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FULL PAPER

Optically active cyclopalladated derivatives of arylimines. Crystal structures of (+)-[{Pd[*p*-MeOC$_6$H$_3$CH=NCH$_2$-(1*S*,2*R*,5*S*)-CHCH$_2$CH$_2$CHC(Me)$_2$CHCH$_2$](μ-X)}$_2$] (X = Cl or Br), (+)-[Pd{*p*-MeOC$_6$H$_3$CH=NCH$_2$-(1*S*,2*R*,5*S*)-CHCH$_2$-CH$_2$CHC(Me)$_2$CHCH$_2$}Cl(PPh$_3$)] and (+)-[{Pd[*p*-Me-OC$_6$H$_3$CH=NCH$_2$-(1*S*,2*R*,5*S*)-CHCH$_2$CH$_2$CHC(Me)$_2$CHCH$_2$]Cl}$_2$-{Fe(η^5-C$_5$H$_4$PPh$_2$)$_2$}]

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4-Methoxybenzaldehyde reacted with (−)-(1*S*,2*R*,5*S*)-2-aminomethyl-6,6-dimethylbicyclo[3.1.1]heptane in benzene to give the new chiral arylimine *p*-MeOC$_6$H$_4$CH=NCH$_2$-(1*S*,2*R*,5*S*)-CHCH$_2$CH$_2$CHC(CH$_3$)$_2$CHCH$_2$ [(−)-**I**]. Cyclopalladation of the imine with Pd(O$_2$CMe)$_2$ in MeCO$_2$H, followed by treatment with LiCl, LiBr or KI, gave the corresponding di-μ-halide-bridged organometallics (+)-[{Pd[*p*-MeOC$_6$H$_3$CH=NCH$_2$-(1*S*,2*R*,5*S*)-CHCH$_2$CH$_2$CHC(Me)$_2$CHCH$_2$](μ-X)}$_2$] [X = Cl (+)-**1a**, Br (+)-**1b** or I (+)-**1c**]. Subsequent treatment of these compounds with triphenylphosphine, pyridine (py) or 1,1′-bis(diphenylphosphino)ferrocene (dppf) in acetone yielded the corresponding cyclopalladated derivatives (+)-[Pd{*p*-MeOC$_6$H$_3$CH=NCH$_2$-(1*S*,2*R*,5*S*)-CHCH$_2$CH$_2$CHC(Me)$_2$CHCH$_2$}X(PPh$_3$)] [X = Cl (+)-**2a**, Br (+)-**2b** or I (+)-**2c**], (+)-[Pd{*p*-MeOC$_6$H$_3$CH=NCH$_2$-(1*S*,2*R*,5*S*)-CHCH$_2$CH$_2$CHC(CH$_3$)$_2$CHCH$_2$}X(py)] [X = Cl (+)-**3a**, Br (+)-**3b** or I (+)-**3c**] and (+)-[{Pd[*p*-MeOC$_6$H$_3$CH=NCH$_2$-(1*S*,2*R*,5*S*)-CHCH$_2$CH$_2$CHC(Me)$_2$CHCH$_2$)]X}$_2$(dppf)] [X = Cl (+)-**4a**, Br (+)-**4b** or I (+)-**4c**], which have been characterized by NMR and mass spectrometry, optical rotation and elemental analysis. The crystal structures of (+)-**1a**, (+)-**1b**, (+)-**2a** and (+)-**4b**·CH$_2$Cl$_2$ have been determined.

The synthesis and structure analysis of orthopalladated complexes containing N-donor ligands have received considerable recent attention.[1,2] Although a large number of cyclopalladated compounds have been described, few of them are optically active.[3] The preparation of such compounds is of great interest as a consequence of their useful applications. It has been shown that (*R* or *S*) bis(μ-chloro)bis[2-(1-dimethylamino)ethylphenyl-*C*^{2},*N*]dipalladium(II), bis(μ-chloro)bis[2-(1-dimethylamino)-ethyl-3-naphthyl-*C*^{3},*N*]dipalladium(II) and bis(μ-chloro)bis-[1-(2,6-dichlorobenzylideneamino)ethylphenyl]dipalladium(II) may be applied not only to optical resolution of racemic phosphines and arsines,[2e,n,3b,4] but also to the determination of the optical purity of chiral phosphines and amines,[2e,5] and the absolute configuration of chiral phosphines by NMR spectroscopy and single-crystal X-ray analysis.[6] In addition, some studies dealing with the anti-tumor activity of such derivatives have also been published.[7] Recently, chiral cyclopalladated compounds have been used to promote asymmetric Diels–Alder reaction in the asymmetric synthesis of (P-chiral) As–P and P–P bidentate ligands,[2m,8] and metallomesogens displaying cholesteric behavior or improved ferroelectric properties have been obtained from cyclopalladated imine derivatives containing a chiral center in the carboxylate ligand[9] or in an alkyl chain.[10]

On the other hand, although the general utility of cyclopalladated complexes in asymmetric synthesis is well known, few optically active cyclopalladated compounds have been synthesized.[3] Albert *et al.*[3b] have prepared optically active halide-bridged exocyclic cyclopalladated dimers, but no optically active endocyclic cyclopalladated compound has been reported. Here we present the synthesis and single-crystal X-ray analysis of optically active halide-bridged endocyclic cyclopalladated dimers which react readily with a wide range of Lewis bases to afford monomeric complexes.

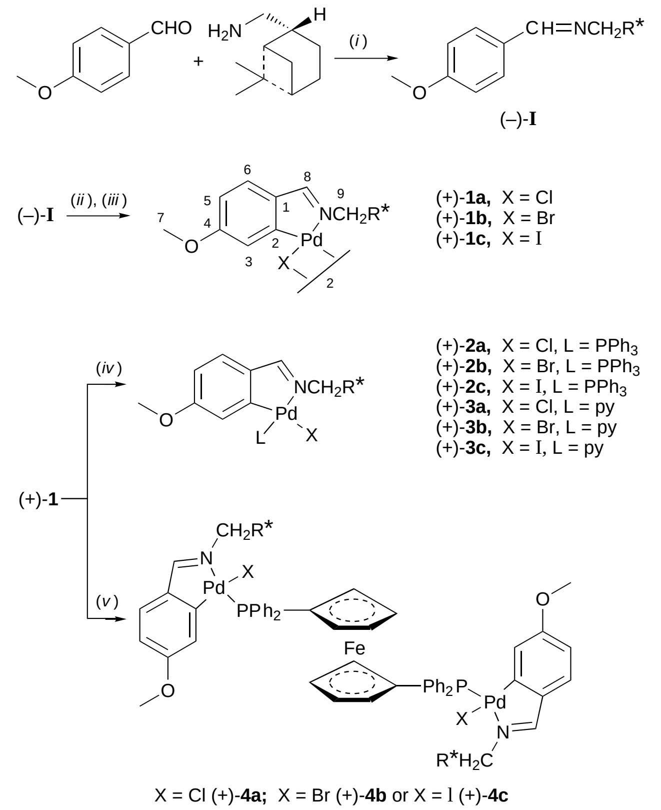
Results and Discussion

Ligand synthesis

The optically active phenylimine (−)-**I** was obtained as an oil in *ca.* 75% yield from the reaction between 4-methoxybenzaldehyde and (−)-*cis*-myrtanylamine {(−)-(1*S*,2*R*,5*S*)-2-aminomethyl-6,6-dimethylbicyclo[3.1.1]heptane} in benzene (Scheme 1).[3b] The presence of molecular sieves (5 Å) was needed to displace equilibrium (*i*) to the right (Scheme 1), as the ligand might suffer appreciable decomposition in the purification procedure using column chromatography. Proton and ^{13}C-{^{1}H} NMR spectroscopy in CDCl$_3$ of compound (−)-**I** provided useful information about its structure and behavior in solution (see Experimental section).

