FULL PAPER

Preparation and characterization of palladium and platinum complexes bearing 1,8-bis[(diphenylphosphino)methyl]naphthalene

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Reaction of MCl₂(cod) (M = Pd, Pt) with 1,8-bis[(diphenylphosphino)methyl]naphthalene (1,8-dpmn) gave MCl₂(1,8-dpmn) **1** (M = Pd), **2** (M = Pt), as confirmed by X-ray analyses. Complex **1** reacted with xylyl isocyanide **a** (XylNC) in the presence of NaPF₆ to give [Pd(1,8-dpmn)(XylNC)₂](PF₆)₂ **3a**. Reactions of dinuclear complexes $[M_2(RNC)_6](PF_6)_2$ (4: M = Pd, **5**: M = Pt; R = Xyl (**a**) or 2,4,6-Me₃C₆H₂ (**b**) (Mes)) with one or two equiv. of 1,8-dpmn gave $[M_2(1,8-dpmn)(RNC)_4](PF_6)_2$ **6** (M = Pd) and **7** (M = Pt), or $[M_2(1,8-dpmn)_2(RNC)_2](PF_6)_2$ **8** (M = Pd) and **9** (M = Pt). The structures of **6b**, **7b** and **8b** were confirmed by X-ray analyses. Reaction of $[Pd_2Cl_2(XylNC)_4]$ with two equiv. of 1,8-dpmn in the presence of NaPF₆ gave **8a**, whereas the reaction in the presence of NH₄PF₆ produced **10a** together with **7a**. It was confirmed by an X-ray analysis of **10a** that the crystal lattice is constructed by two types of cations (**3a** and two 2,2,6,6-tetramethyl-4-piperidonium) and four PF₆ anions. Photochemical reaction of **6a** or **8a** in CH₂Cl₂ led to cleavage of the Pd–Pd bond, giving [PdCl(XylNC)₃](PF₆) and [PdCl(1,8-dpmn)(XylNC)](PF₆).

Introduction

1,8-Bis(diphenylphosphino)naphthalene (1,8-dppn) and its derivatives are rigid in their manner of co-ordination because of the direct binding of the phosphorus atoms to the naphthalene rings, and form chelate complexes, $MCl_2(1,8-dppn)$ (M = Pd, Pt).^{1,2} 1,8-Bis[(diphenylphosphino)methyl]naphthalene (1,8-dpmn), formed by introduction of a methylene group between the naphthalene ring and phosphorus atom, is less rigid than 1,8-dppn and has the potential for co-ordination modes other than chelation.

We have studied the electrochemical or chemical preparation of di-, tri-, and poly-nuclear platinum and palladium complexes of isocyanides bearing various diphosphines³⁻¹¹ or triphosphine.¹² Controlled potential electrolysis of [Pt(diphos)-(RNC)₂]²⁺ at a mercury-pool electrode gave [Pt₂(diphos)₂- $(\text{RNC})_2^{2+}(\text{diphos} = \text{Ph}_2(\text{CH}_2)_n\text{PPh}_2(n = 2-4); \text{R} = 2,6-\text{Me}_2\text{C}_6\text{H}_3$ (Xyl), 2,4,6-Me₃C₆H₂ (Mes)), $[Pt_2(\mu$ -dppm)₂(RNC)₂]²⁺, $[Pt_3$ - $(\mu$ -dppm)₂(RNC)₄]²⁺ (A-frame) and [HgPt₆(dppb)₂(RNC)₈], depending on the coulometric conditions or diphosphines. One-electron reduction of $[Pd(diphos)(RNC)_2]^{2+}$ (diphos = $Ph_2(CH_2)_nPPh_2$, n = 2-4) at a platinum electrode formed the chelate dimers [Pd₂(diphos)₂(RNC)₂]^{2+,6} Chemical reduction of $[Pt(dpphex)(RNC)_2]^{2+}$ (dpphex = $Ph_2P(CH)_6PPh_2$) with Na/Hg also gave the Pt-Hg mixed cluster [Hg2Pt6(dpphex)3(RNC)6]. These complexes could be prepared by the substitution reactions of $[M_2(RNC)_4]^{2+}$ (M = Pd, Pt) or $[Pt_3(RNC)_8]^{2+}$ with appropriate diphosphines.

We report here the preparations and characterization of four-co-ordinate palladium and platinum complexes bearing 1,8-dpmn. The chemistry of metal complexes bearing 1,8-dpmn is limited to the synthesis of ruthenium complexes of 1,8-dpmn by Tin *et al.*¹³

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Results and discussion

Reactions of MCl₂(cod) (M = Pd, Pt) with 1,8-dpmn gave MCl₂(1,8-dpmn) (1: M = Pd, 2: M = Pt) in good yields. X-Ray analyses of 1 and 2 were undertaken. The perspective drawings of 1 and 2 with the atomic numbering schemes are given in Figs. 1 and 2. Selected bond lengths and angles are listed in Table 1. Complexes 1 and 2 are isomorphous. The molecules have *cis* structures with bite angles (P–M–P) of 93.5° for 1 and 94.4° for 2, compared with those of RuH₂(CO)(PPh₃)(1,8-dpmn) (95.96°)¹³ and dppb (Ph₂P(CH₂)₄PPh₂) complexes (94.51°).¹⁴ The dihedral angles between the MP₂Cl₂ plane and the naphthalene ring are 89.0° for 1 and 86.5° for 2, respectively. The MP₂Cl₂ plane is also perpendicular to two phenyl rings among four phenyl rings (86–88°). The average Pt–P bond length of 2.236 Å is shorter than the average Pd–P length of 2.263 Å,



Fig. 1 Structure of [PdCl₂(1,8-dpmn)] 1.

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Table 1 Selected bond lengths (Å) and angles (°) for cis-PdCl₂(1,8-dpmn) 1 and cis-PtCl₂(1,8-dpmn) 2





Fig. 2 Structure of [PtCl₂(1,8-dpmn)] 2.



3a (R = Xyl)

Scheme 1 Reaction of *cis*-PdCl₂(1,8-dpmn) 1 with xylyl isocyanide in the presence of NaPF₆. The PF₆ anions are omitted for clarity.

whereas the average M-Cl bond lengths for Pd and Pt complexes are identical.

Complex 1 was treated with xylyl isocyanide (XylNC) in the presence of NaPF₆ at room temperature to give [Pd(1,8dpmn)(XylNC)₂](PF₆)₂ **3a** in high yield (Scheme 1). The IR spectrum showed a characteristic band at 2213 cm⁻¹, corresponding to the terminal isocyanide groups.

