Kinetics and Mechanisms of Formation, and of Reactions, of Intermediates in the Iron(II)–1,10-Phenanthroline–Cyanide and Related Systems †

By **John Burgess** * and **Robert I. Haines**, Chemistry Department, University of Leicester, Leicester LE1 7RH

Rate laws and rate constants are reported for the two stages of the reactions of $[Fe(L\text{–}L)_2(CN)_2]$ (L–L = 1,10-phenanthroline, 5-chloro-1,10-phenanthroline, or 2,2′-bipyridyl) with cyanide ion in aqueous solution. The preparation of $[Fe(5NO_2\text{-phen}\cdot CN)_2(5NO_2\text{-phen})]$, an intermediate in the reaction of $[Fe(5NO_2\text{-phen})_3]^{2+}$ with cyanide to give $[Fe(5NO_2\text{-phen})_2(CN)_2]$, is described, and the kinetics and mechanisms of some of its reactions, especially with hydroxide and with cyanide, are reported and discussed.

LOW-SPIN iron(II) complexes of the $[Fe(phen)_3]^{2+}$ type ‡ react with cyanides to give successively dicyano- and

$$[Fe(phen)_3]^{2+} \xrightarrow{2[CN]^-} [Fe(phen)_2(CN)_2] \xrightarrow{2[CN]^-} [Fe(phen)(CN)_4]^{2-} \quad (1)$$

tetracyano-products [equation (1)].[1] The kinetics of the first stage have been thoroughly studied;[2,3] the rate law is shown in equation (2). The dominant term in this rate law is usually the k_2 term, which corresponds to

$$-d[Fe(phen)_3{}^{2+}]/dt = (k_1 + k_2\,[CN^-])[Fe(phen)_3{}^{2+}] \quad (2)$$

bimolecular attack of cyanide ion at the complex. This applies to iron(II) complexes of, for example, 2,2′-bipyridyl,[4] 2,2′:6′,2″-terpyridyl,[5] and Schiff bases,[6] as

---

† No reprints available.

‡ phen = 1,10-Phenanthroline, bipy = 2,2′-bipyridyl.

[1] A. A. Schilt, *J. Amer. Chem. Soc.*, 1960, **82**, 3000.

[2] D. W. Margerum and L. P. Morgenthaler, *J. Amer. Chem. Soc.*, 1962, **84**, 706.

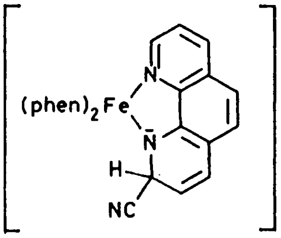
[3] J. Burgess, *Inorg. Chim. Acta*, 1971, **5**, 133.

[4] J. Burgess, *J.C.S. Dalton*, 1972, 1061.

[5] J. Burgess and M. V. Twigg, *J.C.S. Dalton*, 1974, 2032.

[6] J. Burgess, G. E. Ellis, D. J. Evans, A. Porter, R. Wane, and R. D. Wyvill, *J. Chem. Soc.* (*A*), 1971, 44; E. R. Gardner, F. M. Mekhail, and J. Burgess, *Internat. J. Chem. Kinetics*, 1974, **6**, 133.

well as of 1,10-phenanthroline. Originally it was assumed that the cyanide attacked at the iron atom in such complexes,[2,3] but more recently extensive and persuasive arguments have been advanced to support an alternative mechanism in which the cyanide (or hydroxide or alkoxide) attacks at the co-ordinated ligand, giving (1), with subsequent transfer of cyanide to the iron and finally formation of the product, $[\mathrm{Fe(phen)_2(CN)_2}]$.[7] Evidence has since been presented to support the formation of species of the type (1) in reactions of phen and bipy complexes of $\mathrm{Pt^{II}}$ with hydroxide[8] and of $\mathrm{Ru^{II}}$ with hydroxide, cyanide, methoxide, and ethoxide.[9] 5-Nitro-substituted complexes are especially suitable for the detection of such species, as for example in platinum(II)–hydroxide[10] and ruthenium(II)–nucleophile[9] systems. Similar intermediates are thought to occur in reactions of low-spin iron(II) complexes of the $[\mathrm{Fe(phen)_3}]^{2+}$ type with hydroxide or cyanide, but it is more difficult to obtain convincing evidence since these reactions are relatively fast. An early hint[11] of an intermediate in the $[\mathrm{Fe(5NO_2\text{-}phen)_3}]^{2+} + [\mathrm{OH}]^-$ reaction was eventually followed by a kinetic study of the build-up and decay of an intermediate.[12] Complexes of the type $[\mathrm{Fe(phen)_2(CN)_2}]$ react much more slowly than those of the $[\mathrm{Fe(phen)_3}]^{2+}$ type, and are therefore attractive for investigations in search of intermediates.



