Cyanide Ligand Basicities in Cp′M(L)$_2$CN Complexes (M = Ru, Fe). Correlation between Heats of Protonation and *ν*CN

Chip Nataro, Jiabi Chen,† and Robert J. Angelici*

Department of Chemistry and Ames Laboratory, Iowa State University, Ames, Iowa 50011

Received September 4, 1997

Basicities of the cyanide ligands in a series of Cp′M(L)$_2$CN complexes were investigated by measuring their heats of protonation ($-\Delta H_{CNH}$) by CF_3SO_3H in 1,2-dichloroethane solution at 25.0 °C to give Cp′M(L)$_2$(CNH)$^+CF_3SO_3^-$, in which the N−H$^+$ group is probably hydrogen-bonded to the $CF_3SO_3^-$ anion. Basicities ($-\Delta H_{CNH}$) of the CpRu(PR$_3$)$_2$CN complexes increase from 20.5 (PPh$_3$) to 22.4 (PMe$_3$) kcal/mol with increasing donor abilities of the phosphine ligands. Basicities of all the Cp′Ru(PR$_3$)$_2$CN complexes, where Cp′ = Cp or Cp*, are linearly correlated with their *ν*CN values; the nonphosphine complexes, CpRu(1,10-phen)CN and CpRu(COD)CN, do not follow the same correlation. For a large number of Cp′M(L)$_2$CN complexes (M = Ru, Fe, L$_2$ = mono- and bidentate phosphines, CO, 1,10-phen, and COD), their *ν*CN values parallel *ν*CN values of their protonated Cp′M(L)$_2$(CNH)$^+$ analogues. Also, ^{31}P NMR chemical shifts of the unprotonated Cp′M(PR$_3$)$_2$-CN and protonated CpM(PR$_3$)$_2$(CNH)$^+$ complexes are linearly related. Despite the high basicity of Ru in Cp*Ru-(PMe$_3$)$_2$Cl (30.2 kcal/mol), the CN$^-$ in Cp*Ru(PMe$_3$)$_2$CN (25.0 kcal/mol) is the site of protonation; factors that determine whether protonation occurs at the Ru or the CN$^-$ are discussed.

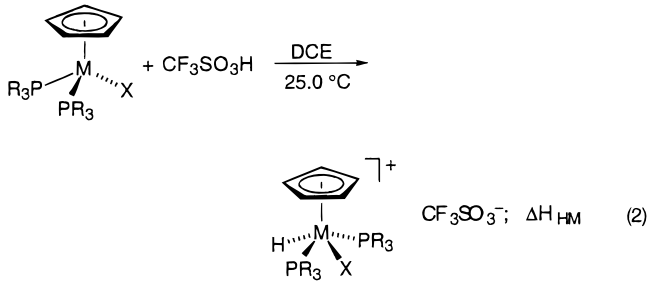
Introduction

The cyanide ligand in transition metal complexes undergoes a variety of reactions, particularly those with electrophiles.[1] The nitrogen is alkylated by R_3O^+ and RX reagents to give alkyl isocyanide complexes. Reactions with other transition metal complexes have yielded numerous cyanide-bridged di- and polynuclear compounds.[1,2] The cyanide ligand is also readily protonated to give hydrogen isocyanide (CNH) complexes. Despite the existence of a large number of protonated cyanide−ligand complexes,[1] only two quantitative measurements of cyanide ligand donor ability have been reported.[3] In one study,[3a] the complexes M(bipy)$_2$(CN)$_2$, where M = Fe, Ru, or Os, were protonated by *o*-$ClC_6H_4NH_3^+$ in acetic acid solvent. Equilibrium constants for protonation of the first CN$^-$ ligand increased slightly with the metal in the following order: Fe (0.9) < Os (1.3) < Ru (2.8). Protonation of the second CN$^-$ occurred with substantially smaller equilibrium constants and the metal-dependence changed to the following: Fe (0.005) < Ru (0.008) < Os (0.026). In the other study,[3b] the basicities of the M(CN)$_6^{4-}$ complexes in water were found to increase with the metals, as indicated by the pK_a of their protonated forms (in parentheses), in the following order: Ru (3.2) < Os (3.3) < Fe (3.4). Thus, the basicity trend is different in the two systems, but the effect of the metal is not large.

In the present paper, we describe studies of the basicity of the cyanide ligand in the family of Cp′M(L)$_2$CN complexes, where M = Ru or Fe, Cp′ = Cp or Cp*(η^5-C_5Me_5), (L)$_2$ = phosphines, 1,5-cyclooctadiene (COD), or 1,10-phenanthroline (1,10-phen). The basicity of the cyanide ligand in these complexes is defined as the enthalpy of protonation (ΔH_{CNH}) for the reaction (eq 1) of the cyanide complex with CF_3SO_3H

$$Cp'M(L)_2CN + CF_3SO_3H \xrightarrow[25\ °C]{DCE} Cp'M(L)_2(CNH)^+CF_3SO_3^-;\ \Delta H_{CNH} \quad (1)$$

in 1,2-dichloroethane (DCE) solvent at 25.0 °C. Previously, heats of protonation of the metal (ΔH_{HM}) in the related non-cyanide complexes Cp′M(PR$_3$)$_2$X, where M = Ru or Os, Cp′ = Cp or Cp*, and X = Cl, Br, I, or H, were reported.[4] It was observed



(2)

that the basicity ($-\Delta H_{HM}$) of the Ru increased by 9.0 kcal/mol when the Cp in CpRu(PMe$_3$)$_2$Cl (21.2(4) kcal/mol) was substituted by Cp* in Cp*Ru(PMe$_3$)$_2$Cl (30.2(2) kcal/mol). A large increase in basicity was also noted when the PPh$_3$ ligands in CpOs(PPh$_3$)$_2$Br (16.3(1) kcal/mol) were replaced by PMe$_3$ in CpOs(PMe$_3$)$_2$Br (29.4(4) kcal/mol). In addition, the replacement of Br$^-$ in CpOs(PPh$_3$)$_2$Br (16.3(1) kcal/mol) by H$^-$ in CpOs(PPh$_3$)$_2$H (37.3(1) kcal/mol) resulted in an enormous increase (21.0 kcal/mol) in the basicity of the Os. Also, replacement of the Ru in CpRu(PMe$_3$)$_2$Br (20.9(3) kcal/mol) by Os in CpOs(PMe$_3$)$_2$Br (29.4(4) kcal/mol) increased the basicity of the metal center by 8.5 kcal/mol. Thus, variations

† Permanent address: Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, PRC.

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S0020-1669(97)01124-5 CCC: $15.00
Published on Web 03/31/1998

in the Cp′, M, PR_3, and X units of the Cp′M$(PR_3)_2$X complexes lead to large changes in the basicity ($-\Delta H_{HM}$) of the metal center.

In the cyanide complexes, Cp′ML$_2$CN, there is also the possibility that protonation would occur at the metal rather than at the cyanide ligand. It is known,[5] for example, that the trigonal bipyramidal complexes (L)RhCN, where L = N$(CH_2CH_2PPh_2)_3$ or P$(CH_2CH_2PPh_2)_3$, are protonated by CF_3SO_3H at the Rh instead of the CN to give (L)Rh(CN)(H)$^+$. Although CpRu$(PPh_3)_2$CN is known[6,7] to protonate at the cyanide, it seemed possible that protonation might occur at the metal if its basicity were sufficiently enhanced by strongly donating ligands, as in Cp*Ru$(PMe_3)_2$CN.

Although the cyanide ligand protonation reaction (eq 1) suggests that the ΔH_{CNH} value simply represents the Lewis basicity of the ligand, there is excellent X-ray evidence[7] for hydrogen bonding between the CN−H$^+$ proton and an oxygen of the $CF_3SO_3^-$ anion (Ru−CN−H- - -OSO_2CF_3) in the solid-state structure of CpRu$(PPh_3)_2(CNH)^+{}^-O_3SCF_3$, which is one of the complexes studied in the present investigation. In addition, there are other examples of hydrogen bonding between protonated cyanide ligands and the oxygen atom in ethers, as for example in the tetrahydrofuran adduct $(CO)_5$Cr−CN−H- - -THF.[1,8] If such hydrogen-bonding were to occur between the Cp′M$(L)_2(CNH)^+$ and $^-O_3SCF_3$ ions in solution under the conditions of the calorimetric studies, the measured ΔH_{CNH} values would include the enthalpies associated with hydrogen bonding. It was therefore important to determine whether hydrogen bonding was a consideration in the interpretation of the ΔH_{CNH} results. Finally, these investigations required the synthesis of a broad range of Cp′M$(L)_2$CN complexes which provided an opportunity to examine correlations among ΔH_{CNH}, νCN, ^{31}P NMR chemical shifts, and other ligand parameters.