Cyclopalladation of imine (−)-I: synthesis of chiral cyclopalladated compounds

Cyclopalladation of the imine with Pd(O$_2$CMe)$_2$ in MeCO$_2$H, followed by treatment with LiCl, LiBr or KI, gives the corresponding di-μ-halide-bridged dimers (+)-[{Pd[*p*-MeOC$_6$H$_3$-CH=NCH$_2$-(1*S*,2*R*,5*S*)-CHCH$_2$CH$_2$CHC(Me)$_2$CHCH$_2$]-(μ-X)}$_2$] [X = Cl (+)-**1a**, Br (+)-**1b** or I (+)-**1c**] which contain



Scheme 1 R* = (1*S*,2*R*,5*S*)-$\mathrm{CHCH_2CH_2CHC(Me)_2CHCH_2}$. (*i*) Benzene, 5 Å molecular sieves, reflux, 6 h; (*ii*) Pd(O$_2$CMe)$_2$, MeCO$_2$H, 95 °C, 1 h; (*iii*) LiCl, LiBr or KI, EtOH, room temperature, 30 min; (*iv*) PPh$_3$ or pyridine, acetone, reflux, 30 min; (*v*) dppf, acetone, room temperature, 3 h

endocyclic five-membered metallacycles with a σ(Pd–C$_{sp^2}$) bond. Owing to the high insolubility of this kind of compound, they are usually treated with neutral Lewis bases such as triphenylphosphine, pyridine (py) and 1,1′-bis(diphenylphosphino)ferrocene (dppf) in acetone and converted into more soluble monomeric compounds (+)-[Pd{*p*-$\mathrm{MeOC_6H_3CH{=}NCH_2}$-(1*S*,2*R*,5*S*)-$\mathrm{CHCH_2CH_2CHC(Me)_2CHCH_2}$}X(PPh$_3$)] [X = Cl (+)-**2a**, Br (+)-**2b** or I (+)-**2c**], (+)-[Pd{*p*-$\mathrm{MeOC_6H_3CH{=}NCH_2}$-(1*S*,2*R*,5*S*)-$\mathrm{CHCH_2CH_2CHC(Me)_2CHCH_2}$}X(py)] [X = Cl **3a**, Br (+)-**3b** or I (+)-**3c**] and ferrocene-bridged dimers (+)-[{Pd[*p*-$\mathrm{MeOC_6H_3CH{=}NCH_2}$-(1*S*,2*R*,5*S*)-$\mathrm{CHCH_2CH_2CHC(Me)_2CHCH_2}$]X}$_2$(dppf)] [X = Cl (+)-**4a**, Br (+)-**4b** or I (+)-**4c**], respectively. Evidence of the cleavage of the Pd–N bond was not observed in any of the cases, even when a large excess (up to 4 molar equivalents) of Lewis base was used. All compounds can be obtained in pure form after purification by SiO$_2$ column chromatography, using CHCl$_3$ as the eluent.

Characterization

Microanalysis and mass spectra indicated that compounds **1** were dimeric cyclopalladated complexes, whereas their ^{1}H NMR spectra and of the imine (−)-**I** in CDCl$_3$ showed that the two doublets due to the pairs H^2, H^6 and H^3, H^5 of the phenylimine split into three signals (H^3, H^5, H^6), which were shifted further upfield upon cyclopalladation, thus indicating that the palladium atom results in a decrease in the ring current of the substituted phenyl moiety.[2h] The large variation observed for the chemical shifts of protons H^3, H^5 and H^6 provided evidence for Pd–N association as well as cyclometallation through the phenyl ring. The ^{1}H NMR spectra in CDCl$_3$ show well resolved signals in the aromatic region, so these compounds are halide-bridged cyclopalladated complexes with a slightly folded structure. Although *cis* and *trans* isomers are possible,[11] we conclude that compounds **1** exist only in the *trans* configuration, since mixtures of *trans* and *cis* isomers for each dimer would result in more complex ^{1}H NMR spectra at 300 MHz with doublet signals. This was confirmed by crystal structure determination in the case of (+)-**1a** and (+)-**1b**. Variation of the chemical shift of the CH=N proton is indicative of the structure and configuration of the ligand (*cis* or *trans*) in the palladated complex.[12,13] It is well known that for the endocyclic palladacycles (which can be formed only if the imine has an *trans* conformation) the signal is shifted to high field.[2k] In our case the chemical shift of the CH=N proton is shifted upfield by 0.52 ppm. One of the most relevant differences observed in the ^{13}C-{^{1}H} NMR spectra of free (−)-**I** and its cyclopalladated complexes is the splitting of the resonance due to the C^2, C^6 and C^3, C^5 pairs of carbon atoms, since the formation of the metallacycle involves a decrease in the symmetry of the substituted cyclopentadienyl ring. There are only a few papers in the literature about the influence of the metal on carbon chemical shifts in orthopalladation reactions. When a Pd–C (aliphatic) bond is formed a small deshielding ($\Delta\delta \approx 5$ ppm)[14] is observed, which becomes larger in the case of a Pd–C (aromatic) bond ($\Delta\delta \approx 18$ ppm),[14] probably due to Pd–C back bonding. This effect is substantially larger for azobenzene and benzylideneamine complexes, where $\Delta\delta$ is higher than 30 ppm. As Pople's equation[15] indicates, an increase in M–C bond order due to π-back bonding increases the deshielding term, σ^{para}. The signals of the palladated carbon atoms (C^2) always appear between δ 160 and 164, corresponding to a 30–34 ppm downfield shift from the signal of the parent imine. The ^{31}P-{^{1}H} NMR spectra of complexes **2** and **4** showed a singlet in the range δ 43.43–55.28 (see Experimental section), which is consistent with the values reported for related five-membered cyclopalladated derivatives containing a σ(Pd–C$_{sp^2,\ phenyl}$) bond in which the imino nitrogen and the phosphine ligand are in a *trans* arrangement.[2k]

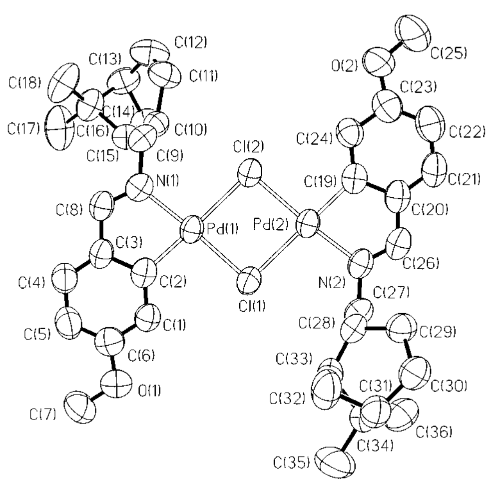


Fig. 1 Molecular structure (30% thermal ellipsoids) and absolute configuration of complex (+)-**1a** with the atom numbering scheme. Molecule (+)-**1b** has the same structure except that the chloride ligands are replaced by bromide ligands

Crystal and molecular structures of complexes (+)-1a and (+)-1b

Fig. 1 shows the molecular structure of isostructural complexes (+)-**1a** (X = Cl) and (+)-**1b** (X = Br) with the atom numbering scheme, and Table 1 gives selected bond distances and angles. The halide-bridged cyclopalladated dimer has a slightly folded structure [the angle between the two planes defined by atoms Pd(1), X(1), X(2) and Pd(2), X(1), X(2) is 171.5° for (+)-**2a**, and

Table 1 Selected bond lengths (Å) and bond angles (°) for complexes **1a**, **1b**, **2a** and **4b**

