SYNTHESIS AND COORDINATION BEHAVIOUR OF A PHOSPHANYL(VINYL)FERROCENE

Petr ŠTĚPNIČKA[1,*] and Ivana CÍSAŘOVÁ[2]

Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030, 128 40 Prague 2, Czech Republic; e-mail: [1] stepnic@natur.cuni.cz, [2] cisarova@natur.cuni.cz

Received November 30, 2005
Accepted January 4, 2006

Dedicated to Professor Jaroslav Podlaha on the occasion of his 70th birthday.

Donor properties of 1-(diphenylphosphanyl)-1′-vinylferrocene (**1**) were investigated in a series of reactions with palladium(II), rhodium(I), and copper(I) compounds. In all complexes obtained, compound **1** coordinates exclusively as a monodentate phosphorus donor, giving *trans*-[$PdCl_2$(**1**-κ*P*)$_2$] (**3**) with [$PdCl_2$(cod)], [PdCl(L^{NC})(**1**-κ*P*)] (**4**) with [{Pd(L^{NC})}$_2$(μ-Cl)$_2$], and *trans*-[RhCl(CO)(**1**-κ*P*)$_2$] (**5**) with [{$Rh(CO)_2$}$_2$(μ-Cl)$_2$] (cod = cycloocta-1,5-diene, L^{NC} = 2-[(dimethylamino)methyl-κ*N*]phenyl-κ*C*[1]). Copper(I) precursors CuI and [$Cu(MeCN)_4$]PF_6 reacted with **1** in a similar manner, yielding at appropriate molar ratios heterocubane [(μ_3-I)$_4${Cu(**1**-κ*P*)}$_4$] (**6**) and the bis(phosphane) complex [Cu(MeCN)(**1**-κ*P*)$_2$]PF_6 (**7**), respectively. The structures of 1-(diphenylthiophosphoryl)-1′-vinylferrocene (**2**), **3**, **4**·$CHCl_3$, **6**·C_6H_6, and **7** have been determined by single-crystal X-ray diffraction.

Keywords: Ferrocenes; Phosphinoalkene; Palladium(II); Rhodium(I); Copper(I) complexes; Structure elucidation; P-ligands; X-ray diffraction.

Bidentate phosphanylferrocene ligands derived from 1,1′-disubstituted ferrocene, Ph_2PfcY (**I**), where fc denotes ferrocen-1,1′-diyl and Y a donor group, have found numerous applications as ligands in the synthesis of organometallic and coordination compounds and in transition metal-catalyzed organic transformations[1]. Nevertheless, their coordination chemistry remains still rather a virgin field, particularly if one considers the wealthy chemistry of the single symmetric representative, 1,1′-bis(diphenylphosphanyl)ferrocene (Y = PPh_2)[2].

Many heterobidentate phosphanylferrocenes of the **I**-type are known; the prominent examples include compounds, where Y is CO_2H and CO_2Me (ref.[3]), CHO (ref.[4]), C(O)Me (ref.[5]), CR_2OH (refs[4c,5]), OR (ref.[6]), $P(OR)_2$ (ref.[7]), $P(E)Ph_2$ (E = O, S, Se) (refs[4b,8]), SR (ref.[9]), $CH(Me)NMe_2$ (refs[4a,5]), or

Collect. Czech. Chem. Commun. 2006, Vol. 71, No. 2, pp. 215–236

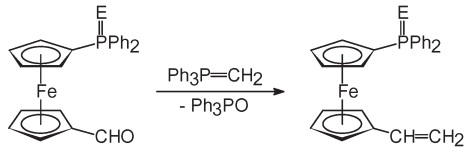
doi:10.1135/cccc20060215

some N-heterocyclic moieties[10]. However, only several representatives of these potential donors have been tested as ligands or catalyst components, the compounds typically serving as intermediates for further syntheses. A closer look at the above list of the Y groups reveals it to contain only a few soft-donor functional groups and no π-donor systems. This prompted our interest in the syntheses and ligating properties of ferrocene phosphanes bearing unsaturated groups. First, we turned to 1-(diphenylphosphanyl)-1′-vinylferrocene (**1**). Compound **1** – the archetype of this kind of mixed donors – has already been mentioned in the literature as a serendipitous by-product arising from acid-catalyzed dehydration of $Ph_2PfcCH(Me)OH$ (ref.[5]), and later utilized in reactions with alkylideneruthenium complex $[(Cy_3P)_2Cl_2Ru{=}CHPh]$ (Cy = cyclohexyl)[11]. However, neither rational synthesis of **1** nor systematic study into its donor properties have been reported to date. This contribution deals with the synthesis and coordination behavior of **1** towards palladium(II), rhodium(II), and copper(I).

RESULTS AND DISCUSSION

*Ligand **1** and Its P-sulfide*

As indicated in Scheme 1, 1-(diphenylphosphanyl)-1′-vinylferrocene (**1**) was obtained by a Wittig reaction between 1′-(diphenylphosphanyl)ferrocene-1-carbaldehyde and ylide $Ph_3P{=}CH_2$ prepared in situ from methyl(triphenyl)phosphonium bromide and butyllithium. The product was isolated by column chromatography in high yield as a dark amber oil that slowly solidified to a rusty brown solid. A similar reaction with 1′-(diphenylthiophosphoryl)ferrocene-1-carbaldehyde gave the corresponding (diphenylthiophosphoryl)vinylferrocene (**2**) as a rusty brown solid. Both compounds were characterized by standard methods and the solid-state structure of **2** was determined by X-ray diffraction methods.



SCHEME 1

^{1}H NMR spectra of the compounds show signals typical of the AMX spin system of the vinyl group and characteristic multiplets attributable to two spin systems arising from the cyclopentadienyls of the 1,1′-disubstituted ferrocene unit (AA′BB′ and AA′BB′X, where A, B = ^{1}H, and X = ^{31}P). Likewise, the ^{13}C NMR spectra are consistent with the formulation, exerting signals due to vinyl groups (δ_C ca. 112 (=CH_2) and ca. 134 (=CH)), and phosphorus-coupled resonances of the cyclopentadienyl and phenyl carbons. The nature of the phosphorus group is best reflected in ^{31}P NMR spectra, showing single resonances at δ_P –16.3 and +42.1 for **1** and **2**, respectively, and by the magnitude of the J_{PC} coupling constants in the ^{13}C NMR spectra.

Mass spectra of **1** and **2** are dominated by the molecular ions (base peaks) and show many common features (e.g., ions $[C_5H_5Fe]^+$ and Fe^+, and fragments at *m/z* 183, 170/171; ref.[12]). However, whereas in fragmentation of $\mathbf{2}^{\bullet+}$ elimination of vinyl-substituted cyclopentadienyl ring predominates ($\mathbf{2}^{\bullet+} \rightarrow$ *m/z* 337), compound **1** shows no such pronounced fragmentation preference: in addition to the common fragments, only ions at *m/z* 319 ([M – Ph]$^+$) with relative abundance higher than 10% can be observed.

As mentioned above, the solid-state structure of **2** has been determined by single-crystal X-ray diffraction analysis. The unit cell of **2** accommodates two symmetrically independent but practically identical molecules. A view of molecule **1** is shown in Fig. 1 together with selected geometric data for both molecules.

The 1,1′-disubstituted ferrocene moieties in **2** are quite regular and adopt conformations close to synclinal eclipsed with torsion angles C(1)–Cg(1)–Cg(2)–C(6) (molecule **1**) and C(31)–Cg(3)–Cg(4)–C(36) (molecule **2**) of 81.3(1) and –79.7(1)°, respectively (cf. the ideal value of 72°)[13]. The double bonds are tilted from the plane of the parent cyclopentadienyl rings, the angles subtended by the double bonds and the planes being 18.5(2)° (C(23)=C(24) vs Cp(1)) and 15.2(2)° (C(53)=C(54) vs Cp(3)). The double bond lengths, 1.314(3) Å in both molecules, are similar to those in, e.g., 1′,1‴-divinylbiferrocene (1.300(7) Å)[14] and dicarbonylnitrosyl{η^5-[(1′-vinylferrocen-1-yl)methyl]cyclopentadienyl}chromium(0) (1.296(8) Å)[15].

Preparation and Structural Characterization of Complexes

Coordination behavior of phosphanyl(vinyl)ferrocene **1** was investigated in reactions with several palladium(II), rhodium(I), and copper(I) compounds. Regardless of the metal source, the reactions afforded only com-

plexes with monodentate **1**. Thus, $[PdCl_2(cod)]$ (cod = cycloocta-1,5-diene) reacts with two molar equivalents of **1** under replacement of the cod ligand to give the diphosphine complex *trans*-$[PdCl_2(\mathbf{1}\text{-}\kappa P)_2]$ (**3**) while the dimer $[\{Pd(L^{NC})\}_2(\mu\text{-}Cl)_2]$, where L^{NC} = 2-[(dimethylamino)methyl-κ*N*]phenyl-κC^1, yields the expected bridge-cleavage product, $[PdCl(L^{NC})(\mathbf{1}\text{-}\kappa P)]$ (**4**) (Scheme 2). Attempts to prepare complexes with chelating (i.e., η^2:κ*P*-bound) **1** either by reacting the ligand with $[PdCl_2(cod)]$ at 1:1 molar ratio or by halide removal with silver perchlorate from **3**, failed.

