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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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In solution the complexes [(ring)CrCl2]2 (ring = Cp, Cp*) with excess KCl in water affords the complexes [(ring)Cr(CN)]3, which have been isolated as PPh3 salts and characterized by elemental (C, H) analysis, 1H NMR, magnetic susceptibility, and an X-ray investigation for the Cr* species. The interaction of these complexes with excess CN− generates equilibrium amounts of the EPR-active, 17-electron [(ring)Cr(CN)]3− adducts. The equilibrium constant for this addition process is 2.3 ± 0.1 M−1 for ring = Cp and (4.4 ± 0.2) × 10−3 M−1 for ring = Cp* at 298 K. Either treatment of [CpCr(CN)]3− with monodentate (L) or bidentate (L2) tertiary phosphine ligands (e.g. PMe3, PMe2Ph, dmpe, dppe) or reaction between CpCrCl2η−L2 or [CpCrCl2L + L] and excess Me3SiCN 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)2L2. The thermal accessibility of these 17-electron Cr(III) cyanide derivatives, as compared with the inaccessibility of the corresponding 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(η3-allyl), which thermally decomposes, however, above 0 °C.5,9 Recent attempts in this laboratory at using the chelate effect of bidentate phosphine ligands have only resulted in the formation of CpCrX2(η3-L-L) (X = Cl, CH3; L-L = dmpe, dppe, dpmp) complexes with one coordinated and one dangling P donor and a 15-electron configuration, the alternative 17-electron CpCrX2(η2-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 Cr3+ and Mo3+ do not appear to play a major role.10–12 It is expected that the introduction of softer and less electronnegative ligands (such as Cp and allyl groups) lowers the cost of pairing the electrons, whereas harder and more electronnegative 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 CpCr11+ 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 underdemanding. 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)$_3$]$^+$ complex,$^{13}$ and $d^2$ Nb(III) and Mo(IV) complexes are typically six-coordinate spin triplet systems with many ligands, whereas eight-coordinate [Nb(CN)$_8$]$^{3-}$ and [Mo(CN)$_8$]$^{4-}$ are stable diamagnetic 18-electron complexes.$^{14,15}$ For Cr(III), a [Cr(CN)$_3$]$^3^-$ complex does not appear to exist. In this contribution we report the synthesis and characterization of the 15-electron [CpCr(CN)$_3$]$_2^-$ 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)$_2$L$_2$ 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$_2$O from Na/benzophene, heptane from Schlenk-line techniques. Solvents were dried by conventional methods (THF and Et$_2$O from Na/benzophene, heptane from Schlenk-linetechniques. Solventsweredriedbyconventional under an atmosphere of dinitrogen or argon with standard treatment.

Preparation of [PPh$_4$][Cr(CN)$_3$].] By a procedure analogous to that reported above for the Cp salt, CrCl$_3$(THF)$_x$ (130 mg, 0.35 mmol) and CpCl$_2$(THF)$_{0.66}$ (83 mg, 0.37 mmol) were reacted in 15 mL of THF to give a solution of CpCrCl$_2$(THF), which was then reacted with KCN (100 mg, 1.53 mmol) in 25 mL of H$_2$O. The resulting red solution had an EPR signal at g = 1.99 (ac$_b$ = 30 G). Addition of this solution to an aqueous solution of PPh$_4$Cl (260 mg, 0.69 mmol), followed by filtration, washing, and drying afforded 73 mg (35%) of the product. Anal. Calc. for [PPh$_4$][CpCr(CN)$_3$]: 3.55 µmol (solution in CD$_3$CN). A single crystal of this compound for the X-ray analysis was obtained from a CH$_2$Cl$_2$/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)$_3$]$_2^-$ was prepared by dissolving 30.0 mg of the compound in 1.50 mL of CH$_2$Cl$_2$. A stock solution of Et$_4$N CN$^-$ was prepared by dissolving 50.0 mg of the salt in 3 mL of CH$_2$Cl$_2$. 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$_2$Cl$_2$ 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)$_3$]$^{2-}$, 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$_2$Cl$_2$.

