www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 582 (1999) 352–357

1-Dialkylamino-1-phospha-[1]ferrocenophanes—synthesis and characterisation

Max Herberhold *, Frank Hertel, Wolfgang Milius, Bernd Wrackmeyer

Laboratorium für Anorganische Chemie, Universität Bayreuth, Postfach 10 12 51, D-95440 Bayreuth, Germany

Received 19 November 1998

Abstract

1-Diisopropylamino-1-phospha-[1]ferrocenophane, fc[P–N^{i}Pr$_2$] (**1**), has been prepared from 1,1′-dilithioferrocene and diisopropylamino-dichlorophosphane. A complete set of NMR data (^{1}H-, ^{13}C-, ^{15}N-, ^{31}P-NMR) supports the monomeric structure of **1** in solution, which has been confirmed by an X-ray structure analysis for the solid state. The nitrogen atom is in a planar environment (sum of angles 359.3°); the distorted sandwich structure contains ecliptic cyclopentadienyl rings which include an angle of $\alpha = 27.89°$. The reactions of **1** with sulfur, selenium and bis(triphenylphosphane)(ethene)platinum(0) are discussed.

Keywords: Ferrocene; [1]Ferrocenophane; Phosphorus; NMR; X-Ray analysis

1. Introduction

Structural distortions in [1]ferrocenophanes as compared with ferrocene have recently attracted considerable interest [1,2]. The synthetic potential due to the strained bonding situation in such compounds has been exploited in insertion reactions [3,4] and in ring-opening polymerisations (ROP) [4–10], which can be conducted under thermal [7,8], anionic [9] or coordination-catalysed [10] conditions. Although 1-organo-1-phospha-[1]ferrocenophanes have been known since 1980 [11,12], the first P-functionally substituted derivative, 1-chloro-1-phospha-[1]ferrocenophane (fc[P–Cl]) was prepared and structurally characterised only recently [8]. However, it appears that its limited stability in solution may prevent a more widespread synthetic application. We report here on the synthesis and characterisation of the first 1-amino-substituted 1-phospha-[1]ferrocenophanes.

2. Results and discussion

2.1. Synthesis and reactivity of 1-diisopropylamino-1-phospha-[1]ferrocenophane (1) and 1-(2,2,6,6,-tetramethylpiperidino)-1-phospha[1]ferrocenophane (2)

In principle, the reaction of 1,1′-dilithioferrocene with amino-dichlorophosphanes, $R_2N–PCl_2$, should provide a straightforward route to 1-amino-1-phospha-[1]ferrocenophanes, fc[P–NR$_2$]. However, so far only dichlorophosphanes bearing a bulky diisopropylamino- or 2,2,6,6-tetramethylpiperidino group, respectively, could be converted to the desired [1]ferrocenophanes **1** and **2** (Scheme 1). The analogous reaction with diethylamino-dichlorophosphane was not successful.

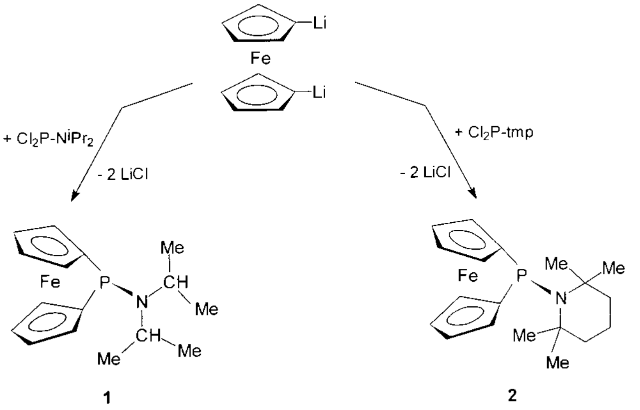
The [1]ferrocenophanes **1** and **2** were isolated as dark-red solids which, in pure crystalline state, can be handled in air. Their solutions in hexane or benzene are stable for weeks at room temperature if air and moisture are rigorously excluded. However, THF solutions of **1** decompose within several hours, and **1** is converted into a brown insoluble solid. Some typical reactions of **1** are presented in Scheme 2.

---

* Corresponding author. Tel.: +49-921-552-540; fax: +49-921-552-157.

