Doubly Cyclopalladated Complexes of *N,N,N′,N′*-Tetraethylbenzene-1,3-bis(methylamine)†

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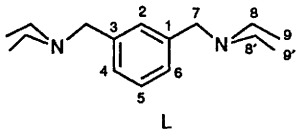
N,N,N′,N′-Tetraethylbenzene-1,3-bis(methylamine) (L) undergoes regiospecific double cyclopalladation with $Li_2[PdCl_4]$ at the 4,6 positions of the benzene ring to produce the chloro-bridged polymeric complex $[Pd_2(L - 2H)Cl_2]$. Reactions of this complex with PPh_3, methylpyridines, acetylacetone, ethylacetoacetate, monothiodibenzoylmethane and trifluoro(thenoyl)acetone have been studied and the products characterized by ^1H and ^{13}C NMR spectroscopy. Treatment of $[Pd_2(L - 2H)(PPh_3)_2Cl_2]$ with $MeCO_2H$ and LiCl produces at room temperature the nitrogen-protonated species $[Pd_2L(PPh_3)_2Cl_4]$, but *trans*-$[Pd_2(PPh_3)_2Cl_4]$ and the metal-free ligand (L) are formed at 80 °C. The complex $[Pd_2(L - 2H)Cl_2]$ undergoes exchange reaction with ligands capable of forming monocyclopalladated complexes. The crystal structure of $[Pd_2(L - 2H)(PPh_3)_2Cl_2]$ has been determined: monoclinic, space group *C*2/*c*, $a = 20.676(4)$, $b = 12.436(3)$, $c = 19.445(4)$ Å, $\beta = 104.29(3)°$ and $Z = 4$; refinement led to $R = 0.035$ and $R' = 0.043$ using 3533 unique reflections with $I > 2\sigma(I)$.

The chemistry of C⁻,N-chelated cyclopalladated compounds has received sustained attention[1,2] over the past two decades. The focus of attention has ranged from exploring substrates that may be subjected to cyclometallation reaction to the reactivities of these compounds and their applications in organic synthesis.[3–5]

Orthopalladated complexes constitute the major bulk of known palladocycles. Double cyclometallation occurring at two different phenyl rings of azobenzene,[6,7] benzalazines,[8] 4,6-diphenylpyrimidine[9] and 2-phenyl-4,6-bis(pyrazolylmethyl)-pyrimidine[10] have also been reported. However, whether two different sites of the same benzene ring can be involved in double cyclometallation reaction has so far received far less attention. Trofimenko[11] was the first to explore this possibility and briefly reported doubly orthopalladated compounds of *N,N,N′,N′*-tetraalkyl-*p*-(or -*m*)xylene-α,α′-diamines. We have recently made extensive studies[12] on the dipalladiobenzene derivatives of *N,N′*-dialkylbenzene-1,3-dicarbaldimines (L′) and have reported the structures of $[Pd_2(L' - 2H)(py)_4]Cl_2$[12a] and $[Pd_2(L' - 2H)(btac)_2]$[12c] [alkyl = ethyl (L′), py = pyridine, Hbtac = benzoyltrifluoroacetone]. Phillips and Steel[13] have also recently observed that 1,3- and 1,4-diacetylbenzene dioximes undergo double cyclopalladation reaction. The present study is concerned with the reactions of the chloro-bridged doubly orthopalladated complex $[Pd_2(L - 2H)Cl_2]$ of *N,N,N′,N′*-tetraethylbenzene-1,3-bis(methylamine) (L). The structure of $[Pd_2(L - 2H)(PPh_3)_2Cl_2]$ is also reported.

Results and Discussion

Cyclometallation Reaction.—*N,N,N′,N′*-Tetraethylbenzene-1,3-bis(methylamine) on reaction with 2 equivalents each of $Li_2[PdCl_4]$ and NEt_3 in methanol afforded the doubly cyclometallated compound $[Pd_2(L - 2H)Cl_2]$ **1** in nearly quantitative yield. When this reaction was carried out in the absence of NEt_3 a mixture of **1** and a non-cyclometallated polymeric product $[Pd_2LCl_4]$ was obtained in an overall yield of 60%. Complex **1**, which is insoluble in common organic solvents, is also polymeric. Its IR spectrum showed two ν(Pd–Cl) vibrations at 330 and 260 cm^{-1}. Although dipalladation of the diamine was possible at either the 4,6 or 2,4 positions, subsequent reactions of the chloro-bridged complex with monodentate donors (see later) disclosed that the 4,6 isomer was formed regiospecifically. Apparently, reaction at the 2,4 positions is sterically more demanding. Attempts to restrict the cyclopalladation reaction to the 4 or 6 position were unsuccessful, indicating that both of these C–H bonds are equally activated towards electrophilic attack of palladium. Exclusive metallation at the 2 position of benzene-1,3-bis(methylamines) was achieved[14] through a different synthetic approach.

