

Optically active cyclopalladated derivatives of arylimines. Crystal structures of (+)-[Pd(*p*-MeOC₆H₃CH=NCH₂-(1*S*,2*R*,5*S*)-CHCH₂CH₂CHC(Me)₂CHCH₂)](μ-X)₂] (X = Cl or Br), (+)-[Pd{*p*-MeOC₆H₃CH=NCH₂-(1*S*,2*R*,5*S*)-CHCH₂-CH₂CHC(Me)₂CHCH₂}Cl(PPh₃)] and (+)-[Pd(*p*-MeOC₆H₃CH=NCH₂-(1*S*,2*R*,5*S*)-CHCH₂CH₂CHC(Me)₂CHCH₂)]Cl₂·{Fe(η⁵-C₅H₄PPh₂)₂}

Gang Zhao, Qi-Guang Wang and Thomas C. W. Mak *

Department of Chemistry, The Chinese University of Hong Kong, Shatin, N. T., Hong Kong

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*-MeOC₆H₄CH=NCH₂-(1*S*,2*R*,5*S*)-CHCH₂CH₂CHC(CH₃)₂CHCH₂ [(–)-**I**]. Cyclopalladation of the imine with Pd(O₂CMe)₂ in MeCO₂H, followed by treatment with LiCl, LiBr or KI, gave the corresponding di-μ-halide-bridged organometallics (+)-[Pd{*p*-MeOC₆H₃CH=NCH₂-(1*S*,2*R*,5*S*)-CHCH₂CH₂CHC(Me)₂CHCH₂}](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*-MeOC₆H₃CH=NCH₂-(1*S*,2*R*,5*S*)-CHCH₂CH₂CHC(Me)₂CHCH₂}X(PPh₃)] [X = Cl (+)-**2a**, Br (+)-**2b** or I (+)-**2c**], (+)-[Pd{*p*-MeOC₆H₃CH=NCH₂-(1*S*,2*R*,5*S*)-CHCH₂CH₂CHC(CH₃)₂CHCH₂}X(py)] [X = Cl (+)-**3a**, Br (+)-**3b** or I (+)-**3c**] and (+)-[Pd{*p*-MeOC₆H₃CH=NCH₂-(1*S*,2*R*,5*S*)-CHCH₂CH₂CHC(Me)₂CHCH₂}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**·CH₂Cl₂ 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-C²,*N*]dipalladium(II), bis(μ-chloro)bis[2-(1-dimethylamino)ethyl-3-naphthyl-C³,*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 ligand⁹ 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.

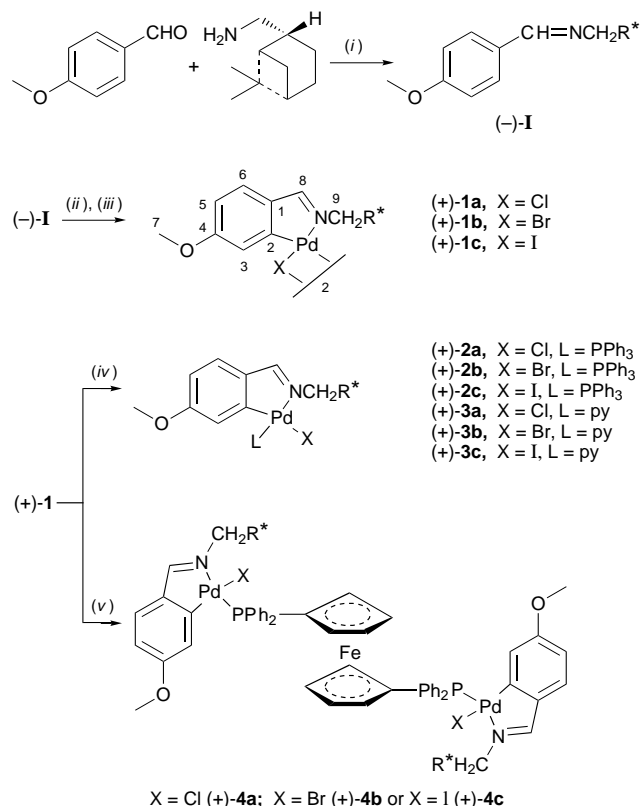
Results and Discussion

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 ¹³C-¹H} NMR spectroscopy in CDCl₃ 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(O₂CMe)₂ in MeCO₂H, followed by treatment with LiCl, LiBr or KI, gives the corresponding di-μ-halide-bridged dimers (+)-[Pd{*p*-MeOC₆H₃-CH=NCH₂-(1*S*,2*R*,5*S*)-CHCH₂CH₂CHC(Me)₂CHCH₂}](μ-X)₂] [X = Cl (+)-**1a**, Br (+)-**1b** or I (+)-**1c**] which contain