E-mail address: max.herberhold@uni-bayreuth.de (M. Herberhold)

0022-328X/99/$ - see front matter © 1999 Elsevier Science S.A. All rights reserved.
PII: S0022-328X(99)00078-9



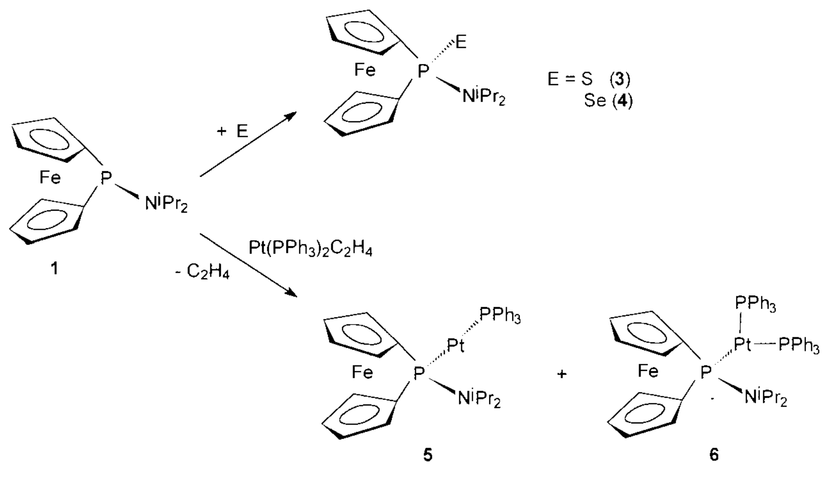
Scheme 1.

Like other phosphanes, **1** reacts with sulfur and selenium in a 1:1 ratio to give the sulfide **3** and the selenide **4**, respectively. There was no reaction of **1** with tellurium at room temperature or after heating in benzene at 60°C for several minutes. The potential of **1** as a ligand in transition metal complexes has been tested in the reaction of **1** with bis(triphenylphosphane)(ethene)platinum, $Pt(PPh_3)_2C_2H_4$. A mixture of two platinum complexes **5** and **6** is obtained, independent of the molar ratio of the reactants and of the reaction conditions. This mixture is stable in solution for several weeks, even in the presence of an excess of **1**.

2.2. NMR Spectra of ***1*** *and* ***2*** *and of some derivatives of* ***1*** *in solution*

A fairly complete NMR data set of **1** and **2** proves that they possess monomeric structures in solution (Table 1). The inversion at the phosphorus atom in both **1** and **2** is apparently slow on the NMR time scale, and four different ^{1}H and ^{13}C signals are therefore observed for the ferrocene core; the assignments are based on 2D $^{1}H/^{1}H$ COSY and NOESY and $^{13}C/^{1}H$ HETCOR spectra. In the case of **1**, the Hahn-echo extended (HEED [15]) INEPT experiment [16] is readily applied to record the ^{15}N satellites and to measure the isotope induced chemical shift $^{1}\Delta^{14/15}N(^{31}P)$ at natural abundance in the ^{31}P-NMR spectra with high accuracy (± 1 ppb). This technique suppresses the intensity of the parent signal belonging to the $^{31}P-^{14}N$ isotopomer (Fig. 1). The normal $^{31}P\{^{1}H\}$-NMR spectra serve for detecting the ^{13}C and ^{15}N satellites and for determining with slightly lower accuracy (± 2 ppb), using more spectrometer time, both $^{1}\Delta^{12/13}C(^{31}P)$ and $^{1}\Delta^{14/15}N(^{31}P)$ as shown for **2** in Fig. 2. The ^{15}N satellites are significantly sharper than the ^{13}C satellites since the latter belong to the $^{13}C-^{31}P-^{14}N$ isotopomer in which the ^{31}P-NMR signals are broadened by partially relaxed scalar $^{31}P-^{14}N$ coupling. The magnitude of $^{1}\Delta^{14/15}N(^{31}P)$ is in the range known for aminophosphanes [15,17]. However, $^{1}\Delta^{12/13}C(^{31}P)$ is more negative than in comparable organophosphanes (e.g. Ph_3P: $^{1}\Delta^{12/13}C(^{31}P) = -22.7$ ppb [18]). Although the data set available for these parameters is still limited, the outlook is promising since it appears that extreme bonding situations, such as in [1]ferrocenophanes, are reflected by noticeable changes in the magnitude of isotope induced chemical shifts. Therefore, it might be worthwhile to determine $^{1}\Delta^{12/13}C(M)$ for $M = {}^{13}C$, ^{29}Si, ^{119}Sn in other [1]ferrocenophanes.