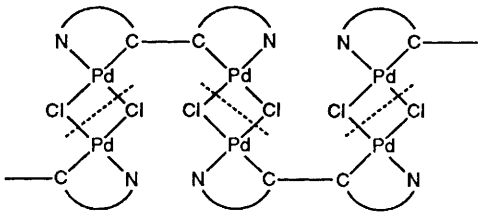


L

The chloro bridges of complex **1** can be substituted by other halides or bridging anions. Thus, complexes of composition $[Pd_2(L - 2H)X_2]$ (X = Br **2**, N_3 **3** or NCS **4**) were obtained by treating a suspension of **1** in MeCN with the stoichiometric amount of $Ag[ClO_4]$ followed by the addition of an aqueous solution of the appropriate alkali-metal salt. The presence of $\nu_{asym}(N_3^-)$ at 2080 cm^{-1} for **3** and ν(NCS^-) at 2050 cm^{-1} for **4** confirmed the involvement of these anions in the bridge formation.[15]

Reactions of Complex **1** *with Mono- and Bi-dentate Ligands.*—A suspension of $[Pd_2(L - 2H)Cl_2]$ in CH_2Cl_2 on treatment with 2 equivalents of PPh_3 readily turned into a clear solution from which the bis(phosphine) complex $[Pd_2(L - 2H)(PPh_3)_2Cl_2]$ **5** was isolated almost quantitatively. The relative molecular mass of this non-electrolytic compound determined in $CHCl_3$ (1040) was in agreement with that required (1055) for **5**. The IR spectrum, in contrast to **1**, showed a single ν(Pd–Cl) at 280 cm^{-1}. There are three possible ways to juxtapose the PPh_3

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



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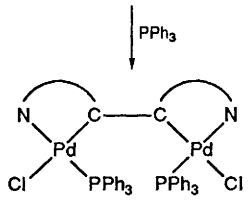

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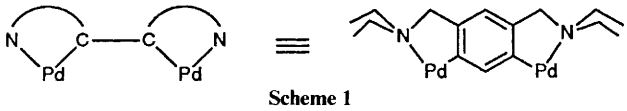
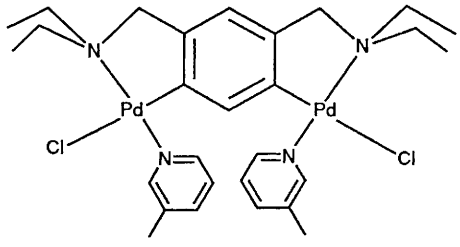


Scheme 1



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molecules and Cl atoms in **5**: (*i*) each of the PPh_3 is *trans* to a nitrogen, *i.e.* they are in the *endo* position; (*ii*) each of the PPh_3 is *trans* to a Pd–C bond, *i.e.* they are in the *exo* position; (*iii*) a situation midway between (*i*) and (*ii*), *i.e.* the donor atoms are in the sequence P,Cl,P,Cl. A symmetric structure was indicated by a single resonance at δ 35.2 in the ^{31}P NMR spectrum. The ^1H NMR spectrum showed a triplet at δ 5.52 and a singlet at δ 6.70, each of which corresponded to a single proton. The more shielded one can be assigned to 5-CH because this proton experiences maximum anisotropic shielding by the neighbouring PPh_3 molecules. The triplet splitting pattern of this proton also arises due to its coupling (through space) with the two adjacent ^{31}P nucleus. The coupling constant, J(P–H) = 5.5 Hz, may be compared with J(P–H) = 4.0 Hz observed for the cyclopalladated complex of 8-methylquinoline.[16] The singlet at δ 6.70 is obviously due to 2-CH. Details of the ^1H and ^{13}C NMR spectra of this and the other complexes are given in the Experimental section.

The formation of complex **5** from **1** (Scheme 1) is based on the simple rationale that the nucleophilic attack of PPh_3 leads to cleavage of the chloro bridge *trans* to the Pd–N bond. It may be noted that neither the alternative structure for **1** involving metallation at the 2,4 positions nor a dimeric 4,6 species would produce a single isomer for **5**.

The chloride ions in complex **5** can be readily substituted with other anions (Br^-, N_3^-, NCS^-, *etc.*). For example, $[Pd_2(L - 2H)(PPh_3)_2(N_3)_2]$ **6** was obtained either by treating **3** directly with PPh_3 or by treating **5** with $Ag[ClO_4]$ in MeCN followed by NaN_3. Complex **6** showed characteristic $\nu_{asym}(N_3^-)$ and $\nu_{sym}(N_3^-)$ vibrations due to terminal azide[15] at 2040 and 1340 cm^{-1}. The ^1H NMR spectrum was again almost identical with that of **5**. In contrast to PPh_3, *o*-tolylphosphine failed to give a definite reaction product with **1**. As will be evident from the molecular structure of **5** (see later) this is due to steric overcrowding.

Monodentate nitrogen donors such as 3- and 4-methylpyridine (3Me- or 4Me-py) reacted with complex **1** in the same way as did PPh_3 to produce complexes **7** and **8**, in which the pyridines are *trans* to the Pd–N bonds. As reported earlier,[12a,b] here also the 5-CH proton is very much shielded (δ 4.71 **7**, 4.95 **8**) relative to the other aromatic proton, 2-CH (δ 6.62 for both **7** and **8**). The remarkably low chemical shift observed for **7** is perhaps worth mentioning; to our knowledge, this is unprecedented for an aromatic proton in orthopalladated compounds.

Unlike 3Me- or 4Me-py, 2Me-py failed to produce any isolable product with complex **1** showing again profound steric involvements between the two adjacent 2Me-py molecules. To see whether any sort of steric interaction is also involved in the 3Me-py derivative, variable-temperature ^1H NMR spectral measurements of **7** over the range −50 to +50 °C (at 25 °C intervals) were undertaken. In **7** the relative orientation of the methyl groups in two 3Me-py moieties could be *syn-syn*, *syn-anti* and *anti-anti*, the latter conformation being of lowest energy. Since over the entire temperature range no stereochemical change was observed the *anti-anti* conformation may be assumed. In fact, temperature had practically no effect on the chemical shifts due to the CH_2NEt_2 and 3Me-py moieties. The only observable effects were on the aromatic protons; while the chemical shift due to 5-CH monotonically decreased from δ 4.75 at 50 °C to 4.64 at −50 °C, the shift for 2-CH increased from δ 6.58 to 6.66.

