Transition-metal–Carbon Bonds. Part 43.[1] Some Long-chain and Large-ring Complexes of Nickel, Palladium, or Platinum with Tetramethylene- and Hexamethylene-dioxydiphenyl †

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The dibromo-ethers 1,4-bis(*o*-bromophenoxy)butane and 1,6-bis(*o*-bromophenoxy)hexane are dilithiated by n-butyl-lithium (halogen–metal exchange). The dilithio-derivative $LiC_6H_4O[CH_2]_4OC_6H_4Li$ (Li_2L) reacts with *trans*-$[NiBr_2Y_2]$ ($Y = PEt_2Ph$ or PEt_3) to give yellow $[NiLY_2]$ where L acts as a *trans*-bonded bidentate chelate giving an 11-membered ring. In contrast, $LiC_6H_4O[CH_2]_6OC_6H_4Li$ (Li_2L') gives a green unidentified product. Corresponding complexes of platinum are not formed: instead binuclear species of the type $[Y_2XPt(C_6H_4O[CH_2]_n\text{-}OC_6H_4)PtY_2X]$ (X = Br or I) are obtained ($Y = PEt_2Ph$, PMe_2Bu^t, or $AsMe_2Bu^t$). The dibromo-complexes $[(Bu^t\text{-}Me_2P)_2XPt(C_6H_4O[CH_2]_nOC_6H_4)PtX(PMe_2Bu^t)_2]$ (X = Br) react with $Na[BH_4]$ to give the corresponding dihydrides (X = H). Palladium complexes of the type $[(Et_3P)_2XPd(C_6H_4O[CH_2]_4OC_6H_4)PdX(PEt_3)_2]$ (X = Cl or Br) have also been synthesized. Treatment of *trans*-$[PdBr_2(PEt_3)_2]$ with Li_2L(1 : 1 mol proportion) gives an impure product of the approximate composition $[\{PdL(PEt_3)_2\}_x]$ (x = ?). Hydrogen-1 and ^{31}P n.m.r. data and i.r. data are given.

SEVERAL transition-metal complexes are now known which have a large chelate ring involving a *trans*-bonded bidentate ligand. Most of these large rings have two tertiary phosphine donor atoms; *e.g.* we have prepared from 12- to 45-membered rings using the flexible diphosphines $Bu^t_2P[CH_2]_nPBu^t_2$ (n = 8—10 or 12) with

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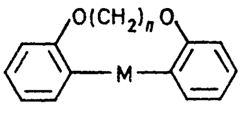
† No reprints available.

[1] Part 42, C. J. Moulton and B. L. Shaw, *J.C.S. Dalton*, 1976, 1020.

platinum, palladium, iridium, rhodium, and ruthenium.[2-6] Venanzi and his co-workers[7] have reported a rigid bidentate diphosphine which spans *trans* positions in 'square-planar' complexes. Long-chain ether diphosphines can also act as chelates as in the mononuclear low-spin nickel(II) complex $[NiI_2(Ph_2P[CH_2]_2O[CH_2]_2O[CH_2]_2PPh_2)]$ in which the co-ordination about the nickel is intermediate between square planar and tetrahedral.[8] Complexes of Rh^I of type $[Rh(CO)Cl\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2\}]$ (n = 1—3) have also been described and structures determined: the long-chain ether diphosphine ligand is *trans*-bonding.[9] Complexes of the type *trans*-$[MX_2L]$ (M = Pd or Pt; X = Cl, Br, or I; L = $Me_2As[CH_2]_3S[CH_2]_3S[CH_2]_3AsMe_2$) have also been described.[10]

