

Synthesis of a new bidentate ferrocenyl *N*-heterocyclic carbene ligand precursor and the palladium (II) complex *trans*-[PdCl₂(C^{fc}C)], where (C^{fc}C) = 1,1'-di-*tert*-butyl-3,3'-(1,1'-dimethyleneferrocenyl)-diimidazol-2-ylidene

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Received 21 September 2004; accepted 8 October 2004

Available online 11 November 2004

Abstract

A new ferrocenyl-*N*-heterocyclic carbene ligand precursor 1,1'-bis[(1-*tert*-butylimidazolium)-3-methyl]ferrocene dichloride has been synthesised and structurally characterised. The imidazolium salt was readily deprotonated in situ with KN(SiMe₃)₂ and reacted with [PdCl₂(cod)] to afford the structurally characterised palladium (II) complex *trans*-[PdCl₂(C^{fc}C)], where (cod) = 1,5-cyclooctadiene and (C^{fc}C) = 1,1'-di-*tert*-butyl-3,3'-(1,1'-dimethyleneferrocenyl)-diimidazol-2-ylidene.

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Keywords: Carbene; *N*-heterocyclic carbene; Ferrocene; Palladium; Trans chelating

1. Introduction

N-heterocyclic carbenes have attracted considerable attention as a new class of ligand over the last few years with their ligating characteristics comparable to the well-studied tertiary phosphines [1–6]. Such carbene ligands have been shown to be effective in a range of transition metal catalyzed processes. Bidentate *N*-heterocyclic carbene ligands offer an alternative to bidentate diphosphines for the promotion of catalytic activity in their transition metal complexes [7–13].

A diphosphine ligand that often shows superior catalytic activity in some of its metal complexes, when compared to complexes containing other types of bidentate diphosphine ligands, is 1,1'-bis(diphenylphosphino)fer-

rocene (dppf) [14]. Carbenes with ferrocenyl substituents have attracted interest because the ferrocene group has unique electronic properties, such as stabilising α -carbocations, and has an unusual cylindrical shape [15]. Metal complexes (W(0), Pd(II) and Hg(II)) containing a monodentate ferrocenyl substituted imidazolylidene ligand have been prepared by in situ deprotonation of the imidazolium precursor 1-(ferrocenylmethyl)-3-methyl imidazolium iodide [16], Fig. 1(a). This ferrocene imidazolium salt has been subsequently shown to act as an anion receptor [17,18]. Similarly, the general structure of the ferrocene substituted imidazolium salt has also been used to prepare chiral carbene ligands [19–21], Fig. 1(b) and (c). An imidazolium precursor containing a ferrocenyl substituent attached directly to each of the the ring nitrogen atoms has also been prepared [22], Fig. 1(d).

Continuing our interests in imidazolylidenes that are linked to a cyclopentadienyl group, bidentate imidazolylidenes [6] and substituted ferrocenes [23], herein, we

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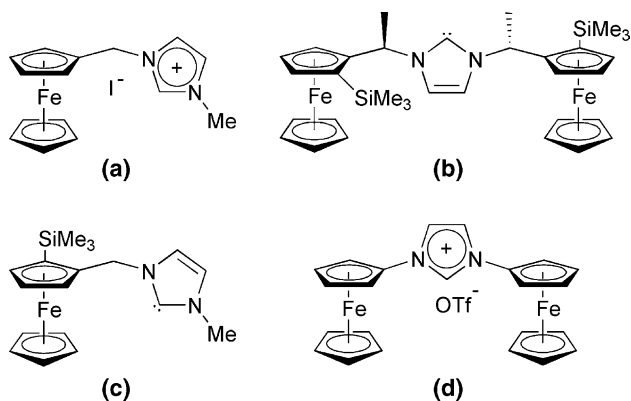


Fig. 1. Ferrocenyl substituted *N*-heterocyclic carbene ligands (ligand precursors).

report the synthesis of ferrocene bridged bidentate carbene ligand precursors and their metal complexes.

