J. Am. Chem. Soc. 1993, 115, 8660–8668

Methyl Transfers. 15. $Co^{I}Pc^{-}$ as a Nucleophile and Leaving Group

Wlodzimierz Galezowski,[†] Prabha N. Ibrahim,[‡] and Edward S. Lewis*

Contribution from the Department of Chemistry, Rice University, P.O. Box 1892, Houston, Texas 77251

Received October 14, 1992. Revised Manuscript Received May 25, 1993[⊛]

Abstract: Many complexes of cobalt in the +1 oxidation state are excellent nucleophiles. The complex with phthalocyanine, Pc^{2-}, is an example; the rates of reaction of complex $(Co^{I}Pc)^{-}$, $\mathbf{1}^{-}$, with MeI and other alkylating agents in dimethylacetamide (DMA) solution are reported. In contrast to previous studies with other Co(I) complexes, the rate of reaction of the methylated product, ($MeCo^{III}Pc$, **3**) with I^{-} is also readily measured, allowing a kinetic evaluation of the equilibrium constant $K = [\mathbf{1}^{-}][MeI]/[\mathbf{3}][I^{-}] = 0.004$ in DMA at 25 °C. Similarly, Br^{-} also reacts with **3** reversibly, and the rate and equilibrium constants are reported. Thus $\mathbf{1}^{-}$ is also a good leaving group. With CN, **3** gives complex $MeCo^{III}PcCN^{-}$ reversibly and slowly gives MeCN in a reaction zero order in CN^{-}. The fast identity rate constants for I^{-} attack on MeI as well as that for Br^{-} attack on MeI are given. Two different paths to the identity methyl transfer rate constant, k_{CoCo}, for the $\mathbf{1}^{-} + \mathbf{3}$ reaction with use of the Marcus equation gave $k_{CoCo} = 4.4\ M^{-1}\ s^{-1}$ from the $\mathbf{3} + I^{-}$ data but $k_{CoCo} = 0.088\ M^{-1}\ s^{-1}$ from the $\mathbf{3} + Br^{-}$ data. This discrepancy, which is outside of experimental error, constitutes a deviation from the Marcus treatment; it is discussed.

Introduction

Nucleophilic reactivity has been of interest for many years. An early quantitative treatment of Swain and Scott[1] established a scale of nucleophilicities based on the relative reactivities with MeBr in methanol, a scale later modified and extended with MeI as the reference.[2]

A relation between nucleophilicity and oxidation potential with basicity had some success,[3] but the realization that even orders of nucleophilicity were solvent dependent[4] led to a loss of interest in any absolute scales or universal rate correlations. In this laboratory, a series of measurements of both rates and equilibria of methyl transfers between nucleophiles in sulfolane solution showed some rate–equilibrium correlations, but wide ranges of nucleophiles or leaving groups did not correlate.[5] Correspondingly, the identity rates for methyl transfer between two identical nucleophiles were quite variable. Albery and Kreevoy[6] successfully applied the Marcus equation to methyl transfers in protic solvents. With experimental equilibrium constants in sulfolane, we were able to reconcile the rates, equilibria, and identity rates and showed that in this dipolar aprotic solvent the Marcus equation fit very well.[7,8]

When equilibrium constants are not far from unity, the quadratic term in the Marcus equation can be neglected. The apparently plausible assumption was made initially that work terms for the forward and reverse reactions are the same for cases with no formation or destruction of charge. Then the Marcus equation for the methyl transfer reaction 1, with the related identity reactions 2 and 3, reduces to the simple form, eq 4,[9] where $K_{YX} = k_{YX}/k_{XY}$.

$$X^{-} + MeY \underset{k_{XY}}{\overset{k_{YX}}{\rightleftarrows}} MeX + Y^{-} \qquad (1)$$

$$X^{-} + MeX \underset{k_{XX}}{\overset{k_{XX}}{\rightleftarrows}} MeX + X^{-} \qquad (2)$$

$$Y^{-} + MeY \underset{k_{YY}}{\overset{k_{YY}}{\rightleftarrows}} MeY + Y^{-} \qquad (3)$$

$$k_{YX} = (k_{XX}k_{YY}K_{YX})^{1/2} \qquad (4)$$

The applicability of eq 4 and deviations from it have been of continuing interest.[10]

The assumption of equal work terms W_R and W_P for forward and reverse reactions was appropriate for earlier work with structurally very similar leaving groups and nucleophiles, but it is inappropriate for the present work and unnecessarily stringent. A less restrictive assumption is derived here.

The Marcus equation without the quadratic term is eq 5, where $\Delta G^{\ddagger}_{YX}$ and ΔG°_{YX} are the experimental free energy of activation and the experimental free energy of the reaction, and $\lambda_{YX}/4$ is the intrinsic barrier.

$$\Delta G^{\ddagger}_{YX} = W_R + \lambda_{YX}/4 + (\Delta G^{\circ}_{YX} - W_R + W_P)/2 = (W_R + W_P)/2 + \lambda_{YX}/4 + \Delta G^{\circ}_{YX}/2 \qquad (5)$$

The free energies of activation for the identity reactions 2 and 3, $\Delta G^{\ddagger}_{XX}$ and $\Delta G^{\ddagger}_{YY}$, according to eq 5 are

$$\Delta G^{\ddagger}_{XX} = W_{XX} + \lambda_{XX}/4 \qquad (6)$$

and a corresponding one for Y, simpler because ΔG°_{XX} (and ΔG°_{YY}) are zero and the forward and reverse work terms are necessarily the same.

[†] Present address: Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland.

[‡] Present address: Department of Chemistry, University of Colorado, Boulder, CO 80309.

[⊛] Abstract published in *Advance ACS Abstracts*, August 15, 1993.

(1) Swain, C. G.; Scott, C. B. *J. Am. Chem. Soc.* **1953**, *75*, 141.

(2) Pearson, R. G.; Sobel, H.; Songstad, J. *J. Am Chem. Soc.* **1968**, *90*, 319.

(3) Edwards, J. O. *J. Am. Chem. Soc.* **1954**, *76*, 1540.

(4) Parker, A. J. *Chem. Rev.* **1969**, *69*, 1.

(5) Lewis, E. S.; Kukes, S. *J. Am. Chem. Soc.* **1979**, *101*, 417. Lewis, E. S.; Kukes, S.; Slater, C. D. *J. Am. Chem. Soc.* **1980**, *102*, 1619.

(6) Albery, W. J.; Kreevoy, M. M. *Adv. Phys. Org. Chem.* **1978**, *16*, 87.

(7) Lewis, E. S.; McLaughlin, M. L.; Douglas, T. A. *J. Am. Chem. Soc.* **1985**, *107*, 6668.

(8) Lewis, E. S. *J. Phys. Chem.* **1986**, *90*, 3796.

(9) This equation is not new. In connection with methyl transfers it appears in logarithmic form as eq 4 in the following: Lewis, E. S.; Douglas, T. A.; McLaughlin, M. L. In *Nucleophilicity*; Harris, J. M., McManus, S. P., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 3.

(10) Recent emphasis has been on the effect of structural changes on identity reaction rates in both methyl transfers (Lewis, E. S.; Yousaf, T. I.; Douglas, T. A. *J. Am. Chem. Soc.* **1987**, *109*, 2152) and phenacyl transfers Yousaf, T. I.; Lewis, E. S. *J. Am. Chem. Soc.* **1987** *109*, 6137).

0002-7863/93/1515-8660$04.00/0

The average of these is

$$(\Delta G^{\ddagger}{}_{XX} + \Delta G^{\ddagger}{}_{YY})/2 = (W_{XX} + W_{YY})/2 + (\lambda_{XX} + \lambda_{YY})/8 = (W_{XX} + W_{YY})/2 + \lambda_{YX}/4 \quad (7)$$

The Marcus identification of the average of the identity intrinsic barriers with the cross reaction intrinsic barrier gives the second equality in (7). Eliminating $\lambda_{YX}/4$ between eqs 5 and 7 gives

$$\Delta G^{\ddagger}{}_{YX} = (W_R + W_P)/2 + (\Delta G^{\ddagger}{}_{XX} + \Delta G^{\ddagger}{}_{YY})/2 - (W_{XX} + W_{YY})/2 + \Delta G^{\circ}{}_{YX}/2 \quad (8)$$

All the work terms fall out of eq 8 if eq 9 is obeyed, even if

$$W_R + W_P = W_{XX} + W_{YY} \quad (9)$$

$W_R \neq W_P$, and eq 8 becomes equivalent to eq 4. Charge-creating reactions such as the Menschutkin reaction must be excluded from this treatment.