	(+)-**1a** (X = Cl)	(+)-**1b** (X = Br)		(+)-**1a** (X = Cl)	(+)-**1b** (X = Br)
Pd(1)–C(2)	1.981(5)	1.967(8)	Pd(2)–X(2)	2.346(1)	2.454(1)
Pd(1)–N(1)	2.037(4)	2.048(7)	Pd(2)–X(1)	2.495(1)	2.564(1)
Pd(1)–X(1)	2.340(1)	2.457(1)	N(1)–C(8)	1.275(6)	1.29(1)
Pd(1)–X(2)	2.462(1)	2.602(1)	N(1)–C(9)	1.470(6)	1.44(1)
Pd(2)–C(19)	1.968(5)	1.999(8)	N(2)–C(26)	1.291(7)	1.31(1)
Pd(2)–N(2)	2.034(4)	1.045(7)	N(2)–C(27)	1.476(6)	1.46(1)
C(2)–Pd(1)–N(1)	81.5(2)	81.1(3)	C(2)–Pd(1)–X(1)	95.5(1)	95.1(2)
N(1)–Pd(1)–X(1)	176.3(1)	175.2(2)	C(2)–Pd(1)–X(2)	178.1(1)	176.9(2)
N(1)–Pd(1)–X(2)	96.6(1)	98.2(2)	X(1)–Pd(1)–X(2)	86.42(4)	85.81(3)
C(19)–Pd(2)–N(2)	81.2(2)	81.3(3)	C(19)–Pd(2)–X(2)	94.9(1)	95.8(2)
N(2)–Pd(2)–X(2)	175.8(1)	176.7(2)	C(19)–Od(2)–X(1)	177.8(1)	177.3(2)
N(2)–Pd(2)–X(1)	98.45(1)	96.2(2)	X(2)–Pd(2)–X(1)	85.53(4)	86.70(3)
Pd(1)–X(1)–Pd(2)	93.33(4)	93.81(3)	Pd(2)–X(2)–Pd(1)	94.06(4)	92.97(3)
C(8)–N(1)–Pd(1)	114.1(3)	113.4(6)	C(26)–N(2)–Pd(2)	115.1(3)	113.2(6)
N(1)–C(8)–C(3)	118.2(4)	117.0(8)	C(20)–C(19)–Pd(2)	113.3(4)	112.0(6)

(+)-**2a**				(+)-**2a**			
Pd(1)–C(1)	2.011(5)	Pd(1)–N(1)	2.082(4)	Pd(2)–N(2)	2.111(4)	Pd(2)–P(2)	2.250(2)
Pd(1)–P(1)	2.264(1)	Pd(1)–Cl(1)	2.380(2)	Pd(2)–Cl(2)	2.364(2)	P(2)–C(59)	1.792(6)
P(1)–C(19)	1.785(5)	P(1)–C(25)	1.825(5)	P(2)–C(71)	1.847(6)	P(2)–C(65)	1.856(5)
P(1)–C(31)	1.858(5)	N(1)–C(7)	1.299(7)	N(2)–C(47)	1.247(8)	N(2)–C(48)	1.429(8)
N(1)–C(8)	1.511(6)	Pd(2)–C(41)	2.055(6)				
C(1)–Pd(1)–N(1)	78.8(2)	C(1)–Pd(1)–P(1)	95.6(1)	N(1)–C(7)–C(6)	114.2(4)	C(41)–Pd(2)–N(2)	82.4(2)
N(1)–Pd(1)–P(1)	173.9(1)	C(1)–Pd(1)–Cl(1)	170.7(1)	C(41)–Pd(2)–P(2)	91.9(1)	N(2)–Pd(2)–P(2)	173.9(2)
N(1)–Pd(1)–Cl(1)	92.9(1)	P(1)–Pd(1)–Cl(1)	92.82(5)	C(41)–Pd(2)–Cl(2)	172.8(1)	N(2)–Pd(2)–Cl(2)	92.3(2)
C(7)–N(1)–Pd(1)	115.7(3)	C(6)–C(1)–Pd(1)	115.1(3)	P(2)–Pd(2)–Cl(2)	93.58(6)	C(47)–N(2)–Pd(2)	110.7(4)

(+)-**4b**			(+)-**4b**		
	Molecule I	Molecule II		Molecule I	Molecule II
Pd(1)–C(12)	2.044(6)	1.972(6)	P(1)–C(1)	1.815(6)	1.806(7)
Pd(1)–N(1)	2.082(6)	2.106(6)	P(1)–C(47)	1.834(6)	1.840(7)
Pd(1)–P(1)	2.269(2)	2.282(2)	P(2)–C(65)	1.798(7)	1.798(7)
Pd(1)–Br(1)	2.529(1)	2.547(1)	P(2)–C(6)	1.799(6)	1.821(7)
Pd(2)–C(30)	2.050(7)	2.003(7)	P(2)–C(59)	1.831(6)	1.822(6)
Pd(2)–N(2)	2.114(5)	2.148(6)	N(1)–C(17)	1.329(8)	1.250(9)
Pd(2)–P(2)	2.266(2)	2.273(2)	N(1)–C(18)	1.466(9)	1.457(9)
Pd(2)–Br(2)	2.540(1)	2.538(1)	N(2)–C(35)	1.286(9)	1.267(1)
P(1)–C(53)	1.801(6)	1.804(6)	N(2)–C(36)	1.459(8)	1.436(9)
C(12)–Pd(1)–N(1)	80.1(2)	79.8(2)	N(2)–Pd(2)–P(2)	171.4(2)	175.3(2)
C(12)–Pd(1)–P(1)	96.9(2)	96.0(2)	C(30)–Pd(2)–Br(2)	167.8(2)	172.3(2)
N(1)–Pd(1)–P(1)	171.4(2)	168.5(2)	N(2)–Pd(2)–Br(2)	92.8(2)	93.0(2)
C(12)–Pd(1)–Br(1)	163.3(2)	164.5(2)	P(2)–Pd(2)–Br(2)	92.08(5)	91.59(6)
N(1)–Pd(1)–Br(1)	91.5(2)	93.3(2)	C(17)–N(1)–Pd(1)	113.1(4)	110.9(5)
P(1)–Pd(1)–Br(1)	93.33(5)	93.32(5)	C(35)–N(2)–Pd(2)	113.0(4)	113.9(5)
C(30)–Pd(2)–N(2)	79.5(2)	80.3(3)	C(11)–C(12)–Pd(1)	112.5(4)	111.4(5)
C(30)–Pd(2)–P(2)	96.8(2)	95.2(2)	N(1)–C(17)–C(11)	116.5(6)	122.9(7)

171.2° for (+)-**1b**]. The palladium atom is bonded to an imino nitrogen, an *ortho*-carbon of the phenyl ring (forming an *endo* structure), and two bridging halogen atoms in a slightly distorted square-planar geometry, as can be seen in the deviation (Å) from the plane defined by atoms C(2), N(1), X(1), X(2) and Pd(1) [Pd(1), −0.020; C(2), −0.012; Cl(1), 0.019; Cl(2), −0.009; N(1), 0.022 for (+)-**1a**; and Pd(1), 0.002; C(2), −0.066; Br(1), 0.049; Br(2), −0.046; N(1), 0.060 for (+)-**1b**]. The bond angles (Table 1) between adjacent atoms in the co-ordination sphere of the palladium lie in the range 81.2(2)–98.4(1)° for (+)-**1a**, and 81.1(3)–98.2(2)° for (+)-**1b**. The Pd(1)–X(2) and Pd(2)–X(1) bonds are significantly longer than the Pd(1)–X(1) and Pd(2)–X(2) bonds, which is a consequence of different *trans* influences of the aromatic C(2) and imino N(1) atoms. The palladium–ligand bond lengths (Table 1) are similar to those found in five-membered palladocyclic compounds containing organic imines.

Crystal and molecular structures of complex (+)-2a

A perspective drawing of the molecular structure of compound (+)-**2a** and the atom labelling scheme are presented in Fig. 2. Selected bond lengths and angles are given in Table 1. The crystal structure consists of discrete molecules of (+)-[Pd{*p*-MeOC$_6$H$_3$CH=NCH$_2$-(1*S*,2*R*,5*S*)-CHCH$_2$CH$_2$CHC(Me)$_2$CHCH$_2$}Cl(PPh$_3$)] held by van der Waals forces. The palladium atom is bound to a chloride, the phosphorus atom of the PPh$_3$, the imino nitrogen, and the C(1) atom of the phenyl moiety in a slightly distorted square-planar co-ordination geometry. The deviations from the plane defined by atoms Pd, P, Cl, N and C(1) are 0.013, 0.050, −0.055, 0.064 and −0.072 Å, respectively. The *endo* five-membered palladated ring is practically coplanar with the metallated aryl ring as reflected by the dihedral angle of 2.9° between them. The Pd–N and Pd–C bond lengths [2.082(4) and 2.011(5) Å] are longer than those of the dimers (+)-**1a** and (+)-**1b** [2.037(4), 1.981(5) and 2.048(7), 1.967(8) Å]. The P–Pd–N bond angle is 173.9(1)°, thus confirming the *trans* arrangement of the imino nitrogen and the phosphine ligand.

