

Synthesis and structure determination of stereoisomeric 2,2'-dibenzoyl-3,3',4,4'-tetramethyl-1,1'-diphosphaferrocenes

Arkadiusz Klys,^a Magdalena Malecka,^b and Janusz Zakrzewski^{a*}

^aDepartment of Organic Chemistry, University of Łódź, 90-136 Łódź, Narutowicza 68, Poland

^bDepartment of Crystallography and Crystal Chemistry, University of Łódź, 90-236 Łódź,

Pomorska 149/153, Poland

E-mail: janzak@uni.lodz.pl

Dedicated to Professor Jan Epsztajn on the occasion of its 75th anniversary

Abstract

Reaction of 3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene **1** with an excess of benzoyl chloride and AlCl₃ afforded a ~1:1 mixture of *meso*- and *rac*-2,2'-dibenzoyl-3,3',4,4'-tetramethyl-1,1'-diphosphaferrocenes **2**, which were separated by column chromatography. The less polar diastereomer was transformed into its *bis*-W(CO)₅- complex **3**. The single crystal X-ray study revealed that this complex contains the *meso*-**2** ligand. Therefore, the more polar diastereomer must be *rac*-**2**. It has been suggested that the splitting pattern of the phospholyl protons signal in the ¹H NMR spectra can be used for stereochemistry assignments.

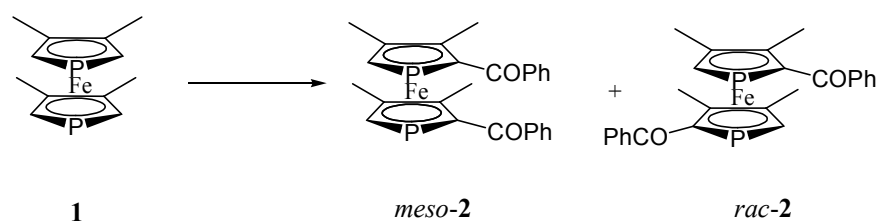
Keywords: Friedel-Crafts acylation, 1,1'-diphosphaferrocene, stereochemistry, X-ray diffraction

Introduction

Friedel-Crafts acylation of ferrocene constitutes a direct synthetic route to monoacyl- and heteroannular 1,1'-diacylferrocenes,¹ versatile starting materials in syntheses of numerous ferrocene derivatives.²⁻⁷ Similarly, Friedel-Crafts acylation of 1,1'-diphosphaferrocene gives, depending on the reaction conditions, either 2-acyl- or heteroannular 2,2'-diacyl derivatives.⁸ However, in this case, because of the planar chirality of the metallocene moiety,⁹ formation of mixtures of the *meso* (*R_p,S_p*)- and racemic (*R_p,R_p* and *S_p,S_p*) stereoisomers is expected. Mathey et al.⁸ separated stereoisomers of 2,2'-diacetyl-3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene by column chromatography but were unable to assess their stereochemistry.

Herein we report the 2,2'-dibenzoylation of **1** along with the separation of the *meso*- and *rac*-stereoisomers via column chromatography. We determined the structure of one of the

stereoisomers after its transformation into crystalline *bis*-W(CO)₅- complex by single-crystal X-ray diffraction.



Results and Discussion

We found that **1** reacts with benzoyl chloride and AlCl₃ (2.5-2.7 molar equivalents) in dichloromethane at room temperature to afford a ~1:1 mixture of *meso*-**2** [*(R_p,S_p)-2*] and *rac*-**2** [*(R_p,R_p)-2* and [*(S_p,S_p)-2*] in 79% overall yield. The stereoisomers were separated *via* column chromatography. They are deep red solids giving elemental analyses, IR and ³¹P NMR spectra corroborating their structures. Interestingly, their ¹H NMR spectra show substantial difference in the splitting pattern of the phospholyl protons (H-5 and H-5'). Whereas the less polar isomer shows expected two-proton doublet (*J*_{P-H} = 37.1 Hz) for these protons, its more polar counterpart displays more complex splitting pattern (Fig.1).

