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Kinetic Studies of the Alkylation of Metal Cyanide Complexes: $M(CO)_x(L)_{5-x}CN$ (M = Mn, Re) and $CpM'(CO)_x(L)_{2-x}CN$ (M′ = Fe, Ru)

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Reaction rates for the alkylation of $Mn(CO)(dppm)_2CN$ (dppm = $PPh_2CH_2PPh_2$), $Mn(CO)_2(tripod)CN$ [tripod = $(PPh_2CH_2)_3CCH_3$], $Re(CO)_3(dppm)CN$, $(\eta^6\text{-}C_6Me_6)Mn(CO)_2CN$, CpFe(dppe)CN (dppe = $PPh_2CH_2CH_2PPh_2$), CpRu(dppe)CN, and $CpRu(CO)(PPh_3)CN$ with methyl 4-nitrobenzenesulfonate (MeONs) to produce complexes of the type $[L_nM{-}CNMe]^+ \ {}^-ONs$ were investigated in 1,2-dichloroethane (DCE) at 30.0 °C. The reactions are first order in both the complex and the alkylating agent, which is consistent with a mechanism that involves nucleophilic attack of the cyanide nitrogen on the methyl of the MeONs. The second-order rate constants (k_2) correlate approximately with the stretching frequency of the cyanide ligand ν(CN) in the complexes. There is a somewhat better correlation between ν(CN) of the $CNCH_3$ ligands in the products and k_2. There is also a good correlation between the rate constant (k_2) and the calculated force constant (k_{CO}) for the ν(CO) vibrational mode of the analogous $[L_nM{-}CO]^+$ complex. These correlations appear to be useful for predicting nucleophilicities of metal cyanide complexes of different metals, in different oxidation states, and with ligands exhibiting a range of electronic and steric properties.

Introduction

Transition metal cyanide complexes have been the subject of numerous studies since the discovery of Prussian blue in the early 1700s.[1−5] Of special interest is the ability of the nitrogen atom of the cyanide ligand to behave as a nucleophile toward various organic and inorganic electrophiles to form alkyl isocyanide complexes[3,4] and multinuclear cyanide-bridged metal complexes.[3−5] However, quantitative investigations of cyanide ligand nucleophilicity have not been reported.

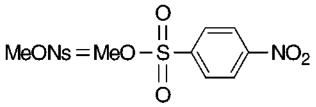
Related to the nucleophilicity of a cyanide ligand is its basicity. Recently this group reported basicities of cyanide ligands in $CpM(L)_2CN$ complexes, where M = Fe or Ru, from a study of heats of protonation (ΔH_{CNH}) of the complexes with $HOSO_2CF_3$ in 1,2-dichloroethane (DCE) (eq 1).[6] It was observed

$$CpM(L)_2CN + HOSO_2CF_3 \xrightarrow[25.0\ ^\circ C]{DCE} CpM(L)_2(CNH)^+\ {}^-OSO_2CF_3; \quad \Delta H_{CNH} \quad (1)$$

that while the basicity ($-\Delta H_{CNH}$) of the cyanide ligand increased from $CpRu(PPh_3)_2CN$ (20.5 kcal/mol) to $CpRu(PMe_3)_2CN$ (22.4 kcal/mol) with increasing donor ability of the PR_3 ligand, the changes in $-\Delta H_{CNH}$ were relatively small. It was observed that for the CpM(dppe)CN complexes, where dppe = $Ph_2PCH_2CH_2PPh_2$, the Fe (20.9 kcal/mol) derivative was slightly more basic than the Ru (19.5 kcal/mol) analogue.[6] However, the basicity determinations were somewhat complicated by hydrogen bonding between the protonated product and the triflate anion as shown in the structure of $CpRu(PPh_3)_2CN{-}H^+\cdots{}^-OSO_2CF_3$, which was determined by an X-ray diffraction study.[7]

In this paper we describe kinetic studies of the nucleophilicities of cyanide ligands by determining the rates of reactions (eq 2) of a series of d^6, 18-electron transition metal complexes with methyl 4-nitrobenzenesulfonate (MeONs) in 1,2-dichloroethane at 30 °C,

$$\underset{\mathbf{1CN}-\mathbf{7CN}}{L_nM{-}CN} + MeONs \longrightarrow \underset{\mathbf{1CNCH_3^+}-\mathbf{7CNCH_3^+}}{L_nM{-}CN{-}Me^+\ ONs^-} \qquad (2)$$



where $L_nM{-}CN$ = $Mn(CO)(dppm)_2CN$ (**1CN**), $Mn(CO)_2(tripod)CN$ (**2CN**), $Re(CO)_3(dppm)CN$ (**3CN**), $(\eta^6\text{-}C_6Me_6)Mn(CO)_2CN$ (**4CN**), CpFe(dppe)CN (**5CN**), CpRu(dppe)CN (**6CN**), and $CpRu(CO)(PPh_3)CN$ (**7CN**).

