ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 598 (2000) 329–338

Journal of Organometallic Chemistry

P,*N*-Heterodifunctional ligands by selective Staüdinger reaction of β-substituted vinylazides with (*Z*)-1,2-bis(diphenylphosphanyl)-ethene and formation of cyclometalled complexes of palladium(II) of these ligands — crystal and molecular structure of a new chiral cyclometallaphosphoraniminophosphane of palladium(II)

Antonio Arques* [a,1], Pedro Molina* [a,2], David Auñón [a], María Jesús Vilaplana [a], M. Desamparados Velasco [a], Francisco Martínez [b], Delia Bautista [c], Fernando J. Lahoz [d]

[a] *Departamento de Química Orgánica, Facultad de Química, Universidad de Murcia, Campus de Espinardo, E-30071 Murcia, Spain*
[b] *Departamento de Química Física, Facultad de Química, Universidad de Murcia, Campus de Espinardo, E-30071 Murcia, Spain*
[c] *Servicio de Apoyo a las Ciencias Experimentales (SACE), Universidad de Murcia, Campus de Espinardo, E-30071 Murcia, Spain*
[d] *Departamento de Química Inorgánica, Instituto de Ciencia de los Materiales de Aragón, Facultad de Ciencias, Universidad de Zaragoza, E-50009 Zaragoza, Spain*

Received 20 September 1999; accepted 24 November 1999

Abstract

Staüdinger reactions of the β-aryl-, heteroaryl- and ferrocenylvinylazides (**2**) with (*Z*)-1,2-bis(diphenylphosphanyl)ethene afford the *P*,*N*-ligands (**3**) in good yields. Reaction of **3** with dichlorobis(benzonitrile)palladium(II) leads to the Pd(II) metallacycle derivatives **5**. The molecular structure of **5e** has been determined by X-ray crystallography. The electrochemical behavior of this compound is also reported.

Keywords: β-Arylvinyl azides; β-Ferrocenylvinylazide; (*Z*)-1,2-bis(Diphenylphosphanyl)ethene; *P*,*N*-Difunctional ligands; Cyclometalled complexes; Palladium; X-ray structure analysis

1. Introduction

The design of difunctional ligands which can form heterodinuclear transition-metal complexes, with well-defined geometries, is of considerable interest considering the rapidly evolving area of bimetallic catalysis [1]. In this context, heterodifunctional ligands that incorporate both a trivalent phosphorus atom and a ferrocene moiety have proven to be suitable for the construction of heterobimetallic systems with well-defined geometry, in which the two metals remain sufficiently close to allow a multisite activation of organic substrates [2].

We have recently reported [3] an efficient preparation of *P*,*N*-heterodifunctional ferrocene-based ligands by means of the Staüdinger imination [4] of trivalent phosphorus compounds with azides to produce an iminophosphorane function after nitrogen evolution. This method, which allows the selective oxidation of diphosphanes using the β-ferrocenylvinyl azide [5], is also applicable to diphosphanes of various chain lengths, and even to tri- and tetraphosphanes. The resulting asymmetrically substituted (iminophosphorane)phosphane ligands are good complexing agents, utilizing the phosphane and iminophosphorane nitrogen centers, and the Pd(II) complex derived from the 1,2-bis(diphenylphosphanyl)methane catalyzed aryl amination reactions [3a]. In this context, it has been described [6] the selective azide mono-oxidation of the (*Z*)-1,2-bis(diphenylphosphanyl)ethene using aryl, benzyl and heterosubstituted azides. It has been postulated that the failure to induce reaction at the second phos-

[1] *Corresponding author. E-mail: arques@fcu.um.es
[2] *Corresponding author. E-mail: pmolina@fcu.um.es

0022-328X/00/$ - see front matter
PII: S0022-328X(99)00731-7

phane center is a direct result of steric crowding created by the rigid *Z* configuration of the phosphorus centers, which inhibits the formation of the intermediate phosphazide.

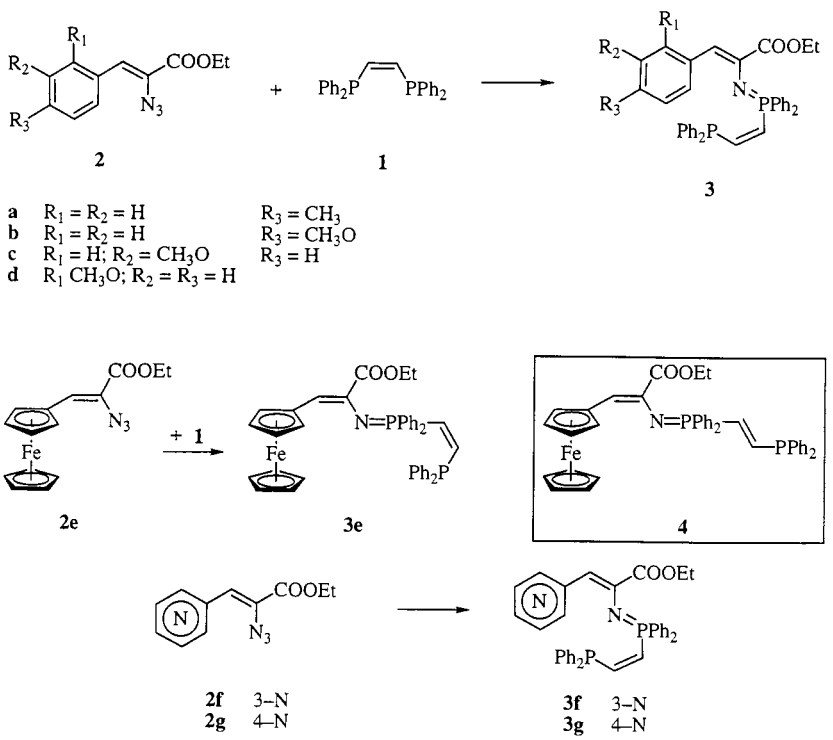
We now wish to report the preparation of *P*,*N*-heterodifunctional ligands derived from (*Z*)-1,2-bis-(diphenylphosphanyl)ethene and β-aryl-, heteroaryl- and ferrocenylvinylazides and subsequent formation of Pd(II)-metallacycle derivatives.

2. Results and discussion

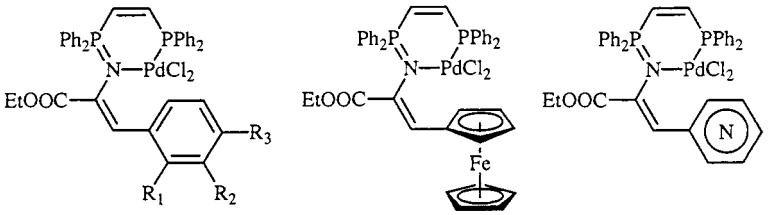
Reaction of (*Z*)-1,2-bis(diphenylphosphanyl)ethene (**1**) with β-(4-methylphenyl)vinyl azide [7] **2a** (1:1 molar ratio) in dry dichloromethane at room temperature provides the monoiminophosphorane **3a** in 94% yield. The reaction of **1** with several others vinylazides [5,7,8] **2b**–**2g** also proceeded smoothly in a similar straightforward fashion to give the corresponding iminophosphoranes **3b**–**3g** in yields ranging from 55 to 85% after purification by column chromatography (Scheme 1). The ^{1}H- and ^{13}C{^{1}H}-NMR data of compounds **3a**–**3d** and **3f**–**3g** are in good agreement with the proposed structures. The ^{31}P{^{1}H}-NMR spectrum of **3** features two doublets in the regions δ −5.75 to −0.1 and δ −25.49 to −23.14 ($^{3}J_{PP}$ = 11.8–13.2 Hz) attributable to the pentavalent and trivalent phosphorus atoms, respectively. Comparison of the ^{31}P{^{1}H}-NMR spectra of **3e** and the isomeric monoiminophosphorane [3b] **4** showed change only slightly for the P(III) atom (+2 ppm) compared with the much larger chemical shift change experienced by the P(V) center (−26.5 ppm). The $^{3}J_{PP}$ coupling constants in **3e** and **4** are similar in magnitude, with the *trans* coupling in **4** being slightly longer (by approximately 7 Hz) than in the *cis*.

With the new ligands **3** in hand, we investigated their suitability for complexation to transition metals. Representative palladium complexes were prepared by reaction of **3** with dichlorobis(benzonitrile)palladium(II) in dichloromethane at room temperature to form the corresponding complexes **5** in yields higher than 60% (Scheme 2). In this reaction the iminophosphorane unit acts as an N-donating side arm with a pendent ferrocenylvinyl group arm. Compounds **5** show a limited solubility in polar solvent and are insoluble in nonpolar solvent, but **5e** was readily recrystallized from chloroform. The best method for the isolation of pure samples of **5** was simply to use precise stoichiometry with careful control of reaction conditions and, upon completion of the reaction, to remove the solvent under reduced pressure. This method produced an amorphous powder of **5** of sufficient purity for subsequent structural characterization. Analytical samples were purified by column chromatography using the appropriate eluent.