Low oxidation number metal complexes are often powerful nucleophiles.[11] Reduction of vitamin B_{12} leads to a Co(I) complex called B_{12s}. This, various cobaloxime complexes in the +1 oxidation state, and the Co(I) complex of phthalocyanine (1^-) are examples of these nucleophiles. Their very high nucleophilic reactivity has resulted in the name "supernucleophiles"; quantitatively the Pearson n_{CH_3I} values in methanol are 14.8, 10.5–14.1, and 10.8, respectively.[12,13]

These "supernucleophiles" are interesting for several reasons. First, the high reactivity puts them well outside the range of the nucleophiles which we have previously included in Marcus equation correlations. Second, the ease of oxidation makes them candidates for outer sphere single electron transfer reactions, including those believed to give products like those of nucleophilic substitution. However, it has been shown that outer sphere SET mechanisms and obedience to the Macus equation are incompatible.[14] Third, they are very "soft", giving an opportunity for seeing additonal examples of the soft–soft interactions that have previously shown small deviations from eq 4. Finally, the analogy to B_{12s} and methyl B_{12} chemistry, especially the enzymatic methionine synthesis, has been initially extensively explored by Schrauzer.[15] We have previously suggested that these Co(I) complexes have good leaving group reactivity and fast identity rates,[16] a combination previously seen only in iodide ion. The combination is required for nucleophilic catalysis of nucleophilic substitution, such as the B_{12} mediated transfer of methyl from nitrogen to sulfur.

In this paper we study nucleophile 1^-, choosing this phthalocyanine ligand because of the absence of extraneous functional groups, the near-irreversible ligation of cobalt, and the commercial accessibility of $Co^{II}Pc$ (**2**). The solvent chosen is dimethylacetamide (DMA), mostly because of prior work[17] and because the solubility of the sodium salt of 1^-, **2**, and the Co-methyl derivative **3** is adequate for spectrophotometric studies. The structures of **1**, **2**, and **3** are depicted in Figure 1. DMA, as a typical dipolar aprotic solvent, also allows a relationship to earlier work in other aprotic solvents to be made. Furthermore, the extent of ion pairing in DMA is negligible[18] compared to that in the solvent THF used by Casey[19] and by Wang and Atwood.[20] A major emphasis is on methyl transfer from **3**, in which 1^- is a leaving group. A brief study of a possible protonation of 1^- is included, since some cobalt hydrides are isolable and evolve hydrogen with excess acid.[21]

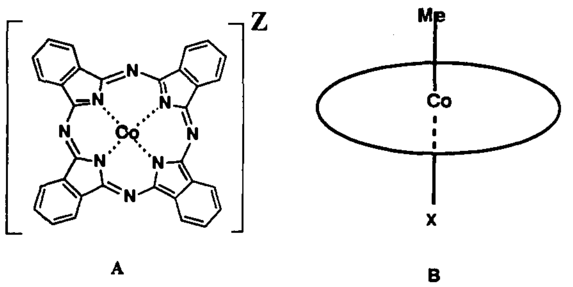

Figure 1. (A) $Z = -1$, Co^IPc^- (1^-); $Z = 0$, $Co^{II}Pc$ (**2**). (B) The ellipse indicates the same phthalocyanine ring as in A; X absent or solvent, $MeCo^{III}Pc$ (**3**).

The recent report[20] of the methyl transfer from a variety of methyl–molybdenum complexes to $CpFe(CO)_2^-$ in THF is highly relevant to this work. First, these are additional examples of fast nucleophilic substitution with metal complexes as leaving groups. Second, an attempt was made to see if the Marcus equation as used for methyl transfers was applicable. The identity rate for the methyl transfer between two $CpFe(CO)_2^-$ nucleophiles was estimated from NMR line broadening to be about 50 M^{-1} s^{-1}, giving an example of very fast methyl transfer identity rates. The identity rate for direct methyl transfer between two $CpMo(CO)_3^-$ was not measured, but it was slower than a competing first-order reaction of the methyl–molybdenum complex with a rate constant of 5×10^{-6} s^{-1}. The equilibrium constant for reaction with the complex iron anion also was not measurable, and a reasonable estimate based on acidities was substituted. A rigorous test of the Marcus treatment was thus not possible, although the applicability was not excluded.

Results

Alkylation of 1^-. Solutions of 1^- in the sodium salt of DMA are stable in concentrated solutions down to *ca.* 10^{-3} M. If such a solution is diluted by a factor of *ca.* 100 in the absence of reducing substances (such as $NaBH_4$ or traces of sodium amalgam) it is oxidized to **2** at a rather nonreproducible rate, as shown by a drop in absorbance at 700 nm and an increase at 660 nm. This oxidation was not prevented by using DMA that had been vacuum distilled from calcium hydride in an atmosphere of argon nor by sparging with argon for several hours. The concentrated solution could be introduced into the 1-cm cell stoppered with a serum cup containing DMA and argon as the gas phase with a gas-tight syringe and the oxidation was not noticeably suppressed compared to using a cell open to the laboratory air. A similar sensitivity in dilute solution was shown in experiments on demethylation of **3** where 1^- was never observed in 10^{-6}–10^{-5} M solutions of **3** but was readily detected with 10^{-3} M solutions.

Reaction 10 was followed by the disappearance of peaks at 466 and 698 nm in DMA solution. The reasons for not following the

$$RX + 1^- \rightarrow RCo^{III}Pc + X^- \quad (10)$$

increase of the $RCo^{III}Pc$ peak at 660 nm are presented in the Experimental Section. Absorbance values at several wavelengths could be measured every second with the Hewlett Packard 8452A diode array spectrophotometer. The resulting listings of A vs time could be presented on an attached PC, and the Hewlett Packard software allowed calculation of the pseudo-first-order rate constant, k_ψ (RX was at a large and constant excess). The second-order constants were obtained from the slope of a plot

---

(11) Henderson, S.; Henderson, R. A. *Adv. Phys. Org. Chem.* **1987**, *23*, 1.

(12) Schrauzer, G. N.; Deutsch, E.; Windgassen, R. J. *J. Am. Chem. Soc.* **1968**, *90*, 2441.

(13) Eckert, H.; Ugi, I. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 825.

(14) Lewis, E. S. *J. Am. Chem. Soc.* **1989**, *111*, 7576.

(15) Schrauzer, G. N. *Acc. Chem. Res.* **1968**, *1*, 97.

(16) McCortney, B. A.; Jacobson, B. M.; Vreeke, M.; Lewis, E. S. *J. Am. Chem. Soc.* **1990**, *112*, 3554.

(17) Day, P.; Hill, H. A. O.; Price, M. G. *J. Chem. Soc. A* **1968**, 90.

(18) Popovych, O. *Nonaqueous Solution Chemistry*; John Wiley and Sons: New York, 1981; p 284.

(19) Casey, C. P.; Cyr, C. R.; Anderson, R. L.; Martin, D. F. *J. Am. Chem. Soc.* **1975**, *97*, 3053.

(20) Wang, P.; Atwood, J. D. *J. Am. Chem. Soc.* **1992**, *114*, 6424.

(21) Chao, T.-H.; Espenson, J. H. *J. Am. Chem. Soc.* **1987**, *100*, 129.

Table I. Rate Constants for Alkylation of 1^- by RX

solvent	R	X	temp, °C	k_2, M^{-1} s^{-1}
DMA	Me	I	25.0	105 ± 6.0
DMA	Me	Br	25.0	1.45
DMA	*n*-Bu	I	24[a]	0.3
DMSO	Me	I	24[a]	62
sulfolane	Me	I	24[a]	162[b]
sulfolane	Me	OSO_3Me	24[a]	0.8[c]

[a] These runs, while done without much temperature change during the runs, were carried out at ambient temperature, which was on different days 24 ± 2 °C. [b] This rate constant, while not believed to be in serious error, does lie at the upper limit measurable by this method. The solution contained NaI. [c] Dimethyl sulfate reacts slowly with DMA, but enough to make DMA an unsuitable solvent; sulfolane is inert to dimethyl sulfate.

Table II. Solvolysis of **3**

solvent	temp, °C	10^6k, s^{-1}	solvent	temp, °C	10^6k, s^{-1}
DMA[a]	70	2.27	pyridine	91	69.9
DMA[a]	100	127	pyridine	100	272
DMA[a]	110	361	pyridine	115.5	1490
pyridine	85.5	37.8			

[a] The solvent was heated over CaH_2 and then distilled at 90 °C. See the Experimental section for need for this treatment.

