Complexes of Palladium and Platinum with Substituted Benzo-[15-crown-5] ‡ Ethers containing Nitrogen-donor Ligand Atoms

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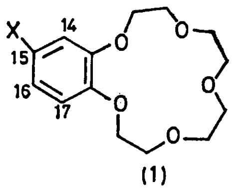
Some benzo-crown ethers substituted in the arene ring are described, *e.g.* the 15-X-substituted benzo-[15-crown-5] ethers (1; X = CN, CH=NOH, or $CH_3C=NOH$) and 15-CH=NOH,16-CH_3-substituted benzo-[15-crown-5] (8). The nitrile (1; X = CN) (L) reacts with $PtCl_2$ to give $[PtCl_2L_2]$. For comparison the 'model' compound $[PtCl_2\{NCC_6H_3(OMe)_2\text{-}3,4\}_2]$ has also been prepared. Both react with hydrazine in air to give very stable, dark blue, triazabutadiene–platinum complexes [Pt{HN=NC(R)=NH}$_2$] (2), where R = the benzo-crown radical (3) (free valence at 15-position) or 3,4-dimethoxyphenyl. The crown triazabutadiene–platinum complex gives a deep blue complex with sodium iodide. Both triazabutadiene–platinum complexes give green diacetates, and the crown diacetate interacts with sodium iodide or sodium thiocyanate in solution. The oximes (1; X = CH=NOH or $CH_3C=NOH$) are cyclopalladated by treatment with $Na_2[PdCl_4]$–$Na[O_2CMe]$ exclusively in the 16-position to give chloro-bridged complexes (6). These complexes react with PPh_3 or PMe_2Ph to give mononuclear complexes (7). 3,4-Dimethoxybenzaldoxime is also cyclopalladated to give a product (4) which when treated with PPh_3 or PMe_2Ph gives mononuclear complexes (5). Complexes of the type $[PdCl_2L_2]$, where L = 3,4-dimethoxybenzaldoxime or (1; X = CH=NOH or $CH_3C=NOH$) have also been prepared. Nuclear magnetic resonance, i.r., and mass spectral data are given.

WE have described in two previous papers [1,2] some new functionalised crown ethers and their complexes with platinum-group metals. We thereby combined together in the same molecules features of transition-metal coordination chemistry and crown ether chemistry. In the first paper [1] crown ether–tertiary phosphine complexes were described and in the second [2] crown ether–transition-metal complexes containing metal–carbon bonds (*e.g.* metal–aryl, –acyl, –olefin, and –acetylene). In the present paper we describe some new functionalised crown ethers containing nitrogen-donor atoms and their complexes to platinum(II) and palladium(II).

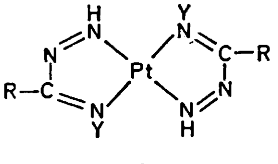
RESULTS AND DISCUSSION

Since nitriles form useful complexes with palladium(II) [3] or platinum(II) [4] chlorides we first attempted to make complexes of this type using a cyano-substituted crown ether. The 15-cyano-derivative of benzo-[15-crown-5] (1; X = CN) was made by dehydrating the oxime of 15-formylbenzo-[15-crown-5] (1; X = CHO) [1] with acetic anhydride: see Experimental section and Table 1 for details. The complex $[PtCl_2L_2]$ was readily prepared by heating platinum(II) chloride with the nitrile (L) (1; X = CN) in 1,1,2,2-tetrachloroethane.



(1)

For comparison we also made $[PtCl_2\{NCC_6H_3(OMe)_2\text{-}3,4\}_2]$ using 3,4-dimethoxybenzonitrile. Both complexes showed strong bands at 340 [ν(Pt–Cl)] and 2 290 cm^{-1} [ν(CN)]. Both reacted with sodium iodide in acetone to give the corresponding iodides $[PtI_2L_2]$, no anomalous behaviour due to interaction of the Na^+ ions with the crown being observed. A solution of the crown complex iodide in either acetone or chloroform showed a band at 2 280 cm^{-1} due to ν(CN). This band was unaffected by the addition of an excess of sodium iodide to the solution.



