Synthesis and Reactions of Cyclopalladated Compounds derived from *N,N'*-Dialkylbenzene-1,3-dicarbaldimines [Alkyl = Ethyl (H_2L^1), Butyl or Octyl] and *N,N'*-Dibenzylbenzene-1,3-dicarbaldimine. Crystal Structure of $[Pd_2L^1(py)_4][ClO_4]_2$ (py = pyridine)†

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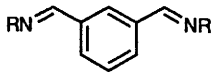
The reactions of *N,N'*-dialkylbenzene-1,3-dicarbaldimines (alkyl = Et, H_2L^1; Bu, H_2L^2 or C_8H_{17}, H_2L^3) and *N,N'*-dibenzylbenzene-1,3-dicarbaldimine (H_2L^4) with $Pd(O_2CMe)_2$ have been studied. In all cases tetra-μ-acetato cyclopalladated compounds, $[Pd_4L_2(O_2CMe)_4]$, were obtained in which metallation had occurred at the 4,6 positions of the benzene ring. The μ-chloro analogues, $[Pd_4L_2Cl_4]$, can be obtained either by reaction of the Schiff bases with $Li_2[PdCl_4]$ or by metathesis of the acetato complexes. Bridge-splitting reactions of $[Pd_4L_2Cl_4]$ with pyridine(py), 4-methylpyridine, pyrazole, 3,5-dimethylpyrazole, amines, and a number of monoprotic bidentate chelating ligands, *viz.* acetylacetone, dibenzoylmethane and its monothio analogue, ethylacetoacetate, salicylaldehyde, *N*-methylsalicylideneimine and sodium *N,N*-dipropyldithiocarbamate have also been investigated. The products have been characterized by ^1H and ^{13}C NMR spectroscopy. The X-ray crystal structure of $[Pd_2L^1(py)_4][ClO_4]_2$ has been determined which crystallizes in the triclinic space group $P\bar{1}$ with a = 10.889(1), b = 16.981(2), c = 10.227(1) Å, α = 92.99(1), β = 93.14(1), γ = 73.65(1)° and Z = 2; refinement led to R = 0.059 and R' = 0.062 using 3620 unique reflections with $I > 3\sigma(I)$.

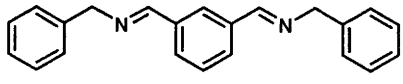
Cyclometallation reactions offer one of the facile pathways for the activation of C–H bonds in hetero-substituted organic molecules. The chemistry of cyclopalladated compounds, especially of N-donor ligands,[1–8] is extensive. The ease with which these compounds are formed and their stability to homolytic cleavage have made them attractive for reactivity studies.[9–18] Many such reactions[19–21] are useful in regio- and stereo-selective organic synthesis and in the formation of heterocyclic compounds. Cyclopalladated compounds are also being developed as liquid crystals[22,23] and are used as catalysts in hydrogenation reactions.[24]

Schiff bases are useful ligands for cyclopalladation reactions.[25,26] Recently the formation of *endo- vs. exo*-palladacycles with five- or six-membered rings has been explored.[27–30] The present study is concerned with the syntheses and reactions of the dipalladiobenzene derivatives obtained from the Schiff bases, *N,N'*-dialkylbenzene-1,3-dicarbaldimines, H_2L^1–H_2L^3 **I**, and *N,N'*-dibenzylbenzene-1,3-dicarbaldimine, H_2L^4 **II**. While the variation of the alkyl substituents in H_2L^1–H_2L^3 influences the solubility behaviour of the cyclopalladated derivatives, H_2L^4 has been used to observe whether cyclometallation occurs to the central phenyl ring or the terminal phenyl rings.



I

H_2L^1: R = Et
H_2L^2: R = Bu
H_2L^3: R = C_8H_{17}



II

H_2L^4

Results and Discussion

The cyclopalladation reaction with the Schiff bases H_2L^1–H_2L^4 takes place readily when a chloroform solution of $Pd(O_2CMe)_2$ and the ligand in a 2:1 molar ratio is heated under reflux. The analytical data (Table 1) for the resulting complexes **1**–**4** correspond to a Pd:L:O_2CMe ratio of 2:1:2, indicating that di-*ortho*-metallation has occurred at the 3,5 positions of the benzene ring. Although complexes **1**, **2** and **4** are sparingly soluble in CH_2Cl_2 or $CHCl_3$, complex **3** is readily soluble in these solvents. The relative molecular mass determined for complex **3** in $CHCl_3$ (1340) is in agreement with a tetranuclear composition $[Pd_4(L^3)_2(O_2CMe)_4]$ (1370). Complexes **1**–**4** exhibit two IR absorptions at 1570 and 1410 cm^{-1} due to the bridging acetate groups. The ^1H NMR spectrum of complex **3** (Table 2) reveals the presence of two types of bridging acetate groups (δ 1.95, 2.20) as shown in the palladacycle **III**. The endocyclic acetate (α) is more shielded relative to that of the

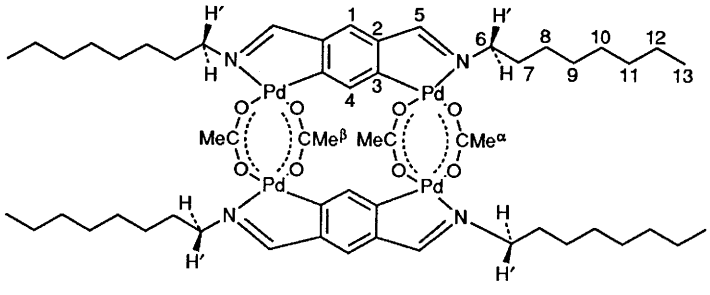
† μ-4,6-Bis(*N*-ethyliminomethyl)-1,3-phenylene-1κ²*C*¹,*N*:2κ²*C*³,*N*'-bis[dipyridinepalladium(II)] diperchlorate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Analytical data * for the complexes

