PERKIN 2

Sandmeyer reactions. Part 6.[1] A mechanistic investigation into the reduction and ligand transfer steps of Sandmeyer cyanation

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For Sandmeyer cyanation at 298 K in 50% v/v aqueous acetonitrile buffered at pH 8, absolute rate constants have been obtained for the reduction of 4-methoxybenzenediazonium tetrafluoroborate by the cyanocuprate(I) anions $Cu^I(CN)_4^{3-}$, $Cu^I(NCMe)(CN)_3^{2-}$ and $Cu^I(NCMe)_2(CN)_2^-$ as (0.50 ± 0.05), (0.12 ± 0.03) and 0.0 $dm^3\ mol^{-1}\ s^{-1}$, respectively. The relative reactivity of the two reactive cyanocuprates reflects the estimated difference in their standard reduction potentials. Ligand transfer to the aryl radical from the cyanocuprate(II) anions produced in the reaction occurs within the solvent cage. By use of radical clocks, first order rate constants of the order of $1 \times 10^8\ s^{-1}$ for ligand transfer between the caged reactants can be evaluated although the transfer rate may vary from one aryl radical to another. No difference was discerned in ligand transferring reactivity between the two cyanocuprate(II) complexes involved.

Although the general mechanism of the Sandmeyer reaction is well understood (Scheme 1),[2,3] most previous studies in this field have focused on the ligand transfer;[3–8] in recent times less work has been devoted to the initial reduction step.[9–12]

$$ArN_2^+ + Cu^IX_n^{(n-1)-} \longrightarrow ArN_2^{\bullet} + Cu^{II}X_n^{(n-2)-}$$

$$ArN_2^{\bullet} \longrightarrow Ar^{\bullet} + N_2$$

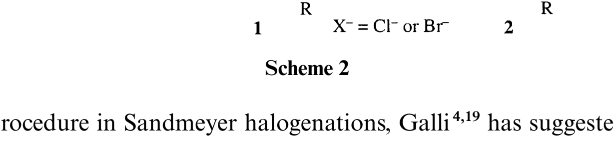
$$Ar^{\bullet} + Cu^{II}X_n^{(n-2)-} \longrightarrow ArX + Cu^IX_{(n-1)}^{(n-2)-}$$

$$Cu^IX_{(n-1)}^{(n-2)-} + X^- \longrightarrow Cu^IX_n^{(n-1)-}$$

$X^- = Cl^-$, Br^- or CN^-

Scheme 1

Customarily, Sandmeyer reactions are carried out in Cu^I-containing aqueous solutions in the presence of chloride, bromide or cyanide ions.[13] The Cu^{II} needed in the ligand transfer step is produced *in situ* and the copper cycles between the two oxidation states.[3] The low concentration of Cu^{II} under these conditions constrains the ligand transfer step and it is possible for the intermediate aryl radical to react alternatively. Indeed, if reaction is carried out in the presence of an alkene, when copper(I) chloride or bromide is used as the reductant, the intermediate aryl radical can add to the double bond giving a radical adduct **1** which subsequently reacts with Cu^{II} and the product is the corresponding haloalkylbenzene **2** (Meerwein reaction, Scheme 2).[14–18] As an improvement to synthetic procedure in Sandmeyer halogenations, Galli[4,19] has suggested the use of mixed Cu^I and Cu^{II} salts: the ligand transfer is thereby no longer dependent on just the Cu^{II} formed concomitantly with the aryl radical and the efficiency of the ligand transfer step is increased.



Scheme 2

When cyanide is the ligand, only the Sandmeyer product, the benzonitrile, is obtained in the presence of alkene,[20] demonstrating that the transfer of cyanide from concomitantly formed Cu^{II} is sufficiently fast to prevent competition from other bimolecular reactions of the aryl radical. By contrast, for Sandmeyer hydroxylation, the ligand transfer step is so slow that the resting state of the copper has to be $Cu(OH_2)_6^{2+}$ and the lower oxidation state required for reducing the diazonium ion is supplied either from Cu_2O in suspension[21] or by reduction of a small part of the Cu^{II} by addition of ascorbic acid or other initiating reductant.[6–8]

Cowdrey and Davies[11] attempted to measure the kinetics of the chlorination reaction using Cu^I solutions. They recognised that in aqueous solutions Cu^I would form a series of complexes with chloride ions according to the equilibria shown in Scheme 3 and from their kinetic evidence they deduced $Cu^ICl_2^-$ to be the most active reducing agent but the mechanism they proposed is at odds with that now accepted.[2,3]

$$Cu^+ + X^- \rightleftharpoons Cu^IX$$

$$Cu^IX + X^- \rightleftharpoons Cu^IX_2^-$$

$$Cu^IX_2^- + X^- \rightleftharpoons Cu^IX_3^{2-}$$

$$Cu^IX_3^{2-} + X^- \rightleftharpoons Cu^IX_4^{3-}$$

$$H^+ + X^- \rightleftharpoons HX$$

$X^- = Cl^-$, Br^- or CN^-

Scheme 3

Galli[12] carried out a study in which he decomposed pairs of diazonium ions in solutions containing excess of chloride but less than equivalent amounts of Cu^{II} and various reductants including Cu^I. He confirmed that diazonium ions bearing electron withdrawing substituents react the faster, which is consistent with the acceptance of an electron from a reducing agent, and he suggested the reaction to be an outer sphere reduction where the rate is dependent on the reduction potential of the reductant. In non-Sandmeyer (*i.e.* copper-free) conditions,

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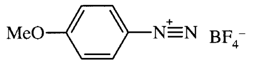
outer-sphere reductions of diazonium ions by ferrocyanide in aqueous solution and by decamethylferrocene in MeCN have been reported by Doyle and co-workers[22] and we have previously inferred comparable behaviour in their reduction by Fe^{2+} ligated by EDTA in aqueous solution at pH 9.[23]

No kinetic study of Sandmeyer cyanation has been carried out, perhaps because of the formation of the intermediate solid or oily phases which have been reported for the reaction in aqueous solution.[24] Nevertheless, cyanide being a ‘pseudohalide’, the reaction is believed to occur in a manner comparable to that of the copper(I) halides and there may well be more than one active cyanocuprate species. In this paper we report the evaluation of absolute rate constants for the reduction of 4-methoxybenzenediazonium ion, **3**, by various cyanocuprate(I) complexes in 50% v/v aqueous acetonitrile at pH 8 and 298 K.



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Results

(i) Identification of the intermediate phase in Sandmeyer cyanation

Synthetically, Sandmeyer cyanation is usually carried out in aqueous solution where the diazonium ion is added to a cyanocuprate(I) solution.[13] There have been reports of the formation of solid or oily intermediate phases, an explanation for which has been suggested to be the reversible formation of the diazocyanide (ArN=N–CN).[24] However, diazonium salts of halocuprate anions which are relatively stable to oxidation are well known and the structure of a benzenediazonium bromocuprate(I) ($PhN_2^+\ Cu_2Br_3^-$) has been resolved by X-ray crystallography;[25] it is hence possible that the intermediate observed in Sandmeyer cyanation is merely a simple salt of the diazonium ion and a cyanocuprate anion. Investigations were carried out to confirm this suggestion by comparing the spectroscopic properties of the isolated solid with those of appropriate diazocyanide and diazonium and cyanocuprate salts. In order to minimise contamination by decomposition products derived from the diazonium ion, **3** (as its tetrafluoroborate) was chosen as it is relatively stable to heterolysis[26] and the solid formed in its Sandmeyer cyanation reaction (using a solution of CuCN in aqueous KCN with $[CN^-] : [Cu^+] = 3 : 1$) was collected. (*E*)-4-Methoxybenzenediazocyanide was synthesised following the procedure of Ignasiak and coworkers.[27] The two solids have different solubilities in $CHCl_3$ and different IR spectra which clearly indicate that the isolated solid is not the diazocyanide. Moreover, the intermediate solid isolated from the Sandmeyer reaction has IR and solid phase ^{13}C CP-MAS NMR spectra which are consistent with it being the simple salt $(ArN_2^+)_2\ Cu(CN)_3^{2-}$ containing some Sandmeyer product, 4-methoxybenzonitrile, as contaminant (see Experimental). The suggested presence of the ion $Cu(CN)_3^{2-}$ is based merely on the stoichiometric ratio of Cu^+ and CN^- used and not on rigorous proof but the observation of a single signal for the CN component in both the ^{13}C-NMR and IR spectra of the intermediate precipitate and the potassium salt is consistent with this formulation.