Scheme 1 R* = (1*S*,2*R*,5*S*)-CHCH₂CH₂CHC(Me)₂CHCH₂. (i) Benzene, 5 Å molecular sieves, reflux, 6 h; (ii) Pd(O₂CMe)₂, MeCO₂H, 95 °C, 1 h; (iii) LiCl, LiBr or KI, EtOH, room temperature, 30 min; (iv) PPh₃ or pyridine, acetone, reflux, 30 min; (v) dppf, acetone, room temperature, 3 h

endocyclic five-membered metallacycles with a $\sigma(\text{Pd}-\text{C}_{\text{sp}^2})$ 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*-MeOC₆H₃CH=NCH₂-(1*S*,2*R*,5*S*)-CHCH₂CH₂CHC(Me)₂CHCH₂}X(PPh₃)] [X = Cl (+)-2a, Br (+)-2b or I (+)-2c], (+)-[Pd{*p*-MeOC₆H₃CH=NCH₂-(1*S*,2*R*,5*S*)-CHCH₂CH₂CHC(Me)₂CHCH₂}X(py)] [X = Cl 3a, Br (+)-3b or I (+)-3c] and ferrocene-bridged dimers (+)-[Pd{*p*-MeOC₆H₃CH=NCH₂-(1*S*,2*R*,5*S*)-CHCH₂CH₂-CHC(Me)₂CHCH₂}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 SiO₂ column chromatography, using CHCl₃ as the eluent.

Characterization

Microanalysis and mass spectra indicated that compounds **1** were dimeric cyclopalladated complexes, whereas their ¹H NMR spectra and of the imine (-)-**I** in CDCl₃ showed that the two doublets due to the pairs H², H⁶ and H³, H⁵ of the phenylimine split into three signals (H³, H⁵, H⁶), 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 H³, H⁵ and H⁶ provided evidence for Pd-N association as well as cyclometallation through the phenyl ring. The ¹H NMR spectra in CDCl₃ show well resolved

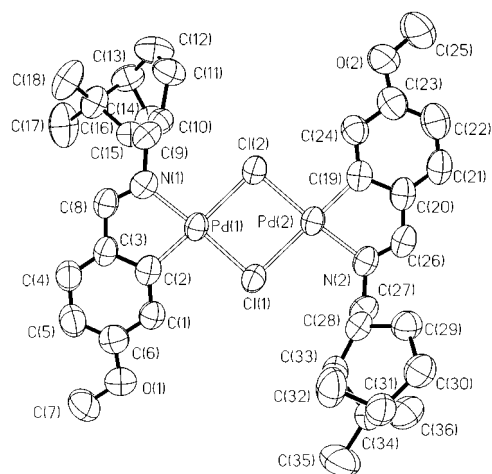


Fig. 1 Molecular structure (30% thermal ellipsoids) and absolute configuration of complex (+)-**1a** with the atom numbering scheme. Molecule (+)-**1b** has the same structure except that the chloride ligands are replaced by bromide ligands

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 ¹H 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 a *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 ¹³C-¹H NMR spectra of free (-)-**I** and its cyclopalladated complexes is the splitting of the resonance due to the C², C⁶ and C³, C⁵ 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 People's equation¹⁵ 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 (C²) always appear between δ 160 and 164, corresponding to a 30–34 ppm downfield shift from the signal of the parent imine. The ³¹P-¹H 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 $\sigma(\text{Pd}-\text{C}_{\text{sp}^2, \text{phenyl}})$ bond in which the imino nitrogen and the phosphine ligand are in a *trans* arrangement.^{2k}

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)–Pd(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*-MeOC₆H₃CH=NCH₂-(1*S*,2*R*,5*S*)-CHCH₂CH₂CHC(Me)₂CHCH₂}Cl(PPh₃)] held by van der Waals forces. The palladium atom is bound to a chloride, the phosphorus atom of the PPh₃, 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**·CH₂Cl₂

