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Accessibility of 17-Electron Structures for Cyclopentadienylchromium(III) Compounds. 2.[†] Cyanide Derivatives with 15- and 17-Electron Configurations

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Ion metathesis of $[(\text{ring})CrCl_2]_2$ (ring = Cp, Cp*) with excess KCN in water affords the complexes $[(\text{ring})Cr(CN)_3]^-$, which have been isolated as PPh_4^+ salts and characterized by elemental (C, H) analysis, ^{1}H NMR, magnetic suceptibility, and an X-ray investigation for the Cp* species. The interaction of these complexes with excess CN^- generate equilibrium amounts of the EPR-active, 17-electron $[(\text{ring})Cr(CN)_4]^{2-}$ adducts. The equilibrium constant for this addition process is 2.3 ± 0.1 M^{-1} for ring = Cp and $(4.4 \pm 0.2) \times 10^{-3}$ M^{-1} for ring = Cp* at 298 K. Either treatment of $[CpCr(CN)_3]^-$ with monodentate (L) or bidentate (L_2) tertiary phosphine ligands (e.g. PMe_3, PMe_2Ph, dmpm, dmpe) or reaction between $CpCrCl_2(\eta^1\text{-}L_2)$ or $[CpCrCl_2L + L]$ and excess Me_3SiCN leads to solutions containing small equilibrium amounts of EPR-active species which are characterized by hyperfine coupling to two equivalent P nuclei and are interpreted as the 17-electron $CpCr(CN)_2L_2$. The thermal accessibility of these 17-electron Cr(III) cyanide derivatives, as compared with the inaccessibility of the correponding chloride and methyl systems, is analyzed energetically in terms of the ligand steric and electronic effects.

Introduction

With only one reported exception,[2] known monocyclopentadienyl compounds of Cr(III) do not exceed the 15-electron configuration, in which they adopt a three-legged piano-stool structure and a spin quartet ground state.[3−5] When the Cp^- ligand is viewed as occupying three coordination sites, these molecules can be considered analogues of the large class of octahedral Cr(III) Werner-type complexes. On the other hand, monocyclopentadienyl Mo(III) compounds are most stable as 17-electron, spin doublet, pseudo-seven-coordinate systems.[6] Although spin quartet octahedral Mo(III) Werner-type complexes are quite common, corresponding 15-electron CpMo(III) complexes have not been isolated to date and attempts to generate them have demonstrated their high reactivity.[7,8]

The only known 17-electron half-sandwich Cr(III) system is the bis(allyl) compound $CpCr(\eta^3\text{-allyl})_2$, which thermally decomposes, however, above 0 °C.[2,9] Recent attempts in this laboratory at using the chelate effect of bidentate phosphine ligands have only resulted in the formation of $CpCrX_2(\eta^1\text{-L-L})$ (X = Cl, CH_3; L-L = dmpe, dppe, dmpm) complexes with one coordinated and one dangling P donor and a 15-electron configuration, the alternative 17-electron $CpCrX_2(\eta^2\text{-L-L})$ structure not being present in spectroscopically observable concentrations at equilibrium.[10]

The different behaviors of Cr(III) and Mo(III) have been attributed to the greater cost of pairing electrons in the smaller 3d orbitals of Cr(III) and to the smaller energy gain associated with the formation of a new Cr−L bond, whereas differences in steric requirements around Cr^{3+} and Mo^{3+} do not appear to play a major role.[10−12] It is expected that the introduction of softer and less electronegative ligands (such as Cp and allyl groups) lowers the cost of pairing the electrons, whereas harder and more electronegative ligands such as those ubiquitous in Werner chemistry should have the opposite effect. The formation of stronger covalent Cr−L bonds should also favor the formation of more saturated configurations.

In search of other ligand systems that could lead to a 17-electron configuration for $CpCr^{III}$ systems by reduction of the energetic cost of electron pairing and/or formation of stronger bonds, we have considered the cyanide ligand. Cyanide is a soft, low-electronegativity ligand, and in addition, it is sterically quite undemanding. A look at the literature reveals that CN^- leads to

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greater coordination numbers and lower spin states with respect to other typical Werner-type ligands for systems of many metal ions. For instance, while Werner-type complexes of d^3 Mo(III) are six-coordinate spin quartet systems, cyanide yields the seven-coordinate spin doublet $[Mo(CN)_7]^{4-}$ complex,[13] and d^2 Nb(III) and Mo(IV) complexes are typically six-coordinate spin triplet systems with most ligands, whereas eight-coordinate $[Nb(CN)_8]^{5-}$ and $[Mo(CN)_8]^{4-}$ are stable diamagnetic 18-electron complexes.[14,15] For Cr(III), a $[Cr(CN)_7]^{4-}$ complex does not appear to exist.

In this contribution we report the synthesis and characterization of the 15-electron $[CpCr(CN)_3]^-$ complex and its Cp* analogue and their equilibrium reactions with excess CN^-. We also report spectroscopic evidence for the existence of 17-electron, $S = {}^1/_2$, phosphine-containing $CpCr(CN)_2L_2$ compounds in solution.

