Complexes of Platinum Metals with Crown Ethers containing Tertiary Phosphine-substituted Benzo Groups

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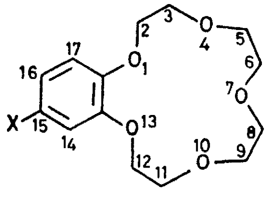
Some benzo-crown ethers substituted in the arene ring are described, *e.g.* some 15-X-substituted benzo-[15-crown-5] ethers [1; X = I, CHO, CH_2OH, CH_2Cl, CH_2Ph_2(Q), or $CH_2PBu^t_2$(Q′)]: 18-iodobenzo-[18-crown-6] (2; X = I) and 15-iodo-16-methylbenzo-[15-crown-5] (3; X = I) are also described. We have failed, however, to lithiate or to prepare a Grignard derivative of a benzo-crown ether. The model phosphines $PR_2[C_6H_3(OMe)_2$-3,4] [4; R = Ph(L) or Bu^t(L′)] have also been synthesized. Reduction of (1; X = CHO) by $Li[AlH_4]$ gives, in addition to (1; X = CH_2OH), a dicrown ether dibenzyl ether derivative (5; X = H). Similar reduction of 15-formyl-16-methylbenzo-[15-crown-5] (3; X = CHO) gives only a dicrown diphenylmethane derivative (6). The chloromethyl derivatives react with $Li[PPh_2]$ to give the corresponding phosphines (4; R = Ph) and (1; X = CH_2PPh_2), and with $PBu^t_2H + I^-$ followed by base (Na[OH]) their Bu^t analogues. Adducts of the substituted crown ethers (1; X = CHO, Me, or I) with Na[SCN] have been prepared and some conductimetric studies made of complex formation with NaI. Complexes of the phosphines L, L′, Q, or Q′ of the types *trans*-[MCl(CO)(phosphine)$_2$] (M = Rh or Ir), *trans*-$[IrCl_2H(CO)Q_2]$, and *trans*-$[IrMe(Cl)I(CO)Q_2]$ (also with L) have been prepared. The complex $[PdCl_2(NCPh)_2]$ reacts with ether Q or L to give $[PdCl_2Q_2]$ or $[PdCl_2L_2]$ (*cis* + *trans* isomers). When treated with $Na[O_2CMe]$ in 2-methoxyethanol, $[PdCl_2L_2]$ undergoes cyclometallation to give $[\overline{Pd_2\{C_6H_2(P}Ph_2\text{-}2)(OMe)_2\text{-}4,5\}_2Cl_2]$ (8; R = Ph, M = Pd). The complex $[PdCl_2(NCPh)_2]$ with the bulky crown phosphine Q′ gives a mixture of *trans*-$[PdCl_2Q'_2]$ and the corresponding cyclometallated complex; the complex (8; R = Bu^t, M = Pd) has also been prepared. A similar but more extensive series of platinum complexes has been made including mononuclear species formed by splitting the chloride-bridged systems with PPh_3. Infrared, ^1H and ^{31}P n.m.r., and mass spectral data are given.

SINCE the work of Pederson[1] great interest has been shown in the chemistry of crown ethers.[2-6] Crown ethers form complexes with alkali-metal, alkaline-earth metal, and with some other metal ions, with oxonium ions, with protonated amines including amino-acids, and also with some neutral rod-like molecules such as acetonitrile. They are particularly useful in phase-transfer catalysis. The crown ether moiety is, however, a very poor ligand for transition-metal ions (except Ag^+).[7,8] We therefore set out to synthesize ligands which would complex to transition metals and which contained crown ether moeities. We hoped to combine together in the same molecule some of the features of transition-metal complexes with some of the features of crown ethers mentioned above. In this paper we describe some new functionalized crown ethers, in particular some crown ethers substituted by tertiary phosphines in their arene rings, and some of their complexes to rhodium, iridium, palladium, and platinum. We have mainly studied derivatives of 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxocyclopentadecin * (1; X = H) which is easily synthesized and is commonly known as benzo-[15-crown-5].[1-6] In this paper we will use this more convenient and widely used 'crown' nomenclature introduced by Pederson. When we began this work derivatives of (1; X = H) functionalized on the benzene ring had not been described. Two approaches to their synthesis could be used. (*i*) To perform a crown ether synthesis on a substituted 1,2-dihydroxybenzene. This method has since been used to synthesize some 15-substituted derivatives of benzo-[15-crown-5] (1) with for example X = CHO or COMe.[9] (*ii*) To effect substitution on benzo-[15-crown-5], which is the method we have used. Several aromatic substitution reactions of 1,2-dimethoxybenzene give high yields, *e.g.* lithiation,[10] iodination, chloromethylation, *etc.*, and we hoped to be able to effect similar high-yield syntheses on benzo-[15-crown-5].



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RESULTS AND DISCUSSION

We first attempted to lithiate benzo-[15-crown-5] and to treat the resulting lithio-derivative with a phosphinous chloride, PR_2Cl. This is an excellent method of synthesizing tertiary phosphines of the type $PR_2[C_6H_3(OMe)_2$-2,3].[10] However, Pederson[1] reported very briefly that n-butyl-lithium opens the ring of dibenzo-[18-crown-6] to produce a phenoxide group. We have treated benzo-[15-crown-5] with $LiBu^n$ in a variety of solvents [diethyl ether, tetrahydrofuran (thf), benzene, *etc.*] at or below room temperature. On adding PPh_2Cl, H_2O, or D_2O we found that at room temperature the crown ether ring was destroyed, as

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* This nomenclature is the one used by Chemical Abstracts.

[1] C. J. Pederson, *J. Amer. Chem. Soc.*, 1967, **89**, 7017.

[2] C. J. Pederson and H. K. Frensdorff, *Angew. Chem. Internat. Edn.*, 1972, **11**, 16.

[3] G. W. Cokes and H. D. Durst, *Synthesis*, 1976, 168.

[4] D. J. Cram and J. M. Cram, *Science*, 1974, **183**, 801.

[5] L. F. Lindoy, *Chem. Soc. Rev.*, 1975, **4**, 421.

[6] M. R. Truter and C. J. Pederson, *Endeavour*, 1971, **11**, 16.

[7] A. C. L. Su and J. F. Weiher, *Inorg. Chem.*, 1968, **7**, 176.

[8] D. DeVos, J. van Daalen, A. C. Knegt, Th. C. Van Hegningen, L. P. Otto, and M. W. Vonk, *J. Inorg. Nuclear Chem.*, 1975, **37**, 1319.

[9] R. Ungaro, B. Elhaj, and J. Smid, *J. Amer. Chem. Soc.*, 1976, **98**, 5198.

[10] H. D. Empsall, P. N. Heys, and B. L. Shaw, *J.C.S. Dalton*, 1978, 257.

deduced by the absence of the characteristic crown ether ^1H n.m.r. patterns between δ 3.0 and 4.5 p.p.m. At low temperatures (−30 to −50 °C) the benzo-[15-crown-5] was either unaffected (and recovered unchanged) or partially destroyed. There was no evidence for the formation of any of the hoped for Ph_2P-substituted crown ether.

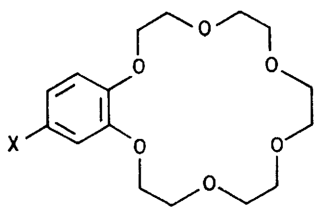
We next tried to make a halogeno- and thence a magnesium-substituted crown ether, *i.e.* a Grignard reagent which we could use to synthesize a tertiary phosphine. 1,2-Dimethoxybenzene is iodinated in the 4-position by I_2 and HIO_3 in glacial acetic acid.[11] We find that benzo-[15-crown-5] is also readily iodinated by these reagents to give the 15-iodo-derivative (1; X = I) as a white solid in 88% yield (see the Experimental section and Tables for some characterizing data). 15-Iodobenzo-[15-crown-5] showed a strong molecular ion at the expected value of *m/e* 394 in its mass spectrum, and the expected pattern for a 1,2,4-trisubstituted benzene ring in its ^1H n.m.r. spectrum together with the characteristic crown ether pattern between δ 3.0 and 4.5 p.p.m. A medium-strength band at 638 cm^{-1} in its i.r. spectrum (Nujol) is tentatively assigned to ν(C–I). 18-Iodobenzo-[18-crown-6] (2; X = I) and 15-iodo-16-methylbenzo-[15-crown-5] (3; X = I) were similarly synthesized and characterized (see Experimental section and Table 1). We were, however, unable to induce reaction between magnesium turnings and 15-iodobenzo-[15-crown-5] in either thf or diethyl ether under typical conditions for the formation of Grignard reagents. Having failed to introduce a PR_2 group directly on to the arene ring of benzo-[15-crown-5], we attempted to introduce an R_2PCH_2 group. 1,2-Dimethoxybenzene is readily monochloromethylated in the 4-position by $MeOCH_2Cl$ [12] and subsequent treatment with $Li[PPh_2]$ readily gives the tertiary phosphine (4; $X = CH_2PPh_2$) (see below). However, under similar conditions, benzo-[15-crown-5] failed to give any isolable chloromethylated derivative although the crude product showed a small peak at δ 4.45 p.p.m. in its ^1H n.m.r. spectrum which possibly corresponded to the CH_2Cl resonance of the required product (see below). We therefore devised an alternative synthesis of the chloromethylated derivative.