(b) ring = Cp*. A 0.0374 M stock solution of [PPh$_4$][Cp*Cr(CN)$_3$]$_2^-$ was prepared by dissolving 38.0 mg of the compound in 1.7 mL of CH$_2$Cl$_2$. A stock solution of Et$_4$N CN$^-$ was prepared by dissolving 50.0 mg of the salt in 3 mL of CH$_2$Cl$_2$. 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$_2$Cl$_2$ to bring the volume to 0.900 mL (total concentration of CpCr 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)$_3$]$^{2-}$, 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.$^{18}$

**Data Analysis.** Given that, for each solution, [Cp*Cr(CN)$_3$]$^{2-}$ and CN$^-$ 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.$^{18}$

$$y = \frac{1}{2}(z + K_{eq}^{-1} \cdot x) - \frac{1}{2} \cdot 4x^{1/2}$$  (1)
used for the reaction with selected phosphines with EPR monitoring: CpCr(CN)3dmpm (triplet, g = 1.99, a<sub>p</sub> = 34 G), CpCr(CN)3dmpe (triplet, g = 1.99, a<sub>p</sub> = 34 G), CpCr(N)<sub>2</sub>-(PMe<sub>3</sub>)<sub>2</sub> (triplet, g = 1.99, a<sub>p</sub> = 34 G), CpCr(CN)3(PMe<sub>2</sub>Ph)<sub>2</sub> (triplet, g = 1.99, a<sub>p</sub> = 34 G). Crystalization from CH<sub>2</sub>Cl<sub>2</sub>/heptane of a solution resulting from the dmpe addition gave orange crystals which were analyzed as [PPh<sub>4</sub>][Cp*Cr(CN)3].

EPR Study of the Reaction between [PPh<sub>4</sub>][Cp*Cr(CN)3] and Phosphines. A 0.0106 M solution of [PPh<sub>4</sub>][Cp*Cr(CN)3] was prepared by dissolving 32 mg of the compound in 5 mL of CD<sub>3</sub>CN. Aliquots of this solution (1 mL each) were used for the reaction with PMe<sub>3</sub> 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<sub>4</sub>][Cp*Cr(CN)3] and Phosphines in Solution (Evans’ Method). A 0.076 M solution of [PPh<sub>4</sub>][Cp*Cr(CN)3] was prepared by dissolving 61 mg of the compound in 1.5 mL of CD<sub>3</sub>CN. 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<sub>2</sub>L<sub>1</sub> and Me<sub>3</sub>SiCN (L = PMe<sub>2</sub>Ph). A similar procedure was used for the attempted synthesis of CpCr(CN)3L<sub>2</sub> (L = PMe<sub>2</sub>Ph, PMe<sub>2</sub>Ph, L<sub>2</sub> = dmpm). (a) L<sub>2</sub> = dmpm. To a solution of CpCrCl<sub>2</sub>(dmpm) (65 mg, 0.2 mmol) in 10 mL of THF was added 75 µL (0.56 mmol) of Me<sub>3</sub>SiCN. 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<sub>p</sub> = 35.0 G). No analytically pure solid product could be isolated from this solution.

(b) L = PMe<sub>2</sub>Ph. A similar procedure was used for the attempted synthesis of CpCr(CN)3L<sub>2</sub> (L = PMe<sub>2</sub>Ph, PMe<sub>2</sub>Ph), the only difference in this case being that the reaction between CpCrCl<sub>2</sub>L<sub>1</sub> and Me<sub>3</sub>SiCN was carried out in the presence of excess phosphine ligand. Sharp EPR spectra were observed in both cases for the resulting solutions: L = PMe<sub>3</sub> (triplet, g = 1.99, a<sub>p</sub> = 34.8 G), L = PMe<sub>2</sub>Ph (triplet, g = 1.99, a<sub>p</sub> = 35.0 G).