Experimental Section

General Considerations. All operations were carried out under an atmosphere of dinitrogen or argon with standard Schlenk-line techniques. Solvents were dried by conventional methods (THF and Et_2O from Na/benzophenone, heptane from Na, and CH_2Cl_2 from P_4O_{10}) and distilled under argon prior to use. FT-IR spectra were recorded on a Perkin-Elmer 1800 spectrophotometer with KBr disks (Nujol mulls). NMR spectra were obtained with Bruker WP200 and AF200 spectrometers; the peak positions are reported with positive shifts downfield of TMS as calculated from the residual solvent peaks (^1H) or downfield of external 85% H_3PO_4 (^{31}P). For each ^{31}P NMR spectrum, a sealed capillary containing H_3PO_4 was immersed in the same NMR solvent used for the measurement, and this was used as the reference. EPR spectra were recorded on a Bruker ER200 spectrometer upgraded to ESP300 and equipped with an X-band microwave generator. The elemental analyses were carried out by M-H-W Laboratories, Phoenix, AZ. Solid-state magnetic measurements were carried out with a Johnson Matthey magnetic balance, which operates by a modified Gouy method. Solution magnetic moments were obtained by the Evans method.[16] $CrCl_3(THF)_3$,[17] $CpCrCl_2(dmpm)$,[10] and $CpCrCl_2(PMe_3)$ and $CpCr(CH_3)_2(PMe_3)$[4] were prepared according to the procedures described in the literature. $CpCrCl_2(PMe_2Ph)$ was prepared *in situ* by an adaptation of the literature procedure.[4] CpNa was prepared from freshly cracked CpH and sodium sand in THF, isolated as a white CpNa·*x*THF solid by precipitation with heptane from a concentrated THF solution, and titrated with 0.1 M HCl to determine the effective molecular weight. KCp*·*x*THF was prepared by reacting Cp*H and K in refluxing THF, and isolated and the molecular weight determined as for the CpNa salt. dppe, dmpm, and dmpe (Strem) were used without further purification. Et_4NCN, Me_3SiCN, and a 1.4 M solution of MeLi in heptane (Aldrich) were used as received.

Preparation of $[PPh_4][CpCr(CN)_3]$. $CpCrCl_2(THF)$ was prepared in situ from $CrCl_3(THF)_3$ (225 mg, 0.6 mmol) and $CpNa(THF)_{0.38}$ (83 mg, 0.72 mmol) in 20 mL of THF. This solution was evaporated to dryness, and to the residue was added KCN (160 mg, 2.42 mmol) dissolved in 10 mL of H_2O at room temperature. The residue dissolved, giving a red solution. EPR of the solution at room temperature showed a sharp singlet at $g = 1.98$ ($a_{Cr} = 15$ G). After ca. 20 min of stirring, the solution was added dropwise to a solution of PPh_4Cl (500 mg, 1.33 mmol) in 20 mL of H_2O, resulting in the formation of an orange-red crystalline precipitate. This was filtered off, washed with ether, and dried under vacuum. Yield: 181 mg (56.5%). Anal. Calcd for $C_{32}H_{25}CrN_3P$: C, 71.90 ; H, 4.70. Found: C, 71.84; H, 5.04. ^1H NMR ($CDCl_3$, δ): 255 (br, $w_{1/2} = 5500$ Hz, Cp), 7.4 (m, PPh_4). $\mu_{eff} = 3.88\ \mu_B$ (solid state), 3.55 μ_B (solution in CD_3CN).

Preparation of $[PPh_4][Cp^*Cr(CN)_3]$. By a procedure analogous to that reported above for the Cp salt, $CrCl_3(THF)_3$ (130 mg, 0.35 mmol) and $Cp^*K(THF)_{0.60}$ (83 mg, 0.37 mmol) were reacted in 15 mL of THF to give a solution of $Cp^*CrCl_2(THF)$, which was then reacted with KCN (100 mg, 1.53 mmol) in 25 mL of H_2O. The resulting red solution had an EPR signal at $g = 1.99$ ($a_{Cr} = 30$ G). Addition of this solution to an aqueous solution of PPh_4Cl (260 mg, 0.69 mmol), followed by filtration, washing, and drying afforded 73 mg (35%) of the product. Anal. Calcd for $C_{37}H_{35}CrN_3P$: C, 73.50; H, 5.70. Found: C, 73.12; H, 5.77. ^1H NMR ($CDCl_3$, δ): 10.3 (br, $w_{1/2} = 600$ Hz, Cp*), 7.2 (m, PPh_4). $\mu_{eff} = 3.60\ \mu_B$ (solution in CD_3CN). A single crystal of this compound for the X-ray analysis was obtained from a CH_2Cl_2/ether layer.

Equilibrium Studies of the Reaction between $[(ring)Cr(CN)_3]^-$ and CN^-. (a) ring = Cp. A 0.0374 M stock solution of $[PPh_4][CpCr(CN)_3]$ was prepared by dissolving 30.0 mg of the compound in 1.50 mL of CH_2Cl_2. A stock solution of $Et_4N^+CN^-$ was prepared by dissolving 50.0 mg of the salt in 3 mL of CH_2Cl_2. To 100 μL of the solution of the Cp complex was added varying amounts (1, 2, 3, and 5 equiv) of the solution of the CN^- salt, and each solution was further diluted with the required amount of CH_2Cl_2 to bring the volume to 0.275 mL (total concentration of CpCr species 0.0136 M). Each solution was investigated by EPR spectroscopy. The intensity of the resonance was obtained by double integration, and the concentration of the EPR-active species, i.e. $[CpCr(CN)_4]^{2-}$, was calculated by calibration against the EPR intensity of a standard solution of $CpMoCl_2(PMe_3)_2$, which is a pure 17-electron $S = {}^1/_2$ system,[18] in CH_2Cl_2.

