Functionalized Isocyanides as Ligands. Part 5.† Syntheses and Reactions of 3-(Benzylphosphonio)indolin-2-ylidene Complexes of Platinum(II). *X*-Ray Crystal Structure of *trans*-[Pt{*o*-$\overline{\mathrm{CN(H)C_6H_4C}}$[P(CH$_2$Ph)$_2$Ph]}X(PPh$_3$)$_2$]BF$_4$·2C$_2H_4Cl_2$ (X = Cl or Br)‡

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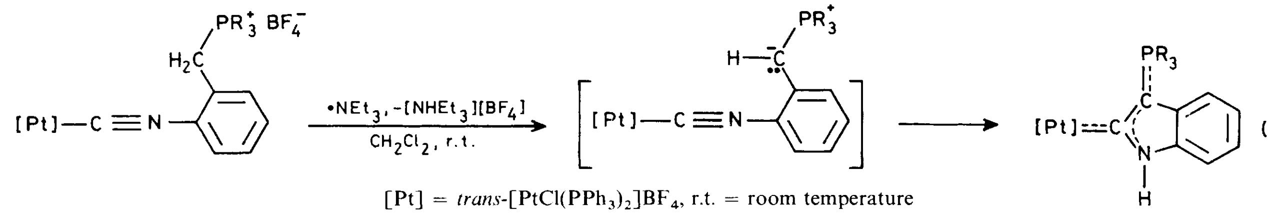
Reactions of the isocyanide o-ClCH$_2$C$_6$H$_4$NC with benzylphosphines, PR$_3$ = P(CH$_2$Ph)Ph$_2$, P(CH$_2$Ph)$_2$Ph, or P(CH$_2$Ph)$_3$, in acetone at room temperature in the presence of excess of LiBr, yield the benzylphosphonium-substituted isocyanides [o-R$_3$PCH$_2$C$_6$H$_4$NC]Br, which are converted to the less hygroscopic tetrafluoroborate salts [o-R$_3$PCH$_2$C$_6$H$_4$NC]BF$_4$ (L) [PR$_3$ = P(CH$_2$Ph)Ph$_2$ (L^1), P(CH$_2$Ph)$_2$Ph (L^2), or P(CH$_2$Ph)$_3$ (L^3)] upon reaction with excess NaBF$_4$ in acetone. The ligands, L, react with a mixture of *cis*- and *trans*-[PtCl$_2$(PPh$_3$)$_2$] and NaBF$_4$ to form the cationic complexes *trans*-[Pt(L)Cl(PPh$_3$)$_2$]BF$_4$ [(**1a**)—(**3a**) for L^1—L^3]. Treatment of complexes (**1a**)—(**3a**) with a 10-fold excess of NEt$_3$ in CH$_2$Cl$_2$ at room temperature leads to the cyclization reaction of the isocyanide ligands *via* phosphorus-ylide intermediates with the formation of 3-(benzylphosphonio)indolin-2-ylidene derivatives *trans*-[Pt{o-$\overline{\mathrm{CN(H)C_6H_4C}}$(PR$_3$)}Cl(PPh$_3$)$_2$]BF$_4$ [PR$_3$ = P(CH$_2$Ph)Ph$_2$ (**1b**), P(CH$_2$Ph)$_2$Ph (**2b**), or P(CH$_2$Ph)$_3$ (**3b**)]. Complexes (**1a**)—(**3a**) and (**1b**)—(**3b**) were characterized by their elemental analyses, i.r., ^{1}H, and ^{31}P n.m.r. spectra. The structure of *trans*-[Pt{o-$\overline{\mathrm{CN(H)C_6H_4C}}$[P(CH$_2$Ph)$_2$Ph]}X(PPh$_3$)$_2$]BF$_4$·2C$_2H_4Cl_2$ (X = Cl or Br) was determined by *X*-ray diffraction: space group *C*2, a = 21.946(1), b = 14.097(3), c = 19.801(1) Å, β = 96.95(1)°, Z = 4, R = 0.037 (R' = 0.041) for 4 802 independent reflections. The co-ordination geometry around the Pt^{II} atom is square planar with the indole ligand perpendicular to the plane. The Pt–C(sp^2) distance is 2.036(8) Å. The bond lengths within the condensed system indicate extensive electronic delocalization. Complex (**1b**) reacts with aqueous KOH in acetone at room temperature to give, in high yield, the platinaheterocycle [Pt{o-CN(H)C$_6$H$_4$C[P(CHPh)Ph$_2$]}Cl(PPh$_3$)] (**1c**). Chloride abstraction by AgBF$_4$ from (**1c**) and reaction of the cationic intermediate with OH$^-$, CO, and PPh$_3$ afford the corresponding derivatives (**1d**), (**1e**), and (**1f**), respectively.

As part of our programme on the synthesis, reactivity, and cyclization reactions of isocyanide ligands,[1–6] we recently described[3,4] the formation of indole systems by base-promoted intramolecular cyclization of either free or metal-co-ordinated phosphonium-substituted isocyanides of the type [o-R$_3$PCH$_2$-C$_6$H$_4$NC]BF$_4$ (R = Me or Ph). The proposed mechanism for the platinum(II)-co-ordinated ligands [equation (1)] entails initial nucleophilic attack on the activated methylene group of the phosphonium moiety, $-\mathrm{CH_2\overset{+}{P}R_3}$, to produce a highly reactive ylide–isocyanide–metal intermediate, which undergoes intramolecular ring closure by ylide carbanion attack on the electrophilic isocyanide carbon to give the final 3-(phosphonio)indolin-2-ylidene derivative. This mutual interaction between ylide and isocyanide functionalities appears to be unprecedented in transition-metal organometallic chemistry.[7,8]



(1)

[Pt] = *trans*-[PtCl(PPh$_3$)$_2$]BF$_4$, r.t. = room temperature

In order to explore the generality of the synthetic strategy developed in equation (1), we tested reactions with benzylphosphonium-substituted isocyanide ligands of the type [o-R$_3$PCH$_2$C$_6$H$_4$NC]BF$_4$ [PR$_3$ = P(CH$_2$Ph)Ph$_2$, P(CH$_2$Ph)$_2$-Ph, or P(CH$_2$Ph)$_3$] co-ordinated to Pt^{II} species [structure (**I**),

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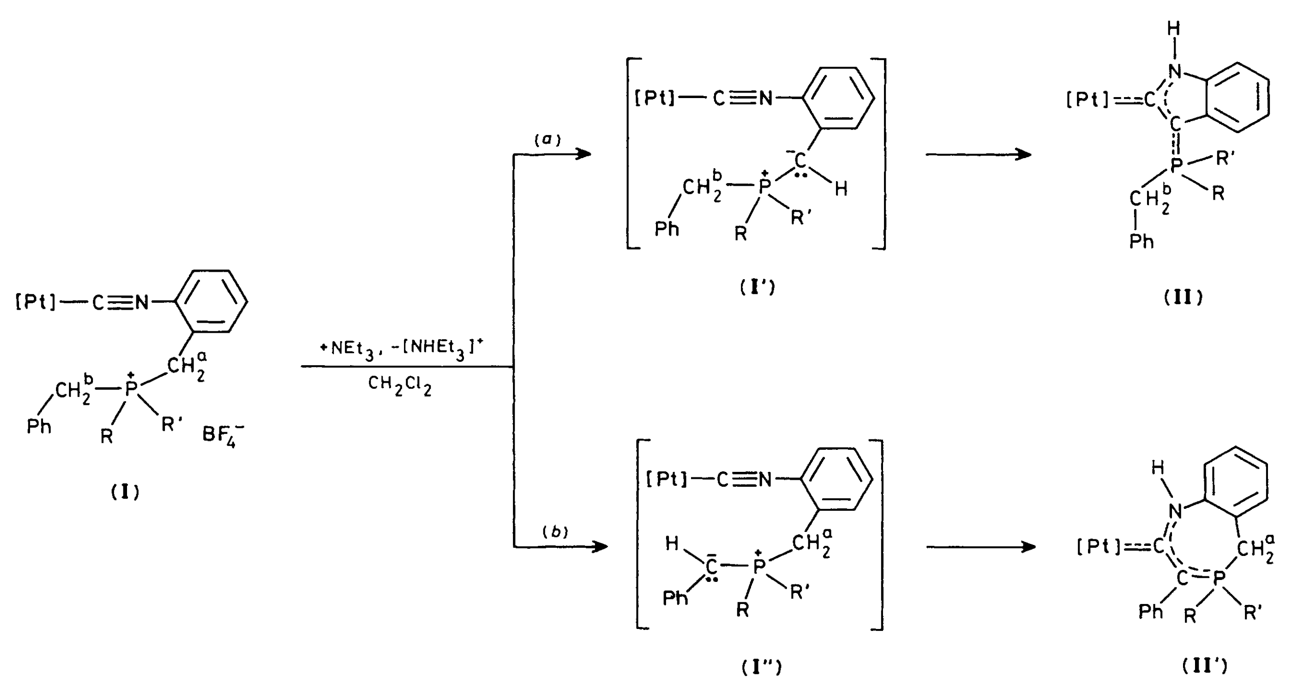
† For Part 4, see ref. 5.