Evidence for the stability of the ligands **3** and their complexes **5** comes from their lack of the aza Wittig reaction with isocyanates up to reflux temperature in dichloromethane even for an extended reaction time.



Scheme 1.



5a-d **5e** **5f** 3–N
5g 4–N

Scheme 2.

This fact is in contrast to the observed behavior of the iminophosphoranes derived from azides **2** and triphenylphosphane, which led to the expected carbodiimides by reaction with isocyanates [7] under the same reaction conditions. We think that the failure to induce the aza Wittig reaction, which needs the initial formation of a cyclic intermediate, could be due either to the steric crowding created by the *cis* configuration of the diphenylphosphino group, which inhibits the reaction mechanism, or to the conjugation of the nitrogen lone pair with the C=C double bond of the phosphine backbone.

It is well known that coordination of a *P*,*N*-ligand to palladium causes shifts of the ^{31}P resonance of the complex ligand to higher frequency [9]. The magnitude of the coordination chemical shift ($\Delta\delta$ ^{31}P coordinated–δ ^{31}P free ligand) in complexes **5a**–**5d** and **5f**–**5g** for the P(III) ($\Delta P(III) = 29.0–32.5$) is higher than for the P(V) ($\Delta P(V) = 13.2–18.6$). However, in the complex **5e** these values for the two phosphorus atoms ($\Delta P(III) = 25.7$ and $\Delta P(V) = 21.5$) are quite close. An interesting feature of complexes **5** is the variability of the $^3J_{PP}$ coupling constant, which increases significantly from 11.8–13.2 to 37.7–51.7 Hz upon complexation to palladium, the smallest observed value in the complex **5e** being from 13.2 to 37.0 Hz.

The ^1H-, $^{13}C\{^1H\}$-NMR and MS in FAB mode of the complexes **5a**–**5d** and **5f**–**5g** are in accord with the proposed structure. However, a rather astonishing aspect of the ^1H-NMR spectrum of the heterobimetallic complex **5e** was the appearance of the O–CH_2–CH_3 protons as an ABX_3 system ($J_{AX} = J_{BX} = 7.0$ Hz, $J_{AB} = -9.8$ Hz), the diastereotopicity and anisochrony of the methylene protons reflecting the chiral nature of compound **5e** (racemic). This spectrum also showed two broad singlets for two protons of the substituted Cp ring, whereas the signals for the two remaining protons are overlapped with the signal corresponding to the unsubstituted Cp rings. The olefinic resonances of the bridging ethylene backbone are apparently embedded in the broad aromatic region and hence cannot be seen.

Further evidence for the ordered conformation in **5e** was obtained from the $^{13}C\{^1H\}$-NMR data for the Cp carbon atoms. In the $^{13}C\{^1H\}$-NMR spectrum of the ligand **3e**, only three resonances were observed for the substituted Cp ring (δ 83.25 (q), 69.7 and 67.87) and only one resonance for the unsubstituted Cp ring (δ 68.9). In contrast, the complex **5e** clearly showed five separated resonances for the substituted Cp ring (δ 78.29 (q), 71.62, 70.52, 70.33 and 69.44) and one resonance for the unsubstituted Cp ring (δ 68.92). This structural information suggested that the complex **5e** might exist as atropoisomers due to the restricted rotation about the C–N bond.

The fact that the anisochrony of the methylene protons in the aromatic analogs **5a**–**5d** and heteroaromatic **5f**–**5g** was not observed could be due to the ferrocene subunit, which sterically represents a quite bulky group with unique spatial requirements due to its cylindrical geometry and its fixed interannular spacing. In retrospect, the typical cone volume of the ferrocenyl unit is about 17 Å [10]. The pendent ferrocenylvinyl arm is not chiral, but is prochiral in the sense that chirality is produced upon coordination and adoption of a particular conformation.

3. Crystal structure of the complex 5e

In order to get a better knowledge of the relative spatial distribution of the different groups conforming the **5e** molecule, a single crystal X-ray analysis was carried out (Fig. 1). This analysis revealed the conformation of the six-membered heteroatom ring and the effect of coordination upon the iminophosphorane bond. Compound **5e** crystallizes in a centrosymmetric space group with the palladium atom exhibiting a slightly distorted square-planar coordination. The metal environment is formed by the *P*,*N*-chelate iminophosphorane ligand and two *cis*-disposed chloride atoms. Distortions from ideal square-planar metal coordination concern fundamentally the *cis*-angles (range 84.35(3)–95.80(8)°) and minor deviations out of the calculated least-square plane (maximum deviation for P(1), 0.032(1) Å).

The two Pd–Cl bond distances are significantly different, 2.3615(9) and 2.3016(8), but both are within the usual range of terminal Pd–Cl bond separations (mean

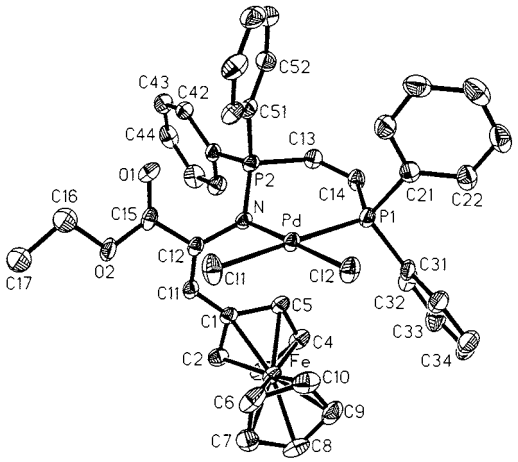


Fig. 1. ORTEP plot of compound **5e**. 50% probability ellipsoids. Selected bond lengths (Å) and angles (°): Pd–N 2.077(2), Pd–P(1) 2.2287(9), Pd–Cl(2) 2.3016(8), Pd–Cl(1) 2.3615(9), P(1)–C(14), 1.804(3), C(14)–C(13) 1.326(4), C(13)–P(2) 1.800(3), P(2)–N 1.605(3), N–(12) 1.426(4) N–Pd–P(1) 95.80(8), N–Pd–Cl(1) 90.33(8), Cl(1)–Pd–Cl(2) 89.56(3), Cl(2)–Pd–P(1) 84.35(3), Pd–P(1)–C(14) 114.35(11), P(1)–C(14)–C(13) 125.4(3), C(14)–C(13)–P(2) 128.2(3), C(13)–P(2)–N 107.7(2), P(2)–N–Pd 115.00(14), P(2)–N–C(12) 121.0(2).

value 2.321(6) Å) [11]. They clearly reflect the different *trans*-influences of the iminophosphorane donor atoms: the longest Pd–Cl(1) distance is located *trans* to the stronger π-acceptor P(1), meanwhile the shorter one, Pd–Cl(2), is opposite to the imino nitrogen atom. The dihedral angle between the main plane of the Pd–N–P(2)–C(13)–C(14)–P(1) and the palladium coordination plane is 20.65(2)°.

The analysis of the molecular structure of **5e** has also shown the puckering of the six-membered metallacycle.

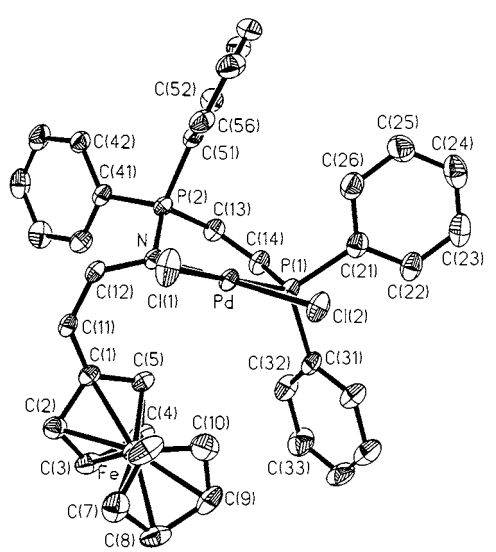


Fig. 2. View of **5e** along the coordination plane showing the conformation of the metallacycle as well as the disposition of the substituent on the ring, with hydrogen atoms and ethoxycarbonyl group omitted for clarity.

Cremer and Pople parameters ($Q = 0.643(2)$ Å, $\phi_2 = 69.2(2)°$, $\theta_2 = 59.5(2)°$) [12] characterize this heteroatomic ring, Pd–N–P(2)–C(13)–C(14)–P(1), as having an envelope conformation E_2 — with the nitrogen out-of-plane — slightly distorted toward a half-chair conformation [13].

