complex is higher than in the bulk solution. Saturation is observed when most complexes have a solvation sphere that contains the necesary number of acetonitrile molecules. After this bulk concentration (~10 M) is reached, further increases in the bulk concentration of acetonitrile have a smaller effect.

To establish that the complex *is* preferentially solvated in CH_2Cl_2 and to a much lesser extent in CH_3NO_2, ^1H NMR spectra of $[(HMB)Ru(anth)]^{2+}$ were obtained (Table II) for a range of concentrations of CD_3CN in both CD_2Cl_2 and CD_3NO_2. The normalized ^1H NMR resonance positions of the coordinated HMB peak (referenced to TMS) were then plotted vs the acetonitrile concentration (shown in Figure 3). The similarity between the NMR and kinetic data is immediately apparent. The gentle curvature that is observed in the nitromethane data is probably due to a slight residual amount of preferential solvation even in this high dielectric solvent. The difference between the kinetic and NMR data in methylene chloride solutions at higher concentrations of acetonitrile (i.e. the continued shift in the ^1H NMR signal when the maximum k_{obs} has been reached) can be explained by considering that the number of acetonitrile molecules required to form the transition state is less than the total number in the solvation sphere. Once the transition state requirement is met, no further rate increase is observed, but the HMB peak continues to shift as acetonitrile completes the solvation sphere.

Conclusions

We propose a mechanism that is consistent with the kinetic and NMR data for both solvent systems and that takes into account preferential solvation:

$$[(HMB)Ru(anth)]^{2+} + CH_3CN \overset{K}{\rightleftharpoons} [(HMB)Ru(anth)]^{2+}\cdot CH_3CN \quad (7)$$

$$[(HMB)Ru(anth)]^{2+}\cdot CH_3CN \xrightarrow[2CH_3CN]{k_2} [(HMB)Ru(CH_3CN)_3]^{2+} + \text{anthracene} \quad (8)$$

where $K_{CH_2Cl_2} > K_{CH_3NO_2}$ and $k_{2(CH_2Cl_2)} < k_{2(CH_3NO_2)}$. The equilibrium constant K refers to replacement of a solvent molecule in the solvation sphere by CH_3CN while k_2 is the first-order rate constant for the release of anthracene from the preferentially (CH_3CN) solvated complex, $[(HMB)Ru(anth)]^{2+}\cdot CH_3CN$. We plan further work in this area designed to investigate the analogous photochemical reaction of $[(HMB)Ru(anth)]^{2+}$.

Acknowledgment. We thank Professor Warren Reynolds for several stimulating discussions concerning the preferential solvation of ions. D.A.F. acknowledges support from the Sohio-Lando program. This material is based upon work supported in part by the National Science Foundation under Grant No. CHE-8722843. The U.S. Government has certain rights in this material.

Registry No. $[(HMB)Ru(anth)][PF_6]_2$, 122270-02-4; $[RuCl_2(HMB)]_2$, 67421-02-7; anthracene, 120-12-7.

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Nucleophilicities of the Metal Carbonyl Anions: Effects of Ligands, Solvent, and Countercation

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Received March 30, 1989

Nucleophilicity has been, and remains, a major focus of organic reactions.[1] The concept has had more limited use in inorganic reactions with the primary focus on metal carbonyl anions.[2,3] The most often used measure of nucleophilicities is the rate of displacement of iodide from MeI. In this note we report the effects of ligand environment, solvent, and countercation on the nucleophilicity of metal carbonyl anions.

Table I. Rate Constants for Reactions of Metal Carbonyl Anions and CH_3I in CH_3CN at 25 °C

complex	CH_3CN[a]	glyme[b]	THF[c]
$(PPN)CpFe(CO)_2$	very rapid		2.8×10^6
$(PPN)Re(CO)_5$	74 ± 7	254	1.0×10^3
$(PPN)Mn(CO)_4(PBu_3)$	89 ± 8		
$(PPN)Mn(CO)_4(PEt_3)$	62 ± 4		
$(PPN)Mn(CO)_3(PPh_3)_2$	44 ± 5		
$(PPN)Mn(CO)_4(PPh_2Me)$	19 ± 1		
$(PPN)Mn(CO)_4(PPh_3)$	7.8 ± 0.4		
$(PPN)Mn(CO)_4[P(OPh)_3]$	1.9 ± 0.1		
$(PPN)Mn(CO)_5$	1.5 ± 0.2	0.77	7.4
$(PPN)CpW(CO)_3$	0.51 ± 0.009	5.0	2.4
$(PPN)CpMo(CO)_3$	0.39 ± 0.05	0.67	1.5
$(PPN)CpCr(CO)_3$	0.058 ± 0.005	0.04	0.075
$(PPN)Co(CO)_3(PPh_3)$	0.37 ± 0.004		
$(PPN)Co(CO)_3(PBu_3)$	0.012 ± 0.002		
$(PPN)Co(CO)_4$	0.009 ± 0.001	0.01	0.0437

[a] This work; errors are quoted as 95% confidence limits. [b] Estimated data from ref 3. [c] Na^+ countercation; ref 2.

