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Note

Palladium(II) complexes containing symmetrical diphosphine ligands based on ferrocene. Sterically enforced palladium–iron bonds

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Abstract

Methylpalladium chloride, cationic methyl- and acylpalladium triflate complexes were synthesised containing bis(dialkyl) and bis(diphenyl)phosphine ferrocene ligands. *Trans*-coordinated cationic methylpalladium complexes containing 1,1′-bis(di-*tert*-butylphosphino)ferrocene, form a palladium–iron bond. The less bulky 1,1′-bis(di-*iso*-propylphosphino)ferrocene ligand coordinates in a *cis* fashion in methylpalladium chloride complexes. A palladium–iron bond was indicated in the cationic acylpalladium complexes of both alkylphosphine ligands. 1,1′-Bis(diphenylphosphino)ferrocene does not form a palladium–iron bond in the monocationic acyl- and methylpalladium complexes. The complexes were characterised by ^{1}H-, ^{31}P-, ^{13}C-NMR spectroscopy, elemental analysis, and UV–vis spectroscopy. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Palladium–iron bonds; Phosphine ligands; NMR spectroscopy

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1. Introduction

Phosphine ligands based on the ferrocene backbone can support a variety of coordination geometries in transition metal chemistry [1]. These ligands are very efficient in many palladium-catalysed reactions, e.g. cross-coupling reactions [2], Heck reaction [3], amination reaction [4], and enantioselective synthesis [5]. Palladium(II) dichloride complexes which contain the frequently used symmetrical arylphosphine ligand, 1,1′-bis(diphenylphosphino)ferrocene (dppf), and ferrocene-based alkylphosphine ligands have already been reported [3]. In all cases, the ligand coordinates in a *cis* fashion to palladium. A particularly interesting example of an unusual coordination mode of the dppf ligand has been reported by Sato et al. Dicationic palladium(II) complexes, such as $[(dppf)Pd(PPh_3)]^{2+}[BF_4^-]_2$, were shown to contain a palladium–iron bond [6,7]. These compounds are strongly coloured, and the UV–vis spectrum showed three absorptions with large extinction coefficients. Here, we present the first example for the occurrence of palladium–iron bonds in monocationic methyl and acylpalladium(II) complexes.

2. Experimental

1,1′-Bis(di-*tert*-butylphosphino)ferrocene (dtpf) [8], 1,1′-bis(di-*iso*-propylphosphino)ferrocene (dipf) [9], (dppf)Pd(CH_3)Cl [10] and (COD)Pd(CH_3)Cl [10] were prepared according to literature procedures. ^{13}CO (99%) was purchased from Isotec Inc. Solvents were distilled from a drying agent prior to use. The phosphine ligands were air-sensitive and handled under an argon atmosphere.

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2.1. Preparation of (dppf)Pd(CH_3)Cl (**1**) [10], (dtpf)Pd(CH_3)Cl (**2**) and (dipf)Pd(CH_3)Cl (**3**)

The ligand (0.37 mmol, 1.03 equivalents) was added to a solution of 0.36 mmol (COD)Pd(CH_3)Cl in 5 ml of benzene. The solution was stirred for 1 h. The suspension was filtered and the residue was washed with benzene and Et_2O. The orange product was dried in vacuo.

2. Yield: 0.35 mmol (97%). ^{1}H-NMR ($CDCl_3$, 300 MHz, 25 °C, δ ppm): 5.45 (m, 4H, *Cp*); 4.20 (m, 4H, *Cp*); 1.69 (m, 3H, PdCH_3); 1.47 (dd, 36H, [$^3J_{PH} = 7.4$ Hz], C(CH_3)$_3$). ^{31}P-NMR ($CDCl_3$, 121.5 MHz, 25 °C, δ ppm): 29.4 (s). Anal. Found: C, 51.84; H, 6.12. Calc. for ($C_{27}H_{39}ClFeP_2Pd$): C, 52.03; H, 6.31%.

