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DI-μ-CHLORODICHLOROBIS(η^4-TETRAKIS-*p*-METHOXYPHENYLCYCLOBUTADIENE)DIPALLADIUM: X-RAY STRUCTURE DETERMINATION, SPECTROSCOPIC PROPERTIES, AND REACTIONS WITH NUCLEOPHILES

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Summary

Reaction of bis-*p*-methoxyphenylacetylene (An_2C_2) with $Na_2[PdCl_4]$ gave $[(\eta^4\text{-}An_4C_4Pd)_2Cl_3][Pd_2Cl_6]_{0.5}$ which with HCl gave $[(An_4C_4Pd)_2Cl_4]$ (6). The complexes $[(An_4C_4Pd)_2Y_4]$ (Y = Br, I, NCS, or NCO) were obtained by metathesis. Reaction of 6 with NaN_3 gave the η^3-cyclobutenyl complex $Na[\{(N_3)An_4C_4Pd\}(N_3)Cl]$. With other nucleophiles OR^- (6) gave the dinuclear η^3-cyclobutenyl complexes $[\{(RO)An_4C_4Pd\}_2Cl_2]$ (R = H, Me, Et, Pr^i or $COCH_3$); $AgPF_6$ in the presence of L (MeCN, Bu^tNC, Me_2NC, Me_2C_2 or py) gave $[(\eta^4\text{-}An_4C_4Pd)_2Cl_2L_2][PF_6]_2$ and in the presence of bipy gave $[\eta^4\text{-}An_4C_4Pd(bipy)Cl]PF_6$. The X-ray crystal structure of the dinuclear complex 6 showed each Pd to be η^4-coordinated to a square planar cyclobutadiene, and bound to three chlorines (two bridging and one terminal). The far IR spectra provide a useful guide to the structures of many of these complexes, but 6 is remarkable in that the spectrum between 200 and 300 cm^{-1} changes dramatically on grinding.

Introduction

Some years ago one of us reported on the synthesis and characterisation of a number of tetraarylcyclobutadienepalladium(II) complexes [1,2] which arise easily from the reaction of the appropriate diarylacetylene with palladium chloride or a derivative thereof [3]. The early work indicated some unexpected features for the complex $[(R_4C_4Pd)_2Cl_4]$ (**1**) where R = *p*-methoxyphenyl (anisyl) [2], and which merited clarification. Further, there is to date only one X-ray crystal structure of a cyclobutadienepalladium complex, namely of the rather unusual compound **2** which is monomeric [4]. By contrast, molecular weight measurements showed complexes **1** to be dinuclear [1,2], and a structure similar to that established many years ago for $[(Me_4C_4Ni)_2Cl_4]$ (**3**) [5] was proposed. The present work was undertaken in order to resolve the anomalies

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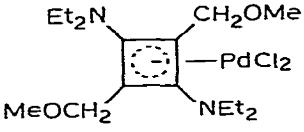
[2] and to definitively determine the structure



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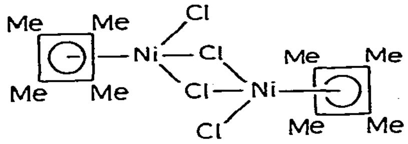

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Results and discussion

Reaction of di-*p*-anisylacetylene (An_2C_2) with sodium tetrachloropalladate in ethanol gave a complex which is now identified as **4** by microanalysis, IR and far IR spectroscopy (Table 1) and NMR spectroscopy (Table 2) and its relationship to $[(Bu^t_2Me_2C_4Pd)_2Cl_3][Pd_2Cl_6]_{0.5}$, the structure of which has been established [6,7].

Reaction of **4** with HPF_6 or HBF_4 in dichloromethane gave **5a** or **5b**, respectively; reaction with HY in DMF gave **6**, **7a** or **7b**, while reaction of **6** with either KSCN or KCNO gave **7c** or **7d**. These complexes were all characterised by microanalysis and spectroscopy.

Good crystals of complex **6** were obtained by slow evaporation from a dichloromethane diethyl ether solution and their structure was determined. This showed (Fig. 1) that the complex was centrosymmetric and dinuclear with the

