Pairing Energy Effects in Cyanide Complexes of $CpCr^{III}$

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The steric and electronic factors responsible for the reactivity differences between CN and Cl complexes of $CpCr^{III}$ were examined by DFT/B3LYP computational techniques. The energy difference between quadruplet and doublet $[CpCr(CN)_2(PH_3)]$, ΔE_{D-Q}, was calculated to be 21.2 kcal mol^{-1} with the LanL2DZ basis set. Although the high-spin configuration is still the ground state for the cyanide complex, the energy gap is 8.7 kcal mol^{-1} less than that found for the corresponding chloride species. The difference between quadruplet $[CpCr(CN)_2(PH_3)]$ and doublet $[CpCr(CN)_2(PH_3)_2]$ less free PH_3, ΔE_{Cr-P}, is also smaller than for the Cl system. The components of ΔE_{Cr-P} for CN and Cl were analyzed by calculating energies at fixed geometries in both spin states, which indicated that the influence of the cyanide group on the pairing energy was more important than changes in Cr–PH_3 bond strength or steric effects.

Introduction

The study of transition metal compounds containing cyanide ligands has experienced a recent resurgence due in large part to the ability of these ligands to form M−CN−M′ bridges.[1] Extending these bridges in one, two, or three dimensions results in novel materials often possessing microporous structures and interesting magnetic properties.[2] As an alternative to homoleptic cyanometalates, anionic $[CpM(CN)_n]^-$ complexes have also been investigated in which the Cp or Cp* ligand serves to enhance the overall inertness of the complex as well as to limit polymerization.[3][4]

We have recently examined the reactivity of cyanide complexes of $CpCr^{III}$ as part of our ongoing investigation of spin-state effects in organometallic chemistry.[5] Cyanide ligands confer a greater stability on the resulting highly coordinated monometallic compounds than the halide ligands on the corresponding, relatively unsaturated analogues. For example, in the case of complexes of $CpMo^{IV}$, the cyanometalate exists as the 18-electron dianion,[6] $[CpMo(CN)_5]^{2-}$, while with the chloride ion the 16-electron monoanion,[7] $[CpMoCl_4]^-$, is observed. The same trend between CN and Cl ligation is observed for $CpCr^{III}$ complexes.[8] For cyanide, equilibrium concentrations of the 17-electron spin-doublet $[CpCrL_4]$ species $[CpCr(CN)_2(PR_3)_2]$ and $[CpCr(CN)_4]^{2-}$ have been detected in solution by ESR spectroscopy,[9] whereas similar 17-electron species were *not* spectroscopically observed for the analogous chloride complex.[10] A kinetic and theoretical investigation of the PR_3 exchange reactions for $[CpCrCl_2(PR_3)]$ complexes demonstrated that, although exchange proceeds by an associative pathway, the reaction proceeds solely on the quadruplet spin hypersurface by an S_N2-type mechanism.[11] Previously, density functional theory (DFT) calculations have been used to compare the relative energies of $[CpCrX_2(PH_3)_n]$ (X = Cl, CH_3; n = 1, 2) and $[CpMoCl_2(PH_3)_n]$ systems in the doublet and quadruplet spin states.[12] In this study, DFT calculations were used to determine the relative importance of the possible factors which contribute to the anomalous stability of the 17-electron doublet CN species relative to the Cl analogues. Possible factors which we have previously considered include: (a) steric considerations (since CN is smaller than Cl), (b) the Cr−L bond strength (the relative electron-withdrawing ability of CN could increase the relative strength of the additional Cr−PR_3 bond in the 17-electron species), (c) changes in ΔE_{D-Q} (by modifying the orbital splitting and/or the pairing energy, CN could influence the relative stabilities of the doublet and quadruplet spin states).[9]

Results and Discussion

Optimized LanL2DZ Geometries and Energies

The geometries of doublet $[CpCr(CN)_2(PH_3)_2]$, and doublet and quadruplet $[CpCr(CN)_2(PH_3)]$ were optimized in the C_s symmetry with DFT using the three-parameter form of the Becke, Lee, Yang and Parr functional (B3LYP)[13a] and the LanL2DZ basis set.[13b−d] The bond lengths and angles are shown in Table 1. A comparison of the two 15-electron monophosphane compounds reveals that the doublet complex has slightly shorter bond lengths and deviates further from an idealized three-legged piano-stool structure.[14] The relative difference between the two geometries is comparatively small and is much less pronounced than the difference between doublet and quadruplet $[CpCrCl_2(PH_3)]$.[11,12b]