The ferrocene-bridged compound (+)-**4b**·CH₂Cl₂ crystallizes in

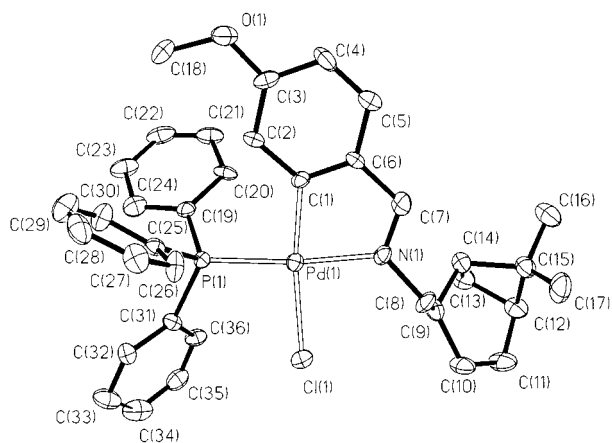


Fig. 2 Molecular structure (30% thermal ellipsoids) and absolute configuration of complex (+)-**2a** with the atom numbering scheme

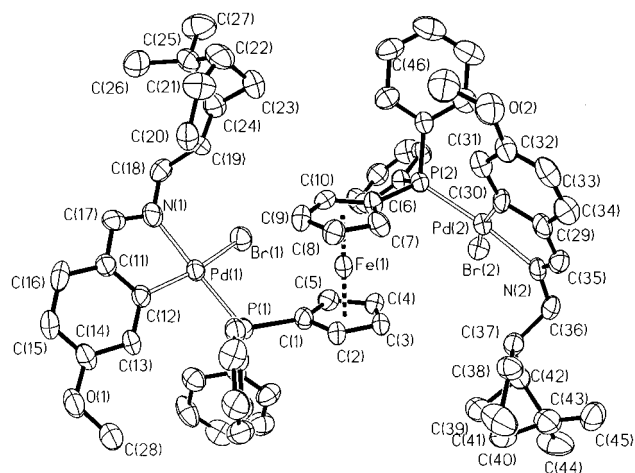


Fig. 3 Molecular structure (30% thermal ellipsoids) and absolute configuration of complex (+)-**4b** with the atom-numbering scheme for independent molecule I. For molecule II the same scheme is used except that a prime is added to each atom label

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 interligand 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*-MeOC₆H₄CH=NCH₂-(1*S*,2*R*,5*S*)-

CHCH₂CH₂CHC(Me)₂CHCH₂ (-)-I. 4-Methoxybenzaldehyde

(1.36 g, 10 mmol) and (-)-*cis*-myrtanylamine (1.53 g, 10 mmol) were dissolved in dry benzene (100 cm³). 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%). $[\alpha]_D -6.19^\circ$ (c 1.0 g cm⁻³, $CHCl_3$). 1H NMR (selected data): δ 8.12 (1 H, s, H⁸), 7.60 (2 H, d, $J = 15$, H³, H⁵), 6.85 (2 H, d, $J = 15$ Hz, H², H⁶), 3.76 (3 H, s, H⁷) and 3.53 (2 H, m, NCH₂). ^{13}C - $\{^1H\}$ NMR (selected data): δ 160.6 (C⁸), 162.0 (C¹), 130.5 (C⁴), 130.0 (C², C⁶), 114.5 (C³, C⁵), 68.6 (C⁹) and 55.8 (C⁷). Mass spectrum m/z 271 (M^+) (Found: C, 79.63; H, 9.36; N, 4.96. Calc. for C₁₈H₂₅NO: C, 79.70; H, 9.22; N, 5.17%).

(+)-[Pd(*p*-MeOC₆H₃CH=NCH₂-(1*S*,2*R*,5*S*)-

CHCH₂CH₂CHC(Me)₂CHCH₂)(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 cm³) 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 cm³), 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**: $[\alpha]_D +38.78^\circ$ (c 1.0, $CHCl_3$); 1H NMR (selected data) δ 7.60 (2 H, s, H⁸), 7.08 (2 H, d, $J = 6$, H³), 6.90 (2 H, s, H⁵), 6.55 (2 H, d, $J = 12$ Hz, H⁶), 3.81 (6 H, s, H⁷) and 3.50 (4 H, m, H⁹); ^{13}C - $\{^1H\}$ NMR (selected data) δ 172.9 (C⁸), 160.0 (C²), 139.3 (C¹), 128.8 (C⁴), 119.4 (C⁶), 119.0 (C³), 111.0 (C⁵), 68.7 (C⁹) and 55.9 (C⁷); mass spectrum m/z 824 (M^+) (Found: C, 52.56; H, 5.99; N, 3.15. Calc. for C₁₈H₂₄ClNOPd: C, 52.43; H, 5.82; N, 3.40%). Complex (+)-**1b**: $[\alpha]_D +46.11^\circ$ (c 1.0, $CHCl_3$); 1H NMR (selected data) δ 7.64 (2 H, s, H⁸), 7.16 (2 H,