Crystal and molecular structures of complex (+)-4b·CH$_2$Cl$_2$

The ferrocene-bridged compound (+)-**4b**·CH$_2$Cl$_2$ crystallizes in

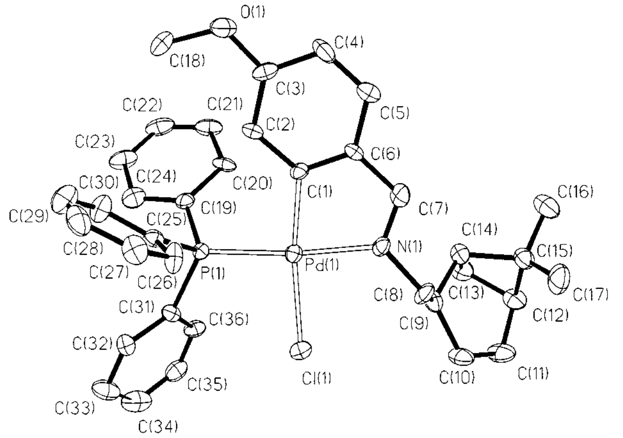


Fig. 2 Molecular structure (30% thermal ellipsoids) and absolute configuration of complex (+)-**2a** with the atom numbering scheme

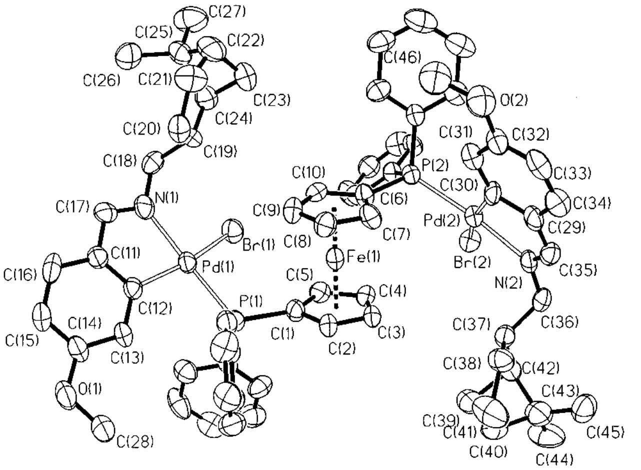


Fig. 3 Molecular structure (30% thermal ellipsoids) and absolute configuration of complex (+)-**4b** with the atom-numbering scheme for independent molecule I. For molecule II the same scheme is used except that a prime is added to each atom label

the monoclinic space group $P2_1$ with $Z = 4$. The X-ray analysis confirmed that the desired compound has been formed, and both independent molecules I and II have virtually the same structure (Fig. 3). Each palladium atom is bound to a bromide, a phosphorus atom of dppf, the imino nitrogen, and the *ortho*-carbon atom of the phenyl moiety, exhibiting a slightly distorted square-planar configuration, as can be seen in the deviations (in Å, values for molecule II given in parentheses) from the planes [Pd(1), 0.05 (0.024); P(1), 0.063 (0.187); Br(1), −0.184 (−0.184); N(1), 0.218 (0.239); C(12), −0.247 (−0.266); Pd(2), 0.012 (0.020); P(2), 0.135 (0.043); Br(2), −0.135 (−0.037); N(2), 0.171 (−0.045); C(30), −0.183 (0.056)]. The structure confirms the *trans* relationship of the phosphine ligand and the imino nitrogen in each cyclopalladated unit. The palladium-ligand bond lengths (Table 1) are similar to those obtained in five-membered palladocyclic compounds containing organic imines. The bond angles (Table 1) between adjacent atoms in the co-ordination sphere lie in the range 80.0(2)–96.8(2)°. The two rings of the bicyclic system resulting from fusion of the palladocycle with the C_6H_3 moiety are each practically planar, forming dihedral angles of 7.9 and 5.1° in molecule I and 9.2 and 5.0° in II. The angles between the two palladacycles are 73.8 and 71.2° in molecule I and II, respectively. The *trans* arrangement of the two palladacycles helps to ease the inter-ligand repulsion otherwise imposed. Since the Pd–P distances [2.266(2)–2.282(2) Å] are not indicative of any significant bond weakening as compared to the corresponding value of 2.264(1) Å in compound (+)-**2a**, the steric demand of a local $Ph_2PC_5H_4$ site cannot be considered as unfavourably high and hence the *trans* configuration of (+)-**4b** originates from the spatial diffuseness of the metalloligand as a whole. Interestingly, molecules I and II exhibit different conformations caused by rotation about the Pd–P bonds: the torsion angles Br(1)–Pd(1)–P(1)–C(1) and Br(2)–Pd(2)–P(2)–C(6) take the values 42.7 and 115.0°, respectively, in molecule I, but change in sign to −47.2 and −112.6°, respectively, in II.

Experimental

Proton and $^{13}C-\{^1H\}$ NMR spectra were recorded on a Bruker DPX 300 instrument using $CDCl_3$ (99.8%) and $SiMe_4$, respectively, as solvent and internal standard, $^{31}P-\{^1H\}$ NMR spectra on a Bruker ARX 500 spectrometer using $CDCl_3$ (99.8%) as solvent, $SiMe_4$ and H_3PO_4 (85%) as internal standard, respectively. Optical rotations were measured in chloroform solution in a 1 dm cell at 20 °C with a Perkin-Elmer model 341 polarimeter. Mass spectra were recorded on a Hewlett-Packard 5989B mass spectrometer. Elemental analyses were performed by MEDAC Ltd. of the Department of Chemistry at Brunel University. *p*-Anisaldehyde and (−)-*cis*-myrtanylamine (Aldrich) were used as received.

Syntheses

(−)-*p*-MeOC$_6$H$_4$CH=NCH$_2$-(1*S*,2*R*,5*S*)-CHCH$_2$CH$_2$CHC(Me)$_2$CHCH$_2$ (−)-I. 4-Methoxybenzaldehyde (1.36 g, 10 mmol) and (−)-*cis*-myrtanylamine (1.53 g, 10 mmol) were dissolved in dry benzene (100 cm^3). The flask containing the reaction mixture was connected to a condenser equipped with a Dean–Stark apparatus. The solution was refluxed on an oil-bath for about 6 h. The hot solution was carefully transferred to a Schlenk tube, in which 5 Å molecular sieve (3.0 g, Aldrich) was introduced. The mixture was refluxed for 5–6 h then the hot solution was carefully filtered and the filtrate reduced to a colourless oil. Yield: 2.08 g (76.8%). $[\alpha]_D$ −6.19° (*c* 1.0 g cm^{-3}, $CHCl_3$). ^1H NMR (selected data): δ 8.12 (1 H, s, H^8), 7.60 (2 H, d, $J = 15$, H^3, H^5), 6.85 (2 H, d, $J = 15$ Hz, H^2, H^6), 3.76 (3 H, s, H^7) and 3.53 (2 H, m, NCH$_2$). $^{13}C-\{^1H\}$ NMR (selected data): δ 160.6 (C^8), 162.0 (C^1), 130.5 (C^4), 130.0 (C^2, C^6), 114.5 (C^3, C^5), 68.6 (C^9) and 55.8 (C^7). Mass spectrum *m*/*z* 271 (M^+) (Found: C, 79.63; H, 9.36; N, 4.96. Calc. for $C_{18}H_{25}NO$: C, 79.70; H, 9.22; N, 5.17%).

