Journal of Organometallic Chemistry, 367 (1989) 117–132
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09791

β-Keto phosphines derived from ferrocene. Syntheses and structures of $[Ph_2PCH_2C(O)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]$ (L^1) and *trans*-$[PdCl_2L^1_2]$

Pierre Braunstein, Tânia Mara Gomes Carneiro, Dominique Matt,

*Laboratoire de Chimie de Coordination, Associé au CNRS (U.A. 416), Université Louis Pasteur,
4 rue Blaise Pascal, F-67070 Strasbourg Cédex (France)*

Fadila Balegroune, and Daniel Grandjean

*Laboratoire de Cristallochimie, Associé au CNRS (U.A. 254), Université de Rennes I,
Avenue du Général Leclerc, F-35042 Rennes Cédex (France)*

(Received October 28th, 1988)

Abstract

The keto-phosphines $[Ph_2PCH_2C(O)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]$ (L^1), $[\{Ph_2PCH_2C(O)(\eta^5\text{-}C_5H_4)\}_2Fe]$ (L^2) and $[\{Ph_2PCH_2C(O)(\eta^5\text{-}C_5H_4)\}Fe\{(\eta^5\text{-}C_5H_4)C(O)CH_3\}]$ (L^3) were respectively prepared by the reaction of Ph_2PCl with the lithium enolates derived from acetylferrocene for L^1, and 1, 1′-bis(acetyl)ferrocene for L^2 and L^3. Ligand L^1 crystallizes in the space group $P\bar{1}$ with a 8.526(2), b 10.915(3), c 12.822(3) Å, α 63.75(2), β 69.04(2), γ 70.77(2)°, V 978.4 Å^3 and Z 2. The structure was solved and refined to $R = 0.034$ and $R_w = 0.042$. The C_5-rings are eclipsed (3.2°) and the plane of the keto group forms a dihedral angle of 13.1° with the C_5H_4 plane. In the complexes *cis*- and *trans*-$[PdCl_2L^1_2]$ (*cis*-**1** and *trans*-**1**), $[(o\text{-}C_6H_4CH_2NMe_2)PdClL^1]$ (**2**), *cis*-$[PtCl_2L^1_2]$ (**3**), and $[AuClL^1]$ (**4**) the phosphine ligand(s) behave as *P*-monodentate(s). The structure of *trans*-**1** has been determined by X-ray diffraction at −145 °C. The complex crystallizes in the monoclinic space group $P2_1/c$ with a 10.622(7), b 12.647(7), c 15.59(1) Å, β 103.20(6)°, V 2039 Å^3 and $Z = 2$. The structure was solved and refined to $R = 0.037$ and $R_w = 0.053$. The palladium atom lies on a centre of symmetry and the Pd–P and Pd–Cl bond lengths are respectively 2.314(1) and 2.287(1) Å. The C_5-rings of each ligand are slightly staggered (10.5°) and, as for L^1, each keto group is almost parallel to the C_5H_4 plane (dihedral angle 8.9°). For the complex $[CuL^1_2)]BF_4$, NMR and IR solution spectroscopy has shown that there is a dynamic exchange between chelating and P-monodentate L^1. The possibility of using L^2 as a binucleating ligand was demonstrated by the preparation of the trinuclear complex $[\{(C_{10}H_8N)PdCl\}_2(\mu\text{-}L^2\text{-}P,P')]$ (**6**). The enolato complexes *cis*-$[M\{Ph_2PCH{=}C(O)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}_2]$ (M = Pd (**7**), M = Pt (**8**)), and $[(o\text{-}C_6H_4CH_2NMe_2)Pd\{Ph_2PCH{=}C(O)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}$

0022-328X/89/$03.50

$C_5H_5)\}]$ (**9**) were prepared in high yield by the reaction of NaH with complexes **1**, **3**, and **2**, respectively. Complex **9** reacts with dimethylacetylenedicarboxylate to yield the alkenyl complex $[(o\text{-}C_6H_4CH_2NMe_2)Pd\{Ph_2PCH[C(O)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)](MeO_2CC{=}CCO_2Me)\}]$ (**10**), resulting from carbon–carbon coupling between the P bound enolate-carbon atom and the alkyne. All the complexes were characterized by elemental analysis, and ^1H and $^{31}P\{^1H\}$ NMR and IR spectroscopy.

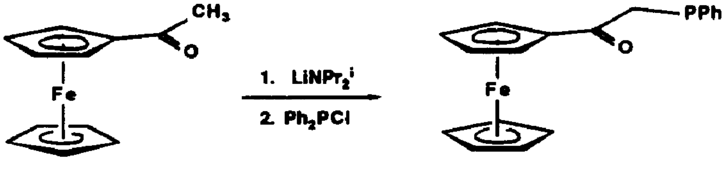
Introduction

Ligands which incorporate both a trivalent phosphorus atom and an anionic cyclopentadienide moiety have recently attracted considerable interest [1]. Such ligands are important for several reasons. For example they are suitable for the construction of polymetallic systems in which the metals are not necessarily linked together by direct metal–metal bonds but remain sufficiently close to allow a multisite activation of organic substrates or to give rise to a long range metal–metal interaction. Furthermore, since metallocenes often display high electron-transfer rates, such ligands offer interesting possibilities as systems capable of acting as redox catalysts by allowing enhancement of electron transfer properties or by acting as electron storage devices. Finally, phosphorus-substituted ferrocenes can be very efficient ligands in catalytic chemistry, in particular for those derivatives in which chelation may occur via the phosphorus atom and another functional group attached to the opposite C_5-ring [2]. In this paper we describe the synthesis and coordination properties of some new β-keto phosphines in which the carbonyl group is directly attached to a ferrocenyl group. The structure of one of them, namely $[Ph_2PCH_2C(O)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]$ (L^1), as well as that of its palladium(II) complex [*trans*-$PdCl_2L^1{}_2$] are also described.

Results and discussion

A. Synthesis of the new ligands and of related complexes

The keto-phosphine L^1 was prepared in high yield by the reaction of the lithium enolate derived of acetyl ferrocene with diphenylchlorophosphine (eq. 1). It is

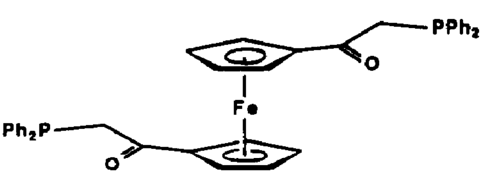


(1)

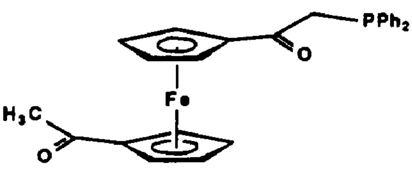
L^1

noteworthy that under the reaction conditions no O–P coupling occurred. The spectroscopic data for L^1 are given in the Experimental Section and in Table 1. Its molecular geometry has been determined by an X-ray diffraction study (see below).

The new 1, 1′-disubstituted ferrocene with two pendant keto-phosphine groups L^2 was prepared in the same way as L^1 by use of 2 equivalents of $LiNPr^i{}_2$; however the yield was not as good as that of L^1. One of the characterized by-products is the functional phosphine L^3 (for details see Experimental).