(ii) Optimisation of conditions for the measurement of Sandmeyer cyanation kinetics

In order to measure kinetics for the Sandmeyer cyanation reaction, a homogenous solution is required in which the concentrations of the various reducing cyanocuprates are known. A 50% v/v aqueous acetonitrile solvent provides the requisite conditions: formation constants have been reported[28] for the various cyanocuprate complexes (Scheme 3) and these allow calculation of the concentration of each species at the start of the reaction (Table 1),[29] hence allowing estimation of the rate of reduction of **3** by each copper complex. (For convenience, only the cyanide ligands on Cu^I will be indicated whereas, in fact, in aqueous acetonitrile solutions at low and intermediate pH values, coordination sites not occupied by CN^- are occupied by MeCN.)[28,30] Cyanide ions and protons, however, exist in an equilibrium with hydrogen cyanide ($pK_a = 9.93$ in 50% v/v aqueous MeCN)[28] and so the pH must be known and maintained in order to determine accurately the concentration of cyanide available for co-ordinating Cu^I. The solution was therefore buffered and a pH of 8 was chosen. Practically, a solution of KH_2PO_4 (0.1 mol dm^{-3}) and K_2HPO_4 (0.062 mol dm^{-3}) was used to buffer the reaction and, although this mixture gives a pH of 7 in a purely aqueous medium, it was found that in 50% v/v aqueous MeCN the co-solvent perturbs the buffering equilibria so that a value closer to 8 was measured. This value could then be adjusted to 8 precisely by the addition of a solution of H_2SO_4 or NaOH (in 50% v/v aqueous MeCN) as appropriate. The pH of the mixture was measured using a pH meter previously calibrated with aqueous standard solutions and it was assumed that the measured value obtained for the mixed solvent remained representative of the true oxonium ion concentration. Reaction at higher pH was found not to give good kinetic results perhaps owing to the intervention of species of the type $Cu^I(CN)_n(OH)_m^{(m+n-1)-}$ which have been suggested to be present in these conditions.[28]

(iii) Measurement of the rates of reduction in the Sandmeyer cyanation

Experimentally, the rate of reduction of **3** was determined by measuring the evolution of N_2 over times up to *ca.* 2 h at 298 K, the amount evolved being quantified continuously by use of an apparatus adapted from an original design by Crossley and co-workers.[31] The system operates so that the nitrogen produced displaces from a glass cell an equal volume of water, which is collected and weighed continuously by an electronic top-pan balance. The mass of water is equated to the volume of nitrogen which is evolved and the molar quantity, at 298 K, can hence be calculated using the ideal gas law. Experiments were restricted to total concentrations of cyanide between 0.099 and 0.152 mol dm^{-3} (for $[Cu^+]_{total} = 0.038$ mol dm^{-3} and $[ArN_2^+] = 0.0095$ mol dm^{-3}) as at lower values a white precipitate of CuCN formed[28] and at higher values the solution separated into two phases, presumably because the salt concentration rises to the point where MeCN is no longer miscible. It is evident from Fig. 1 and Table 1 that, in the accessible range of cyanide concentration, the concentrations of free Cu^+ and CuCN are negligible but those of the three anionic cyanocuprates are significant and all should be considered as potential reductants of **3**.

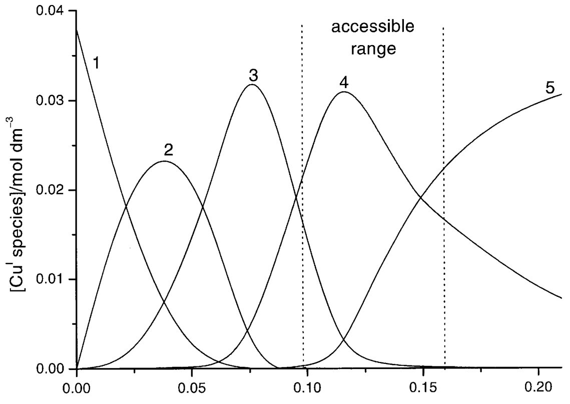


Fig. 1 Distribution of Cu^I species as a function of cyanide concentration in aqueous MeCN (1 : 1). 1, Cu^+; 2, CuCN; 3, $Cu(CN)_2^-$; 4, $Cu(CN)_3^{2-}$; 5, $Cu(CN)_4^{3-}$.

Table 1 Initial species distribution[a]/mol dm^{-3} and observed first order rate constants for Sandmeyer cyanation of 4-methoxybenzenediazonium tetrafluoroborate in 50% v/v aqueous acetonitrile containing Cu$^+$ (0.038 mol dm^{-3}) and various concentrations of KCN at 298 K and pH 8

$[CN^-]_{total}$	$10^6[CN^-]$	$10^4[HCN]$	$10^{11}[Cu^+]$	$10^7[CuCN]$	$10^3[Cu(CN)_2^-]$	$10^2[Cu(CN)_3^{2-}]$	$10^3[Cu(CN)_4^{3-}]$	10^3k_{obs}[b]
0.0991	2.78	2.37	6240	999	15.3	2.23	0.333	2.34 ± 0.11
0.107	6.40	5.45	654	241	8.48	2.85	0.981	2.74 ± 0.11
0.114	15.4	13.1	52.5	46.3	3.91	3.15	2.60	3.80 ± 0.17
0.122	38.2	32.5	3.26	7.18	1.51	3.03	6.22	6.20 ± 0.32
0.130	72.6	61.8	0.423	1.77	0.705	2.68	10.5	7.08 ± 0.36
0.137	110	93.5	0.107	0.679	0.410	2.36	13.9	9.12 ± 0.43
0.145	160	136	0.0298	0.275	0.242	2.03	17.5	9.56 ± 0.62
0.152	210	179	0.0115	0.140	0.161	1.78	20.1	11.8 ± 0.60

[a] Calculated using equilibrium constants for ionic strength 1.0 mol dm^{-3} from ref. 28; the actual ionic strength varied in the range *ca.* 0.3–0.5 mol dm^{-3}. [b] The uncertainties are the 95% confidence limits.

If it is assumed that the reduction of **3** by each cyanocuprate is a second order process overall, the rate of evolution of N_2 is given by eqn. (1):

$$d[N_2]/dt = -d[\mathbf{3}]/dt = k_2[Cu(CN)_2^-][\mathbf{3}] + k_3[Cu(CN)_3^{2-}][\mathbf{3}] + k_4[Cu(CN)_4^{3-}][\mathbf{3}] = k_{obs}[\mathbf{3}] \quad (1)$$

i.e.

$$k_{obs} = k_2[Cu(CN)_2^-] + k_3[Cu(CN)_3^{2-}] + k_4[Cu(CN)_4^{3-}] \quad (2)$$

where k_{obs} is the observed combined first order rate constant.

Eqn. (3) follows from the first order condition:

$$[N_2] = [\mathbf{3}]_0\{1 - \exp(-k_{obs}t)\} \quad (3)$$

where $[N_2]$ is the amount of N_2 (in units of concentration) produced at time t and $[\mathbf{3}]_0$ is the initial concentration of **3**. For decompositions involving 1 mmol of **3**, this expression is adapted to eqn. (4), where v_t is the volume of N_2, in cm^3, evolved at time t and v_m is the millimolar volume at SATP (*i.e.* 24.790 cm^3 mmol^{-1}).

$$100v_t/v_m = A\{1 - \exp(-k_{obs}t)\} + C \quad (4)$$

Eqn. (4) thus expresses the percentage of the theoretical evolution of N_2 as a function of time in terms of three constants A, C and k_{obs}; C represents the amount of nitrogen which does not displace water immediately the timing commences ($t = 0$) and A represents $[\mathbf{3}]_0$ adjusted for this inertial factor and for minor side reactions (*ca.* 10%) which reduce the theoretical nitrogen yield.