(b) ring = Cp*. A 0.0374 M stock solution of $[PPh_4][Cp^*Cr(CN)_3]$ was prepared by dissolving 38.0 mg of the compound in 1.7 mL of CH_2Cl_2. A stock solution of $Et_4N^+CN^-$ was prepared by dissolving 50.0 mg of the salt in 3 mL of CH_2Cl_2. To 200 μL of the solution of the Cp* complex was added varying amounts (3, 5, 8, and 10 equiv) of the solution of the CN^- salt, and each solution was further diluted with the required amount of CH_2Cl_2 to bring the volume to 0.900 mL (total concentration of Cp*Cr species 0.0082 M). Each solution was investigated by EPR spectroscopy. The intensity of the resonance was obtained by double integration, and the concentration of the EPR-active species, i.e. $[Cp^*Cr(CN)_4]^{2-}$, was calculated by calibration against the EPR intensity of a standard solution of $CpMoCl_2(PMe_3)_2$, which is a pure 17-electron $S = {}^1/_2$ system.

(c) Data Analysis. Given that, for each solution, $[(ring)Cr(CN)_4{}^{2-}] = y$ (ring = Cp, Cp*), $[(ring)Cr(CN)_3{}^-] + [(ring)Cr(CN)_4{}^{2-}] = z$ ($z = 0.0136$ M (Cp), 0.0082 M (Cp*)), and $[CN^-] = x - y$ (x = analytical $[Et_4N^+CN^-]$), the equilibrium constant expression becomes eq 1 for both Cp and Cp* systems. The value of K_{eq} was obtained by the nonlinear least-squares fit (quasi-Newtonian method) of the experimental (x, y) data with the program Curve Fit.[19]

$$y = {}^1/_2\{z + K_{eq}{}^{-1} + x - [(z + K_{eq}{}^{-1} + x)^2 - 4zx]^{1/2}\} \quad (1)$$

EPR Study of the Reaction between $[PPh_4][CpCr(CN)_3]$ and Phosphines. A 0.076 M solution of $[PPh_4][CpCr(CN)_3]$ was prepared by dissolving 61 mg of the compound in 1.5 mL of CD_3CN. Aliquots of this solution (200 μL each) were

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used for the reaction with selected phosphines with EPR monitoring: $CpCr(CN)_2dmpm$ (triplet, $g = 1.99$, $a_P = 34$ G), $CpCr(CN)_2dmpe$ (triplet, $g = 1.99$, $a_P = 34$ G), $CpCr(CN)_2(PMe_3)_2$ (triplet, $g = 1.99$, $a_P = 34$ G), $CpCr(CN)_2(PMe_2Ph_2)_2$ (triplet, $g = 1.99$, $a_P = 34$ G). Crystallization from CH_2Cl_2/heptane of a solution resulting from the dmpe addition gave orange crystals which were analyzed as $[PPh_4][CpCr(CN)_3]$. Found: C, 71.41; H, 5.02.

EPR Study of the Reaction between $[PPh_4][Cp^*Cr(CN)_3]$ and Phosphines. A 0.0106 M solution of $[PPh_4][Cp^*Cr(CN)_3]$ was prepared by dissolving 32 mg of the compound in 5 mL of CD_3CN. Aliquots of this solution (1 mL each) were used for the reaction with PMe_3 and dmpe with EPR monitoring. No EPR signal was observed in these cases, even in the presence of a large excess of the phosphine ligand.

Magnetic Moment Studies of the Reaction between $[PPh_4][CpCr(CN)_3]$ and Phosphines in Solution (Evans' Method). A 0.076 M solution of $[PPh_4][CpCr(CN)_3]$ was prepared by dissolving 61 mg of the compound in 1.5 mL of CD_3CN. Aliquots of this solution (200 μL each) were used for the reaction with selected phosphines and the subsequent determination of the magnetic moment in solution. The results are summarized in Table 1.

EPR Study of the Reaction between $CpCrCl_2L_x$ and Me_3SiCN ($L = PMe_3$, PMe_2Ph_2; L_2 = dmpm). (a) L_2 = dmpm. To a solution of $CpCrCl_2(dmpm)$ (65 mg, 0.2 mmol) in 10 mL of THF was added 75 μL (0.56 mmol) of $SiMe_3CN$. The solution was stirred overnight at room temperature, resulting in a color change from blue to red-brown. This solution exhibited a sharp EPR signal (triplet, $g = 1.99$, $a_P = 35.0$ G). No analytically pure solid product could be isolated from this solution.

(b) $L = PMe_3$, PMe_2Ph. A similar procedure was used for the attempted synthesis of $CpCr(CN)_2L_2$ ($L = PMe_3$, PMe_2Ph), the only difference in this case being that the reaction between $CpCrCl_2L$ and $SiMe_3CN$ was carried out in the presence of excess phosphine ligand. Sharp EPR spectra were observed in both cases for the resulting solutions: $L = PMe_3$ (triplet, $g = 1.99$, $a_p = 34.8$ G), $L = PMe_2Ph$ (triplet, $g = 1.99$, $a_p = 35.0$ G).

^1H and ^{31}P NMR Study of the Reaction between $CpCrCl_2(dmpm)$ and $SiMe_3CN$. $CpCrCl_2(dmpm)$ (20 mg, 0.062 mmol) and $SiMe_3CN$ (25 μL, 0.25 mmol) were dissolved in 1 mL of CD_3CN. After ca. 3 h the resonances due to $CpCrCl_2(dmpm)$[10] had completely disappeared and had been replaced by the resonances of free dmpm (^1H NMR δ 1.5 (s, 2H, CH_2), 1.0 (s, 12H, CH_3); ^{31}P NMR: δ -54).