2. Results and discussion

2.1. Synthesis and characterisation of the ligand precursor 1,1'-bis[(1-*tert*-butylimidazolium)-3-methyl]ferrocene dichloride (**1**)

The ferrocenyl imidazolium precursor 1,1'-bis[(1-*tert*-butylimidazolium)-3-methyl]ferrocene dichloride (**1**) was prepared from the reaction of 1,1'-bis(chloromethyl)ferrocene, in a THF solution, with two equivalents of 1-*tert*-butylimidazole, Scheme 1. The ligand (**1**) was characterised by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, elemental analysis and mass spectrometry.

The ^1H NMR spectrum exhibits three resonances at δ 7.38, 7.61 and 10.66, characteristic of an imidazolium species. The adjacent methylene side chain protons are at δ 5.70 and are shifted to high frequency upon comparison with 1,1'-bis(chloromethyl)ferrocene (δ 4.43) [24]. The cyclopentadienyl resonances were observed as multiplets at δ 4.20 and 4.57. The remaining ^1H NMR signals and the $^{13}\text{C}\{^1\text{H}\}$ NMR data were consistent with the formation of the desired ligand precursor (**1**). The electrospray mass spectrum (MeOH) further supported the formation of the imidazolium product with the

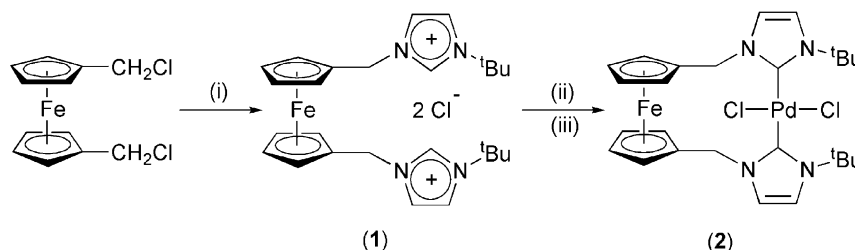
observation of the parent ion minus the chloride anion at $m/z = 495$.

2.2. Molecular structure of 1,1'-bis[(1-*tert*-butylimidazolium)-3-methyl]ferrocene dichloride (**1**)

Crystals of the ferrocenyl imidazolium salt (**1**), suitable for single crystal X-ray diffraction, were obtained by layering a dichloromethane solution of (**1**) with diethyl ether. An ORTEP view of the molecular structure is shown in Fig. 2, and crystallographic data given in Table 1. Selected bond lengths and angles are listed in Table 2. The asymmetric unit contains one molecule of dichloromethane and half of molecule of (**1**) with the rest generated by symmetry.

The bond lengths and angles of the imidazolium ring attached to the side chain are unexceptional and are comparable to previously reported imidazolium structures [6]. The C–N bonds attaching the *tert*-butyl and ferrocenylmethyl substituents to the ring are almost identical in length, N(1)–C(4) is 1.486(7) Å compared to N(2)–C(10) at 1.488(8) Å. This similarity in length is probably due to the large steric bulk of both substituents. The imidazolium rings project up above the planes of the Cp rings in order to avoid one another and to minimise steric interactions with the ferrocene unit. These rings are linked to the ferrocene backbone by the C(5)–C(4) bond (1.495(7) Å) which is similar in length to that in other ferrocene methylene containing compounds [25].

The average C–C bond length of the η^5 -cyclopentadienyl ring is 1.412 Å (bond lengths range from 1.38(1) to 1.445(8) Å) and the average internal ring angle is an expected 108° (the bond angles range from 106.7(5)° to 109.2(5)°). The distance between the Fe atom and the η^5 -Cp rings, given by the mean Fe–C bond length (2.040 Å) or the Fe–C_{pcentroid} distance (1.646 Å) are similar to values found in other ferrocene based compounds [25,26]. The Cp rings of the ferrocene unit are eclipsed, however, the substituents at the Cp rings are staggered about the Cp centroid by an angle of 72° avoiding eclipsing interactions. The remaining bond lengths and angles are unexceptional and are within expected limits.