Another interesting feature determined by the structural analysis concerns the modifications of the iminophosphorane ligand upon coordination to the metal. Thus, the P(2)–N–C(12) bond angle has been seriously reduced from 131.6(2)° in a related free ligand [3b] to a value of 121.0(2)° in **5e**. Additionally, both P(2)–N and N–C(12) bonds have been lengthened from 1.566(2) and 1.384(3) Å to 1.605(3) and 1.426(4) Å, respectively. These data compare well with those observed in related iminophosphorane metal complexes [14] and support that coordination of iminophosphorane to the metal significantly reduces the double-bond character of the P–N bond [6,15]. The directional donation of the lone pair of the sp^2 nitrogen atom upon formation of complex **5e** restores the trigonal planar geometry at the nitrogen. The Pd–P bond length 2.2287(9) is shorter than the single bond 2.41 Å, suggesting a π-bonding interaction [16], which is similar to the other found earlier [17].

Considering the best idealized coordinating plane of the palladium, it is instructive to analyze the position of the different parts of the molecule with respect to this plane (Fig. 2). Observing that (a) the ferrocene subunit lies below this plane and (b) completing the ring by joining the phosphorus and nitrogen atoms with the palladium atom, one arrives at a propeller-type position of the four P-phenyl groups, two pseudoaxial and two pseudoequatorial. The pseudoaxial Ph–P(1) and pseudoequatorial Ph–P(2) are edge-on exposed, whereas the pseudoequatorial Ph–P(1) and pseudoaxial Ph–P(2) are face-on exposed [18]. (c) The structure **5e** presents a chiral axis, the helical sense of which is maintained through hindered rotation around the N–C(12) single bond. Thus, anti-clockwise rotation around this bond is hindered by the chlorine atom that lies on the Pd–N–P(2) plane, whereas clockwise rotation is hindered by the pseudoequatorial Ph–P(2).

4. Electrochemistry

Compounds **3e** and **5e** were further characterized by cyclic voltammetry. All potentials are referenced to the SCE. $E_{1/2} = (E_{pa} + E_{pc})/2$ for reversible electron transfer processes and oxidation peak potentials (E_{pa}) for irreversible processes are given.

The complex **5e** exhibits an uncomplicated reversible electron-transfer pattern involving the ferrocenyl subunit. The cyclic voltammogram of **5e** in dimethylformamide solution displayed a simple reversible

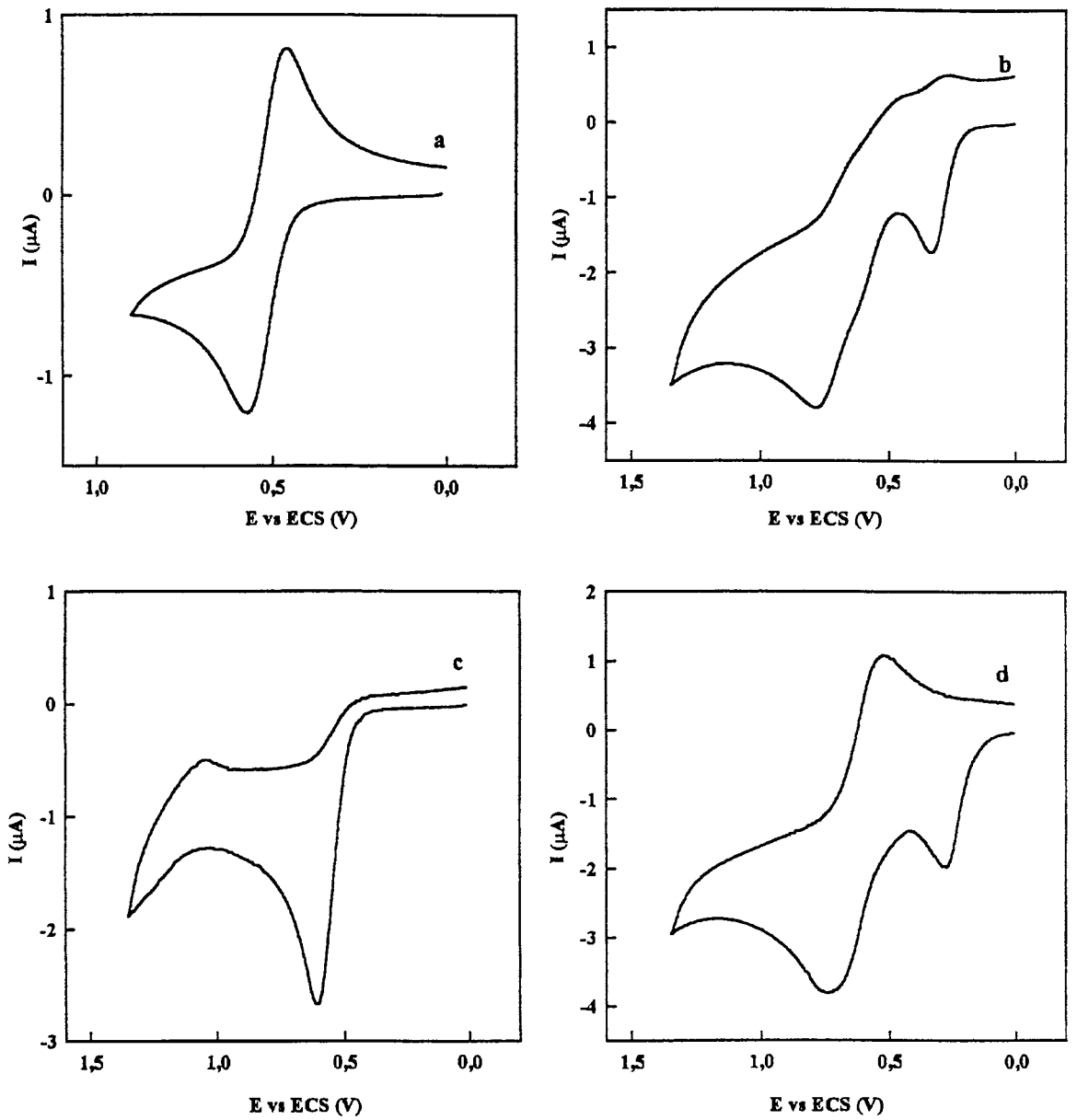


Fig. 3. Cyclic voltammograms of: (a) **5e** in DMF solution; (b) **3e** in DMF solution; (c) **3d** in DMF solution, (d) **3e** in acetonitrile solution. Experimental conditions: 1×10^{-3} M, Pt disk working electrode, SCE reference electrode, 0.1 M [n-Bu_4N][ClO_4], scan rate: 200 mV s^{-1}.

one-electron transfer process at $E_{1/2} = 0.517$ V versus SCE, ($\Delta E_p = 116$ mV) less anodic than that displayed by the free ligand **3e**, $E_{pa} = 0.782$ V versus SCE. No peaks corresponding to the oxidation process of the Pd(II)/Pd(III) couple were observed [19] (Fig. 3(a)). It has been reported [20] that in heterobimetallic ferrocene–palladium complexes the potential of the Fe(II)/Fe(III) couple is shifted to a high-potential region. This fact is probably due to a dative iron–palladium bond, which decreases the electron density on the iron atom. As the potential oxidation value in the complex **5e** ($E_{1/2} = 0.517$ V) is quite similar to that of the ferrocene itself ($E_{1/2} = 0.485$ V, $\Delta E_p = 80$ mV) and it is shifted to a lower-potential region with respect to the free ligand **3e** ($E_{pa} = 0.782$ V), we conclude that there is only, if any, bonding interaction between the Fe and Pd atoms in complex **5e**.

In striking contrast with the electrochemical behavior observed in the complex **5e**, the redox pattern for the free ligand **3e** is much more complicated under identical experimental conditions. The cyclic voltammogram of **3e** shows two oxidation peaks at 0.337 and 0.780 V versus SCE at a scan rate of 200 mV s^{-1} and a very low response in the cathodic scan (Fig. 3(b)). Taking into account that in the cyclic voltammogram of the aromatic analog **3d** (Fig. 3(c)), in which the ferrocene group has been replaced by an aromatic ring, only an oxidation peak at 0.610 V appears due to the irre-

versible oxidation of the iminophosphorane group [21], it would be reasonable to assign the first oxidation peak to the iminophosphorane oxidation. Fig. 3(d) also shows that the diphenylphosphino group does not undergoes electrochemical oxidation under these conditions.

The second electron transfer concerns the iron center [Fe(II)/Fe(III)] which gives an irreversible wave. This observation, coupled with the above-mentioned absence of any chemical complication when both diphenylphosphino and iminophosphorane groups are coordinated by palladium, would lead to the conclusion that the ferrocene–ferrocinium electron transfer in the free ligand **3e** might be complicated by chemical reactions.

The observed lack of a coupled cathodic peak after the last oxidation is probably due to the fast disappearance of the ferricinium cation. This behavior has also been found in several ferrocenylphosphanes in which the diphenylphosphino group is directly linked to the ferrocene ring, and it has been attributed to an oxidation of the phosphorus atom via a ferrocinium cation by a fast intramolecular electron transfer with regeneration of Fe(II) [22]. However, in the free ligand **3e**, the diphenylphosphino group is not directly linked to the ferrocene ring, so that the absence of the cathodic peak is not likely to be due to this type of interaction. This idea was supported by changing the solvent. Thus, the cyclic voltammogram of **3e** in acetonitrile solution displayed a first irreversible electron process ($E_{pa} = 0.275$ vs. SCE) corresponding to the iminophosphorane group oxidation, and a second quasi-reversible electron process ($E_{1/2} = 0.634$ V vs. SCE) due to the oxidation Fe(II) to Fe(III). This observation could suggest coupled reactions between the resulting product of the initial iminophosphorane group oxidation with the ferrocene ring, and the loss of the cathodic peak observed in DMF solution could be due to low stability of the ferrocinium cation in this solvent. The quantitative electrochemical studies of **3e** and others types of ferrocenylimino–phosphorane compounds are under active investigation.

