Journal of Organometallic Chemistry, 421 (1991) 299–304
Elsevier Sequoia S.A., Lausanne
JOM 22179

Synthesis and nonlinear optical properties of new bimetallic iron/palladium complexes

G. Doisneau [a], G. Balavoine [*,a], T. Fillebeen-Khan [a], J.-C. Clinet [a], J. Delaire [b], I. Ledoux [c], R. Loucif [b] and G. Puccetti [c]

[a] *Institut de Chimie Moléculaire d'Orsay (URA-CNRS no 255), Université Paris-Sud, 91405 Orsay Cedex (France)*
[b] *Laboratoire de Physicochimie des Rayonnements (URA-CNRS no 75), Université Paris-Sud, 91405 Orsay Cedex and ENS 94230 Cachan (France)*
[c] *C.N.E.T. Laboratoire de Bagneux (URA-CNRS no 250), 196 Avenue Henri Ravera, 92220 Bagneux (France)*

(Received June 11th, 1991)

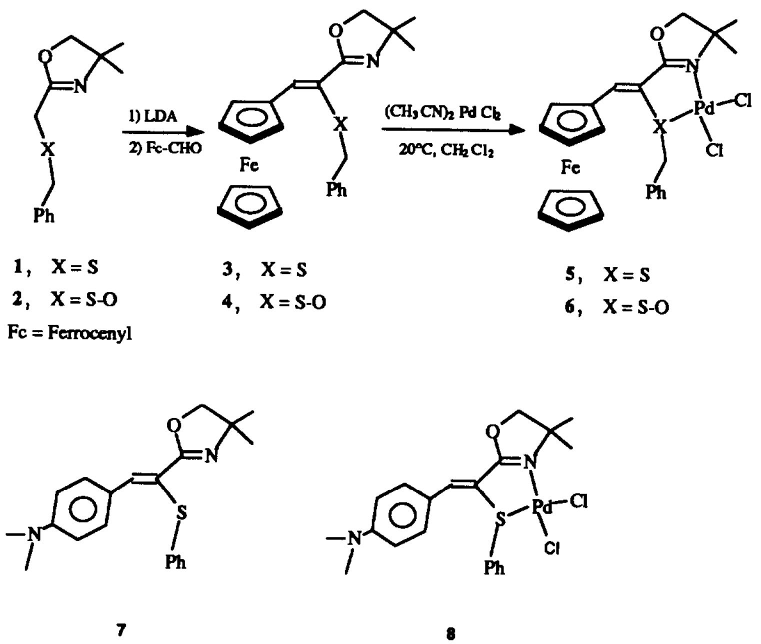
Abstract

Two new ferrocenyl derivatives, (*Z*)-[1-(benzylthio)-1-(4′,4′-dimethyl-oxazolinyl)-2-ferrocenyl]ethylene (**3**) and (*Z*)-[1-(benzylsulfino)-1-(4′,4′-dimethyloxazolinyl)-2-ferrocenyl]ethylene (**4**) have been synthesized. On complexation with $PdCl_2$ these yield new bimetalllic complexes **5** and **6** respectively. Non-linear optical properties measured by the EFISH technique show an enhanced molecular hyperpolarizability upon complexation, leading to higher values for β_0.

Introduction

There has been considerable interest in recent years in the development of new materials with non-linear optical (NLO) properties. This is due to the higher polarizability of π-electronic systems under an applied electric field associated with laser beam. Future photonic devices for communications and information processing might be derived from such materials. Although several inorganic [1,2] and organic materials have been shown to display substantial NLO properties, reports on such properties for organometallic complexes are scarce [3–8].

We describe here some novel ferrocene derivatives and the corresponding palladium complexes that exhibit promising NLO properties. We prepared (*Z*)-[1-(benzylthio)-1-(4′,4′-dimethyloxazolinyl)-2-ferrocenyl]ethylene (**3**) and (*Z*)-[1-(benzylsulfino)-1-(4′,4′-dimethyloxazolinyl)-2-ferrocenyl]ethylene (**4**). In these complexes an electron-releasing organometallic moiety (i.e. ferrocenyl group) is attached to the electron-attracting oxazoline via an ethylenic linkage. A sulfur function adjacent to the oxazoline ring provides a bidentate ligand for further complexation to another transition metal. Furthermore chirality could be readily introduced in this ligand either at the sulfur center or in the oxazoline ring in



1, X = S
2, X = S-O
Fc = Ferrocenyl

3, X = S
4, X = S-O

5, X = S
6, X = S-O

7

8

Scheme 1.

order to give non-centrosymmetric crystals, an essential requirement for NLO properties in the solid state.

