Preparation of Hydroxo- and Cyano-complexes of Platinum(II) by the Use of (Crown Ether)Potassium Hydroxide and Cyanide †

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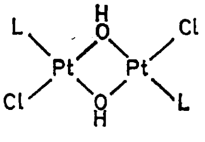
Phase-transfer catalysis using crown ethers has been used to obtain $[Pt_2Cl_2(OH)_2L_2]$ (L = PEt_3, PMe_2Ph, and PEt_2Ph), $[Pt_2(OH)_2(C_6H_4Me\text{-}4)_2(PEt_2Ph)_2]$, and [Pt(OH)Ph(dppe)] from chloro-complexes and aqueous KOH. Crown ethers catalyse the reaction between solid KCN and platinum(II) complexes and salts containing the anions $[PtR_2(CN)_2]^{2-}$ (R = benzofuran-2-yl, 2-thienyl, 4-methoxyphenyl, and Me), $[PtMe_2(CN)(PEt_3)]^-$, and $[PtMe(CN)_2(PEt_3)]^-$ have been obtained.

PLATINUM(II) complexes of tertiary phosphines are usually soluble in organic solvents, but insoluble in water, and since the reverse is true for most simple alkali-metal salts, difficulties can arise in carrying out reactions between them. These difficulties have sometimes been overcome by the use of acetone or an alcohol as solvent, but a much wider range of organic solvents can now be used if crown ethers [1] are added to complex the alkali-metal cation. We report the use of crown ether–KOH and –KCN in the preparation of some platinum(II) hydroxo- and cyano-complexes.

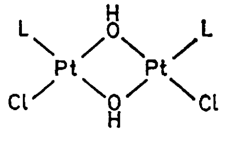
RESULTS AND DISCUSSION

Hydroxo-complexes.—Although hydroxide ion is a strong nucleophile and should be capable of cleaving chloride bridges or displacing the terminal chloride of (phosphine)platinum(II) complexes, few platinum(II) hydroxo-complexes appear to have been obtained by this route. In the presence of hydroxide, alcohols as solvents become strongly reducing and, instead of forming hydroxo-complexes, reactions between KOH in alcohols and chloro(phosphine)platinum(II) complexes give platinum metal, platinum(0) complexes, or platinum(II) hydrides.[2]

We have found that reactions between (phosphine)-platinum(II) complexes and crown ether–KOH in benzene or dichloromethane are most conveniently carried out in a phase-transfer system.[3] The complex (*ca.* 0.5 g) and crown ether (either 18-crown-6 [1] or dicyclohexyl 18-crown-6,[1] *ca.* 0.1 g) were dissolved in benzene or dichloromethane (*ca.* 10 cm^3), an approximately equal volume of aqueous KOH (2 mol dm^{-3}) was added, and the two-phase mixture stirred vigorously at ambient temperature. After some time (usually several hours) the organic layer was separated, washed with water, dried, and evaporated to dryness to give in favourable instances a solid which was purified by recrystallisation. With the chloride-bridged complexes *sym-trans*-$[Pt_2Cl_4L_2]$ (L = PEt_3, PMe_2Ph, and PEt_2Ph) in benzene, this procedure gave complexes (**1**)—(**3**) with analyses corresponding to $[Pt_2Cl_2(OH)_2L_2]$ in yields that increased with decreasing solubility of the product. The presence of the hydroxo-ligand was indicated by ν(OH) at *ca.* 3 450—3 600 cm^{-1} [ν(OD) 2 665 cm^{-1} in a deuteriated sample, L = PEt_3] in the i.r. spectra of thoroughly dried samples, and the hydroxo-ligands are evidently in bridging positions, since the band at *ca.* 270 cm^{-1} characteristic of bridging chloride, which was present in the spectra of the starting complexes, was absent in the spectra of the products. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of the products (**1**)—(**3**) in dichloromethane comprised two resonances of unequal intensity with very similar chemical shifts and each having ^{195}Pt satellites with fairly similar values of ^1J(PtP) (Table). The parameters of each resonance are different from those of the starting complex. It appears therefore that in solution the hydroxo-bridged complexes are mixtures of isomers [(a) and (b)] the proportions of which depend on the nature of L.