3. Yield: 0.34 (94%). ^{1}H-NMR ($CDCl_3$, 300 MHz, 25 °C, δ ppm): 4.4–4.3 (m, 8H, *Cp*); 2.69 and 2.43 (m, 4H, [$^3J_{HH} = 7.1$ Hz], C*H*(CH_3)$_2$); 1.50 (dd, 6H, [$^3J_{HH} = 7.1$ Hz and $^3J_{PH} = 15.9$ Hz], CH(C*H*$_3$)$_2$); 1.29–1.13 (m, 18H, CH(C*H*$_3$)$_2$); 0.91 (dd, [$^3J_{PH} = 3.0$ Hz and $^3J_{PH} = 6.9$ Hz], 3H, PdC*H*$_3$). ^{31}P-NMR ($CDCl_3$, 121.5 MHz, 25 °C, δ ppm): 49.5 (d, [$^2J_{PP} = 21.6$ Hz]); 29.5 (d, [$^2J_{PP} = 21.6$ Hz]). Anal. Found: C, 48.21; H, 6.98. Calc. for $C_{23}H_{39}ClFeP_2Pd$: C, 48.03; H, 6.83%.

2.2. Preparation of [(dppf)PdCH_3(CH_3CN)]$^+$ [CF_3SO_3]$^-$ (**4**) [10], [(dtpf)Pd(CH_3)]$^+$ [CF_3SO_3]$^-$ (**5**) and [(dipf)PdCH_3(CH_3CN)]$^+$ [CF_3SO_3]$^-$ (**6**)

A suspension of **1**–**3** (0.18 mmol) and silver triflate (0.18 mmol) in 10 ml of CH_2Cl_2–MeCN (10:1, v/v) was stirred in the dark for 1 h. The suspension was filtered over Celite, and the filtrate was concentrated in vacuo to ca. 5 ml. Diethyl ether (10 ml) was added resulting in the formation of orange crystals. The orange crystals were dried in vacuo.

5. Yield: 0.15 mmol (83%). ^{1}H-NMR ($CDCl_3$, 300 MHz, 25 °C, δ ppm): 5.25 (m, 4H, *Cp*); 4.20 (m, 4H, *Cp*); 1.70 (t, [$^3J_{PH} = 4.8$ Hz], 3H, PdC*H*$_3$); 1.46 (dd, [$^3J_{PH} = 7.5$ Hz], 36H, C(C*H*$_3$)$_3$). ^{31}P-NMR ($CDCl_3$, 121.5 MHz, 25 °C, δ ppm): 29.3 (s). Anal. Found: C, 45.14; S, 4.32; H, 6.47. Calc. for ($C_{28}H_{47}F_3FeO_3P_2SPd$): C, 45.15; S, 4.30; H, 6.36%.

6. Yield: 0.10 mmol (56%). ^{1}H-NMR ($CDCl_3$, 300 MHz, -40 °C, δ ppm): 4.49, 4.48, 4.41, 4.35 (s, 8H, *Cp*); 2.58 (s, 3H, C*H*$_3$CN); 2.43, 2.31 (q, [$^3J_{HH} = 6.9$ Hz], 2H, C*H*(CH_3)$_2$); 2.06 (br s, 2H, C*H*(CH_3)$_2$); 1.36–1.06 (dd, [$^3J_{HH} = 6.9$ Hz and $^3J_{PH} = 14$ Hz], 24H, CH(C*H*$_3$)$_2$); 0.73 (br d, [$^3J_{PH} = 4.8$ Hz], 3H, PdC*H*$_3$). ^{31}P-NMR ($CDCl_3$, 121.5 MHz, -40 °C, δ ppm): 54.1 (d, [$^2J_{PP} = 21.3$ Hz]); 32.7 (d, [$^2J_{PP} = 21.3$ Hz]). Anal. Found: C, 42.72; H, 5.97; N, 1.78; S, 4.11. Calc. for $C_{26}H_{42}F_3FeNO_3P_2SPd$: C, 42.78; H, 5.84; N, 1.92; S, 4.39%.

2.3. Preparation of [(dppf)PdC(O)CH_3(CH_3CN)]$^+$ [CF_3SO_3]$^-$ (**7**) [10], [(dtpf)PdC(O)CH_3)]$^+$ [CF_3SO_3]$^-$ (**8**) and [(dipf)PdC(O)CH_3]$^+$ [CF_3SO_3]$^-$ (**9**)

An NMR tube was charged with 20 mg of **4**–**6** and 0.7 ml of $CDCl_3$. CO was bubbled through the orange solution at room temperature (r.t.) for 20 min. NMR spectra were recorded at r.t. In case of complex **5**, 100% conversion could not be obtained. ^{13}C-enriched CO was used to determine the chemical shifts of the acylpalladium complexes.

8. ^{1}H-NMR ($CDCl_3$, 300 MHz, 25 °C, δ ppm): 4.98, 4.26 (s, 8H, *Cp*); 2.78 (s, 3H, C(O)C*H*$_3$); 2.39 (br m, 4H, C*H*(CH_3)$_2$); 1.29 (br m, 24H, CH(C*H*$_3$)$_2$). ^{31}P-NMR ($CDCl_3$, 121.5 MHz, 25 °C, δ ppm): 11.9 (s).