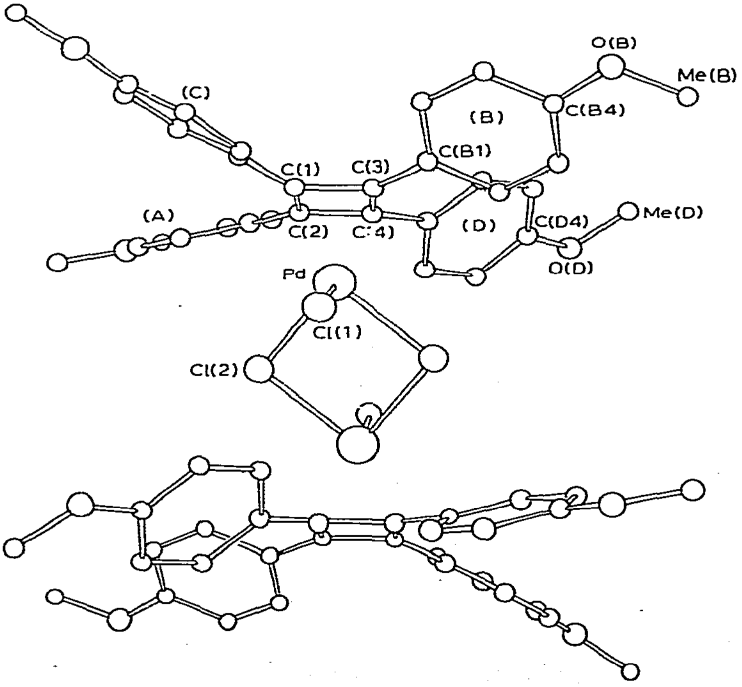
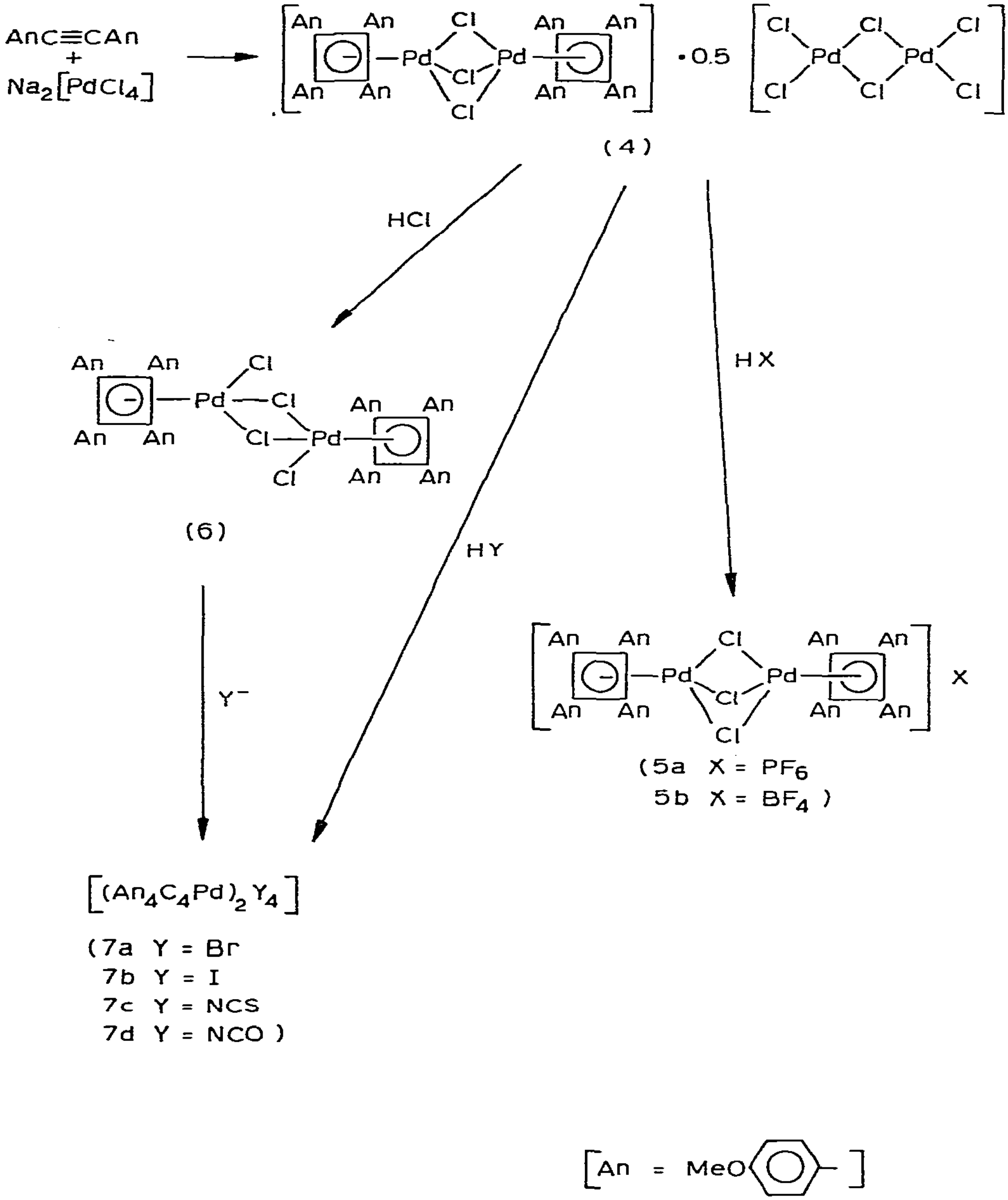


Fig. 1. The structure of $[(An_4C_4Pd)_2Cl_4]$, complex **6**.



SCHEME 1

palladium atoms bridged by two chlorines, and each palladium η^4-bonded to the cyclobutadiene ring of the An_4C_4 ligand as well as to a terminal chlorine. The C_4 ring is square planar within the limits of accuracy of the determination [mean C—C, 1.448(18) Å] and the metal is 1.878(18) Å away from the plane of the ring. The Pd—C bond lengths vary slightly [2.092—2.189(13) Å] but this probably arises from the asymmetry induced by the three chlorine ligands on the other side. The terminal chlorine is at 2.419(4) Å from the metal while the two bridging chlorines are slightly further away, at 2.510 and 2.533(3) Å. The *p*-methoxyphenyl substituents are bent back away from the ring.

This structure is very similar to the one found for the nickel complex **3** but contrasts sharply with that for the mononuclear **2**. While the ring C—C distances in **2** are all similar [mean 1.470(5) Å] and close to those in **6**, the ring in **2** is not planar but has a fold of 155° about the diagonal $MeOCH_2C\cdots CCH_2OMe$, with the palladium attached to the convex side.