(a)



(b)

From the organic layer of the reaction mixture (L = PEt_3) we also isolated a yellow complex, shown by analysis and comparison of its ^{31}P n.m.r. parameters with known values[4] to be $[K(18\text{-crown-}6)][PtCl_3L]$ (**4**; L = PEt_3). This complex was soluble in water and a variety of organic solvents. Concentration of the aqueous layer of the reaction mixture (L = PEt_3) led to some decomposition, but $^{31}P\text{-}\{^1H\}$ spectra of the concentrated aqueous layer showed the presence of $[PtCl_3L]^-$ and an approximately equal amount of a compound with ^{31}P n.m.r. parameters [δ 140.1 p.p.m., ^1J(PtP) 4 026 Hz] different from (1a), (1b), or known chloro(phosphine)-platinum(II) complexes.[4] From the method of preparation it is probable that this complex is *trans*-$[PtCl_2(OH)L]^-$ (L = PEt_3) and the value of ^1J(PtP) is consistent with this formulation. It is presumed that this anion is formed by cleavage of the chloride bridge of the starting complex and that two such anions combine to form the hydroxide-bridged complexes with elimination of chloride. The anion $[PtCl_3L]^-$ is known to be formed from the chloride-bridged complex in the presence of chloride.[4]

Unlike the compounds $[Pt_2(OH)_2L_4]^{2+}$, which are inert in the presence of nucleophiles,[5] the complexes

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† No reprints available.

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$[Pt_2Cl_2(OH)_2L_2]$ (L = PEt_3 or PEt_2Ph) reacted rapidly with amines or phosphines. However, the initial products decomposed, giving black deposits and dark-coloured solutions; the solution from the reaction between PEt_2Ph and $[Pt_2Cl_2(OH)_2(PEt_2Ph)_2]$ was shown from ^{31}P-$\{^1H\}$ n.m.r. spectra to contain $P(O)Et_2Ph$ and *cis*-$[PtCl_2(PEt_2Ph)_2]$ and a variety of unidentified phosphorus-containing compounds.

With the chloride-bridged complex $[Pt_2Cl_2(C_6H_4Me\text{-}4)_2(PEt_2Ph)_2]$ in benzene the above procedure gave a stable crystalline complex with ν(OH) 3 600 cm^{-1}, ν(PtCl) absent, and with an analysis corresponding to $[Pt_2(OH)_2(C_6H_4Me\text{-}4)_2(PEt_2Ph)_2]$ (5). In CH_2Cl_2, ^{31}P-$\{^1H\}$ n.m.r. spectra showed that this reacted with PEt_2Ph (2 mol) to give mainly *trans*-$[Pt(C_6H_4Me\text{-}4)(OH)(PEt_2Ph)_2]$ (6) (see Table). Complexes of this type have been prepared by other routes.[6] The spectrum also showed the presence of a minor component containing three phosphine ligands, two of which were equivalent. This complex is probably $[Pt(C_6H_4Me\text{-}4)(PEt_2Ph)_3]^+$, but it was not positively identified because the ^{195}Pt satellites of the triplet resonance were too weak to be observed. The complex (5) did not react with $[NBu_4]Cl$.