The complexes were chosen so as to represent metals with varying degrees of electron richness, which was adjusted using different auxiliary ligands (L) in the $L_nM{-}CN$ complexes. A major goal of the study was to determine whether the nucleophilicity of the cyanide ligand, as represented by the rate constant (k_2) for reaction 2, could be correlated with parameters that reflect electron richness at the metal center.

Experimental Section

General Procedures. All preparative reactions, chromatography, and manipulations were carried out under an inert atmosphere of nitrogen or argon using standard Schlenk techniques. Solvents were purified under nitrogen using standard methods.[8] Hexanes and dichloromethane

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(DCM) were refluxed over CaH_2 and then distilled. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone. Methanol was dried over magnesium turnings and iodine and distilled. Hexanes and dichloromethane were stored under nitrogen over molecular sieves (4 Å). 1,2-Dichloroethane (DCE) was purified by washing consecutively with concentrated sulfuric acid, distilled deionized water, 5% NaOH, and water again; after the solvent was predried over anhydrous $MgSO_4$, it was distilled from P_4O_{10} and then stored in the dark under nitrogen. Neutral Al_2O_3 (Brockmann activity I) was deoxygenated at room temperature under high vacuum for 12 h, deactivated with 5% (w/w) N_2-saturated water, and stored under N_2.

All solution infrared spectra were recorded on samples in CH_2Cl_2 or 1,2-dichloroethane in NaCl cells using a Nicolet 560 infrared spectrophotometer; ^{1}H NMR spectra were obtained on compounds in $CDCl_3$ using a Bruker 200 AC MHz or a Varian VXR 300 MHz spectrometer using TMS (δ = 0.00 ppm) as the internal reference. $^{31}P\{^1H\}$ NMR spectra were obtained in $CDCl_3$ on the Bruker AC 200 MHz instrument with 85% phosphoric acid (δ = 0.00 ppm) as an external reference. Elemental microanalyses were performed on a Perkin-Elmer 2400 series II CHNS/O analyzer. Electron ionization mass spectra (EIMS at 70 eV), chemical ionization (NH_3) mass spectra (CIMS), and electrospray ionization mass spectra (ESI in CH_2Cl_2) were obtained on a Finnigan 4000 spectrometer.

The alkylating agent methyl 4-nitrobenzenesulfonate (MeONs) was purchased from Aldrich or Sigma. The metal complexes, $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, as well as the phosphines $(Ph_2PCH_2)_3CCH_3$ (tripod), $Ph_2PCH_2CH_2PPh_2$ (dppe), and $Ph_2PCH_2PPh_2$ (dppm) were purchased from Strem Chemical Co. NaCN and KCN were purchased from Fisher Chemical Co. The complexes $Mn(CO)_5Br$,[9] $(C_6Me_6)Mn(CO)_2CN$ (**4CN**),[10] $Mn(CO)(dppm)_2Br$,[11] CpFe(dppe)CN (**5CN**),[12] CpRu(dppe)CN (**6CN**),[13] $CpRu(CO)(PPh_3)CN$ (**7CN**),[6] and $Re(CO)_3(dppm)(OSO_2CF_3)$[14] were prepared by literature methods. IR spectra in the ν(CN) region of the L_nM-CN and $L_nM-CNCH_3^+$ complexes are given in the Discussion section. The ν(CN) bands of the CN^- ligands are of weak to medium intensity, while those of the $CNCH_3$ ligands are of medium to strong intensity.

Preparation of *trans*-$Mn(CO)(dppm)_2CN$ (1CN). To a 50 mL Schlenk flask containing $Mn(CO)(dppm)_2Br$ (415 mg, 0.69 mmol) and CH_2Cl_2 (10.0 mL) was added a 3-fold molar excess of KCN (135 mg, 2.07 mmol) in methanol (20.0 mL) under nitrogen. The solution was stirred for 3 h, at which time the solution had changed from dark orange to orange-yellow. The solvent was removed under vacuum. The remaining residue was treated with 10 mL of water, and the $Mn(CO)(dppm)_2CN$ was extracted from the mixture with CH_2Cl_2 (3 × 5 mL). The CH_2Cl_2 solution was dried over anhydrous Na_2SO_4, the solvent was reduced to ∼5 mL under vacuum, and hexanes were added to precipitate the orange product (264 mg, 68%). Spectra of **1CN** are similar to those reported previously for this compound.[15] IR (CH_2Cl_2): ν(CO) 1861 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.84 (m, 4H, CH_2), 7.16−7.31, 7.41−7.46 (m, 40H, Ph). ^{31}P NMR ($CDCl_3$): 41.5 (s). MS (EI): 878 (M^+).