5. Experimental

5.1. General

All experiments were carried out with the exclusion of air and moisture under nitrogen. Solvents were predried over molecular sieves and freshly distilled from appropriate drying agents. Compounds **2a** and **2d–g** were prepared according to the literature procedure [5,7,8]. NMR: Bruker AC200 or Varian Unity 300. MS: Fisons Autospec 5000 VG. IR: Nicolet Impact 400. Elemental analyses: Perkin–Elmer 240c. Melting points were determined on a Kofler hot-plate and are uncorrected. Electrochemistry: Quiceltron potentiostat/galvanostat controlled by a personal computer and driven by dedicated software. Experiments were carried out in a three-electrode cell. Electrochemical experiments were performed on 1 mM dimethylformamide or acetonitrile solutions containing 0.1 M [n-Bu_4N][ClO_4] as supporting electrolyte. Deoxygenation of the solutions was achieved by bubbling nitrogen for at least 10 min. All of the potential values are referred to SCE. Cyclovoltammetric tests were performed at scan rates from 50 to 500 mV s^{-1}.

5.2. Preparation of azides **2b–c** and **2g** — general procedure

To a well-stirred solution containing sodium (0.76 g, 33 mmol) in dry ethanol (10 ml), a solution of ethyl azidoacetate (4.3 g, 33 mmol) in dry ethanol (3 ml) and the appropriate aldehyde (15 mmol) were added dropwise at −15°C under nitrogen. The reaction mixture was stirred at this temperature for 7 h. After this it was poured into aqueous 30% ammonium chloride (30 ml) and was extracted with diethyl ether (3 × 30 ml). The combined extracts were washed with water (3 × 10 ml), dried (Na_2SO_4) and evaporated under reduced pressure at 30°C. The residual material was chromatographed on a silica gel column using ethylacetate–n-hexane (2:1).

2b: (78%), yellow prisms, m.p. 57–58°C, $R_f = 0.50$. IR (Nujol): $\nu = 2122$, 1700, 1605, 1515, 1334, 1313, 1266, 1218, 1180, 1124, 1085, 1033, 900, 840, 762, 728 cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 7.29$ (d, 2H, $^3J = 8.7$ Hz), 6.90 (d, 2H, $^3J = 8.7$ Hz), 6.88 (s, 1H, CH=C), 4.35 (q, 2H, $^3J = 7.2$ Hz, CH_2), 3.83 (s, 3H, CH_3O), 1.39 (t, 3H, $^3J = 6.9$ Hz, CH_2CH_3). ^{13}C-NMR ($CDCl_3$): $\delta = 163.16$ (CO), 160.42 (C-4), 132.34 (C-2), 127.73 (C-1), 126.02 (CH=*C*), 125.37 (*C*H=C), 113.88 (C-3), 62.03 (CH_2), 55.28 (CH_3O), 14.21 (CH_2CH_3). MS (EI, 70 eV); m/z (%): 219 (45) [$M^+ - N_2$], 174 (20), 173 (100), 158 (16), 146 (33), 145 (34). $C_{12}H_{13}N_3O_3$ (247.25): Anal. Calc. C, 58.29; H, 5.30; N, 16.99; found C, 58.20; H, 5.35; N, 16.85%.

2c: (69%), yellow prisms, m.p. 46–48°C, $R_f = 0.54$. IR (Nujol): $\nu = 2124$, 2104, 1714, 1624, 1581, 1305, 1285, 1260, 1237, 1163, 1108, 1098, 1049, 1030, 943, 914, 888, 862, 787, 762 cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta =$ 7.42 (m, 1H, 2-H), 7.37–7.22 (m, 2H), 6.93–6.85 (m, 1H), 6.87 (s, 1H, CH=C), 4.36 (q, 2H, $^3J = 7.1$ Hz, CH_2), 3.83 (s, 3H, CH_3O), 1.39 (t, 3H, $^3J = 7.1$ Hz, CH_2CH_3). ^{13}C-NMR ($CDCl_3$): $\delta = 163.45$ (CO), 159.41 (C-3), 134.38 (C-1), 129.32 (C-5), 125.74 (*C*H=C), 125.09 (CH=*C*), 123.34 (C-6), 115.42 (C-2)*, 115.24 (C-4)*, 62.25 (CH_2), 55.25 (CH_3O), 14.16 (CH_2CH_3). MS (EI, 70 eV); m/z (%): 219 (60) [$M^+ - N_2$], 174 (29), 173 (100), 158 (29), 147 (53), 146 (39). $C_{12}H_{13}N_3O_3$ (247.25): Anal. Calc. C, 58.29; H, 5.30; N, 16.99; found C, 58.40; H, 5.38; N, 16.75%. *Interchangeable.

2g: (5%), brown viscous oil, $R_f = 0.10$. IR (Nujol): $\nu = 2129$, 1723, 1618, 1595, 1343, 1273, 1250, 1201, 1121, 1098, 1076, 1022, 999, 906, 892, 874, 823, 765, 726 cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 8.62$ (m, 2H; 2-H/6-H), 7.63 (m, 2H; 3-H/5-H), 6.76 (s, 1H; CH=C), 4.39 (q, 2H, $^3J = 7.2$ Hz, CH_2), 1.41 (t, 3H, $^3J = 7.2$ Hz, CH_2CH_3). ^{13}C-NMR ($CDCl_3$): $\delta = 162.65$ (CO), 150.06 (C-2/C-6), 140.14 (C-4), 129.92 (CH=*C*), 123.89 (C-3/C-5), 121.31 (*C*H=C), 62.73 (CH_2), 14.09 (CH_2CH_3). MS (EI, 70 eV); m/z (%): 218 (9) [M^+], 190 (55) [$M^+ - N_2$], 145 (22), 144 (100), 116 (19). $C_{10}H_{10}N_4O_2$ (218.21): Anal. Calc. C, 55.04; H, 4.62; N, 25.67; found C, 55.12; H, 4.60; N, 25.80%.

5.3. Preparation of monoiminophosphoranes **3** — general procedure

To a solution of the appropriate β-substituted vinylazide **2** (1.53 mmol) in 10 ml of dry CH_2Cl_2, an equimolecular amount of (*Z*)-1,2-bis(diphenylphosphoranyl)ethene **1** in 10 ml of dry CH_2Cl_2 was added at room temperature. The reaction mixture was stirred for 24 h. The solvent was then removed in vacuo and the remaining residue was chromatographed on a silica gel column using ethyl acetate–*n*-hexane (1:5) as eluent for **3a**–**3e** and ethyl acetate–*n*-hexane (2:1) for **3f**–**3g**.

3a: (94%), yellow prisms, m.p. 42–43°C, $R_f = 0.26$. IR (Nujol): $\nu = 1684$, 1588, 1561, 1326, 1236, 1198, 1113, 1038, 851, 824, 744, 717, 696 cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 8.13$ (d, 2H, $^3J = 8.4$ Hz), 7.79 (ddd, 4H, $^3J_P = 12.0$, $^3J = 7.8$, $^4J = 1.5$), 7.58 (ddd, 1H, $J_P = 29.1$, $J_P = 22.5$, $^3J_{cis} = 13.8$ Hz), 7.46–7.09 (m, 19H), 6.67 (d, 1H, $^4J = 8.1$ Hz, CH=C–CO), 3.92 (q, 2H, $^3J = 7.2$ Hz, CH_2); 2.35 (s, 3H, CH_3Ar), 1.10 (t, 3H, $^3J = 7.2$ Hz, CH_2CH_3). ^{13}C{^{1}H}-NMR ($CDCl_3$): $\delta = 168.34$ (d, $^3J =$ 8.7 Hz, CO), 148.08 (dd, $^1J = 23.0$, $^2J = 2.3$ Hz, CH–P(III)), 138.80 (dd, $^1J = 84.2$, $^2J = 23.6$ Hz, CH–P(V)), 138.63 (dd, $^1J = 12.0$, $^4J = 1.1$ Hz, C-1″), 135.74 (C-4), 135.28 (dd, $^2J = 8.1$, $^5J = 1.1$ Hz, =*C*–CO), 135.26 (d, $^1J = 110.1$ Hz, C-1′), 135.18 (C-1), 132.79 (d, $^2J = 19.5$ Hz, C-2″), 131.19 (dd, $^2J = 9.2$, $^5J = 1.2$ Hz, C-2′), 130.42 (d, $^4J = 2.1$ Hz, C-4′), 129.50* (C-2), 128.24 (C-4″), 128.20 (d, $^3J = 6.4$ Hz, C3″), 128.14 (d, $^3J = 12.0$ Hz, C-3′), 128.03* (C-3), 116.25 (d, $^3J = 20.7$ Hz, *C*H=C–CO), 60.83 (CH_2), 21.36 (CH_3–Ar), 14.15 (CH_2CH_3). ^{31}P-NMR ($CDCl_3$): $\delta = -$ 3.28 (d, P(V)), $-$23.93 (d, P(III)), $^3J_{PP} = 12.3$ Hz. HR-MS (EI, 70 eV); m/z (%): 599.2128 (15) [M^+, Anal. Calc. for $^{12}C^1_{38}H^{14}_{35}N^{16}O^{31}_2P_2$ 599.2143], 570.1803 (4), 543.1836 (4), 542.1804 (11), 523.1793 (18), 522.1757 (49), 415.1642 (29), 414.1609 (100), 396.1158 (10), 335.0731 (21). MS (EI, 70 eV); m/z (%): 600 (6) [$M^+ +$ 1], 599 (15) [M^+], 570 (4), 543 (4), 542 (11), 523 (18), 522 (49), 415 (29), 414 (100), 396 (10), 335 (21). *Interchangeable.

