$OC_2H_5]BF_4$, 104507-16-6; [CpCo(dppe)C(O)OC_2H_5]PF_6, 104507-18-8; [CpCo(dppe)C(O)OC_3H_7]PF_6, 104507-20-2; [CpCo(dppe)C(O)OC_4H_9]PF_6, 104507-22-4; [CpCo(dppe)C(O)$CH_2CH(CH_3)_2$]PF_6, 104507-24-6; [CpCo(dppe)C(O)C_3H_{11}]PF_6, 104507-26-8; [CpCo(dppe)C(O)C_6H_{13}]PF_6, 104507-28-0; CO, 630-08-0; [CpCo(dppe)I]I, 32842-39-0; [Cp*Co(dppe)I]I, 104507-29-1; [CpCo(dppp)I]I, 89463-02-5; CH_3OH, 67-56-1; C_2H_5OH, 64-17-5; C_6H_7OH, 71-23-8; C_4H_9OH, 71-36-3; $(CH_3)_2CHCH_2OH$, 78-83-1; $C_kH_{11}OH$, 71-41-0; $C_6H_{13}OH$, 111-27-3; $C_1H_5NH_2$, 62-53-3; C_6H_5SH, 108-98-5.

Supplementary Material Available: Tables of bond distances and angles and anisotropic thermal parameters for the three structures described in this paper (12 pages); listings of calculated and observed structure factors for the three structures described in this paper (51 pages). Ordering information is given on any current masthead page.

Functionalized Isocyanides as Ligands. 4.[1] Base-Promoted Cyclization Reactions of Free and Platinum(II)-Coordinated *o*-(Phosphoniomethyl)phenyl Isocyanide Tetrafluoroborates, *o*-($BF_4^-R_3P^+$–CH_2)C_6H_4NC. Synthesis and Spectroscopic Characterization of 1- and 2-Platinum(II)-Substituted Indole Derivatives and X-ray Structure of *trans*-{$(PPh_3)_2Pt[\overline{CN(H)\text{-}o\text{-}C_6H_4C(PMe_3)}]Cl\}BF_4\cdot C_2H_4Cl_2$

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The chloromethyl substituent of the isocyanide *o*-($ClCH_2$)C_6H_4NC easily reacts in CH_2Cl_2 with the tertiary phosphines PMe_3 and PMe_2Ph or in acetone in the presence of excess LiBr with the phosphines $PMePh_2$ and PPh_3 to give quantitatively the novel phosphonium-substituted isocyanides *o*-($X^-R_3P^+$–CH_2)C_6H_4NC (X = halide), which are more conveniently converted into their less hygroscopic tetrafluoroborate salts *o*-($BF_4^-R^3P^+$–CH_2)C_6H_4NC (L) (PR_3 = PMe_3 (L^1), PMe_2Ph (L^2), $PMePh_2$ (L^3), PPh_3 (L^4)). Attack of an appropriate base to the activated methylene group of the R_3P^+–CH_2– substituent produces the highly reactive ylide function R_3P^+–CH^-– which undergoes ring closure with the adjacent isocyano group via intramolecular attack of the ylide carbanion to the electrophilic isocyanide carbon (either free or metal-coordinated), affording an indole derivative. Thus, upon treatment in CH_2Cl_2 at room temperature with a 10-fold excess of the mild base NEt_3, the Pt(II)-coordinated ligands L in cationic complexes of the type *trans*- and *cis*-[$P_2Pt(L)X]BF_4$ (X = Cl, L = L^1–L^4, P = PPh_3 (**1**–**4**); X = CH_3, L = L^1, P = $PMePh_2$ (**5**), PMe_2Ph (**6**), PCy_3 (**7**); X = Cl, L = L^1, P_2 = *cis*-$Ph_2PCH{=}CHPPh_2$ (**8**)) undergo cyclization reactions to 2-Pt(II)-substituted indole derivatives of the type *trans*- and *cis*-{$P_2Pt[\overline{CN(H)\text{-}o\text{-}C_6H_4C(PR_3)}]X\}BF_4$ (**9**–**15**), with reaction times depending on steric and electronic factors due to the ligand and metal substituents. The structures of the final compounds have been assigned on the basis of analytical, spectroscopic (IR and ^1H and ^{31}P NMR), and structural data. The solid-state structure of *trans*-{$(PPh_3)_2Pt[\overline{CN(H)\text{-}o\text{-}C_6H_4C(PMe_3)}]Cl\}BF_4\cdot C_2H_4Cl_2$ (**9**) has been determined by single-crystal X-ray diffractometry: space group $P2_1/m$, a = 10.434 (1) Å, b = 23.465 (2) Å, c = 11.725 (1) Å, β = 112.88 (2)°, Z = 2. The structural model was refined to R = 0.040 (R_w = 0.045) for 3961 independent reflections. The coordination geometry around the Pt(II) atom is square-planar with the carbenoid ligand perpendicular to the plane. The Pt–C(sp^2) and Pt–Cl bond lengths are 1.99 (1) and 2.369 (1) Å, respectively. Bond lengths within the indole system, which constitutes the carbenoid ligand, indicate extensive electronic delocalization. As a consequence, β-protonation at the indole ring occurs on treating **9** with HBF_4. Reaction of the stronger base $NaNH_2$ in THF at room temperature with the uncoordinated isocyanide L^4 affords the 3-(triphenylphosphonio)indolyl ligand: $\overline{N(o\text{-}C_6H_4)C(PPh_3)C(H)}$, which is found to coordinate to Pt(II) at the N(1) position of the indole ring as in the complexes *cis*-{$(PPh_3)_2Pt[\overline{N(o\text{-}C_6H_4)C(PPh_3)C(H)}]Cl\}BF_4$ and *trans*-$(PPh_3)Cl_2Pt[\overline{N(o\text{-}C_6H_4)C(PPh_3)C(H)}]$.