(through the origin) of k_ψ *vs* [RX] and are shown in Table I for R = CH_3, X = I or Br. The table also shows some preliminary results obtained before temperature control in the cell was available. They are adequate to illustrate only qualitatively some effects of variation in R and in X. In the solvents MeCN, MeOH, and THF, major side reactions allowed only the conclusion that reaction 10 with MeI, to the extent that it occurred, was within an order of magnitude the same as that in DMA.

It is relevant that the reaction of very low I_2 concentrations in MeI is extremely fast. Distilled, colorless MeI is necessary.

Attempted Protolysis of 1^-. The possible correlation of nucleophilicity with base strength led us to explore the reaction of 1^- with acids in DMA. There is a highly nonreproducible acid promoted oxidation of 1^- to **2** in 10^{-5}–10^{-6} M 1^-, presumably by unavoidable traces of oxygen, but in much more concentrated solutions where trace contamination becomes negligible, the spectrum of 1^- in DMA is unchanged by a large excess of trifluoroacetic acid, hence DMA is a stronger base than 1^-.

Solvolysis and Photolysis of 3. Compound **3** is somewhat thermally and photochemically unstable, giving **2**. All studies of **3** were therefore done at low light levels. In solution in DMA and pyridine there is a slow reaction usually giving $Co^{II}Pc$. The first-order rate constants, determined spectrophotometrically, are shown in Table II. The data in Table II yield the following Eyring equation constants: in DMA, $\Delta H^\ddagger = 32.7 \pm 0.6$ kcal/mol and $\Delta S^\ddagger = +10.6 \pm 1.6$ cal K^{-1} moll^{-1}; in pyridine, $\Delta H^\ddagger = 33.7 \pm 1.3$ kcal/mol and $\Delta S^\ddagger = +14.9 \pm 3.5$ cal K^{-1} mol^{-1}.

The stoichiometry and the fate of the methyl group is not known, but in DMA a degassed solution of **3** in an evacuated sealed cell gave some 1^- initially on heating to 110 °C for 2 h as shown by 700-nm absorption along with **2**. The 1^- was destroyed by overnight heating at 110 °C; only **2** could be detected. The instability of 1^-, even in this rigorously degassed and sealed system, is notable.

Reaction of 3 with CN^-. When excess NaCN in DMA is added to **3**, $MeCo^{III}PcCN^-$, Figure 1B with X = CN, is formed very rapidly, with a spectrum as previously observed.[17] After long heating the spectrum changes to that of $Co^{III}Pc(CN)_2^-$, also known. The first-order rate constants for this conversion are presented in Table III. The reaction is clearly zero order in CN^-, and the Eyring equation constants are $\Delta H^\ddagger = 29.7 \pm 1.1$ kcal/mol and $\Delta S^\ddagger = +7.8 \pm 3.2$ cal K^{-1} mol^{-1}.

At very low [CN^-], reaction 11 was not quantitative. When

$$3 + CN^- \rightleftarrows CH_3Co^{III}PcCN^- \qquad (11)$$

small volumes of dilute (~10^{-5} M) NaCN solutions were used, reproducible meaningful results were not obtained. However, the solvent (not distilled from CaH_2) may have contained traces of acid. In the presence of the added base DBU, a "titration" of **3** at 1 × 10^{-5} M with dilute NaCN gave results shown in Figure 2. This plot, made with [DBU] = 0.01 M, allowed the evaluation as described in the Experimental Section of an equilibrium constant $K_{11} = (1.6 \pm 0.2) \times 10^6$ for reaction 11 at 25 °C. A similar run with [DBU] = 0.1 M gave $K_{11} = (2.1 \pm 0.2) \times 10^6$. The difference is not considered significant. At 50 °C the solution was less stable, and the value calculated was $K_{11} = (2 \pm 0.1) \times 10^5$. In spite of the agreement shown, this value is for experimental reasons less reliable than the 25 °C value. This leads to the following estimate for reaction 11: $\Delta H^\circ = -17 \pm 2$ kcal/mol and $\Delta S^\circ = -16 \pm 6$ cal K^{-1} mol^{-1}. The error estimates are very rough.

Table III. Rate Constants for $MeCo^{III}PcCN^- \rightarrow Co^{III}Pc(CN)_2^-$

temp, °C	10^3[NaCN], M	10^6k, s^{-1}	temp, °C	10^3[NaCN], M	10^6k, s^{-1}
50	2.69	2.27	60	5–13	12.2 ± 0.4
50	5.38	2.83	70	5–13	43.1 ± 0.3
50	13.5	2.82	80	5	145 ± 3
50	67.3	2.74			

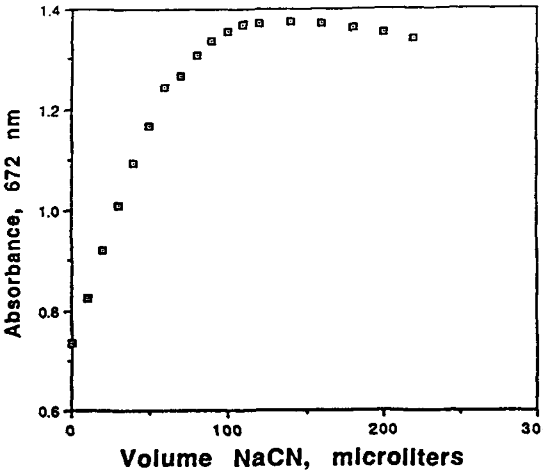

Figure 2. Plot of the spectrophotometric "titration" of **3** with NaCN in the presence of DBU, giving the equilibrium constant for reaction 11.

Product from CN^- Reaction. The nature of the demethylation of **3** by CN^- cannot be ascertained from the spectrophotometric observations. The fate of the methyl group was shown by the isolation of MeCN. A solution of **3** heated at 50 °C for 48 h with NaCN gave a GC yield of 35% of MeCN. The amount expected in this time calculated from the rate constant in Table III is 38.6%, and the agreement shows that the disappearance of $MeCo^{III}PcCN^-$ corresponds to the formation of MeCN.

Reaction of 3 with Bromide Ion. At spectrophotometric concentrations, of the order of 10^{-5} M, **3** is quantitatively destroyed by tetrabutylammonium bromide in DMA. The reaction follows a first-order course, but the spectrophotometric rate constants appear to depend on the wavelength of measurement, especially at temperatures greater than 20 °C. The problem was ultimately traced to a series of consecutive reactions 12, 13, and 14 of which

$$3 + Br^- \rightarrow 1^- + MeBr \qquad (12)$$

$$1^- + [O_2] \rightarrow 2 \qquad (13)$$

$$2 + 2\,Br^- + [O_2] \rightarrow Co^{III}PcBr_2^- \qquad (14)$$

(12) is rate determining, (13) is always fast, but (14) is variable, depending on the purification of the solvent, the temperature, and presumably the content of trace oxidizing agents. As a

Table IV. Rate Constants for **3** + Br$^-$ → **1**$^-$ + MeBr

temp, °C	k,[a] M^{-1} s^{-1}	temp, °C	k,[a] M^{-1} s^{-1}
20	0.0379	35	0.294
25	0.0677	40	0.471

[a] k calculated from the slope of a plot of pseudo-first-order constants *vs* [Br$^-$].

Table V. Equilibrium Constants for **3** + X$^-$ ⇄ **1**$^-$ + MeX at *ca.* 25 °C in DMA

X$^-$	[X$^-$]	K	method[a]
Br$^-$	0.0119	0.0387	A
Br$^-$	0.0299	0.0326	A
Br$^-$	0.050	0.0225	A
Br$^-$		0.0467	B
I$^-$	0.0067	0.00482	A
I$^-$	0.0182	0.00788	A
I$^-$	0.027	0.0104	A
I$^-$	0.0532	0.00972	A
I$^-$		0.00469	B
I$^-$	0.0063	0.0079	C
I$^-$	0.0063	0.0047	C
I$^-$		0.0035	D

[a] A, spectrophotometric study of concentrated solutions in thin cells; B, ratio of forward and reverse rate constants; C, derived from yields of MeI, neglecting equilibrium shift in isolation. (these values are not used in any computations); D, the value from the rate ratio for Br$^-$ divided by K for reaction 15.

consequence, the final A depends on the extent of (14). **1**$^-$ was never detected. The identity of the oxidizing agent, denoted as [O$_2$] in (13) and (14), is not known, although the notation indicates a plausible candidate. The identity of the product of reaction 14 was shown by the similarity of the spectrum (in DMA) to the reported spectrum of this substance in CH_2Cl_2,[22] especially with respect to the major peak at 664 nm and the broad weak band at 435 nm. The spectrum showed numerous differences from that of **2**, with several isosbestic points. Measurement at any of these isosbestic points would allow following the disappearance of **3** without complication from reaction 14. However, only the 658-nm peak was different enough from the spectrum of **3** to be a useful wavelength to follow. Measurements made at 660 nm, close enough to this isosbestic point to make the rate constants insensitive to the variable occurrence of reaction 14, are reported in Table IV. The rate constants measured at 660 nm followed a first-order course well, and the pseudo-first-order rate constants were proportional to [Br$^-$]. The temperature dependencies yield $\Delta H^{\ddagger} = 23.2 \pm 1.2$ kcal/mol and $\Delta S^{\ddagger} = 13.9 \pm 3.5$ cal K^{-1} mol^{-1}.

