New mono- and di-nuclear complexes of PdII, PtII and NiII of PNNP ligands with a 2,2′-biaryl bridging unit

Alette G. J. Ligtenbarg,[a] Esther K. van den Beuken,[a] Auke Meetsma,[a] Nora Veldman,[b] Wilberth J. J. Smeets,[b] Anthony L. Spek[b] and Ben L. Feringa *,[a]

[a] Department of Organic and Molecular Inorganic Chemistry, Groningen Center for Catalysis and Synthesis, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
[b] Crystal and Structural Chemistry, Bijvoet Center for Biomolecular Research, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

The Schiff bases 2,2′-bis{N-[(2-diphenylphosphino)phenyl]formimidoyl}biphenyl (L^1) and 2,2′-bis{[(2-diphenyl-phosphino)benzylidene]amino}biphenyl (L^2) were synthesized from the appropriate amine and aldehyde. Their co-ordination behaviour towards PdII, PtII and NiII has been studied. Dinuclear complexes were formed when treating L^1 with 2 equivalents of [PdCl(Me)(cod)] (cod = cycloocta-1,5-diene) and $Pd(O_2CMe)_2$. In the case of the reaction of L^1 with $Pd(O_2CMe)_2$ an unexpected double cyclopalladated complex was formed. However, treatment of L^1 with 2 equivalents of $[PtCl_2(MeCN)_2]$ resulted in hydrolysis of the ligand and a mononuclear complex of (2-diphenylphosphino)benzenamine was obtained. The structure of $[Pd_2L^1Cl_2Me_2]$ **1** has been established by an X-ray diffraction study. The dihedral angle between the biphenyl rings is 49.2(8)° and the intramolecular Pd···Pd distance is 7.165(3) Å. The biphenyl bridging moiety shows a remarkable bending of 169.2(8)°. Treatment of **1** with carbon monoxide resulted in a double CO insertion, yielding the bis(acetyl)palladium compound $[Pd_2L^1Cl_2\{C(O)Me\}_2]$ **2**. The structure of $[Pd_2L^1(O_2CMe)_2]\cdot4CH_2Cl_2$ **3** was also determined by X-ray diffraction. The dihedral angle between the biphenyl rings is 75.9(14)° while the intramolecular Pd···Pd distance is 8.655(2) Å. The reaction of L^2 with 2 equivalents of anhydrous $[PdCl_2(MeCN)_2]$ or $NiCl_2$ afforded mononuclear complexes. The crystal and molecular structure of $[PdL^2]Cl_2\cdot3.5CH_2Cl_2$ was determined. The compound has an approximately square-planar P_2N_2 geometry.

The chemistry of dinuclear transition-metal complexes has attracted considerable interest in recent years.[1] In particular dinuclear models of metalloproteins[2] have received great attention[3] and a variety of new homo-[4] and hetero-dinuclear[5] complexes has been synthesized. In the design of these types of compounds the choice of the ligand system is of prime importance.[6] When the two metal centres are incorporated in close proximity the complexes have the potential of catalysing reactions either more efficiently, or with different chemo-, regio- or stereo-selectivity than those of corresponding mononuclear ones, due to co-operation of the two metals in the transition state of the catalytic reaction.[7] An excellent example of a dinuclear catalyst which exhibits higher regioselectivity and reactivity than those of the related mononuclear system by bimetallic co-operation is the dirhodium system reported by Stanley and co-workers[8] for the hydroformylation of α-olefins. In our group oxygen activation on dinuclear copper complexes contain a *meta*-arene-bridged ligand system was investigated.[9] Recently dinuclear rhodium phosphite complexes based on a tetranaphthol skeleton were studied as catalysts in hydroformylation reactions.[10] In the systems studied so far ligands are often either highly flexible or rigid; in the second case the two metal centres are in a fixed orientation towards each other. It was envisaged that when the distance between the two metal ions is flexible this might result in optimum co-operation of the metal centres in the transition state of a catalytic reaction. A building block for this approach is a biphenyl unit, which can act as a bridging moiety between two ligating groups. Réglier *et al.*[11] have reported a dinuclear complex of a bis(pyridyl)-substituted biphenyl ligand which acts as a functional mimic of tyrosinase, a copper-containing monooxygenase. However, in most cases where a biaryl backbone is used, mononuclear complexes are obtained *e.g.* with NiII, CuII, CoII, ZnII and PdII.[12,13] In the approach described here a biphenyl ligand system is developed consisting of two fairly rigid arms connected to
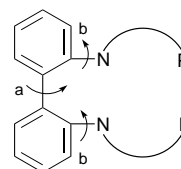

the backbone which has flexibility at point a. Owing to the bulky 2,2′ substituents, however, hindered rotation is expected around the biaryl bond (atropisomerism), which might result in stereoisomers of these ligands or complexes. As donor sets phosphorus and imino-nitrogen atoms were chosen, and the co-ordination behaviour of these ligands with metals of Group VIII, *e.g.* PdII, PtII and NiII, was studied. The co-ordination geometry of the metals will largely be determined by the angle between the two phenyl rings in the biphenyl moiety (a) and by rotation around the single bonds connecting the side-arms to this unit (b).

Results

Synthesis of 2,2′-bis{N-[(2-diphenylphosphino)phenyl]-formimidoyl}biphenyl (L^1)

The tetradentate diimine ligand 2,2′-bis{N-[(2-diphenyl-phosphino)phenyl]formimidoyl}biphenyl (L^1) was synthesized by the Schiff-base formation of 2 equivalents of biphenyl-2,2′-dicarbaldehyde with (2-diphenylphosphino)benzenamine[14] (Scheme 1). The synthesis of biphenyl-2,2′-dicarbaldehyde by phenanthrene ozonolysis is a known literature procedure[15] but the yields are often low. Therefore we developed a more convenient route towards this compound starting from diphenic acid ([1,1′-biphenyl]-2,2′-dicarboxylic acid).[16] In a first step the dimethyl ester **I** was formed in 80% yield. Subsequently reduction with lithium aluminium hydride gave the corresponding
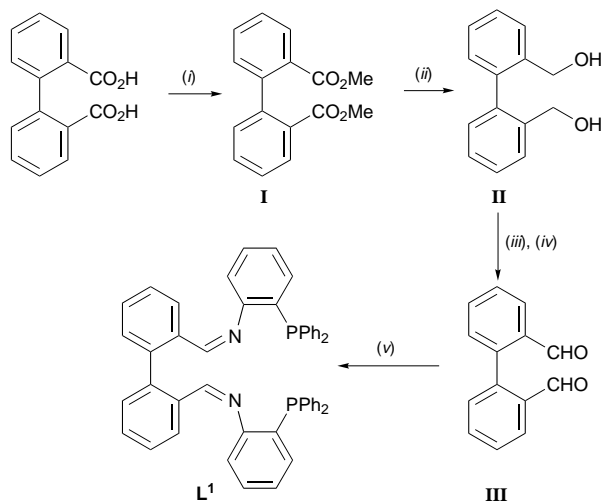
Scheme 1 (*i*) MeOH, H_2SO_4, reflux, 16 h, yield 80%; (*ii*) LiAlH$_4$, tetrahydrofuran (thf), reflux, 17 h, 90%; (*iii*) ClCOCOCl, dimethyl sulfoxide (dmso), −60 °C, 45 min; (*iv*) NEt$_3$, 90%; (*v*) (2-diphenyl-phosphino)benzenamine, toluene-*p*-sulfonic acid, benzene, molecular sieves (4 Å), Dean–Stark, reflux, 24 h, 65%
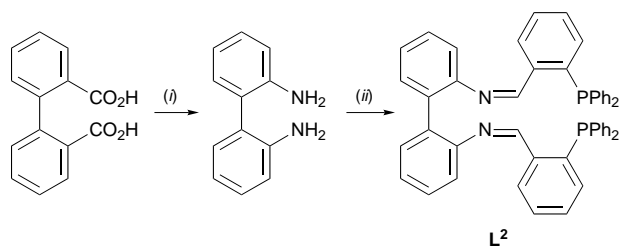

