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Journal of Organometallic Chemistry 691 (2006) 2044–2047

Journal of Organo metallic Chemistry

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Note

1,1′-Bis(phosphoranylidenamino)ferrocene palladium(II) complexes: An unusual case of dative Fe → Pd bonding

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Received 21 November 2005; received in revised form 9 January 2006; accepted 9 January 2006
Available online 20 February 2006

Abstract

Subtle differences in the electron-richness of nitrogen atoms in 1,1′-bis(phosphoranylidenamino)ferrocenes can change the coordination geometry of their palladium(II) complexes from *cis* to *trans*. *Trans* complexation results in concomitant formation of a relatively short dative Fe–Pd bond of 2.67 Å.

Keywords: Ferrocene; Iminophosphorane; Palladium; Complex; Dative bond

1. Introduction

In recent years there has been a surge of interest in the preparation of homobidentate transition metal complexes of bisiminophosphoranes [1,2] as alternatives to more commonly used sp^2-hybridized nitrogen donor ligands such as bis-imines and bis-oxazolines [3]. Among the two basic structural types of iminophosphoranes, the coordination chemistry of those of exemplified by type I (Fig. 1) have been studied more extensively than ligands of type II. The study of type II iminophosphoranes received a boost with the report by Reetz [4] that the chiral binaphthyl-derived bisiminophosphorane (**1**) can be used as a ligand for asymmetric cyclopropanation. Although ferrocenyl bisiminophosphoranes of type I (**2**) [5–7], and ferrocenes bearing pendant [8] iminophosphorane moieties are known, there are few examples of ferrocenyl iminophosphoranes of type II (**3**) (1,1′-bis(phosphoranylidenamino)ferrocenes) in which the nitrogen atoms are directly attached to the cyclopentadienyl rings. To the best of our knowledge, only three such compounds have been reported [9,10], one of which is the potentially bidentate ligand **3a**, R = Ph [11]. The coordination chemistry of type II ferrocenyl bisiminophosphoranes has not been explored [12].

2. Results and discussion

As part of an investigation into the potential of type II ferrocenyl bisiminophosphoranes as ligands for palladium, two homobidentate compounds were prepared by the Staudinger [13] reaction of triphenylphosphine and tricyclohexylphosphine with 1,1′-diazidoferrocene [14] (**4**) to provide **3a** and **3b** as brick-red solids (Scheme 1). Iminophosphoranes **3a** and **3b** were readily coordinated to Pd(II) by treatment with dichlorobis(acetonitrile)palladium(II) in toluene to give the corresponding complexes **5a** and **5b** which were characterized spectroscopically (see Section 3). Notably, a slight downfield shift was observed in the ^{31}P NMR spectra for both **5a** and **5b** (δ 35.0 and 45.2, respectively) compared to the free iminophosphoranes **3a**,**b** (δ 27.2 and 39.8, respectively).

Initially, the *cis* coordination geometry was assigned to both **5a** and **5b** based on the reported crystal structure of bisiminoferrocene palladium(II) complex (**6**) [15], which

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0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.01.012

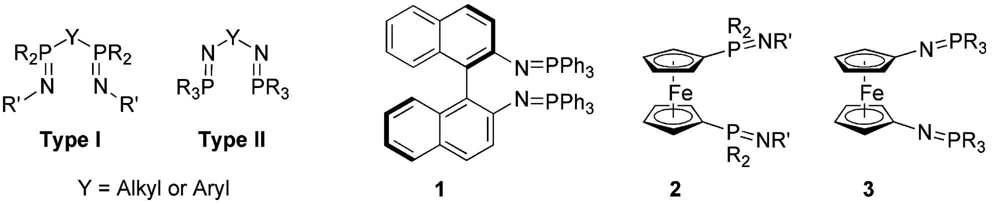
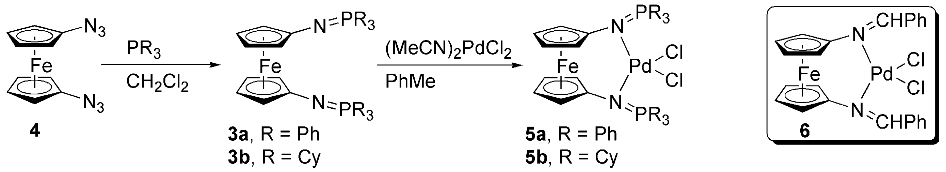


Fig. 1. Structural types of iminophosphoranes.



