Journal of Organometallic Chemistry, 317 (1986) 301–306
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SYNTHESIS OF DIFERROCENYLGLYOXIME AND SOME OF ITS TRANSITION METAL COMPLEXES

MÜMTAZ ERTAS, ALI R. KORAY, VEFA AHSEN

Department of Chemistry, Tübitak - Research Institute for Basic Sciences, P.O. Box 74, Gebze - Kocaeli (Turkey)

and ÖZER BEKÂROĞLU*

Department of Chemistry, Technical University of Istanbul, Maslak-Instanbul and Tübitak - Research Institute for Basic Sciences, P.O. Box 74, Gebze-Kocaeli (Turkey)

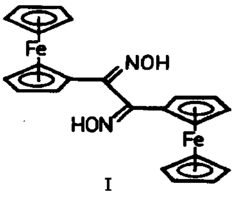
(Received July 9th, 1986)

Summary

Diferrocenylglyoxime has been prepared by the reaction of monolithioferrocene or dilithioferrocene with *anti*-dichloroglyoxime. Characterization of this novel *vic*-dioxime and some of its transition metal complexes are described.

Introduction

We have recently described the synthesis and characterization of various types of *vic*-dioximes and their transition metal complexes [1]. As part of our current programme on the preparation of novel systems that combine features of both coordination and organometallic chemistry we have obtained the first *vic*-dioxime bearing two ferrocenyl groups. We describe here the synthesis and characterization of diferrocenylglyoxime (I) and some of its transition metal complexes.



I

Results and discussion

As our primary goal was to synthesize a ferrocenophanedioxime (II) we carried out the reaction of 1,1′-dilithioferrocene with *anti*-dichloroglyoxime (DCGO) as outlined in Scheme 1.

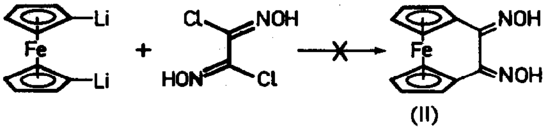
Work up, however, gave an orange cystalline product in 11% yield, which was shown by elemental analysis, IR, ^{1}H NMR and mass spectra to be unequivocally *anti*-diferrocenylglyoxime (I).

This unexpected result prompted us to investigate the reaction of monolithioferrocene with DCGO, which we expect to give I directly (Scheme 2).

Several ways of preparing monolithioferrocene free from dilithioferrocene are described in the literature [2]. The three routes most commonly used are: (a) reaction of ferrocene with an equimolar amount of butyllithium [3]; (b) exchange between chloromercuriferrocene and butyllithium [4]; and (c) reaction of bromoferrocene with butyllithium [5]. The reaction with DCGO of monolithioferrocene prepared by the first two procedures yielded no trace of I; the failure of these reactions must be attributed to the high reactivity of dichloroglyoxime towards the excess of butyllithium and some by-products (e.g. dibutylmercury) which are present in the reaction mixtures. We therefore treated bromoferrocene with a stoichiometric amount of butyllithium in n-hexane and removed the solvent by cannula after the formation of the orange precipitate of monolithioferrocene [6]. This precipitate was dissolved in THF, then treated with a solution of DCGO in THF, and this gave I in 6% yield.

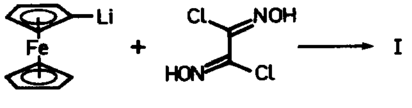
In the ^{1}H NMR spectrum of I, the signal from the OH protons appears as a broad singlet at 10.4 ppm, which disappears on D$_2$O exchange. The presence of only one singlet for the OH protons is consistent with the assumption that I has a *trans*-configuration, as do all known symmetrically substituted *vic*-dioximes.

Two triplets are observed for the protons of the monosubstituted rings (δ 4.29, 4.77 ppm, 8H), and a singlet for the protons of the free cyclopentadienyls (δ 4.21 ppm, 10H). In the IR spectrum ν(OH), ν(C=N) and ν(N–O) stretches are found at 3260, 1631, and 910 cm^{-1} respectively. The characteristic bands of a monosubstituted ferrocene are also present. The mass spectrum of I gives a molecular ion at 456 and the elemental analysis (C, H, N, Fe) is in excellent accord with the proposed structure.



(II)

SCHEME 1



SCHEME 2

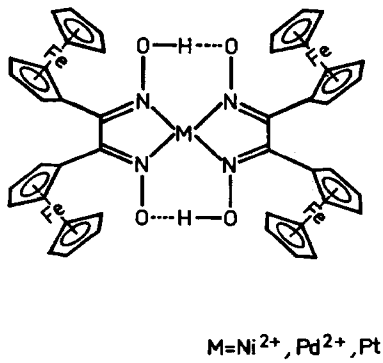


Fig. 1

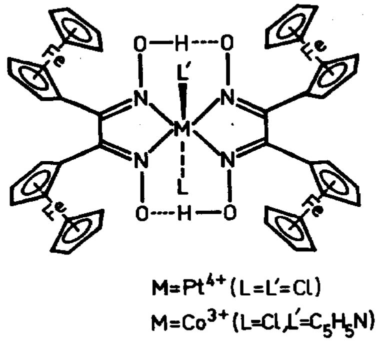


Fig. 2

As is the case for most *anti*-dioximes, I forms complexes, in which the metal/ligand ratio is 1 : 2, with metal ions like Ni^{2+}, Pd^{2+}, Pt^{2+} (Fig. 1), Co^{3+} and Pt^{4+} (Fig. 2).