We have examined the reactions of the metal carbonyl anions[4] listed in Table I with MeI by infrared stopped-flow spectrophotometry.[6,7] The product in each case is the methyl complex, MeM. The reactions are first order in metal carbonyl anion and in MeI.

$$\text{rate} = k[M^-][MeI]$$

The rate constants reported (Table I) are obtained as the slope of plots of pseudo-first-order rate constants, k_{obs}, versus [MeI]. Representative data are given in the supplemental data. The rates of reaction of some of the metal carbonyl anions with MeI have been previously reported and are also listed in Table I.[2,3] Considering the difference in solvent and counterion, the three studies show reasonable agreement in rates and agreement in the order of nucleophilicities:

$$Co(CO)_4^- < CpCr(CO)_3^- < CpMo(CO)_3^- < Mn(CO)_5^- < Re(CO)_5^- < CpFe(CO)_2^-$$

As shown by the data in Table II, the nucleophilicity is relatively unaffected by changes in solvent. The data also show a rather small effect of the countercation with a slower rate for the more interacting cation.

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(1) See for instance: (a) Bunnett, J. F. *Annu. Rev. Phys. Chem.* **1963**, *14*, 271. (b) Ritchie, C. D. *Acc. Chem. Res.* **1972**, *5*, 348. (c) Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1983**, *48*, 2206. (d) Eberson, L. *Acta Chem. Scand.* **1984**, *B38*, 439. (e) Jencks, W. P.; Gilchrist, M. *J. Am. Chem. Soc.* **1968**, *90*, 2622. (f) Bordwell, F. G.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 1052.

(2) Pearson, R. G.; Figdore, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 1541.

(3) Dessy, R. E.; Pohl, R. L.; King, R. B. *J. Am. Chem. Soc.* **1966**, *88*, 5121.

(4) The metal carbonyl anions were prepared as previously described.[5]

(5) (a) Lai, C. K.; Atwood, J. D. Submitted for publication. (b) Zhen, Y.; Atwood, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 1506. (c) Zhen, Y.; Feighery, W. G.; Lai, C. K.; Atwood, J. D. *J. Am. Chem. Soc.*, in press.

(6) Corraine, M. S.; Atwood, J. D. *Inorg. Chem.*, in press.

(7) All the kinetic experiments were performed on an IR stopped-flow spectrophotometer as described previously.[6] All reactions that had been previously[2,3,8] shown to be second order were run under pseudo-first-order conditions with excess alkyl halide. Typical concentrations of metal anion and CH_3I for kinetic studies were 0.001–0.010 and 0.01–10.0 M in CH_3CN at 25 °C, depending on the reaction rates of different metal anions. The rates were monitored by the observed decrease in intensity of the infrared absorbance at 1865, 1860, 1794, 1790, 1751, 1805, 1807, 1830, 1830, 1860, 1788, 1768, 1886, and 1880 cm^{-1} for the metal anions $CpFe(CO)_2^-$, $Re(CO)_5^-$, $Mn(CO)_4(PBu_3)^-$, $Mn(CO)_4(PEt_3)^-$, $Mn(CO)_3(PPh_3)_2^-$, $Mn(CO)_4(PPh_2Me)^-$, $Mn(CO)_4(PPh_3)^-$, $Co(CO)_3(PPh_3)^-$, $Mn(CO)_4[P(OPh)_3]^-$, $Mn(CO)_5^-$, $CpMo(CO)_3^-$, $CpCr(CO)_3^-$, $Co(CO)_3(PBu_3)^-$, and $Co(CO)_4^-$, respectively. The observed rate constants, the standard deviation, and the error at the chosen confidence limit were calculated by using the OLIS computer programs.[6] The second-order rate constants, k, were obtained as the slope of plots of k_{obs} versus $[CH_3I]$.

(8) (a) Darensbourg, M. Y.; Darensbourg, D. J; Burns, D.; Drew, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 3127. (b) Gladysz, J. A.; Williams, G. M.; Tam, W.; Johnson, D. L.; Parker, D. W.; Selover, J. C. *Inorg. Chem.* **1979**, *18*, 553. (c) Darensbourg, M. Y.; Jimenez, P.; Sackett, J. R.; Hanckel, J. M.; Kump, R. L. *J. Am. Chem. Soc.* **1982**, *104*, 1521.