(1)

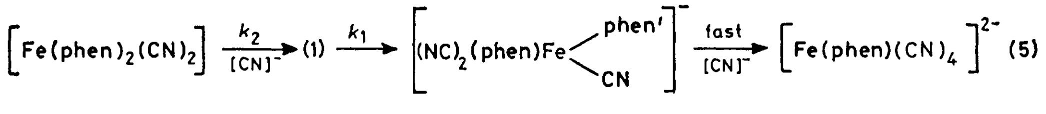
We have presented a preliminary report of the kinetics of generation and rearrangement of an intermediate in the reaction of $[\mathrm{Fe(5Cl\text{-}phen)_2(CN)_2}]$ with cyanide.[13] We now describe our kinetic results for the reactions of $[\mathrm{Fe(L\text{-}L)_2(CN)_2}]$ (L–L = bipy, phen, or 5Cl-phen) with cyanide. We also report the generation of an intermediate, $[\mathrm{Fe(5NO_2\text{-}phen{\cdot}CN)_2(5NO_2\text{-}phen)}]$, in the reaction of the $[\mathrm{Fe(5NO_2\text{-}phen)_3}]^{2+}$ cation with cyanide, and the kinetics of some reactions of this intermediate.

RESULTS AND DISCUSSION

$[\mathrm{Fe(phen)_2(CN)_2}]$ *and* $[\mathrm{Fe(5Cl\text{-}phen)_2(CN)_2}]$ *plus Cyanide.*—Repeat scan monitoring of the reaction of the complexes $[\mathrm{Fe(L\text{-}L)_2(CN)_2}]$ (L–L = phen, 5Cl-phen, or bipy) with cyanide ion showed that in each case there were two consecutive steps *en route* to the respective $[\mathrm{Fe(L\text{-}L)(CN)_4}]^{2-}$ products. For the bipy complex the changes in the spectra during the first stage were too small for any kinetic deductions to be possible, but for the phen and 5Cl-phen complexes the two steps were associated with marked changes in spectra. Moreover, the second step was in both cases sufficiently slower than the first for the reactions to be kinetically distinguishable and for individual rate constants to be obtained. All the runs were carried out with the cyanide in considerable excess, under which conditions first-order kinetics were followed for each stage. Observed first-order rate constants are reported in Table 1. The variation of rates with cyanide concentration indicates the rate laws shown in equation (3) for the first stage and in equation (4) for the second stage. Thus the first stage is first order in $[\mathrm{CN^-}]$, the second is zero order. This is

$$-\mathrm{d}[\mathrm{Fe(phen)_2(CN)_2}]/\mathrm{d}t = k_2[\mathrm{Fe(phen)_2(CN)_2}][\mathrm{CN^-}] \quad (3)$$

$$-\mathrm{d}[\text{intermediate}]/\mathrm{d}t = k_1[\text{intermediate}] \quad (4)$$



$$\left[\mathrm{Fe(phen)_2(CN)_2}\right] \xrightarrow[\mathrm{[CN]^-}]{k_2} (1) \xrightarrow{k_1} \left[(\mathrm{NC})_2(\mathrm{phen})\mathrm{Fe}\begin{smallmatrix}\mathrm{phen}'\\ \mathrm{CN}\end{smallmatrix}\right]^- \xrightarrow[\mathrm{[CN]^-}]{\text{fast}} \left[\mathrm{Fe(phen)(CN)_4}\right]^{2-} \quad (5)$$

TABLE 1

Observed first-order rate constants ($k_{\mathrm{obs.}}$) for the reactions of $[\mathrm{Fe(phen)_2(CN)_2}]$ and of $[\mathrm{Fe(5Cl\text{-}phen)_2(CN)_2}]$ with cyanide ion in aqueous solution at 373.5 K and I = 0.10 mol dm^{-3} (K[NO$_3$])