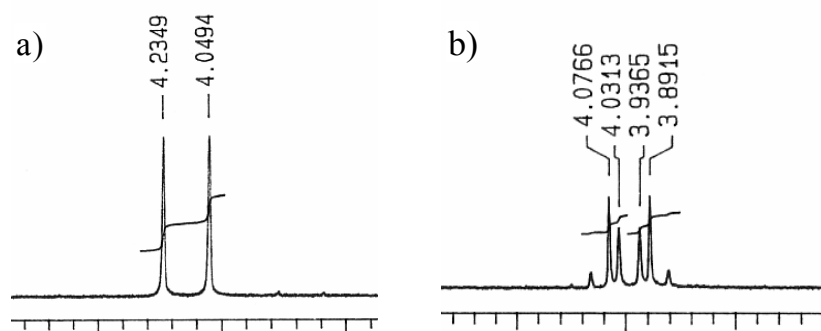
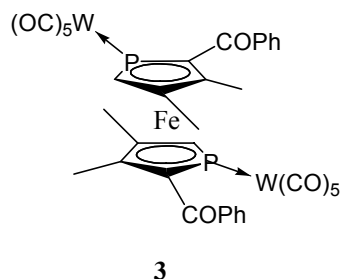


Figure 1. Signal of the phospholyl protons in the ¹H NMR spectra of less polar (a) and more polar diastereomer (b) of **2**.

The more complex and apparently higher-order splitting pattern observed for the more polar stereoisomer may suggest its lower symmetry i.e. the *rac* stereochemistry as was suggested by Mathey *et al.* for 2,2'-(diphenylphosphino) derivative of **1**.¹⁰ However, to provide a direct evidence for the suggested stereochemistry X-ray diffraction study of at least one stereoisomer of **2** was necessary. Unfortunately, attempts to grow crystals of any stereoisomer suitable for such a study failed. Since earlier we often used transformation of a 1,1'-diphosphaferrocene derivative

into its *bis*-W(CO)₅ complexes, which easily gave X-ray quality crystals,¹¹ we transformed the less polar diastereomer of **2** into a such derivative *via* reaction with photochemically generated W(CO)₅(THF). The single crystal X-ray study revealed the structure **3** (*vide infra*).



The metallocene ligand in **3** has a *meso*- configuration, and therefore the less polar and more polar diastereomers of **2** must be *meso*-**2** and *rac*-**2**, respectively.

It is worthy noting that diastereomeric 2,2'-diacetyl-3,3',4,4'-tetramethyl-1,1'-diphosphaferrocenes also shown a very similar difference in the splitting patterns of phospholyl protons, the less polar displaying a doublet and the more polar a higher-order multiplet similar to that shown in Figure 1b. This suggests that this difference may be used as a tool for stereochemistry determination.

X-Ray diffraction study of **3**

Crystals of **3** suitable for X-ray diffraction study were grown from layered dichloromethane-hexane. The crystal data and structure refinement are collected in Table 1. Some relevant bond lengths and angles are gathered in Table 2. The molecular structure of **3** is shown in Fig.2.

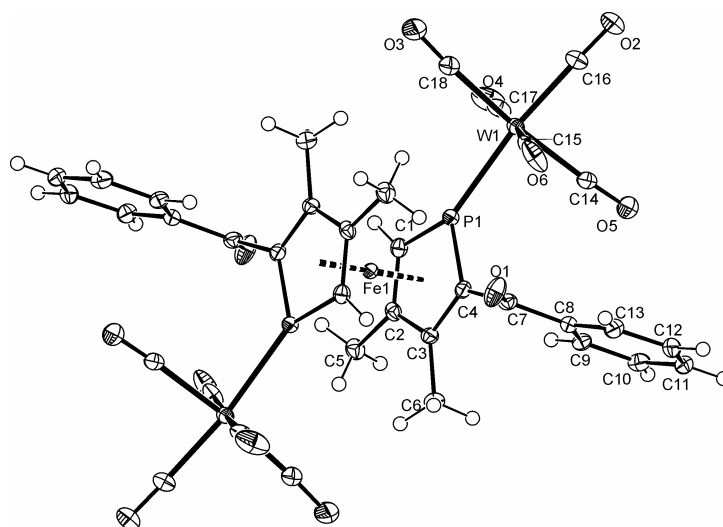


Figure 2. Ortep drawing of **3** with atom numbering scheme.

