Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Organometallic Chemistry 676 (2003) 38–42

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

New stable cyclopentadienyl iron(II) complexes containing 3,5-dimethylpyrazolyl phosphine X-ray structure of $[FeCp(CO)_2PPh_2(Me_2Pz)]BF_4$

Rosa-María Tribó [a], Josep Ros [a], Josefina Pons [a], Ramón Yáñez [*],
Angel Álvarez-Larena [b], Joan-Francesc Piniella [b]

[a] Departament de Química, Universitat Autònoma de Barcelona, 08193 Cerdanyola del Vallès, Barcelona, Spain
[b] Departament de Geología, Unitat de Cristal lografía, Universitat Autónoma de Barcelona, 08193 Cerdanyola del Vallès, Barcelona, Spain

Received 25 October 2002; received in revised form 12 February 2003; accepted 12 February 2003

Abstract

Very stable complexes of general formula $[FeCp(CO)_xPh_2P(Me_2Pz)]BF_4$, where $x = 1(\mathbf{1})$–$2(\mathbf{2})$ were prepared by room temperature reaction of the 3,5-dimethylpyrazolylphosphine ligand with $[Fe_2(CO)_2(C_5H_5)_2]$. When $[FeCp(CO)_2Ph_2P(Me_2Pz)]BF_4$ (**1**) was treated with $(CH_3)_3NO\cdot 2H_2O$, one coordinated CO was lost and complex **2** was formed. ^1H-, ^{13}C- and ^{31}P-NMR spectra supported a structure of **2** with pyrazolyl ligand chelated to iron forming a four-membered metallocycle.

Keywords: Iron complexes; Pyrazole complexes; Crystal structures

1. Introduction

The chemistry of metal complexes containing hemilabile ligands has received considerable attention in recent years [1]. Hemilabile ligands are those polydentate chelates which contain at least two types of bonding groups with different properties in substitution reactions. One of groups could be strongly bonded to one metal atom while the other could be displaced easily by others ligands. Interest in such ligands stems from their potential use in catalysis and organometallic-based synthetic chemistry. Recently [2], we have been interested in the synthesis, structural characterization, and reactivity of 3,5-dimethylpyrazol N-substituted organometallic complexes which show hemilabile ligand behaviour. Our observation of the reaction of diphenylpyrazolylphosphine ligand with $[RuCl_2(p\text{-cymene})]_2$ has shown that the coordination of the ligand was possible but the P–N(pyrazole) bond remained highly reactive towards ROH molecules, giving a rapid cleavage of P–N bond in the same way as free phosphine ligands [3]. In an attempt to clarify this kind of reaction we have now prepared a cyclopentadienyl dicarbonyl complex of iron with the same $(PPh_2(Me_2Pz))$ phosphine. The fact that CO ligands are more π-electron withdrawing than chlorides could mean that the lone-pair on the nitrogen azine less basic and the P–N bond more resistant to hydrolysis.

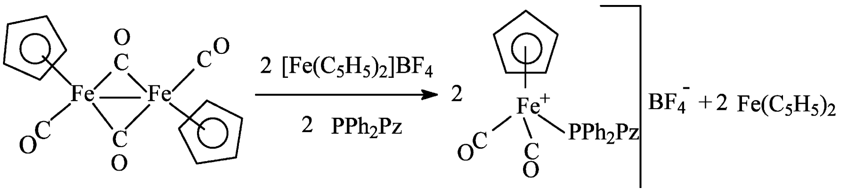
2. Results and discussion

The cationic P-coordinated diphenylpyrazolylphosphino $PPh_2(Me_2Pz)$ complex $[FeCp(CO)_2PPh_2(Me_2Pz)]BF_4$ was prepared in high yield by oxidation of starting cyclopentadienyl complex $[Fe_2(CO)_2(C_5H_5)_2]$

---

[*] Corresponding author.
E-mail address: ramon.yanez@uab.es (R. Yáñez).