TABLE

Phosphorus-31 n.m.r. parameters of complexes dissolved in dichloromethane [a]

Complex	δ [b] p.p.m.	^1J(PtP)/Hz	Notes
$[PtCl_2(OH)_2(PEt_3)_2]$ (1a) [c]	141.9	4 097	Isomer ratio (a)/(b) 0.08
(1b)	142.7	4 067	
$[Pt_2Cl_2(OH)_2(PMe_2Ph)_2]$ (2a)	165.9	4 116	Isomer ratio (a)/(b) 1.1
(2b)	165.5	4 042	
$[Pt_2Cl_2(OH)_2(PEt_2Ph)_2]$ (3a) [c]	144.5	4 145	Isomer ratio (a)/(b) 1.6
(3b)	144.1	4 057	
$[K(18\text{-crown-}6)][PtCl_3(PEt_3)]$ (4)	138.4	3 706	
$[Pt_2Cl_2(C_6H_4Me\text{-}4)_2(PEt_2Ph)_2]$	148.3	4 865	^2J(PtPt) 105, ^3J(PtP) −6, ^4J(PP) 3 Hz
$[Pt_2(OH)_2(C_6H_4Me\text{-}4)_2(PEt_2Ph)_2]$ (5)	135.8	4 425	
trans-$[Pt(OH)(C_6H_4Me\text{-}4)(PEt_2Ph)_2]$ (6)	126.5	2 883	
$[PtCl(Ph)(dppe)]$	100.3	1 650	P *trans* to Ph
	102.0	4 164	P *trans* to Cl
$[Pt(OH)Ph(dppe)]$ (7)	103.1	1 784	P *trans* to Ph
	108.6	3 425	P *trans* to OH
$[Pt(CH_2COCH_3)Ph(dppe)]$ (8) [d]	96.7	1 709	P *trans* to Ph
	98.5	2 309	P *trans* to CH_2COCH_3
cis-$[PtCl(OH)(PMe_2Ph)_2]$ (9) [e]	152.1	3 899	^2J(PP) = 24 Hz
	164.1	3 066	

[a] Obtained from ^{31}P-$\{^1H\}$ spectra (40.5 MHz). [b] Positive shifts are to high field of the external reference $P(OMe)_3$ in C_6D_6. [c] Complex with larger ^1J(PtP) tentatively assigned structure (1) by analogy with chloride-bridged complexes (ref. 8). [d] In acetone. [e] See text.

A compound analogous to the reported[6] [Pt(OH)Me(dppe)] [dppe = 1,2-bis(diphenylphosphino)ethane] was obtained by the reaction of hydroxide with [PtCl(Ph)(dppe)] in dichloromethane using the procedure described earlier with a short reaction time to minimise the extent of reaction of the product with dichloromethane. The product [Pt(OH)Ph(dppe)] (7), obtained as a white crystalline material, was so formulated on the basis of analytical results, ν(OH) at 3 608 cm^{-1}, the absence of a band due to ν(PtCl), and the ^{31}P n.m.r. parameters given in the Table. From ^{31}P-$\{^1H\}$ n.m.r. spectra it was shown that (7) reacted with acetone to form $[Pt(CH_2COCH_3)Ph(dppe)]$ (8).[6]

Attempts to isolate hydroxo-complexes by the above procedure from *cis*-$[PtCl_2L_2]$ in CH_2Cl_2 (L = PMe_2Ph or PEt_3) led to much decomposition and recovery of some starting complex. The ^{31}P-$\{^1H\}$ n.m.r. spectrum of the organic phase (L = PMe_2Ph) after 30 min showed the presence of a complex (9) with non-equivalent phosphines each *trans* to a ligand of low *trans*-influence. This complex is presumably *cis*-$[PtCl(OH)(PMe_2Ph)_2]$ or $[Pt_2Cl(OH)(PMe_2Ph)_4]^{2+}$. At longer reaction times this complex disappeared and $[Pt_2(OH)_2(PMe_2Ph)_4]^{2+}$ was detected.[7] In an attempt to isolate this as the tetrafluoroborate salt, an excess of $Na[BF_4]$ was added to the reaction mixture after 2 h. A colourless crystalline product (10) was obtained on working up the organic phase. This melted at a temperature (245—249 °C) different from that reported[7] for $[Pt_2(OH)_2(PMe_2Ph)_4][BF_4]_2$ (155—157 °C), it had i.r. bands characteristic of $[BF_4]^-$, but bands due to ν(PtCl) or ν(OH) were not detected. The molar conductivity implied a 2 : 1 electrolyte and the analytical results were consistent with a trinuclear formulation $[Pt_3(O)_2(PMe_2Ph)_6][BF_4]_2$. Consistent with this, the ^{31}P-$\{^1H\}$ n.m.r. spectrum showed the phosphines to be equivalent and was similar in form to that obtained[8] for the trinuclear complex $[Pt_3(S)_2(PMe_2Ph)_6]^{2+}$.[9]