	[KCN]/mol dm^{-3}			
	0.02	0.04	0.06	0.10
	$10^2k_{\mathrm{obs.}}/\mathrm{s^{-1}}$			
First stage				
$[\mathrm{Fe(phen)_2(CN)_2}]$	0.14	0.45	0.55	1.10
$[\mathrm{Fe(5Cl\text{-}phen)_2(CN)_2}]$	0.65	1.7	3.3	5.2
	$10^4k_{\mathrm{obs.}}/\mathrm{s^{-1}}$			
Second stage				
$[\mathrm{Fe(phen)_2(CN)_2}]$	3.0	3.1	3.0	2.8
$[\mathrm{Fe(5Cl\text{-}phen)_2(CN)_2}]$	5.3	5.4	5.4	5.3

---

[7] R. D. Gillard, *Inorg. Chim. Acta*, 1974, **11**, L21; *Co-ordination Chem. Rev.*, 1975, **16**, 67.

[8] R. D. Gillard and J. R. Lyons, *J.C.S. Chem. Comm.*, 1973, 585.

[9] R. D. Gillard, C. T. Hughes, L. A. P. Kane-Maguire, and P. A. Williams, *Transition Metal Chem.*, 1976, **1**, 226; R. D. Gillard, L. A. P. Kane-Maguire, and P. A. Williams, *ibid.*, 1977, **2**, 12.

[10] E. Bielli, R. D. Gillard, and D. W. James, *J.C.S. Dalton*, 1976, 1837; K. H. Al-Obaidi, R. D. Gillard, L. A. P. Kane-Maguire, and P. A. Williams, *Transition Metal Chem.*, 1977, **2**, 64.

[11] J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1965, 4697.

[12] R. D. Gillard, C. T. Hughes, and P. A. Williams, *Transition Metal Chem.*, 1976, **1**, 51.

[13] J. Burgess, A. J. Duffield, and R. I. Haines, *Transition Metal Chemistry*, 1977, **2**, 276.

consistent with the reaction sequence shown in equation (5). In this sequence phen′ indicates unidentate phenanthroline; any intermediate containing such a species is likely to be transient. The first stages of the reactions of the $[Ru(5NO_2\text{-phen})_3]^{2+}$ cation with methoxide or ethoxide [9] and of $[Mo(CO)_4(5NO_2\text{-phen})]$ with cyanide [13] are reversible. It is therefore quite likely that the first stage of sequence (5) is also reversible, but that in this case the back reaction does not make a significant contribution to the observed kinetics.

The second-order rate constants, k_2, of equation (3) for the first stages of the reactions of $[Fe(phen)_2(CN)_2]$ and $[Fe(5Cl\text{-phen})_2(CN)_2]$ are 1.0 and 5.2 dm^3 mol^{-1} s^{-1} respectively at 373.5 K. The faster reaction of the 5Cl-phen complex is as expected from the established faster rate for $[Fe(5Cl\text{-phen})_3]^{2+}$ than for the $[Fe(phen)_3]^{2+}$ cation with cyanide.[3] The first-order rate constants for the transfer of cyanide from ligand to metal are 3.0×10^{-4} and 5.3×10^{-4} s^{-1} at 373.5 K for the phen and 5Cl-phen complexes respectively. Again the chloro-derivative is the more reactive, as expected.

$[Fe(bipy)_2(CN)_2]$ *plus Cyanide*.—As mentioned above, it is only possible to obtain rate constants for the second stage of this reaction. Observed first-order rate constants, obtained over a range of temperature, are reported in Table 2. As for the analogous phen complexes, the rate law is zero order in $[CN^-]$ [*cf.* equation (4)]. First-order rate constants for $[Fe(bipy)_2(CN)_2]$ (second stage) are considerably greater than those for the analogous phen and 5Cl-phen complexes at 373.5 K (Table 1); extrapolation of Table 2 data indicates a rate constant of 61×10^{-4} s^{-1} for $[Fe(bipy)_2(CN)_2]$ at the same temperature.