When dimeric palladium or platinum complexes $[M_2(RNC)_6]$ -(PF₆)₂ (4: M = Pd, 5: M = Pt; a: R = Xyl, b: R = Mes) were



Fig. 3 The ${}^{31}P{}^{1}H$ NMR spectrum of 7a.

treated with an equiv. of 1,8-dpmn, yellow crystals formulated as $[M_2(1,8-dpmn)(RNC)_4](PF_6)_2$ (6: M = Pd; 7: M = Pt) were formed (Scheme 2). The IR spectra of 6 and 7 showed a strong band at *ca*. 2165 cm⁻¹ and a very weak band at *ca*. 2190 cm⁻¹, due to the N–C triple bond. The ¹H NMR spectra of 6 and 7 showed the presence of four kinds of isocyanide ligands, suggesting that all isocyanide ligands are nonequivalent. The ³¹P{¹H} NMR spectra of 6 showed a doublet around δ 21 and 13 with ²J_{PP'} = 54.5 Hz, respectively; the former is assignable to the phosphorus atom in a *trans*-position to the Pd atom and the latter to that in a *cis*-position, based on the chemical shift in the ³¹P{¹H} NMR spectrum of $[Pt_2(1,8-dpmn)(RNC)_4](PF_6)_2$ (*vide infra*).

The ³¹P{¹H} NMR spectrum of [Pt₂(1,8-dpmn)(XylNC)₄]- $(PF_6)_2$ 7a indicated two sets of resonances centered at δ 28.0 and 9.2, which are accompanied by satellite peaks due to ¹⁹⁵Pt (I =1/2) atom (Fig. 3). The observed spectrum is explicable as a combination of four isotopomers, P2Pt-Pt, P2Pt-¹⁹⁵Pt, P2¹⁹⁵Pt-Pt and P_2^{195} Pt-¹⁹⁵Pt (their ratios calculated from the natural abundance are 4:2:2:1). From the higher field set (A) centered at δ 9.2, the values of ${}^{1}J_{PPt}$, ${}^{2}J_{PPt}$ and ${}^{2}J_{PP'}$ were estimated to be 3076, 53 and 25 Hz, respectively. From the lower field set (B) centered at δ 28.0, the values of ${}^{1}J_{P'Pt}$, ${}^{2}J_{P'Pt}$ and ${}^{2}J_{PP'}$ were estimated to be 2275, 440 and 25 Hz, respectively. From analogy to the ³¹P{¹H} NMR spectra of $[Pt_2(diphos)_2(RNC)_2](PF_6)_2$ bearing the chelate structure and comparison with the values of the ${}^{2}J_{PPt}$ coupling constants, the resonance A was assigned to the phosphorus atom occupying the position cis to the Pt-Pt bond and the resonance B, to the phosphorus atom in the trans position to the Pt-Pt bond. A similar pattern was observed in 7b.

X-Ray crystallographic analyses of **6b** and **7b** were undertaken. The perspective drawings of the complex cations of **6b** and **7b** with the atomic numbering schemes are given in Figs. 4 and 5. Some selected bond lengths and angles are listed in Table 2. The complex cations consist of two palladium or platinum atoms joined by a metal–metal σ -bond. The Pd(2) or Pt(2) atom



Scheme 2 Reaction of $[M_2(RNC)_4](PF_6)_2$ (M = Pd, Pt) with 1,8-dpmn. The PF₆ anions are omitted for clarity.



Fig. 4 Structure of $[Pd_2(1,8-dpmn)(MesNC)_4](PF_6)_2$ 6b. The PF₆ anions are omitted for clarity.



Fig. 5 Structure of $[Pt_2(1,8\text{-dpmn})(MesNC)_4](PF_6)_2$ 7b. The PF₆ anions are omitted for clarity.

is co-ordinated by two phosphorus atoms of a bidentate 1,8dpmn ligand, a terminal carbon atom of isocyanide and another Pd(1) or Pt(1) atom, which is surrounded by the terminal carbon atoms of three isocyanide ligands. The structures are in good agreement with the nonequivalence of isocyanide ligands in the ¹H NMR spectra.

A dihedral angle between the $[MP_2C]$ and $[MC_3]$ coordination planes is 99(1)° for **6b** and 83(1)° for **7b**, nearly perpendicular as observed in other dinuclear complexes, minimizing the repulsion between the ligands. Similar structures have been observed in the nonbridged dimer.

The naphthalene ring has a dihedral angle of 69(1)° for the Pd(2)P(1)P(2)C(31) plane compared to 108(1)° for the Pt(2)P(1)P(2)C(31) plane. The Pd(1)-Pd(2) (2.568(3) Å) and Pt(1)-Pt(2) (2.61(4) Å) bond lengths are significantly longer than those for isocyanide dimers without phosphine ligands, $\begin{array}{c} [Pd_2Cl_2({}^tBuNC)_4] \ (2.532(2) \ \text{\AA}), {}^{15} \ [Pd_2(MeNC)_6](PF_6)_2 \ (2.531(1) \ \text{\AA}), {}^{16-18} \ [Pd_2I_2(MeNC)_4] \ (2.533(1) \ \text{\AA}) {}^{19} \ \text{and} \ [Pt_2Cl_2(2,4{}^tBu_2{}^{-6-16} \ \text{H})_2(2,4{}^tBu_2{}^{-6-16} \ \text{H})_2(2,4{$ $MeC_6H_2NC)_4$] (2.532(2) Å).²⁰ The Pd(2)–P(1) bond length of 2.351(7) Å and Pt(2)-P(2) bond length of 2.39(4) Å in a transposition to the metal atom are longer than those found in another M-P bond in a cis-position, due to the strong transinfluence of the metal-metal bond. The P-M-P bite angles for both complexes are typical. The average M(2)-M(1)-C bond angles in the M(1)C₃ plane are 84° for both 6b and 7b and the M(1)-M(2)-C(31) angles in the $M(2)P_2C(31)$ plane are $72.8(10)^{\circ}$ for **6b** and $80(1)^{\circ}$ for **7b**. Each isocyanide ligand is bent toward another metal atom. The large inward bend of the latter depends on the steric bulk of the diphosphine. This trend has been noted in $[M_2(diphos)_2(RNC)_2](PF_6)_2$ (M = Pd,⁹ Pt¹⁰). The M-C-N and C-N-C bond angles, except Pt(1)-C(1)-N(1) $(165(4)^{\circ})$, C(1)–N(1)–C(2) $(166(4)^{\circ})$ and C(11)–N(2)–C(12) (167(4)°), are linear (171–179°).

When the reactions between $[M_2(RNC)_8](PF_6)_2$ and 1,8dpmn were carried out in a 1 : 2 molar ratio, further substitution reactions occurred to form $[M_2(1,8\text{-dpmn})_2(RNC)_2](PF_6)_2$ (8: M = Pd; a: R = Xyl; b: R = Mes. 9: M = Pt; a: R = Xyl; b: R = Mes) (Scheme 2). The IR spectra showed the band due to the terminal isocyanide groups at *ca*. 2130 cm⁻¹. It is reasonable, given the high electron donation ability of diphosphines, that the v(N=C) frequency is shifted to *ca*. 30 cm⁻¹ lower energy than for the monochelate complexes 6 and 7. The ¹H NMR spectra of 8 and 9 showed the presence of only one type of isocyanide ligand.