Scheme 2 (*i*) NaN$_3$, H_2SO_4, 30–40 °C, 95 min, yield 65%; (*ii*) 2-(diphenylphosphino)benzaldehyde, toluene-*p*-sulfonic acid, benzene, Dean–Stark, reflux, 4 h, 92%

diol **II** in 90% yield. Next, a mild Swern oxidation was performed, affording the dialdehyde **III** in high yield (90%). The synthesis of L^1 was carried out under a nitrogen atmosphere in dry benzene. The reaction was followed by ^{31}P NMR spectroscopy, which revealed that imine formation was rather slow and was complete after 24 h. Besides a Dean–Stark trap, addition of molecular sieves was necessary in order to remove all the water produced during the reaction and to drive it to completion. Even small amounts of water in the reaction mixture caused oxidation of the product. The compound L^1 was purified by crystallisation from a dichloromethane–pentane solvent mixture. It showed in the ^{31}P NMR spectrum an absorption at δ −14.9 and is air-stable in the solid state. Furthermore, the ligand was characterised by ^{1}H NMR spectroscopy, elemental analysis and mass spectrometry (see Experimental section).

Synthesis of 2,2′-bis{[2-(diphenylphosphino)benzylidene]amino}-biphenyl (L^2)

A related tetradentate Schiff-base ligand (L^2) with phosphorus and imino-nitrogen donor sets was also synthesized. In L^2 the imino nitrogen atom is attached to the biphenyl moiety, instead of the imino carbon atom in L^1. We expected this ligand to be more stable towards oxidation and more easily synthesized. Furthermore, upon co-ordination of the phosphorus and nitrogen atoms to a metal ion, a six-membered chelate ring will be formed instead of a five-membered ring in the case of L^1. Ligand L^2 was synthesized by a Schiff-base reaction of 2,2′-diaminobiphenyl[17] and 2-(diphenylphosphino)benzaldehyde (Scheme 2).[18] After 4 h reflux in benzene under Dean–Stark conditions with a catalytic amount of toluene-*p*-sulfonic acid L^2 was obtained in 92% yield. It showed an absorption at δ
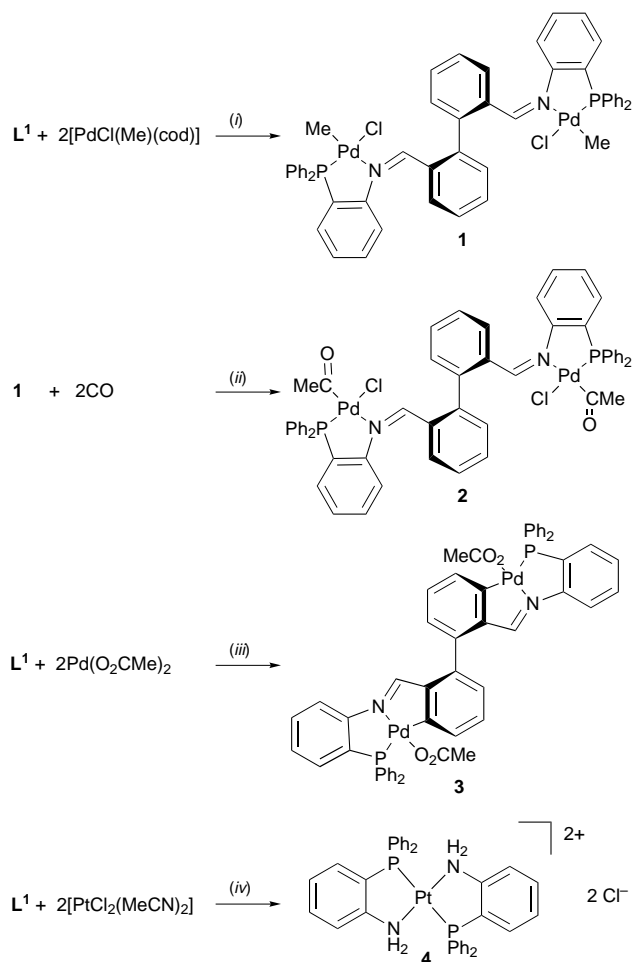
Scheme 3 (*i*) thf, room temperature (r.t.), 16 h, yield 65%; (*ii*) CDCl$_3$, r.t., 15 min; (*iii*) CH$_2$Cl$_2$, r.t.; (*iv*) CH$_2$Cl$_2$, r.t., 1 h

−15.2 in the ^{31}P NMR spectrum. The product was also characterised as for L^1.

Compound L^2 was air-stable in the solid state as well as in solution. The Schiff-base reaction yielding it was much faster than the imine formation affording L^1 as only 4 h for complete conversion for L^2 and 24 h for L^1 were required. In addition, a larger overall yield for L^2 compared to L^1 (60 and 45%, respectively) was found.

Palladium and platinum complexes based on L^1

Ligand L^1 was allowed to react with 2 equivalents of [PdCl(Me)(cod)][19] (cod = cycloocta-1,5-diene) in tetrahydrofuran for 16 h at room temperature yielding a precipitate, which was crystallised from dichloromethane–pentane as pale yellow crystals in 65% yield. The cod group of the starting material was replaced by L^1, giving rise to dinuclear complex **1** (Scheme 3). The ^{31}P NMR spectrum shows a singlet at δ 35.4 (CDCl$_3$), which indicates that the two phosphorus atoms are identical. Compared with the free biphenyl (δ −14.9, CDCl$_3$) a strong downfield shift is observed. The ^{1}H NMR spectrum of **1** revealed that the methyl groups on the metal ions are equivalent giving a sharp doublet at δ 0.86 due to phosphorus proton coupling [*J*(P–H) = 2.93 Hz]. The magnitude of this coupling indicates a *cis* relationship[20] between two groups having a large *trans* influence,[21] *i.e.* the phosphorus atom and the methyl group. The crystal structure of [Pd$_2$L^{1}Cl$_2$Me$_2$] **1** was established by an X-ray diffraction study (Fig. 1). Selected bond lengths, angles and torsion angles are listed in Table 1.