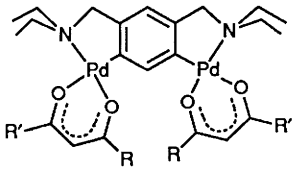
Reaction of complex **1** with acetylacetone (Hacac) gave the bis(chelate) $[Pd_2(L - 2H)(acac)_2]$ **9**, the ^1H and ^{13}C NMR spectra of which were consistent with the expected C_{2v} symmetry. The compounds $PhCOCH_2CSPh$ and $MeCOCH_2CO_2Et$ also smoothly reacted with **1** and in both the cases a single isomer, **10** and **11**, was obtained. While in the case of **10** the sulfur atom is *trans* to the Pd–N bond, in **11** the oxygen atom of the ester moiety is *trans* to the Pd–C bond. The binding mode of these two ligands is in accord with their enolizing behaviour. By contrast, trifluoro(thenoyl)acetone (Htta) gave a mixture of the isomers **12** and **13**, which could not be separated either by fractional crystallization or by column chromatography. The notable feature in the ^1H NMR spectra of this mixture was the occurrence of two overlapping singlets due to the benzylic CH_2 protons at δ 3.96 and 3.98 and at 6.20 and 6.26 due to the CH proton of tta^-. The relative heights of these signals (5.3:4.7) indicated that the two isomers were formed almost in equal amount.

Protolytic Reaction of Complex **5**.—There is considerable interest in the mechanism of electrophilic cleavage of transition metal–carbon bonds.[17] Homolytic cleavage of the Pd–C bond in cyclometallated compounds has been carried out in several ways, *viz.* reduction,[18,19] reductive carbonylation under basic conditions,[20] cyanide-induced dissociation[21] and protonolysis with HCl.[22] More recently, Ryabov and co-workers[23] have reported chloride-ion-induced protolytic reaction with acetic acid. We studied this last reaction with $[Pd_2(L - 2H)(PPh_3)_2Cl_2]$ **5**.

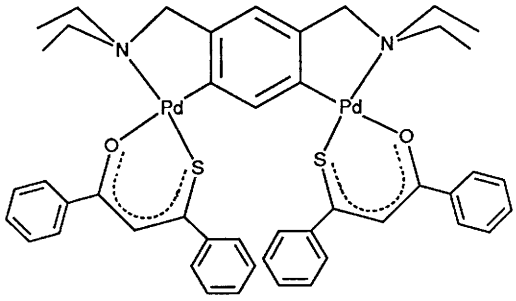
A solution of complex **5** in $CHCl_3$–$MeCO_2H$ (1:1) on stirring with 2 equivalents of LiCl at room temperature gave a white product of composition $[Pd_2L(PPh_3)_2Cl_4]$ **14**. The IR spectrum showed two ν(Pd–Cl) vibrations at 320 and 280 cm^{-1}, indicating the presence of a *cis*-dichloro linkage.[24] Moreover, a group of bands at 2750, 2680 and 2630 cm^{-1} indicated the formation of a trialkylammonium ion.[25] These observations led us to suggest the structure of the protonated complex shown in **14**. In polar solvents **14** reverted back to **5** on treatment with a base, showing the reversible nature of reaction (1). It appears

$$[Pd_2(L - 2H)(PPh_3)_2Cl_2] + 2Cl^- + 2H^+ \rightleftharpoons [Pd_2L(PPh_3)_2Cl_4] \quad (1)$$

that the nucleophilic attack of Cl^- ion is immediately followed



9 R = R′ = Me
11 R = Me, R′ = OEt



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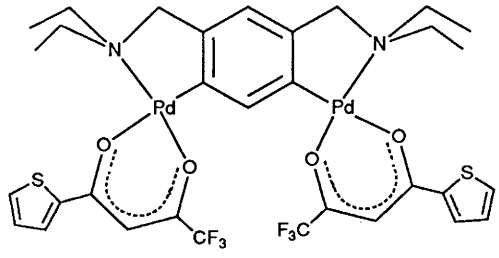

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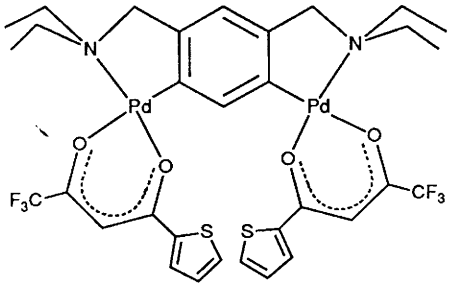

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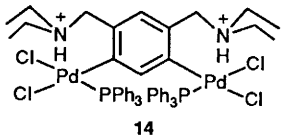

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by transfer of protons to the nitrogen donors. The driving force for the reaction seems to be the strong labilizing influence of the phosphine ligand and complex **14** is additionally stabilized in the solid state by the intramolecular N^+–H ··· Cl^- hydrogen bonds.