These transition metal complexes, which represent a new class of heteropolynuclear compounds, possess some properties not observed for the previously described *vic*-dioxime complexes. In contrast to the red-yellow complexes with d^8 metal ions of *vic*-dioximes, e.g. dimethyl glyoxime etc., the Ni^{2+} complex is black,

TABLE 1

^{1}H NMR SPECTRAL DATA FOR I AND ITS Co^{3+} AND Pt^{2+} COMPLEXES

Compound	O--H-O	N-OH	Bound Cp	Free Cp
I [a]	–	10.6 (s,2H)	4.31 (t,4H) 4.73 (t,4H)	4.21 (s,10H)
Co^{III}-complex [b,c]	19.27 (s,2H)	–	4.26 (t,16H) 4.61(t,16H)	4.08 (s,20H)
Pd^{II}-complex [b]	not observed	–	4.34 (t,16H) 4.58 (t,16H)	4.20 (s,20H)

[a] In acetone-d_6. [b] In tetrahydrofuran-d_8. [c] Coordinated pyridine: δ = 7.26(m), 7.86(m), 8.62(m).

while the Pd^{2+} and Pt^{2+} compounds are dark-purple. On the other hand, the new complexes are soluble in slightly polar organic solvents such as acetone and THF, and we could record their ^1H NMR spectra (Table 1).

Experimental

Reactions were carried out under purified argon. Solutions of n-butyllithium (1.6 molar in hexane), *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), and ferrocene were obtained from the Merck Co. Hexane was dried by distillation over sodium under nitrogen. Tetrahydrofuran, diethyl ether and 1,2-dimethoxyethane were purified by distillation from $LiAlH_4$ under nitrogen. All solvents were purged with argon before use. *Anti*-dichloroglyoxime (DCGO) was prepared by a published procedure [7]. All other chemicals were of commercial reagent grade and were used without further purification.

(a) Reaction of 1,1′-dilithioferrocene with DCGO

A solution of n-butyllithium in hexane (25.6 ml, 0.042 mol), and freshly distilled TMEDA (0.042 mol) were added separately with stirring via a cannula to ferrocene (3.72g, 0.02 mole). Stirring was continued for 22 h at room temperature. The resulting orange slurry 1,1′-dilithioferrocene · TMEDA was diluted with 200 ml of 1,2-dimethoxyethane then the solution was cooled to −78°C and a solution of DCGO (3.9 g, 0.025 mol) in 40 ml of 1,2-dimethoxyethane was added dropwise during 0.5 h. During the addition the mixture turned from orange to yellowish-brown with precipitation of LiCl. The mixture was allowed to warm to room temperature with stirring and was then treated with 100 ml of water. Diethyl ether was added, and the insoluble material was filtered off, then thoroughly extracted with CH_2Cl_2. The combined Et_2O and CH_2Cl_2 extracts were dried over anhydrous Na_2SO_4 and then evaporated to dryness. Flash chromatography of the residue on silica, with hexane as eluant gave 1.37 g ferrocene (36.8% based on initial ferrocene), and subsequent elution with 3 : 1 hexane : ether afforded I. This was recrystallized from ethanol to give red-brown crystals, 500 mg (~ 11%); m.p. 203°C (dec.). (Found: C, 57.78; H, 4.41; N, 6.05; Fe, 23.85. $C_{22}H_{20}N_2O_2Fe_2$ calc: C, 57.89; H, 4.39; N, 6.14; Fe, 24.56%)

(b) Reaction of monolithioferrocene with DCGO

n-Butyllithium (3.4 ml, 5.5 mmol) was added slowly from a syringe to a solution of bromoferrocene (1.3 g, 5 mmol) in 20 ml of hexane at −12°C. The mixture was stirred at room temperature for an additional 5 h, during which an orange precipitate of monolithioferrocene was formed. Then stirring was interrupted and the solvent was carefully removed through a cannula. The residual orange intermediate was dissolved in 50 ml of THF, the solution was cooled to −50°C, and a solution of DCGO (470 mg, 3 mmol) in 20 ml of THF was added dropwise. The mixture was allowed to warm to room temperature. Work up as described above for (a) gave 65 mg of I (6%).