Complex	Colour	Analysis (%) C	H	N	Pd
1 $[Pd_4(L^1)_2(O_2CMe)_4]$	Orange	37.60 (37.15)	3.65 (3.85)	5.60 (5.40)	41.05 (41.20)
2 $[Pd_4(L^2)_2(O_2CMe)_4]$	Orange	41.45 (41.90)	5.10 (4.90)	5.20 (4.90)	37.40 (37.15)
3 $[Pd_4(L^3)_2(O_2CMe)_4]$	Orange	48.80 (49.05)	6.50 (6.40)	3.85 (4.10)	31.45 (31.05)
4 $[Pd_4(L^4)_2(O_2CMe)_4]$	Orange	49.30 (48.70)	4.05 (3.75)	4.05 (4.35)	32.95 (33.20)
5 $[Pd_4(L^1)_2Cl_4]$	Light yellow	30.80 (30.65)	3.35 (3.00)	6.20 (5.95)	45.45 (45.30)
6 $[Pd_4(L^2)_2Cl_4]$	Light yellow	36.05 (36.50)	4.05 (4.20)	5.60 (5.35)	40.20 (40.50)
7 $[Pd_4(L^3)_2Cl_4]$	Light yellow	44.60 (45.15)	6.15 (5.95)	4.20 (4.40)	33.45 (33.35)
8 $[Pd_4(L^4)_2Cl_4]$	Light yellow	44.00 (44.45)	3.20 (3.05)	4.50 (4.70)	36.20 (35.85)
9 $[Pd_2L^1(py)_2Cl_2]$	White	41.50 (42.05)	4.00 (3.80)	9.25 (8.90)	33.65 (33.90)
10 $[Pd_2L^2(4Me\text{-}py)_2Cl_2]$	White	47.05 (47.20)	5.30 (5.05)	7.55 (7.85)	30.00 (29.90)
11 $[Pd_2L^1(py)_4][ClO_4]_2$	Light yellow	42.40 (42.00)	3.80 (3.70)	9.00 (9.20)	23.60 (23.30)
12 $[Pd_2L^1(NH_2Bu)_2Cl_2]$	White	38.60 (39.00)	5.60 (5.85)	9.00 (9.10)	34.85 (34.55)
13 $[Pd_2L^1(NHEt_2)_2Cl_2]$	White	38.50 (39.00)	6.15 (5.85)	9.35 (9.10)	34.75 (34.55)
14 $[Pd_2L^1\{NMe_2(CH_2Ph)\}_2Cl_2]$	White	49.25 (48.65)	5.60 (5.40)	7.25 (7.55)	28.50 (28.75)
15 $[Pd_2L^1(Hpz)_2Cl_2]$	White	36.15 (36.65)	3.90 (3.65)	13.50 (13.85)	34.45 (35.15)
16 $[Pd_2L^2(Hdmpz)_2(\mu\text{-}dpmz)]Cl{\cdot}CH_2Cl_2$	White	44.15 (44.55)	5.60 (5.45)	12.75 (13.00)	24.50 (24.70)
17 $[Pd_2L^1(acac)_2]$	Yellow	44.45 (44.25)	4.80 (4.70)	4.90 (4.70)	35.50 (35.65)
18 $[Pd_2L^4(acac)_2]$	Yellow	53.00 (53.25)	4.60 (4.45)	4.10 (3.90)	29.30 (29.50)
19 $[Pd_2L^1(dbm)_2]$	Yellow	60.20 (59.65)	4.40 (4.25)	3.50 (3.30)	25.55 (25.20)
20 $[Pd_2L^1(sdbm)_2]$	Orange yellow	57.05 (57.50)	4.30 (4.10)	3.45 (3.20)	24.60 (24.25)
21 $[Pd_2L^1(eaa)_2]$	Yellow	44.25 (43.85)	4.70 (4.85)	4.15 (4.25)	32.35 (32.40)
22 $[Pd_2L^1(sal)_2]$	Yellow	49.00 (48.70)	4.00 (3.75)	4.60 (4.35)	33.00 (33.20)
23 $[Pd_2L^2(msaln)_2]$	Yellow	53.05 (53.15)	5.10 (5.25)	8.05 (7.75)	29.20 (29.45)
24 $[Pd_2L^1(S_2CNPr_2)_2]$	Deep yellow	41.30 (41.55)	5.75 (5.60)	7.30 (7.45)	28.20 (28.35)

* Required values are given in parentheses.



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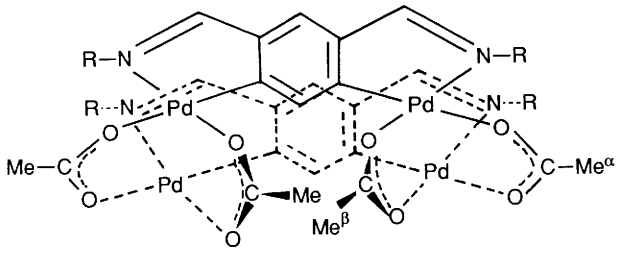

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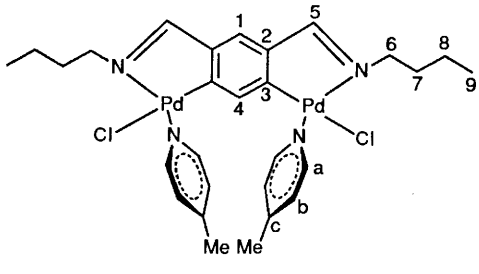
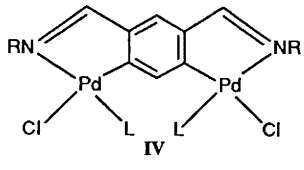


10

exocyclic acetate (β). It may also be noted that for the two aromatic proton singlets (δ 6.56 and 6.72), that appearing at lower field is assignable to C^4H due to its closer proximity to the metallated sites.

The acetato complexes can be converted smoothly to their chloro analogues **5**–**8** by reaction with LiCl in MeOH. The chloro complexes can also be obtained directly by reaction of $Li_2[PdCl_4]$ with the Schiff bases. The tetranuclear composition of these compounds was again verified by determining the relative molecular mass of $[Pd_4(L^3)_2Cl_4]$ **7** in $CHCl_3$ (Found: 1310, **7** requires 1275). The chloro-bridged complexes exhibit bands due to ν(C=N) and ν(C···C) at *ca.* 1600 and 1560 cm^{-1}, respectively.

A number of bridge-cleavage reactions of the μ-chloro



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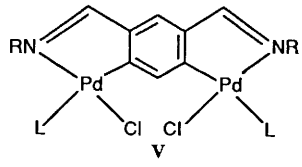

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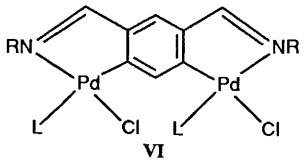


VI

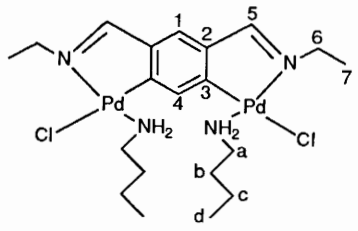
	L	R
9	py	Et
10	4-Mepy	Bu

Table 2 Proton and ^{13}C proton noise-decoupled NMR spectra of the complexes[a]