Scheme 1. Preparation of type II 1,1′-bis(phosphoranylidenamino)ferrocene palladium(II) complexes.

was also prepared by reaction of the free ligand with $(MeCN)_2PdCl_2$. However, complexes **5a** and **5b** showed significant differences in the number and position of signals arising from the cyclopentadienyl (cp.) rings in their ^{1}H and ^{13}C NMR spectra. Whereas **5b** exhibited four cp. ring proton signals, consistent with the ^{1}H NMR data reported for the *cis*-coordinated bisimine **6** [15], the ^{1}H NMR spectrum of **5a** showed only two cp. ring signals at δ 5.46 and 3.02, a difference of 2.44 ppm. Similar differences were observed in the ^{13}C NMR spectra, where **5a** displayed three cp. ring signals, versus five for **5b**. A two-dimensional ^{1}H–^{13}C correlation experiment (HSQC) verified the coherence of two ^{13}C signals for **5a** at 79.2 and 69.3 ppm with the signals at 5.46 and 3.02 ppm, respectively, in the ^{1}H NMR spectrum.

The observation of only two cp. ^{1}H NMR signals with a large chemical shift difference for **5a** was a strong indication of *trans* coordination and the possible presence of a dative Fe–Pd bond. Although uncommon [16], several ferrocenyl palladium complexes with dative Fe–Pd bonds, especially those derived from bidentate phosphorus [17] or sulfur [18] donors, have been characterized crystallographically. It is typical in these complexes to observe a large difference in chemical shift of approximately 2 ppm or more for the cp. protons. For example, the 1,1′-diphosphinoferrocenepalladium(II) iodide (**7**) (Fig. 2) has resonances at δ 6.08 and 4.10 [19]. Similarly, 1,1′-dithiolatoferrocenepalladium(II) complex (**8**) has resonances at δ 5.16 and 2.86 [20]. A third example, the 1,1′-ferrocenedioxalatopalladium(II) complex (**9**) has been reported to have cp. ring resonances at δ 4.90 and 3.00, although its structure has not been confirmed by X-ray analysis [21].

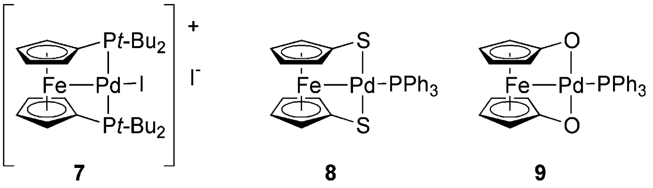


Fig. 2.

To verify whether complex **5a** did indeed possess a dative Fe–Pd bond, crystals were grown from CH_2Cl_2/MeOH. Subjection of **5a** to X-ray analysis revealed what had been suspected, that the Pd center was cationic and nearly square planar (bond angles: N1–Pd–N2 = 162.07(14)°; Fe1–Pd1–Cl1 = 177.15(3)°) with the nitrogen atoms in a pseudo-*trans* coordination geometry. The *trans* geometry brings the iron atom in close proximity to palladium, resulting in the formation of a dative bond (Fig. 3). To the best of our knowledge, **5a** is the first example of a bidentate ferrocene with dative Fe–Pd bonding in which the coordinating heteroatoms are nitrogen. Interestingly,