‡ [3-(Dibenzylphenylphosphonio)indolin-2-ylidene]halogenobis(triphenylphosphine)platinate(II) tetrafluoroborate–1,2-dichloroethane (1/2).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.



Scheme 1. R, R′ = CH_2Ph or Ph, [Pt] = *trans*-$[PtCl(PPh_3)_2]BF_4$

Scheme 1]. Interest in these ligands stems from the presence of several (up to four) potentially reactive $-CH_2\overset{+}{P}R_3$ moieties, one of which belongs to the isocyanide ligand [$-CH^a_2$-type, structure (I)] and all the others to the benzylphosphine ligand ($-CH^b_2$-type). Since $-CH^a_2$ and $-CH^b_2$ methylene protons are electronically similar, the two groups can each generate a ylide functionality by attack of base. Molecular models indicate that either of the ylide carbanions of the ylide–isocyanide–metal intermediates (I′) and (I″) is in a favourable position to interact with the isocyanide carbon to give ring closure to (II) and (II′), respectively. However, steric factors such as crowding around the reacting centres may influence, to a different extent, routes (*a*) and (*b*) of the reaction pathway, the results of which are reported herein.

Experimental

General Procedures and Materials.—All reactions were performed under an N_2 atmosphere using Schlenk techniques. Unless otherwise noted, reagent grade chemicals were used as received. The solvent Et_2O was distilled from sodium–benzophenone; CH_2Cl_2 was dried over CaH_2 and distilled under N_2. Acetone was dried over $CaSO_4$ and degassed before use.

Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer. ^1H and ^{31}P-$\{^1H\}$ n.m.r. spectra were obtained on a Varian FT-80A spectrometer. Melting points were taken on a hot-plate apparatus and are uncorrected. Elemental analyses were performed by the Department of Analytical Chemistry of the University of Padua. Mass spectra were recorded on a VG ZAB 2F spectrometer. Molecular weight measurements were determined on a Knauer osmometer using 1,2-dichloroethane as solvent.

The isocyanide ligand *o*-$ClCH_2C_6H_4NC$ was prepared as recently described.[4] The complex $[PtCl_2(PPh_3)_2]$ was obtained as a mixture of *trans*-[9] and *cis*-[10] forms (*ca.* 9:1 ratio from i.r. and ^{31}P n.m.r. data) in 90% yield by reaction of $[PtCl_2(cod)]$[11] (cod = cyclo-octa-1,5-diene) with two equivalents of PPh_3 in CH_2Cl_2 at room temperature for 3 h, followed by precipitation with Et_2O.

Synthesis of the Ligands.—[*o*-$R_3PCH_2C_6H_4NC$]Br [PR_3 = $P(CH_2Ph)Ph_2$, $P(CH_2Ph)_2Ph$, *or* $P(CH_2Ph)_3$]. All these ligands were prepared by a standard procedure which is described below for the $P(CH_2Ph)Ph_2$ derivative. To a solution of LiBr (1.31 g, 15 mmol) dissolved in acetone (40 cm^3) was added, in one portion, solid *o*-$ClCH_2C_6H_4NC$ (0.76 g, 5.00 mmol) and $P(CH_2Ph)Ph_2$ (1.66 g, 6.00 mmol), and the reaction mixture was stirred overnight at room temperature. It was then dried under reduced pressure and the solid residue dissolved in CH_2Cl_2 (30 cm^3). After filtration, addition of Et_2O (50 cm^3) to the solution gave the product as a white precipitate. Yield 1.79 g (76%), m.p. 209—210 °C (Found: C, 67.10; H, 5.00; N, 2.70. Calc. for $C_{27}H_{23}BrNP{\cdot}0.5H_2O$: C, 67.35; H, 5.25; N, 2.90%). I.r. (CH_2Cl_2): 2 121s cm^{-1} (ν_{NC}). N.m.r.: $\delta_H(CD_2Cl_2)$, 5.30 [2 H, d, CH_2, ^2J(HP) 15.5], 5.07 [2 H, d, CH_2, ^2J(HP) 14.6]; $\delta_P(CD_2Cl_2)$, 25.11 [1 P, s, $P(CH_2Ph)Ph_2$]. PR_3 = $P(CH_2Ph)_2Ph$: yield 75%, m.p. 154—156 °C (Found: C, 66.40; H, 5.30; N, 2.80. Calc. for $C_{28}H_{25}BrNP{\cdot}H_2O$: C, 66.65; H, 5.40; N, 2.80%). I.r. (CH_2Cl_2): 2 119 cm^{-1} (ν_{NC}). N.m.r.: $\delta_H(CD_2Cl_2)$, 4.71 [2 H, d, CH_2 ^2J(HP) 14.8], 4.68 [2 H, d, CH_2, ^2J(HP) 15.7], 4.58 [2 H, d, CH_2, ^2J(HP) 14.8]; $\delta_P(CD_2Cl_2)$ 22.25 [1 P, s, $P(CH_2Ph)_2Ph$]. PR_3 = $P(CH_2Ph)_3$: yield 68%, m.p. 159—163 °C (Found: C, 67.30; H, 5.40; N, 2.60. Calc. for $C_{29}H_{27}BrNP{\cdot}H_2O$: C, 67.20; H, 5.65; N, 2.70%). I.r. (CH_2Cl_2): 2 117 cm^{-1} (ν_{NC}). N.m.r.: $\delta_H(CD_2Cl_2)$, 4.21 [8 H, d, CH_2, ^2J(HP) 14.4]; $\delta_P(CD_2Cl_2)$, 25.69 [1 P, s, $P(CH_2Ph)_3$].

[*o*-$R_3PCH_2C_6H_4NC$]BF_4 [PR_3 = $P(CH_2Ph)Ph_2$ (L^1), $P(CH_2Ph)_2Ph$ (L^2), *or* $P(CH_2Ph)_3$ (L^3)]. The tetrafluoroborate salts were prepared according to the following procedure, described for L^1. To a suspension of $NaBF_4$ (1.91 g, 17.40 mmol) in acetone (50 cm^3) was added, in one portion, solid [*o*-$Ph_2(PhCH_2)PCH_2C_6H_4NC$]Br (1.64 g, 3.48 mmol). After stirring for 2 h at room temperature the solvent was evaporated under vacuum, and the residue was dissolved in CH_2Cl_2 (50

Table 1. I.r., ^{1}H, and ^{31}P-{^{1}H} n.m.r. spectral data for the ligands and their Pt^{II} derivatives

	I.r./cm^{-1}			N.m.r. data	
Compound	ν(N≡C)[a]	ν(Pt–Cl)[b]	ν(N–H)[b]	δ(^{1}H)/p.p.m.[c]	δ(^{31}P)/p.p.m.[d]
L^1	2 121s			5.34 [2 H, d, CH_2, ^2J(HP) 16.0] 5.13 [2 H, d, CH_2, ^2J(HP) 15.0]	25.82 [1 P, s, $P(CH_2Ph)Ph_2$]
L^2	2 119s			4.32 [4 H, d, CH_2, ^2J(HP) 14.9] 4.37 [2 H, d, CH_2, ^2J(HP) 14.4]	22.49 [1 P, s, $P(CH_2Ph)_2Ph$]
L^3	2 117s			4.15 [6 H, d, CH_2, ^2J(HP) 14.5] 4.10 [2 H, d, CH_2, ^2J(HP) 14.5]	25.55 [1 P, s, $P(CH_2Ph)_3$]
(**1a**)	2 190s	347w		4.07 [2 H, d, CH_2, ^2J(HP) 14.0] 3.40 [2 H, d, CH_2, ^2J(HP) 14.3]	25.65 [1 P, s, $P(CH_2Ph)Ph_2$], 18.51 [2 P, s, PPh_3, ^1J(PPt) 2 170]
(**2a**)	2 191s	341w		3.97 [4 H, d, CH_2, ^2J(HP) 14.8] 3.56 [2 H, d, CH_2, ^2J(HP) 14.3]	23.40 [1 P, s, $P(CH_2Ph)_2Ph$], 16.98 [2 P, s, PPh_3, ^1J(PPt) 2 256]
(**3a**)	2 187s	330w		3.50 [6 H, d, CH_2, ^2J(HP) 14.1] 3.31 [2 H, d, CH_2, ^2J(HP) 15.0]	*e*
(**1b**)		307w	3 312w	9.15 [1 H, d, NH, ^3J(HPt) 26.0, ^4J(HP) 3.6] 5.37 [2 H, d, CH_2, ^2J(HP) 15.5]	18.28 [2 P, d, PPh_3, ^1J(PPt) 2 720, ^4J(PP) 1.5] 13.41 [1 P, t, $P(CH_2Ph)Ph_2$, ^3J(PPt) 28.6, ^4J(PP) 1.5]
(**2b**)		296w	3 316w	9.20 [1 H, d, NH, ^3J(HPt) 20.0, ^4J(HP) 3.3] 4.81 [2 H, t, CH_2, ^2J(HP) 14.5] 3.38 [2 H, t, CH_2, ^2J(HP) 14.5]	16.84 [2 P, d, PPh_3, ^1J(PPt) 2 725, ^4J(PP) 1.7] 12.20 [1 P, t, $P(CH_2Ph)_2Ph$, ^3J(PPt) 32.2, ^4J(PP) 1.7]
(**3b**)		301w	3 349w	8.98 [1 H, br, NH, ^3J(HPt) 24.0] 3.81 [2 H, d, CH_2, ^2J(HP) 14.1] 3.73 [4 H, d, CH_2, ^2J(HP) 14.1]	16.13 [2 P, d, PPh_3, ^1J(PPt) 2 727, ^4J(PP) 1.7] 13.87 [1 P, t, $P(CH_2Ph)_3$, ^3J(PPt) 33.0, ^4J(PP) 1.7]