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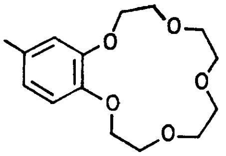

(3)

We have shown previously that complexes of the type *trans*-$[PtCl_2(NCR)_2]$ when treated with hydrazine in the presence of air give intensely blue and very stable triazabutadiene–platinum complexes of the type [Pt{HN=NC(R)=NH}$_2$].[5] We now find that the crown complex $[PtCl_2\{$15-cyanobenzo-[15-crown-5]$\}_2]$ and the model complex $[PtCl_2\{NCC_6H_3(OMe)_2\text{-}3,4\}_2]$ react similarly to give dark blue complexes of type (2) where Y = H and R = (3) or 3,4-dimethoxyphenyl, respectively. The model complex was sufficiently volatile to give a mass spectrum with the most intense molecular ion at the expected value *m*/*e* = 581. A mass spectrum could not be obtained for the crown ether complex, presumably because it was insufficiently volatile. Sodium iodide in acetone had no effect on the model complex but when an acetone solution of the crown complex [2; Y = H, R = (3)] was treated with sodium iodide a dark blue precipitate formed. This was not soluble in common organic solvents and could not be purified. After exhaustive washing with water to remove any excess of sodium iodide, microanalysis gave the following results: C, 32.45; H, 4.15; I, 20.85; N, 7.45; Na, 3.50%. Calculated values for the 1 : 2 sodium iodide adduct $C_{30}H_{42}I_2N_6Na_2O_{10}Pt$ are: C, 31.55; H, 3.70; I, 22.2; N, 7.35; Na, 4.00%. The i.r. spectrum of this product differed markedly from the starting complex (2) in the region 1 000—1 400 cm^{-1}, a

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† No reprints available.

‡ 2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin.

TABLE 1

Melting-point and microanalytical data [a]