Results and discussion

Complexes **3** and **4** were prepared by condensation of ferrocene carboxaldehyde with the anions of **1** and **2** respectively [9a]. Complexes **5** and **6** were obtained in almost quantitative yields by treating the ferrocene derivatives **3** and **4** with $(CH_3CN)_2PdCl_2$ [10] in CH_2Cl_2 (Scheme 1).

A comparison of the ^1H NMR spectra of compounds **3**, **4** and **4**, **5** reveals the influence of the acceptor palladium group upon the chemical shift of the Cp ligand protons (see Experimental section).

The palladium complexes **5** and **6** display solvatochromic behavior [11]. The UV visible absorption spectra of the uncomplexed compounds **3** and **4** exhibit a band at ca. 470 nm, and the complexes **5** and **6** a band at ca. 550 nm. This low energy band shows a bathochromic shift when the solvent polarity is increased. The solvatochromism is larger for complexes **5** and **6** than for the uncomplexed compounds **3** and **4**. Complex **8**, similar to **5**, was prepared for comparison; in this the ferrocenyl group has been replaced by the organic electron releasing *p*-*N*,*N*-dimethylaminophenyl group. Application of the MacRae relationship [12] gives the excited state dipole moments (see Table 1). This solvent effect was the first indication of probable SHG properties. Measurements of β at 1.34 μm by the electric-field-induced second harmonic generation (EFISH) technique [13,14] gave values in the range $4.5\text{–}37.0 \times 10^{-30}$ esu ($\pm 10\%$) for compounds **3** to **6**. These

Table 1

Values of measured ground state and excited state dipole moments, first hyperpolarizabilities at 1.34 μm and the extrapolated β_0 from the wavelength absorption band involved in the Internal Charge Transfer (ICT) process

	3	**4**	**5**	**6**	**7**	**8**
μ_g [a] (Debye)	3.85	5.7	13.2	12.2	3.5	13.5
$\Delta\mu$ [b] $= \mu_e - \mu_g$ (Debye)	2.0	2.1	3.0	6.0	17.2	9.0
β [c] 1.34 μm (10^{-30} esu)	4.5	8.4	12.2	30.2	23.0	37.0
β_0 [d] (10^{-30} esu)	2.0	3.7	3.9	7.6	15.0	20.0
Peak wavelength [e] involved in ICT (μm)	472	470	530	559	371	442

[a] Ground state dipole moments μ_g have been measured in chloroform in a dipolemeter by using the Guggenheim equation [16]. [b] μ_e: excited state dipole moment. $\Delta\mu$ is determined by measuring the solvatochromism shift and appplying MacRae relationship [12]. [c] Second order hyperpolarizability β was measured in chloroform solution by the EFISH technique. [d] β_0 is given by $\beta(\omega) = \beta_0 F(W, \omega)$ where W is the energy of the first maximum band of the molecule, ω is the fundamental wave frequency, and $F(W, \omega)$ is the dispersion function [17]. [e] In chloroform.

values of β are comparable to those for the very few reported for organo-transition metal complexes. For instance, the highest values of β reported for such compounds are 52×10^{-30} esu at 1.9 μm for 1-ferrocenyl-4-(4-nitrophenyl)-*trans*-butadiene [8] and 108×10^{-30} esu at 1.06 μm for Ru-CTP complexes studied by the Langmuir–Blodgett technique [15]. Measurements of third harmonic generation at 1.9 μm revealed a negligible contribution from the third order polarizability in the EFISH experiment [13,14]. Complexes **3** and **4** show NLO properties that are further enhanced upon coordination with Pd^{II} by a factor of 2 in terms of the measured polarizabilities. The increase in the value of β_0 upon complexation is related to the increased value of $\Delta\mu$. The metal ion withdraws electrons from the lone pairs of the heteroatoms. Thus compounds **5** and **6** provide the first example of the influence of complexation on NLO properties (Table 1).