Heating of complex **14** alone in $CHCl_3$–$MeCO_2H$ solvent at 80 °C or carrying out reaction (1) at this temperature gave an orange-brown compound **15** and the metal-free ligand, L. Complex **15** was characterized as the well known chloride-bridged *trans*-$[Pd_2(PPh_3)_2Cl_4]$.[26] The protolytic cleavage of the Pd–C bonds is shown in Scheme 2

Cyclopalladation Exchange Reactions.—The splitting of the Pd–C bond in $MeCO_2H$–$CHCl_3$ suggests the possibility of a ligand-exchange reaction between a cyclopalladated complex and a free ligand to afford a new metallocycle, as first realized by Ryabov and co-workers.[27] A number of such reactions has been studied[27–29] with different leaving and entering ligands, and thermodynamic and kinetic aspects have been examined.[29] However, whether a doubly cyclopalladated complex would undergo exchange reaction with a monocyclopalladating ligand was not previously studied.

The exchange reaction (2) of complex **1** with azobenzene, 2-phenylpyridine, 2-benzylpyridine, benzo[*h*]quinoline, 8-methyl-

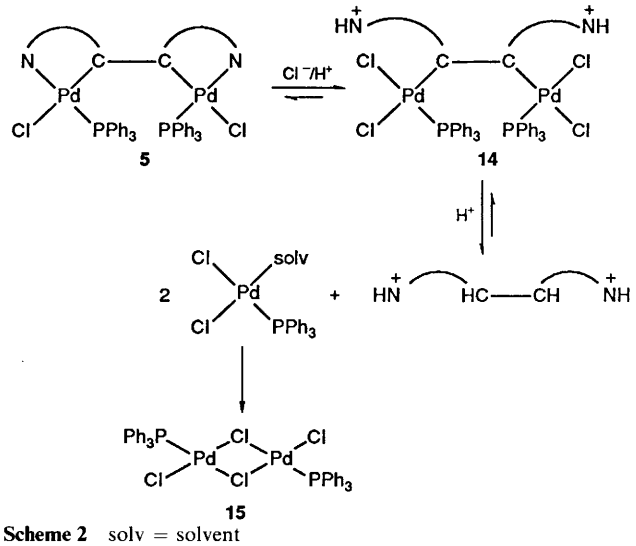
$$[Pd_2(L - 2H)Cl_2] + 2L^* \rightleftharpoons [\{Pd(L^* - H)Cl\}_2] + L \quad (2)$$

quinoline and *N*,*N*-diethyl-4-nitrobenzylamine as the entering ligands (L*) was carried out in $CHCl_3$–$MeCO_2H$ (1:1) at 60 °C over an extended time period. In all the cases the products isolated (30–55%) were of the composition $[\{Pd(L^* - H)Cl\}_2]$ and were characterized as the authentic cyclometallated compounds by converting them into their known soluble derivatives.[1,2] The exchange reaction with 2-benzylpyridine resulted in the conversion of a five- into a six-membered metallocycle. It is also of interest that although *N*,*N*-diethyl-4-nitrobenzylamine cannot be directly cyclometallated, under exchange-reaction conditions orthopalladation occurs.[27] Except for 8-methylquinoline, the exchange reactions entailed cleavage and generation of sp^2 C–H bonds. In the case of 8-methylquinoline, Pd–C bond formation occurs to give sp^3 C–H bonds. The transfer of palladium from one ligand to the other has been suggested[29] to take place according to the different extents of resistance shown by the two ligands towards protonolysis, *i.e.* a cyclopalladate more susceptible to acidolysis is more prone to exchange reaction.

Molecular Structure of Complex **5**.—The crystal structure of complex **5** consists of discrete $[Pd_2(L - 2H)(PPh_3)_2Cl_2]$ molecules separated by van der Waals distances. An ORTEP[30] view of the complex along with the atom labelling scheme is shown in Fig. 1. Positional parameters and selected bond lengths and angles are given in Tables 1 and 2, respectively. Since a crystallographic two-fold axis of symmetry passes through C(1) and C(2) of the cyclometallated benzene ring the asymmetric unit consists of half the molecule. The metal atom in the asymmetric unit is in an appreciably distorted square-planar environment provided by the C(3), N, Cl and P donors. These atoms are alternately displaced from the mean plane: C(3) −0.278(4), N 0.263(4), Cl −0.080(3) and P 0.086(3) Å. The metal centre itself lies 0.064(2) Å below the plane. The angles between adjacent atoms lie in the range 80.8(2)–95.3(2)°, of which N–Pd–C(3) angle is the most acute. The bond angles about Pd are dictated by the large PPh_3 ligand, which to avoid contact with the cyclometallated benzene ring and the other PPh_3 ligand compresses the five-membered chelate ring. Steric involvements are also prevented by twisting of the *trans* angles, Cl–Pd–C(3) 170.8(1)° and P–Pd–N 166.4(2)° from the expected linearity. The Pd–Cl distance 2.396(3) Å, which is on the high side of the range 2.24–2.45 Å reported for various palladium(II) complexes,[31] indicates the large *trans* influence of the σ-bonded carbon. The relatively long Pd–N bond distance 2.159(4) Å, which may be compared with other Pd–N(sp^3) bonds (2.06–2.22 Å),[2,32] also reflects the fairly large *trans* influence of PPh_3. The Pd–P [2.251(3) Å] and Pd–C(3) distances [1.997(5) Å] are, however, typical of complexes belonging to this category.[2,12a,31c,32a,33] The molecular structure of **5** reveals that introduction of further steric constraints would abruptly decrease the thermodynamic stability of the complex. In retrospect, the failure of *o*-tolylphosphine to afford a definite reaction product with **1** appears consistent.

