Asymmetric synthesis of a chiral tetradentate ligand based on a bis[diphenylphosphinoferrocenyl] moiety. Electrochemical behavior of free ligand and its Ru^{II} and Cu^{I} complexes [1]

Anne Masson-Szymczak, Olivier Riant, Aurore Gref, Henri B. Kagan [*]

*Laboratoire de Synthèse Asymétrique associé au CNRS, Institut de chimie moléculaire d'Orsay, Université de Paris-Sud,
91405 Orsay Cedex, France*

Abstract

α-Diphenylphosphino carboxaldehyde 4, prepared by asymmetric synthesis, was reacted with ethane diamine to give bisimine bisphosphine 5. Ruthenium(II) complex 6 and copper(I) complex 8 were easily formed and their electrochemical properties studied.

Keywords: Asymmetric synthesis; Tetradentate ligand; Ruthenium; Copper; Ferrocenyl phosphine; Cyclic voltammetry

1. Introduction

We recently described [1] an efficient asymmetric synthesis of orthosubstituted ferrocene carboxaldehydes 4 (*ee* > 98%) from ferrocene carboxaldehyde 1 via the preparation of chiral acetal 2. The ortholithiation of acetal 2 followed by addition of ClPPh$_2$ and acidic hydrolysis of the acetal moiety provided phosphinoaldehyde 4 (E=PPh$_2$) in good yield with *ee* > 98%. We wish to show the use of this latter for the preparation of the C$_2$ symmetric bis-ferrocenylphosphine 5 which can act as a tetradentate ligand of some transition metals.

2. Results and discussion

Diphosphine 5 is easily prepared by adding 1,2-diaminoethane to aldehyde 4 (E=PPh$_2$) in boiling ethanol (Scheme 1). The diphosphine 5 precipitates and is recovered in 83% yield. The spectroscopic data are in full agreement with the structure. The C$_2$ symmetry is evidenced by ^{1}H and ^{31}P NMR, which show only one signal (singlet) for both CH=N and phosphorus.

The synthesis of the ruthenium(II) complex 6 (56% isolated yield) has been realized by reacting 5 and RuCl$_2$(DMSO)$_4$ [2] in refluxing chloroform. ^{1}H NMR shows δ = 8.7 ppm for CH=N (against 8.6 ppm in 5) and ^{31}P NMR indicates a singlet at δ = 34.8 ppm (against −22.2 ppm in 5). These two data are in agreement with a tetradentate C$_2$-symmetrical ligand, the two phosphorus being equivalent. Treatment of ruthenium complex 6 with excess AgPF$_6$ in hot acetonitrile gave the biscationic complex 7 mixed with another complex, attributed to silver(I) [5Ag]$^+$PF$_6^-$ complex. ^{31}P NMR gave a singlet at δ = 35.7 ppm for 7 and an AB system of two doublets at δ = 34.53 and 38.44 ppm (J(P–P) = 30.7 Hz) for the monocationic silver complex (two non-equivalent phosphorus, see Experimental section).

The copper(I) complex 8 is easily obtained from diphosphine 5 and copper(I) triflate in acetonitrile at room temperature.

Electrochemical behavior of the different compounds has been investigated in anhydrous dichloromethane n-Bu$_4$NBF$_4$ (0.1 M) solutions, using a glassy carbon working electrode in a three electrode cell and a 263-Model PAR equipment. The cyclic voltammograms of 4, 5, 6 and 8 species are shown in Figs. 1 and 2.