The notion that the ligand has imposed C_2 symmetry on the palladium complex was confirmed by the X-ray diffraction analysis showing a two-fold axis dividing the C(25)–C(25a)

Table 1 Selected bond distances (Å) and angles (°) and torsion angles (°) of complex **1** with estimated standard deviations (e.s.d.s) in parentheses

Pd–N	2.237(4)	Pd–C(26)	2.020(6)
Pd–Cl	2.3625(15)	C(25)–C(25a)	1.486(6)
Pd–P	2.1963(16)	Pd(1)⋯Pd(1a)	7.165(3)
Cl–Pd–N	98.57(11)	Cl–Pd–P	178.21(5)
P–Pd–N	79.70(11)	N–Pd–C(26)	169.6(2)
P–Pd–C(26)	92.0(2)	C(20)–C(25)–C(25a)	126.0(4)
Cl–Pd–C(26)	89.8(2)	C(24)–C(25)–C(25a)	116.5(4)
C(20)–C(25)–C(25a)–C(20a)	49.2(8)		

Table 2 Selected bond distances (Å) and angles (°) and torsion angles (°) of complex **3** with e.s.d.s in parentheses

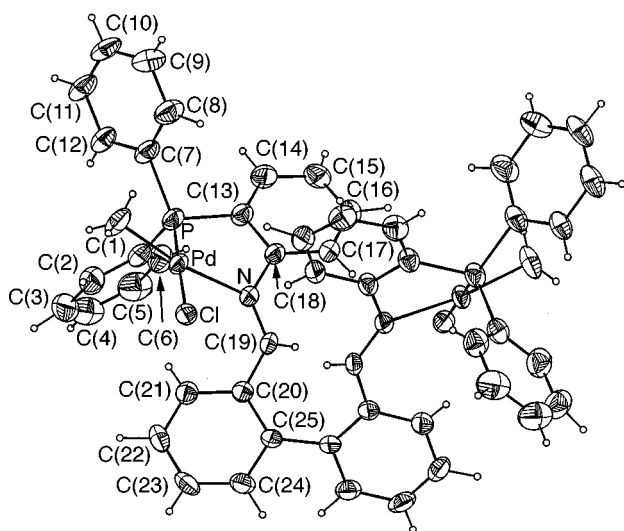|			
Pd(1)–N(1)	2.000(7)	Pd(1)–C(21)	1.978(10)
Pd(1)–O(1)	2.051(7)	C(25)–C(25a)	1.508(14)
Pd(1)–P(1)	2.319(2)	Pd(1)⋯Pd(1a)	8.655(2)
P(1)–Pd(1)–O(1)	100.0(2)	O(1)–Pd(1)–N(1)	172.7(3)
P(1)–Pd(1)–N(1)	84.5(2)	P(1)–Pd(1)–C(21)	166.6(3)
O(1)–Pd(1)–C(21)	93.4(2)	C(20)–C(25)–C(25a)	122.5(8)
N(1)–Pd(1)–C(21)	82.0(3)	C(24)–C(25)–C(25a)	119.8(9)
C(20)–C(25)–C(25a)–C(20a)	75.9(14)		

Fig. 1 An ORTEP[22] plot of complex **1** (50% probability level)

bond. The metals adopt a distorted square-planar co-ordination geometry. The P–Pd–N angle of 79.70(11)° is significantly smaller than the ideal 90° angle, whereas the Cl–Pd–N angle of 98.57(11)° is significantly larger than 90°. The distances between palladium and the donor atoms are within the normal range;[20b,23,24a] Pd–N and Pd–P distances are 2.237(4) and 2.1963(16) Å, respectively whereas Pd–Cl and Pd–CH₃ are 2.3625(15) and 2.020(6) Å, respectively. The Pd⋯Pd distance is 7.165(3) Å and the metal ions are directed to the outside (anti-folding, see Scheme 5, structure **A**). The two phenyl rings of the biphenyl are twisted with respect to each other resulting in a dihedral angle of 49.2(8)° for C(20)–C(25)–C(25a)–C(20a). A remarkable feature of the biphenyl moiety is the significant non-linearity as shown by the orientation of the atoms C(22), C(25), C(25a) and C(22a). The angle C(22)–C(25)–C(22a) is 169.2(8)° instead of the ideal 180°. The carbon atoms of the phenyl ring of C(20) to C(25) deviate 0.022 Å from the mean plane. Carbon atom C(22a) is 0.366(6) Å and C(25a) 0.123(5) Å out of that plane.

Complexes containing a metal–carbon σ bond can undergo insertion reactions with *e.g.* carbon monoxide[24] and isocyanides.[25] Treatment of a solution of **1** with carbon monoxide in CDCl₃ at room temperature for 15 min resulted smoothly and nearly quantitatively in double CO insertion leading to the formation of the dinuclear acetylpalladium compound [Pd₂L¹Cl₂{C(O)Me}₂] **2** which was characterised by IR and NMR spectroscopy. The CO stretching vibration at 1697 cm⁻¹ indicates inserted carbon monoxide.[24a] In the ¹H NMR spectrum the methyl absorption is shifted to δ 2.25 compared with δ 0.86 in **1** and the coupling pattern has disappeared. The ¹³C NMR spectrum shows an additional carbonyl absorption at δ 210.8 and an acetyl methyl signal at δ 10.93 whereas the methyl resonance in **1** was located at δ −1.42. The ³¹P resonance has shifted upfield to δ 14.29. Reaction of **1** with *tert*-butyl

isocyanate resulted in the formation of some palladium(0) and a complex reaction mixture, according to NMR spectroscopy, which was not further identified.

Reaction of 2 equivalents of Pd(O₂CMe)₂ with L¹ was carried out in dichloromethane at room temperature under a nitrogen atmosphere for 1.5 h. Subsequently, the solvent was removed *in vacuo* and the resulting dark yellow-brown oil was crystallised from dichloromethane–pentane. Dark red crystals of the cyclopalladated complex **3** were obtained after a few weeks and its structure confirmed by X-ray crystallography (Fig. 2). The ³¹P NMR spectrum shows a singlet at δ 44.9 (CDCl₃), which indicates that the two phosphorus atoms are identical.

The complex has C_2 symmetry with a two-fold axis dividing the C(25)–C(25a) bond. The two phenyl rings of the biphenyl moiety are twisted with respect to each other with a dihedral angle of 75.9(14)° for C(20)–C(25)–C(25a)–C(20a). Atoms C(22), C(25) and C(25a), C(22a) show a nearly linear arrangement. For example the angle between C(22), C(25) and C(25a) is 179.1(9)°. The distances between palladium and the co-ordinated donor atoms in complex **3** are in the normal range, Pd–N and Pd–P are 2.000(7) and 2.319(2) Å, respectively and Pd–O and Pd–C are respectively 2.051(7) and 1.978(10) Å.[26] The intramolecular metal–metal distance is 8.655(2) Å. The metal adopts a distorted square-planar co-ordination geometry: the angles P(1)–Pd(1)–N(1) [84.5(2)°] and N(1)–Pd(1)–C(21) [82.0(3)°] are significantly less than the ideal 90°. The angles P(1)–Pd(1)–O(1) and O(1)–Pd(1)–C(21) are respectively 100.0(2) and 93.4(3)°. Selected bond lengths and angles are listed in Table 2.

From ³¹P and ¹H NMR studies it can be concluded that cyclometallation of L¹ with Pd(O₂CMe)₂ in dichloromethane is a very slow process. Initially, upon addition of Pd(O₂CMe)₂, a mixture of products is formed. These products eventually rearrange to give the more stable cyclopalladated compound together with acetic acid. The formation of [Pd₂(O₂CMe)₂L¹] is irreversible.

