

Structural and NMR spectroscopic characterization of ferrocene-containing η^3 -allylpalladium complexes

Yang Jie Wu ^{a,*}, Yuan Hong Liu ^a, Han Zhen Yuan ^b, Xi An Mao ^b

^a Department of Chemistry, Zhengzhou University, Zhengzhou 450052, People's Republic of China

^b Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics, The Chinese Academy of Sciences, Wuhan 430071, People's Republic of China

Received 10 January 1996; in revised form 14 February 1996

Abstract

The reaction of 1,3-diferrocenylbut-2-en-1-one **1** with Li_2PdCl_4 in methanol in the presence of NaOAc produced μ -chloro-bridged η^3 -allylpalladium complex **2** in high yield. Treatment of **2** with PPh_3 afforded the monomeric triphenylphosphine derivative **3**. The *anti* conformation of **3** was confirmed by 2D ^1H NMR spectroscopy and also by X-ray crystallography.

Keywords: η^3 -Allylpalladium complex; Ferrocene; Palladium; Crystal structure

1. Introduction

The η^3 -allyl ligand, formally a four-electron donor occupying two coordination sites, is one of the most common of carbon ligands, forming moderately stable complexes with virtually all the transition metal series. The versatile reaction paths and pronounced reactivity of the π -allyl group account for the large number of synthetic and catalytically important reactions manifested by η^3 -allyl complexes [1]. Recently, ferrocenyl derivatives have attracted much attention for applications in areas including non-linear optical materials, molecular switches in controlling supramolecular assemblies and mixed-valence complexes with the possibility of producing high temperature and superconducting materials, etc. [2]. In this paper we describe the preparation and structural characterization of one group of ferrocene-containing η^3 -allylpalladium complexes.

2. Results and discussion

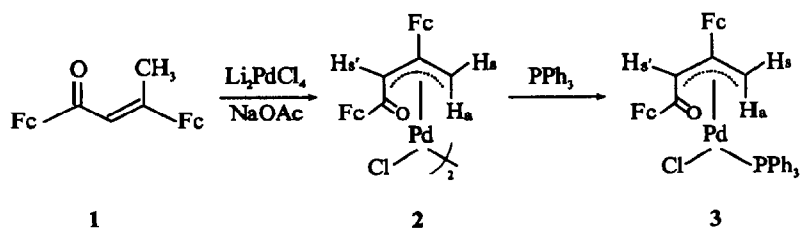
The η^3 -allyl ligand **1** is metalated by the palladium(II) salt Li_2PdCl_4 in methanol in the presence of anhydrous sodium acetate to afford the corresponding stable η^3 -allylpalladium complex **2** in good yield. It was subjected

to bridge-splitting reaction with triphenylphosphine to produce the monomeric triphenylphosphine derivative **3**. These are examples of palladium-mediated C–H activation reactions in which there is abstraction of a proton that is delivered to the basic reaction medium.

The ^1H NMR spectra of **2** is very complicated, we can only assign the singlets at δ 4.95 and 4.03 to the protons of the terminal CH_2 group and the broad singlet at δ 5.51 to the methine proton of π -allyl. The ^1H NMR data of **1** has been reported, but the signals of the protons of the ferrocenyl part have not been well separated using a 80 MHz spectrometer [3]. 2D NOESY spectra (Figs. 1, 2) helped us to determine the ferrocenyl protons of compounds **1** and **3**. It was confirmed for compound **1** that the triplet at δ 4.60 corresponds to the C(2') proton and the singlet at δ 4.15 to the C(4') proton due to the appearance of negative cross-peaks representing the NOE between them and methyl protons. The downfield triplet at δ 4.81 corresponds to the C(2) proton due to the NOE peak between the C(2) proton and the methine proton on the π -allyl unit. The cross-peak between protons 2 and 3, 2' and 3' allowed the assignment of signals at δ 4.48 and 4.42 to protons 3 and 3' respectively.

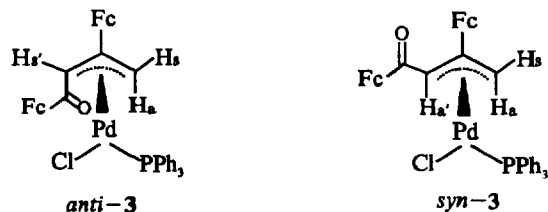
It is well known that a 1,2-disubstituted η^3 -allyl moiety can exist in two isomeric configurations [4], in our case a *syn* configuration where the ferrocenyl group is *cis*- to the ferrocenyl group or an *anti* configura-

* Corresponding author.



