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The Effect of the Methyl Group on the Nucleophilic Attack by n-Butylamine on *cis*-Dichlorobis(tolunitrile)platinum(II) Complexes

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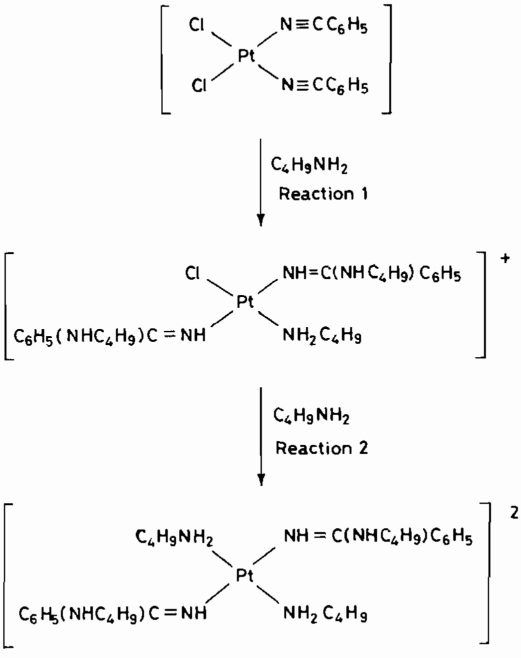
The activation of molecules by coordination to transition metal ions has for some time been of considerable interest, in particular the activation of ligands with respect to nucleophilic attack [1, 2]. Recently, we reported our investigations into the nucleophilic attack by amines on *cis*-dichlorobis(benzonitrile)platinum(II) [3]. The reaction with n-butylamine was shown to occur in two stages, resulting in the formation of the amidine complex $[Pt(n\text{-}C_4H_9NH_2)_2\{C_6H_5C(NHC_4H_9){=}NH\}_2]Cl_2$ via the sequence shown in Scheme 1.



Scheme 1.

The kinetics of these processes, carried out in chloroform at 30 °C, suggest that reaction (2) is second-order, with a calculated rate-constant k_2 of $(1.07 \pm 0.04) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}, whereas reaction (1) was overall third-order, obeying the rate expression

$$\text{rate} = k_1[Pt(C_6H_5CN)_2Cl_2][C_4H_9NH_2]^2$$

where $k_1 = (71.9 \pm 1.9)$ dm^6 mol^{-2} s^{-1}.

To explain the second-order dependence on amine concentration in reaction (1), we suggested a rate-determining step involving an amine dimer attack on the carbon of one of the nitrile ligands, as reported for a similar system by Uguagliati *et al.* [4, 5]. Subsequent reactions involving rapid addition of amine to the second nitrile group, replacement of chloride *trans* to the amidine by amine and isomerization give the final product of reaction (1).

We now report the results of our investigations into the reaction of the three ligand-isomers of the complex *cis*-dichlorobis(tolunitrile)platinum(II) with n-butylamine under identical conditions. The purpose of the study was to determine whether or not a similar reaction scheme to the one outlined above was followed and to investigate the steric/electronic effects associated with the introduction of methyl substituents in the phenyl ring of the nitrile ligand.

The complexes were prepared as described in the literature for *cis*-dichlorobis(benzonitrile)platinum(II) [6], using the relevant *ortho*-, *meta*- or *para*-tolunitrile and platinum(II) chloride. After heating for ~40 min at 100 °C, the yellow–green product sublimed and condensed on the sides of the reaction vessel and was isolated. In each case, the reaction gave a yield of between 40–65%.

The reaction of each complex with various concentrations of n-butylamine inchloroform at 30 °C was followed spectrophotometrically under pseudo-first-order conditions, and an IR spectrum of the final product was recorded. From the appearance of the repeat-scan UV spectra for these reactions and the IR spectrum of the final product, it would seem that the nucleophilic attack of n-butylamine on the tolunitrile complexes follows the two-stage reaction sequence that we reported for the corresponding reaction of the benzonitrile complex. The kinetic data for these reactions are summarised in Table I, together with those for the benzonitrile complex for comparison.

The second-order rate constant k_2 does not vary significantly on introduction of a methyl group to the phenyl ring. This is consistent with the mechanism proposed previously for chloride replacement by amine [3]. However, the first reaction, which directly involves the coordinated tolunitrile ligand, shows a reduction in the third-order rate constant k_1 compared with that for the benzonitrile complex of ~39% for *para*, ~65% for *meta* and ~93% for *ortho*. In terms of the proposed mechanism for such a process, a variation of this type is to be expected

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TABLE I. Rate Constants for the Reaction between *cis*-Dichlorobis(tolunitrile)platinum(II) Complexes and n-Butylamine in Chloroform at 30 °C

	k_1[a] ($dm^6\ mol^{-2}\ s^{-1}$)	k_2[b] ($dm^3\ mol^{-1}\ s^{-1}$)
ortho-tolunitrile complex	4.8 ± 0.2	$(3.9 \pm 0.1) \times 10^{-2}$
meta-tolunitrile complex	25.3 ± 0.3	$(1.78 \pm 0.01) \times 10^{-2}$
para-tolunitrile complex	44.0 ± 1.0	$(1.52 \pm 0.02) \times 10^{-2}$
benzonitrile complex [3]	71.9 ± 1.9	$(1.07 \pm 0.04) \times 10^{-2}$

[a] k_1 Rate constant for reaction (1) followed at four different concentrations of n-butylamine in the range 0.0025–0.0250 mol dm^{-3}. [b] k_2 Rate constant for reaction (2) followed at three different concentrations of n-butylamine in the range 0.1–0.5 mol dm^{-3}.

on the basis of steric and electronic effects. The reduced reactivity of the *p*-tolunitrile relative to the unsubstituted complex may be attributed to the electronic effect of the methyl substituent. The positive inductive effect of this group would reduce the partial positive charge of the nitrile carbon, making it less susceptible to a nucleophilic attack by amine, *i.e.* the rate-determining step of the reaction [7, 8]. This electronic effect is more evident for the *meta*- and *ortho*-tolunitrile complexes, and in the latter case, steric hindrance by the methyl group causes a further reduction in the observed rate constant. Such steric effects have been previously noted in the reaction of *cis*-dichlorobis(benzonitrile)-platinum(II) with the bulkier nucleophile, diethylamine [3].

For the second reaction, the effect of methyl substitution in the phenyl ring on complex reactivity is much less pronounced than it is in the case of the first reaction.

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References

1 D. A. Buckingham, F. R. Keene and A. M. Sargeson, *J. Am. Chem. Soc., 95,* 5649 (1973).
2 D. A. Buckingham, P. Morris, A. M. Sargeson and A. Zanella, *Inorg. Chem., 16,* 1910 (1977).
3 C. A. Amodio and K. B. Nolan, *Inorg. Chim. Acta, 113,* 27 (1986).
4 L. Calligaro, R. A. Michelin and P. Uguagliati, *Inorg. Chim. Acta, 76,* L83 (1983).
5 P. Uguagliati, U. Belluco, R. A. Michelin and P. Guerriero, *Inorg. Chim. Acta, 81,* 61 (1984).
6 F. R. Hartley, 'The Chemistry of Palladium and Platinum', Applied Science, London, 1973, p. 462.
7 J. Chatt and B. L. Shaw, *J. Chem. Soc.,* 1718 (1960).
8 F. Basolo and R. G. Pearson, 'Mechanism of Inorganic Reactions', 2nd edn., Wiley, New York, 1968, p. 649.