The ³¹P{¹H} NMR spectra of **8** showed two sets of resonances at δ *ca.* 9.0 and 20.0. The ³¹P{¹H} NMR spectrum of **8b** has been satisfactorily simulated using a computer analysis based on a AA'XX' spin system. The observed and calculated ³¹P{¹H} NMR spectrum for **8b** is depicted in Fig. 6, but attempts to simulate the spectrum **8a** were unsuccessful due to spectral overlapping. Analogously, the analyses of the ³¹P{¹H} NMR spectra of **9** were unsuccessful because of the very complicated patterns.

A structure of the complex cation of **8b** with the atomic numbering scheme is given in Fig. 7. Selected bond lengths and angles are listed in Table 3. The molecule has a crystallographically imposed inversion center in the middle of the $Pd \cdots Pd^*$ vector. The complex cation consists of two palladium atoms joined by a Pd–Pd σ -bond. Each palladium atom is surrounded by two phosphorus atoms from the bidentate 1,8-dpmn ligand, a terminal carbon atom from the isocyanide, and another palladium atom in a nearly planar array. The dihedral angle between two [PdP₂C] co-ordination planes is 79.8°, being smaller by 6° than those of [Pd₂(MesNC)₂(dppp)₂](PF₆)₂ (86°)⁹ and [Pt₂(MesNC)₂(dppp)₂](PF₆)₂ (86°).

The Pd-Pd bond length of 2.670(3) Å is significantly longer

Table 2 Selected bond lengths (Å) and angles (°) for $[Pd_2(1,8-dpmn)(MesNC)_4](PF_6)_2 \cdot (CH_3)_2 CO$ **6b** $\cdot (CH_3)_2 CO$ and $[Pt_2(1,8-dpmn)(MesNC)_4](PF_6)_2 \cdot (CH_3)_2 CO$ **7b**

(a) [Pd ₂ (1,8-dpmn)(Me	sNC) ₄](PF ₆) ₂ ·(C	CH ₃) ₂ CO 6b ·(CH ₃) ₂ CO			
Pd(1)-Pd(2)	2,568(3)	Pd(1)-C(1)	2.07(3)	Pd(1)-C(11)	2.02(2)
Pd(1)-C(21)	1.99(2)	Pd(2) - P(1)	2.351(7)	Pd(2) - P(2)	2.291(8)
Pd(2)-C(31)	1.85(3)	C(1) = N(1)	1.15(3)	C(11) - N(2)	1.12(2)
C(21) - N(3)	1.12(2)	C(31) = N(4)	1.22(3)		(-)
Pd(2)-Pd(1)-C(1)	178.5(6)	Pd(2)-Pd(1)-C(11)	83.6(7)	Pd(2)-Pd(1)-C(21)	84.4(7)
C(1) - Pd(1) - C(11)	94.9(10)	C(1) - Pd(1) - C(21)	97.1(9)	C(11) - Pd(1) - C(21)	167(1)
Pd(1) - Pd(2) - P(1)	171.5(2)	Pd(1) - Pd(2) - P(2)	93.8(2)	Pd(1) - Pd(2) - C(31)	72.8(10)
P(1) - Pd(2) - P(2)	93.2(3)	P(1) - Pd(2) - C(31)	101(1)	P(2) - Pd(2) - C(31)	163.1(9)
Pd(1)-C(1)-N(1)	176(2)	C(1)-N(1)-C(2)	179(2)	Pd(1)-C(11)-N(2)	170(2)
C(11) - N(2) - C(12)	172(3)	Pd(1)-C(21)-N(3)	178(2)	C(21) - N(3) - C(22)	175(2)
Pd(2) - C(31) - N(4)	171(2)	C(31) - N(4) - C(32)	170(2)	P(1)-C(65)-C(66)	109(1)
P(2) - C(76) - C(74)	106(1)				
(b) [Pt ₂ (1,8-dpmn)(Mes	sNC) ₄](PF ₆) ₂ 7b				
Pt(1)-Pt(2)	2.61(4)	Pt(1)-C(1)	1.97(6)	Pt(1)-C(11)	1.83(3)
Pt(1) - C(21)	1.99(3)	Pt(2) - P(1)	2.24(4)	Pt(2)-P(2)	2.39(4)
Pt(2) - C(31)	2.03(5)	C(1) = N(1)	1.08(7)	C(11) - N(2)	1.22(3)
C(21) - N(3)	1.13(3)	C(31) - N(4)	1.17(5)		
			~ /		
Pt(2)-Pt(1)-C(1)	176(1)	Pt(2)-Pt(1)-C(11)	84(1)	Pt(2)-Pt(1)-C(21)	84(1)
C(1) - Pt(1) - C(11)	93(1)	C(1) - Pt(1) - C(21)	97(1)	C(11) - Pt(1) - C(21)	167(2)
Pt(1)Pt(2)-P(1)	94(1)	Pt(1)-Pt(2)-P(2)	171(1)	Pt(1) - Pt(2) - C(31)	80(1)
P(1) - Pt(2) - P(2)	93.3(10)	P(1) - Pt(2) - C(31)	168.7(8)	P(2) - Pt(2) - C(31)	92(1)
Pt(1)-C(1)-N(1)	165(4)	C(1)-N(1)-C(2)	166(4)	Pt(1)-C(11)-N(2)	175(2)
C(11) - N(2) - C(12)	167(4)	Pt(1)-C(21)-N(3)	175(4)	C(21)-N(3)-C(22)	171(3)
Pt(1)-C(31)-N(4)	173(2)	C(31) - N(4) - C(32)	172(4)	P(1)-C(65)-C(67)	112(2)
P(2)-C(66)-C(74)	106(2)		. /		

Table 3 Selected bond lengths (Å) and angles (°) for $[Pd_2(1,8-dpmn)_2(MesNC)_2](PF_4)_2 \cdot (CH_3)_2 \cdot (CH_3)_3 \cdot (CH_$

Pd(1)–Pd(2) Pd(1)–C(1)	2.670(3) 1.95(2)	Pd(1)–P(1) C(1)–N(1)	2.330(5) 1.18(2)	Pd(1)–P(2)	2.387(5)	
Pd(1)*–Pd(1)–P(1) P(1)–Pd(1)–P(2) Pd(1)–C(1)–N(1) P(2)–C(111)–C(101)	103.7(1) 91.4(2) 167(1) 106(1)	Pd(1)-Pd(1)-P(2) P(1)-Pd(1)-C(1) C(1)-N(1)-C(11)	164.6(1) 171.2(5) 174(2)	Pd(1)*-Pd(1)-C(1) P(2)-Pd(1)-C(1) P(1)-C(112)-C(109)	72.4(5) 93.0(5) 109(1)	



C18 C19 C54 053 C55 C42 C56 CI Pd1 C10 C10) C102 C112 C103) C104 C109

Fig. 6 (a) Observed and (b) calculated $^{31}P\{^1H\}$ NMR spectrum for $[Pd_2(1,8\text{-}dpmn)_2(MesNC)_2](PF_6)_2$ 8b.