The formation of the sulfide **3** and the selenide **4** follows unambiguously from the NMR data (Section 3), the [1]ferrocenophane structure being retained. Similarly, this strained structure is retained in the platinum complexes **5** and **6**, although one might have expected that insertion into one of the P–C bonds could have taken place (cf. [3,4]). However, complementary ^{31}P- and ^{195}Pt-NMR data (Section 3) provide clear evidence for the presence of a two-coordinate (**5**) and a three-coordinate Pt(0) complex (**6**). The magnitude of the cou-



Scheme 2.

Table 1
NMR data[a] of the 1-dialkylamino-1-phospha-[1]ferrocenophanes **1** and **2**

No.	δ ^{1}H (C_5H_4)	δ ^{1}H (NR_2)	δ ^{13}C (C_5H_4)	δ ^{13}C (NR_2)	δ ^{31}P[b]	δ ^{15}N
1	4.37 (2/7) 4.30 (3/8) 4.16 (4/9) 4.36 (5/10)	3.47 (11.5) CH 1.22 (<1) (Me)	78.1 (7.8) (2/7) 78.2 (1.0) (3/8) 75.1 (12.1) (4/9) 76.1 (49.0) (5/10) 34.7 (53.2) (1/6)	49.5 (10.1) (CH) 24.2 (8.1) (Me)	31.1	−310.6 (64.7)
2	4.49 (2/7) 4.16 (3/8) 4.01 (4/9) 4.37 (5/10)	1.41 (<1) (Me) 1.36 (<1) (CH_2) 1.18 (<1) (–CH_2–)	79.8 (11.7) (2/7) 76.9 (3.0) (3/8) 74.5 (16.6) (4/9) 79.1 (68.0) (5/10) 40.9 (69.6) (1/6)	57.3 (12.5) NC 42.7 (2.3) (C–*CH_2*) 32.6 (13.2) (C–*Me*) 17.6 (0.8) (–CH_2–)	28.3	−286.5 (86.4)

[a] The numbering scheme corresponds to that of the molecular structure of **1** (Fig. 3). Coupling constants $J(^{31}P, ^1H)$, $J(^{31}P,^{13}C)$ and $J(^{31}P, ^{15}N)$ are given in parentheses.

[b] Isotope induced chemical shifts; **1**: $^1\Delta^{12/13}C(^{31}P) = -40.0 \pm 2$ ppb; $^1\Delta^{14/15}N(^{31}P) = -35.0 \pm 1$ ppb (Hahn-echo experiment; Fig. 1); **2**: $^1\Delta^{12/13}C(^{31}P) = -35.7 \pm 2$ ppb; $^1\Delta^{14/15}N(^{31}P) = -39.0 \pm 2$ ppb (Fig. 2).

pling constants $^1J(^{195}Pt, ^{31}P)$ is typical of Pt(0) complexes, and the ^{195}Pt resonances at low frequency (δ^{195} Pt: −502.7) and high frequency (δ^{195} Pt: −28.6) are characteristic of two-coordinate and three-coordinate Pt(0) phosphane complexes, respectively [19].

2.3. X-ray structural analysis of fc[P–N^{i}Pr$_2$] (1)

Dark red prisms of **1** were grown from hexane solution in the refrigerator (8°C). The complex **1** crystallises in the monoclinic system with four molecules in the unit cell. The distorted sandwich structure of **1** is shown in Fig. 3; selected bond lengths and angles are given in Table 2.

The nitrogen atom of the diisopropylamino group has a planar environment, the sum of the angles at N being 359.3°. The plane containing P, N, C(11), C(14) and also the two single hydrogen atoms of the isopropyl substituents forms an angle of 8.3° with the Fe, P, N plane and is arranged almost perpendicular (82.1°) with respect to the line connecting C(1) and C(6). This indicates that the lone pair of electrons at the nitrogen atom can interact ($n-\sigma^*$) with the P–C(1) and P–C(6) bonds.

Table 3 contains a collection of typical molecular parameters of **1** together with those of related 1-phospha-[1]ferrocenophanes, fc[P–R], which have been structurally characterised by X-ray crystallography.