Complex	
3	δ_H[b] 0.84 (12 H, t, $C^{13}H_3$), 1.20 (40 H, m, $C^{8-12}H_2$), 1.80 (8 H, m, C^7H_2), 1.95 (6 H, s, α-CH_3), 2.20 (6 H, s, β-CH_3), 3.12 (4 H, m, C^6H), 3.50 (4 H, m, C^6H), 6.56 (2 H, s, C^1H), 6.72 (2 H, s, C^4H), 7.50 (4 H, s, C^5H)
10	δ_H[b] 0.82 (6 H, t, C^9H_3), 1.39 (4 H, m, C^9H_2), 1.84 (4 H, m, C^7H_2), 2.24 (6 H, s, C^cH_3), 3.76 (4 H, t, C^6H_2), 5.20 (1 H, s, C^4H), 7.16, 7.20 (4 H, s + m, C^1H + C^bH), 7.80 (2 H, s, C^5H), 8.46 (4 H, m, C^aH)
12	δ_H[b] 0.90 (6 H, t, C^dH_3), 1.30 (6 H, t, C^7H_3), 1.60 (8 H, m, C^cH_2 + C^bH_2), 3.00 (4 H, br, NH_2), 3.68 (8 H, m, C^aH_2 + C^6H_2), 6.84 (1 H, s, C^1H), 6.96 (1 H, s, C^4H), 7.58 (2 H, s, C^5H)
14	δ_H[c,d] 1.28 (6 H, t, C^7H_3), 3.40 (12 H, s, NMe_2), 3.68 (4 H, q, C^6H_2), 4.00 (4 H, m, C^aHH'), 6.86 (1 H, s, C^1H), 7.28, 7.30 (7 H, m + s, C^bH + C^dH + C^4H), 7.41 (4 H, m, C^cH), 8.16 (2 H, s, C^5H)
17	δ_H[b] 1.36 (6 H, t, C^7H_3), 1.94 (6 H, s, C^aH_3), 2.04 (6 H, s, C^cH_3), 3.65 (4 H, q, C^6H_2), 5.36 (2 H, s, C^bH), 7.08 (1 H, s, C^1H), 7.84 (2 H, s, C^5H), 7.90 (1 H, s, C^4H)
18	δ_H[c] 1.96 (6 H, s, C^aH_3), 2.06 (6 H, s, C^cH_3), 4.85 (4 H, s, C^6H_2), 5.36 (2 H, s, C^bH), 7.02 (1 H, s, C^1H), 7.36 (10 H, m, $C^{8-10}H$), 7.76 (2 H, s, C^5H), 7.90 (1 H, s, C^4H)
	δ_C[e] 27.2 (C^a), 27.8 (C^c), 60.5 (C^6), 100.2 (C^c), 124.0 (C^1), 127.8 (C^{10}), 128.7 (C^9), 129.0 (C^8), 133.9 (C^7), 137.1 (C^2), 141.7 (C^4), 164.7 (C^3), 173.7 (C^5), 186.6 (C^b), 188.0 (C^d)
21	δ_H[c] 1.26 (6 H, t, $C^{13}H_3$), 1.38 (6 H, t, C^7H_3), 2.04 (6 H, s, C^8H_3), 3.66 (4 H, q, C^6H_2), 4.20 (4 H, q, $C^{12}H_2$), 4.80 (2 H, s, $C^{10}H$), 7.05 (1 H, s, C^1H), 7.82 (2 H, s, C^5H), 7.88 (1 H, s, C^4H)
	δ_C[e] 14.6 (C^{13}), 15.7 (C^7), 27.1 (C^8), 53.2 (C^6), 53.4 (C^{12}), 84.3 (C^{10}), 123.4 (C^1), 133.6 (C^2), 141.6 (C^4), 162.2 (C^3), 171.6 (C^5), 171.9 (C^9), 187.6 (C^{11})
22	δ_C[b] 1.44 (6 H, t, C^7H_3), 3.80 (4 H, q, C^6H_2), 6.60 (2 H, t, $C^{11}H$), 7.10 (1 H, s, C^1H), 7.20 (2 H, d, C^9H), 7.34 (1 H, s, C^4H), 7.40 (4 H, m, $C^{10}H$ + $C^{12}H$), 7.90 (2 H, s, C^5H), 9.24 (2 H, s, C^8H)
23	δ_H[c] 0.96 (6 H, t, C^9H_3), 1.42 (4 H, m, C^8H_2), 1.82 (4 H, m, C^7H_2), 3.70 (4 H, t, C^6H_2), 3.87 (6 H, s, $C^{10}H_3$), 6.54 (2 H, t, $C^{14}H$), 6.86 (2 H, d, $C^{13}H$), 7.12 (1 H, s, C^1H), 7.24 (4 H, m, $C^{15}H$ + $C^{16}H$), 7.66 (1 H, s, C^4H), 7.84 (4 H, C^5H + $C^{11}H$)
	δ_C[e] 13.8 (C^9), 20.2 (C^8), 32.8 (C^7), 52.7 (C^6), 57.1 (C^{10}), 113.6 (C^{14}), 121.7, 122.0, 132.8, 134.0, 134.7 (aromatic), 141.9 (C^2), 143.1 (C^{12}), 164.2 (C^{17}), 166.2 (C^5), 167.7 (C^3), 172.8 (C^4)
24	δ_H[c] 0.96, 0.99 (12 H, m, $C^{11}H_3$ + $C^{11'}H_3$), 1.35 (6 H, t, C^7H_3), 1.73 (8 H, m, $C^{10}H_2$ + $C^{10'}H_2$), 3.69, 3.71, 3.73 (12 H, m, C^9H_2 + $C^{9'}H_2$ + C^6H_2), 7.00 (1 H, s, C^1H), 7.98 (3 H, s, C^4H + C^5H)
	δ_C[e] 11.2 ($C^{11,11'}$), 14.9 (C^7), 16.10 ($C^{10,10'}$), 51.6 (C^9), 52.7 ($C^{9'}$), 56.1 (C^1), 125.1 (C^1), 139.2 (C^4), 142.6 (C^2), 168.1 (C^3), 172.6 (C^5), 211.3 (C^8)

[a] Unless otherwise stated spectra recorded in $CDCl_3$. [b] 100 MHz. [c] 270 MHz. [d] In [$^2H_6$]Me_2SO. [e] 67.9 MHz.

cyclopalladates has been investigated. Thus, pyridine (py) and 4-methylpyridine (4Me-py) react with $[Pd_4(L^1)_2Cl_4]$ **5** and $[Pd_4(L^2)_2Cl_4]$ **6** to afford $[Pd_2L^1(py)_2Cl_2]$ **9** and $[Pd_2L^2(4Me\text{-}py)_2Cl_2]$ **10** respectively. The dinuclear composition of these non-electrolytic complexes was verified by determining the relative molecular mass of complex **10** in $CHCl_3$ (Found: 730, **10** requires 712). There are three possible structures for **9** and **10**, *viz* **IV**, **V** or **VI**. The ^1H NMR spectral data for the 4-methylpyridine derivative **10** (Table 2) are consistent with structure **IV**. The most remarkable feature is that the C^4H proton resonance has experienced a considerable upfield shift (δ 5.20) relative to that for C^1H (δ 7.16) which would only be



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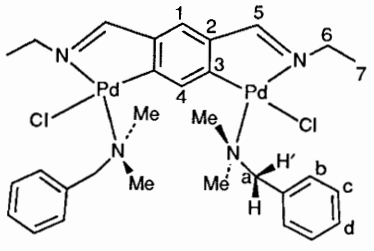

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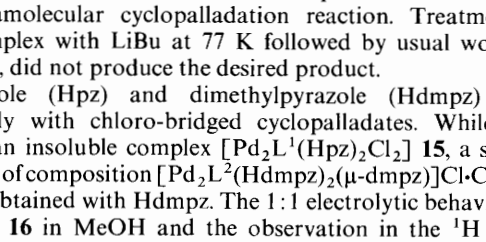
expected for structure **IV** due to the anisotropic shielding effect of the adjacent pyridine rings. The ν(Pd–Cl) value of 305 cm^{-1} observed in these compounds is also closer to the range 300–280 cm^{-1} reported[31] for a series of cyclopalladated compounds in which Cl is *trans* to the Pd–C bond rather than those (355–320 cm^{-1}) for the corresponding *cis* isomers.

The complex $[Pd_4(L^1)_2Cl_4]$ **5** on treatment with py in the presence of $AgClO_4$ produces $[Pd_2L^1(py)_4][ClO_4]_2$ **11**. The ^1H NMR spectrum of this compound again showed[32] that C^4H (δ 4.94) is much more shielded than C^1H (δ 7.50). Confirmation of the orientation of the pyridine rings with respect to the cyclometallated benzene ring has been obtained by determination of the crystal structure of this complex (see later).