TABLE 1

Microanalytical,* melting-point, and yield data for some 15-substituted crown ethers, some adducts with sodium thiocyanate, and also for 1-(diphenylphosphinomethyl)-3,4-dimethoxybenzene (L)

Compound		M.p.	Analysis (%)		
No.	Substituent X	(θ_c/°C)	C	H	Halogen [Nitrogen]
(1)	I	87—88	42.95 (42.65)	5.10 (4.85)	32.05 (32.2)
(1)	CHO	78—81	60.4 (60.8)	6.85 (6.80)	
(1)	$CH{=}NNHC_6H_3(NO_2)_2$-2,4	222—225	52.9 (52.9)	4.90 (5.00)	[11.6 (11.75)]
(1)	CH_2OH	52—54	60.3 (60.4)	7.35 (7.40)	
(5)		107—109	61.95 (62.2)	7.25 (7.30)	
(1)	CH_2Cl	65—66	56.35 (56.8)	6.60 (6.70)	10.5 (11.2)
(1)	CH_2PPh_2	108—109	69.75 (69.5)	6.50 (6.70)	
(4)	CH_2PPh_2	88—90	74.8 (75.0)	6.10 (6.30)	
(2)	I	92—94	44.05 (43.85)	5.25 (5.30)	28.8 (28.95)
(3)	I	69—71	44.45 (44.1)	5.25 (5.20)	30.65 (31.0)
(3)	CHO	82—83	62.1 (61.9)	7.05 (7.15)	
(6)		111—112	64.25 (64.5)	7.40 (7.70)	
Na[SCN] adducts					
(1)	CHO	124—125	50.9 (50.9)	5.40 (5.30)	[4.0 (3.70)]
(1)	Me	125—126	52.6 (52.2)	5.70 (5.65)	[3.90 (3.85)]
(1)	I	148—150	38.7 (37.9)	4.05 (4.00)	26.05 (16.7) [3.00 (2.95)]

* Calculated values are given in parentheses.



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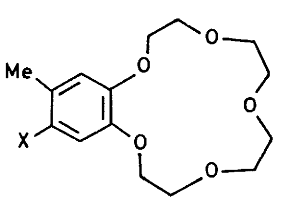

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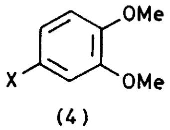

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We find that benzo-[15-crown-5] is readily formylated in the 15-position to give (1; X = CHO) by treatment with *N*-methylformanilide in the presence of $POCl_3$ (the Vilsmeir reaction).[13] The crude oily product (see Experimental section) could not be induced to crystallize. However, we found that a sodium hydrogensulphite addition compound formed readily and this was an excellent method of removing non-aldehydic material. The hydrogensulphite addition compound is white and crystalline and slowly loses SO_2 at room temperature. In the i.r. spectrum the aldehyde band ν(C=O) at 1 688 cm^{-1} is absent and replaced by a strong broad band between 3 350 and 3 550 cm^{-1} due to ν(O–H): this

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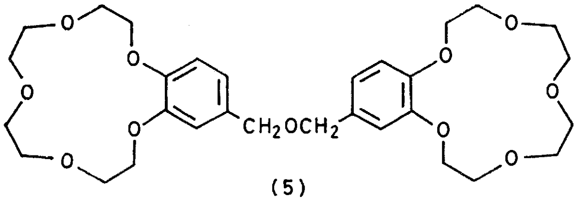
[11] H. O. Wirth, O. Königstein, and W. Kern, *Annalen*, 1960, **634**, 101.

[12] O. Gawron, *J. Amer. Chem. Soc.*, 1949, **71**, 744.

[13] V. I. Minkin and G. N. Dorofenko, *Russ. Chem. Rev.*, 1969, **29**, 599.

confirms that the compound is an aldehyde–hydrogen-sulphite adduct and not just a sodium ion–crown ether complex. When treated with strong sulphuric acid the free solid aldehyde (1; X = CHO) was readily obtained (see Experimental section and Table 1). In the i.r. spectrum (Nujol) a strong band at 1 688 cm^{-1} is assigned to ν(C=O) and a strong molecular-ion peak in the mass spectrum is at the expected value of *m/e* 296. In the ^1H n.m.r. spectrum the aldehyde proton absorbed at δ 9.84 p.p.m. and trisubstituted aromatic and crown ether resonances of the expected intensity were also observed. 15-Formylbenzo-[15-crown-5] gave a red 2,4-dinitrophenylhydrazone and was reduced by Li[AlH_4] to 15-hydroxymethylbenzo-[15-crown-5] in moderate (64%) yield. The ^1H n.m.r. and i.r. data for this hydroxymethyl derivative are in agreement with the structure, *e.g.* in the ^1H n.m.r. spectrum ($CDCl_3$) there is a sharp singlet at δ 4.48 p.p.m. (CH_2OH) and a broad singlet at 2.5 p.p.m. (CH_2O*H*) which disappears on addition of D_2O and in the i.r. spectrum a broad band at 3 200—3 450 cm^{-1} is assigned to ν(OH). A strong molecular ion at the expected value of *m/e* 298 is shown in the mass spectrum. 15-Hydroxymethylbenzo-[15-crown-5] was purified by recrystallization from propan-2-ol–light petroleum: the mother liquors from this recrystallization gradually gave a white crystalline precipitate. This was identified as the dicrown ether dibenzyl ether derivative (5; X = H). This formulation follows from the microanalytical and ^1H n.m.r. data, with the aromatic, benzylic, and crown ether hydrogen resonances being of the expected relative areas, and molecular weight [602 (osmometry). Calc. for $C_{30}H_{42}O_{11}$: 578]. The mass spectrum showed a strong molecular ion at the expected value of *m/e* 578. This dicrown ether was obtained in a yield of 25% which explains why the yield of the accompanying benzyl alcohol derivative (1; X = CH_2OH) was only moderate (64%). We cannot, however, suggest a mechanism to explain the formation of this dibenzyl ether derivative.



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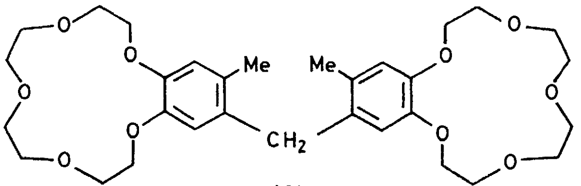


(6)

15-Methylbenzo-[15-crown-5] (3; X = H) was similarly converted into the formyl derivative (3; X = CHO) by treatment with *N*-methylformanilide–$POCl_3$. In this case the required formyl derivative was readily crystallized without the need for isolation *via* the Na[HSO_3] adduct. The formulation follows from the mass spectrum which exhibits a strong molecular ion at *m/e* 310, as expected, and also from the microanalytical (Table 1) and spectroscopic data, *e.g.* ν(C=O) at 1 675 cm^{-1} (Nujol) and singlet ^1H n.m.r. resonances at 10.2 (CHO), 7.35 and 6.67 (aromatic CH), and 2.6 p.p.m. (CH_3) in addition to the crown ether pattern. However, Li[AlH_4] reduction of this aldehyde gave as the only isolable product a dicrown diphenylmethane derivative (6) in 53% yield (analytical data in Table 1), molecular ion at *m/e* 576, as expected. In the ^1H n.m.r. spectrum this derivative showed two sharp singlets at δ 6.69 and 6.40 p.p.m. due to the two pairs of equivalent aromatic hydrogens, a singlet at 2.13 p.p.m. due to the two methyl groups, and a complex pattern between 3.0 and 4.5 p.p.m. due to the crown ether hydrogens and presumably the methylene group of the diphenylmethane residue. Integration gave relative areas of 4.0 (aromatic) : 33.5 (crown ether + CH_2) : 6.0 (methyls), calc. 4 : 34 : 6. In the ^{13}C n.m.r. spectrum (in $CDCl_3$) the methyl carbons absorb at 18.9 p.p.m., the central methylene carbon at 35.8 p.p.m., the crown ether methylene carbons at 67.0—72.0 p.p.m., and the aromatic carbons at 114—150 p.p.m. We cannot explain how derivative (6) is formed.