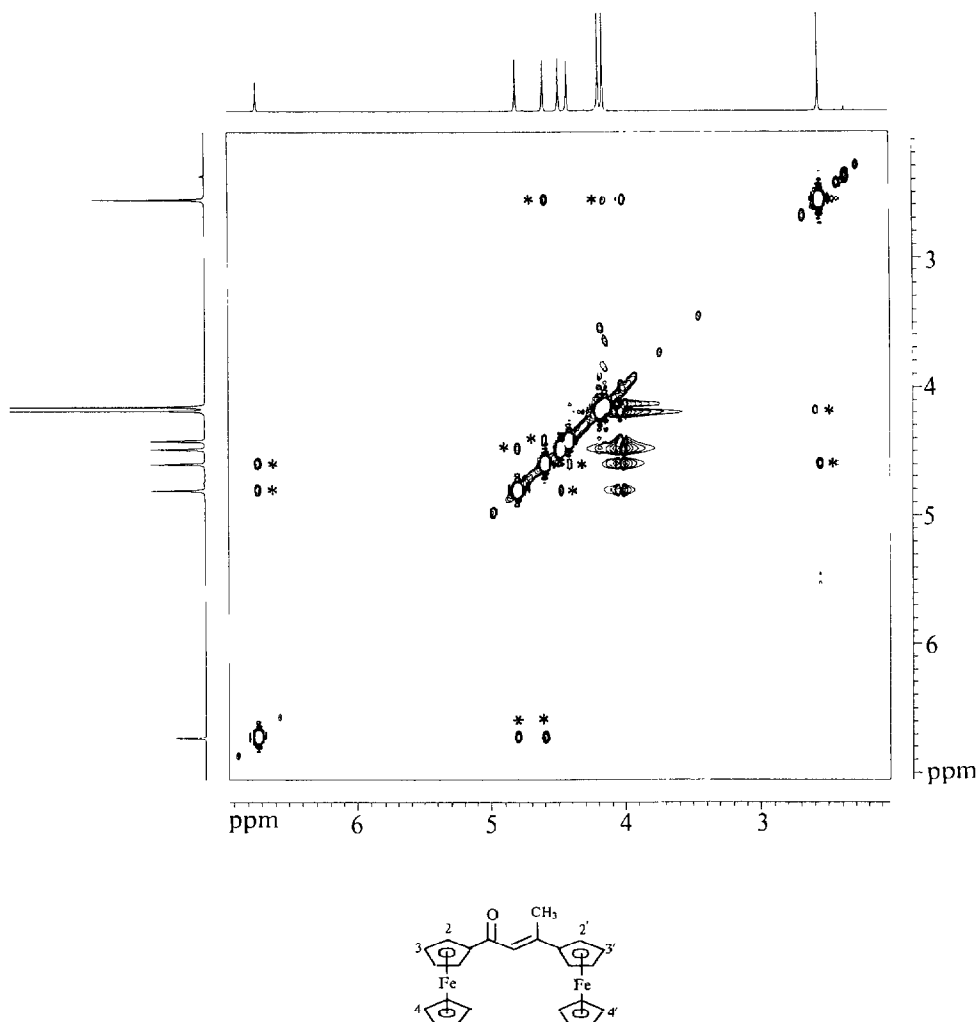
Form 1.

ration where the ferrocenyl group is *trans* to the ferrocenyl group, both of which are chiral:



Form 2.

The ^1H NMR spectra of **3** indicated the presence of only one isomer in solution. In the same way as described above, based on 2D NOESY spectra, we can assign the protons of ferrocenyl moieties accurately and confirm the *anti* configuration of **3**. That is, the singlets at δ 5.18 and 4.30 due to the protons 2 and 2', the triplets at δ 4.56 and 4.38 due to the protons 3 and 3' respectively. If **3** exists in the *syn* configuration, then there would be an NOE cross-peak between proton $\text{H}_{a'}$ and H_a , and no-cross peak between $\text{H}_{a'}$ and the protons

Fig. 1. 2D NOESY spectra of compound **1**; "*" NOE peaks.