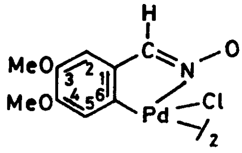
Compound	M.p. (θ_c/°C)	Analysis (%)			
		C	H	N	Halogen
(1; X = CH=NOH)·$\frac{1}{2}H_2O$ [b]	79—83	56.3 (56.3)	7.0 (6.9)	4.4 (4.4)	
(1; X = CH_3C=NOH)	123—126	58.9 (59.0)	7.1 (7.1)	4.35 (4.3)	
(1; X = CN)	94—95	60.8 (61.4)	6.4 (6.5)	4.45 (4.7)	
$[PtCl_2L_2]$ L = (1; X = CN)	190—194	42.05 (42.25)	4.65 (4.5)	3.1 (3.3)	8.7 (8.3)
$[PtCl_2\{NCC_6H_3(OMe)_2\text{-}3,4\}_2]$	220—223	36.75 (36.5)	3.4 (3.05)	4.55 (4.7)	12.25 (12.0)
$[PtI_2L_2]$ L = (1; X = CN)	200—203 (decomp.)	34.35 (34.8)	3.6 (3.7)		24.7 (24.5)
$[PtI_2\{NCC_6H_3(OMe)_2\text{-}3,4\}_2]$	146—150 (decomp.)	27.95 (27.9)	2.4 (2.35)	3.5 (3.6)	33.3 (32.75)
Substituted triazabutadiene complexes					
[2; Y = H, R = $C_6H_3(OMe)_2$-3,4]	277—278 (decomp.)	37.5 (37.2)	3.7 (3.8)	13.9 (14.4)	
[2; Y = $COCH_3$, R = $C_6H_3(OMe)_2$-3,4]	244—245	40.4 (39.7)	4.5 (3.95)	12.4 (12.6)	
[2; Y = H, R = (3)]	243—245	43.3 (42.8)	5.3 (5.0)	9.5 (10.0)	
[2; Y = $COCH_3$, R = (3)]	253—254	44.3 (44.1)	5.1 (5.0)	9.05 (9.05)	
Substituted benzaldoxime complexes of type $[PdCl_2L_2]$					
L = CH(=NOH)$C_6H_3(OMe)_2$-3,4	192—198 (decomp.)	39.8 (40.05)	4.2 (4.1)	5.2 (5.2)	13.3 (13.1)
L = (1; X = CH=NOH)	168—170	44.65 (45.0)	5.35 (5.3)	3.3 (3.5)	9.1 (8.85)
L = (8)	190—193 (decomp.)	46.75 (46.4)	5.7 (5.6)	3.35 (3.35)	8.8 (8.55)
Cyclometallated palladium–oxime complexes					
(4)	165—170 (decomp.)	33.95 (33.35)	3.35 (3.13)	4.9 (4.35)	11.45 (11.0)
(6; R′ = H)	168—170	39.35 (39.85)	4.6 (4.45)	3.15 (3.1)	8.05 (7.85)
(6; R′ = CH_3)	246—256 (decomp.)	40.85 (41.2)	5.15 (4.75)	3.0 (3.0)	7.5 (7.6)
(5; X = Cl, L = PPh_3)	200—201	55.85 (55.5)	4.45 (4.3)	2.95 (2.4)	6.25 (6.05)
(7; X = Cl, L = PPh_3)	210—211	55.2 (55.5)	5.0 (4.9)	1.95 (1.95)	4.85 (4.95)
(7; R′ = CH_3, L = PPh_3, X = Cl)	115—118	55.75 (56.0)	5.35 (5.1)	1.85 (1.9)	4.75 (4.85)
(5; L = PMe_2Ph, X = Cl)	108—110	45.0 (44.35)	4.4 (4.6)	3.1 (3.05)	7.75 (7.7)
(7; R′ = H, L = PMe_2Ph, X = Cl)	95—97	46.95 (46.8)	5.4 (5.3)	2.4 (2.35)	5.9 (6.0)
(5; X = I, L = PPh_3)	183—185 (decomp.)	46.8 (46.0)	3.65 (3.85)	2.0 (2.15)	19.05 (19.45)
(7; R′ = CH_3, L = PMe_2Ph, X = I)	119—121	40.65 (40.5)	4.45 (4.55)	2.0 (2.05)	18.5 (18.6)
(5; X = I, L = PMe_2Ph)	146—148 (decomp.)	36.9 (37.0)	3.65 (3.85)	2.6 (2.55)	23.35 (23.0)

[a] Calculated values are given in parentheses. [b] This hemihydrate when dried gave a gum, which in moist air gave back the highly crystalline hemi hydrate.

region giving a qualitative indication of ionic co-ordination to the crown ether ring. Although values of ν(C=N) were virtually the same for the crown complex (2) and the 1 : 2 sodium iodide adduct (each complex showed two bands at 1 585 ± 2 and 1 604 ± 2 cm^{-1}), values of ν(N–H) were significantly different being at 3 365s for the crown complex and 3 230br and 3 400br cm^{-1} for the 1 : 2 sodium iodide adduct (br = broad). Both the model and the crown complexes of type (2; Y = H) reacted with acetic anhydride to give green acetates (2; Y = $COCH_3$). Both complexes showed a strong i.r. absorption due to ν(C=O) at 1 686 cm^{-1}. The model complex (2; Y = $COCH_3$, R = 3,4-dimethoxyphenyl) gave a mass spectrum with the expected five-peak molecular ion and a base peak at $m/e = 655$, also as expected. The crown complex acetate [2; Y = $COCH_3$, R = (3)] is almost insoluble in acetone but when its acetone suspension was treated with an excess of sodium iodine or sodium thiocyanate an intense green solution was formed. This was probably produced by interaction of the sodium ions with the crown complex although NaI or Na[SCN] adducts could not be isolated.