[a] In CH_2Cl_2 solution; s = strong. [b] Nujol mull; w = weak. [c] Spectra recorded in CD_2Cl_2; proton chemical shifts are reported relative to $SiMe_4$ by taking the chemical shift of CD_2Cl_2 as +5.32 p.p.m.; *J* in Hz; d = doublet; t = triplet; br = broad. [d] Spectra recorded in CD_2Cl_2; phosphorus chemical shifts referenced to external H_3PO_4(85%); s = singlet; d = doublet; t = triplet. [e] Too insoluble for ^{31}P n.m.r. measurements.

cm^3), and stirred with activated charcoal. After filtration, the filtrate was evaporated under reduced pressure to *ca.* 10 cm^3, and subsequently treated with Et_2O (50 cm^3). A cream solid precipitated which was filtered off, recrystallized from CH_2Cl_2–Et_2O, and dried under vacuum. Yield 1.38 g (83%), m.p. 171—173 °C (Found: C, 67.80; H, 4.65; N, 2.90. Calc. for $C_{27}H_{23}BF_4NP$: C, 67.65; H, 4.85; N, 2.90%). L^2: yield 75%, m.p. 144—146 °C (Found: C, 67.90; H, 5.35; N, 2.80. Calc. for $C_{28}H_{25}BF_4NP$: C, 68.15; H, 5.10; N, 2.85%). L^3: yield 81%, m.p. 142—144 °C (Found: C, 68.40; H, 5.55; N, 2.60. Calc. for $C_{29}H_{27}BF_4NP$: C, 68.65; H, 5.35; N, 2.75%). I.r. and n.m.r. spectral data for the ligands L^1—L^3 are listed in Table 1.

Synthesis of the Complexes.—trans-$[Pt(L)Cl(PPh_3)_2]BF_4$ [(**1a**)—(**3a**) *for* L = L^1—L^3, *respectively*]. A typical procedure is given below for compound (**1a**). To a suspension of $NaBF_4$ (0.97 g, 8.88 mmol) in acetone (50 cm^3) was added solid *cis-* and *trans*-$[PtCl_2(PPh_3)_2]$ (1.75 g, 2.22 mmol). The mixture was then treated dropwise at 0 °C with a solution of L^1 (1.06 g, 2.22 mmol) in acetone (30 cm^3) over a period of 30 min, and stirred for an additional 30 min at room temperature. The solvent was removed under vacuum and the residue dissolved in CH_2Cl_2 (50 cm^3). A white solid precipitated which was filtered off and recrystallized from CH_2Cl_2–Et_2O. Yield 2.82 g (96%), m.p. 256—258 °C (Found: C, 59.40; H, 4.50; N, 1.20. Calc. for $C_{63}H_{53}B_2ClF_8NP_3Pt{\cdot}0.5CH_2Cl_2$: C, 59.80; H, 4.25; N, 1.10%). (**2a**): yield 86%, m.p. 175—177 °C (Found: C, 57.25; H, 4.10; N, 1.05. Calc. for $C_{64}H_{55}B_2ClF_8NP_3Pt$: C, 57.60; H, 4.15; N, 1.05%). (**3a**): yield 75%, m.p. 162—165 °C (Found: C, 56.25; H, 4.25; N, 0.90. Calc. for $C_{65}H_{57}B_2ClF_8NP_3Pt{\cdot}0.5CH_2Cl_2$: C, 56.50; H, 4.20; N, 1.00%). I.r. and n.m.r. data for (**1a**)—(**3a**) are given in Table 1.

trans-$[Pt\{o\text{-}CN(H)C_6H_4C(PR_3)\}Cl(PPh_3)_2]BF_4$ [PR_3 = $P(CH_2Ph)Ph_2$ (**1b**), $P(CH_2Ph)_2Ph$ (**2b**), *or* $P(CH_2Ph)_3$ (**3b**)]. These complexes were prepared by an analogous procedure, described here for (**1b**). A solution of (**1a**) (2.30 g, 1.74 mmol) in CH_2Cl_2 (50 cm^3) was treated with NEt_3 (2.44 cm^3, 1.77 g, 17.4 mmol) and the reaction mixture stirred at room temperature. The course of the reaction was followed by i.r. by monitoring the decrease of the ν(N≡C) absorption. After 30 min, no ν(N≡C) band of the starting material was present. The reaction mixture was taken to dryness and the residue washed with small amounts of H_2O to remove inorganic salts. The resulting solid residue was dissolved in CH_2Cl_2 (50 cm^3), and the solution dried over anhydrous Na_2SO_4. After filtration, the solution was concentrated under vacuum to *ca.* 15 cm^3. On addition of Et_2O (50 cm^3), the product precipitated as a white solid. Yield 1.78 g (83%), m.p. 290—293 °C (Found: C, 59.55; H, 4.05; N, 1.10. Calc. for $C_{63}H_{52}BClF_4NP_3Pt{\cdot}0.5CH_2Cl_2$: C, 59.80; H, 4.20; N, 1.10%). (**2b**): yield 96%, m.p. 253—255 °C (Found: C, 59.75; H, 4.25; N, 1.15. Calc. for $C_{64}H_{54}BClF_4Pt{\cdot}0.5CH_2Cl_2$: C, 60.05; H, 4.30; N, 1.10%). (**3b**): yield 92%, m.p. 181—184 °C (Found: C, 57.25; H, 4.15; N, 1.00. Calc. for $C_{65}H_{56}BClF_4NP_3Pt{\cdot}1.5CH_2Cl_2$: C, 57.50; H, 4.30; N, 1.00%). I.r. and n.m.r. data for (**1b**)—(**3b**) are given in Table 1.

$[Pt\{o\text{-}CN(H)C_6H_4C[P(CHPh)Ph_2]\}Cl(PPh_3)]$ (**1c**). To a solution of complex (**1b**) (1.76 g, 1.43 mmol) dissolved in acetone (30 cm^3) was added dropwise at room temperature an aqueous solution (3 cm^3) of KOH (0.01 g, 1.72 mmol). The mixture was stirred for 30 min. The white solid formed was filtered off and washed with acetone (3 × 20 cm^3) and recrystallized from CH_2Cl_2–n-hexane. Yield 1.02 g (81%), m.p. 248—251 °C (Found: C, 60.90; H, 4.05; N, 1.55. Calc. for $C_{45}H_{36}ClNP_2Pt$: C, 61.20; H, 4.10; N, 1.60%). The i.r. and n.m.r. spectral data for this complex and its derivatives described below are reported in Table 2. The mass spectrum of (**1c**) showed M^+ at *m/e* 883. The molecular weight measurement in 1,2-dichloroethane gave a value of 892 (calculated 883).

$[Pt\{o\text{-}CN(H)C_6H_4C[P(CHPh)Ph_2]\}(OH)(PPh_3)]$ (**1d**). To a solution of complex (**1c**) (0.30 g, 0.33 mmol) in CH_2Cl_2 (30 cm^3) was added dropwise a solution of $AgBF_4$ (0.064 g, 0.33

Table 2. I.r., ^1H, and ^{31}P-{^1H} n.m.r. data for platinaheterocycle derivatives[a]

	I.r./cm^{-1} [b]		^1H N.m.r.[c]					
Compound	ν(N–H)	ν(other)	δ(CH)	$^2J(H\overset{+}{P})$	$^3J(HP_A)$	$^2J(HPt)$	$^3J(HP_B)$	δ(NH)
(1c)	3 414m	300w[e]	4.63 (t)	8.2	8.2	81.2		*f*
(1d)[g]	3 419m	3 604w[h]	4.41 (t)	8.8	8.8	83.2		*f*
(1e)	3 415m	2 107s[i]	5.00 (dd)	11.8	7.8	66.7		*f*
(1f)	3 409m		3.83 (ddd)	11.2	11.2	58.2	4.7	*f*