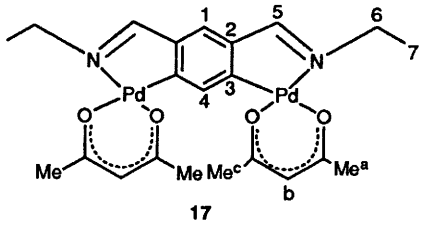
Amines (primary, secondary or tertiary) react in the same manner as pyridine. In this way $[Pd_2L^1(NH_2Bu)_2Cl_2]$ **12**, $[Pd_2L^1(NHEt_2)_2Cl_2]$ **13** and $[Pd_2L^1\{NMe_2(CH_2Ph)\}_2Cl_2]$ **14** have been obtained. As may be noted from the ^1H NMR spectral data of these compounds the incoming ligands are *trans* to Pd–N bonds. The ν(C=N) and ν(Pd–Cl) absorptions of these compounds are observed at *ca.* 1605 and 310 cm^{-1}, respectively. We were interested to see whether complex **14** could undergo an intramolecular cyclopalladation reaction. Treatment of this complex with LiBu at 77 K followed by usual work-up, however, did not produce the desired product.

Pyrazole (Hpz) and dimethylpyrazole (Hdmpz) react differently with chloro-bridged cyclopalladates. While Hpz affords an insoluble complex $[Pd_2L^1(Hpz)_2Cl_2]$ **15**, a soluble complex of composition $[Pd_2L^2(Hdmpz)_2(\mu\text{-}dmpz)]Cl\cdot CH_2Cl_2$ **16** was obtained with Hdmpz. The 1:1 electrolytic behaviour of complex **16** in MeOH and the observation in the ^1H NMR spectrum of three singlets (δ 2.20, 2.24 and 2.32) due to the methyl groups of pyrazole are consistent with structure **VII**.



VII

A variety of neutral, soluble dipalladiobenzene derivatives $[Pd_2L(A\text{–}B)_2]$ has been obtained with monoprotic bidentate chelating ligands such as acetylacetone (Hacac), dibenzoylmethane (Hdbm), the monothio analogue of dibenzoylmethane (Hsdbm), ethylacetoacetate (eaa), salicylaldehyde (Hsal), *N*-



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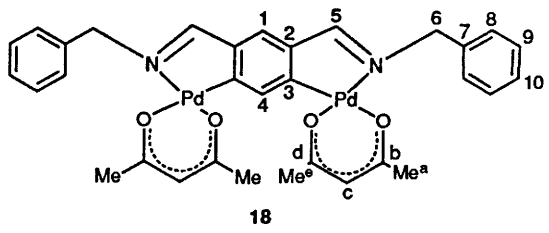

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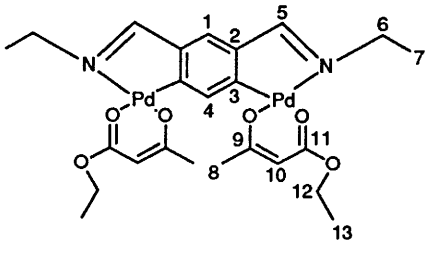

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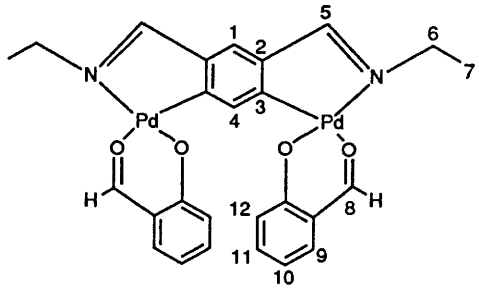

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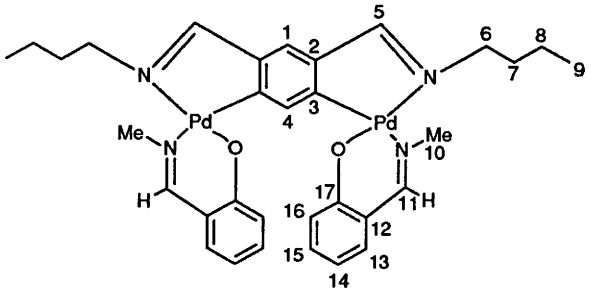

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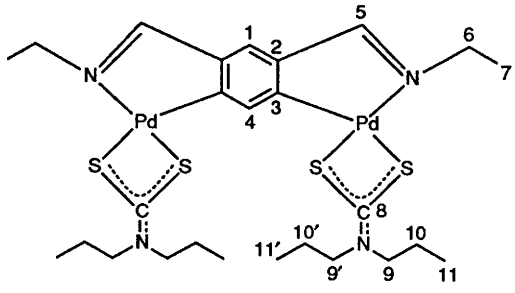

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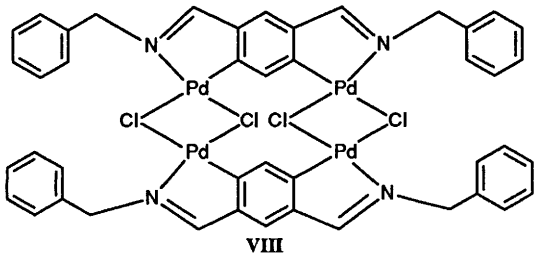
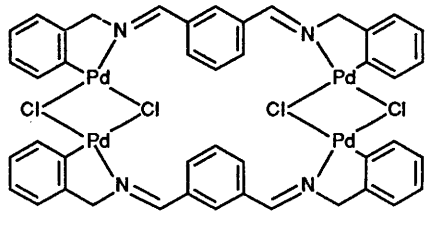
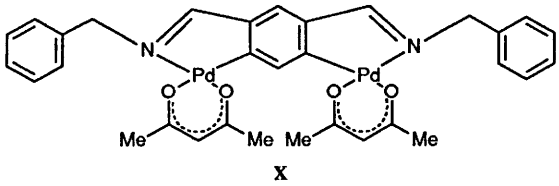


VIII



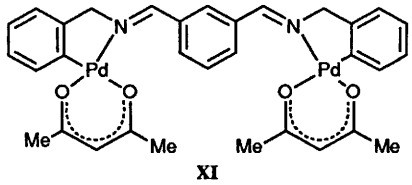
IX

acac⁻



X

acac⁻



XI

methylsalicylideneimine (Hmsaln), and sodium *N,N*-dipropyldithiocarbamate $Na(S_2CNPr_2)$. In all cases a single isomer was obtained, which was characterized by its ^1H and ^{13}C NMR spectra (Table 2). With the asymmetric ligands, ethylacetoacetate, salicylaldehyde and *N*-methylsalicylideneimine the enolic or phenolic oxygen of the product remains *trans* with respect to the nitrogen atom of the cyclopalladated ring.

As already mentioned the ligand H_2L^4 was investigated to see whether *ortho*-palladation occurs to the central or terminal phenyl rings. Since $[Pd_4(L^4)_2Cl_4]$ **8** can have either structure

VIII or **IX**, accordingly $[Pd_2L^4(acac)_2]$ **18** should be either **X** or **XI**. These two structures can be differentiated on the basis of the number of resonances observed in the ^{13}C NMR spectrum; **X** should exhibit 15 lines as against 17 for **XI**. The data given in Table 2 substantiate structure **X**.