Complexes **3** and **4** are air-stable crystalline solids that tend to bind traces of solvents used in the syntheses or crystallization. Their structures were determined from NMR spectra and further corroborated by X-ray crystallography. Exclusive P-coordination of **1** in these compounds is manifested by virtually unaffected ^{1}H signals due to the vinyl group ($\Delta\delta_H < 0.2$, $|\Delta\delta_C| < 1$ ppm) and by the shift of the ^{31}P NMR resonances to lower field. The ob-

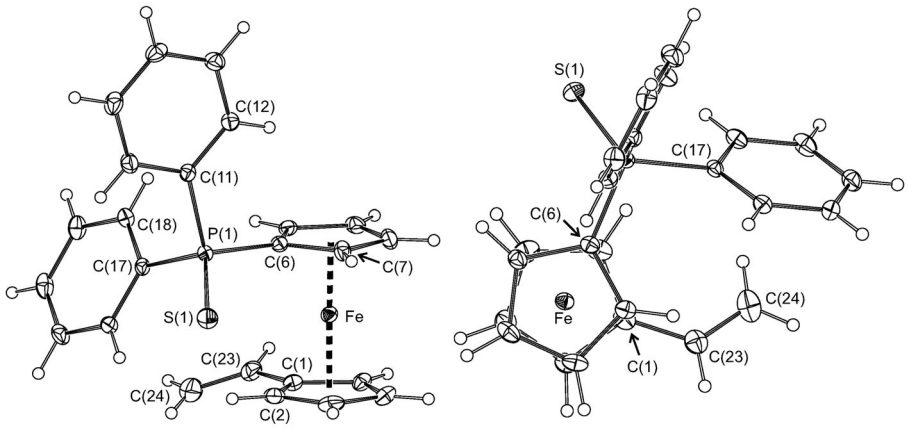
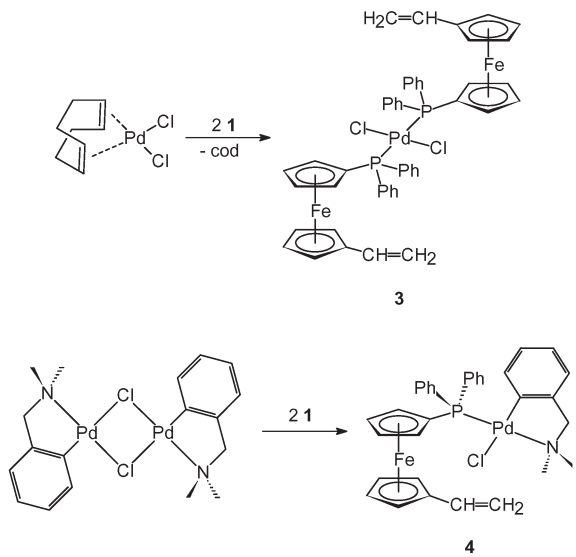


FIG. 1

Side (left) and top (right) views of molecule **1** in the structure of P-sulfide **2**. Displacement ellipsoids enclose 30% probability level. Selected geometric data for **1**: Fe(1)–Cg(1) 1.6474(9), Fe(1)–Cg(2) 1.6387(8), P(1)–S(1) 1.9513(6), P(1)–C(6) 1.790(2), P(1)–C(11) 1.820(2), P(1)–C(17) 1.815(2), C(1)–C(23) 1.459(3), C(23)–C(24) 1.314(3) Å; Cg(1)–Fe–Cg(2) 178.88(4), ∠Cp(1),Cp(2) 1.6(1), C(1)–C(23)–C(24) 125.8(2)°; for **2**: Fe(2)–Cg(3) 1.6477(9), Fe(2)–Cg(4) 1.6377(9), P(2)–S(2) 1.9551(7), P(2)–C(36) 1.790(2), P(2)–C(41) 1.821(2), P(2)–C(47) 1.814(2), C(31)–C(53) 1.458(3), C(53)–C(54) 1.314(3) Å; Cg(3)–Fe–Cg(4) 178.70(5), ∠Cp(3),Cp(4) 1.6(1), C(31)–C(53)–C(54) 125.0(2)°. Notes: ring atoms are numbered consecutively and the labelling scheme is retained for all compounds studied. Atom labels for molecule **2** are obtained by adding 30 to the respective atom label in molecule **1** (except for Fe(2), P(2), and S(2)). Cyclopentadienyl ring planes are defined as follows: C(1–5) Cp(1), C(6–10) Cp(2), C(31–35) Cp(3), and C(36–40) Cp(4). Cg(*n*) (*n* = 1–4) stand for the respective ring centroids

served ^{31}P coordination shifts ($\Delta_P = \delta_P(\text{complex}) - \delta_P(\text{ligand})$) of +31.9 (**3**) and +49.3 (**4**) are similar to those of *trans*-[$PdCl_2$(Hdpf-κ*P*)$_2$] (Hdpf = 1′-(diphenylphosphanyl)ferrocene-1-carboxylic acid; Δ_P +35.1 in DMSO-d_6)[16] and [PdCl(L^{NC})(Ph_2PfcCO_2Me-κ*P*)] (Δ_P +50.0 in $CDCl_3$)[17], respectively. Besides, the $^4J_{PH}$ and $^3J_{PC}$ coupling constants observed for **4** clearly indicate *trans*-P–N arrangement of the donors (cf. refs[17,18] and references cited therein). ^{13}C NMR spectrum of **3** shows the signals due to the carbon atoms within the phosphorus-substituted cyclopentadienyl and benzene rings as triplets characteristic of bis(phosphane) complexes that arise due the presence of ABX spin systems ^{12}C–$^{31}P_A$–(metal)–$^{31}P_B$–$^{13}C_X$ with relatively large J_{AB} values[19]. Similar features were reported for the mentioned Hdpf–palladium(II) complex[16].

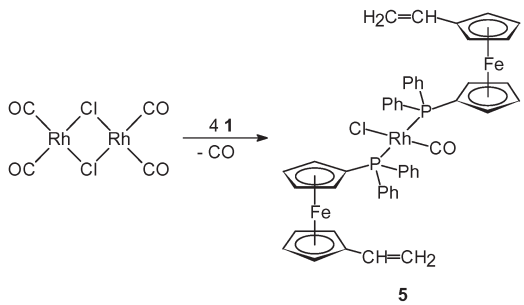


SCHEME 2

A reaction between **1** and [{$Rh(CO)_2$}$_2$(μ-Cl)$_2$] (Scheme 3) in diethyl ether afforded *trans*-[RhCl(CO)(**1**-κ*P*)$_2$] (**5**), which was isolated as crystalline solvate **5**·0.4Et_2O. Similar reactions at 1:1 metal-to-phosphane ratio under various conditions gave only complicated mixtures.

^{31}P NMR spectrum of **5** shows a rhodium-coupled doublet at δ_P 22.1. Both the ^{31}P coordination shift (Δ_P +38.4) and the $^1J_{RhP}$ value (126 Hz) compare very well with those of *trans*-[RhCl(CO)(Hdpf-κ*P*)$_2$] (Δ_P +37.8 in $CDCl_3$)[20], indicating *trans*-position of the phosphine donors (see also ref.[21]). The ^{13}C

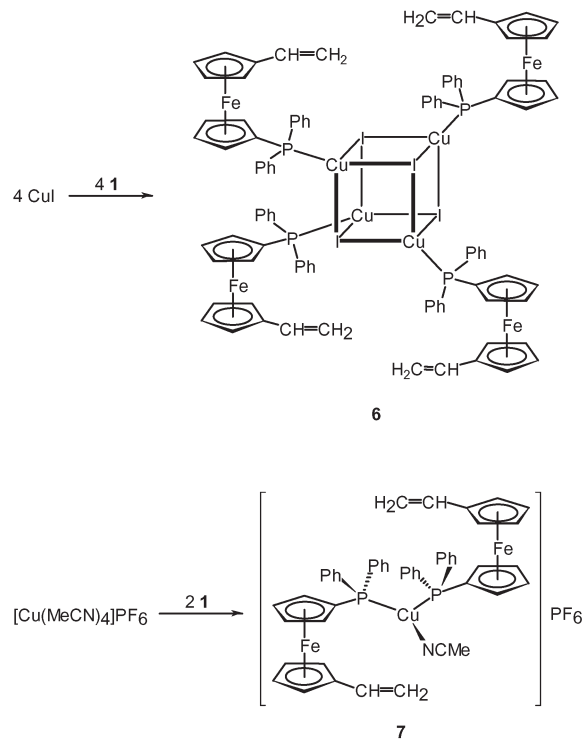
NMR signals due to the phosphanylated aromatic rings appear as virtual triplets, similar to those in **3** (vide supra). On the other hand, the resonance of rhodium-bonded carbonyl is observed as a normal doublet of triplets at δ_C 187.60 due to coupling with the rhodium and two equivalent phosphorus atoms ($^1J_{RhC}$ = 74, $^2J_{PC}$ = 16; cf. ref.[20]). The terminal carbonyl group also gives rise to a characteristic strong ν(C≡O) band at 1954 cm^{-1} in the IR spectra. The *trans*-bis(phosphane) structure was confirmed by X-ray diffraction analysis. However, the structural data[22] will not be discussed in detail because the structure shows a statistical disorder of the chloride and carbonyl ligands, preventing satisfactory refinement of their positional parameters.



5

SCHEME 3

Reactions between **1** and CuI (1:1 molar ratio) or $[Cu(MeCN)_4]PF_6$ (2:1 molar ratio) as copper(I) precursors gave, respectively, heterocubane $[(\mu_3\text{-I})_4\{Cu(\mathbf{1}\text{-}\kappa P)\}_4]$ (**6**) and cationic bis(phosphane) complex $[Cu(MeCN)(\mathbf{1}\text{-}\kappa P)_2]PF_6$ (**7**) (Scheme 4). Formulation of these complexes comes mainly from X-ray crystallography because these compounds are fairly unstable. Complex **7**, in particular, decomposes during isolation, losing probably the coordinated acetonitrile. Moreover, the complexes are insoluble in nonpolar solvents, while in polar ones they seem to dissociate. Consequently, the spectral data should be taken as more indicative of individual components than of the overall structure of the products. For instance, the IR and NMR spectra clearly confirm the presence of the ligands and, for **7**, the counter-ion (IR: ν(C≡N) and ν(C=C) bands, ν_3 and ν_4 bands of the PF_6^- ion; ^{1}H NMR: signals due to coordinated **1** and MeCN; $^{31}P\{^1H\}$ NMR: **1** and PF_6^-). The FAB^+ mass spectra exhibit, in addition to $\mathbf{1}^+$, only the following metal-containing fragments: $[Cu_2I_x(\mathbf{1})_y]^+$ (x/y = 1/2, 1/1) for **6**, and $[Cu(\mathbf{1})_n]^+$ (n = 1, 2) for both compounds.