The binding of L¹ to Pt^II was briefly examined by treating a solution of L¹ in dichloromethane with 2 equivalents of bis-(acetonitrile)platinum(II) chloride. After 1 h at room temperature ³¹P NMR spectroscopy showed the presence of various compounds. After 1 night this composition had not changed. Attempts to isolate either a mono- or a di-nuclear complex of L¹ failed. The only complex that was isolated according to ¹H, ¹³C NMR spectroscopy and elemental analysis was the platinum complex **4** of (2-diphenylphosphino)benzenamine **IV**. Obviously, the complexes formed initially are highly water sensitive. During work-up by filtering the solution in the presence of air the ligand was hydrolysed, followed by complexation of Pt to form **4**.

Palladium and nickel complexes based on L²

To study the co-ordination behaviour of L², 2 equivalents of [PdCl₂(MeCN)₂] were added to a solution of L² in dichloromethane at room temperature. Remarkably, in this case no
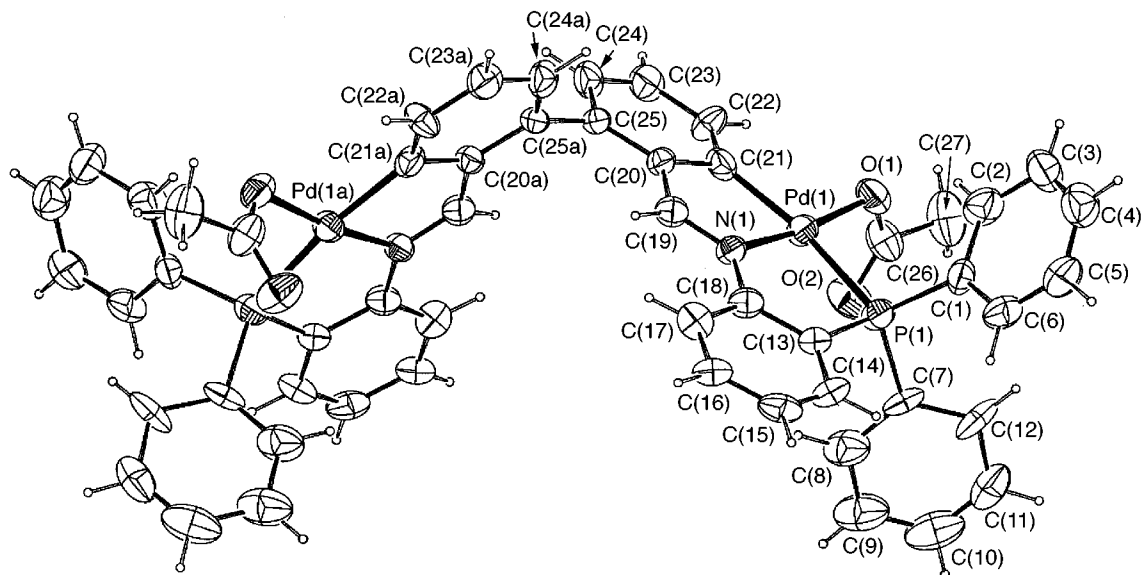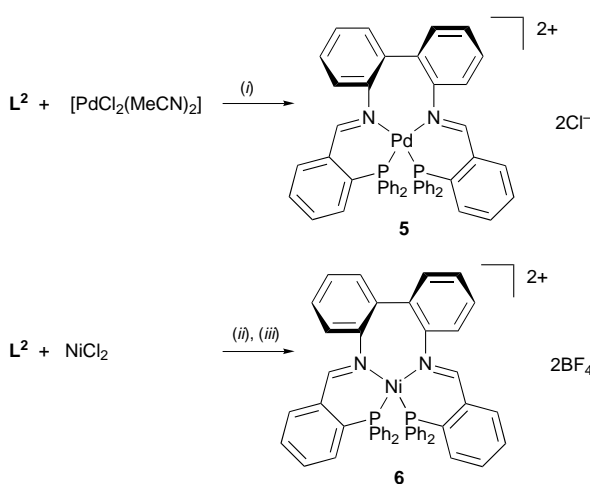
Fig. 2 An ORTEP plot of complex **3** (50% probability level)

Scheme 4 (*i*) CH$_2$Cl$_2$, r.t., 1.5 h, yield 66%; (*ii*) absolute EtOH, reflux, 3 h; (*iii*) CH$_2$Cl$_2$, 4 NaBF$_4$, r.t., 2 h, 53%
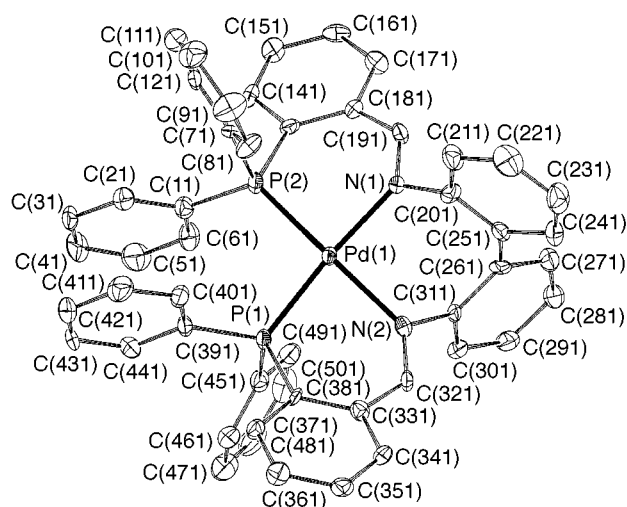

Fig. 3 An ORTEP plot of one of the two independent molecules in the crystals of complex **5** (50% probability level)

Table 3 Selected bond distances (Å) and angles (°) and torsion angles (°) of complex **5*** with e.s.d.s in parentheses

|			
Pd(1)–N(1)	2.086(6)	Pd(1)–P(2)	2.262(2)
Pd(1)–N(2)	2.164(6)	Pd(1)···Cl(1)	2.8025(19)
Pd(1)–P(1)	2.243(2)	C(251)–C(261)	1.470(11)
P(1)–Pd(1)–N(2)	85.08(18)	P(1)–Pd(1)–N(1)	175.08(17)
P(1)–Pd(1)–P(2)	96.56(8)	P(2)–Pd(1)–N(2)	161.98(16)
N(1)–Pd(1)–N(2)	90.0(2)	C(201)–C(251)–C(261)	122.6(7)
P(2)–Pd(1)–N(1)	88.29(17)	C(241)–C(251)–C(261)	119.5(7)
C(241)–C(251)–C(261)–C(271)	51.4(11)		

* Values for only one crystallographically independent molecule are given. The dimensions of the second are very similar.

formation of a dinuclear species was observed. According to ^{31}P NMR spectroscopy, mononuclear complex **5** (Scheme 4) was formed quantitatively, giving rise to a ^{31}P NMR absorption at δ 31.1 (free biphenyl δ −15.2). Crystallisation from dichloromethane–pentane afforded orange crystals suitable for X-ray analysis. The crystal structure of **5** is shown in Fig. 3. Selected bond lengths, angles and torsion angles are listed in Table 3.