15-Hydroxymethylbenzo-[15-crown-5] (1; X = CH_2OH) was converted into the 15-chloromethyl derivative (1; X = CH_2Cl) by treatment with thionyl chloride in benzene. The chloromethyl compound was characterized by microanalytical data (Table 1) and the mass spectrum showed a parent molecular ion at *m/e* 316 (for ^{35}Cl) and *m/e* 318 (for ^{37}Cl). In the ^1H n.m.r. ($CDCl_3$) the CH_2Cl protons absorb at 4.45 p.p.m.

As briefly mentioned above, 1-chloromethyl-3,4-dimethoxybenzene when treated with Li[PPh_2] gave the solid phosphine $PPh_2[CH_2C_6H_3(OMe)_2$-3,4] (4; X = CH_2PPh_2). This phosphine showed a molecular ion at the expected value of *m/e* 336, the expected ^1H n.m.r. spectrum, and a singlet in the ^{31}P n.m.r. spectrum at -9.8 p.p.m. The analogous 15-(diphenylphosphinomethyl)benzo-[15-crown-5] (1; X = CH_2PPh_2) was prepared similarly. It shows a parent molecular ion at *m/e* 466 in the mass spectrum (as would be expected), a singlet ^{31}P n.m.r. resonance at -9.65 p.p.m., the expected trisubstituted phenyl ^1H n.m.r. pattern, and broad resonances due to the crown ether methylenes which obscured the benzylic methylene resonance. When treated with PBu^t_2H, $ClCH_2C_6H_3(OMe)_2$ in acetone in the presence of sodium iodide gave a quantitative yield of the phosphonium salt $[PBu^t_2\{C_6H_3(OMe)_2\}H]I$. This salt was isolated but not characterized by analysis, *etc.* With sodium hydroxide solution it readily gave 1-(di-t-butylphosphinomethyl)-3,4-dimethoxybenzene, purified by distillation. It was characterized by ^1H n.m.r. spectroscopy, *e.g.* two singlets at δ 3.16 and 3.22 p.p.m. (OMe), a doublet at 2.5 p.p.m. [^2J(PH) 2 Hz] (benzylic CH_2), and a doublet at 0.80 p.p.m. [^3J(PH)

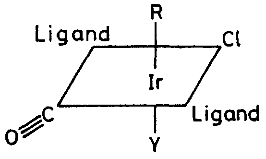
10.5 Hz (Bu^t)], by a singlet ^{31}P n.m.r. resonance (31.75 p.p.m.), and a molecular ion peak in the mass spectrum at *m*/*e* 328. A similar treatment of 15-chloromethylbenzo-[15-crown-5] with PBu$^t_2$H in acetone in the presence of NaI gave a rapid precipitate of the acetone-insoluble sodium iodide complex of 15-chloromethylbenzo-[15-crown-5]. This adduct was also prepared in the absence of PBu$^t_2$H (see Experimental section). We therefore carried out the treatment with PBu$^t_2$H in the presence of tetra-n-butylammonium iodide. No phosphonium iodide was precipitated and when the solvent was removed by evaporation an oil was obtained. This was treated with sodium hydroxide solution and the product extracted into diethyl ether to give a light yellow oil. Attempts to distil this oil at high vacuum (5 × 10^{-3} Torr)* caused extensive decomposition. However, the oil showed a singlet ^{31}P n.m.r. resonance at 32.0 p.p.m. together with a small peak at 57.0 p.p.m. assigned as the phosphine oxide (when the sample was allowed to stand in air this peak increased in intensity). The ^{1}H n.m.r. spectrum of the oil showed an aromatic hydrogen pattern of the expected form for 1,2,4-trisubstitution, crown ether resonances between 3.0 and 4.5 p.p.m., a broad singlet at 2.74 p.p.m. due to the benzylic methylene hydrogens, and a doublet at 1.10 p.p.m. [^3J(PH) 11 Hz] due to the t-butyl groups. The product oil appeared to be of sufficient purity to use as a ligand (the small amount of the phosphine oxide should not interfere) and was used without further purification as a solution in ethanol (see Experimental section).

As mentioned above the adduct between NaI and 15-chloromethylbenzo-[15-crown-5] forms rapidly at room temperature as a dense white precipitate on mixing the two components in acetone solution. This is the only example of such rapid solid-adduct formation that we have encountered. It is soluble in water but not in acetone or chloroform. It melts at 146—150 °C without apparent decomposition and we cannot offer an explanation for this high stability and very low solubility. We have also prepared sodium thiocyanate adducts of 15-substituted benzo-[15-crown-5] ethers (1; X = CHO, Me, or I) (see Experimental section). These were very soluble in acetone but could be crystallized from acetone–diethyl ether mixtures. Their melting points are considerably higher than those of the free crown ether ligands. The i.r. spectra of all these complexes in the ' fingerprint ' region are different from those of the uncomplexed crowns. It has been shown previously that the i.r. spectrum of benzo-[15-crown-5] is sensitive to conformational change, although individual assignments were not made.[14] The carbonyl-stretching frequencies of the sodium thiocyanate adducts of the formyl- and acetyl-substituted crowns of type (1) were essentially the same as the free ligands suggesting that the carbonyl groups are not involved in co-ordination. We were unable to make sodium thiocyanate complexes of dicrown ethers of types (5) and (6).

We have also made some conductimetric studies on complex formation between NaI and the 15-substituted benzo-[15-crown-5] ethers of type (1). Using 0.05 mol dm^{-3} crown ether in acetone as titrant and 0.001 mol dm^{-3} NaI in acetone at 21 °C a change in gradient of the curve of conductivity against moles of crown ether added per mol of NaI was observed with benzo-[15-crown-5] and with 15-hydroxymethylbenzo-[15-crown-5], corresponding to 1 : 1 complex formation. With the 15-formyl- or 15-iodo-benzo-[15-crown-5] and also with the dicrown (5) the titration curves show a more gradual change in gradient: this indicates that complex formation is less strong.

We have synthesized and characterized several kinds of transition-metal complexes with crown ether tertiary phosphines of type (1; X = CH$_2$PPh$_2$ or CH$_2$PBu$^t_2$) ligands Q and Q′ respectively, with the metals rhodium, iridium, palladium, and platinum. For comparison we also made complexes from the [(3,4-dimethoxyphenyl)methyl]phosphines (4; X = CH$_2$PPh$_2$ or CH$_2$PBu$_2{}^t$), ligands L and L′ respectively. Details of the preparative procedures are given in the Experimental section, microanalytical and molecular-weight data in Table 2, and ^{1}H and ^{31}P n.m.r. data in Table 3.

Thus treatment of [Rh$_2$Cl$_2$(CO)$_4$] in methanol with 2 mol of these ligands gave the complexes *trans*-[RhCl(CO)Q$_2$] and *trans*-[RhCl(CO)L$_2$]. The crown ether complex had ν(Rh–Cl) at 298 cm^{-1} and ν(C≡O) at 1 950 cm^{-1}. The ^{31}P n.m.r. spectrum shows a doublet at 29.3 p.p.m. with ^1J(RhP) 124 Hz, and the ^{1}H n.m.r. spectrum showed complex patterns at 6.54—7.36 (aromatic protons) and 3.0—4.5 p.p.m. (crown ether + benzylic protons) of the correct relative intensities. This rhodium(I) complex showed no tendency to undergo oxidative addition with methyl iodide. The characterizing data for *trans*-[RhCl(CO)L$_2$] are i.r. (Nujol mull) ν(Rh–Cl) at 299 cm^{-1} and ν(C≡O) at 1 960 cm^{-1}, a ^{31}P n.m.r. doublet at 29.6 p.p.m. [^1J(RhP) 127 Hz], and ^{1}H n.m.r. singlets at 3.76 and 3.38 p.p.m. (OMe), a ' virtually ' coupled triplet {|^2J(PH) + ^4J(PH)| = 6 Hz} at 3.95 p.p.m. due to the benzylic methylene protons, and a complex aromatic proton resonance. It also showed no tendency to react with MeI. The corresponding complexes of iridium, *trans*-[IrCl(CO)Q$_2$] and *trans*-[IrCl(CO)L$_2$], were made in excellent yields *via* their adducts (7; R = H, Y = Cl), *i.e.* by treating sodium chloroiridate(IV) in ethanol with carbon monoxide followed by the addition of the ligand (Q or L). Subsequent treatment with triethylamine removed the elements of



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* Throughout this paper: 1 Torr = (101 325/760) Pa.