SCHEME 4

Description of the Crystal Structures

Structure determination for **3** confirms the ordinary square-planar coordination around the palladium with *trans* ligands. Since the palladium atom resides on the crystallographic inversion centre, only half of the molecule is structurally independent and the coordination sphere perfectly planar. The overall structure of **3** (Fig. 2) compares nicely with that of other complexes featuring monodentate (diphenylphosphanyl)ferrocenyl ligands *trans*-[$PdCl_2(Ph_2PfcY)$], where Y = CO_2H (Hdpf) (ref.[16]), SMe (ref.[9c]), $P(O)Ph_2$ (ref.[8b]), or (*S*)-4-isopropyl-4,5-dihydrooxazol-2-yl (ref.[23]) – not only in terms of the Pd–donor bond lengths and interligand angles, but also in the conformation of the whole dichlorobis{(diphenylphoshanyl)ferrocenyl}palladium moiety.

The proximity of the bulky phosphane donors likely results in deviation of the interligand angles from the right angle and leads to displacement of the phosphorus atom from the plane of the bonded cyclopentadienyl ring

by 0.117(1) Å outwards the iron atom (i.e., from the ferrocene moiety). The whole ferrocene moiety is rotated with respect to the coordination plane at a dihedral angle of the phosphanylated cyclopentadienyl and coordination planes of 55.06(8)°. Cyclopentadienyl rings in monodentate **1** exert a tilt angle of ca. 4° and an almost ideal eclipsed conformation with *syn*-arranged substituents: the torsion angle τ(C(1)–Cg(1)–Cg(2)–C(6)) is –75.2(1)°. The vinyl group is directed away from the coordination plane and, as evidenced by the angle between the C(23)=C(24) vector and the Cp(1) plane of 11.5(2)°, it is rotated from the arrangement coplanar with its parent cyclopentadienyl ring.

The molecular structure of **4**·$CHCl_3$ is shown in Fig. 3 and the pertinent geometric parameters are listed in Table I. The structure corroborates the expected *trans*-P–N square-planar coordination environment around the palladium atom. When compared with the structure of bis(phosphane) complex **3**, the coordination sphere in **4** is markedly distorted. The defor-

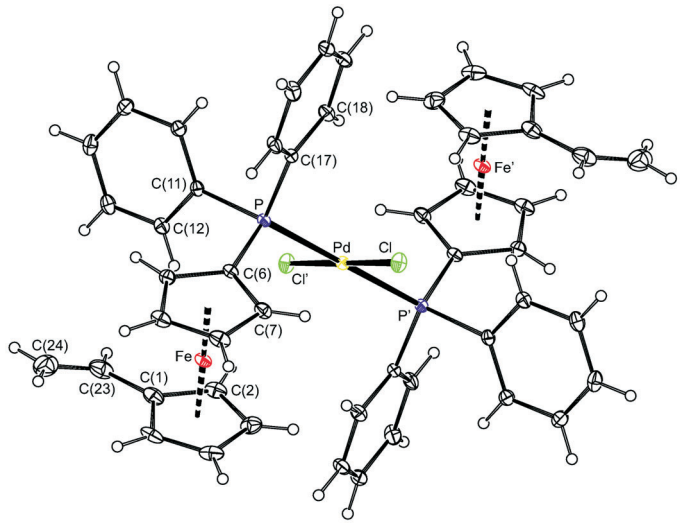


FIG. 2

The molecular structure of complex **3**. Displacement ellipsoids are scaled to the 30% probability level. Selected geometric parameters: Pd–Cl 2.3017(4), Pd–P 2.3406(5), P–C(6) 1.803(2), P–C(11) 1.832(2), P–C(17) 1.816(2), C(1)–C(23) 1.448(3), C(23)–C(24) 1.334(4) Å; Cl–Pd–P 86.81(1), Cl–Pd–P^{i} 93.19(1), C(6)–P–C(11) 102.40(8), C(6)–P–C(17) 105.70(8), C(11)–P–C(17) 101.95(8), C(1)–C(23)–C(24) 125.5(2)°; ferrocene unit: Fe–Cg(1) 1.659(1), Fe–Cg(2) 1.6510(9) Å; ∠Cp(1),Cp(2) 3.9(1)°. Symmetry operations: i. (2 – *x*, –*y*, 2 – *z*). Cp(1,2) and Cg(1,2) are defined as for **2** (see Fig. 1)

TABLE I
Selected geometric parameters for **4**·$CHCl_3$ (in Å and °)[a]

Pd–Cl	2.4074(9)	Cl–Pd–P	91.40(3)
Pd–P	2.2531(8)	Cl–Pd–N	91.62(7)
Pd–N	2.143(2)	P–Pd–C(25)	96.43(9)
Pd–C(25)	2.014(3)	N–Pd–C(25)	81.4(1)
Fe–Cg(1,2)	1.645(1)[b]	∠Cp(1),Cp(2)	2.0(2)
P–C(6)	1.807(3)	C(6)–P–C(11)	99.5(1)
P–C(11)	1.828(3)	C(6)–P–C(17)	104.2(1)
P–C(17)	1.816(3)	C(11)–P–C(17)	105.5(1)
C(1)–C(23)	1.456(5)	Pd–P–C(6,11,17)	110.39(8)–118.20(9)
C(23)–C(24)	1.317(5)	C(1)–C(23)–C(24)	125.5(3)
N–C(31)	1.485(4)	C(31)–N–C(32)	110.0(2)
N–C(32)	1.485(3)	C(31)–N–C(33)	109.3(3)
N–C(33)	1.473(4)	C(32)–N–C(33)	109.2(2)

[a] Definitions: Cp(1) (Cp(2)) are the C(1–5) (C(6–10)) cyclopentadienyl rings. Cg(1) and Cg(2) denote the respective ring centroids. [b] Fe–Cg(1) = Fe–Cg(2).

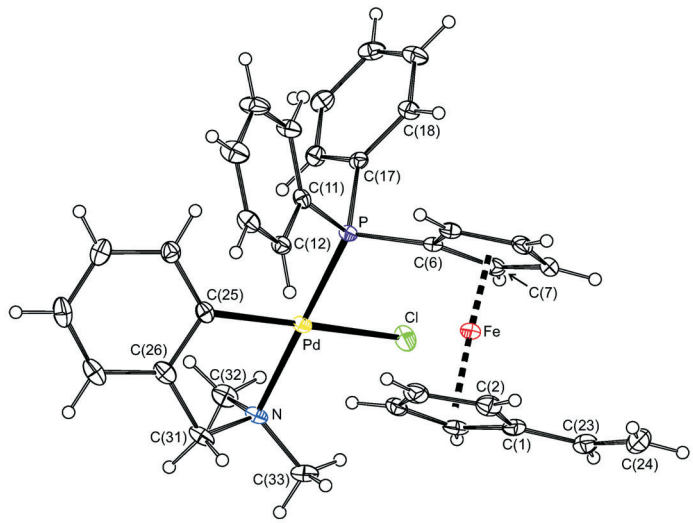


FIG. 3
The molecular structure of **4**·$CHCl_3$. Solvating chloroform was omitted for clarity. Displacement ellipsoids are scaled to the 30% probability level

mation can be accounted for by steric interactions of the ligands: spatial limitations imposed by the relatively rigid 2-[(dimethylamino)methyl]-phenyl (L^{NC}) chelating group and bulkiness of the diphenylphosphanyl moiety lead to closure of the N–Pd–C(25) angle and to opening of the adjacent interligand P–Pd–C(25) angle. In addition, palladium and its four ligating atoms, {Pd,Cl,P,N,C(25)}, deviate significantly from planarity: the donor atoms are displaced by as much as 0.119(1)–0.175(3) Å from their least-squares plane. Excluding the C(25) atom from this set markedly lowers the deviations of the plane atoms (to ca. 0.05 Å). Then, the Pd–C(25) bond and the {Pd,Cl,P,N} plane intersect at an angle of 12.1(1)°, with the distance from the plane of the C(25) atom being as long as 0.475(3) Å.

The Pd–donor bond lengths correspond well with those in the related compounds featuring other ferrocene phosphanes: $[Pd(L^{NC})(MeCN\text{-}\kappa N)(Ph_2PfcCO_2Me\text{-}\kappa P)]ClO_4$ (ref.[17]) and *rac*-$[PdCl(L^{NC})\{Fe(\eta^5\text{-}C_5H_3(PPh_2\text{-}\kappa P)(CH_2CO_2Me)\text{-}1,2)(\eta^5\text{-}C_5H_3)\}]$ (ref.[18]). In accordance with a lower *trans*-influence[24] of the nitrogen and chloride donors as compared with phosphane and phenyl, respectively, the Pd–P bond is shorter and the Pd–Cl bond longer than those in **3** (both by ca. 0.1 Å).

The five-membered palladacycle in **4** has an envelope conformation with the nitrogen displaced from the plane of the remaining ring atoms. The metallated ring C(25–30), which is a part of the chelate ring, is rotated from the coordination plane {Pd,Cl,P,N,C(25)} by 25.4(1)°. The C–C bond lengths in the palladated benzene ring span a range of 1.374(7)–1.406(4) Å, the extreme values corresponding to the C(27)–C(28) (shortest) and C(25)–C(26) (longest) bonds. Finally, the ferrocene unit in monodentate **1** is rotated with respect to the coordination plane, the dihedral angle of the phosphanyl-substituted cyclopentadienyl ring and the coordination plane being 49.1(1)°. The ferrocene framework has regular geometry, showing identical Fe–Cg(1,2) distances and a negligible tilt of the cyclopentadienyl rings. The rings adopt a near-to-eclipsed conformation, bearing the substitutents in *anti*-positions (cf. the torsion angle τ(C(1)–Cg(1)–Cg(2)–C(6)) 141.5(2)°), and the vinyl group is nearly coplanar with the parent ring (the C(23)=C(24) vs Cp(1) angle is only 2.2(3)°).