	^{31}P N.m.r.[d]								
Compound	$\delta(P_A)$	$^1J(P_APt)$	$^3J(P_A\overset{+}{P})$	$\delta(\overset{+}{P})$	$^2J(\overset{+}{P}Pt)$	$\delta(P_B)$	$^1J(P_BPt)$	$^2J(P_AP_B)$	$^3J(P_B\overset{+}{P})$
(1c)	20.96 (d)	2 584	14.7	26.42 (d)	50.5				
(1d)[g]	23.05 (d)	2 693	14.7	26.38 (d)	44.5				
(1e)	14.87 (d)	2 123	10.3	30.61 (d)	19.7				
(1f)	21.59 (dd)	2 369	18.9	27.86 (dd)	3.0	17.48 (dd)	2 320	18.0	11.5

[a] For details about the P_A, P_B, and $\overset{+}{P}$ moieties see equation (3) and Scheme 3. [b] Nujol mull unless otherwise stated; w = weak; m = medium; s = strong. [c] Experimental conditions as in footnote *c* of Table 1. [d] As footnote *d* of Table 1. [e] Pt–Cl. [f] Not observed. [g] δ(OH) not located. [h] Pt–OH; i.r. (CH_2Cl_2): ν(PtOH) 3 597w. [i] Pt–CO.

mmol) in acetone (10 cm^3) and the mixture was stirred for 15 min. The AgCl formed was filtered off and the solvent evaporated under vacuum. The solid residue was dissolved in acetone (15 cm^3) and an aqueous solution (3 cm^3) of KOH (0.019 g, 0.33 mmol) added at 0 °C. The solution was allowed to reach room temperature and the solvent evaporated under reduced pressure. The solid residue was dissolved in benzene (30 cm^3). After filtration, the filtrate was treated with n-hexane (50 cm^3) to give the product. Yield 0.25 g (86%), m.p. 227—230 °C (Found: C, 62.5; H, 4.35; N, 1.35. Calc. for $C_{45}H_{37}NOP_2Pt$: C, 62.50; H, 4.30; N, 1.60%).

[Pt{*o*-$\overline{CN(H)C_6H_4C}$[P(CHPh)Ph_2]}(CO)(PPh_3)]BF_4 **(1e)**. A solution of $AgBF_4$ (0.064 g, 0.33 mmol) in acetone (10 cm^3) was added dropwise to a solution of **(1c)** (0.30 g, 0.33 mmol) in CH_2Cl_2 (30 cm^3) under CO. The mixture was stirred for 30 min with active charcoal. After filtration the filtrate was evaporated under vacuum to 10 cm^3 and Et_2O (50 cm^3) was added. The pale yellow product was filtered off and recrystallized from CH_2Cl_2–Et_2O. Yield 0.25 g (77%), m.p. 160—163 °C (Found: C, 57.05; H, 3.70; N, 1.50. Calc. for $C_{46}H_{36}BF_4NOP_2Pt$: C, 57.40; H, 3.75; N, 1.45%).

[Pt{*o*-$\overline{CN(H)C_6H_4C}$[P(CHPh)Ph_2]}(PPh_3)$_2$]BF_4 **(1f)**. To a solution of **(1c)** (0.23 g, 0.25 mmol) in CH_2Cl_2 (20 cm^3) was added dropwise $AgBF_4$ (0.049 g, 0.25 mmol) in acetone (10 cm^3) and the mixture stirred for 15 min. The AgCl formed was filtered off and solid PPh_3 (0.07 g, 0.25 mmol) added to the filtrate. The solution was stirred for an additional 30 min, and then Et_2O (50 cm^3) added. The white solid formed was filtered off and dried under vacuum. Yield 0.24 g (81%), m.p. 174—177 °C (Found: C, 63.20; H, 4.30; N, 1.15. Calc. for $C_{63}H_{51}BF_4NP_3Pt$: C, 63.00; H, 4.20; N, 1.10%).

X-Ray Structural Determination.—Crystal data for **(2b)** are summarized in Table 3 together with some experimental details. Crystals suitable for *X*-ray analysis were obtained by slow diffusion of Et_2O into a solution of **(2b)** in 1,2-dichloroethane kept at room temperature.

Diffraction intensities were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer with Mo-K_α radiation (λ = 0.710 69 Å) and reduced to F_o values. Absorption correction was applied using the Walker and Stuart method,[12] once a complete structural model had been obtained and all atoms refined isotropically. The relative correction factor varied from 1.0 to 0.945. The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least squares, the minimized function being $\Sigma w(|F_o| - |F_c|)^2$. The weighting scheme employed was $w = k/[\sigma^2(F_o) + |g|F_o^2]$, where *k* and *g* were refined (4.296 and 0.000 43, respectively). The SHELX 76 package of crystallographic programs[13] was used for all computations with the analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, taken from ref. 13*b*. Thermal vibrations were treated anisotropically for all non-hydrogen atoms of the cation, except the two disordered halogen images (see below) and the phenyl rings which were treated as 'rigid bodies' (C–C = 1.40 Å, C–C–C = 120°). Hydrogen atoms were added in calculated positions (C–H = 1.08 Å) and refined 'riding' on the corresponding C or N atoms. As mentioned above, the crystal was found to contain disordered Cl and Br atoms bound to Pt^{II}. In fact, a peak appearing at a distance of 2.46 Å from Pt was at

Table 3. Crystal data and intensity collection parameters for **(2b)**

Formula	$C_{67.2}H_{60.4}BBr_{0.4}Cl_{3.8}F_4NP_3Pt$
M	1 423.52
Crystal system	Monoclinic
Space group	*C*2
a/Å	21.946(1)
b/Å	14.097(3)
c/Å	19.801(1)
β/°	96.95(1)
U/Å^3	6 080.9
Z	4
D_c/g cm^{-3}	1.56
μ(Mo-K_α)/cm^{-1}	30.1
Crystal dimensions/mm	0.3 × 0.55 × 0.35
Scan mode	ω–2θ
θ range/°	2.5—25
Octants of reciprocal space explored	±*h*, *k*, *l*
Measured reflections	5 025
Observed unique reflections with $I > 2.5\sigma(I)$	4 802
Final *R* and *R'* indices	0.037, 0.041
ω scan width/°	0.8 + 0.35 tan θ
Pre-scan speed/° min^{-1}	5
Pre-scan acceptance σ(*I*)/*I*	0.5
Maximum scan time/s	120
Requested σ(*I*)/*I*	0.01
Parameters refined	338