The stronger donor–acceptor interaction in compound **7** than in compounds **3** and **4**, accounts for the weak increase (ca. 30%) of β_0 in the Pd-complexed **8**. The effect of metal complexation will then be relatively lowered in compound **8**. The ICT contribution localized on the ligand is much stronger than in compounds **5** and **6**, in which the electron-donating ability of the ferrocenyl group is substantially weaker than that of the dimethylaminophenyl group of compound **8**. This is confirmed by the values of β_0 for the corresponding ligands (**3**, **4** and **7**). Finally, the ligands which already display high β_0 values, as a consequence of strong ICT, seem to be less affected by metal complexation than the organometallic compounds showing only moderate β_0 values.

Conclusion

The presence of a metal ion in complexes **3** and **4** results in a net increase in the measured polarizability. Complexes **5** and **6** provide the first examples of the influence of complexation on NLO properties.

Experimental

All manipulations were carried out under an inert atmosphere. ^1H NMR spectra were recorded on a Bruker 200 MHz spectrometer with tetramethylsilane as internal standard IR spectra were obtained with a Perkin–Elmer 883 IR spectrophotometer. Elemental analyses were performed by the Microanalysis Service of CNRS at Gif-sur-Yvette. Ferrocene carboxaldehyde was purchased from Aldrich. The oxazoline derivatives **1** and **2** as well as $(CH_3CN)_2PdCl_2$ were prepared by published methods [9,10]. The solvents were purified prior to use.

(Z)-[1-(Benzylthio)-1-(4′,4′-dimethyloxazolinyl)-2-ferrocenyl]ethylene (3)

A solution of **1**, 4.8 g (20 mmol), in 50 ml of THF was cooled to −78 ° C and 13.5 ml (21.6 mmol) of 1.6 *M* n-butyllithium in hexane was added dropwise. After 1 h of stirring a solution of ferrocene carbaldehyde, 4.5 g (21 mmol) in THF was added. After 1.5 h of stirring at −78 ° C, the solution was warmed to room temperature. Hydrolysis was carried out at 0 ° C and the mixture was then extracted several times with CH_2Cl_2, and the extract washed with water and dried over $MgSO_4$. The extract phase contained the intermediate alcohol, which was not isolated, but dehydrated as follows. 6.6 ml (2.5 equiv.) of Et_3N was added to the above CH_2Cl_2 solution at 0 ° C and 3.6 ml of trifluoroacetic anhydride was added dropwise. The solution was stirred for 1 h at 0 ° C and then overnight at room temperature, washed with water and dried, and the solvent removed to leave a red oil. This was purified by flash chromatography with pentane/ether (7/3) as eluent. The red band eluted gave bright red crystals of the desired compound (7.1 g, 16.5 mmol, 81%). ^1H NMR ($CDCl_3$) δ 7.4 (s, 1H, vinylic), 7.1–7.2 (m, 5H, aromatic), 4.8 (m, 2H, η-C_5H_4), 4.35 (m, 2H, η-C_5H_4), 4.1 (s, 2H, benzylic), 4.05 (s, 2H, CH_2-oxazoline), 4.0 (s, 5H, η-C_5H_5), 1.4 (s, 6H, CH_3) ppm. IR (KBr) (cm^{-1}): 2969, *1626*, 1584, 1000. Anal. Found: C, 66.62; H, 5.97; N, 3.48. $C_{24}H_{25}NOSFe$ calc.: C, 66.81; H, 5.84; N, 3.24%.