Oxidation of 4 gives (Fig. 1(A)a) a first irreversible wave at 1.04 V and a quasi-reversible one of $E_{1/2}$ at
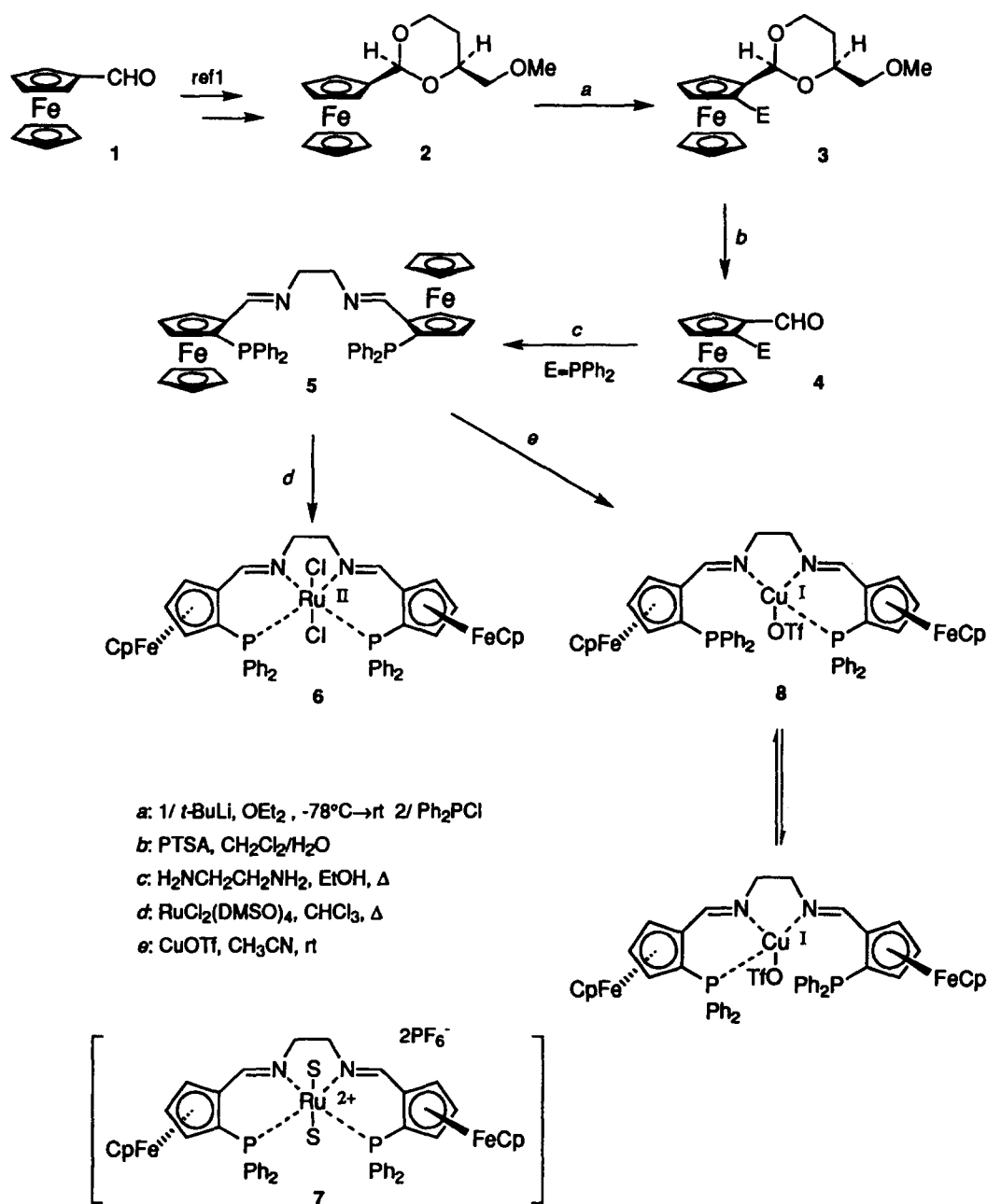
---

[1] Dedicated to Professor H. Brunner on his 60th birthday.
[*] Corresponding author.