Reactions were carried out for solutions of Cu^I (0.038 mol dm^{-3}) containing various cyanide concentrations within the homogeneous range and at least two runs were carried out for each total cyanide concentration. All the kinetic data were fitted to eqn. (4) using non-linear regression. Excellent fits were obtained in every case (*e.g.* Fig. 2) and the average combined first order rate constants, k_{obs}, found for the various initial total cyanide concentrations are given in Table 1.

Preliminary estimates of the second order rate constants k_2–k_4 were obtained by a multiple linear regression of k_{obs} upon the initial equilibrium concentrations of cyanocuprate anions taken from Table 1 [eqn. (2)]. Inclusion of the term for $Cu(CN)_2^-$ led to a value of k_2 which is not significantly different from zero. Hence it is inferred that $Cu(CN)_2^-$ plays no part in the reduction process and the dependence of k_{obs} on cyanocuprates is given by eqn. (5).

$$k_{obs} = k_3[Cu(CN)_3^{2-}] + k_4[Cu(CN)_4^{3-}] \quad (5)$$

In the reaction, Cu^I is recycled (*i.e.* Cu^{II} formed in the rate-determining step is rapidly returned to Cu^I by ligand transfer) and the total Cu^I concentration remains essentially constant. However, owing to the limited practical range of cyanide concentrations and the need to use a quantity of **3** sufficient to produce enough N_2 for measurement, $[CN^-]_{total}$ falls significantly during the reaction (by *ca.* 10% in the worst case) as the ion is diverted to the product, 4-MeOC$_6$H$_4$CN, and such loss from the inorganic reservoir results in a significant change in the distribution of Cu^I species over the course of the reaction. For each decomposition reaction the amount of diazonium salt used is known (1 mmol). It is thus possible to calculate the amounts of cyanide lost from the inorganic reservoir for various extents of reaction (assuming all diazonium ion is converted to 4-methoxybenzonitrile, a reasonable assumption since the yields of the latter are typically *ca.* 90%). For each chosen extent of reaction, the distribution of cyanocuprate ions can be recalculated and the corresponding values of k_3 and k_4 found *via* eqn. (5). The values found for five different percentage extents of reaction are given in Table 2. Numerically both constants show an apparent upward trend though the value of k_4 is constant within the quoted uncertainty (95% confidence interval); the apparent increase in k_3 is somewhat outside this interval. We suggest this variation has its origin in the change in ionic strength over the course of reaction. However, the mean values of both constants do not differ significantly from the

Table 2 Second order rate constants for various extents of conversion of **3** into 4-methoxybenzonitrile

Conversion of **3** (%)	k_3/dm^3 mol^{-1} s^{-1}	k_4/dm^3 mol^{-1} s^{-1}
0	0.086 ± 0.044	0.486 ± 0.054
25	0.100 ± 0.044	0.496 ± 0.057
50	0.116 ± 0.046	0.502 ± 0.062
75	0.131 ± 0.047	0.507 ± 0.068
100	0.145 ± 0.047	0.511 ± 0.075
Mean	0.116 ± 0.026	0.500 ± 0.049

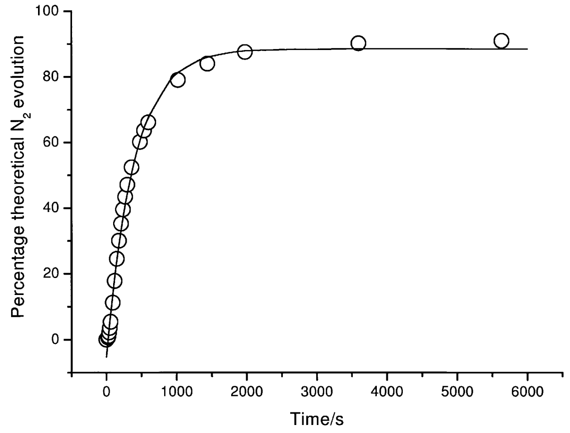


Fig. 2 Evolution of N_2 as a function of time for a run with [Cu^I] = 0.038 mol dm^{-3}, $[CN^-]_{total}$ = 0.0991 mol dm^{-3} fitted by eqn. (4) with A = 93.75%, C = −5.25% and k_{obs} = 2.5 × 10^{-3} s^{-1}.

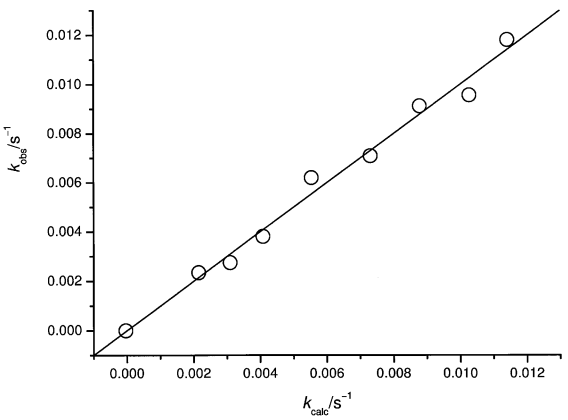


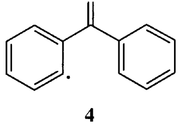
Fig. 3 Plot of k_{obs} *versus* k_{calc} given by eqn. (5).

values for 50% conversion and we propose they be taken as the best estimates of k_3 and k_4. Fig. 3 shows the plot of k_{obs} *versus* k_{calc}, the latter being the calculated combined first order rate constant obtained using these values of k_3 and k_4 and the cyanocuprate concentrations appropriate at 50% conversion of **3**.

In summary, for the Sandmeyer cyanation of 4-methoxybenzenediazonium ion in 50% v/v aqueous acetonitrile at pH 8 and 298 K, of the potential reductants in the system, Cu^+ and CuCN were not present in significant concentrations in the conditions employed; $Cu(CN)_2^-$ was present but unreactive whereas both $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ reacted with respective rate constants of (0.12 ± 0.03) and (0.50 ± 0.05) $dm^3\ mol^{-1}\ s^{-1}$; *i.e.* $Cu(CN)_4^{3-}$ reacts some 4.3-fold faster than $Cu(CN)_3^{2-}$.

(iv) Estimation of rates of caged cyanide ligand transfer

In previous studies[7,8] we have estimated rate constants for the transfer of ligands from Cu^{II} to aryl radicals by use of the 2-benzoylphenyl radical, **4**, as a radical clock. Using a prior estimate of the rate of cyclisation of the radical, second order rate constants for ligand transfer were calculated from measurements of the variation in the ratio of the substituted to cyclised products as a function of the concentration of the Cu^{II} ligand-transfer agent. This procedure cannot be applied to find second order rate constants for cyanide ligand transfer because cyanocuprate(II) complexes are unstable, addition of cyanide to an aqueous solution of Cu^{2+} resulting in the formation of cyanogen and cyanocuprate(I) *via* transient cyanocuprate(II) in a reaction which is of second order in the latter.[32,33] It is therefore impossible to observe variation in product ratio as a function of the concentration of added cyanocuprate(II).