(+)-[{Pd[*p*-MeOC$_6$H$_3$CH=NCH$_2$-(1*S*,2*R*,5*S*)-CHCH$_2$CH$_2$CHC(Me)$_2$CHCH$_2$](μ-X)}$_2$] [X = Cl (+)-1a, Br (+)-1b or I (+)-1c]. A mixture of palladium(II) acetate (0.44 g, 2.0 mmol) and the imine (0.49 g, 2.0 mmol) in acetic acid (10 cm^3) was stirred for 1 h at 95 °C, then cooled to room temperature and dried in vacuum. The dark brown solid was added to a solution of LiCl, LiBr or KI in anhydrous ethanol (10 cm^3), and the yellow suspension stirred at room temperature for 30 min. The solid was then filtered off, successively washed with water, ethanol, diethyl ether, and dried under high vacuum. The product was extracted into chloroform and isolated as a colourless [(+)-**1a**] or light yellow [(+)-**1b**, (+)-**1c**] solid *via* column chromatography (silica 60 and chloroform as eluent). The solid was subsequently recrystallized from dichloromethane by addition of *n*-hexane. Yield: 0.68 (82), 0.78 (85) and 0.74 g (73%), respectively. Complex (+)-**1a**: $[\alpha]_D$ +38.78° (*c* 1.0, $CHCl_3$); ^1H NMR (selected data) δ 7.60 (2 H, s, H^8), 7.08 (2 H, d, $J = 6$, H^3), 6.90 (2 H, s, H^5), 6.55 (2 H, d, $J = 12$ Hz, H^6), 3.81 (6 H, s, H^7) and 3.50 (4 H, m, H^9); $^{13}C-\{^1H\}$ NMR (selected data) δ 172.9 (C^8), 160.0 (C^2), 139.3 (C^1), 128.8 (C^4), 119.4 (C^6), 119.0 (C^3), 111.0 (C^5), 68.7 (C^9) and 55.9 (C^7); mass spectrum *m*/*z* 824 (M^+) (Found: C, 52.56; H, 5.99; N, 3.15. Calc. for $C_{18}H_{24}ClNOPd$: C, 52.43; H, 5.82; N, 3.40%). Complex (+)-**1b**: $[\alpha]_D$ +46.11° (*c* 1.0, $CHCl_3$); ^1H NMR (selected data) δ 7.64 (2 H, s, H^8), 7.16 (2 H, d, $J = 9$, H^3), 6.99 (2 H, s, H^5), 6.54 (2 H, d, $J = 15$ Hz, H^6), 3.81 (6 H, s, H^7) and 3.58 (4 H, m, H^9); ^{13}C-{^{1}H} NMR (selected data) δ 173.3 (C^8), 160.3 (C^2), 158.1 (C^1), 139.6 (C^4), 129.1 (C^6), 121.2 (C^3), 110.6 (C^5), 67.2 (C^9) and 55.9 (C^7); mass spectrum *m/z* 914 (M^+) Found: C, 47.43; H, 5.41; N, 2.92. Calc. for $C_{18}H_{24}BrNOPd$: C, 47.26; H, 5.25; N, 3.06%). Complex (+)-**1c**: [α]$_D$ +56.99° (*c* 1.0, CHCl$_3$); ^{1}H NMR (selected data) δ 7.71 (2 H, s, H^8), 7.22 (2 H, d, $J = 8$, H^3), 6.96 (2 H, s, H^5), 6.54 (2 H, d, $J = 8$ Hz, H^6), 3.82 (6 H, s, H^7) and 3.72 (4 H, m, H^9); ^{13}C-{^{1}H} NMR (selected data) δ 174.0 (C^8), 161.0 (C^2), 141.3 (C^1), 129.5 (C^4), 118.9 (C^6), 116.1 (C^3), 110.2 (C^5), 66.9 (C^9) and 56.0 (C^7); mass spectrum *m/z* 1007 (M^+) (Found: C, 42.66; H, 4.92; N, 2.57. Calc. for $C_{18}H_{24}INOPd$: C, 42.91; H, 4.77; N, 2.78%).

(+)-[Pd{*p*-MeOC$_6$H$_3$CH=NCH$_2$-(1*S*,2*R*,5*S*)-CHCH$_2$CH$_2$CHC(Me)$_2$CHCH$_2$}X(PPh$_3$)] [X = Cl (+)-2a, Br (+)-2b or I (+)-2c]. Triphenylphosphine (0.105 g, 0.4 mmol) was added to an acetone suspension (15 cm^3) containing the dimeric complex **2** (0.1 mmol). The resulting mixture was refluxed for 30 min during which the starting material dissolved gradually. After cooling to room temperature the solution was filtered and the filtrate concentrated to dryness in vacuum. Addition of diethyl ether to the residue resulted in precipitation of the desired compound, which was recrystallized from dichloromethane–*n*-hexane (1 : 3). Yield: 0.24 (91), 0.25 (87) and 0.24 g (79%), respectively. Complex (+)-**2a**: [α]$_D$ +58.36° (*c* 1.0, CHCl$_3$); ^{1}H NMR (selected data) δ 7.91 (1 H, s, H^8), 7.73 (6 H, m, PPh$_3$), 7.39 (9 H, m, PPh$_3$), 7.20 (1 H, d, $J = 9$, H^3), 5.96 (1 H, s, H^5), 6.42 (1 H, d, $J = 12$ Hz, H^6), 3.96 (1 H, m, H^9), 3.74 (1 H, m, H^9) and 2.95 (3 H, s, H^7); ^{13}C-{^{1}H} NMR (selected data) δ 174.2 (C^8), 161.2 (C^2), 141.3 (C^1), 129.2 (C^4), 128.7 (C^6), 123.7 (C^3), 111.4 (C^5), 65.2 (C^9), 55.2 (C^7), 160.0, 141.4, 136.1, 136.0, 132.1, 131.3 (PPh$_3$); ^{31}P-{^{1}H} NMR δ 55.02 (s); mass spectrum *m/z* 674 (M^+) (Found: C, 63.75; H, 5.79; N, 1.89. Calc. for $C_{36}H_{39}ClNOPPd$: C, 64.09; H, 5.79; N, 2.08%). Complex (+)-**2b**: [α]$_D$ +41.59° (*c* 1.0, CHCl$_3$); ^{1}H NMR (selected data) δ 7.87 (1 H, d, $J = 8.1$, H^8), 7.70 (6 H, m, PPh$_3$), 7.35 (9 H, m, PPh$_3$), 7.15 (1 H, d, $J = 8.1$, H^3), 6.37 (1 H, d, $J = 10.2$, H^6), 5.90 (1 H, d, $J = 6.6$ Hz, H^5), 4.06 (1 H, m, H^9), 3.84 (1 H, m, H^9) and 2.90 (3 H, s, H^7); ^{13}C-{^{1}H} NMR (selected data) δ 174.6 (C^8), 162.3 (C^2), 141.4 (C^1), 129.0 (C^4), 128.6 (C^6), 123.3 (C^3), 111.6 (C^5), 66.4 (C^9), 55.2 (C^7), 160.0, 136.2, 136.0, 132.8, 132.2, 131.3 (PPh$_3$); ^{31}P-{^{1}H} NMR δ 55.27 (s); mass spectrum *m/z* 716 (M^+) (Found: C, 60.39; H, 5.60; N, 1.96. Calc. for $C_{36}H_{39}BrNOPPd$: C, 60.38; H, 5.45; N, 1.89%). Complex (+)-**2c**: [α]$_D$ +34.22° (*c* 1.0, CHCl$_3$); ^{1}H NMR (selected data) δ 7.92 (1 H, s, H^8), 7.68 (6 H, m, PPh$_3$), 7.33 (9 H, m, PPh$_3$), 7.14 (1 H, d, $J = 8.4$, H^3), 6.38 (1 H, d, $J = 10.5$ Hz, H^6), 5.84 (1 H, s, H^5), 4.28 (1 H, m, H^9), 4.10 (1 H, m, H^9) and 2.90 (3 H, s, H^7); ^{13}C-{^{1}H} NMR (selected data) δ 175.0 (C^8), 163.7 (C^2), 141.6 (C^1), 128.9 (C^4), 128.7 (C^6), 122.8 (C^3), 111.7 (C^5), 68.9 (C^9), 55.3 (C^7), 159.9, 136.0, 135.9, 134.4, 133.8, 131.2 (PPh$_3$); ^{31}P-{^{1}H} NMR δ 55.28 (s); mass spectrum *m/z* 763 (M^+) (Found: C, 55.28; H, 5.42; N, 1.89. Calc. for $C_{36}H_{39}INOPPd$: C, 55.62; H, 5.11; N, 1.83%).