Results

(a) Synthesis and Characterization of [(ring)-Cr(CN)=3] Complexes. The addition of 4 equiv of KCN to (ring)CrCl<sub>2</sub>(THF) precursors (ring = Cp, Cp*) in water generates red solutions which exhibit sharp EPR singlets with the expected Cr satellites (J = 9/2, 9.55%) at room temperature (see Figure 1). The addition of PPh<sub>4</sub>Cl to these solutions results in the precipitation of [PPh<sub>4</sub>][(ring)Cr(CN)3] in good yields. These complexes are quite soluble in CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN and can conveniently be recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. The products have been characterized by elemental analysis, <sup>1</sup>H 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.

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.

Figure 1. Room-temperature EPR spectra of (a) [Cp-Cr(CN)=3]<sup>2-</sup> and (b) [Cp*Cr(CN)=3]<sup>2-</sup> in water.

Figure 2. View of the [Cp*Cr(CN)=3]<sup>-</sup> anion from the single-crystal X-ray structure of the NEt<sub>4</sub> salt.

(20) Crystal data for [PPh<sub>4</sub>][Cp*Cr(CN)3] (M<sub>r</sub> = 604.65): orthorhombic, space group Pbca, a = 17.398(4) Å, b = 17.457(4) Å, c = 20.997(4) Å, V = 6377(2) Å³, Z = 8, d<sub>calc</sub> = 1.260 Mg/m³, 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, the electronic relaxation is apparently much faster for spin quartet, lower symmetry half-sandwich compounds, leading to EPR-silent isomeric solutions. For instance, the compounds CpCrX$_2$(η$^1$-L-L) (X = Cl, CH$_3$) do not show EPR resonances down to the freezing point of the solvent. The nature of the EPR-active species will be examined in the next section.

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

(b) Addition of CN$^-$. 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 tetra-cyano complex [(ring)Cr(CN)$_4$]$^2^-$. The 17-electron configuration necessarily leads to an orbital 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$_3$)$_2$. A quartet ground state for a 17-electron Cr(III) complex would require the occupation of metal–ligand d$^{*}$ 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)). The only previously reported example of a half-sandwich 17-electron Cr(III) complex, i.e. CpCr(C$_3$H$_5$)$_2$, has a reported magnetic moment of 1.8 $\mu_B$.^3

Every attempt to crystallize the 17-electron dianion only afforded back the EPR-silent and $^1$H-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 Cr(CN)$_3$$^3$ ion. The EPR spectrum of a genuine sample of [Cr(CN)$_3$]$^3$–, 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 cyclopenta-dienyl 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$^0$, or Cr(−I), d$^{-1}$),^28 whereas oxidized species (Cr(V), d$^4$) 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 $^{53}$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 × $^{13}$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. 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

\[
[(\text{ring})\text{Cr(CN)}_3]^- + \text{CN}^- \leftrightarrow [(\text{ring})\text{Cr(CN)}_4]^2^- \tag{2}
\]

solutions of [(ring)Cr(CN)$_3$]$^-$ with known excess amounts of CN$^-$. The concentration of the [(ring)Cr(CN)$_3$]$^-$ 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


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

(c) Generation of 17-Electron Phosphine Derivatives of (ring)Cr(CN)\textsubscript{3}. The reaction between [CpCr(CN)\textsubscript{3}]\textsuperscript{-} and tertiary phosphine ligands (PMe\textsubscript{3}, PMe\textsubscript{2}Ph, dmpe, dmpm) in CH\textsubscript{2}Cl\textsubscript{2} results in the formation of products characterized by well-defined room-temperature EPR spectra. These spectra consist of 1:2:1 triplets at \( g = 1.99 \) (\( a_p = 34 \text{ G} \)) 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\textsuperscript{-} to [(ring)Cr(CN)\textsubscript{3}]\textsuperscript{-}, the solutions obtained by adding tertiary phosphine ligands to [CpCr(CN)\textsubscript{3}]\textsuperscript{-} 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)\textsubscript{3}L]\textsuperscript{-} species (L = tertiary phosphine). A magnetic susceptibility study of equilibrium 3 was carried out in solution by the Evans method;\textsuperscript{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., \( S = \frac{1}{2} \text{CpCr(CN)\textsubscript{2}L} \). This result also indicates that equilibrium 3, like equilibrium 2 shown in the previous section, is largely shifted to the left.