than those in the bis-diphosphine complexes, $[Pd_2(MesNC)_2-(dppp)_2](PF_6)_2 (2.617(2) Å)^9$ and $[Pd_2(XyINC)_2(dppen)_2](PF_6)_2$ (dppen = Ph₂PCH=CHPPh₂) (2.602(1) Å)⁹ and $[Pd_2(XyINC)_2-(dppf)_2](PF_6)_2$ (dppf = 1,1'-bis(diphenylphosphino)ferrocene (2.602(1) Å),²¹ probably due to minimization of the steric repulsion between the naphthalene ring and the isocyanide connected to another palladium atom. The average Pd–Pd–P_{ax}

Fig. 7 Structure of $[Pd_2(1,8-dpmn)_2(MesNC)_2](PF_6)_2$ 8b. The PF₆ anions are omitted for clarity.

angle is 165.3°, comparable to that in $[Pd_2(XyINC)_2(dppf)_2]-(PF_6)_2 (163.75^\circ).$

The P(1)–Pd(1)–P(2) bite angle of 91.4(2)° is narrower than that of **6b** (93.2(3)°). The Pd(1)*–Pd(1)–C(1) angle of 72.4(5)° is similar to the corresponding angles for **6b** and **7b**. A characteristic feature is that the Pd(1)*–Pd(1)–P(1) angle of 103.7(1)° is wider by *ca*. 10° than those of the mono-substituted diphosphine complexes **6b** and **7b**, minimizing the repulsive

 $\label{eq:table_$

Pd(1) - P(1)	2.312(7)	Pd(2)–P(2)	2.305(8)	Pd(1)–C(37)	1.89(3)
Pd(1)–C(46)	1.96(3)	C(37)–N(1)	1.15(3)	C(46)–N(2)	1.15(3)
P(1)–Pd(1)–P(2)	93.3(3)	P(1)-Pd(1)-C(37)	171.2(9)	P(1)–Pd(1)–C(46)	88.0(7)
P(2)-Pd(1)-C(37)	91.1(9)	P(2)-Pd(1)-C(46)	172.4(8)	C(37) - Pd(1) - C(46)	86(1)
Pd(1)-C(37)-N(1)	175(2)	C(37)-N(1)-C(38)	169(2)	Pd(2)-C(46)-N(2)	176(2)
C(36) - N(2) - C(47)	178(2)	P(1)-C(11)-C(1)	115(1)	P(2)-C(24)-C(9)	110(1)
[2,2,6,6-Tetramethyl-4	4-piperidonium]				
N(3)-C(57)	1.49(4)	N(3)-C(60)	1.51(4)	C(55)–O(1)	1.29(4)
N(4)-C(66)	1.48(3)	N(4)-C(69)	1.52(4)	C(64) - O(2)	1.11(3)



Scheme 3 Reaction of $[Pd_2Cl_2(Xy|NC)_4]$ with 1,8-dpmn in the presence of NH_4PF_6 or $NaPF_6$ (L = Xy|NC). The PF₆ anions are omitted for clarity.

interaction with another 1,8-dpmn ligand. The structure of platinum complex **9** is considered to be similar to that of **8**.

When two equiv. of 1,8-dpmn was added to a CH_2Cl_2 solution of trinuclear complex $[Pd_3(XyINC)_8](PF_6)_2$ at room temperature, the reaction solution changed rapidly from yellow to violet and finally to yellow. This color change suggested the occurrence of a substitution reaction with 1,8-dpmn but attempts to isolate the violet species were unsuccessful because the change proceeded very quickly, suggesting that a trinuclear complex bearing diphosphine is very unstable. This trend has also been observed in the reaction of $[Pd_3(XyINC)_8](PF_6)_2$ with the bulky phosphine, $[2,6-(MeO)_2C_6H_3)]_3P^{22}$

Reactions of $[Pd_2Cl_2(XyINC)_4]$ with 1,8-dpmn in the presence of $NaPF_6$ or NH_4PF_6

When the neutral dinuclear complex $[Pd_2Cl_2(XyINC)_4]$, was treated in acetone, with two equiv. of 1,8-dpmn in the presence of excess NaPF₆, **8a** was obtained. However on treatment with an excess of NH₄PF₆, two complexes, **8a** and **10a** formulated as $[{Pd(1,8-dpmn)(XyINC)_2} {HN(CH_2)_2(CMe_2)_2CO}_2](PF_6)_4$, were formed (Scheme 3).

It was confirmed by X-ray analysis that **10a** consists of two kinds of cations, $[Pd(1,8-dpmn)(XyINC)_2]^{2+}$ and two 2,2,6,6-tetramethyl-4-piperidonium, and four PF₆ anions (Fig. 8 and Table 4). It is very rare that two kinds of cations are incorporated into the crystal lattice. The complex cation, $[Pd(1,8-dpmn)(XyINC)_2]^{2+}$ was surrounded by two phosphorus atoms of 1,8-dpmn and the terminal carbon atoms of two isocyanide ligands. The dihedral angle between the PdP₂C₂ and naphthalene planes is 104.3°, comparable with that for **7b**. The P(1)–Pd–P(2) bite angle is 93.3(3)°, comparable with those of **1** and **2**. The piperidonium cation adopted a typical chair-form. The bond lengths and angles fall within the usual values.

The IR spectrum of **10a** showed characteristic absorption bands at 3198, 3135, 2218 and 1725 cm⁻¹. The band at *ca.* 2200 cm⁻¹ is assigned to terminal isocyanide ligands. Two bands around 3160 cm⁻¹ and the bond at 1725 cm⁻¹ are due to the N–H and C=O groups, respectively. The presence of PF₆ anions was confirmed by a broad band at 847 cm⁻¹. In the ¹H NMR spectrum, the methyl and methylene protons of the piperidonium cation and *o*-methyl protons of isocyanide appeared at δ 1.69, 2.87 and 1.99, respectively. Multiplets of the P–CH₂ protons appeared at δ *ca.* 4.63 and *ca.* 5.86. The ³¹P{¹H} NMR spectrum indicated a singlet at δ 30.3, in close agreement with that of **3a**. After several crystallizations of **10a 3a** and a piperidonium cation as a PF₆ salt could be isolated separately.



Fig. 8 Structures of two cations, $[Pd(1,8-dpmn)(Xy|NC)_2]^{2+}$ and 2,2,6,6-tetramethyl-4-piperidonium in **10a**. The PF₆ anions are omitted for clarity.