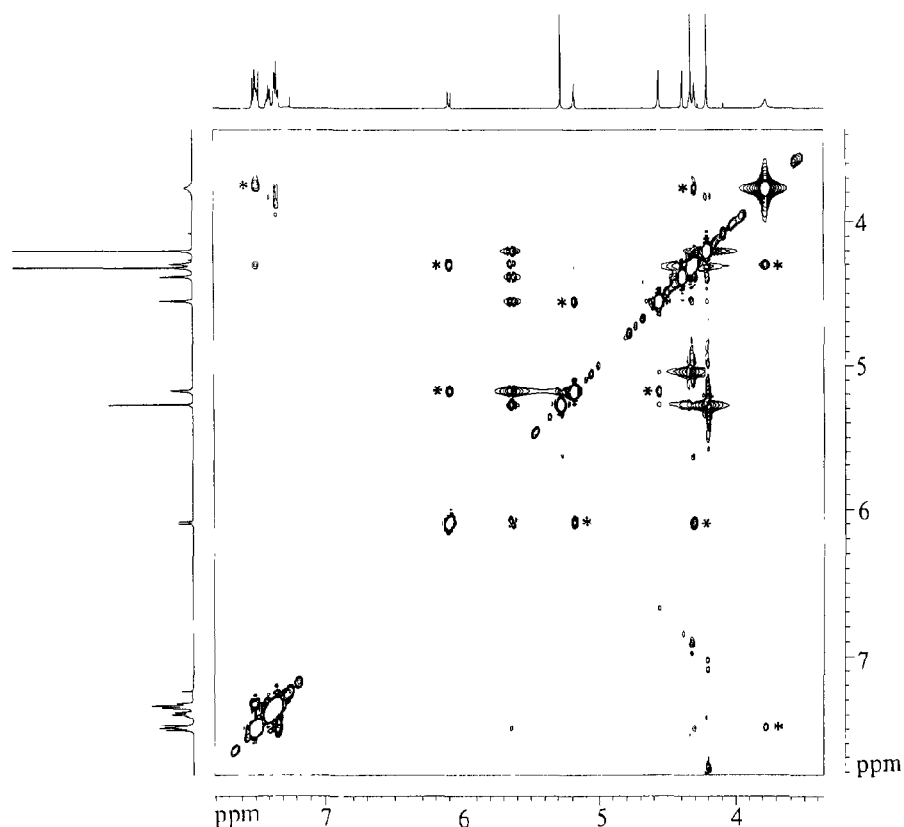


Fig. 2. 2D NOESY spectra of compound **3**: “*” NOE peaks.

of the ferrocenyl group on the central carbon atom. In our case there is an NOE cross-peak between H_a and the protons of the ferrocenyl group on the central carbon atom without the cross-peak between H_a and

H_b . So the assignment of the *anti* configuration is correct. In comparison with the starting material **1**, the chemical shift (δ 3.77) of one of the terminal CH_2 group protons of **3** has experienced a considerable

Table 1
Selected bond distances (Å) for **3**

| | | | | | |
|------------|----------|-------------|----------|-------------|----------|
| Pd–Cl(1) | 2.345(1) | C(4)–C(5) | 1.476(6) | Fe(1)–C(23) | 2.027(5) |
| Pd–P(1) | 2.310(1) | C(2)–C(15) | 1.474(6) | Fe(1)–C(24) | 2.020(5) |
| Pd–C(1) | 2.146(4) | O(1)–C(4) | 1.229(5) | Fe(2)–C(5) | 2.034(4) |
| Pd–C(2) | 2.156(4) | C(15)–C(16) | 1.431(6) | Fe(2)–C(6) | 2.036(4) |
| Pd–C(3) | 2.200(4) | Fe(1)–C(15) | 2.025(4) | Fe(2)–C(7) | 2.044(5) |
| Pd–O(1) | 3.427(3) | Fe(1)–C(16) | 2.047(5) | Fe(2)–C(8) | 2.051(5) |
| P(1)–C(25) | 1.828(4) | Fe(1)–C(17) | 2.054(5) | Fe(2)–C(9) | 2.041(4) |
| P(1)–C(36) | 1.821(4) | Fe(1)–C(18) | 2.031(4) | Fe(2)–C(10) | 2.023(7) |
| P(1)–C(37) | 1.823(4) | Fe(1)–C(19) | 2.030(4) | Fe(2)–C(11) | 2.038(6) |
| C(1)–C(2) | 1.437(6) | Fe(1)–C(20) | 2.032(5) | Fe(2)–C(12) | 2.032(6) |
| C(2)–C(3) | 1.396(6) | Fe(1)–C(21) | 2.035(5) | Fe(2)–C(13) | 2.015(7) |
| C(3)–C(4) | 1.495(6) | Fe(1)–C(22) | 2.041(5) | Fe(2)–C(14) | 2.007(7) |