Preparation of *fac*-$Mn(CO)_2(tripod)Br$ (2Br). To a 50 mL Schlenk flask containing $Mn(CO)_5Br$ (704 mg, 2.56 mmol) and tripod (1.76 g, 2.82 mmol) was added toluene (20 mL) under nitrogen. While the solution was refluxed with stirring, it turned from light orange to dark orange-red. After 1 h, the solution was allowed to cool to room temperature. The volume of toluene was reduced under vacuum to 10 mL, and hexanes were added; a dark orange solid precipitated. The solution was filtered, and the solid was washed with hexanes (4 × 5 mL), dried under vacuum, and recrystallized from CH_2Cl_2/hexanes to give 1.86 g (89%) of **2Br**.[16] IR (CH_2Cl_2): ν(CO) 1951 (s), 1893 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.49 (s, 3H, CCH_3), 2.47 (m, 6H, CH_2), 7.02−7.29, 7.49, 7.71 (m, 30H, Ph). ^{31}P NMR ($CDCl_3$): δ 21.89 (d, J_{PP} = 88.0 Hz, 2P), 69.88 (t, J_{PP} = 90.0 Hz, 1P). MS (ESI): *m*/*e* 680 (M^+).

Preparation of *fac*-$Mn(CO)_2(tripod)CN$ (2CN). A solution of $Mn(CO)_2(tripod)Br$ (495 mg, 0.61 mmol) in CH_2Cl_2 (15 mL) was treated with NaCN (119 mg, 2.42 mmol) dissolved in MeOH (32.0 mL). After the solution was refluxed for 2 h, the opaque orange solution turned clear yellow-orange. This solution was cooled (−10 °C), the solvent mixture was evaporated, and water (10 mL) was added to the residue; then CH_2Cl_2 (3 × 5 mL) was added. The CH_2Cl_2 layer was decanted, dried over anhydrous Na_2SO_4 and filtered through Celite. The solvent was reduced to 5 mL under vacuum, and hexanes were added to precipitate the product, which was recrystallized from CH_2Cl_2/hexanes to give a light yellow solid (390 mg, 84%). IR (CH_2Cl_2): ν(CO) 1954 (vs), 1897 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.49 (s, 3H, CCH_3), 2.24−2.33 (m, 6H, CH_2), 7.09−7.25, 7.52, 7.70 (m, 30H, Ph). ^{31}P NMR ($CDCl_3$): δ 31.0 (br, 2P), 49.0 (br, 1P). MS (ESI): *m*/*e* 761 (M^+). Anal. Calcd for $C_{44}H_{39}MnNO_2P_3$: C, 69.38; H, 5.16; N, 1.84. Found: C, 68.78; H, 5.46; N, 1.79.

Preparation of *fac*-$Re(CO)_3(dppm)CN$ (3CN). To a solution of $Re(CO)_3(dppm)OSO_2CF_3$ (1.95 g, 2.42 mmol) in acetone (20.0 mL) was added a 2-fold molar excess of KCN or NaCN. After the solution was stirred for 3 h at room temperature, the solvent was removed under vacuum. The resulting white solid was washed with water (10 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The CH_2Cl_2 layer was filtered and dried over Na_2SO_4. A white solid (**3CN**) was obtained from the CH_2Cl_2 solution after recrystallization from CH_2Cl_2/hexanes (1.31 g, 80%). IR (CH_2Cl_2): ν(CO) 2032 (vs), 1952 (s, sh) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.60−4.80 (m, 1H, CH*H*), 5.32−5.61 (m, 1H, C*H*H), 7.31−7.48, 7.69 (m, 30H, Ph). ^{31}P NMR ($CDCl_3$): δ −39.5 (s).

Reactions of 1CN−7CN with MeONs. The compounds **1CN−7CN** were reacted with MeONs for infrared characterization of the $[L_nM-CNMe]$ONs products by dissolving approximately 10 mg of L_nM-CN in 2.0 mL of DCE in a 16 mm Pyrex test tube under nitrogen. To the solution was added 10 equiv of MeONs. The color of the solution lightened upon alkylation within the reaction time (45 min to 7 days). The yields of the alkylated products were quantitative as determined by the complete disappearance of the reactant IR spectrum and the appearance of the spectrum for only the $L_nM-CNMe^+$ product.

Isolation of the alkylated products was accomplished by reaction of the metal cyanide complexes (100 mg) with equimolar MeONs in refluxing 1,2-dichloroethane (30 mL). These reactions were monitored by IR spectroscopy until only the product peaks were visible. The solvent was reduced to 5 mL, and the product was precipitated by the addition of 50 mL of hexanes. The product was recrystallized from MeOH/diethyl ether. Spectroscopic data for the alkylated complexes $[L_nM-CNMe]$ONs are given below.