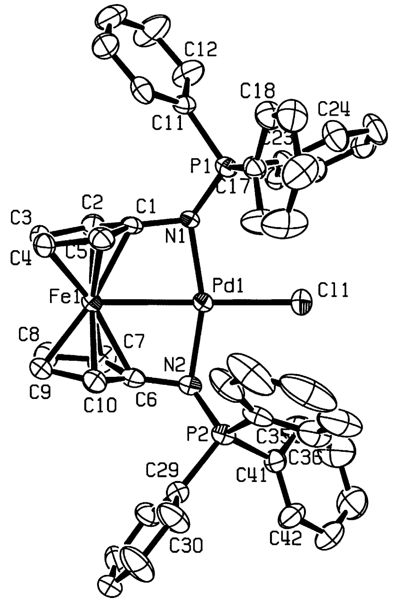


Fig. 3. ORTEP® plot of **5a**. Thermal ellipsoids are shown at 50% probability.

unlike in previous cases where the length of the Fe–Pd bond has ranged from approximately 2.8–3.0 Å [22], the length of the Fe–Pd bond in **5a** is significantly shorter at 2.67 Å. This value is at the long end of the range for what is usually observed in clusters containing Fe–Pd single bonds (2.6–2.7 Å) [18,23]. The shortness of the Fe–Pd bond in **5a** is presumably a result of the smaller atomic radius of nitrogen compared to phosphorus or sulfur.

The difference in coordination geometry of **5a** versus **5b** may be tentatively attributed to the relative electron richness of nitrogen in the two ligands. In complex **5a**, the presence of three phenyl rings on each phosphorus atom may curtail electron donation to the nitrogen atoms through resonance, thus leaving the Pd(II) center electronically unsaturated and favoring the formation of a dative bond with iron. The same delocalization of phosphorus electrons is not possible in the case of **5b** where there is resonance only with nitrogen, making the nitrogen atoms stronger electron donors, enough to satisfy the electronic requirements of Pd(II). This subtle difference in the electronic environment of nitrogen in type II ferrocenyl iminophosphorane complexes as a potential determinant of coordination geometry warrants further study.

3. Experimental

3.1. General

All reagents were purchased from Aldrich, Fisher Scientific or Strem and used as received unless otherwise indicated. Dichloromethane was distilled over CaH_2 under an atmosphere of nitrogen. Toluene was distilled over sodium under a nitrogen atmosphere. All reactions were performed under argon in flame- or oven-dried glassware using syringe-septum cap techniques or Schlenk conditions unless otherwise indicated. NMR spectra were obtained on a Bruker Aspect 200, Avance 300 or Avance 600 instrument and are referenced to TMS or to the residual proton signal of the deuterated solvent for ^1H spectra, and to the carbon multiplet of the deuterated solvent for ^{13}C spectra according to values given in *Spectrometric Identification of Organic Compounds, sixth ed., p. 200,240*. FTIR spectra were recorded on an ATI Mattson Research Series spectrometer. Low and high-resolution mass spectral data were obtained on a Kratos Concept 1S Double Focusing spectrometer. Elemental analyses were performed by Canadian Microanalytical Service, Delta, BC, Canada. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected.