upfield shift relative to that of **2** (δ 4.95) and, moreover, there exist NOE peaks between the protons H_a (or H_s) and the protons of triphenylphosphine. These results are consistent with a *cis* arrangement of triphenylphosphine and the terminal CH₂ group of **3**. It can be considered that the shielding effect of the phenyl ring in PPh₃ is very large.

The X-ray crystal structure of *anti*- η^3 -1-ferrocenylformyl-2-ferrocenylallyl (triphenylphosphine) chloropalladium **3** was determined, which contains a CH₂Cl₂ molecule as solvate. A perspective view of the molecular structure of **3** is shown in Fig. 3. The selected bond distances and angles are listed in Tables 1 and 2.

The structure determined is completely consistent with that proposed for the compound **3**, which has been supported by the spectral data. That is, the ferrocenyl group and the ferroceneformyl group are located in the *syn* position with respect to the methine hydrogen atom of the π -allyl group. In certain compounds, the steric factors may also influence the choice of *anti* or *syn* isomer [4], so only the *anti* isomer of **3** was obtained. The coordination about the Pd atom is essentially planar if the central allyl C atom (C2) is neglected. Indeed the

Table 2
Selected bond angles (deg) for **3**

| | | | |
|------------------|----------|------------------|----------|
| Cl(1)–Pd–P(1) | 97.52(5) | Pd–C(2)–C(1) | 70.1(2) |
| Cl(1)–Pd–C(1) | 163.8(1) | Pd–C(2)–C(3) | 73.0(2) |
| Cl(1)–Pd–C(3) | 96.3(1) | Pd–C(3)–C(2) | 69.6(2) |
| P(1)–Pd–C(1) | 98.2(1) | C(1)–C(2)–C(3) | 117.8(4) |
| P(1)–Pd–C(3) | 165.9(1) | C(2)–C(3)–C(4) | 124.3(4) |
| C(1)–Pd–C(2) | 39.0(2) | C(3)–C(4)–C(5) | 117.0(4) |
| C(1)–Pd–C(3) | 67.9(2) | C(4)–C(5)–C(6) | 129.3(4) |
| C(2)–Pd–C(3) | 37.4(2) | C(4)–C(5)–C(9) | 122.6(4) |
| Pd–P(1)–C(25) | 116.5(1) | C(1)–C(2)–C(15) | 118.5(4) |
| Pd–P(1)–C(36) | 117.3(1) | C(3)–C(2)–C(15) | 121.6(4) |
| Pd–P(1)–C(37) | 109.9(1) | C(2)–C(15)–C(16) | 125.0(4) |
| C(25)–P(1)–C(36) | 102.9(2) | C(2)–C(15)–C(19) | 126.3(4) |
| C(25)–P(1)–C(37) | 103.9(2) | O(1)–C(4)–C(3) | 122.9(4) |
| C(36)–P(1)–C(37) | 104.9(2) | O(1)–C(4)–C(5) | 120.1(4) |
| Pd–C(1)–C(2) | 70.8(2) | C(5)–C(6)–C(7) | 107.7(4) |

inclination of the C₃ plane defined by the C(1), C(2) and C(3) atoms to the square coordination plane at the metal Pd is ca. 105°, close to the 110° value typical of η^3 -allyl Pd complexes [5]. The Pd–C(3) distance (*trans* to P) of 2.200(4) Å is longer than the Pd–C(1) distance (*trans* to Cl) of 2.146(4) Å, which is probably due to