TABLE 2

Observed first-order rate constants ($k_{obs.}$) for the second stage of the reaction of $[Fe(bipy)_2(CN)_2]$ with cyanide ion in aqueous solution at $I = 0.67$ mol dm^{-3} ($K[NO_3]$)

	[KCN]/mol dm^{-3}			
	0.17	0.33	0.50	0.67
	$10^5k_{obs.}/s^{-1}$			
T/K				
343.9	2.6	2.6	2.4	2.6
348.7	6.9	6.5	6.5	6.7
350.6	10.1	9.7	10.2	9.8
352.1	12.9	12.8	11.6	12.8
356.7	31	31	29	31

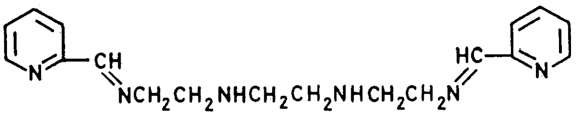
The observed rates for this reaction of $[Fe(bipy)_2(CN)_2]$ with cyanide are faster than those reported for the reactions of this complex with phen or its 5-sulphonato-derivative [14] or in acidic aqueous solution.[15] These comparisons favour the assignment of this step as an intramolecular transfer of cyanide ion rather than rate-determining dissociation of $[Fe(bipy)_2(CN)_2]$ itself. Iron–nitrogen bond breaking in the bipy analogue of (1) should be easier and faster than in $[Fe(bipy)_2(CN)_2]$. The very low sensitivity of the rate constant for the second stage of the $[Fe(bipy)_2(CN)_2] + [CN]^-$ reaction to solvent variation (Table 3) is also consistent with the proposed intramolecular nature of this process. Activation parameters for this reaction, computed using a standard unweighted least-mean-squares program, are $E^‡ = 197 \pm 3$ kJ mol^{-1} and $\log_{10}A = 30.4 \pm 0.4$ (or $\Delta H^‡ = 195 \pm 3$ kJ mol^{-1} and $\Delta S^‡ = 233 \pm 9$ J K^{-1} mol^{-1}). The activation energy (enthalpy) is unusually high, consistent with great difficulty in stretching and breaking the strong iron–nitrogen bonds in the complex. The very large positive activation entropy indicates an unexpectedly large increase in entropy in going from the initial to the transition state.

TABLE 3

Variation of the observed first-order rate constant ($k_{obs.}$) for the second stage of the $[Fe(bipy)_2(CN)_2] + [CN]^-$ reaction with solvent composition in binary aqueous mixtures at 356.6 K and [KCN] = 0.667 mol dm^{-3}

Solvent	$10^4k_{obs.}/s^{-1}$
Water	3.1
30% v/v n-Propanol	3.2
30% v/v Ethylene glycol	3.0
30% v/v Dimethyl sulphoxide	3.4

$[Fe(bpdo)(CN)_2]$ *plus Cyanide*.—The reaction between the iron(II) complex of the sexidentate Schiff base, 1,8-bis(2-pyridylmethyleneamino)-3,6-diazaoctane (bpdo), derived from pyridine-2-carbaldehyde and 3,6-diaza-octane-1,8-diamine, and cyanide obeys the usual rate law and produces a complex believed to be $[Fe(bpdo)(CN)_2]$, in which the originally sexidentate Schiff base ligand is quadridentate.[16] This ternary complex undergoes further reaction with cyanide, for which observed first-order rate constants are recorded in Table 4. This process is zero order in $[CN^-]$ and presumably corresponds to the second stage in the reaction between $[Fe(bipy)_2(CN)_2]$ and cyanide. Initial bimolecular attack of cyanide, difficult to detect for $[Fe(bipy)_2(CN)_2]$ (*cf.* above), could not be seen for the reaction of $[Fe(bpdo)(CN)_2]$. The reaction of $[Fe(bpdo)(CN)_2]$ is faster than that of $[Fe(bipy)_2(CN)_2]$ having a rate constant of 4×10^{-5} s^{-1} at 318 K compared with the $[Fe(bipy)_2(CN)_2] + [CN]^-$ reaction which has this rate constant at 345 K. The higher reactivity of the bpdo



bpdo

TABLE 4

Observed first-order rate constants ($k_{obs.}$) for the reaction of $[Fe(bpdo)(CN)_2]$ with cyanide in aqueous solution at 317.8 K and $I = 0.333$ mol dm^{-3} (KCl).