0022-328X/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0022-328X(03)00261-4



Scheme 1.

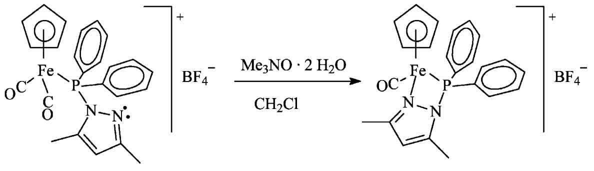
([Fp_2]) with ferricinium cation in the presence of one equivalent of $PPh_2(Me_2Pz)$ (Scheme 1) according to the reaction

$$\tfrac{1}{2}[Fp_2] + [FeCp_2]^+ + PPh_2(Me_2Pz) \rightarrow [(Fp)(PPh_2(Me_2Pz))]^+ \ (\mathbf{1}) + FeCp_2$$

In the infrared spectrum, complex **1** exhibited two bands: 2064, 2021 cm^{-1} assigned to the $\nu(CO)$ of the fragment $[CpFe(CO)_2]^+$ and one band at 1568 cm^{-1} corresponding to the $\nu(C{=}C)+\nu(C{=}N)$ absorption of pyrazole. Moreover, the ^1H- and ^{13}C-NMR spectra of **1** in CD_3Cl solution show the signals corresponding to the presence of η^5-cyclopentadienyl ligand; the two methyl groups attached to the pyrazole ring appear at 1.47 and 2.30 ppm in the ^1H-NMR spectrum. The $\{^1H\}^{31}P$-NMR spectrum of **1** shows a signal a 121.2 ppm which is assigned to the phosphorus atom coordinated to an iron atom.

It is noticeable that complex **1** did not react at room temperature or reflux with ROH ($R = H$, CH_3, CH_3CH_2). This behaviour contrasts with that of complex [$RuCl_2$(*p*-cymene) $PPh_2(Me_2Pz)$]$^+$, which reacts with ROH molecules resulting in a cleavage of the P–N bond [3]. This trend could be explained by the less basic character of the lone pair over N2 in pyrazol due to the coordination of phosphorus atom to a more electrophilic iron metal [4,5].

Treatment of **1** dissolved in CH_2Cl_2 with $Me_3NO \cdot 2H_2O$ in molar ratio 1:1 gave $[FeCp(CO)PPh_2Pz]BF_4$ complex (**2**) (Scheme 2). The $\{^1H\}^{31}P$-NMR spectrum of **2** in $CDCl_3$ solution showed a singlet at δ 115.6 ppm slightly shifted to a higher field than phosphorus in complex **1**. The corresponding ^1H-NMR spectrum in $CDCl_3$ also showed a signal a 4.4 ppm which was assigned to the Cp ligand. The $PPh_2(Me_2Pz)$ ligand showed signals at 2.28(CH_3), 2.36(CH_3) and 5.83(CH) ppm. In the infrared spectrum, complex **2** exhibited a band at 1936 assigned to the $\nu(CO)$ of the fragment $[CpFe(CO)]^+$ and one band at 1581 corresponding to $\nu(C{=}C)+\nu(C{=}N)$ absorption of pyrazole. This shifting to high energy of the $\nu(C{=}C)+\nu(C{=}N)$ band is attributable of a strained pyrazol [6]. The methyl resonances of $PPh_2(Me_2Pz)$ are quite sensitive to complexation. For the ligand, the higher field resonance is assigned to 5-methyl group, on the basis of relatively greater paramagnetic shielding by the phenyl rings. The 5-methyl group on complex **1** is 'locked' in place, in close proximity to two phenyl rings (Fig. 1) and experiences a strong shielding effect (1.47 ppm). Moreover the shift of the 5-methyl group of the pyrazole ring ^1H resonance to low field (2.3 ppm) is attributable to the less paramagnetic shielding effect of phenyl groups attached to the phosphorus atom on that methyl, as a result of coordination of both phosphorus and N atoms forming a PNNFe metallocyclic structure [5,7–9]. Efforts to grow crystals from solutions of complex **2** were unsuccessful. In order to preclude other possible structures like, for instance, that corresponding to a dicationic dimer $[CpFe(CO)_2PPh_2(Me_2Pz)]_2[BF_4]_2$, electrospray mass spectra of complexes **1** and **2** in NCMe were recorded, but not reliable data were obtained.