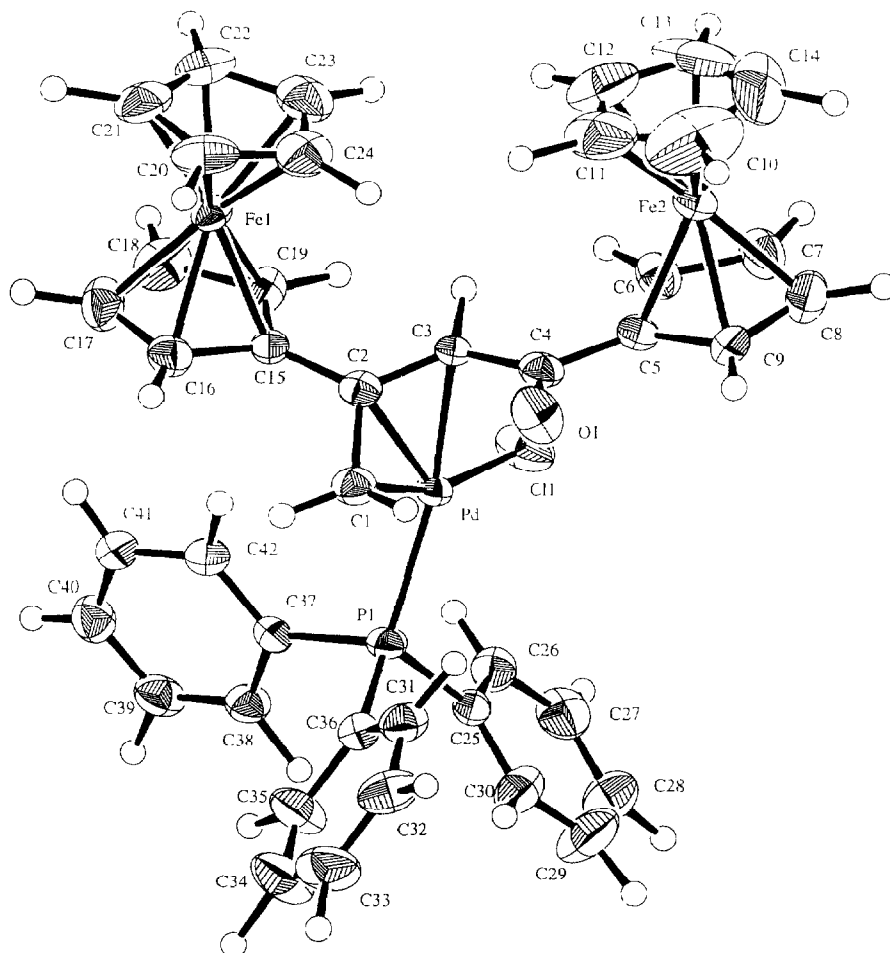


Fig. 3. Molecular structure of **3**.

the *trans* influence of the PPh₃ ligand. The Pd···O distance is 3.427(3) Å, which indicates that there is no direct interaction between them. The π -allyl plane (C₃ plane) and one of the substituted Cp rings forms a dihedral angle of 97.81°, 64.30° with the nearest phenyl ring of the PPh₃ group respectively, which accounts for the shielding effect observed in NMR studies.

The cyclopentadienyl groups are planar within the limits of experimental error. The dihedral angle between the planes C(15)–C(19) and C(20)–C(24) at Fe(1) is 2.71°, and only 1.78° in the other ferrocenyl fragment at Fe(2). The Fe(1) atom is at the same distance (1.635 Å) from the C(15)–C(19) and C(20)–C(24) planes. (1.642 and 1.647 Å for Fe(2) with respect to the C(5)–C(9) and C(10)–C(14) planes). Fe–C (cyclopentadienyl ring) distances range from 2.007(7) to 2.054(5) Å (av. 2.03 Å) and intracyclopentadienyl C–C bond lengths lie in the range 1.34(1)–1.47(1) Å (av. 1.41 Å), the geometry of the ferrocenyl fragments being very similar to that observed in ferrocene itself. The dihedral angle between the two substituted Cp rings and the C₃ plane is 35.50° at Fe(1) and 37.79° at Fe(2) respectively, and that between the two substituted Cp rings and the plane defined by atoms C(2), C(3), C(4), C(5) and C(15) is 18.66° at Fe(1) and 11.17° at Fe(2) respectively.