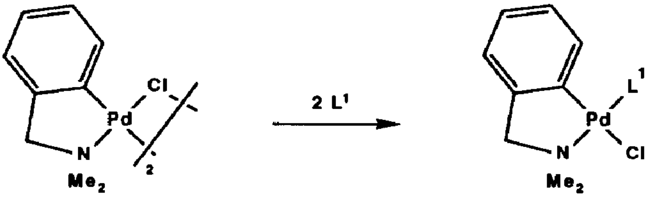
L²



L³

$$\mathrm{PdCl_2(PhCN)_2} \xrightarrow{2\,\mathrm{L^1}} \text{cis and trans-}\mathrm{PdCl_2L^1_2} \quad (2)$$

1



(3)

2

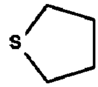
$$\mathrm{PtCl_2(PhCN)_2} \xrightarrow{2\,\mathrm{L^1}} \text{cis-}\mathrm{PtCl_2L^1_2} \quad (4)$$

3

$$\mathrm{AuCl(tht)} \xrightarrow{\mathrm{L^1}} \mathrm{AuClL^1} \quad (5)$$

4

tht =



For all three free phosphine ligands described in this work the observed $^2J(\mathrm{PH})$ coupling constant is zero. This appears to be a general feature of β-carbonylphosphines of formula $\mathrm{Ph_2PCH_2C(O)R}$, and was previously encountered for $\mathrm{Ph_2PCH_2C(O)Ph}$ and $\mathrm{Ph_2PCH_2C(O)OEt}$ [3a,4].

Phosphine $\mathrm{L^1}$ readily reacts with $[\mathrm{PdCl_2(PhCN)_2}]$, $[(\overline{o\text{-}\mathrm{C_6H_4CH_2NMe_2})\mathrm{Pd}}(\mu\text{-}\mathrm{Cl})]_2$, $[\mathrm{PtCl_2(PhCN)_2}]$ or $[\mathrm{AuCl(tht)}]$ (tht = tetrahydrothiophene) to yield complexes **1**–**4**, respectively (eq. 2–5). The spectroscopic data for these complexes are given in Table 1 and in the Experimental.

The reaction leading to complex $[\mathrm{PdCl_2L^1_2}]$ gives mixtures of the *cis* and *trans* isomers, as shown by ^{1}H and $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectroscopy. The solid state structure of *trans*-**1** was determined by a X-ray diffraction study (see below).

The cationic complex $[\mathrm{CuL^1_2}]\mathrm{BF_4}$ (**5**) was obtained by reaction of $[\mathrm{Cu(MeCN)_4}]\mathrm{BF_4}$ with 2 equivalents of $\mathrm{L^1}$. The presence in the IR spectrum of **5** in solution in $\mathrm{CH_2Cl_2}$ of absorption bands at 1650 and 1615 cm^{-1} indicates the presence of two bonding modes for $\mathrm{L^1}$, P-monodentate and P,O-chelate. From the ^{1}H and $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$) spectra, however, both ligands appear to be

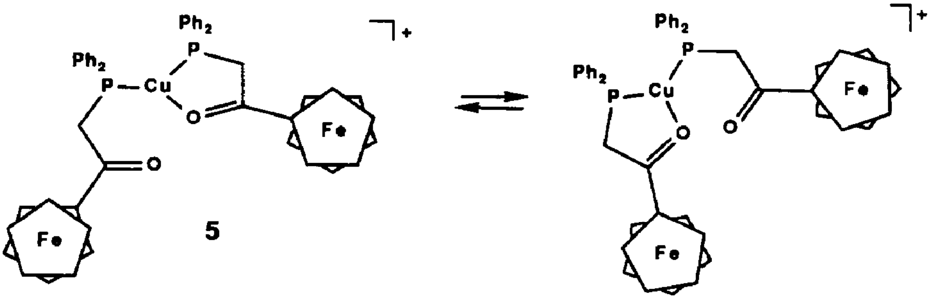
Table 1

Spectroscopic data of phosphines L^1–L^3 and their complexes

Compound	IR (KBr) (cm^{-1}) ν(C=O) or ν(C–O) + ν(C=C)	^{1}H NMR, δ(ppm) (J(PH)(Hz)) [a] PCH_2 or PCH	^{31}P{H} NMR, δ (ppm) [b]
L^1	1642	3.72(0)	−19.1
L^2	1650sh, 1632	3.45(0)	−17.5
L^3	1652, 1672	3.48(0)	−17.6
1	1654 (*trans*)	4.17 [c]	12.8 (*trans*), 22.6 (*cis*)
2	1652	4.36(12)	27.6
3	1654	4.12(13)	2.9
4	1638	3.95(11)	22.6
5	1650, 1616 [d]	3.51	−13.7
6	1660, 1651	4.37(10)	26.3
7	1522	4.24(2)	38.1
8	1530	4.37(6)	13.1
9	1510	4.47(2)	32.4
10	1682, 1653	3.53(3.5) and 4.57(14)	61.6

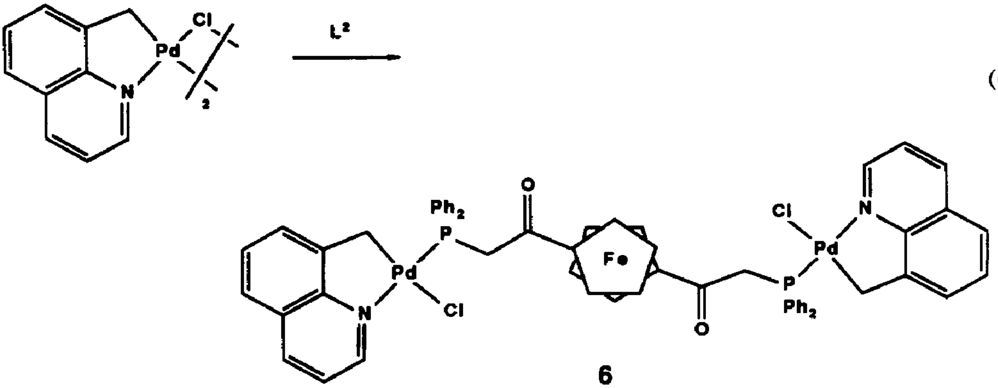
[a] Spectra in $CDCl_3$ except for L^1 (acetone-d_6). [b] Spectra in CH_2Cl_2/C_6D_6 except for L^1 (THF/D_2O ext), **1** and **4** ($CDCl_3$). [c] Overlapping signals. [d] In CH_2Cl_2.

equivalent in the temperature range −80 to 25 °C, suggesting a rapid exchange between them around a tricoordinate metal centre:



5

Obviously L^2 should be suitable for complexation of two metal centers, and the trinuclear complex **6** was indeed isolated in 87% yield when L^2 was treated with 1 equivalent of $[(\overline{C_{10}H_8N})Pd(\mu\text{-}Cl)]_2$ (eq. 6).



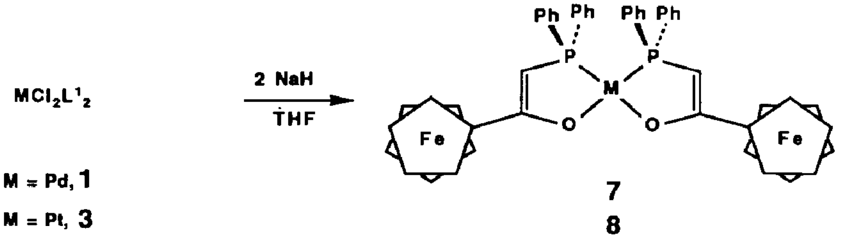
(6)

6

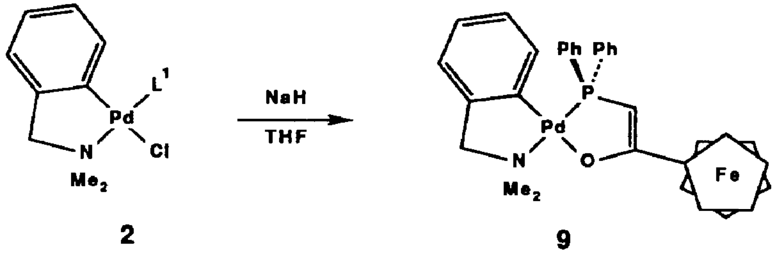
In view of the considerable interest in polynuclear ferrocenyl-based complexes [5], further studies are planned with this and related binucleating bridging ligands.