The molecular distortions in phospha-[1]ferrocenophanes, fc[P–R], can be conveniently described [1a,8] by a set of four angles (α, β, δ and θ) which are defined in Fig. 4.

Compared with 1-chloro-1-phospha-[1]ferrocenophane, fc[P–Cl] [8], the (non-bonding) iron–phosphorus distance in **1** is slightly longer (280.2(1) versus 271.5(6) pm, Table 3), and concomitantly, both the angles δ at iron and θ at phosphorus in **1** become slightly smaller. The angles β which describe the inclination of the C(1)–P and C(6)–P connections relative to their respective cyclopentadienyl planes are significantly larger (41.2° average in **1**) than the analogous angles in the other fc[P–R] complexes (R = Cl [8], ^{t}Bu [13], and Ph [13,14]) where average β values between 31.9 and 32.8° have been observed. Apparently, the phosphorus atom in fc[P–N^{i}Pr$_2$] (**1**) is shifted closer to the ferrocenophane cave although the iron atom tries to avoid close Fe···P contacts. The distance of the Fe atom from the line connecting the two midpoints of the cyclopentadienyl rings, Z(1) and Z(6), is 30.4 pm in fc[P–N^{i}Pr)$_2$] (**1**) as compared with 27.7(8) pm in fc[P–Cl] [8]; the distances Fe–Z(1) (163.8 pm) and Fe–Z(6) (163.3 pm) are very close to the value of 166 pm in ferrocene [20]. Both cyclopentadienyl rings are planar (within experimental

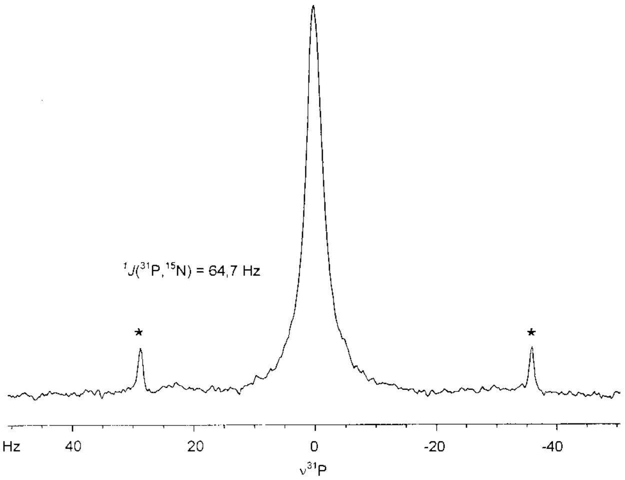


Fig. 1. 103.1 MHz ^{31}P-NMR spectrum of fc[P–N^{i}Pr$_2$] (**1**) in C_6D_6, recorded by using the HEED-INEPT pulse sequence with ^{1}H decoupling [15] (Hahn-echo delay of 0.18 s; result of 200 transients, spectrometer time 8 min). The ^{15}N satellites are marked by asterisks ($^1\Delta^{14/15}N(^{31}P) = -35.0 \pm 1$ ppb).

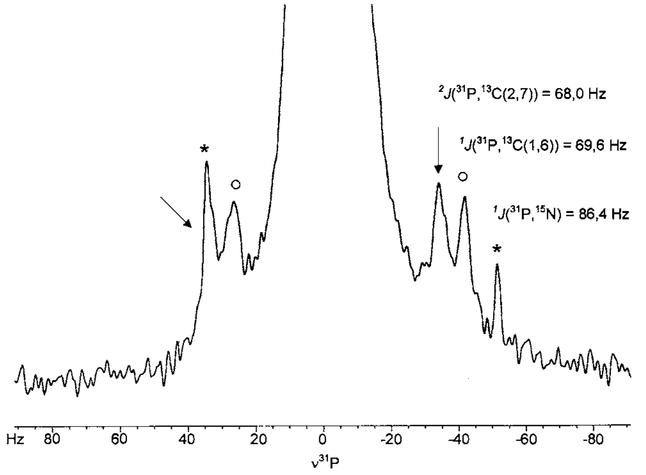


Fig. 2. 202.5 MHz $^{31}P\{^1H\}$-NMR spectrum of **2** showing the parent line together with ^{13}C and ^{15}N satellites (2716 transients; 2 h of spectrometer time). Note that the ^{15}N satellites (marked by asterisks; $^1\Delta^{14/15}N(^{31}P) = -39 \pm 2$ ppb) are much sharper than the ^{13}C satellites for $^1J(^{31}P, ^{13}C(1,6))$ (marked by open circles; $^1\Delta^{12/13}C(^{31}P) = -36 \pm 2$ ppb) and $^2J(^{31}P, ^{13}C(2,7))$ (marked by arrows; $^2\Delta^{12/13}C(^{31}P) < 2$ ppb).

error), and they are arranged in an ecliptic position, the angle τ describing the deviation from the ideal ecliptic arrangement being only 1.4°.