(+)-[Pd{*p*-MeOC$_6$H$_3$CH=NCH$_2$-(1*S*,2*R*,5*S*)-CHCH$_2$CH$_2$CHC(Me)$_2$CHCH$_2$}X(py)] [X = Cl (+)-3a, Br (+)-3b or I (+)-3c]. Colourless needles of **3** were prepared according to the procedure described above using pyridine and **2** as starting materials. Yield: 0.16 (81), 0.19 (90) and 0.17 g (73%), respectively. Complex (+)-**3a**: [α]$_D$ +35.72° (*c* 1.0, CHCl$_3$); ^{1}H NMR (selected data) δ 8.81 (2 H, d, $J = 5.1$, py), 7.78 (1 H, t, $J = 7.6$, py), 7.62 (1 H, s, H^8), 7.36 (2 H, t, $J = 7.6$, py), 7.18 (1 H, d, $J = 8.4$, H^3), 5.57 (1 H, s, H^5), 6.49 (1 H, d, $J = 10.5$ Hz, H^6), 3.73 (2 H, m, H^9) and 3.57 (3 H, s, H^7); ^{13}C-{^{1}H} NMR (selected data) δ 174.0 (C^8), 160.8 (C^2), 140.2 (C^1), 129.1 (C^4), 126.0 (C^6), 119.6 (C^3), 108.9 (C^5), 66.3 (C^9), 55.6 (C^7), 160.3, 153.7, 138.6 (py); mass spectrum *m/z* 491 (M^+) (Found: C, 56.02; H, 6.03; N, 5.47. Calc. for $C_{23}H_{29}ClN_2OPd$: C, 56.21; H, 5.91; N, 5.70%). Complex (+)-**3b**: [α]$_D$ +40.13° (*c* 1.0, CHCl$_3$); ^{1}H NMR (selected data) δ 8.82 (2 H, d, $J = 5.1$, py), 7.77 (1 H, t, $J = 7.6$, py), 7.63 (1 H, s, H^8), 7.36 (2 H, t, $J = 7.6$, py), 7.18 (1 H, d, $J = 8.1$, H^3), 6.49 (1 H, d, $J = 10.8$ Hz, H^6), 5.45 (1 H, s, H^5), 3.80 (1 H, m, H^9), 3.68 (1 H, m, H^9) and 3.42 (3 H, s, H^7); ^{13}C-{^{1}H} NMR (selected data) δ 174.1 (C^8), 161.1 (C^2), 140.2 (C^1), 129.1 (C^4), 126.0 (C^6), 119.1 (C^3), 109.0 (C^5), 67.6 (C^9), 55.6 (C^7), 160.8, 153.9, 138.6 (py); mass spectrum *m/z* 536 (M^+) (Found: C, 51.4; H, 5.54; N, 4.97. Calc. for $C_{23}H_{29}BrN_2OPd$: C, 51.54; H, 5.42; N, 5.23%). Complex (+)-**3c**: [α]$_D$ +46.82° (*c* 1.0, CHCl$_3$); ^{1}H NMR (selected data) δ 8.84 (2 H, d, $J = 5.1$, py), 7.75 (1 H, t, $J = 7.3$, py), 7.66 (1 H, s, H^8), 7.35 (2 H, t, $J = 7.4$, py), 7.18 (1 H, d, $J = 7.5$, H^3), 6.48 (1 H, d, $J = 8.1$ Hz, H^6), 5.25 (1 H, s, H^5), 3.97 (1 H, m, H^9), 3.78 (1 H, m, H^9) and 3.55 (3 H, s, H^7); ^{13}C-{^{1}H} NMR (selected data) δ 174.4 (C^8), 160.8 (C^2), 140.3 (C^1), 129.0 (C^4), 126.0 (C^6), 118.2 (C^3), 109.2 (C^5), 69.7 (C^9), 55.7 (C^7), 154.1, 152.4, 138.4 (py); mass spectrum *m/z* 583 (M^+) (Found: C, 47.18; H, 5.01; N, 4.46. Calc. for $C_{23}H_{29}IN_2OPd$: C, 47.38; H, 4.98; N, 4.81%).

(+)-[{Pd[*p*-MeOC$_6$H$_3$CH=NCH$_2$-(1*S*,2*R*,5*S*)-CHCH$_2$CH$_2$CHC(Me)$_2$CHCH$_2$]X}(dppf)] [X = Cl (+)-4a, Br (+)-4b or I (+)-4c]. An acetone solution (5 cm^3) of 1,1′-bis(diphenylphosphino)ferrocene (0.11 g, 0.2 mmol) was added dropwise to an acetone suspension (5 cm^3) containing the dimeric complex **1** (0.2 mmol). The resulting mixture was stirred at room temperature for 3 h. After the red suspension became clear upon stirring, the solution was filtered and the filtrate concentrated to dryness in vacuum. Addition of diethyl ether to the residue resulted in precipitation of the desired compound, which was recrystallized as orange plates from CH$_2$Cl$_2$–*n*-hexane (3 : 1). Yield: 0.17 (62), 0.19 (68) and 0.22 g (74%), respectively. Complex (+)-**4a**: [α]$_D$ +55.78° (*c* 1.0, CHCl$_3$); ^{1}H NMR (selected data) δ 7.85 (2 H, s, H^8), 7.58 (8 H, m, PPh$_2$), 7.39 (4 H, m, PPh$_2$), 7.28 (10 H, m, H^3, PPh$_2$), 6.48 (2 H, d, $J = 9.0$, H^6), 5.99 (2 H, d, $J = 6.0$, H^5), 5.21 (4 H, d, $J = 9.0$, C$_5$H$_4$), 4.52 (4 H, d, $J = 18.0$ Hz, C$_5$H$_4$), 3.93 (2 H, m, H^9), 3.76 (2 H, m, H^9) and 2.99 (3 H, s, H^7); ^{13}C-{^{1}H} NMR (selected data) δ 174.6 (C^8), 161.9 (C^2), 141.8 (C^1), 129.7 (C^4), 128.9 (C^6), 127.5 (C^3), 109.2 (C^5), 72.5, 71.3 (C$_5$H$_4$), 59.6 (C^9), 55.6 (C^7), 135.8, 132.5, 131.0, 129.2 (PPh$_2$); ^{31}P-{^{1}H} NMR δ 43.43 (s); mass spectrum *m/z* 1378 (M^+) (Found: C, 60.85; H, 5.51; N, 1.92. Calc. for $C_{70}H_{76}Cl_2FeN_2O_2P_2Pd_2$: C, 60.95; H, 5.51; N, 2.03%). Complex (+)-**4b**: [α]$_D$ +64.07° (*c* 1.0, CHCl$_3$); ^{1}H NMR (selected data) δ 7.83 (2 H, d, $J = 8.7$, H^8), 7.55 (8 H, m, PPh$_2$), 7.35 (4 H, m, PPh$_2$), 7.28 (10 H, m, H^3, PPh$_2$), 6.43 (2 H, d, $J = 10.5$, H^6), 5.88 (2 H, d, $J = 8.7$ Hz, H^5), 5.15 (2 H, s, C$_5$H$_4$), 5.07 (2 H, s, C$_5$H$_4$), 4.48 (4 H, d, $J = 15.3$ Hz, C$_5$H$_4$), 4.08 (2 H, m, H^9), 3.80 (2 H, m, H^9) and 2.94 (3 H, s, H^7); ^{13}C-{^{1}H} NMR (selected data) δ 174.3 (C^8), 161.9 (C^2), 141.3 (C^1), 129.3 (C^4), 128.8 (C^6), 123.6 (C^3), 111.8 (C^5), 74.6, 73.8 (C$_5$H$_4$), 65.9 (C^9), 55.2 (C^7), 134.8, 132.6, 131.2 and 128.2 (PPh$_2$); ^{31}P-{^{1}H} NMR δ 44.20 (s); mass spectrum *m/z* 1467 (M^+) (Found: C, 54.64; H, 5.20; N, 1.74. Calc. for $C_{70}H_{76}Br_2FeN_2O_2P_2Pd_2\cdot CH_2Cl_2$: C, 54.90; H, 5.03; N, 1.80%). Complex (+)-**4c**: [α]$_D$ +73.66° (*c* 1.0, CHCl$_3$); ^{1}H NMR (selected data) δ 7.87 (2 H, d, $J = 8.7$, H^8), 7.52 (8 H, m, PPh$_2$), 7.45 (4 H, m, PPh$_2$), 7.26 (10 H, m, H^3, PPh$_2$), 6.42 (2 H, d, $J = 9.8$, H^6), 5.85 (2 H, d, $J = 8.7$, H^5), 5.15 (2 H, s, C$_5$H$_4$), 5.03 (2 H, s, C$_5$H$_4$), 4.44 (4 H, d, $J = 13.8$ Hz, C$_5$H$_4$), 2.90 (3 H, s), 4.08 (2 H, m, H^9), 3.78 (2 H, m, H^9) and 2.90 (3 H, s, H^7); ^{13}C-{^{1}H} NMR (selected data) δ 174.0 (C^8), 161.1 (C^2), 141.8 (C^1), 129.6 (C^4), 128.0 (C^6), 123.4 (C^3), 110.9 (C^5), 74.0, 73.2 (C$_5$H$_4$), 65.4 (C^9), 55.5 (C^7), 134.1, 132.8, 131.1, 128.8 (PPh$_2$); ^{31}P-{^{1}H} NMR δ 45.38 (s); mass spectrum *m/z* 1561 (M^+) (Found: C, 53.69; H, 5.06; N, 1.83. Calc. for $C_{70}H_{76}FeI_2N_2O_2P_2Pd_2$: C, 53.81; H, 4.87; N, 1.79%).