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Table II. Rate Constants for Reactions of $Mn(CO)_5^-$ with Different Counterions and CH_3I at 25 °C[a]

complex	CH_3CN	CH_3COCH_3	CH_2Cl_2	THF	toluene
$(PPN)Mn(CO)_5$	1.5 ± 0.2	1.0 ± 0.1	3.2 ± 0.2	2.5 ± 0.3	
$NaMn(CO)_5$	0.66 ± 0.01				
$LiMn(CO)_5$	0.64 ± 0.04				
$Mg[Mn(CO)_5]_2\cdot 4py$	0.7 ± 0.2				0.092 ± 0.007

[a] Errors are quoted as 95% confidence limits.

Table III. Peak Potentials for Oxidations of Anions

metal anion	E_{anode}, mV	metal anion	E_{anode}, mV
$CpFe(CO)_2^-$	-1303	$Mn(CO)_4P(OPh)_3^-$	-617
$Re(CO)_5^-$	-656	$Mn(CO)_5^-$	-480
$Mn(CO)_4PEt_3^-$	-951	$CpMo(CO)_3^-$	-434
$Mn(CO)_3(PPh_3)_2^-$	-1133	$CpCr(CO)_3^-$	-568
$Mn(CO)_4PPh_2Me^-$	-895	$Co(CO)_3PPh_3^-$	-642
$Mn(CO)_4PPh_3^-$	-851	$Co(CO)_4^-$	-206

The ligand effect on nucleophilicity is shown by the data for $Mn(CO)_4L^-$ (L = PEt_3, PPh_2Me, PPh_3, $P(OPh)_3$) and $Mn(CO)_3(PPh_3)_2^-$ in Table I. The rate of reaction with MeI directly parallels the donor capability of the ligand with nucleophilicity for $Mn(CO)_4L^-$ varying as L = CO < $P(OPh)_3$ < PPh_3 < PPh_2Me < PEt_3.

To further examine the nucleophilicity, we have also measured the oxidation potentials of the anions.[9] These are shown in Table III and are correlated with ln *k* in Figure 1. The oxidation is irreversible; the values reported are the peak potentials. While the peak potentials have no true thermodynamic significance, since they are recorded under identical conditions, they may provide a useful correlation with the nucleophilicity. As shown in Figure 1, the E_p values correlate reasonably well with ln *k*. The correlation is especially good if the anions with phosphine substituents are omitted (r^2 improves from 0.70 to 0.94). All of the anions with a phosphine ligand have reactivity lower by 2 orders of magnitude than expected from the E_p values for oxidation. This strongly indicates that in the reaction of $Mn(CO)_4L^-$ with MeI the phosphine ligand provides a steric inhibition to the expansion of the manganese from five-coordinate to six-coordinate. The $P(OPh)_3$ complex has reduced reactivity from that expected for the potential, but by only half the magnitude of the phosphines. The only non-phosphine-substituted metal carbonyl anion that has appreciably lower reactivity toward MeI is $CpCr(CO)_3^-$. It is likely that expansion of the first-row metal to seven-coordinate is sterically hindered. The steric inhibition of the reaction with MeI continues to $Mn(CO)_3(PPh_3)_2^-$, which reacts 4 orders of magnitude more slowly than expected from the E_p value. Thus, the electron-donor character of the phosphine, which is responsible for the increase in nucleophilicity, is partially offset by the greater steric interactions. Steric interactions for reaction with MeI are well-known in organic reactions.[1]