Experimental Section

General Procedures. All preparative reactions, chromatography and manipulations were carried out under an atmosphere of nitrogen or argon using standard Schlenk techniques. Solvents were purified under nitrogen using standard methods.[9] Diethyl ether (Et_2O) and THF were distilled over sodium benzophenone, while benzene, hexanes, and CH_2Cl_2 were distilled from CaH_2. The C_2H_5OH and CH_3OH were deoxygenated using four or five freeze−pump−thaw cycles and stored under N_2. Acetone was deoxygenated and dried with 4 Å molecular sieves; CD_2Cl_2 was stored over molecular sieves under nitrogen. 1,2-Dichloroethane (DCE) was purified by washing with concentrated sulfuric acid, distilled deionized water, 5% NaOH, and again with water. The solvent was then predried over anhydrous $MgSO_4$ and stored in amber bottles over molecular sieves (4 Å). The DCE was distilled from P_4O_{10} under argon immediately before use. Triflic acid (CF_3SO_3H) was purchased from 3M Co. and purified by fractional distillation under argon prior to use. The neutral Al_2O_3 (Brockman, Activity I, 80−100 mesh) used for chromatography was deoxygenated under high vacuum at room temperature for 16 h, deactivated with 5% (w/w) N_2-saturated water, and stored under N_2. Chromatography columns were 1.5 × (5−15) cm. The phosphines, PPh_3, P$(p$-$MeOC_6H_4)_3$, P$(p$-$MeC_6H_4)_3$, P$(m$-$MeC_6H_4)_3$, P$(p$-$FC_6H_4)_3$, P$(p$-$CF_3C_6H_4)_3$, $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PCH_2CH_2PPh_2$ (dppe), $Ph_2PCH_2CH_2CH_2PPh_2$ (dppp), PMe_3, PEt_3, $PMePh_2$, PMe_2Ph, PCy_3, PEt_3, and P$(i$-Pr$)_3$, were purchased from either Strem Chemical Co. or Aldrich Chemical Co. Dicyclopentadiene was purchased from Aldrich. NaCN and 1,10-phenanthroline were purchased from Fisher Chemical Co. The complexes CpRu$(P(OMe)_3)_2$Cl (**1Cl**),[10] CpRu$(PMe_3)_2$Cl (**5Cl**),[11] CpRu$(PPh_3)_2$Cl (**8Cl**),[12] CpRu$(PPh_3)_2$-CN (**8CN**),[13] CpRu(CO)(PPh_3)Cl (**9Cl**),[14] CpRu$(CO)_2$CN (**10CN**),[15] CpRu(dppm)Cl (**17Cl**),[10] CpRu(dppe)Cl (**18Cl**),[10] CpRu(dppe)CN (**18CN**),[16] CpRu(COD)Cl (**20Cl**),[11] CpFe$(CO)_2$Br (**22Br**),[17] CpFe(dppe)-CN (**23CN**),[18] Cp*Ru$(PMe_3)_2$Cl (**5*Cl**),[19] Cp*Ru(dppe)Cl (**18*Cl**),[20] Cp*Ru(dppp)Cl (**19*Cl**),[20] and Cp*Ru(COD)Cl (**20*Cl**)[20,21] were prepared by literature methods.

Table 1. IR Data (CH_2Cl_2 Solvent) for the Cp′M$(L)_2$CN and Cp′M$(L)_2(CNH)^+$ Complexes

complex	Cp′ML$_2$	ν(CN)	complex	ν(CN)
2CN	CpRu$(PEt_3)_2$	2065 (m)	**2CNH**$^+$	2015 (vw)
5CN	CpRu$(PMe_3)_2$	2065 (m)	**5CNH**$^+$	2017 (vw)
6CN	CpRu$(PMe_2Ph)_2$	2069 (m)	**6CNH**$^+$	2017 (vw)
7CN	CpRu$(PMePh_2)_2$	2071 (m)	**7CNH**$^+$	2021 (vw)
8CN	CpRu$(PPh_3)_2$	2072 (m)	**8CNH**$^+$	2023 (vw)
9CN	CpRu(CO)(PPh_3)	2105 (m)	**9CNH**$^+$	2092 (vw)
10CN	CpRu$(CO)_2$	2129 (m)	**10CNH**$^+$	obscured
11CN	CpRu$(P(p$-$MeOC_6H_4)_3)_2$	2067 (m)	**11CNH**$^+$	2016 (vw)
12CN	CpRu$(P(p$-$MeC_6H_4)_3)_2$	2069 (m)	**12CNH**$^+$	2019 (vw)
13CN	CpRu$(P(m$-$MeOC_6H_4)_3)_2$	2069 (m)	**13CNH**$^+$	2021 (vw)
14CN	CpRu$(P(p$-$CF_3C_6H_4)_3)_2$	2080 (m)	**14CNH**$^+$	2032 (vw)
15CN	CpRu$(P(p$-$FC_6H_4)_3)_2$	2075 (m)	**15CNH**$^+$	2021 (vw)
17CN	CpRu(dppm)	2076 (m)	**17CNH**$^+$	2033 (vw)
18CN	CpRu(dppe)	2075 (m)	**18CNH**$^+$	2023 (vw)
19CN	CpRu(dppp)	2067 (m)	**19CNH**$^+$	2022 (vw)
20CN	CpRu(COD)	2100 (m)	**20CNH**$^+$	2055 (vw)
21CN	CpRu(1,10-phen)	2073 (m)	**21CNH**$^+$	2024 (vw)
23CN	CpFe(dppe)	2063 (m)	**23CNH**$^+$	2015 (vw)
5*CN	Cp*Ru$(PMe_3)_2$	2057 (m)	**5*CNH**$^+$	2001 (vw)
18*CN	Cp*Ru(dppe)	2065 (m)	**18*CNH**$^+$	2019 (vw)
19*CN	Cp*Ru(dppp)	2057 (m)	**19*CNH**$^+$	2017 (vw)
20*CN	Cp*Ru(COD)	2092 (m)	**20*CNH**$^+$	2046 (vw)

Elemental analyses were performed on a Perkin-Elmer 2400 Series II CHNS/O analyzer at Iowa State University or at the Shanghai Institute of Organic Chemistry. IR spectra were measured on a Nicolet 710 FTIR or Magna-IR560 spectrophotometer; values for the ν(CN) band of the Cp′M$(L)_2$(CN) and Cp′M$(L)_2(CNH)^+$ $CF_3SO_3^-$ complexes are given in Table 1. All ^{1}H NMR spectra were recorded on compounds dissolved in CD_2Cl_2 solution with TMS ($\delta = 0.00$) as the internal reference using a Bruker AC 200 MHz spectrometer; the abbreviation pst refers to a pseudo-triplet. ^{31}P{^{1}H} NMR spectra were obtained in CD_2Cl_2 on a Bruker AC 200 MHz spectrometer with H_3PO_4 ($\delta = 0.00$) as the external reference. Electron ionization mass spectra (EIMS) were run on a Finnigan 4500 spectrometer at 70 eV, and fast atom bombardment (FAB) spectra were run on a Kratos MS-50 mass spectrometer with samples in a 3-nitrobenzyl alcohol/CH_3NO_2 matrix. Melting points were recorded on compounds in sealed N_2-filled capillaries and are uncorrected. Conductivity measurements were made with a YSI 3100 Conductivity Instrument and are corrected to 25.0 °C.

Preparation of CpRu[P(OMe)$_3$]$_2$CN (1CN). A mixture of **1Cl** (0.51 g, 1.1 mmol) and NaCN (0.22 g, 4.5 mmol) in 50 mL of CH_3OH

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was refluxed with stirring for 1.5 h, during which time the orange solution gradually turned yellow. The solvent was removed under vacuum, and the residue was extracted with CH_2Cl_2 (2 × 10 mL). The extract was reduced to about 5 mL, and hexanes (ca. 50 mL) were added to precipitate the product. The resulting mixture was cooled at −20 °C overnight to give 0.32 g (64%, based on **1Cl**) of yellow crystals of **1CN**. Mp 133−134 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 4.81 (s, 5H, Cp), 3.64 (pst, 18H, CH_3). ^{31}P NMR (CD_2Cl_2): δ 38.45 (s). MS (EI): *m*/*e* 440 (M^+). Anal. Calcd for $C_{12}H_{23}NO_6P_2Ru$: C, 32.73; H, 5.27; N, 3.18. Found: C, 32.88; H, 5.10; N, 3.22. Complex CpRu[P(*i*-Pr)$_3$]$_2$CN(**3CN**) was prepared by a similar procedure (see Supporting Information).

Preparation of CpRu(PEt$_3$)$_2$Cl (2Cl). To a suspension of **20Cl** (0.50 g, 1.6 mmol) in 50 mL of acetone was added 0.50 g (4.2 mmol) of PEt_3. The mixture was stirred at room temperature for 1.5 h, during which time the solid material dissolved and the solution became orange-red in color. After removal of the solvent, the residue was recrystallized from hexanes at −20 °C to give orange-red crystals of **2Cl**. Yield: 0.60 g (85%, based on **20Cl**). Mp 66−68 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 4.45 (s, 5H, Cp), 1.98 (m, 6H, −(CH$_2$)−), 1.57 (m, 6H, −(CH$_2$)−), 1.09 (m, 18H, CH_3). ^{31}P NMR (CD_2Cl_2): δ 34.79 (s). MS (FAB): *m*/*e* 438 (M^+). Anal. Calcd for $C_{17}H_{35}ClP_2Ru$: C, 46.62; H, 8.06. Found: C, 46.60; H, 8.30. The complexes CpRu[P(*i*-Pr)$_3$]$_2$Cl (**3Cl**), CpRu[P(Cy)$_3$]$_2$Cl (**4Cl**), CpRu(PMe$_2$Ph)$_2$Cl (**6Cl**), and CpRu(PMePh$_2$)$_2$Cl (**7Cl**) were prepared by similar procedures.

Preparation of CpRu(PEt$_3$)$_2$CN (2CN). To a solution of **2Cl** (0.60 g, 1.4 mmol) in 50 mL of CH_3OH was added 0.17 g (3.5 mmol) of NaCN. The red solution quickly turned yellow. The mixture was stirred under reflux for 0.5 h. After cooling, the solvent was removed in vacuo and the residue was extracted with CH_2Cl_2 (2 × 10 mL). The combined CH_2Cl_2 extracts were evaporated to a volume of ca. 5 mL, to which hexanes (ca. 50 mL) were added to precipitate the light yellow product. The solid product was removed by filtration, washed with hexanes and then dried under vacuum. Yield: 0.42 g (71%, based on **2Cl**). Mp 84−86 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 4.74 (s, 5H, Cp), 1.95 (m, 6H, −(CH$_2$)−), 1.45 (m, 6H, −(CH$_2$)−), 1.05 (m, 18H, CH_3). ^{31}P NMR (CD_2Cl_2): δ 42.25 (s). MS (FAB): 428, 429 (M^+). Anal. Calcd for $C_{18}H_{35}NP_2Ru$: C, 50.45; H, 8.23; N, 3.27. Found: C, 50.46; H, 8.51; N, 3.17. The complexes CpRu[P(Cy)$_3$]$_2$CN (**4CN**), CpRu(PMe$_3$)$_2$CN (**5CN**), CpRu(PMe$_2$Ph)$_2$CN (**6CN**), CpRu(PMePh$_2$)$_2$CN (**7CN**), and CpRu(CO)(PPh$_3$)(CN) (**9CN**) were prepared by similar methods.