(Z)-[1-(Benzylsulfino)-1-(4′,4′-dimethyloxazolinyl)-2-ferrocenyl]ethylene (4)

Compound **4** was prepared analogously from 5.1 g (20 mmol) of compound **2** and LDA (prepared by addition of 13.2 ml of (1.6 *M* in hexane) butyllithium to 3.12 ml of diisopropylamine at 0 ° C in THF). Yield 7 g (15.6 mmol) 78%. ^1H NMR (C_6D_6) δ 7.25 (s, 1H, vinylic), 7.0–7.4 (m, 5H, aromatic), 4.6 (m, 1H, η-C_5H_4), 4.5 (m, 1H, η-C_5H_4), 4.22 (d, *J* 12 Hz, 1H, CH_2-benzylic), 4.13 (d, *J* 12 Hz, 1H, CH_2-benzylic), 4.05 (m, 2H, η-C_5H_4), 3.85 (s, 5H, η-C_5H_5), 3.53 (d, *J* 8 Hz, 1H, CH_2-oxazoline), 3.48 (d, *J* 8 Hz, 1H, CH_2-oxazoline), 1.1 (3H, CH_3), 1.05 (3H, CH_3) ppm. IR (KBr) (cm^{-1}): 2968, *1635*, 1595, 992. Anal. Found: C, 64.51; H, 5.56; N, 3.26. $C_{24}H_{25}NO_2SFe$ calc.: C, 64.43; H, 5.63; N, 3.13%.

(Z)-[1-(Benzylthio)-1-(4′,4′-dimethyloxazolinyl)-2-ferrocenyl]ethylene palladium dichloride complex (5)

To a mixture of 250 mg (0.6 mmol) of **3** and 150 mg (0.6 mmol) of $(CH_3CN)_2PdCl_2$ was added 20 ml of CH_2Cl_2. A violet color immediately appeared. After 1 h stirring the volume was reduced by one-third and an excess of ether was added. The solution was cooled and the precipitate washed with ether. Yield 360 mg (0.59 mmol) 98%. ^1H NMR (CD_2Cl_2) δ 7.35–7.65 (m, 4H, aromatic), 7.25 (s, 1H, vinylic), 5.2, 4.95, 4.8, 4.65 (s, 4H, η-C_5H_4), 4.5 (d, *J* 10 Hz, 1H, CH_2-oxazoline), 4.3 (s, 5H, η-C_5H_5), 4.1 (bs, 1H, CH_2-benzylic), 3.85 (bs, 1H, CH_2-benzylic), 3.75 (d, *J* 10 Hz, 1H, CH_2-oxazoline), 1.5 (s, 3H, CH_3), 1.1 (s, 3H, CH_3) ppm. IR (KBr) (cm^{-1}): 2966, *1600*, 1413. Anal. Found: C, 46.85; H, 4.37; N, 2.28; Cl, 11.53. $C_{24}H_{25}FePdSONCl_2$ calc.: C, 47.35; H, 4.13; N, 2.30; Cl, 11.64%.

*(Z)-[1-(Benzylsulfino)-1-(4'4'-dimethyloxazolinyl)-2-ferrocenyl]ethylene palladium dichloride complex (**6**)*

The complex **6** was prepared similarly to **5**. Yield 90%. ^1H NMR (CD_2Cl_2) δ 7.24–7.7 (m, 6H, 5 aromatic + 1 vinylic), 5.2 (d, *J* 11 Hz, 1H, CH_2-benzylic), 5.0, 4.95, 4.75 (m, 1H, 2H, and 1H, η-C_5H_4), 4.42 (d, *J* 11 Hz, 1H, benzylic), 4.35 (s, 5H, η-C_5H_5), 4.3 (d, *J* 7 Hz, 1H, CH_2-oxazoline), 1.5 (s, 3H, CH_3), 1.0 (s, 3H, CH_3) ppm. IR (KBr) (cm^{-1}): *1575*, 1545, 1426, 968. Anal. Found: C, 46.33; H, 4.00; N, 2.40; Cl, 11.42. $C_{24}H_{25}FeSO_2NPdCl_2$ calc.: C, 46.17; H, 4.03; N, 2.24; Cl , 11.35%.

*(Z)-[1-(Phenylthio)-1-(4',4'-dimethyl oxazolinyl)-2-(p-N,N-dimethylaminophenyl)]-ethylene (**7**)*

Compound **7** was prepared by a procedure similar to that used for compound **3**. Yield 90%. ^1H NMR ($CDCl_3$) δ 7.85 (s, 1H, vinylic), 7.8 (d, *J* 9 Hz, 2H, aromatic) 7.1–7.3 (m, 5H, phenyl), 6.6 (d, *J* 9 Hz, 2H, aromatic), 3.95 (s, 2H, CH_2-oxazoline), 3.0 (s, 6H, $(CH_3)_2N$-), 1.2 (s, 6H, $(CH_3)_2$-oxazoline) ppm.