Introduction

Suitably functionalized isocyanide ligands have proved synthetically useful reagents in organometallic chemistry to form a variety of heterocyclic systems. The two general routes reported so far to such cyclization reactions are closely related to the role of the function which can (i) spontaneously interact with the isocyanide[2] or (ii) activate the neighboring C–H bonds to form α-metalated iso-

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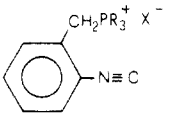
cyanides[3,4] or metal–carbon[5–7] bonds which subsequently undergo cycloadditions with 1,3-dipolarophiles or intramolecular migratory rearrangements, respectively.

We have recently reported[8] the synthesis of functionalized isocyanides of the type *o*-$(XCH_2)C_6H_4NC$ (X = Cl, I) and shown that the isocyanide and halomethyl functions in these ligands can selectively interact with an appropriately chosen metal substrate to give mononuclear or homo- and heteropolynuclear complexes.[8,9] Nucleophilic substitution of halide in the halomethyl isocyanide ligands with other potentially reactive functionalities would therefore appear to be an attractive approach to the preparation of other functionalized isocyanides. Here we describe a detailed study of the synthesis of novel phosphonium-substituted isocyanide ligands of the type



X = halide, BF_4; PR_3 = tertiary monophosphine

derived from the reactions of *o*-(chloromethyl)phenyl isocyanide with tertiary monophosphines such as PMe_3, PMe_2Ph, $PMePh_2$, and PPh_3. Interest in these ligands stems also from the following reasons. First, the R_3P^+–CH_2– phosphonium moiety in these ligands can be regarded as a suitable source of the corresponding ylide function R_3P^+–$\ddot{C}H^-$–[10] which may potentially undergo further reactions. Thus, molecular models indicate that the nucleophilic ylide carbon is in a favorable position to interact intramolecularly with the electrophilic isocyanide carbon (either free or metal-coordinated) to afford novel substituted indole derivatives. Secondly, there appear to be no examples in the literature of the interaction of phosphorus ylides with transition-metal-coordinated isocyanides.[11,12] It has been recently shown[13] that the reactions of P-ylides with mixed isocyanide–carbonyl complexes of the type $[Cp(CO)_2(MeNC)Fe]BF_4$ and $[Cp(CO)(RNC)_2Fe]BF_4$ (Cp = η^5-C_5H_5; R = Me, *t*-Bu) occur only via ylide attack at the carbonyl carbon with formation of iron acyl ylides.

A preliminary communication on the synthesis and reactivity of phosphonium-substituted isocyanides has already appeared.[14]

Experimental Section

General Procedures. All reactions were carried out under a nitrogen atmosphere. Dichloromethane, diethyl ether, and tetrahydrofuran (THF) were distilled under Ar from sodium benzophenone ketyl. *N,N*-Dimethylformamide (DMF) was distilled under N_2 from BaO. Acetone was dried over $CaSO_4$ and degassed before use. All other solvents were of reagent grade purity and dried over molecular sieves without further purification. IR spectra were taken on a Perkin-Elmer 983 spectrophotometer. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian FT-80A spectrometer. Melting points were taken on a hot plate apparatus and are uncorrected. Elemental analyses were performed by the Institute of Analytical Chemistry of the University of Padua.