[KCN]/mol dm^{-3}	0.133	0.200	0.267	0.333
$10^5k_{obs.}/s^{-1}$	3.9	3.5	4.1	3.7

---

[14] J. Burgess, *J.C.S. Dalton*, 1972, 203.

[15] V. Balzani, V. Carassiti, and L. Moggi, *Inorg. Chem.*, 1964, **3**, 1252.

[16] J. Burgess and G. M. Burton, accepted for publication in *Rev. Latinoamer. Quim.*

complex is in line with other comparisons of Schiff base complexes and bipy or phen complexes in iron(II) kinetics.

$[Fe(5NO_2\text{-phen})_3]^{2+}$ *plus Cyanide.*—The advantages of the presence of a 5-nitro-substituent in facilitating detection of intermediates containing cyanide, hydroxide, or alkoxide bonded to a co-ordinated di-imine ligand,[9,10] and the detection of two stages in the reaction of the $[Fe(5NO_2\text{-phen})_3]^{2+}$ cation with hydroxide ion,[12] prompted us to examine the reaction of cyanide with this cation. We have not been able to establish the detailed kinetic pattern for the reaction sequence to $[Fe(5NO_2\text{-phen})_2(CN)_2]$, but we have isolated an intermediate and been able to investigate kinetics of reactions of this intermediate.

When Schilt's method [1] for the preparation of complexes $[Fe(L\text{-}L)_2(CN)_2]$ is used for L–L = 5-nitro-1,10-phenanthroline, the product of treating $[Fe(5NO_2\text{-phen})_3]^{2+}$ with cyanide is not the expected $[Fe(5NO_2\text{-phen})_2(CN)_2]$ but a red complex sparingly soluble in all the common solvents. Microanalysis indicates the presence of three $5NO_2$-phen molecules and two cyanide ions per iron atom {Found: C, 53.7; H, 3.20; N, 17.8. Calc. for $[Fe(5NO_2\text{-phen}{\cdot}CN)_2(5NO_2\text{-phen})]$: C, 54.5; H, 3.25; N, 18.4%}, but cannot distinguish between the salt $[Fe(5NO_2\text{-phen})_3][CN]_2$, the salt $[Fe(5NO_2\text{-phen})_2(5NO_2\text{-phen}{\cdot}CN)][CN]$, and the uncharged complex $[Fe(5NO_2\text{-phen})(5NO_2\text{-phen}{\cdot}CN)_2]$. However, this complex cannot be the first mentioned, as might be expected in view of the known low solubility of analogous thiocyanate salts,[17] since the visible-absorption spectrum of its saturated aqueous solution has $\lambda_{max.}$ 532 nm in contrast to 510 nm for the $[Fe(NO_2\text{-phen})_3]^{2+}$ cation.[18] The i.r. spectrum of our red complex is consistent with the formulation $[Fe(5NO_2\text{-phen})(5NO_2\text{-phen}{\cdot}CN)_2]$. It has $\nu(C{\equiv}N)$ at 2 190—2 200 cm^{-1}, close to the range 2 220—2 240 cm^{-1} characteristic of a cyano-group substituted in an aromatic ring [aliphatic $\nu(C{\equiv}N)$ at 2 250—2 260 cm^{-1}]. For cyanide bonded directly to Fe^{II} $\nu(C{\equiv}N)$ is, for example, at 2 040—2 090 cm^{-1} in the $[Fe(CN)_6]^{4-}$ anion and at 2 060 cm^{-1} in $[Fe(phen)_2(CN)_2]$. Ionic cyanide also has $\nu(C{\equiv}N)$ in this region, 2 070—2 100 cm^{-1}. There is only a very small peak here in quickly run spectra of freshly prepared samples of our red complex; this small peak grows quickly due to the build-up of $[Fe(5NO_2\text{-phen})_2(CN)_2]$. There are many differences in the aromatic 'fingerprint' region (665—805 cm^{-1}) between the spectrum of our complex and those of the $[Fe(5NO_2\text{-phen})_3]^{2+}$ cation and of $[Fe(5NO_2\text{-phen})_2(CN)_2]$. Indeed, the i.r. spectroscopic characteristics of our complex are analogous to those reported in the ruthenium(II)–5-nitro-1,10-phenanthroline–cyanide system,[9] and we assign the formula $[Fe(5NO_2\text{-phen}{\cdot}CN)_2(5NO_2\text{-phen})]$ to our complex by analogy with the ruthenium(II) assignment. Since the low solubility of our complex precludes the recording of satisfactory n.m.r. spectra, we are unable to decide whether the cyano-groups are bonded to C^2 or C^9 of the ligands.