$[Mn(CO)(dppm)_2(CNCH_3)]$ONs ($1CNCH_3^+$). IR (DCE): ν(CO) 1901 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.70 (s, 3H, $CNCH_3$), 4.88 (m, 2H, CH*H*), 4.76 (m, 4H, C*H*H), 7.01, 7.11, 7.23−7.74 (m, 40H, Ph), 8.15 (s, 4H, $C_6H_4NO_2$). ^{31}P NMR ($CDCl_3$): 38.8 (s).

$[Mn(CO)_2(tripod)(CNCH_3)]$ONs ($2CNCH_3^+$). IR (DCE): ν(CO) 1975 (vs), 1924 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.80 (s, 3H, CCH_3), 2.83 (s, 6H, CH_2), 2.49 (s, 3H, $CNCH_3$), 7.26 (s, 30H, Ph), 8.15 (s, 4H, $C_6H_4NO_2$). ^{31}P NMR ($CDCl_3$): δ 34.5 (s, br).

$[Re(CO)_3(dppm)(CNCH_3)]$ONs ($3CNCH_3^+$). IR (DCE): ν(CO) 2049 (vs), 1977 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.24−5.45 (m, 2H, CH*H*), 6.18−6.32 (m, 2H, C*H*H), 2.78 (s, 3H, $CNCH_3$), 7.28, 7.33−7.87 (m, 20H, Ph; 4H, $C_6H_4NO_2$). ^{31}P NMR ($CDCl_3$): δ −43.7 (s).

$[(C_6Me_6)Mn(CO)_2(CNCH_3)]$ONs ($4CNCH_3^+$). IR (DCE): ν(CO) 2007 (vs), 1962 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.40 (s, 18H, CCH_3), 3.73 (s, 3H, $CNCH_3$), 8.18 (s, 4H, $C_6H_4NO_2$).

$[CpFe(dppe)(CNCH_3)]$ONs ($5CNCH_3^+$). ^{1}H NMR ($CDCl_3$): δ 2.55, 2.62 (m, 4H, CH_2), 2.88 (s, 3H, $CNCH_3$), 4.54 (s, 5H, C_5H_5), 7.27, 7.43−7.69 (m, 20H, Ph; 4H, $-C_6H_4NO_2$). ^{31}P NMR ($CDCl_3$): δ 97.1 (s).

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[CpRu(dppe)(CNCH$_3$)]ONs (6CNCH$_3^+$). ^{1}H NMR (CDCl$_3$): δ 2.61−2.71 (m, 4H, CH$_2$), 2.71 (s, 3H, CNCH$_3$), 4.98 (s, 5H, C$_5$H$_5$), 7.09−7.72 (m, 20H, Ph; 4H, C$_6$H$_4$NO$_2$). ^{31}P NMR (CDCl$_3$): δ 77.7 (s).

[CpRu(CO)(PPh$_3$)(CNCH$_3$)]ONs (7CNCH$_3^+$). IR (DCE): ν(CO) 2006 (s) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 3.34 (s, 3H, CNCH$_3$), 5.38 (s, 5H, C$_5$H$_5$), 7.28−7.73 (m, 15H, Ph; 4H, C$_6$H$_4$NO$_2$). ^{31}P NMR (CDCl$_3$): δ 49.3 (s).

Attempted Alkylations of Nitriles. To compare the reactivities of the cyano complexes with those of organic nitriles, acetonitrile and benzonitrile (4−5 μL) were treated with a 10-fold excess of methyl 4-nitrobenzene sulfonate in a solution of DCE (3.0 mL) at 30.0 °C in a 16 mm Pyrex test tube under nitrogen. Periodic monitoring of the reaction solutions by infrared spectroscopy showed that no reaction occurred for either reaction over a 7 day period. Benzonitrile was previously reported to be ethylated with the strong electrophilic reagents [Et$_3$O]BF$_4$ and diethoxycarbonium hexachloroantimonate.[17−19]

Kinetic Studies of the Reactions of L$_n$M−CN with MeONs. In a typical experiment, 10−15 mg of L$_n$M−CN was dissolved in DCE in a 16 mm Pyrex test tube under nitrogen. This solution was placed in a constant-temperature bath at 30.0 ± 0.2 °C for 20−30 min. The Cryo Therm variable-temperature IR cell (International Crystal Laboratories, No. 2405-4763) was placed in a constant-temperature jacket also at 30.0 ± 0.2 °C for 30 min before it was used. To the solution of L$_n$M−CN was added 0.5−1.5 mL of the desired concentration of MeONs also at 30.0 ± 0.2 °C. This reaction solution was then injected into the IR cell. The formation of the methylated product was monitored to completion by measuring the increase in the ν(CNMe) peak intensity of the methylated product. Rate constants were calculated from the 15−50 spectra taken during the first two half-lives of the reactions. In the experiments, where at least a 10-fold excess of alkylating agent was utilized, the absorbances (P) of the ν(CNMe) product band were fitted to eq 3[20] utilizing Kaleidagraph (Synergy Software) to obtain a pseudo-first-order rate constant k_{obs} (s^{-1}). The bimolecular rate constants

$$P_\infty - P_t = (P_\infty - P_0)\exp(-k_{\mathrm{obs}}t) \qquad (3)$$

k_2 (M^{-1} s^{-1}) were calculated using the expression $k_2 = k_{\mathrm{obs}}/[\mathrm{MeONs}]_{\mathrm{av}}$, where [MeONs]$_{\mathrm{av}}$ is the average of the [MeONs] at the beginning and the end of the reaction.