Complex **5** exists in two forms in the unit cell which slightly differ from one another, together with seven solvent molecules

(dichloromethane). In both structures the chlorides are non-co-ordinating. The palladium ion adopts a slightly distorted square-planar geometry. The twist in the biphenyl moiety is 51.4(11)° for C(241)–C(251)–C(261)–C(271) and 51.5(11)° for the corresponding carbon atoms in the second structure. The distances between palladium and the donor atoms are within the normal range.[23] The distances between Pd(1) and P(1) and P(2) are 2.243(2) and 2.262(2) Å, respectively. The Pd–N distances are 2.086(6) Å for Pd(1)–N(1) and 2.164(6) Å for Pd(1)–N(2). Also in this compound the atoms C(221)–C(251)–C(261)–C(291) show a non-linear arrangement, but the bending in the biaryl unit is significantly less than in complex **1** (see above). The angle between C(251), C(261) and C(291) is 175.5(6)° and for the corresponding atoms in the second structure 175.2(6)°. For a related mononuclear rhodium(I) complex of an asymmetric 6,6′-dimethyl-2,2′-bis{[2-diphenylphosphino)benzylidene]amino}biphenyl ligand[27] no bend in the biphenyl moiety was reported, whereas the dihedral angle between the rings was larger (69°).

Upon reaction of L^2 with anhydrous nickel(II) chloride mononuclear complex **6** was formed which was characterised by ^{31}P and ^{1}H NMR spectroscopy, elemental analysis and mass spectrometry (see Experimental section). The complex shows an absorption in the ^{31}P NMR spectrum at δ 31.3.
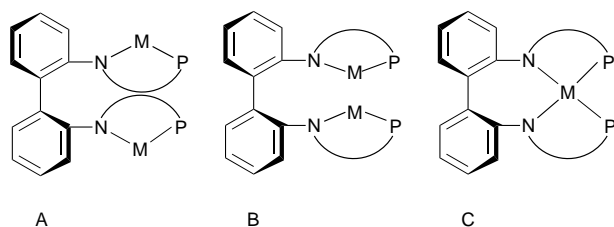
Scheme 5 Representation of the geometries of mono- and di-nuclear complexes based on PNNP ligands

Discussion

From these results it can be concluded that L^1 is an excellent dinucleating ligand for palladium. When [PdCl(Me)(cod)] is added to L^1 a geometry is adopted in which the ligating groups at each phenyl ring point to the 'inside' and the two metal centres are directed to the 'outside' as illustrated in Scheme 5, structure **A**. Probably steric interactions between the two side-arms disfavour the formation of a *syn*-folded geometry as indicated in structure **B**, although it must be emphasised that in solution rotation around the single bonds connecting the side-arms to the backbone is still possible. In geometry **B** the two metals are in closer proximity, yielding a complex in which they might be able to co-operate in a catalytic reaction. However, in the double cyclometallated complex **3** (Fig. 2), despite the biaryl rotation, the formation of a *syn*-folded geometry is not possible because the palladium ions are directly attached to the biphenyl backbone *via* C(21)–Pd(1) [C(21a)–Pd(1a)] aryl–metal bonds.

In the case of L^2 only mononuclear complexes were formed with the general structure as shown in Scheme 5, **C**. In spite of the possibility of adopting a conformation able to accommodate two metal ions simultaneously, by rotation around the single bond in the biphenyl backbone, only mononuclear complexes are formed. Apparently, these are very stable. Once a metal ion is complexed between the four donor atoms in the ligand, the binding of a second metal ion is disfavoured.

Conclusion

Two new ligand systems, L^1 and L^2, were developed containing a PNNP donor-atom sequence and a biphenyl backbone. We have shown that L^1 can readily accommodate two palladium ions. Furthermore, a mild double cyclometallation reaction was observed with $Pd(O_2CMe)_2$ although the process is rather slow. In contrast, L^2 only affords mononuclear complexes of palladium and nickel. Notably, the crystal structures of [Pd$_2$-L^{1}Cl$_2$Me$_2$] **1** and [Pd$_2$L^2]Cl$_2$ **5** obtained by X-ray analyses showed that the biphenyl moiety is twisted to approximately the same degree (about 50°) for both complexes. However, the twist in the biphenyl moiety of [Pd$_2$L^1(O$_2$CMe)$_2$] **3** is much larger (75.9°). Another remarkable feature of these compounds is the significant non-linearity in the biphenyl entity leading to significant biphenyl bending. Finally with complex **1** a successful double-insertion reaction was performed with carbon monoxide yielding [Pd$_2$L^{1}Cl$_2${C(O)Me}$_2$] **2**.

Experimental

Melting points (uncorrected) were determined on a Mettler FP-2 apparatus equipped with a FP-21 microscope and are uncorrected. Proton NMR spectra were recorded on a Varian Gemini-200 (at 200 MHz), on a VXR-300 (at 300 MHz) or on a Unity 500 spectrometer (at 500 MHz). Chemical shifts are reported in δ units (ppm) relative to the solvent and converted into the SiMe$_4$ scale (δ 0) using δ (CHCl$_3$) 7.26. Carbon-13 NMR spectra were recorded on a Varian Gemini-200 (at 50.3 MHz), on a VXR-300 (at 75.4 MHz) or on a Unity 500 spectrometer (at 125 MHz), ^{31}P NMR spectra on a Varian Gemini-

200 spectrometer (at 80.95 MHz) with triphenyl phosphate as an external reference (δ −18). High-resolution mass spectra were obtained on an AEI MS-902 spectrometer by electron impact (EI), electron spray (ES) mass spectra on a NERMAG mass spectrometer. Infrared spectra were recorded on a Perkin-Elmer 841 spectrometer. Elemental analyses were performed in the Microanalytical Department of our laboratory.

All manipulations were carried out under an atmosphere of dry dinitrogen except for the synthesis of compound **I**. Dichloromethane, pentane and hexane were distilled from phosphorus pentaoxide, methanol from magnesium, benzene from sodium wire and tetrahydrofuran from sodium–benzophenone. Dimethyl sulfoxide was dried by stirring over barium oxide during 18 h before use. (2-Diphenylphosphino)-benzenamine,[14] 2,2′-diaminobiphenyl,[17] 2-(diphenylphos-phino)benzaldehyde [18] and [PdCl(Me)(cod)][19] were synthesized using literature procedures. Diphenic acid, 2-bromo-benzaldehyde and chlorodiphenylphosphine obtained from Aldrich were used without further purification.

Preparations

Biphenyl-2,2′-dicarboxylic acid dimethyl ester I. To biphenyl-2,2′-dicarboxylic acid (25.0 g, 103 mmol) in methanol (250 cm³) was added sulfuric acid (4 cm³) and the solution was heated under reflux for 16 h. The resulting dark brown reaction mixture was poured into a water–ice mixture (300 cm³) and subsequently ethyl acetate (300 cm³) was added. Evaporation of most of the methanol yielded a two-phase system. The dark green aqueous layer was extracted with ethyl acetate (2 × 75 cm³) and the combined organic layers were subsequently washed with saturated sodium hydrogencarbonate solution (2 × 75 cm³), water (1 × 75 cm³) and brine (1 × 50 cm³). Drying (MgSO$_4$) and evaporation of the solvent yielded a pale brown solid which was crystallised from ethyl acetate (10 cm³). Yield: 22.6 g as white crystals (80%). M.p. 76.7–77.7 °C; ^{1}H NMR (CDCl$_3$) δ 8.05–8.00 (m, 2 H), 7.60–7.40 (m, 4 H), 7.24–7.20 (m, 2 H) and 3.63 (s, 6 H); ^{13}C NMR (CDCl$_3$) δ 167.4 (C), 143.3 (C), 131.4 (CH), 130.2 (CH), 129.8 (CH), 129.3 (C), 127.2 (CH) and 51.8 (CH$_3$).