The flexible diphosphines $Ph_2P[CH_2]_nPPh_2$ (n = 4 or 5), however, give tetrahedral nickel(II) complexes.[11] Some binuclear complexes of type $[\{Mo(CO)_4(Me_2P[CH_2]_nPMe_2)\}_2]$ (n = 5 or 6) containing large rings have also been synthesized.[12] Long-chain α,ω-diamines $H_2N[CH_2]_nNH_2$ (n = 10, 12, or 14) can give large chelate rings with Co^{III}, *e.g.* $[Co(en)_2(H_2N[CH_2]_nNH_2)]X_3$ (en = ethylenediamine),[13] and a long-chain bidentate nitrogen–olefin donor ligand (L), $H_2C{:}CH[CH_2]_mCOO[CH_2]_3C_5H_3NMe_2$ (m = 1, 2, 4, or 8), gives mononuclear but unstable complexes of the type *trans*-$[PtCl_2L]$ under high dilution conditions[14] (the nitrogen and olefin donors are co-ordinated in mutually *trans* positions).

Previously no complexes have been reported which contain large chelate rings involving mutually *trans*-σ-bonded carbon-donor ligand atoms. We therefore attempted to synthesize complexes containing such a ring system, *i.e.* of type (1) (n = 4 or 6), and have been successful for Ni^{II}. Such a system seemed suitable since diarylmetal complexes of the type *trans*-$[M(aryl)_2(PR_3)_2]$ (M = Ni, Pd, or Pt) are especially stable and inert when the aryl rings carry *ortho* substituents.[15,16] The orientation of the aryl groups and their rigidity would also help to stabilize the large ring.

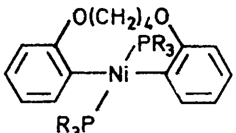


(1)

RESULTS AND DISCUSSION

We prepared 1,4-bis(*o*-bromophenoxy)butane and 1,6-bis(*o*-bromophenoxy)hexane by treating sodium *o*-bromophenoxide with 1,4-dibromobutane or 1,6-dibromohexane, respectively. The dilithio-derivatives were prepared by treating the diaryl dibromides with n-butyllithium (halogen–metal exchange). We hoped that by treating complexes of the type $[MX_2Y_2]$ (M = Ni, Pd, or Pt; X = halogen; Y = tertiary phosphine) with these dilithio-derivatives we would obtain complexes containing the desired systems (1).

When a red slurry of $[NiBr_2(PEt_2Ph)_2]$ in benzene was added to an excess of 1,4-di(2-lithiophenoxy)butane in tetrahydrofuran (thf) at room temperature a yellow solution was formed almost immediately. The mixture was stirred overnight to ensure that equilibration was complete. A yellow complex was isolated and recrystallized from n-heptane. The analytical and molecular-weight data (Table 1) fit the formulation $[NiL(PEt_2Ph)_2]$ (L = $C_6H_4O[CH_2]_4OC_6H_4$). The integration of the ^1H n.m.r. spectrum of the complex shows that there is a ratio of one L to two phosphine species. The spectrum showed two broad signals of equal intensity due to the tetramethylene protons; the signal to low field presumably being due to the methylene protons adjacent to oxygen. The phosphorus-ethyl proton region was complex, but double irradiation of the PCH_2CH_3 proton signal caused the PCH_2CH_3 signal to collapse into a triplet. This indicates that the phosphines are mutually *trans* $[|^3J(PH) + {}^5J(PH)|$ *ca.* 13 Hz] and that the complex has configuration (2). The ^{31}P spectrum in C_6D_6 solution showed only one signal (at δ 16.1 p.p.m.).



(2)

A similar treatment of $[NiBr_2(PEt_3)_2]$ gave a complex formulated as $[NiL(PEt_3)_2]$, from analytical and molecular-weight data (Table 1). The complex was crystallized with difficulty from light petroleum (b.p. 60—80 °C) at −10 °C which may account for the rather poor yield (43%). The ^1H n.m.r. spectrum of the phosphorus-ethyl proton region was complex, and double-resonance experiments were not feasible since the PCH_2CH_3 and PCH_2CH_3 proton signals overlapped.