The relative energies calculated for the $CpCr^{III}$ cyanide compounds are depicted in Figure 1. As expected, based on 15-electron $CpCr^{III}$ monophosphane compounds containing halide or alkyl groups,[15] the quadruplet state is favored over the doublet. In the present case, the high-spin configuration is 21.2 kcal mol^{-1} more stable than the ΔE_{D-Q} value

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Table 1. Optimized geometries for doublet and quadruplet $[CpCr(CN)_2(PH_3)_n]$ (n = 1, 2)[a]

Structural Parameter[b]	$[CpCr(CN)_2(PH_3)_2]$ doublet	$[CpCr(CN)_2(PH_3)]$ doublet	$[CpCr(CN)_2(PH_3)]$ quadruplet
CNT−Cr	1.918	1.958	1.979
Cr−CN	2.004	1.986	1.993
Cr−P	2.470	2.495	2.521
CNT−Cr−CN	116.50	121.44	122.72
CNT−Cr−P	115.58	129.30	128.00
NC−Cr−P	78.39	85.53	87.23
NC−Cr−CN	126.98	104.06	98.92
NC−Cr−CNT−P	90.6	112.5	115.4
NC−Cr−CNT−CN	178.8	135.0	129.2

[a] Bond lengths in Å and angles in degrees. − [b] CNT = center of gravity of the Cp ring.

of 29.9 kcal mol^{-1} previously calculated for $[CpCrCl_2(PH_3)]$ with the same functional and basis set.[11] Similar differences between cyanide and chloride complexes are observed when comparing the energy of doublet $[CpCrX_2(PH_3)_2]$ to the sum of quadruplet $[CpCrX_2(PH_3)]$ and free PH_3. This energy difference, labelled ΔE_{Cr-P} in Figure 1, provides an indication of how readily the quadruplet species will accommodate another *phosphane* ligand. In qualitative agreement with experimental results, ΔE_{Cr-P} is smaller for X = CN (10.3 kcal mol^{-1}) than for X = Cl (ΔE_{Cr-P} = 21.2 kcal mol^{-1}).

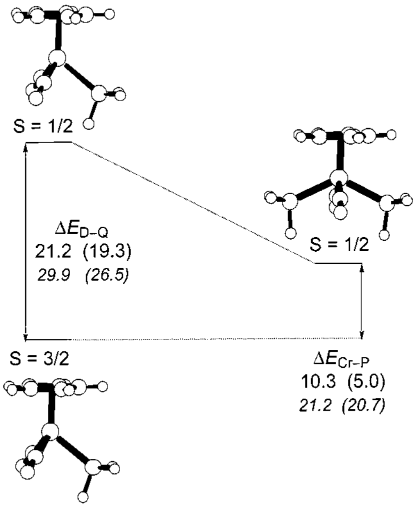

Figure 1. Relative energies of doublet and quadruplet $[CpCr(CN)_2(PH_3)_n]$ (n = 1, 2); energies calculated at the B3LYP/LanL2DZ level of theory, with B3LYP/6−311+G(2d,2p) values indicated in parentheses, and the corresponding $[CpCrCl_2(PH_3)_n]$ energies in italics

Larger Basis Set Calculations

Recent work with $[CpCo(PH_3)_n]$ complexes (n = 1, 2) has showed the importance of the size of the basis set on $[ML_n]$ ligand dissociation energies.[16] Smaller basis sets tend to underestimate metal−ligand bond strengths, thereby causing the relative stability of unsaturated compounds to be overstated. To account for this effect, the energies of the $[CpCr(CN)_2(PH_3)_n]$ compounds optimized at the B3LYP/LanL2DZ level were recalculated with the larger 6−311+G(2d,2p) basis set; the resulting energies are indicated in parentheses in Figure 1. The energy difference between the quadruplet and doublet 15-electron compounds decreased slightly to 19.3 kcal mol^{-1}, and the expected decrease in ΔE_{Cr-P} was also observed, from 10.3 to 5.0 kcal mol^{-1}. For comparison, the B3LYP/LanL2DZ geometries previously obtained for $[CpCrCl_2(PH_3)_n]$ were used to recalculate their energies at the B3LYP/6−311+G(2d,2p) level, and the resulting values are also displayed in Figure 1.