A useful tool for the investigation of metal—halogen binding is far IR spectroscopy. In general, though there are many exceptions, $\nu(Pd—Cl_{terminal})$ are usually found above 300 cm^{-1} while $\nu(Pd—Cl_{bridge})$ come below. This in principle allows a ready identification of the mode of bonding from the far IR spectrum. For example, $[(Ph_4C_4Pd)_2Cl_4]$ which is anticipated to have the same structure as **6** shows bands at 213m, 300sh, and 306vs, while $[(Ph_4C_4Pd)_2Cl_3]$-$[PF_6]$, isostructural with **5**, shows bands at 214 and 237 cm^{-1} [7]. However, the spectrum of **6** in the region 150—400 cm^{-1} varied substantially from one sample to another. In particular, it was found that on dissolution in dichloromethane and reprecipitation the complex **6** darkened, had higher Pd and Cl

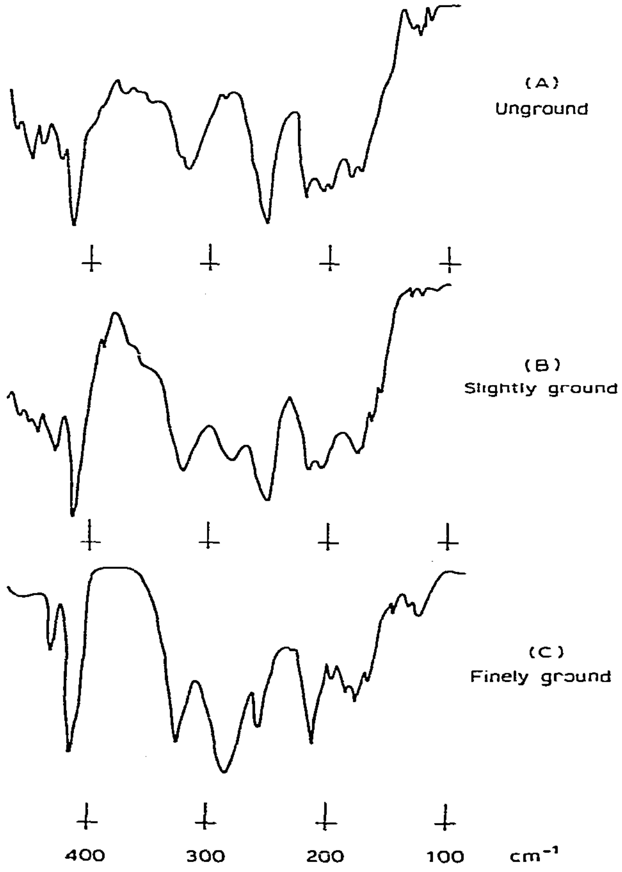


Fig. 2. The effect of grinding on the far IR spectrum of $[(An_4C_4Pd)_2Cl_4]$, complex **6**.

contents, and developed bands in the region of 325 cm^{-1}. These effects were intensified when the reprecipitation were repeated. These results may be taken to indicate the slow reformation of **4** from **6**; unfortunately these reactions are not very clean and it has not been possible to establish what the (organic) by-products are.

Even more surprising are the changes that occur in the far IR spectra on grinding. Figure 2 shows the results of one such series of experiments; the same sample was used in each. In the first one (Fig. 2a) a freshly precipitated microcrystalline sample was used in a Nujol mull with essentially no grinding. Figures 2b and 2c show the spectra of the same sample with some grinding (ca. 30 sec) and considerable grinding (5 min). The most dramatic effect is the emergence of a peak at 280 cm^{-1} on repeated grinding, but other minor changes also occur [*].

The cause of these changes is not clear but may be related to surface effects in the smaller (more well-ground) crystallites and, possibly, to the breaking and reforming of Pd—Cl bonds. The phenomenon seems to be very localised; for example $[(Ph_4C_4Pd)_2Cl_4]$ does not show any changes in the far IR spectrum on grinding nor have we come across other examples of it in other systems.

Reaction of **6** with sodium azide did not give **7** ($Y = N_3$). Instead, nucleophilic attack occurred both at the metal and at the C_4 ring to give the η^3-cyclobutenyl complex **8**. Elemental analysis was consistent with the structure shown as were the strong bands at 372 ($Pd—Cl_{terminal}$), 2050 (metal-bonded azide [8]) and at 2095 cm^{-1} (assigned to C-bonded azide [9]) in the IR. The ^1H NMR spectrum showed a complex pattern for the phenyl protons and two peaks for the methoxy hydrogens. The ^1H NMR spectra of complexes **4**—**7** all showed a singlet for the methoxy protons and one double doublet for the *o*- and *m*-phenyl protons. Clearly, therefore, the symmetry of the C_4 ring has been lost in **8**. Products with similar ^1H NMR spectra were obtained when the cyclobutadiene complex **6** was reacted with other nucleophiles; water (OH^-), acetate, methoxide, ethoxide, and isopropoxide. These are formulated as the η^3-cyclobutenyl complexes **9a**—**9d** with the OR^- having attacked at the ring *exo*- to the metal, by analogy to the *exo*-ethoxytetraphenylcyclobutenyl complex which has been shown to result from reaction of $[(Ph_4C_4Pd)_2Cl_4]$ with ethanol [10].