The dilithio-reagent reacted with a red benzene slurry of $[NiBr_2(PMe_2Ph)_2]$ to give a yellow solution. A yellow solid was isolated, smelling strongly of free phosphine, but we were unable to purify it. The solid rapidly turned green when exposed to the air, and became insoluble in organic solvents. When a red slurry of $[NiBr_2(PEt_2Ph)_2]$ in benzene was treated with 1,6-di(2-lithiophenoxy)hexane a dark green solution was formed. The

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[5] B. L. Shaw and I. Shepherd, unpublished work.

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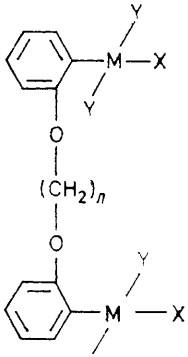
solution was evaporated to give a green air-sensitive oil, smelling strongly of phosphine. Possibly the ligand constrained the nickel to adopt an unstable configuration. We next turned our attention to platinum since arylplatinum complexes are generally much more stable than corresponding arylnickel complexes.

Treatment of a yellow solution of *trans*-[$PtI_2(PEt_2Ph)_2$] in benzene with 1,4-di(2-lithiophenoxy)butane gave a colourless solution after a few minutes. A white, slightly oily, complex was isolated. The integration of the ^1H n.m.r. spectrum showed that there was a ratio of one L to four phosphines. The phosphorus-ethyl proton region of the spectrum was complex. The complex could not be obtained analytically pure although its ^1H n.m.r. and ^{31}P n.m.r. spectra indicated that only one species was present. The analytical data (Table 1) approximately fit the formulation [{$PtI(PEt_2Ph)_2$}$_2$L], configuration (**3**; Y = PEt_2Ph, X = I). The *trans* arrangement of phosphorus atoms follows from the low value of ^1J(PtP) 2 788 Hz; δ 7.77 p.p.m. in $CDCl_3$ solution. Metathesis of [{$PtI(PEt_2Ph)_2$}$_2$L] with potassium thiocyanate in boiling acetone gave the white thiocyanate complex [{$Pt(PEt_2Ph)_2(SCN)$}$_2$L] in 70% yield, which was analytically pure (see Table 1). The i.r. spectrum of this complex showed a strong band at 2 100 cm^{-1} due to ν(CN), indicating that the thiocyanate ligand is probably S-bonded.[17]



(**3**)

TABLE 1

Analytical, molecular-weight, yield, and melting-point data for $BrC_6H_4O[CH_2]_nOC_6H_4Br$ (n = 4 and 6), and for nickel(II), platinum(II), and palladium(II) complexes containing the ligands $\cdot C_6H_4O[CH_2]_nOC_6H_4\cdot$ [n = 4(L), n = 6(L′)]

Compound	Yield (%)	M.p. (θ_c/°C)	Analysis (%) ^{a} C	H	Halogen	M(in $CHCl_3$) ^{a}
$BrC_6H_4O[CH_2]_4OC_6H_4Br$	60	97—100	47.7 (48.0)	3.8 (4.0)	40.0 (39.95)	
$BrC_6H_4O[CH_2]_6OC_6H_4Br$	84	89—92	50.35 (50.5)	4.8 (4.7)	37.2 (37.3)	
[$NiL(PEt_2Ph)_2$]	75	132—136 ^{b}	68.65 (68.5)	7.45 (7.35)	0	613 (631) ^{c}
[$NiL(PEt_3)_2$]	43	141—144 ^{b}	62.8 (62.8)	8.7 (8.65)		560 (535) ^{c}
[{$PtI(PEt_2Ph)_2$}$_2$L]	53	159—161	44.65 (43.4)	4.9 (4.95)	15.95 (16.35)	
[{$Pt(PEt_2Ph)_2(SCN)$}$_2$L]	70	161—163	49.3 (49.35)	5.35 (5.45)	N: 2.1 (2.0)	1 449 (1 411)
[{$PtBr(PMe_2Bu^t)_2$}$_2$L]	57	244—260	38.05 (38.05)	6.05 (6.05)	12.5 (12.65)	1 223 (1 263)
[{$PtI(PMe_2Bu^t)_2$}$_2$L]	96	238—244	35.55 (35.4)	5.75 (5.65)	18.95 (18.7)	1 359 (1 357)
[{$PtBr(PMe_2Bu^t)_2$}$_2$L′]	70	145—156	38.7 (39.05)	6.25 (6.25)		
[{$Pt(AsMe_2Bu^t)_2Br$}$_2$L]	58	152—155	34.6 (33.4)	5.4 (5.3)	10.7 (11.1)	1 465 (1 439)
[{$PtH(PMe_2Bu^t)_2$}$_2$L]	87	134—139 ^{b}	43.95 (43.5)	7.1 (7.1)		1 075 (1 105)
[{$PtH(PMe_2Bu^t)_2$}$_2$L′]	77	53—57	44.9 (44.6)	7.3 (7.15)		1 180 (1 131)
[{$PdBr(PEt_3)_2$}$_2$L]	47	154—158	44.25 (44.25)	7.15 (7.05)		1 000 (1 085)
[{$PdCl(PEt_3)_2$}$_2$L]	21	125—130	49.2 (48.2)	8.4 (7.7)	6.6 (7.1)	