Preparation of CpRu[P(*p*-MeOC$_6$H$_4$)$_3$]$_2$Cl (11Cl). The reaction was carried out under an N_2 atmosphere in a 500 mL, three-necked, round-bottom flask equipped with a 50 mL dropping funnel and a reflux condenser topped with a nitrogen bypass. The P(*p*-MeOC$_6$H$_4$)$_3$ (2.40 g, 6.81 mmol) was dissolved in 150 mL of absolute ethanol by heating. Hydrated ruthenium trichloride, $RuCl_3 \cdot 3H_2O$, (0.45 g, 1.7 mmol) was dissolved in ethanol (15 mL) by bringing the mixture to a boil and then allowing the solution to cool to room temperature. Freshly distilled cyclopentadiene (C_5H_6) (0.86 mL, 0.69 g, 10 mmol) was added to the $RuCl_3$ solution, and the mixture was transferred to the dropping funnel. The dark-brown solution was then added to the P(*p*-CH$_3$OC$_6$H$_4$)$_3$ solution over a period of 10 min while the temperature was maintained at reflux. An additional 1.5 h of refluxing caused the solution to lighten to a dark red-orange. The solution was filtered quickly while hot. The filtrate was evaporated under vacuum to about two-thirds of its volume and then cooled overnight at −20 °C. The resulting fine orange crystals were filtered, washed with ethanol (ca. 10 mL) and then with hexanes (10 mL), and dried in vacuo. Yield: 1.10 g (86%, based on $RuCl_3 \cdot 3H_2O$). Mp 140−141 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 7.32−7.23 (m, 12H, C$_6$*H*$_4$), 6.69−6.64 (m, 12H, C$_6$*H*$_4$), 4.08 (s, 5H, Cp), 3.77 (s, 18H, C*H*$_3$O). ^{31}P NMR (CD_2Cl_2): δ 38.90 (s). MS (FAB): *m*/*e* 906 (M^+). Anal. Calcd for $C_{47}H_{47}ClO_6P_2Ru$: C, 62.28; H, 5.23. Found: C, 62.72; H, 5.43. The complexes CpRu[P(*p*-MeC$_6$H$_4$)$_3$]$_2$Cl (**12Cl**), CpRu[P(*m*-MeC$_6$H$_4$)$_3$]$_2$Cl (**13Cl**), CpRu[P(*p*-CF$_3$C$_6$H$_4$)$_3$]$_2$Cl (**14Cl**), and CpRu[P(*p*-FC$_6$H$_4$)$_3$]$_2$Cl (**15Cl**), were prepared by similar procedures.

Preparation of CpRu[P(*p*-MeOC$_6$H$_4$)$_3$]$_2$CN (11CN). A mixture of **11Cl** (0.70 g, 0.77 mmol) and NaCN (0.19 g, 3.9 mmol) in 60 mL of CH_3OH was refluxed with stirring. Although the orange suspension became a bright yellow solution after 10 min, refluxing was continued for a total of 2 h to ensure complete conversion. After the solvent was removed under vacuum, the residue was extracted with CH_2Cl_2 (2 × 15 mL). The combined CH_2Cl_2 extracts were evaporated to a small volume (ca. 5 mL). To this solution was added an excess of hexanes (ca. 50 mL) which caused the precipitation of a yellow powder. After filtration, washing with hexanes and drying under vacuum, **11CN** was isolated in 80% yield (0.55 g) as a yellow powder. Mp 148−150 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 7.34−7.24 (m, 12H, C$_6$*H*$_4$), 6.70−6.66 (m, 12H, C$_6$*H*$_4$), 4.37 (s, 5H, Cp), 3.77 (s, 18H, C*H*$_3$O). ^{31}P NMR (CD_2Cl_2): δ 49.71 (s). MS (FAB): *m*/*e* 897 (M^+). Anal. Calcd for $C_{48}H_{47}NO_6P_2Ru$: C, 64.28; H, 5.28; N, 1.56. Found: C, 64.11; H, 5.36; N, 1.54. The complexes CpRu[P(*p*-MeC$_6$H$_4$)$_3$]$_2$CN (**12CN**), CpRu[P(*m*-MeC$_6$H$_4$)$_3$]$_2$CN (**13CN**), CpRu[P(*p*-CF$_3$C$_6$H$_4$)$_3$]$_2$CN (**14CN**), and CpRu[P(*p*-FC$_6$H$_4$)$_3$]$_2$CN (**15CN**) were prepared by similar procedures.

Preparation of CpRu[P(OPh)$_3$]$_2$Cl (16Cl). A mixture of **8Cl** (1.50 g, 2.07 mmol) and P(OPh)$_3$ (1.92 g, 6.19 mmol) in decalin (60 mL) was heated under reflux for 20 min, during which time the solution turned from brick-red to yellow. The cooled solution was directly chromatographed on Al_2O_3 (neutral). After the decalin and excess P(OPh)$_3$ were washed out of the column with hexanes, the yellow band was eluted with hexanes/CH_2Cl_2/Et_2O (20:1:1) and collected. The solvent was removed, and the residue was recrystallized from hexanes/CH_2Cl_2 at −20 °C to afford 0.40 g (24%, based on **8Cl**) of yellow crystals of **16Cl**. Mp 142−144 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 7.34−6.86 (m, 30H, OPh), 4.02 (s, 5H, Cp). ^{31}P NMR (CD_2Cl_2): δ 55.65 (s). MS (FAB): *m*/*e* 822 (M^+). Anal. Calcd for $C_{41}H_{35}ClO_6P_2Ru$: C, 59.89; H, 4.29. Found: C, 60.08; H, 4.11.

Preparation of CpRu[P(OPh)$_3$]$_2$CN (16CN). Similar to the synthesis of **1CN**, 0.32 g (0.39 mmol) of **16Cl** and 0.067 g (1.4 mmol) of NaCN in 50 mL of CH_3OH were refluxed for 2 h, during which time the orange solution turned light yellow. Further treatment of the resulting solution as described in the preparation of **1CN** gave 0.27 g (84%, based on **16Cl**) of **16CN** as a yellow powder. Mp 135−137 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 7.34−7.10 (m, 30H, OPh), 4.02 (s, 5H, Cp). ^{31}P NMR (CD_2Cl_2): δ 55.63 (s). MS (FAB): 813, 814 (M^+). Anal. Calcd for $C_{42}H_{35}NO_6P_2Ru$: C, 62.07; H, 4.34; N, 1.72. Found: C, 62.45; H, 4.08; N, 1.31.

Preparation of CpRu(dppm)CN (17CN). NaCN (0.31 g, 6.3 mmol) was added to a suspension of **17Cl** (1.12 g, 1.91 mmol) in 60 mL of CH_3OH. The mixture was heated under reflux for 0.5 h, during which time the bright red solution faded to yellow. The solvent was removed under vacuum and the resulting solid was extracted with CH_2Cl_2 (2 × 10 mL). After the combined CH_2Cl_2 extracts were evaporated to a small volume (ca. 5 mL), 50 mL of hexanes were added to precipitate a yellow solid. The crude product was recrystallized from CH_2Cl_2/hexanes at −20 °C to give 0.45 g (41%, based on **17Cl**) of **17CN** as orange-red crystals. Mp 244−246 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 7.40−7.19 (m, 20H, Ph), 4.99 (s, 5H, Cp), 4.35 (m, 2H, −CH$_2$−). ^{31}P NMR (CD_2Cl_2): δ 19.82 (s). MS (FAB): *m*/*e* 576, 578 (M^+). Anal. Calcd for $C_{31}H_{27}NP_2Ru$: C, 64.58; H, 4.72; N, 2.43. Found: C, 64.26; H, 4.71; N, 2.28. The complex CpRu(dppp)CN (**19CN**) was prepared by a similar method.

Preparation of CpRu(dppp)Cl (19Cl). A mixture of **8Cl** (1.50 g, 2.07 mmol) and dppp (0.85 g, 2.1 mmol) in 250 mL of benzene was refluxed for 8 h, during which time the brown-yellow solution turned orange. The solution was reduced to ca. 40 mL in vacuo and a 4:1 Et_2O/hexanes mixture was added until a light yellow precipitate formed (ca. 40−50 mL of Et_2O/hexanes). After filtration, further addition of hexanes to the filtrate gave 0.65 g (52%, based on **8Cl**) of **19Cl** as a yellow powder. Mp 140−146 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 7.65 (m, 4H, Ph), 7.34 (m, 8H, Ph), 7.16 (m, 8H, Ph), 4.43 (s, 5H, Cp), 2.88−2.69 (m, 4H, −(CH$_2$)$_3$−), 2.41−2.23 (m, 2H, −(CH$_2$)$_3$−). ^{31}P NMR (CD_2Cl_2): δ 41.99 (s). MS (FAB): *m*/*e* 614 (M^+). Anal. Calcd for $C_{32}H_{31}ClP_2Ru$: C, 62.59; H, 5.09. Found: C, 62.47; H, 5.01.

Preparation of CpRu(COD)CN (20CN). A mixture of **20Cl** (0.40 g, 1.3 mmol) and NaCN (0.19 g, 3.9 mmol) in 50 mL of CH_3OH was heated under reflux for 1 h. After removal of the solvent, the residue was chromatographed on Al_2O_3 (neutral) with CH_2Cl_2/Et_2O (10:1) as eluent. The yellow band was collected. After removal of the solvent,

0.18 g (46%, based on **20Cl**) of **20CN** was obtained as a yellow powder. Mp 173−175 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 5.04 (s, 5H, Cp), 4.64 (m, 2H, C_8H_{12}), 3.91 (m, 2H, C_8H_{12}), 2.60 (m, 2H, C_8H_{12}), 2.23 (m, 2H, C_8H_{12}), 2.15 (m, 2H, C_8H_{12}), 1.91 (m, 2H, C_8H_{12}). MS (FAB): *m*/*e* 300 (M^+). Anal. Calcd for $C_{14}H_{17}NRu$: C, 55.98; H, 5.71; N, 4.66. Found: C, 55.55; H, 5.84; N, 4.53.