It is evident from this and other work[6,10] that the 'soft' character of co-ordination sites in phosphine-platinum(II) complexes does not prevent the formation of stable hydroxo-complexes, although in some situations there appears to be a decomposition route that results in the formation of phosphine oxide and unstable complexes, which are possibly platinum(II) hydrides. Hydroxide

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[8] K. J. Odell, personal communication.

[9] J. Chatt and D. M. P. Mingos, *J. Chem. Soc. (A)*, 1970, 1243.

[10] J. Chatt and B. T. Heaton, *J. Chem. Soc. (A)*, 1968, 2745.

co-ordinated to platinum(II) is sufficiently nucleophilic to displace chloride ligand with formation of dinuclear hydroxo-bridged complexes. Complexes with terminal hydroxo-ligands have been obtained [6,10] only when the remaining ligands are more strongly held than chloride.

Cyano-complexes.—Although the displacement of anionic ligands from platinum(II) by cyanide is well known, the displacement of uncharged ligands has been relatively neglected. Displacement of halide in tertiary phosphine complexes by cyanide is normally carried out with nearly stoicheiometric quantities of reagents, since otherwise phosphine displacement occurs, but this reaction appears to have been exploited only once previously to prepare *trans*-$[Pt(CN)_2(GePh_3)_2]^{2-}$ from $[Pt(GePh_3)_2(PEt_3)_2]$.[11] Since displacement by cyanide of aryl or alkyl ligands would release radicals or carbanions, it is likely to be a high-activation-energy process even if thermodynamically favoured. We therefore investigated the action of an excess of cyanide on various alkyl and aryl complexes in the expectation that other neutral or anionic ligands such as chloride would be displaced. Since the products of some preliminary investigations were hygroscopic and there was also a possibility of hydrolytic cleavage of the alkyl or aryl ligands from the cyanide complexes, anhydrous conditions were used throughout. The complex and an approximately stoicheiometric quantity of 18-crown-6 were dissolved in dry benzene and treated with an excess of anhydrous KCN. Reaction mixtures were stirred and sometimes heated under reflux, filtered to remove excess of KCN, evaporated to dryness, and washed with diethyl ether to remove crown ether and its complex with KCN. Larger quantities of crown ether are required in this procedure because it is consumed by co-ordination to the potassium ion of the product salts.

The cyclo-octa-1,5-diene (cod) ligand of complexes $[PtR_2(cod)]$ (R = 2-thienyl, benzofuran-2-yl, 4-methoxyphenyl, and methyl) was easily displaced by this procedure to give complexes $[K(18\text{-crown-}6)]_2[Pt(CN)_2R_2]$ (**11**). These, apart from (**11**; R = Me), were obtained in good yield as colourless, crystalline, solids with analytical results, conductivities, and ^1H n.m.r. spectra consistent with the assigned formulae. The i.r. spectra showed characteristic bands for the crown ether at 1 120 cm^{-1} and doublet $\nu(CN)$ bands indicating a *cis*-configuration for the anions. The complex (**11**; R = Me) was hygroscopic and although analytical results were not obtained, the i.r. and ^1H n.m.r. spectra were satisfactory.