Materials. *o*-Aminobenzyl alcohol was purchased from Fluka and used without further purification. Phosphines were Strem Chemicals products and used as purchased. The following compounds were prepared according to literature methods: acetic formic anhydride (AFA),[15] *cis*-$(PPh_3)_2PtCl_2$,[16] *trans*-$(PR_3)_2Pt(CH_3)Cl$ (PR_3 = $PMePh_2$,[17] PMe_2Ph,[18] PCy_3[19]). The complex *cis*-$(Ph_2PCH{=}CHPPh_2)PtCl_2$ was prepared in 90% yield by reacting equivalent amounts of $(COD)PtCl_2$[20] (COD = 1,5-cyclooctadiene) and *cis*-$Ph_2CH{=}CHPPh_2$ in CH_2Cl_2 at room temperature for 3 h, followed by precipitation with Et_2O.

Synthesis of Ligands. (*o*-(Hydroxymethyl)phenyl)formamide, *o*-$(HOCH_2)C_6H_4NHCHO$. A three-neck, 3-L, round-bottom flask equipped with mechanical stirrer, dropping funnel, and inlet–outlet for N_2 was charged with *o*-aminobenzyl alcohol (84.60 g, 0.68 mol), Et_2O (1.2 L), and *n*-hexane (1.2 L) and the resultant mixture cooled to 0 °C with an ice–water bath. AFA (65.60 g, 0.74 mol) was added dropwise under vigorous stirring over a period of 1 h. After the addition was complete, the reaction mixture was stirred for 30 min at 0 °C and then at room temperature for an additional 30 min. The off-white solid formed was filtered off and washed with *n*-hexane (3 × 50 mL). It was then dried under vacuum to yield 92.10 g (90%) of the product: mp 79–80 °C; IR (CH_2Cl_2, cm^{-1}) ν(OH) 3588 (m), ν(NH) 3358 (m), ν(C=O) 1696 (vs); ^1H NMR ($CDCl_3$) δ(OH) 3.32 (br), $\delta(CH_2)$ 4.65 (s), δ(NH) 8.81 (br), δ(CHO) 8.28 (s). Anal. Calcd for $C_8H_9NO_2$: C, 63.56; H, 6.00; N, 9.96. Found: C, 63.20; H, 5.78; N, 8.85.

(*o*-(Chloromethyl)phenyl)formamide, *o*-$(ClCH_2)C_6H_4NHCHO$. A three-neck, round-bottom flask equipped with mechanical stirrer, dropping funnel and inlet–outlet for N_2 was charged with (*o*-(hydroxymethyl)phenyl)formamide (70.80 g, 0.47 mol) and THF (1.25 L) and the resultant mixture cooled to −40 °C in a dry ice–acetone bath. After being stirred at the low temperature for 30 min, a solution of $SOCl_2$ (35.8 mL, 0.49 mol) in THF (200 mL) was added dropwise under vigorous stirring in a period of 3 h. After the addition was complete, the reaction mixture was left stirring at −40 °C for an additional hour and then kept at −20 °C overnight. It was then filtered and the solution treated with Et_2O (3.2 L) and a 2 M aqueous solution of Na_2CO_3 (1.2 L) and H_2O (4 × 300 mL) and then dried over anhydrous Na_2SO_4. After filtration, evaporation under reduced pressure gave an oily residue which was taken up with CH_2Cl_2 (200 mL). Addition of Et_2O (200 mL) and *n*-hexane (200 mL) gave 44.40 g (56%) of a cream solid which was filtered and dried under vacuum. The crude product can be chromatographed on a silica gel column (3 × 20 cm) with CH_2Cl_2 as eluant. The cream band developed was collected and taken to dryness to yield the off-white product, yield 38.60 g (49%). Analytical and spectral data for this compound are identical with those previously reported.[8]

***o*-(Chloromethyl)phenyl Isocyanide, *o*-$(ClCH_2)C_6H_4NC$.** The isocyanide was prepared by the $SOCl_2$–DMF method as previously reported.[8] Purification of the isocyanide may be achieved both by sublimation[8] or by column chromatography on silica gel eluting with a solution of CH_2Cl_2–*n*-hexane (1:1, v/v). The yellow band which is formed is collected and taken to dryness (yield ca. 65%).