The molecular structure of complex **6** as found in solvate **6**·C_6H_6 (Fig. 4) resembles in many respects that of previously characterized complex $[Cu(\mu_3\text{-}I)_4\{Cu(Hdpf\text{-}\kappa P)\}_4]\cdot 2AcOH$ (ref.[25]). Even in the case of **6**, compound **1** coordinates as a simple monodentate phosphane. The four independent ligand moieties show no unexpected features; their vinyl substituents are neither coordinated nor involved in intermolecular interactions. This results in enhanced mobility of the peripheral parts, which apparently in-

creases on going from the inner core to the external ferrocene moieties, finally resulting in a disorder at the vinylcyclopentadienyl moieties (N.B.: the whole crystal assembly is essentially molecular, devoid of any polar interactions such as hydrogen bonding). All this makes the heterocubane core the only part of interest (Fig. 5 and Table II).

The tetranuclear core as well as the whole molecule of **6** lack any external (i.e., crystallographic) symmetry. Because of its compactness, the distortion of the Cu_4I_4 cluster from idealized cubic symmetry should be sought mainly in the different radii of the involved atoms (Cu vs I). Although the bulky phosphane ligands certainly play some role, their influence can be significantly relaxed by their conformational flexibility. The Cu_4I_4 unit appears as if consisting of two mutually rotated Cu_2I_2 rhomboids (Fig. 5) connected by Cu–I bonds into the final cuboidal body. Individual rhomboids, {Cu(1)I(4)Cu(3)I(2)} and {Cu(2)I(1)Cu(4)I(2)}, are markedly compressed along the Cu···Cu axis; the lengths of the diagonals differ on average by as much as 60% (cf. Cu(1)···Cu(3) 2.7570(9) vs I(2)···I(4) 4.5311(5) Å and Cu(2)···Cu(4) 2.8506(9) vs I(1)···I(3) 4.4879(5) Å). Besides, the Cu(1)···Cu(3)

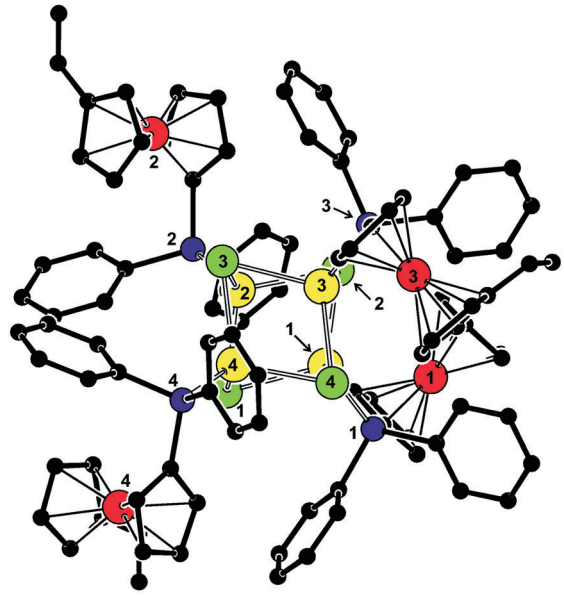


FIG. 4

The molecular structure of **6**·C_6H_6. Hydrogen atoms and the molecule of solvating benzene were omitted. The numbers are the atom labels (for copper (yellow) and iodine (green) atoms) and ligand moieties (iron (red) and phosphorus (violet))

and Cu(2)···Cu(4) distances are significantly shorter that other Cu···Cu contacts within the Cu_4I_4 unit (see Table II).

Apart from this close-approach approximation, the heterocubane core can be equally well but perhaps more conveniently described as a distorted Cu_4 tetrahedron with all triangular faces capped by triply bridging iodine atoms. Phosphane donors, attached to the metal vertexes, then complete distorted tetrahedral coordination around each copper atom.

The structure of the cation in complex **7** (Fig. 6) shows a distorted trigonal coordination geometry for the central atom, similar to that in $[Cu(MeCN)(Ph_2PfcOMe\text{-}\kappa P)_2]PF_6$ (ref.[6a]). Although the Cu–donor atom bond lengths are very similar in both structurally characterized complexes, compound **7** shows somewhat higher angular distortion of the coordination sphere: the P(1)–Cu–P(2) angle is more opened (by ca. 5°) and the N–Cu–P(1,2) angles are noticeably different (cf. the absolute difference of the N–Cu–P(1,2) angles of 12.3° in **7** and ca. 0.2° in the reference compound). The copper atom is displaced by 0.147(1) Å from the plane of its ligating atoms and its acetonitrile ligand is bent away from the {Cu,P(1),P(2),N} coordination plane.

The P-bonded ferrocene ligands show different orientation towards the coordination plane: the angles formed by the planes of their phosphanylated cyclopentadienyl rings (Cp^P) and the coordination plane are 71.9(1) and 20.0(2)° for ligands **1** and **2**, respectively. The ferrocene units are practically perpendicular to each other, as exemplified by the dihedral angle of their Cp^P planes, 88.5(2)°. Similar to previous case, the vinyl groups are

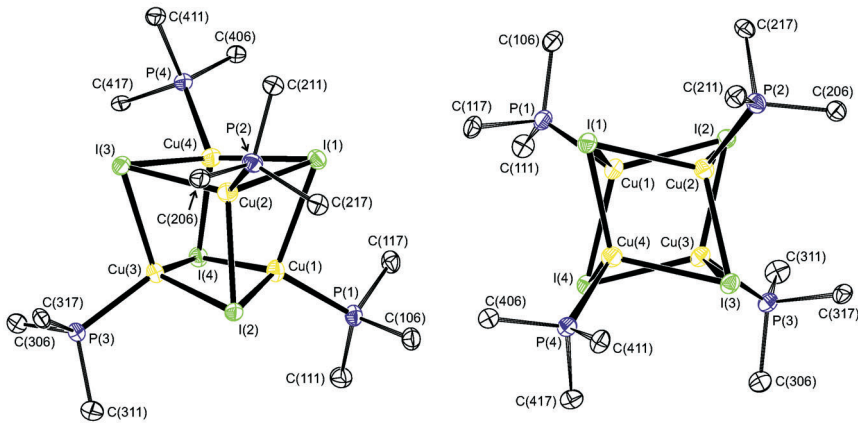


FIG. 5

Views of the core geometry in $\mathbf{6}\cdot C_6H_6$ showing only the pivotal carbon atoms for the P-bonded aromatic rings. Displacement ellipsoids are scaled to the 30% probability level

directed away from the coordination centre and one of them (molecule **2**) exhibits a disorder.

CONCLUSIONS

In the series of Pd(II), Rh(I), and Cu(I) complexes presented in this contribution, ligand **1** coordinates exclusively via phosphane group. The fact that the vinyl group does not participate in the coordination can be ascribed to unfavorable steric properties of this potentialy bidentate donor, not allowing for chelate coordination due to steric requirements of the central atoms and/or spatial properties of the ferrocene unit. Free vinyl groups thus behave as spectator dangling substituents and are often disordered in the solid state due to a lack of intermolecular interactions that would fix their position in the crystal lattice. Further investigations into the coordination properties of **1**, aimed at its bidentate coordination in either chelate or bridging modes, are currently under way.

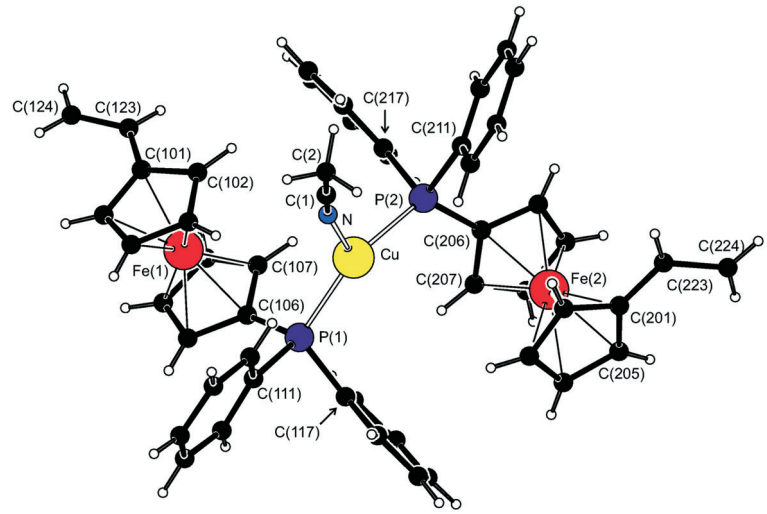


FIG. 6

The structure of the complex cation in **7**. For clarity, hydrogen atoms were omitted and only one orientation of the disordered vinylcyclopentadienyl ring in ligand **2** is shown. Selected geometric data: Cu–P(1) 2.2431(9), Cu–P(2) 2.2551(8), Cu–N 1.993(3), N–C(1) 1.110(6), C(1)–C(2) 1.46(1), P(1)–C(106) 1.801(3), P(1)–C(111) 1.827(3), P(1)–C(117) 1.826(3), P(2)–C(206) 1.795(3), P(2)–C(211) 1.828(3), P(2)–C(217) 1.831(3) Å; P(1)–Cu–P(2) 133.66(3), P(1)–Cu–N 118.64(8), P(2)–Cu–N 106.27(8), Cu–N–C(1) 163.8(4), N–C(1)–C(2) 176.9(6)°; ferrocene moieties in ligands **1**/**2**: Fe–Cg(P) 1.641(1)/1.636(2), Fe–Cg(C) 1.652(2)/(disorder) Å; ∠Cp(P),Cp(C) 1.1(2)°/(disorder) (Cp(P) and Cp(C) are the phosphanyl- and vinyl-substituted cyclopentadienyl rings; Cg denotes the respective ring centroid)

TABLE II
Selected interatomic distances and angles describing the geometry of the heterocubane core in **6**·C_6H_6 (in Å and °)