Phosphine ligands were also displaced using a similar procedure. At ambient temperature *cis*-$[PtMe_2(PEt_3)_2]$ gave a colourless crystalline complex with analysis corresponding to $[K(18\text{-crown-}6)][Pt(CN)Me_2(PEt_3)]$ (**12**). The conductivity in nitromethane corresponded to a 1 : 1 electrolyte and there was a single band at 2 090 cm^{-1} due to $\nu(CN)$. The ^1H n.m.r. spectrum comprised a singlet (δ 3.8 p.p.m.) due to OCH_2CH_2O groups of the crown ether and multiplets (δ 1.9, 1.2 p.p.m.) from PEt_3. The methyl ligands were non-equivalent (δ 0.6, 0.2 p.p.m.) with closely similar values of coupling constants to platinum [$^2J(PtCH)$ 68 Hz] and phosphorus [$^3J(PPtCH)$ 8 Hz], so the anion has methyl ligands in a *cis* configuration. The ^{31}P-{^1H} n.m.r. spectrum was the expected single line (δ 132 p.p.m.) with ^{195}Pt satellites, and the coupling constant [$^1J(PtP)$ 1 863 Hz] was similar to the phosphorus ***trans*** to Me in *cis*-$[PtMe_2(PEt_3)_2]$ [$^1J(PtP)$ 1 856 Hz].[12]

A similar procedure with *cis*-$[PtCl_2(PMe_2Ph)_2]$ led to the isolation of a material which was shown from ^{31}P-{^1H} n.m.r. spectra to contain two ***trans*** complexes whose formulations as ***trans***-$[PtCl(CN)(PMe_2Ph)_2]$ [δ 148.2 p.p.m., $^1J(PtP)$ 2 292 Hz] and ***trans***-$[Pt(CN)_2(PMe_2Ph)_2]$ [δ 152.9 p.p.m., $^1J(PtP)$ 2 197 Hz] are based upon the comparison of magnitudes of $^1J(PtP)$ with known complexes.[13] Reactions under reflux led to complete displacement of phosphine ligands with formation of $K_2[Pt(CN)_4]$.

It appears probable that a wide range of transition-metal alkyl- or aryl-complexes containing cyanide ligands would be accessible from this procedure. One difficulty was noted, however, when the product complex was anionic. The counter ion $[K(\text{crown ether})]^+$ gave products of very high solubility with consequent difficulties in isolation and purification. There are in general no such difficulties when the role of $[K(\text{crown ether})]^+$ is purely catalytic.

EXPERIMENTAL

General.—Reactions were carried out under dry nitrogen using dry oxygen-free solvents. Potassium cyanide was dried under vacuum at 100 °C for at least 24 h. I.r. spectra were recorded as Nujol mulls between CsI plates on a Perkin-Elmer 457 grating spectrometer. Molar conductances were measured in nitromethane solutions at *ca.* 10^{-3} mol dm^{-3}. The ^1H n.m.r. spectra were obtained with Varian T60 or A60 or Perkin-Elmer R32 (90 MHz) instruments using $SiMe_4$ as internal standard. The ^{31}P-{^1H} n.m.r. spectra were obtained with a JEOL PFT-100 instrument with 8-mm tubes and $P(OMe)_3$ in C_6D_6 as external reference and lock. Elemental analyses were by Mrs. G. Olney of this laboratory.

Starting Materials.—Dicyclohexyl 18-crown-6 (m.p. 49—57 °C; Found: C, 64.3; H, 9.5. Calc. for $C_{20}H_{36}O_6$: C, 64.5; H, 9.7%) [1] and 18-crown-6 (m.p. 36—39 °C) [14] were obtained as described in the literature. Methyl complexes were obtained from the corresponding chloro-complex and methyl-lithium, and aryl complexes by use of aryltin compounds.[15] Other complexes were obtained by established methods.[2]

Hydroxo-complexes.—*Preparation of* $[Pt_2Cl_2(OH)_2L_2]$ (L = PEt_3, PMe_2Ph, PEt_2Ph, *or* PBu_3). Aqueous KOH (10 cm^3,