Equilibrium of Reaction 12. When the concentration of **3** was much increased, the concentration of oxidant, [O$_2$], in reactions 13 and 14 was negligible, and the position of the equilibrium of reaction 12 could be measured in a 0.1-mm cell from the absorption spectrum. Table V shows the equilibrium constant of reaction 12 at three bromide concentrations, as well as a value from the ratio of forward to reverse rates. Table V also shows the corresponding values of the equilibrium with I$^-$, determined analogously, as well as an indication of equilibrium from MeI yields.

Reaction of 3 with I$^-$. In dilute solutions **3** is also quantitatively demethylated by NaI in DMA. Reactions analogus to reactions 12–14 appear to take place. A difference is that even with long times and added I$_2$, there is no reproducible spectrum of the product of reaction 14. The spectrum appears to shift much the same as with bromide, but we have no evidence for the formation of Co^{III}PcI$_2$$^-$. However, the 660-nm peak of **2** in the presence of I$_3$$^-$ undergoes a slow shift to the red. The spectra of **2** and this new product, while not very different, show an isosbestic point at 662 nm. Again, the rate constants for the demethylation of **3**, measured at 660 nm, are reported in Table VI. The *A vs t* curves showed no extrema at this wavelength. At other wavelengths, *A vs t* plots often showed maxima or minima, especially with higher concentrations of I$^-$ and higher temperatures, attributable to a follow-up reaction perhaps like reaction 14.

Table VI. Reaction Rates of **3** with NaI

temp, °C	10^3[I$^-$]	10^3k_ψ, s^{-1}	k_2,[a] M^{-1} s^{-1}
20	0.8–5		0.327
25	1–4		0.492
30	1.01	0.998	
30	2.01	1.872	
30	3.00	3.058	
30	3.985	3.987	
30	4.96	4.979	0.998
35	0.8–4		1.74

[a] Obtained from the slopes of plots of at least five pseudo-first-order rate constants, k_ψ, *vs* [I$^-$]. Only one of such data sets, the one at 30 °C, is shown.

The second-order rate constants from Table VI fit the Eyring equation well with $\Delta H^{\ddagger} = 19.7 \pm 0.8$ kcal/mol and $\Delta S^{\ddagger} = 6 \pm 2.7$ cal K^{-1} mol^{-1}.

No **1**$^-$ could be detected at the spectrometric concentrations of *ca.* 10^{-5} M cobalt. Assuming that the reaction observed is really the reverse of the methylation of **1**$^-$ by MeI, the reaction of **3** with NaI in the presence of added MeI was studied, with the aim of intercepting **1**$^-$ by remethylation. Initially, as expected, there was no overall reaction, then a slow reaction was seen, and if I$_3$$^-$ was added, the effect of MeI disappeared. The MeI was not consumed.

MeI was the other postulated product of the demethylation, but at the spectrophotometric concentration (in 1-cm cells) the amount produced was too small to find. At much higher concentrations MeI was detected in yields of about 20%, which turned out to be equilibrium limited, leading to the equilibrium estimates by method C in Table V, which were crude because equilibrium could be shifted during isolation. In the presence of added I$_2$, the yield of MeI was quantitative within experimental error.

Equilibria were measured as in the case of the Br$^-$ equilibrium by using concentrated solutions in a thin cell, denoted as method A in Table V.

A value of the equilibrium constant was established (method B) by using the ratio of the forward to reverse rates. This is probably the most precise value, and it will be used hereafter.

Reaction of MeI with Br$^-$. The equilibria for attack of Br$^-$ and I$^-$ on **3** are related; the ratio of their equilibrium constants is the equilibrium constant of reaction 15. The equilibrium constant

$$\mathrm{Br^- + MeI \rightleftarrows MeBr + I^-} \qquad (15)$$

from the Br$^-$ to I$^-$ ratio, determined by potentiometric titration, gives a value at 25 °C in DMA of $K_{15} = 13.5 \pm 0.6$. The rate constant for this reaction was also measured as 13.4 M^{-1} s^{-1} at 25 °C in DMA.

Iodide Ion Identity Rate. Another different methyl transfer rate was measured for the purposes of application of the Marcus equation, that of identity reaction 16. The rate constants measured

$$\mathrm{{}^{125}I^- + MeI \xrightarrow{DMA} {}^{125}IMe + I^-} \qquad (16)$$

with an ^{125}I tracer were 4.42 M^{-1} s^{-1} at 15 °C and 11.8 M^{-1} at 25 °C.

Discussion

Powerful cobalt nucleophiles are not new, and cobalt phthalocyanine in the +1 oxidation state, **1**$^-$, reacts very rapidly with MeI in MeOH.[13] The evidence of **1**$^-$ as a leaving group in substitution reactions is less well documented. Elimination reactions with **1**$^-$ as a leaving group have been observed and

---

(22) Homberg, H.; Kalz, W. *Z. Naturforsch.* **1984**, *39b*, 1490–1499.

utilized[23] as part of a protecting group sequence. Methylcobaloximes have been shown[24] to react with some nucleophiles including I$^-$ to methylate the nucleophile, although the cobalt product was not identified. Presumably the methylation of cobaloxime anions by MeI is therefore reversible. The methyl transfer between two very similar Co(I) cobaloximes was fast;[25] only a lower limit was established for the rate constant. Similarly, methyl B_{12} reacts with B_{12s} with a high but not measured rate of identity methyl transfer.[26] Methyl transfer rates between Rh(I) dioxime complexes are also measurably fast.[27] Nevertheless, it is not widely recognized that Co(I) complex anions are practical leaving groups in S_N2 reactions using more familiar nucleophiles.

Table I shows that the rapid alkylation of **1**$^-$ by RX shows reactivities with changes in R and X about what would be expected for ordinary (S_N2) substitution. The methyl to butyl rate ratio of about 350 is high but not unprecedented. The ratio of MeI to $(MeO)_2SO_2$ of about 200 is also high but not as high as with another soft nucleophile.[28] This conformity with S_N2 behavior allows rejection of any possible SET mechanism.

DMA is a dipolar aprotic solvent in which S_N2 rates are very close to those in acetone.[4] It is quite basic compared to most solvents. It is difficult to purify, and trace impurities appear to be important in some of the secondary reactions observed in this work; however, no impurities could be detected by GC. In spite of these problems no better solvent seemed available. We looked for evidence of dimerization, known to occur in some solvents with phthalocyanine derivatives, by looking for Beer's law deviations. Over a concentration range of over a factor of 100, no changes in spectrum were seen with either **2** or **1**$^-$, thus dimerization is not a problem in this solvent.

The demethylation of **3** by nucleophiles appears to be general, since it is accomplished by CN$^-$ I$^-$, Br$^-$, pyridine, and DMA, as well as by PhS$^-$ in a fast reaction not described here. In the case of CN$^-$ and pyridine, no **1**$^-$ was detected, in the case of I$^-$, Br$^-$, and DMA, **1**$^-$ was observed only in relatively concentrated solutions with extreme care to exclude air. It is reasonable to assume that the primary reaction in every case is

$$3 + Nu^- \rightarrow MeNu + 1^- \qquad (17)$$

followed rapidly under spectrophotometric conditions by reactions probably analogous to (13) and (14). The failure to observe **1**$^-$ as a product in dilute solution is obviously related to the difficulty of obtaining stable dilute solutions of **1**$^-$ in the absence of reducing agents mentioned earlier. It is tempting to suggest that **1**$^-$ is protected by some ligand which dissociates off at low concentrations. However, the insensitivity of the spectrum to concentration makes this explanation less likely. We therefore prefer the explanation in terms of trace oxidants.