^{a} Calculated values are given in parentheses. ^{b} With decomposition. ^{c} In benzene solution.

Even prolonged treatment of *trans*-[$PtI_2(PEt_2Ph)_2$] with 1,4-di(2-lithiophenoxy)butane (1 : 1 mol proportion) gave only the binuclear complex (**3**) containing monosubstituted platinums. The large *ortho* substituent on the platinum-bonded aryl group would markedly reduce the rate of replacement of the second iodide ligand,[15] but it seemed possible that the rather large phosphine (PEt_2Ph) might also lower the reactivity. We therefore treated *trans*-[$PtBr_2(PMe_2Bu^t)_2$] with the dilithioreagent. (We have found that PMe_2Bu^t complexes are more reactive than PEt_2Ph complexes and have the advantage that the t-butyl ^1H n.m.r. pattern is very useful in determining the stereochemistry.) Again, however, a white binuclear species was obtained formulated as [{$PtBr(PMe_2Bu^t)_2$}$_2$L], configuration (**3**) (see Table **1**). Metathesis of this complex with sodium iodide in boiling ethyl methyl ketone gave the corresponding iodo-complex [{$PtI(PMe_2Bu^t)_2$}$_2$L]. The ^1H n.m.r. spectra for these complexes show that there is a ratio of one L to four phosphines (from the integration). The phosphine-t-butyl protons give rise to a triplet signal due to the *trans* arrangement of phosphorus atoms but, as expected, the phosphine-methyl protons give rise to two triplet signals, each with ^{195}Pt satellites. The aryl protons of L are spread over a region of 1.0 p.p.m. and are capable of approximately first-order analysis.

In order to investigate the effect of increasing the chain length in the diaryl ligand, *trans*-[$PtBr_2(PMe_2Bu^t)_2$] was treated with 1,6-di(2-lithiophenoxy)hexane. A white complex was isolated and shown to be [{$PtBr(PMe_2Bu^t)_2$}$_2$L′] (**3**; n = 6) from analytical and molecular-weight data (Table 1), and ^1H n.m.r. data (Table 2). The ^1H n.m.r. spectrum of the complex showed two signals due to phosphorus-methyl protons.

Both the tetra- and hexa-methylene complexes of type [{$PtBr(PMe_2Bu^t)_2$}$_2$L] were reduced by sodium

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[17] J. Chatt and L. A. Duncanson, *Nature*, 1956, **178**, 997; 'Metal–Ligand and Related Vibrations,' ed. D. M. Adams, Edward Arnold, London, 1967, p. 327.

tetrahydroborate in benzene–ethanol to give the hydrides $[\{\mathrm{PtH(PMe_2Bu^t)_2}\}_2\mathrm{L}]$ (see Table 1 for analytical and molecular-weight data). The ^{1}H n.m.r. data (Table 2) are in agreement with the assigned structures. The i.r. absorption bands due to ν(PtH) (Table 2) are strong. The 220- and 90-MHz ^{1}H n.m.r. spectra showed a doublet of triplets signal for the metal hydride proton (see Table 2 for data) with ^{195}Pt satellites. In each case the doublet splitting is the same (*ca.* 2.0 Hz), and is therefore probably due to coupling with the *ortho*-hydrogen and not due to a difference in chemical shift (caused perhaps by two conformations). The ^{31}P n.m.r. data for the hydride complexes are given in Table 2. The low values of ^1J(PtP) are consequent on the *trans* arrangement of phosphorus atoms.