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ca. 2 mol dm^{-3}) was added to a benzene solution of [$Pt_2Cl_4L_2$] (0.5 g) and dicyclohexyl 18-crown-6 or 18-crown-6 (*ca.* 0.1 g). The two-phase system was stirred vigorously for 12 h. The organic layer was separated, washed with water until the washings were neutral, and stirred with $MgSO_4$ and charcoal. After filtration, the solution was evaporated to dryness and the residue recrystallised from benzene–pentane. Thus obtained were *di-μ-hydroxo-bis[chloro(triethylphosphine)platinum*(II)], (1), m.p. 151—153 °C, in 27% yield; i.r., ν(OH) 3 607 and 3 618 cm^{-1}, n.m.r. δ(OH) 4 p.p.m., ^2J(PtH) 40 Hz (Found: C, 19.8; H, 4.6. $C_{12}H_{32}Cl_2O_2P_2Pt_2$ requires C, 19.7; H, 4.4%); *di-μ-hydroxo-bis[chloro(dimethylphenylphosphine)platinum*(II)], (2), m.p. 185—186 °C, in 88% yield (complex precipitates from reaction mixture), i.r., ν(OH) 3 550 cm^{-1} (Found: C, 24.6; H, 3.1; Cl, 9.4. $C_{16}H_{32}Cl_2O_2P_2Pt_2$ requires C, 24.9; H, 3.1; Cl, 9.2%), and *di-μ-hydroxo-bis[chloro(diethylphenylphosphine)platinum*(II)], (3), m.p. 138—141 °C, in 86% yield, i.r., ν(OH) 3 450 cm^{-1} (Found: C, 28.9; H, 4.0; Cl, 9.1. $C_{20}H_{32}Cl_2O_2P_2Pt_2$ requires C, 29.0; H, 3.9; Cl, 8.6%). The complex with L = PBu_3, m.p. 124—125 °C was obtained in low yield and was not analysed.

Evaporation of the supernatant liquor from the recrystallisation of (1) gave a small amount of [K(18-crown-6)][$PtCl_3(PEt_3)$], (4), as yellow crystals, m.p. 130—131 °C (Found: C, 30.5; H, 5.5; Cl, 12.9. $C_{18}H_{39}Cl_3KO_6PPt$ requires C, 29.9; H, 5.4; Cl, 14.7%), soluble in $CHCl_3$, CH_2Cl_2, C_6H_6, and H_2O. Concentration of the aqueous phase of the reaction mixtures gave dark precipitates and solutions. One solution (L = PEt_3) was examined by ^{31}P-{^1H} n.m.r. spectroscopy and contained approximately equal amounts of [$PtCl_3(PEt_3)$]$^-$ [parameters identical to (4)] and a compound with δ 140.1 p.p.m. and ^1J(PtP) 4 026 Hz (see text).

Reactions of (1) and (3) with PPh_3, pyridine, or NEt_3 (2 mol) in dichloromethane at ambient temperature gave precipitates and dark solutions with complex ^{31}P-{^1H} n.m.r. spectra. A mixture of (3) and PEt_2Ph gave a solution containing $P(O)Et_2Ph$ (δ 97.9 p.p.m.), and *cis*-[$PtCl_2(PEt_2Ph)_2$][δ 137.5 p.p.m., ^1J(PtP) 3 545 Hz], identified by comparison of ^{31}P n.m.r. parameters with those of authentic samples.