It was previously noted [2] that **9d** could not be isolated from reaction of ethanol with complex **6**; in fact, the reactions with alcohols in the presence of base are fast and give the desired product in good yield, when they are carried out carefully. Decomposition occurs readily and the product must be isolated quickly.

In the presence of silver hexafluorophosphate complex **6** loses one chlorine per palladium. When the reaction is carried out in the presence of a suitable ligand, L, the complexes **10a**—**10d** may be isolated. Both the C_4 ring and the Pd_2Cl_2 are retained and only the terminal chlorines are lost. The structures $[(An_4C_4Pd)_2Cl_2L_2][PF_6]_2$ are shown by the presence of medium to weak bands at 220—240 cm^{-1} in the ($Pd—Cl_{bridge}$) region in the far IR spectra of these com-

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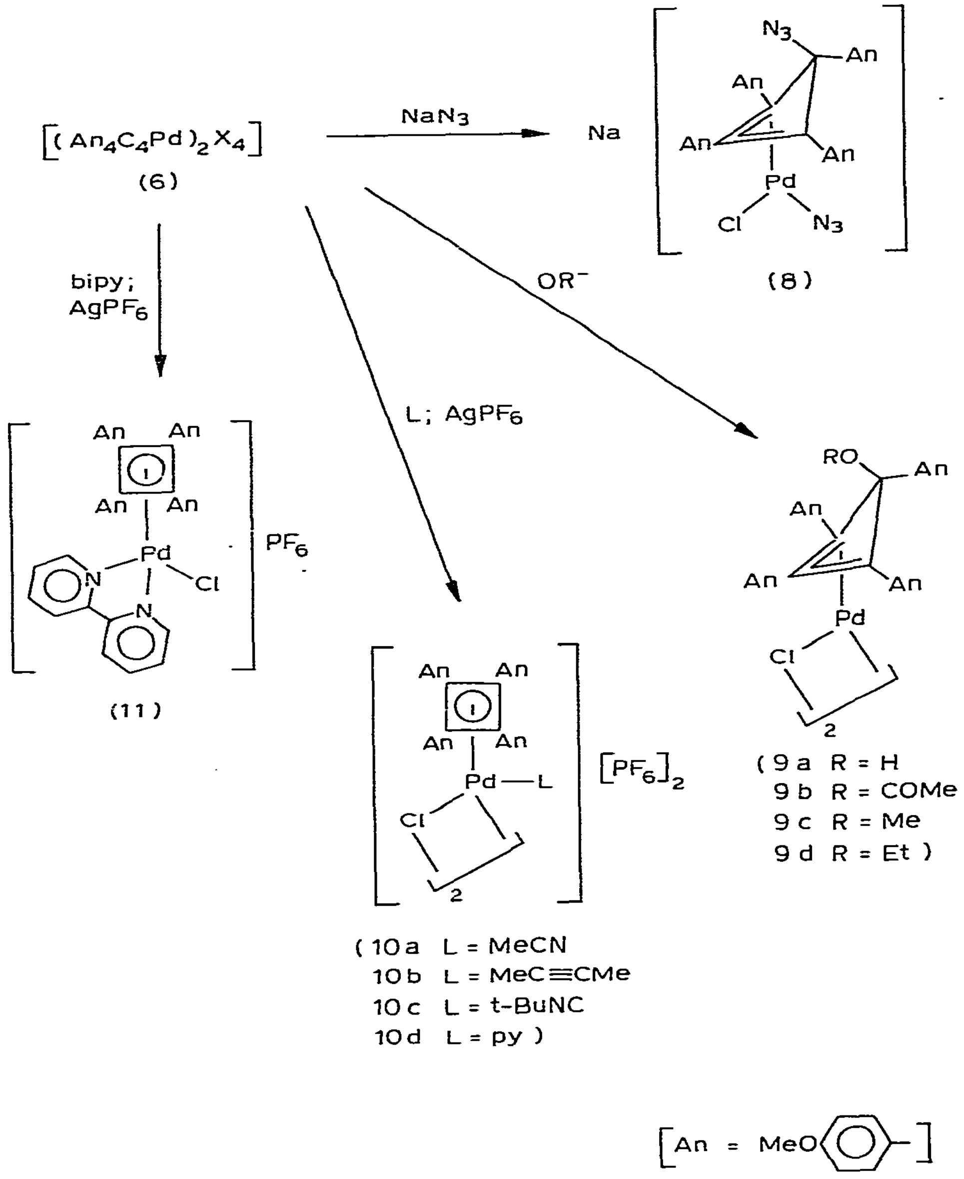
[*] We thank Professor S.F.A. Kettle for first drawing our attention to these changes.



SCHEME 2

plexes and by the very clean ^{1}H NMR spectra, double doublets in the aromatic region and only a singlet for the methoxy protons. By contrast, the bipyridyl complex $[(An_4C_4Pd)Cl(bipy)][PF_6]$ is probably mononuclear since it shows ν(PdCl) at 350 cm^{-1} which is well in the Pd—Cl$_{\text{terminal}}$ region. However, the C_4 ring still remains intact.