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\textsubscript{2}]\textsuperscript{+}CN\textsuperscript{-} species does not appear reasonable because (i) by analogy with other previously investigated half-sandwich 15-electron complexes, including [CpCr(CN)\textsubscript{3}]\textsuperscript{-}, such a species is not expected to give rise to an isotropic EPR spectrum at room temperature, (ii) the CN\textsuperscript{-} 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)L\textsubscript{2}]\textsuperscript{+}, 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)\textsubscript{3}]\textsuperscript{-} 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.

Crystalization from the equilibrium solutions obtained as described in eq 3 only allowed the recovery of solid [PPh\textsubscript{3}][CpCr(CN)\textsubscript{3}]. A \(^1\text{H}\) NMR monitoring experiment in CDC\textsubscript{13} showed only a slight decrease of the paramagnetically shifted resonance at \( \delta \) 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. Cr(CN)\textsubscript{2}L or Cr(CN)\textsubscript{2}(η\textsuperscript{1}-L-L). Previously reported phosphine-contain-
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)L2. 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(n2-C3H5)2 decomposes at temperatures above 0 °C,2 Ligand adducts of sandwich or pseudosandwich (e.g. half-open) Cr(III) complexes with a 17-electron configuration are also known, e.g. [CpCr(Pd′)-(CO)]+ (Pd′ = 2,4-dimethylpenta-2,4-dien-1-y1).30 Steric effects are manifested by the smaller equilibrium concentration of [CpCr(P)2]+ relative to the corresponding Cp derivative, the absence of an interaction between [CpCr(CN)3]+ and the bulkier ligands PEt3 (cone angle, θ = 132°) and PPh3 (θ = 145°),31 and by the absence of an interaction between [CpCr(CN)3]+ and any phosphine ligand.

We have recently reported that the compounds CpCrX2(L-L) (X = Cl, CH3; L-L = dmpp, dppe) adopt only a three-legged piano-stool, 15-electron CpCrX2(η1-L-L) structure, both in the solid state and in solution.10 The results reported here indicate that the energy difference between CpCrX2L2 or CpCrX2(η2-L-L) and the [CpCr(CN)L2 + L+] or CpCrX2(η1-L-L) system is less for X = CN relative to X = Cl, CH3. 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 CH3. However, we have already argued10,11 that steric effects alone should not prevent a 15-electron CpCrX2(PR3) system with X = Cl or CH3 to coordinate another PR3 ligand, because the corresponding V(III) center of similar size forms the stable four-legged piano-stool complexes CpVX2(PR3)2 (X = Cl, CH3) even with relatively encumbering ligands such as PEt3.33

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
duly producing solutions that show once again the characteristic EPR signals assigned to the CpCr(CN)L2 species and weak NMR resonances indicative of the presence of CpCrCl2L (see eq 5; L = PMe3 or PMe2Ph).

\[
[CpCr(CN)(μ-Cl)]_2 + 3L \rightleftharpoons CpCr(CN)_2L_2 + CpCrCl_2L. \tag{5}
\]

**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)L2. 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(n2-C3H5)2 decomposes at temperatures above 0 °C,2 Ligand adducts of sandwich or pseudosandwich (e.g. half-open) Cr(III) complexes with a 17-electron configuration are also known, e.g. [CpCr(Pd′)-(CO)]+ (Pd′ = 2,4-dimethylpenta-2,4-dien-1-y1).30 Steric effects are manifested by the smaller equilibrium concentration of [CpCr(P)2]+ relative to the corresponding Cp derivative, the absence of an interaction between [CpCr(CN)3]+ and the bulkier ligands PEt3 (cone angle, θ = 132°) and PPh3 (θ = 145°),31 and by the absence of an interaction between [CpCr(CN)3]+ and any phosphine ligand.