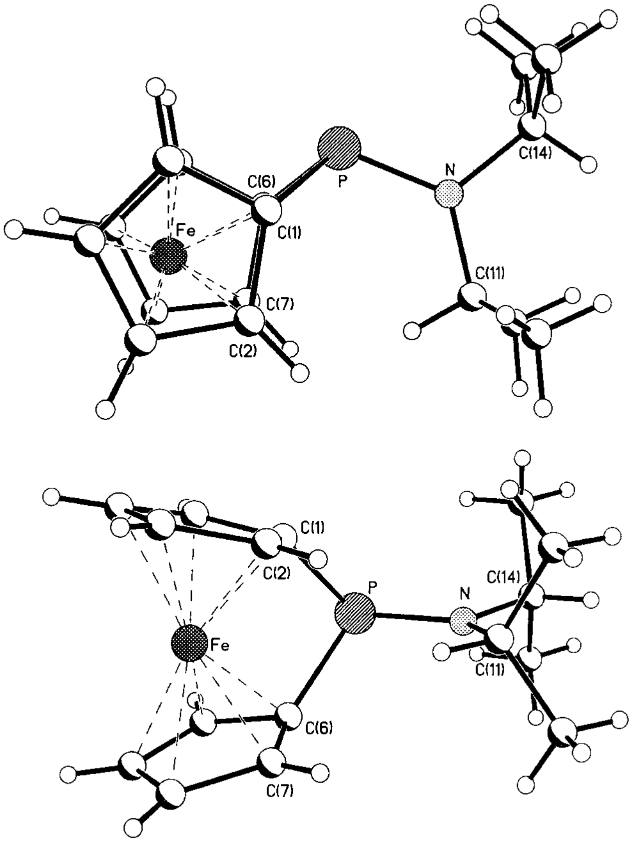


Fig. 3. Two views of the molecular structure of fc[P–N^{i}Pr$_2$] **1**.

Table 2
Selected bond lengths and angles in fc[P–N^{i}Pr$_2$] (**1**)

Bond lengths (pm)			
Fe···P	280.2(1)	P–N	166.9(2)
Fe–C(1)	197.7(2)	Fe–C(6)	198.2(2)
Fe–C(2)	201.6(2)	Fe–C(7)	200.8(2)
Fe–C(3)	208.8(3)	Fe–C(8)	207.6(3)
Fe–C(4)	208.9(3)	Fe–C(9)	208.5(3)
Fe–C(5)	203.1(2)	Fe–C(10)	203.0(1)
P–C(1)	187.4(2)	P–C(6)	185.5(2)
N–C(11)	147.1(3)	N–C(14)	148.7(2)
Bond angles (°)			
Fe···P–N	125.3(1)		
C(1)–P–N	110.0(1)	P–N–C(11)	125.0(1)
C(6)–P–N	109.8(1)	P–N–C(14)	117.9(1)
C(1)–P–C(6)	88.8(1)	C(11)–N–C(14)	116.4(2)

3. Experimental

3.1. Materials and instruments

All reactions were performed in an atmosphere of dry nitrogen, using carefully dried solvents and oven-dried glassware. Starting materials such as ferrocene, BuLi in hexane (1.6 M) and PCl_3 were used as commercial products; the amino-dichlorophosphanes [21] and 1,1′-dilithioferrocene [22] were prepared following the literature procedures. EI–MS (70 eV): Varian MAT CH7 with direct inlet. ^1H-, ^{13}C-, ^{15}N- (INEPT refocused [16], based on $^3J(^{15}N, ^1H) = 2.5$ Hz, ^1H decoupled) and ^{31}P-NMR spectra were measured using Bruker ARX 250 and DRX 500 instruments, equipped with multinuclear units; chemical shifts are given with respect to Me_4Si [δ $^1H(C_6D_5H) = 7.15$, $(C_6D_5CD_2H) = 2.03$: δ $^{13}C(C_6D_6) = 128.0$, $(C_6D_5CD_3) = 20.4$], neat $MeNO_2$ (δ $^{15}N = 0$ for $\Xi(^{15}N) = 10.136767$ MHz), H_3PO_4 85%(aq.) [δ $^{31}P = 0$ for $\Xi(^{31}P) = 40.480747$ MHz], and δ $^{195}Pt = 0$ for $\Xi(^{195}Pt) = 21.4$ MHz.