TABLE 2

Hydrogen-1 n.m.r. data (s = singlet, t = triplet, dt = doublet of triplets; *J* values in Hz); ^{31}P n.m.r. data and values of ν(Ph–H) are given as footnotes

Complex	$\delta(\mathrm{C}H_2)$ [a]	$\delta(\mathrm{OC}H_2)$ [a]	$\delta(\mathrm{PBu^t})$	J(PH) [b]	δ(PMe)	J(PH) [c]	^3J(PtH)	Solvent (frequency)
$[\{\mathrm{PtBr(PMe_2Bu^t)_2}\}_2\mathrm{L}]$	2.09	3.94	1.22 (t)	14.5	0.80 (t)	6.7	34.4	$\mathrm{CDCl_3}$ (60)
					1.48 (t)	6.8	27.8	
$[\{\mathrm{PtI(PMe_2Bu^t)_2}\}_2\mathrm{L}]$	2.17	3.95	1.19 (t)	14.1	0.78 (t)	6.8	34.4	$\mathrm{C_6D_6}$ (90)
					1.71 (t)	6.6	27.8	
$[\{\mathrm{PtBr(PMe_2Bu^t)_2}\}_2\mathrm{L'}]$	1.65	3.78	1.13 (t)	14.2	0.73 (t)	7.0	33.2	$\mathrm{CDCl_3}$ (60)
					1.38 (t)	7.0		
$[\{\mathrm{Pt(AsMe_2Bu^t)_2Br}\}_2\mathrm{L}]$	2.16	3.95	1.19 (s)		0.78 (s)		23.4	$\mathrm{C_6D_6}$ (90)
					2.29 (s)		21.9	
$[\{\mathrm{PtH(PMe_2Bu^t)_2}\}_2\mathrm{L}]$ [d]	1.88	3.94	1.15 (t)	14.4	1.07 (t)	6.1	33.2	$\mathrm{CDCl_3}$ (90)
					1.23 (t)	5.8	33.4	
$[\{\mathrm{PtH(PMe_2Bu^t)_2}\}_2\mathrm{L'}]$ [e]	1.60	1.83	1.11 (t)	14.6	1.05 (t)	6.1	33.0	$\mathrm{C_6D_6}$ (220)
					1.20 (t)	6.1	33.0	

	$\delta(\mathrm{C}H_2)$ [a]	$\delta(\mathrm{OC}H_2)$ [a]	$\delta(\mathrm{PC}H_2\mathrm{CH_3})$ [a]	$\delta(\mathrm{PCH_2C}H_3)$ [a]	Solvent (frequency)
$[\mathrm{Ni(PEt_2Ph)_2L}]$	2.04	3.95	1.62	0.95	$\mathrm{C_6H_6}$ (60)
$[\mathrm{Ni(PEt_3)_2L}]$	2.12	4.10	1.22	1.12	$\mathrm{C_6H_6}$ (60)
$[\{\mathrm{PtI(PEt_2Ph)_2}\}_2\mathrm{L}]$	2.00	3.78	2.00	0.94	$\mathrm{CDCl_3}$ (60)
$[\{\mathrm{Pt(PEt_2Ph)_2(SCN)}\}_2\mathrm{L}]$	1.85	3.90	1.85	0.87	$\mathrm{CDCl_3}$ (60)
$[\{\mathrm{PdBr(PEt_3)_2}\}_2\mathrm{L}]$	1.95	3.82	1.50	1.04	$\mathrm{CDCl_3}$ (60)

