Inorganica Chimica Acta, 33 (1979) 11–14
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Substitution Reactions of Chlorobis[1,2-bis(diphenylphosphino)ethane] cobalt(II) Chloride with Bidentate Amines

MICHAEL J. HYNES and PATRICIA F. BRANNICK
Chemistry Department, University College, Galway, Ireland

Received March 2, 1978

The substitution reactions of five-co-ordinate [Co(Ph$_2$PC$_2$H$_4$PPh$_2$)$_2$Cl]Cl with bipyridine, 1,10-phenanthroline and 2,9 dimethyl-1,10-phenanthroline have been investigated in dichloromethane at a temperature of 25 °C. A detailed mechanism is proposed to account for the kinetic data. Evidence is presented to show that the complex reacts by a dissociative mechanism, with a dissociation rate constant of 62.5 s^{-1}.

Introduction

There has been considerable interest recently in the kinetics and mechanisms of the substitution reactions of five-co-ordinate transition metal complexes [1–22]. An assessment of the published results indicates that these reactions can proceed by either dissociative or associative mechanisms. The limited data available suggest that five-co-ordinate d^8 metal complexes follow dissociative mechanisms except in the case of the high spin complex [Ni(S$_2$P(OMe)$_2$)$_2$-(2,9-dimethyl-1,10-phenanthroline)] which appears to substitute by an associative mechanism [19]. It has been suggested that five-co-ordinate systems having less than 8 d-electrons will generally react via associative pathways [11–13, 20]. However, a dissociative contribution is present in the substitution reactions of many of the five-co-ordinate cobalt(III) complexes which have been investigated. There have only been two quantitative studies of the substitution reactions of five-co-ordinate cobalt(II) complexes [21, 22]. One of these proposes an associative mechanism, while the other suggests that the substitution is dissociatively controlled.

In this present investigation we report the kinetics and mechanism of the substitution reactions of the low-spin five-co-ordinate complex [Co(Ph$_2$PC$_2$H$_4$-PPh$_2$)$_2$Cl]Cl with bidentate amines in dichloromethane. Two structural isomers of the complex [Co-(Ph$_2$PC$_2$H$_4$PPh$_2$)$_2$Cl]SnCl$_3$ can be isolated as red and green crystals and an X-ray investigation has shown that the red form has a square pyramidal structure while the green crystals possess a trigonal bipyramidal structure [23, 24]. The structure of the green complex [Co(Ph$_2$PC$_2$H$_4$Ph$_2$)$_2$Cl]Cl has not been determined but by analogy it is likely to have the trigonal bipyramidal structure. The u.v.–visible spectrum in CH$_2$Cl$_2$ is similar to the mull spectrum suggesting that the geometry of the ligands in the solid state is maintained in solution [25].

Experimental

[Co(Ph$_2$PC$_2$H$_4$PPh$_2$)$_2$Cl]Cl was prepared as described in the literature [25] and analysed satisfactorily. Reagent grade dichloromethane was dried and purified by distillation prior to use. The rate constants were measured using an Applied Photophysics stopped-flow device and the data were recorded using a Tektronix model 5100 storage oscilloscope and Polaroid camera. All the reactions were run under pseudo-first-order conditions with the nucleophile present in excess. The temperature was maintained constant at 25.0 ± 0.1 °C. The substrate concentration was varied between 4×10^{-5} and 1×10^{-4} mol dm^{-3}. Standard errors were calculated as described in the literature [26]. The conductivities were measured in 1×10^{-3} mol dm^{-3} acetone solutions using a Radiometer conductivity meter equipped with a type CDC 314 conductivity cell. The product of the reaction between [Co(Ph$_2$PC$_2$H$_4$PPh$_2$)$_2$Cl]Cl and 2,9-dimethyl-1,10-phenanthroline (dmphen) was isolated. It was characterized as [Co(dmphen)Cl$_2$]. *Anal.:* Calculated for CoC$_{14}$H$_{12}$N$_2$Cl$_2$: C, 49.9; H, 3.5; N, 8.31. Found: C, 49.4; H, 3.4; N, 8.3. This complex has been previously investigated [27].