Reaction 17 with Nu$^-$ = CN$^-$ has some special features. The cobalt product observed is exclusively Co^{III}Pc(CN)$_2^-$ in good yield, and MeCN is formed in a yield comparable to that expected from the reaction time. However, the reaction is very slow, because complexation reaction 11 is very extensive. Thus reaction 17 can occur only to the extent that free **3** is available. The kinetics of the conversion of the complex, MeCo^{III}PcCN$^-$, to MeCN and ultimately to Co^{III}Pc(CN)$_2^-$ is zero order in cyanide, showing that the rate-determining transition state has the composition of the complex. This is compatible with the presence of a small equilibrium concentration of **3** reacting according to reaction 17 as the rate-determining step. It is also apparently compatible with a rate-determining reverse of reaction 11, a mechanism that we reject, because the equilibrium for (11) was rapidly established at 25 °C, allowing the measurement of the equilibrium constant. Thus reaction 11 is quite fast at 25 °C in both directions. The reaction giving MeCN is very slow at 25 °C; the calculated rate from the temperature dependence is 6.1×10^{-8} s^{-1}. However, assuming that the reaction is slow because of the low concentration of **3**, we calculate for reaction 17, Nu$^-$ = CN$^-$, $k = 0.098$ M^{-1} s^{-1}. This calculation is based on extrapolation from a good Eyring equation fit to data between 50 and 80 °C and the reliable 25 °C value of the equilibrium constant. The Eyring parameters for reaction 17, $\Delta H^{\ddagger} = 13$ kcal/mol and $\Delta S^{\ddagger} = -10$ eu, are less reliable, because they use the more uncertain value of K_{11} at 50 °C.

Table VII. Nucleophile and Solvent Effects on λ_{max} of Co^{III}Pc Species

ligand	λ_{max}, nm	ligand	λ_{max}, nm
(CN$^-$)$_2$	671	Me, Py	666
Me, CN$^-$	671	Me, DMA	660
Br$^-$ Br$^-$	664		

This high reactivity in reaction 17 but the low overall reactivity may account in part for the notion that these organometallic nucleophiles are not good leaving groups. If a nucleophile is also a good ligand for **3**, then the ligated complex can be expected to be far less reactive. It was fortunate that the particular system of **3** and CN$^-$ allowed the establishment of both the equilibrium and the rate.

The ligation of **3** by CN$^-$, which was consipicuous in the spectrum, brings up the question of whether an octahedral ligand is always present. In the solid state **3** recrystallized from THF has this as a ligand, as shown by preliminary X-ray diffraction, but the ligation is not strong, since most of the THF is lost under vacuum at room temperature. Perhaps in DMA solution the DMA is a ligand. A possible clue to solvent ligation may be found in the visible spectrum. The position of the maximum for Co^{III}Pc complexes near 660 nm is somewhat sensitive to the ligands, as shown in the Table VII. If the position of the maximum indicates the importance of strength of complexation, then **3** in DMA is the least strongly complexed of the species in the list, since the cyano complexes are clearly strong, and shows the longest wavelength peak.

An argument for substantial complexation by solvent lies in the substantial positive entropy of activation for the reactions with I$^-$ and Br$^-$. The positive $\Delta S^{\ddagger}$ for the reaction of iodide and bromide might, if corrected for the DMA ligation equilibrium, have a much more negative $\Delta S^{\ddagger}$, as is expected for an $S_N{}^2$ reaction. The positive $\Delta S^{\ddagger}$ for the cyanide reaction similarly became negative when corrected for CN$^-$ ligation. Should this be the case, the conclusion would be that MeCo^{III}PcDMA is not reactive with I$^-$ or Br$^-$, but it possibly may react with CN$^-$. The argument is not a rigorous demonstration of specific solvation (ligation) of **3**. Obvious alternatives to this solvent ligation explanation for the positive $\Delta S^{\ddagger}$ values for the reactions of **3** with I$^-$ or Br$^-$ include the desolvation of the halide ions (which in this solvent is usually considered unimportant) or an SET mechanism,[29] which was rejected for other reasons. Curiously, in methanol, the reaction of **1**$^-$ with MeI is also reported[13] to have a positive $\Delta S^{\ddagger}$. The extensive reactions of **3** with iodide and bromide came as a surprise, since the reverse reaction appeared quantitative. However, scavenging of **1**$^-$ by reaction 13 allows the reaction to go to complete loss of **3**. In the case of the I$^-$ reaction, I_2 and I_3^- are very effective scavengers, in agreement with the observation of fast oxidation of **1**$^-$ by traces of I_2 in MeI. The adventitious scavenger does not compete with MeI as a trap for **1**$^-$. However in the presence of MeI, after some time the demethylation of **3**

---

(23) Eckert, H.; Ugi, I. *Liebigs Ann.* **1989**, 278.

(24) Stadlbauer, E. A.; Holland, R. J.; Amon, F. P.; Schrauzer, G. N. *Bioinorg. Chem.* **1974**, *4*, 67.

(25) Dodd, D.; Johnson, M. D.; Lockman, B. L. *J. Am. Chem. Soc.* **1977**, *99*, 3664.

(26) Imhoff, M. Dissertation, Eidgenössische Technische Hochschule, 1980.

(27) Collman, J. P.; Brauman, J. I.; Madonik, M. A. *Organometallics* **1986**, *5*, 215.

(28) Whitmire, K. H.; Lee, F. R.; Lewis, E. S. *Organometallics* **1986**, *5*, 987.

(29) Lexa, D.; Savéant, J.-M.; Su, K.-B.; Wang, D.-L. *J. Am. Chem. Soc.* **1988**, *110*, 7617.

resumes, at first slowly, even though no MeI is lost, and if I_3^- is added, the demethylation rate is the same as in the absence of MeI. The resumption of reaction after inhibition can be attributed to the oxidation of I^- by the aventitious scavenger, giving the excellent scavenger I_3^-. This inhibition of demethylation by MeI is the best kinetic evidence that **1**$^-$ is indeed the product, confirmed of course by the detection of **1**$^-$ in the equilibrium studies with much higher concentration of **3**.

Equilibrium constants by direct measurement (method A in Table V) show some dependence on halide ion concentration, but in opposite directions for Br^- and I^-. A suggestion of a possible but unestablished source of the Br^- case is made later; in the rest of this work we shall use the equilibrium constants for the kinetic method B as the most reliable. The ratio of equilibrium constants for **3** with Br^- and with I^- should be the equilibrium constant of reaction 15. The equilibria of **3** with Br^- and I^- give $K_{15} = 10$, compared to the directly measured value of 13.5 ± 0.6, perhaps in adequate agreement considering concentration variations. The observation of the facile reactions of **3** with CN^-, Br^-, and I^- emphasizes the previously unrecognized fact that **1**$^-$ is a very good leaving group.

One aim of this work has been to test the applicability of the modified Marcus equation, eq 4. This can be done by calculating the identity rate k_{CoCo} for the reaction between **1**$^-$ and **3** both from the **3** + I^- system and again for the **3** + Br^- combination. The data for the first system are $k_{CoI} = 0.492$ M^{-1} s^{-1}, $K_{CoI} = 4.7 \times 10^{-3}$, and $k_{II} = 11.8$ M^{-1} s^{-1}; they give $k_{CoCo} = 4.4$ M^{-1} s^{-1} with eq 4.

In order to calculate k_{CoCo} from the bromide system, we first calculate k_{BrBr} using $k_{IBr} = 13.4$ M^{-1} s^{-1} and $K_{IBr} = 13.5$ and the same k_{II} value; these give $k_{BrBr} = 1.13$ M^{-1} s^{-1}. This value is very close to the values of Parker[30] in acetone of 1.3 and 0.78 measured directly or calculated as above from Parker's values given for k_{IBr}, k_{BrI}, and k_{II}. Thus, since rates in acetone and DMA are usually close,[30] our value of k_{BrBr} in DMA is very reasonable.

By using this value for k_{BrBr} and the measured values for k_{CoBr} and K_{CoBr}, a value of $k_{CoCo} = 0.088$ is calculated with use of eq 4. There is thus a discrepancy of a factor of 50 between the two values of k_{CoCo} in DMA at 25 °C.

This appears to be a real discrepancy. There are errors, some of poorly established magnitude. The discrepancy can be reduced but not nearly eliminated by unjustifiable selection of some extreme values of the data. Experimental error does not account for the discrepancy.

Another possible source of the discrepancy is that all the reactions starting with I^- use Na^+ as the counterion. Those starting with Br^- use tetrabutylammonium ion as the counterion. Kinetics using **1**$^-$ also have the Na^+ counterion. Activity coefficient effects may differ somewhat, but since the solutions are quite dilute, especially for the kinetics, this difference must be quite small; it would not lead to the discrepancy.