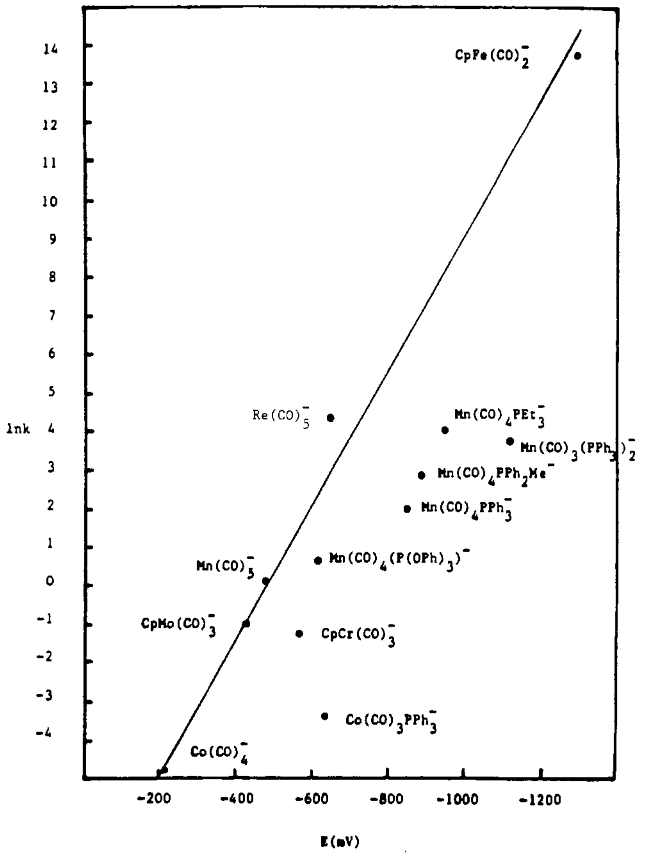

Figure 1. Correlation of ln *k* for reactions of the metal carbonyl anions with MeI and the peak potentials for oxidations of the anion. The rate constant for $CpFe(CO)_2^-$ ($6 \times 10^6\ M^{-1}\ s^{-1}$) was estimated from previously reported data. The line is given to illustrate the lowered reactivity of sterically constrained anions but is not a best fit of the data.

The bond from Mg^{2+} to the oxygen of $Mn(CO)_5^-$ in $Mg(Mn(CO)_5)_2\cdot 4py$[9] causes a significant decrease in the nucleophilicity of the $Mn(CO)_5^-$ anion in toluene. This decrease in k_2 for reaction with MeI is by a factor of 7. Reaction in CH_3CN, where the bond to oxygen is broken by solvation, gives a rate equivalent to that of $NaMn(CO)_5$.

This study shows that the solvent and countercation have a relatively small effect on the nucleophilicity of metal carbonyl anions, as measured by the rate of reaction with MeI. The effect of replacing a CO with a phosphine ligand is more significant, with the increase in rate from the donation partially offset by the increased size.

Acknowledgment. We acknowledge support from the Department of Energy (Grant ER 13775) for this research, donation of anions by Shauna Corraine, and helpful discussions with Janet Osteryoung.

Supplementary Material Available: A plot of k_{obs} versus $[CH_3I]$, plots of kinetic data for the reaction of $(PPN)Mn(CO)_4(PPh_3)$ with CH_3I in CH_3CN, a table of observed rate constants, and a table of infrared data for $CH_3M(CO)_k$ compounds (9 pages). Ordering information is given on any current masthead page.

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(9) Cyclic voltammetric measurements on the oxidation of the anions were performed on a BAS 100 electrochemical analyzer under an atmosphere of argon. Acetonitrile (freshly distilled from P_2O_5 and stored under N_2) was the solvent. The supporting electrolyte was TBATFB (Kodak, 0.1 M, tetrabutylammonium tetrafluoroborate), which was recrystallized three times from an ethanol solution and vacuum-dried. The working electrode was a 3-mm platinum-disk electrode, and the auxiliary electrode was a platinum wire. The reference electrode was a Ag/Ag^+ electrode (0.01 M $AgNO_3$/0.25 M TBATFB in acetonitrile) separated from the cell by a Vycor tip. All potentials were measured and are reported versus this electrode. The cell was set up to minimize the effects of solution resistance; however, no *iR* compensation was employed in the measurements. The concentration of analyte was 10^{-3} M in all cases. All measurements were recorded at a scan speed of 100 mV/s. Under these conditions ferrocene exhibited a reversible couple at $E_{1/2}$ = 84 mV.

(10) $Mg[Mn(CO)_5]_2(C_5H_5N)_4$ was prepared by a modified procedure:[11] A mixture of $Mn_2(CO)_{10}$ (0.78 g) and magnesium amalgam (2.0 mmol) in 30 mL of THF was stirred overnight at room temperature. The solution was concentrated, and light yellow $Mg[Mn(CO)_5]_2(C_4H_8O)_4$ was recrystallized from toluene. IR (toluene): 2015 (m), 1928 (s), 1907 (s), 1727 (s) cm^{-1}. To a solution of $Mg[Mn(CO)_5]_2(C_4H_8O)_4$ (1.0 g) in 10 mL of THF was added 0.2 mL of pyridine. The sparingly soluble $Mg[Mn(CO)_5](C_4H_8O)_4$ became very soluble upon addition of pyridine, and the color of the solution changed from light yellow to orange. The compound was recrystallized twice from toluene. IR (toluene): 2010 (w), 1928 (s), 1904 (s), 1721 (s) cm^{-1}.

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