In summary, the method reported here has been proved to be a mild, chemoselective way of activating an allylic C–H bond in an olefinic substrate. To complete the sequence, it is now necessary to achieve C–C or C–N bond formation, which is the subject of the accompanying manuscript.

3. Experimental section

Melting points were determined on a WC-1 microscopic apparatus and are uncorrected. ¹H NMR spectra were recorded using a Bruker ARX 500 spectrometer, in chloroform-*d*, and all *J* values are in Hz. IR spectra were recorded on a Shimadzu IR 435 spectrophotometer. Elemental analyses were determined with a Carlo Erba 1106 elemental analyzer, and some of the palladium complexes crystallized as solvates from methylene chloride; the analytical data for these crystalline compounds are calculated on the basis of the quantity of methylene chloride observed in individual samples by ¹H NMR measurements. The 2D NOESY spectra were recorded in CDCl₃ at room temperature with a mixing time of 300 ms. Chromatographic work was carried out using a silica gel packed dry column under reduced pressure.

3.1. Syntheses

3.1.1. 1,3-Diferrocenylbut-2-en-1-one (1) [3]

Red needles, m.p. 118–119°C. IR (KBr pellet): 1633, 1587, 1445, 1240, 1100, 997, 819 cm⁻¹. ¹H NMR: δ

2.56 (s, 3H, CH₃), 4.15 (s, 5H, H(4')), 4.19 (s, 5H, H(4)), 4.42 (t, 2H, *J* = 1.7 Hz, H(3')), 4.48 (t, 2H, *J* = 1.75 Hz, H(3)), 4.60 (t, 2H, *J* = 1.7 Hz, H(2')), 4.81 (t, 2H, *J* = 1.75 Hz, H(2)), 6.72 (s, 1H, methine proton on the π -allyl group). Anal. Found: C, 66.15; H, 5.10. C₂₄H₂₂Fe₂O Calc.: C, 65.79; H, 5.06%.

3.1.2. Di- μ -chlorobis(η^3 -1-ferrocenylformyl-2-ferrocenyl- π -allyl)dipalladium (2)

A solution of lithium tetrachloropalladate(II) in 10 ml of methanol (0.26 g of Li₂PdCl₄, 1 mmol) was added to a solution of molar equivalents of NaOAc and **1** in 20 ml methanol, the resulting red solution was stirred at room temperature for about 20 h and then filtered, the solid obtained was recrystallized from CH₂Cl₂–petroleum ether (60–90°C) to produce **2**. Yield 89%, m.p. > 220°C (dec.). IR (KBr pellet): 1630, 1490, 1445, 1100, 1000, 820 cm⁻¹. ¹H NMR: δ 4.03 (s, 2H, CH₂ group), 4.16–4.88 (36H, ferrocenyl group), 4.95 (s, 2H, CH₂ group), 5.51 (bs, 2H, the methine protons on the π -allyl unit). Anal. Found: C, 49.55; H, 3.68. C₄₈H₄₂Cl₂Fe₄O₂Pd₂ Calc.: C, 49.70; H, 3.82.

3.1.3. anti- η^3 -1-Ferrocenylformyl-2-ferrocenyl-allyl(tri-phenylphosphine)chloropalladium (3)

The μ -chloro-bridged complex **2** was treated with molar equivalents of PPh₃ in CH₂Cl₂ at room temperature for 0.5 h, the product was purified by passing rapidly through a short silica gel column, then recrystallized from CH₂Cl₂–petroleum ether (60–90°C) as red platelets. Yield 82% (calculated on the basis of **1**), m.p. 153–155°C. IR (KBr pellet): 1620, 1490, 1450, 1432, 1097, 1000, 825, 740, 690 cm⁻¹. ¹H NMR: δ 3.77 (bs, 2H, CH₂ group), 4.20 (s, 5H, H(4)), 4.30 (s, 2H, H(2')), 4.32 (s, 5H, H(4')), 4.38 (t, 2H, *J* = 1.8 Hz, H(3')), 4.56 (t, 2H, *J* = 1.9 Hz, H(3)), 5.18 (s, 2H, H(2)), 5.27 (s, 2H, CH₂Cl₂), 6.08 (d, 1H, *J* = 9.35 Hz, methine proton on the π -allyl group). 7.33–7.51 (m, 15H, PPh₃-H). Anal. Found: C, 56.00; H, 4.13. C₄₂H₃₆ClFe₂OPPd · CH₂Cl₂ Calc.: C, 55.76; H, 4.14%.