Table 1. Crystal data and structure refinement for **3**

Empirical formula	$C_{36}H_{24}FeO_{12}P_2W_2$
Formula weight	1134.04
Temperature [K]	100(2)
Wavelength	0.71073
Crystal system	monoclinic
Space group	
Unit cell dimensions	
a [Å]	9.750(1)
b [Å]	14.716(2)
c [Å]	12.802(2)
β [°]	94.83(1)
Volume [Å ³]	1830.2(2)
Z	2
Density (calculated) [Mg/m ³]	2.058
Absorption coefficient [mm ⁻¹]	6.811
Absorption correction	gaussian
F(000)	1080
Crystal size [mm]	0.9 x 0.16 x 0.32
θ min/max for data collection [°]	2.10 / 29.21
Index ranges	-13 ≤ h ≤ 13, -20 ≤ k ≤ 20, -17 ≤ l ≤ 17
Reflections collected	17514
Independent reflections	4934 [R(int) = 0.0460]
Completeness	100.0 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4934 / 0 / 243
Goodness-of-fit on F ²	0.891
Final R indices [I > 2σ(I)]	R1 = 0.0226, wR2 = 0.0476
R indices (all data)	R1 = 0.0351, wR2 = 0.0498
Largest diff. peak and hole [e/ Å ³]	1.488 and -1.751

Table 2. Selected bond lengths [Å] and angles [°] for **3**

C(1)-C(2)	1.419(4)	C(4)-Fe(1)	2.086(3)
C(1)-P(1)	1.758(3)	C(7)-O(1)	1.222(3)
C(1)-Fe(1)	2.092(3)	C(7)-C(8)	1.493(4)
C(2)-C(3)	1.436(4)	C(8)-C(13)	1.395(4)
C(2)-C(5)	1.504(4)	C(8)-C(9)	1.403(4)
C(2)-Fe(1)	2.085(3)	C(9)-C(10)	1.380(4)
C(3)-C(4)	1.426(4)	C(10)-C(11)	1.386(4)
C(3)-C(6)	1.503(4)	C(11)-C(12)	1.385(4)
C(3)-Fe(1)	2.079(3)	C(12)-C(13)	1.388(4)
C(4)-C(7)	1.503(4)	Fe(1)-P(1)	2.2673(8)
C(4)-P(1)	1.762(3)	P(1)-W(1)	2.4719(8)
C(2)-C(1)-P(1)	112.6(2)	P(1)-C(4)-Fe(1)	71.64(10)
C(2)-C(1)-Fe(1)	69.86(15)	C(3)-Fe(1)-C(1)	69.27(11)
P(1)-C(1)-Fe(1)	71.56(9)	C(2)-Fe(1)-C(1)	39.71(11)
C(1)-C(2)-C(3)	112.3(2)	C(4)-Fe(1)-C(1)	73.67(11)
C(1)-C(2)-C(5)	123.2(3)	O(1)-C(7)-C(8)	121.3(2)
C(3)-C(2)-C(5)	124.5(3)	C(8)-C(7)-C(4)	117.1(2)
C(1)-C(2)-Fe(1)	70.43(15)	C(13)-C(8)-C(9)	119.4(3)
C(3)-C(2)-Fe(1)	69.61(15)	C(13)-C(8)-C(7)	118.7(2)
C(5)-C(2)-Fe(1)	129.7(2)	C(9)-C(8)-C(7)	121.9(2)
C(4)-C(3)-C(2)	111.8(2)	C(10)-C(9)-C(8)	120.0(3)
C(4)-C(3)-C(6)	122.4(3)	C(12)-C(11)-C(10)	120.4(3)
C(2)-C(3)-C(6)	125.7(3)	C(12)-C(13)-C(8)	120.1(3)
C(4)-C(3)-Fe(1)	70.25(16)	C(4)-Fe(1)-P(1)	47.52(8)
C(2)-C(3)-Fe(1)	70.03(16)	C(1)-Fe(1)-P(1)	47.36(8)
C(6)-C(3)-Fe(1)	128.0(2)	C(1)-P(1)-C(4)	90.74(14)
C(3)-C(4)-C(7)	123.6(3)	C(1)-P(1)-Fe(1)	61.08(9)
C(3)-C(4)-P(1)	112.5(2)	C(4)-P(1)-Fe(1)	60.84(10)
C(7)-C(4)-P(1)	123.7(2)	C(1)-P(1)-W(1)	137.66(10)
C(3)-C(4)-Fe(1)	69.71(16)	C(4)-P(1)-W(1)	127.83(10)
C(7)-C(4)-Fe(1)	130.6(2)	Fe(1)-P(1)-W(1)	148.22(3)