1.21 V. Loss of the first one-electron concerns the phosphorus atom [3], which is oxidized via ferricinium by fast intramolecular electron transfer with Fe^{II} regeneration. The second one-electron transfer concerns the iron center ($Fe^{II} \rightleftarrows Fe^{III}$) which gives the quasi-reversible wave ($E_{1/2} = 1.21$ V). This agrees with results recently described in the oxidation of other types of mono-ferrocenyl phosphines [4]. The comparison with the voltammogram of ferrocenyl carboxaldehyde ($E_{1/2} = 0.83$ V) (Fig. 1(A)b) shows that the first oxidation in 4 really concerns the iron center. So, the backward

quasi-reversible wave of the ferrocene entity in 4 is due to the presence in the charge transfer of a less electron-rich species.

A similar intramolecular transfer exchange has been observed in cyclic voltammetry of bis-ferrocenyl phosphine 5 (Fig. 1(B)). Containing two ferrocene units and two phosphino groups, this compound is more electron-rich and the oxidation starts at a lower potential when compared with monoferrocene species as 4. The oxidation takes place in a similar way, consistent with a successive one-electron oxidation at 0.66 V and 0.80 V

a: 1/ t-BuLi, OEt₂, -78°C→rt 2/ Ph₂PCl

b: PTSA, CH₂Cl₂/H₂O

c: H₂NCH₂CH₂NH₂, EtOH, Δ

d: RuCl₂(DMSO)₄, CHCl₃, Δ

e: CuOTf, CH₃CN, rt

Scheme 1.

($Fe^{II} \rightleftarrows Fe^{III}$) of each ferrocene unit chemically not identical, followed by fast chemical oxidation of phosphorus atoms by the two ferricinium species. The second one-electron oxidation of ferrocenes takes place in the same zone of potential as for **4**. Nevertheless, the voltammogram shows two practically irreversible superposed waves (oxidation peaks 1.16 V and 1.37 V; reduction peaks 0.97 V and 0.83 V). Such a differentiation of two iron centers is often encountered with bis-ferrocene species [5]. The drastic irreversibility observed in oxidation of **5**, consistent with the fast disappearance of ferricinium cations, is due to a chemical reaction, probably the subsequent oxidation of phosphine radical cation [6].

The cyclic voltammogram of ruthenium(II) complex **6** shows (Fig. 1(C)) two quasi-reversible oxidation waves at $E_{1/2}^1$ of 0.45 V and $E_{1/2}^2$ of 1.04 V. The first one-electron wave ($E_{1/2}^1$) corresponds to $Ru^{II} \rightleftarrows Ru^{III}$ oxidation and the second two-electron wave ($E_{1/2}^2$) to $Fe^{II} \rightleftarrows Fe^{III}$ oxidation. In this complex, the two ferrocenyl units are full equivalents, there is no internal electron transfer from phosphorus to ferricinium, good evidence that both phosphorus atoms are strongly coordinated to ruthenium. This complex is chemically stable at the time-scale of analysis.

The cyclic voltammogram of copper(I) complex **8** is given in Fig. 2(A). When compared with ruthenium complex there is a similar wave corresponding to the oxidation of the two ferrocenyl units (oxidation peak at 1.14 V, reduction peak at 0.98 V), but this is irreversible and shows two iron centers not completely
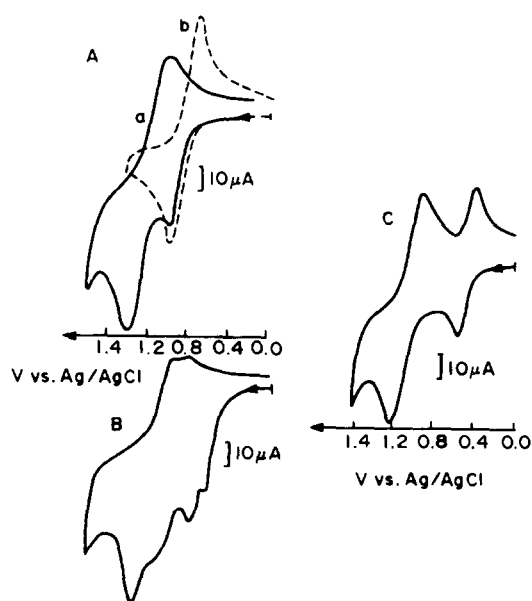