Preparation of CpRu(1,10-phen)Cl (21Cl). A solution of **20Cl** (0.50 g, 1.61 mmol) and 1,10-phenanthroline (0.32 g, 1.61 mmol) in 50 mL of acetone was stirred at room temperature for 7.5 h. The dark purple precipitate that formed was filtered off, washed with Et_2O (2 × 25 mL), and dried in vacuo. This gave 0.55 g (89%, based on **20Cl**) of the dark purple product, **21Cl**. Mp > 250 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 9.90 (dd, J = 5 and 1 Hz, 2H), 8.28 (dd, J = 8 and 1 Hz, 2H), 7.90 (s, 2H), 7.72 (dd, J = 8 and 5 Hz, 2H), 4.32 (s, 5H, Cp). MS (FAB): *m*/*e* 382 (M^+). Anal. Calcd for $C_{17}H_{13}ClN_2Ru$: C, 53.48; H, 3.43; N, 7.34. Found: C, 53.49; H, 3.37; N, 7.30.

Preparation of CpRu(1,10-phen)CN (21CN). A mixture of **21Cl** (0.52 g, 1.4 mmol) and NaCN (0.13 g, 3.7 mmol) in 50 mL of CH_3OH was refluxed for 2 h, during which time the dark purple solution turned red-purple. After evaporation of the solvent, the dark purple residue was washed with EtOH/H_2O (3:1) (2 × 10 mL) and then with EtOH (10 mL), and finally dried in vacuo to give 0.45 g (88%, based on **21Cl**) of brick-red crystals of **21CN**. Mp > 280 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 9.63 (dd, J = 5 and 1 Hz, 2H), 8.30 (dd, J = 8 and 1 Hz, 2H), 7.93 (s, 2H), 7.63 (dd, J = 8 and 5 Hz, 2H), 4.61 (s, 5H, Cp). MS (FAB): *m*/*e* 372, 373 (M^+). Anal. Calcd for $C_{18}H_{13}N_3Ru$: C, 58.06; H, 3.52; N, 11.28. Found: C, 57.71; H, 3.50; N, 11.31.

Preparation of Cp*Ru(PMe$_3$)$_2$CN (5*CN). To a solution of **5*Cl** (0.60 g, 1.4 mmol) in 40 mL of CH_3OH was added 0.13 g (2.7 mmol) of NaCN. The solution turned from orange to yellow after stirring for 10 min at room temperature. The mixture was refluxed for 5 min to ensure complete conversion. The resulting light yellow solution was evaporated to dryness, and the residue was extracted with CH_2Cl_2 (2 × 20 mL). After the combined extracts were reduced to a volume of about 3 mL, hexanes (50 mL) were added to precipitate **5*CN** as a light yellow powder. Yield: 0.45 g (76%, based on **5*Cl**). Mp 166−168 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 1.80 (s, 15H, Cp*), 1.40 (pst, 18H, CH_3). ^{31}P NMR (CD_2Cl_2): δ 9.41 (s). MS (EI): *m*/*e* 414, 415 (M^+). Anal. Calcd for $C_{17}H_{33}NP_2Ru$: C, 49.26; H, 8.03; N, 3.38. Found: C, 48.74; H, 8.28; N, 3.34. The complexes Cp*Ru(dppe)CN (**18*CN**), Cp*Ru(dppp)CN (**19*CN**), and Cp*Ru(COD)CN (**20*CN**), were prepared by similar methods.

Preparation of CpFe(CO)$_2$CN (22CN). To a suspension of $CpFe(CO)_2Br$ (0.50 g, 2.0 mmol) in 40 mL of CH_3OH was added 0.28 g (5.7 mmol) of NaCN. The mixture was refluxed for 15 min during which time the mixture changed to an orange-yellow solution. After removal of the solvent, the residue was extracted with CH_2Cl_2 (2 × 10 mL). The combined extracts were evaporated to a volume of about 5 mL, and hexanes (50 mL) were added to precipitate a brown-yellow solid. The product was filtered off and dried in vacuo to give 0.30 g (75%, based on $CpFe(CO)_2Br$) of **22CN** as a brown-yellow powder. Mp 104−107 °C (dec). ^{1}H NMR (CD_2Cl_2): δ 5.16 (s, Cp). MS (EI): 203 (M^+). Anal. Calcd for $C_8H_5O_2NFe$: C, 47.34; H, 2.48; N, 6.90. Found: C, 47.30; H, 2.51; N, 6.59.

Protonation Reactions. Compounds **2CN**, **3CN**, **5CN**−**15CN**, **17CN**−**21CN**, **23CN**, **5*CN**, and **18*CN**−**20*CN** were protonated for characterization of the $[CpML_2(CNH)]^+CF_3SO_3^-$ products by dissolving approximately 10 mg of the complex in 0.50 mL of either CD_2Cl_2 (for NMR) or CH_2Cl_2 (for IR) in an NMR tube under nitrogen. To the solution was added 1 equiv of CF_3SO_3H through the rubber septum using a gas-tight microliter syringe. The solutions did not change color significantly, unless otherwise noted. Yields of the protonated products were quantitative as indicated by the disappearance of the reactant signals and appearance of the product signals in IR and ^{1}H NMR spectra of the solutions. No precipitates formed, and no ^{1}H NMR signals for other products were detected. The absence of a signal at fields higher than δ 0.0 ppm showed that protonation did not occur at the metal. No resonance[6,7] for the proton on the CNH ligand was observed, as was previously reported for $CpRu(PPh_3)_2(CNH)^+$.

[CpRu(PEt$_3$)$_2$(CNH)$^+$]CF$_3$SO$_3^-$ (2CNH$^+$CF$_3$SO$_3^-$). The color of the solution changed from light yellow to faint green upon addition of the acid. ^{1}H NMR (CD_2Cl_2): δ 5.00 (s, 5H, Cp), 1.95 (m, 6H, −(CH_2)−), 1.56 (m, 6H, −(CH_2)−), 1.06 (m, 18H, CH_3). ^{31}P NMR (CD_2Cl_2): δ 39.36 (s).

[CpRu(P(*i*-Pr)$_3$)$_2$(CNH)$^+$]CF$_3$SO$_3^-$ (3CNH$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 4.86 (s, 5H, Cp), 2.29 (m, 6H, C*H*$(CH_3)_2$), 1.25 (m, 36H, CH_3). ^{31}P NMR (CD_2Cl_2): δ 76.50 (s).

[CpRu(PMe$_3$)$_2$(CNH)$^+$]CF$_3$SO$_3^-$ (5CNH$^+$ CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 4.69 (s, 5H, Cp), 1.49 (pst, 18H, CH_3). ^{31}P NMR (CD_2Cl_2): δ 11.77 (s).

[CpRu(PMe$_2$Ph)$_2$(CNH)$^+$]CF$_3$SO$_3^-$ (6CNH$^+$ CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.35 (m, 10H, Ph), 4.83 (s, 5H, Cp), 1.60 (pst, 12H, CH_3). ^{31}P NMR (CD_2Cl_2): δ 20.21 (s). IR (DCE): ν(CN) (cm^{-1}) 2013 (vw).

[CpRu(PMePh$_2$)$_2$(CNH)$^+$]CF$_3$SO$_3^-$ (7CNH$^+$ CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.23 (m, 20H, Ph), 4.87 (s, 5H, Cp), 1.46 (pst, 6H, CH_3). ^{31}P NMR (CD_2Cl_2): δ 35.79 (s).

[CpRu(PPh$_3$)$_2$(CNH)$^+$]CF$_3$SO$_3^-$ (8CNH$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.24 (m, 30H, Ph), 4.63 (s, 5H, Cp). ^{31}P NMR (CD_2Cl_2): δ 48.91 (s).

[CpRu(PPh$_3$)(CO)(CNH)$^+$]CF$_3$SO$_3^-$ (9CNH$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.41 (m, 15H, Ph), 5.19 (s, 5H, Cp). ^{31}P NMR (CD_2Cl_2): δ 51.23 (s). IR (CH_2Cl_2): ν(CO) (cm^{-1}) 2004 (s).

[CpRu(CO)$_2$(CNH)$^+$]CF$_3$SO$_3^-$ (10CNH$^+$CF$_3$SO$_3^-$). The color of the solution changed from light yellow to orange-yellow upon addition of the acid. ^{1}H NMR (CD_2Cl_2): δ 5.70 (s, 5H, Cp). IR (CH_2Cl_2): ν(CO) (cm^{-1}) 2084 (s), 2024 (s).

[CpRu(P(*p*-MeOC$_6$H$_4$)$_3$)$_2$(CNH)$^+$]CF$_3$SO$_3^-$ (11CNH$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.57 (m, 12H, Ph), 7.33 (m, 12H, Ph), 4.77 (s, 5H, Cp), 2.31 (s, 18H, C*H*$_3$). ^{31}P NMR (CD_2Cl_2): δ 45.25 (s).

[CpRu(P(*p*-MeC$_6$H$_4$)$_3$)$_2$(CNH)$^+$]CF$_3$SO$_3^-$ (12CNH$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.05 (m, 24H, C$_6$*H*$_4$), 4.60 (s, 5H, Cp), 2.34 (s, 18H, C*H*$_3$). ^{31}P NMR (CD_2Cl_2): δ 46.80 (s).

[CpRu(P(*m*-MeC$_6$H$_4$)$_3$)$_2$(CNH)$^+$]CF$_3$SO$_3^-$ (13CNH$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.01 (m, 24H, C$_6$*H*$_4$), 4.63 (s, 5H, Cp), 2.18 (s, 18H, C*H*$_3$). ^{31}P NMR (CD_2Cl_2): δ 48.57 (s).