Reaction between $CpCrCl_2(THF)$ and Excess Me_3SiCN. Synthesis of $[CpCr(CN)Cl]_2$. $CpCrCl_2(THF)$ was prepared *in situ* from $CrCl_3(THF)_3$ (940 mg, 2.40 mmol) and $CpNa(THF)_{0.38}$ (310 mg, 2.69 mmol) in 40 mL of THF. The resulting blue solution was evaporated to dryness and extracted in CH_3CN (40 mL). To this solution was added Me_3SiCN (1.5 mL, 11.0 mmol) at room temperature. The solution turned from blue to red-brown in ca. 1 h with formation of a brown precipitate. The solution was then refluxed overnight. After it was cooled, the red-brown suspension was filtered and the precipitate was washed with ether and dried under vacuum. Yield: 236 mg (55%). Anal. Calcd for C_6H_5ClCrN: H, 40.4; H, 2.8; Cl, 19.8. Found: C, 40.0, H, 2.5; Cl, 20.7. $\mu_{eff} = 2.03$ μ_B.

Results

(a) Synthesis and Characterization of $[(ring)Cr(CN)_3]^-$ (ring = Cp, Cp*) Complexes. The addition of 4 equiv of KCN to $(ring)CrCl_2(THF)$ precursors (ring = Cp, Cp*) in water generates red solutions which exhibit sharp EPR singlets with the expected Cr satellites ($I = {}^3/_2$, 9.55%) at room temperature (see Figure 1). The addition of PPh_4Cl to these solutions results in the precipitation of $[PPh_4][(ring)Cr(CN)_3]$ in good yields. These complexes are quite soluble in CH_2Cl_2 and CH_3CN and can conveniently be recrystallized from CH_2Cl_2/Et_2O. The products have been characterized by elemental analysis, ^1H NMR spectroscopy, and magnetic susceptibility measurements. In addition, a single crystal X-ray structure has been obtained for the Cp* derivative (see Figure 2), although the poor quality of the crystal did not allow a satisfactory refinement of the intensity data. The structure is shown here only as proof of chemical connectivity.[20]

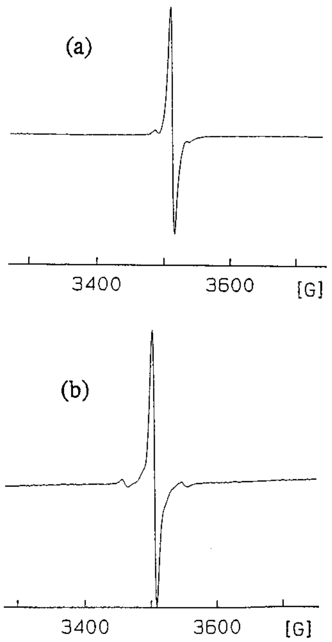

Figure 1. Room-temperature EPR spectra of (a) $[CpCr(CN)_4]^{2-}$ and (b) $[Cp^*Cr(CN)_4]^{2-}$ in water.

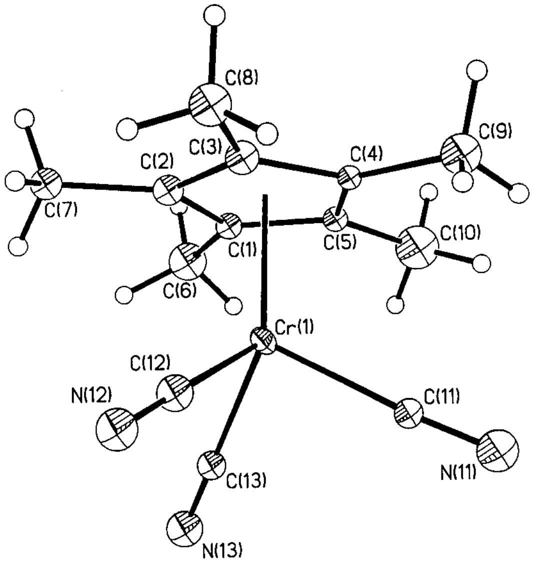

Figure 2. View of the $[Cp^*Cr(CN)_3]^-$ anion from the single-crystal X-ray structure of the NEt_4^+ salt.

The EPR spectrum observed in solution before isolation is *no longer observed* after redissolution of the isolated solids, both of them giving EPR-silent solutions

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(20) Crystal data for $[PPh_4][Cp^*Cr(CN)_3]$ ($M_r = 604.65$): orthorhombic, space group *Pbca*, $a = 17.398(4)$ Å, $b = 17.457(4)$ Å, $c = 20.997(4)$ Å, $V = 6377(2)$ Å^3, $Z = 8$, $d_{calc} = 1.260$ Mg/m^3, μ(Mo Kα) = 0.439 mm^{-1}.

at room temperature. Although relatively sharp EPR spectra are sometimes observed for Werner-type octahedral complexes of Cr(III) with a $^4A_{2g}$ ground state,[21] the electronic relaxation is apparently much faster for spin quartet, lower symmetry half-sandwich compounds, leading to EPR-silent isotropic solutions.[22] For instance, the compounds $CpCrX_2(\eta^1\text{-L-L})$ (X = Cl, CH_3) do not show EPR resonances down to the freezing point of the solvent.[10] The nature of the EPR-active species will be examined in the next section.

The room-temperature ^1H NMR spectrum for the Cp complex shows a paramagnetically shifted resonance for the Cp protons at δ 255 ($w_{1/2}$ = 5500 Hz). This resonance is similar to those of other $CpCr^{III}$ compounds with a 15-electron configuration and an $S = {}^3/_2$ ground state, e.g. δ 231 for $CpCrCl_2(PMe_3)$ and 233.6 for $[CpCrCl_3]^-$.[4,23] The Cp* resonance for the $[Cp^*Cr(CN)_3]^-$ complex is observed at δ 10.3 ($w_{1/2}$ = 600 Hz). The Cp complex has a magnetic moment of 3.88 μ_B in solid state and 3.55 μ_B in solution, in agreement with the presence of three unpaired electrons.