Rate data obtained when [MeONs]$_0$ was less than 10 times as large as [L$_n$M−CN]$_0$ were fitted to linear plots of eq 4,[20] ln([B]/[A]) vs t, where the rate constant was determined by first converting the absorbance for L$_n$M−CNCH$_3$ ([Mn(CO)(dppm)$_2$CNMe]ONs, ϵ = 708 cm^{-1} M^{-1}; [Mn(CO)$_2$(tripod)CNMe]ONs, ϵ = 1033 cm^{-1} M^{-1}) to concentration. The second-order rate constant k_2 (M^{-1} s^{-1}) was obtained from the slope of the best fit straight line.

$$\ln\frac{[\mathrm{MeONs}]_0 - [\mathrm{L}_n\mathrm{M{-}CNCH_3}]_t}{[\mathrm{L}_n\mathrm{M{-}CN}]_0 - [\mathrm{L}_n\mathrm{M{-}CNCH_3}]_t} = \ln\frac{[\mathrm{MeONs}]_0}{[\mathrm{L}_n\mathrm{M{-}CN}]_0} + k_2\Delta_0 t \qquad (4)$$

where [B] = [MeONs]$_0$ − [L$_n$M−CNCH$_3$]$_t$, [A] = [L$_n$M−CN]$_0$ − [L$_n$M−CNCH$_3$]$_t$ and Δ_0 = [MeONs]$_0$ − [L$_n$M−CN]$_0$.

Results

Preparation of Mn(CO)(tripod)Br (2Br). This complex was previously prepared by Ellermann et al.[16] by an indirect method. A more efficient route involves refluxing a solution of Mn(CO)$_5$Br with 1 equiv of tripod in toluene (eq 5).

$$\mathrm{Mn(CO)_5Br + (Ph_2PCH_2)_3CCH_3 \xrightarrow[\text{reflux}]{\text{toluene}} \underset{\textbf{2Br}}{Mn(CO)_2[(Ph_2PCH_2)_3CCH_3]Br}} \qquad (5)$$

Preparation of 1CN, 2CN, and 3CN. Two common methods for the preparation of metal cyanide complexes from metal halides L$_n$M−X involve either (i) refluxing L$_n$M−X in methanol with an alkali metal cyanide[6,12,13] or (ii) stirring L$_n$M−X with AgCN in CH$_2$Cl$_2$.[15] The preparation of *fac*-Mn(CO)$_2$(tripod)CN **(2CN)** gave the highest yield following the first method by refluxing a MeOH/CH$_2$Cl$_2$ solution of Mn(CO)$_2$(tripod)Br with an excess of NaCN.

The synthesis of complex **1CN** from *trans*-Mn(CO)(dppm)$_2$Br **(1Br)** and silver cyanide has been described previously by Riera et al.[15] However, **1Br** is also oxidized by AgCN, producing a black solution with only a small quantity of the desired product **1CN**. To avoid this oxidation, KCN or NaCN was reacted with **1Br** to give **1CN** in 68% yield.

Because there was no reaction between *fac*-Re(CO)$_3$(dppm)-Br and excess AgCN even after 48 h, the triflate complex Re(CO)$_3$(dppm)(OSO$_2$CF$_3$) was reacted with KCN or NaCN to produce **3CN** (eq 6) in 80% yield. Two ν(CO) bands were

$$\underset{\textbf{3Br}}{\mathrm{Re(CO)_3(dppm)Br}} \xrightarrow[\text{DCM}]{\mathrm{AgOSO_2CF_3}} \mathrm{Re(CO)_3(dppm)(OSO_2CF_3)} \xrightarrow[\text{acetone}]{\text{NaCN}} \underset{\textbf{3CN}}{\mathrm{Re(CO)_3(dppm)CN}} \qquad (6)$$

observed in the IR spectrum of **3CN**; they are at lower wavenumber than those of Re(CO)$_3$(dppm)(OSO$_2$CF$_3$). One phosphorus signal was observed in the ^{31}P NMR spectrum, and ^{1}H NMR signals for Ph and both CH*H* protons were similar in appearance to those of the facial complexes Re(CO)$_3$(dppm)-(OSO$_2$CF$_3$)[14] and Re(CO)$_3$(dppm)Br.[14] Complexes (C$_6$Me$_6$)Mn-(CO)$_2$CN (**4CN**),[10] CpFe(dppe)CN (**5CN**),[12] CpRu(dppe)CN (**6CN**),[13] and CpRu(CO)(PPh$_3$)CN (**7CN**)[6] were prepared by previously reported methods.