[a] Signals were complex. [b] $J(\mathrm{PH}) = {}^3J(\mathrm{PH})$. [c] $J(\mathrm{PH}) = {}^2J(\mathrm{PH}) + {}^4J(\mathrm{PH}) + {}^5J(\mathrm{PH})$. [d] $\delta(\mathrm{Pt}H)(\mathrm{CDCl_3})$ −6.87 (dt) p.p.m.; ^2J(PtH) 18.4, ^1J(PtH) 657, ^4J(HH) *ca.* 1.8 Hz. Phosphorus-31 n.m.r. data: δ 17.21 p.p.m., ^1J(PtP) 2 813 Hz. ν(Pt–H) at 1 965s cm^{-1} ($\mathrm{CHCl_3}$). [e] δ(PtH)($\mathrm{CDCl_3}$) −6.86 (dt) p.p.m.; ^2J(PtH) 18.3, ^1J(PtH) 659, ^4J(HH) 1.8 Hz. Phosphorus-31 n.m.r. data: δ 17.24 p.p.m., ^1J(PtP) 2 815 Hz. ν(Pt–H) at 1 970s cm^{-1} ($\mathrm{CHCl_3}$).

We treated $[\mathrm{Pt(AsMe_2Bu^t)_2Br_2}]$ with 1,4-di(2-lithiophenoxy)butane, hoping that both bromine atoms would be replaced, since the arsine should create less steric hindrance than the corresponding phosphine. However, only $[\{\mathrm{Pt(AsMe_2Bu^t)_2Br}\}_2\mathrm{L}]$ (3) was isolated and in good yield (see Tables 1 and 2). Dimethylphenylphosphine is less sterically demanding still, so we treated *cis*-$[\mathrm{PtCl_2(PMe_2Ph)_2}]$ with 1,4-di(2-lithiophenoxy)butane and obtained an oily solid. The ^{31}P n.m.r. spectrum of this showed it to consist of about four species with one major constituent. The values of ^1J(PtP) for the species were in the range 1 923—1 944 Hz, showing that the phosphorus atoms in each species were mutually *trans*. Only partial separation of these species could be effected by column chromatography. Possibly the oily solid obtained was a mixture of mono- and poly-nuclear species.

Because of the different behaviour of corresponding nickel and platinum complexes towards the dilithio-reagents, it was clearly worthwhile investigating analogous complexes of palladium. When *trans*-$[\mathrm{PdBr_2(PEt_3)_2}]$ was treated with $\mathrm{LiC_6H_4O[CH_2]_4OC_6H_4Li}$ (0.5 mol per palladium atom) a binuclear species of type (3) was readily obtained (M = Pd, X = Br, Y = $\mathrm{PEt_3}$) (see Experimental section and Tables). A similar treatment of *trans*-$[\mathrm{PdCl_2(PEt_3)_2}]$ with the dilithio-reagent gave a slightly impure sample of the corresponding chloro-complex (3; X = Cl). This chloro-complex reacted with lithium bromide in acetone (15 h, 20 °C) to give the bromo-complex (3), described above. Treatment of *trans*-$[\mathrm{PdBr_2(PEt_3)_2}]$ with the dilithio-reagent (in 1 : 1 mol proportions) gave a white benzene-soluble product. We were unsuccessful in isolating crystalline material from this white product in spite of many attempts with several different solvents. Microanalytical data (C and H) were erratic but not far from the values calculated for $[\{\mathrm{PdL(PEt_3)_2}\}_x]$ (Found: C, 56.55, 59.65%; H, 8.15, 7.85. Calc. for $\mathrm{C_{23}H_{46}O_2P_2Pd}$: C, 57.7; H, 7.95%). The ^{1}H n.m.r. data in $\mathrm{CDCl_3}$, including the integrated intensities, were also in agreement with this formulation: *viz.* $\delta(\mathrm{OC}H_2)$ 3.98(br), $\delta(\mathrm{OCH_2C}H_2)$ 2.0(br), and $\delta(\mathrm{PC}H_2\mathrm{C}H_3)$ *ca.* 1.15(br) p.p.m. (br = broad). The product was clearly a mixture and may have contained both high-molecular-weight material (the specimens were slightly sticky) and a mononuclear product analogous to (2). The complex *trans*-$[\mathrm{PdBr_2(PMe_2Ph)_2}]$ behaved differently from *trans*-$[\mathrm{PdBr_2(PEt_3)_2}]$ when treated with the dilithio-reagent (2 : 1 proportion). Initially a deep red solution formed and a dark red product was isolated. However, this blackened above 100 °C and decomposed readily in solution at room temperature giving back some *trans*-$[\mathrm{PdBr_2(PMe_2Ph)_2}]$ and a black material. We do not know the nature of the dark red material and were unable to isolate it pure.