3.2. X-ray crystal structure determination of 3

Crystal data: C₄₃H₃₈Cl₃Fe₂OPPd, *M*_r = 926.20, triclinic, *P*1 (No. 2), *a* = 12.378(3), *b* = 14.884(4), *c* = 11.974(3) Å, α = 94.49(2), β = 107.70(2), γ = 109.61(2)°, *V* = 1939.3(9) Å³, *Z* = 2, *D*_c = 1.59 g cm⁻³, *F*(000) = 936, λ = 0.71069 Å, μ (Mo K α) = 14.78 cm⁻¹.

A red plate crystal of **3** with approximate dimensions 0.30 × 0.30 × 0.40 mm³ was mounted on a Rigaku AFC7R diffractometer. Unit cell parameters were determined from the angular setting of 21 reflections with 2 θ

angles in the range 23.33–26.46°. Intensities were collected with graphite monochromated Mo K α radiation, using the ω - 2θ scan technique. A total of 4936 reflections were measured, 4146 reflections were considered as observed with $I > 3\sigma(I)$. Three reflections were measured after every 200 reflections as orientation and intensity control, and no significant intensity decay was observed. Data were corrected for Lorentz and polarisation effects and also for absorption by an empirical method on the basis of a zimuthal scan of several reflections. The structure was solved by heavy atom Patterson methods, expanded using Fourier techniques and refined by full-matrix least-squares methods. All calculations were performed using the teXsan program package [6]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final R factor was 0.035 ($R_w = 0.049$). The maximum and minimum peaks on the final difference Fourier map corresponded to 0.53 and $-0.80 \text{ e} - \text{\AA}^{-3}$ respectively.

4. Supplementary material available

Tables of atomic coordinates and thermal parameters, bond lengths and angles, anisotropic thermal parameters and hydrogen atom coordinates for **3** are available from the authors.

Acknowledgements

We are grateful to the National Natural Science Foundation of China and the Natural Science Foundation of Henan Province for financial support of this work.

References

- [1] (a) P.A. Van der Schaaf, J.P. Sutter, M. Grellier, G.P.M. Van Mier, A.L. Spek, G. Van Koten and M. Pfeffer, *J. Am. Chem. Soc.*, **116** (1994) 5134; (b) T. Ohta, T. Hosokawa, S.I. Murahashi, K. Miki and N. Kasai, *Organometallics*, **4** (1985) 2080; (c) G. Gatti, J.A. López, C. Mealli and A. Musco, *J. Organomet. Chem.*, **483** (1994) 77.
- [2] (a) B.J. Coe, C.J. Jones, J.A. McCleverty, D. Bloor, P.V. Kolinsky and R.J. Jones, *J. Chem. Soc., Chem. Commun.*, (1989) 1485; (b) G. Doisneau, G. Balavoine, T. Fillebeen-Kahn, J.C. Clinet, J. Delaire, I. Ledoux, R. Loucif and G. Puccetti, *J. Organomet. Chem.*, **421** (1991) 299; (c) S. Ghosal, M. Samoe, P.N. Prasad and J.J. Tufariello, *J. Phys. Chem.*, **94** (1990) 2847; (d) M. Sato, Y. Hayashi, H. Shintate, M. Katada and S. Kawata, *J. Organomet. Chem.*, **471** (1994) 179; (e) D.B. Broen (ed.), *Mixed-Valence Compounds*, Reidel, Boston, MA, 1980.
- [3] Y.K. Zhou, Y.Z. Li and S.Z. Wu, *Huaxue Xuebao*, **46** (1988) 1042.
- [4] J.W. Faller, M.E. Thomsen and M.J. Mattina, *J. Am. Chem. Soc.*, **93** (1971) 2642.
- [5] A.E. Smith, *Acta Crystallogr.*, **18** (1965) 331.
- [6] *teXsan: Crystal Structure Analysis Package*, Molecular Structure Corporation, 1985 and 1992.