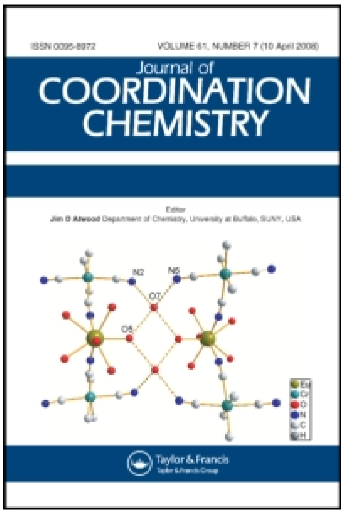

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

FACILE LIGAND DISPLACEMENT IN THE COMPLEX CATION BY DIPHOSPHINES BIS (1, IO-PHENANTHROLINE-COPPER(1)

T. S. Andy Hor[a]; Elina B. C. Luar[a]
[a] Depurlmenl of Chemistry, Faculty .f Science, National University of Singapore, Kent Ridge, OSl, Singapore

To cite this Article Hor, T. S. Andy and Luar, Elina B. C.(1988) 'FACILE LIGAND DISPLACEMENT IN THE COMPLEX CATION BY DIPHOSPHINES BIS (1, IO-PHENANTHROLINE-COPPER(1)', Journal of Coordination Chemistry, 18: 4, 335 — 337

To link to this Article: DOI: 10.1080/00958978808080973

URL: http://dx.doi.org/10.1080/00958978808080973

J. Coord. Chem. 1988, Vol. 18. pp. 335–337
Reprints available directly from the publisher
Photocopying permitted by license only

FACILE LIGAND DISPLACEMENT IN THE BIS(1,10-PHENANTHROLINE)-COPPER(I) COMPLEX CATION BY DIPHOSPHINES

T. S. ANDY HOR* and ELINA B. C. LUAR

Department of Chemistry, Faculty of Science, National University of Singapore, Kent Ridge, 0511, Singapore

(Received April 27, 1988; in final form June 13, 1988)

Ligand substitution occurs readily at room temperature upon mixing stoichiometric quantities of $[Cu(phen)_2]NO_3$ and free triphenylphosphine or diphosphines $Ph_2P(CH_2)_nPPh_2$ (n = 1–3). The resultant cationic complexes [Cu(phen)(PP)]X are isolated as PF_6^- or NO_3^- salts in high yields.

Keywords: copper, phenanthroline, phosphine, substitution

INTRODUCTION

In the recent development of copper(I) chemistry, much attention has been focussed on α-diimine complexes;[1–6] this owes largely to their luminescence or photo-redox properties[7–11] which are related to solar energy conversion.[12,13] Most of the reported systems are confined to the triphenylphosphine species,[7–10,14–16] which is understandable in view of the ready accessibility of starting materials such as $[Cu(PPh_3)_n]BF_4$[9] and $Cu(PPh_3)_2(NO_3)$.[17,18] In the present communication, we wish to report facile ligand dissociation in the complex $[Cu(phen)_2]NO_3$ (phen = 1,10-phenanthroline)[19,20] thus making it an attractive reagent for the synthesis of other phosphine-substituted Cu(I) phenanthroline derivatives.

EXPERIMENTAL

General Procedures

All reactions were performed under an atmosphere of pure dry dinitrogen using standard Schlenk techniques. NMR spectra in $CDCl_3$ were recorded on a JEOL 90Q instrument with H_3PO_4 as the external ^{31}P reference. Conductivity (10^{-3} mol dm^{-3}) of the sample in nitromethane was determined using a CM-115 Kyoto Electronic conductivity meter with a cell constant of 1.23 cm^{-1}. The complexes $Cu(PPh_3)_2NO_3$[17] and $[Cu(phen)_2]NO_3$[19] were prepared according to literature methods. Other reagents were supplied from commercial sources.

Reactions

The preparation of $[Cu(phen)(dppp)]PF_6$ (dppp = 1,3-bis(diphenylphosphino)-propane) represents a typical procedure and is described below.

---

* Author for correspondence

A brownish red suspension of [Cu(phen)$_2$]NO$_3$ (0.54 g: 1.04 mmol) in methanol (20 cm^3) immediately turned to a clear yellow solution upon addition of solid dppp (0.43 g; 1.04 mmol). Excess of a solution of NH$_4$PF$_6$ in methanol was added after the solution was stirred for 1½ h at room temperature (28°C), followed by evaporation to *ca* 5 cm^3 under vacuum. Filtration and recrystallization from CH$_2$Cl$_2$/CH$_3$OH led to the isolation of yellow microcrystals of [Cu(phen)(dppp)]PF$_6$ (0.73 g; 64%).

All the other products were made by following similar procedures and their melting points, yields and recrystallization solvents are listed in Table I. The nitrate salts were isolated directly from the reaction mixtures without the addition of NH$_4$PF$_6$.

TABLE I
Preparative, conductance and analytical data for the complexes.

Complexes (colour, melting point (°C))	Recrystallization solvent; yield (%)	Elemental analyses (%)	Λ_M (ohm^{-1} cm^2 M^{-1})^a	δ^{31}P (PR$_3$) (ppm)^b
[Cu(phen)(PPh$_3$)$_2$]NO$_3$ (pale yellow; 203–204)	ethanol/ether; 77	C, 68.44(69.43) H, 4.38(4.61) N, 5.57(5.06)	77	3.77(br)
[Cu(phen)(dppp)] PF$_6$ (yellow; 232–234)	CH$_2$Cl$_2$/methanol; 64	C, 58.36(58.43) H, 4.08(4.28) N, 3.01(3.49)	74	−18.44(br)
[Cu(phen)(dppe)]PF$_6$ (pale yellow; 229–230)	CH$_3$CN/ethanol; 91	C, 58.32(57.98) H, 3.87(4.09) N, 3.67(3.56)	78	−5.52(br)
[Cu(phen)(dppm)]NO$_3$–·¼CH$_2$Cl$_2$ (pale yellow; 248–249)	CH$_2$Cl$_2$; 73	C, 62.47(62.78) H, 4.05(4.28) N, 6.04(5.91)	84	−11.44(br)

^{a} Nitromethane. ^{b} CDCl$_3$.