Preparation of complex **10a** consists of an initial formation of **8a**, accompanied by cleavage of the metal-metal bond and generation of NH_4Cl as shown in Scheme 4. This mechanism has also been observed in the reaction of $[Pd_2Cl_2(Xy|NC)_4]$ with tris(2,6-dimethoxyphenyl)phosphine (L) in the presence of NH_4PF_6 to give $[PdCl(L)(Xy|NC)_2](PF_6)$.²² Finally, complex **3a**



Scheme 4 A possible path for the formation of 10a. The PF_6 anions are omitted for clarity. L = XyINC; $P^{\circ}P = 1,8$ -dpmn.

was obtained by the reaction of [PdCl(1,8-dpmn)(XylNC)]-(PF₆) with xylyl isocyanide. In order to examine the origin of 2,2,6,6-tetramethyl-4-piperidonium, a mixture of NH₄PF₆ and acetone was treated at room temperature for 24 h and led to the formation of a PF₆ salt of 2,2,6,6-tetramethyl-4-piperidonium, [HN(CH₂)₂(CMe₂)₂CO](PF₆), in high yield, suggesting that the palladium complex is unnecessary for the formation of a piperidonium salt. No piperidonium derivative was obtained when the reaction was carried out for a short time. In fact, a short reaction gave only **8a**. The reaction consists of an amination of NH₃, generated by an equilibrium of NH₄PF₆, to a diol arising from the trimerization of acetone, accompanied by a ring closure (Scheme 4).

Photochemical reactions of dinuclear palladium complexes

In the UV-vis spectra of **6** and **8**, the lowest energy absorption band appeared at *ca.* 385 nm for **6** and *ca.* 460 nm for **8**, assigned to the $\sigma \rightarrow \sigma^*$ transition of the Pd–Pd bond. It is reasonable, given the high electron-donating ability of diphosphines, that the metal–metal bonds of **8** are weaker than those of **6**. This was traced back to the Pd–Pd bond lengths; the Pd–Pd length is 2.568 Å for **6b** and 2.670 Å for **8b**. The $\sigma \rightarrow \sigma^*$ transitions of [Pd₂(diphos)₂(RNC)₂](PF₆)₂ (diphos = Ph₂P(CH₂)_nPPh₂; n = 2-4), having a structure similar to **8**, have been observed in the range from 421 to 434 nm,⁹ suggesting that 1,8-dpmn is a stronger electron-donating ligand than diphosphines bearing methylene groups, such as dppe, dppp, *etc.* This observation is in agreement with the fact that the bond length of **8b** is longer than that found for [Pd₂{Ph₂P(CH₂)₃PPh₂}₂-(XylNC)₂](PF₆)₂.

When **6a** was irradiated in CH₂Cl₂, the solution changed from yellow to colorless. The $\sigma \rightarrow \sigma^*$ transition around 385 nm decreased and finally no appreciable absorption was observed in the region $\lambda > 380$ nm. This reaction was monitored spectroscopically, and the formation of two complexes, [PdCl(XylNC)₃](PF₆) and [PdCl(1,8-dpmn)(XylNC)](PF₆), was confirmed (Scheme 5). Photochemical reaction of **8a** also showed a similar color-change and cleaved a Pd–Pd bond to give [PdCl(1,8-dpmn)(XylNC)](PF₆). The bond-cleavage rate of **8a** is faster than that of **6a**.

Experimental

All reactions were carried out under a nitrogen atmosphere.



Scheme 5 Photochemical reactions of **6a** and **8a**. The PF_6 anions are omitted for clarity. $P^{\circ}P = 1,8$ -dpmn.

Isocyanides,²³ 1,8-bis(dichloromethyl)naphthalene,²⁴ [Pd₂Cl₂-(RNC)₄],²⁵ [Pd₂(RNC)₆](PF₆)₂,²⁰ [Pt₂(RNC)₆](PF₆)₂,²⁰ and [Pd₃(RNC)₈](PF₆)₂²⁰ were prepared according to the literature. Dichloromethane was distilled over CaH₂ and diethyl ether was distilled over LiAlH₄. The IR spectra were measured on an FT/IR-5300 instrument. The ¹H NMR spectra were measured at 250 MHz and ³¹P{¹H}-NMR spectra were measured at 101 MHz using 85% H₃PO₄ as an external reference.

Syntheses

Preparation of 1,8-bis[(diphenylphosphino)methyl]naphthalene. Triphenylphosphine (7.6 g, 29.0 mmol) and lithium (0.6 g, 86.5 mmol) in tetrahydrofuran (THF) (40 mL), were stirred for one day at room temperature, and lithium was removed by filtration. tert-Butyl chloride (3.4 mL, 31 mmol) in THF (10 mL) was added to the ice cooled solution which was then heated at reflux for 10 min. After cooling in an ice-bath, 1,8-[bis(dichloromethyl)]naphthalene (3.5 g, 15.6 mmol) in THF (40 mL) was added dropwise and the mixture was refluxed for 30 min. The solvent was removed and a mixture of H₂O (200 mL) and Et₂O (200 mL) was added to form white solids. The solids were filtered and washed with EtOH to give 1,8-dpmn (3.0 g, 37%). ¹H NMR (CDCl₃): δ 4.21 (d, PCH₂, 4H), 6.6–7.7 (c, napthalene, 26H). ${}^{31}P{}^{1}H$ NMR (CDCl₃): $\delta -11.4$ (s). Anal. calc. for C₃₆H₃₀P₂: C, 82.43; H, 5.78. Found: C, 82.62; H, 5.55%.

Preparation of $PdCl_2(1,8-dpmn) \cdot 1.5CH_2Cl_2 \cdot 1.1.5CH_2Cl_2$. To a solution of $PdCl_2(cod)$ (50 mg, 0.18 mmol) in CH_2Cl_2 (5 mL), 1,8-dpmn (96 mg, 0.18 mmol) in CH_2Cl_2 (10 mL) was added at room temperature. After stirring for 2 h, the mixture was filtered on a glass filter (G4) and the solvent was concentrated to *ca.* 3 mL and diethyl ether was added to give pale yellow crystals of 1·1.5CH₂Cl₂ (112 m, 77%). ¹H NMR (CDCl₃): δ 4.97 (d, $J_{PH} = 11.3$ Hz, 4H, CH₂), 5.27 (s, CH₂Cl₂), 7.02–7.93 (m, 26H, napthalene). ³¹P NMR (CDCl₃): δ 33.4. Anal. calc. for C₃₆H₃₀P₂Cl₂Pd·1.5CH₂Cl₂: C,54.31; H, 4.01. Found: C, 53.81; H, 4.27%.

Preparation of PtCl₂(1,8-dpmn)·3H₂O 2·3H₂O. To a solution of PtCl₂(cod) (59 mg, 0.16 mmol) in CH₂Cl₂ (5 mL), 1,8-dpmn (84 mg, 0.16 mmol) in CH₂Cl₂ (10 mL) was added at room temperature. After stirring for 2 h, the solvent was removed under reduced pressure and the residue was crystallized from CH₂Cl₂ and acetone to give white crystals of $2\cdot3H_2O$ (58 mg, 43%). Anal. calc. for C₃₆H₃₀P₂Cl₂Pt·3H₂O: C, 51.19; H, 4.30. Found: C, 50.56; H, 3.87%.