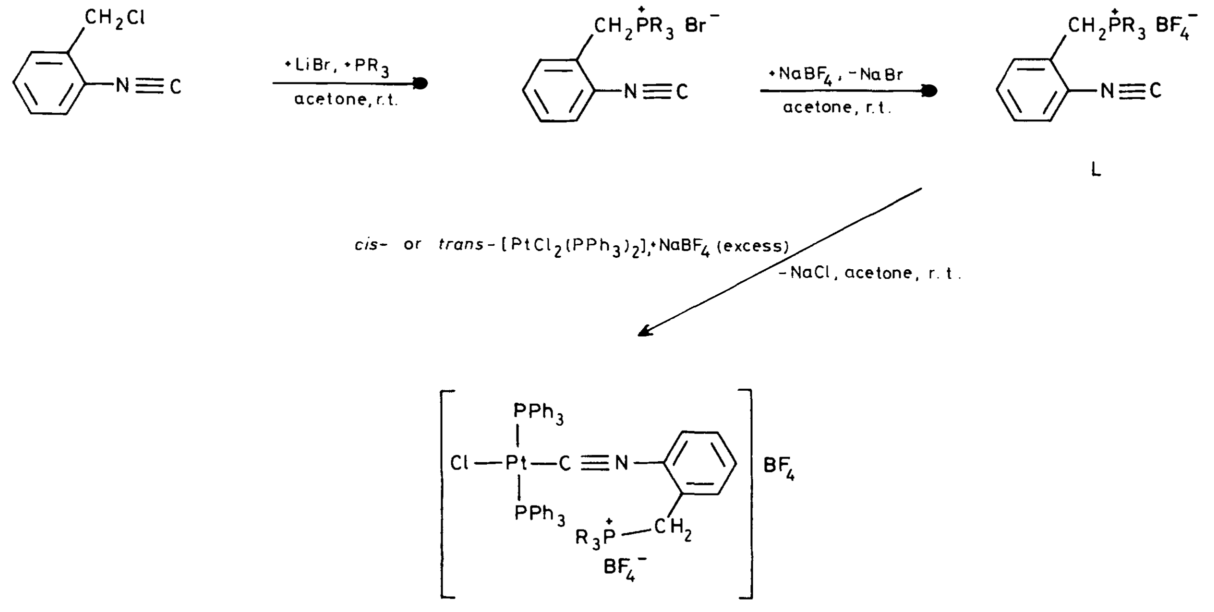
Table 4. Fractional atomic co-ordinates for **(2b)**, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	−0.251 33(1)	0.000 00	−0.199 53(1)	C(34)	−0.169 8(4)	−0.105 7(3)	−0.373 1(4)
Cl	−0.202 7(3)	−0.063 4(6)	−0.096 5(2)	C(35)	−0.096 9(3)	0.060 4(6)	−0.217 8(3)
Br	−0.198 15(13)	−0.048 45(18)	−0.865 7(7)	C(36)	−0.047 9(3)	0.068 8(6)	−0.256 2(3)
P(1)	−0.288 96(11)	0.253 69(18)	−0.274 20(12)	C(37)	0.003 0(3)	0.123 9(6)	−0.232 2(3)
P(2)	−0.159 29(11)	−0.019 72(15)	−0.244 87(13)	C(38)	0.004 8(3)	0.170 6(6)	−0.169 8(3)
P(3)	−0.343 98(11)	−0.019 08(17)	−0.156 12(14)	C(39)	−0.044 3(3)	0.162 2(6)	−0.131 5(3)
N	−0.320 8(3)	−0.009 2(9)	−0.333 1(4)	C(40)	−0.095 1(3)	0.107 1(6)	−0.155 5(3)
C(1)	−0.295 7(4)	0.053 7(7)	−0.287 5(4)	C(41)	−0.128 8(3)	−0.136 1(6)	−0.219 1(4)
C(2)	−0.309 8(4)	0.143 6(6)	−0.310 9(4)	C(42)	−0.066 8(3)	−0.149 1(5)	−0.196 2(4)
C(3)	−0.348 2(5)	0.134 5(8)	−0.377 0(5)	C(43)	−0.044 6(3)	−0.239 6(5)	−0.178 4(4)
C(4)	−0.376 9(5)	0.196 7(10)	−0.425 1(5)	C(44)	−0.084 4(3)	−0.317 0(5)	−0.183 5(4)
C(5)	−0.412 9(6)	0.159 8(12)	−0.480 1(6)	C(45)	−0.146 5(3)	−0.304 0(5)	−0.206 5(4)
C(6)	−0.419 2(6)	0.064 8(14)	−0.490 4(6)	C(46)	−0.168 7(3)	−0.213 6(5)	−0.224 3(4)
C(7)	−0.390 2(4)	−0.003 4(15)	−0.443 8(5)	C(47)	−0.344 9(4)	−0.133 9(7)	−0.113 0(4)
C(8)	−0.354 5(4)	0.037 4(8)	−0.388 8(5)	C(48)	−0.320 2(4)	−0.211 9(7)	−0.143 6(4)
C(9)	−0.353 4(5)	0.321 2(8)	−0.246 6(5)	C(49)	−0.319 0(4)	−0.300 5(7)	−0.112 2(4)
C(10)	−0.402 0(3)	0.354 9(5)	−0.298 5(4)	C(50)	−0.342 3(4)	−0.311 3(7)	−0.050 1(4)
C(11)	−0.395 5(3)	0.438 5(5)	−0.334 6(4)	C(51)	−0.366 9(4)	−0.233 3(7)	−0.019 5(4)
C(12)	−0.442 1(3)	0.467 9(5)	−0.384 4(4)	C(52)	−0.368 2(4)	−0.144 6(7)	−0.050 9(4)
C(13)	−0.495 3(3)	0.413 6(5)	−0.398 0(4)	C(53)	−0.413 0(4)	−0.025 1(4)	−0.217 2(4)
C(14)	−0.501 9(3)	0.329 9(5)	−0.361 9(4)	C(54)	−0.439 1(4)	0.057 6(4)	−0.246 6(4)
C(15)	−0.455 2(3)	0.300 6(5)	−0.312 2(4)	C(55)	−0.491 0(4)	0.052 2(4)	−0.294 7(4)
C(16)	−0.233 3(6)	0.230 0(9)	−0.197 4(5)	C(56)	−0.516 8(4)	−0.035 9(4)	−0.313 3(4)
C(17)	−0.207 1(3)	0.319 3(6)	−0.163 2(4)	C(57)	−0.490 6(4)	−0.118 5(4)	−0.283 9(4)
C(18)	−0.150 6(3)	0.352 8(6)	−0.178 6(4)	C(58)	−0.438 8(4)	−0.113 2(4)	−0.235 8(4)
C(19)	−0.125 6(3)	0.435 5(6)	−0.148 0(4)	C(59)	−0.358 7(3)	0.075 2(6)	−0.095 5(4)
C(20)	−0.157 2(3)	0.484 7(6)	−0.101 9(4)	C(60)	−0.309 2(3)	0.122 5(6)	−0.059 3(4)
C(21)	−0.213 8(3)	0.451 2(6)	−0.086 5(4)	C(61)	−0.319 8(3)	0.194 9(6)	−0.014 2(4)
C(22)	−0.238 7(3)	0.368 6(6)	−0.117 2(4)	C(62)	−0.379 8(3)	0.220 0(6)	−0.005 2(4)
C(23)	−0.252 7(4)	0.328 4(5)	−0.329 5(4)	C(63)	−0.429 2(3)	0.172 7(6)	−0.041 4(4)
C(24)	−0.235 0(4)	0.293 5(5)	−0.390 1(4)	C(64)	−0.418 6(3)	0.100 3(6)	−0.086 5(4)
C(25)	−0.205 2(4)	0.352 7(5)	−0.432 0(4)	B	−0.327 2(8)	−0.290 7(8)	−0.341 3(9)
C(26)	−0.193 1(4)	0.446 9(5)	−0.413 4(4)	F(1)	−0.311 7(7)	−0.207 4(8)	−0.320 7(8)
C(27)	−0.210 8(4)	0.481 8(5)	−0.352 8(4)	F(2)	−0.298 0(11)	−0.346 1(14)	−0.297 9(12)
C(28)	−0.240 6(4)	0.422 6(5)	−0.310 8(4)	F(3)	−0.324 0(18)	−0.332 5(22)	−0.397 8(11)
C(29)	−0.165 6(4)	−0.020 2(3)	−0.337 3(4)	F(4)	−0.382 4(10)	−0.305 5(22)	−0.330 3(20)
C(30)	−0.165 4(4)	0.065 6(3)	−0.372 4(4)	C(65)	−0.084 6(7)	−0.061 1(10)	−0.903 3(8)
C(31)	−0.169 3(4)	0.065 9(3)	−0.443 2(4)	C(66)	−0.043 0(6)	−0.029 4(10)	−0.956 4(8)
C(32)	−0.173 5(4)	−0.019 5(3)	−0.479 0(4)	C(67)	−0.437 7(7)	−0.215 4(11)	−0.564 4(8)
C(33)	−0.173 7(4)	−0.105 3(3)	−0.443 9(4)	C(68)	−0.459 4(8)	−0.318 5(11)	−0.576 7(12)

Table 5. Relevant bond distances (Å) and angles (°) for **(2b)**

Pt–Cl	2.360(5)	C(9)–C(10)	1.47(1)	P(3)–C(47)	1.83(1)	C(3)–C(8)	1.39(1)
Pt–Br	2.490(2)	P(1)–C(16)	1.86(1)	P(3)–C(53)	1.82(1)	C(4)–C(5)	1.37(1)
Pt–C(1)	2.036(8)	C(16)–C(17)	1.51(1)	P(3)–C(59)	1.84(1)	C(5)–C(6)	1.36(2)
Pt–P(2)	2.324(3)	P(1)–C(23)	1.78(1)	C(1)–N	1.34(1)	C(6)–C(7)	1.43(2)
Pt–P(3)	2.317(3)	P(2)–C(29)	1.82(1)	C(1)–C(2)	1.37(1)	C(7)–C(8)	1.39(1)
P(1)–C(2)	1.75(1)	P(2)–C(35)	1.80(1)	C(2)–C(3)	1.47(1)	N–C(8)	1.41(1)
P(1)–C(9)	1.84(1)	P(2)–C(41)	1.82(1)	C(3)–C(4)	1.39(1)		
C(1)–Pt–Cl	178.3(3)	C(35)–P(2)–C(41)	104.0(3)	C(2)–P(1)–C(9)	114.2(5)	C(2)–C(3)–C(4)	135(1)
C(1)–Pt–Br	173.8(3)	Pt–P(3)–C(47)	109.6(3)	C(2)–P(1)–C(16)	107.0(5)	C(2)–C(3)–C(8)	105.6(8)
C(1)–Pt–P(2)	93.6(2)	Pt–P(3)–C(53)	117.1(3)	C(2)–P(1)–C(23)	112.6(4)	C(4)–C(3)–C(8)	118.6(9)
C(1)–Pt–P(3)	90.6(2)	Pt–P(3)–C(59)	112.8(2)	C(9)–P(1)–C(16)	107.6(5)	C(3)–C(4)–C(5)	118(1)
Cl–Pt–P(2)	88.0(2)	C(47)–P(3)–C(53)	102.3(3)	C(9)–P(1)–C(23)	107.1(5)	C(4)–C(5)–C(6)	122(1)
Br–Pt–P(2)	88.8(1)	C(47)–P(3)–C(59)	108.7(4)	C(16)–P(1)–C(23)	108.1(5)	C(5)–C(6)–C(7)	122(1)
Cl–Pt–P(3)	87.8(2)	C(53)–P(3)–C(59)	105.6(3)	Pt–P(2)–C(29)	115.1(3)	C(6)–C(7)–C(8)	113(1)
Br–Pt–P(3)	88.4(1)	C(1)–N–C(8)	110(1)	Pt–P(2)–C(35)	118.3(3)	C(7)–C(8)–N	128(1)
Pt–P(2)–C(41)	107.8(3)	Pt–C(1)–C(2)	134.2(7)	Pt–C(1)–N	116.5(7)	C(3)–C(8)–C(7)	125(1)
C(29)–P(2)–C(35)	105.3(3)	N–C(1)–C(2)	109.1(8)	P(1)–C(2)–C(3)	122.6(7)	C(3)–C(8)–N	107(1)
C(29)–P(2)–C(41)	105.0(3)	C(1)–C(2)–P(1)	130.0(7)	C(1)–C(2)–C(3)	107.5(8)		

first treated as a chlorine atom, but the distance remained too long after several refinement cycles and the thermal parameter suspiciously low. It was then treated as a bromine atom, yielding a higher *R* factor and an unreliable thermal parameter. Because of this rather contradictory situation, the occurrence of disorder was suspected. In fact a residual peak of *ca.* 2 e Å^{-3} at a distance of 0.5 Å from the previous one could be detected in the final Fourier map and was attributed to a small fraction of bromine. Site occupation factors for Cl and Br converged to 0.6 and 0.4, respectively. Both halogens were then refined, fixing their