We have also studied reactions of the crown oxime (1; X = CH=NOH) and a model oxime, 3,4-dimethoxybenzaldoxime, with palladium(II). It has been shown that oximes of aromatic aldehydes and ketones undergo *ortho* *C*-palladation.[6] We hoped originally that cyclopalladation of (1; X = CH=NOH) would occur at least in part in the 14-position because with this position ions or molecules complexed by the crown ether moiety would lie close to some of the co-ordination sites of the palladium and might have considerable influence on the chemistry. We thought that palladation in the 16-position was more likely and this is in fact what occurs, exclusively, as far as we can determine.

The model aldoxime, 3,4-dimethoxybenzaldoxime, reacted with sodium tetrachloropalladate(II)–sodium acetate in methanol at room temperature to give the binuclear complex (4). This was characterised by microanalytical data (Table 1) but was too insoluble for its ^1H n.m.r. spectrum to be determined. It reacted readily with PPh_3 or PMe_2Ph to give the yellow mononuclear complexes of type (5), where L = PPh_3 or PMe_2Ph respectively. Both these complexes were characterised by microanalytical (Table 1) and by ^1H and ^{31}P n.m.r. spectroscopy (Table 2). The ^1H n.m.r. data, in particular the absence of *ortho* spin–spin coupling (which would be of the order of 10 Hz) between the two hydrogens of the benzene ring, show that palladation has occurred in the 6-position, as shown in (5), and not the 2-position. Complexes (5) gave the corresponding iodides when treated with sodium iodide in acetone (characterising data in the Tables). Both PMe_2Ph complexes of type (5; X = Cl or I) gave good mass spectra, the chloride showed a base peak at $m/e = 425$ corresponding to $M - 35$ (*i.e.* loss of Cl). The pattern of the molecular ion had the most intense peak at $m/e = 460$, the remainder of the pattern corresponding closely with that calculated using the isotope abundances for Pd, Cl, and C. The spectrum of the iodide showed a base peak at $m/e = 509$, *i.e.* loss of CNO from the parent molecular ion, which had a maximum at $m/e = 551$.



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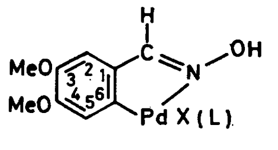
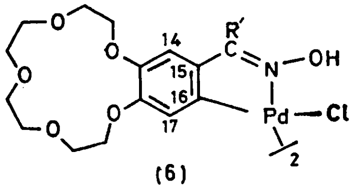


(5)

When the oxime of 15-formylbenzo-[15-crown-5] was added to $Na_2[PdCl_4]$ in methanol a heavy brown precipitate formed immediately. This was probably a salt containing a sodium ion adduct of the crown ether. We therefore devised a method of palladating this crown ether oxime which did not involve sodium ions. The oxime was treated with palladium(II) chloride in ethanol in the presence of a small amount of lithium chloride and tetra-n-butylammonium acetate as base to take up the hydrogen chloride liberated by palladation. This method was also used for palladating the oxime of 15-acetylbenzo-[15-crown-5] to give (6; R′ = CH_3). Thic cyclopalladated product was also prepared by the action of the oxime of 15-acetylbenzo-[15-crown-5] on $[PdCl_2(NCPh)_2]$. It reacted with PPh_3 in ethanol to give the mononuclear complex (7; R′ = CH_3, L = PPh_3, X = Cl) (see Tables for characterising data). Spin–spin coupling between the two protons of the benzene ring could not be observed (Table 2). This showed that the two hydrogens were not mutually *ortho* and that palladation of (1) occurred in the 16- and not the 14-position, *i.e.* the configuration of the cyclometallated product is as shown in (7) [or (6)]. From the values of ν(Pd–Cl), *viz.* at 272 and 275 cm⁻¹, we cannot



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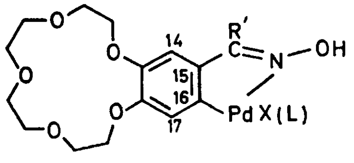


(7)