B. Enolato Complexes.

The transformation of coordinated L^1 into the corresponding enolate $(L^1)^-$ was performed by treating complexes $[MCl_2L^1_2]$ (M = Pd, **1** or M = Pt, **3**) or $[(o\text{-}C_6H_4CH_2NMe_2)PdClL^1]$ (**2**) with NaH (eq. 7, 8).



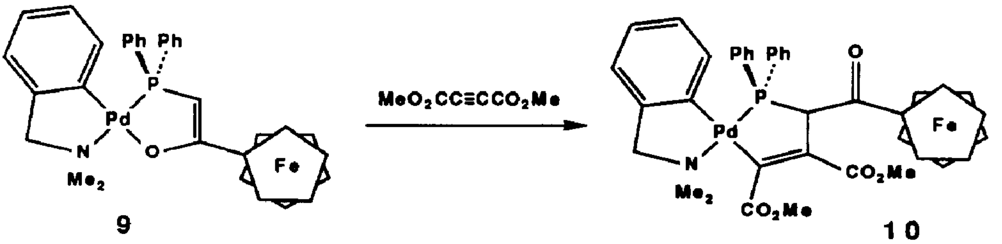
(7)



(8)

Characteristic features of these complexes include: (i) the presence in the IR spectrum of ν(C–O) + ν(C=C) bands in the region 1500–1530 cm^{-1} typical for O-coordinated enolates; (ii) the presence in the ^1H NMR spectra of **7** and **8** of a PCH doublet indicative of a *cis* arrangement.

We have shown previously that enolates of the type $[Ph_2PCH{=}C(O)R]^-$ can act as P,O chelates towards transition metal ions to form stable complexes which react with electrophilic species such as the heterocumulenes CO_2 [3] or ArNCO [6]. Such reactions proceed by carbon–carbon bond formation and are therefore particularly relevant to the activation of these heterocumulenes and to the metal-assisted generation of new polyfunctional ligands. As an extension of this reaction we have now found that complex **9** reacts with dimethylacetylenedicarboxylate ($MeO_2CC{\equiv}CCO_2Me$, DMAD) to yield the alkyne coupling product **10** (eq. 9).



(9)

This reaction generates a chiral carbon atom in the position α to the phosphorus atom, and as a consequence of this both N–CH_3 groups as well as both NC*H* protons as diastereotopic; for the same reason all the protons of the C_5H_4 ring

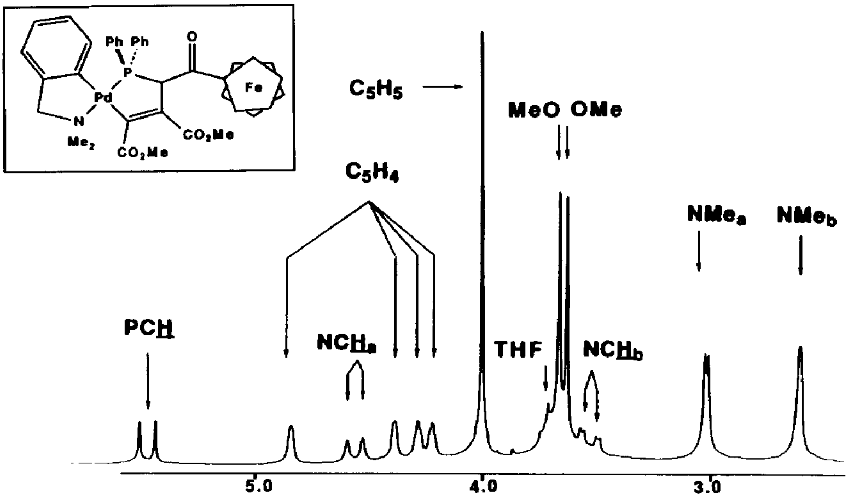


Fig. 1. Part of the ^1H NMR ($CDCl_3$) spectrum of complex **10**.

display different chemical shifts (ABCD spin system (see ^1H NMR spectrum, Fig. 1). Interestingly this reaction illustrates that the carbon atom in position α to the phosphorus atom of the enolato complex **9** has strong carbanionic character even though the complex is air-stable in the solid state.

Description of the structure of L^1

An ORTEP drawing of this molecule is shown in Fig. 2. Selected bond distances and angles are given in Table 2. The ferrocenyl moiety is very similar to that in other monosubstituted ferrocene derivatives: the rings are planar and parallel to each other within experimental error, and the CCC angles in the two C_5 rings range from 107.3(3) to 109.1(3)° and the C–C distances from 1.398(5) to 1.436(5) Å. These values are unexceptional. The Fe–C distances to the C_5 rings range from

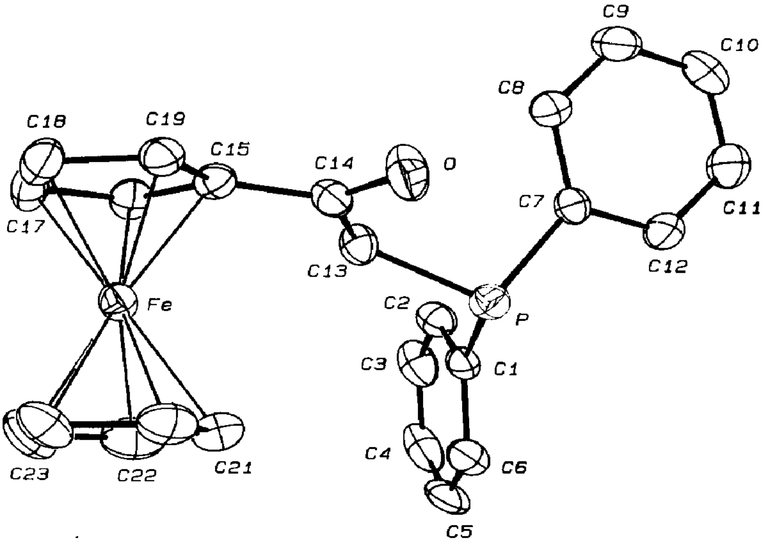


Fig. 2. ORTEP view of L^1.