d, $J = 9$, H³), 6.99 (2 H, s, H⁵), 6.54 (2 H, d, $J = 15$ Hz, H⁶), 3.81 (6 H, s, H⁷) and 3.58 (4 H, m, H⁹); ¹³C-¹H NMR (selected data) δ 173.3 (C⁸), 160.3 (C²), 158.1 (C¹), 139.6 (C⁴), 129.1 (C⁶), 121.2 (C³), 110.6 (C⁵), 67.2 (C⁹) and 55.9 (C⁷); mass spectrum m/z 914 (M^+) Found: C, 47.43; H, 5.41; N, 2.92. Calc. for C₁₈H₂₄BrNOPd: C, 47.26; H, 5.25; N, 3.06%. Complex (+)-**1c**: [α]_D +56.99° (c 1.0, CHCl₃); ¹H NMR (selected data) δ 7.71 (2 H, s, H⁸), 7.22 (2 H, d, $J = 8$, H³), 6.96 (2 H, s, H⁵), 6.54 (2 H, d, $J = 8$ Hz, H⁶), 3.82 (6 H, s, H⁷) and 3.72 (4 H, m, H⁹); ¹³C-¹H NMR (selected data) δ 174.0 (C⁸), 161.0 (C²), 141.3 (C¹), 129.5 (C⁴), 118.9 (C⁶), 116.1 (C³), 110.2 (C⁵), 66.9 (C⁹) and 56.0 (C⁷); mass spectrum m/z 1007 (M^+) (Found: C, 42.66; H, 4.92; N, 2.57. Calc. for C₁₈H₂₄INOPd: C, 42.91; H, 4.77; N, 2.78%).

(+)-[Pd{*p*-MeOC₆H₃CH=NCH₂-(1*S*,2*R*,5*S*)-CHCH₂CH₂CHC(Me)₂CHCH₂}X(PPh₃)] [X = Cl (+)-**2a**, Br (+)-**2b** or I (+)-**2c**]. Triphenylphosphine (0.105 g, 0.4 mmol) was added to an acetone suspension (15 cm³) 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, CHCl₃); ¹H NMR (selected data) δ 7.91 (1 H, s, H⁸), 7.73 (6 H, m, PPh₃), 7.39 (9 H, m, PPh₃), 7.20 (1 H, d, $J = 9$, H³), 5.96 (1 H, s, H⁵), 6.42 (1 H, d, $J = 12$ Hz, H⁶), 3.96 (1 H, m, H⁹), 3.74 (1 H, m, H⁹) and 2.95 (3 H, s, H⁷); ¹³C-¹H NMR (selected data) δ 174.2 (C⁸), 161.2 (C²), 141.3 (C¹), 129.2 (C⁴), 128.7 (C⁶), 123.7 (C³), 111.4 (C⁵), 65.2 (C⁹), 55.2 (C⁷), 160.0, 141.4, 136.1, 136.0, 132.1, 131.3 (PPh₃); ³¹P-¹H NMR δ 55.02 (s); mass spectrum m/z 674 (M^+) (Found: C, 63.75; H, 5.79; N, 1.89. Calc. for C₃₆H₃₉ClNOPd: C, 64.09; H, 5.79; N, 2.08%). Complex (+)-**2b**: [α]_D +41.59° (c 1.0, CHCl₃); ¹H NMR (selected data) δ 7.87 (1 H, d, $J = 8.1$, H⁸), 7.70 (6 H, m, PPh₃), 7.35 (9 H, m, PPh₃), 7.15 (1 H, d, $J = 8.1$, H³), 6.37 (1 H, d, $J = 10.2$, H⁶), 5.90 (1 H, d, $J = 6.6$ Hz, H⁵), 4.06 (1 H, m, H⁹), 3.84 (1 H, m, H⁹) and 2.90 (3 H, s, H⁷); ¹³C-¹H NMR (selected data) δ 174.6 (C⁸), 162.3 (C²), 141.4 (C¹), 129.0 (C⁴), 128.6 (C⁶), 123.3 (C³), 111.6 (C⁵), 66.4 (C⁹), 55.2 (C⁷), 160.0, 136.2, 136.0, 132.8, 132.2, 131.3 (PPh₃); ³¹P-¹H NMR δ 55.27 (s); mass spectrum m/z 716 (M^+) (Found: C, 60.39; H, 5.60; N, 1.96. Calc. for C₃₆H₃₉BrNOPd: C, 60.38; H, 5.45; N, 1.89%). Complex (+)-**2c**: [α]_D +34.22° (c 1.0, CHCl₃); ¹H NMR (selected data) δ 7.92 (1 H, s, H⁸), 7.68 (6 H, m, PPh₃), 7.33 (9 H, m, PPh₃), 7.14 (1 H, d, $J = 8.4$, H³), 6.38 (1 H, d, $J = 10.5$ Hz, H⁶), 5.84 (1 H, s, H⁵), 4.28 (1 H, m, H⁹), 4.10 (1 H, m, H⁹) and 2.90 (3 H, s, H⁷); ¹³C-¹H NMR (selected data) δ 175.0 (C⁸), 163.7 (C²), 141.6 (C¹), 128.9 (C⁴), 128.7 (C⁶), 122.8 (C³), 111.7 (C⁵), 68.9 (C⁹), 55.3 (C⁷), 159.9, 136.0, 135.9, 134.4, 133.8, 131.2 (PPh₃); ³¹P-¹H NMR δ 55.28 (s); mass spectrum m/z 763 (M^+) (Found: C, 55.28; H, 5.42; N, 1.89. Calc. for C₃₆H₃₉INOPd: C, 55.62; H, 5.11; N, 1.83%).