[CpRu(P(*p*-CF$_3$C$_6$H$_4$)$_3$)$_2$(CNH)$^+$]CF$_3$SO$_3^-$ (14CNH$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.57 (m, 12H, C$_6$*H*$_4$), 7.33 (m, 12H, C$_6$*H*$_4$), 4.77 (s, 5H, Cp). ^{31}P NMR (CD_2Cl_2): δ 51.68 (s).

[CpRu(P(*p*-FC$_6$H$_4$)$_3$)$_2$(CNH)$^+$]CF$_3$SO$_3^-$ (15CNH$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.19 (m, 12H, C$_6$*H*$_4$), 7.01 (m, 12H, C$_6$*H*$_4$), 4.68 (s, 5H, Cp). ^{31}P NMR (CD_2Cl_2): δ 48.11 (s).

[CpRu(dppm)(CNH)$^+$]CF$_3$SO$_3^-$ (17CNH$^+$CF$_3$SO$_3^-$). The color of the solution changed from orange-yellow to yellow upon addition of the acid. ^{1}H NMR (CD_2Cl_2): δ 7.45 (m, 20H, Ph), 5.25 (s, 5H, Cp), 4.36 (m, 2H, −(CH_2)−). ^{31}P NMR (CD_2Cl_2): δ 13.31 (s).

[CpRu(dppe)(CNH)$^+$]CF$_3$SO$_3^-$ (18CNH$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.48 (m, 20H, Ph), 4.96 (s, 5H, Cp), 2.59 (d, J = 24.0 Hz, 4H, −(CH_2)−). ^{31}P NMR (CD_2Cl_2): δ 83.14 (s).

[CpRu(dppp)(CNH)$^+$]CF$_3$SO$_3^-$ (19CNH$^+$CF$_3$SO$_3^-$). The color of the solution changed from yellow to faint green upon addition of the acid. ^{1}H NMR (CD_2Cl_2): δ 7.33 (m, 20H, Ph), 4.91 (s, 5H, Cp), 2.68 (m, 4H, −(CH_2)−), 2.53 (m, 2H, −(CH_2)−). ^{31}P NMR (CD_2Cl_2): δ 42.69 (s).

[CpRu(COD)(CNH)$^+$]CF$_3$SO$_3^-$ (20CNH$^+$CF$_3$SO$_3^-$). The color of the solution changed from yellow to faint green upon addition of the acid. ^{1}H NMR (CD_2Cl_2): δ 5.20 (s, 5H, Cp), 4.98 (m, 2H, C_8H_{12}), 4.18 (m, 2H, C_8H_{12}), 2.56 (m, 2H, C_8H_{12}), 2.41 (m, 2H, C_8H_{12}), 2.35 (m, 2H, C_8H_{12}), 2.17 (m, 2H, C_8H_{12}).

[CpRu(1,10-phen)(CNH)$^+$]CF$_3$SO$_3^-$ (21CNH$^+$CF$_3$SO$_3^-$). The color of the solution changed from purple to orange upon addition of the acid. ^{1}H NMR (CD_2Cl_2): δ 9.41 (dd, J = 5 and 1 Hz, 2H), 8.46 (dd, J = 8 and 1 Hz, 2H), 8.01 (s, 2H), 7.75 (dd, J = 8 and 5 Hz, 2H), 4.86 (s, 5H, Cp).

[CpFe(dppe)(CNH)$^+$]CF$_3$SO$_3^-$ (23CNH$^+$CF$_3$SO$_3^-$). ^{1}H NMR (CD_2Cl_2): δ 7.49 (m, 20H, Ph), 4.52 (s, 5H, Cp), 2.54 (m, 4H, −(CH_2)−). ^{31}P NMR (CD_2Cl_2): δ 98.30 (s).

[Cp*Ru(PMe$_3$)$_2$(CNH)$^+$]CF$_3$SO$_3^-$ (5*CNH$^+$CF$_3$SO$_3^-$). The color of the solution changed from yellow to faint green upon addition of the acid. ^{1}H NMR (CD_2Cl_2): δ 1.83 (s, 15H, Cp*), 1.46 (pst, 18H, CH_3). ^{31}P NMR (CD_2Cl_2): δ 6.43 (s).

[Cp*Ru(dppe)(CNH)$^+$]CF$_3$SO$_3^-$ (18*CNH$^+$CF$_3$SO$_3^-$). The color of the solution changed from yellow to faint green upon addition of

the acid. ^{1}H NMR (CD_2Cl_2): δ 7.56 (m, 20H, Ph), 2.46 (m, 4H, $-(CH_2)-$), 1.55 (s, 15H, Cp*). ^{31}P NMR (CD_2Cl_2): δ 78.98 (s).

[Cp*Ru(dppp)(CNH)$^+$]CF$_3$SO$_3^-$ (19*CNH$^+$CF$_3$SO$_3^-$). The color of the solution changed from yellow to faint green upon addition of the acid. ^{1}H NMR (CD_2Cl_2): δ 7.33 (m, 20H, Ph), 2.59 (m, 6H, $-(CH_2)-$), 1.43 (s, 15H, Cp*). ^{31}P NMR (CD_2Cl_2): δ 39.85 (s).

[Cp*Ru(COD)(CNH)$^+$]CF$_3$SO$_3^-$ (20*CNH$^+$CF$_3$SO$_3^-$). The color of the solution changed from yellow to faint green upon addition of the acid. ^{1}H NMR (CD_2Cl_2): δ 3.72 (m, 4H, C_8H_{12}), 2.51 (m, 4H, C_8H_{12}), 2.30 (m, 2H, C_8H_{12}), 2.06 (m, 2H, C_8H_{12}), 1.75 (s, 15H, Cp*).

Calorimetric Studies. Heats of protonation (ΔH_{CNH}) of the CpML$_2$CN complexes were determined with 0.1 M CF_3SO_3H in DCE solvent at 25.0 °C. Titrations were performed using a Tronac model 458 isoperibol calorimeter as originally described[22] and then modified.[23] A typical calorimetric run consisted of three sections:[24] initial heat capacity calibration, titration, and final heat capacity calibration. Each section was preceded by a baseline acquisition period. During the titration, 1.2 mL of a 0.1 M CF_3SO_3H solution (standardized to a precision of ±0.0002 M) in DCE was added at a rate of 0.3962 mL/min to 50 mL of a 2.6 mM solution of the complex (5−10% excess) in DCE at 25.0 °C. Infrared spectra of the titrated solutions exhibited ν(CN) bands characteristic of the CpM(L)$_2$(CNH)$^+$ products.

Two separately standardized acid solutions were used for determining ΔH_{CNH} values of each complex. The reported values are the average of at least four titrations and as many as five. The reaction enthalpies were corrected for the heat of dilution (ΔH_{dil}) of the acid in DCE (−0.2 kcal/mol).[23] The reported error in ΔH_{CNH} is the average deviation from the mean of all of the determinations. Titrations of 1,3-diphenylguanidine (GFS Chemicals) with CF_3SO_3H in DCE (−36.9 ± 0.3 kcal/mol; lit.[22] −37.2 ± 0.4 kcal/mol) were used to monitor the performance of the calorimeter before each set of determinations.

Results

Preparations of 2Cl-4Cl, 6Cl, 7Cl, 11Cl−16Cl, 19Cl and 21Cl. Three different routes were used to prepare these CpRuL$_2$Cl complexes. Compounds **2Cl−4Cl**, **6Cl**, and **7Cl** were prepared by using 2 equiv of the appropriate phosphine to displace cyclooctadiene from CpRu(COD)Cl (**20Cl**) (eq 3).

$$\underset{\textbf{20Cl}}{\text{CpRu(COD)Cl}} + 2\text{PR}_3 \xrightarrow[\text{or THF}]{\text{acetone}} \text{CpRu(PR}_3)_2\text{Cl} + \text{COD} \quad (3)$$

This route was developed by Albers et al.[11] to prepare CpRuL$_2$Cl (L = CO, PPh_3, PMe_3, $^1/_2$ dppe, $P(OMe)_3$, or PPh_2H). Compounds **11Cl−15Cl** were prepared in a two-step synthesis developed by Bruce et al. for the synthesis of CpRu(PPh$_3$)$_2$Cl.[12] In the first step, $RuCl_3 \cdot 3H_2O$ and C_5H_6 were heated to reflux in ethanol to give [CpRu(Cl)$_2$]$_n$,[12] which was then reacted with approximately 3 equiv of the desired triarylphosphine to give CpRu(PR$_3$)$_2$Cl (eq 4). Compound **12Cl** was prepared by

$$\text{RuCl}_3 \cdot 3\text{H}_2\text{O} + \text{xs } \text{C}_5\text{H}_6 + \text{xs PR}_3 \xrightarrow{\text{ethanol}} \text{CpRu(PR}_3)_2\text{Cl} \quad (4)$$

a similar route reported previously;[25] however, our synthesis resulted in a higher yield. Compounds **16Cl**, **19Cl**, and **21Cl** were prepared using a modification of the reported[10] preparations of CpRuL$_2$Cl (L = P(OMe)$_3$, $^1/_2$ dppm or $^1/_2$ dppe). Both PPh_3 ligands in **8Cl** were displaced by P(OPh)$_3$ (**16Cl**), dppp (**19Cl**), or 1,10-phen (**21Cl**) to give the desired product (eq 5).

$$\underset{\textbf{8Cl}}{\text{CpRu(PPh}_3)_2\text{Cl}} + \text{L}_2 \xrightarrow[\text{benzene}]{\text{acetone}} \text{CpRuL}_2\text{Cl} + 2\text{PPh}_3 \quad (5)$$

Preparation of Compounds 1CN−7CN, 9CN, 11CN−17CN, 19CN−22CN, 5*CN, 19*CN and 20*CN. The reaction of CpRu(PPh$_3$)$_2$Cl and NaCN in refluxing methanol gives CpRu(PPh$_3$)$_2$CN (**8CN**) in high yield.[13] Related cyanide complexes have been prepared by a similar method except KCN was used instead of the sodium salt.[9] We have found that the synthesis developed by Laidlaw and Denning[13] is a useful general procedure for the preparation of the CpRuL$_2$CN compounds (eq 6). Successful synthesis occurs when the L$_2$ ligands are a variety

$$\text{CpRuL}_2\text{Cl} + \text{xs NaCN} \xrightarrow[\text{reflux}]{\text{methanol}} \text{CpRuL}_2\text{CN} + \text{NaCl} \quad (6)$$

of monodentate and bidentate phosphines or other four-electron donors such as COD or 1,10-phenanthroline. Yields are typically greater than 70% and the pure products are obtained by column chromatography.