TABLE 2

Infrared (cm⁻¹) and ^{31}P [a] and ^{1}H [b] n.m.r. data

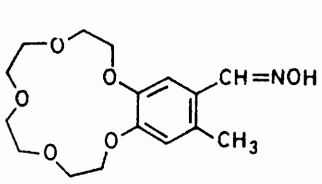
Compound	I.r. (Nujol)		^{31}P N.m.r.	^{1}H N.m.r.				
	ν(Pd–Cl)	ν(O–H)	(δ)	δ(H_a)	δ(H_b)	δ(CH=N)	δ(O–H)	Others
(4)	257 288	3 490 3 360	[c]	[c]				
(5; X = Cl, L = PPh_3)	295	3 400	41.3	5.88	6.76	7.92	10.2(br)	2.75, 2.84 (OCH_3)
(5; X = Cl, L = PMe_2Ph)	290	3 170, 3 460	12.75	5.92	6.78	7.88	9.8(br)	3.69, 3.16 (OCH_3) 1.86(br) (PCH_3)
(5; X = I, L = PPh_3)		3 240	41.7	5.82	6.71	8.00	9.18(br)	3.72, 2.79 (OCH_3)
(5; X = I, L = PMe_2Ph)		3 220	14.6	5.88(d) (6 Hz)	6.73		9.11(d) (3 Hz)	3.73, 3.14 (PCH_3) 2.06(d) (10.4 Hz)
(6; R′ = H)	250 234	3 400	[c]	[c]				
(6; R′ = CH_3)	245	3 400		6.13	6.98		8.42(br)	
(7; R′ = H, L = PPh_3, X = Cl)	275	3 200	42.7	5.82	6.76	7.6	10.5(br)	
(7; R′ = H, L = PMe_2Ph, X = Cl)	272	3 280	11.7	5.89(d) (5 Hz)	6.78	[d]	9.92(br)	1.88(d) (10 Hz) PCH_3
(7; R′ = H, L = PMe_2Ph, X = I)		3 240	41.2	5.87(d) (6 Hz)	6.74	[d]	9.23(d) (3 Hz)	2.04(d) (10 Hz) PCH_3
(7; R′ = CH_3, L = PPh_3, X = Cl)	267	3 160	42.9	5.88(d) (6 Hz)	6.75		10.4(d) (3.5 Hz)	

[a] In $CDCl_3$ at 27 °C and 36.43 Mz. δ ±0.1 p.p.m. shifts relative to 85% H_3PO_4 (external). All singlets. [b] In $CDCl_3$ at 34 °C and 60 MHz. δ ±0.01 p.p.m., J ±0.5 Hz; d = doublet, t = triplet, br = broad. The resonances are singlets unless otherwise stated. [c] Too insoluble. [d] Obscured by phenyl proton resonances.

assign configuration (7) more completely, *i.e.* whether Cl is *trans* to N or *trans* to C. The mononuclear chloride complex from the formyl oxime reacted with sodium iodide in acetone to give the corresponding iodide (7; R′ = H, L = PMe_2Ph, X = I). In the mass spectrum of the chloride complex the molecular ion could not be observed: the base peak in the spectrum at *m*/*e* 452 corresponded to *M* — 138, *i.e.* loss of PMe_2Ph. The mass spectrum of the iodide complex also showed no molecular ion and for it the base peak was at *m*/*e* = 511, corresponding to loss of both PMe_2Ph and C=N–O from the molecular ion. When treated with sodium iodide in acetone the mononuclear chloro-complex (7; R′ = H, L = PPh_3, X = Cl) gave an orange solid which appeared to be the corresponding iodo-complex complexed to sodium iodide. Analytical data agreed quite well with one sodium iodide associated with two complexes of type (7; X = I) (Found: C, 45.5; H, 4.15; I, 22.5; N, 1.50. Calc. for $C_{66}H_{70}I_3N_2NaO_2P_2Pd_2$: C, 45.3; H, 4.05; I, 21.5; N, 1.60%). The molar conductivity in nitrobenzene solution at 23 °C was 19 Ω^{-1} cm^2 mol^{-1} compatible with a 1 : 1 electrolyte.