3.2. 1-Diisopropylamino-1-phospha-[1]ferrocenophane, fc[P–N^{i}Pr$_2$] (1)

A suspension of fcLi$_2$(TMEDA) (11.4 mmol) in hexane (200 ml) is cooled to −78°C and a solution of ^{i}Pr$_2$N–PCl$_2$ (2.30 g; 11.4 mmol) in hexane (30 ml) is added dropwise. The reaction mixture is allowed to warm up to 15°C, and insoluble material is immediately removed by filtration. The filtrate is kept at −78°C for 12 h to give deep red needles of **1** [1.33 g; 42%; m.p. dec. = 133°C] which are dried in vacuo after decanting the reddish solution. EI–MS: m/z (%) = 315 (100) [M$^+$], 230 (40) [fcPMe$^+$], 215 (50) [fcP$^+$].

1-(2,2,6,6-Tetramethylpiperidino)-1-phospha-[1]ferrocenophane, fc[P–tmp] (**2**), was obtained in the same way as a bright red powder [yield 50%; m.p. dec. = 116°C], using 2,2,6,6-tetramethylpiperidino-dichloro-

Table 3
Characteristic molecular parameters in 1-phospha-[1]ferrocenophanes, fc[P–R]

	R = Cl [8]	R = ^{t}Bu [13]	R = Ph [14]	R = Ph [13]	R = N^{i}Pr$_2$ This work
Bond lengths (pm)					
Fe···P	271.5(6)	276.3(1)	277.4(3)	277.4(1)	280.2(1)
Fe–C(1)	195.4(17)	198.3(3)	197.5(9)	198.2(4)	197.7(2)
Fe–C(6)	196.0(14)	197.8(4)	198.3(9)	197.9(4)	198.2(6)
C(1)···C(6)	260.6(17)	263.3(5)	261.9(12)	263.2(6)	261.0(2)
P–C(1)	184.0(15)	185.4(3)	183.6(9)	184.9(5)	187.4(2)
P–C(6)	183.4(20)	187.0(4)	184.9(10)	185.0(5)	185.5(2)
Bond angles (°)[a]					
α	27.0(6)	27.1	26.7	26.9	27.8
β(average)	31.9(7)	32.8	32.5	32.3	41.2(2)
δ	160.4(6)	159.8	160	159.8	157.1
ϑ	90.1	90.5(2)	90.6(3)	90.7(2)	88.8(1)

[a] See Fig. 4.

phosphane. EI–MS: m/z (%) = 355 (82) [M$^+$], 230 (100) [fcPMe$^+$], 215 (68) [fcP$^+$].

3.3. Reactions of **1** with sulfur, selenium and [Pt(PPh$_3$)$_2$(C$_2$H$_4$)]

The reactions were carried out on a small scale in NMR tubes. The sulfide **3** and the selenide **4** were formed quantitatively, and in the case of the platinum complex, a mixture of the Pt(0) complexes **5** and **6** was identified. The latter reaction was carried out by mixing the components either at room temperature or at −78°C; the result was the same.

3: ^{31}P-NMR: δ ^{31}P = 65.4. **4**: ^{31}P-NMR: δ ^{31}P = 54.7, ^1J(^{77}Se, ^{31}P) = 792 Hz; **5**: ^{31}P-NMR: δ ^{31}P = 97.6 d (^2J(^{31}P, ^{31}P) = 68.0 Hz), [^1J(^{195}Pt, ^{31}P) = 4320 Hz] 1-phospha-[1]ferrocenophane; 36.5 d (^2J(^{31}P, ^{31}P) = 68.0 Hz), [^1J(^{195}Pt, ^{31}P) = 3525 Hz] PPh$_3$; ^{195}Pt-NMR: δ ^{195}Pt = −502.7 dd [^1J(^{195}Pt, ^{31}P) = 4320 and 3525 Hz]; **6**: δ ^{31}P = 119.0 t (^2J(^{31}P, ^{31}P) = 172.0 Hz), [^1J(^{195}Pt, ^{31}P) = 5336 Hz] 1-phospha-[1]ferrocenophane; 50.8 d (^2J(^{31}P, ^{31}P) = 172.0 Hz), [^1J(^{195}Pt, ^{31}P) = 4135 Hz] PPh$_3$; ^{195}Pt-NMR: δ ^{195}Pt = −28.6 dt [^1J(^{195}Pt, ^{31}P) = 5336 (d) and 4135 Hz (t)].