Scheme 1. (i) 2 eq. 1-*tert*-butyl imidazole, THF, reflux. (ii) 2 eq. $\text{KN}(\text{SiMe}_3)_2$, THF, -78°C . (iii) $\text{Pd}(\text{cod})\text{Cl}_2$.

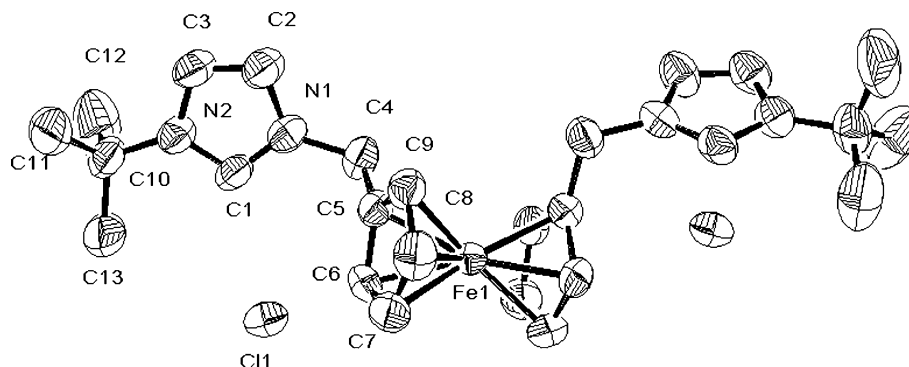


Fig. 2. ORTEP diagram of the molecular structure of (1). Thermal ellipsoids are set at 40%. Hydrogen atoms and solvent of crystallisation are omitted for clarity.

Table 1
Summary of crystallographic data for compounds 1 and 2

	1	2
Empirical formula	C ₂₆ H ₃₆ Cl ₂ FeN ₄ .CH ₂ Cl ₂	C ₂₆ H ₃₄ Cl ₂ FeN ₄ Pd.2CH ₂ Cl ₂
<i>M_r</i>	616.26	805.60
<i>T</i> (K)	250	150
λ (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	C12/c1	C2/c
Unit cell dimensions		
<i>a</i> (Å)	22.4679(6)	18.5202(3)
<i>b</i> (Å)	12.9832(5)	14.4781(3)
<i>c</i> (Å)	12.5423(5)	14.3248(2)
α (°)	90	90
β (°)	117.7483(15)	119.8020(10)
γ (°)	90	90
<i>V</i> (Å ³)	3237.9(2)	3333.03(10)
<i>Z</i>	4	4
<i>D_c</i> (mg m ⁻³)	1.268	1.605
μ (mm ⁻¹)	0.817	1.481
<i>F</i> ₀₀₀	1291.836	1631.785
Crystal size (mm)	0.15 × 0.15 × 0.40	0.05 × 0.06 × 0.25
Description of crystal	Orange-yellow plate	Orange-yellow needle
Absorption correction	Multi-scan	Multi-scan
Transmission coefficients (minimum, maximum)	0.92, 0.93	0.69, 0.93
θ Range for data collection (°)	5.17 ≤ θ ≤ 27.76	5.0 ≤ θ ≤ 27.5
Index ranges, <i>hkl</i>	−29 ≤ <i>h</i> ≤ 29, −16 ≤ <i>k</i> ≤ 17, −16 ≤ <i>l</i> ≤ 16	−24 ≤ <i>h</i> ≤ 20, 0 ≤ <i>k</i> ≤ 18, 0 ≤ <i>l</i> ≤ 18
Reflections measured	6729	15474
Unique reflections	3701	3949
<i>R</i> _{int}	0.073	0.045
Observed reflections (<i>I</i> > 3 σ (<i>I</i>))	2320	2703
Refinement method	Full-matrix least-squares on <i>F</i>	Full-matrix least-squares on <i>F</i>
Parameters refined	174	182
Weighting scheme	Chebychev 3-term polynomial	Chebychev 3-term polynomial
Goodness of fit	0.9648	1.0769
<i>R</i>	0.1125	0.0319
<i>wR</i>	0.0964	0.0335
Residual electron density (minimum, maximum) (e Å ⁻³)	−0.97, 2.62	−0.61, 0.68