3b: (86%), yellow prisms, m.p. 121–122°C, $R_f = 0.18$. IR (Nujol): $\nu = 1743$, 1690, 1599, 1556, 1310, 1198, 1177, 1113, 1033, 856, 824, 728, 701 cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 8.19$ (d, 2H, $^3J = 8.8$ Hz, 3-H/5-H), 7.83–7.68 (m, 4H), 7.52–7.11 (m, 18H), 6.85 (d, 2H, $^3J = 8.8$ Hz, 2-H/4-H), 6.85 (d, 1H, $^4J = 8.2$ Hz, CH=C–CO), 3.93 (q, 2H, $^3J = 7.0$ Hz, CH_2), 3.82 (s, 3H, CH_3O), 1.10 (t, 3H, $^3J = 7.0$ Hz, CH_2CH_3). ^{13}C{^{1}H}-NMR ($CDCl_3$): $\delta = 168.39$ (d, $^3J = 8.7$ Hz, CO), 157.63 (C-4), 148.02 (dd, $^1J = 23.0$, $^2J = 2.2$ Hz, CH–P(III)), 139.79 (dd, $^1J = 85.1$, $^2J = 23.7$ Hz, CH–P(V)), 138.65 (dd, $^1J = 12.3$, $^4J = 1.1$ Hz, C-1″), 135.32 (d, $^1J = 110.7$ Hz, C-1′), 134.30 (dd, $^2J = 8.1$, $^5J = 1.1$ Hz, =*C*–CO), 132.78 (d, $^2J = 19.3$ Hz, C-2″), 131.54 (d, $^4J = 0.9$ Hz, C-1), 131.18 (dd, $^2J = 9.4$, $^5J = 1.4$ Hz, C-2′), 130.84 (C-2), 130.40 (d, $^4J = 2.8$ Hz, C-4′), 128.25 (C-4″), 128.19 (d, $^3J = 6.3$ Hz, C-3″), 128.13 (d, $^3J = 11.9$ Hz, C-3′), 116.14 (d, $^3J = 21.1$ Hz, *C*H=C–CO), 113.10 (C-3), 60.76 (CH_2), 55.21 (CH_3O), 14.18 (CH_2CH_3). ^{31}P-NMR ($CDCl_3$): $\delta = -3.20$ (d, P(V)), -23.88 (d, P(III)), $^3J_{PP} = 11.8$ Hz. HR-MS (EI, 70 eV); m/z (%): 615. 2118 (31) [M^+, Anal. Calc. for $^{12}C^1_{38}H^{14}_{35}N^{16}O^{31}_3P_2$ 615.2092], 558.1755 (9), 539.1743 (19), 538.1708 (53), 431.1594 (27), 430.1558 (100), 429.1487 (42), 396.1192 (14), 335.0750 (31). MS (EI, 70 eV); m/z (%): 616 (14) [$M^+ + 1$], 615 (31) [M^+], 558 (9), 539 (19), 538 (53), 431 (27), 430 (100), 429 (42), 396 (14), 335 (31).

3c: (86%), yellow prisms, m.p. 45–47°C, $R_f = 0.24$. IR (Nujol): $\nu = 1693$, 1591, 1476, 1465, 1299, 1265, 1243, 1220, 1190, 1160, 1115, 1044, 999, 957, 882, 848, 788, 739, 694 cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 8.23$ (dd, 1H, $^4J = 2.0$, $^4J = 1.5$ Hz, 2-H), 7.76 (ddd, 4H, $^3J_P =$ 12.3, $^3J = 8.1$, $^4J = 1.5$ Hz), 7.55–7.10 (m, 20H), 6.71 (dd, 1H, $^3J = 8.4$, $^4J = 2.0$ Hz, 4-H), 6.66 (d, 1H $^4J =$ 8.1 Hz, CH=C–CO), 3.94 (q, 2H, $^3J = 7.5$ Hz, CH_2), 3.58 (s, 3H, CH_3O), 1.11 (t, 3H, $^3J = 7.5$ Hz, CH_2CH_3). ^{13}C{^{1}H}-NMR ($CDCl_3$): $\delta = 168.29$ (d, $^3J = 9.2$ Hz, CO), 159.23 (C-3), 148.40 (dd, $^1J = 23.6$, $^2J = 2.0$ Hz, CH–P(III)), 139.98 (C-1), 138.60 (dd, $^1J = 12.0$, $^4J = 1.1$ Hz, C-1″), 138.60 (dd, $^1J = 84.2$, $^2J = 22.2$ Hz, CH–P(V)), 136.33 (dd, $^2J = 8.0$, $^5J = 1.1$ Hz, =*C*–CO), 135.18 (d, $^1J = 110.7$ Hz, C-1′), 132.79 (d, $^2J = 19.5$ Hz, C-2″), 131.18 (dd, $^2J = 9.2$, $^5J = 1.7$ Hz, C-2′), 130.48 (d, $^4J = 2.9$ Hz, C-4′), 128.33 (C-4″ + C-5), 128.26 (d, $^3J = 6.3$ Hz, C-3″), 128.18 (d, $^3J = 12.0$ Hz; C-3′), 122.57 (C-6), 115.91 (d, $^3J = 21.3$; *C*H=C–CO), 113.21 (C-2), 112.90 (C-4), 60.94 (CH_2), 55.12 (CH_3O), 14.14 (CH_2CH_3). ^{31}P-NMR ($CDCl_3$): $\delta = -1.93$ (d, P(V)), -24.00 (d, P(III)), $^3J_{PP} = 11.8$ Hz. MS (EI, 70 eV); m/z (%): 615 (11) [M^+], 586 (5), 558 (14), 538 (47), 431 (30), 430 (100), 396 (14), 335 (22), 201 (44), 185 (38), 183 (63). $C_{38}H_{35}NO_3P_2$ (615.65): Anal. Calc. C, 74.14; H, 5.73; N, 2.28; found C, 74.28; H, 5.70; N, 2.31.

3d: (85%), yellow prisms, m.p. 47–49°C, $R_f = 0.22$. IR (Nujol): $\nu = 1738$, 1684, 1599, 1567, 1310, 1241, 1113, 1033, 750, 696 cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 9.22$

(dd, 1H, $^3J_{H5} = 7.5$, $^4J_{H4} = 1.8$ Hz, 6-H), 7.82–7.75 (m, 4H), 7.70–7.09 (m, 20H), 6.97 (t, 1H, $^3J = 8.1$ Hz), 6.85 (d, 1H, $^3J = 7.5$ Hz, 3-H), 3.94 (q, 2H, $^3J = 7.2$ Hz, CH_2), 3.84 (s, 3H, CH_3O), 1.09 (t, 3H, $^3J = 7.2$ Hz, CH_2CH_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta = 168.42$ (d, $^3J =$ 8.9 Hz, CO), 156.28 (C-2), 147.99 (dd, $^1J = 23.3$, $^2J =$ 2.3 Hz, CH–P(III)), 138.82 (dd, $^1J = 84.7$, $^2J = 23.5$ Hz, CH–P(V)), 138.55 (dd, $^1J = 12.3$, $^4J = 1.6$ Hz, C-1″), 135.91 (d, $^2J = 6.9$ Hz, =*C*–CO), 135.29 (d, $^1J = 111.0$ Hz, C-1′), 132.73 (d, $^2J = 19.2$ Hz, C-2″), 131.19 (dd, $^2J = 9.9$, $^5J = 1.3$ Hz, C-2′), 130.72 (C-6), 130.34 (d, $^4J = 2.6$ Hz, C-4′), 128.23 (C-4″), 128.17 (d, $^3J = 6.3$ Hz, C-3″), 128.06 (d, $^3J = 12.0$ Hz, C-3′), 127.42 (C-1), 126.41 (C-4), 119.92 (C-5), 109.59 (C-3), 108.78 (d, $^3J = 20.6$ Hz, *C*H=C–CO), 60.84 (CH_2), 55.47 (CH_3O), 14.16 (CH_2CH_3). ^{31}P-NMR ($CDCl_3$): $\delta = -3.59$ (d, P(V)), -25.84 (d, P(III)), $^3J_{PP} = 12.3$ Hz. MS (EI, 70 eV); *m*/*z* (%): 615 (14) [M^+], 558 (15), 538 (46), 431 (43), 430 (100), 396 (18), 356 (48), 335 (31), 201 (56), 185 (59), 183 (91), 108 (38), 107 (21). $C_{38}H_{35}NO_3P_2$ (615.65): Anal. Calc. C, 74.14; H, 5.73; N, 2.28; found C, 74.08; H, 5.67; N, 2.32.