[14] D. G. Parsons, M. R. Truter, and J. N. Wingfield, *Inorg Chim. Acta*, 1975, **14**, 45.

hydrogen chloride to give the yellow square-planar iridium(I) complexes.[15] The addition of hydrogen chloride was reversible and both these iridium(I) complexes added MeI to give the colourless iridium(III) adducts (7; R = Me, Y = I). Both iridium(I) complexes showed a u.v. absorption at $\lambda_{max.}$ 387 nm. A preliminary study of the additions of MeI to these complexes in toluene solution at 298 K, followed by the disappearance of the peak at 387 nm, showed that they both reacted at virtually the same rate with a half-life of 30 min (the solution was initially 0.001 mol dm^{-3} in complex and 0.01 mol dm^{-3} in MeI). Thus the crown ether moiety seems to exert virtually the same electronic and/or steric effect as the 1,2-dimethoxy-groups in the ' model ' complex.

TABLE 2

Microanalytical,[a] molecular-weight,[a] and melting-point data for some rhodium, iridium, palladium, and platinum complexes

Complex [b]	M.p. (θ_c/°C)	Microanalysis (%) C	H	Halogen [c]	M [d]
[RhCl(CO)L_2]	154—155	60.8 (61.5)	4.85 (5.00)	4.80 (4.20)	
[RhCl(CO)Q_2]	137—138	59.95 (60.1)	5.55 (5.65)	3.30 (3.20)	
[IrCl$_2$H(CO)L_2]	Decomp.	53.3 (53.5)	4.50 (4.50)	7.35 (7.35)	
[IrCl$_2$H(CO)Q_2]	Decomp.	53.65 (53.9)	5.10 (5.10)	5.40 (5.80)	
[IrCl(CO)L_2]	178—180	55.4 (55.6)	4.45 (4.55)	4.10 (3.80)	
[IrCl(CO)Q_2]	146—147	55.05 (55.55)	5.10 (5.25)	2.95 (2.95)	
[IrMe(Cl)I(CO)L_2]	203—205 [e]	49.55 (49.4)	4.20 (4.20)	2.95 (3.30) 11.5 (11.8) (I)	
[IrMe(Cl)I(CO)Q_2]	193—195 [e]	49.9 (50.1)	4.75 (4.95)	2.80 (2.70) 9.70 (9.60) (I)	
[PdCl$_2$L$_2$]	193—195	58.65 (59.3)	5.05 (5.00)	8.00 (8.35)	840 (850)
[PdCl$_2$Q$_2$]	181—184	57.85 (58.4)	5.50 (5.60)	6.20 (6.40)	1 092 (1 110)
(8; M = Pd, R = Ph)	237—238	53.1 (52.85)	4.30 (4.20)	7.10 (7.40)	963 (954)
[PdCl$_2$L$'_2$]	227—228	53.35 (53.0)	7.40 (7.60)	9.45 (9.20)	758 (770)
[PdCl$_2$Q$'_2$]	230—233	54.0 (53.6)	7.65 (7.65)	7.20 (6.90)	1 006 (1 030)
(8; M = Pd, R = Bu^t)	258—260 [e]	46.15 (47.6)	6.35 (6.45)	7.90 (8.10)	872 (874)
(9; M = Pd)	250—253	49.3 (48.7)	6.85 (6.75)	6.05 (6.25)	1 131 (1 134)
(10; M = Pd)	169—171	60.0 (60.1)	6.00 (6.20)	4.75 (5.05)	704 (699)
[PtCl$_2$L$_2$]	236—237	53.95 (53.7)	4.45 (4.50)	7.50 (7.55)	984 (938)
[PtCl$_2$Q$_2$]	154—157	53.7 (54.1)	5.25 (5.20)	6.30 (5.90)	1 253 (1 199)
(11)	139—141	56.15 (55.9)	4.60 (4.60)	4.20 (3.90)	997 (902)
(8; M = Pt, R = Bu^t)	280 [e]	39.2 (38.8)	5.35 (5.35)	6.95 (6.75)	987 (1 051)
(9; M = Pt)	177—183	41.45 (42.1)	5.75 (5.80)	5.00 (5.40)	1 314 (1 312)
(10; M = Pt)	223—225	53.7 (53.3)	5.40 (5.50)	4.40 (4.50)	
(12; X = Cl	Glass	54.0 (53.6)	5.90 (5.80)	3.65 (3.85)	
(12; X = I)	Glass	49.4 (48.75)	5.30 (5.30)	12.9 (12.55)	

[a] Calculated values are given in parentheses. [b] L = (4; X = CH$_2$PPh$_2$), L$'$ = (4; X = CH$_2$PBu$^t_2$), Q = (1; X = CH$_2$PPh$_2$), and Q$'$ = (1; X = CH$_2$PBu$^t_2$). [c] Chlorine unless indicated otherwise. [d] Measured in chloroform solution. [e] Melts with decomposition.

TABLE 3

I.r. (cm^{-1}) and ^{31}P [a] and ^{1}H [b] n.m.r. data for some iridium and palladium complexes [c]

Complex	I.r. (Nujol) ν(Ir–Cl)	ν(C≡O)	ν(Ir–H)	^{31}P N.m.r.	^{1}H N.m.r. δ(PCH$_2$)	^2J(PH) + ^4J(PH)	δ(IrH)	^2J(PH)	δ(IrCH$_3$)
(a) Iridium									
[IrCl(CO)L$_2$]	307	1 945		22.6	4.03 (t)	8			
[IrCl(CO)Q$_2$]	306	1 940		22.4	d				
[IrCl$_2$H(CO)L$_2$]	264, 300	2 050	2 190	−0.1	4.46 (t)	12	16.3 (t)	10	
[IrCl$_2$H(CO)Q$_2$]	258, 305	2 050	2 200	0.1	4.4b [e]		16.3 (t)	10	
[IrMe(Cl)I(CO)L$_2$]	300	2 040		−10.0	4.75b [e]				0.88 [e]
[IrMe(Cl)I(CO)Q$_2$]	297	2 040		−10.2	4.6b [e]				0.83 [e]

(b) Palladium	ν(Pd–Cl)	^{31}P N.m.r.	δ(OCH$_3$)	δ(PCH$_2$)	^2J(PH)	δ(Bu^t)	^3J(PH)
[PdCl$_2$L$'_2$]	346	43.5	3.84	3.56 (t)	7 [f]	1.52 (t)	13 [g]
(8; R = Bu^t)	260	100.7	3.74 3.78	3.13 (d)	10	1.42 (d)	14
(10)	280	h	3.27 3.70	3.27 (d)	9	1.40 (d)	12.5
[PdCl$_2$Q$'_2$]	345	43.7		d		1.50 (t)	13 [g]
(9)	250	h		3.08 (d)	10	1.38 (d)	14

[a] In CDCl$_3$ at 27 °C and 36.43 MHz. $\delta \pm 0.1$ p.p.m. [b] In CDCl$_3$ at 34 °C and 60 MHz. $\delta \pm 0.01$ p.p.m., $J \pm 0.5$ Hz. t = triplet, q = quartet, and b = broad. [c] Data for rhodium and the extensive data for the platinum complexes are given in the text. [d] Obscured by other resonances. [e] Unresolved. [f] $|^2J(PH) + {}^4J(PH)|$. [g] $|^3J(PH) + {}^5J(PH)|$. [h] See Discussion section.

Treatment of [PdCl$_2$(NCPh)$_2$] with either L or Q in methanol gave products of the type [PdCl$_2$(ligand)$_2$] as mixtures of *cis* and *trans* isomers. These seemed to readily interconvert in solution and we did not prepare the pure isomers. The products [PdCl$_2$L$_2$] and [PdCl$_2$Q$_2$] shown in Table 2 are therefore mixtures. Thus both mixtures showed three strong bands due to ν(Pd–Cl) at 275 and 296 (*cis*) and 350 cm^{-1} (*trans*). The ^{31}P

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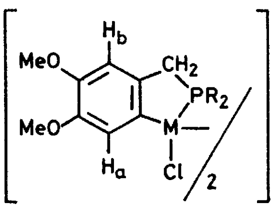
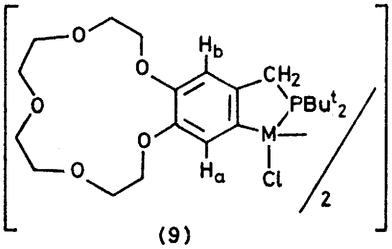
[15] A. J. Deeming and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 1887.

n.m.r. spectrum of $[PdCl_2Q_2]$ showed two peaks at 32.4 and 20.5 p.p.m., probably corresponding to the *cis* and the *trans* isomers, respectively. Similarly $[PdCl_2L_2]$ showed peaks at 32.0 and 20.4 p.p.m.