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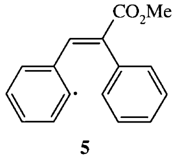

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Under the conditions of Sandmeyer cyanation, cyanocuprate(II) is formed in the first propagation step, *i.e.* by the overall rate-determining reduction of diazonium ion by cyanocuprate(I) (Scheme 1) and the fact that the derived aryl radical is not captured by alkene in a Meerwein reaction[20] indicates that it does not escape from the solvent cage which also contains the concomitantly formed cyanocuprate(II). If an aryl radical clock is produced during Sandmeyer cyanation, the ligand transfer and the cyclisation of the radical clock can therefore be regarded as competitive first order reactions of the caged pair of reactants and, as neither of the competing processes is likely to be reversible, the molar ratio of their products may be taken to equal the ratio of their rate constants. Under the assumption that the radical clock undergoes cyclisation at the same rate irrespective of whether or not it is caged with cyanocuprate, a first order rate constant for the caged ligand transfer may then be evaluated from the product ratio (Scheme 4). The rate of fragmentation of the intermediate diazenyl radical is of no consequence as neither of the two competitive reactions can occur until after it has occurred.

Table 3 gives the molar product ratios obtained using two radical clocks in Sandmeyer cyanation: the 2-benzoylphenyl radical, **4**, and the stilbene-derived radical, **5**, for which cyclisation rate constants, k^{Cyc}, have been given previously as (8 ± 0.9) × 10^5 and (3 ± 0.5) × $10^9\ s^{-1}$, respectively.[7,34] It is apparent from the product ratios that neither clock is ideal for obtaining a ligand transfer rate, **4** cyclising rather slowly relative to ligand transfer and **5** rather fast with the consequence that both give product ratios in which the proportion of minor product is small. Nevertheless, each clock gives a characteristic mean ratio of aryl nitrile to cyclised product which is independent of the concentration of the reducing agent and, for **4**, of the proportion of copper to ligand. It is easily shown for each clock that the ligand transfer rate constant, k^{CN}, is given by $k^{CN} = k^{Cyc} \times$ product ratio. Inserting values, **4** gives $k^{CN} = (3.5 \pm 0.5) \times 10^7\ s^{-1}$ and **5** gives $k^{CN} = (1.8 \pm 0.3) \times 10^8\ s^{-1}$, values which agree within a factor of 5 although, given the difference in the substituents *ortho* to the radical centre in **4** and **5**, the difference is probably significant; we have shown previously that second order ligand transfer rate constants of simply substituted aryl radicals are sensitive to variation in substitution[8] and that methylation of the radical ring of **4** *meta* to the radical centre doubles the rate at which it undergoes Sandmeyer hydroxylation.[1] The radical **4** reacts in bimolecular chloride ligand transfers with $Cu^{II}Cl_2$ and $Cu^{II}Cl_3^-$ with a statistically corrected second order rate constant of 1 × $10^8\ dm^3\ mol^{-1}\ s^{-1}$. Since, in buffered conditions, the product ratio from **4** shows no significant variation as the $[CN^-]/[Cu^I]$ ratio is varied, it appears that the ligand transfer rate is independent of the particular cyanocuprate with which the radical is caged. The first order rate constants obtained are thus global values applicable to caged ligand transfer from either of the two cyanocuprate(II) anions which may be produced together with the particular radical clock.

Discussion

(i) Reduction of 4-methoxybenzenediazonium tetrafluoroborate by $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$

We have shown that $Cu(CN)_4^{3-}$ reduces 4-methoxybenzenediazonium ion, **3**, 4.3-fold faster than $Cu(CN)_3^{2-}$. Galli[12] has previously related the rate of the reduction step for diazonium ions to the standard reduction potential of the reductant invoking a threshold potential of *ca.* 1 V above which reduction fails and suggesting that the lower the reduction potential, the faster the rate of reduction. In order to ascertain whether this trend is followed by the cyanocuprates, information on the reduction potentials of $Cu^I(CN)_3^{2-}$ and $Cu^I(CN)_4^{3-}$ is required as they have not been measured experimentally in 50% v/v aqueous MeCN.

From the Nernst equation it follows that the standard reduction potential, E_n, of a general cyanocuprate redox couple, $Cu^{II}(CN)_n^{(n-2)-}/Cu^I(CN)_n^{(n-1)-}$ in aqueous solution, is given by eqn. (6):

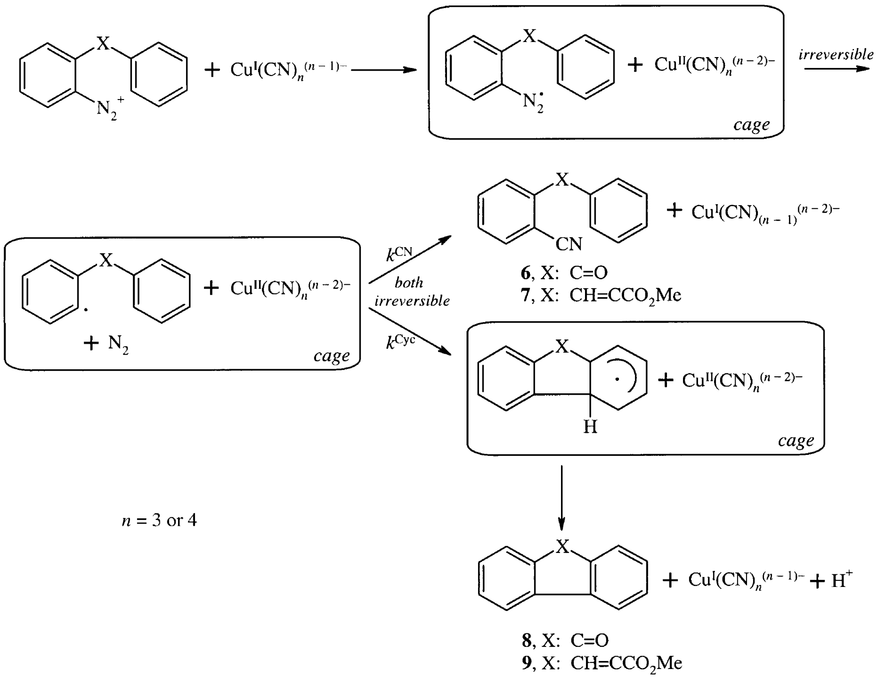
$$E_n = E\{Cu^{2+}/Cu^+\} - (RT/F)\ln(\beta^{II}_n/\beta^{I}_n) \quad (6)$$

Where $E\{Cu^{2+}/Cu^+\}$ is the standard reduction potential for the aquated ions, β^{I}_n and β^{II}_n are the appropriate overall formation constants of the cyanocuprate complexes comprising the couple, R is the gas constant, T the absolute temperature and F the Faraday constant.

Table 3 Molar product ratios from competitive caged cyanide ligand transfer and cyclisation of radical clocks **4** and **5**

Radical clock **4**[a]			Radical clock **5**[b]		
$[Cu^I]$/mol dm^{-3}	$[CN^-]$/mol dm^{-3}	[**6**]/[**8**]	$[Cu^I]$/mol dm^{-3}	$[CN^-]$/mol dm^{-3}	[**7**]/[**9**]
0.03	0.09	42.9	0.17	0.50	0.061
0.04	0.12	41.3	0.25	0.75	0.055
0.06	0.18	42.6	0.33	1.00	0.061
0.08	0.24	45.5	0.42	1.25	0.062
0.042	0.100	47.0			*Mean* 0.060 ± 0.006
0.042	0.117	42.5			
0.042	0.133	41.4			
0.042	0.166	42.3			
		Mean 43.2 ± 0.4			

[a] Solvent 50% v/v aqueous MeCN buffered at pH 8. [b] Solvent 10% v/v aqueous MeCN, unbuffered.