Scheme 2.

In conclusion we have shown that the coordination of $PPh_2(Me_2Pz)$ ligand can coordinate the 'CpFe' centre in P-monodentate and P,N-bidentate modes. The coordination of $PPh_2(Me_2Pz)$ to Fe(II) in complex $[CpFe(CO)_2(PPh_2(Me_2Pz))]^+$ (**1**) leads to a significant stabilisation of the P–N bond towards polar ROH

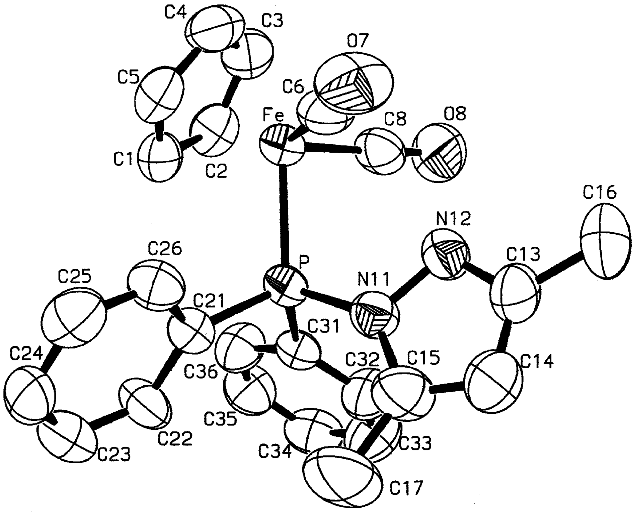


Fig. 1. An ORTEP view of the structure of cation $[FeCp(CO)_2(Ph_2P(Me_2pz))]^+$. The thermal ellipsoids enclose 50% probability.

Table 1
Crystal data and structure refinement for **1**

Empirical formula	$C_{24}H_{22}BF_4FeN_2O_2P$
Formula weight	544.074
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	8.9540(20)
b (Å)	10.1840(50)
c (Å)	14.1220(30)
α (°)	91.42(3)
β (°)	103.21(2)
γ (°)	91.32(3)
V (Å^3)	1252.75(73)
Z	2
ρ_{calc} (g cm^{-3})	1.4424
Absorption coefficient (mm^{-1})	0.719
F(000)	556.0
Crystal size (mm)	0.2 × 0.2 × 0.15
θ Range for data collection (°)	1.78–24.98
Reflections collected	4390
Independent reflections	2437 [$I > 2\sigma(I)$]
Refinement method	Least-squares
Data/parameters	4390/16/316
Goodness-of-fit on F^2	0.883
Final R_1 indices [$I > 2\sigma(I)$]	$R_1 = 0.0498$, $wR_2 = 0.11$
R indices (all data)	$R_1 = 0.1120$, $wR_2 = 0.11$
Largest difference peak and hole	0.275 and −0.246

molecules. This behaviour differs from that observed in a previously reported *p*-cymene-Ru(II) complex and should be originated by the strong π-acceptor character of CO ligands coordinated to the metal. The displacement of one CO of complex **1** produces a new compound $[CpFe(CO)(PPh_2(Me_2Pz))]^+$ (**2**) whose analytical and spectroscopic data are congruent with the formation of a four membered PNNFe ring. This study proves that, in spite of results of previously reported works, the very available $PPh_2(Me_2Pz)$ can be used, in some cases, as ancillary ligand to give stable organometallic compounds.