(+)-[Pd{*p*-MeOC₆H₃CH=NCH₂-(1*S*,2*R*,5*S*)-CHCH₂CH₂CHC(Me)₂CHCH₂}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, CHCl₃); ¹H 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, H⁸), 7.36 (2 H, t, $J = 7.6$, py), 7.18 (1 H, d, $J = 8.4$, H³), 5.57 (1 H, s, H⁵), 6.49 (1 H, d, $J = 10.5$ Hz, H⁶), 3.73 (2 H, m, H⁹) and 3.57 (3 H, s, H⁷); ¹³C-¹H NMR (selected data) δ 174.0 (C⁸), 160.8 (C²), 140.2 (C¹), 129.1 (C⁴), 126.0 (C⁶), 119.6 (C³), 108.9 (C⁵), 66.3 (C⁹), 55.6 (C⁷), 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 C₂₃H₂₉ClN₂OPd: C, 56.21; H, 5.91; N, 5.70%). Complex (+)-**3b**: [α]_D +40.13° (c 1.0, CHCl₃); ¹H 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, H⁸), 7.36 (2 H, t, $J = 7.6$, py), 7.18 (1 H, d, $J = 8.1$, H³), 6.49 (1 H, d, $J = 10.8$ Hz, H⁶), 5.45 (1 H, s, H⁵), 3.80 (1 H, m, H⁹), 3.68 (1 H, m, H⁹) and 3.42 (3 H, s, H⁷); ¹³C-¹H NMR (selected data) δ 174.1 (C⁸), 161.1 (C²), 140.2 (C¹), 129.1 (C⁴), 126.0 (C⁶), 119.1 (C³), 109.0 (C⁵), 67.6 (C⁹), 55.6 (C⁷), 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 C₂₃H₂₉BrN₂OPd: C, 51.54; H, 5.42; N, 5.23%). Complex (+)-**3c**: [α]_D +46.82° (c 1.0, CHCl₃); ¹H 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, H⁸), 7.35 (2 H, t, $J = 7.4$, py), 7.18 (1 H, d, $J = 7.5$, H³), 6.48 (1 H, d, $J = 8.1$ Hz, H⁶), 5.25 (1 H, s, H⁵), 3.97 (1 H, m, H⁹), 3.78 (1 H, m, H⁹) and 3.55 (3 H, s, H⁷); ¹³C-¹H NMR (selected data) δ 174.4 (C⁸), 160.8 (C²), 140.3 (C¹), 129.0 (C⁴), 126.0 (C⁶), 118.2 (C³), 109.2 (C⁵), 69.7 (C⁹), 55.7 (C⁷), 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 C₂₃H₂₉IN₂OPd: C, 47.38; H, 4.98; N, 4.81%).