The *meso-2* ligand in **3** adopts a centrosymmetric antiperiplanar conformation with the largest distance between phosphorus atoms. The W-P bonds length, 2.4719(8) Å, is similar to those observed in similar complexes.^{11,12} Interestingly, the carbonyl groups in positions 2 and 2' are almost perpendicular to the phospholyl ligands planes (torsional angle C3-C4-C7-O1 is equal to -104(4)° and P1-C4-C7-O1 to 81.4(4)°). It seems therefore that there is no conjugation between these groups and the metallocene moiety. On the other hand, the C7=O1 carbonyl group

are almost coplanar with the phenyl rings (torsional angle O1-C7-C8-C13 is equal to $-6.6(4)^\circ$ and O1-C7-C8-C9 to $173.1(3)^\circ$), indicating extensive conjugation between these groups.

Experimental Section

General Procedures. All reactions were carried out under argon. All reagents used in this work are commercially available (Aldrich) and were used without further purifications. Compound **1** was prepared according to the literature procedure.¹³ Dichloromethane was distilled over calcium hydride and THF over sodium-benzophenone before use. Chromatographic separations were carried out using Silica gel 60 (Merck, 230-400 mesh ASTM). The NMR spectra were run on a Varian Gemini 200 BB (200 MHz for ^1H) and IR spectra on a FT-IR Nexus spectrometer. Elemental analyses were performed by Analytical Services of the Center of Molecular and Macromolecular Studies of the Polish Academy of the Sciences (Łódź).

2-Benzoyl-3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene 2. Benzoyl chloride (0.81 ml, 6.75 mmol) and AlCl_3 (0.85 g, 6.22 mmol) in dichloromethane (5 ml) were stirred at rt for 5 min and 3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene (690 mg, 2.48 mmol) was added and to the resulting mixture was stirred at rt for 4h. Dichloromethane (10ml) was then added and the reaction mixture was poured into 3N aq. HCl. The organic layer was separated, washed with aq. Na_2CO_3 and evaporated to dryness. Column chromatography (silica gel, eluent: hexane-ethyl acetate 9:1) afforded in order of elution: a small amount of starting metallocene, 2-benzoyl-3,3',4,4'-tetramethyl-1,1'-diphosphaferrocene, and two fractions containing 2,2'-dibenzoyl derivatives.

First fraction: Deep red solid. Yield 267 mg (44%). M.p. $114-116^\circ$. ^1H NMR (CDCl_3 , δ ppm): 7.83- 7.87 (m, 10H, Ph), 4.14 (d, $J = 37.1$ Hz, 2H, phospholyl H's), 2.30 (s, 6H, 2 x Me), 2.25 (s, 6H, 2 x Me). ^{31}P NMR (CDCl_3 , δ ppm): -38.30. IR (KBr, cm^{-1}): 1641. Elemental analysis: Calcd for $\text{C}_{26}\text{H}_{24}\text{FeO}_2\text{P}_2$: C, 64.22, H, 4.97. Found. C, 64.16, H, 5.29.

Second fraction: Deep red solid. Yield 208 mg (35%). M.p. $129-131^\circ$. ^1H NMR (CDCl_3 , δ ppm): 7.33-7.75(m, 10H, aromatic H's), 3.73- 4.09(m (see Fig 1b), 2H, phospholyl H's), 2.20 (s,6H, 2 x Me), 2.16 (s,6H, 2 x Me). ^{31}P NMR (CDCl_3 , δ ppm):- 54.22. Elemental analysis: Calcd for $\text{C}_{26}\text{H}_{24}\text{FeO}_2\text{P}_2$: C, 64.22, H, 4.97. Found. C, 64.31, H, 4.91.

