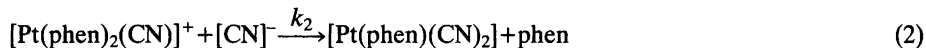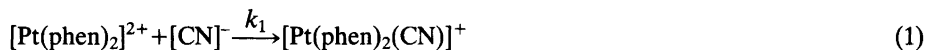# Short Communication

Studies on Five-coordinated d^8 Metal Ions. Part II*. The Displacement of 1,10-Phenanthroline by the Reaction of the Five-coordinate Cyanobis(1,10-phenanthroline)platinum(II) Cation with Cyanide

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In an earlier paper,[1] it was shown that $[Pt(phen)_2]^{2+}$ ** rapidly adds cyanide giving the ion $[Pt(phen)_2(CN)]^+$. In the solid state, as its nitrate salt, this ion has a square-pyramidal structure with an apical Pt−N bond which is 30 % longer than the basal Pt−N bonds. The platinum atom is displaced 0.0069 nm in the direction of the apical donor-atom, as predicted by theory for a five-coordinate, square-pyramidal d^8 complex with an apical bond which is longer and weaker than the basal bonds.[2] Therefore, even for this system where the apically bonded donor group forms a part of a rigid chelate, the central atom is probably bonded to all five donor atoms and therefore does not necessarily contain a "half-bonded" η^1 chelate. The salt $[PtCl(PEt_3)_2(phen)]BF_4]$, the cation of which has a similar structure and reactivity, was originally reported as containing a five-coordinate complex,[3] but was later incorrectly (*vide infra*) reformulated as a "half-bonded" system on the basis of the structure alone.[4] It may also be relevant that in the ^{13}C NMR spectra of $[Pt(phen)_2(CN)]^+$,[1] both in nitromethane and aqueous solution, the four halves of the phen ligands are equivalent on the NMR time-scale. The $J(^{195}Pt—^{13}C)$ coupling constants of the peaks assignable to phen in the spectra are only between 5 and 15 % smaller than for $[Pt(phen)_2]^{2+}$. Thus, the Pt−N bonds, although presumably weaker in the five-coordinate complex than in $[Pt(phen)_2]^{2+}$, should not correspond to those of a system with only three Pt−N bonds and one "half-bonded" η^1 phen molecule, and still give such high values of $J(Pt−C)$.

The present work is an attempt to use *reactivity* as an alternative means of characterising the five-coordinate complex. An obvious choice of reaction was that between $[Pt(phen)_2]^{2+}$ and an excess of $[CN]^-$, which preliminary observation revealed to occur in two stages:

$$[Pt(phen)_2]^{2+} + [CN]^- \xrightarrow{k_1} [Pt(phen)_2(CN)]^+ \tag{1}$$

$$[Pt(phen)_2(CN)]^+ + [CN]^- \xrightarrow{k_2} [Pt(phen)(CN)_2] + phen \tag{2}$$

The kinetics of reaction (1) were measured under standard acidic conditions (buffered with aqueous 0.05 mol 1^{-1} $K[C_2O_4H].C_2O_4H_2$), and these results are summarised in Table 1. The effect of pH upon this reaction will be the subject of a future publication;[5] the rate law is:

$$\text{Rate} = k_1[\{Pt(phen)_2\}^{2+}][CN^-];$$
$$k_1 = 1.87 \times 10^8 \ 1 \ \text{mol}^{-1} \ \text{s}^{-1} \ (\text{at } 25 \ °C)$$
$$\Delta H_1^{\ddagger} = 11.3 \ \text{kJ mol}^{-1}$$
$$\Delta S_1^{\ddagger} = -50 \ \text{J mol}^{-1} \ \text{K}^{-1}$$

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* Part 1. See Ref. 1.
** 1,10-Phenanthroline is abbreviated to phen throughout this Communication.

Table 1. Kinetic Data.

	T /°C	[Pt complex] /mol l^{-1}	[KCN] range /10^{-3} mol l^{-1}	No. of runs	$k_{av.obs}$ /l mol^{-1} s^{-1}	k^a /l mol^{-1} s^{-1}
Reaction (1) in 0.05	17.1	1.15×10^{-4}	2.12–5.31	4	3.63	$1.63(3) \times 10^8$
mol l^{-1} aqueous	18.9		2.04–4.09	7	3.92	$1.60(2) \times 10^8$
K[C$_2$O$_4$H].C$_2$O$_4$H$_2$	22.6		2.98	6	5.70	$1.86(15) \times 10^8$
	29.9		0.68–1.9	7	9.47	$1.97(6) \times 10^8$
	31.7		1.01–2.02	6	10.4	$2.01(7) \times 10^8$
	33.6		1.31–3.5	6	13.8	$2.31(17) \times 10^8$
Reaction (2) in 0.10	18.2	1.00×10^{-5}	0.5–4.5	13		2.95(7)
mol l^{-1} methanolic	23.2		0.6–11.0	5		3.65(20)
Na[O$_2$CMe]	27.4		1.9–11.6	6		2.3(2)
	30.1		1.9–7.7	10		5.6(2)
	35.2		1.9–7.6	6		7.3(3)