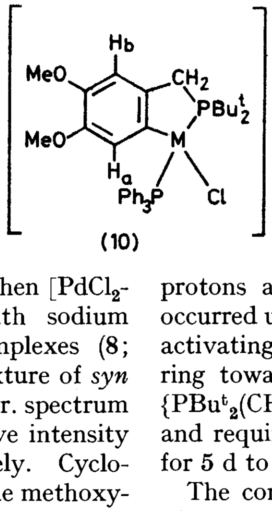
Cyclometallation of either $PPh_2(CH_2Ph)$ or $PPh(CH_2Ph)_2$ has not been observed with Pd^{II} although the aromatic ring of the more bulky phosphine $PBu^t_2(CH_2Ph)$ can be cyclopalladated.[16] However, the cyclometallation of aromatic rings has been shown to be promoted by methoxy-substituents *e.g.* the cyclopalladation of substituted azobenzenes[17] and the cyclo-iridation of substituted triphenylphosphines.[18] We thus hoped that our ligands Q and L could be cyclopalladated. However, both $[PdCl_2Q_2]$ and $[PdCl_2L_2]$ were recovered unchanged after being heated under reflux in 2-methoxyethanol solution for 4 h. It has also been shown, however, that cyclometallation of tertiary phosphines can be promoted by sodium acetate[19] and when $[PdCl_2L_2]$ was heated in 2-methoxyethanol with sodium acetate the chloride-bridged binuclear complexes (8; R = Ph, M = Pd) were produced, *i.e.* a mixture of *syn* and *anti* isomers as evidenced by the ^{31}P n.m.r. spectrum in $CDCl_3$ which showed two peaks of relative intensity *ca.* 5 : 1 at 54.4 and 48.3 p.p.m. respectively. Cyclometallation probably occurs *para* to one of the methoxy-groups by analogy with the PBu^t_2 complexes described below. In the ^1H n.m.r. spectrum of this *syn–anti* mixture the benzylic methylenes absorb at 3.76(d) p.p.m. [^2J(PH) 12 Hz], both OMe groups absorb at 3.72(s) p.p.m., and both aromatic protons of the 1,2-dimethoxybenzene ring absorb at 6.62(s) p.p.m. Unfortunately, attempted preparation of the analogous crown ether complex in a similar manner led to extensive decomposition and only an intractable glass could be isolated. It is possible that complexation of sodium ions by the crown ether moiety caused decomposition.



(8)



(9)



(10)

When $[PdCl_2(NCPh)_2]$ was treated with the bulky crown phosphine 15-(di-t-butylphosphinomethyl)benzo-[15-crown-5] (1; $X = CH_2PBu^t_2$) in ethanol it gave an amorphous yellow product. This when recrystallized from chloroform–ethanol gave a mixture of two types of crystals which could be separated mechanically or by fractional crystallization (see Experimental section and Table 1). One product (yellow needles) was $[PdCl_2Q'_2]$ exclusively in the *trans* configuration, and the other (lemon-yellow prisms) the chloride-bridged cyclometallated complex (9; M = Pd). This cyclometallated product showed ^{31}P n.m.r. resonances at 100.2 and 99.8 p.p.m. indicating only two species to be present in the ratio *ca.* 10 : 6; these are probably *syn* and *anti* isomers. In the ^1H n.m.r. spectrum a broad unresolved multiplet between 3.5 and 4.5 p.p.m. is due to the crown ether methylene protons and resonances at 7.39 and 6.59 p.p.m. correspond to the two, mutually *para*, aromatic protons as shown in (9). Since the cyclometallation occurred under such mild conditions it shows the marked activating effect of the ether oxygens on the aromatic ring towards cyclometallation. The complex $[Pd_2Cl_4\{PBu^t_2(CH_2Ph)\}_2]$ resists prolonged boiling in methanol and requires heating under reflux in 2-methoxyethanol for 5 d to effect metallation.[16]

The complex $[PdCl_2L'_2]$ was prepared by the action of (4; $X = CH_2PBu^t_2$), *i.e.* L′, on $[PdCl_2(NCPh)_2]$ in ethanol. The spectroscopic data (Table 3) indicate it to be exclusively in the *trans* configuration. When heated under reflux in 2-methoxyethanol it underwent cyclometallation with loss of phosphine ligand to give the binuclear complex $[Pd_2\{C_6H_2(CH_2PBu^t_2\text{-}2)(OMe)_2\text{-}4,5\}_2Cl_2]$ (8; M = Pd, R = Bu^t). Cyclometallation in boiling 2-methoxyethanol was faster in the presence of sodium acetate. Cyclometallation also occurred in boiling ethanol although less readily, *e.g.* after reflux for 3 h a mixture of unchanged $[PdCl_2L'_2]$ and cyclometallated product was obtained. Complex (8; M = Pd,

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[16] B. L. Shaw and M. M. Truelock, *J. Organometallic Chem.*, 1975, **102**, 517.

[17] H. Takahashi and J. Tsuji, *J. Organometallic Chem.*, 1967, **10**, 511.

[18] M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, 1969, **91**, 6983.

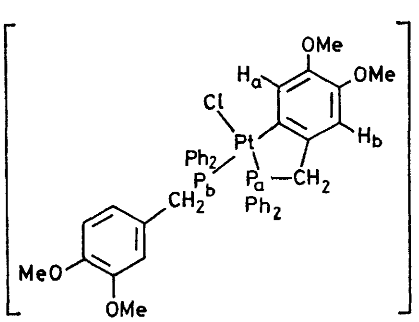
[19] J. M. Duff and B. L. Shaw, *J.C.S. Dalton*, 1972, 2219.

$R = Bu^{t}$) reacted with PPh_3 to give mononuclear $[\overline{Pd\{C_6H_2(CH_2P}Bu^{t}_2\text{-}2)(OMe)_2\}Cl(PPh_3)]$ (10) with mutually *trans* P-donor atoms: this follows from the ^{31}P n.m.r. spectrum which shows a large value for $^{2}J(PP)$ (395 Hz), the two ^{31}P chemical shifts being 88.3 and 28.2 p.p.m. In the ^{1}H n.m.r. spectrum two singlets at 6.66 and 6.27 p.p.m. are assigned as H_b and H_a respectively by analogy with the corresponding platinum complex (see below).

The binuclear cyclometallated complexes (8; $M = Pd$, $R = Bu^{t}$) and (9; $M = Pd$) gave good mass spectra, *e.g.* the crown complex gave a 15-line molecular ion with the most intense peak at *m/e* 1 134 as calculated from the assigned molecular formula (six isotopes of Pd, two of Cl, and two of C). Similarly, complex (8; $M = Pd$, $R = Bu^{t}$) showed a 15-line molecular ion with the most intense line at *m/e* 874.

Several platinum complexes including cyclometallated derivatives were also prepared, *e.g.* the complexes *cis*-$[PtCl_2L_2]$ and *cis*-$[PtCl_2Q_2]$ were readily formed by the action of the appropriate dimethoxy- and crown-phosphines on $[PtCl_2(NCPh)_2]$ in methanol. The dimethoxybenzyl complex $[PtCl_2L_2]$ showed ν(Pt–Cl) at 273 and 298 cm^{-1} and a ^{31}P n.m.r. singlet with satellites at 11.3 p.p.m. [$^{1}J(PtP)$ 3 758 Hz]. The ^{1}H n.m.r. spectrum was as expected with a trisubstituted phenyl pattern at 6.0—6.7 p.p.m., two sharp OMe singlets at 3.73 and 3.82 p.p.m., and a doublet at 3.98 p.p.m. [$^{2}J(PH)$ 11 Hz] with ^{195}Pt satellites [$^{3}J(PH)$ 48 Hz] due to the CH_2-$C_6H_3(OMe)_2$ protons. The crown ether complex $[PtCl_2Q_2]$ shows a ^{31}P resonance at 11.1 p.p.m. with satellites [$^{1}J(PtP)$ 3 762 Hz]: in the ^{1}H n.m.r. spectrum a broad multiplet between 3.0 and 4.5 p.p.m. due to the CH_2 protons of the crown ether ring obscured the resonance of the benzylic methylene protons.

Cyclometallation of $PPh_2(CH_2Ph)$ by platinum has not been observed.[20] However, treatment of *cis*-$[PtCl_2L_2]$ with sodium acetate in boiling 2-methoxyethanol gave a good yield of the cyclometallated complex $[\overline{Pt\{C_6H_2(CH_2P}Ph_2\text{-}2)(OMe)_2\text{-}4,5\}Cl\}\{PPh_2[CH_2C_6H_3\text{-}(OMe)_2\text{-}3,4]\}]$ (11). This again illustrates the increased tendency towards metallation of the benzene ring brought about by the methoxy-groups. This complex is unusual in that the two phosphorus donor atoms are mutually *cis* [$^{2}J(PP)$ 12 Hz, $\delta(P_a)$ 38.0 p.p.m., $\delta(P_b)$ 19.5 p.p.m., $^{1}J(PtP_a)$ 4 255 Hz, $^{1}J(PtP_b)$ 1 823 Hz]. In the ^{1}H n.m.r. spectrum a doublet at 8.18 p.p.m. [$^{4}J(PH)$ 7 Hz] with ^{195}Pt satellites [$^{3}J(PtH)$ 42 Hz] is probably due to proton H_a (11) and a broad singlet at 7.75 p.p.m. is assigned to H_b. In the i.r. spectrum a strong band at 289 cm^{-1} is assigned to ν(Pt-Cl): this value is typical of ν(Pt-Cl) *trans* to a phosphorus donor atom. Attempts to effect a similar cyclometallation of the crown ether complex $[PtCl_2Q_2]$ by treatment with sodium acetate caused decomposition to platinum metal or the starting complex was recovered unchanged.