Table 2

Selected interatomic distances (Å) and angles (deg) in L^1 and *trans*-**1**

	L^1	*trans*-**1**
P–C(1)	1.833(4)	1.819(4)
P–C(7)	1.833(3)	1.816(5)
P–C(13)	1.849(3)	1.824(5)
C(13)–C(14)	1.504(5)	1.518(6)
C(14)–O	1.221(4)	1.207(6)
C(14)–C(15)	1.459(4)	1.458(6)
C(15)–C(19)	1.435(5)	1.420(7)
C(17)–C(18)	1.410(5)	1.411(7)
C(21)–C(22)	1.401(5)	1.399(8)
C(22)–C(23)	1.405(6)	1.406(8)
C(23)–C(24)	1.407(6)	1.408(8)
Pd–P		2.314(1)
Pd–Cl		2.287(1)
C(7)–P–C(13)	103.5(2)	107.6(2)
C(1)–P–C(13)	97.6(1)	100.2(2)
C(1)–P–C(7)	100.2(2)	100.9(2)
P–C(13)–C(14)	113.6(2)	116.0(3)
C(13)–C(14)–O	120.8(3)	120.3(4)
O–C(14)–C(15)	121.6(3)	123.8(4)

2.018(3) to 2.050(4) Å, and are also in agreement with those for other ferrocenyl-containing complexes. The cyclopentadienyl rings are almost perfectly eclipsed (eclipse angle: 3.2°). The relatively short C(14)–C(15) distance (1.459(4) Å, vs. 1.504(5) for C(13–C(14)) suggests that the carbonyl group is conjugated with the functionalized C_5-ring, and this is consistent with the angle of only 13.1° between this C_5-ring and the O–C(14)–C(13) plane. The geometry around the phosphorus

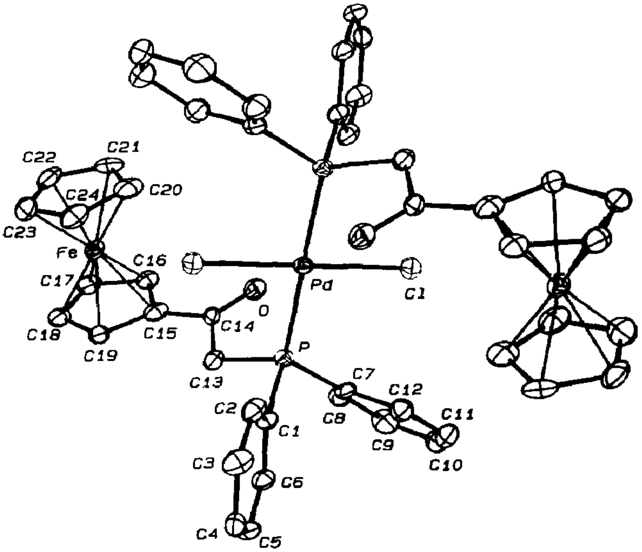


Fig. 3. ORTEP view of *trans*-$PdCl_2L^1{}_2$.

atom corresponds to that of a somewhat compressed tetrahedron (the angles between the substituents are respectively C(1)–P–C(7) 100.2(2), C(1)–P–C(13) 97.6(1), C(7)–P–C(13) 103.5(2)) but this is not unusual, and has been observed for other aryl substituted phosphines.

Description of the structure of trans-[PdCl$_2$L$^1{}_2$] (3)

An ORTEP drawing of this molecule is shown in Fig. 3. Selected bond distances and angles are given in Table 2 for comparison with those found for free L^1. This complex has a *trans* geometry, the metal atom lying on a crystallographic centre of symmetry. The distances and angles within this molecule are normal. The cyclopentadienyl moieties of the coordinated ligands are slightly staggered (10.5°). The keto group of each ligand is, as in the free phosphine, almost in perfect conjugation with the C_5H_4 ring (the dihedral angle between the C_5 ring and the OC(14)C(15) plane is 8.9°).

Conclusion

The formation of P–C coupling products is observed when the lithium enolates derived from acetyl and diacetylferrocene react with Ph_2PCl, and this extends the previously reported reactions of enolates acting as C-nucleophiles towards chlorophosphines. This allows the synthesis of a new class of β-keto ferrocenyl phosphines. These can readily be converted into coordinated phosphino enolates having a P,O bonding mode by reaction of chloro complexes of the related phosphines with NaH. All the enolate complexes described in the account are air-stable in the solid state. One of them, $[(\overline{o\text{-}C_6H_4CH_2NMe_2)\dot{P}d}\{\overline{Ph_2PCH{=}C(O})(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}]$ (**9**), reacts regioselectively with $MeO_2CC{\equiv}CCO_2Me$ to yield the palladium complex **10**, which results from a nucleophilic attack by the carbon atom of the enolate on one of the alkyne carbon atoms, with formation of a chelating phosphinoalkenyl three electron donor ligand containing also a chiral carbon atom. We are currently examining the possibility of "inserting" other organic substrates into this masked metal–carbon bond.

Experimental

General procedures

The preparations and manipulation of all compounds were carried out by use of standard techniques and equipment (Schlenk flasks, etc.) for handling air- and moisture-sensitive materials, as previously described [3]. Acetyl- and diacetyl-ferrocene [7] and $[(\overline{C \sim N)\dot{P}d}(\mu\text{-}Cl)]_2$ (where CH ~ N = dimethylbenzylamine [8], and 8-methylquinoline [9]) and $[Cu(MeCN)_4](BF_4)$ [10] were made by standard procedures. Dimethylacetylene dicarboxylate, from Aldrich, was degassed by bubbling nitrogen through it and used without further purification. Chemical shifts are in ppm, and coupling constants in Hz. A positive sign denotes a value downfield from the reference ($SiMe_4$ or H_3PO_4).

[{Ph$_2$PCH$_2$C(O)(η^5-C$_5$H$_4$)}Fe(η^5-C$_5$H$_5$)] (L^1)

A 1.6 *M* hexane solution of n-C_4H_9Li (4.9 ml, 7.9 mmol) was added dropwise to a solution of dry diisopropylamine (0.810 g, 8.0 mmol) in Et_2O (20 ml) at −78°C.

The mixture was than stirred for 0.5 h and a solution of acetylferrocene (1.802 g, 7.90 mmol) in Et_2O (30 ml) was subsequently added dropwise in 3 min with the temperature kept at −78 °C. After 1 h stirring of the mixture a solution of Ph_2PCl (1.743 g, 7.9 mmol) in Et_2O (20 ml) was added slowly. The temperature was then raised, and a brick-red precipitate gradually appeared. The mixture was stirred for 3 h at room temperature and the solvent then removed in vacuo. The residue was treated with toluene and the resulting suspension was filtered to remove LiCl. Cooling of the toluene solution afforded brick-red crystals of L^1 (2.996 g, 92%) (m.p. 142–143 °C). Anal. Found: C, 69.87; H, 5.21. $C_{24}H_{21}FeOP$ ($M_r = 412.25$) calcd.: C, 69.92; H, 5.13%. IR(KBr): 1642 s (ν(CO)) cm^{-1}. ^1H NMR (acetone-d_6): δ 3.72 (s, 2H, PCH_2), 4.20 (s, 5H, C_5H_5), 4.54 and 4.85 (two t, AA′BB′ spin system, 4H, C_5H_4), 7.37–7.57 (10H, aromatic H). $^{31}P\{^1H\}$ NMR (THF/D_2O ext.): δ − 19.1 (s).

$[\{Ph_2PCH_2C(O)(\eta^5\text{-}C_5H_4)\}_2Fe]$ (L^2) and $[\{Ph_2PCH_2C(O)(\eta^5\text{-}C_5H_4)\}Fe\{(\eta^5\text{-}C_5H_4)C(O)CH_3\}]$ (L^3)

A 1.6 *M* hexane solution of n-C_4H_9Li (11.6 ml, 18.5 mmol) was added dropwise to a solution of dry diisopropylamine (1.860 g, 18.5 mmol) in THF (40 ml) at −78 °C. After 0.5 h stirring, a solution of diacetylferrocene (2.500 g, 9.2 mmol) in THF (30 ml) was slowly added within 15 min at −78 °C. The mixture was stirred for 2 h at −78 °C then a cold (ca. −20 °C) solution of Ph_2PCl (4.080 g, 18.5 mmol) in THF (30 ml) was slowly added via a cannula. The temperature was then raised gradually and the solution stirred for 12 h at room temperature. The solvent was removed in vacuo, the brown residue was treated with toluene (40 ml), and the resulting suspension was filtered through Celite. The filtered solution was evaporated to dryness in the presence of 3 g of Kieselgel (Kieselgel 60, Merck). The resulting powder was then transferred to a chromatography column containing 400 g of Kieselgel. The column was first eluted with mixtures of AcOEt/cyclohexane (3/97–7.5/92.5 v/v) in order to remove some minor products (ca. 0.400 g) which were not identified. Then the red-brown compound L^2 (1.620 g) was obtained by elution with a mixture of ethyl acetate/cyclohexane (10/90 v/v), and the orange compound L^3 (1.210 g) by elution with ethyl acetate/cyclohexane (25/75 v/v).