Results

A single reaction was observed when dichloromethane solutions of [Co(Ph$_2$PC$_2$H$_4$PPh$_2$)$_2$Cl]Cl were reacted with 1,10-phenanthroline (phen), 2,2′-bipyridyl (bipy) and 2,9-dimethyl-1,10-phenanthroline (dmphen). The measured absorbance change was equal to the calculated absorbance change between reactants and products. The kinetic data are given in Tables I and II. The results are consistent with a mechanism in which [Co(Ph$_2$PC$_2$H$_4$PPh$_2$)$_2$Cl]$^{+1}$

TABLE I. Pseudo-first-order Rate Constants for Substitution Reactions of $[Co(Ph_2PC_2H_4PPh_2)_2Cl]Cl$ with Bipy, Phen, and Dmphen in Dichloromethane at λ = 360 nm.

$10^4[Co(Ph_2PC_2H_4PPh_2)_2Cl]^+$ mol dm^{-3}	10^3[phen] mol dm^{-3}	k_{obs}/s^{-1}
0.4	0.5	16.4
	1.0	25.0
	2.0	40.0
	3.0	42.9
	5.0	48.3
	10.0	57.0
	16.0	62.5
1.0	1.0	10.2
	2.0	18.9
	4.0	25.8
	8.0	37.0
1.0[a]	2.0	3.7
	4.0	7.3
	6.0	10.2
	10.0	17.0

$10^4[Co(Ph_2PC_2H_4PPh_2)_2Cl]^+$ mol dm^{-3}	10^3[bipy] mol dm^{-3}	k_{obs}/s^{-1}
0.4	1.0	14.0
	2.0	20.0
	4.0	26.3
	40.0	52.3
1.0	1.0	9.8
	2.0	18.9
	4.0	24.0
	10.0	38.5
	40.0	47.0

$10^4[Co(Ph_2PC_2H_4PPh_2)_2Cl]^+$ mol dm^{-3}	10^3[dmphen] mol dm^{-3}	k_{obs}/s^{-1}
0.4	1.0	0.80
	2.0	1.52
	4.0	3.3
	6.0	3.7
	10.0	7.6
1.0	2.0	1.2
	4.0	2.3
	6.0	3.3
	10.0	5.5

[a] $[Ph_2PC_2H_4PPh_2] = 1 \times 10^{-2}$ mol dm^{-3}.

reacts with the nucleophile by the dissociative mechanism outlined in the Scheme.

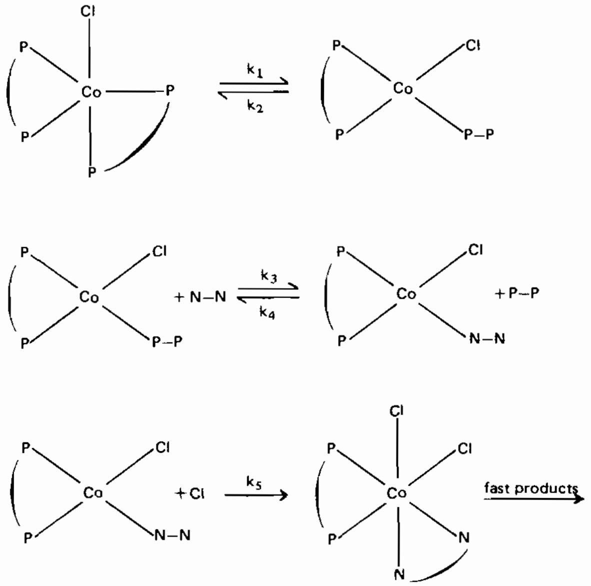
Assuming B and C to be in steady states and that the concentrations of B and C are negligible, equation 1 is obtained for k_{obs}:

$$k_{obs} = \frac{k_1k_3k_5[N\text{–}N][Cl]}{k_3k_5[N\text{–}N][Cl] + k_2k_4[P\text{–}P] + k_2k_5[Cl]} \tag{1}$$

TABLE II. Rate Data for the Substitution of $[Co(Ph_2PC_2H_4PPh_2)_2Cl]Cl$ with Bidentate Amines in Dichloromethane at λ = 360 nm.