(b) Addition of CN^- to $[(ring)Cr(CN)_3]^-$. The EPR signals observed during the syntheses of $[(ring)Cr(CN)_3]^-$ (Figure 1) are obtained again upon addition of CN^- to solutions of the EPR-silent $[(ring)Cr(CN)_3]^-$ complexes. The resulting solutions are stable at room temperature, no change in the intensity of the EPR signal being observed over several hours.

These spectra are assigned to the 17-electron tetracyano complex $[(ring)Cr(CN)_4]^{2-}$. The 17-electron configuration necessarily leads to an orbitally nondegenerate spin doublet ground state, for which relatively sharp EPR signals are expected at room temperature, as is well established for the corresponding Mo(III) systems, e.g. $CpMoCl_2(PR_3)_2$.[18,24,25] A quartet ground state for a 17-electron Cr(III) complex would require the occupation of metal−ligand σ^* orbitals. This is unprecedented for organometallic complexes, except for a very limited number of complexes of first-row metals with d^5 and d^6 configurations (for instance, Mn(II) and Fe(II)).[11] The only previously reported example of a half-sandwich 17-electron Cr(III) complex, i.e. $CpCr(\eta^3\text{-}C_3H_5)_2$, has a reported magnetic moment of 1.8 μ_B.[9]

Every attempt to crystallize the 17-electron dianion only afforded back the EPR-silent and ^1H-NMR-active 15-electron complex in the solid state. Other reasonable assignments for the EPR spectra shown in Figure 1 are excluded: an alternative reaction pathway may involve displacement of the Cp^- ligand, to yield the known[26] $Cr(CN)_6{}^{3-}$ ion. The EPR spectrum of a genuine sample of $[Cr(CN)_6]^{3-}$, which was prepared according to the literature procedure,[27] has an identical g value of 1.99 relative to the signals reported in Figure 1 but is much broader (peak-to-peak separation of 24 vs 6 G for both Cp and Cp* systems in Figure 1) and has no discernible Cr hyperfine splitting. In addition, a hypothetical ring replacement reaction should give rise to the same EPR spectra for both systems. Although the g value and the line widths are the same for both signals in Figure 1, the a_{Cr} hyperfine constant is 15 G in one case and 30 G in the other, indicating the presence of the cyclopentadienyl ring in the products. Since the value of g is significantly lower than 2.0023, it excludes the assignment of the EPR signals of Figure 1 to reduced chromium species (e.g. Cr(I), d^5, or Cr(−I), d^7),[28] whereas oxidized species (Cr(V), d^1) are not expected under the conditions used for these studies.

It has been pointed out to us by one of the reviewers that coupling of the unpaired electron to the ^{13}C nucleus of the cyanide ligand at natural abundance could give rise to satellite resonances of approximately the same relative intensity as the two outer ^{53}Cr satellites. Indeed, simulation of the spectrum for one ^{53}Cr vs four ^{13}C nuclei with suitable values of the hyperfine constants produces almost indistinguishable results. That the observed satellites are due to coupling to Cr and not to the cyanide C nuclei, however, is shown by two independent arguments. First, the spectrum of the Cp* derivative (Figure 1b) has noticeable shoulders on the central line that can only be attributed to the two inner Cr satellites. These shoulders are reproducible in the simulated ^{53}Cr spectrum and not in the simulated ($4 \times {}^{13}C$) spectrum. Second, the attribution of the observed satellites to the ^{13}C nuclei requires hyperfine couplings of 45 G for the Cp compound and 90 G for the Cp* compound. These are completely unreasonable values. As points of reference, a number of π-radical anions of aromatic hydrocarbons have a_C in the 4−10 G range and the methyl radical has a_C = 38.34 G.[29] The spin density is expected to be mostly residing on the Cr orbitals in the above complexes, leading to the expectation of much smaller couplings to the cyanide carbon nuclei. Given the experimental line width of the resonance (Figure 1), such coupling is unobservable. Therefore, the use of ^{13}C-enriched cyanide ligands, for instance, would not lead to the gathering of any additional information, such as the observation of a coupling pattern consistent with the presence of four cyanide groups. The only (indirect) evidence for the presence of four cyanide ligands in the EPR-active species is their formation by addition of excess cyanide to solutions of the corresponding tricyano complexes and the fitting of the intensity data to the expected equilibrium relationships, which is now examined in detail.

The equilibrium constant for CN^- addition to the Cp and Cp* systems (eq 2) was determined by EPR spectroscopy. The experiment was carried out by treating

$$[(ring)Cr(CN)_3]^- + CN^- \rightleftharpoons [(ring)Cr(CN)_4]^{2-} \quad (2)$$

$$ring = Cp, Cp^*$$

solutions of $[(ring)Cr(CN)_3]^-$ with known excess amounts of CN^-. The concentration of the $[(ring)Cr(CN)_4]^-$ species was calculated by calibration of the doubly integrated EPR signal against a standard solution of $CpMoCl_2(PMe_3)_2$. For both ring systems, equilibrium