Characterization of Products in Reaction 2. The methylated products were prepared by reaction of the L$_n$M−CN complexes **1CN**−**7CN** with excess (10-fold) MeONs in DCE. The large increase in ν(CN) and small increase in ν(CO) indicate that the alkylation occurs at the cyanide ligand. For example, ν(CN) in [(C$_6$Me$_6$)Mn(CO)$_2$(CNMe)]ONs increases by 103 cm^{-1} from that in (C$_6$Me$_6$)Mn(CO)$_2$CN, but ν(CO) increases by only 27 and 33 cm^{-1}. The coordination geometries of the alkylated complexes were established to be the same as those of their precursor cyanide complexes, L$_n$M−CN, by the similar appearance of their IR and ^{31}P and ^{1}H NMR spectra. Also *trans*-[Mn-(CO)(dppm)$_2$(CNMe)]ONs (**1CNCH$_3^+$**), [(C$_6$Me$_6$)Mn(CO)$_2$-(CNMe)]ONs (**4CNCH$_3^+$**), and CpFe(dppe)(CNMe)]ONs (**5CNCH$_3^+$**) have spectra very similar to those of the following reported compounds that contain the same cationic complexes: *trans*-[Mn(CO)(dppm)$_2$(CNMe)]PF$_6$,[15] [CpFe(dppe)(CNMe)]-BF$_4$,[13] and (C$_6$Me$_6$)Mn(CO)$_2$(CNMe)]OTf.[10] In the ^{31}P NMR spectra of **6CNCH$_3^+$** and **7CNCH$_3^+$**, the ^{31}P signal is shifted upfield from that of the precursor cyanide complexes. The ^{1}H NMR spectra of **6CNCH$_3^+$** and **7CNCH$_3^+$** show a Cp resonance that is downfield with respect to the nonalkylated starting complexes **6CN** and **7CN**, as is also observed in the methylation of CpFe(dppe)(CN) (**5CN**). Overall shifts in the IR and ^{31}P and ^{1}H NMR bands are similar to those reported for the methylation of CpFe(dppe)(CN) with [Me$_3$O]BF$_4$.[13] Upon methylation, the ^{31}P NMR spectrum of Mn(CO)$_2$(tripod)CN (**2CNCH$_3^+$**) shows an upfield shift in the signal of the phosphorus trans to the cyanide ligand and a slight downfield shift in the signal for the

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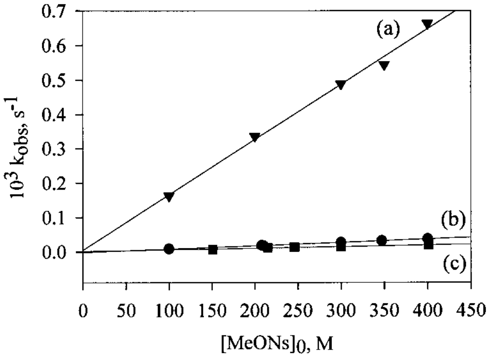

Figure 1. Plots of k_{obs} vs $[MeONs]_0$ for reactions (eq 2) of (a) CpFe(dppe)CN (▼), (b) $(C_6Me_6)Mn(CO)_2CN$ (●), and (c) $Re(CO)_3(dppm)$-CN (■) with MeONs at 30.0 °C.

Table 1. Second-Order Rate Constants (k_2) for Reaction 2 and k_{CO} for L_nM-CN Complexes

metal complex	10^5k_2,[a] M^{-1} s^{-1}	k_{CO}, N m^{-1}
$Re(CO)_3(dppm)CN$ (**3CN**)	0.54(3)	1724
$(C_6Me_6)Mn(CO)_2CN$ (**4CN**)	0.97(1)	1650
$CpRu(CO)(PPh_3)CN$ (**7CN**)	1.09(4)	1691
CpRu(dppe)CN (**6CN**)	16.1(4)	1617
CpFe(dppe)CN (**5CN**)	16.7(4)	1615
$Mn(CO)_2(tripod)CN$ (**2CN**)	20(2)	1634
$Mn(CO)(dppm)_2CN$ (**1CN**)	152(6)	1551

[a] Average of the values in Table S1 of Supporting Information; numbers in parentheses are average deviations.

two phosphorus atoms cis to the cyanide ligand. The resulting spectrum contains only one broad peak. The ^{31}P NMR spectrum of $\mathbf{3CNCH_3}^+$ shows only one signal similar in position to those of the related facial complexes *fac*-$Re(CO)_3(dppm)Br$ and *fac*-$Re(CO)_3(dppm)OTf$.[14]