Compound L^2 (m.p. 112–114 °C). Anal. Found: C, 71.82; H, 5.52. $C_{38}H_{32}FeO_2P_2$ ($M_r = 638.47$) calcd.: C, 71.49; H, 5.05%. IR (KBr): 1650 sh, 1632 vs cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.45 (s, 4H, PCH_2), 4.40 and 4.69 (two s, AA′BB′ spin system, 8H), 7.32–7.46 (20H, aromatic H). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): −17.5 (s). MS (CI/CH_4): 639 ($(M + H)^+$).

Compound L^3 (m.p. 94–96 °C). Anal. Found: C, 68.68; H, 5.06. $C_{26}H_{23}FeO_2P$ ($M_r = 454.29$) calcd.: C, 68.74; H, 5.10%. IR (KBr): 1672 vs, 1652 vs. cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.29 (s, 3H, CH_3), 3.48 (s, 2H, PCH_2), 4.42 and 4.69 (two s, AA′BB′ spin system, C_5H_4), 4.47 and 4.75 (two s br, AA′BB′ spin system, 7.34–7.48 (10H, aromatic H). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ − 17.6 (s). MS (CI/CH_4): 455 ($(M + H)^+$).

$[PdCl_2\{Ph_2PCH_2C(O)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}_2]$ (1)

To a solution of $[PdCl_2(PhCN)_2]$ (0.153 g, 0.40 mmol) in CH_2Cl_2 (15 ml) was added a solution of L^1 (0.330 g, 0.80 mmol) in CH_2Cl_2 (15 ml). The mixture first became dark red then rapidly turned to red-orange. After 0.5 h stirring the solvent was removed in vacuo. The residue was then recrystallized from CH_2Cl_2/pentane, affording red crystals of **1** (0.330 g, 82%). Anal. Found: C, 57.51; H, 4.21%. $C_{48}H_{42}Cl_2Fe_2O_2P_2Pd$ (M_r = 1001.83) calcd.: C, 57.55; H, 4.23%. IR (KBr, *trans* isomer): 1654 s br (ν(CO)) cm^{-1}. Irrespective of the mode of formation of this complex, the solution spectra always revealed the presence of the *cis* and *trans* isomers. ^1H NMR ($CDCl_3$): δ 4.05 (s, C_5H_5, first isomer), 4.16 (s, C_5H_5, second isomer), 4.17 (overlapping signals due to PCH_2), 4.37 and 4.61 (two t, AA′BB′ spin system, C_5H_4 of first isomer), 4.47 and 4.71 (two s br, AA′BB′ spin system, C_5H_4 of second isomer), 7.16–7.87 (aromatic H). $^{31}P\{^1H)\}$ NMR ($CDCl_3$): δ 12.8 (s, *trans* isomer), 22.6 (s br, *cis* isomer).

$[(o\text{-}\overline{C_6H_4CH_2NMe_2)Pd}Cl\{Ph_2PCH_2C(O)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}]$ (2)

To a solution of $[(o\text{-}C_6H_4CH_2NMe_2)Pd(\mu\text{-}Cl)]_2$ (0.980 g, 1.78 mmol) in THF (30 ml) was added a solution of L^1 (1.465 g, 3.55 mmol) in THF (15 ml). After 15 min stirring, the solution was concentrated to ca. 15 ml and the product was precipitated with pentane (ca. 100 ml). Recrystallization from THF/pentane gave **2** as a pale orange powder (2.080 g, 85%) (m.p. 165–166 °C, dec). Anal. Found: C, 59.06; H, 5.06; N, 2.09. $C_{33}H_{33}ClNFeOPPd$ (M_r = 688.31) calcd.: C, 57.52; H, 4.83; N, 2.03%. IR (KBr): 1660 sh, 1652 s (ν(CO)) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.82 (d, 6H, NMe_2, ^4J(PH) 2 Hz), 4.04 (signal overlapping with Cp, NCH_2), 4.06 (s, 5H, C_5H_5), 4.36 (d, 2H, PCH_2, ^2J(PH) 12 Hz), 4.38 and 4.73 (two s, AA′BB′ spin system, 4H), 6.33–7.93 (14H, aromatic H). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 27.6 (s).

cis-$[PtCl_2\{Ph_2PCH_2C(O)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}_2]$ (3)

A mixture of L^1 (0.410 g, 0.99 mmol) and $[PtCl_2(PhCN)_2]$ (0.235 g, 0.50 mmol) in toluene (30 ml) was refluxed for 5 min. The clear solution was then concentrated to ca. 10 ml and the orange precipitate formed was filtered off, washed with pentane, and was recrystallized from CH_2Cl_2/pentane (0.436 g, 80%) (m.p. 168–170 °C). Anal. Found: C, 52.61; H, 3.99%. $C_{48}H_{42}Cl_2Fe_2O_2P_2Pt$ (M_r = 1090.50) calcd.: C, 52.87; H, 3.89%. IR (KBr): 1654 vs (ν(CO)) cm^{-1}. ^1H NMR($CDCl_3$): δ 4.11 (s, 10H, Cp), ca. 4.12 (d, 4H, PCH_2, ^2J(PH) ca. 13 Hz (estimated because overlapping with Cp signal), 4.43 and 4.64 (two t, AA′BB′ spin system, 8H, C_5H_4), 7.11–7.58 (20H, aromatic H). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 2.9 (s with Pt satellites, J(PPt) 3770 Hz).

$[AuCl\{Ph_2PCH_2C(O)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}]$ (4)

[AuCl(tht)] (0.155 g, 0.48 mmol) was treated with L^1 (0.200 g, 0.48 mmol) in THF (35 ml). After 2 h stirring, the solution was concentrated and the product precipitated with pentane. Recrystallization from CH_2Cl_2/pentane gave **4** as orange microcrystals (0.248 g, 80%) (m.p. 203–204 °C, dec). Anal. Found: C, 44.79; H, 3.33. $C_{24}H_{21}AuClFeOP$. (M_r = 644.67) calcd.: C, 44.71; H, 3.28%. IR (KBr): 1638 s (ν(CO)) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.95 (d, 2H, PCH_2, ^2J(PH) 11 Hz), 4.16 (s, 5H, C_5H_5), 4.55 and 4.74 (two t, AA′BB′ spin system, 4H, C_5H_4), 7.43–7.74 (12H, aromatic H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 22.6 (s).

$[Cu\{Ph_2PCH_2C(O)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}_2](BF_4)$ (5)

A solution of L^1 (0.160 g, 0.39 mmol) in CH_2Cl_2 (5 ml) was added to a solution of $[Cu(MeCN)_4](BF_4)$ (0.061 g, 0.19 mmol) in CH_2Cl_2 (5 ml). After 1 h stirring the red solution was concentrated and the product was precipitated with pentane. Recrystallization from CH_2Cl_2/pentane gave **5** as carmine red microcrystals (0.150 g, 77%). Anal. Found: C, 57.55; H, 4.40. $C_{48}H_{42}BCuF_4Fe_2O_2P_2 \cdot 0.5\ CH_2Cl_2$ ($M_r = 1017.32$) calcd.: C, 57.85; H, 4.26%. IR (CH_2Cl_2): 1650 s, 1616 m cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.51 (s br, 4H, PCH_2), 3.95 (s, 10H, C_5H_5), 4.41 and 4.62 (two s br, 8H, C_5H_4), 7.15–7.33 (20 H, aromatic H). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6, 25 °C): δ −13.7 (s).