3.4. X-ray structure analysis of fc[P–N^{i}Pr$_2$] (**1**)

The crystal of C$_{16}$H$_{22}$FeNP was a dark red prism with dimensions 0.25 × 0.20 × 0.12 mm^3; space group $P2_1/c$ (monoclinic) with lattice parameters a = 1895.6(2), b = 754.5(2), c = 1089.1(2) pm, β = 95.62(2)°, and Z = 4; absorption coefficient 1.062 mm^{-1}. Data collection: Siemens P4 diffractometer (Mo–K$_\alpha$ radiation, λ = 71.073 pm, graphite monochromator); T = 296 K; 7946 reflections measured with ω scan mode in the range $3° \leq 2\vartheta \leq 55°$; 3554 independent reflections and 3029 were assigned to be observed ($F_o \geq 3.0\ \sigma(F_o)$). Structure solution and refinement: after applying Lorentz, polarisation, and absorption corrections (Ψ-scans, min/max transmission factors: 0.4224/0.4556) the position of Fe could be found by Patterson synthesis, and the remaining atoms were located by consecutive difference Fourier synthesis (Siemens SHELXTL-PLUS); all non-hydrogen atoms were refined anisotropically; the hydrogen atoms (on calculated positions) were treated isotropically applying the riding model with a fixed temperature factor (0.08 Å^2); refinement of 173 parameters converged at R/wR-values of 0.037/0.041; the max/min residual electron density was 0.55/−0.32 e Å^{-3}.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 107105. Copies of this information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

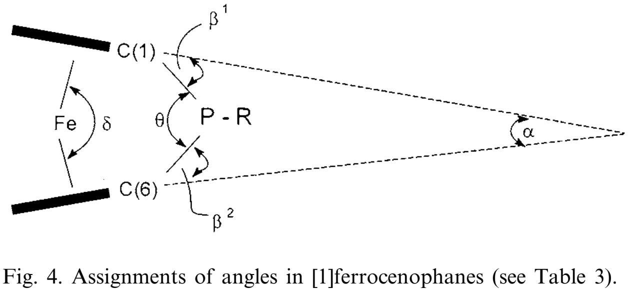


Fig. 4. Assignments of angles in [1]ferrocenophanes (see Table 3).

Acknowledgements

Support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

References

[1] (a) M. Herberhold, Angew. Chem. 107 (1995) 1985; Angew. Chem. Int. Ed. Engl. 34 (1995) 1937. (b) M. Herberhold, T. Bärtl, Z. Naturforsch. Teil B 50 (1995) 1692.

[2] (a) J.K. Pudelski, D.P. Gates, R. Rulkens, A.J. Lough, I. Manners, Angew. Chem. 107 (1995) 1633; Angew. Chem. Int. Ed. Engl. 34 (1995) 1506; (fc[S]). (b) R. Rulkens, A.J. Lough, I. Manners, Angew. Chem. 108 (1996) 1929; Angew. Chem. Int. Ed. Engl. 35 (1996) 1805, (fc[Sn^{t}Bu$_2$]); cf. [4]. (c) H. Braunschweig, R. Dirk, M. Müller, P. Nguyen, R. Resendes, D.P. Gates, I. Manners, Angew. Chem. 109 (1997) 2433; Angew. Chem. Int. Ed. Engl. 36 (1997) 2338; (fc[B–N(SiMe$_3$)$_2$]).

[3] (a) J.B. Sheridan, A.J. Lough, I. Manners, Organometallics, 15 (1996) 2195. (b) J.B. Sheridan, K. Temple, A.J. Lough, I. Manners, J. Chem. Soc. Dalton Trans. (1997) 711.

[4] F. Jäkle, R. Rulkens, G. Zech, D.A. Foucher, A.J. Lough, I. Manners, Chem. Eur. J. 4 (1998) 2117.