$10^4[Co(Ph_2PC_2H_4PPh_2)_2Cl]^+$ mol dm^{-3}	Nucleophile	$10^2 \frac{1}{k_1}$/s	$10^{-1}k_1$/s^{-1}
0.4	phen[a]	1.60 ± 0.40	6.25
1.0	phen	1.66 ± 0.30	6.02
0.4	bipy[b]	1.90 ± 0.40	5.26
1.0	bipy	1.70 ± 0.45	5.88
0.4	dmphen[c]	1.67 ± 0.35	6.00
1.0	dmphen	1.62 ± 0.20	6.17
1.0[d]	phen	1.59 ± 0.22	6.30

[a] 1,10-phenathroline. [b] 2,2′-bipyridyl. [c] 2,9-dimethyl-1,10-phenanthroline. [d] The concentration of added $Ph_2PC_2H_4PPh_2$ was 1×10^{-2} mol dm^{-3}.



Scheme. All charges are omitted, P–P = $Ph_2PC_2H_4PPh_2$, and N–N = bidentate nucleophile.

Equation 1 can be rearranged to give equation 2:

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{1}{[N\text{–}N]}\left[\frac{k_2k_4[P\text{–}P]}{k_1k_3k_5[Cl]} + \frac{k_2}{k_1k_3}\right] \tag{2}$$

Thus plots of $1/k_{obs}$ *versus* $1/[N\text{–}N]$ should yield straight lines of intercept $1/k_1$ and slope $\{k_2/k_1k_3 + k_2k_4[P\text{–}P]/k_1k_3k_5[Cl]\}$. It was possible to isolate the reaction product $[Co(dmphen)Cl_2]$ when dmphen was the nucleophile. In the case of the reactions of $[Co(Ph_2PC_2H_4PPh_2)_2Cl]^+$ with both bipy and phen it was not possible to isolate reaction products.

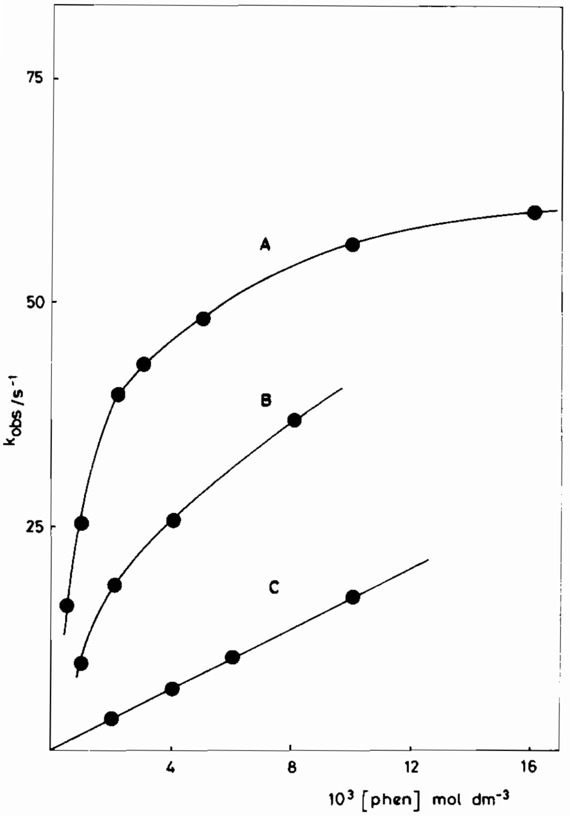


Figure 1. Plot of k_{obs} *versus* nucleophile concentration for reaction of 1,10-phenanthroline with $[Co(Ph_2PC_2H_4PPh_2)_2Cl]Cl$ in dichloromethane at 25 °C. (A) $[Co(Ph_2PC_2H_4PPh_2)_2Cl]^{1+} = 4 \times 10^{-5}$ mol dm^{-3}; (B) $[Co(Ph_2PC_2H_4PPh_2)_2Cl]^{1+} = 1 \times 10^{-4}$ mol dm^{-3}; (C) $[Co(Ph_2PC_2H_4PPh_2)_2Cl]^{1+} = 1 \times 10^{-4}$ mol dm^{-3}, $[Ph_2PC_2H_4PPh_2] = 1 \times 10^{-2}$ mol dm^{-3}.