An unstable acetone solvate species, presumably $[(An_4C_4Pd)_2Cl_2(Me_2CO)_2]$-$[PF_6]$, could be generated in acetone solution but could not be isolated. The ^{1}H NMR spectrum of this species in $(CD_3)_2CO$ showed the usual double doublet at δ 7.55 (J 9 Hz) and a singlet at 3.98. If used quickly, this solution can serve as a convenient precursor to **10a**—**10d**. An intriguing complex is that incorporating dimethylacetylene (but-2-yne) **10b** in which each palladium appears to bind one acetylene, acting as a 2-electron donor. The weak peak in the IR at 2020 cm^{-1} may be due to $\nu(C{\equiv}C)$ of the coordinated acetylene; with more confidence we can assign the ^{13}C resonance at δ 67.9 to coordinated $MeC{\equiv}CMe$ [11].

This complex did not give the benzene, $C_6An_4Me_2$, supporting our previous contention that benzenes do not arise directly from reactions of cyclobutadienes and acetylenes in palladium-mediated reactions [3]. All these cationic and dicationic complexes were extremely susceptible to reaction with nucleophiles, which usually led to decomposition. Pure dry solvents were required in order to prepare and crystallise them.

The ^{13}C spectra of the cyclobutadiene complexes **4**, **7c**, **10b** and **11** as well as of the cyclobutenyl complexes **8** and **9b** support the structural assignments; the multiplicity shown by the phenyl carbons was particularly helpful.

Experimental

All reactions were carried under nitrogen, though few of the complexes isolated were air-sensitive. All solvents were carefully dried before use. Microanalyses were carried out by the Department of Chemistry Microanalysis Service (Table 1), NMR spectra were determined on PE-12B (^1H, 60 MHz) and PFT-100 (^{13}C, 25 MHz) spectrometers (Table 2), and far IR spectra (Table 1) were determined on a PE-180 with far IR attachment. Typical preparations are given.

$[(An_4C_4Pd)_2Cl_3][Pd_2Cl_6]_{0.5}$ (4)

Di-*p*-anisylacetylene (26.1 g, 0.11 mol) in dichloromethane (50 cm^3) was added to a stirred solution of $Na_2[PdCl_4]$ (14.7 g, 0.005 mol) in 95% aqueous EtOH (50 cm^3). After 0.5 h the solution was filtered and the filtrate reduced to dryness. The residue was dissolved in the minimum dichloromethane and the product precipitated with petroleum ether (50 cm^3). Yield 30.5 g (68%).

$[(An_4C_4Pd)_2Cl_3][PF_6]$ (5a)

Hexafluorophosphoric acid (5 cm^3, 11 N) was added dropwise to a stirred solution of complex **4** (2 g, 1.4 mmol) in dichloromethane (50 cm^3). After 3 h the dichloromethane solution was washed with water (3 × 50 cm^3) and dried over anhydrous sodium sulphate. The product was precipitated using petroleum ether (50 cm^3). Yield 1.18 g (60%).

$[(An_4C_4Pd)_2Cl_4]$ (6)

Aqueous HCl (5 cm^3, 11 N) was added dropwise to a stirred solution of complex **4** (5 g, 3.3 mmol) in DMF (20 cm^3). After 0.5 h the mixture was cooled to 0°C and the insoluble product filtered off. After washing the residue with DMF (2 × 5 cm^3) and water (2 × 5 cm^3) the product was precipitated from a dichloromethane solution with petroleum ether (20 cm^3). Yield 2.77 g (63%).

(continued on p. 383)

TABLE 1

MICROANALYTICAL AND IR SPECTROSCOPIC DATA

Complex	Yield (%)	Microanalyses ^{a}				IR (cm^{-1})	
		C (%)	H (%)	N (%)	Other (%)	ν(Pd—Cl)	Other
$[(An_4C_4Pd)_2Cl_3][Pd_2Cl_6]_{0.5}$ (4)	68	51.6 (51.8)	3.6 (3.8)		Cl, 15.1 (14.3)	218s, 324vs	
$[(An_4C_4Pd)_2Cl_3][PF_6]$ (5a)	60	53.8 (54.2)	3.9 (3.9)		Cl, 7.8 (7.5)	213s	ν(PF) 842vs
$[(An_4C_4Pd)_2Cl_3][BF_4]$ (5b)	54	56.2 (56.5)	4.1 (4.1)		Cl, 8.0 (7.8)	205s	ν(BF) 1100vs
$[(An_4C_4Pd)_2Cl_4]$ (6)	63	58.8 (58.8)	4.3 (4.3)		Cl, 11.0 (10.9)	variable, see Fig. 2	
$[(An_4C_4Pd)_2Br_4]$ (7a)	59	52.1 (51.7)	3.7 (3.8)		Br, 21.9 (21.6)		ν(PdBr) 142s, 165s
$[(An_4C_4Pd)_2I_4]$ (7b)	38	46.0 (45.9)	3.4 (3.3)		I, 31.0 (30.4)		ν(PdI) 129m
$[(An_4C_4Pd)_2(NCS)_4]$ (7c)	76	58.5 (58.4)	4.4 (4.0)	4.0 (4.0)	S, 9.0 (9.2)		ν(SCN) 2095s, 2130s
$[(An_4C_4Pd)_2(NCO)_4]$ (7d)	61	61.2 (61.2)	4.2 (4.2)	4.3 (4.3)			ν(NCO) 2195vs, 2255vs