Scheme 4

Hence,

$$E_3 - E_4 = (RT/F)\ln[(\beta^{II}_4/\beta^{I}_4)/(\beta^{II}_3/\beta^{I}_3)] = (RT/F)\ln(K^{II}_4\beta^{I}_3/\beta^{I}_4) \quad (7)$$

where K^{II}_4 is the stepwise stability constant for the formation of $Cu^{II}(CN)_4^{2-}$ from $Cu^{II}(CN)_3^-$ and CN^-. An expression analogous to eqn. (7) is expected to hold for solutions in 50% v/v aqueous MeCN. The overall formation constants for $Cu^I(CN)_3^{2-}$ (β^I_3) and $Cu^I(CN)_4^{3-}$ (β^I_4) in this solvent are $10^{22.21}$ (dm^3 mol^{-1})^3 and $10^{25.95}$ (dm^3 mol^{-1})^4, respectively.[28] In order to evaluate K^{II}_4 for aqueous solution, Katagiri and co-workers[32,33] first used eqn. (6) with an experimental value for $E_4\{Cu(CN)_4^{2-}/Cu(CN)_4^{3-}\}$ of 0.54 V *vs.* NHE to evaluate β^{II}_4 as $10^{24.0}$ (dm^3 mol^{-1})^4; however, Beck[35] has pointed out that the value taken for β^I_4 [$10^{30.53}$ (dm^3 mol^{-1})^4] was too high. Adopting the recommended value[35] for β^I_4 [$10^{27.9}$ (dm^3 mol^{-1})^4] we re-evaluate β^{II}_4 as $10^{21.35}$ (dm^3 mol^{-1})^4. Then, from this value, after the manner of Katagiri and co-workers,[32,33] by assuming that the ratios of consecutive stepwise stability constants of cyanocuprate(II) complexes $K_{(n+1)}/K_n$ equal[36] the means of those of chlorocuprate(II) complexes[37] and amminecopper(II) complexes,[38] we estimate the stepwise stability constants of cyanocuprate(II) complexes in water to be: $K_1 = 10^{6.16}$ dm^3 mol^{-1}, $K_2 = 10^{5.54}$ dm^3 mol^{-1}, $K_3 = 10^{5.23}$ dm^3 mol^{-1} and $K_4 = 10^{4.43}$ dm^3 mol^{-1}. If we then further assume that MeCN has negligible effect in stabilising Cu^{II} and adopt the value of $10^{4.43}$ dm^3 mol^{-1} for K_4 in 50% aqueous MeCN, then $E_3 - E_4 = 0.04$ V. This indicates that $E_4 < E_3$, and our finding that $Cu(CN)_4^{3-}$ reduces **3** more rapidly than $Cu(CN)_3^{2-}$ is in agreement with Galli's suggestion. If the difference in free energies of activation for reduction of **3** by the two complexes were to equal the difference in their reduction potentials (*i.e.* $0.04F = 3.86$ kJ mol^{-1}), all other things being equal, the relative reduction rate would be 4.75; our experimental value of 4.3 is therefore of a reasonable magnitude. Since coordination by MeCN stabilises Cu^I,[30] it is to be expected that in aqueous solution the aquacyanocuprates, $Cu^I(OH_2)_{4-n}(CN)_n^{(n-1)-}$ should show somewhat higher reactivity than the corresponding MeCN complexes studied here if their reactivity is also determined principally by the reduction potential; on the other hand, $Cu^I(CN)_4^{3-}$ might be expected to exhibit similar reactivity in both aqueous and mixed solvents since the inner coordination sphere remains the same in both media and any difference can stem only from secondary solvation effects.

The standard reduction potential for the couple $Cu^{II}(CN)_4^{2-}/Cu^I(CN)_4^{3-}$ (in water) found by Katagiri and co-workers[32,33] was 0.54 V *vs.* NHE and, on the basis of the argument given above, that for $Cu^{II}(CN)_3^-/Cu^I(CN)_3^{2-}$ in aqueous MeCN is 0.58 V. These are similar to the values for the couples $Cu^{II}Cl_3^-/Cu^ICl_3^{2-}$ and $Cu^{II}Cl_2/Cu^ICl_2^-$ (0.52 and 0.50 V, respectively, *vs.* NHE)[8] indicating their reactions with any particular diazonium ion to be almost isoergonic. We indicated that, other things being equal, a difference in reduction potential of 0.04 V might, at most, be manifest as a 4.75-fold difference in reduction rate. On this basis, these chloro- and cyano-copper(I) complexes would be expected to react with a given substrate at rates falling within the same order of magnitude, yet chlorocuprates reduce diazonium ions much more rapidly than cyanocuprates. (We estimate a factor of about 10^3 for solutions containing comparable total concentrations of Cu^I and chloride or cyanide). Evidently, when comparing the differently ligated cuprates, there is no correspondence of reactivity with reduction potential (assuming the various stability constants from which the latter are derived are soundly based). The question arises as to what is the mechanism of these reductions. The marked difference in rates could arise from a variety of circumstances: (i) if the reduction steps in both Sandmeyer reactions were to occur by outer-sphere mechanisms but with that in cyanation manifesting a significantly higher intrinsic barrier to electron transfer or, (ii) if the reduction step of Sandmeyer cyanation were to occur by an outer-sphere mechanism whereas that of chlorination were to occur by an inner-sphere mechanism or, (iii) if both reduction steps were inner-sphere processes but with differing conductivity of the bridging ligands in electron transfer. In the ensuing paper, we shall adduce evidence that chlorocuprates reduce diazonium ions by an inner-sphere mechanism precluding circumstance (i) but not circumstance (ii). Circumstances (ii) and (iii) both depend on the relative ability of cyanide and chloride to act as a bridging ligand, the difference being merely one of degree. In order for a ligand to act as a bridge, a lone pair on the ligand is required to participate at a suitable electrophilic site on the diazonium ion. It is expected that the polarisable lone-pair orbitals on chloride should be better able to do this than the less polarisable lone-pair of sp-character on the nitrogen atom of cyanide. Furthermore, on account of the contracted, filled *d* orbitals in d^{10} Cu^I complexes, it is likely that in an inner-sphere process the electron will be conducted *via* the σ-framework rather than *via* π-orbital interactions. Again the orbitals of chloride are expected to be the better fitted for the role. Circumstance (iii) could therefore hold. The simplest interpretation of the available circumstantial evidence (Occam's razor) is that it does hold and that both chloro- and cyanocuprates reduce diazonium ions by inner-sphere mechanisms in which the activation barriers differ significantly in favour of the chlorocuprates on account of their possession of ligands of higher electron conductivity.† There is a possibility that cyanocuprates may react by an outer-sphere mechanism but with only approximate reduction potentials and no self-exchange rates it cannot be tested *via* Marcus theory.

(ii) The mechanism of the ligand transfer step

Although many reagents are capable of reducing diazonium ions, Cu^{II} is virtually unique in its ability to transfer certain ligands to the derived aryl radicals. Three distinct mechanisms can be envisaged for the transfer of a ligand L. The first is atom transfer where the aryl radical abstracts $L^\bullet$ from the coordination shell of Cu^{II} in an S_H2 type of process simultaneously producing a new C–L bond and reducing Cu^{II} to Cu^I. The second mechanism is an electron transfer from the radical to the Cu^{II} complex which reduces it to Cu^I and the aryl cation which results from the electron transfer then captures a ligand L^- liberated by the metal centre on its change of oxidation state; in order to account for the unique transferring ability of copper, the electron transfer must be an inner-sphere process in the sense that the ligand which provides the bridge between the aryl radical and the metal for transmission of the electron is also the ligand which is transferred. The third mechanism is penetration of the aryl radical into the primary coordination shell of the metal, formally to give $L–Cu^{III}–Ar$, which then undergoes reductive elimination to Ar–L and Cu^I.

The first two mechanisms differ only in the synchrony of electron and atom transfer. Previously, we have envisaged them as the end-members of a gradation in the character of ligand transfer which is dependent on the extent of decoupling of the transfer of the electron from that of the ligand itself such that the electron transfer aspect is enhanced by factors such as nucleophilicity of the aryl radical (influenced by substitution) or high reduction potential of the Cu^{II} complex.[8] The third mechanism differs from the others in the site of attack of the aryl radical on the Cu^{II} complex. Although there is spectroscopic evidence of organocopper intermediates formed in the reaction of alkyl radicals with Cu^{2+}aq,[41,42] we are aware of no such evidence regarding aryl radicals. There is evidence that organocopper intermediates are involved in the production of by-products associated with Sandmeyer reactions (*e.g.* azoarenes and *n*,*n*-biaryls)[43,44] but there is no evidence that requires their involvement in the steps of Sandmeyer reaction proper.