Kinetic Studies. Second-order rate constants (k_2) for the methylation (eq 2) of L_nM-CN, **1CN**−**7CN,** were determined from rate studies conducted under pseudo-first-order (>10-fold excess of MeONs) or second-order (<10-fold excess) conditions in 1,2-dichloroethane (DCE) at 30.0 °C. The rate constants k_2 (Table S1) were obtained by one of two methods: (i) indirectly from the relationship $k_2 = k_{obs}/[MeONs]_{av}$ or (ii) directly from a linear plot of the data for a second-order reaction using eq 4. Plots (Figure 1) of k_{obs} vs $[MeONs]_0$ gave straight lines with *y*-intercepts near 0, within experimental error. Rate constants k_2 for the 5−13 runs for each complex are within at least 17% of the average values listed in Table 1. All reactions were shown to follow the second-order rate law: rate = k_2 $[L_nM-CN]$-[MeONs]. No ν(CN) or ν(CO) bands other than those of the reactant and product were detected during the course of the reactions.

Discussion

Prior to performing the kinetic studies, we compared qualitative rates of reactions of $Mn(CO)_2(tripod)CN$ (**2CN**) with 10-fold excesses of several electrophiles in CH_2Cl_2 solvent at room temperature. After 3 h of reaction with MeI, approximately 25% of **2CN** was converted to $\mathbf{2CNCH_3}^+$. Under the same conditions, approximately 60% of **2CN** was converted to $\mathbf{2CNCH_3}^+$ after 7 h of reaction with methyl tosylate (MeOTs). With MeONs, 50% of **2CN** reacted in 1.1 h. With CF_3SO_3Me (MeOTf), 100% of **2CN** was converted to $\mathbf{2CNCH_3}^+$ in less than 3 min. Thus, the reaction rates increase with the alkylating agent in the order MeI $\leq$ MeOTs $<$ MeONs $\ll$ MeOTf. A similar order of reactivity has been observed in reactions with organic nucleophiles.[21] On the basis of these and other studies, MeONs was chosen as the electrophile for detailed study because it gave the most convenient rates for the reactions with the cyanide complexes.

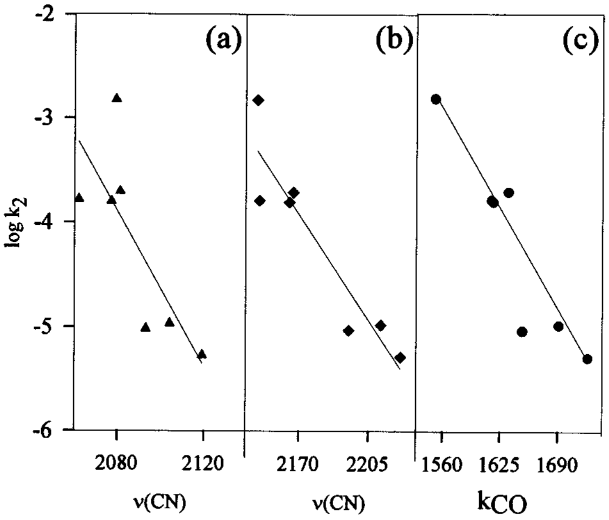

Figure 2. Correlation between log k_2 rate constants for reaction 2 and (a) ν(CN) for the L_nM-CN complexes (▲), (b) ν(CN)for the $L_nM-CNMe^+$ products (◆), and (c) calculated force constants (k_{CO}) for L_nM-CO^+ corresponding to the L_nM-CN complexes **1CN**−**7CN** (●).

Alkylation (eq 2) of the CN^- ligand in complexes **1CN**−**7CN** with MeONs follows a second-order rate law which is consistent with a mechanism that involves nucleophilic attack of the nitrogen atom of the cyanide ligand on the carbon of the MeONs methyl group. This attack results in the displacement of the nosylate anion (^-ONs) and the formation of the product $[L_nM-CNMe]^+$ ^-ONs. As shown in Table 1, rate constants k_2 for the reaction in eq 2 increase with the nucleophilic complex in the order (10^5k_2 in parentheses) **3CN** (0.54) < **4CN** (0.97) < **7CN** (1.09) < **6CN** (16.1) ∼ **5CN** (16.7) < **2CN** (20) < **1CN** (152). In an attempt to explain the 280-fold increase in rate from the slowest **3CN** to the fastest **1CN** reaction, we first considered the possibility that ν(CN) values of the complexes would serve as a guide. It was observed previously that there is a correlation between the basicity ($-\Delta H_{CNH}$, eq 1) and ν(CN) for a series of (η^5-Cp)$Ru(PR_3)_2CN$ complexes;[6] the lower ν(CN), the higher the basicity. For the present series of complexes, the ν(CN) values (measured in CH_2Cl_2 except for **5CN** and **6CN** in DCE) decrease in the order **3CN** (2119 cm^{-1}) > **7CN** (2104) > **4CN** (2093) > **2CN** (2081) > **1CN** (2079) > **6CN** (2077) > **5CN** (2065). The correlation ($R = 0.615$) of ν(CN) with log k_2 is shown in Figure 2. A somewhat better correlation ($R = 0.934$) is observed (Figure 2) between ν(CN) values of the CN−CH_3 ligands in the products and the k_2 rate constants. These ν(CN) values (measured in DCE solvent) decrease in the order $\mathbf{3CNCH_3}^+$ (2221 cm^{-1}) > $\mathbf{7CNCH_3}^+$ (2211) > $\mathbf{4CNCH_3}^+$ (2195) > $\mathbf{2CNCH_3}^+$ (2167) > $\mathbf{6CNCH_3}^+$ (2165) > $\mathbf{5CNCH_3}^+$ (2150) > $\mathbf{1CNCH_3}^+$ (2149).