$[\{\overline{(C_{10}H_8N)Pd}Cl\}_2(\mu\text{-}L^2\text{-}P,P')]$ *(6)*

To a solution of $[\overline{C_{10}H_8N)Pd}(\mu\text{-}Cl)]_2$ (0.213 g, 0.37 mmol) in CH_2Cl_2 (10 ml) was added a solution of L^2 (0.240 g, 0.38 mmol) in CH_2Cl_2 (10 ml). After 15 min stirring the solution was filtered and the solvent removed in vacuo. Recrystallization from CH_2Cl_2/pentane gave **6** as an orange-brown powder (0.388 g, 87%) (m.p. ca. 165 °C). Anal. Found: C, 57.16; H, 3.75. $C_{58}H_{48}Cl_2FeN_2O_2P_2Pd_2$ ($M_r = 1206.53$) calcd.: C, 57.74; H, 4.01; N: 2.32%. IR (KBr): 1660 s (ν(CO)), 1651 s (ν(CO)) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.86 (d, 4H, CH_2Pd, ^3J(PH) 3 Hz), 4.37 (d, 4H, PCH_2, ^2J(PH) 10 Hz), 4.43 and 4.66 (two signals, AA′BB′ spin system, 8H, C_5H_4), 7.30–9.61 (32H, aromatic H). $^{31}P\{^1H\}$NMR (CH_2Cl_2/C_6D_6): δ 26.3 (s).

cis-$[\overline{Pd\{Ph_2PCH{=}C(O}){(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}_2}]$ *(7)*

A THF (35 ml) solution of $[PdCl_2(SEt_2)_2]$ (0.114 g, 0.32 mmol) and L^1 (0.263 g; 0.64 mmol) was stirred with NaH (ca. 0.016 g; 0.66 mmol). After 12 h, a microcrystalline precipitate had formed. The iridescent suspension was filtered, and the orange precipitate recrystallized from CH_2Cl_2/pentane to afford **7** as an orange powder (0.282 g, 95%) (mp > 230 °C). Anal. Found: C, 60.23; H, 4.41. $C_{48}H_{40}Fe_2O_2P_2Pd \cdot 0.5\ CH_2Cl_2$ ($M_r = 971.36$) calcd.: C, 59.97; H, 4.25%. IR (KBr): 1522 s (ν(C–O) + ν(C=C)) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 4.17 (s, 10 H, C_5H_5), 4.24 (d, 2H, PCH, ^2J(PH) 2 Hz), 4.30 and 4.71 (two t, AA′BB′ spin system, 8H, C_5H_4), 7.07–7.40 (24H, aromatic H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 38.1 (s).

$[\overline{Pt\{Ph_2PCH{=}C(O}){(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}_2}]$ *(8)*

A solution of complex **3** (0.410 g, 0.38 mmol) in THF (50 ml) was stirred with NaH (0.019 g, 0.8 mmol) for 15 h. The iridescent suspension was then filtered, and the precipitate was washed with water then dried in vacuo. Recrystallization from CH_2Cl_2/pentane gave a pale orange powder (0.340 g, 85%) (m.p. > 230 °C). Anal. Found: C, 55.15; H, 4.23. $C_{48}H_{40}Fe_2O_2P_2Pt \cdot 0.5\ CH_2Cl_2$ ($M_r = 1055.03$) calcd.: C, 55.21; H, 3.91%. IR (KBr): 1530 s (ν(C–O) + ν(C=C)). ^1H NMR ($CDCl_3$): δ 4.14 (s, 10H, C_5H_5), 4.24 and 4.74 (two t, AA′BB′ spin system, 8H, C_5H_4), 4.37 (d with Pt satellites, 2H, PCH, ^2J(PH) 6 Hz, ^3J(PtH) ≈ 32 Hz), 7.01–7.38 (20 H, aromatic H). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 13.1 (s with Pt satellites, J(PPt) 3528 Hz).

$[(o\text{-}\overline{C_6H_4CH_2NMe_2)}\overline{Pd\{Ph_2PCH{=}C(O}){(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)\}}]$ *(9)*

A solution of complex **2** (0.932 g, 1.35 mmol) in THF (20 ml) was stirred with NaH (0.033 g, 0.37 mmol) for 15 h. The turbid mixture was then concentrated to half volume and pentane was added. The product and NaCl were filtered off on a glass frit, washed with pentane and dried. Complex **9** was then dissolved in toluene from the frit and the solution passed directly into another Schlenk flask. Addition of pentane to the toluene solution afforded **9** as a pale orange powder (0.696 g, 78%)

(m.p. 203–205 °C, dec). Anal. Found: C, 62.14; H, 5.86; N, 1.98. $C_{33}H_{32}NFeOPPd$ (M_r = 651.85) calcd.: C, 60.81; H, 4.95; N, 2.15%. IR (KBr): 1510 s (ν(C–O) + ν(C=C)) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.92 (d, 6H, NMe_2, ^4J(PH) 2 Hz), 3.99 (s br, 2H, NCH_2), 4.10 (s, 5H, C_5H_5), 4.17 and 4.63 (two t, AA′BB′ spin system, 4H, C_5H_4), 4.47 (d, 1H, PCH, ^2J(PH) 3 Hz), 6.69–7.79 (14H, aromatic H). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 32.4 (s).

[(o-$C_6H_4CH_2NMe_2$)Pd{$Ph_2PCH[C(O)(\eta^5$-$C_5H_4)Fe(\eta^5$-$C_5H_5)](MeO_2CC=CCO_2Me)$}] (10)

Complex **9** (0.250 g, 0.38 mmol) was treated with $MeO_2CC{\equiv}CCO_2Me$ (0.057 g, 0.40 mmol) in THF (15 ml) for 72 h. The product was then precipitated with pentane, filtered off, and washed several times with pentane. Recrystallization from THF/pentane gave **10** as an analytically pure orange powder (0.259 g, 86%) (m.p.