Following on from the above, the transfer of a cyanide ligand could result from attack by the aryl radical upon a ligand of the cyanocuprate(II) which co-occurs within its solvent cage. Since Sandmeyer cyanation is regioselective yielding only nitrile and not isonitrile,‡ the attack must be adjacent, *i.e.* on the carbon atom which is bonded to the metal. In a wholly inorganic context, adjacent attack on a cyanide ligand does not occur as the ligating carbon atom possesses no additional lone pair with which to coordinate a second metal. In the present context, where the reaction partner is an organic radical, no such restriction need apply, the attacking radical being able to interact at carbon with both occupied and/or unoccupied bonding orbitals associated with the ligand, whichever affords the greater stabilisation. On the other hand, the regioselectivity of nitrile formation might be construed as circumstantial evidence of organometallic involvement. For example, if the aryl radical were to attack square planar tetracyanocuprate(II)[46] in the axial direction, reductive elimination from the penta-coordinate adduct would result in the formation of ArCN. A theoretical analysis of the relative energetics of different reaction paths would be informative.

Conclusion

Of the various copper(I) species present when $[Cu^I(NCMe)_4](BF_4)$ and KCN are dissolved in 50% v/v aqueous acetonitrile at pH 8 only $Cu^I(NCMe)(CN)_3{}^{2-}$ and $Cu^I(CN)_4{}^{3-}$ reduce 4-methoxybenzenediazonium ion and their respective rate constants are (0.12 ± 0.03) and (0.5 ± 0.05) $dm^3\ mol^{-1}\ s^{-1}$ at 298 K. The relative reactivity closely reflects the estimated difference in the reduction potentials of the two ions but the cyanocuprate ions are significantly less reactive than chlorocuprates which have similar reduction potentials. The balance of circumstantial evidence seems to favour cyanocuprates reducing diazonium ions by an inner-sphere mechanism but an outer-sphere mechanism is not ruled out. When a diazonium ion is reduced by one of the reactive cyanocuprate(I) complexes, the derived aryl radical undergoes ligand transfer from the cyanocuprate(II) anion with which it shares its solvent cage. The first order rate constant for ligand transfer within the caged pair of reactants is *ca.* $1 \times 10^8\ s^{-1}$ but may vary with substitution in the aryl radical like bimolecular ligand transfer rates; no difference in reactivity of the two concerned cyanocuprate(II) complexes is detectable.

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† An account of the causes of differing conductivities of halide ions as bridging ligands has been given by Cannon.[39] We are not aware of any comparable analysis of the relative conductivities of chloride and cyanide as bridging ligands but note that in the inner-sphere reduction of $Co^{III}(NH_3)_5X^{2+}$ by Cu^+aq, the rate for $X = Cl^-$ exceeds that for $X = CN^-$ by seven orders of magnitude.[40]

‡ Synthetically, PhNC has been reported as a contaminant of PhCN[45] but this can be ascribed to minor heterolysis of the diazonium precursor under the high temperature conditions of the procedure. No isonitrile is detected in the cyanation conditions used here.

Experimental

(i) Materials

Tetrakis(acetonitrile)copper(I) tetrafluoroborate. This was synthesised from copper(I) oxide and fluoroboric acid by the method of Kubas.[47]

4-Methoxybenzenediazonium tetrafluoroborate, 3. 4-Anisidine (12.3 g), dissolved in fluoroboric acid (50%, 34 cm^3) and diluted with water (40 cm^3), was diazotised by portion-wise addition of sodium nitrite (6.9 g) in water (15 cm^3) at 0–5 °C. After stirring for 15 min, the thick precipitate was collected and re-dissolved in acetone. *4-Methoxybenzenediazonium tetrafluoroborate*, **3**, (21 g, 95%) was precipitated by addition of diethyl ether, mp 141–142 °C, lit.[48] 142 °C; ν_{max}(Nujol)/cm^{-1} 2253 (N≡N$^+$), 1044br (BF$_4^-$); δ_H[270 MHz, (CD$_3$)$_2$CO] 4.24 (s, 3H), 7.60 (d, *J* 9.5, 2H), 8.82 (d, *J* 9.5, 2H); δ_C[67.9 MHz, (CD$_3$)$_2$CO] 58.0, 103.6, 118.3 (2C), 137.0 (2C) and 170.6, lit.[49,50]

(*E*)-4-Methoxybenzenediazocyanide. This was prepared from potassium cyanide and 4-methoxybenzenediazonium tetrafluoroborate by the method of Ignasiak and co-workers.[27] An aqueous solution of potassium cyanide (1.63 g in 7.5 cm^3) was added slowly to a stirred aqueous solution of 4-methoxybenzenediazonium tetrafluoroborate (2.78 g in 10 cm^3) at 0 °C until the reaction solution when tested with potassium cyanide on a piece of filter paper failed to give an orange-coloured product. The mixture was diluted with ice-water (13 cm^3) and then filtered through a Buchner funnel. The wet, coloured residue was extracted into chloroform and dried over anhydrous magnesium sulfate. After filtration to remove the desiccant, the solution was heated on a steam bath [which completes the *Z* to *E* isomerisation of the diazocyanide] and then evaporated. *(E)-4-Methoxybenzenediazocyanide* was recrystallised from hexane, mp 105–108 °C, lit.[27] 124 °C [low owing to a remaining trace of (*Z*)-form]; ν_{max}(Nujol)/cm^{-1} 2172 (CN), 1599, 1258, 1154, 1017, 843, 723; δ_H[270 MHz, CDCl$_3$] 3.90 (s, 3H), 6.97 (d, 2H), 7.87 (d, 2H); δ_C[67.9 MHz, CDCl$_3$] 56.6, 115.5, 116.9, 128.2, 148.8 and 167.8, in good agreement with precedent.[51]

4-Methoxybenzenediazonium tricyanocuprate, [ArN$_2^+$]$_2$-[Cu^I(CN)$_3^{2-}$]. A similar procedure was followed to that given for (*E*)-4-methoxybenzenediazocyanide in which the potassium cyanide solution was replaced by an aqueous cyanocuprate solution (2.24 g Cu^{I}CN and 3.26 g KCN in 10 cm^3). The precipitate was collected by filtration, washed with CHCl$_3$ and dried in a vacuum desiccator. In Table 4 a comparison of the ^{13}C CP-MAS NMR and IR spectra of this solid is made with spectra of **3**, K$_2$Cu^I(CN)$_3$ and 3-methoxybenzonitrile.

Dipotassium tricyanocuprate. To an aqueous suspension of CuCN (1 g, 0.011 mol in 10 cm^3) was added KCN (1.45 g, 0.022 mol) with vigorous stirring. The solution was filtered and the water removed by rotary evaporation. The resultant white powder was dried at 100 °C under vacuum, ν_{max}(Nujol)/cm^{-1} 2078 [*cf.* the CN stretching frequency at 2094 cm^{-1} reported for disodium tricyanocuprate in aqueous solution];[52] δ_C[67.9 MHz, D$_2$O] 152.5.

2-Benzoylbenzenediazonium tetrafluoroborate[7] and methyl (*E*)-3-(2-diazoniophenyl)-2-phenylpropenoate tetrafluoroborate.[34] These precursors to the radical clocks **4** and **5** were prepared as previously described as was methyl phenanthrene-9-carboxylate,[34] **9**, the cyclisation product of the latter. Fluoren-9-one, **8**, the cyclisation product of **4**, was a commercial material (Lancaster).