9. ^{1}H-NMR ($CDCl_3$, 300 MHz, 25 °C, δ ppm): 5.19, 4.37 (*Cp*, s, 8H); 2.91 (t, [$^4J_{PH} = 1.5$ Hz], 3H, C(O)C*H*$_3$); 1.48 (m, 36 H, C(C*H*$_3$)$_3$). ^{31}P-NMR ($CDCl_3$, 121.5 MHz, 25 °C, δ ppm): 30.2 (s).

2.4. NMR spectra

NMR spectra were recorded on a Bruker DRX 300 spectrometer. ^{1}H-NMR spectra were recorded at 300 MHz, ^{31}P-NMR spectra at 121.5 MHz and ^{13}C-NMR spectra at 75.4 MHz. Me_4Si was used as a standard for ^{1}H- and ^{13}C-NMR. H_3PO_4 was used as a standard for ^{31}P-NMR spectra.

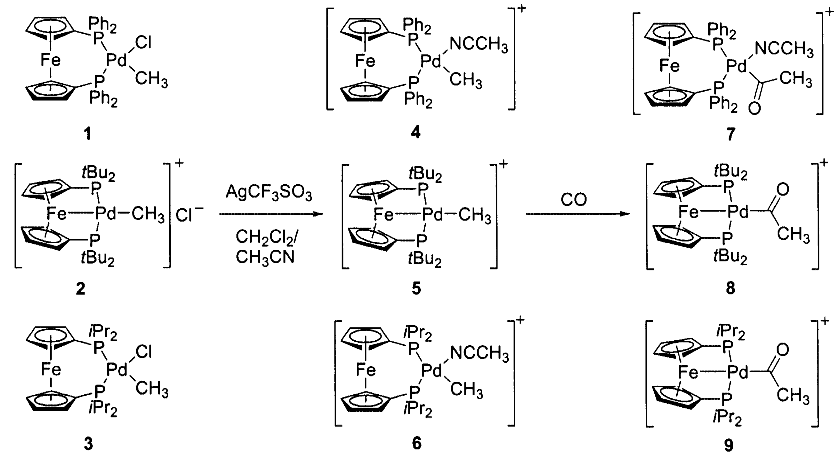
3. Results and discussion

Complexes **1**–**3** were readily obtained from the reaction of (COD)Pd(CH_3)Cl and the ferrocene-based diphosphine ligand. The ^{1}H- and ^{31}P-NMR spectra of complexes **1** and **3** in $CDCl_3$ show two inequivalent phosphorus atoms, a double doublet for the methyl group and four signals of the hydrogen atoms of the cyclopentadienyl (*Cp*) rings, indicating that the ligands coordinate in a *cis* fashion to palladium (Table 1). (Scheme 1).

In contrast, complex **2** has two equivalent phosphorus atoms and shows a triplet for the methyl group and only two signals for the hydrogen atoms of the *Cp* rings. This indicates that the phosphorus atoms in complex **2** are coordinated in a *trans* fashion to palladium. A *trans*-coordination mode of the dtpf ligand implies that either the dtpf ligand is positioned above the square planar palladium complex or that the iron atom of the ferrocene unit is bonded to palladium. In the latter case, the 14e configuration that forms after loss of the chloride ligand would be alleviated by a dative palladium–iron bond and the strong basicity of the phosphine ligand. A study by Sato et al. [6] showed that formation of a palladium–iron bond leads to tilting of the *Cp* rings. This causes a large chemical-shift

Table 1
NMR data in $CDCl_3$. Chemical shift in ppm (multiplicity) {coupling in Hz}

Compound	^{1}H-NMR for CH_3/C(O)CH_3 δ, $\{J_{PH}\}$	$^{31}P\{^1H\}$-NMR δ, $\{^2J_{PP}\}$	Cp rings, no. of signals, [$\Delta\delta$]
1 [10]	0.79 (dd) {7.7} {3.7}	37.8, d {34} 11.9, d	4
2	1.69 (br, t)	29.4 (s)	2, [1.2]
3	0.91 (dd) {6.9}{3.0}	49.5, d {22} 29.5, d	4
4 [10]	0.71 (dd) {7.1} {3.3}	39.6, d {34} 15.9, d	4
5	1.68 (t) {5.8}	29.1 (s)	2, [1.1]
6	0.73 (dd)	54.1, d {21} 32.7, d	4
7 [10]	2.01 (s)	23.2, d {56} 4.5, d	4
8	2.91 (t) {1.5}	30.2 (s)	2, [0.81]
9	2.78 (s)	11.9 (s)	2, [0.72]



Scheme 1.

difference ($\Delta\delta$) between the α- and β-H atoms of the Cp rings (≈ 1 ppm) compared to the chemical-shift difference in the free ligand (≈ 0.2 ppm). A very large $\Delta\delta$ was indeed observed for complex **2** (Table 1).