2.3. Synthesis of the palladium (II) complex *trans*-[PdCl₂(C[^]fc[^]C)] (2), where C[^]fc[^]C = 1,1'-bis[(1-*tert*-butylimidazol-2-ylidene)-3-methyl]ferrocene

The palladium (II) complex *trans*-[PdCl₂(C[^]fc[^]C)] (2), where C[^]fc[^]C = 1,1'-bis[(1-*tert*-butylimidazol-2-ylidene)-3-methyl]ferrocene was prepared by firstly gen-

erating the carbene from the imidazolium precursor (1), by reaction with two equivalents of KN(SiMe₃)₂, followed by reaction with a THF suspension of Pd(cod)Cl₂ at −78 °C, Scheme 1. The product was readily characterised by elemental analysis, mass spectrometry [ES+ (parent ion observed at *m/z* = 636)] and ¹H and ¹³C{¹H} NMR spectroscopy. The ¹H NMR spectrum is

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

Compound 1			
Fe(1)–C _{mean}	2.040	N(1)–C(4)	1.486(7)
Fe(1)–C _{pcentroid}	1.646	N(2)–C(10)	1.488(8)
C(5)–C(4)	1.495(7)	Fe(1)–C(5)–C(4)	124.5(4)
N(2)–C(1)	1.325(7)	C(7)–N(2)–C(3)	107.5(5)
N(1)–C(1)	1.326(7)	N(1)–C(1)–N(2)	109.1(5)
N(1)–C(2)	1.374(7)	C(1)–N(1)–C(2)	108.7(4)
C(2)–C(3)	1.338(9)	N(1)–C(2)–C(3)	106.7(5)
N(2)–C(3)	1.380(8)	N(2)–C(3)–C(2)	108.0(5)
Compound 2			
Pd(1)–C(1)	2.058(3)	C(4)–C(5)	1.495(4)
Pd(1)–Cl(1)	2.3206(7)	C(1)–Pd(1)–C(1')	173.46(17)
C(1)–N(2)	1.359(4)	Cl(1)–Pd(1)–C(1)	89.41(8)
C(1)–N(1)	1.363(4)	Cl(1)–Pd(1)–C(1')	90.68(8)
N(1)–C(2)	1.389(4)	Cl(1)–Pd(1)–Cl(1')	178.42(5)
C(2)–C(3)	1.343(5)	N(1)–C(1)–N(2)	104.7(2)
C(3)–N(2)	1.392(4)	C(1)–N(1)–C(2)	111.1(3)
N(1)–C(4)	1.460(4)	N(1)–C(2)–C(3)	106.3(3)
N(2)–C(10)	1.502(4)	C(2)–C(3)–N(2)	107.7(3)
Fe(1)–C _{mean}	2.050	C(1)–N(2)–C(3)	110.2(3)
Fe(1)–C _{pcentroid}	1.652	C(4)–C(5)–Fe(1)	123.1(2)

consistent with the coordination of the carbene moiety to a palladium metal centre with the disappearance of the NCHN imidazolium resonance observed in (**1**) at δ 10.66. Similarly, the NCHCHN resonances were shifted to lower frequency, δ 6.83 and 7.06 compared to the corresponding protons (δ 7.38 and 7.61) in the imidazolium precursor (**1**). In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum the complexed carbene resonance is observed as a singlet at δ 166.5 and is typical of an imidazolylidene ligand coordinated to palladium [10]. The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra showed the expected peaks for the ferrocene ligand framework with the methylene group that attaches the imidazolylidene ring to the ferrocene backbone observed at δ 5.95 and 48.11 respectively. The *trans* geometry of the palladium (II) complex (**2**) was confirmed by single crystal X-ray diffraction.