Na[{(N_3)An_4C_4Pd}Cl(N_3)Cl] (**8**)	78	53.0 (53.0)	5.2 (3.9)	10.5 (11.6)	Cl,	5.0 (4.9)	372vs	ν(N_3) 2050s, 2095s
[{(HO)An_4C_4Pd}$_2$$Cl_2$] (**9a**)	92	60.3 (60.5)	4.5 (4.6)		Cl,	5.7 (5.6)	244s	ν(OH) 3490w
[{(AcO)An_4C_4Pd}$_2$$Cl_2$] (**9b**)	69	60.3 (60.3)	4.7 (4.6)		Cl,	5.3 (5.2)	255m	ν(CO_2) 1660br
[{(MeO)An_4C_4Pd}$_2$$Cl_2$] (**9c**)	96	61.0 (61.0)	4.8 (4.8)		Cl,	5.9 (5.5)	248m	
[{(EtO)An_4C_4Pd}$_2$$Cl_2$] (**9d**)	69	61.0 (61.4)	5.0 (5.0)		Cl,	5.8 (5.4)	233m	
[(An_4C_4Pd)$_2$$Cl_2$(MeCN)$_2$][$PF_6$]$_2$ (**10a**)	65	50.6 (50.8)	3.8 (3.9)	1.7 (1.7)	Cl,	4.6 (4.4)	230m	ν(CN) 2315, 2330s ν(PF) 845vs
[(An_4C_4Pd)$_2$$Cl_2$($Me_2C_2$)$_2$][$PF_6$]$_2$ (**10b**)	67	52.9 (52.9)	4.2 (4.2)		Cl,	4.8 (4.4)	221m	ν(C≡C) 2020w ν(PF) 840vs
[(An_4C_4Pd)$_2$$Cl_2$($Bu^tNC$)$_2$][$PF_6$]$_2$ (**10c**)	80	53.0 (52.6)	4.5 (4.4)	1.8 (1.7)	Cl,	4.0 (4.2)	234m	ν(NC) 2195, 2255s ν(PF) 837vs
[(An_4C_4Pd)$_2$$Cl_2(py)_2$][$PF_6$] (**10d**)	74	53.0 (52.7)	4.1 (3.9)	1.5 (1.7)	Cl,	4.4 (4.3)	238m	ν(PF) 840vs
[(An_4C_4Pd)Cl bipy][PF_6] (**11**)	72	54.3 (54.9)	4.1 (3.9)	3.3 (3.1)	Cl,	4.0 (3.9)	350m	ν(PF) 845vs

[a] Calculated values in parentheses.

TABLE 2

^1H AND $^{13}C\{^1H\}$ NMR SPECTRA (δ) [a]

Complex	^1H			$^{13}C\{^1H\}$
	Phenyl protons	Methoxy protons	Other	
$[(An_4C_4Pd)_2Cl_3][Pd_2Cl_6]_{0.5}$ [a] (4)	7.32 (dd, *J* 9 Hz)	3.87		
$[(An_4C_4Pd)_2Cl_3][PF_6]$ [b,c] (5a)	7.26 (dd, *J* 10 Hz)	3.85		
$[(An_4C_4Pd)_2Cl_3][BF_4]$ [b] (5b)	7.30 (dd, *J* 9 Hz)	3.85		
$[(An_4C_4Pd)_2Cl_4]$ [a,d] (6)	7.38 (dd, *J* 8 Hz)	3.88		56.5 (OCH_3), 110.4 (C_4 ring) 115.6, 116.7, 132.8, 164.1 (aromatics)
$[(An_4C_4Pd)_2Br_4]$ [b] (7a)	7.43 (dd, *J* 10 Hz)	3.95		
$[(An_4C_4Pd)_2I_4]$ [b] (7b)	7.44 (dd, *J* 9 Hz)	3.90		
$[(An_4C_4Pd)_2(SCN)_4]$ [b] (7c)	7.06 (dd, *J* 9 Hz)	3.88		55.6 (OCH_3, 108.2 (C_4 ring) 114.9, 117.0, 131.9, 162.4 (aromatic ring), 232.3 (*SC*N)
$[(An_4C_4Pd)_2(CNO)_4]$ [b] (7d)	7.08 (dd, *J* 9 Hz)	3.93		
$Na[\{(N_3)An_4C_4Pd\}Cl(N_3)]$ [b] (8)	7.85—6.73) (m)	3.87, 3.71		55.1 (ArO*Me*), 79.6 and 87.5 (*C*$_4$ ring), 112—160 (⩾15 lines, aromatics)
$[\{(HO)An_4C_4Pd\}_2Cl_2]$ [b] (9a)	8.24—6.64 (m)	3.91, 3.77	1.55 (1H, —O*H*)	
$[\{(AcO)An_4C_4Pd\}_2Cl_2]$ [b] (9b)	7.80—6.45 (m)	3.79, 3.68, 3.61	3.70 (3H, OOCCH_3)	
$[\{(MeO)An_4C_4Pd\}_2Cl_2]$ [b] (9c)	8.12—6.59 (m)	3.85, 3.79, 3.69	3.28 (3H, —OCH_3)	51.8 (C_4O*Me*), 55.1 (ArO*Me*), 88.9 and 89.9 (*C*$_4$ ring), 113—160 (⩾15 lines, aromatics)
$[\{(EtO)(An_4C_4)Pd\}_2Cl_2]$ [b] (9d)	8.09—6.66 (m)	3.87, 3.83, 3.23	3.57 (q, 2H, —CH_2—) 1.08 (q, 3H, —CH_3)	
$[(An_4C_4Pd)_2Cl_2(MeCN)_2][PF_6]_2$ [e] (10a)	7.43 (dd, *J*(HH) 8 Hz)	3.95	2.29 (3H, CH_3CN)	
$[(An_4C_4Pd)_2Cl_2(MeC_2)_2][PF_6]_2$ (10b)	7.40 (dd, *J* 8 Hz)	3.95	2.41 (6H, CH_3C ; CCH_3)	22.1 (*Me*C≡), 55.7 (O*Me*), 67.9 (Me*C*≡), 129.5 (C_4 ring), 115.3, 130.3, 131.9 and 163.6 (aromatics)
$[(An_4C_4Pd)_2Cl_2(Bu^tNC)_2][PF_6]_2$ (10c)	7.42 (dd, *J* 9 Hz)	3.96	1.56 (9H, br, ^{t}*Bu*NC)	
$[(An_4C_4Pd)_2Cl_2(py)_2][PF_6]_2$ [e] (10d)	7.48 (dd, *J* 9 Hz)	3.90	7.80—7.33 (m, 5H, pyridine)	
$[(An_4C_4Pd)Cl(bipy)][PF_6]$ (11)	7.41 (dd, *J* 10 Hz)	3.92	8.80—7.49 (m, 6H, bipy)	56.1 (ArO*Me*), 107.4 (*C*$_4$ ring), 115.9, 117.8, 132.8 and 163.7 (*Ar*OMe), 124.2, 128.2, 141.2, 151.3, 153.3 (bipy)