2,2′-Di(hydroxymethyl)biphenyl II. Dimethyl ester **I** (7.0 g, 25.9 mmol) in thf (100 cm³) was added slowly to a suspension of LiAlH$_4$ (2.0 g, 0.21 mol) in thf (150 cm³) at 0 °C. The reaction mixture was refluxed for 17 h. After cooling to 0 °C, aqueous 1.4 M KOH (20 cm³) was added carefully. After refluxing for 1 h, filtering, drying (MgSO$_4$) and evaporation of the solvent, **II** was obtained in 94% yield as a white solid which was recrystallised from ethyl acetate (10 cm³). Yield: 5.0 g as white needles (90%). M.p. 112.4–113.5 °C; ^{1}H NMR (CDCl$_3$) δ 7.36 (m, 6 H), 7.13 (dd, $J = 0.9$, $J = 3.6$ Hz, 2 H), 4.27 (s, 4 H) and 3.66 (s, OH, 2 H); ^{13}C NMR (CDCl$_3$) δ 140.0 (C), 138.6 (C), 129.61 (CH), 129.55 (CH), 128.0 (CH), 127.6 (CH) and 62.7 (CH$_2$).

Biphenyl-2,2′-dicarbaldehyde III. A solution of oxalyl chloride (2.75 cm³, 0.032 mol, 2.7 equivalents) in dichloromethane (50 cm³) was cooled to −60 °C and a mixture of dmso (3 cm³, 0.042 mol, 3.5 equivalents) and dichloromethane (10 cm³) was added carefully. After stirring for 5 min, **II** (2.6 g, 0.012 mol) in dmso (1 cm³) and dichloromethane (50 cm³) was added in less than 5 min. The resulting white solution was stirred for 45 min at −60 °C. Next a large excess of triethylamine (10 cm³, 0.072 mol, 6.0 equivalents) was added carefully. The mixture was allowed to warm to room temperature and subsequently washed with 5% HCl solution (30 cm³), aqueous NaHCO$_3$ (saturated, 30 cm³) and brine (30 cm³). Drying (MgSO$_4$) and evaporation of the solvent gave dialdehyde **III** as a pale yellow oil that solidified upon standing. Yield: 2.3 g as a yellow solid (90%). M.p. 63.2–64.3 °C (lit.,[15] 62.5–63.5 °C); ^{1}H NMR

(CDCl$_3$) δ 9.80 (s, CHO, 2 H), 8.02 (d, $J = 4$, 2 H), 7.70–7.57 (m, 4 H) and 7.33 (d, $J = 3$ Hz, 2 H); ^{13}C NMR (CDCl$_3$) δ 191.0 (CH), 141.2 (C), 134.5 (C), 133.4 (CH), 131.7 (CH), 128.8 (CH) and 128.5 (CH).

2,2′-Bis{N-[(2-diphenylphosphino)phenyl]formimidoyl}-biphenyl L^1.

To a mixture of biphenyl-2,2′-dicarbaldehyde **III** (0.31 g, 1.49 mmol), (2-diphenylphosphino)benzenamine **IV** (0.83 g, 2.98 mmol, 2.0 equivalents) and a catalytic amount of toluene-p-sulfonic acid in dry benzene (40 cm^3) were added molecular sieves (4 Å). The reaction mixture was refluxed under Dean–Stark conditions for 16 h. After 90% completion of the reaction according to ^{31}P NMR spectroscopy (16 h), the mixture was filtered over Celite and the yellow solution refluxed for 6 h. Evaporation of the solvent yielded a pale yellow foam. Pure L^1 was obtained upon crystallisation from dichloromethane–pentane (1 : 2). Yield: 0.76 g as a pale yellow powder (65%). M.p. 183.3–185.3 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 8.10–8.05 (m, 2 H), 7.87 (s, 2 H), 7.41–7.32 (m, 4 H), 7.31–7.20 (m, 22 H), 7.08 (t, $J = 7.5$, 2 H), 7.00–6.95 (m, 2 H), 6.79 (d, $J = 1.2$, 1 H), 6.77 (d, $J = 1.5$, 1 H), 6.74 (d, $J = 4.4$, 1 H), 6.71 (d, $J = 1.0$, 2 H) and 6.69 (d, $J = 1.2$ Hz, 1 H); ^{13}C NMR (CDCl$_3$, 50.3 MHz) δ 157.9 (CH, $^4J_{PC} = 1.5$), 154.0 (C, $^1J_{PC} = 17.9$), 140.3 (C), 136.8 (C, $^2J_{PC} = 10.7$), 134.4 (C), 134.0 (CH, $^2J_{PC} = 20.6$), 132.6 (C, $^1J_{PC} = 11.4$), 132.3 (CH), 130.7, 130.2 (CH), 129.7 (CH), 128.4 (CH), 128.2 (CH, $^3J_{PC} = 7.3$ Hz), 128.0 (CH), 127.2 (CH), 125.8 (CH) and 117.0 (CH); ^{31}P NMR (CDCl$_3$, 80.95 MHz) δ −14.9. High-resolution mass spectrum: m/z 728.251 (calc. for C$_{50}$H$_{38}$N$_2$P$_2$: 728.251) (Found: C, 82.04; H, 5.47; N, 3.75; P, 8.29. Calc. for C$_{25}$H$_{19}$NP: C, 82.40; H, 5.26; N, 3.84; P, 8.50%).

2,2′-Bis{[2-(diphenylphosphino)benzylidene]amino}biphenyl L^2.

A mixture of 2-(diphenylphosphino)benzaldehyde (1.01 g, 3.44 mmol), 2,2′-diaminobiphenyl (0.322 g, 1.72 mmol) and a catalytic amount of toluene-p-sulfonic acid in benzene (40 cm^3) was refluxed for 4 h under Dean–Stark conditions. The solvent was evaporated and the product crystallised from absolute ethanol (15 cm^3). Yield: 1.15 g as a pale yellow powder (92%). M.p. 170.8–171.2 °C; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 8.98 (d, $J = 5.6$ Hz, 2 H), 7.86–7.79 (m, 2 H), 7.38–7.15 (m, 30 H), 6.85–6.78 (m, 2 H) and 6.39 (m, 2 H); ^{13}C NMR (CDCl$_3$, 50.3 MHz) δ 158.4 (CH, $^3J_{PC} = 25.2$), 150.6 (C), 139.4 (C, $^1J_{PC} = 17.2$), 138.0 (C, $^1J_{PC} = 19.5$), 136.2 (C, $^2J_{PC} = 10.7$), 134.0 (CH, $^2J_{PC} = 20.2$), 133.7 (C), 132.7 (CH), 131.0 (CH), 130.4 (CH), 129.0 (CH), 128.7 (CH), 128.5 (CH, $^3J_{PC} = 7.3$), 128.1 (CH), 127.4 (CH, $^2J_{PC} = 4.2$ Hz), 124.9 (CH) and 118.2 (CH); ^{31}P NMR (CDCl$_3$, 80.95) δ −15.2. High-resolution mass spectrum: m/z 728.251 (calc. for C$_{50}$H$_{38}$N$_2$P$_2$: 728.251) (Found: C, 82.08; H, 5.43; N, 3.82; P, 8.35. Calc. for C$_{25}$H$_{19}$NP: C, 82.40; H, 5.26; N, 3.84; P, 8.50%).