Experimental

Materials.—The compound $PdCl_2 \cdot xH_2O$ was obtained from



Scheme 2 solv = solvent

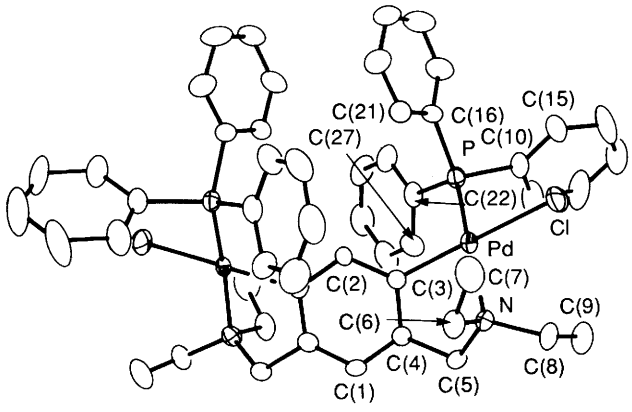


Fig. 1 An ORTEP view of $[Pd_2(L - 2H)(PPh_3)_2Cl_2]$ **5**

Aurora-Matthey, Calcutta. Other chemicals were available commercially and used as received. The ligand $PhCOCH_2CSPh$ was prepared according to the method given in ref. 34 and *N*,*N*-diethyl-4-nitrobenzylamine was prepared by refluxing *N*,*N*-diethyl-4-nitrobenzyl bromide [35] with diethylamine.

Physical Measurements.—Proton and ^{13}C NMR spectra were recorded on either a Bruker WH 270 or JEOL-FX 100 spectrometer; the former had a facility for variable-temperature measurements. The spectra were obtained as $CDCl_3$ solutions using $SiMe_4$ (δ 0) as the internal reference. Assignments of ^{13}C NMR spectra were made from a combination of ^{13}C-$\{^1H\}$ and proton-noise decoupled spectra. The ^{31}P NMR spectra were recorded with a JEOL-FX100 spectrometer, using $CDCl_3$ solutions and H_3PO_4 as the external reference. Infrared spectra were recorded with a Perkin Elmer 783 spectrophotometer. Relative molecular mass determinations were made with $CHCl_3$ solutions by a Knauer vapour-phase osmometer using benzil as the calibrant. Carbon, H and N analyses were performed on a Perkin Elmer model 240C ememental analyser. Palladium was determined gravimetrically with dimethylglyoxime.

Syntheses.—*Ligand* L. To 2,6-bis(bromomethyl)benzene (10 g) was slowly added with stirring diethylamine (30 g) and the mixture was heated under reflux for 2 h. After cooling, the solution was poured into water (300 cm^3) and enough NaOH added to neutralize the HBr liberated. The ligand was extracted with Et_2O and after removal of the solvent it was distilled under reduced pressure [b.p. 82–84 °C at 0.1 mmHg) (*ca.* 13.3 Pa)] δ_H 1.07 (12 H, t, 9,9′-CH_3), 2.54 (8 H, m, 8,8′-CH_2), 3.54 (4 H, s, 7-CH_2) and 7.20 (4 H, m, aromatic).

Table 1 Fractional atomic coordinates of $[Pd_2(L - 2H)(PPh_3)_2Cl_2]$ **5** with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Pd	0.127 40(1)	0.140 88(2)	0.195 12(1)
Cl	0.230 11(6)	0.207 71(10)	0.175 61(8)
P	0.068 62(5)	0.270 19(9)	0.125 88(5)
N	0.171 1(2)	−0.008 0(3)	0.241 7(2)
C(1)*	0	−0.086 7(4)	0.25
C(2)*	0	0.138 2(4)	0.25
C(3)	0.505 0(2)	0.082 3(2)	0.225 7(2)
C(4)	0.052 1(2)	−0.030 1(3)	0.232 9(2)
C(5)	0.113 5(2)	−0.084 3(3)	0.221 1(3)
C(6)	0.190 9(2)	−0.000 5(4)	0.321 6(2)
C(7)	0.237 9(3)	0.089 5(6)	0.348 7(3)
C(8)	0.229 9(2)	−0.047 6(4)	0.217 6(3)
C(9)	0.216 3(3)	−0.064 6(5)	0.138 3(3)
C(10)	0.096 8(2)	0.284 6(3)	0.044 3(1)
C(11)	0.068 9(2)	0.219 5(3)	−0.013 8(1)
C(12)	0.094 6(2)	0.221 3(3)	−0.073 7(1)
C(13)	0.148 3(2)	0.288 3(3)	−0.075 5(1)
C(14)	0.176 2(2)	0.353 5(3)	−0.017 4(1)
C(15)	0.150 5(2)	0.351 7(3)	0.042 5(1)
C(16)	0.075 0(2)	0.403 4(2)	0.166 0(1)
C(17)	0.063 4(2)	0.497 7(2)	0.126 0(1)
C(18)	0.067 4(2)	0.597 2(2)	0.159 9(1)
C(19)	0.083 0(2)	0.602 4(2)	0.233 8(1)
C(20)	0.094 6(2)	0.508 2(2)	0.273 9(1)
C(21)	0.090 6(2)	0.408 6(2)	0.240 0(1)
C(22)	−0.020 8(1)	0.246 5(2)	0.090 8(2)
C(23)	−0.065 9(1)	0.331 7(2)	0.074 4(2)
C(24)	−0.132 8(1)	0.311 7(20)	0.041 5(2)
C(25)	−0.154 6(1)	0.206 5(2)	0.025 0(2)
C(26)	−0.109 5(1)	0.121 3(2)	0.041 5(2)
C(27)	−0.042 6(1)	0.141 3(2)	0.074 3(2)

* Occupancy factor 0.5.