(11)

Treatment of $[PtCl_2(NCPh)_2]$ with 1 mol of PBu^{t}_2-$[CH_2C_6H_3(OMe)_2\text{-}3,4]$ (L′) per Pt atom gave the binuclear complex (8; $M = Pt$, $R = Bu^{t}$). The microanalytical data (Table 2) are in agreement with this formulation: the i.r. spectrum showed bands at 276 and 252 cm^{-1} attributed to ν(Pt–Cl) and the ^{31}P n.m.r. spectrum (in $CDCl_3$) showed a peak at 71.3 p.p.m. with satellites [$^{1}J(PtP)$ 4 762 Hz]. The ^{1}H n.m.r. spectrum in $CDCl_3$ gave a doublet at 1.48 p.p.m. [$^{3}J(PH)$ (Bu^{t}) 13.5 Hz], a singlet at 3.79 p.p.m. (OCH_3), a doublet at 2.98 p.p.m. [$^{2}J(PH)$ 10 Hz] with satellites [$^{3}J(PtH)$ 42 Hz (PCH_2)], a singlet at 7.29 p.p.m. with satellites [$^{3}J(PtH)$ 60 Hz (H_a)], and a singlet at 6.78 p.p.m. [$^{3}J(PtH)$ 21 Hz (H_b)]; the assignments to H_a and H_b are based on the relative values of $J(PtH)$. When treated with PPh_3 in ethanol the chloride-bridged system is split and the mononuclear complex (10; $M = Pt$) was formed. This complex showed ν(Pt–Cl) at 276 cm^{-1}, $\delta(P_a)$ 74.0 p.p.m. [$^{1}J(PtP)$ 3 100 Hz], $\delta(P_b)$ 35.3 p.p.m. [$^{1}J(PtP)$ 2 932 Hz], $^{2}J(PP)$ 413 Hz. The ^{1}H n.m.r. spectrum gave a doublet at 1.45 p.p.m. [$^{3}J(PH)$ 12 Hz (Bu^{t})], two singlets at 3.74 and 2.77 p.p.m. (OCH_3), a doublet of doublets at 3.23 p.p.m. [$^{2}J(P_aH)$ 9, $^{4}J(P_bH)$ 2 Hz] with ^{195}Pt satellites [$^{3}J(PtH)$ 27 Hz] due to PCH_2, a doublet at 6.4 p.p.m. [$^{4}J(PH)$ 3 Hz] with ^{195}Pt satellites [$^{3}J(PtH)$ 61 Hz (H_a)], and a singlet at 6.72 p.p.m. with ^{195}Pt satellites [$^{4}J(PtH)$ 16 Hz (H_b)].

The crown phosphine (1; $X = CH_2PBu^{t}_2$) was similarly cyclometallated by $[PtCl_2(NCPh)_2]$ to give the binuclear complex (9; $M = Pt$). This probably was present in solution as *syn* and *anti* isomers since the ^{31}P n.m.r. spectrum in $CDCl_3$ showed two resonances each with satellites, one at 71.0 p.p.m. [$^{1}J(PtP)$ 4 729 Hz] and the other which was only *ca.* 40% the intensity of the first at 71.2 p.p.m. [$^{1}J(PtP)$ 4 756 Hz]. The ^{1}H n.m.r. spectrum gave a doublet at 1.37 p.p.m. [$^{3}J(PH)$ 14 Hz (Bu^{t})], a doublet at 2.95 p.p.m. [$^{2}J(PH)$ 9 Hz] with ^{195}Pt satellites [$^{3}J(PtH)$ 42 Hz (CH_2)], an unresolved multiplet at 3.5—4.5 p.p.m. due to crown ether methylenes, a singlet at 7.2 p.p.m. [$^{3}J(PtH)$ 60 Hz (H_a)], and a singlet at 6.67 p.p.m. [$^{4}J(PtH)$ 21 Hz (H_b)]. The value of $^{3}J(PtH)$ for H_a is typical for the group $Pt{-}\overset{|}{C}{=}\overset{|}{C}H$, *e.g.* in cycloplatinated arylphosphines[21] and *cis*-protonated acetylene (*i.e.* vinylic)[22] complexes. Triphenyl-

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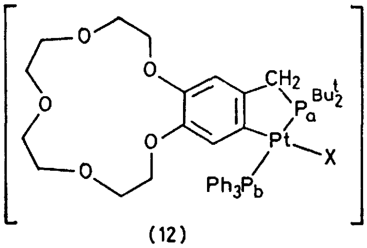
[20] B. L. Shaw and M. M. Truelock, unpublished work.

[21] A. J. Cheney, B. E. Mann, B. L. Shaw, and R. M. Slade, *J. Chem. Soc.* (*A*), 1971, 3833.

[22] B. E. Mann, B. L. Shaw, and N. I. Tucker, *Chem. Comm.*, 1970, 1333.

phosphine splits the chloride-bridged system to give only one product, the mononuclear complex (12) in good yield, *i.e.* the *syn* and *anti* isomers of (9) give the same product. The i.r. and ^{31}P n.m.r. data for this crown complex are very similar to those for the model complex, *i.e.* ν(Pt–Cl) at 275 cm^{-1}, δ(P_a) 73.8 [^1J(PtP) 3 100 Hz], and δ(P_b) 34.6 p.p.m. [^1J(PtP) 2 928 Hz] and the ^1H n.m.r. spectrum is similar apart from the broad unresolved signal at 3.5—4.5 p.p.m. due to the crown ether methylenes and the absence of OMe resonances.



(12)

Complex (12; X = Cl) in deuteriochloroform solution reacted slowly when shaken with solid NaI to give the corresponding iodide (12; X = I), whereas a $CDCl_3$ solution of the model dimethoxyphenyl analogue (10; M = Pt) was unaffected by NaI. Thus the crown ether complex is active as its own phase-transfer agent. Conversion was essentially complete after 24 h at 25 °C. The ^{31}P n.m.r. data for complex (12; X = I), which was isolated from solution (see Experimental section), are δ(P_a) 77.4 p.p.m. [^1J(PtP) 3 008 Hz] and δ(P_b) 28.2 p.p.m. [^1J(PtP) 2 969 Hz], ^2J(P_AP_B) 413 Hz. The ^1H n.m.r. data for this complex are very similar to those of the corresponding chloride. In the presence of NaI the ^{31}P parameters changed slightly, δ(P_a) 77.3 p.p.m. [^1J(PtP) 2 978 Hz] and δ(P_b) 28.5 p.p.m. [^1J(PtP) 2 935 Hz], ^2J(P_aP_b) 411 Hz. These changes are probably due to uptake of NaI and complexation of sodium ions by the crown ether moieties.

Apart from the example of internally promoted phase-transfer catalysis and the probable uptake of NaI discussed above, we have not studied the effects of added ions (Na^+, $[H_3O]^+$, $[NRH_3]^+$, *etc.*) on the properties of these crown ether–tertiary phosphine–transition-metal complexes. The effects could lead to some unusual chemistry and we hope to study them in the future.

EXPERIMENTAL

The general techniques and instruments were the same as those used previously.[23] Percentage yields, m.p.s, and characterizing data are given in the Tables.

15-*Iodo*-2,3,5,6,8,9,11,12-*octahydro*-1,4,7,10,13-*benzopentaoxacyclopentadecin* (1; X = I).—Benzo-[15-crown-5] (6.0 g, 22.3 mmol), iodine (2.26 g, 8.94 mmol), and periodic acid (1.02 g, 4.47 mmol) were added to a mixture of glacial acetic acid (25 cm^3), water (5 cm^3), and concentrated sulphuric acid (0.6 cm^3). The mixture was stirred at 65—70 °C for 16 h, cooled, and diluted to 250 cm^3 with water. The product was isolated with diethyl ether, the ether extract being washed with sodium thiosulphate solution and then sodium hydrogencarbonate solution. It formed needles (7.73 g, 19.6 mmol) from light petroleum (b.p. 60—80 °C).

18-Iodo-2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclo-octadecin (2; X = I) and 15-iodo-16-methyl-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin (3; X = I) were prepared similarly.