Unfortunately, deprotonation of the imidazolium salt (**1**) using only KN(SiMe₃)₂ or BuLi, followed by subsequent work-up, failed to afford the free carbene in any significant concentration and resulted in a mixture of intractable products.

2.4. Molecular structure of *trans*-[PdCl₂(C^{fc}C)] (**2**)

Crystals suitable for X-ray structure determination were grown by layering a concentrated dichloromethane solution of (**2**) with pentane. The molecular structure is shown in Fig. 3, and crystallographic data given in Table 1. Selected bond lengths and angles are listed in Table 2. The asymmetric unit contains a molecule of dichloromethane and half a molecule of (**2**), which is situated on a crystallographic twofold axis of rotation, which passes through the Pd(1) and Fe(1) atoms.

The bidentate ferrocenyl NHC ligand adopts a *trans* arrangement in the palladium complex (**2**). The C(1)–

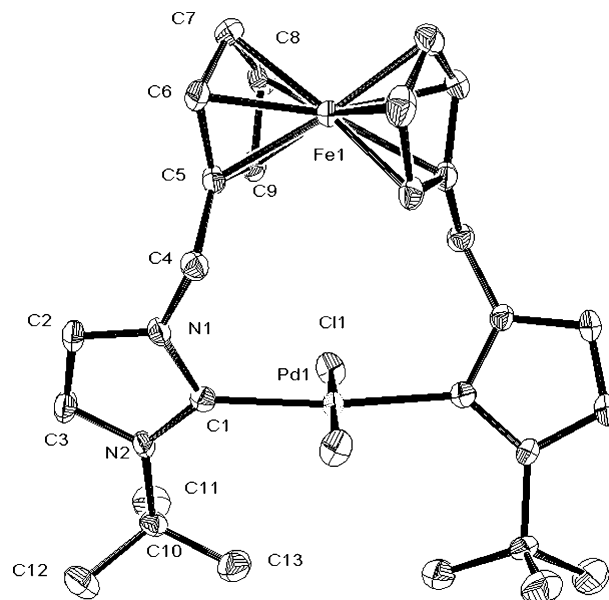


Fig. 3. ORTEP diagram of the molecular structure of (**2**). Thermal ellipsoids are set at 40%. Hydrogen atoms and solvent of crystallisation are omitted for clarity.

Pd(1)–C(1') bond angle was determined to be 173.46 (17)°. The coordination geometry at the Pd atom is approximately square planar, with the imidazolylidene ring tilted out of the Pd(1)–Cl(1)–Cl(1')–C(1)–C(1') plane by 72.9°, presumably to avoid eclipsing interactions with the chlorine atoms. Metal complexes with chelating bis-carbene ligands in the *trans* arrangement are rare. Most monodentate and bidentate palladium-carbene complexes contain the imidazolylidene ligands coordinated *cis* to one another. There are only two other reported examples of *trans* chelating bis-imidazolylidene ligands, based on 1,2-diamidecyclohexane and 1,1-binaphthyl chiral frameworks, coordinated to palladium [27,28].

The Pd(1)–C(1) distance of 2.058(3) Å and the Pd(1)–Cl(1) distance of 2.3206(7) Å are as expected for square planar Pd(II) complexes. The carbene centred, N(1)–C(1)–N(2) ring angle is smaller (104.7(2)°) than the corresponding angle (109.1(5)°) in the imidazolium ring of the ligand precursor (**1**). The bonds C(1)–N(2) and C(1)–N(1) to the carbene centre (1.359(4) and 1.363(4) Å, respectively) are slightly longer than the corresponding bonds (1.324(7) and 1.326(6) Å) in the imidazolium ring of the ligand precursor (**1**). Elongated C–N bond lengths to the carbene carbon atom and a reduction of the N–C–N bond angle are typical geometric features of an imidazolylidene coordinated to a metal centre, when compared to the imidazolium precursor [2], and are presumed to be due to the reduction of π -electron delocalisation.