		Distances	
I(1)–Cu(1)	2.7503(7)	I(2)–Cu(1)	2.6297(7)
I(1)–Cu(2)	2.7000(7)	I(2)–Cu(2)	2.7068(7)
I(1)–Cu(4)	2.6341(7)	I(2)–Cu(3)	2.7195(7)
I(3)–Cu(2)	2.6418(7)	I(4)–Cu(1)	2.6838(8)
I(3)–Cu(3)	2.6881(7)	I(4)–Cu(3)	2.6410(7)
I(3)–Cu(4)	2.7248(7)	I(4)–Cu(4)	2.7104(7)
Cu(1)–P(1)	2.251(2)	Cu(2)–P(2)	2.255(2)
Cu(3)–P(3)	2.250(2)	Cu(4)–P(4)	2.254(2)
Cu(1)···Cu(2)	3.0203(9)	Cu(2)···Cu(3)	3.0204(9)
Cu(1)···Cu(3)	2.7570(9)	Cu(2)···Cu(4)	2.8506(9)
Cu(1)···Cu(4)	2.9944(9)	Cu(3)···Cu(4)	3.0405(9)
P(1)–C(106)	1.790(6)	P(2)–C(206)	1.801(5)
P(1)–C(111)	1.823(6)	P(2)–C(211)	1.831(6)
P(1)–C(117)	1.829(6)	P(2)–C(217)	1.831(5)
P(3)–C(306)	1.799(6)	P(4)–C(406)	1.804(5)
P(3)–C(311)	1.820(6)	P(4)–C(411)	1.821(5)
P(3)–C(317)	1.827(5)	P(4)–C(417)	1.820(5)
		Angles	
Cu(1)–I(1)–Cu(2)	67.30(2)	Cu(1)–I(2)–Cu(2)	68.92(2)
Cu(1)–I(1)–Cu(4)	67.54(2)	Cu(1)–I(2)–Cu(3)	62.02(2)
Cu(2)–I(1)–Cu(4)	64.60(2)	Cu(2)–I(2)–Cu(3)	67.65(2)
Cu(2)–I(3)–Cu(3)	69.03(2)	Cu(1)–I(4)–Cu(3)	62.36(2)
Cu(2)–I(3)–Cu(4)	64.15(2)	Cu(1)–I(4)–Cu(4)	67.44(2)
Cu(3)–I(3)–Cu(4)	68.34(2)	Cu(3)–I(4)–Cu(4)	69.23(2)
I(1)–Cu(1)–I(2)	105.58(2)	I(1)–Cu(2)–I(2)	104.86(2)
I(1)–Cu(1)–I(4)	105.60(2)	I(1)–Cu(2)–I(3)	114.31(3)
I(2)–Cu(1)–I(4)	117.03(3)	I(2)–Cu(2)–I(3)	106.77(2)
I(1)–Cu(1)–P(1)	103.43(4)	I(1)–Cu(2)–P(2)	106.57(4)
I(2)–Cu(1)–P(1)	119.25(5)	I(2)–Cu(2)–P(2)	104.90(4)
I(4)–Cu(1)–P(1)	104.40(4)	I(3)–Cu(2)–P(2)	118.24(4)
I(2)–Cu(3)–I(3)	105.11(2)	I(1)–Cu(4)–I(3)	113.74(3)
I(2)–Cu(3)–I(4)	115.40(3)	I(1)–Cu(4)–I(4)	108.17(2)
I(3)–Cu(3)–I(4)	106.37(2)	I(3)–Cu(4)–I(4)	103.44(2)
I(2)–Cu(3)–P(3)	103.98(4)	I(1)–Cu(4)–P(4)	120.39(4)
I(3)–Cu(3)–P(3)	106.09(4)	I(3)–Cu(4)–P(4)	103.38(4)
I(4)–Cu(3)–P(3)	118.79(4)	I(4)–Cu(4)–P(4)	106.26(4)

EXPERIMENTAL

Materials and Methods

Unless noted otherwise, the syntheses were performed under an argon atmosphere and with exclusion of the direct daylight. Tetrahydrofuran (THF) was distilled from potassium-benzophenone ketyl. Toluene, diethyl ether and hexane were dried over potassium metal and distilled. Dichloromethane and chloroform were dried over anhydrous potassium carbonate. 1′-(Diphenylphosphanyl)ferrocene-1-carbaldehyde[4c], $[PdCl_2(cod)]$ (ref.[26]), di-μ-chlorobis{[((2-dimethylamino)methyl-κ*N*)phenyl-κ*C*^{1}]palladium(II)} (ref.[27]), $[\{Rh(CO)_2\}_2(\mu\text{-}Cl)_2]$ (ref.[28]). 1′-(Diphenylthiophosphoryl)ferrocene-1-carbaldehyde was synthesized from the corresponding phosphane and elemental sulfur. $[PPh_3Me]Br$ (Fluka) was dried at 120 °C for 1 h and then stored over phosphorus pentoxide. Other chemicals were used as received from commercial suppliers (Fluka, Aldrich; solvents from Lachema).

NMR spectra were measured on a Varian UNITY Inova 400 spectrometer (^{1}H, 399.95; ^{13}C, 100.58; ^{31}P, 161.90 MHz) at 298 K. Chemical shifts (δ, ppm) are given relative to internal reference tetramethylsilane (^{1}H and ^{13}C) and external reference 85% aqueous H_3PO_4 (^{31}P); coupling constants (*J*) are given in Hz. IR spectra were recorded on an FTIR Nicolet Magna 760 instrument in the range 400–4000 cm^{-1}. Mass spectra were measured on a Varian 3400 (GC)/Finnigan MAT INCOS (MS) GC-MS (EI spectra) or a ZAB-SEQ spectrometer (high resolution (HR) and fast-atom bombardment spectra (FAB)). Melting points were determined on a Kofler apparatus and are uncorrected.

Synthesis of 1-(Diphenylphosphanyl)-1′-vinylferrocene (**1**)

BuLi (2.2 ml, 2.5 M solution in hexanes, 5.5 mmol) was slowly introduced to a suspension of $[PPh_3Me]Br$ (2.146 g, 6.0 mmol) in THF (50 ml) upon cooling in an ice bath. The white phosphonium salt dissolved almost completely to give an orange solution that turned later bright yellow. After stirring at 0 °C for 1 h, a solution of 1′-(diphenylphosphanyl)ferrocene-1-carbaldehyde (1.995 g, 5.0 mmol) in THF (25 ml) was added to the formed ylide. The cooling bath was removed and the mixture was stirred at room temperature for 6 h and then quenched by addition of saturated aqueous $NaHCO_3$ and stirring for another 15 min. The orange organic phase was separated, washed successively with saturated aqueous $NaHCO_3$ and NaCl solutions, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The oily residue was purified by column chromatography (silica gel, hexane–diethyl ether 1:2). The major band of the product is eluted first, slowly followed by a minor band due to the corresponding phosphine oxide. Evaporation of the first band and drying under vacuum (13 Pa for 1 h) gave **1** as an amber oil that solidified upon standing to a pale orange solid. Yield 1.776 g (89%). The product tends to retain traces of the solvents.

^{1}H NMR ($CDCl_3$): 4.01 (apparent q, 2 H), 4.09 (apparent t, 2 H), 4.25 (apparent t, 2 H), 4.29 (apparent t, 2 H) (4 × CH, fc); 4.95 (dd, $^2J_{HH}$ = 1.4, $^3J_{HH}$ = 10.8, 1 H, $=CH_2$), 5.24 (dd, $^2J_{HH}$ = 1.4, $^3J_{HH}$ = 17.5, 1 H, $=CH_2$), 6.23 (dd, $^3J_{HH}$ = 10.7, 17.5, 1 H, =CH), 7.25–7.40 (m, 10 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$): 67.61, 69.97, 72.46 (d, J_{PC} = 4), 73.91 (d, J_{PC} = 15) (4 × CH, fc); 76.18 (d, $^1J_{PC}$ = 7, C-P, fc), 84.11 (C-CH=CH_2, fc), 111.67 ($=CH_2$), 128.06 (d, J_{PC} = 7), 128.40, 133.43 (d, J_{PC} = 20) (3 × CH, Ph); 133.89 (=CH), 139.04 (d, $^1J_{PC}$ = 10, C_{ipso}, Ph). ^{31}P{^{1}H} NMR ($CDCl_3$): –16.3 (s). EI MS, *m/z* (rel.%): 397 (27), 396 ($M^{\bullet+}$, 100), 395 (34), 394 (7), 319 ($[M - Ph]^+$, 19), 305 (5), 288 (6), 241 (9), 229 (9), 210 (5), 198 (6), 183 (8), 171 (22), 170 (16), 133 (7), 121 ($[C_5H_5Fe]^+$, 10), 56 (Fe^+, 18). IR (neat): 3086 m, 3067 s, 3055 s,

3009 m, 3000 m; ν(C=C) 1629 s, 1585 m; 1476 s, 1433 vs, 1308 m, 1241 m, 1159 s, 1090 m, 1027 s, 985 s, 910 s, 890 s, 830 vs, 746 vs, 741 vs, 696 vs, 633 m, 502 s, 482 s. HR MS calculated for $C_{24}H_{21}{}^{56}FeP$: 396.0730, found: 396.0745.

Synthesis of 1-(Diphenylthiophosphoryl)-1′-vinylferrocene (**2**)

BuLi (2.4 ml, 2.5 M solution in hexanes, 6.0 mmol) was added dropwise to a stirred, ice-cooled suspension of $[PPh_3Me]Br$ (2.144 g, 6.0 mmol) in THF (30 ml). Most of the salt dissolved to give an orange solution, that later turned yellow. The ylide solution was stirred at 0 °C for 1 h and then treated with a solution of 1′-(diphenylthiophosphoryl)ferrocene-1-carbaldehyde (2.151 g, 5.0 mmol) in THF (50 ml). After stirring at 0 °C for 30 min and then at room temperature overnight, the reaction was terminated by addition of saturated aqueous $NaHCO_3$ and stirring for 15 min. The organic phase was separated, washed with saturated aqueous $NaHCO_3$, dried over anhydrous $MgSO_4$, and evaporated under vacuum. The oily residue was purified by column chromatography on alumina (Brockmann II) with hexane–diethyl ether (1:1) as eluent. Solvent removal and drying under vacuum (60 °C at 133 Pa for 1 h) afforded pure **2** as an amber oil, which solidified upon standing to give a crystalline, orange brown solid. Yield 1.952 g (91%). M.p. 116.5–117.5 °C (diethyl ether–hexane).