Bis-(tungsten pentacarbonyl) complex of 2 (3). A solution of tungsten hexacarbonyl (352 mg, 1 mmol) in THF (60 ml) was irradiated with the UV light (100 W mercury lamp) through pyrex for 1 h. **2** (less polar fraction, 122mg, 0.25 mmol) was added, the solution refluxed 90 min and evaporated to dryness. Column chromatography (silica gel, eluent: chloroform) afforded in order of elution: a small amount of unchanged tungsten hexacarbonyl and an orange fraction containing **3**. Yield 174 mg (62%). ^1H NMR (CDCl_3 , δ ppm): 7.35-7.72 (m, 10H, aromatic H's), 4.09 (d, $J = 33.8$ Hz, 2H, phospholyl H's), 2.39 (s, 6H, 2 x Me), 2.13 (s, 6H, 2 x Me). IR (KBr,

cm⁻¹): 2075, 1947, 1641. Elemental analysis: Calcd for C₃₆H₂₄FeO₁₂P₂W₂: C, 38.13, H, 2.13. Found. C, 38.37, H, 2.27.

X-Ray structure determination. Crystallographic data (excluding structure factors) for the structure of **3** have been deposited with the Cambridge Crystallographic Data centre as supplementary publication number CCDC 621006. Copies of the data can be obtained, free of charge, via <http://www.ccdc.cam.uk/conts/retrieving.html> or on application to CCDC, 12 Union road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

Financial support from University of Łódź (grant No 706'505 to MM) is gratefully acknowledged. The authors wish to thank Prof. Werner Massa from University of Marburg for skilful experimental assistance.

References

1. Rosenblum, M. In *Ferrocenes, Part I*, Wiley: New York 1965, pp 62-119.
2. Liptau, P.; Tebben, L.; Kehr, G.; Fröhlich, R.; Erker, G.; Hollmann, F.; Rieger, B. *Eur. J. Inorg. Chem.* **2005**, 1909.
3. El-Shiekh, S. M.; Abd-Elzaher, M. M.; Eweis, M. *Appl. Organomet. Chem.* **2006**, *20*, 505.
4. Liu, W. H.; Xu, Q. H.; Chen, B. H.; Liang, Y. M.; Ma, Y. X.; Liu, W. M. *J. Organomet. Chem.* **2001**, *637-639*, 782.
5. Neum, L.; Brouard, H.; Meffre, P.; Larchevêque, Buisson, D.; Demousseau, E.; Azerad, R. *Tetrahedron:Asymmetry* **2000**, *11*, 4055.
6. Locke, A. J.; Richards, C. J. *Tetrahedron Lett.* **1996**, *37*, 7861-7864; Locke, A. J.; Richards, C. J. *Organometallics.* **1999**, *18*, 3750.
7. Sato, W.; Watanabe, H.; Ohtsuka, Y.; Ikeno, T.; Fukuzawa, S. I.; Yamada, T. *Org. Lett.* **2002**, *4*, 3313.
8. De Luzon, G.; Deschamps, B.; Fischer, J.; Mathey, F.; Mitschler, A. *J. Am. Chem. Soc.* **1980**, *102*, 994.
9. Hermann In *Ferrocenes*, Togni, A.; Hayashi, T. Eds.; VCH: Weinheim 1995; pp.173-218.
10. Deschamps, B.; Mathey, F. *Organometallics*, **1992**, *11*, 1411.
11. Sieroń, L.; Tosik, A.; Bukowska-Strzyżewska, M. *J. Chem. Crystallogr.* **1998**, *28*, 621.
12. Zakrzewski, J.; Kłys, A.; Bukowska-Strzyżewska, M.; Tosik, A. *Organometallics* **1998**, *17*, 5880.
13. Mathey, F.; de Lauzon, G. *Organomet. Synth.* **1986**, 251.