Ligation of **3** by Br^- could make the species different in the reactions using both species and hence render the application of eq 4 unjustifiable. Only one rather uncertain piece of evidence suggests that this is important: the variation of K_{CoBr} with $[Br^-]$ by method A could be explained by a small extent of ligation. Also, a search for such a complex (Figure 1B, X = Br) using quite high $[Br^-]$ and low temperature did show a very small shift (1–2 nm) to the red of the 660-nm peak of **3** and the appearance of a very weak broad peak at 470 nm. Both are similar to the larger and more conspicuous shifts shown in Table VII for octahedral dicyano, dibromo, and methylcyano complexes. However, the changes of the spectrum of **3** with Br^- are barely perceptible, and the pseudo-first-order rate constants at a somewhat higher temperature of **3** + Br^- are proportional to $[Br^-]$ up to nearly the concentration used in the search for a complex. If this complexation is real, it cannot be extensive enough to cause the discrepancy.

In reactions such as (1) with X^- = **1**$^-$ and $Y^- = I^-$ or Br^-, it seems unlikely that $W_R = W_P$. However, the less restrictive eq 9 still seems very plausible, and thus work term variations are apparently not expected to be a serious problem.

Deviations from Marcus equation predictions have been seen before in the MeI–ArS$^-$ reaction[31] and in the high reactivity of MeI compared to Me_2SO_4[28] with $HFe(CO)_4^-$ and in the present case with **1**$^-$. A consequence of the application of eq 4 or its equivalent has previously been shown to predict slightly higher reactivity of Me_2SO_4 than MeI.[32] These deviations have been attributed to the "soft–soft" interactions of Pearson.[33] However, a study of the application of the Marcus equation to the reaction of I^- with a number of methyl sulfonates showed only small random deviations,[7] and the relative reactivities of the same methyl sulfonates with thiophenoxides and phenoxides were about the same.[31] Thus deviations resulting from "softness" only appear when both the leaving groups and the nucleophiles are soft. It is tempting to regard the effect as a favorable partial innersphere net electron transfer in the transition state, which cannot of course contribute to symmetrical identity reactions. Such an electron transfer is reminiscent of the "state correlation diagrams" of Shaik[34] in which a high energy state described by a complete electron transfer from the nucleophile contributes to the transition state.

It is worthwhile to compare k_{CoCo} for the methyl transfer between the cobalt(I) phthalocyanine ligand and others. It is slower than the substantially faster but not quantitatively measured near identity cobaloxime case[25] and the B_{12} case,[26] both in methanol. Regardless of choice of values our k_{CoCo} is larger than the corresponding rhodoxime case,[27] much faster than the $CpMo(CO)_3^-$ case, and much slower than the $CpFe(CO)_2^-$ case,[20] all measured in MeCN.

Conclusions

In DMA, **1**$^-$ rapidly reacts with MeI, and the reverse reaction is also rapid. An equilibrium constant can be established. Bromide reactions with **3** similarly, but CN^- is a good ligand for **3**, and this complex must dissociate before a fast reaction giving MeCN can take place. The organometallic nucleophile is thus also an excellent leaving group. Data allowing a rigorous check of the modified Marcus equation are collected, but this equation yields two different values for the identity reaction of methyl transfer between two **1**$^-$ ions, thus the modified equation fails. Possible explanations of the discrepancy are offered; the most reasonable uses a transition state interaction of a soft leaving group and a soft nucleophile. Special transition state interactions not found in reagent or product are unlikely to fit the Marcus equation, and these can be expected when these "soft" metal complex anions are used. The simplified Marcus equation is still useful, and the combination of a thermodynamic contribution and a contribution from the average identity barriers is still an excellent first approximation in dealing with rates of methyl transfer between nucleophiles.

Because the identity rate for methyl transfer between the **1**$^-$ ions is so much slower than for the B_{12s} example, it is unlikely that it will show the nucleophilic catalysis of methyl transfer from nitrogen to sulfur that is seen in the natural methionine synthesis pathway.[35]

---

(30) Parker, A. J. *J. Chem. Soc.* **1961**, 1328.

(31) Lewis, E. S.; Vanderpool, S. H. *J. Am. Chem. Soc.* **1978**, *100*, 6421.

(32) Reference 9, Table IV.

(33) Pearson, R. G.; Songstad, J. *J. Am. Chem. Soc.* **1967**, *89*, 1827.

(34) Shaik, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 3692 and later papers.

(35) Zydowsky, T. M.; Courtney, L. F.; Frasca, V.; Kobayashi, K.; Yuen, L.-D.; Matthews, R. G.; Benkovic, S. J.; Floss, H. G. *J. Am. Chem. Soc.* **1986**, *108*, 3152.

Experimental Section

There is an enormous literature on phthalocyanines, and a review volume[36] has been very helpful.

Absorption Spectra. Model 8452A Hewlett Packard diode array spectrometers were used throughout this work. Some of the data in Table I on alkylation rates were obtained on an instrument, courtesy of Prof. P. S. Engel, not providing thermostating or stirring. All other data were obtained on another instrument which provided stirring and thermostating when 1-cm square cells were used but not when 1- or 0.1-mm cells were used.

Materials. Cobalt(II) phthalocyanine ($Co^{II}Pc$, **2**) partly was prepared following Eckert,[23] and commerical (Aldrich) β-form, 97% pure, was used for most of the later work. Most solvents were either good grades of commercial products or those purified by literature methods. *N,N*-Dimethylacetamide (DMA) was "spectrometric grade", and for some purposes it was stirred for *ca.* 4 h with CaH_2 at 100 °C and then distilled under vacuum with an argon leak at 90 °C and kept under argon. The GC traces for both samples and for a sample only vacuum distilled were indistinguishable and showed no extraneous peaks. Tetrahydrofuran was either freshly opened or distilled conventionally from sodium benzophenone ketyl. 1,8-Diazabicyclo[5.4.0]undec-7-ene, DBU, was vacuum distilled. Iodomethane was distilled to remove iodine, a highly reactive impurity. 1-Iodobutane and dimethyl sulfate were distilled. Sodium iodide, sodium cyanide, and tetrabutylammonium bromide were commercial materials, dried, and the solutions were assayed by potentiometric titration with silver nitrate or in the case of cyanide titration by Liebig's method.

Sodium Cobalt(I) Phthalocyanine, 1^-. Cobalt(II) phthalocyanine, **2**, in suspension in DMA and protected by argon or N_2 was reduced by an excess of 5% sodium amalgam for a period of 4 h or more with stirring. The intensely colored green solution contained suspended solids and reducing substances and was basic. For some purposed this was filtered, which removed much of the solid, but not all of the reducing substances. As long as the solution contained both excess base and reducing material, it was reasonably stable, often when diluted to 10^{-6} to 10^{-5} M. Such solutions were used for many of the alkylation studies. Neutral or acidic solutions were extremely sensitive even to traces of oxygen, and time stable dilute solutions were not obtained. A 10^{-3} M solution of 1^-, protected from air, was unaltered in spectral properties by the addition of excess trifluoroacetic acid.

Sodium borohydride would also reduce **2** cleanly, but not as fast as it reduced **3**. Thus solutions of **1** prepared in this way would react rapidly with MeI, but residual excess $NaBH_4$ would then reduce the product **3** fast enough to make the system unsuitable for kinetic studies on the MeI + 1^- reaction.

Methylcobalt(III) Phthalocyanine, 3. Cobalt(II) phthalocyanine (**2**) (14 g, 0.0245 mol) was reduced by sodium amalgam following the procedure given by Eckert and Ugi.[23] The green solution, containing 1^-, was decanted from the residue into a reaction flask which was flushed with N_2 and covered with aluminum foil. Freshly distilled MeI (15 mL, 0.241 mol) was added and stirred for 2 h. The mixture was then stirred with water (300 mL) and the purple solid was isolated by filtration and washed consecutively with methanol, water, and methanol. The yield at this stage was 12 g in one case, but it was much lower in several repetitions when the solution of 1^- was filtered before methylation. About 1 g of this product was extracted into THF by using a Soxhlet extractor to separate it from the less soluble **2**, yielding a purple solid which was recrystallized from THF. A preliminary crystallographic study showed that THF was ligated to cobalt in the vacant octahedral position (Figure 1B, X = THF). but the THF was lost during the X-irradiation. Elemental analysis at this stage was not entirely satisfactory. Calcd (as **3**·THF) for $CoC_{37}H_{27}N_8O$: C, 67.48; H, 4.10; N, 17.02; Co, 8.97. Found: C, 66.07; H, 4.06; N, 17.20; Co, 8.71. The samples of **3** used in subsequent work were vacuum dried samples which lost most of the THF. ^1H NMR (250 MHz, DMSO-d_6) δ 9.4 (8 H, m), 8.2 (8 H, m), 3.6 (m), 1.8 (m), -4.8 (3 H br s). The peaks at δ 3.6 and 1.8, corresponding to residual THF, were weak and difficult to integrate, corresponding roughly to 0.2 molecule of THF per phthalocyanine molecule.