^{1}H NMR ($CDCl_3$): 4.19 (apparent t, 2 H), 4.34 (apparent q, 2 H), 4.36 (apparent t, 2 H), 4.42 (apparent q, 2 H) (4 × CH, fc); 4.95 (dd, $^2J_{HH}$ = 1.5, $^3J_{HH}$ = 10.7, 1 H, =CH_2), 5.23 (dd, $^2J_{HH}$ = 1.5, $^3J_{HH}$ = 17.5, 1 H, =CH_2), 6.18 (dd, $^3J_{HH}$ = 10.7, 17.5, 1 H, =CH), 7.38–7.76 (m, 10 H, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 68.39, 70.97, 73.51 (d, J_{PC} = 10), 73.97 (d, J_{PC} = 13) (4 × CH, fc); 75.31 (d, $^1J_{PC}$ = 98, C-P, fc), 84.92 (C-CH=CH_2, fc), 112.39 (=CH_2), 128.16 (d, J_{PC} = 12), 131.15 (d, J_{PC} = 3), 131.59 (d, J_{PC} = 11) (3 × CH, Ph); 133.30 (=CH), 134.55 (d, $^1J_{PC}$ = 87, C_{ipso}, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$): +42.1 s. EI MS, *m/z* (rel.%): 429 (29), 428 (M^+, 100), 427 (7), 426 (7), 402 ($[M - C_2H_2]^+$, 7), 339 (7), 338 (22), 337 ($[Ph_2P(S)C_5H_4Fe]^+$, 98), 335 (7), 273 (11), 229 (9), 183 (10), 414 (5), 121 ($[C_5H_5Fe]^+$, 5), 56 (Fe^+, 10). IR (Nujol): ν(C=C) 1632 m; 1308 m, 1169 s, 1101 s, 1033 m, 1026 m, 984 m, 841 m, 816 m, 752 s, 715 vs, 694 s, 658 vs, 542 s, 521 m, 498 s, 486 s. For $C_{24}H_{21}FeP$ calculated: 67.30% C, 4.94% H; found: 66.95% C, 4.87% H.

Synthesis of *trans*-Dichlorobis[1-(diphenylphosphanyl-κ*P*)-1′-vinylferrocene]-palladium(II) (**3**)

A solution of **1** (166 mg, 0.42 mmol) in chloroform (5 ml) was added to solid $[PdCl_2(cod)]$ (57 mg, 0.20 mmol). The resulting red solution was stirred at room temperature for 90 min and then evaporated under reduced pressure. (The characteristic smell of liberated cycloocta-1,5-diene was clearly detectable immediately after mixing the reactants.) The residue was redissolved in chloroform and crystallized by diffusion of hexane. The crystalline product formed after several days was filtered off, washed with hexane and dried in air. Yield of **3**·0.15$CHCl_3$ 182 mg (92%), dark red crystals.

^{1}H NMR ($CDCl_3$): 4.31 (apparent t, 2 H), 4.53 (m, 4 H), 4.65 (apparent t, 2 H) (4 × CH, fc); 5.05 (dd, $^3J_{HH}$ = 10.7, $^2J_{HH}$ = 1.4, 1 H, =CH_2), 5.34 (dd, $^3J_{HH}$ = 17.5, $^2J_{HH}$ = 1.4, 1 H, =CH_2), 6.39 (dd, $^3J_{HH}$ = 17.5, 10.7, 1 H, =CH), 7.32–7.68 (m, 10 H, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 68.22 (CH, fc), 71.20 (virtual t, J' = 28, C-P, fc), 71.95 (CH, fc), 73.96 (virtual t, J' = 8, CH, fc), 76.00 (virtual t, J' = 5, CH, fc), 84.97 (C-CH=CH_2, fc), 112.45 (=CH_2), 127.69

(virtual t, J' = 5, CH of PPh_2), 130.22 (CH of PPh_2), 131.24 (virtual t, J' = 25, C_{ipso} of PPh_2), 133.76 (=CH), 134.14 (virtual t, J' = 6, CH of PPh_2). $^{31}P\{^1H\}$ NMR ($CDCl_3$): +15.6 s. IR (Nujol): ν(C=C) 1622 m; 1304 m, 1165 s, 1105 m, 1092 m, 1053 m, 1036 m, 1020 m, 989 m, 918 s, 822 s, 750 vs, 692 vs, 619 m, 542 m, 515 vs, 508 s, 492 s, 472 s. For $C_{48}H_{42}Cl_2Fe_2P_2Pd \cdot 0.15CHCl_3$ calculated: 58.55% C, 4.30% H; found: 58.45% C, 4.37% H.

Synthesis of Chloro{2-[(dimethylamino)methyl-κ*N*]phenyl-κC^1}-[1-(diphenylphosphanyl-κ*P*)-1′-vinylferrocene]palladium(II) (**4**)

A solution of **1** (83 mg, 0.21 mmol) in dichloromethane (2 ml) was added to di-μ-chlorobis-{[(2-dimethylamino)methyl-κ*N*)phenyl-κC^1]palladium(II)} (55 mg, 0.10 mmol) in the same solvent (2 ml). The resulting solution was allowed to stand for 15 min and then crystallized by layering with hexane and diffusion at 4 °C for several days. The separated crystals were filtered off, washed with hexane and dried under vacuum. Yield of **4** 124 mg (85%), well-developed rusty orange crystals.

^1H NMR ($CDCl_3$): 2.85 (d, $^4J_{PH}$ = 2.7, 6 H, NMe_2), 4.12 (d, $^4J_{PH}$ = 2.2, 2 H, NCH_2), 4.25 (d of apparent t, 2 H), 4.36 (apparent q, 2 H), 4.54 (apparent t, 2 H), 4.71 (apparent t, 2 H) (4 × CH, fc); 5.03 (dd, $^3J_{HH}$ = 10.8, $^2J_{HH}$ = 1.5, 1 H, $=CH_2$), 5.32 (dd, $^3J_{HH}$ = 17.5, $^2J_{HH}$ = 1.5, 1 H, $=CH_2$), 6.40 (dd, $^3J_{HH}$ = 17.5, 10.8, 1 H, =CH), 6.26–7.04 (m, 4 H, C_6H_4; overlaps with the =CH multiplet), 7.28–7.60 (m, 10 H, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 50.13 (d, $^3J_{PC}$ = 3, NMe_2), 68.10, 72.22 (2 × CH, fc); 73.16 (d, $^1J_{PC}$ = 60, C-P, fc), 73.58 (d, $^3J_{PC}$ = 7, NCH_2), 73.95 (d, J_{PC} = 7), 75.96 (d, J_{PC} = 10) (2 × CH, fc); 84.82 (**C**-CH=CH_2, fc), 112.35 ($=CH_2$), 122.42, 123.66, 124.81 (d, J_{PC} = 6) (3 × CH of C_6H_4); 127.82 (d, J_{PC} = 11), 130.43 (d, J_{PC} = 2) (2 × CH of PPh_2); 131.72 (d, $^1J_{PC}$ = 49, C_{ipso} of PPh_2), 133.74 (=CH), 134.33 (d, J_{PC} = 12, CH of PPh_2), 138.40 (d, J_{PC} = 10, CH of C_6H_4), 148.14 (d, J_{PC} = 2), 152.19 (2 × C_{ipso} of C_6H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): +33.0 s. FAB MS, *m/z* (rel.%): 671 (M^+), 636 ($[M - Cl]^+$), 591, 502, 396 ($[Ph_2PfcCHCH_2]^+$). IR (Nujol): ν(C=C) 1626 m, 1579 m; 1304 m, 1165 s, 1100 s, 1045 m, 1028 m, 996 m, 984 w, 970 m, 918 m, 849 s, 739 vs, 691 s, 627 m, 544 m, 517 s, 498 s, 474 m. HR MS calculated for $C_{33}H_{33}{}^{56}FeNP^{106}Pd$ ($[M - Cl]^+$): 636.0735, found: 636.0732. For $C_{33}H_{33}ClFeNPPd \cdot 0.67CH_2Cl_2$ calculated: 55.46% C, 4.75% H, 1.92% N; found: 55.41% C, 4.84 H, 1.85% N.

Synthesis of *trans*-Carbonylchlorobis[1-(diphenylphosphanyl-κ*P*)-1′-vinylferrocene]-rhodium(I) (**5**)

A solution of di-μ-chlorobis[dicarbonylrhodium(I)] (39 mg, 0.10 mmol) in diethyl ether (10 ml) was added to solid **1** (166 mg, 0.42 mmol). The ligand dissolved with copious effervescence (CO evolution) and the product started to separate as an orange microcrystalline solid. The mixture was allowed to stand at room temperature for 1 h and then at –18 °C overnight. The solid product was filtered off, washed with diethyl ether and dried in air. Yield of **5**·0.4Et_2O 189 mg (96%), rusty orange crystalline solid.