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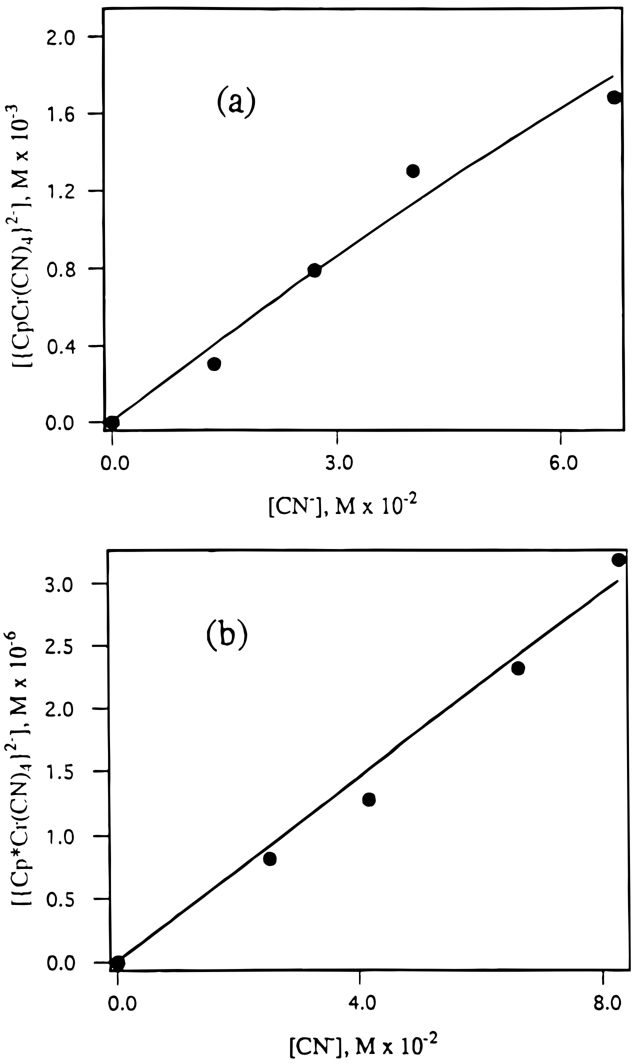

Figure 3. Experimental data for equilibrium 2 and least-squares fitting according to eq 1: (a) Cp system; (b) Cp* system.

2 is well shifted to the left, since addition of 5 equiv of CN^- gave only 12% of the 17-electron species for a solution which is 0.0136 M in the CpCr system, and addition of 10 equiv of CN^- gave only 0.04% of the 17-electron species for a solution which is 0.0082 M in the Cp*Cr system. Fitting of the data (Figure 3) gave a K_{eq} value of 2.3 ± 0.1 M^{-1} for the Cp system and (4.4 ± 0.2) × 10^{-3} M^{-1} for the Cp* system.

(c) Generation of 17-Electron Phosphine Derivatives of (ring)Cr(CN)$_2$. The reaction between $[CpCr(CN)_3]^-$ and tertiary phosphine ligands (PMe_3, PMe_2Ph, dmpe, dmpm) in CH_2Cl_2 results in the formation of products characterized by well-defined room-temperature EPR spectra. These spectra consist of 1:2:1 triplets at $g = 1.99$ ($a_P = 34$ G) due to coupling to two equivalent phosphorus nuclei and the expected Cr satellites. A representative spectrum for the dmpm adduct is shown in Figure 4. Like the solutions obtained by addition of excess CN^- to $[(ring)Cr(CN)_3]^-$, the solutions obtained by adding tertiary phosphine ligands to $[CpCr(CN)_3]^-$ are stable at room temperature. The EPR spectra are assigned to 17-electron bis(phosphine) derivatives, obtained by the equilibrium shown in eq 3. For no phosphine and solvent system investigated was there any evidence of an EPR resonance exhibiting a hyperfine doublet splitting, as would be expected for a $[CpCr(CN)_3L]^-$ species (L = tertiary phosphine). A magnetic susceptibility study of equilibrium 3 was carried out in solution by the Evans method;[16] a slight decrease of the magnetic moment upon addition of phosphine was observed (see Table 1), in agreement with the formation of small amounts of magnetically less active phosphine adducts, e.g., $S = {}^1/_2$ $CpCr(CN)_2L_2$. This result also indicates that equilibrium 3, like equilibrium 2 shown in the previous section, is largely shifted to the left.

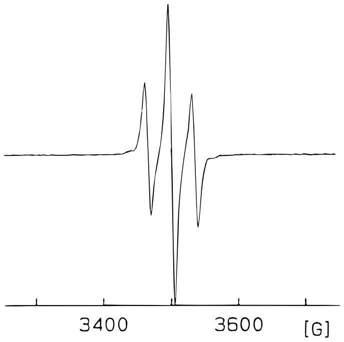

Figure 4. EPR spectrum of a solution generated as described in eq 3 from $CpCr(CN)_3^-$ and dmpm (solvent CH_2Cl_2).

$$[CpCr(CN)_3]^- + 2L \rightleftharpoons CpCr(CN)_2L_2 + CN^- \quad (3)$$

$$L = PMe_3, PMe_2Ph; L_2 = dmpe, dmpm$$

Alternative formulations for the species responsible for the triplet EPR resonances appear extremely unlikely. The EPR hyperfine splitting pattern demonstrates that two phosphorus donor atoms are bonded to the metal center. The formulation as a 15-electron $[CpCr(CN)L_2]^+CN^-$ species does not appear reasonable because (i) by analogy with other previously investigated half-sandwich 15-electron complexes, including $[CpCr(CN)_3]^-$, such a species is not expected to give rise to an isotropic EPR spectrum at room temperature, (ii) the CN^- anion should be displaced from the coordination sphere with greater difficulty than the tertiary phosphine ligand, and (iii) the EPR-active complex is quite soluble in relatively nonpolar organic solvents such as toluene, in disagreement with an ionic formulation. An alternative formulation with a displaced Cp ring, e.g. $[Cr(CN)_4L_2]^-$, is not possible because, if such were the case, the same products should be obtained for the Cp* system. Instead, the complex $[Cp^*Cr(CN)_3]^-$ does not give rise to any EPR signal upon addition of phosphine ligands. Furthermore, the alternative generation method which is illustrated later leads to the demonstrated loss of phosphine ligand, rather than Cp.