Table 3

Crystal data and data collection for L^1 and *trans*-$PdCl_2L^1_2$

	L^1	*trans*-$PdCl_2L^1_2$
formula	$C_{24}H_{21}FeOP$	$C_{48}H_{42}Cl_2Fe_2O_2P_2Pd$
fw	412.25	1001.83
cryst syst.	triclinic	monoclinic
space group	$P\bar{1}$, no. 2	$P2_1/c$, no. 14
a, Å	8.526 (2)	10.622 (7)
b, Å	10.915 (3)	12.647 (7)
c, Å	12.822 (3)	15.59 (1)
α, deg	63.75 (2)	90.00
β, deg	69.04 (2)	103.20 (6)
γ, deg	70.77 (2)	90.00
V, $Å^3$	978.4	2039
Z	2	2
ρ_{calcd}, g/cm^3	1.399	1.632
cryst dimens, mm	0.38 × 0.25 × 0.13	0.40 × 0.28 × 0.20
$F(000)$	428	1016
systematic absences	none	$h0l$ $l \neq 2n$; $0k0$ $k \neq 2n$
Temperature, °C	23 ± 2	− 145 ± 2
diffractometer	Enraf–Nonius CAD 4	Enraf–Nonius CAD 4
radiation (graphite monochromator)	(λ(Mo-K_α) 0.71073)	(λ(Mo-K_α) 0.71073)
linear abs coeff, cm^{-1}	8.595	13.823
scan type	$\omega/2\theta$	$\omega/2\theta$
scan range, deg	$1 + 0.35 \tan\theta$	$1 + 0.35 \tan\theta$
θ limits, deg	1–25	1–25
no. of data collected	3121	3985
no. of unique data used	2048 $[F_o^2 > 3\sigma(F_o^2)]$	2414 $[F_o^2 > 4\sigma(F_o^2)]$
no. of variables	245	260
decay, %	< 2	< 4
$R = \Sigma(\lVert F_o \rvert - \lvert F_c \rVert)/\Sigma \lvert F_o \rvert$	0.034	0.037
$R_w = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2/\Sigma w \lvert F_o \rvert^2]^{1/2}$	0.042	0.053
GOF = $[\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2/N$ observ. $- N$ param.$]^{1/2}$	1.219	1.278
largest shift/esd, final cycle	0.01	0.01
largest peak, e/$Å^3$	0.58	1.50
fudge factor	0.05	0.07

Table 4

Positional parameters and their estimated standard deviations for L^1

Atom	x	y	z	$B(\mathrm{\AA}^2)$	Atom	x	y	z	$B(\mathrm{\AA}^2)$ [a]
Fe	0.05796(6)	0.25758(5)	0.31417(4)	2.69(1)	C22	0.0619(5)	0.3846(4)	0.3917(3)	4.9(1)
P	−0.5116(1)	0.60349(9)	0.29580(7)	3.02(2)	C23	0.2072(5)	0.2756(4)	0.3992(3)	5.1(1)
O	−0.3860(3)	0.3231(2)	0.2760(2)	4.68(8)	C24	0.1498(5)	0.1490(4)	0.4639(3)	4.3(1)
C1	−0.4694(4)	0.7707(3)	0.2684(3)	3.01(8)	H2	−0.4266	0.8569	0.0863	5*
C2	−0.4290(4)	0.8725(3)	0.1542(3)	3.6(1)	H3	−0.3644	1.0616	0.0585	5*
C3	−0.3927(5)	0.9946(4)	0.1373(4)	4.8(1)	H4	−0.3733	1.1044	0.2217	5*
C4	−0.3971(5)	1.0195(4)	0.2334(4)	5.5(1)	H5	−0.4386	0.9390	0.4146	5*
C5	−0.4360(5)	0.9215(4)	0.3477(3)	5.4(1)	H6	−0.4972	0.7287	0.4444	5*
C6	−0.4715(5)	0.7963(4)	0.3655(3)	4.3(1)	H8	−0.5226	0.5571	0.0869	5*
C7	−0.6562(4)	0.6632(3)	0.1984(3)	2.66(8)	H9	−0.7188	0.6378	−0.0268	5*
C8	−0.6263(4)	0.6203(3)	0.1050(3)	3.39(9)	H10	−0.9768	0.7883	0.0169	5*
C9	−0.7436(5)	0.6673(4)	0.0379(3)	4.1(1)	H11	−1.0362	0.8580	0.1769	5*
C10	−0.8961(5)	0.7561(4)	0.0636(3)	4.4(1)	H12	−0.8365	0.7826	0.2874	5*
C11	−0.9304(5)	0.7978(4)	0.1574(3)	4.8(1)	H13A	−0.2999	0.5882	0.1236	5*
C12	−0.8115(4)	0.7523(4)	0.2232(3)	3.9(1)	H13B	−0.2142	0.5562	0.2237	5*
C13	−0.3024(4)	0.5387(3)	0.2064(3)	3.27(9)	H16	0.0580	0.4737	0.1028	5*
C14	−0.2682(4)	0.3852(3)	0.2319(3)	2.99(9)	H17	0.3199	0.2782	0.1133	5*
C15	−0.0900(4)	0.3142(3)	0.2012(3)	2.79(9)	H18	0.2239	0.0487	0.2270	5*
C16	0.0583(4)	0.3767(3)	0.1404(3)	3.23(9)	H19	−0.0999	0.0977	0.2872	5*
C17	0.2042(4)	0.2671(4)	0.1466(3)	4.0(1)	H20	−0.1015	0.1135	0.5410	5*
C18	0.1506(5)	0.1385(4)	0.2100(3)	3.8(1)	H21	−0.2007	0.3769	0.4591	5*
C19	−0.0302(4)	0.1657(3)	0.2439(3)	3.16(9)	H22	0.0631	0.4814	0.3529	5*
C20	−0.0295(5)	0.1797(4)	0.4964(3)	4.0(1)	H23	0.3234	0.2855	0.3663	5*
C21	−0.0851(5)	0.3268(4)	0.4509(3)	4.1(1)	H24	0.2206	0.0582	0.4824	5*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{4}{3}[a^2\beta_{1,1} + b^2\beta_{2,2} + c^2\beta_{3,3} + ab(\cos\gamma)\times\beta_{1,2} + ac(\cos\beta)\times\beta_{1,3} + bc(\cos\alpha)\times\beta_{2,3}]$.

169–170 °C). Anal. Found: C, 59.18; H, 4.94; N, 1.68. $C_{39}H_{38}NFeO_5PPd$ calcd.: C, 59.00; H, 4.82; N, 1.76%. IR (KBr): 1682 vs, 1653 s cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.63 (d, 3H, NMe, ^4J(PH) 1.4 Hz), 3.03 (d, 3H, NMe, ^4J(PH) 3 Hz), δ_A 4.57 and δ_B 3.53 (ABX spin system (X = P), 2H, NCH_2, ^2J(AB) 14 Hz, ^4J(PA) 0 Hz, ^4J(PB) 3.5 Hz), 3.64 (s, 3H, OMe), 3.67 (s, 3H, OMe), 4.01 (s, 5H, C_5H_5), 4.22 (m, 1H of C_5H_4), 4.29 (m, 1H of C_5H_4), 4.39 (m, 1H of C_5H_4), 4.85 (m, 1H of C_5H_4) 5.48 (d, 1H, PCH, ^2J(PH) 14 Hz), 6.45–8.13 (14 H, aromatic H). $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 61.6 (s).

Crystal structure determination of L^1

Single crystals of L^1 (red prisms with hexagonal shape) were obtained by cooling a toluene solution. Cell constants and other pertinent data are listed in Table 3. Data collection was at room temperature (23 ± 2 °C). Precise lattice parameters were determined by standard Enraf–Nonius least-squares methods using 25 carefully selected reflections. Intensity data were collected on an automatic four-circle diffractometer. No intensity decay was observed during the data collection period.