We attempted to force cyclopalladation to occur in the 14-position by blocking the 16-position with a methyl group. However, treatment of the aldoxime (8) with $PdCl_2$ and LiCl in the presence of tetra-n-butylammonium acetate caused extensive decomposition (to metallic palladium) and we were unable to detect a cyclopalladated product.

We have also prepared complexes of the type *trans*-[$PdCl_2L_2$] by treating [$PdCl_2(NCPh)_2$] with the oxime (L) (1; X = CH=NOH), the oxime (8), and 3,4-dimethoxybenzaldoxime. These are stable yellow solids almost insoluble in common organic solvents. The *trans* configuration follows from the presence of one very strong band within the range 329—333 cm^{-1} due to the *trans*-Cl–Pd–Cl grouping. Many complexes of the type *trans*-[$PdCl_2$(oxime)$_2$] have previously been described in the literature.[7,8]



(8)

EXPERIMENTAL

The general techniques and instruments were the same as those used previously.[9] Percentage yields, m.p.s, and characterising data are given in the Tables.

Oxime of 15-*Formyl*-2,3,5,6,8,9,11,12-*octahydro*-1,4,7,10,-13-*benzopentaoxacyclopentadecin*, (1; X = CH=NOH).—A 15-mixture of formylbenzo-[15-crown-5] (6.00 g, 20.2 mmol), hydroxylamine hydrochloride (15.0 g, 202 mmol), and sodium hydroxide (6.0 g, 150 mmol) was heated in a mixture of water (120 cm^3) and ethanol (6 cm^3) for 15 min under reflux. Water (100 cm^3) was then added and the mixture allowed to cool. The product (6.48 g) separated as a prismatic hydrate (see Table 1).

The oximes of 15-formyl-16-methylbenzo-[15-crown-5] (8) and 15-acetylbenzo-[15-crown-5] (1; X = CH_3C=NOH) were prepared similarly except that the ketoxime was isolated with chloroform and recrystallised from light petroleum (b.p. 60—80 °C).

(1; X = CN).—The aldoxime (1; X = CH=NOH) (5.15 g, 16.5 mmol) was heated under reflux in acetic anhydride (8 cm^3) for 1 h. The resulting mixture was added to water (40 cm^3) and when the excess of acetic anhydride had hydrolysed the product was isolated by chloroform extraction and recrystallised from propan-2-ol.

[$PtCl_2L_2$] [L = (1; X = CN)].—A mixture of platinum(II) chloride (0.63 g, 2.32 mmol) and 15-cyanobenzo-[15-crown-5] (2.04 g, 6.96 mmol), suspended in 1,1,2,2-tetrachloroethane (15 cm^3), was stirred at *ca.* 130 °C for 2 h. The mixture was then filtered and methanol (50 cm^3) added to the filtrate to give the product (1.64 g, 1.92 mmol) as light yellow plates from dichloromethane–ethanol. *Dichlorobis*(3,4-*dimethoxybenzonitrile*)*platinum*(II) was prepared similarly as yellow needles.

[PtI_2L_2] [L = (1; X = CN)].—A mixture of the corresponding dichloride (see above; 0.38 g, 0.44 mmol) and sodium iodide (0.66 g, 4.40 mmol) was heated under reflux in acetone (15 cm^3) for 1 h. The acetone was then evaporated. The required product formed orange prisms from dichloromethane–methanol. *Bis*(3,4-*dimethoxybenzonitrile*)*di-iodoplatinum*(II) was prepared and purified similarly.

[2; Y = H, R = (3)].—A mixture of dichlorobis(15-cyanobenzo-[15-crown-5])platinum(II) (0.72 g, 0.84 mmol) and hydrazine hydrate (1.47 g, 2.95 mmol) in ethanol (10 cm^3) was stirred at room temperature for 16 h. The product formed dark blue microcrystals (0.55 g, 0.65 mmol). trans-*Bis*[2-(3,4-*dimethoxyphenyl*)-1,3,4-*triazabuta*-1,3-*diene*]-*platinum*, [(2); Y = H, R = 3,4-*dimethoxyphenyl*], was prepared in a similar manner.