(1)

	PR3
L[1], (**1a**)	$P(CH_2Ph)Ph_2$
L[2], (**2a**)	$P(CH_2Ph)_2Ph$
L[3], (**3a**)	$P(CH_2Ph)_3$

Scheme 2.

distances from Pt at 2.36 for Cl and 2.49 Å for Br, in agreement with average values found in similar platinum–carbene complexes. Both the BF_4^- anion and the two $C_2H_4Cl_2$ solvent molecules were also affected by disorder, although to a different extent. In the former case, slight rotational displacement of the F atoms was reflected by the high values of their thermal parameters, whereas for the latter the Cl atoms could not be located, indicating random orientation of the Cl–C–C–Cl system, so that partial occupancies could be refined only for the C atoms (0.8 at convergence). The refinement of a structural model related by inversion to the present one was attempted to determine the absolute configuration. The rejected enantiomer gave the following agreement indices: 0.042 and 0.046 for R and R', respectively *vs.* values of 0.037 and 0.041 for the appropriate configuration.

The atomic co-ordinates are listed in Table 4 and relevant bond distances and angles in Table 5. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

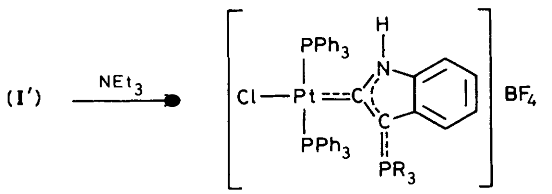
Results and Discussion

Synthesis of the Ligands and their Platinum(II) *Complexes*.— The phosphonium–isocyanide ligands L^1—L^3 and their Pt^{II} complexes (**1a**)—(**3a**) were prepared according to Scheme 2. The synthesis of the ligands L^1—L^3 involves the reaction in acetone at room temperature of *o*-$ClCH_2C_6H_4NC$[1,4] with 1.2 equivalents of the appropriate benzylphosphine in the presence of a three-fold excess of LiBr to give, in *ca.* 68—76% yield, the corresponding bromide salts. As previously reported for similar reactions,[4] it is suggested that either the more reactive bromo intermediate *o*-$BrCH_2C_6H_4NC$ or chloride–bromide exchange between phosphonium and lithium salts are involved during the reaction. The bromide–phosphonium–isocyanide salts are finally converted, in *ca.* 75—83% yield, to the corresponding, less hygroscopic tetrafluoroborates L^1—L^3 by reaction in acetone with excess $NaBF_4$. The ligands are white, odourless solids, soluble in chlorinated and alcoholic solvents, and slightly soluble in acetone. They were characterized by elemental analyses (Experimental section), i.r., ^1H, and ^{31}P n.m.r. spectra (Table 1). The ligands L^1—L^3 display the $\nu(N{\equiv}C)$ as a strong absorption in the range 2 117—2 121 cm^{-1} in CH_2Cl_2 solution. The ^1H n.m.r. spectra show the $-CH_2\overset{+}{P}R_3$ methylene protons as doublets [$^2J(HP)$ = 14.4—16.0 Hz] in the range δ 4.10—5.34. The ^{31}P n.m.r. spectra show the phosphonium group as a singlet in the range δ 22.49—25.82, typical of phosphonium salts.[14]

Reactions of the ligands L^1—L^3 with equimolar amounts of a mixture of *cis*- and *trans*-$[PtCl_2(PPh_3)_2]$ in acetone, in the presence of a four- or five-fold excess of $NaBF_4$, afford the corresponding cationic complexes *trans*-$[Pt(L)Cl(PPh_3)_2]BF_4$ [(**1a**)—(**3a**)] in > 75% yield. The isocyanide complexes [(**1a**)—(**3a**)] gave satisfactory C, H, and N elemental analyses (see Experimental section), and they have been characterized by i.r., ^1H, and ^{31}P n.m.r. spectra (Table 1). As expected for Pt^{II} co-ordination,[4—6] $\nu(N{\equiv}C)$ increases on passing from the unbound (2 117—2 121 cm^{-1}) to the co-ordinated isocyanide (2 187—2 191 cm^{-1}), with $\Delta\nu = \nu(N{\equiv}C)_{co\text{-}ord} - \nu(N{\equiv}C)_{free}$[15] = *ca.* 70 cm^{-1}, reflecting the electrophilic character[16] of the isocyanide carbon and therefore its ability to undergo nucleophilic attack to form carbene complexes.[17] The *trans* geometry of (**1a**) and (**2a**) has been determined by ^{31}P n.m.r. spectroscopy (Table 1), (**3a**) was insufficiently soluble for such measurements. Assignment of the *trans* configuration for (**3a**) is based on the absence of the characteristic strong i.r. band at 549 cm^{-1} attributed to the first overtone of the asymmetric PC_3 deformation mode in *cis*-bis(triphenylphosphine)platinum(II) complexes, as proposed by Mastin.[18] The ^1H n.m.r. spectra of (**1a**)—(**3a**) (Table 1) display the $-CH^a_2$ and $-CH^b_2$ resonances [see structure (**I**) of Scheme 1] as doublets in the range δ 3.56—3.31 [$^2J(HP)$ = 14.3—15.0 Hz] and δ 3.50—4.07 [$^2J(HP)$ = 14.0—14.8 Hz], respectively. The $-CH^b_2$ methylene protons of (**1a**) are tentatively assigned at δ 4.07 by comparison with values of the chemical shifts found for the parent complexes (**2a**) and (**3a**), which could be unambiguously assigned on the basis of integration ratios with the corresponding $-CH^a_2$ protons. The $-CH^a_2$ and $-CH^b_2$ chemical shifts in (**1a**)—(**3a**) are shifted upfield with respect to the free ligands L^1—L^3, probably as a consequence of shielding effects due to the presence of the phenyl rings of the two metal-co-ordinated PPh_3 ligands, as observed for other Pt^{II} species of similar structure.[4]

Cyclization Reactions.—Treatment of complexes (**1a**)—(**3a**) with a 10-fold excess of NEt_3 in CH_2Cl_2 at room temperature leads to almost instantaneous disappearance of the ν(N≡C) absorption, as evidenced by monitoring the course of the reaction by i.r. spectroscopy in the range 2 100—2 200 cm^{-1}. After work-up of the reaction mixtures (see Experimental section), the resulting reaction products [(**1b**)—(**3b**), Table 1] were isolated in *ca.* 83—96% yield. On the basis of their elemental analyses, i.r., ^1H, and ^{31}P n.m.r. spectra (Table 1), and of a single-crystal structure determination carried out for (**2b**) (see below), they have all been assigned the structure (**II**) in Scheme 1.