Protonation of the Cp′ML$_2$CN Complexes. The reactions of **2CN, 3CN, 5CN−15CN, 17CN−21CN, 23CN, 5*CN**, **and 18*CN−20*CN** with 1 equiv of triflic acid in CD_2Cl_2 gave quantitatively the N-protonated cationic isocyanide complexes **2CNH$^+$**, **3CNH$^+$**, **5CNH$^+$−15CNH$^+$**, **17CNH$^+$−21CNH$^+$**, **23CNH$^+$**, **5*CNH$^+$**, and **18*CNH$^+$−20*CNH$^+$**. This protonation causes the Cp resonances in the ^{1}H NMR spectra to shift downfield by approximately 0.3 ppm, while protonation of the Cp* complexes causes the Cp* resonances to shift downfield by approximately 0.03 ppm. The ^{31}P signals of the compounds containing phosphorus ligands shift upfield approximately 5.0 ppm upon protonation of the CN$^-$ ligand. At the same time, the ν(CN) bands move approximately 50 cm^{-1} to lower wavenumbers. IR data in the ν(CN) region for the protonated compounds are shown in Table 1. Previously, [CpRu(PPh$_3$)$_2$(CNH)]$^+$ PF_6^- was isolated and characterized by elemental analysis and IR and NMR spectroscopy;[6] recently [CpRu(PPh$_3$)$_2$(CNH)]$^+$ $CF_3SO_3^-$ was isolated and its structure established by X-ray diffraction studies.[7] Also, the isolation and characterization of [CpFe(dppe)(CNH)]$^+$ BF_4^- have been reported.[26]

Complexes **2CNH$^+$**, **3CNH$^+$**, **5CNH$^+$−15CNH$^+$**, **17CNH$^+$−21CNH$^+$**, **23CNH$^+$**, **5*CNH$^+$**, and **18*CNH$^+$−20*CNH$^+$** are deprotonated quickly and quantitatively with 1 equiv of diphenylguanidine (DPG) in CH_2Cl_2 or DCE solution to give the original complexes. The compounds were separated from the DPGH$^+$CF$_3$SO$_3^-$ by passing the solution through a short (5 cm) alumina column using CH_2Cl_2 as the eluent. Evaporation of the solution to dryness gave the pure compounds. Compound **3CN** is sparing soluble in CH_2Cl_2 and DCE and therefore, the basicity of this compound could not be determined by calorimetry. The reactions of CF_3SO_3H with **1CN**, **4CN**, **16CN**, and **22CN** in CD_2Cl_2 gave products other than CpML$_2$(CNH)$^+$ as indicated by their ^{1}H NMR spectra.

Calorimetry Studies. Heats of protonation (ΔH_{CNH}) determined by calorimetric titration of complexes **5CN**, **8CN**, **12CN**, **18CN**, **20CN**, **21CN**, **5*CN**, **18*CN**, and **23CN** with CF_3SO_3H in DCE solvent at 25.0 °C according to eq 1 are presented in Table 2. Plots of temperature vs amount of acid added during the titrations were linear, indicating that the protonations occurred rapidly and stoichiometrically.[24] Normal pre- and post-titration traces were evidence that no decomposition of the neutral or protonated species occurred.

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(24) Eatough, D. J.; Christensen, J. J.; Izatt, R. M. *Experiments in Thermometric and Titration Calorimetry*; Brigham Young University: Provo, UT, 1974.
(25) Bruce, M. I.; Windsor, N. J. *Aust. J. Chem.* **1977**, *30*, 1601.
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Table 2. Heats of Protonation (ΔH_{CNH}) of Cp′M(L)$_2$CN Complexes

metal complex	$-\Delta H_{CNH}$,[a,b] (kcal/mol)
Cp*Ru(PMe$_3$)$_2$CN, **5*CN**	25.0(2)
Cp*Ru(dppe)CN, **18*CN**	22.6(4)
CpRu(PMe$_3$)$_2$CN, **5CN**	22.4(2)
CpRu(P(*p*-CH$_3$C$_6$H$_4$)$_3$)$_2$CN, **12CN**	21.0(3)
CpFe(dppe)CN, **23CN**	20.9(3)
CpRu(PPh$_3$)$_2$CN, **8CN**	20.5(2)
CpRu(COD)CN, **20CN**	20.2(3)
CpRu(dppe)CN, **18CN**	19.5(5)
CpRu(1,10-phen)CN, **21CN**	13.3(3)

[a] For protonation with 0.1 M CF_3SO_3H in DCE solvent at 25.0 °C. [b] Numbers in parentheses are average deviations from the mean of at least four titrations.

Since the CNH^+ ligand is known to form hydrogen bonds with ethers,[1] we sought to determine if H-bonded species were formed during titrations of the CpRuL$_2$CN complexes with CF_3SO_3H. In a recent study,[7] the addition of 1 equiv of CpRu(PPh$_3$)$_2$CN to 1 equiv of CpRu(PPh$_3$)$_2$(CNH)$^+$ $CF_3SO_3^-$ gave [(CpRu(PPh$_3$)$_2$(CN))$_2$(μ-H)]$^+$ $CF_3SO_3^-$ in which there is a C−N−H−N−C hydrogen bonding bridge between the two CN^- ligands. This dimer, which was structurally characterized by X-ray diffraction studies,[7] is easily detected by IR spectroscopy (poly(chlorotrifluoroethylene) mull) as the ν(CN) band is located at higher wavenumbers (2084 cm^{-1}) than those in either CpRu(PPh$_3$)$_2$CN (2070 cm^{-1}) or CpRu(PPh$_3$)$_2$(CNH)$^+$$CF_3SO_3^-$ (2016 cm^{-1}). To determine whether such a species exists in solution during the titration, 2.6 mM solutions (the same concentrations as in the titrations) of CpRu(PMe$_2$Ph)$_2$CN (**6CN**) and CpRu(PMe$_2$Ph)$_2$(CNH)$^+$ $CF_3SO_3^-$ (**6CNH$^+$CF$_3$SO$_3^-$**) in DCE were prepared. After the solution of **6CNH$^+$** was added to the **6CN** solution, the resulting mixture was allowed to sit for 10 min. An IR spectrum of the solution showed peaks only for **6CN** (2071 cm^{-1}) and **6CNH$^+$** (2013 cm^{-1}), but no peak was observed at higher frequency which would indicate the presence of a hydrogen-bridging dimer. This evidence, in addition to the observation that the calorimetric titration plots were linear over the entire titration, strongly suggests that [(CpRuL$_2$(CN))$_2$(μ-H)]$^+$$CF_3SO_3^-$ is not formed during the titrations.

As noted in the Introduction, the recently determined[7] structure of CpRu(PPh$_3$)$_2$(CNH)$^+$$CF_3SO_3^-$ shows hydrogen bonding CpRu(PPh$_3$)$_2$CN−H···OSO$_2$CF$_3$ between the proton on the cyanide and an oxygen atom of the triflate, as indicated by the short (2.747 Å) N···O distance. We sought to determine using conductivity measurements if there was hydrogen bonding between the CNH ligand and $CF_3SO_3^-$ in the products of the titrations (eq 1) in DCE solution in this study. A 0.020M solution of [Bu$_4$N]I in DCE was used as the standard; its Λ value was measured as 18 cm^2/Ω mol which is in good agreement with 19 cm^2/Ω mol obtained previously for [Bu$_4$N]Br in DCE.[27] In general, 1:1 electrolytes in DCE give values of Λ in the range 14−30 cm^2/Ω mol. The Λ value determined for a 0.020 M solution of **15CNH$^+$CF$_3$SO$_3^-$** was 2.4 cm^2/Ω mol. This low value suggests that **15CNH$^+$CF$_3$SO$_3^-$** does not exist as ions in solution but is present primarily in a hydrogen-bonded form similar to that found in the solid-state structure[7] of [CpRu(PPh$_3$)$_2$(CNH)$^+$]$CF_3SO_3^-$ (**8CNH$^+$CF$_3$SO$_3^-$**). On the basis of these results, it is likely that the other Cp′M(L)$_2$CNH$^+$$CF_3SO_3^-$ products formed in the calorimetric titrations also exist at least in part in hydrogen-bonded forms.

(27) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81 and references therein.