Preparation of [Pd(1,8-dpmn)(XyINC)₂](PF₆)₂ 3a. To a solution of PdCl₂(1,8-dpmn)·1.5CH₂Cl₂ (100 mg, 0.12 mmol) in CH₂Cl₂ (10 mL), XyINC (33 mg, 0.25 mmol) in CH₂Cl₂ (10 mL) and NH₄PF₆ (98 mg, 0.60 mmol) in acetone (10 mL) was added at room temperature. After stirring for 2 h, the solvent was removed to dryness and the residue was extracted with CH₂Cl₂. Recystallization from CH₂Cl₂ and diethyl ether gave pale yellow crystals of **3a** (137 mg, 87%) (contained CH₂Cl₂ as a solvated molecule). IR (Nujol): 2213 (N≡C), 835 (PF₆) cm⁻¹. ¹H NMR(CD₃COCD₃): δ 1.97 (s, *o*-Me, 12H), 4.60 (center of an AB quartet, *J*_{HH} = 10.0 Hz, 4H, CH₂), 5.27 (s, CH₂Cl₂), 5.6–8.2. ³¹P NMR (CDCl₃): δ 30.1 (s), −143.4 (sep., *J*_{PF} = 707 Hz). Anal. Calc. for C₅₄H₄₈N₂P₄F₁₂Pd·1.5CH₂Cl₂: C, 50.86; H, 3.92; N, 2.13. Found: C, 50.44; H, 3.65; N, 1.99%.

Preparation of [Pd₂(1,8-dpmn)(XyINC)₄](PF₆)₂ 6a. To a solution of [Pd₂(XyINC)₆](PF₆)₂ (100 mg, 0.08 mmol) in CH₂Cl₂ (10 mL) was added 1,8-dpmn (43.6 mg, 0.08 mmol) in CH₂Cl₂ (5 mL) at room temperature. After stirring for 2 h, the solvent was removed to dryness and the residue was extracted with benzene. Recystallization of the residue from CH₂Cl₂ and diethyl ether gave yellow crystals of 6a (71 mg, 57%) (contained CH₂Cl₂ as a solvated molecule). IR (Nujol): 2187 (w), 2160 (st.) (N=C), 837 (PF₆) cm⁻¹. UV-vis (CH₂Cl₂): λ_{max} 385 nm. ¹H NMR (CD₃COCD₃): δ 2.11 (s, *o*-Me, 6H), 2.21 (s, *o*-Me, 6H), 2.30 (s, *o*-Me, 6H), 2.38 (s, Me, 6H), *ca.* 4.1, *ca.* 4.8, *ca.* 5.2, *ca.* 5.5 (b, CH₂, 1H), 6.8–7.8. ³¹P{¹H} NMR (CD₃COCD₃): δ 21.3 (d, ²J_{PP'} = 54.5 Hz), 13.4 (d, ²J_{PP'} = 54.5 Hz), -143.4 (sep., ¹J_{PF} = 710 Hz). Anal. calc. for C₇₂H₆₆N₄P₄F₁₂Pd₂·0.5CH₂Cl₂: C, 54.61; H, 4.24; N, 3.51. Found: C, 54.35; H, 4.21; N, 3.53%.

Preparation of [Pd₂(1,8-dpmn)(MesNC)₄](PF₆)₂ 6b. Yellow crystals (56%) of 6b, recrystallized from acetone and diethyl ether, were obtained from [Pd₂(MesNC)₆](PF₆)₂ and 1,8-dpmn, according to a procedure similar to that for 6a. IR (Nujol): 2189 (w), 2162 (st.) (N≡C), 837 (PF₆) cm⁻¹. UV-vis. (CH₂Cl₂): λ 385 nm. ¹H NMR (CD₃COCD₃): δ 2.02 (s, Me, 3H), 2.08 (s, Me, 6H), 2.15 (s, Me, 6H), 2.22 (s, Me, 9H), 2.3 (s, Me, 12H), 3.88–5.15 (m, CH₂, 4H), 5.6–8.2. ³¹P{¹H} NMR (CDCl₃): δ 21.2 (d, ²J_{PP'} = 54.5 Hz), 12.4 (d, ²J_{PP'} = 54.5 Hz), -143.4 (sep., ²J_{PF} = 710 Hz). Anal. calc. for C₇₆H₇₄N₄P₄F₁₂Pd₂·(CH₃)₂CO: C, 56.95; H, 4.84; N, 3.36. Found: C, 57.09; H, 4.81; N, 3.34%.

Preparation of [Pt₂(1,8-dpmn)(XyINC)₄](PF₆)₂ 7a. 1,8-Dpmn (20 mg, 0.038 mmol) was added to a solution of [Pt₂(XyINC)₆]-(PF₆)₂ (50 mg, 0.034 mmol) in acetone (10 mL mL) at room temperature and stirred for 2 h. The solvent was concentrated to *ca.* 3 mL and diethyl ether was extracted with benzene. Recrystallization of the residue from acetone and diethyl ether gave pale yellow crystals of 7a (38 mg, 65%). IR (Nujol): 2202 (w), 2164 (st) (N=C), 835 (PF₆) cm⁻¹. ¹H NMR (CD₃COCD₃): δ 2.13 (s, *o*-Me, 6H), 2.22 (s, *o*-Me, 6H), 2.24 (s, *o*-Me, 6H), 2.37

(s, *o*-Me, 6H), 4.38 (c, CH₂, 2H), 5.45 (c, CH₂, 2H), 6.8–7.9 (m, Ph, 54H). ³¹P{¹H} NMR(CD₃COCD₃): δ 9.17 (¹J_{P'Pt} = 3076 Hz, ²J_{P'Pt} = 53 Hz, ²J_{PP'} = 25 Hz), 28.0 (¹J_{P'Pt} = 2275 Hz, ²J_{P'Pt} = 440 Hz, ²J_{PP'} = 25 Hz), -143.4 (sep. ¹J_{PF} = 710 Hz). Anal. calc. for C₇₂H₆₆N₄P₄F₁₂Pt₂: C, 50.02; H, 3.85; N, 3.24. Found: C, 50.90; H, 4.00; N, 3.09%.

Preparation of [Pt₂(1,8-dpmn)(MesNC)₄](PF₆)₂ 7b. Pale yellow crystals of 7b (72%) were prepared from the reaction of [Pt₂(MesNC)₆](PF₆)₂ with 1,8-dpmn. IR (Nujol): 2206 (w), 2170 (st) (N≡C), 835 (PF₆) cm⁻¹. ¹H NMR (CDCl₃): δ 1.79, 1.99, 2.02, 2.19 (s, *o*-Me, 24H), 2.17, 2.26, 2.30, 2.43 (s, *p*-Me, 12H), 4.20, 4.93 (c, PCH₂, 4H), 6.0–7.7 (m, Ph, 34H). ³¹P{¹H} NMR (CDCl₃): δ 8.90 (¹*J*_{PFt} = 3070 Hz, ²*J*_{PFt} = 50 Hz, ²*J*_{PF'} = 25 Hz), 26.8 (¹*J*_{P'Ft} = 2272 Hz, ²*J*_{P'Ft} = 450 Hz, ²*J*_{P'F} = 25 Hz), −143.6 (¹*J*_{PF} = 707 Hz). Anal. calc. for C₇₆H₇₄N₄P₄F₁₂Pt₂: C, 51.13; H, 4.18; N, 3.14. Found: C, 52.10; H, 4.43; N, 2.99%.