Table 2 Selected bond lengths (Å) and angles (°) in $[Pd_2(L - 2H)(PPh_3)_2Cl_2]$ **5**

Pd–C(3)	1.997(5)	P–C(16)	1.822(3)
Pd–N	2.159(4)	P–C(22)	1.829(3)
Pd–P	2.251(3)	N–C(5)	1.498(6)
Pd–Cl	2.396(3)	N–C(6)	1.509(5)
P–C(10)	1.829(4)	N–C(8)	1.491(7)
N–Pd–C(3)	80.8(2)	C(10)–P–C(16)	106.1(2)
P–Pd–C(3)	95.3(2)	C(10)–P–C(22)	101.6(2)
Cl–Pd–P	91.5(2)	C(16)–P–C(22)	105.4(3)
Cl–Pd–N	93.9(2)	Pd–N–C(5)	102.0(3)
Cl–Pd–C(3)	170.8(1)	Pd–N–C(6)	111.0(3)
P–Pd–N	166.4(2)	Pd–N–C(8)	116.2(3)
Pd–P–C(10)	110.3(3)	C(5)–N–C(6)	108.1(5)
Pd–P–C(16)	115.0(2)	C(5)–N–C(8)	111.3(4)
Pd–P–C(22)	117.1(2)	C(6)–N–C(8)	108.0(4)

$[Pd_2(L - 2H)Cl_2]$ **1**. To a methanol solution (100 cm^3) of the ligand (1.24 g, 5 mmol) and triethylamine (1 g, 10 mmol) was added in small portions with stirring a methanol solution (50 cm^3) of $Li_2[PdCl_4]$ (2.62 g, 10 mmol). The light yellow product that deposited was filtered off after 1 h and washed thoroughly with water, MeOH and Me_2CO; yield 2.5 g, 95% (Found: C, 36.6; H, 5.05; N, 5.3; Pd, 40.25. $C_{16}H_{26}Cl_2N_2Pd_2$ requires C, 36.25; H, 4.9; N, 5.3; Pd, 40.15%).

$[Pd_2(L - 2H)X_2]$ (X = Br **2**, N_3 **3** or NCS **4**). To a stirred suspension of complex **1** (0.53 g, 1 mmol) in MeCN (50 cm^3) was added $Ag[ClO_4]$ (0.36 g, 2 mmol). The AgCl precipitated was filtered off and the filtrate treated with an aqueous solution of NaX (3 mmol). The product that separated from the solution was filtered off and washed successively with water, MeOH and Me_2CO (Found: C, 34.8; H, 4.9; N, 20.4; Pd, 39.4. $C_{16}H_{26}N_8Pd_2$ **3** requires C, 35.35; H, 4.8; N, 20.65; Pd, 39.2%).

$[Pd_2(L - 2H)(PPh_3)_2Cl_2]$ **5**. A stirred suspension of complex **1** (1.06 g, 2 mmol) in CH_2Cl_2 (50 cm^3) was treated with PPh_3 (1.05 g, 4 mmol). When all the material dissolved the solution was filtered. The filtrate on rotary evaporation gave yellow crystals of the complex, which was recrystallized from CH_2Cl_2–MeOH; yield 2 g, 95% (Found: C, 59.3; H, 5.4; N, 2.7; Pd, 20.3. $C_{52}H_{56}Cl_2N_2P_2Pd_2$ requires C, 59.2; H, 5.3; N, 2.65; Pd, 20.2%). δ_H 1.30 (12 H, m, 9,9′-CH_3), 2.75 (4 H, m, 8-CH_2), 2.95 (4 H, m, 8′-CH_2), 4.01 (4 H, s, 7-CH_2), 5.52 (1 H, t, 5-CH), 6.70 (1 H, s, 2-CH) and 7.2–7.5 (30 H, m, PPh_3); δ_C 12.5 (9,9′-C), 52.1 (8,8′-C), 66.2 (7-C), 116.9 (2-C), 130.5 (5-C), 143.1 (1,3-C), 152.9 (4,6-C), 127.9, 128.3, 131.1, 133.0, 135.1, 135.6 (PPh_3); δ_P 35.2.

$[Pd_2(L - 2H)(PPh_3)_2(N_3)_2]$ **6**. This compound was prepared from complex **3** in the same way as **5**. It was also obtained by stirring a mixture of **5** (0.53, 0.5 mmol) and $Ag[ClO_4]$ (0.2 g, 1 mmol) in MeCN (20 cm^3) followed by the addition of an aqueous solution (5 cm^3) of NaN_3 (0.1 g, 1.5 mmol) to the filtrate. The compound was recrystallized from $CHCl_3$–MeOH (Found: C, 58.2; H, 5.15; N, 10.4; Pd, 19.8. $C_{52}H_{56}N_8P_2Pd_2$ requires C, 58.5; H, 5.25; N, 10.5; 19.95%). δ_H 1.32 (12 H, m, 9,9′-CH_3), 2.84 (8 H, m, 8,8′-CH_2), 4.02 (4 H, s, 7-CH_2), 5.60 (1 H, t, 5-CH), 6.68 (1 H, s, 2-CH) and 7.1–7.7 (30 H, m, PPh_3).