The ferrocene fragment is unexceptional (Fe–C_{pcentroid} distance of 1.652 Å) and is geometrically similar to the structure of the ligand precursor (**1**). Similar to the

ligand precursor, the carbon atoms of the Cp rings of the ferrocene unit are eclipsed, with the substituents attached to the ring staggered by an angle of 76.1° about the Cp centroid, to avoid one another.

3. Conclusions

The synthesis of a new *trans* chelating bidentate *N*-heterocyclic carbene ligand coordinated to palladium (II), *trans*-[PdCl₂(C^{fc}C)], where (C^{fc}C) = 1,1'-di-*tert*-butyl-3,3'-(1,1'-dimethyleneferrocenyl)-diimidazol-2-ylidene, has been demonstrated by reaction of the imidazolium salt with a strong base and subsequent reaction with a suitable labile Pd(II) precursor. The complex *trans*-[PdCl₂(C^{fc}C)] represents a rare example a chelating bidentate carbene ligand coordinating to a metal centre with a *trans* geometry.

4. Experimental

4.1. General procedures

All manipulations were carried out under an inert atmosphere of dinitrogen using standard Schlenk line techniques, or in an inert atmosphere dry box containing dinitrogen. All solvents were dried over the appropriate drying agents and distilled under nitrogen. NMR spectra were recorded using either a Varian Mercury 300 (¹H: 300 MHz, ¹³C: 75.5 MHz) or a Varian UNITYplus (¹H: 500 MHz, ¹³C: 125.7 MHz) spectrometer, and at room temperature unless otherwise stated. The spectra were referenced internally relative to the residual protio-solvent (¹H) and solvent (¹³C) resonances and chemical shifts reported relative to tetramethylsilane (¹H, ¹³C, δ = 0). Electrospray mass spectra were recorded in acetonitrile or methanol on a Micromass LC TOF MS. Microanalyses were performed by the microanalytical department of the Inorganic Chemistry Laboratory, University of Oxford.

All reagents were purchased from Aldrich and used as received. The reagents 1,1'-bis(chloromethyl)ferrocene [29], Pd(cod)Cl₂ [30] 1-*tert*-butylimidazole [31] were prepared using published procedures.

4.2. Preparation of 1,1'-bis[(1-*tert*-butylimidazolium)-3-methyl]ferrocene dichloride (1)

1,1'-bis(chloromethyl)ferrocene (5.30 g, 18.7 mmol) was dissolved in 120 ml of THF and 1-*tert*-butylimidazole (5.12 g, 41.2 mmol) added to the yellow solution. The reaction mixture was heated to reflux for 48 h during which time a precipitate slowly formed. After cooling the reaction to room temperature the yellow precipitate was isolated by filtration, washed with

Et₂O (3 × 30 ml) and dried under vacuum. The solid was purified by crystallisation from CH₂Cl₂ layered with Et₂O. Yield = 5.60 g (57%).

¹H NMR (CDCl₃, 300 MHz): δ 1.64 [s, 18H, (CH₃)₃C], 4.20 [m, 4H, Cp-H], 4.57 [m, 4H, Cp-H], 5.70 [s, 4H, Cp-CH₂-N-], 7.38 [s, 2H, -NCHCHN-], 7.61 [s, 2H, -NCHCHN-], 10.66 [s, 2H, -NCHN-]. ¹³C{¹H} NMR (CDCl₃, 75.5 MHz): δ 29.86 [s, C(CH₃)₃], 48.45 [s, Cp-CH₂-N-], 59.57 [s, C(CH₃)₃], 67.45 [s, Cp-C], 69.58 [s, Cp-C], 70.81 [s, Cp-C], 119.43 [s, -NCHCHN-], 122.30 [s, -NCHCHN-], 135.02 [s, -NCHN-]. MS (ES, MeOH) *m/z* 495 [M⁺ - Cl] (29%). Elemental analysis (%): Found (Calc. (1) · CH₂Cl₂): C, 51.11 (52.62); H, 6.25 (6.23); N, 8.75 (9.09)%.