Seeking a more general parameter that would account for the rates of reactions (eq 2) involving these complexes containing four different metals (Mn, Re, Fe, Ru), two oxidation states, and several different ligands (Cp, C_6Me_6, tripod, dppe, dppm, PPh_3, and CO), we turned to a parameter (k_{CO}) that this research group used previously[22] to correlate nucleophilic attack on coordinated ethylene and benzene ligands. The k_{CO} in its present

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usage is simply the C−O stretching force constant for a CO ligand that occupies the site of the CN^- ligand in a L_nM-CN complex. Thus, the k_{CO} value for $[CpRu(dppe)(CO)]^+$ is the parameter for CpRu(dppe)CN and is a measure of the electron richness of the $CpRu(dppe)^+$ fragment. Complexes with the lowest k_{CO} values have the highest electron richness at the metal center. A high electron richness at the metal center should make the CN^- ligand more electron rich and therefore more nucleophilic. In principle, k_{CO} values for the L_nM-CO^+ complexes can be calculated from experimental ν(CO) values for the complexes or they can be more easily estimated by an empirical procedure (eq 7) developed by Timney.[23] He noted that k_{CO} values depend on the following parameters: k_d (associated with the metal and its number of d electrons), $\epsilon_L{}^\theta$ (contributions from each of the ligands L in the complex),[24] and 197 N m^{-1} for the effect of the charge on ionic complexes. Using Timney's eq 7

$$k_{CO} = k_d + \sum_L \epsilon_L{}^\theta + (197\ \mathrm{N\ m^{-1}}) \tag{7}$$

and parameters,[23] we calculated k_{CO} values for the L_nM-CO^+ complexes corresponding to each of the cyanide complexes in Table 1, except for **4CN**. In Figure 2 is shown a plot of the ln k_2 rate constant (eq 2) vs k_{CO} values for the complexes, where the line is a least-squares fit of all of the compounds except **4CN**. Only the complex $(C_6Me_6)Mn(CO)_2CN$ (**4CN**) deviates significantly from the otherwise very good correlation (R = 0.986). The reason for this deviation is not obvious, but it is perhaps related to the method of estimating k_{CO}. Because Timney parameters for the η^6-C_6Me_6 ligand are not available,[23] the previously reported[25] k_{CO} value, calculated from experimental ν(CO) data for $[(\eta^6\text{-}C_6Me_6)Mn(CO)_3]^+$, was used. Thus, with the exception of **4CN**, there is a clear correlation between a high rate of reaction and a low k_{CO}. This correlation, together with those of ν(CN) values for the CN^- and $CNCH_3$ ligands, supports the proposed S_N2 nucleophilic mechanism. The correlation also suggests that it is the electronic, rather than the steric, properties of the complexes that control the rate of nucleophilic attack.

In conclusion, results described in this paper show that the nucleophilicities of transition metal cyanide complexes L_nM-CN depend substantially upon the metals and ligands (L) in the complexes and that these nucleophilicities are generally correlated with ν(CN) for the CN^- and $CNCH_3$ ligands and with the k_{CO} parameter. Low values of all of these parameters indicate complexes with more highly nucleophilic CN^- ligands.

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Supporting Information Available: Rate constants for the reactions (eq 2) of L_nM-CN with MeONs in DCE at 30.0 ± 0.2 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) The $\epsilon_L{}^\theta$ parameter for the phosphorus donor groups in dppm, dppe, and tripod were approximated by the $\epsilon_L{}^\theta$ value for PPh_2Me, which was estimated from $\epsilon_L{}^\theta$ values for PPh_3 and PMe_3 as follows: $(2\epsilon_{PPh3}{}^\theta + \epsilon_{PMe3}{}^\theta)/3$.

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