(1; X = CHO).—Phosphoryl chloride (57.2 g, 0.37 mol) was added to *N*-methylformanilide (50.4 g, 0.37 mol) and the resulting mixture was put aside for 20 min. Benzo-[15-crown-5] (50.0 g, 0.18 mol) was then added and the mixture was heated to *ca.* 90 °C for 4 h. The resulting dark brown mixture was cooled, added to water (600 cm^3), and the crude product extracted into chloroform (6 × 75 cm^3). The chloroform was removed under reduced pressure and the residual brown oil in ethanol solution (150 cm^3) was added to a solution of sodium hydrogensulphite (70 g, 0.31 mol) in water (150 cm^3) and ethanol (120 cm^3). The resulting solution was warmed and stirred to give the sodium hydrogensulphite adduct of the product as a heavy white precipitate. This was collected, suspended in a mixture of water (400 cm^3) and chloroform (200 cm^3) at 0 °C. Concentrated H_2SO_4 (*ca.* 80 cm^3) was added carefully to the stirred suspension until all the solid had dissolved. The chloroform layer was separated, the aqueous layer extracted with chloroform (4 × 75 cm^3), and the combined chloroform extracts evaporated under reduced pressure. The resulting yellow oil was dissolved in a boiling mixture of propan-2-ol (150 cm^3) and light petroleum (b.p. 60—80 °C) (100 cm^3). The required product crystallized as white needles on cooling and could be further purified by recrystallization from propan-2-ol, yield 29.8 g (0.10 mol).

When treated with an equivalent quantity of 2,4-dinitrophenylhydrazine in boiling ethanol it gave the 2,4-dinitrophenylhydrazone as red needles.

The compound (3; X = CHO) was prepared in a similar manner without treatment with $Na[HSO_3]$. The oil isolated with chloroform readily gave needles of the required product from propan-2-ol.

(1; X = CH_2OH).—15-Formylbenzo-[15-crown-5] (1.75 g, 5.9 mmol) was added to a suspension of lithium tetrahydridoaluminate (0.58 g, 15.3 mmol) in diethyl ether (60 cm^3). The resulting mixture was stirred at room temperature for 24 h, aqueous sodium hydroxide solution (1 mol dm^{-3}, 2.64 cm^3) was then added over 10 min, and the ether layer was separated from a gum. The gum was extracted with chloroform (2 × 30 cm^3) and the combined organic extracts dried ($Mg[SO_4]$). The product was isolated from the organic layer and formed needles from propan-2-ol –light petroleum (b.p. 40—60 °C) (1 : 1) at −20 °C, yield 1.12 g (3.76 mmol). The mother liquors from this recrystallization were put aside for several weeks at *ca.* 20 °C and gradually deposited a white precipitate identified as 15,15′-oxydimethylenebis(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin) (5) (0.42 g, 0.72 mmol) which formed needles from ethanol.

15,15′-*Methylenebis*(16-*methyl*-2,3,5,6,8,9,11,12-*octahydro*-1,4,7,10,13-*benzopentaoxacyclopentadecin*) (6).—Similar treatment of 15-formyl-16-methylbenzo-[15-crown-5] with $Li[AlH_4]$ in diethyl ether gave only the dicrown ether which formed needles from ethanol.

(1; X = CH_2Cl).—A solution of thionyl chloride (1.8 g,

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[23] H. D. Empsall, E. M. Hyde, and B. L. Shaw, *J.C.S. Dalton*, 1975, 1690.

1.10 cm^3, 15.2 mmol) in dry benzene (15 cm) was added to a stirred solution of 15-hydroxymethylbenzo-[15-crown-5] (2.26 g, 7.59 mmol) in benzene (15 cm^3). The resulting mixture was stirred for 2 h at *ca.* 20 °C, water (20 cm^3) was then added, and the benzene layer separated. The aqueous layer was extracted with chloroform (3 × 30 cm^3) and the product isolated from the combined organic layers. It formed prisms from light petroleum (b.p. 40—60 °C).

(1; X = CH_2PPh_2).— 15-(Chloromethyl)benzo-[15-crown-5] (1.45 g, 4.59 mmol) in dry diethyl ether (35 cm^3) was added at 20 °C over 20 min to a stirred solution of lithium diphenylphosphide, prepared from diphenylphosphine (0.85 g, 4.59 mmol) in diethyl ether (10 cm^3) and butyl-lithium (3.12 cm, 1.47 mol dm^{-3}) in hexane. The resulting mixture was stirred at *ca.* 20 °C for 1 h and then heated under reflux for 2 h. Water (20 cm^3) was then added and the product isolated with diethyl ether. It formed needles from ethanol, yield 1.61 g (3.45 mmol).

1-(Diphenylphosphinomethyl)-3,4-dimethoxybenzene was prepared similarly and formed plates from methanol.

1-(*Di-t-butylphosphinomethyl*)-3,4-*dimethoxybenzene*.— Di-t-butylphosphine (7.04 g, 48.15 mmol) in acetone (10 cm^3) was added to a solution of 1-chloromethyl-3,4-dimethoxybenzene (8.98 g, 48.15 mmol) and sodium iodide (8 g, 53 mmol) in acetone (30 cm^3) with external ice cooling. After the vigorous reaction had subsided the mixture was stirred at 20 °C for 2 h and the white precipitate of the phosphonium salt isolated, yield 20.4 g (48.15 mmol, 100%). A portion of this solid (14.0 g, 33.0 mmol) was suspended in diethyl ether (50 cm^3) and shaken with a solution of sodium hydroxide (13 g, 33 mmol) in water (25 cm^3) for 5 min. The product was isolated as a colourless liquid from the ether by distillation, yield 7.98 g (27.0 mmol, 84%), b.p. 155—165 °C (0.05 Torr).

The compound (1; X = $CH_2PBu^t_2$) was prepared similarly but could not be distilled and was used as an ethanol solution (see Discussion section).

(1; X = CHO)·Na[SCN] *Adduct*.—A solution of 15-formylbenzo-[15-crown-5] (0.24 g, 0.81 mmol) and sodium thiocyanate (0.065 g, 0.81 mmol) in ethanol (15 cm^3) was filtered and then evaporated to low bulk (*ca.* 4 cm^3) on a water-bath. Diethyl ether (5 cm^3) was added to the cooled solution giving the required adduct (0.27 g, 0.71 mmol) as a microcrystalline white solid. The adducts (1; X = COMe)·Na[SCN], (1; X = Me)·Na[SCN], and (1; X = I)·Na[SCN] were prepared similarly.

(1; X = CH_2Cl)·NaI *Adduct*.—A solution of 15-(chloromethyl)benzo-[15-crown-5] (0.25 g, 0.79 mmol) in acetone (5 cm^3) was added to a solution of NaI (0.24 g, 1.58 mmol) in acetone (5 cm^3). White prisms of the adduct separated immediately, yield 0.33 g (0.71 mmol).

trans-(*Carbonyl*)*chlorobis*{15-(*diphenylphosphinomethyl*)-2,3,5,6,8,9,11,12-*octahydro*-1,4,7,10,13-*benzopentaoxacyclopentadecin*}*rhodium*(I).—The phosphine ligand (0.58 g, 1.25 mmol) was added to a solution of μ-dichloro-tetracarbonyldirhodium(I) (0.12 g, 0.30 mmol) in methanol (15 cm^3) at *ca.* 20 °C. After 30 min the product was filtered off and formed yellow prisms from chloroform–ethanol, yield 0.58 g (0.53 mmol, 88%).

trans-Carbonylchlorobis{1-(diphenylphosphinomethyl)-3,4-dimethoxybenzene)}rhodium(I) was prepared similarly as yellow prisms, yield 92%.

trans-*Carbonyldichlorobis*{15-(*diphenylphosphinomethyl*)-2,3,5,6,8,9,11,12-*octahydro*-1,4,7,10,13-*benzopentaoxacyclopentadecin*}*hydridoiridium*(III), $[IrCl_2H(CO)Q_2]$.—A solution containing $Na_2[IrCl_6]$ (0.35 g, 0.61 mmol), rhodium trichloride trihydrate (0.02 g), and concentrated hydrochloric acid (0.5 cm^3) was stirred at 80 °C in an atmosphere of carbon monoxide for 24 h. The resulting mixture was stirred with the phosphine ether ligand (0.62 g, 1.34 mmol) for 1 h and the resulting precipitate was filtered off and washed with water and ethanol. The product was obtained as white microcrystals (0.74 g, 0.60 mmol) which decomposed on attempted recrystallization, yield 98%.

trans-Carbonyldichlorobis{1-(diphenylphosphinomethyl)-3,4-dimethoxybenzene}hydridoiridium(III), $[IrCl_2H(CO)L_2]$, was prepared similarly as white prisms yield 98%.

trans-$[IrCl(CO)Q_2]$.—The complex *trans*-$[IrCl_2H(CO)Q_2]$ (0.60 g, 0.49 mmol) suspended in ethanol (8 cm^3) was treated with triethylamine (0.049 g, 0.49 mmol) and the resulting mixture heated on a water-bath for 30 min. The required product separated on cooling and formed yellow prisms from dichloromethane–ethanol, yield 0.51 g (0.43 mmol, 88%).