Crystallization from the equilibrium solutions obtained as described in eq 3 only allowed the recovery of solid $[PPh_4][CpCr(CN)_3]$. A ^1H NMR monitoring experiment in $CDCl_3$ showed only a slight decrease of the paramagnetically shifted resonance at δ 255 of the starting material, again in agreement with equilibrium 3 being shifted to the left, while no new resonances are present except for those of the excess phosphine ligand, indicating the absence of phosphine-containing half-sandwich 15-electron species, e.g. $CpCr(CN)_2L$ or $CpCr(CN)_2(\eta^1\text{-L-L})$. Previously reported phosphine-contain-

Table 1. Effective Magnetic Moments (Evans Method) per Cr Atom for Solutions Containing [Et$_4$N][CpCr(CN)$_3$] and Excess Phosphine Ligand (Solvent CD$_3$CN)

[[Et$_4$N][CpCr(CN)$_3$]]/M	phosphine (concn/M)	μ_{eff}/μ_B
0.076		3.55
0.074	dmpm (0.15)	3.40
0.075	dmpe (0.074)	3.29
0.074	PMe$_3$ (0.24)	3.30
0.074	PMe$_2$Ph (0.17)	3.44

ing compounds of this type, e.g. CpCrX$_2$(PMe$_3$) and CpCrX$_2$(η^1-L-L) (X = Cl, CH$_3$; L-L = dmpe, dmpm),[4,10] show contact-shifted but relatively sharp ^{1}H NMR resonances for the phosphine protons. The interaction between [CpCr(CN)$_3$]$^-$ and PEt$_3$ or PPh$_3$ did not give rise to any EPR signal, nor was any EPR-active species generated by the interaction of [PPh$_4$][Cp*Cr(CN)$_3$] with any of the forementioned phosphine ligands.

The same EPR spectra obtained as described in eq 3 were also obtained by an alternative strategy, i.e. from the reaction of CpCrCl$_2$(η^1-L-L) (for the bidentate phosphine dmpe and dmpm), or CpCrCl$_2$L and excess L (for the monodentate phosphine PMe$_3$ and PMe$_2$Ph), with Me$_3$SiCN in CH$_2$Cl$_2$ (see eq 4).

$$\mathrm{CpCrCl_2L + L \text{ or } CpCrCl_2(\eta^1\text{-L-L}) \xrightarrow{Me_3SiCN} CpCr(CN)_2L_2} \quad (4)$$

^{31}P NMR monitoring shows the increase with time of the free dmpm resonance. Crystallization by addition of toluene yielded only impure solids which do not show any EPR resonance and no ^{1}H NMR signals attributable to phosphine ligands. The analytical data are most consistent with materials of formula CpCr(CN)$_x$Cl$_{2-x}$ (x ca. 1). Even when an excess amount of Me$_3$SiCN and long reaction times were used, materials that are richer in CN and poorer in Cl could not be obtained. The more extensively this product is worked up, the lower its solubility. The addition of phosphine ligands to solutions of these materials, however, generates once again the EPR spectra that we assign to the CpCr(CN)$_2$L$_2$ species and weak ^{1}H NMR resonances in the expected region for compounds CpCrCl$_2$L. The reaction is relatively rapid when the freshly prepared material is used, whereas longer reaction times and/or higher temperatures are necessary when using the worked-up, less soluble material.

The direct reaction of [CpCrCl$_2$]$_2$ and excess Me$_3$SiCN in CH$_2$Cl$_2$ also yielded a product whose analysis is consistent with “CpCr(CN)Cl”. In an attempt to force the Cl/CN exchange, the reaction was carried out in refluxing MeCN, giving a completely insoluble brown product whose analysis corresponds once again to CpCr(CN)Cl. The magnetic moment of this material is μ_{eff} = 2.03 μ_B/Cr atom, indicating substantial quenching of the expected moment for magnetically diluted d^3 Cr(III) and suggesting antiferromagnetic coupling in an oligonuclear structure. It is possible that the first product of the exchange is the dinuclear species [CpCr(CN)(μ-Cl)]$_2$ and workup or warming converts this species into an oligomeric or polymeric structure. Perhaps the last Cl ligand is not exchanged because the CN ligand would not be able to bridge the two metals. The addition of free phosphine to this insoluble [CpCr(CN)(μ-Cl)]$_n$ material requires prolonged heating, eventually producing solutions that show once again the characteristic EPR signals assigned to the CpCr(CN)$_2$L$_2$ species and weak NMR resonances indicative of the presence of CpCrCl$_2$L (see eq 5; L = PMe$_3$ or PMe$_2$Ph).

$$\mathrm{[CpCr(CN)(\mu\text{-Cl})]_2 + 3L \rightleftarrows CpCr(CN)_2L_2 + CpCrCl_2L} \quad (5)$$

Discussion

The above results show that the addition of CN$^-$ or tertiary phosphine ligands to the 15-electron [(ring)-Cr(CN)$_3$]$^-$ species (ring = Cp, Cp*) affords small equilibrium amounts of the 17-electron species [(ring)-Cr(CN)$_4$]$^{2-}$ or CpCr(CN)$_2$L$_2$. In all cases investigated, the 17-electron complex is the minor species in solution and could not be isolated in the solid state. Nonetheless, these equilibrium species are the first 17-electron half-sandwich Cr(III) systems that are stable at room temperature. As mentioned in the Introduction, compound CpCr(η^3-C$_3$H$_5$)$_2$ decomposes at temperatures above 0 °C.[2] Ligand adducts of sandwich or pseudo-sandwich (e.g. half-open) Cr(III) complexes with a 17-electron configuration are also known, e.g. [CpCr(Pdl′)-(CO)]$^+$ (Pdl′ = 2,4-dimethylpenta-2,4-dien-1-yl).[30] Steric effects are manifested by the smaller equilibrium concentration of [Cp*Cr(CN)$_4$]$^{2-}$ relative to the corresponding Cp derivative, by the absence of an interaction between [CpCr(CN)$_3$]$^-$ and the bulkier ligands PEt$_3$ (cone angle, θ = 132°) and PPh$_3$ (θ = 145°),[31] and by the absence of an interaction between [Cp*Cr(CN)$_3$]$^-$ and any phosphine ligand.