^1H NMR ($CDCl_3$): 1.21 (t, $^3J_{HH}$ = 7.0, 2.4 H, $OCH_2C\mathbf{H}_3$), 3.48 (q, $^3J_{HH}$ = 7.0, 1.6 H, $OC\mathbf{H}_2CH_3$), 4.30 (apparent t, 2 H), 4.44 (br m, 2 H), 4.45 (apparent t, 2 H), 4.52 (apparent t, 2 H) (4 × CH, fc); 5.02 (dd, $^3J_{HH}$ = 10.8, $^2J_{HH}$ = 1.5, 1 H, $=CH_2$), 5.31 (dd, $^3J_{HH}$ = 17.5, $^2J_{HH}$ = 1.5, 1 H, $=CH_2$), 6.36 (dd, $^3J_{HH}$ = 17.5, 10.8, 1 H, =CH), 7.31–7.72 (m, 10 H, PPh_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 15.28 ($OCH_2\mathbf{C}H_3$), 65.85 ($O\mathbf{C}H_2CH_3$), 68.08, 71.88, 73.52 (virtual t, J' = 3) (3 × CH, fc); 74.78 (virtual t, J' = 26) (C-P, fc), 75.24 (virtual t, J' = 5) (CH, fc), 84.68

(C-CH=CH_2, fc), 112.15 (=CH_2), 127.79 (virtual t, J' = 5), 129.85, 133.95 (virtual t, J' = 6) (3 × CH of PPh_2); 134.76 (virtual t, J' = 24, C_{ipso} of PPh_2), 187.60 (dt, $^1J_{RhC}$ = 74, $^2J_{PC}$ = 16, C≡O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 22.1 (d, $^1J_{RhP}$ = 126). FAB MS, *m/z* (rel.%): 958 (M^+), 895, 839, 748, 527 ([Rh(CO)(Ph_2PfcCH=CH_2)]$^+$), 396 ([Ph_2PfcCH=CH_2]$^+$). IR (Nujol): ν(C≡O) 1954 vs; ν(C=C) 1635 w, 1620 w; 1304 m, 1163 m, 1097 m, 1030 m, 987 w, 904 w, 933 m, 752 m, 696 s, 627 w, 509 s, 498 s, 469 m. HR MS calculated for $C_{49}H_{42}{}^{35}Cl^{56}Fe_2OP_2{}^{103}Rh$ (M^+): 958.0153, found: 958.0116.

Synthesis of Tetra-μ_3-iodotetrakis{[1-(diphenylphosphanyl-κ*P*)-1′-vinylferrocene]-copper(I)} (**6**)

CuI (38 mg, 0.20 mmol) was added to a solution of **1** (83 mg, 0.21 mmol) in chloroform (5 ml) and the mixture was stirred overnight (the solid dissolved completely within 1–2 h). Then, the reaction solution was evaporated under reduced pressure, the residue dissolved in chloroform (3 ml) and the solution layered with hexane (ca. 12 ml). Crystallization at +4 °C gave a fine microcrystalline solid, which was filtered off, washed with hexane and dried under vacuum. Yield of **6** 99 mg (83%), orange microcrystalline solid.

^1H NMR (C_6D_6): 4.18 (apparent t, 2 H), 4.24 (br apparent t, 2 H), 4.26 (apparent t, 2 H), 4.61 (apparent q, 2 H) (4 × CH, fc); 4.90 (dd, $^3J_{HH}$ = 10.7, $^2J_{HH}$ = 1.6, 1 H, =CH_2), 5.18 (dd, $^3J_{HH}$ = 17.4, $^2J_{HH}$ = 1.6, 1 H, =CH_2), 6.05 (dd, $^3J_{HH}$ = 17.4, 10.7, 1 H, =CH), 7.08–7.87 (m, 10 H, PPh_2). $^{31}P\{^1H\}$ NMR (C_6D_6): –25.4 (br s, $\Delta\nu_{1/2} \approx 350$). FAB MS, *m/z* (rel.%): 1045 ([Cu_2I(**1**)$_2$]$^+$), 855 ([Cu(**1**)$_2$]$^+$), 649 ([Cu_2I(**1**)]$^+$), 459 ([Cu(**1**)]$^+$), 396 (**1**$^+$). For $C_{96}H_{84}Cu_4Fe_4I_4P_4 \cdot 0.25CHCl_3$ calculated: 47.24% C, 3.47% H; found: 47.25% C, 3.38% H.

X-ray quality crystals of solvate **7**·C_6H_6 were obtained exactly as described above except that benzene was used as solvent. Since the crystalline product rapidly decomposed in air (most likely by the loss of solvent), it was covered with deoxygenated mineral oil prior to further manipulation.

Synthesis of (Acetonitrile-κ*N*)bis[1-(diphenylphosphanyl-κ*P*)-1′-vinylferrocene]copper(I) Hexafluorophosphate (**7**)

A solution of **1** (83 mg, 0.21 mmol) in dichloromethane (3 ml) was added to solid tetrakis-(acetonitrile)copper(I) hexafluorophosphate (37 mg, 0.10 mmol). The mixture was stirred at room temperature for 90 min whereupon a clear orange solution resulted. The solution was filtered through PTFE syringe filter (0.45 μm pore size) and the filtrate layered with hexane. Crystallization over several days yielded a solid product, which was filtered off, washed with hexane and dried under vacuum. Yield of **7** 102 mg (93%), orange microcrystalline solid.

^1H NMR (C_6D_6): 1.51 (s, 3 H, MeCN), 4.06 (apparent t, 2 H), 4.07 (apparent q, 2 H), 4.15 (apparent t, 2 H), 4.17 (apparent t, 2 H) (4 × CH, fc); 5.08 (br dd, $^3J_{HH}$ = 10.7, $^2J_{HH} \approx 1.3$, 1 H, =CH_2), 5.23 (br dd, $^3J_{HH}$ = 17.4, $^2J_{HH} \approx 1.3$, 1 H, =CH_2), 6.28 (br dd, $^3J_{HH}$ = 17.4, 10.7, 1 H, =CH), 7.08–7.87 (m, 10 H, PPh_2). $^{31}P\{^1H\}$ NMR (C_6D_6): –6.5 (br s, $\Delta\nu_{1/2} \approx 30$), –142.2 (sept, $^1J_{PF}$ = 712). FAB MS, *m/z* (rel.%): 1025, 855 ([Cu(**1**)$_2$]$^+$), 629 ([1025 – **1**]$^+$), 459 ([Cu(**1**)]$^+$), 396 (**1**$^+$). IR (Nujol): ν(C≡N) 2271 w; 1626 w, 1586 v, 1570 w; 1310 m, 1194 w, 1166 s, 1098 s, 1029 s, 914 m, $\nu_3(PF_6)$ 839 br, vs; 745 vs, 698 vs, $\nu_4(PF_6)$ 558 vs, 514 s, 491 s, 468 m. The compound readily decomposes (probably by oxidation to Cu(II) and loss of coordinated MeCN), which did not allow for obtaining reliable microanalytical data.

TABLE III
Crystallographic data, data collection and structure refinement parameters for **2**, **3**, **4**·$CHCl_3$, **6**·C_6H_6, and **7**

Parameter	**2**	**3**	**4**·$CHCl_3$	**6**·C_6H_6	**7**
Formula	$C_{24}H_{21}FePS$	$C_{48}H_{42}Cl2Fe_2P_2Pd$	$C_{34}H_{34}Cl_4FeNPPd$	$C_{102}H_{90}Cu_4Fe_4I_4P_4$	$C_{50}H_{45}CuF_6Fe_2NP_3$
M	428.29	969.76	791.64	2424.78	1042.02
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a, Å	13.3177(2)	9.3885(2)	11.2719(3)	16.7516(2)	13.0746(1)
b, Å	17.5592(2)	11.5325(2)	12.3840(3)	15.4286(1)	25.5498(3)
c, Å	17.3493(3)	18.2658(4)	12.9910(3)	36.0600(4)	13.6385(2)
α, °			80.176(2)		
β, °	102.7613(8)	93.8253(9)	69.996(2)	93.6262(4)	101.7992(6)
γ, °			89.748(2)		
V, Å^3	3956.9(1)	1973.28(7)	1676.18(7)	9301.2(2)	4459.72(9)
Z	8	2	2	4	4
D, g ml^{-1}	1.438	1.632	1.569	1.732	1.552
μ(MoKα), mm^{-1}	0.955	1.429	1.361	2.945	1.285
T [a]	–[b]	0.620–0.723	0.759–0.912	0.572–0.835	0.772–0.827
Diffrns total	57750	25404	25119	118501	72250
Unique/obsd[c] diffrns	9025/6859	4508/4142	7698/6273	21284/16145	10200/8593
R_{int}, %[d]	3.40	3.22	4.33	5.22	3.60
No. of parameters	487	250	381	923	542
R obsd diffrns, %[e]	3.15	2.40	3.73	4.58	5.00
R, *wR* all data, %[e]	4.89, 8.65	2.72, 5.76	5.25, 9.37	6.81, 12.7	6.15, 12.5
Δρ, eÅ^{-3}	0.36, –0.40	0.49, –0.49	1.35, –0.85	2.35, –1.30	0.99, –0.72
CCDC reference No.	289215	289216	289217	289218	289219

[a] The range of transmission coefficients. [b] Not corrected. [c] Diffractions with $I_o > 2\sigma(I_o)$. [d] $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma F_o^2$, where $F_o^2(\text{mean})$ is the average intensity for symmetry equivalent diffractions. [e] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma w(F_o^2)^2]^{1/2}$.

X-ray Crystallography

Single crystals suitable for X-ray diffraction analysis were obtained by crystallization from diethyl ether–hexane (**2**: orange prism, 0.18 × 0.35 × 0.45 mm^3), chloroform–hexane (**3**: red prism, 0.30 × 0.33 × 0.45 mm^3; **4**·$CHCl_3$: red plate, 0.08 × 0.15 × 0.35 mm^3, **7**: orange plate, 0.15 × 0.20 × 0.43 mm^3), and from benzene–hexane (see also above; **6**·C_6H_6: orange plate, 0.05 × 0.28 × 0.30 mm^3). The selected crystals were mounted onto glass fibres with wax and transferred to a Nonius KappaCCD diffractometer equipped with Cryostream Cooler (Oxford Cryosystems). Full-set diffraction data ($\pm h$, $\pm k$, $\pm l$, $2\theta \leq 55°$) were collected at 150(2) K using graphite monochromatized MoKα radiation (λ = 0.71073 Å) and analyzed with the HKL program package[29] (Table III). The data were corrected for absorption using Gaussian (**3** and **6**·C_6H_6) or multiscan (**4**·$CHCl_3$ and **7**) methods incorporated in the diffactometer software (the ranges of transmission factors are given in Table III).