Discussion

Effects of Phosphine Ligands on Cyanide Basicity (-ΔH_{CNH}) in CpRuL$_2$CN. For reactions of the phosphine complexes CpRuL$_2$CN with CF_3SO_3H (eq 1), the $-\Delta H_{CNH}$ values (Table 2) increase in the following order: **18CN** (dppe, 19.5 kcal/mol) < **8CN** (2 PPh$_3$, 20.5 kcal/mol) < **12CN** (2 P(*p*-C$_6$H$_4$Me)$_3$, 21.0 kcal/mol) < **5CN** (2 PMe$_3$, 22.4 kcal/mol). The phosphine ligand effect in the Cp*RuL$_2$CN complexes is much the same (**18*CN** (dppe, 22.6 kcal/mol) < **5*CN** (2PMe$_3$, 25.0 kcal/mol)). Particularly notable is the fact that the $-\Delta H_{CNH}$ values are relatively insensitive to the nature of the phosphine ligands. For example, the difference in $-\Delta H_{CNH}$ values for CpRu(PPh$_3$)$_2$CN and CpRu(PMe$_3$)$_2$CN is only 1.9 kcal/mol, whereas for protonation at the metal in CpOs(PR$_3$)$_2$Br, the $-\Delta H_{HM}$ value increases by 13.1 kcal/mol when PPh$_3$ is substituted by PMe$_3$.[4] The relative insensitivity of $-\Delta H_{CNH}$ to the donor ability of the phosphine may be due to the substantial distance between the phosphine and the site of protonation at the CN^- nitrogen atom. However, it may also be due to the effect of hydrogen bonding. The overall $-\Delta H_{CNH}$ may be considered (eq 7) as

$$\mathrm{M{-}CN} + \mathrm{CF_3SO_3H} \xrightarrow{-\Delta H_p} \mathrm{M{-}CN{-}H^+CF_3SO_3^-} \xrightarrow{-\Delta H_{HB}} \mathrm{M{-}CN{-}H\text{- - -}OSO_2CF_3} \quad (7)$$

the sum of the simple enthalpy of protonation (ΔH_p) and the enthalpy of hydrogen bonding ΔH_{HB}. More strongly donating phosphines (e.g., PMe$_3$) will make $-\Delta H_p$ *more* positive but the proton in M−CN−H$^+$ will be less acidic which will make $-\Delta H_{HB}$ *less* positive. Thus, the increased basicity provided by PMe$_3$ in the first step ($-\Delta H_p$) is at least partially canceled by weaker hydrogen bonding ($-\Delta H_{HB}$) in the second step. That hydrogen bonding between an acid and base becomes less favorable as the acidity of the acid decreases is well-documented in a variety of other systems.[28]

Despite the opposing effects of $-\Delta H_p$ and $-\Delta H_{HB}$, the $-\Delta H_{CNH}$ values for the CpRuL$_2$CN complexes increase as the donor ability ($-\Delta H_{HP}$) of the phosphine increases. Thus, the phosphine basicity, as defined by the enthalpy of protonation ($-\Delta H_{HP}$) of the free monophosphine (eq 8) increases,[29] PPh$_3$

$$\mathrm{PR_3} + \mathrm{CF_3SO_3H} \xrightarrow[25.0\ ^\circ\mathrm{C}]{\mathrm{DCE}} \mathrm{HPR_3^+CF_3SO_3^-};\ \Delta H_{HP} \quad (8)$$

(21.2 kcal/mol) < P(*p*-CH$_3$C$_6$H$_4$)$_3$ (23.2 kcal/mol) < PMe$_3$ (31.6 kcal/mol), in the same order as the basicity of their CpRu(PR$_3$)$_2$CN complexes. Thus, the protonation step ($-\Delta H_p$) in eq 7 appears to dominate the trend in $-\Delta H_{CNH}$ values.

Since an increase in phosphine basicity is expected[7] to lower the νCN values for the CpRu(PR$_3$)$_2$CN complexes by reducing CN^- σ donation to the metal and increasing π back-bonding from the metal to the CN^-, a correlation between the phosphine basicity ($-\Delta H_{HP}$) and νCN is expected and observed (Figure 1). This correlation (eq 9) ($r = 0.9611$) allows one to estimate

$$\nu(\mathrm{CN})\ (\mathrm{cm^{-1}}) = 2088.7 - 0.731\,55(-\Delta H_{HP}) \quad (9)$$

basicities ($-\Delta H_{HP}$) for the range of phosphines whose CpRu(PR$_3$)$_2$CN complexes have reported ν(CN) values (Table

(28) (a) March, J. *Advanced Organic Chemistry*; 3rd ed.; John Wiley & Sons: New York, 1985; p 72. (b) Epshtein, L. M. *Russ. Chem. Rev.* **1979**, *48*, 854.

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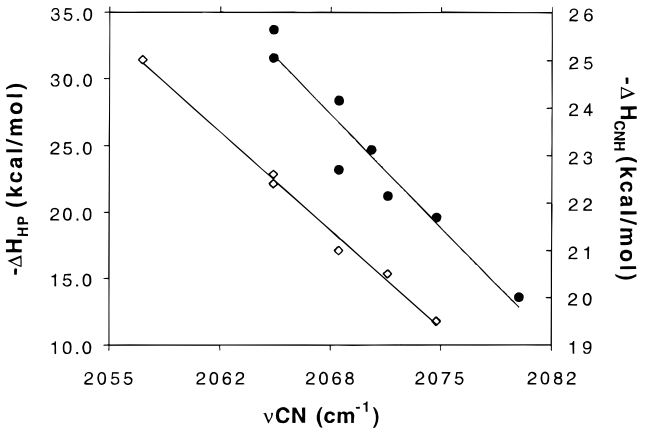

Figure 1. (a) Correlation (filled circles) of ν(CN) and phosphine basicity ($-\Delta H_{HP}$) (left axis) for the $CpRu(PR_3)_2CN$ complexes **2CN**, **5CN**−**8CN**, **12CN**, **14CN**, and **15CN**. (b) Correlation (open squares) of ν(CN) and cyanide basicity ($-\Delta H_{CNH}$) (right axis) for the mono- and diphosphine $Cp'Ru(L)_2CN$ complexes **5CN**, **8CN**, **12CN**, **18CN**, **5*CN**, and **18*CN**.

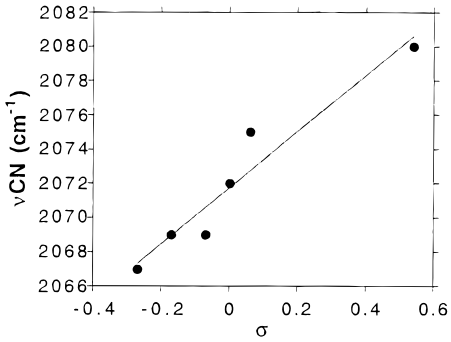

Figure 2. Correlation of the Hammett parameter (σ) and ν(CN) for the $CpRu[P(aryl)_3]_2CN$ complexes, **8CN** and **11CN**−**15CN**.

1). Similarly, there is a correlation (eq 10) (r = 0.971 88)

$$\nu(\mathrm{CN})\ (\mathrm{cm}^{-1}) = 2072.2 + 16.82\sigma \qquad (10)$$

between the Hammett σ parameters[30] of the substituent in the aryl phosphines and the ν(CN) values of their $CpRu[P(aryl)_3]_2CN$ complexes (Figure 2). As their donor abilities increase, their σ values decrease in the order *p*-CF_3 (0.54) > *p*-F (0.06) > H (0.00) > *m*-CH_3 (−0.07) > *p*-CH_3 (−0.17) > *p*-MeO (−0.27).

Of particular interest is the correlation (eq 11) (r = 0.996 75)

$$-\Delta H_{CNH} = 653.13 - 0.305\ 39(\nu(\mathrm{CN})\ (\mathrm{cm}^{-1})) \qquad (11)$$

between $-\Delta H_{CNH}$ and ν(CN) (cm^{-1}) (Figure 1), which shows that an increase in the phosphine basicity increases the basicity ($-\Delta H_{CNH}$) of the CN^- ligand and decreases its ν(CN) value in a linear fashion. This correlation, which includes both the Cp and Cp* derivatives as well as mono- and diphosphine $Cp'Ru(PR_3)_2CN$ complexes, allows one to estimate $-\Delta H_{CNH}$ values for other $Cp'Ru(PR_3)_2CN$ complexes whose ν(CN) values are known (Table 1). The $-\Delta H_{CNH}$ values are very sensitive to changes in ν(CN) since a decrease of 1.0 cm^{-1} in ν(CN) increases $-\Delta H_{CNH}$ by approximately 0.3 kcal/mol.

It is also interesting that there is a correlation (eq 12) (r =

$$\nu\mathrm{CN}[\mathrm{MCNH}^+] = -177.54 + 1.0623(\nu\mathrm{CN}[\mathrm{MCN}]) \qquad (12)$$

0.948 21) (Figure 3) between ν(CN) values for the unprotonated

(30) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemsitry,* 3rd ed.; Harper Collins Publishers: New York, 1987.

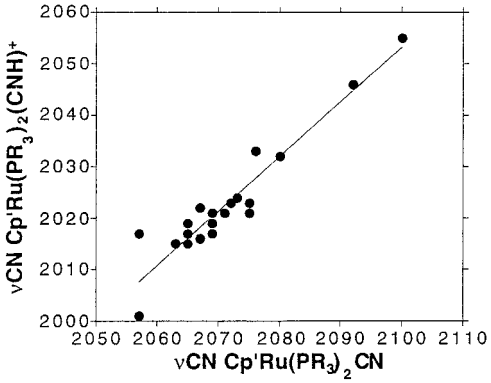

Figure 3. Correlation of ν(CN) for $Cp'M(PR_3)_2CN$ and for $Cp'M(PR_3)_2(CNH)^+$ for **2CN**, **5CN**−**8CN**, **11CN**−**21CN**, **23CN**, **5*CN**, **18*CN**, and **19*CN** and their protonated analogues.

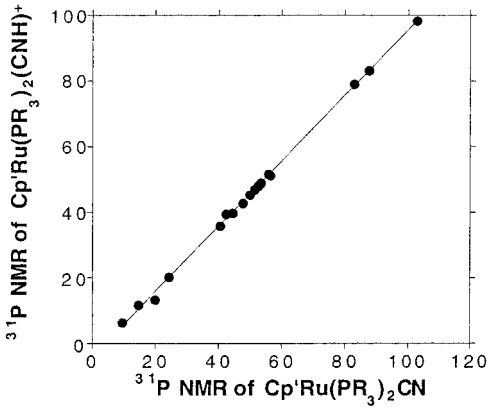

Figure 4. Correlation of the ^{31}P chemical shifts for $Cp'M(PR_3)_2CN$ and for $Cp'M(PR_3)_2(CNH)^+$ for **2CN**, **5CN**−**9CN**, **11CN**−**19CN**, **23CN**, **5*CN**, **18*CN**, and **19*CN** and their protonated analogues.