Preparation of [Pd₂(1,8-dpmn)₂(MesNC)₂](PF₆)₂ 8b. To a solution of 4b (86 mg, 0.06 mmol) in acetone (10 mL) was added 1,8-dpmn (72 mg, 0.13 mmol) at room temperature. After stirring for 2 h, the solvent was removed *in vacuo* and the residue was extracted with acetone. Reddish orange complex 8b (30 mg, 55%) was isolated by recrystallization from acetone-diethyl ether. IR (Nujol): 2133 (N≡C), 838 (PF₆) cm⁻¹. UV-vis (CH₂Cl₂): λ_{max} 460 nm. ¹H NMR (CDCl₃): δ 1.72 (s, *o*-Me, 12H), 2.44 (s, *p*-Me, 6H), 4.20, 3.8–5.9 (c, PCH₂, 8H), 6.6–8.1 (m, Ph, 56H). ³¹P₁¹H} NMR (CDCl₃): δ 22.16 (²J_{P1P2} = -75 Hz, ²J_{P1P2} = 60 Hz, ³J_{P1P1} = 264 Hz), 9.09 (¹J_{P2P1} = -75 Hz, ³J_{P2P2} = 17 Hz, ³J_{P2P1} = 60 Hz), −143.6 (¹J_{PF} = 707 Hz). Anal. calc. for C₉₂H₈₂N₂P₆F₁₂Pd₂: C, 59.98; H, 4.49; N, 1.52. Found: C, 59.65; H, 4.18; N, 1.43%.

Preparation of [Pd₂(1,8-dpmn)₂(XyINC)₂](PF₆)₂ 8a. Reddish orange complex 8a (55%) was prepared from the reaction of [Pd₂(XyINC)₆](PF₆)₂ with 1,8-dpmn according to a similar procedure to 8b. IR (Nujol): 2132 (N≡C), 841 (PF₆) cm⁻¹. UV-vis (CH₂Cl₂): λ_{max} 463 nm. ¹H NMR (CD₃COCD₃): δ 1.79 (s, *o*-Me, 12H), 3.74–5.90 (b, CH₂, 8H), 6.2–8.0. ³¹P{¹H} NMR (CD₃COCD₃): δ *ca.* 19.0 (c), *ca.* 9.0 (c), -144.4 (sep. ¹J_{PF} = 710 Hz). Anal. calc. for C₉₀H₇₈N₂P₆F₁₂Pd₂·0.5CH₂Cl₂: C, 58.54; H, 4.29; N, 1.15. Found: C, 58.68; H, 4.29; N, 1.31%.

Preparation of $[Pt_2(1,8-dpmn)_2(XyINC)_2](PF_6)_2$ **9a.** To a solution of **5a** (50 mg, 0.034 mmol) in acetone (10 mL) was added 1,8-dpmn (37 mg, 0.07 mmol) at room temperature. After stirring for 2 h, the solvent was removed *in vacuo* and the residue was extracted with acetone. Recrystallization from acetone–diethyl ether gave yellow crystals of **9a** (17 mg, 25%). IR (Nujol): 2152 (N=C), 841 (PF_6) cm⁻¹. UV-vis (CH₂Cl₂): λ_{max} 461 nm. ¹H NMR (CD₃COCD₃): δ 1.80 (s, *o*-Me, 12H), 4.2–5.90 (b, CH₂, 8H), 6.2–8.0. Anal. calc. for C₉₀H₇₈N₂P₆F₁₂Pt₂: C, 54.28; H, 3.95; N, 1.41. Found: C, 54.58; H, 4.00; N, 1.66%.

Preparation of $[Pt_2(1,8-dpmn)_2(MesNC)_2](PF_6)_2$ **9b.** Pale yellow crystals (49%) of **9a** recrystallized from acetone and diethyl ether, were obtained from $[Pd_2(MesNC)_6](PF_6)_2$ and 1,8-dpmn, according to a similar procedure to **9b**. IR (Nujol): 2154 (N=C), 837 (PF_6) cm⁻¹. UV-vis (CH_2Cl_2): λ 463 nm. ¹H NMR (CD_3COCD_3): δ 1.77 (s, *o*-Me, 12H), 2.86 (s, *p*-Me, 6H), 4.2–5.90 (b, CH_2, 8H), 6.2–8.0. Anal. calc. for $C_{92}H_{82}N_2P_6F_{12}Pt_2$: C, 54.71; H, 4.09; N, 1.39. Found: C, 54.38; H, 4.20; N, 1.55%.

Preparation of [{Pd(1,8-dpmn)(XyINC)₂)}{HN(CH₂)₂-(CMe₂)₂CO}₂](PF₆)₄ 10a. To a solution of [Pd₂Cl₂(XyINC)₄] (48 mg, 0.059 mmol) in acetone (10 mL) was added 1,8-dpmn (72 mg, 0.13 mmol) and NH₄PF₆ (100 mg, 0.61 mmol) at room temperature and the mixture was stirred for 24 h. After the solvent was removed *in vacuo*, the residue was extracted with CH₂Cl₂. Recrystallization from CH₂Cl₂ and diethyl ether gave