2-Cyanobenzophenone, 6. Tetrakis(acetonitrile)copper(I) tetrafluoroborate in MeCN solution (48 cm^3, 0.2 mol dm^{-3}) was added to KCN (1.95 g) dissolved in mixed MeCN and aqueous phosphate buffer [KH$_2$PO$_4$ (0.1 mol dm^{-3}), K$_2$HPO$_4$ (0.062 mol dm^{-3}), pH 7] to give a solution (225 cm^3) of 50% v/v aqueous MeCN solvent composition. 2-Benzoylbenzenediazonium tetrafluoroborate (0.74 g) dissolved in solvent of the same composition (25 cm^3) was added and the mixture was stirred. After 2 h. it was added to a solution of disodium 2-naphthol-3,6-disulfonate (100 cm^3, 0.17 mol dm^{-3}) and the organic product was extracted with ethyl acetate (3 × 25 cm^3). Removal of the solvent and chromatography of the residue on a silica column, eluting with light petroleum (40–60 °C)–ethyl acetate (5 : 1), gave *2-cyanobenzophenone*, mp 78 °C, lit.[53] 84.5–85.5 °C (Found: M^+ 207.0693. C$_{14}$H$_9$NO requires 207.0684); *m/z* 207 (34%, M^+), 130 (17), 105 (100), 102 (19), 77 (56), 51 (34); ν_{max}(Nujol)/cm^{-1} 2229 (C≡N), 1660 (C=O); δ_H(270 MHz, CDCl$_3$) 7.50 (m, 2H), 7.68 (m, 4H), and 7.83 (m, 3H); δ_C(67.9 MHz, CDCl$_3$) 118.8, 117.0, 128.6 (2C), 130.0, 130.2 (2C), 131.3, 132.0, 133.8, 134.2, 135.8, 141.3 and 193.7 in excellent agreement with precedent.[54]

Methyl (*E*)-3-(2-cyanophenyl)-2-phenylpropenoate, 7. 2-Cyanobenzaldehyde and phenylacetic acid were reacted by DeTar's procedure[55] to give *(E)-3-(2-cyanophenyl)-2-phenylpropenoic acid* (47%), mp 184–186 °C, lit.[56] 191.5–192.5 °C. This acid was methylated by refluxing overnight in methanol acidified with H$_2$SO$_4$. After addition of water, the ester was extracted into ether, washed with a saturated solution of Na$_2$CO$_3$, and with water, and the solution dried. On removal of the solvent *methyl (E)-3-(2-cyanophenyl)-2-phenylpropenoate* was obtained as colourless crystals (93%), mp 94.5–95 °C; (Found: M^+ 263.09450. C$_{17}$H$_{13}$NO$_2$ requires 263.09463); *m/z* 263 (95%, M^+), 232 (12), 204 (100), 203 (65), 176 (15), 146 (51) 102 (9), 77 (10), 51 (10); ν_{max}(Nujol)/cm^{-1} 2229 (C≡N), 1703 (C=O), 1245 (C–O); δ_H(270 MHz, CDCl$_3$) 3.78 (s, 3H), 6.8 (m, 1H), 7.07–7.27 (m, 8H), 7.58 (m, 1H), and 8.00 (s, 1H); δ_C(67.9 MHz, CDCl$_3$) 52.7, 113.0, 117.0, 127.5, 128.0, 128.4, 128.6, 128.9, 129.3 129.5, 133.4, 135.5, 136.0, 173.2, and 167.0.

(ii) Kinetic measurements

Sandmeyer cyanation. The following procedure is typical of those carried out to measure rates of the Sandmeyer cyanation reaction. A master solution of KCN was made (fresh, daily) by dissolving 5.2 g in water (100 cm^3) buffered at pH 7, the composition of the buffer being KH$_2$PO$_4$ (0.1 mol dm^{-3}) and K$_2$HPO$_4$ (0.062 mol dm^{-3}). Tetrakis(acetonitrile)copper(I) tetrafluoroborate in an acetonitrile solution (20 cm^3, 0.20 mol dm^{-3}) was then added to a chosen aliquot of the cyanide solution and the volume increased to approximately 90 cm^3 by the addition of more acetonitrile and buffer as necessary to ensure a final composition of 1 : 1 MeCN–water. The pH was adjusted to a measured value of 8 by the addition of acid or base (0.01 mol dm^{-3} H$_2$SO$_4$ or NaOH in 1 : 1 MeCN–water). The total volume was then adjusted to 100 cm^3, ensuring that a 1 : 1 MeCN–water ratio was maintained, and the pH re-measured to ensure it remained 8. The solution was placed in a three necked flask and stirred from overhead (through a gas tight seal) and allowed to equilibrate at 298 K. One arm of the flask was connected to the gas displacement cell and the other to a pressure equalising funnel containing 4-methoxybenzenediazonium tetrafluoroborate, **3**, (0.22 g, 1 mmol) in 1 : 1 MeCN–aqueous pH 7 buffer (5 cm^3).

Once the setup had been made gas-tight (all joints were sealed with labfilm), the diazonium solution was added to the cyanocuprate solution giving a total reaction volume of 105 cm^3 with [Cu^I] = 0.038 mol dm^{-3}, [CN$^-$] according to the aliquot of master solution taken, [**3**] = 0.0095 mol dm^{-3} and pH 8. The volume of evolved nitrogen was measured at suitable intervals by weighing the water which was displaced from the gas cell into a beaker placed on a top pan balance. After 2 hours the reaction mixture was added to a solution of disodium

Table 4 Spectroscopic comparison of the intermediate precipitate from Sandmeyer cyanation with that of component ions and the Sandmeyer product

^{13}C Chemical shifts/ppm				IR Frequencies/cm$^{-1\,a}$		
Precipitate^b	**3**^{c}	$K_2Cu(CN)_3$^{d}	4-MeOC$_6$H$_4$CN^e	Precipitate	**3**	$K_2Cu(CN)_3$
57.0			55.5	2234	2247	
58.9	58.0			2105		2078
99.5	103.6			1576	1583	
103.1			103.9	1297	1293	
117.5			114.7	1095	1098	
Broad	118.3			1009	999^f	
			119.2	842	840	
134.0			133.9	522	522	
137.3	137.0					
152.0		152.5				
162.0			162.8			
170.0	170.6					

[a] IR spectra were obtained for Nujol mulls. [b] CP-MAS spectrum; the absorptions assigned to 4-methoxybenzonitrile appeared during acquisition of the spectrum. [c] Spectrum obtained for solution in $(CD_3)_2CO$. [d] Spectrum obtained for solution in D_2O. [e] Spectrum obtained for solution in $CDCl_3$. [f] Shoulder on broad absorption due to BF_4^-.

2-naphthol-3,6-disulfonate (50 cm^3, 0.17 mol dm^{-3}). The buffer provided sufficiently basic conditions for azo-coupling to remove any unreacted **3**. The mixture was extracted with diethyl ether and the extract analysed by GC on an SE-54 capillary column (temperature program 60 °C for 5 min then 16 °C min^{-1} until 290 °C). The main product (*ca.* 95%) was 4-methoxybenzonitrile (retention time 10.2 min) giving a mass spectrum agreeing with precedent:[57] m/z 133 (100%, M^+), 118 (12), 103 (35), 90(62) and 64 (20). Each run was repeated at least once.

Caged ligand transfer. For the evaluation of the rate constants for caged ligand transfer to **4**, buffered cyanocuprate(I) solutions in 1 : 1 aqueous MeCN were made up as above but on a one quarter scale (25 cm^3) as measurement of nitrogen evolution was not required. 2-Benzoylbenzenediazonium tetrafluoroborate (0.05 g) in the same solvent was added and the solution stirred for 2 h after which the solution was added to a solution of disodium 2-naphthol-3,6-disulfonate to ensure removal of any traces of unreacted diazonium ion. The products were extracted into ethyl acetate and analysed by GC as above. The relative response factor for the products of ligand transfer, **6**, and cyclisation, **8**, was determined by use of the authentic materials.