Fig. 2. Cyclic voltammograms in CH_2Cl_2-n-Bu_4NBF_4 (0.1 M) at glassy carbon electrode, reference electrode Ag/AgCl of **8** (1 mM): A sweep rate 100 mV s^{-1}; B sweep rate 2 V s^{-1}.

equivalent. Concerning the copper(I) center there is one wave in oxidation at 0.82 V and two waves in reduction at 0.73 V and 0.55 V. Because the coordination of Cu(I) by P_2N_2 ligand is not well established [7] it is more difficult to assign the electron transfer at this center.

However, because there is a precedent in oxidation of free phosphine by Cu^{II} [10], and we show here that ferricinium also has this oxidation (in free ligand), we think that the electrochemical oxidations at 0.82 V ($Cu^I \rightarrow Cu^{II}$) and 1.14 V ($Fe^{II} \rightarrow Fe^{II}$) are followed by a slow chemical oxidation of one free phosphine by Cu^{II} or ferricinium. At a low sweep rate (100 mV s^{-1}, Fig. 2(A)), there is only one species of Cu^I in oxidation and two species of Cu^{II} in reduction, one containing the unoxidized phosphine and the other containing oxidized phosphine. When the sweep rate increases to 2 V s^{-1}, the extent of chemical oxidation is attenuated because chemical oxidation is slow, the two waves $Fe^{II} \rightarrow Fe^{III}$ and $Cu^I \rightarrow Cu^{II}$ became practically quasi-reversible and the peak at 0.55 V is very attenuated (Fig. 2(B)).

This is compatible with an apparent C_2 symmetry of **8** (^1H NMR spectra) if there is a fast equilibrium between the two complexes where only one phosphorus binds to copper. This interpretation is also in agreement with the broad singlet observed in ^{31}P NMR [6]. The quantitative electrochemical studies and catalytic properties of complexes **6–8** and other types of complex prepared from **5** are under active investigation [11].

Fig. 1. Cyclic voltammograms in CH_2Cl_2-n-Bu_4NBF_4 (0.1 M) at glassy carbon electrode, reference electrode Ag/AgCl, sweep rate 100 mV s^{-1} at room temperature under argon: A, (a) **4** (2 mM); (b) ferrocenylcarboxaldehyde (2 mM); B, **5** (2 mM) C, **6** (2 mM).
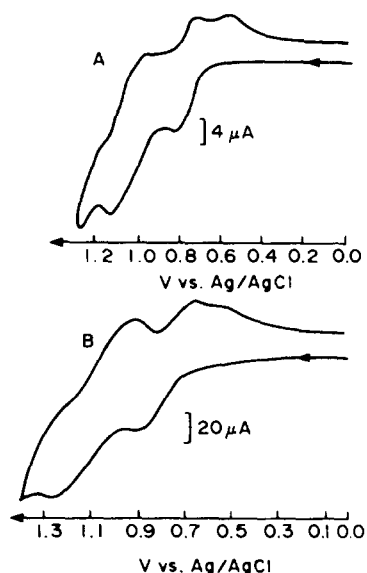
3. Experimental