The shapes of the UV spectra of 1^-, **2**, and **3** in DMA are close to those reported by Day,[17] and that of **2** was quite insensitive to pyridine concentrations from 0 to 50%. It was difficult to obtain an extinction coefficient based on solutions of **2**, since the rate of solution is small and the presence of undissolved solid is difficult to detect. Extinction coefficients are therefore based on gravimetrically prepared solutions of **3**·0.2THF. The extinction coefficients of 1^- and **3** were related by methylation of 1^-, giving from several measurements of $\epsilon^3{}_{660}/\epsilon^1{}_{700}$ a value of 2.53. The extinction coefficient of **3** at 660 nm obtained directly was taken as 180 000 from several independent measurements. These measurements agreed within 5%. This gives ϵ_{700} = 71 000 for 1^-. This extinction coefficient is about 40% larger than Day's value. Studies of **2** (and 1^-) showed no dependence of λ_{max} or ϵ over a concentration range of more than 100. This range was achieved by using cells from 1 cm to 0.1 mm in path length. Thus dimerization is not significant in this solvent. The peaks for **3** and **1** are occasionally seen at 658 and 698 nm, respectively. The instrument has diodes every 2 nm, so this difference was ignored.

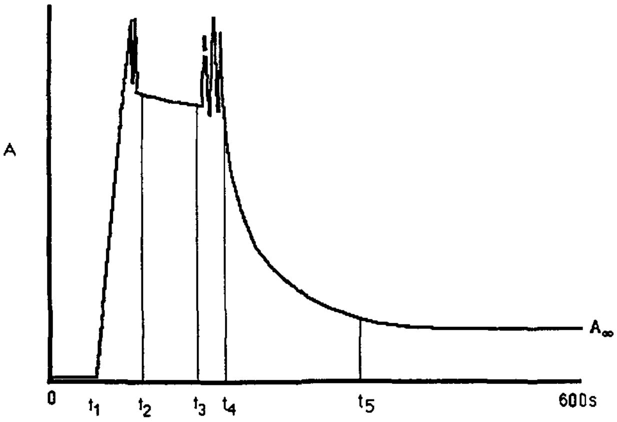

Figure 3. Sketch of a typical trace of A (at 466 nm) *vs* time for the reaction of 1^- with MeI. The range of the A axis is very roughly A = 0.6 to 0, and the time axis generally ran to 600 s. At t_1 the 1^- solution was added, from t_2 to t_3 the "background" rate constant (k_b) was established, MeI was added, and the solution was mixed well, the period t_4 to t_5 was used to establish k_t, and the reaction was continued to establish A_∞. The jagged portions have the light beam interrupted by the hypodermic needles.

The extinction coefficient of **2** was less certain. Photolysis (4 min near a fluorescent light) of **3** led to a fall in the 660nm absorbance by a factor of 1.3, but much longer photolysis leads to complete bleaching, so this factor probably is a lower limit. The so calculated value at 660 nm is ϵ = 138 000 for **2**.

Alkylation Kinetics. The rates in Table I were measured by adding a small volume of a solution of RX to a 2-mL solution of 1^- in DMA (about 5×10^{-6} M) contained in a stirred 1-cm cell protected by a serum cap in the spectrophotometer. In the case of RX = MeI, 50–150 μL of 0.01 M MeI in DMA was used (the slower reactions used more RX). The HP 8452A spectrophotometer was equipped with a filter passing light >300 nm to minimize photolysis of **3**; the disappearance of the peak of 1^- at 698 nm or better the one at 466 nm was followed until there was no additional change (except as noted below), giving A_∞.

The rather erratic behavior of 1^- in dilute solution allowed a simple direct method of following the kinetics when 1^- did not disappear too fast. To the 2 mL of reasonably stable *ca.* 5×10^{-6} M **1** solution in the cell was added RX solution in DMA, usually 50–150 μL of a 0.010 M solution for MeI and more for slower reacting RX. The exponential decay of the peak at 700 or 466 nm was recorded and converted to a pseudo-first-order rate constant, k_ψ, by the PC interfaced to the spectrophotometer. It is necessary to stop using data before $A_t - A_\infty$ begins to lose precision, otherwise the software gives a rate constant too low. Cutting off the data at still earlier times does not change the rate constant except that the precision becomes low if the extent of reaction is too small. The second-order rate constant is then $k_2 = k_\psi/[RX]$.

In the case of faster decay, the following method gave reproducible results. The method is illustrated by the stretch in Figure 3. The solvent (variously purified and protected from air), 2 mL, was placed in the cell and allowed to come to the controlled temperature, and then (in the sketch at t_1) about 10 μL of a stable 1^- solution in contact with 5% sodium amalgam was introduced. After the injection (at t_2) the absorbance decreased, at least 20 s elapsed, and then *ca.* 100 μL of MeI was added. Immediately a 5-mL syringe (kept at the measurement temperature) was used to withdraw a major portion of the cell contents, which was immediately rapidly expelled back into the cell, thus providing a well-stirred solution at t_4. For fairly fast reactions the magnetic stirring was inadequate. The reaction was then followed to completion. A first-order rate constant, k_b, was established for the t_2 to t_3 period and another one

---

[36] Leznoff, C. C.; Lever, A. B. P., Eds. *Phthalocyanines, Properties and Applications*; VCH Publishers, Inc.: New York, 1989.

for the t_4 to $t5$ period (k_t) using the same A_∞ for both periods; the pseudo-first-order rate constant was $k_\psi = k_t - k_b$. In all cases k_b was less than 0.1 k_t, but this correction was still necessary to get good reproducible rates. The jagged parts of the sketch correspond mostly to hypodermic needle interruptions of the light beam. The time t_5 was selected to avoid the software problem mentioned above. This technique was used in the first entry in the table. In the others k_b (which was not measured) was small enough to ignore. In a few runs not reported, A would rise very slowly after apparent completion, especially with lower [RX]. This was traced to the presence of traces of reducing material, which reduced **3** to **1**$^-$.

The reaction of a small volume of **1**$^-$ in DMA sulfolane in the cell followed by MeI gave a plot of rate constants k_ψ against [MeI] that was concave downward. Addition of a little NaI solution gave the same value of k_ψ in the low concentrations, but now linear with [MeI]. This unexplained phenomenon was also seen when a small volume of a solution of **1**$^-$ in MeCN was used for runs in DMA.

In the reaction of MeBr, a solution of MeBr was made by passing MeBr gas into DMA and weighing before and after. A more precise measure of [MeBr] was obtained by hydrolysis in aqueous base, followed by acidification and silver nitrate titration.

Solvolysis of 3 in DMA and Pyridine. In this, and all work on **3**, the ease of photolysis demands that a very low light level prevails. At higher temperatures **3** was slowly converted to **2** in solution in pyridine. A solution of **3** in pyridine was placed in a closed flask in the dark in an oil thermostat. Periodic samples were withdrawn and the spectrum taken, and then the samples were photolyzed and the spectrum taken again, given A_∞. This determination of A_∞ by photolysis is similar to that used in the MeB_{12} system.[37] This gave the amount of **3** remaining, and the linear plot of log [**3**] *vs* time (or ln $|A - A_\infty|$ *vs* time) then gave the rate constant. These and other rate constants involving slow reactions with intermittent sampling were evaluated with use of "Cricketgraph" software. The highest temperature rate was obtained from a boiling solution rather than a flask immersed in the oil thermostat.

The same procedure was used in DMA, using DMA that had been treated with and distilled from CaH_2. Without this treatment the solution became practically colorless in time; even **2** is totally destroyed, presumably by traces of acid in the solvent.[36] This total loss of all phthalocyanine compounds is a problem only at high temperatures, although solutions of **2** in untreated DMA did fade after months at room temperature.

The rate constants are presented in Table II. When untreated DMA and **3** were heated with small concentrations of DBU, the fading was prevented, but the rate was faster than with the DMA distilled from CaH_2, and the rate increased with [DBU].

When a carefully vacuum degassed spectrophotometer cell containing a fairly high concentration of **3** in DMA was sealed and then heated at 110 °C, the solution showed the presence of **1**$^-$ as well as **2**, but 1 day later, only **2** was present.

Methyl Iodide–Iodide Ion Identity Reaction. This was followed in DMA solution by using the same method used earlier in sulfolane.[7] The order of magnitude faster reaction at 25 °C required that samples be collected every 10 s with an automatic pipet. The determination at 15 °C was less hectic and more precise. The initial concentration of trace labeled NaI was 1.5×10^{-3} M, and the MeI was 3×10^{-3} M.