*3.2. 1,1′-Bis(triphenylphosphoranylidenamino)ferrocene (**3a**) [11]*

An oven-dried 25 mL round-bottomed flask containing a solution of 1,1′-diazidoferrocene (**4**) [14] (80 mg, 0.298 mmol) in dry CH_2Cl_2 (4 mL) was cooled to 0 °C in subdued light. The resulting solution was treated with a solution of triphenylphosphine (155 mg, 0.594 mmol, 1.98 equiv) in CH_2Cl_2 (2 mL), transferred by cannula over 10 min, resulting in a color change from orange to cherry red. The flask was removed from the ice bath, wrapped in foil and left to stir behind a blast shield for 24 h. The reaction mixture was concentrated in vacuo to give a dark brown oil. The oil was taken up in a minimum quantity of CH_2Cl_2, and hexane was added to induce precipitation of the product. The product was isolated by suction filtration, washed with cold hexane and recrystallized from CH_2Cl_2/hexane to give **3a** (110 mg, 50%) as a red powder; m.p. >230 °C (CH_2Cl_2/hexane); IR (KBr) ν_{max} 3426, 3046, 2999, 1470, 1433 cm^{-1}; ^{31}P NMR (243 MHz, CD_2Cl_2) δ 27.2; EIMS [*m*/*z* (%)] 736 (M^+, 1.3), 277 ($HNPPh_3^+$, 100); Anal. calcd for $C_{46}H_{38}FeN_2P_2$: C, 75.01; H, 5.20; N, 3.80; found C, 74.03; H, 4.81; N, 3.89%.

*3.3. 1,1′-Bis(tricyclohexylphosphoranylidenamino)ferrocene (**3b**)*

An oven-dried 50 mL round-bottomed flask containing a solution of 1,1′-diazidoferrocene (**4**) [14] (100 mg, 0.37 mmol) in dry CH_2Cl_2 (10 mL) under argon was cooled to 0 °C in subdued light. The resulting solution was treated with a solution of tricyclohexylphosphine (207 mg, 0.74 mmol) in CH_2Cl_2 (2 mL), transferred by cannula over 10 min, resulting in a color change from orange to cherry red. The flask was removed from the ice bath, wrapped in foil and left to stir behind a blast shield for 12 h. The dark brown reaction mixture was concentrated in vacuo to give a dark brown oil. The oil was taken up in a minimum quantity of CH_2Cl_2 and cold hexane (−30 °C) was added to induce precipitation of the product. The product was isolated by suction filtration and washed with cold hexane to give **3b** (113 mg, 39%) as an orange powder; m.p. 92–94 °C (CH_2Cl_2/hexane); IR (KBr) ν_{max} 2929, 2852, 1447, 1113 cm^{-1}; ^{31}P NMR (121.5 MHz, CD_2Cl_2) δ 39.8; ^1H NMR (300 MHz, CD_2Cl_2) δ 4.48 (t, 4H, $J = 1.9$ Hz), 4.05 (t, 4H, $J = 1.9$ Hz), 2.36–2.26 (m, 6H), 2.01–1.97 (m, 12H), 1.87 (m, 12H), 1.76 (m, 6H), 1.58–1.54 (m, 12H), 1.34–1.28 (m, 18H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 108.2, 67.2, 61.6, 32.9 (d, $^1J_{^{13}C-^{31}P} = 51.2$ Hz), 26.7 (d, $^2J_{^{13}C-^{31}P} = 10.6$ Hz), 26.3 (d, $^3J_{^{13}C-^{31}P} = 4.4$ Hz), 25.7; EIMS [*m*/*z* (%)] 772(M^+, 4), 280(6), 214(100); HRMS (EI) calcd for $C_{46}H_{74}FeN_2P_2$: 772.4677; found 772.4619.

*3.4. [1,1′-Bis(triphenylphosphoranylidenamino)ferrocene Pd(II)Cl]Cl · H_2O (**5a**)*

An oven-dried 25 mL round-bottomed flask containing iminophosphorane **3a** (100 mg, 0.136 mmol), $Pd(MeCN)_2Cl_2$ (35.3 mg, 0.136 mmol) and PhMe (4 mL) under an atmosphere of argon was stirred at ambient temperature for 18 h. The solvent was removed in vacuo to give **5a** (102 mg, 82%) as a light orange-brown powder; m.p. >230 °C (CH_2Cl_2/hexanes); IR (KBr) ν_{max} 3049, 1459, 1435 cm^{-1}; ^{31}P NMR (243 MHz, CD_2Cl_2) δ 35.0; ^1H