It is difficult to rationalize and explain all the results: clearly a number of factors are involved. Of the three metals studied nickel is the most labile and gave the desired large-ring compounds involving *trans*-bonded bidentate σ-C-donor ligands. Platinum is the most inert and gave only monoaryl-substituted, and therefore binuclear, complexes. Palladium gave binuclear complexes analogous to those of platinum but also some disubstituted and impure material.

EXPERIMENTAL

The spectrometers, techniques, and other apparatus used were the same as those given in recent papers from this laboratory.[18]

1,4-*Bis*(o-*bromophenoxy*)*butane*.—*o*-Bromophenol (20.0 g, 0.117 mol) was treated with a solution of sodium ethoxide (0.117 mol) in ethanol (60 cm^3). 1,4-Dibromobutane (12.6 g, 0.058 mol) was then added and the mixture was heated under reflux for 8 h. The ethanol was removed by distillation and the residue was extracted with diethyl ether (500 cm^3) and water (100 cm^3). The organic layer was washed with dilute sodium hydroxide solution (2 × 100 cm^3) and then evaporated to an oil. This was triturated with methanol (100 cm^3) to give a white solid which was recrystallized from dichloromethane–methanol to give the *product* (13.8 g) as white prisms. 1,6-*Bis*(o-*bromophenoxy*)*hexane* was prepared similarly, as white prisms, using 1,6-dibromohexane.

Bis(*diethylphenylphosphine*)[2,2′-(*tetramethylenedioxydiphenyl*)]*nickel*(II), *Configuration* (2).—A solution of 1,4-bis(*o*-bromophenoxy)butane (1.60 g, 4.00 mmol) in dry thf (15 cm^3) was treated with n-butyl-lithium (8 mmol) in hexane (2.86 cm^3) and the mixture was stirred for 15 min. A slurry of the red dibromobis(diethylphenylphosphine)nickel(II) (1.00 g, 1.82 mmol) in dry benzene (25 cm^3) was added to give a pale orange solution. The mixture was stirred for 20 h but no further colour change occurred. The solution was evaporated to a brown oil which was extracted with hot n-heptane (50 cm^3). The yellow solution was reduced in volume to 5 cm^3, when a yellow solid formed. This was filtered off to give the *product* (0.86 g) as needles. The corresponding *bis*(*triethylphosphine*) derivative was prepared similarly as orange prisms from light petroleum (b.p. 60—80 °C).

μ-2,2′-*Tetramethylenedioxydiphenyl-bis*[*iodobis*(*diethylphenylphosphine*)*platinum*(II)]. *Configuration* (3).—A yellow solution of *trans*-di-iodobis(diethylphenylphosphine)platinum(II) (1.00 g, 1.28 mmol) in dry benzene (25 cm^3) was treated with a solution of the dilithio-reagent (1.54 mmol) *in* dry thf (7 cm^3) and n-heptane (3 cm^3). The mixture was stirred for 5 h to give a colourless solution which was then evaporated to dryness. The residue was extracted with dichloromethane and water. The organic layer was evaporated to dryness and the residue recrystallized from acetone–methanol to give the *product* (0.524 g) as white needles.