[Pd$_2$L^{1}Cl$_2$Me$_2$] 1.

To L^1 (100 mg, 0.14 mmol) in thf (1.5 cm^3) was added [PdCl(Me)(cod)] (72.7 mg, 0.28 mmol, 2.0 equivalents). After stirring for 16 h at r.t., the yellow solution was concentrated under reduced pressure until a white precipitate was formed. Filtration and crystallisation from dichloromethane–pentane yielded pale yellow crystals, 95 mg (65%). ^{31}P NMR (CDCl$_3$): δ 35.4. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 9.16 (d, $J = 5.1$, 2 H), 8.86 (s, 2 H), 7.65–7.34 (m, 30 H), 7.21–7.15 (m, 2 H), 7.05–7.00 (m, 2 H) and 0.86 (d, $J = 2.9$ Hz, 6 H). ^{13}C NMR (CDCl$_3$, 75.4 MHz): δ 167.43 (CH), 155.89 (d, C, $^2J_{PC} = 15.9$), 140.90 (C), 134.32 (s, CH), 133.56 (d, CH, $^2J_{PC} = 13.4$), 133.40 (d, CH, $^2J_{PC} = 11.0$), 133.51 (C), 132.39 (CH), 131.97 (CH), 131.32 (CH), 131.06 (CH), 131.03 (CH), 130.45 (CH), 130.14 (CH), 129.53 (d, C, $^1J_{PC} = 40.3$ Hz), 129.01 (d, CH, $^3J_{PC} = 11.0$), 128.85 (d, CH, $^3J_{PC} = 11.0$), 128.81 (d, C, $^1J_{PC} = 37.9$), 128.35 (d, CH, $^2J_{PC} = 6.1$), 128.07 (C), 120.51 (d, CH, $^2J_{PC} = 7.3$ Hz) and −1.42 (CH$_3$). ES mass spectrum: m/z 1007 (M − Cl), 1039 (M − Cl + MeOH) and 486 (M − 2Cl) (Found: C, 59.29; H,

4.26; N, 2.64. Calc. for C$_{26}$H$_{22}$ClNPPd: C, 59.90; H, 4.25; N, 2.69%).

[Pd$_2$L^{1}Cl$_2${C(O)Me}$_2$] 2.

The complex [Pd$_2$L^{1}Cl$_2$Me$_2$] (25 mg, 0.02 mmol) in CDCl$_3$ was stirred for 15 min under 1 bar (10^5 Pa) CO at r.t. According to NMR data the conversion was nearly quantitative. IR (CDCl$_3$); ν_{CO} 1687 cm^{-1}. ^{31}P NMR (CDCl$_3$): δ 14.3. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 9.35 (d, $J = 7.8$ Hz, 2 H), 8.57 (s, 2 H), 7.76–7.42 (m, 30 H), 7.36–7.26 (m, 2 H), 7.22–7.09 (m, 2 H) and 2.25 (s, 6 H). ^{13}C NMR (CDCl$_3$, 75.4 MHz): δ 223.39 (d, C, $^2J_{PC} = 7.3$), 167.10 (CH), 155.03 (d, C, $^2J_{PC} = 15.9$), 140.83 (C), 134.37 (CH), 133.57 (d, CH, $^2J_{PC} = 13.4$), 133.17 (C), 133.11 (d, C, $^2J_{PC} = 13.4$), 132.60 (CH), 132.15 (CH), 131.31 (CH), 131.00 (CH), 130.39 (CH), 129.98 (CH), 129.66 (CH), 129.15 (d, CH, $^3J_{PC} = 11.0$), 129.01 (C), 128.91 (d, CH, $^3J_{PC} = 9.8$), 128.41 (CH), 128.36 (CH), 120.50 (d, CH, $^2J_{PC} = 7.3$) and 37.43 (d, CH$_3$, $^3J_{PC} = 21.8$ Hz); one C$_q$ was not resolved.

[Pd$_2$L^1(O$_2$CMe)$_2$] 3.

To L^1 (100 mg, 0.14 mmol) in CH$_2$Cl$_2$ (4 cm^3) was added Pd(O$_2$CMe)$_2$ (62 mg, 0.28 mmol, 2.0 equivalents) and the resulting clear dark red solution was stirred for 1.5 h at r.t. The product was precipitated as a yellow powder by adding the solution dropwise to pentane while stirring vigorously. The pentane was decanted and the powder crystallised from dichloromethane–pentane to yield orange-red crystals suitable for X-ray analysis. ^{31}P NMR (CDCl$_3$): δ 44.9. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 8.14–7.98 (m, 4 H), 7.90–7.76 (m, 6 H), 7.60–7.21 (m, 24 H), 7.20–7.00 (m, 4 H) and 1.92 (s, 6 H).

[Pt(H$_2$NC$_6$H$_4$PPh$_2$-2)$_2$]Cl$_2$ 4.

To L^1 (100 mg, 0.14 mmol) in CH$_2$Cl$_2$ (1 cm^3) was added [PtCl$_2$(MeCN)$_2$] (49 mg, 0.14 mmol, 2.0 equivalents). The resulting yellow solution was stirred for 1 h at r.t. The solution was quickly filtered in the presence of air to remove undissolved material. Evaporation of the solvent and crystallisation from dichloromethane–pentane yielded pale yellow crystals. ^{31}P NMR (CDCl$_3$): δ 25.8 (s), 25.8 (d, $J_{PPt} = 3334$ Hz). ^{1}H NMR (CDCl$_3$, 200 MHz): δ 7.79 (dd, $J = 3.4$ Hz, 2 H), 7.46 (m, 2 H), 7.40–7.30 (m, 14 H) and 7.26–7.11 (m, 14 H). ^{13}C NMR (CDCl$_3$, 50.3 MHz): δ 147.30 (C), 134.12 (CH), 133.13 (t, CH, $^2J_{PC} = 11.8$), 132.16 (CH), 132.06 (CH), 103.19 (d, C, $^1J_{PC} = 64.9$), 128.95 (t, CH, $^3J_{PC} = 11.8$), 128.34 (t, CH, $^3J_{PC} = 7.6$), 127.01 (t, CH, $^3J_{PC} = 14.1$) and 125.84 (d, C, $^1J_{PC} = 67.1$ Hz) (Found: C, 51.26; H, 4.02; N, 3.34. Calc. for C$_{36}$H$_{32}$Cl$_2$N$_2$P$_2$Pt·1.5CH$_2$Cl$_2$: C, 51.35; H, 3.85; N, 3.31%).

[PdL^2]Cl$_2$ 5.