[a] In CD_2Cl_2. [b] In $CDCl_3$. [c] Unchanged at −80°C. [d] At 30°C the 220 MHz spectrum shows two doublets (δ 6.96, 7.80); at −90°C the lower field resonance was split into doublets (δ 7.70, 7.81, *J* 10 Hz) probably due to restricted rotation. [e] In acetone-d_6.

Crystal structure determination of (**6**)

Crystals of complex **6** were obtained by the gradual evaporation of solvent from a dichloromethane/diethyl ether solution at 5°C. The crystals were small but generally well shaped, but they lost their diffracting ability after about 24 h. A stable specimen was obtained by totally encapsulating the crystal in glue.

Crystal Data. ($\bar{\lambda}$ 0.71069 Å). μ(Mo-K_α) 14.75 cm^{-1}: $C_{64}H_{56}O_8Pd_2Cl_4$. M = 1307.8; Triclinic, a 13.81(1), b 12.75(1), c 12.40(1), α 67.20(3), β 123.91(4), γ 107.88(2), U 1658(3) Å^3. D_m 1.29 g cm^{-3}. $Z = 1$. D_c 1.31 g cm^{-3}. $F(000)$ = 664. Space group, $p_{\bar{1}}$.

A Stoe Stadi-2 two circle diffractometer was used to collect the data. Intensity data was collected within a sphere $6.5 < 2\theta < 50°$ (layers 0*kl* to 14*kl*). 4575 Independent reflections with $I > 3\sigma(I)$ and background difference $\Delta <$

TABLE 3

FRACTIONAL COORDINATES OF THE NON-HYDROGEN ATOMS IN THE UNIT CELL OF $[(An_4C_4Pd)_2Cl_4]$ (6)

Pd	0.47886	0.3008	0.03494
Cl(1)	0.29250	0.29809	0.02492
Cl(2)	0.57663	0.48792	0.16668
C(A1)	0.68484	0.45567	−0.09771
C(A2)	0.62419	0.34460	−0.09902
C(A3)	0.72171	0.51695	−0.19198
C(A4)	0.69707	0.46645	−0.28568
C(A5)	0.63692	0.35514	−0.28903
C(A6)	0.59995	0.29672	−0.19470
O(A)	0.73585	0.53187	−0.37380
Me(A)	0.69999	0.48781	−0.48366
C(B1)	0.50832	0.07950	0.23162
C(B2)	0.39422	0.03432	0.20311
C(B3)	0.37262	−0.05947	0.29582
C(B4)	0.46506	−0.10672	0.41663
C(B5)	0.57971	−0.06212	0.44941
C(B6)	0.59976	0.03023	0.35592
O(B)	0.43460	−0.19927	0.49895
Me(B)	0.53052	−0.25823	0.62331
C(C1)	0.38364	0.15243	−0.12065
C(C2)	0.33913	0.22626	−0.25171
C(C3)	0.34068	0.03681	−0.09802
C(C4)	0.25399	−0.00580	−0.20774
C(C5)	0.21244	0.06561	−0.33829
C(C6)	0.25084	0.18068	−0.36109
O(C)	0.13559	0.01346	−0.43689
Me(C)	0.09302	0.08607	−0.57641
C(D1)	0.74974	0.28660	0.24952
C(D2)	0.76473	0.27735	0.37321
C(D3)	0.87460	0.30471	0.47626
C(D4)	0.96880	0.34430	0.45630
C(D5)	0.95393	0.35372	0.33045
C(D6)	0.84706	0.32803	0.22897
O(D)	1.07662	0.37593	0.54726
Me(D)	1.10335	0.36151	0.68281
C(1)	0.48212	0.20024	−0.01089
C(2)	0.58367	0.28206	−0.00321
C(3)	0.53248	0.17201	0.13361
C(4)	0.63451	0.25383	0.14000