Fixed Geometry Calculations

In order to analyze the various components that make up ΔE_{Cr-P}, single-point calculations were performed at the B3LYP/LanL2DZ level as illustrated in Figure 2. One PH_3 ligand was removed from the optimized structure of doublet $[CpCr(CN)_2(PH_3)_2]$ without altering any of the other structural parameters. The single-point calculations on these complexes with one or three unpaired electrons yield energies for the doublet-fixed and quadruplet-fixed complexes, respectively, as indicated in Table 2. The Bond Energy Term (BET) is equal to the difference between the 17-electron doublet-optimized and 15-electron doublet-fixed structures plus free PH_3, and provides an indication of the $Cr-PH_3$ bond strength without additional factors due to spin-state change. Since the doublet-fixed and quadruplet-fixed energies are based on exactly the same geometry, the difference in energy between these species reflects the Pairing Energy (PE). The Relaxation Energy (RE), obtained from the difference between quadruplet-fixed and quadruplet-optimized energies, accounts for the reorganization required for the 15-electron species to accommodate an additional phosphane ligand, and is directly related to the steric bulk of the adjacent cyanide ligands. These energies were also calculated for the chloride species, and the values obtained are collected in Table 2.

Direct comparison of the factors that contribute to ΔE_{Cr-P} for the two $[CpCrX_2(PH_3)_n]$ systems helps identify the ligand properties responsible for the observed experimental differences between the cyanide and chloride compounds. The BET is only slightly greater for X = CN than for X = Cl, a variation which might be attributable to the

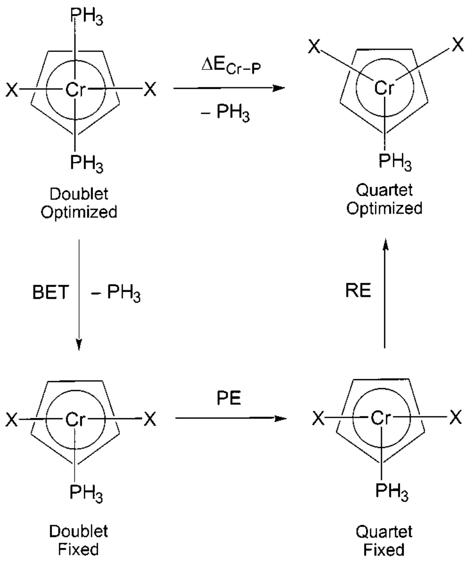

Figure 2. Schematic representation of fixed and optimized geometries used for B3LYP/LanL2DZ energy calculations of $[CpCrX_2(PH_3)_n]$ (X = CN, Cl; n = 1, 2)

Table 2. Relative energies of $[CpCrX_2(PH_3)_n]$ (X = CN, Cl; n = 1, 2) complexes in optimized and fixed geometries[a]

	$[CpCr(CN)_2(PH_3)_n]$	$[CpCrCl_2(PH_3)_n]$
Bond Energy Term	20.2	17.1
Pairing Energy	−17.1	−25.5
Relaxation Energy	−13.4	−12.8

[a] ΔE (in kcal mol^{-1}) calculated at the B3LYP/LanL2DZ level of theory.

different electron-withdrawing capacity of the two X ligands which affects the ability of the metal center to accommodate the strong σ-donor phosphane ligand. The anticipated difference in steric requirements for CN vs. Cl apparently does not play an appreciable role, since the RE is roughly the same in each case. The key factor seems to be the ability of the cyanide ligand to facilitate the electron pairing required to cross over from the quadruplet-spin to the doublet-spin potential energy surface, as reflected in the PE which is −17.1 kcal mol^{-1} for X = CN in contrast to −25.5 kcal mol^{-1} for X = Cl. The same trend is seen in the values obtained for ΔE_{D-Q} in the two systems.