2.1. X-ray structure determination of $[FeCp(CO)_2PPh_2(Me_2Pz)]BF_4$ (**1**)

Suitable single crystals of the $[FeCp(CO)_2PPh_2(Me_2Pz)]BF_4$ complex were obtained by slow evaporation of a dichloromethane–methanol solution at room temperature. The structure is composed of complex cations and $[BF_4]^-$ anions held by Coulomb forces. Final atomic parameters are presented in Table 1. Significant bond distances and angles are shown in Table 2.

The structure of the cation $[FpFePPh_2(Me_2Pz)]^+$ with the adopted numbering scheme is shown in Fig. 1 and consists of a $[CpFe(CO)_2]^+$ fragment bonded to a $PPh_2(Me_2Pz)$ ligand through a Fe–P bond leading to a classical ‘piano-stool’ configuration. Structural parameters of the $CpFe(CO)_2$ fragment are very similar to those found in $[FpEPh_3]^+$ E = P, As, Sb, Bi) complexes [10–12]. The most significant feature of this structure is the Fe–P bond distance of 2.11(1) Å, which is shorter than in related complexes. This effect could be attributed to the strong π-acceptor nature of the pyrazole group [13,14].

3. Experimental

3.1. General data

All reactions were performed under nitrogen by using standard Schlenk tube techniques. All the solvents were distilled and dried before use. Infrared spectra were recorded on a Perkin–Elmer FT 1710 spectrophotometer on KBr disks or with CH_2Cl_2 solutions. Mass spectra were obtained on a Hewlett Packard H.P. 2985

Table 2
Selected bond lengths (Å) and angles (°) for **1**

Bond lengths	
Fe–C(1)	2.093(5)
Fe–C(2)	2.083(5)
Fe–C(3)	2.090(5)
Fe–C(4)	2.085(4)
Fe–C(5)	2.086(5)
Fe–Cp	2.088(5)
Fe–C(6)	1.776(5)
C(6)–O(7)	1.131(6)
Fe–C(8)	1.775(5)
C(8)–O(8)	1.138(6)
Fe–P	2.211(1)
P–N(11)	1.711(4)
N(11)–N(12)	1.396(5)
N(11)–C(15)	1.380(6)
N(12)–C(13)	1.314(6)
C(13)–C(14)	1.391(7)
C(14)–C(15)	1.343(8)
C(13)–C(16)	1.514(8)
C(15)–C(17)	1.499(8)
Bond angles	
C(8)–Fe–P	91.61(15)
C(6)–Fe–P	93.02(15)
C(6)–Fe–C(8)	95.07(22)
Fe–C(6)–O(7)	176.23(42)
Fe–C(8)–O(8)	176.96(45)
Fe–P–C(21)	115.12(14)
Fe–P–C(31)	115.23(13)
Fe–P–N(11)	111.02(12)
N(11)–P–C(21)	104.49(18)
C(21)–P–C(31)	106.25(18)
C(31)–P–N(11)	103.57(17)
P–N(11)–N(12)	114.61(26)
N(11)–N(12)–C(13)	105.38(35)
N(12)–C(13)–C(14)	111.62(42)
C(13)–C(14)–C(15)	106.55(48)
C(14)–C(15)–N(11)	107.55(42)
C(15)–N(11)–N(12)	108.87(34)

GC/MS. NMR spectra were recorded on a Bruker AC-250 (^{1}H, 250 MHz; ^{13}C, 62 MHz) spectrometer in $CDCl_3$ solutions. Elemental analyses were obtained by the staff of the Chemical Analysis Service of the Universitat Autonoma de Barcelona. $[Fe_2(CO)_2Cp_2]$ was purchased commercially. $PPh_2(Me_2Pz)$ was prepared by using previously published procedures [15,2]. Crystal structure determination was performed by the X-ray Diffraction Service of the University Autonoma de Barcelona.