We have recently reported that the compounds CpCrX$_2$-(L-L) (X = Cl, CH$_3$; L-L = dmpm, dmpe, dppe) adopt only a three-legged piano-stool, 15-electron CpCrX$_2$(η^1-L-L) structure, both in the solid state and in solution.[10] The results reported here indicate that the energy difference between CpCrX$_2$L$_2$ or CpCrX$_2$(η^2-L-L) and the [CpCr(CN)$_2$L + L] or CpCrX$_2$(η^1-L-L) system is less for X = CN relative to X = Cl, CH$_3$. There are several reasons for half-sandwich, 17-electron, spin doublet Cr(III) compounds to be more accessible when cyanide ligands are used. One reason is steric: the cyanide ligand is smaller than either Cl or CH$_3$. However, we have already argued[10,11] that steric effects alone should not prevent a 15-electron CpCrX$_2$(PR$_3$) system with X = Cl or CH$_3$ to coordinate another PR$_3$ ligand, because the corresponding V(III) center of similar size forms the stable four-legged piano-stool complexes CpVX$_2$(PR$_3$)$_2$ (X = Cl, CH$_3$) even with relatively encumbering ligands such as PEt$_3$.[32,33]

Electronic effects can also increase the accessibility of 17-electron cyanide derivatives. We can identify three different types of electronic effects. We can ideally separate the process of ligand coordination to the 15-electron spin quartet complex in two steps: (i) promotion to an excited spin doublet state and (ii) coordination of the ligand along the spin doublet energy surface (see Scheme 1). Let us analyze the second step first. The

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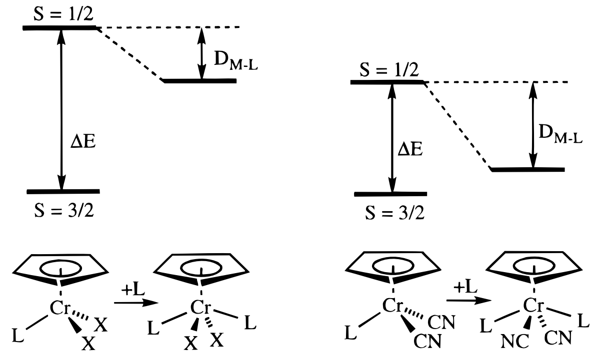
Scheme 1



(X = Cl or CH$_3$, L = X$^-$ or PR$_3$) (L = CN$^-$ or PR$_3$)

strength of the Cr−L interaction along the spin doublet surface (D_{M-L}) may be greater when L = CN$^-$ relative to L = Cl$^-$, CH$_3^-$; this fact alone may rationalize the existence (accessibility) of the complex [CpCr(CN)$_4$]$^{2-}$ *vis à vis* the nonexistence of complexes [CpCrX$_4$]$^{2-}$ with X = Cl, CH$_3$. Concerning the formation of neutral CpCrX$_2$L$_2$ complexes (L = tertiary phosphine), the Cr−PR$_3$ bond may be stronger when X = CN relative to X = Cl, CH$_3$ because of the π-acidic nature of the CN ligand, making the Cr center better able to accept electron density from the phosphine donor.

The promotion energy (i.e. ΔE, related to the electron-pairing process from a quartet to a doublet state) evidently plays a dominant role in this system,[11,12] and the nature of the X ligand may also affect this step. In monoelectronic terms, ΔE can be expressed as a combination of an orbital gap and a series of coulombic and exchange integrals.[34] While it is difficult to predict the effect of X on the orbital gap, the Coulombic and exchange contributions to the pairing energy are smaller as the nephelauxetic effect of the ligand becomes greater. Thus cyanide, because of its low electronegativity and its ability to disperse the metal electron density via π back-bonding, is a highly nephelauxetic ligand and should lead to smaller promotion energies. By using the same argument, Hall *et al.* have rationalized the electronic structure of TiX$_2$(dmpe)$_2$ as a spin triplet for X = Cl and singlet for X = CH$_3$.[35] Theoretical calculations at various levels on the CpCrX$_2$(PH$_3$)$_n$ (n = 1, 2) system in both the quartet and doublet spin states for X = Cl, CH$_3$, CN are underway and will be reported in due course.[12,36]

Conclusions

The most typical electronic configuration for half-sandwich Cr(III) complexes features 15 valence electrons and a spin quartet ground state for a three-legged piano-stool structure, and previous studies have shown the accessibility of even less electronically saturated (13-electron) structures by the use of weakly coordinating or sterically encumbering ligands.[22,37,38] We have shown here that the use of the small, strongly binding, and highly nephelauxetic CN$^-$ ligand also allows access in solution to thermally stable, pseudo-seven-coordinate, 17-electron compounds with a spin doublet ground state. Whether 17-electron CpCr^{III} compounds may be accessible transition states for reactions of complexes containing ligands of lower nephelauxetic power will be the subject of future investigations.

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