RESULTS AND DISCUSSION

Ligand displacement occurs rapidly upon mixing stoichiometric quantities of [Cu(phen)$_2$]NO$_3$ with free monophosphine (PPh$_3$) or diphosphines [Ph$_2$PC$_3$H$_6$PPh$_2$ (dppp), Ph$_2$PC$_2$H$_4$PPh$_2$ (dppe) and Ph$_2$PCH$_2$PPh$_2$ (dppm)] at room temperature corresponding to (*1*).

$$[\mathrm{Cu(phen)_2}]\mathrm{NO_3} \xrightarrow{\text{P–P}} [\mathrm{Cu(phen)(P{-}P)}]\mathrm{NO_3} \xrightarrow{\mathrm{PF_6}^-} [\mathrm{Cu(phen)(P{-}P)}]\mathrm{PF_6}$$

$$(\text{P–P} = 2 \times \mathrm{PPh_3}, \text{ dppm, dppe and dppp}) \qquad (1)$$

The substitution is accompanied by an almost instantaneous dissolution and decolourization of the charge transfer bis(phen) complex in methanol upon introduction of the phosphines. The resultant mixed-ligand complexes, which are isolated as NO$_3$$^-$ or PF$_6$$^-$ salts, are stable to air oxidation and ligand dissociation except for the dppm analogue which decomposes readily in solution. The diphosphine complexes are novel but the PPh_3 species has been isolated from a substitution reaction of $[Cu(PPh_3)_n]^+$ with phen.[7,10,21]

The uncoordinated natures of the anions are inferred from their IR absorptions. In nitromethane the complexes display conductance which typifies a 1:1 electrolyte (Table I).[22] In the ^{31}P-NMR spectra, though the PF_6^- septuplets are sharp [J(PF) = 713 Hz], resonances from the coordinated phosphines are broad, as expected from quadrupolar relaxation.

Synthesis of other novel bis-chelating Cu(I) α-diimines could be motivated by the ligand lability of the title bis(phen) complex. Emission and excitation spectral studies of these potentially redox active systems are of some interest.

ACKNOWLEDGEMENTS

The authors express their gratitude to the National University of Singapore for financial support (RP 850030).

REFERENCES

1. C.C. Phifer and D.R. McMillin, *Inorg. Chem.*, **35**, 1329 (1986).
2. S. Goldstein and G. Czapski, *Inorg. Chem.*, **24**, 1087 (1985).
3. S. Kitagawa, M. Munakata and A. Higashie, *Inorg. Chim. Acta*, **84**, 79 (1984).
4. C.-W. Lee and F.C. Anson, *Inorg. Chem.*, **23**, 837 (1984).
5. L.E. Pope and D.S. Sigman, *Proc. Nat. Acad. Sci. USA*, **81**, 3 (1984).
6. S. Goldstein and G. Czapski, *J. Amer. Chem. Soc.*, **105**, 7276 (1983).
7. R.A. Rader, D.R. McMillin, M.T. Buckner, T.G. Matthews, D.J. Casadonte, R.K. Lengel, S.B. Whittaker, L.M. Darmon and F.E. Lytle, *J. Amer. Chem. Soc.*, **103**, 5906 (1981).
8. P.A. Breddels, P.A.M. Berdowski and G. Blasse, *J. Chem. Soc., Faraday Trans.*, **78**, 595 (1982).
9. A.A. Del Paggio and D.R. McMillin, *Inorg. Chem.*, **22**, 691 (1983).
10. M.T. Buckner, T.G. Matthews, F.E. Lytle and D.R. McMillin, *J. Amer. Chem. Soc.*, **101**, 5846 (1979).
11. V. Balzani, F. Bolletta, M.T. Gandolfi and M. Maestri, *Top. Curr. Chem.*, **75**, 1 (1978).
12. V. Balzani, F. Bolletta, F. Scandola and R. Ballardini, *Pure Appl. Chem.*, **51**, 299 (1979).
13. M.W. Blaskie and D.R. McMillin, *Inorg. Chem.*, **19**, 3519 (1980).
14. S. Sakaki, G. Koga and K. Ohkubo, *Inorg. Chem.*, **25**, 2330 (1986).
15. L.M. Engelhardt, C. Pakawatchai, A.H. White and P.C. Healy, *J. Chem. Soc., Dalton Trans.*, 125 (1985).
16. G. Blasse and D.R. McMillin, *Chem. Phy. Lett.*, **70**, 1 (1980).
17. H.J. Gysling, in D.F. Shriver (ed.), 'Inorganic Syntheses', Vol. 19 (Wiley, New York, 1979), Chap. 3, p. 92.
18. G.G. Messmer and G.J. Palenik, *Inorg. Chem.*, **8**, 2750 (1969).
19. F.H. Jardine, A.G. Vohra and F.J. Young, *J. Inorg. Nucl. Chem.*, **33**, 2941 (1971).
20. M. Munakata and J.F. Endicott, *Inorg. Chem.*, **23**, 3693 (1984).
21. M.T. Buckner and D.R. McMillin, *Chem. Comm.*, 759 (1978).
22. W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).