Table 5

Positional parameters and their estimated standard deviations for *trans*-$PdCl_2L^1_2$

Atom	x	y	z	$B(\text{Å}^2)$ [a]
Pd	0.000	0.000	0.000	1.292(9)
Fe	0.34607(7)	0.15891(5)	0.31200(5)	1.63(1)
Cl	−0.0148(1)	0.0385(1)	−0.14532(8)	1.98(2)
P	−0.0684(1)	0.1674(1)	0.02858(8)	1.35(2)
O	0.2129(3)	0.2242(3)	0.0765(2)	2.39(8)
C1	−0.2297(4)	0.1653(4)	0.0501(3)	1.48(9)
C2	−0.2898(5)	0.0707(4)	0.0627(3)	1.9(1)
C3	−0.4106(5)	0.0706(4)	0.0800(4)	2.2(1)
C4	−0.4744(5)	0.1645(4)	0.0856(3)	1.8(1)
C5	−0.4140(5)	0.2595(4)	0.0744(3)	1.9(1)
C6	−0.2937(5)	0.2602(4)	0.0567(3)	1.8(1)
C7	−0.0878(5)	0.2682(4)	−0.0563(3)	1.6(1)
C8	−0.0118(5)	0.3583(4)	−0.0489(4)	2.1(1)
C9	−0.0378(6)	0.4344(4)	−0.1148(4)	2.7(1)
C10	−0.1343(6)	0.4199(5)	−0.1894(4)	2.8(1)
C11	−0.2059(6)	0.3281(5)	−0.1984(4)	2.8(1)
C12	−0.1829(5)	0.2531(4)	−0.1325(4)	2.2(1)
C13	0.0224(5)	0.2259(4)	0.1311(3)	1.7(1)
C14	0.1670(5)	0.2369(4)	0.1398(3)	1.51(9)
C15	0.2424(5)	0.2663(4)	0.2269(4)	1.9(1)
C16	0.3793(5)	0.2923(4)	0.2479(3)	1.8(1)
C17	0.4160(5)	0.3080(4)	0.3404(4)	2.1(1)
C18	0.3073(5)	0.2915(4)	0.3764(4)	2.1(1)
C19	0.2011(5)	0.2659(4)	0.3074(3)	1.8(1)
C20	0.3423(6)	0.0139(4)	0.2522(4)	2.6(1)
C21	0.4710(5)	0.0439(4)	0.2896(4)	2.5(1)
C22	0.4847(6)	0.0603(4)	0.3800(4)	2.7(1)
C23	0.3646(6)	0.0405(5)	0.4003(4)	2.8(1)
C24	0.2763(6)	0.0110(4)	0.3221(4)	2.6(1)

[a] Anisotropic parameters are given in the form of the isotropic equivalent displacement parameter defined as $\frac{4}{3}[a^2\beta_{1,1} + b^2\beta_{2,2} + c^2\beta_{3,3} + ab(\cos\gamma)\times\beta_{1,2} + ac(\cos\beta)\times\beta_{1,3} + bc(\cos\alpha)\times\beta_{2,3}]$.

For all subsequent computations the Enraf–Nonius SDP package was used [11]. Intensities were corrected for Lorentz polarization factors. Absorption corrections were omitted in view of the low linear absorption coefficient. The crystal structure was solved by using the MULTAN [12] program and refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. The function minimized was $\Sigma(w|F_o| - |F_c|)^2$, where the weight w is $[1/4(\sigma^2(I)/I + (0.05I)^2/I)]^{-1}$. Hydrogen atoms were placed at their calculated positions (C–H distance 0.95 Å) for structure factor calculations and were assigned isotropic thermal parameters of B 5.0 Å^2. The neutral-atom scattering factors used for all atoms and anomalous scattering factors for all non-hydrogen atoms were obtained from standard source. The results of refinements are given in Table 3. Atomic coordinates with estimated standard deviations corresponding to the final least-squares refinement cycles are given in Table 4. Hydrogen atom coordinates, anisotropic thermal parameters for all non-hydrogen atoms, a complete list of bond distances and angles, a list of angles between selected planes, and lists of observed and calculated structure factors are available from the authors.

Crystal structure determination of trans-$PdCl_2L^1{}_2$

Single red parallelepipeds of *trans*-$PdCl_2L^1{}_2$ (*trans*-**1**) were obtained by slow diffusion of pentane into a CH_2Cl_2 solution of the complex. Data collection was performed at −145 °C to avoid the intensity decay otherwise observed [13]. The structure was solved by using the Patterson and Fourier difference methods and refined as for L^1. The weighting scheme was $[1/4(\sigma^2(I)/I + (0.07I)^2/I)]^{-1}$. Hydrogen atoms were placed at calculated positions (C–H 0.95 Å) in the structure factor calculations and were assigned isotropic thermal parameters of B 3.0 Å^2. The results of refinement are given in Table 3, and atomic coordinates in Table 5. All other data are available on request from the authors.

Acknowledgments

We are grateful to Prof. J. Fischer for the drawings, Dr. R. Bender for interesting discussions, and Madame A. Degrémont for experimental assistance. We thank the CNPq (Brazil) for a grant to T.M.G.C.

References

1 See for example: (a) N.E. Shore, J. Am. Chem. Soc., 101 (1979) 7410; (b) D. Seyferth and H.P. Withers, Jr., J. Organomet. Chem., 185 (1980) C1; (c) J.C. Leblanc, C. Moise, A. Maisonnat, R. Poilblanc, C. Charrier and F. Mathey, ibid., 231 (1982) C43; (d) I.R. Butler and W.R. Cullen, Can. J. Chem., 61 (1983) 147; (e) M.D. Rausch, B.H. Edwards, R.D. Rogers and J.L. Atwood, J. Am. Chem. Soc., 105 (1983) 3882; (f) C.P. Casey, R.M. Bullock and F. Nief, ibid., 105 (1983) 7574; (g) T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi and K. Hirotsu, ibid., 106 (1984) 158; (h) E. Român, V. Castro and M. Camus, J. Organomet. Chem., 293 (1985) 93; (i) V.I. Losilkina, M.N. Estekhina, N.K. Baranetskaya and V.N. Setkina, ibid., 299 (1986) 187; (j) D.L. DuBois, C.W. Eigenbrot, Jr., A. Miedaner and J.C. Smart, Organometallics, 5 (1986) 1405; (k) X. He, A. Maisonnat, F. Dahan and R. Poilblanc, ibid., 6 (1987) 67; (l) R.M. Bullock and C.P. Casey, Acc. Chem. Res., 20 (1987) 167.

2 (a) T. Hayashi, M. Konishi, K.-I. Yokota and M. Kumada, J. Organomet. Chem., 285 (1985) 359; (b) T. Hayashi, Pure & Appl. Chem., 60 (1988) 7.

3 (a) P. Braunstein, D. Matt, Y. Dusausoy, J. Fischer, A. Mitschler and L. Ricard, J. Am. Chem. Soc., 103 (1981) 5115; (b) P. Braunstein, D. Matt and D. Nobel, ibid., 110 (1988) 3207.
4 S.-E. Bouaoud, P. Braunstein, D. Grandjean, D. Matt and D. Nobel, Inorg. Chem., 25 (1986) 3765.
5 (a) G. Marr and B.W. Rockett, J. Organomet. Chem., 343 (1988) 79; (b) M. Onishi, K. Hiraki, S. Wada and Y. Ohana, Polyhedron, 6 (1987) 1243.
6 S.-E. Bouaoud, P. Braunstein, D. Grandjean, D. Matt and D. Nobel, Inorg. Chem., 2 (1988) 2279.
7 M. Rosenblum and R.B. Woodward, J. Am. Chem. Soc., 80 (1958) 5443.
8 A.C. Cope and E.C. Friedrich, J. Am. Chem. Soc., 90 (1968) 909.
9 G.E. Hartwell, R.V. Lawrence and H.J. Smas, J. Chem. Soc. D, (1970) 912.
10 G.J. Kubas, Inorg. Synth., (1979) 90.
11 B.A. Frenz in H. Schenk, Olthof-Hazekamp, H. van Konigsveld, G.S. Bassi (Eds.), The Enraf–Nonius CAD4-SDP, Computing in Crystallography, University Press, Delft, The Netherlands, 1979, p. 64.
12 G. Germain, P. Main and M.M. Woolfson, Acta Crystallogr. A, 27 (1971) 368.
13 J. Fischer, personal communication.