Bisimine **5**. Phosphinoaldehyde **4** (796 mg, 2 mmol) was mixed with 20 ml of ethanol under argon and the

mixture was heated to reflux until dissolution of the red–orange solid. Freshly distilled 1,2-diaminoethane (67 μl) was injected and the imine immediately started to precipitate. After 3 h standing at room temperature the orange crystals were collected on a glass fritt, washed with cold ethanol and dried in vacuo (685 mg, 83% yield). M.p. 209°C; $[\alpha]_D = +372$ ($c = 0.5$, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 3.55 (4H, m, CH_2), 3.80 (2H, s, C_5H_3), 4.15 (10H, s, C_5H_5), 4.45 (2H, s, C_5H_3), 5.05 (2H, s, C_5H_3), 7.0–7.60 (20H, m, Ar), 8.40 (2H, s, CH=N). ^{31}P NMR: δ −22.26 ppm (s, 1P). MS (Cl, NH_3) m/e 825 (32.8%), 824 (73.5), 823 (100), 822 (52.8), 821 (19.2), 820 (6.6). IR (cm^{-1}) 1640 (C=N). Anal. Found: C, 69.26; H, 5.49; N, 3.35; P, 7.19. $C_{48}H_{42}Fe_2N_2P_2$. Calc.: C, 70.26; H, 5.16; N, 3.41; P, 7.55.

Ruthenium complex **6**. A dry Schlenk tube was charged with bisimine **5** (150 mg, 0.18 mmol) under argon and dissolved in 10 ml of degased chloroform, $RuCl_2(DMSO)_4$ [2]. (88.5 mg, 1 equiv.) were added and the deep orange solution was refluxed for 40 min under argon. The reaction mixture was cooled and the solvent was removed on the vacuum line. The complex was precipitated by addition of a small amount of degased acetone. After filtration under nitrogen using a filter canula and drying in vacuo, the complex **6** (100 mg, 56% yield) was isolated as a bright orange powder. The solid was stable enough to be handled for a short time in air but was readily decomposed in solution if oxygen was present. M.p. 245°C (dec.). $[\alpha]_D = -3098$ ($c = 0.43$, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 3.47 (2H, m, CH_2), 3.72 (5H, s, C_5H_5), 3.75 (2H, m, CH_2), 4.30 (2H, s, C_5H_3), 4.55 (2H, s, C_5H_3), 4.80 (2H, s, C_5H_3), 6.80–7.20 (m, Ar), 8.73 (2H, m, CH=N). ^{31}P NMR: δ +34.86 (s, 1P). MS (CI, NH_3) m/e 994 (M + 2, 3.5%), 993 (M + 1, 3.6), 992 (4.5), 991 (4.0). IR (cm^{-1}) 1641 (C=N). Anal. Found: H, 4.39; N, 2.45; P, 5.77. $C_{48}H_{42}Cl_2Fe_2N_2P_2Ru$. Calc.: H, 4.26; N, 2.82; P, 6.24.

Attempted preparation of complex **7**. To a stirred solution of complex **6** (50 mg, 50 μmol) in 15 ml of dry acetonitrile under argon was added dropwise a solution of silver hexafluorophosphate (81 mg) in 5 ml of acetonitrile and the reaction mixture was refluxed in the dark for 2 h. After cooling, the mixture was filtered on Celite under argon to remove the precipitated silver salts and the resulting orange solution was concentrated on the vacuum line. Dry degased diethyl ether was added dropwise to precipitate a brown solid which was filtered under nitrogen using a filter canula and dried in vacuo. The brown solid was then directly analysed by ^{31}P NMR in CD_3CN ($\delta = 35.7$ ppm (s) for the biscationic complex **7**, $\delta = 34.53$ and 38.44 ppm (AB, J(P–P) = 30.5 Hz) for the monocationic silver(I) complex). The NMR indicates a 1/4 ratio for the silver(I)/ruthenium(II) complexes. This reaction was run several times under different conditions (temperature, silver salt,

equiv. of silver salt) but we were unable to isolate the pure biscationic complex. The silver(I) complex was in situ prepared from equimolecular amounts of silver hexafluorophosphate and ligand **5** in acetonitrile and analysed by ^{31}P NMR.