(c) Preparation of the nickel(II) complex of I

A solution of $NiCl_2 \cdot 6H_2O$ (11.9 mg, 0.05 mmol) in ethanol (10 ml) was added to a solution of I (45.6 mg, 0.1 mmole) in ethanol (40 ml). The solution was warmed to

60 °C 0.1 *N* NaOH in EtOH was added until the pH of the solution was 5.0. The precipitated black complex was filtered off, washed with ethanol then diethyl ether, and dried under vacuum. Yield: 58 mg (60%); m.p. > 210 °C (dec.). Found: C, 52.27; H, 3.89; N, 6.37; N, 6.37. $C_{44}H_{38}N_4O_4NiFe_4$ calc: C, 52.17; H, 4.16; N, 6.08%.

(d) Preparation of the palladium(II) complex of I

A mixture of $PdCl_2$ (8.8 mg, 0.055 mmol) and NaCl (6.6 mg, 0.11 mmol) in ethanol (25 ml) was stirred at 70 °C until the $PdCl_2$ completely dissolved and solution was added with stirring to a warm solution of I (50 mg, 0.11 mmol) in ethanol, 0.9 ml of a 0.1 *N* NaOH solution in ethanol was added dropwise to bring the pH to 5.0. The dark-purple precipitate was filtered off, washed with ethanol then diethyl ether, and dried under vacuum. Yield: 78 mg (70%), m.p. > 225 °C, (dec.). Found: C, 50.21; H, 3.86; N, 6.02. $C_{44}H_{38}O_4N_4Fe_4Pd$ calc: C, 49.60; H, 3.95; N, 5.78%.

(e) Preparation of the platinum(II) complex of I

A solution of K_2PtCl_4 (22 mg, 0.055 mmol) in water was added to a solution of I (50 mg, 0.11 mmole) in ethanol (40 ml), and 0.1 *N* solution of KOH in ethanol was added to bring the pH to 5.0. The purple-black precipitate was filtered off, washed with ethanol then diethyl ether, and dried under vacuum. Yield: 69 mg (57%), m.p. > 210 °C, (dec.). Found: C, 47.30; H, 3.45; N, 4.91. $C_{44}H_{38}O_4N_4Fe_4Pt$ calc: C, 47.76; H, 3.43; N, 5.06%.

(f) Preparation of the cobalt(III) complex of I

A solution of $CoCl_2 \cdot 6H_2O$ (13 mg, 0.055 mmol) in ethanol (5 ml) was added to a solution of I (50 mg, 0.11 mmol) in ethanol (40 ml) followed by a solution of pyridine (30 mg), in ethanol (10 ml). The solution was warmed gently and air was bubbled through for 1 h. The dark brown precipitate was filtered off, washed with ethanol then diethyl ether, and dried. Yield: 77 mg (65%), m.p. > 200 °C (dec.). Found: C, 53.97; H, 3.95; N, 5.89. $C_{49}H_{43}ClO_4N_5Fe_4Co$ calc: C, 54.36; H, 3.91; N, 6.47%.

(g) Preparation of the platinum(IV) complex of I

A solution of $Na_2PtCl_6 \cdot 6H_2O$ (30.9 mg, 0.055 mmol) in ethanol (10 ml) was added to a solution of I (50 mg, 0.11 mmol) in ethanol (40 ml), and 0.1 *N* ethanolic KOH was added slowly to bring the pH to 5.0. The black precipitate was filtered off, washed with ethanol then diethyl ether, and dried. Yield: 71 mg (55%), m.p. > 225 °C (dec.). Found: C, 44.55; H, 3.13; N, 5.01. $C_{44}H_{38}Cl_2O_4N_4Fe_4Pt$ calc: C, 44.94; H, 3.23; N, 4.77%.

References

1 A. Gül, A.I. Okur, A. Cihan, N. Tan and Ö. Bekâroğlu, J. Chem. Res. S, (1986) 90 and references cited therein.

2 M.D. Rausch and D.J. Ciappenelli, J. Organomet. Chem. 10, (1967) 127; D.W. Slocum, T.R. Engelmann, C. Erust, C.A. Jennings, W. Jones, B. Koonsvitsky, J. Lewis and P. Shenkini, J. Chem. Educ., 46 (1969) 144.

3 R.A. Benkaser, D. Goggin and G. Schroll, J. Am. Chem. Soc., 76 (1954) 4025; M. Rausch, M. Vogel and H. Rosenberg, J. Org. Chem., 22 (1957) 900; S.I. Goldberg, L.H. Keith and T. Prokopov, J. Org. Chem., 28 (1963) 850.

4 D. Seyferth and J.F. Helling, Chem. Ind., (1961), 1568; D. Seyferth, H.P. Hofmann, R. Burton and J.F. Helling, Inorg. Chem., 1 (1962) 227.

5 A.N. Nesmeyanov, N.N. Sedova, V.A. Sazonova and S.K. Moiseev, J. Organomet. Chem., 185 (1980) C6; F.L. Hedberg and H. Rosenberg, Tetrahedron Lett., (1969) 4011.

6 M.T. Lee, B.M. Foxman and M. Rosenblum, Organometallics, 3 (1985) 539.

7 G. Ponzio and F. Baldrocco, Gazz. Chim. Ital., 60 (1930) 415.