The complex *trans*-$[IrCl(CO)L_2]$ was prepared similarly as yellow prisms, yield 96%.

$[IrMe(Cl)I(CO)Q_2]$.—Iodomethane (3 cm^3) was added to a solution of *trans*-$[IrCl(CO)Q_2]$ (0.16 g, 0.13 mmol) in benzene (5 cm^3) and the mixture put aside at room temperature for 30 min. The resulting colourless solution was reduced to *ca.* 2 cm^3 by evaporation under reduced pressure and light petroleum (b.p. 60—80 °C, 15 cm^3) added. The resulting precipitate was recrystallized from dichloromethane–light petroleum (b.p. 60—80 °C) as white microcrystals, yield 0.14 g (0.11 mmol, 81%). The complex $[IrMe(Cl)I(CO)L_2]$ was similarly prepared as white microcrystals, yield 94%.

$[PdCl_2Q_2]$.—A mixture of the phosphine ether (0.61 g, 1.3 mmol) and bis(benzonitrile)dichloropalladium(II) (0.24 g, 0.63 mmol) in methanol (10 cm^3) was shaken at *ca.* 20 °C for 24 h. The resulting yellow precipitate was recrystallized from dichloromethane–methanol to give the required product as yellow microcrystals (0.37 g, 0.33 mmol, 53%). The complex $[PdCl_2L_2]$ was similarly prepared as light yellow plates from chloroform–methanol, yield 91%.

Di-μ-chloro-bis{[2-(*diphenylphosphinomethyl*)-4,5-*dimethoxyphenyl*-C^1P]*palladium*(II)}, *Configuration* (8; M = Pd, R = Ph).—A mixture of $[PdCl_2L_2]$ (0.28 g, 0.33 mmol) and sodium acetate (0.27 g, 3.3 mmol) in 2-methoxyethanol (12 cm^3) was heated under reflux for 2 h. The solution was cooled and the small amount of black precipitate filtered off. The filtrate was added to water (80 cm^3) giving the required product as light yellow needles (0.14 g, 0.15 mmol) from chloroform–ethanol.

trans-*Dichlorobis*[1-(*di-t-butylphosphinomethyl*)-3,4-*dimethoxybenzene*]*palladium*(II), $[PdCl_2L'_2]$.—Bis(benzonitrile)dichloropalladium(II) (0.93 g, 2.44 mmol) was added to a solution of the phosphine L′ (1.52 g, 5.13 mmol) in ethanol (15 cm^3) and the mixture was shaken at *ca.* 20 °C for 15 h. The required product precipitated and formed deep yellow prisms from chloroform–ethanol.

The Action of (1; X = $CH_2PBu^t_2$), Q′, *on* $[PdCl_2(NCPh)_2]$.—A solution of the phosphine ether (0.68 g, 1.6 mmol) in ethanol (7 cm^3) was added to $[PdCl_2(NCPh)_2]$ (0.29 g, 0.77 mmol) and the resulting mixture was shaken for 24 h. The resulting yellow solid was recrystallized by allowing its solution in chloroform–ethanol to slowly evaporate over 6 weeks. This gave a mixture of two sets of well formed crystals which were readily separated mechanically as *trans*-$[PdCl_2Q'_2]$, yellow needles (0.16 g, 0.15 mmol, 20%), and *di-μ-chloro-bis*{[16-(*di-t-butylphosphinomethyl*)-2,3,5,6,8,9,11,12-*octahydro*-1,4,7,10,13-*benzopentaoxacyclopentadecin*-15-*yl*-C^{15}P]*palladium*(II)} (9; M = Pd) as lemon-yellow prisms (0.18 g, 0.16 mmol, 10%).

(8; M = Pd, R = Bu^t).—A mixture of $[\mathrm{PdCl_2L'_2}]$ (0.53 g, 0.68 mmol) and sodium acetate (0.56 g, 6.8 mmol) in 2-methoxyethanol (20 cm^3) was heated under reflux for 30 min. The resulting solution was cooled and poured into water (80 cm^3) giving the product as lemon-yellow prisms (0.25 g, 0.29 mmol) from chloroform–ethanol.

Chloro[2-(*di-t-butylphosphinomethyl*)-4,5-*dimethoxyphenyl*-C^{1}P](*triphenylphosphine*)*palladium*(II), *Configuration* (10; M = Pd).—A mixture of complex (8; M = Pd, R = Bu^t) (0.13 g, 0.15 mmol) and triphenylphosphine (0.08 g, 0.33 mmol) in ethanol (10 cm^3) was heated under reflux for 10 min. The required product separated on cooling as light yellow needles which were recrystallized from ethanol, yield 0.14 g (0.20 mmol, 67%).

cis-$[\mathrm{PtCl_2Q_2}]$.—A mixture of bis(benzonitrile)dichloroplatinum(II) (0.14 g, 0.31 mmol) and the phosphine ether (0.30 g, 0.64 mmol) in methanol (10 cm^3) was heated under reflux for 5 min. The required product separated from the cooled solution and formed white prisms from dichloromethane–methanol, yield 0.34 g (0.29 mmol, 92%). The complex *cis*-$[\mathrm{PtCl_2L_2}]$was prepared similarly as white plates, yield 65%.

Chloro[(3,4-*dimethoxyphenylmethyl*)*diphenylphosphine*]-[2-(*diphenylphosphinomethyl*)-4,5-*dimethoxyphenyl*-C^{1}P]-*platinum*(II), *Configuration* (11).—The complex $[\mathrm{PtCl_2L_2}]$ (0.33 g, 0.35 mmol) and sodium acetate (0.29 g, 3.5 mmol) were heated together in 2-methoxyethanol (20 cm^3) for 3.5 h. The solution was cooled and added to water (100 cm^3), precipitating the required product which formed as white prisms from dichloromethane–methanol, yield 0.29 g (0.32 mmol, 94%).

(8; M = Pt, R = Ph).—A mixture of $[\mathrm{PtCl_2(NCPh)_2}]$ (0.81 g, 1.72 mmol) and 1-(di-t-butylphosphinomethyl)-3,4-dimethoxybenzene (L′) (0.51 g, 1.72 mmol) was heated under reflux in ethanol (12 cm^3) for 3 h. The small amount of a black precipitate was filtered off and the required product separated from the filtrate. It formed white needles (0.29 g, 0.28 mmol) from dichloromethane–ethanol.

(9; M = Pt).—A mixture of dichlorobis(t-butyl cyanide)-platinum(II) (0.38 g, 0.87 mmol) and (1; X = $\mathrm{CH_2PBu^t{}_2}$) (0.78 g, 1.84 mmol) in ethanol (8 cm^3) was heated under reflux for 5 h. The solvent was then removed under reduced pressure and the residue triturated with pentane. The resulting solid was recrystallized from methanol to give the required complex (9) (0.49 g, 0.37 mmol) as off-white prisms.

(10; M = Pt).—Complex (8; M = Pt, R = Bu^t) (0.12 g, 0.11 mmol) in hot ethanol (5 cm^3) was heated with triphenylphosphine (0.06 g, 0.24 mmol) for 15 min. The required product crystallized on cooling and formed colourless needles from ethanol, yield 0.16 g (0.20 mmol, 82%).

Chloro[16-(*di-t-butylphosphinomethyl*)-2,3,5,6,8,9,11,12-*octahydro*-1,4,7,10,13-*benzopentaoxacyclopentadecin*-15-*yl*-C^{15}P](*triphenylphosphine*)*platinum*(II) *Configuration* (12; X = Cl).—A solution of complex (9; M = Pt) (0.097 g, 0.074 mmol) in hot ethanol (5 cm^3) was treated with triphenylphosphine (0.038 g, 0.147 mmol) and the resulting mixture warmed to *ca.* 60 °C for 15 min. The product was isolated as a glass by evaporation but could not be induced to crystallize. It was characterized by n.m.r. and i.r. spectroscopy (see text).

(12; X = I).—Complex (12; X = Cl) (0.025 g, 0.082 mmol) in deuteriochloroform (0.6 cm^3) was shaken with NaI (0.12 g, 0.82 mmol) at 25 °C and the progress of reaction followed by ^{31}P n.m.r. spectroscopy (see Discussion section). After 48 h the solvent was evaporated and the residue washed with water and dried. It was isolated as a glass which could not be induced to crystallize but was characterized by microanalysis (Table 1) and ^{31}P n.m.r. spectroscopy (see Discussion section).

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