In the dithiocarbamato chelate $[Pd_2L^1(S_2CNPr)_2]$ **24** owing to the partial double-bond character of the $Pr_2N\cdots CS_2^-$ moiety, the alkyl groups experience hindered rotation in solution. As a result, the proton chemical shifts due to C^9H_2, $C^{10}H_2$ and $C^{11}H_3$ are slightly different from their counterparts for $C^{9'}H_2$, $C^{10'}H_2$ and $C^{11'}H_3$.

Table 3 summarizes the variation in chemical shifts due to the C^1H, C^4H and CH=N protons in the $[Pd_2L(A–B)_2]$ chelates. It may be noted that the δ values for C^1H (7.00–7.12) are rather insensitive to the nature of the chelating ligand. The variation of δ for CH=N (7.76–7.98) is also marginal. However, considerable variation in chemical shift is observed for protons C^4H ranging from δ 7.34 for $[Pd_2L^1(sal)_2]$ **22** to 7.98 for $[Pd_2L^1(S_2CNPr_2)_2]$ **24** with decreasing order in downfield shift

Table 3 Chemical shifts due to the aromatic and azomethine protons in the cyclometallated ring of the chelates $[Pd_2L(A–B)_2]$

	δ		
Compound	C^1H	C^4H	CH=N
17 $[Pd_2L^1(acac)_2]$	7.08	7.90	7.84
18 $[Pd_2L^4(acac)_2]$	7.02	7.90	7.76
21 $[Pd_2L^1(eaa)_2]$	7.05	7.88	7.82
22 $[Pd_2L^1(sal)_2]$	7.10	7.34	7.90
23 $[Pd_2L^2(msaln)_2]$	7.12	7.66	7.84
24 $[Pd_2L^1(S_2CNPr_2)_2]$	7.00	7.98	7.98

Table 4 Positional parameters of $[Pd_2L^1(py)_4][ClO_4]_2$ **11** with estimated standard deviations in parentheses

Atom	x	y	z	Atom	x	y	z
Pd(1)	0.355 89(8)	0.062 65(5)	0.813 14(9)	C(8)	0.886(1)	−0.343 5(8)	0.482(2)
Pd(2)	0.632 78(9)	−0.290 28(5)	0.639 58(9)	C(9)	0.977(1)	−0.387(1)	0.590(2)
Cl(1)	0.762 3(5)	0.535 1(3)	0.123 3(5)	C(10)	0.559(1)	0.086 5(8)	0.675(1)
Cl(2)	0.110 2(3)	0.857 3(2)	0.432 9(3)	C(11)	0.441(1)	0.217 0(7)	0.767(2)
O(1)	0.856(3)	0.508(2)	0.201(3)	C(12)	0.530(2)	0.256 5(8)	0.712(2)
O(2)	0.780(2)	0.481(1)	0.013(2)	C(13)	0.235(1)	0.191 9(9)	1.024(1)
O(3)	0.637(2)	0.534(1)	0.159(2)	C(14)	0.154(1)	0.259(1)	1.081(2)
O(4)	0.745(1)	0.610(2)	0.068(2)	C(15)	0.051(1)	0.301 8(9)	1.011(2)
O(5)	−0.013(1)	0.901 9(9)	0.470(1)	C(16)	0.031(1)	0.274 7((9)	0.888(2)
O(6)	0.209(1)	0.881 6(8)	0.505(1)	C(17)	0.116(1)	0.205 6(8)	0.837(1)
O(7)	0.119(2)	0.778(1)	0.442(2)	C(18)	0.161(11)	−0.027 8(7)	0.793(1)
O(8)	0.114(2)	0.877(1)	0.309(2)	C(19)	0.084(1)	−0.072 8(9)	0.834(2)
N(1)	0.464 3(9)	0.127 7(5)	0.743(1)	C(20)	0.102(1)	−0.099 3(9)	0.958(2)
N(2)	0.782 4(9)	−0.276 7(6)	0.542(1)	C(21)	0.199(2)	−0.084(1)	0.039(2)
N(3)	0.219 6(9)	0.165 3(6)	0.904 2(9)	C(22)	0.269(1)	−0.038 9(8)	0.991(1)
N(4)	0.252 6(9)	−0.010 8(5)	0.870 3(9)	C(23)	9.367(1)	−0.272 0(8)	0.697(2)
N(5)	0.482(1)	−0.294 3(6)	0.746(1)	C(24)	0.261(1)	−0.280 5(9)	0.760(2)
N(6)	0.677(1)	−0.420 8(5)	0.612(1)	C(25)	0.284(2)	−0.315(1)	0.871(2)
C(1)	0.483(1)	−0.028 2(6)	0.726(1)	C(26)	0.407(2)	−0.341(1)	0.931(2)
C(2)	0.496(1)	−0.112 8(7)	0.722(1)	C(27)	0.503(2)	−0.328 6(9)	0.864(1)
C(3)	0.593(1)	−0.168 9(6)	0.658(1)	C(28)	0.651(1)	−0.453 4(7)	0.498(1)
C(4)	0.684(1)	−0.138 8(7)	0.597(1)	C(29)	0.667(1)	−0.535 9(8)	0.473(2)
C(5)	0.676(1)	−0.056 0(7)	0.599(1)	C(30)	0.710(2)	−0.4586 3(9)	0.575(2)
C(6)	0.577(1)	−0.001 9(6)	0.665(1)	C(31)	0.736(2)	−0.555(1)	0.692(2)
C(7)	0.783(1)	−0.202 7(7)	0.535(1)	C(32)	0.718(2)	−0.471 1(9)	0.706(2)

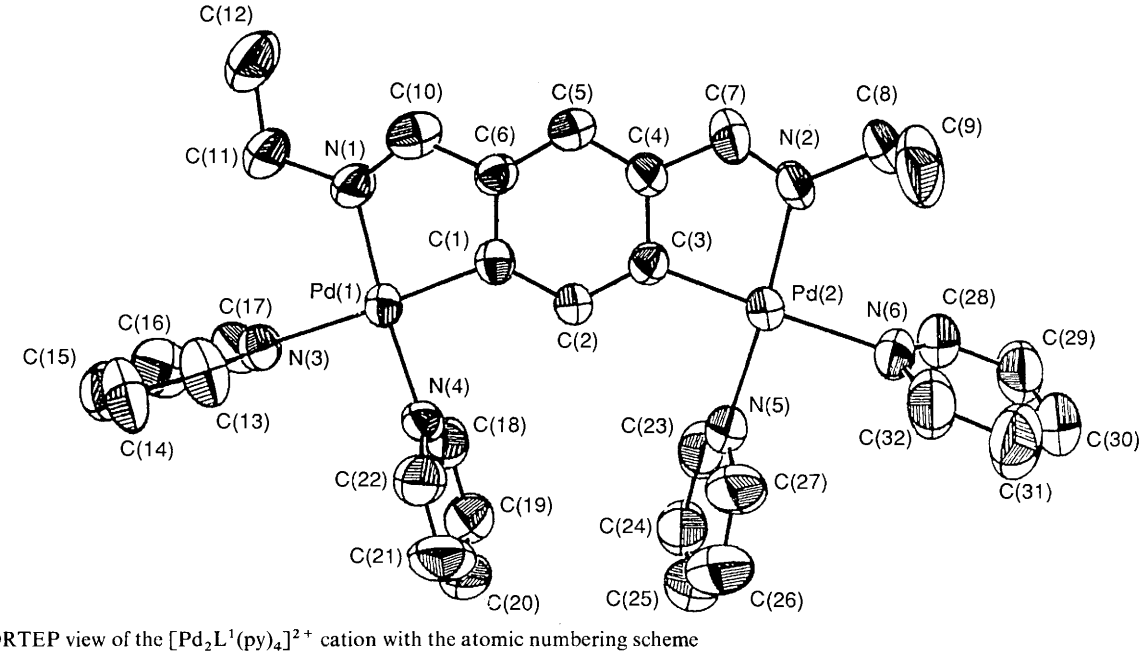


Fig. 1 ORTEP view of the $[Pd_2L^1(py)_4]^{2+}$ cation with the atomic numbering scheme