The structures were solved by direct methods (SIR97 [30]) and refined by weighted full-matrix least squares on F^2 (SHELXL97 [31]). The non-hydrogen atoms were refined with anisotropic displacement parameters unless specified otherwise for disordered molecular parts. The disorder was typically observed for vinylcyclopentadienyl moieties (particularly in **6**·C_6H_6 and **7**). These nonpolar groups do not participate in the coordination nor take part in any substantial intermolecular interactions; consequently, they behave as dangling peripheral groups. The disorder was treated as follows: for **6**·C_6H_6, the vinylcyclopentadienyl moieties in all four ligand moieties were constrained to have the same geometry, whereas for **7**, one of the vinylcyclopentadienyl units (ligand **2** comprising the Fe(2) atom) was refined over two positions, where the terminal $=CH_2$ carbon atom acts as a pivot, with idealized geometry for the five-membered ring and identical displacement parameters for the pairs of corresponding atoms. Carbon atoms within the mentioned disordered moieties were refined isotropically. The geometry of **2** as well as that of the ligand moieties in **3** and **4**·$CHCl_3$ were refined without such constraints. Furthermore, the solvating chloroform molecule in **4**·$CHCl_3$ was refined over two positions with the anisotropic displacement parameters restrained to the same values for each pair of the related atoms.

All hydrogen atoms were included in idealized positions with U_{iso}(H) assigned to 1.2U_{eq}(C) (aromatic and methylene) or 1.5U_{eq}(C) (methyl), and allowed to 'ride' on their adjacent carbon atom during the refinenemt. Final geometric calculations were carried out with a recent version of Platon program[32]; the values were rounded to one decimal digit in the estimated standard deviation.

CCDC 289215 (for **2**), 289216 (for **3**), 289217 (for **4**), 289218 (for **6**), 289219 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

This work was supported by the Grant Agency of the Czech Republic (grant No. 203/05/0276).

REFERENCES AND NOTES

1. Atkinson R. C. J., Gibson V. C., Long N. J.: *Chem. Soc. Rev.* **2004**, *33*, 313.

2. a) Gan K. S., Hor T. S. A. in: *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science* (A. Togni and Hayashi T., Eds), Chap. 1, p. 3–104. VCH, Weinheim 1995; b) Bandoli G., Dolmella A.: *Coord. Chem. Rev.* **2000**, *209*, 161.
3. Štěpnička P.: *Eur. J. Inorg. Chem.* **2005**, 3787.
4. a) Wright M. E.: *Organometallics* **1990**, *9*, 853; b) Butler I. R., Davies R. L.: *Synthesis* **1996**, 1350; c) Štěpnička P., Baše T.: *Inorg. Chem. Commun.* **2001**, *4*, 682.
5. Butler I. R., Cullen W. R.: *Can. J. Chem.* **1983**, *61*, 147.
6. a) Atkinson R. C. J., Gibson V. C., Long N. J., White A. J. P., Williams D. J.: *Organometallics* **2004**, *23*, 2744; b) Atkinson R. C. J., Gibson V. C., Long N. J., White A. J. P., Williams D. J.: *Dalton Trans.* **2004**, 1823.
7. Laly M., Broussier R., Gautheron B.: *Tetrahedron Lett.* **2000**, *41*, 1183.
8. a) Hor T. S. A., Chan H. S. O., Tan K. L., Phang L. T., Yan Y. K., Liu L. K., Wen Y. S.: *Polyhedron* **1991**, *10*, 2437; b) Phang L. T., Gan K. S., Lee H. K., Hor T. S. A.: *J. Chem. Soc., Dalton Trans.* **1993**, 2697; c) Pilloni G., Longato B., Bandoli G.: *Inorg. Chim. Acta* **1998**, *277*, 163; d) Coyle R. J., Slovokhotov Y. L., Antipin M. Y., Grushin V. V.: *Polyhedron* **1998**, *17*, 3059; e) Broussier R., Laly M., Perron P., Gautheron B., Nifantev I. E., Howard J. A. K., Kuzmina L. G., Kalck P.: *J. Organomet. Chem.* **1999**, *587*, 104; f) Broussier R., Bentabet E., Laly M., Richard P., Kuzmina L. G., Serp P., Wheatley N., Kalck P., Gautheron B.: *J. Organomet. Chem.* **2000**, *613*, 77; g) Grushin V. V.: *Organometallics* **2001**, *20*, 3950; h) Gusev O. V., Peganova T. A., Kalsin A. M., Vologdin N. V., Petrovskii P. V., Lyssenko K. A., Tsvetkov A. V., Beletskaya I. P.: *J. Organomet. Chem.* **2005**, *690*, 1710 (only representative examples).
9. a) Adeleke J. A., Chen Y.-W., Liu L.-K.: *Organometallics* **1992**, *11*, 2543; b) Long N. J., Martin J., Opromolla G., White A. J. P., Williams D. J., Zanello P.: *J. Chem. Soc., Dalton Trans.* **1999**, 1981; c) Gibson V. C., Long N. J., White A. J. P., Williams C. K., Williams D. J., Fontani M., Zanello P.: *J. Chem. Soc., Dalton Trans.* **2002**, 3280; d) Gibson V. C., Long N. J., White A. J. P., Williams C. K., Williams D. J.: *Organometallics* **2002**, *21*, 770; e) Aguado J. E., Canales S., Gimeno M. C., Jones P. G., Laguna A., Villacampa M. D.: *Dalton Trans.* **2005**, 3005.
10. a) Yoshida T., Tani K., Yamagata T., Tatsuno Y., Saito T.: *J. Chem. Soc., Chem. Commun.* **1990**, 292; b) Butler I. R.: *Polyhedron* **1992**, *11*, 3117; c) Butler I. R.: *Organometallics* **1992**, *11*, 74; d) Butler I. R., Kalaji M., Nehrlich L., Hursthouse M., Karaulov A. I., Malik K. M. A.: *J. Chem. Soc., Chem. Commun.* **1995**, 459.
11. Butler I. R., Coles S. J., Hursthouse M. B., Roberts D. J., Fujimoto N.: *Inorg. Chem. Commun.* **2003**, *6*, 760.
12. Polášek M., Štěpnička P.: *J. Mass Spectrom.* **1998**, *33*, 739.
13. Opposite sings of the torsion angles indicate the opposite configurations of the molecules chosen for the refinement (enantiomers). The molecules show planar chirality in the solid state owing to fixed geometry of the ferrocene unit.
14. Dong T.-Y., Hwang M.-Y., Hsu T.-L., Schei C.-C., Yeh S.-K.: *Inorg. Chem.* **1990**, *29*, 80.
15. Wang Y.-P., Lin T.-S., Shyu R.-S., Hwu J.-M., Wang Y., Cheng M.-C.: *J. Organomet. Chem.* **1989**, *371*, 57.
16. Štěpnička P., Podlaha J., Gyepes R., Polášek M.: *J. Organomet. Chem.* **1998**, *552*, 293.
17. Štěpnička P., Lamač M., Císařová I.: *Polyhedron* **2004**, *23*, 921.
18. Štěpnička P., Císařová I.: *Organometallics* **2003**, *22*, 1728.
19. Pregosin P. S., Kunz R. W. in: *NMR Basic Principles and Progress* (P. Diehl, E. Fluck and R. Kosfeld, Eds), Vol. 16, Sect. E, p. 65. Springer, Berlin 1979; and references therein.

20. Štěpnička P., Císařová I.: *J. Chem. Soc., Dalton Trans.* **1998**, 2807.
21. Ref.[19], Sect. G, Table 16 on p. 110 ff; and references therein.
22. Triclinic, space group $P\bar{1}$ (No. 2); unit cell parameters: a = 9.6874(3) Å, b = 11.6241(3) Å, c = 11.8603(4) Å; α = 66.139(2)°, β = 71.360(2)°, γ = 65.363(2)°; Z = 1. The rhodium atom resides on the crystallographic inversion centre and its chloride and carbonyl ligands are distributed over *trans* positions of the square-planar coordination sphere around rhodium(I). The shape of the whole molecule seems to be determined by the bulky (diphenylphosphanyl)ferrocenyl ligand with the Cl/CO donors acting just as small, embedded moieties.
23. Drahoňovský D., Císařová I., Štěpnička P., Dvořáková H., Maloň P., Dvořák D.: *Collect. Czech. Chem. Commun.* **2001**, *66*, 588.
24. Hartley F. R.: *The Chemistry of Platinum and Palladium*, p. 209–303. Aplied Science, London 1973.
25. Štěpnička P., Gyepes R., Podlaha J.: *Collect. Czech. Chem. Commun.* **1998**, *63*, 64.
26. Drew D., Doyle J. R., Shaver A. G.: *Inorg. Synth.* **1972**, *13*, 47.
27. Cope A. C., Friedrich E. C.: *J. Am. Chem. Soc.* **1968**, *90*, 909.
28. McCleverty J. A., Wilkinson G.: *Inorg. Synth.* **1966**, *8*, 214.
29. Otwinowski Z., Minor W.: *HKL Denzo and Scalepack Program Package*. Nonius BV, Delft 1997. For a reference, see: Otwinowski Z., Minor W.: *Methods Enzymol.* **1997**, *276*, 307.
30. Altomare A., Burla M. C., Camalli M., Cascarano G. L., Giacovazzo C., Guagliardi A., Moliterni A. G. G., Polidori G., Spagna R.: *J. Appl. Crystallogr.* **1999**, *32*, 115.
31. Sheldrick G. M.: *SHELXL97. Program for Crystal Structure Refinement from Diffraction Data*. University of Göttingen, Göttingen 1997.
32. Spek A. L.: *Platon, A Multipurpose Crystallographic Tool*. Utrecht University, Utrecht 2003; and updates. Distributed via Internet; home page http://www.cryst.chem.uu.nl/platon/.