Reactions of $[Fe(5NO_2\text{-phen}{\cdot}CN)_2(5NO_2\text{-phen})]$ *with Nucleophiles.*—The complex reacts with cyanide or hydroxide ion. In 30% methanol these reactions follow first-order kinetics (nucleophile in considerable excess). Plots of observed first-order rate constants (Table 5) against nucleophile concentration are linear with non-zero intercepts, indicating a rate law as shown in equation (6). The values of k_1 for the two reactions are equal within experimental error (2.5×10^{-3} s^{-1} at 317.7 K), indicating a common dissociative rate-determining step for this reaction path. Values of k_2 are 0.26 and 0.033 dm^3 mol^{-1} s^{-1} at 317.7 K for the reactions with cyanide and hydroxide respectively. Faster reaction with cyanide here parallels the faster reaction of cyanide than of hydroxide with the $[Fe(5NO_2\text{-phen})_3]^{2+}$ cation.[3,11]

TABLE 5

Observed first-order rate constants, $k_{obs.}$, for the reaction of $[Fe(5NO_2\text{-phen}{\cdot}CN)_2(5NO_2\text{-phen})]$ with cyanide and with hydroxide ions in 30% v/v aqueous methanol at 317.7 K and I = 0.21 mol dm^{-3} (NaCl)

	Nucleophile	
	$[CN]^-$	$[OH]^-$
$\frac{[\text{Nucleophile}]}{\text{mol dm}^{-3}}$	$10^2k_{obs.}/s^{-1}$	
0.002	0.298	0.273
0.004	0.349	
0.006	0.436	
0.008	0.491	0.289
0.010		0.297
0.020	0.770	
0.040	1.31	
0.050		0.412
0.100		0.581
0.150		0.753
0.180		0.859

$$-d[\text{complex}]/dt = (k_1 + k_2\,[\text{nucleophile}])[\text{complex}] \quad (6)$$

The mean value for k_1 from the cyanide and hydroxide reactions is considerably greater than the rate constants for disappearance of $[Fe(5NO_2\text{-phen}{\cdot}CN)_2(5NO_2\text{-phen})]$ in acid solution or in an aqueous solution containing the disodium salt of ethylenediaminetetra-acetic acid (H_4edta). At 317.7 K the rate constants in acid solution are 0.7×10^{-3} and 0.8×10^{-3} s^{-1} in 0.05 and 0.10 mol dm^{-3} sulphuric acid, and in edta solution 0.5×10^{-3} s^{-1} at edta concentrations both of 10^{-2} and 5×10^{-3} mol dm^{-3}. Presumably these rate constants refer to rate-determining dissociation of the complex, whereas the k_1 term in equation (6) can be ascribed to more rapid intramolecular cyanide transfer from ligand to iron. This argument is the same as that developed for the reaction of $[Fe(bipy)_2(CN)_2]$.

However, there is an important difference between the $[Fe(bipy)_2(CN)_2] + [CN]^-$ and the $[Fe(5NO_2\text{-phen}{\cdot}CN)_2(5NO_2\text{-phen})] + [CN]^-$ reactions. It appears (see above) that the reaction of, for example, $[Fe(bipy{\cdot}CN)(bipy)(CN)_2]^-$ or $[Fe(5Cl\text{-phen}{\cdot}CN)(5Cl\text{-phen})(CN)_2]^-$

---

[17] K. Madeja and E. König, *J. Inorg. Nuclear Chem.*, 1963, **25**, 377.

[18] M. L. Moss, M. G. Mellon, and G. F. Smith, *Analyt. Chem.*, 1942, **14**, 931.

with cyanide is zero order in $[\mathrm{CN}^-]$, whereas the reaction of $[\mathrm{Fe(5NO_2\text{-}phen{\cdot}CN)_2(5NO_2\text{-}phen)}]$ with cyanide has a rate law with a significant first-order term in cyanide concentration [equation (6)]. The explanation may lie in the strong electron-withdrawing and thereby ligand-activating properties of the 5-nitro-substituent facilitating attack by cyanide at this complex.