^{a} The rate constants were obtained from the slope of a linear plot of pseudo-first-order rate constants versus [KCN]. The pseudo-first-order rate constants were calculated from logarithmic first-order plots which were linear for more than three half-lives. The reactions were monitored spectrophotometrically at 375 and 325 nm, respectively. ^{b} A preliminary report of these data was given at the 13th meeting of the Royal Society of Chemistry Inorganic Mechanisms Group, Cardiff, Great Britain, 1980. ^{c} [Pt(phen)$_2$][NO$_3$]$_2$ was prepared according to Ref. 1. A freshly prepared solution of K[CN] (A.R. grade) was used. All reagent solutions were saturated with dinitrogen. The pH of the medium was *ca.* 1.7.

However, the product of the second reaction, (2), is virtually insoluble in water. Thus, the rate was measured in methanol (in the presence of a Na$_2$[B$_4$O$_7$].10H$_2$O buffer), ensuring that the fraction of total cyanide which was protonated was a constant. The pK of HCN in methanol is not accurately known, so the rate law (but *not* k_2) could be established:

Rate $= k_2'[\{Pt(phen)_2(CN)\}^+][CN^-]$

In a constant ionic strength medium, sodium ethanoate (0.10 mol l^{-1}) in methanol with [KCN] $> 10^{-3}$ mol l^{-1}, the HCN concentration can be ignored. From a study of the kinetics in this medium (Table 1), the rate law was explicitly:

Rate $= k_2[\{Pt(phen)_2(CN)\}^+][CN^-]$;
$k_2 = 4.06$ l mol^{-1} s^{-1} (at 25 °C)
$\Delta H_2^{\ddagger} = 39$ kJ mol^{-1}
$\Delta S_2^{\ddagger} = -105$ J mol^{-1} K^{-1}

From these data, it can be seen that the rate constant for reaction (2) is in the range normally observed for nucleophilic substitution by cyanide in platinum(II) comlexes.[6,7] In contrast, the rate constant, k_1, for the *formation* of the five-coordinate species is many orders of magnitude larger than k_2, suggesting that no ligand displacement is involved. This argument is further supported by consideration of the activation parameters. $\Delta H_2^{\ddagger}$, at 40 kJ mol^{-1}, is typical of values for substitution reactions,[6,7] whereas $\Delta H_1^{\ddagger}$ is about one quarter of typical values (40–60 kJ mol^{-1})[6,7] for such processes as:

$$[PtL_4]^{2+} + X^- \rightarrow [PtL_3X]^+ + L \tag{3}$$

These data clearly support the proposition that no Pt–N bond is broken during reaction (1), thus arguing strongly against formulating species such as [Pt(phen)$_2$(CN)]$^+$ and [PtCl(PEt$_3$)$_2$(phen)]$^+$ as four-coordinate complexes containing η^1-phen. For some substitu-

tion reactions where phen is the leaving group, it has been suggested[8] (on the basis of kinetic data) that "half-bonded" η^1-phen exists in intermediates, but the existence of such a species has never been demonstrated; the kinetic data described above remove the only possible argument which remained in support of such complexes.

It is of interest that the value of $\Delta S_2^{\ddagger}$ is in a range normally considered as typical for an associative reaction,[6,7] suggesting the formation of a six-coordinate activated complex, $[Pt(\eta^2\text{-phen})_2(CN)_2]$. The displacement of phen from $[Ir(1,5\text{-cyclooctadiene})(phen)]^+$ with 1,2-diaminoethane as the nucleophile has $\Delta S^{\ddagger} = -25$ J mol^{-1} K^{-1}.[9] This reaction was described as a *dissociative* displacement of phen from the stable five-coordinate intermediate containing η^1-1,2-diaminoethane. The results presented here clearly indicate the possibility of an alternative interpretation of these results, *viz.* an *associative* mechanism with a six-coordinate activated complex. Both these reactions present examples of a reaction type which is not accord with Tolman's rule (*i.e.* the number of electrons in the activated complex must be either sixteen or eighteen).[10]

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