3.2. X-ray crystal structure determination of 1

3.2.1. Data collection and processing

Data collected on an Enraf–Nonius CAD4 diffractometer using graphite-monochromated Mo–K_α radiation ($\lambda = 0.71069$ A) and an ω–2θ scan, ω scan width $= 0.80 + 0.35\tan\theta$. ω Scan speed 1.3–5.5°. Reflection ranges for the data collection: $1 < \theta < 25$, $-10 < h < 10$, $-12 < k < 12$, $0 < l < 16$. Lp and empirical absorption corrections were applied, $T_{\min} = 0.817$, $T_{\max} = 1.000$. Four thousand six hundred and ninety-nine reflections were measured in the range $1.78 < \theta < 24.98°$. Four thousand four hundred and twenty with $I > 2(\sigma(I))$. The structure was solved by direct methods (SHELXS-86) [16] and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97) [17]. All non-hydrogen atoms of **1** were refined anisotropically, hydrogen atoms bonded to carbon atoms were placed in calculated positions with isotropic temperature factors 1.5 (methyl hydrogens) or 1.2 times (the rest). The U_{eq} values of corresponding carbons, and hydrogen atoms bonded to oxygen or nitrogen atoms were localized in a difference electron density map and refined with isotropic temperature factors 1.5 times the U_{eq} values of corresponding oxygen or nitrogen atoms. The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.0580P)^2 + 0.000P]$ where $= [\max(F_o^2, 0) + 2F_c^2]/3$. Final $R(F)$ and $Rw(F^2)$ values were 0.0498 and 0.11 for reflections with $I > 2\sigma(I)$.

3.2.2. Synthesis of complex [FeCp(CO)$_2$PPh$_2$(Me$_2$Pz)]BF$_4$ (1)

Dichloromethane (20 ml) was added to a mixture of PPh_2Pz (0.28 g, 1.0 mmol) and $[FeCp(CO)_2]_2$ (0.177 g. 0.50 mmol). After 2 min of stirring, $[Fe(C_5H_5)_2][BF_4]$ (0.273 g, 1.0 mmol) in CH_2Cl_2 (10 ml) was added an the resulting solution was stirred for 5 h at room temperature, the solution was reduced in vacuo to a volume of 1 ml. Addition of hexane (5 ml) afforded precipitation of a brown solid, which was then washed with three portions of hexane and recrystallized from CH_2Cl_2–diethyl ether at −20 °C. The yellow crystals that separated were collected, washed with diethyl ether, and dried in vacuo. 60% Yield.

Anal. Calc. for $C_{24}H_{22}BF_4FeN_2O_2P$: C, 52.9; H, 4.08; H, 4.08; N, 5.15. Found: C, 52.18; H, 4.07; N, 4.98%. IR ν(CO) ($CDCl_3$): 2064(s), 2021(s) (cm^{-1}); ν(C=C)+ν(C=N) (KBr): 1568 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.47 (s, CH_3), 2.30 (s, CH_3), 5.24 (s, 5H, C_5H_5), 6.13 (s, CH), 7.4–7.6 (m, Ph) ppm. ^{13}C-NMR ($CDCl_3$), except phenyl resonances: δ 13.8–14.0 (CCH$_3$), 89.1 (C_5H$_5$), 113.1 (CH middle pyrazole), 208–208.6 (C≡O) ppm. ^{31}P-NMR ($CDCl_3$): δ 121.2 (s, PPh_2Pz) ppm.

3.2.3. Synthesis of complex [FeCp(CO)PPh$_2$(Me$_2$Pz)]BF$_4$ (2)

The solid compound $(CH_3)_3NO\cdot 2H_2O$ (0.04 g, 0.36 mmol) was added to a solution of **1** (0.1 g, 0.37 mmol) in dichloromethane (15 ml). The reaction was monitored by IR spectroscopy (ν_{CO} region), and after nearly 2 h of stirring at room temperature, the solution was filtered off and evaporated to dryness. The residual solid was extracted with hexane (3 × 10 ml), and the resulting solution was evaporated to dryness. The residual product was loaded on a silica gel column. After elution with CH_2Cl_2 a red complex that eluted with CH_2Cl_2–methanol (10/1) was collected and dried in vacuo to give a red powder of **2**. 35% yield.