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	$1 \cdot CH_2 CI_2$	2.CH ₂ Cl ₂ ,	6b ·(CH ₃) ₂ CO	Tb	8b·2(CH ₃) ₂ CO	10a
Formula Molecular weight	$C_{37}H_{32}P_2Cl_4Pd$ 786.8	C ₃₇ H ₃₂ P ₂ Cl ₄ Pt 875.5	$C_{79}H_{80}N_4OF_{12}P_4Pd_2$ 1666.2	$C_{76}H_{74}N_4F_{12}P_4Pt_2$ 1785.5	$C_{98}H_{94}N_2F_{12}O_2P_6Pd_2$ 1958.46	C ₇₂ H ₈₄ N ₄ O ₂ P ₆ F ₂₄ Pd 1785.69
Color	Pale yellow	White	Yellow	Pale yellow	Orange	Pale yellow
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$ (no. 14)	$P2_{1}/n$ (no. 14)	$P2_1$ (no. 4)	$P2_1$ (no. 4)	<i>C</i> 2/ <i>c</i> (no. 15)	$P\overline{1}$ (no. 2)
aĨÅ	14 414(2)	14.45(1)	10.919(6)	11.06(5)	27.18(2)	15.660(4)
b/Å	9.871(2)	9.898(2)	25.859(9)	25.823(10)	18.653(3)	23.72(1)
$c/{ m \AA}$	24.796(4)	24.74(1)	14.502(9)	14.292(10)	25.17(2)	11.793(4)
a°						101.72(4)
β_{γ^0}	101.87(1)	101.72(6)	108.13(5)	108.1(1)	124.42(5)	91.57(3) 105 34(3)
wA^3	3453(1)	3464(6)	3891(3)	3881(12)	10527(10)	4120(2)
Ζ	4	4	0	0	4	2
$D_{ m call}/{ m gcm^{-3}}$	1.513	1.679	1.422	1.53	1.236	1.439
μ/cm^{-1}	9.59	45.2	6.19	37.4	4.89	4.41
Scan rate/° min ⁻¹	16	16	8	8	16	16
No. of reflections (< 2θ)	6456 (<50°)	6488 (<50°)	7413 (<50°)	13652 (<50°)	6998 (<45°)	13161 (<50°)
No. of data $(I > 3.0\sigma(I))$	$2162 (I > 3.0\sigma(I))$	$1842(I > 3.0\sigma(I))$	$7343 (I > -10.0\sigma(I))$	$3887 (I > 2.0\sigma(I))$	$3018 (I > 3.0\sigma(I))$	$3198(I > 2.5\sigma(I))$
No. of variables	382	212	895	411	520	482
$R; R_w$	$0.071; 0.075^a$	$0.062; 0.061^{a}$	$0.233; 0.231^b$	$0.120: 0.167^{b}$	$0.072; 0.086^{a}$	$0.108; 0.128^a$
RI			$0.101 \text{ (for 3493 refs)}^{b}$	$0.078 \text{ (for } 3887 \text{ refs})^b$		
${ m GOF}^c$	1.73	1.23	1.34	1.40	2.68	1.81
^{<i>a</i>} $R = \Sigma F_0 - F_0 /\Sigma F_0 $, $R_w = \Sigma w(F_0 - F_0)$ $N_0 = \text{number of data}$, $N_v = \text{number of variably}$	${}^{2}/\Sigma w F_{o} ^{2}]^{1/2}$ ($w = 1/\sigma^{2}(F_{o})$. sles.	$R = \Sigma (F_{\rm o}^2 - F_{\rm c}^2) / \Sigma F_{\rm o}^2,$	$R_{\rm w} = [\Sigma w (F_{\rm o}^2 - F_{\rm c}^2)^2 / \Sigma w (F_{\rm o}^2)$	$2^{-1} L^{-2}, R^{-1} = \Sigma \ F_{ m o}\ - \ F_{ m o}\ /\Sigma \ F_{ m o}\ $	for $I > 2.0\sigma(I)$ data. ^e GOF	$= [\Sigma w(F_o - F_c)^2 / \Sigma (N_o - N_v)]^{1/2}$, where

1780

yellow crystals (135 mg, 64.1%) of **10a**. IR (Nujol): 3198, 3135 (N–H), 2218 (N=C), 1725 (C=O), 847 (PF₆) cm⁻¹. ¹H NMR (CDCl₃): δ 1.69 (s, Me, 24H), 1.99 (s, *o*-Me, 12H), 2.87 (s, CH₂, 8H), 4.63, 5.86 (c, PCH₂, 4H), 6.7–8.2 (m, Ph, 32H). ³¹P NMR (CDCl₃): δ 30.3 (s), –143.1 (sep., PF₆). Anal. calc. for C₇₂H₈₄-N₄O₂P₆F₂₄Pd: C, 48.43; H, 4.74; N, 3.14. Found: C, 48.11; H, 4.55; N, 2.97%.

Each cationic compound, $[Pd(XyINC)_2(1,8-dpmn)](PF_6)_2$ and $[HN(CH_2)_2(CMe_2)_2CO](PF_6)$ can be separately isolated by several recrystallizations.

Photochemical reaction of [Pd₂(1,8-dpmn)₂(XylNC)₂](PF₆)₂ 8a in CH₂Cl₂

A solution of **8a** (50 mg, 0.028 mmol) in CH₂Cl₂ (10 mL) was irradiated with sunlight. After 3 h, the solvent was removed and the residue was crystallized from CH₂Cl₂ and diethyl ether to give yellow crystals of [PdCl(1,8-dpmn)(XylNC)](PF₆) (45 mg, 85%). IR (Nujol): 2001 (N≡C), 845 (PF₆) cm⁻¹. ¹H NMR (CDCl₃): δ 1.83 (s, *o*-Me, 6H), 3.82, 5.40 (c, PCH₂, 4H), 6.2–8.0 (m, Ph, 28H). ³¹P NMR (CDCl₃): δ 32.1 (d, J_{PP} = 35.4 Hz), 32.6 (d, J_{PP} = 35.4 Hz), -143.1 (sep., J_{PF} = 710 Hz, PF₆). Anal. calc. for C₄₅H₃₉NClP₃F₆Pd: C, 57.34; H, 4.17; N, 1.49. Found: C, 57.26; H, 3.95; N, 1.35%.

Data collection

Complexes, 1·CH₂Cl₂, 2·CH₂Cl₂ 6b·(CH₃)₂CO, 7b, 8b·2(CH₃)₂-CO and 10a, were recrystallized from CH₂Cl₂-diethyl ether. Cell constants were determined from 20-25 reflections on a Rigaku four-circle automated diffractometer AFC5S. The crystal parameters along with data collections are summarized in Table 5. Data collection was carried out by a Rigaku AFC5S refractometer at 27 °C. Intensities were measured by the $2\theta - \omega$ scan method using Mo-Ka radiation ($\lambda = 0.71069$ Å). Throughout the data collection the intensities of three standard reflections were measured every 200 reflections as a check of the stability of the crystals and no decay was observed. Intensities were corrected for Lorentz and polarization effects. The absorption correction was made with the ψ scan method. Atomic scattering factors were taken from Cromer and Waber, the usual tabulation.²⁶ Anomalous dispersion effects were included in F_{calc} ;²⁷ the values of $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.²⁸ All calculations were performed using the TEXSAN crystallographic software package.29

Determination of the structures. All structures except 1·CH₂Cl₂, 2·CH₂Cl₂ and 8b·2(CH₃)₂CO (solved by Direct methods) were solved by Patterson methods (DIRDIF92, PATTY).³⁰ The positions of all nonhydrogen atoms except nonhydrogen atoms from the CH2Cl2 solvent for 1·CH2Cl2 and six F atoms for 8b·2(CH₃)₂CO, were refined with anisotropic thermal parameters by using full-matrix least-squares methods. The positions of all nonhydrogen atoms except the Pt, Cl and P atoms for 2, and the Pt and P atoms for 7b were refined with isotropic thermal parameters by using full-matrix leastsquares methods. The positions of all nonhydrogen atoms of 6b·(CH₃)₂CO were refined with anisotropic thermal parameters by using full-matrix least-squares methods. The positions of the Pd, P and two N atoms for 10a were refined anisotropically and other nonhydrogen atoms were refined isotropically. All hydrogen atoms were calculated at the ideal positions with the C–H distance of 0.95 Å and not refined.

CCDC reference numbers 157470, 157471 and 161769–161772.

See http://www.rsc.org/suppdata/dt/b1/b100860i/ for crystallographic data for $6b \cdot (CH_3)_2 CO$ (157470) and 7b (157471) in CIF or other electronic format.

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