We have recently reported that the compounds CpCrX2(L-L) (X = Cl, CH3; L-L = dmpp, dppe) adopt only a three-legged piano-stool, 15-electron CpCrX2(η1-L-L) structure, both in the solid state and in solution.10 The results reported here indicate that the energy difference between CpCrX2L2 or CpCrX2(η2-L-L) and the [CpCr(CN)L2 + L+] or CpCrX2(η1-L-L) system is less for X = CN relative to X = Cl, CH3. 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 CH3. However, we have already argued10,11 that steric effects alone should not prevent a 15-electron CpCrX2(PR3) system with X = Cl or CH3 to coordinate another PR3 ligand, because the corresponding V(III) center of similar size forms the stable four-legged piano-stool complexes CpVX2(PR3)2 (X = Cl, CH3) even with relatively encumbering ligands such as PEt3.33

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

Table 1. Effective Magnetic Moments (Evans Method) per Cr Atom for Solutions Containing [Et4N][CpCr(CN)3] and Excess Phosphine Ligand (Solvent CD3CN)

<table>
<thead>
<tr>
<th>[[Et4N][CpCr(CN)3]]/M</th>
<th>phosphine (concn/M)</th>
<th>μeff/μB</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.076</td>
<td>dpmm (0.15)</td>
<td>3.55</td>
</tr>
<tr>
<td>0.074</td>
<td>dmpe (0.074)</td>
<td>3.40</td>
</tr>
<tr>
<td>0.075</td>
<td>PMe₃ (0.24)</td>
<td>3.29</td>
</tr>
<tr>
<td>0.074</td>
<td>PMe₂Ph (0.17)</td>
<td>3.30</td>
</tr>
<tr>
<td>0.074</td>
<td>PMe₃ (0.17)</td>
<td>3.44</td>
</tr>
</tbody>
</table>

31P NMR monitoring shows the increase with time of the free dpmm resonance. Crystallization by addition of toluene yielded only impure solids which do not show any EPR resonance and no 31H NMR signals attributable to phosphine ligands. The analytical data are most consistent with materials of formula CpCr(CN)Cl2−x (x ca. 1). Even when an excess amount of Me3SiCN 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)2L2 species and weak 31H NMR resonances in the expected region for compounds CpCrCl2L. 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 reaction of [CpCrCl2]2 and excess Me3SiCN in CH2Cl2 also yielded a product whose analysis is consistent with "CpCr(CN)Cl". In an attempt to force the CI/CN exchange, the reaction was carried out in refluxing Me3CN, giving a completely insoluble brown product whose analysis corresponds once again to CpCr(CN)Cl. The magnetic moment of this material is μeff = 2.03 μB/Cr atom, indicating substantial quenching of the expected moment for magnetically diluted d3 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)2(μ-Cl)]2 and workup or warming converts this species into an oligomeric or polymeric structure. Perhaps the last CI 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)2(μ-Cl)]n material requires prolonged heating, even-

\[
[CpCr(CN)(μ-Cl)]_2 + 3L \rightleftharpoons CpCr(CN)_2L_2 + CpCrCl_2L. \tag{5}
\]
strength of the Cr—L interaction along the spin doublet surface \( \left( D_{M-L} \right) \) may be greater when \( L = \text{CN}^- \) relative to \( L = \text{Cl}^- \), \( \text{CH}_3^- \); this fact alone may rationalize the existence (accessibility) of the complex \([\text{CpCr(CN)}_4]^2-\) vis à vis the nonexistence of complexes \([\text{CpCrX}_4]^2-\) with \( X = \text{Cl}, \text{CH}_3 \). Concerning the formation of neutral \( \text{CpCrX}_2L_2 \) complexes \( (L = \text{tertiary phosphine}) \), the Cr–PR\(_3\) bond may be stronger when \( X = \text{CN} \) relative to \( X = \text{Cl}, \text{CH}_3 \) because of the \( \pi \)-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. \( \Delta E \), 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 monoatomic terms, \( \Delta E \) 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 \( \pi \) 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 \( \text{TiX}_2(\text{dmpe})_2 \) as a spin triplet for \( X = \text{Cl} \) and singlet for \( X = \text{CH}_3 \).\(^{35}\) Theoretical calculations at various levels on the \( \text{CpCr}_2(\text{PH}_3)_n \) \( (n = 1, 2) \) system in both the quartet and doublet spin states for \( X = \text{Cl}, \text{CH}_3, \text{CN} \) 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 coordinating, 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 \( \text{CpCr}^{III} \) 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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