The present isocyanide cyclization is closely related to the conversion of phosphonium–isocyanide ligands to indole derivatives [equation (1)]. As reported for these reactions, in this case also the presumed ylide–isocyanide–metal intermediate (Scheme 1) could not be detected, cyclizing rapidly to the carbene ligand. Thus, there is no evidence for the formation of either of the two forms (**I′**) or (**I″**) (Scheme 1), but only (**I′**) appears to be the reactive intermediate yielding compounds (**1b**)—(**3b**) as the only reaction products [equation (2)].*



(2)

(**II**)

$PR_3 = P(CH_2Ph)Ph_2$ (**1b**), $P(CH_2Ph)_2Ph$ (**2b**), $P(CH_2Ph)_3$ (**3b**)

The diagnostic spectral features of compounds (**1b**)—(**3b**) are as follows. The ^{31}P n.m.r. resonance of the ylide phosphorus of the carbene unit appears as a triplet flanked by ^{195}Pt satellites [$I = \frac{1}{2}$, 34% abundance, $^3J(PPt)$ = 28.6—33.0 Hz], owing to coupling with the two magnetically equivalent metal-co-ordinated phosphines [$^4J(PP)$ = 1.5—1.7 Hz]. The ^{31}P chemical shifts of the ylidic phosphorus of (**1b**)—(**3b**) fall in the range δ 12.20—13.87 with an upfield shift of *ca.* 10—12 p.p.m. with respect to the free and platinum(II)-co-ordinated phosphonium precursors (Table 1), analogous to that found for other phosphorus-ylide systems.[4]

The ^1H n.m.r. spectra of complexes (**1b**)—(**3b**) display the N–H resonance in the range δ 8.98—9.20. The signal is broad for complex (**3b**), but appears as a doublet for complexes (**1b**) and (**2b**), due to coupling with the ylide phosphorus atom [$^4J(HP)$ = 3.3—3.6 Hz]. For complexes (**1b**)—(**3b**) the N–H resonance is further split by ^{195}Pt coupling [$^3J(HPt)$ = 20—26 Hz] as found in other Pt^{II} aminocarbene complexes.[19]

The benzyl protons of the $P(CH_2Ph)Ph_2$ ylide derivative (**1b**) appear as a doublet at δ 5.37 owing to coupling with the adjacent P atom. However, the benzyl resonances of the P ylide derivatives (**2b**) and (**3b**) show different patterns. Thus, the two sets of $-CH_2$ protons of complex (**2b**) each give rise to a triplet at δ 4.81 and 3.38, while the three benzyl groups of (**3b**) display two doublets at δ 3.81 (2 H) and 3.73 (4 H). These data suggest that there is restricted rotation around the P(ylide)–C(indole) bond (see also the description of the structure). The resonance pattern for the benzyl protons of (**2b**) may be explained by the absence of a plane of symmetry (see structure), which makes the benzyl protons magnetically inequivalent. Thus, the observed triplet may arise from the accidental equality of $^2J(HP)$ and geminal $^2J(HH)$ coupling constants.

Finally, the i.r. spectra of (**1b**)—(**3b**) show the ν(N–H) and ν(Pt–Cl) absorptions in the range 3 312—3 349 and 296—307 cm^{-1}, respectively, as weak bands.

To establish conclusively the identity of compounds (**1b**)—(**3b**), the crystal structure of (**2b**) was determined.

Description of the Structure of trans-$[Pt\{o\text{-}CN(H)C_6H_4C[P(CH_2Ph)_2Ph]\}X(PPh_3)_2]BF_4$ (X = Cl *or* Br) (**2b**).—The crystal contains *trans*-$[Pt\{o\text{-}CN(H)C_6H_4C[P(CH_2Ph)_2Ph]\}X(PPh_3)_2]^+$ cations (X = Cl or Br), present as a 6:4 disordered mixture of the two halogens, and $[BF_4]^-$ anions, together with two extensively disordered $C_2H_4Cl_2$ solvent molecules (see Experimental section). The structural characterization of this complex together with its ^1H and ^{31}P n.m.r. spectra revealed the presence of a mixture of chloro and bromo derivatives. The spectral data for the chloro derivative [(**2b**)] are reported in Table 1. The ^{31}P n.m.r. data for *trans*-$[Pt\{o\text{-}CN(H)C_6H_4C[P(CH_2Ph)_2Ph]\}Br(PPh_3)_2]BF_4$ are as follows: δ 15.16 [2 P, d, PPh_3, $^1J(PPt)$ 2 704, $^4J(PP)$ 2.0], 12.14 [1 P, t, $P(CH_2Ph)_2Ph$, $^3J(PPt)$ 29, $^4J(PP)$ 2.0 Hz]. The bromo derivative shows the same ^1H n.m.r. spectrum as (**2b**). Integration ratios between the ^{31}P resonances of the chloro and bromo derivatives show the presence of *ca.* 70% of (**2b**) and 30% of the bromo derivative. A plausible explanation for the formation of the mixture of chloro and bromo derivatives may be the incomplete conversion of the phosphonium–bromide–isocyanide $[o\text{-}Ph(PhCH_2)_2PCH_2C_6H_4NC]Br$ to its tetrafluoroborate salt. Chloride–bromide exchange at the Pt^{II} centre may thus occur as a consequence of the presence of bromide ions in solution.

The molecular structure of the Cl derivative is shown in the Figure. The co-ordination geometry around the Pt^{II} atom is characterized by a slight deviation from planarity of the square planar arrangement [atom elevation from the Cl, P(2), C(1), P(3), Pt plane ranging from 0.09 to −0.15 Å; 0.06 to −0.20 Å for the Br derivative]. The deformation of the square-planar stereogeometry appears to be caused by the presence of the bulky $P(CH_2Ph)_2Ph$ ligand bound to the indole moiety. Interestingly, while the *trans* Cl–Pt–C(1) system approaches linearity [178.3(3)°], the Br–Pt–C(1) system does not [173.8(3)°]. However, the two *trans*-PPh_3 ligands seem to bear most of the steric pressure exerted by the $P(CH_2Ph)_2Ph$ ligand.

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* It should be noted that the absence of (**II′**) (Scheme 1) does not preclude formation of the intermediate (**I″**). This could conceivably rearrange to (**I′**) before cyclization can take place.

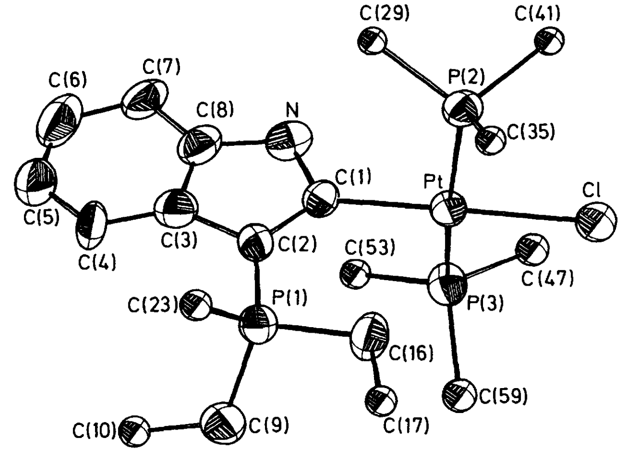


Figure. The molecular structure of *trans*-[Pt{*o*-$\overline{CN(H)C_6H_4C}$-[P(CH$_2$Ph)$_2$Ph]}Cl(PPh$_3$)$_2$]$^+$ (**2b**); only first atoms of the phenyl groups are shown for clarity, H-atoms are also omitted

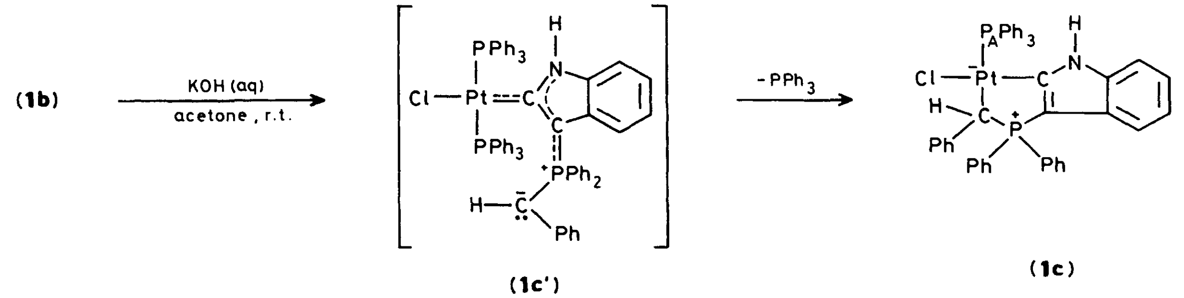
In fact, the value of P(2)–Pt–P(3) [164.4(1)°] shows appreciable deviation from 180° and should be compared with the value observed in the related species *trans*-[Pt{*o*-CN(H)C$_6$H$_4$C(PMe$_3$)}Cl(PPh$_3$)$_2$]BF$_4$ (**A**) [175.0(2)°],[4] where a slight deformation due to the PMe$_3$ ligand could already be detected. Furthermore, the two PPh$_3$ ligands appear to bend slightly towards the Cl atom [Cl–Pt–P(2) 88.0(2), Cl–Pt–P(3) 87.8(2)°]; the values for the Br derivative being Br–Pt–P(2) 88.8(1), Br–Pt–P(3) 88.4(1)°.

The average Pt–P bond length [2.320(3) Å] is shorter than the value previously reported for (**A**) [2.329(1) Å] and those reported for other square planar Pt^{II} complexes such as *trans*-[Pt{CN(C$_6$H$_4$Me-*p*)CH$_2$CH$_2$O}Br(PPh$_3$)$_2$]BF$_4$ [2.327(2) Å].[5] The Pt–C(1) value [2.036(8) Å] is close to the range observed in several other Cl–Pt–C(carbene) systems (1.82—2.01 Å).[20] The indole plane is strictly perpendicular to the Pt^{II} co-ordination square (92.9° for the Cl derivative). The bulky P(CH$_2$Ph)$_2$Ph ligand, co-ordinated to the indole moiety, determines substantial deformations of the whole carbenoid system. The C(1) and C(2) *sp*^{2} centres show larger angular values inside the *cis* Pt–C(1)–C(2)–P(1) system than outside [Pt–C(1)–C(2) 134(1), Pt–C(1)–N 116(1), C(1)–C(2)–P(1) 130(1), C(3)–C(2)–P(1) 123(1)°]. These angular deformations prevent the H-atoms bound to the benzyl carbon atom, and almost coplanar with the Pt atom and the indole system [C(16), see Figure], from getting too close to the Pt atom [Pt ··· H(15) 2.95, Pt ··· H(16) 2.78 Å].