3e: (41%), red prisms, m.p. 48–51°C, $R_f = 0.22$. IR (Nujol): $\nu = 1685$, 1590, 1412, 1213, 1108, 807 cm^{-1}. ^1H-NMR ($CDCl_3$): $\delta = 7.89$ (ddd, 4H, $^3J_P = 12.0$, $^3J =$ 7.5, $^4J = 1.8$ Hz; 2′-H), 7.68 (ddd, 1H, $J_P = 30.3$ Hz, $J_P = 21.6$, $^3J_{cis} = 13.5$ Hz; =CH–P(V)), 7.46–7.33 (m, 6H, 3′-H, 4′-H), 7.26–7.13 (m, 11H, 2″-H, 3″-H, 4″-H, =CH–P(III)), 6.50 (d, 1H, $^4J_P = 8.4$ Hz, CH=C), 5.02 (pt, 2H, $J = 1.8$ Hz, 2-H/5-H), 4.25 (pt, 2H, $J = 1.8$ Hz, 3-H/4-H), 4.07 (s, 5H, Cp), 3.98 (q, 2H, $^3J = 7.2$ Hz, CH_2), 1.16 (t, 3H, $^3J = 7.2$ Hz, CH_2CH_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta = 168.97$ (d, $^3J = 8.5$ Hz, CO), 146.97 (d, $^1J = 22.0$ Hz, =CH–P(III)), 140.17 (dd, $^1J = 84.6$, $^2J = 24.5$ Hz, =CH–P(V)), 138.62 (d, $^1J = 11.5$ Hz, C-1″), 135.65 (d, $^1J = 109.6$ Hz, C-1′), 133.92 (d, $^2J = 8.0$ Hz, =*C*–CO), 132.68 (d, $^2J = 19.0$ Hz, C-2″), 131.21 (dd, $^2J = 9.0$, $^5J = 1.5$ Hz, C-2′), 130.33 (d, $^4J = 2.4$ Hz, C-4′), 128.27 (C-4″), 128.23 (d, $^3J = 6.0$ Hz, C-3″), 128.11 (d, $^3J = 11.5$ Hz, C-3′), 115.86 (d, $^3J = 22.5$ Hz, *C*H=C–CO), 83.25 (C-1), 69.70 (C-2/C-5), 68.92 (Cp), 67.87 (C-3/C-4), 60.62 (CH_2), 14.24 (CH_2CH_3). ^{31}P-NMR ($CDCl_3$): $\delta = -5.72$ (d, P(V)), -25.49 (d, P(III)), $^3J_{PP} = 13.2$ Hz. MS (EI, 70 eV); *m*/*z* (%): 693 (100) [M^+], 616 (12), 224 (23). $C_{41}H_{37}NO_2P_2Fe$ (693.55): Anal. Calc. C, 71.00; H, 5.38; N, 2.02; found C, 70.90; H, 5.41; N, 1.97.

3f: (78%), yellow prisms, m.p. 55–57°C, $R_f = 0.50$. IR (CH_2Cl_2): $\nu = 1694$, 1592, 1560, 1430, 1332, 1268, 1220, 1119, 1043, 899, 737, 713 cm^{-1}. ^1H-NMR ($CDCl_3$): $\delta = 9.00$ (d, 1H, $^4J = 1.8$ Hz, 2-H), 8.85 (dt, 1H, $^3J = 8.1$, $^4J_{H4} = {}^4J_{H2} = 1.8$ Hz, 6-H), 8.32 (dd, 1H, $^3J_{H5} = 4.8$, $^4J_{H2} = 1.8$ Hz, 4-H), 7.75 (ddd, 4H, $^3J_P =$ 12.0, $^3J = 7.5$, $^4J = 1.2$ Hz, 2′-H), 7.54–7.09 (m, 19H), 6.55 (d, 1H, $^4J_P = 8.4$ Hz, CH=C–CO), 3.96 (q, 2H, $^3J = 7.2$ Hz, CH_2), 1.13 (t, 3H, $^3J = 7.2$ Hz, CH_2CH_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta = 167.57$ (dd, $^3J = 9.1$, $^6J =$ 0.7 Hz, CO), 150.41 (C-6), 148.61 (dd, $^1J = 23.2$, $^2J =$ 2.3 Hz, CH–P(III)), 145.66 (C-2), 138.32 (dd, $^1J = 11.9$, $^4J = 1.1$ Hz, C-1″), 138.24 (dd, $^2J = 8.1$, $^5J = 1.2$ Hz, =*C*–CO), 138.00 (dd, $^1J = 85.4$, $^2J = 23.5$ Hz, CH–P(V)), 135.57 (C-4), 134.67 (d, $^1J = 111.3$ Hz, C-1′), 134.62 (d, $^4J = 0.9$ Hz, C-3), 132.64 (d, $^2J = 19.5$ Hz, C-2″), 130.99 (dd, $^2J = 9.5$, $^5J = 1.4$ Hz, C-2′), 130.61 (d, $^4J = 2.7$ Hz, C-4′), 128.24 (d, $^3J = 11.8$ Hz, C-3′), 128.21 (d, $^3J = 6.6$ Hz, C-3″), 128.36 (C-4″), 122.72 (C-5), 111.52 (d, $^3J = 21.3$ Hz, *C*H=C–CO), 61.10 (CH_2), 14.10 (CH_2CH_3). ^{31}P-NMR ($CDCl_3$): $\delta =$ -1.00 (d, P(V)), -23.50 (d, P(III)), $^3J_{PP} = 11.8$ Hz. MS (EI, 70 eV); *m*/*z* (%): 587 (32) [$M^+ + 1$], 586 (36) [M^+], 557 (21), 529 (22), 509 (71), 402 (54), 401 (100), 335 (55), 201 (62), 185 (44), 183 (63). $C_{36}H_{32}N_2O_2P_2$ (586.61): Anal. Calc. C, 73.71; H, 5.50; N, 4.78; found C, 73.80; H, 5.55; N, 4.82.

3g: (62%), yellow prisms, m.p. 58–60°C, $R_f = 0.18$. IR (CH_2Cl_2): $\nu = 1735$, 1699, 1584, 1526, 1329, 1240, 1196, 1113, 1036, 990, 854, 817, 738, 697 cm^{-1}. ^1H-NMR ($CDCl_3$): $\delta = 8.43$ (d, 2H, $^3J = 6.1$ Hz, 2-H/6-H), 7.99 (d, 2H, $^3J = 6.1$ Hz, 3-H/5-H), 7.75 (ddd, 4H, $^3J_P = 12.1$, $^3J = 7.4$, $^4J = 1.5$ Hz, 2′-H), 7.54–7.09 (m, 18H), 6.45 (d, 1H, $^4J_P = 8.2$ Hz, CH=C–N=P(V)), 3.96 (q, 2H, $^3J = 7.0$ Hz, CH_2), 1.29 (t, 3H, $^3J = 7.0$ Hz, CH_2CH_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta = 167.24$ (d, $^3J =$ 9.8 Hz, CO), 149.23 (d, $^1J = 23.0$ Hz, CH–P(III)), 148.56 (C-2/C-6), 146.25 (C-4), 141.04 (d, $^1J = 8.1$ Hz, C-1″), 138.18 (d, $^2J = 11.5$ Hz, =*C*–CO), 137.31 (dd, $^1J = 85.3$, $^2J = 23.1$ Hz, CH–P(V)), 134.22 (d, $^1J =$ 110.7 Hz, C-1′), 132.69 (d, $^2J = 19.6$ Hz, C-2″), 131.06 (d, $^2J = 9.2$ Hz, C-2′), 130.84 (d, $^4J = 2.3$ Hz, C-4′), 128.26 (C-4″), 128.35 (d, $^3J = 12.6$ Hz, C-3′), 128.39 (d, $^3J = 6.9$ Hz, C-3′), 123.25 (C-3/C-5), 111.68 (d, $^3J =$ 20.7 Hz, *C*H=C–CO), 61.35 (CH_2), 14.07 (CH_2CH_3). ^{31}P-NMR ($CDCl_3$): $\delta = -0.10$ (d, P(V)), 23.14 (d, P(III)), $^3J_{PP} = 11.8$ Hz. MS (EI, 70 eV); *m*/*z* (%): 587 (5) [$M^+ + 1$], 586 (10) [M^+], 557 (14), 529 (14), 509 (72), 402 (29), 401 (100), 335 (67), 201 (81), 185 (40), 183 (74). $C_{36}H_{32}N_2O_2P_2$ (586.61): Anal. Calc. C, 73.71; H, 5.50; N, 4.78; found C, 73.68; H, 5.42; N, 4.73.