Conclusions.—The reactions of $[\mathrm{Fe(phen)_2(CN)_2}]$, $[\mathrm{Fe(5Cl\text{-}phen)_2(CN)_2}]$, and $[\mathrm{Fe(5NO_2\text{-}phen)_3}]^{2+}$ with cyanide proceed in two distinct stages, as has been demonstrated for the reaction of the last complex with hydroxide.[19] The first stages of the reactions of $[\mathrm{Fe(phen)_2(CN)_2}]$ and $[\mathrm{Fe(5Cl\text{-}phen)_2(CN)_2}]$ with cyanide and of the $[\mathrm{Fe(5NO_2\text{-}phen)_3}]^{2+}$ cation with hydroxide have rates dependent on the concentration of the attacking nucleophile, suggesting bimolecular attack of the nucleophile. This attack is reversible for the last case, as for the reaction of $[\mathrm{Mo(CO)_4(5NO_2\text{-}phen)}]$ with cyanide;[13] any reverse reaction is not kinetically detectable for the $[\mathrm{Fe(phen)_2(CN)_2}]$ and $[\mathrm{Fe(5Cl\text{-}phen)_2(CN)_2}]$ reactions. The second stages of all these reactions proceed at rates independent of cyanide concentration. The reaction of the $[\mathrm{Fe(5NO_2\text{-}phen)_3}]^{2+}$ plus cyanide reaction intermediate with further cyanide is exceptional in that its rate is dependent on the concentration of cyanide ion.

There are now many examples of this type of mechanism for reactions of di-imine complexes. Apart from the examples already mentioned, other reactions which are thought to proceed by initial attack at the di-imine ligand include thallium(III) oxidation of the $[\mathrm{Os(bipy)_3}]^{2+}$ and $[\mathrm{Os(phen)_3}]^{2+}$ cations,[20] and base hydrolysis of the $[\mathrm{Cr(bipy)_2Cl_2}]^+$ and $[\mathrm{Cr(phen)_2Cl_2}]^+$ cations.[21] Evidence in favour of structures of the type (1) is presented in many of the references cited already. N.m.r. evidence relating to addition to dicyano-complexes of the $[\mathrm{Fe(L{-}L)_2(CN)_2}]$ type has also been presented.[22] The formation of covalent hydrates[7,23] from $[\mathrm{Fe(L{-}L)_3}]^{2+}$, $[\mathrm{Fe(L{-}L)_2(CN)_2}]$, and $[\mathrm{Pt(L{-}L)(CN)_2}]$ di-imine derivatives, and of the closely related complex $[\mathrm{Fe(phen)_2(NCS)_2}]$,[24] and the role of such hydrates in aquation of iron(III) and nickel(II) di-imine complexes[25] provide further supporting evidence. Direct attack of the hydroxyl radical at the co-ordinated phenanthroline of the $[\mathrm{Fe(phen)_3}]^{2+}$ cation is suggested by the similarity of second-order rate constants for reaction of the cation and of 1,10-phenanthroline itself with the hydroxyl radical.[26]

Thus the majority of observations in this area support, or are at least consistent with, the hypothesis of reaction *via* initial attack of the nucleophile (cyanide, hydroxide, or alkoxide) at the co-ordinated di-imine. However, there are systems in which addition of such nucleophiles to co-ordinated di-imines is thought unlikely. Such reactions include those of $[\mathrm{Pt(bipy)_2}]^{2+}$ (ref. 27) and of $[\mathrm{Cr(bipy)_3}]^{3+}$ (ref. 28) with hydroxide, and of $[\mathrm{Pd(2,9Me_2\text{-}phen)_2}]^{2+}$ with cyanide.[29] The $[\mathrm{Pt(bipy)_2}]^{2+}$ case is controversial;[8,27] there is evidence[30] for the existence of an anion $[\mathrm{Pd(phen)(OH)_3}]^-$ to lend some credence to the hypothesis of direct approach of hydroxide to $\mathrm{Pd^{II}}$ or $\mathrm{Pt^{II}}$. The tendency of $\mathrm{Cr^{III}}$ to undergo nucleophilic substitution by an associative mechanism may dictate direct attack of the hydroxide at chromium rather than at the bipyridyl ligand in the $[\mathrm{Cr(bipy)_3}]^{3+}$ case. In the case of the palladium(II) cation, n.m.r. evidence is said to indicate, surprisingly, the bonding of two cyanide ions to the palladium to give six-co-ordinate $\mathrm{Pd^{II}}$. The formulation $[\mathrm{Ir(bipy)_2(bipy')(OH_2)}]^{3+}$ containing unidentate bipyridyl has been preferred to a covalent hydrate structure for the hydrate of the $[\mathrm{Ir(bipy)_3}]^{3+}$ cation.[31]