(+)-[Pd{*p*-MeOC₆H₃CH=NCH₂-(1*S*,2*R*,5*S*)-CHCH₂CH₂CHC(Me)₂CHCH₂}X(dppf)] [X = Cl (+)-**4a**, Br (+)-**4b** or I (+)-**4c**]. An acetone solution (5 cm³) of 1,1'-bis(diphenylphosphino)ferrocene (0.11 g, 0.2 mmol) was added dropwise to an acetone suspension (5 cm³) 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 CH₂Cl₂-*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, CHCl₃); ¹H NMR (selected data) δ 7.85 (2 H, s, H⁸), 7.58 (8 H, m, PPh₂), 7.39 (4 H, m, PPh₂), 7.28 (10 H, m, H³, PPh₂), 6.48 (2 H, d, $J = 9.0$, H⁶), 5.99 (2 H, d, $J = 6.0$, H⁵), 5.21 (4 H, d, $J = 9.0$, C₅H₄), 4.52 (4 H, d, $J = 18.0$ Hz, C₅H₄), 3.93 (2 H, m, H⁹), 3.76 (2 H, m, H⁹) and 2.99 (3 H, s, H⁷); ¹³C-¹H NMR (selected data) δ 174.6 (C⁸), 161.9 (C²), 141.8 (C¹), 129.7 (C⁴), 128.9 (C⁶), 127.5 (C³), 109.2 (C⁵), 72.5, 71.3 (C₅H₄), 59.6 (C⁹), 55.6 (C⁷), 135.8, 132.5, 131.0, 129.2 (PPh₂); ³¹P-¹H NMR δ 43.43 (s); mass spectrum m/z 1378 (M^+) (Found: C, 60.85; H, 5.51; N, 1.92. Calc. for C₇₀H₇₆Cl₂FeN₂O₂P₂Pd₂: C, 60.95; H, 5.51; N, 2.03%). Complex (+)-**4b**: [α]_D +64.07° (c 1.0, CHCl₃); ¹H NMR (selected data) δ 7.83 (2 H, d, $J = 8.7$, H⁸), 7.55 (8 H, m, PPh₂), 7.35 (4 H, m, PPh₂), 7.28 (10 H, m, H³, PPh₂), 6.43 (2 H, d, $J = 10.5$, H⁶), 5.88 (2 H, d, $J = 8.7$ Hz, H⁵), 5.15 (2 H, s, C₅H₄), 5.07 (2 H, s, C₅H₄), 4.48 (4 H, d, $J = 15.3$ Hz, C₅H₄), 4.08 (2 H, m, H⁹), 3.80 (2 H, m, H⁹) and 2.94 (3 H, s, H⁷); ¹³C-¹H NMR (selected data) δ 174.3 (C⁸), 161.9 (C²), 141.3 (C¹), 129.3 (C⁴), 128.8 (C⁶), 123.6 (C³), 111.8 (C⁵), 74.6, 73.8 (C₅H₄), 65.9 (C⁹), 55.2 (C⁷), 134.8, 132.6, 131.2 and 128.2 (PPh₂); ³¹P-¹H NMR δ 44.20 (s); mass spectrum m/z 1467 (M^+) (Found: C, 54.64; H, 5.20; N, 1.74. Calc. for C₇₀H₇₆Br₂FeN₂O₂P₂Pd₂·CH₂Cl₂: C, 54.90; H, 5.03; N, 1.80%). Complex (+)-**4c**: [α]_D +73.66° (c 1.0, CHCl₃); ¹H NMR (selected data) δ 7.87 (2 H, d, $J = 8.7$, H⁸), 7.52 (8 H, m, PPh₂), 7.45 (4 H, m, PPh₂), 7.26 (10 H, m, H³, PPh₂), 6.42 (2 H, d, $J = 9.8$, H⁶), 5.85 (2 H, d, $J = 8.7$, H⁵), 5.15 (2 H, s, C₅H₄), 5.03 (2 H, s, C₅H₄), 4.44 (4 H, d, $J = 13.8$ Hz, C₅H₄), 2.90 (3 H, s), 4.08 (2 H, m, H⁹), 3.78 (2 H, m, H⁹) and 2.90 (3 H, s, H⁷); ¹³C-¹H NMR (selected data) δ 174.0 (C⁸), 161.1 (C²), 141.8 (C¹), 129.6 (C⁴), 128.0 (C⁶), 123.4 (C³), 110.9 (C⁵), 74.0, 73.2 (C₅H₄), 65.4 (C⁹), 55.5 (C⁷), 134.1, 132.8, 131.1, 128.8 (PPh₂); ³¹P-¹H NMR δ 45.38 (s); mass spectrum m/z 1561 (M^+) (Found: C, 53.69; H, 5.06; N, 1.83. Calc. for C₇₀H₇₆FeI₂N₂O₂P₂Pd₂: 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 ₂ Cl ₂