$[Pd_2(L - 2H)(base)_2Cl_2]$ (base = 3Me-py **7** or 4Me-py **8**). To a stirred suspension of complex **1** (0.53 g, 1 mmol) in $CHCl_3$ (20 cm^3) was added the pyridine base (0.19 g, 2 mmol). The clear light yellow solution that resulted was filtered after 0.5 h. On removing the solvent on a rotary evaporator a thick syrup was obtained, which on stirring with Et_2O became a solid mass. The compound was recrystallized from $CHCl_3$–MeOH; yield 0.68 g, 95%. (Found for **7**: C, 46.75; H, 5.55; N, 7.6; Pd, 29.9. $C_{28}H_{40}Cl_2N_4Pd_2$ requires C, 46.95; H, 5.6; N, 7.8; Pd, 29.75%). δ_H for **7** 1.57 (12 H, t, 9,9′-CH_3), 2.22 (6, s, 3-Me of py), 2.77 (4 H, m, 8-CH_2), 3.27 (4 H, m, 8′-CH_2), 3.88 (4 H, s, 7-CH_2), 4.71 (1 H, s, 5-CH), 6.62 (1 H, s, 2-CH), 6.94 (2 H, m, 5-CH of py), 7.33 (2 H, d, 4-CH of py), 8.40 (2 H, d, 6-CH of py) and 8.47 (2 H, s, 2-CH of py). δ_H for **8** 1.58 (4 H, t, 9,9′-CH_3), 2.37 (6 H, s, 4-Me of py), 2.79 (4 H, s, 8-CH_2), 3.27 (4 H, m, 8′-CH_2), 3.90 (4 H, s, 7-CH_2), 4.95 (1 H, s, 5-CH), 6.62 (1 H, s, 2-CH), 6.88 (4 H, d, 3,5-CH of py) and 8.46 (4 H, d, 2,6-CH of py); δ_C 13.5 (9,9′-C), 21.6 (4-Me of py), 56.3 (8,8′-C), 66.3 (7-C), 114.6 (2-C), 125.6 (2,6-C of py), 126.2 (3,5-C of py), 135.7 (5-C), 145.6 (1,3-C), 149.1 (4-C of py) and 153.8 (4,6-C).

$[Pd_2(L - 2H)(dik)_2]$ (Hdik = $MeCOCH_2COMe$ **9**, $PhCOCH_2CSPh$ **10**, $MeCOCH_2CO_2Et$ **11** or $C_4H_3SCOCH_2COCF_3$, **12**, **13**). To a stired suspension of complex **1** (2 mmol, 1.06 g) in CH_2Cl_2 (50 cm^3) were added a methanol solution (20 cm^3) of the appropriate chelating reagent (4 mmol) and an aqueous solution 5 cm^3) of NaOH (0.16 g, 4 mmol). Over a period of 2 h a clear solution was obtained and was filtered. The filtrate on concentration afforded the product, which was washed with water and MeOH and recrystallized from $CHCl_3$–MeOH; yield *ca.* 90%.

Complex **9** (Found: C, 47.75; H, 6.05; N, 4.1; Pd, 32.6. $C_{26}H_{40}N_2O_4Pd_2$ requires C, 47.5; H, 6.1; N, 4.25; Pd, 32.4%): δ_H 1.48 (12 H, t, 9,9′-CH_3), 1.90 (6 H, s, CH_3 of acac), 1.98 (6 H, s, CH_3 of acac), 2.82 (4 H, m, 8-CH_2), 3.10 (4 H, m, 8′-CH_2), 3.88 (4 H, s, 7-CH_2), 5.28 (2 H, s, CH of acac), 6.55 (1 H, s, 2-CH) and 7.22 (1 H, s, 5-CH); δ_C 12.4 (9,9′-C), 27.3 (CH_3 of acac), 28.2 (CH_3 of acac), 54.5 (8,8′-C), 66.6 (7-C), 99.2 (CH of acac), 113.4 (2-C), 131.8 (5-C), 142.3 (1,3-C), 142.9 (4,6-C), 186.5 (CO of acac) and 187.4 (CO of acac).

Complex **10** (Found: C, 58.6, H, 5.2; N, 3.1. $C_{46}H_{48}N_2O_2Pd_2S_2$ requires C, 58.9; H, 5.1; N, 3.0%): δ_H 1.60 (12 H, t, 9,9′-CH_3), 3.04 (8 H, m, 8,8′-CH_2), 4.01 (4 H, s, 7-CH_2), 6.64 (2 H, s, CH of ligand) and 6.8–8.1 (22 H, m, aromatic).

Complex **11** (Found: C, 47.1; H, 6.2; N, 3.8. $C_{28}H_{44}N_2O_6Pd_2$ requires C, 46.85; H, 6.1; N, 3.9%): δ_H 1.23 (6 H, t, CH_2CH_3 of ligand), 1.53 (12 H, t, 9,9′-CH_3), 2.76 (4 H, m, 8-CH_2), 2.88 (4 H, m, 8′-CH_2), 3.55 (6 H, s, CH_2 of ligand), 3.82 (4 H, s, 7-CH_2), 3.99 (4 H, q, CH_2CH_3 of ligand), 4.70 (2 H, s, CH of ligand), 6.47 (1 H, s, 2-CH) and 7.15 (1 H, s, 5-CH).