[(2); Y = $COCH_3$, R = (3)].—The dark blue microcrystals (0.14 g, 0.167 mmol, see above) were heated under reflux with acetic anhydride (3 cm^3) for 10 min. The resulting precipitate which formed on cooling was collected and washed with water, to give the required product (0.097 g, 0.105 mmol) as dark green microcrystals. trans-*Bis*[1-*acetyl*-2-(3,4-*dimethoxyphenyl*)-1,3,4-*triazabuta*-1,3-*diene*]-*platinum* was similarly prepared and formed dark green prisms from chloroform–methanol.

trans-*Dichlorobis*(3,4-*dimethoxybenzaldoxime*)*palladium*-(II).—A mixture of bis(benzonitrile)dichloropalladium(II) (0.69 g, 1.81 mmol) and 3,4-dimethoxybenzaldoxime (0.69 g, 3.81 mmol) in ethanol (15 cm^3) was heated under reflux on a water-bath for 20 min. The required product precipitated as yellow needles (0.98 g, 1.81 mmol). trans-*Dichlorobis*(15-*formylbenzo*-[15-*crown*-5])*platinum*(II) and trans-*dichlorobis*(15-*formyl*-16-*methylbenzo*-[15-*crown*-5])*platinum*(II) were prepared similarly.

(6; R′ = H).—A mixture of palladium(II) chloride (1.15 g, 6.47 mmol), lithium chloride (0.068 g, 1.61 mmol), 15-formylbenzo-[15-crown-5] aldoxime (2.01 g, 6.47 mmol), and tetra-n-butylammonium acetate (1.95 g in 14 cm^3 of water) was heated under reflux in ethanol (80 cm^3) for 2 h. Some black material was filtered off and the filtrate was put aside. The required product separated over 5 d. The yellow-orange microcrystals were collected and washed with ethanol and water. Yields 1.95 g (2.15 mmol).

(4).—A mixture of sodium tetrachloropalladate(II) (1.98

g, 5.42 mmol), sodium acetate (0.44 g, 5.42 mmol), and 3,4-dimethoxybenzaldoxime (0.98 g, 5.42 mmol) in methanol was put aside for 2 weeks. The required product had then separated as yellow-orange microcrystals and was washed with water and dried. Yield 1.28 g (1.98 mmol). The *complex* (6; R′ = Me) was prepared similarly and formed yellow microcrystals from chloroform–ethanol.

(7; R′ = H, L = PPh_3, X = Cl).—A mixture of the chloro-bridged complex (6; R′ = Me) (0.17 g, 0.27 mmol) and triphenylphosphine (0.14 g, 0.55 mmol) was heated under reflux in dichloromethane (5 cm^3). Ethanol was then added and the dichloromethane evaporated off. The required product separated as light yellow prisms (0.24 g, 0.41 mmol) which were recrystallised from ethanol. The *complexes* (7; R′ = H, L = PPh_3, X = Cl) and (7; R′ = CH_3, L = PPh_3, X = Cl) were prepared in a similar manner, and (5; X = Cl, L = PMe_2Ph) and (7; R′ = H, L = PMe_2Ph, X = Cl) were similarly prepared using PMe_2Ph instead of PPh_3.

(5; X = I, L = PPh_3).—A mixture of the corresponding chloro-complex (5) (0.85 g, 1.45 mmol) and sodium iodide (2.17 g, 14.5 mmol) was heated under reflux in acetone (20 cm^3) for 3 h. The acetone was removed, water added, and the product collected and recrystallised from ethanol as yellow plates (0.93 g, 1.43 mmol). The *complexes* (5; X = I, L = PMe_2Ph) *and* (7; PMe_2Ph, X = I) were prepared in a similar manner. However, when (7; R′ = H, L = PPh_3, X = Cl) was treated with NaI in acetone a sodium iodide adduct of (7; R′ = H, L = PPh_3, X = I) was isolated (see Results and Discussion).

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