta^5\text{-}C_5Ph_5)M(CO)_2^-$ (M = Co, Rh) compared to their unsubstituted cyclopentadienyl analogues. As observed previously for isoelectronic Pd π-complexes, the thermodynamic stabilization ($E°$ potentials) is mild (a few hundred millivolts) but the kinetic stabilization is very high. The reduced Rh complex appears to be the best-characterized d^9 Rh(0) π-complex reported to date.

2. $(\eta^5\text{-}C_5Ph_5)Co(CO)_2^-$ shows no tendency to react with PPh_3, implying that the carbonyl ligands are strongly held in the 19-electron cobalt complex.

3. The 19-electron radical anions appear to have pseudo-C_{2v} symmetry, implying symmetrical bonding of the cyclopentadienyl ring to the metal. Half-occupation of the $2b_2(d_{yz})$ molecular orbital in the anion appears to relax the "allyl-ene" Cp distortion found in the neutral 18-electron complexes. McKinney and co-workers have shown[48] that the "allyl-ene" distortion is also absent in $[CpCo(PEt_3)_2]^+$. Thus, a relatively complete picture of the influence of electron count on metal–cyclopentadienyl bonding is now available for this class of compounds, with unsymmetrical metal–Cp interactions being found in the 18-electron complex but not in the 17- or 19-electron complexes.

4. There appears to be sufficient $(n+1)p_y$ admixture in the SOMO to significantly perturb the anisotropy of the *g* tensors for both the Co and Rh radical anions. While the effect of p_y admixture on the hyperfine tensor is probably small for the Co radical anion, it may be quite significant for the Rh species. Thus, our estimate of the 4d spin density for this species, $a^2 = 0.45$, is subject to considerable uncertaintly.

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Registry No. 1, 90502-88-8; **1**$^-$, 103835-69-4; **2**, 102539-06-0; **2**$^-$, 103835-70-7.

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(48) Harlow, R. L.; McKinney, R. J.; Whitney, J. F. *Organometallics* **1983**, *2*, 1839.

$Pd(CH_3CN)_4(BF_4)_2$-Assisted Attack of Nitriles on Olefins. A Pd Analogue of the Ritter Reaction

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Abstract: The strongly electrophilic complex $Pd(CH_3CN)_4(BF_4)_2$ (**1**) activates a variety of olefins to undergo nucleophilic attack by nitriles to give nitrilium salts. These nitrilium salts undergo reaction with a variety of nucleophiles including electron-rich aromatics, alcohols, and amines, ultimately producing a variety of heterocyclic ring systems.

Palladium(II) salts are electrophilic and interact strongly with unsaturated electron-rich organic compounds. Thus, arenes, indoles, and other electron-rich heterocycles undergo direct palladation by palladium(II) acetate or trifluoroacetate.[1] In contrast, highly electrophilic $Pd(CH_3CN)_4(BF_4)_2$[2] (**1**) interacts strongly with olefins, with the proposed formation of incipient carbonium ions as intermediates, in its catalysis of the polymerization of ethylene and styrene,[3] its Friedel–Crafts alkylation of benzene with propene,[3] its rearrangements of *tert*-butylethylene and 1,1,2-trimethylcyclopropane to tetramethylethylene,[3] and its po-

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(1) Fujiwara, Y.; Maruyama, O.; Yoshidomi, M.; Taniguchi, H. *J. Org. Chem.* **1981**, *46*, 851. Itahara, T.; Sakakibara, T. *Synthesis* **1978**, 607. Itahara, T. *Synthesis* **1979**, *151*; *J. Chem. Soc., Chem. Commun.* **1981**, 254. Itahara, T.; Ikeda, M.; Sakakibara, T. *J. Chem. Soc., Perkin Trans 1* **1983**, 1361.

(2) Schramm, R. F.; Wayland, B. B. *Chem. Commun.* **1968**, 898.

(3) Sen, A.; Lai, T.-W. *J. Am. Chem. Soc.* **1981**, *103*, 4627.

0002-7863/86/1508-6224$01.50/0