*(Z)-[1-(Phenylthio)-1-(4',4'-dimethyloxazolinyl)-2-(p-N,N-dimethylaminophenyl)]-ethylene palladium dichloride complex (**8**)*

Complex **8** was prepared in the way described for **5**. Orange crystals. Yield 98%. ^1H NMR (CD_2Cl_2) δ 6.5–7.75 (m, 10H, 9 aromatic + 1 vinylic), 4.4 (d, *J* 9 Hz, 1H, CH_2-oxazoline), 4.29 (d, *J* 9 Hz, 1H, CH_2-oxazoline), 3.05 (s, 6H, $(CH_3)_2N$), 1.7 (s, 6H, $(CH_3)_2$-oxazoline). Anal. Found: C, 47.64; H, 4.65; N, 5.27, Cl, 13.15. $C_{21}H_{24}N_2OSPdCl_2$ calc.: C, 47.617; H, 4.56; N, 5.29; Cl, 13.38%.

Acknowledgement

We are grateful to Dr. J. Zyss and Prof. J. Faure for helpful and stimulating discussions.

References

1 (a) D.S. Chemla and J. Zyss (Eds.) Non Linear Optical Properties of Organic Molecules and Crystals, Vols. 1 and 2, Academic Press, New York, 1987; (b) D.J. Williams, Angew. Chem. Int. Ed. Engl., 23 (1984) 690.

2 (a) C. Fouquey, J.-M. Lehn and J. Malthete, J. Chem. Soc., Chem. Commun., (1987) 1424; (b) J.-M. Lehn, Angew. Chem. Int. Ed. Engl., 29 (1990) 1304.

3 (a) C.-C. Frazier, M.A. Harvey, M.P. Cockerham, H.M. Hand, E.A. Chauchard and Chi H. Lee, J. Phys. Chem., 90 (1986) 5703; (b) J.C. Calabrese and W. Tam, Chem. Phys. Lett., (1987) 244.

4 Z. Yuan, N.J. Taylor, T.B. Marder, I.D. Williams, S.K. Kurtz and L.T. Cheng, J. Chem. Soc., Chem. Commun., 133 (1990) 1489.

5 J.A. McCleverty, D. Bloor, P.V. Kolnisky and R.J. Jones, J. Chem. Soc., Chem. Commun., (1989) 1485.

6 M.L.H. Green, S.R. Marder, M.E. Thompson, J.A. Bandy, D. Bloor, P.V. Kolinsky and R.J. Jones, Nature, 330 (1987) 360.

7 L.-T. Cheng, W. Tam and D.F. Eaton, Organometallics, 9 (1990) 2856.

8 D.R. Kanis, M.A. Ratner and T.J. Marks, J. Am Chem. Soc., 112 (1990) 8203.

9 (a) J.-C. Clinet and G. Balavoine, Tetrahedron Lett., 28 (1987) 5509; (b) J.A. Frump, Chem. Rev., 71 (1971) 483.

10 F.R. Hartley, S.G. Murray, and C.A. McAuliffe, Inorg. Chem., 18 (1979) 1394.

11 G. Balavoine, J. Delaire, G. Doisneau, T. Fillebeen-Khan and R. Loucif, unpublished results.

12 E.G. McRae, J. Phys. Chem., 61 (1957) 562.

13 B.F. Levine and C.G. Bethea, Appl. Phys. Lett., 24 (1974) 445.

14 I. Ledoux and J. Zyss, Chem. Phys., 73 (1982) 203.

15 (a) T. Richardson, G.G. Roberts, M.E.C. Polywka and S.G. Davies, Thin Solid Films, (1988) 160 and 231; (b) T. Richardson, G.G. Roberts, M.E.C. Polywka and S.G. Davies, ibid., (1989) 179 and 405.

16 E.A. Guggenheim, Trans. Faraday Soc., 45 (1949) 714.

17 J.-F. Nicoud, C. Serbutoviez, G. Puccetti, I. Ledoux and J. Zyss, Chem. Phys. Lett., 175 (1990) 257.