When the ferrocene unit is positioned above the coordination plane of the palladium centre and the phosphorus atoms are coordinated in a *trans* fashion, the rings can still be tilted as a result of the large intramolecular P–P distance. This could give rise to the observation of a large $\Delta\delta$ as well. Evidence for the palladium–iron bond was provided by performing conductivity measurements. The large molar conductivity observed for complex **2** in CH_2Cl_2 ($\Lambda_m = 56$ S cm^{-2} mol^{-1}, compared to **1** and **3** ($\Lambda_m = 0$ S cm^{-2} mol^{-1})) proved that this complex was cationic. Apparently, the *tert*-butyl groups are too bulky for the ligand to allow coordination in a *cis* fashion. Presumably, the larger phosphine substituents cause steric crowding which favours dissociation of one ligand and the coordinative unsaturation results in the formation of a Pd–Fe dative bond.

The compounds prepared by Sato et al. are strongly coloured (dark-green, dark-red or purple) [6]. In contrast, complex **2** is orange and UV–vis experiments show only an absorption at 349 nm. This absorption was also present in complexes **1**and **3** and the complexes reported by Sato. Absorptions at higher wavelengths were not observed. Therefore, the presence of a palladium–iron bond could not be proven by UV–vis spectroscopy in the monocationic methylpalladium complexes.

When solutions of complexes **1**–**3** in dichloromethane–acetonitrile (10:1, v/v) were made to react with one equivalent of silver triflate, silver chloride precipitated and the cationic complexes **4**–**6** were formed. The isolated complexes were all shown to be cationic by conductivity measurements ($\Lambda_m = 52$–62 S cm^{-2} mol^{-1}). ^{1}H-NMR spectroscopy showed that complexes **4** and **6** contained coordinated acetonitrile

($\delta(CH_3CN) = 1.83$ and 2.58 ppm, respectively), whereas complex **5** did not bind acetonitrile ($\delta(CH_3CN) = 1.98$ ppm, free acetonitrile). The large $\Delta\delta$ of the α- and β-H atoms of the Cp rings (Table 1) and the conductivity measurements showed that only the ionic complex containing the dtpf ligand, **5**, had a palladium–iron bond whereas complexes **4** and **6** did not.

The reaction of **4**–**6** with CO or ^{13}CO in $CDCl_3$ gave the acylpalladium complexes **7**–**9**. The ^{13}C-NMR spectra of complexes **7**–**9** showed signals corresponding to the carbonyl carbon atom around 220 ppm, which is characteristic of an acylpalladium complex. The *trans*-complex, **5**, undergoes insertion of CO significantly more slowly than complexes **4** and **6**. The complex containing the dppf ligand, **7**, remained a *cis*-complex without a palladium–iron interaction and an acetonitrile-coordinated palladium centre. The complex containing the dtpf ligand, **8**, remained a *trans*-complex containing a palladium–iron bond. The dipf ligand coordinated complex, **9**, however, underwent a change in coordination behaviour. The hydrogen atoms of the *Cp* ring showed only two signals in the ^{1}H-NMR spectrum at 4.98 and 4.26 ppm ($\Delta\delta = 0.72$ ppm). The ^{31}P-NMR spectra showed one singlet. Furthermore, free acetonitrile (1.98 ppm) was observed in the ^{1}H-NMR spectrum. These spectroscopic data indicated that a palladium–iron bond had formed. Obviously, not only the bulkiness of the ligand is important, but the electronic properties of the metal centre are important as well. A more electron-deficient metal centre has a higher tendency to form a palladium–iron bond. This is in agreement with the results of Sato et al. as their complexes are very electron-deficient.

4. Conclusions

Changes in the substituents of the phosphorus atoms of diphosphine ferrocene ligands can have a large effect on their coordination behaviour. A palladium–iron interaction is favoured by bulky alkyl substituents on phosphorus and a lower electron density at palladium.

Acknowledgements

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