The value of the N–C(1)–C(2) angle [109(1)°] falls within the range of values observed in Pt^{II} co-ordinated penta-atomic cyclic complexes, such as (**A**) [106.3(5)°], which contains a very similar indole ligand, or *trans*-[Pt{CN(C$_6$H$_4$Me-*p*)CH$_2$CH$_2$O}Br(PPh$_3$)$_2$]BF$_4$ [112(1)°], which contains an amino–oxy penta-atomic ring, or *cis*-[Pt{CN(C$_6$H$_4$Me-*p*)CH$_2$CH$_2$N(H)}Br$_2$(PPh$_3$)] [107(1)°] for a diamino penta-atomic ring[6] and *trans*- and *cis*-dichloro(1,3-diphenylimidazolidin-2-ylidene)(triethylphosphine)platinum(II) [107(1) and 111(1)°, respectively], where the ligand is an imidazoline.[21] However, the indole system retains planarity [max. deviation 0.07 Å for C(1)]. The bond length values within the condensed system indicate extensive electronic delocalization, as already observed in (**A**). Although the C(1)–N bond distance is considerably shorter than in the related complex (**A**) [1.34(1) *vs.* 1.40(1) Å], the distances C(8)–N are of comparable length [1.41(1) *vs.* 1.38(1) Å in (**2b**) and (**A**), respectively]. These differences suggest a slightly increased *sp*^{2} character for the N atom with respect to (**A**), while the P–C interaction between the indole system and the outer P(CH$_2$Ph)$_2$Ph group is strictly comparable to the value observed for the PMe$_3$ ligand in (**A**) [P(1)–C(2) 1.75(1) and 1.73(1) Å, respectively], where substantial multiple-bond character for this interaction has been inferred.

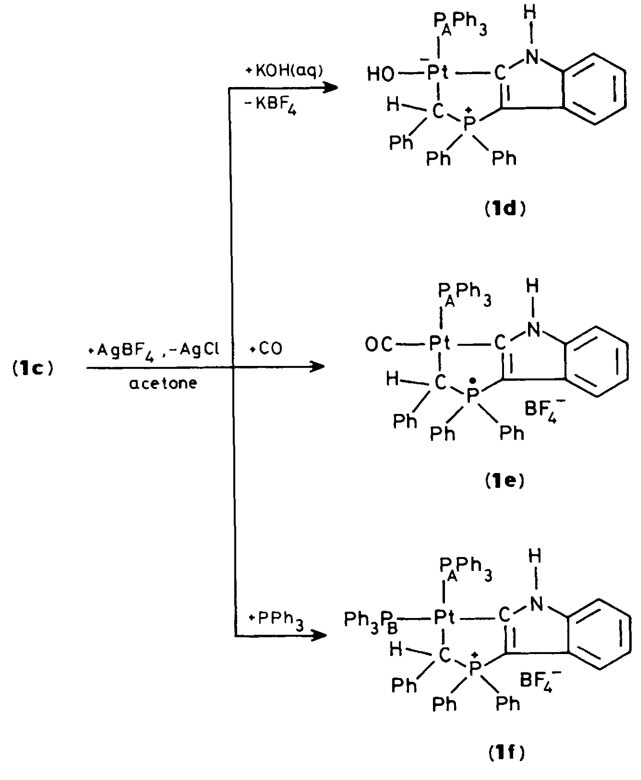
Finally, it is interesting to speculate about the 'asymmetric' location of the P(CH$_2$Ph)$_2$Ph ligand which might have chosen to have the Ph ring coplanar with the carbenoid system and the two benzyl groups above and below the plane. A more regular C_s-*m* location for the P(CH$_2$Ph)$_2$Ph group is very likely prevented by the steric interactions which would arise between the phenyl group and the neighbouring indole moiety (an ideal 61° rotation to achieve co-planarity would bring H ··· H contacts to about 0.7 Å).

Platinaheterocycles with Ylide-chelate Ligands.—The –CH$^b_2$ protons in structure (**II**) (Scheme 1), which are unreactive towards NEt$_3$ under the experimental conditions employed in the preparation of compounds (**1b**)—(**3b**), do, however undergo nucleophilic attack by a stronger base such as KOH. Thus, (**1b**) rapidly reacts with 1.2 equivalents of aqueous KOH in acetone at room temperature to give the platinaheterocycle complex (**1c**) in 81% isolated yield [equation (3)]. Presumably, the formation of (**1c**) in equation (3) occurs by initial deprotonation of the methylene protons by OH$^-$ ions to give the ylide–carbene–metal intermediate (**1c′**), followed by nucleophilic attack of the ylide carbanion on the platinum centre. Final ring closure to give (**1c**) results in loss of a PPh$_3$ ligand.



(**1c′**) (**1c**) (3)

Compound (**1c**) is air-stable in the solid state and in solution for a period of at least several months. Its structure has been fully determined by mass spectroscopy, elemental analysis (Experimental section), i.r., ^{1}H and ^{31}P n.m.r. spectroscopy (Table 2). The ^{1}H n.m.r. spectrum of (**1c**) shows the platinum(II)-co-ordinated –CH methine proton at δ 4.63 as a triplet, flanked by ^{195}Pt satellites, owing to accidental equality of ^2J(HP) and ^3J(HP) coupling constants (8.2 Hz). The ^2J(HPt) coupling constant of 81.2 Hz may be compared with the values found for the co-ordinated Ph$_3$PCH$_2$ ylide ligand in the cationic complex *cis*-[PtCl(CH$_2$PPh$_3$)(PPh$_3$)$_2$]I[22] [^2J(HPt)



Scheme 3.

69 Hz] or in the acyl ylide-chelate complexes of the type [Pt{CH[C(O)R]PPh$_2$(CH$_2$)$_2$PPh$_2$}Cl$_2$][23] [^2J(HPt) 108—116 Hz]. In the ^{31}P n.m.r. spectrum the resonances of the PPh$_3$ ligand and the phosphonium phosphorus each occur as doublets, flanked by ^{195}Pt satellites, with ^3J(PP) of 14.7 Hz. The magnitude of the ^1J(PPt) coupling constant for the phosphine ligand (2 584 Hz) is consistent with the values found for phosphine ligands *trans* to ylide-carbon donor groups as in the complexes *cis*-[Pt(CH$_2$PPh$_3$)Cl(PPh$_3$)$_2$]X [X = I[22] or AlCl$_4$;[24] ^1J(PPt) 2 244 Hz]. The ^{195}Pt–^{31}P ylide coupling constant is 50.5 Hz, which is 20 Hz lower with respect to values found for the above-mentioned Ph$_3$PCH$_2$-ylide–Pt^{II} complexes.[22,24] The ^{31}P resonance of the phosphonium group in (**1c**) falls at δ 26.42 with a downfield shift of 13 p.p.m. with respect to (**1b**). The observed value is similar to those found for the free and the Pt^{II}-co-ordinated ligand L^1 (Table 1) and also to those reported for other metal-co-ordinated phosphorus ylide systems.[22,24]

The Nujol mull i.r. spectrum of (**1c**) shows ν(N–H) at 3 414 cm^{-1} as a medium absorption. This value compares well with those observed for free 2-alkyl(aryl)indoles [ν(N–H) 3 390—3 435 cm^{-1}], which were obtained by Cu$_2$O catalyzed cyclization reactions of *o*-tolyl isocyanide.[25] Thus, all the reported spectroscopic data for (**1c**) appear to support the platinaheterocycle structure depicted in equation (3).

Chloride abstraction from (**1c**) by AgBF$_4$ and subsequent treatment of the cationic intermediate with nucleophiles such as OH$^-$, CO, and PPh$_3$ leads to the formation of the platinaheterocycles (**1d**), (**1e**), and (**1f**), respectively (Scheme 3). They were characterized by their elemental analyses, i.r., ^{1}H, and ^{31}P n.m.r. spectra. The spectroscopic data are reported in Table 2 and compare well with those of the precursor compound (**1c**). These complexes are stable in the solid state and in solution. Compound (**1d**) shows ν(OH) at 3 604 cm^{-1} (Nujol mull) as a weak band. Similar values have been found for other Pt^{II}-hydroxo complexes.[26] No CO insertion into the Pt–C(ylide) bond occurs in the synthesis of (**1e**) at room temperature. Its Nujol mull i.r. spectrum shows ν(CO) at 2 107 cm^{-1} as a strong absorption. Also compounds (**2b**) and (**3b**) react with KOH under experimental conditions analogous to those reported for (**1b**). However, the resulting reaction products display spectral features significantly different to those reported for (**1c**). A detailed investigation of their structures is underway.

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