5.4. Synthesis of complexes **5** — general procedure

To a solution of the appropriate monoiminophosphorane **3** (0.367 mmol) in 15 ml of dry dichloromethane, a suspension of dichlorobis(benzonitrile)-palladium(II) (0.14 g, 0.367 mmol) in 10 ml of the same solvent was added dropwise. The resulting mixture was stirred at room temperature for 4 h. The precipitated solid was collected by filtration and chromatographed on a silica gel column using 1:9 methanol–dichloromethane as eluent.

5a: (83%), yellow prisms, m.p. 262–264°C, $R_f = 0.40$. IR (Nujol): $\nu = 1706$, 1615, 1316, 1252, 1161, 1102,

1049, 1006, 888, 846, 824, 739, 712, 701 cm^{-1}. ^{31}P-NMR ([D$_6$]DMSO): $\delta = 11.6$ (d, P(V)), 5.07 (d, P(III)), $^3J_{PP} = 48.1$ Hz. MS (FAB); m/z (%): 745 (23), 744 (58), 743 (39), 742 (99), 741 (56), 740 (100) [$M^+ - Cl$], 739 (67), 738 (30), 705 (21) [$M^+ - 2Cl$], 632 (14), 502 (22), 425 (21). $C_{38}H_{35}NCl_2O_2P_2Pd$ (776.96): Anal. Calc. C, 58.74; H, 4.54; N, 1.80; found C, 58.63; H, 4.40; N, 1.85.

5b: (97%), yellow prisms, m.p. 251–253°C, $R_f = 0.70$. IR (Nujol): $\nu = 1706$, 1602, 1509, 1316, 1305, 1246, 1173, 1155, 1117, 1030, 996, 884, 846, 832, 737, 691 cm^{-1}. ^{31}P-NMR ([D$_6$]DMSO): $\delta = 12.66$ (d, P(V)), 6.78 (d, P(III)), $^3J_{PP} = 51.7$ Hz. MS (FAB); m/z (%): 762 (14), 761 (22), 760 (56), 759 (42), 758 (99), 757 (57), 756 (100) [$M^+ - Cl$], 755 (68), 754 (30), 721 (17) [$M^+ - 2Cl$], 648 (10), 502 (17), 425 (17). $C_{38}H_{35}NCl_2O_3P_2Pd$ (792.96): Anal. Calc. C, 57.56; H, 4.45; N, 1.77; found C, 57.42; H, 4.32; N, 1.70.

5c: (80%), yellow prisms, m.p. 249–251°C, $R_f = 0.60$. IR (Nujol): $\nu = 1711$, 1614, 1592, 1306, 1268, 1245, 1121, 1045, 1002, 911, 858, 752, 735, 701 cm^{-1}. ^1H-NMR ([D$_6$]DMSO): $\delta = 3.99$ (q, 2H, $^3J = 6.6$ Hz, CH_2), 1.09 (t, 3H, $^3J = 6.6$ Hz, CH_2CH_3). ^{31}P-NMR ([D$_6$]DMSO): $\delta = 14.98$ (d, P(V)), 5.21 (d, P(III)), $^3J_{PP} = 41.3$ Hz. MS (FAB); m/z (%): 762 (14), 761 (22), 760 (56), 759 (42), 758 (99), 757 (57), 756 (100) [$M^+ - Cl$], 755 (68), 754 (30), 721 (17) [$M^+ - 2Cl$], 648 (10), 502 (17), 425 (17). $C_{38}H_{35}NCl_2O_3P_2Pd$ (792.96): Anal. Calc. C, 57.56; H, 4.45; N, 1.77; found C, 57.39; H, 4.38; N, 1.80.

5d: (89%), yellow prisms, m.p. 239–241°C, $R_f = 0.63$. IR (Nujol): $\nu = 1707$, 1597, 1308, 1288, 1256, 1183, 1160, 1110, 1033, 1005, 941, 897, 882, 837, 745, 700 cm^{-1}. ^{31}P-NMR ([D$_6$]DMSO): $\delta = 12.48$ (d, P(V)), 6.69 (d, P(III)), $^3J_{PP} = 51.7$ Hz. MS (FAB); m/z (%): 762 (16), 761 (23), 760 (59), 759 (39), 758 (100), 757 (54), 756 (100) [$M^+ - Cl$], 755 (64), 754 (29), 721 (16) [$M^+ - 2$ Cl], 502 (15). $C_{38}H_{35}NCl_2O_3P_2Pd$ (792.96): Anal. Calc. C, 57.56; H, 4.45; N, 1.77; found C, 57.66; H, 4.48; N, 1.72.

5e: (56%), red prisms, m.p. > 300°C, $R_f = 0.53$. IR (Nujol): $\nu = 1692$, 1613, 1595, 1261, 1149 cm^{-1}. ^1H-NMR (CD_2Cl_2): $\delta = 8.43$ (dd, 2H, $^3J_P = 12.7$, $^3J = 7.1$ Hz, 2″-H), 7.97 (dd, 2H, $^3J_P = 11.1$, $^3J = 7.2$ Hz, 2′-H), 7.72–7.44 (m, 6H), 7.39–6.95 (m, 13H), 5.14 (s, 1H, H_2/H_5), 4.27 (s, 1H, H_3/H_4), 4.30 (s, 7H, Cp + 2H), 4.00–3.83 (m, 2H, $^2J_{AB} = 9.8$, $^3J_{AX} = {}^3J_{BX} = 7.0$ Hz), 1.16 (t, 3H, $^3J = 7.0$ Hz, CH_2CH_3). $^{13}C\{^1H\}$-NMR (CD_2Cl_2): $\delta = 167.61$ (d, $^3J = 1.4$ Hz, CO), 141.02 (dd, $^1J_{P(V)} = 104.5$, $^2J_{P(III)} = 7.2$ Hz, =CH–P(V)), 135.63 (dm, $^1J_{P(III)} = 34.6$ Hz, =CH–P(III)), 134.44 (d, $^2J = 11.1$ Hz, C-2″), 133.78 (d, $^3J = 11.8$ Hz, C-3″), 133.76 (d, $^2J = 9.7$ Hz, C-2′), 131.57 (d, $^4J = 3.0$ Hz, C-4″)*, 130.92 (d, $^4J = 2.7$ Hz, C-4′)*, 128.16 (d, $^3J = 12.1$ Hz, C-3′), 78.29 (C-1), 71.62, 70.52, 70.33, 69.51 (Cp), 69.44, 61.07 (CH_2), 13.78 (CH_2CH_3). ^{31}P-NMR (CD_2Cl_2): $\delta = 15.80$ (d, P(V)), 0.26 (d, P(III)), $^3J_{PP} = 37.0$ Hz. MS (FAB); m/z (%): 839 (23), 838 (54), 837 (41), 836 (97), 835 (58), 834 (100) [$M^+ - Cl$], 833 (63), 832 (30), 798 (25) [$M^+ - 2Cl$], 678 (86), 502 (69), 425 (86). $C_{41}H_{37}NCl_2O_2P_2FePd$ (869.00): Anal. Calc. C, 56.55; H, 4.28; N, 1.61; found C, 56.40; H, 4.16; N 1.70. *Interchangeable.

5f: (56%), yellow prisms, m.p. 145–148°C, $R_f = 0.40$. IR (CH_2Cl_2): $\nu = 1714$, 1620, 1590,1440, 1326, 1267, 1158, 1108, 1038, 885, 808, 736, 701 cm^{-1}. ^{31}P-NMR (CD_2Cl_2): $\delta = 12.20$ (d, P(V)), 6.27 (d, P(III)), $^3J_{PP} = 45.6$ Hz. MS (FAB); m/z (%): 733 (19), 732 (26), 731 (59), 730 (40), 729 (100), 728 (55), 727 (100) [$M^+ - Cl$], 726 (70), 725 (34), 692 (49) [$M^+ - 2Cl$], 615 (20), 502 (67). $C_{36}H_{32}N_2Cl_2O_2P_2Pd$ (763.92): Anal. Calc. C, 56.60; H, 4.22; N, 3.67; found C, 56.73; H, 4.30; N, 3.61.