NMR (300 MHz, CD_2Cl_2) δ 7.79 (dd, 12 H, $J = 12.9$, 7.8 Hz), 7.69 (t, 6H, $J = 7.2$ Hz), 7.56–7.52 (m, 12 H), 5.46 (s, 4H), 3.02 (s, 4H); ^{13}C NMR (150.9 MHz, CD_2Cl_2) δ 133.6 (d, $J = 10.6$ Hz), 133.5, 128.9 (d, $J = 12.1$ Hz), 125.9 (d, $^{1}J_{^{13}C-^{31}P} = 102.6$ Hz), 96.1 (d, $J = 4.5$ Hz), 79.2, 69.3 (d, $J = 6$ Hz); FABMS [m/z (%)] 877 ($M^{+}-^{35}Cl$, 27.5), 736 ($M^{+}-PdCl_2$, 70.9), 340 (100), 262 (30); Anal. calcd for $C_{46}H_{38}Cl_2FeN_2P_2Pd$: C, 59.28; H, 4.33; N, 3.01; found C, 59.77; H, 3.83; N, 2.90%.

*3.5. 1,1′-Bis(tricyclohexylphosphoranylidenamino)ferrocene Pd(II)Cl$_2$ (**5b**)*

An oven-dried 25 mL round-bottomed flask containing iminophosphorane **3b** (50.0 mg, 0.065 mmol), $Pd(MeCN)_2Cl_2$ (16.8 mg, 0.065 mmol) and PhMe (3 mL) under an atmosphere of argon was stirred at ambient temperature for 18 h. The solvent was removed in vacuo to give **5b** (51.6 mg, 84%) as an orange-brown powder; m.p. >190 °C (decomp.) (hexanes/CH_2Cl_2); ^{31}P NMR (81 MHz, CD_2Cl_2) δ 45.2; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 5.92 (s, 2H), 4.49 (s, 2H), 4.30 (s, 2H), 3.97 (s, 2H), 2.41–2.34 (m, 6H), 2.13–1.23 (m, 60H); ^{13}C NMR (75.5 MHz, CD_2Cl_2) δ 112.4, 67.5, 66.3, 66.1, 65.4, 32.1 (d, $^{1}J_{^{13}C-^{31}P} = 50.0$ Hz), 26.6 (d, $^{2}J_{^{13}C-^{31}P} = 10.9$ Hz), 25.9 (d, $^{3}J_{^{13}C-^{31}P} = 3.8$ Hz), 25.5.

3.6. Crystallography

X-ray analysis of **5a** was performed on a dark red plate fragment ($0.32 \times 0.21 \times 0.07$ mm) which was obtained by recrystallization from CH_2Cl_2/MeOH: $C_{46}H_{40}Cl_2FeN_2OP_2Pd$, $M = 931.94$, orthorhombic, $Pca2_1$, $a = 19.0488(15)$ Å, $b = 11.8259(9)$ Å, $c = 35.916(3)$ Å, $V = 8090.7(11)$ Å^3, $Z = 8$; $D_c = 1.530$ g/cm^3, $F(000) = 3808$, $T = 180(1)$ K. Data were collected on a Bruker APEX CCD system with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å); 19302 data were collected. The structure was solved by Direct Methods (SHELXTL) and refined by full-matrix least squares on F^2 resulting in final R, R_w and GOF (for 16210 data with $F > 2\sigma(F)$) of 0.0384, 0.0708 and 1.481, respectively. N.B: Each asymmetric unit contains two molecules and some phenyl rings are disordered over two positions.

Acknowledgements

We thank NSERC Canada for support of our research program, and Mr. Tim Jones and Mr. Razvan Simionescu for assistance with NMR and MS determinations. D.T. thanks NSERC for an Undergraduate Student Research Award (2004). F.B. thanks Career Services at Brock University for an Experience Works award, which made his contribution possible.

Appendix A. Supplementary data

Crystallographic data for **5a** have been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 277349). Copies of this data may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336 033; email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.01.012.

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