TABLE 4

IMPORTANT BOND LENGTHS AND BOND ANGLES FOR $[(\mathrm{An_4C_4Pd})_2\mathrm{Cl_4}]$ (6) (e.s.d.s in parentheses) [a]

	(Å)		(°)
Pd—Cl(1)	2.419(4)	Cl(1)—Pd—Cl(2)	99(1)
Pd—Cl(2)	2.533(3)	Cl(1)—Pd—Cl(2′)	95(1)
Pd—Cl(2′)	2.510(3)	Cl(2)—Pd—Cl(2′)	83(1)
Pd—C(1)	2.092(13)	Pd—Cl(2)—Pd′	96(1)
Pd—C(2)	2.145(13)	C(1)—C(3)—C(4)	89(1)
Pd—C(3)	2.141(13)	C(2)—C(1)—C(3)	91(1)
Pd—C(4)	2.189(13)	C(4)—C(2)—C(1)	90(1)
C(1)—C(2)	1.453(18)	C(3)—C(4)—C(2)	91(1)
C(1)—C(3)	1.445(18)		
C(2)—C(4)	1.431(18)		
C(3)—C(4)	1.462(18)		

[a] Primed positions refer to $(1-x, 1-y, -z)$.

$4\sigma(B)$ were corrected for Lorentz and polarisation effects. No allowance was made for absorption or primary and secondary extinction. The structure was solved using Patterson and Fourier methods.

Refinement of the positional and isotropic vibration parameters by block diagonal matrix least squares refinement reduced R to 0.098. The introduction of anisotropic factors reduced R to 0.062.

A final difference Fourier showed small peaks of electron density due to disordered solvent molecules which resisted refinement. The atomic coordinates with e.s.d.s are listed in Table 3, key bond lengths and bond angles in Table 4 and the structure is shown in Fig. 1. Structure factors and anisotropic thermal parameters may be obtained from the authors.

$[(An_4C_4Pd)_2(SCN)_4]$ (7c)

Excess potassium thiocyanate (0.25 g, 2.5 mmol) was added to a stirred solution of complex **6** (0.325 g, 0.25 mmol) in acetone (25 cm^3). After 15 h the solution was filtered through a short column packed with cellulose and the filtrate reduced to dryness. The product was precipitated from a dichloromethane solution with petroleum ether. Yield 0.26 g (76%).

$Na[\eta^3\text{-}\{(N_3)An_4C_4Pd\}(N_3)Cl]$ (8)

Sodium azide (0.1 g, 1.5 mmol) was added to a stirred solution of complex **6** (0.325 g, 0.25 mmol) in acetone (15 cm^3). The solution immediately became lighter and after 10 min was evaporated to dryness. The residue was dissolved in dichloromethane and filtered to remove unreacted sodium azide. The filtrate was evaporated to dryness and the product crystallised from acetone. Solvent of crystallisation was removed by drying in vacuo. Yield 0.28 g (78%).

Crystallisation of the acetone mother liquors afforded octakis-*p*-anisyl-cyclooctatetraene ($\mathrm{An_8C_8}$, [2], 0.036 g, 8%).

$[\eta^3\text{-}\{(HO)An_4C_4Pd\}_2Cl_2]$ (9a)

Water (5 cm^3) was added to a stirred solution of complex **6** (0.325 g, 0.25

mmol) in acetone (15 cm^3). The red solution immediately became lighter in colour, reaction being complete in 5 min. After a further 0.5 h the product precipitated from solution as a very fine yellow powder. The product was collected by filtration and air dried. Yield 0.297 g (92%). The complex could also be made, but less satisfactorily, using THF in place of acetone (78%), or by reacting **6** in a mixture of dichloromethane and aqueous sodium carbonate (16%).

$[\eta^3\text{-}\{(MeO)An_4C_4Pd\}_2Cl_2]$ **(9c)**

Clean sodium metal (0.011 g, 0.5 mmol) was added to methanol (10 cm^3) and allowed to dissolve. This solution was then added to complex **6** (0.325 g, 0.25 mmol) and stirred. Reaction was complete within 1 min. The yellow solution was reduced to dryness and the product crystallised from acetone. Yield 0.31 g (96%).

$[(\eta^4\text{-}An_4C_4Pd)_2Cl_2(MeCN)_2][PF_6]_2$ **(10a)**

Silver hexafluorophosphate (0.126 g, 0.5 mmol) was added to a stirred solution of complex **6** (0.325 g, 0.25 mmol) in acetonitrile (15 cm^3). An immediate reaction occurred with precipitation of silver chloride. This was removed by filtration and the filtrate reduced to dryness. The product was obtained as a deep red microcrystalline solid by crystallisation from acetone. Yield 0.26 g (65%).

$[(\eta^4\text{-}An_4C_4Pd)(bipy)Cl][PF_6]$ **(11)**

Silver hexafluorophosphate (0.126 g, 0.5 mmol) was added to a stirred solution of complex **6** (0.325 g, 0.25 mmol) in acetone (15 cm^3). Silver chloride precipitated immediately and was filtered off; the filtrate was treated with bipyridyl (0.08 g, 5.1 mmol). After 5 min the orange solution was reduced to dryness and the residue crystallised from dichloromethane at 5°C to give red crystals. Yield 0.33 g (72%).

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