Table 5 Selected bond lengths (Å) and angles (°) in the $[Pd_2L^1(py)_4]^{2+}$ ion

Pd(1)–N(1)	2.01(2)	Pd(2)–N(2)	2.04(2)
Pd(1)–N(3)	2.152(8)	Pd(2)–N(5)	2.04(1)
Pd(1)–N(4)	2.03(2)	Pd(2)–N(6)	2.138(9)
Pd(1)–C(1)	1.969(9)	Pd(2)–C(3)	1.98(2)
N(1)–Pd(1)–N(3)	96.4(4)	N(2)–Pd(2)–N(6)	96.5(5)
N(1)–Pd(1)–N(4)	174.7(3)	N(2)–Pd(2)–N(5)	175.0(4)
N(1)–Pd(1)–C(1)	81.4(4)	N(2)–Pd(2)–C(3)	82.0(4)
N(3)–Pd(1)–N(4)	88.4(4)	N(6)–Pd(2)–N(5)	88.2(4)
N(3)–Pd(1)–C(1)	177.9(4)	N(6)–Pd(2)–C(3)	177.9(4)
N(4)–Pd(1)–C(1)	93.7(4)	N(5)–Pd(2)–C(3)	93.4(4)

being S_2CNPr_2 > acac ≈ eaa > msaln > sal. Since the deshielding of C^4H with respect to C^1H can be related to the electrophilicity of the palladium centres and hence to electron delocalization in the chelate ring, the above trend therefore indicates the relative electron delocalizing ability of the chelating ligands.

Structure of $[Pd_2L^1(py)_4][ClO_4]_2$ **11**.—An ORTEP[33] diagram of the complex cation $[Pd_2L^1(py)_4]^{2+}$ with the atom labelling scheme is shown in Fig. 1. Positional parameters and selected bond lengths and angles are given in Tables 4 and 5, respectively. The molecular structure shows that the palladium atoms are in distorted square-planar environments. The Pd–N distances can be divided into two groups. The first four, varying between 2.01(2) and 2.04(2) Å, are those involving nitrogen atoms which are *trans* to each other. The two other distinctly longer distances of 2.138(9) and 2.152(8) Å involve nitrogens *trans* to carbon illustrating the higher *trans* effect of the aryl carbon. The Pd–C distances, 1.969(9) and 1.98(2) Å, are comparable to those of other related *ortho*-palladated compounds.[29,30,34–37] In the co-ordination polyhedra the maximum deviations of the atoms from the planes Pd(1)C(1)-N(1)N(3)N(4) (plane A) and Pd(2)N(2)C(3)N(5)N(6) (plane B) are 0.020 and 0.024 Å, respectively. The *cis* angles in these planes vary from 81.4(4) to 96.5(4)°, while the *trans* angles vary from 174.7(4) to 177.9(4)°; the larger angles involve nitrogens and carbons in *trans* positions. The cyclometallated rings Pd(1)-N(1)C(1)C(6)C(10) (plane C) and Pd(2)N(2)C(7)C(4)C(3) (plane D) are also planar within 0.016 and 0.008 Å, respectively. The benzene ring has an inclination of 2.5, 0.4, 1.0 and 2.0° with the planes A, B, C and D respectively. The dihedral angles between the pyridine rings bound to each of the palladium centres are 92.6 [Pd(1)] and 83.4° [Pd(2)].

Experimental

Materials.—Reagents were those available commercially and were used as received. The compound $Pd(O_2CMe)_2$ was prepared by the method of Stephenson *et al.*;[38] benzene-1,3-dicarbaldehyde was prepared by a minor modification of the method of Johnston and Williams;[39] $Na(S_2CNPr_2)$ and $PhCSCH_2COPh$ (Hsdbm) were prepared according to the methods given in refs. 40 and 41 respectively.

Syntheses.—Ligands H_2L^1–H_2L^4. The Schiff bases were prepared by refluxing a benzene solution (50 cm^3) of benzene-1,3-dicarbaldehyde (2.7 g, 20 mmol) and the appropriate amine (40 mmol) for 3 h in a Dean-Stark apparatus. The solvent was removed on a rotary evaporator and the oily residue dried at room temperature at a reduced pressure (0.01 mmHg, *ca.* 1.33 Pa). The ligands thus obtained were essentially pure and used directly for cyclometallation reactions.

$[Pd_4L_2(O_2CMe)_4]$ (L = L^1, **1**; L^2, **2**; L^3, **3**; *or* L^4, **4**). A $CHCl_3$ solution (30 cm^3) of $Pd(O_2CMe)_2$ (0.89 g, 4 mmol) was treated with a $CHCl_3$ solution (5 cm^3) of the Schiff base (2.2 mol) and refluxed for 2 h. Complexes **1**, **2** and **4** which deposited as orange crystals were collected by filtration, washed with $CHCl_3$ and MeOH, and finally dried in vacuum; yield *ca.* 80%. Complex **3** was isolated as an oily residue after removing the solvent on a rotary evaporator. The viscous material became solid on stirring vigorously with Et_2O. After washing with Et_2O, hexane and EtOH it was recrystallized from $CHCl_3$–MeOH; yield 0.82 g (60%).

$[Pd_4L_2Cl_4]$ (L = L^1, **5**; L^2, **6** or L^4, **8**. A mixture of $[Pd_4L_2(O_2CMe)_4]$ (1 mmol) and LiCl (0.17 g, 4 mmol) was refluxed in MeOH (30 cm^3) for 1 h, during which time the bright yellow starting complex became pale yellow. The product was collected by filtration and washed successively with MeOH, water and Me_2CO; the yield was almost quantitative.

$[Pd_4(L^3)_2Cl_4]$ **7**. The salt $Li_2[PdCl_4]$ (1.04 g, 4 mmol) and H_2L^3 (0.72 g, 2 mmol) dissolved in MeOH (50 cm^3) were stirred for 4 h. The solution was filtered and allowed to evaporate slowly. After 24 h the product was collected by filtration, washed with EtOH and Et_2O, and recrystallized from CH_2Cl_2–MeOH; yield 0.5 g (40%).

$[Pd_2L^1(py)_2Cl_2]$ **9**. A stirred suspension of $[Pd_4(L^1)_2Cl_4]$ **5** (0.94 g, 1 mmol) in MeOH (40 cm^3) was treated with pyridine (0.5 cm^3) at room temperature. The material slowly went into solution followed by precipitation of the product which was collected by filtration after 2 h and washed with MeOH and Et_2O; yield 1.1 g (88%).

$[Pd_2L^2(4Me\text{-}py)_2Cl_2]$ **10**. The reaction was carried out in the same way as for **9**, but in this case the product did not precipitate. The solution was evaporated nearly to dryness on a rotary evaporator and triturated with Et_2O. The product was collected by filtration and recrystallized from $CHCl_3$; yield 85%.