Formula	C ₃₆ H ₄₈ Cl ₂ N ₂ O ₂ Pd ₂	C ₃₆ H ₄₈ Br ₂ N ₂ O ₂ Pd ₂	(C ₃₆ H ₃₉ ClN ₂ O ₂ Pd) ₂	C ₇₁ H ₇₈ Br ₂ Cl ₂ FeN ₂ O ₂ P ₂ Pd ₂
<i>M</i>	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	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (no. 19)	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (no. 19)	<i>P</i> 1 (no. 1)	<i>P</i> 2 ₁ (no. 4)
<i>a</i> /Å	13.518(3)	13.548(3)	12.138(2)	16.703(3)
<i>b</i> /Å	25.105(5)	24.965(5)	13.909(3)	16.415(3)
<i>c</i> /Å	10.797(2)	10.945(2)	10.066(2)	25.250(5)
<i>α</i> /°			91.75(3)	
<i>β</i> /°			97.35(3)	90.70(3)
<i>γ</i> /°			104.22(3)	
<i>U</i> /Å ³	3664(1)	3702(1)	1630.4(5)	6934(2)
<i>Z</i>	4	4	1	4
<i>F</i> (000)	1672	1824	1432	3152
<i>D</i> /g cm ⁻³	1.491	1.639	1.394	1.489
<i>μ</i> (Mo-Kα)/mm ⁻¹	1.160	3.163	0.729	2.040
2θ Range/°	3–55	3–55	3–55	3–52
Reflections collected, <i>n</i>	11 888	10 561	6049	20 315
Independent reflections (<i>R</i> _{int})	6486 (0.023)	6258 (0.065)	6049 (0.00)	12 097 (0.062)
<i>R</i> 1 ^a	0.0378	0.0607	0.0316	0.0695
<i>wR</i> 2 ^b	0.0997	0.1695	0.0788	0.1707
Weighting scheme ^c	<i>a</i> = 0.0741, <i>b</i> = 0.0754	<i>a</i> = 0.1188, <i>b</i> = 1.2471	<i>a</i> = 0.0312, <i>b</i> = 0.2202	<i>a</i> = 0.0898, <i>b</i> = 5.1590
No. parameters refined, <i>p</i>	398	398	739	1514
<i>S</i> (Goodness of fit) ^d	1.043	1.026	1.021	1.088
Maximum, mean <i>Δ</i> /σ	0.002, 0.000	0.225, 0.005	0.077, 0.006	0.019, 0.000
<i>Δρ</i> _{max} /e Å ⁻³	0.841, -0.756	0.870, -0.926	0.285, -0.380	0.858, -0.653

^a *R*1 = (Σ|*F*_o - |*F*_c||)/Σ|*F*_o|. ^b *wR*2 = [Σ*w*(*F*_o² - *F*_c²)/Σ*w*(*F*_o²)²]^{1/2}. ^c *w*⁻¹ = σ²(*F*_o²) + (*aP*)² + *bP* where *P* = (*F*_o² + 2*F*_c²)/3. ^d *S* = [Σ*w*(*F*_o² - *F*_c²)²/(*n* - *p*)]^{1/2}.

Crystallography

Crystallographic data of complexes (+)-**1a**, (+)-**1b** and (+)-**4b**·CH₂Cl₂ 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 (λ = 0.7103 Å) from a rotating-anode generator operating at 50 kV and 90 mA [2θ_{min} = 3°, 2θ_{max} = 55°, sixty 3° oscillation frames for (+)-**1a** and (+)-**4b**·CH₂Cl₂, 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 (λ = 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 *R*1 and *wR*2 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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