5g: (58%), yellow prisms, m.p. 185–189°C, $R_f = 0.33$. IR (Nujol): $\nu = 1715$, 1632, 1613, 1319, 1250, 1156, 1119, 1029, 999, 843, 735, 692 cm^{-1}. ^1H-NMR (CD_2Cl_2): $\delta = 3.99$ (q, 2H, $^3J = 7.2$ Hz, CH_2), 1.05 (t, 3H, $^3J = 7.2$ Hz, CH_2CH_3). ^{31}P-NMR (CD_2Cl_2): $\delta = 18.50$ (d, P(V)), 6.71 (d, P(III)), $^3J_{PP} = 37.7$ Hz. MS (FAB); m/z (%): 733 (18), 732 (26), 731 (61), 730 (42), 729 (100), 728 (57), 727 (99) [$M^+ - Cl$], 726 (72), 725 (28), 692 (14) [$M^+ - 2Cl$], 615 (9), 502 (14). $C_{36}H_{32}N_2Cl_2O_2P_2Pd$ (763.92): Anal. Calc. C, 56.60; H, 4.22; N, 3.67; found C, 56.77; H, 4.15; N, 3.59.

6. X-ray crystallographic studies

Crystal data are given in Table 1. A crystal of **5e** suitable for X-ray diffraction was prepared by slow difussion of methanol–ethanol (1:1) in a dichloromethane solution. A crystal of **5e** was mounted in inert oil on a glass fiber and transferred to the diffractometer (Siemens P4 with LT2 low-temperature attachment). Measurements were made at 100°C using monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å).

Unit cell parameters were determined from a least-squares analysis of ca. 63 accurately centered reflections ($9.4 < 2\theta < 23.7°$). Intensities were measured using ω scans. Absorption corrections were based on ψ scans. The structures were solved by the heavy-atom method and refined anisotropically on F^2 (program SHELXL-93) [23]. Hydrogen atoms were included using a riding model.

7. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-

Table 1
Crystal data for compound **5e** [a]

Empirical formula	$C_{41}H_{37}Cl_2FeNO_4P_2Pd \cdot EtOH \cdot MeOH$
M_r	948.92
a (Å)	11.4729(9)
b (Å)	12.5465(10)
c (Å)	16.2722(12)
α (°)	83.281(5)
β (°)	71.648(6)
γ (°)	64.801(5)
Z	2
$D_{calc.}$ (Mg m^{-3})	1.567
Crystal system	Triclinic
Space group	$P\bar{1}$
Crystal size (mm)	$0.60 \times 0.30 \times 0.20$
θ range (°)	3.16–25.00
Reflections measured	8483
Independent reflections	6985
μ (mm^{-1})	1.065
Max./min. transmission	0.91965/0.83798
Parameters	485
$F(000)$	972
Max. $\Delta\rho$ (e Å^{-3})	0.745
R_1 [a]	0.0334
wR_2 [b]	0.0833

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ for reflections with $I > 2\sigma(I)$.

[b] $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2)+(aP)^2+bP$, where $P = (2F_c^2+F_o^2)/3$ and a and b are constants set by the program.

121658. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

We gratefully acknowledge the financial support of the Dirección General de Investigación Científica y Técnica, project number PB95-1019.

References

[1] (a) M.G. Göbel, Angew. Chem. Int. Ed. Engl. 33 (1994) 1141. (b) H. Steinhagen, G. Helmchem, Angew. Chem. Int. Ed. Engl. 35 (1996) 2339. (c) M.E. Broussard, B. Juma, S.G. Train, W.-J. Peng, S.A. Laneman, G.G. Stanley, Science 260 (1993) 1784.

[2] (a) M. Sawamura, R. Kuwano, Y. Ito, J. Am. Chem. Soc. 117 (1995) 9602. (b) W. Zhang, T. Hirao, I. Ikeda, Tetrahedron Lett. 37 (1996) 4545. (c) W. Zhang, T. Kida, Y. Nakatsuji, I. Ikeda, Tetrahedron Lett. 37 (1996) 7995. (d) A. Togni, U. Burckhardt, V. Gramlich, P.S. Pregosin, R. Salzmann, J. Am. Chem. Soc. 118 (1996) 1031. (e) J.-F. Marcoux, S. Wagan, S.L. Buchwald, J. Org. Chem. 62 (1997) 1568. (f) J.P. Wolfe, S.L. Buchwald, Tetrahedron Lett. 38 (1997) 6359. (g) P. Barbaro, A. Togni, Organometallics 14 (1995) 3570.

[3] (a) P. Molina, A. Arques, A. García, M.C. Ramírez de Arellano, Tetrahedron Lett. 38 (1997) 7613. (b) P. Molina, A. Arques, A. García, M.C. Ramírez de Arellano, Eur. J. Inorg. Chem. (1998) 1359.

[4] (a) H. Staudinger, J. Meyer, Helv. Chim. Acta 2 (1919) 635. (b) Y.G. Gololobov, I.N. Zhmurova, L.F. Kasukhin, Tetrahedron 37 (1981) 437.

[5] (a) P. Molina, A. Pastor, M.J. Vilaplana, M.C. Ramírez de Arellano, Tetrahedron Lett. (1996) 7829. (b) P. Molina, A. Pastor, M.J. Vilaplana, M.D. Velasco, M.C. Ramírez de Arellano, Organometallics 16 (1997) 5836.

[6] R.W. Reed, B. Santarsiero, R.G. Cavell, Inorg. Chem. 35 (1996) 4292.

[7] P. Molina, A. Tárraga, M.J. Lidón, J. Chem. Soc. Perkin Trans. 1 (1990) 1727.

[8] P. Molina, A. Lorenzo, E. Aller, Tetrahedron 48 (1992) 4601.

[9] (a) R.B. King, J.C. Cloyd Jr, Inorg. Chem. 14 (1975) 1550. (b) S. Hietkamp, D.J. Stufkens, K. Urieze, J. Organomet. Chem. 169 (1979) 107. (c) I. McLeod, L. Manojlovic-Muir, D. Millington, K.W. Muir, D.W.A. Sharp, R. Walker, J. Organomet. Chem. 97 (1975) C7. (d) T.G. Appleton, M.A. Bennett, Inorg. Chem. 17 (1978) 738.

[10] H.K. Gupta, S. Brydges, M.J. McGlinchey, Organometallics 18 (1999) 115.

[11] F.H. Allen, O. Kennard, Chem. Des. Autom. News 8 (1993) 31.

[12] D. Cremer, J.A. Pople, J. Am. Chem. Soc. 97 (1975) 1354.

[13] G. Giacovazzo (Ed.), Fundamentals of Crystallography, Oxford University Press, Oxford, UK, 1992, Chapter 7, pp. 490–499.

[14] (a) P. Imhoff, C.J. Elsevier, J. Organomet. Chem. 361 (1989) C61. (b) P. Imhoff, R. van Asselt, C.J. Elsevier, M.C. Zoutberg, C.H. Stam, Inorg. Chim. Acta 184 (1991) 73. (c) M.W. Avis, K. Urieze, H. Kooijman, N. Veldman, A.L. Spek, C.J. Elsevier, Inorg. Chem. 34 (1995) 4092.

[15] (a) K.V. Katti, R.J. Batchelor, F.W.B. Einstein, R.G. Cavell, Inorg. Chem. 29 (1990) 808. (b) M.W. Avis, M.E. van der Boom, C.J. Elsevier, W.J.J. Smeets, A.L. Spek, J. Organomet. Chem. 527 (1997) 263.

[16] W. Oberhauser, C. Bachmann, P. Brueggeller, Inorg. Chem. Acta 238 (1995) 35.

[17] J. Albert, J. Granell, J. Sales, X. Solans, M. Font-Altaba, Organometallics 5 (1996) 2567.

[18] H. Brunner, A. Winter, J. Breu, J. Organomet. Chem. 553 (1998) 285 and references cited therein.

[19] (a) P.D. Harvey, L.L. Gan, Inor. Chem. 31 (1991) 3239. (b) J.C. Kotz, E.E. Getty, L. Lin, Organometallics 4 (1985) 610. (c) T. Kawamoto, Y. Kushi, J. Chem. Soc. Dalton Trans. (1992) 3137.

[20] M. Sato, H. Asano, J. Organomet. Chem. 452 (1993) 105.

[21] (a) M. Pomerantz, D.S. Marynick, K. Rajeshwar, W. Chou, L. Throckmorton, E.W. Tsai, P.C.Y. Chen, T. Cain, J. Org. Chem. 51 (1986) 1223. (b) E.W. Tsai, M.K. Witczack, K. Rajeshwar, M. Pomerantz, J. Electroanal. Chem. 236 (1987) 219.

[22] (a) G. Pilloni, B. Longato, B. Corain, J. Organomet. Chem. 420 (1991) 57. (b) A. Masson-Szymczak, O. Riant, A. Gref, H.B. Kagan, J. Organomet. Chem. 511 (1996) 193. (c) B. Corain, B. Longato, G. Favero, D. Ajó, G. Pilloni, U. Russo, F.R. Kreissl, Inorg. Chim. Acta 157 (1989) 259.

[23] G.M. Sheldrick, SHELXL-93, University of Göttingen, Germany, 1993.