The relative energies of the frontier orbitals for the $[CpCrX_2(PH_3)]$ (X = CN, Cl) fixed-doublet and fixed-quadruplet species are shown in Figure 3. While it is imprudent to assign too much physical significance to the Kohn-Sham orbitals arising from the current DFT calculations,[17] the qualitative trends in orbital energies appear to support our interpretation. The significantly greater energy gap for X = CN than for X = Cl between the highest and lowest energy frontier orbitals for both spin states accounts for the enhanced stability of the doublet spin-state for the cyanide complex. As well as influencing the orbital splitting, the CN group may also favor the doublet species by decreasing the pairing energy, consistent with the known large nephelauxetic effect of the cyanide ligand.[18]

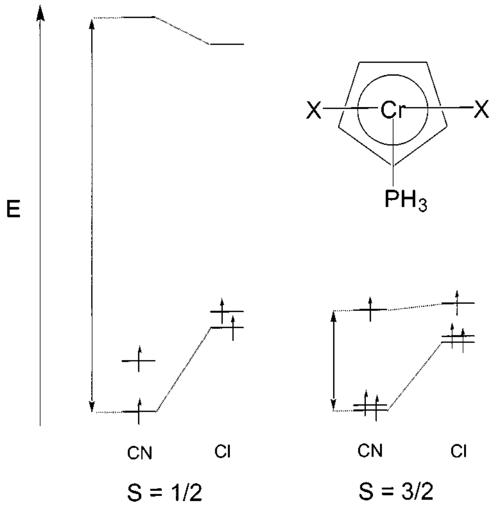

Figure 3. Orbital energies (α orbitals) and occupancies of fixed geometry $[CpCrX_2(PH_3)]$ (X = CN, Cl) species in doublet and quadruplet spin states

Conclusions

Several possible explanations were initially forwarded to rationalize the observation of $[CpCr(CN)_2(PR_3)_2]$ complexes by EPR although the corresponding Cl complexes were not detected. Calculations at the DFT/B3LYP level indicate that the steric differences and variation in Cr−P bond strength are not adequate to account for this discrepancy. The observed differences are best explained by the relative ability of the CN group to encourage spin pairing, as demonstrated by the smaller ΔE_{D-Q} than in the chloride system for both fixed and optimized geometries.

Experimental Section

General Remarks: All calculations were performed with GAUSSIAN 94[19] on an SGI Origin 200 workstation. The geometries of the $[CpCrX_2(PH_3)_2]$ and $[CpCrX_2(PH_3)]$ species and free PH_3 were optimized with B3LYP,[13a] a DFT type of calculation, employing the LanL2DZ basis set. The LanL2DZ basis set includes both Dunning and Hay's D95 sets for H and C and the core potential sets of Hay and Wadt for the heavy atoms.[13b−d] Electrons outside the core were all those for H and C, the 3s and 3p electrons for P, and the 3s, 3p, 3d and 4s electrons for Cr. All geometries were optimized at the B3LYP/LanL2DZ level with imposed C_s symmetry. The B3LYP energy calculations were performed separately with both the LanL2DZ basis set and the larger 6−311+G(2d,2p) basis set, which has two sets of polarization functions on all atoms including two f-sets on the Cr, and also diffuse functions.

The mean value of the first-order electronic wavefunction, which is not an exact eigenstate of S^2 for unrestricted calculations on the open shell systems, was considered suitable for unambiguous identification of the spin state. Spin contamination was carefully monitored and the value of $<S^2>$ for the unrestricted B3LYP (UB3LYP) calculations on the $[CpCrX_2(PH_3)_n]$ species indicated minor spin contamination in most cases. With the exception of doublet [$CpCr(CN)_2(PH_3)$], $\langle S^2 \rangle$ was in the range of 0.7651 to 0.7783 for doublet species, and 3.8196 to 3.8692 for quadruplets. As previously observed for doublet [$CpCr(CH_3)_2(PH_3)$],[12b] the 15-electron doublet cyanide complex exhibited anomalously large $\langle S^2 \rangle$ values: 1.7257 to 1.5558 for fixed and optimized geometries with both basis sets. The energies shown in the Results and Discussion section correspond to UB3LYP calculations, and the frontier orbital energies are those of the occupied (α) orbitals.

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