μ-2,2′-*Tetramethylenedioxydiphenyl-bis*[*bis*(*diethylphenylphosphine*)*thiocyanatoplatinum*(II)]. *Configuration* (3).—A solution of the above iodo-complex (0.20 g, 0.13 mmol) in acetone (10 cm^3) containing potassium thiocyanate (0.20 g) was boiled for 25 min. The resulting solution was evaporated to dryness and the residue was extracted with dichloromethane–water. The organic layer was evaporated to dryness and the residue recrystallized from acetone–methanol to give the *product* (0.13 g) as white prisms.

μ-2,2′-*Tetramethylenedioxydiphenyl-bis*[*bromobis*(*dimethyl-t-butylphosphine*)*platinum*(II)]. *Configuration* (3).—A solution of *trans*-dibromobis(dimethyl-t-butylphosphine)platinum(II) (1.00 g, 1.69 mmol) in benzene (15 cm^3) was treated with 1,4-di(2-lithiophenoxy)butane (1.86 mmol) in tetrahydrofuran–hexane. The resulting colourless solution was stirred for 5 h, when a white suspension had formed. This was evaporated to dryness and the residue extracted with benzene and water. The organic layer was evaporated to dryness and the residue recrystallized from dichloromethane–methanol to give the *product* (0.59 g) as white plates.

The following complexes were prepared similarly: μ-2,2′-*tetramethylenedioxydiphenyl-bis*[*bromobis*(*dimethyl-t-butylarsine*)*platinum*(II)], (3), from dibromobis(dimethyl-t-butylarsine)platinum(II), as white microcrystals. μ-2,2′-*hexamethylenedioxydiphenyl-bis*[*bromo*(*dimethyl-t-butylphosphine*)-*platinum*(II)], (3) from the dilithio-reagent and *trans*-$[PtBr_2(PMe_2Bu^t)_2]$ as white needles.

μ-2,2′-*Tetramethylenedioxydiphenyl-bis*[*iodobis*(*dimethyl-t-butylphosphine*)*platinum*(II)], (3).—A solution of the corresponding bromo-complex (0.20 g) and sodium iodide (an excess) in ethyl methyl ketone (10 cm^3) was heated under reflux for 3 h. The resulting orange solution was cooled to give the *product* (0.207 g) as white plates.

μ-2,2′-*Tetramethylenedioxydiphenyl-bis*[*bis*(*dimethyl-t-butylphosphine*)*hydridoplatinum*(II)], (3).—A suspension of the corresponding dibromo-complex (0.100 g, 0.079 mmol) in benzene (2 cm^3) and ethanol (5 cm^3) was heated under reflux with sodium tetrahydroborate (0.100 g) for 0.5 h. The resulting clear solution was evaporated to dryness and the residue extracted with benzene. The benzene solution was evaporated to an oil which was dissolved in acetone. The acetone solution was allowed to evaporate slowly, giving the *product* (0.076 g) as large white prisms. μ-2,2′-*Hexamethylenedioxydiphenylbis*[*bis*(*dimethyl-t-butylphosphine*)*hydridoplatinum*(II)] was prepared similarly from the corresponding bromo-complex as white prisms.

μ-2,2′-*Tetramethylenedioxydiphenyl-bis*[*bromobis*(*triethylphosphine*)*palladium*(II)]. *Configuration* (3).—A solution of *trans*-dibromobis(triethylphosphine)palladium(II) (0.75 g, 2 mmol) in dry benzene (10 cm^3) was treated with a solution of the dilithio-reagent (1 mmol) (prepared as above). The resulting pale yellow solution was stirred for 1.5 h then evaporated to dryness and the product isolated with benzene. It formed white fibrous needles (0.38 g) from methanol. The dichloro-derivative was prepared similarly from the corresponding dichloride complex and formed white microprisms from light petroleum (b.p. 40—60 °C). When treated with a large excess (*ca.* 20-fold) of lithium bromide in acetone (16 h at 20 °C) it was converted into the dibromide described above.

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