For evaluation of rates of ligand transfer to **5**, a somewhat different procedure was used: CuCN and KCN were dissolved in fixed proportion (1 : 2) but different concentrations in 10% aqueous acetonitrile (25 cm^3). As the solution was stirred vigorously, the diazonium salt (0.025 g) in the same solvent (5 cm^3) was added which resulted in a short-lived orange turbidity. After stirring for 10 minutes, the solution was extracted with ethyl acetate containing dibenzofuran as internal standard for GC analysis, which was performed on an SE30 capillary column at 180 °C, the necessary response factors being obtained on authentic materials.

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References

1 Part 5. S. A. Chandler, P. Hanson, A. B. Taylor, P. H. Walton and A. W. Timms, *J. Chem. Soc., Perkin Trans. 2*, 2001, 214.
2 W. A. Waters, *J. Chem. Soc.*, 1942, 266.
3 J. K. Kochi, *J. Am. Chem. Soc.*, 1957, **79**, 2942.
4 C. Galli, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1459.
5 C. Galli, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1139.
6 P. Hanson, J. R. Jones, B. C. Gilbert and A. W. Timms, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1009.
7 P. Hanson, R. C. Hammond, P. R. Goodacre, J. Purcell and A. W. Timms, *J. Chem. Soc., Perkin Trans. 2*, 1994, 691.
8 P. Hanson, R. C. Hammond, B. C. Gilbert and A. W. Timms, *J. Chem. Soc., Perkin Trans. 2*, 1995, 2195.
9 E. Pfeil and O. Velten, *Justus Liebigs Ann. Chem.*, 1949, **562**, 163.
10 E. Pfeil and O. Velten, *Justus Liebigs Ann. Chem.*, 1949, **565**, 183.
11 W. S. Cowdrey and D. S. Davies, *J. Chem. Soc.*, 1949, S48.
12 C. Galli, *J. Chem. Soc., Perkin Trans. 2*, 1984, 897.
13 See *e.g.* B. S. Furniss, A. J. Hannaford, V. Rogers, P. W. G. Smith and A. R. Tatchell, *Vogel's Textbook of Practical Organic Chemistry*, 4th Edn., Longman, London, 1979, pp. 689–703.
14 S. C. Dickerman, K. Weiss and A. K. Ingberman, *J. Org. Chem.*, 1956, **21**, 380.
15 S. C. Dickerman, K. Weiss and A. K. Ingberman, *J. Am. Chem. Soc.*, 1957, **80**, 1904.
16 S. C. Dickerman, D. J. DeSouza and N. Jacobson, *J. Org. Chem.*, 1969, **34**, 710.
17 C. J. Rondestvedt, *Org. React. (N. Y.)*, 1960, **11**, 189.
18 C. J. Rondestvedt, *Org. React. (N. Y.)*, 1976, **24**, 225.
19 C. Galli, *Chem. Rev.*, 1988, **88**, 765.
20 J. K. Kochi, *J. Am. Chem Soc.*, 1956, **78**, 1228.
21 T. Cohen, A. G. Dietz and J. R. Miser, *J. Org. Chem.*, 1977, **42**, 2053.
22 M. P. Doyle, J. K. Guy, K. C. Brown, S. N. Mahapatro, C. M. VanZyl and J. C. Pladziewicz, *J. Am. Chem. Soc.*, 1987, **109**, 1536.
23 B. C. Gilbert, P. Hanson, J. R. Jones, A. C. Whitwood and A. W. Timms, *J. Chem. Soc., Perkin Trans. 2*, 1992, 629.
24 D. S. Wulfman, *The Chemistry of Diazonium and Diazo groups*, Part 1, Ed. S. Patai, Interscience, 1978, p. 293.
25 C. H. R. Rømming and K. Wærstad, *J. Chem. Soc., Chem. Commun.*, 1965, 299.
26 M. L. Crossley, R. H. Kienle and C. H. Benbrook, *J. Am. Chem. Soc.*, 1940, **62**, 1400.
27 T. Ignasiak, J. Susko and B. Ignasiak, *J. Chem. Soc., Perkin Trans. 1*, 1975, 2123.
28 K. Kurnia, D. E. Giles, P. M. May, P. Singh and G. T. Hefter, *Talanta*, 1996, **43**, 2045.
29 The computer program used, ES4ECI, was kindly provided by Professor S. Sammartano. C. De Stefano, P. Mineo, C. Rigano and S. Sammartano, *Ann. Chim. (Rome)*, 1993, **83**, 243.
30 A. Günter and A. Zuberbühler, *Chemia*, 1970, **24**, 340.
31 M. L. Crossley, R. H. Kienle and C. H. Benbrook, *Ind. Eng. Chem. Anal. Ed.*, 1940, **12**, 216.
32 A. Katagiri, S. Yoshimura and S. Yoshizawa, *Inorg. Chem.*, 1981, **20**, 4143.
33 A. Katagiri, S. Yoshimura and S. Yoshizawa, *Inorg. Chem.*, 1986, **25**, 2278.
34 P. Hanson, P. W. Lövenich, S. C. Rowell, P. H. Walton and A. W. Timms, *J. Chem. Soc., Perkin Trans. 2*, 1999, 49.
35 M. T. Beck, *Pure Appl. Chem.*, 1987, **59**, 1703.
36 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th Edn., Wiley, New York, 1988, p. 44.
37 R. W. Ramette, *Inorg. Chem.*, 1986, **25**, 2481.

38 E. Högfeldt, Stability Constants of Metal-ion Complexes, Part A, Inorganic Ligands, IUPAC Chem. Data Ser., No. 21, Pergamon, Oxford, 1983, p. 111.
39 R. D. Cannon, *Electron Transfer Reactions*, Butterworths, London, 1980, p. 257.
40 O. J. Parker and J. H. Espenson, *J. Am. Chem. Soc.*, 1969, **91**, 1968.
41 J. C. Scaiano, W. J. Leigh and G. Ferraudi, *Can. J. Chem.*, 1984, **62**, 2355.
42 A. Mayouf, L. Lemmetyinen, I. Sychttchikova and J. Koskikallio, *Int. J. Chem. Kinet.*, 1992, **24**, 579.
43 T. Cohen, R. J. Lewarchik and J. Z. Tarino, *J. Am Chem. Soc.*, 1974, **96**, 7753.
44 P. Hanson, A. B. Taylor, P. H. Walton and A. W. Timms, unpublished work.
45 B. S. Furniss, A. J. Hannaford, V. Rogers, P. W. G. Smith and A. R. Tatchell, *Vogel's Textbook of Practical Organic Chemistry*, 4th Edn., Longman, London, 1979, p. 704.
46 A. Longo and T. Buch, *Inorg. Chem.*, 1967, **6**, 556.
47 G. J. Kubas, *Inorg. Synth.*, 1990, **28**, 68.
48 T. J. Broxton, J. F. Bunnett and C. H. Paik, *J. Org. Chem.*, 1977, **42**, 643.
49 G. A. Olah and J. L. Grant, *J. Am. Chem. Soc.*, 1975, **97**, 1546.
50 R. M. Elofson, N. Cyr, J. K. Laidler, K. F. Schultz and F. F. Gadallah, *Can. J. Chem.*, 1984, **62**, 92.
51 R. M. Elofson, N. Cyr, J. K. Laidler and K. F. Schultz, *Tetrahedron Lett.*, 1984, **25**, 3039.
52 C. Kappenstein and R. P. Hugel, *Inorg. Chem.*, 1978, **17**, 1945.
53 H. Bredereck and H. W. Vollmann, *Chem. Ber.*, 1972, **105**, 2271.
54 R. D. Rieke, D. E. Stack, B. T. Dawson and T.-C. Wu, *J. Org. Chem.*, 1993, **58**, 2483.
55 D. F. DeTar, *Org. Synth.*, 1963, **Coll. Vol. 4**, 730.
56 D. F. DeTar and L. A. Carpino, *J. Am. Chem. Soc.*, 1956, **78**, 475.
57 J. R. Hwu, C. H. Hsu, F. F. Wong, C. Chung and G. H. Hakemelahi, *Synthesis*, 1998, 329.