Preparation of [$Pt_2(OH)_2(C_6H_4Me\text{-}4)_2(PEt_2Ph)_2$]. Aqueous KOH (10 cm^3, *ca.* 2 mol dm^{-3}) was added to a dichloromethane solution of [$Pt_2Cl_2(C_6H_4Me\text{-}4)_2(PEt_2Ph)_2$] (0.28 g) and dicyclohexyl 18-crown-6 (*ca.* 0.1 g). A similar procedure with recrystallisation from dichloromethane–pentane gave *di-μ-hydroxo-bis[diethylphenylphosphine(*p*-tolyl)platinum*(II)], (5), as colourless crystals, m.p. 151—155 °C (Found: C, 42.8; H, 4.9. $C_{34}H_{46}O_2P_2Pt_2$ requires C, 43.5; H, 4.9%). Addition of PEt_2Ph (2 mol) to a solution of this complex in dichloromethane gave a mixture of *trans*-[$Pt(C_6H_4Me\text{-}4)_2(PEt_2Ph)_2$] (6, Table) and a small amount of a tris(phosphine) complex [n.m.r.; δ 135.6 p.p.m. (doublet), ^2J(*P*Pt*P*) 22 Hz; δ 142.3 p.p.m. (triplet)] (see text).

Preparation of [Pt(OH)Ph(dppe)]. A similar procedure with [PtCl(Ph)(dppe)] (0.23 g) and 18-crown-6 (*ca.* 0.1 g) in dichloromethane (15 cm^3) and aqueous KOH (15 cm^3, 2 mol dm^{-3}) gave [*1,2-bis(diphenylphosphino)ethane*]*hydroxo*(*phenyl*)*platinum*(II), (7), obtained by addition of diethyl ether to the dried dichloromethane solution as colourless crystals, m.p. 199—203 °C (0.06 g) (Found: C, 54.9; H, 4.8. $C_{32}H_{30}OP_2Pt$ requires C, 55.9; H, 4.4%). A solution of the complex (0.1 g) in acetone (5 cm^3) was put aside at ambient temperature for 12 h, reduced in volume to 1 cm^3, and examined by ^{31}P-{^1H} n.m.r. spectroscopy [(8), Table].

Reactions of cis-[$PtCl_2L_2$]. The complexes were dissolved in benzene (L = PBu_3 and PEt_3) or dichloromethane (L = PMe_2Ph) and treated with aqueous KOH (2 mol dm^{-3}) in the presence of crown ether. The organic phase became lime-green, and that for L = PMe_2Ph was examined by ^{31}P-{^1H} n.m.r. spectroscopy [(9), Table]. Addition of diethyl ether to the dried organic phase precipitated starting complex, and concentration of the resulting solution gave a precipitate of platinum.

A mixture of *cis*-[$PtCl_2(PMe_2Ph)_2$] (0.39 g), 18-crown-6 (0.1 g), dichloromethane (10 cm^3), and aqueous KOH (10 cm^3, 2 mol dm^{-3}) was stirred vigorously for 2 h, then treated with Na[BF_4] (1 g) and stirring continued for 12 h. The organic layer was separated, washed with water (2 × 5 cm^3), dried (Na_2CO_3), and evaporated to dryness. The residue was recrystallised from methanol–water to give the product, tentatively identified as di-μ_3-oxo-tris[bis(dimethylphenylphosphine)platinum(II)] tetrafluoroborate (10) as yellow crystals, m.p. 245—249 °C (decomp.) (0.16 g), Λ_m 201 S cm^2 mol^{-1} (Found: C, 35.8; H, 4.4. $C_{48}H_{66}B_2F_8O_2P_6Pt_3$ requires C, 35.6; H, 4.1%), ^{31}P-{^1H} n.m.r. spectrum: central peak δ 160.4 p.p.m. (I = 1), other lines at ±15 Hz (I = 0.33), ±1 389 Hz (I = 0.02), ±1 389 Hz (I = 0.02), ±1 724 Hz (I = 0.08), ±1 741 Hz (I = 0.12), and ±2 234 Hz (I = 0.02).