Table 2 Crystal data for complexes **1a**, **1b**, **2a** and **4b**

	(+)-**1a**	(+)-**1b**	(+)-**2a**	(+)-**4b**·CH_2Cl_2
Formula	$C_{36}H_{48}Cl_2N_2O_2Pd_2$	$C_{36}H_{48}Br_2N_2O_2Pd_2$	$(C_{36}H_{39}ClNOPPd)_2$	$C_{71}H_{78}Br_2Cl_2FeN_2O_2P_2Pd_2$
M	822.4	913.4	1369.2	1554.7
Shape (color)	Block (yellow)	Block (yellow)	Prism (colorless)	Plate (yellow)
Size/mm	0.20 × 0.30 × 0.50	0.20 × 0.20 × 0.20	0.10 × 0.20 × 0.38	0.20 × 0.15 × 0.20
Crystal system	Orthorhombic	Orthorhombic	Triclinic	Monoclinic
Space group	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)	$P1$ (no. 1)	$P2_1$ (no. 4)
a/Å	13.518(3)	13.548(3)	12.138(2)	16.703(3)
b/Å	25.105(5)	24.965(5)	13.909(3)	16.415(3)
c/Å	10.797(2)	10.945(2)	10.066(2)	25.250(5)
α/°			91.75(3)	
β/°			97.35(3)	90.70(3)
γ/°			104.22(3)	
U/Å^3	3664(1)	3702(1)	1630.4(5)	6934(2)
Z	4	4	1	4
$F(000)$	1672	1824	1432	3152
D_c/g cm^{-3}	1.491	1.639	1.394	1.489
μ(Mo-Kα)/mm^{-1}	1.160	3.163	0.729	2.040
2θ Range/°	3–55	3–55	3–55	3–52
Reflections collected, n	11 888	10 561	6049	20 315
Independent reflections (R_{int})	6486 (0.023)	6258 (0.065)	6049 (0.00)	12 097 (0.062)
$R1^a$	0.0378	0.0607	0.0316	0.0695
$wR2^b$	0.0997	0.1695	0.0788	0.1707
Weighting scheme^c	$a = 0.0741$, $b = 0.0754$	$a = 0.1188$, $b = 1.2471$	$a = 0.0312$, $b = 0.2202$	$a = 0.0898$, $b = 5.1590$
No. parameters refined, p	398	398	739	1514
S (Goodness of fit)^d	1.043	1.026	1.021	1.088
Maximum, mean Δ/σ	0.002, 0.000	0.225, 0.005	0.077, 0.006	0.019, 0.000
$\Delta\rho_{max}$/e Å^{-3}	0.841, −0.756	0.870, −0.926	0.285, −0.380	0.858, −0.653

[a] $R1 = (\Sigma|F_o| - |F_c|)/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$. [c] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ where $P = (F_o^2 + 2F_c^2)/3$. [d] $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{\frac{1}{2}}$.

Crystallography

Crystallographic data of complexes (+)-**1a**, (+)-**1b** and (+)-**4b**·CH_2Cl_2 measured on a MSC/Rigaku RAXIS IIC imaging-plate diffractometer are summarized in Table 2. Intensities were collected at 294 K using graphite-monochromatized Mo-Kα radiation ($\lambda = 0.7103$ Å) from a rotating-anode generator operating at 50 kV and 90 mA [$2\theta_{min} = 3°$, $2\theta_{max} = 55°$, sixty 3° oscillation frames for (+)-**1a** and (+)-**4b**·CH_2Cl_2, forty-two 5° frames for (+)-**1b**, in the range of 0–180°, exposure 8 min per frame].[16] A self-consistent semiempirical absorption correction based on Fourier-coefficient fitting of symmetry-equivalent reflections was applied using the ABSCOR program.[17] Intensity data of compound (+)-**2a** were collected in the variable ω-scan mode on a four-circle diffractometer (Rigaku AFC7R) using Mo-Kα radiation ($\lambda = 0.710\ 73$ Å) at 294 K. For this compound the crystal class and orientation matrix were determined according to established procedures,[18] and unit-cell parameters were calculated from least-squares fitting of 2θ angles for 25 reflections. Crystal stability was monitored by recording three check reflections at intervals of 100/150 data measurements, and no significant variation was detected. The raw data were processed with a learn-profile procedure,[19] and empirical absorption corrections were applied by fitting a pseudo-ellipsoid to the ψ-scan data of selected strong reflections over a range of 2θ angles.[20]

The crystal structures of all four compounds were solved with the Patterson superposition method, and subsequent Fourier-difference syntheses employed to locate the remaining non-hydrogen atoms which did not show up in the initial structure. As the known chirality of the starting material (−)-*cis*-myrtanylamine is retained in the cyclopalladation reaction, the absolute configurations can be ascertained. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all generated geometrically (C–H bond lengths fixed at 0.96 Å), assigned appropriate isotropic thermal parameters and allowed to ride on their parent carbon atoms. All the H atoms were held stationary and included in structure-factor calculation in the final stages of full-matrix least-squares refinement on F^2. The computation was performed on an IBM-compatible 486 personal computer with the SHELXTL PC program package.[21] The final $R1$ and $wR2$ indices and other refinement parameters are presented in Table 2.

CCDC reference number 186/875.

See http://www.rsc.org/suppdata/dt/1998/1241/ for crystallographic files in .cif format.

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References

1 G. R. Newkome, W. E. Puckett, V. K. Gupta and G. E. Kiefer, *Chem. Rev.*, 1986, **86**, 451; I. Omae, *Coord. Chem. Rev.*, 1988, **83**, 137; V. V. Dunina, O. A. Zaleskaya and V. M. Potatov, *Russ. Chem. Rev.*, 1988, 250; A. D. Ryabov, *Chem. Rev.*, 1990, **90**, 403.