Complexes **12** and **13** (Found: C, 42.9; H, 4.0; N, 2.95; Pd, 23.4. $C_{32}H_{34}F_6N_2O_4Pd_2S_2$ requires C, 42.65; H, 3.8; N, 3.1; Pd, 23.6%): δ_H 1.52 (12 H, m, 9,9′-CH_3), 2.88 (8 H, m, 8,8′-CH_2), 3.96, 3.98 (4 H, s, 5-CH_2), 6.20, 6.26 (2 H, s, CH of tta), 6.62 (1 H, s, 2-CH), 7.18 (1 H, s, 5-CH_2) and 7.0–7.8 (3 H, m, C_4H_3S of tta).

Protolytic Reaction of Complex **5**.—To a chloroform solution (25 cm^3) of complex **5** (0.53 g, 0.5 mmol) a solution of LiCl (0.064 g, 1.5 mmol) in acetic acid (25 cm^3) was added. The solution was stirred at room temperature and after a short while a white crystalline product separated. The product **14** was filtered off, washed with $CHCl_3$ and dried in vacuum; yield 0.36 g, 65% (Found: C, 54.9; H, 5.3; N, 2.35; Pd, 19.2. $C_{52}H_{58}Cl_4N_2P_2Pd_2$ requires C, 55.4; H, 5.15; N, 2.5; Pd, 18.9%).

When the above reaction mixture was heated at 80 °C for 0.5 h, brown-orange crystals of complex **15** deposited. They were filtered off and washed successively with $MeCO_2H$, $CHCl_3$ and Et_2O; yield 0.36 g, 80% (Found: C, 49.5; H, 3.2; Pd, 24.35. $C_{36}H_{30}Cl_4P_2Pd_2$ requires C, 49.15; H, 3.4; Pd, 24.2%). Complex **15** was also obtained by heating a suspension of **14** in $CHCl_3$–$MeCO_2H$ at 80 °C.

Cyclopalladation Exchange Reactions.—The following general method was used for the exchange reactions involving $[Pd_2(L - 2H)Cl_2]$ **1** and the entering ligands (L*) azobenzene, 2-phenylpyridine, benzo[*h*]quinoline, 8-methylquinoline, 2-benzylpyridine and *N*,*N*-diethyl-4-nitrobenzylamine. To a suspension of **1** (1.06 g, 2 mmol) in $CHCl_3$–$MeCO_2H$ (1:1, 60 cm^3) was added the entering ligand (4 mmol). The mixture was heated at 60 ± 2 °C for 12–16 h. In the case of azobenzene the solution was filtered hot and from the filtrate red crystals of $[\{Pd(L^* - H)Cl_2\}_2]$ deposited on standing. In all other cases the product $[\{Pd(L^* - H)Cl\}_2]$ being insoluble in the solvent was filtered off and washed with MeOH and Et_2O. The yield varied between 30 and 55%, lowest for *N*,*N*-diethyl-4-nitrobenzylamine and highest for azobenzene.

Crystal Structure Determination of $[Pd_2(L - 2H)(PPh_3)_2Cl_2]$ **5**.—Diffraction-quality crystals were obtained by diffusion of MeOH into a $CHCl_3$ solution of the complex. A suitable crystal was mounted on a glass fibre.

Crystal data. $C_{52}H_{56}Cl_2N_2P_2Pd_2$, M = 1054.7, monoclinic, space group $C2/c$, a = 20.676(4), b = 12.436(3), c = 19.445(4) Å, β = 104.29(3)°, U = 4845(2) Å^3 (by least-squares refinement of diffractometer angles for 20 automatically centred reflections having 2θ 10–25°, λ = 0.710 73 Å), Z = 4, D_c = 1.445 g cm^{-3} $F(000)$ = 1112. Crystal dimensions: 0.25 × 0.30 × 0.45 mm, μ(Mo-Kα) 8.60 cm^{-1}.

Data collection and processing. Intensity data were collected with a Nicolet R3m/V automated diffractometer using graphite-monochromated Mo-Kα radiation. Intensities of three standard reflections monitored after every 97 did not show any appreciable decay during data collection. The intensity data were corrected for Lorentz-polarization effects and for absorption by the empirical method of North *et al.*[36] A total of 4409 reflections were collected in the range $2 < 2\theta < 50°$, of which 3533 independent reflections with $I > 2\sigma(I)$ were used for structure determination.

Structure analysis and refinement. Systematic absences led to the identification of the space group as C_c or $C2/c$. The structure was solved in the latter. The position of the Pd atom was determined from a Patterson map and the remaining non-hydrogen atoms were located from successive Fourier maps. The structure was refined by the full-matrix least-squares method using the program SHELX.[37] In the final stages of refinement all non-hydrogen atoms were made anisotropic while the hydrogen atoms were held fixed in the geometrically calculated positions with isotropic thermal parameters. The

weighting scheme $w = 1/[\sigma^2(F_o) + 0.002F_o^2]$, with $\sigma(F_o)$ from counting statistics, gave satisfactory agreement analyses. The highest peak in the final Fourier difference map was 0.42 e Å^{-3}. Final R and R' values were 0.035 and 0.043. Anomalous dispersion corrections were applied to Pd and scattering factor data from ref. 38. All computations were carried out on Cyber 180/840A and Vax systems.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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