Anal. Calc. for $C_{23}H_{22}BF_4FeN_2O_2P$: C, 53.47; H, 4.30; N, 5.43. Found: C, 53.90; H, 4.50; N, 5.51%. IR ν(CO) (CH_2Cl_2): 1936(s) (cm^{-1}); ν(C=C)+ν(C=N) (KBr): 1581 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 2.28 (s, CH_3), 2.36 (s, CH_3), 4.41 (s, 5H, C_5H_5), 5.86 (s, CH), 6.7–7.8 (m, Ph) ppm. ^{13}C-NMR ($CDCl_3$) except phenyl resonances: δ 11.8–15.8 (CCH$_3$), 84.4 (C_5H$_5$), 107.7 (CH middle pyrazole), 222.0 (C≡O) ppm. ^{31}P-NMR ($CDCl_3$): δ 121.2 (s, PPh_2Pz) ppm.

Acknowledgements

We gratefully acknowledge support from the Ministerio de Educación y Cultura of Spain, project PB96-1146 and BQU2000-0238.

References

[1] (a) A. Bader, E. Lindner, Coord. Chem. Rev. 108 (1991) 27;
(b) C.S. Slone, D.A. Weinberger, C.A. Mirkin, Prog. Inorg. Chem. 48 (1999) 233.
[2] G. Esquius, J. Pons, J. Ros, R. Yánez, J. Organomet. Chem. 619 (2001) 14.
[3] R. Tribó, J. Pons, R. Yánez, J.F. Piniella, A. Alvarez-Larena, J. Ros, Inorg. Chem. Commun. 3 (2000) 545.
[4] S. Fischer, J. Hoyano, L.K. Peterson, Can. J. Chem. 54 (1976) 2710.
[5] H.B. Davis, J.K. Hoyano, P.Y. Leung, L.K. Peterson, B. Wolstenholme, Can. J. Chem. 58 (1980) 151.
[6] A. Chadgan, J. Pons, A. Caubet, J. Casabó, J. Ros, A. Álvarez, J.F. Piniella, Polyhedron 19 (2000) 855.

[7] R.E. Cobbledick, F.W.B. Einstein, Acta Crystallogr. Sect. B. 33 (1977) 2020.

[8] J. Hoyano, L.K. Petersson, Can. J. Chem. 54 (1976) 2697.

[9] L.K. Peterson, H.B. Davis, P.Y. Leung, Inorg. Chim. Acta 47 (1980) 63.

[10] H. Schumman, L. Eguren, J. Organomet. Chem. 403 (1991) 183.

[11] E. Louattani, A. Lledos, J. Suades, A. Alvarez, J.F. Piniella, Organometallics 14 (1995) 1053.

[12] G.A. Sim, D.I. Woodhouse, G.R. Knox, J. Chem. Soc. Dalton Trans. (1979) 629.

[13] M.R. Torres, A. Santos, A. Perales, J. Ros, J. Organomet. Chem. 353 (1988) 221.

[14] A.L. Spek, W.L. Driessen, W.G.R. Wiesmeijer, Acta Crystallogr. Sect. C 44 (1988) 1567.

[15] L.K. Peterson, S. Fischer, J.F. Nixon, Can. J. Chem. 52 (1974) 3981.

[16] G.M. Sheldrick, C. Kruger & R. Goddard, SHELXS86, In Crystallographic Computing, Oxford University Press, Oxford (1985) 175–189.

[17] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Institüt für Anorganische Chemie der Universität, Göttingen, Germany, 1997.