To L^2 (100 mg, 0.14 mmol) in CH$_2$Cl$_2$ (2 cm^3) was added [PdCl$_2$(MeCN)$_2$] (35.6 mg, 0.14 mmol, 1.0 equivalent) and the clear red solution was stirred for 1.5 h at r.t. Crystallisation from dichloromethane–pentane afforded large red crystals suitable for X-ray analysis. Filtration and drying of the crystals *in vacuo* gave 82 mg of analytically pure [PdL^2]Cl$_2$ as an orange-red powder (66%). ^{31}P NMR (CDCl$_3$): δ 31.3. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.17 (d, $J = 11.5$, 2 H), 8.02 (br, 4 H), 7.76 (m, 2 H), 7.67 (t, $J = 7.6$, 4 H), 7.60–7.55 (m, 8 H), 7.45 (t, $J = 7.6$, 2 H), 7.35 (m, 2 H), 7.30 (m, 6 H), 6.94 (br, 2 H), 6.88 (m, 4 H) and 6.58 (d, $J = 7.7$ Hz, 2 H). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 168.96 (CH), 148.45 (C), 138.77 (CH), 135.60 (CH), 134.80 (CH), 133.63 (t, C, $^2J_{PC} = 26.1$), 133.48 (CH), 132.89 (C), 131.87 (CH), 131.68 (CH), 131.34 (C), 131.07 (CH), 129.56 (CH), 129.45 (CH), 129.37 (t, C, $^2J_{PC} = 11.8$), 129.12 (t, CH), 126.3 (d, CH, $^1J_{PC} = 52.5$), 124.52 (d, C, $^1J_{PC} = 53.6$), 123.66 (CH) and 123.30 (d, CH, $^1J_{PC} = 65.5$); one CH was not resolved due to overlap. ES mass spectrum: m/z 869 (M − Cl) and 417 (M − 2Cl).

[NiL^2][BF$_4$]$_2$ 6.

To a suspension of L^2 (100 mg, 0.14 mmol) in absolute EtOH (2 cm^3) was added dry NiCl$_2$ (15 mg, 0.14 mmol, 1.0 equivalent) and the resulting clear dark brown solution was warmed to reflux for 3 h. After evaporation of the

Table 4 Summary of crystal data for compounds **1**, **3** and **5**

	1	**3·4CH₂Cl₂**	**5·3.5CH₂Cl₂**
Formula	$(C_{26}H_{22}\text{-}ClNPPd)_2$	$(C_{27}H_{21}NO_2\text{-}PPd)_2$	$C_{50}H_{38}Cl_2N_2\text{-}P_2Pd$
M	1042.6	1397.45	906.1
Crystal system	Monoclinic	Trigonal	Triclinic
Space group	$C2/c$	$P3_121$	$P\bar{1}$
$a/Å$	17.789(5)	13.009(2)	15.1653(18)
$b/Å$	14.170(4)	13.009(2)	19.369(2)
$c/Å$	19.423(7)	29.706(6)	20.3003(17)
$\alpha/°$			100.755(10)
$\beta/°$	113.02(2)		99.828(8)
$\gamma/°$			111.470(10)
$U/Å^3$	4506(3)	4353.7(13)	5262.1(10)
$D_c/g\,cm^{-3}$	1.537	1.599	1.519
Z	4	3	4
$F(000)$	2104	2106	2436
Crystal size/mm	0.19 × 0.44 × 0.50	0.40 × 0.50 × 0.50	0.45 × 0.70 × 0.70
μ(Mo-Kα)/cm^{-1}	10.26	10.9	9.1
R^a	0.0471	0.0653	0.0673
$wR2^b$	0.1298	0.156	0.174
S	1.083	0.988	1.008

$^a R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|.$ $^b wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}.$

EtOH, CH_2Cl_2 (2 cm³) was added. To the resulting pale brown suspension was added $NaBF_4$ (60 mg, 0.55 mmol, 4 equivalents). After stirring for an additional 2 h at r.t., the reaction mixture was filtered over Celite to remove the excess of $NaBF_4$ and evaporation of the solvent gave a dark brown solid that was crystallised from dichloromethane–pentane to afford complex **6** as dark brown crystals: 63 mg (53%). ^{31}P NMR (CDCl₃): δ 31.3. ^1H NMR (CDCl₃, 200 MHz): δ 8.2–8.0 (br, 2 H), 7.9–7.3 (m, 28 H), 7.3–7.0 (br, 6 H) and 7.0–6.8 (br, 2 H). ES mass spectrum: m/z 873 ($M - BF_4$) and 394 ($M - 2BF_4$) (Found: C, 62.50; H, 4.28; N, 3.12. Calc. for $C_{50}H_{38}B_2F_8N_2NiP_2$: C, 62.48; H, 3.99; N, 2.91%).

Crystallography

X-Ray data for compound **1** were collected at 130 K on an Enraf-Nonius CAD-4F² diffractometer with Mo-Kα radiation ($\lambda = 0.710\,73$ Å). The orange crystal was quickly removed from the wall of the vessel and mounted on top of a glass fibre. The structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF.²⁸ The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined on F^2 with full-matrix least-squares procedures minimising the $Q = \Sigma_h[w(|F_o|^2 - k(F_c)^2|^2]$, where $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$, $P = [\max(F_o,0^2) + 2F_c^2]/3$. Reflections were stated observed if satisfying the $F^2 \geqslant 0$ criterion of observability. A subsequent Fourier-difference synthesis resulted in the location of all hydrogen atoms, the coordinates and isotropic thermal displacement parameters of which were refined. Final refinement on F^2 carried out by full-matrix least-squares techniques converged at $wR(F^2) = 0.1298$ for 4269 reflections with $F^2 \geqslant 0$ and $R(F) = 0.0471$ for 3921 reflections with $F \geqslant 4.0\sigma(F)$ and 359 parameters. A final Fourier-difference map showed residual densities between -1.14 and $+1.22(13)$ e Å^{-3} and one peak of 3.13 e Å^{-3} located near (1.86 Å) the Pd atom. No other significant peaks having chemical meaning were observed in the final Fourier-difference syntheses. Geometrical calculations were done with PLATON.²⁹

X-Ray data for compounds **3** and **5** were collected at 150 K on an Enraf-Nonius CAD4T diffractometer with rotating anode and graphite monochromated Mo-Kα radiation. Orange crystals were cut to size and covered by inert oil to avoid deterioration due to loss of solvent. A total of 12 388 reflections for **3** and 19 488 for **5** were scanned to θ_{max} of 26.0 and

25.4° respectively. Intensity data for **3** were corrected for absorption PLATON/DIFABS.²⁹ The structures of **3** and **5** were solved by Patterson methods (DIRDIF)²⁸ and direct methods (SHELXS 86³⁰), respectively. Least-squares refinement of F^2 was done with SHELXL 96.³¹ Hydrogen atoms were taken into account at calculated positions riding on their carrier atoms. Convergence was reached at $wR2 = 0.1560$ [5513 reflections, $R1 = 0.0653$ for 3793 reflections with $I > 2\sigma(I)$] and 0.1735 [18 889 reflections, $R1 = 0.0673$ for 11 771 reflections with $I > 2\sigma(I)$]. The final difference map did not show any significant residual features. Geometrical calculations and the ORTEP illustrations were done with PLATON.²⁹ The final results were checked for missed symmetry with the PLATON/MISSYM option and solvent-accessible voids with the PLATON/SOLV option.

CCDC reference number 186/754.

See http://www.rsc.org/suppdata/dt/1998/263/ for crystallographic files in .cif format.

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