Copper complex **8**. To a solution of bisimine **5** (150 mg, 0.18 mmol) in 10 ml of degased acetonitrile under argon was added a solution of copper(I) triflate (CuOTf $0.5C_6H_6$, 46 mg, 1 equiv.) in 5 ml of acetonitrile. After 10 min stirring at room temperature the deep red solution was concentrated on the vacuum line and degased diethyl ether was injected dropwise until formation of a precipitate. After filtration under argon and drying in vacuo the complex **8** (157 mg, 84%) was isolated as an orange crystalline solid. M.p. 175°C, $[\alpha]_D = -1380$ ($c = 0.25$, CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 3.50 (4H, m, CH_2), 4.18 (2H, s, C_5H_3), 4.28 (10 H, s, C_5H_5), 4.75 (2H, s, C_5H_3), 4.95 (2H, s, C_5H_3), 7.20–7.60 (20H, m, Ar), 8.70 (2H, s, CH=N). ^{31}P NMR: δ −9.64 ppm (bs, 1P). IR (cm^{-1}) 1638 (C=N). Anal. Found: C, 56.34; H, 4.73; N, 2.37. $C_{48}H_{42}CuF_3Fe_2N_2O_3P_2S$. Calc.: C, 56.46; H, 4.15; N, 2.74.

References and notes

[1] O. Riant, O. Samuel and H.B. Kagan, *J. Am. Chem. Soc.*, *115* (1993) 5835.

[2] I.P. Evans, A. Spencer and G. Wilkinson, *J. Chem. Soc.*, *Dalton Trans.*, (1972) 204.

[3] Oxidation of phosphorus proceeds by phosphonium radical cation ($P^{+\circ}$) formation, which can evolve in the presence of traces of water, and subsequent oxidation to phosphine oxide.

[4] I.R. Butler, M. Kalaji, L. Nehrlich, M. Hursthouse, A.I. Karaulov and K.N Malik, *J. Chem. Soc., Chem. Commun.*, (1995) 459.

[5] (a) T.L. Gilchrist and C.J. Moody, *Chem. Rev.*, *77* (1977) 409.
(b) H. Scholl and K. Sochai, *Electrochim. Acta, 36* (1991) 689.

[6] $Fc^+ + P^{+\circ} + H_2O \rightarrow Fc + P=O + 2H^+$.

[7] The structure of Cu^1 complexes of diiminodiphosphines derived from 2-diphenylphosphinobenzaldehyde and various 1,2- or 1,3-diamines have been studied [8,9]. The authors concluded, on the basis of spectroscopic and X-ray data, that the Cu^1 are four- or three-coordinated by the two phosphino groups and one of the two imino groups, a fast equilibrium occuring between two imino groups. The electrochemical data of our ferrocenyl analogue **8** do not fit with this picture and are better accommodated with a tricoordinate complexation involving a fast equilibrium between the two phosphino groups. More work is needed to confirm this interpretation, the different behavior probably originating from steric and electronic factors not present in the benzene analog.

[8] J.C. Jeffrey, T.B. Rauchfuss and P.A. Tucker, *Inorg. Chem.*, *19* (1980) 3306.

[9] W.K. Wong, J.X. Gao, W.T. Wong and C.M. Che, J. Organomet. Chem., 471 (1994) 277.

[10] S. Daniele, C. Basato, B. Corain, G. Favero and G. Bontempelli, J. Chem. Soc., Dalton Trans., (1988) 1425.

[11] Some C$_2$-symmetric bis-imine ligands have been successfully used as chiral ligands in asymmetric catalysis. See for instance: (a) Z. Li, K.R. Conser and E.N. Jacobsen, J. Am. Chem. Soc., 115 (1993) 5326. (b) D.A. Evans, T. Lectka and S.J. Miller, Tetrahedron Lett., 34 (1993) 7027. (c) J. Knol, A. Meetsma and B.L. Feringa, Tetrahedron: Asymmetry, 6 (1995) 1069.