$[Pd_2L^1(py)_4][ClO_4]_2$ **11**. To a stirred suspension of $[Pd_2L^1(py)_2Cl_2]$ **9** (0.31 g, 0.5 mmol) in MeOH (20 cm^3) $AgClO_4$ (0.21 g, 1 mmol) and pyridine (0.3 cm^3) were added. After 0.5 h AgCl was filtered off and the filtrate deposited light yellow crystals on slow evaporation; yield 0.4 g (87%).

$[Pd_2(L^1)(NH_2Bu)_2Cl_2]$ **12**. To a stirred suspension of $[Pd_4(L^1)_2Cl_4]$ **5** (0.94 g, 1 mmol) in $CHCl_3$ (30 cm^3) NH_2Bu (0.3 g, 4 mmol) was added. When all the material went into solution, it was filtered. The filtrate on concentration (5 cm^3) and cooling afforded a crystalline product, which was recrystallized from $CHCl_3$–MeOH; yield 0.95 g (77%).

$[Pd_2L^1(NHEt_2)_2Cl_2]$ **13**. After carrying out the reaction as above, the $CHCl_3$ solution was evaporated and the residue stirred with Et_2O. The product was recrystallized from $CHCl_3$–MeOH; yield 0.84 g (68%).

$[Pd_2L^1\{NMe_2(CH_2Ph)\}_2Cl_2]$ **14**. The reaction was carried out in the same way as above but in CH_2Cl_2 (50 cm^3). The solution on concentration (20 cm^3) and cooling gave a crystalline product, which was recrystallized from CH_2Cl_2–MeCN; yield 1.05 g (71%).

$[Pd_2L^1(Hpz)_2Cl_2]$ **15**. A stirred suspension of $[Pd_4(L^1)_2Cl_4]$ **5** (0.94 g, 1 mmol) in CH_2Cl_2 (30 cm^3) was treated with pyrazole (0.28 g, 4.1 mmol). The mixture first became clear but soon the product precipitated, which was collected by filtration and washed with MeOH; yield 1.12 g (92%).

$[Pd_2L^2(Hdmpz)_2(\mu\text{-}dmpz)]Cl\cdot CH_2Cl_2$ **16**. The reaction involving $[Pd_4(L^2)_2Cl_4]$ **6** (1.05 g, 1 mmol) and Hdmpz (0.68 g, 6 mmol) in CH_2Cl_2 (30 cm^3) gave a clear solution on stirring the mixture for 3 h. The product was isolated by adding hexane to the concentrated solution (5 cm^3). Recrystallization of the product was from CH_2Cl_2–C_6H_{14}; yield 1.31 g (76%).

$[Pd_2L(acac)_2]$ (L = L^1, **17** or L^4, **18**). To a stirred boiling suspension of $[Pd_4L_2Cl_4]$ (1 mmol) in MeOH (50 cm^3) was added dropwise a methanol solution (10 cm^3) containing acetylacetone (0.4 g, 4 mmol) and sodium metal (0.092 g, 4 mmol). After refluxing the mixture for 4 h it was filtered and the residue washed several times alternately with water and MeOH. The product was dried in vacum and recrystallized from $CHCl_3$–MeOH; yield *ca.* 80%.

$[Pd_2L^1(dbm)_2]$ **19** *and* $[Pd_2L^1(sdbm)_2]$ **20**. To a stirred

suspension of $[Pd_4(L^1)_2Cl_4]$ **5** (0.94 g, 1 mmol) were added in succession an acetone solution (20 cm^3) of $PhCOCH_2COPh$ (0.9 g, 4 mmol) or $PhCOCH_2CSPh$ (0.96 g, 4 mmol) and an aqueous solution (10 cm^3) of NaOH (0.16 g, 4 mmol). The mixture was refluxed for 2 h and filtered. The residue after washing with MeOH and water was dried in vacuum. The product can be recrystallized from a $CHCl_3$ solution obtained by repetitive extraction; yield *ca.* 70%.

$[Pd_2L^1(eaa)_2]$ **21**. A stirred suspension of $[Pd_4(L^1)_2Cl_4]$ **5** (0.94 g, 1 mmol) in CH_2Cl_2 (100 cm^3) was treated with ethyl acetoacetate (0.52 g, 4 mmol) and an ethanol solution (10 cm^3) of KOH (0.22 g, 4 mmol). The almost clear solution obtained after 6 h was filtered. The filtrate on concentration (20 cm^3) and slow evaporation gave the crystalline product, which was purified by column chromatography over silica using $CHCl_3$ as the eluent; yield 0.83 g (63%).

$[Pd_2L^1(sal)_2]$ **22**. The reaction was carried out as above with salicylaldehyde. The product was recrystallized from $CHCl_3$; yield 78%.

$[Pd_2L^2(msaln)_2]$ **23**. To a stirred suspension of $[Pd_4(L^2)_2Cl_4]$ **6** (1.05 g, 1 mmol) in $CHCl_3$ (60 cm^3) was added a solution of *N*-methylsalicylideneimine obtained by refluxing a mixture of salicylaldehyde (0.49 g, 4 mmol) and methylamine (0.6 cm^3, 40% aqueous solution) in MeOH (20 cm^3). When all the material went into solution (*ca.* 1 h) it was filtered. The filtrate on concentration and cooling afforded crystalline product, which was recrystallized from $CHCl_3$–MeCN; yield 1.2 g (83%).

$[Pd_2L^1(S_2CNPr_2)_2]$ **24**. A stirred suspension of $[Pd_4(L^1)_2Cl_4]$ **5** (0.94 g, 1 mmol) in MeOH (30 cm^3) was treated with an MeOH solution (20 cm^3) of freshly prepared $Na_2(S_2CNPr_2)$ (4.5 mmol). The product was collected after 4 h by filtration and recrystallized from $CHCl_3$–MeOH; yield 1.15 g (77%).

Physical Measurements.—Proton and ^{13}C NMR spectra were recorded on either a Bruker WH 270 or JEOL-FX 100 spectrometer. The spectra were obtained as $CDCl_3$ and $[^2H_6]Me_2SO$ solutions using $SiMe_4$ (δ 0) as the internal reference. Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer. A Philips PR 9500 bridge was used for conductivity measurements. 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 elemental analyser in our Department. Palladium was determined gravimetrically with dimethylglyoxime.

X-Ray Crystal Structure Determination of $[Pd_2L^1(py)_4][ClO_4]_2$ **11**.—Diffraction quality crystals were obtained by diffusion of Et_2O into an MeOH solution of the complex.

Crystal data. $C_{32}H_{34}Cl_2N_6O_8Pd_2$, $M = 913.7$, triclinic, $a = 10.889(1)$, $b = 16.981(2)$, $c = 10.227(1)$ Å, $\alpha = 92.99(1)$, $\beta = 93.14(1)$, $\gamma = 73.65(1)°$, $U = 1809.7(5)$ Å^3 (by least-squares refinement of diffractometer angles for 25 automatically centred reflections, $\lambda = 0.710\,78$ Å), space group $P\bar{1}$, $Z = 2$, $D_c = 1.68$ g cm^{-3}. Light yellow air-stable needles. Crystal dimensions: 0.06 × 0.17 × 0.31 mm, μ(Mo-Kα) = 11.856 cm^{-1}, $T = 295$ K.