*Cyano-complexes.—Reactions of cyclo-octa-*1,5*-diene complexes.* An excess of KCN (0.4 g) was added to a solution of [PtR_2(cod)] (R = benzofuran-2-yl) (0.21 g) and 18-crown-6 (0.1 g) in benzene (10 cm^3). The solution was heated under reflux for 3 h. The yellow solution was filtered and reduced to dryness under vacuum. The residue was washed with diethyl ether (2 × 5 cm^3) and the product, (18-crown-6)potassium bis(benzofuran-2-yl)dicyanoplatinate(II), m.p. 155—159 °C (0.28 g, 97%) (Found: C, 46.3; H, 5.4; N, 2.7. $C_{42}H_{58}K_2N_2O_{14}Pt$ requires C, 46.5; H, 5.4; N, 2.6%), ν(CN) 2 117, 2 125 cm^{-1}, Λ_m 138 S cm^2 mol^{-1}, was collected by filtration. The complex was soluble in water and organic solvents. Similarly prepared were (18-crown-6)potassium dicyanobis(2-thienyl)platinate(II) (at ambient temperature), m.p. 163—164 °C (40%) (Found: C, 39.3; H, 5.5; N, 2.9. $C_{34}H_{54}K_2N_2O_{12}PtS_2$ requires C, 40.4; H, 5.4; N, 2.8%), ν(CN) 2 100, 2 119 cm^{-1}, Λ_m 146 S cm^2 mol^{-1}, and (18-crown-6)potassium dicyanobis(4-methoxyphenyl)platinate(II) (5-h reflux), m.p. 100—105 °C (75%) (Found: C, 45.1; H, 6.3; N, 2.5. $C_{40}H_{62}K_2N_2O_{14}Pt$ requires C, 45.0; H, 5.9; N, 2.6%), ν(CN) 2 085 cm^{-1}, 2 100 cm^{-1}, Λ_m 138 S cm^2 mol^{-1} (complex hygroscopic).

A similar procedure (R = Me, 8-h reflux) gave (18-crown-6)potassium dicyanodimethylplatinate(II), as a colourless hygroscopic oil, ν(CN) 2 109, 2 122 cm^{-1}, ^1H n.m.r.; δ(Me) 0.2 p.p.m. ^2J(*PtCH*) 68 Hz.

Reactions of phosphine complexes. An excess of KCN (0.2 g) was added to a solution of *cis*-[$PtMe_2(PEt_3)_2$] (0.26 g) and 18-crown-6 (0.3 g) in benzene (20 cm^3). The mixture was stirred vigorously for 18 h at ambient temperature and then filtered and the filtrate evaporated to dryness. The residue was washed with diethyl ether (2 × 5 cm^3) and pentane (5 cm^3) and dried *in vacuo* to give (18-crown-6)potassium cyanodimethyl(triethylphosphine)platinate(II), (12), m.p. 121—124 °C (0.25 g, 67%) (Found: C, 37.7; H, 7.0; N, 2.3. $C_{21}H_{45}NO_5PPt$ requires C, 37.5; H, 6.7; N, 2.1%), Λ_m 71 S cm^2 mol^{-1}. The complex was very soluble in $CHCl_3$, CH_2Cl_2, C_6H_6, and H_2O.

By a similar procedure at ambient temperature (20 h) *cis*-[$PtMeCl(PEt_3)_2$] gave (18-crown-6)potassium dicyanomethyl(triethylphosphine)platinate(II), obtained from dichloromethane–diethyl ether as colourless needles, m.p. 86—89 °C (52%) (Found: C, 36.2; H, 5.9; N, 4.3. $C_{21}H_{42}KN_2O_6PPt$ requires C, 36.9; H, 6.2; N, 4.1%), ν(CN) 2 116 cm^{-1}, Λ_m 70 S cm^2 mol^{-1}.

A similar procedure with *cis*-$[PtCl_2(PMe_2Ph)_2]$ gave a mixture of two *trans*-bis(phosphine) complexes (see text); under conditions of reflux, $K_2[Pt(CN)_4]$, ν(CN) 2 150 cm^{-1}, was obtained.

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