4.3. Preparation of *trans*-1,1'-di-*tert*-butyl-3,3'-(1,1'-dimethyleneferrocenyl)-diimidazol-2-ylidene palladium dichloride (2)

1,1'-bis[(1-*tert*-butylimidazolium)-3-methyl]ferrocene (1) (0.53 g, 1.0 mmol) and Pd(cod)Cl₂ (0.29 g, 1.0 mmol) were suspended in 40 ml of THF and cooled to -78 °C. A cooled (-78 °C) THF solution (20 ml) of KN(SiMe₃)₂ (0.42 g, 2.1 mmol) was then added dropwise to the suspension. Upon addition, the solution turned orange and the solids began to dissolve. The reaction was stirred at -78 °C for 3 h upon which time the solution gradually darkened. The reaction mixture was then warmed to room temperature and stirred for a further 12 h. The reaction solution was filtered and the solvent removed. The solid was re-dissolved in CH₂Cl₂ and passed through a short silica column. The solvent was removed to afford an orange solid. The solid was purified by crystallisation from CH₂Cl₂ layered with Et₂O. Yield = 0.13 g (21%).

¹H NMR (CD₂Cl₂, 500 MHz): δ 1.96 [s, 18H, C(CH₃)₃], 4.12 [t, ³J = 1.95 Hz, 4H, Cp-H], 4.46 [br s, 4H, Cp-H], 5.95 [s, 4H, Cp-CH₂-N-], 6.83 [d, ³J = 1.98 Hz, 2H, -NCHCHN-], 7.06 [d, ³J = 1.98 Hz, 2H, -NCHCHN-]. ¹³C{¹H} NMR (CD₂Cl₂, 125.7 MHz): δ 31.80 [s, C(C₃)₃], 48.11 [s, Cp-C₂-N-], 58.42 [s, C(CH₃)], 66.98 [s, Cp-C], 69.66 [s, Cp-C], 85.65 [s, Cp-C_{ipso}], 119.62 [s, -NCHCHN-], 120.77 [s, -NCHCHN-], 166.53 [s, Pd-C_{carbene}]. MS (ES, MeCN) *m/z* 636 [M⁺] (48%). Elemental analysis (%): Found (Calc. (1) · CH₂Cl₂): C, 46.00 (45.00); H, 4.96 (5.03); N, 7.82 (7.77)%.

5. X-ray crystallography

Crystals were isolated under dinitrogen, covered with a perfluoropolyether oil, and mounted on the end of a glass fibre. Crystal data are summarised in Table 1.

Data were collected at 250 K for (1) and 150 K for (2) using an Enraf-Nonius KappaCCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å), as summarised in Table 1. The images were processed with the DENZO and SCALEPACK programs [32]. All solution, refinement, and graphical calculations were performed using the CRYSTALS program suite [33]. The crystal structures were solved by direct methods using the SIR 92 program [34] and were refined by full-matrix least squares on F . All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon-bound hydrogen atoms were generated and allowed to ride on their corresponding carbon atoms with fixed thermal parameters.

Data for compound (1) indicated twinning of the crystal, thus the structure was refined with the twin matrix ($H' = H + 1.667L$, $K' = -K$, $L' = -L$) determined from F_o/F_c data. The solvent molecule CH₂Cl₂ was severely disordered over a special position. The largest peaks and deepest troughs of the difference Fourier map lie close to the Fe atoms, suggesting that the structure may be disordered. However, attempts to model this gave no substantial improvements in the agreement of calculated and observed structure factors. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 250465 for compound (1) and 250466 for compound (2). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Acknowledgement

We thank the Royal Society for a University Research Fellowship (K.S.C.), the EPSRC for a studentship (S.T.) and Balliol College for a Dervorguilla Scholarship (S.I.P.).

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