$Cp'ML_2CN$ and protonated $Cp'ML_2(CNH)^+$ complexes. This correlation includes complexes of both Ru and Fe, Cp and Cp*, and L_2 ligands as varied as phosphines, COD and 1,10-phen. Thus, electronic changes in the metal, as well as the Cp′ and L_2 ligands, affect ν(CN) for the unprotonated and protonated complexes in a very similar manner.

Finally, there is an excellent (r = 0.999 39) correlation (eq 13) between the ^{31}P chemical shifts of the phosphine-containing

$$^{31}\mathrm{P}[\mathrm{MCNH}^+] = -4.022 + 0.995\ 34(^{31}\mathrm{P}[\mathrm{MCN}]) \qquad (13)$$

$Cp'ML_2CN$ complexes and their protonated analogues $Cp'ML_2(CNH)^+$; this correlation (Figure 4) includes complexes of both Ru and Fe as well as Cp and Cp*.

Effects of 1,10-phen and COD Ligands on Cyanide Basicity ($-\Delta H_{CNH}$) in $CpRuL_2CN$. The basicities ($-\Delta H_{CNH}$) of the $CpRuL_2CN$ complexes containing the 1,10-phenanthroline and COD ligands are not predicted from their ν(CN) values using the ν(CN) vs $-\Delta H_{CNH}$ correlation (eq 11, Figure 1) that fit the $CpRu(PR_3)_2CN$ phosphine complexes so well. By using eq 11, we predict CpRu(1,10-phen)CN (**21CN**) to have a $-\Delta H_{CNH}$ value (20.1 kcal/mol) very similar to that (20.5 kcal/mol) of $CpRu(PPh_3)_2CN$ (**8CN**); however, its actual value (Table 2) is only 13.3 kcal/mol. There is no obvious reason the basicity of **21CN** is so unusually low unless there is substantially different hydrogen bonding or other interactions between the cation and anion (eq 7) and solvent than occurs in the phosphine complexes.

The predicted (eq 11) $-\Delta H_{CNH}$ value for CpRu(COD)CN (**20CN**) is only 11.8 kcal/mol, but the actual value is 20.2 kcal/

mol. In view of the much lower donor ability of COD as compared with phosphines in $CpIrL_2$ complexes,[29] it is surprising that the CN^- ligand in **20CN** is as basic as that in $CpRu(PPh_3)_2CN$ (20.5 kcal/mol). Clearly, we do not understand the factors that determine CN^- ligand basicities in the nonphosphine $CpRuL_2CN$ complexes.

Effect of Cp and Cp* Ligands on Cyanide Basicity ($-\Delta H_{CNH}$) in $CpRuL_2CN$. Evidence of the more strongly donating nature of Cp* as compared with Cp is seen (Table 2) in the 2.6 kcal/mol higher basicity ($-\Delta H_{CNH}$) of $Cp^*Ru(PMe_3)_2CN$ (25.0 kcal/mol) as compared with $CpRu(PMe_3)_2CN$ (22.4 kcal/mol). Similarly, Cp*Ru(dppe)CN (22.6 kcal/mol) is 3.1 kcal/mol more basic than CpRu(dppe)CN (19.5 kcal/mol). The 2.6−3.1 kcal/mol difference in $-\Delta H_{CNH}$ between the Cp* and Cp complexes is significantly smaller than the 9.0 kcal/mol difference in $-\Delta H_{HM}$ values between $Cp^*Ru(PMe_3)_2Cl$ (30.2 kcal/mol) and $CpRu(PMe_3)_2Cl$ (21.2 kcal/mol) and the 5.5 kcal/mol difference between $Cp^*Ru(PPh_3)_2H$ (35.2 kcal/mol) and $CpRu(PPh_3)_2H$ (29.7 kcal/mol), where protonation occurs at the Ru (eq 2). Protonation at the CN^- ligand is expected to be less sensitive to a change in the Cp′ ligand than protonation at the metal because of the greater distance of the Cp′ from the site of protonation. Also, hydrogen bonding (ΔH_{HB}, eq 7) in the $Cp'Ru(PR_3)_2CN$ protonations is expected, as discussed above, to reduce the difference between $-\Delta H_{CNH}$ values for the Cp and Cp* complexes.

Effect of the Metal (Fe vs Ru) on Cyanide Basicity ($-\Delta H_{CNH}$) in $CpML_2CN$. The somewhat higher basicity ($-\Delta H_{CNH}$) of the Fe complex CpFe(dppe)CN (20.9 kcal/mol) than the Ru analogue CpRu(dppe)CN (19.5 kcal/mol) is unexpected considering the well-known[31] strong π-donating ability of Ru^{II} in its complexes with π-accepting ligands. Molecular orbital calculations[1,7] indicate that CN^- is a weakly π-accepting ligand, but one might expect the hydrogen isocyanide ligand (CNH) in the protonated $CpRu(dppe)(CNH)^+$ product to be stabilized by π donation from the metal as in alkyl and aryl isocyanide complexes.[32] If this occurs, it is not evident in $-\Delta H_{CNH}$ values for the Fe and Ru complexes, **23CN** and **18CN**. On the other hand, the νCN value for CpFe(dppe)CN (2063 cm^{-1}) is lower than that for CpRu(dppe)CN (2075 cm^{-1}) which suggests (eq 11) that the Fe complex (**23CN**) should be more basic than the Ru (**18CN**), as observed. As noted in the Introduction, the Ru analogue of $M(bipy)_2(CN)_2$ is more basic than that of Fe, while the Fe analogue of $M(CN)_6^{4-}$ is slightly more basic than that of Ru.[3] In both of these cases, as well as for CpM(dppe)CN, the differences in basicities between the Fe and Ru derivatives are not large.

Concluding Comments

In this first systematic investigation of the basicity of the cyanide ligand in a series of related complexes (eq 1), we observe that the basicities ($-\Delta H_{CNH}$) of the $CpRu(PR_3)_2CN$ complexes increase as the donor abilities of the phosphines ($-\Delta H_{HP}$) increase. However, the range of basicities is relatively small, e.g., 1.9 kcal/mol between $CpRu(PMe_3)_2CN$ and $CpRu(PPh_3)_2CN$, in part because of hydrogen bonding between the CNH ligand in the protonated product and the $CF_3SO_3^-$ anion. Since the ν(CN) values for the complexes decrease with increasing donor ability of the phosphine, there is a very good correlation (Figure 1) between $-\Delta H_{CNH}$ and ν(CN) for the $CpRuL_2CN$ complexes with mono- and diphosphine ligands. The basicity of the CN^- ligand is increased by 2.6−3.1 kcal/mol when Cp in $CpRuL_2CN$ is replaced by Cp*, and the CpM(dppe)CN complex is slightly (1.4 kcal/mol) more basic when M is Fe rather than Ru.

One of the questions raised in the Introduction was whether it was possible to increase the basicity of the metal center sufficiently to make it, rather than the CN^- ligand, the site of protonation. It is evident that the addition of strongly donating ligands to the complexes increases the basicity of the metal more than it increases the basicity of the CN^-. Thus, it seemed possible to make a $Cp'RuL_2CN$ complex that would be protonated at the Ru. In these studies, the most electron-rich unit is $Cp^*Ru(PMe_3)_2$. Its chloride complex $Cp^*Ru(PMe_3)_2Cl$ is protonated (eq 14) at the Ru with $-\Delta H_{HM} = 30.2$ kcal/mol.

$$Cp^*Ru(PMe_3)_2Cl + CF_3SO_3H \rightarrow Cp^*Ru(PMe_3)_2(Cl)(H)^+CF_3SO_3^-; \quad \Delta H_{HM} = -30.2 \text{ kcal/mol} \quad (14)$$

$$\underset{\textbf{18*CN}}{Cp^*Ru(PMe_3)_2CN} \rightarrow \underset{\textbf{18*CNH}^+}{Cp^*Ru(PMe_3)_2(CNH)^+}{}^-O_3SCF_3; \quad \Delta H_{CNH} = -25.0 \text{ kcal/mol} \quad (15)$$

The analogous cyanide complex is protonated (eq 15) at the nitrogen with $-\Delta H_{CNH} = 25.0$ kcal/mol. Given the favorable protonation at the metal in eq 14, why does protonation occur at the nitrogen, rather than the metal, in eq 15? Complex **18*CNH**$^+$ appears to be the thermodynamic product since it is stable in DCE solution for at least 2 days at room temperature without rearranging to a metal-protonated isomer. If the metal-protonated form were more stable, it seems unlikely that there would be a significant kinetic barrier to this rearrangement. Therefore, it is likely that **18*CNH**$^+$ is the thermodynamic product. That protonation of **18*CN** occurs at the CN^- must mean that the equilibrium constant for protonation at the Ru is significantly smaller than that for protonation at the CN^-. This is possible if CN^- were a less strongly donating ligand than Cl^-. That this is likely is suggested by Lever's ligand electrochemical parameter, $E_L(L)$,[33] which is significantly more negative for Cl^- (−0.24) than CN^- (0.02). Thus, it is reasonable to conclude that the Ru is less electron-rich in $Cp^*Ru(PMe_3)_2CN$ than in $Cp^*Ru(PMe_3)_2Cl$, which possibly explains why protonation occurs at the CN^- ligand. However, it is also possible, although not obvious, that the entropy associated with protonation at the CN^- is significantly more positive than protonation at the Ru, which might also contribute to the observed protonation at the CN^- ligand.

Acknowledgment. We thank the National Science Foundation (Grant CHE-9414242) and the Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract W-7405-Eng-82 to Iowa State University for support of this work. We also thank Johnson-Matthey for the generous loan of $RuCl_3 \cdot nH_2O$.

Supporting Information Available: Experimental procedures for the syntheses of compounds **3CN**, **3Cl**, **4Cl**, **6Cl**, **7Cl**, **4CN**, **5CN**, **6CN**, **7CN**, **9CN**, **12Cl**, **13Cl**, **14Cl**, **15Cl**, **12CN**, **13CN**, **14CN**, **15CN**, **19CN**, **18*CN**, **19*CN**, and **20*CN** (7 pages). Ordering information is given on any current masthead page.

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