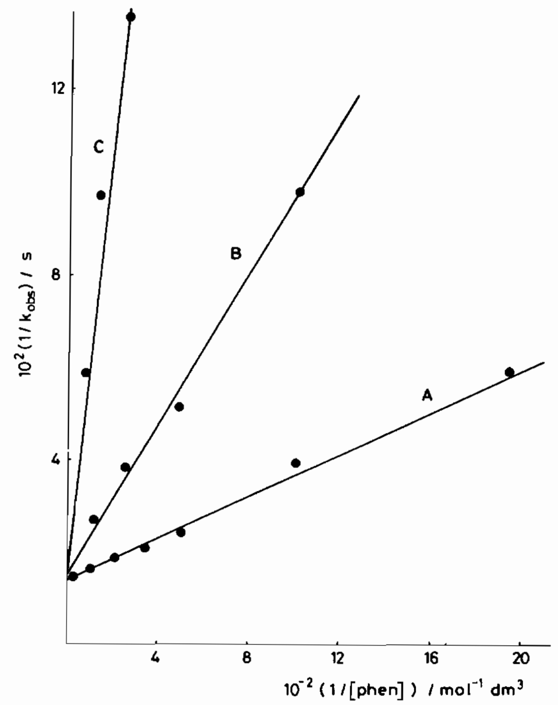


Figure 2. Plot of $1/k_{obs}$ *versus* 1/(nucleophile concentration) for reaction of 1,10-phenanthroline with $[Co(Ph_2PC_2H_4PPh_2)_2Cl]^{1+}$ in dichloromethane at 25 °C. (A) $[Co(Ph_2PC_2H_4PPh_2)_2Cl]^{1+} = 4 \times 10^{-5}$ mol dm^{-3}; (B) $[Co(Ph_2PC_2H_4PPh_2)_2Cl]^{1+} = 1 \times 10^{-4}$ mol dm^{-3}; (C) $[Co(Ph_2PC_2H_4PPh_2)_2Cl]^{1+} = 1 \times 10^{-4}$ mol dm^{-3}, $[Ph_2PC_2H_4PPh_2] = 1 \times 10^{-2}$ mol dm^{-3}.

The experimental data support the proposed mechanism. Figure 1 shows plots of k_{obs} *versus* nucleophile concentration for reaction of $[Co(Ph_2PC_2H_4PPh_2)_2Cl]^{+1}$ with phen, at two different substrate concentrations and at a large excess of leaving group. Equation 1 predicts that the presence of excess leaving group will reduce the observed rate constant at a given nucleophile concentration; increasing the substrate concentration generally has a similar effect. When $(k_2k_4[P\text{–}P] + k_2k_5[Cl]) \gg k_3k_5[N\text{–}N][Cl]$ equation 1 predicts that k_{obs} will vary linearly with nucleophile concentration. Figure 1 shows this to be the case. Figure 2 shows plots of $1/k_{obs}$ *versus* 1/[N–N] for the data in Figure 1. There is good agreement with the proposed mechanism and the intercept $1/k_1$ gives $k_1 = 62.5$ s^{-1}. This is in good agreement with the directly observed limit in Figure 1 *i.e.* $k_{obs} = k_1$ when $k_3k_5[N\text{–}N][Cl] \gg (k_2k_4[P\text{–}P] + k_2k_5[Cl])$. Further support for the proposed mechanism is the fact that the addition of nucleophile to solutions of $[Co(Ph_2PC_2H_4PPh_2)_2Cl]Cl$ causes an instant decrease in the conductivity.

Discussion

Of the two Co^{II} five-co-ordinate complexes whose substitution reactions have been previously reported, one reacts by a dissociative mechanism while the other reacts by an associative mechanism. In the present investigation the mechanism proposed is purely dissociative and there is no evidence to suggest that an associative contribution is present. The reasons for the different mechanistic behaviour of five-co-ordinate Co^{II} complexes is not immediately obvious. Tolman's Rules [28] which relate to 16 and 18 electron systems are not strictly applicable to Co^{II} complexes. A possible reason for the divergence in behaviour is the effect of the structure of the substrate on its reactivity. The five-co-ordinate trigonal bipyramidal species $[Co(2,6\text{ lutidine N-oxide})_5]^{2+}$ was found to react by a dissociative mechanism [22], while a pentaco-ordinate macrocyclic Co^{II} complex, which is believed to have the square pyramidal structure, reacted by an associative mechanism [21]. The evidence strongly suggests that the complex used in the present investigation has a trigonal bipyramidal structure.