Reaction of 3 with NaCN. Solutions of **3** in DMA with excess CN^- rapidly gave the complex $CH_3Co^{III}PcCN^-$, with a spectrum as reported by Day.[17] On long heating the spectrum gradually changed to that of $Co^{III}Pc(CN)_2^-$, the stable form of CoPc in the presence of CN^-. Solutions of this dicyanophthalocyanine complex were only partially reduced to Co^IPc^- even with a large excess of $NaBH_4$. Kinetics were measured at 502, 604, 690, and 684 nm, all of which gave essentially the same result. A solution of **3**, about 1×10^{-5} M in a flask swept with argon, was mixed with a solution of NaCN, in spectrometric grade DMA, leading to concentrations of NaCN from 2.69×10^{-3} to 6.73×10^{-2} M. The tightly stoppered flask covered with aluminum foil was placed in an oil thermostat, which was in a dark location. Samples of about 2 mL were taken from time to time, cooled, and placed in the spectrophotometer. The spectrum was then taken. All kinetics and handling were done at a very low light level. The A_∞ values were determined by photolysis (about 1 min a few centimeters away from a fluorescent light) after the spectrum had been taken. This spectrum of $Co^{III}Pc(CN)_2^-$ after photolysis agreed with that of one sample kept for many half-lives. Rate constants were calculated from the slope of a plot of ln$|A_\infty - A_t|$ *vs* time. The values in Table III are averages of those from different wavelengths and except for the first entries, averages with different [CN^-].

Equilibrium of the 3 + CN$^-$ Reaction. A cell containing about 1×10^{-5} M **3** and 0.01 or 0.1 M DBU in DMA at 25 °C was placed in the spectrophotometer. Samples of a dilute solution of NaCN in DMA, also containing the same concentration of DBU as the **3** solution, were added consecutively and the absorbance at 672 nm was recorded. In the run shown in Figure 2, the end point corresponded to the addition of 72 μL of the NaCN solution, and the equilibrium constant was calculated from the experimental curve in Figure 2. The linear end portions of the concentration *vs* volume of NaCN solution were extrapolated to their intersection, which was taken as the equivalence point. The difference between the experimental A at this equivalence and the intersection corresponds to the amount of **3** not converted to complex, from which with the known concentration of **3** the equilibrium constant is readily calculated. Without the addition of DBU, traces of acidic substances in the solvent protonated some of the CN^- and led to uninterpretable results. It is not clear whether 0.01 M DBU fails to prevent some protonation of CN^- or whether the difference between results with 0.01 and 0.1 M is merely experimental error.

At 50 °C the solutions were not as stable, and a complete curve as shown in Figure 2 could not be attained. The less precise value of the equilibrium constant was based on a few points near the 1:1 ratio of [**3**] to [CN^-]. The same solution of **3** was used at both temperatures.

Kinetics of 3 + NaI. A solution of **3** (recrystallized from THF and dried under vacuum) was prepared in DMA (the purification of DMA was irrelevant to the rates measured at 660 nm). About 50 mL of solution was made up to be about 8×10^{-6} M in **3**. This solution was placed in a well-stoppered 50-mL flask that was covered with aluminum foil and kept in the dark. In the dark 2 mL of this solution was transferred to a 1-cm square UV cell fitted with a serum stopper to allow it to be swept with argon. The cell was then placed in the (dark) cell compartment of the spectrophotometer for about 10 min, and then a measured volume of *ca.* 0.2 M NaI solution (concentration known with precision) was added with a 50- or 100-μL syringe. Stirring with a small stirring bar took about 1 min, and then points were taken such that about 100 points would cover the reaction well. Measurements at 660 nm and rate constants were evaluated by using the HP software, and an end point (A_∞) was determined from the data. Measurements at other wavelengths were unreliable, as described in the Discussion section. Alternative explanations in terms of photolysis of **3** and precipitation of **2** were explored and rejected.

Addition of MeI at a concentration of 0.38 M stopped the reaction for about 30 min, but then the demethylation started slowly and accelerated. When at this point I_3^- was added, the rate in the absence of MeI was restored. The MeI is not consumed (see below).

Reaction of 3 with Br$^-$. The technique of the study of this reaction was the same as that for the reaction with I^-. The source of Br^- was tetrabutylammonium bromide, chosen because NaBr is not very soluble in DMA. The large cation also reduces ion pairing. The reaction is somewhat slower than the iodide reaction, and again the calculated rate constants at most wavelengths were discrepant but measurements at 660 nm were well-behaved, as described in Discussion section.

Product of the Reaction of 3 with CN$^-$. A solution of 6.82×10^{-5} mol of **3** in 2.5 mL of 0.07 M NaCN in DMA was heated at 50 °C for 48 h in the dark. The product was bulb-to-bulb distilled and the distillate was subjected to gas chromatographic analysis after adding a known amount of cyclohexane as an internal standard. MeCN was identified as a product in the distillate by its retention time and inseparability from deliberately added MeCN. A small peak in the GC corresponding to much less than an equivalent of THF in starting **3** was observed.

Product of the Reaction of 3 with I$^-$. The procedure was the same as that with CN^- except that the reaction was fast, so no heating was necessary and only a short reaction time was needed. The yield in several reactions at about 10^{-3} M **3** and various concentrations of I^- gave about 20% yield, and the solution before distillation showed some **1**$^-$ by a green color. When the reaction took place in the presence of I_3^-, no **1**$^-$ was observed and the yield of CH_3I was 95 ± 10%. In the absence of **3**, DMA and NaI yield no detectable MeI. Further controls showed that the recovery of small amounts of MeI by this procedure was virtually quantitative from a solution of **2**.

Ten milliliters of a solution containing *ca.* 10^{-3} M **3**, 0.16 M MeI, and 4×10^{-3} M NaI was kept in the dark for 3 h. It was then bulb-to-bulb distilled after adding cyclohexane as an internal standard, and GC showed MeI at the same concentration as the starting solution. Thus the resumption of reaction with NaI after the initial inhibition by MeI cannot be attributed to destruction of MeI.

---

(37) Martin, B. D.; Finke, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 585.

Equilibria of 3 with Halides. A solution of 3 (*ca.* 7×10^{-4} M) in DMA (distilled from CaH_2) was placed in a small flask equipped with a serum stopper and two cannulae. The first cannula was used an an argon inlet. The second led to a second flask similarly equiped containing the halide solution of known concentration (NaI or Bu_4NBr). The second cannula from the second flask led to a spectrophotometer cell with a 0.095-mm light path. The septum in the cell was also pierced by a needle. Argon was passed through both flasks and the cell for about an hour and then the second cannula in the first flask was pushed to the bottom of the flask, forcing the contents into the second flask. After mixing, the second cannula in the second flask was lowered to the bottom, forcing the mixture into the cell. All the preceding steps were done in near darkness, to prevent photolysis of 3. The needle and the cannula were then removed from the cell which was then placed in the spectrophotometer and the spectrum taken. The concentrations of 3 and I^- were then determined by using the extinction coefficients previously measured, and the equilibrium constant was calculated.

The Reaction of Br^- with MeI. The equilibrium for this reaction is attained within a minute in DMA. The addition of MeI to a solution of Bu_4NBr gave initially a solution of 0.002 M Br^- and 0.0077 M MeI. After 3 min. the solution was quenched with cold water. The relative amounts of I^- and Br^- were determined by potentiometric titration.

The kinetics were more difficult because the reaction is so fast. The rate was determined by using very dilute solutions, sampling every 20 s and after quenching, and titrating with a 1-mL buret containing 0.01 M $AgNo_3$. The starting solution was 2.3×10^{-4} M in CH_3I and 8.3×10^{-4} M in Br^-, and with this excess of Br^-, as well as a favorable equilibrium constant, the rate constant was calculated without complication from any reverse reaction.

Possible Complexation of 3 by Br^-. When 3 is mixed with dilute Br^- at 25 °C, there are no detectable spectral changes, except for that due to the demethylation. When a more concentrated solution of Br^- is used, the reaction is too fast to allow exacting study of the starting material. When 3 at 6×10^{-5} M is mixed with 0.06 M Br^- at 14 °C, there is a very broad and weak band appearing at about 470 nm with an absorbance increase of 0.024 units and the peak at 660 nm appears to be slightly shifted to longer wavelengths. Neither of these changes is unequivocal evidence for any interaction, but by analogy with the formation of $MeCo^{III}PcCN^-$, both are in the same direction. The partial formation of a complex is not incompatible with the small spectral changes observed. However, the kinetics showed no deviation from being strictly first order in bromide at 25 °C with $[Br^-]$ up to 0.04 M.

Acknowledgment. We thank the Robert A. Welch Foundation for support of this work and for postdoctoral fellowship to W.G. and P.N.I.