2 (*a*) G. Balavoine, J. C. Clinet, P. Zerbib and K. Boubekeur, *J. Organomet. Chem.*, 1990, **389**, 259; (*b*) A. D. Ryabov, G. M. Kszankov, A. K. Yatsimirsky, L. G. Kuz'mina, O. Y. Burtseva, N. V. Dvortsova and V. A. Polyakov, *Inorg. Chem.*, 1992, **31**, 3083; (*c*) R. Bosque, C. López, J. Sales, X. Solans and M. Font-Bardía, *J. Chem. Soc., Dalton Trans.*, 1992, 735; (*d*) C. López, J. Sales, X. Solans and R. Zuqiak, *J. Chem. Soc., Dalton Trans.*, 1992, 2321; (*e*) S. Y. M. Chooi, Siah Soh-Yun, P. H. Leung and K. F. Mok, *Inorg. Chem.*, 1993, **32**, 4812; (*f*) C. Navarro-Ranninger, I. López-Solera, A. Alvarez-Valdés, J. H. Rodríguez-Ramos, J. R. Masaguer, J. L. García-Ruano and X. Solans, *Organometallics*, 1993, **12**, 4104; (*g*) C. Navarro-Ranninger, I. López-Solera, A. Alvarez-Valdés, J. H. Rodríguez and J. L. García-Ruano, *J. Organomet. Chem.*, 1994, **476**, 19; (*h*) C. López, J. Sales, X. Solans and R. Zuqiak, *J. Organomet. Chem.*, 1994, **483**, 61; (*i*) S. Q. Huo, Y. J. Wu, C. Y. Zhu, H. Z. Yuan and X. A. Mao, *J. Organomet. Chem.*, 1994, **483**, 139; (*j*) C. López, R. Bosque, X. Solans, M. Font-Bardía, J. Silver and G. Fern, *J. Chem. Soc., Dalton Trans.*, 1995, 1839; (*k*) R. Bosque, C. López, J. Sales, D. Tramuns and X. Solans, *J. Chem. Soc., Dalton Trans.*, 1995, 2445; (*l*) H. L. Holcomb, S. Nakanish and T. C. Flood, *Organometallics*, 1996, **15**, 4228; (*m*) Aw Beng-Hwee, L. Pak-hing, A. J. P. White and D. J. Williams, *Organometallics*, 1996, **15**, 3640; (*n*) Siah Soh-Yun, P. Leung, K. F. Mok and M. G. B. Drew,

Tetrahedron: *Asymmetry*, 1996, **7**, 357; (*o*) C. López, R. Bosque, X. Solans and M. J. Font-Bardía, *J. Organomet. Chem.*, 1997, **535**, 99; (*p*) C. López, R. Bosque, X. Solans and M. Font-Bardía, *J. Organomet. Chem.*, 1997, **539**, 99.

3 (*a*) F. Maassarani, M. Pfeffer, G. L. Borgne, J. T. B. H. Jastrzebski and G. van Koten, *Organometallics*, 1987, **6**, 1111; (*b*) J. Albert, J. Granell, J. Sales, M. Font-Bardía and X. Solans, *Organometallics*, 1995, **14**, 1393 and refs. therein; (*c*) C. López, R. Bosque, X. Solans and M. Font-Bardía, *Tetrahedron*: *Asymmetry*, 1996, **7**, 2527; (*d*) C. López, R. Bosque and D. Sainz, *Organometallics*, 1997, **16**, 3261; (*e*) G. Zhao, F. Xue, Z. Y. Zhang and T. C. W. Mak, *Organometallics*, 1997, **16**, 4023.

4 S. Y. M. Chooi, J. D. Ranford, P. H. Leung and K. F. Mok, *Tetrahedron*: *Asymmetry*, 1994, **5**, 1805; J. Albert, J. Granell, G. Muller, D. Sainz, M. Font-Bardía and X. Solans, *Tetrahedron*: *Asymmetry*, 1995, **6**, 325.

5 S. Otsuka, A. Nakumara, T. Kano and K. Tani, *J. Am. Chem. Soc.*, 1971, **93**, 4301; D. G. Allen, G. M. McLaughin, G. B. Robertson, W. L. Steffen, G. Salem and S. B. Wild, *Inorg. Chem.*, 1982, **21**, 1007; N. Gabbitas, G. Salem, M. Sterns and A. C. Willis, *J. Chem. Soc., Dalton Trans.*, 1993, 3271; N. W. Alcock, J. M. Brown and D. I. Hulmes, *Tetrahedron*: *Asymmetry*, 1993, **4**, 743; S. Gladiali, A. Dore, D. Fabbri, O. De Lucchi, and M. Manassero, *Tetrahedron*: *Asymmetry*, 1994, **5**, 511; K. Tani, H. Tashiro, M. Yoshida and T. Yamagata, *J. Organomet. Chem.*, 1994, **469**, 229.

6 S. Y. M. Chooi, P. H. Leung, C. C. Lim, K. F. Mok, G. H. Quek, K. Y. Sim and M. K. Tan, *Tetrahedron*: *Asymmetry*, 1992, **3**, 529; J. L. Bookham and W. McFarlane, *J. Chem. Soc.*, *Chem. Commun.*, 1993, 1352.

7 C. Navarro-Ranninger, J. López-Solera, J. M. Pérez, J. M. Masaguer and C. Alonso, *Appl. Organomet. Chem.*, 1993, **7**, 57; J. Higgins, *J. Inorg. Biochem.*, 1993, **49**, 149.

8 P. H. Leung, S. Selvaratnam, C. R. Cheng, K. F. Mok, N. H. Rees and W. McFarlane, *Chem. Commun.*, 1997, 751.

9 M. J. Baena, J. Buey, P. Espinet, H. S. Kitzerow and G. Heppke, *Angew. Chem.*, *Int. Ed. Engl.*, 1993, **32**, 1201.

10 M. J. Baena, J. Barberá, P. Espinet, B. M. Ros, J. L. Serrano and A. Ezcurra, *Angew. Chem.*, *Int. Ed. Engl.*, 1993, **32**, 1203; M. J. Baena, J. Barberá, P. Espinet, A. Ezcurra, B. M. Ros and J. L. Serrano, *J. Am. Chem. Soc.*, 1994, **116**, 1899.

11 R. Bosque, C. Lopez, J. Sales and X. Solans, *J. Organomet. Chem.*, 1994, **483**, 61.

12 R. G. Miller, R. D. Stuffer, D. R. Fahey and D. R. Pernell, *J. Am. Chem. Soc.*, 1970, **92**, 1511.

13 J. Albert, J. Granell and J. Sales, *J. Organomet. Chem.*, 1984, **273**, 393; J. Albert, J. Granell, J. Sales, X. Solans and M. Font-Bardía, *Organometallics*, 1986, **5**, 2567; J. Albert, J. Barro and J. Granell, *J. Organomet. Chem.*, 1991, **408**, 115.

14 A. R. Garber, P. E. Garrou, G. E. Hartwell, M. J. Smas, J. R. Wilkinson and L. J. Todd, *J. Organomet. Chem.*, 1975, **86**, 219.

15 B. Crociani, F. Di Bianca and A. Giovenco, *J. Organomet. Chem.*, 1983, **251**, 393.

16 J. Tanner and K. Krause, *Rigaku J.*, 1994, **11**, 4; 1990, **7**, 28; K. Krause and Jr G. N. Phillips, *J. Appl. Crystallogr.*, 1992, **25**, 146; M. Sato, M. Yamamoto, Y. Katsube, N. Tanaka and T. Higashi, *J. Appl. Crystallogr.*, 1992, **25**, 348

17 T. Higashi ABSCOR, An Empirical Absorption Correction Based on Fourier Coefficient Fitting, Rigaku Corporation, Tokyo, 1995.

18 R. A. Sparks, in *Crystallographic Computing Techniques*, ed. F. R. Ahmed, Munksgaard, Copenhagen, 1976, p. 452.

19 R. Diamond, *Acta Crystallogr.*, *Sect. A*, 1968, **25**, 43.

20 G. Kopfmann and R. Huber, *Acta Crystallogr.*, *Sect. A*, 1968, **24**, 348.

21 *SHELXL-PC Version 5.0 Reference Manual*, Siemens Energy & Automation Inc., Madison, WI, 1996; G. M. Sheldrick, in *Computational Crystallography 6*, eds. H. D. Flack, L. Párkányi and K. Simon, International Union of Crystallography and Oxford University Press, Oxford, 1993, pp. 111 and 112.

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