It is probable that a square pyramidal five-coordinate complex would be more susceptible to nucleophilic attack than one having the trigonal bipyramidal structure. Although the number of systems investigated to date is very limited, nevertheless the results suggest the square-pyramidal five-coordinate Co^{II} complexes will react by a predominantly associative mechanism and that trigonal bipyramidal complexes will substitute via a dissociative mechanism. Clearly it will be necessary to investigate many more systems before a general solution is possible.

Acknowledgements

One of us (P.F.B.) thanks the Department of Education for support. We thank a referee for helpful suggestions regarding the mechanism.

References

1 D. A. Sweigart and P. Heidtmann, *Chem. Commun.*, 556 (1973).
2 D. A. Sweigart and P. Heidtmann, *J. Chem. Soc. Dalton*, 1686 (1975).
3 C. G. Grimes and R. G. Pearson, *Inorg. Chem.*, *13*, 970 (1974).
4 P. Meier, A. E. Merbach, M. Dartiguenave and Y. Dartiguenave, *J. Am. Chem. Soc.*, *98*, 6402 (1976).
5 T. D. B. Morgan and M. L. Tobe, *Inorg. Chim. Acta*, *5*, 563 (1971).
6 P. Meakin and J. P. Jesson, *J. Am. Chem. Soc.*, *96*, 5751 (1974).
7 R. F. Heck, *J. Am. Chem. Soc.*, *85*, 651, 657 (1963).
8 F. Basolo, A. T. Brault and A. S. Poe, *J. Chem. Soc.*, 676 (1964).
9 P. M. Enriquez and S. S. Zumdahl, *Inorg. Chem.*, *12*, 2475 (1973).
10 B. F. G. Johnson, J. Lewis and M. V. Twigg, *J. Chem. Soc. Dalton*, 1876 (1975).
11 D. A. Sweigart, D. E. Cooper and J. M. Millican, *Inorg. Chem.*, *13*, 1272 (1974).
12 D. A. Sweigart, *Inorg. Chim. Acta*, *18*, 179 (1976).
13 R. V. Snyder and G. N. La Mar, *J. Am. Chem. Soc.*, *98*, 4419 (1976).
14 D. A. Sweigart, *Inorg. Chim. Acta*, *23*, 113 (1977).
15 H. Waiversik and F. Basolo, *J. Am. Chem. Soc.*, *89*, 4626 (1967).
16 E. Grimley, J. M. Grimley, Tsong-Dsu Li and D. Emerich, *Inorg. Chem.*, *15*, 1716 (1976).
17 D. A. Sweigart and D. G. De Wit, *Inorg. Chem.*, *9*, 1582 (1970).
18 W. J. Louw and J. E. Singleton, *Chem. Commun.*, 520 (1977).
19 M. J. Hynes and P. F. Brannick, *Chem. Commun.*, 942 (1977).
20 D. A. Sweigart, *Chem. Commun.*, 688 (1975).
21 P. M. Enriques, S. S. Zumdahl and L. Forshey, *Chem. Commun.*, 1527 (1970).
22 P. Meier, A. Merbach, S. Burki and T. A. Kaden, *Chem. Commun.*, 36 (1972).
23 J. K. Stalick, P. W. R. Corfield and D. W. Meek, *J. Am. Chem. Soc.*, *94*, 6194 (1972).
24 J. K. Stalick, D. W. Meek, B. Y. K. Ho and J. J. Zuckerman, *Chem. Commun.*, 630 (1972).
25 W. D. Horrocks, Jr., G. R. Van Hecke and D. D. Hall, *Inorg. Chem.*, *6*, 694 (1967).
26 E. S. Swinbourne, 'Analysis of Kinetic Data', Nelson, London (1971).
27 N. Teodorescu and M. Brezeanu, *Rev. Roumaine Chim.*, *22*, 221 (1977).
28 C. A. Tolman, *Chem. Soc. Rev.*, *1*, 337 (1972).