We therefore conclude by accepting the hypothesis of an intermediate in which the incoming nucleophile is bonded initially to the co-ordinated di-imine, as in formula (1), and using this mechanism in the interpretation of our kinetic results. However, we recognise that, while most of the experimental evidence fits this scheme, the case in its favour is not irrefutable and there are a few observations on these and related systems which favour alternative mechanisms.

EXPERIMENTAL

The complexes $[\mathrm{Fe(L{-}L)_2(CN)_2}]$ (L–L = bipy, phen, or 5Cl-phen) were made by Schilt's method.[1] The complex $[\mathrm{Fe(5NO_2\text{-}phen{\cdot}CN)_2(5NO_2\text{-}phen)}]$ was prepared by adding a saturated aqueous solution of potassium cyanide to a strong aqueous solution of $[\mathrm{Fe(5NO_2\text{-}phen)_3}][\mathrm{SO_4}]$ at or below room temperature; the use of more dilute solutions or of higher temperatures leads to contamination by $[\mathrm{Fe(5NO_2\text{-}phen)_2(CN)_2}]$. Pure $[\mathrm{Fe(5NO_2\text{-}phen)_2(CN)_2}]$ is best prepared by heating $[\mathrm{Fe(5NO_2\text{-}phen{\cdot}CN)_2(5NO_2\text{-}phen)}]$ under reflux in methanol. The reagents used in the kinetic studies were all AnalaR grade and used without further purification. Kinetic runs were carried out in the thermostatted cell compartment of a Unicam SP 800A or SP 1800 recording spectrophotometer. Duplicate runs were carried out to obtain the results in Tables 2—4; the rate constants reported in Table 1 are mean values from between three and six determinations.

We thank the Royal Society for the award of a Grant-in-aid for the purchase of the SP 800A spectrophotometer, and Professor R. D. Gillard, Dr. L. A. P. Kane-Maguire, and Dr. P. A. Williams for helpful and interesting discussions.

[7/2066 *Received, 24th November*, 1977]

---

[19] R. D. Gillard, C. T. Hughes, and P. A. Williams, *Transition Metal Chem.*, 1976, **1**, 51.

[20] G. Nord, *Inorg. Chem.*, 1976, **15**, 1921.

[21] J. Josephsen and C. E. Schäffer, *Chem. Comm.*, 1970, 61.

[22] R. D. Gillard, C. T. Hughes, L. A. P. Kane-Maguire, and P. A. Williams, *Transition Metal Chem.*, 1976, **1**, 114.

[23] R. D. Gillard, L. A. P. Kane-Maguire, and P. A. Williams, *Transition Metal Chem.*, 1976, **1**, 247.

[24] M. Teodorescu, *Rev. Roumaine Chim.*, 1976, **21**, 1031.

[25] R. D. Gillard, L. A. P. Kane-Maguire, and P. A. Williams, *Transition Metal Chem.*, 1977, **2**, 47.

[26] E. S. Floryan and P. Pagsberg, *Internat. J. Radiation Phys. Chem.*, 1976, **8**, 425.

[27] G. Nord, *Acta Chem. Scand.*, 1975, **A29**, 270.

[28] M. Maestri, F. Bolletta, N. Serpone, L. Moggi, and V. Balzani, *Inorg. Chem.*, 1976, **15**, 2048.

[29] R. D. Gillard, L. A. P. Kane-Maguire, and P. A. Williams, *Transition Metal Chem.*, 1977, **2**, 55.

[30] V. Parthasarathy and C. K. Jørgenson, *Chimia*, 1975, **29**, 210.

[31] R. J. Watts, J. S. Harrington, and J. Van Houten, *J. Amer. Chem. Soc.*, 1977, **99**, 2179.