[5] I. Manners, Adv. Organometal. Chem. 37 (1995) 131.

[6] I. Manners, Angew. Chem. 108 (1996) 1713; Angew. Chem. Int. Ed. Engl. 35 (1996) 1602.

[7] (a) D.A. Foucher, B.-Z. Tang, I. Manners, J. Am. Chem. Soc. 114 (1992) 6246. (b) W. Finckh, B.-Z. Tang, D.A. Foucher, D.B. Zamble, R. Ziembinski, A.J. Lough, I. Manners, Organometallics 12 (1993) 823. (c) J.K. Pudelski, I. Manners, J. Am. Chem. Soc. 117 (1995) 7265.

[8] C.H. Honeyman, A.D. Foucher, F.Y. Dahmen, R. Rulkens, A.J. Lough, I. Manners, Organometallics 14 (1995) 5503.

[9] (a) R. Rulkens, A.J. Lough, I. Manners, J. Am. Chem. Soc. 116 (1994) 797. (b) R. Rulkens, Y. Ni, I. Manners, J. Am. Chem. Soc. 116 (1994) 12121. (c) Y. Ni, R. Rulkens, I. Manners, J. Am. Chem. Soc. 118 (1996) 4102.

[10] (a) N.P. Reddy, H. Yamashita, M. Tanaka, J. Chem. Soc. Chem. Commun. (1995) 2263. (b) Y. Ni, J.K. Rulkens, J.K. Pudelski, I. Manners, Makromol. Chem. Rapid. Commun. 16 (1995) 637. (c) P. Gómez-Elipe, P.M. Macdonald, I. Manners, Angew. Chem. 109 (1997) 780, Angew. Chem. Int. Ed. Engl. 36 (1997) 762.

[11] A.G. Osborne, R.H. Whiteley, R.E. Meads, J. Organomet. Chem. 193 (1980) 345.

[12] D. Seyferth, H.P. Withers Jr., J. Organomet. Chem. 185 (1980) C1.

[13] I.R. Butler, W.R. Cullen, F.W.B. Einstein, S.J. Rettig, A.J. Willis, Organometallics 2 (1983) 128.

[14] H. Stoeckli-Evans, A.G. Osborne, R.H. Whiteley, J. Organomet. Chem. 194 (1980) 91.

[15] E. Kupce, B. Wrackmeyer, J. Magn. Reson. 97 (1992) 568.

[16] (a) G.A. Morris, R. Freeman, J. Am. Chem. Soc. 101 (1979) 760. (b) D.P. Burum, R.R. Ernst, J. Magn. Reson. 39 (1980) 163. (c) G.A. Morris, J. Am. Chem. Soc. 102 (1980) 428.

[17] (a) B. Wrackmeyer, E. Kupce, G. Kehr, J. Schiller, Magn. Reson. Chem. 30 (1992) 304. (b) B. Wrackmeyer, C. Köhler, Magn. Reson. Chem. 31 (1993) 573. (c) B. Wrackmeyer, C. Köhler, E. Kupce, Magn. Reson. Chem. 31 (1993) 769. (d) B. Wrackmeyer, S. Gerstmann, M. Herberhold, Magn. Reson. Chem. 31 (1993) 499.

[18] C.J. Jameson, in: D.M. Grant, R.K. Harris (Eds.), Encyclopedia of NMR, vol. 4, Wiley, Chichester, 1996, pp. 2638–2655.

[19] (a) R. Benn, H.M. Buch, R.D. Reinhardt, Magn. Reson. Chem. 23 (1985) 559. (b) P.S. Pregosin, Coord. Chem. Rev. 44 (1982) 247. (c) P.S. Pregosin, Annu. Rep. NMR Spectrosc. 17 (1986) 285.

[20] (a) P. Seiler, J. Dunitz, Acta Cryst. B 35 (1979) 1068. (b) F. Takusagawa, T.F. Koetzle, Acta Crystallogr. B 35 (1979) 1074.

[21] N. Gerrard, H.R. Hudson, in: G.M. Kosolapoff, L. Maier (Eds.), Organic Phosphorus Compounds, vol. 5, Wiley, New York, 1973, p. 88.

[22] M.D. Rausch, C.J. Ciappenelli, J. Organomet. Chem. 10 (1967) 127.