Data collection and processing. Data were collected with an Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo-Kα radiation. Orientation and decay during the data collection process were checked by two sets of three control reflections. The intensity data were corrected for Lorentz-polarization effects and for absorption by the empirical method of North *et al.*[42] A total of 5345 reflections were collected in the range $2 < 2\theta < 47°$, of which 3620 independent reflections with $I > 3\sigma(I)$ were used for structure determination.

Structure analysis and refinement. The structure was solved by using the program MULTAN 82[43] in the space group $P\bar{1}$. The *E*-map with the highest combined figure of merit gave the positions of the palladium and chlorine atoms. Isotropic refinement of these atoms, followed by a Fourier difference map led to the location of all the non-hydrogen atom. After reaching convergence in the isotropic mode, all the non-hydrogen atoms refined automatically, except those belonging to the perchlorate ions. Hydrogen atoms were generated using stereochemical constraints. A mixed mode of refinement with all the non-hydrogen atoms varying anisotropically, the perchlorates isotropically, and fixing the hydrogen atoms using a unit weighting scheme with a Dunitz–Seiler factor[44] resulted in convergence at $R = 0.059$ and $R' = 0.062$. The difference map at this stage had maxima of 0.6 e Å^{-3} around the palladium atoms. All computations were carried out using the SDP package of programs[45] for the PDP-11/73 system and scattering factor data given in ref. 46.

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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References

1 J. Dehand and M. Pfeffer, *Coord. Chem. Rev.*, 1976, **18**, 327.
2 M. I. Bruce, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 73.
3 I. Omae, *Chem. Rev.*, 1979, **79**, 287.
4 E. C. Constable, *Polyhedron*, 1984, **3**, 1037.
5 G. R. Newkome, W. E. Puckett, V. K. Gupta and G. E. Kiefer, *Chem. Rev.*, 1986, **86**, 451.
6 I. Omae, *Coord. Chem. Rev.*, 1988, **83**, 187.
7 V. V. Dunina, O. A. Zalevskaya and V. M. Potatov, *Russ. Chem. Rev.*, 1988, **57**, 250.
8 A. Ryabov, *Chem. Rev.*, 1990, **90**, 403.
9 A. Bahsoun, J. Dehand, M. Zinsius, M. Pfeffer, S. E. Bouand and G. I. Borgue, *J. Chem. Soc., Dalton Trans.*, 1979, 547.
10 P. Braunstein, D. Matt, Y. Duasausoy, J. Fischer, A. Mitschler and L. Riaard, *J. Am. Chem. Soc.*, 1981, **103**, 5115.
11 A. K. Mahapatra, D. Bandopadhyay, P. Bandopadhyay and A. Chakravorty, *J. Chem. Soc., Chem. Commun.*, 1984, 999.
12 P. Braunstein, J. Fischer, D. Matt and M. Pfeffer, *J. Am. Chem. Soc.*, 1984, **106**, 410.
13 A. D. Ryabov, I. K. Sakodinskaya and A. J. Yatsimirsky, *J. Chem. Soc., Dalton Trans.*, 1985, 2629.
14 S. E. Bouaoud, P. Braunstein, P. Grandjean, D. Matt and D. Novel, *Inorg. Chem.*, 1986, **25**, 3765.
15 T. Zanecki, J. A. D. Jeffreys, P. L. Pauson, A. Pletrzykowski and K. J. McCullough, *Organometallics*, 1987, **6**, 1553.
16 C. Sinha, D. Bandopadhyay and A. Chakravorty, *Inorg. Chem.*, 1988, **27**, 1173.
17 P. Espinet, G. Garcia, F. J. Herrero, Y. Jeannin and M. Philoche-Levisalles, *Inorg. Chem.*, 1989, **28**, 4207.
18 F. Massarani, M. Pfeffer and G. Van Koten, *Organometallics*, 1989, **8**, 871.
19 A. D. Ryabov, *Synthesis*, 1985, 233.
20 R. F. Heck, *Palladium Reagents in Organic Synthesis*, Academic Press, London, 1985.
21 G. Wu, S. J. Geib, A. L. Rheingold and R. F. Heck, *J. Org. Chem.*, 1988, **53**, 3238.
22 M. Ghedini, S. Armentano, F. Neve and S. Licoccia, *J. Chem. Soc., Dalton Trans.*, 1988, 1565.
23 H. Adams, N. A. Bailey, D. W. Bruce, R. Dhillon, D. A. Dunmur, S. E. Hunt, E. Lalinde, A. A. Maggs, R. Orr, P. Styring, M. S. Wragg and P. M. Maitlis, *Polyhedron*, 1988, **7**, 1861.
24 A. Bose and C. R. Saha, *J. Mol. Catal.*, 1989, **49**, 271.
25 S. P. Molnar and M. Orchin, *J. Organomet. Chem.*, 1969, **16**, 196.
26 H. Onoue and I. Moritani, *J. Organomet. Chem.*, 1972, **43**, 431.
27 J. Albert, J. Granell and J. Sales, *J. Organomet. Chem.*, 1984, **273**, 393.
28 J. Granell, D. Sainz, J. Sales, X. Solans and M. Font, *J. Chem. Soc., Dalton Trans.*, 1986, 1785.
29 P. W. Clark, S. F. Dyke and G. Smith, *J. Organomet. Chem.*, 1987, **330**, 447.

30 J. Albert, M. Gomez, J. Granell, J. Sales and X. Solans, *Organometallics*, 1990, **9**, 1405.
31 B. Crociani, T. Boschi, R. Pietropaolo and U. Belluco, *J. Chem. Soc. A*, 1970, 531.
32 S. Chakladar, P. Paul and K. Nag, *Polyhedron*, 1991.
33 ORTEP, C. K. Johnson, ORTEP II Report ORNL-3794, revised, Oak Ridge National Laboratory, TN, 1971.
34 G. D. Fallon and B. M. Gatehouse, *J. Chem. Soc., Dalton Trans.*, 1974, 1632.
35 J. Dehand, J. Fischer, M. Pfeffer, A. Mitschler and M. Zinsius, *Inorg. Chem.*, 1976, **15**, 2675.
36 G. L. Borgue, S. E. Bouaoud, D. Grandjean, P. Braunstein, J. Dehand and M. Pfeffer, *J. Organomet. Chem.*, 1977, **136**, 375.
37 J. Granell, J. Sales, J. Villarrassa, J. P. Declerq, G. Germain, C. Miravitlles and X. Solans, *J. Chem. Soc., Dalton Trans.*, 1983, 2441.
38 T. A. Stephenson, S. M. Morehouse, A. R. Powell, J. P. Heffer and G. Wilkinson, *J. Chem. Soc.*, 1965, 3632.
39 H. W. Johnston and J. R. Williams, *J. Am. Chem. Soc.*, 1947, **69**, 2065.
40 F. W. Moore and M. L. Larson, *Inorg. Chem.*, 1967, **6**, 998.
41 S. H. H. Chaston, S. E. Livingstone, T. N. Lockyer, V. A. Pickles and J. S. Shanon, *Aust. J. Chem.*, 1965, **18**, 673.
42 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
43 P. Main, G. Germain, J. P. Declercq and M. M. Woolfson, MULTAN 82, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Data, University of York, 1982.
44 J. D. Dunitz and P. Seiler, *Acta Crystallogr., Sect. B*, 1973, **29**, 589.
45 Enraf-Nonius Structure Determination Package, Enraf-Nonius, Delft, 1985.
46 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

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