Synthesis of Phosphonium-Substituted Isocyanides, *o*-$(Cl^-R_3P^+$–$CH_2)C_6H_4NC$ (PR_3 = PMe_3, PMe_2Ph). All these compounds were prepared by a standard procedure which is

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Table I. IR and ^1H and $^{31}P\{^1H\}$ NMR Spectral Data for the Ligands and Their Pt(II) Complexes

	IR, cm^{-1}		^1H NMR[d]				$^{31}P\{^1H\}$ NMR[d]		
compd[a]	$\nu(N{\equiv}C)$[b]	$\nu(PtCl)$[c]	$\delta(CH_2)$	$^2J(HP)$	$\delta(PCH_3)_{ligand}$	$^2J(HP)$	$\delta(P)_{ligand}$	$\delta(P)_{metal}$	$^1J(PPt)$
L^1	2122 (s)		3.85 (d)	16.1	1.91 (d)	14.2	30.18 (s)		
L^2	2121 (s)		4.07 (d)	15.7	2.29 (d)	13.9	25.12 (s)		
L^3	2120 (s)		4.67 (d)	15.6	2.55 (d)	13.4	22.42 (s)		
L^4	2120 (s)		4.96 (d)	14.3			22.72 (s)		
1	2186 (s)	347 (w)	2.90 (d)	16.4	1.49 (d)	14.2	29.13 (s)	18.55 (s)	2183
2	2193 (s)	346 (w)	3.00 (d)	15.6	1.80 (d)	13.8	25.84 (s)	18.76 (s)	2176
3	2187 (s)	345 (w)	3.31 (d)	15.6	1.84 (d)	13.0	21.92 (s)	18.92 (s)	2170
4	2191 (s)	346 (w)	3.57 (d)	15.8			22.21 (s)	19.18 (s)	2156
5[e]	2163 (s)		2.96 (d)	16.3	1.56 (d)	14.2	29.08 (s)	7.45 (s)	2648
6[f]	2157 (s)		2.40 (d)	16.3	1.71 (d)	14.2	29.32 (s)	−6.44 (s)	2534
7[g]	2129 (s)		3.88 (d)	16.2	1.97 (d)	14.2	29.20 (s)	26.02 (s)	2408
8	2209 (s)	315 (w)	3.97 (d)	16.5	1.90 (d)	14.2	30.50 (s)	51.43 (d)[h]	3219
								56.50 (d)[i]	2897

[a] See Scheme II for ligands L and Scheme III for their Pt(II) complexes. [b] CH_2Cl_2; s = strong. [c] Nujol mull; w = weak. [d] Spectra recorded in CD_2Cl_2; proton chemical shifts are reported from Me_4Si by taking the chemical shift of dichloromethane-d_2 as +5.32 ppm; phosphorus chemical shifts referenced to external H_3PO_4 (85%); J in Hz; s = singlet; d = doublet. [e] ^1H NMR: $\delta(PCH_3)_{metal}$ 2.34 (t, $^2J(HP) + {}^4J(HP)$ = 6.5, $^3J(HPt)$ = 34.0); $\delta(CH_3)$ 0.44 (t, $^3J(HP)$ = 8.1, $^2J(HPt)$ = 60.4). [f] ^1H NMR: $\delta(PCH_3)_{metal}$ 1.96 (t, $^2J(HP) + {}^4J(HP)$ = 7.5, $^3J(HPt)$ = 32.6); $\delta(CH_3)$ 0.49 (t, $^3J(HP)$ = 8.2, $^2J(HPt)$ = 61.5). [g] ^1H NMR: $\delta(CH_3)$ 0.58 (t, $^3J(HP)$ = 6.4, $^2J(HPt)$ = 62.0). [h] P trans to Cl, $^2J(PP)$ = 5.8. [i] P cis to Cl, $^2J(PP)$ = 5.8.

described below for the PMe_3 derivative. A solution of *o*-$(ClCH_2)C_6H_4NC$ (1.51 g, 9.98 mmol) in CH_2Cl_2 (25 mL) was treated in one portion with PMe_3 (1.0 mL, ca. 1.0 g, ca. 13 mmol) and the reaction mixture stirred at room temperature overnight. It was then concentrated to half of the volume under reduced pressure, and Et_2O (50 mL) was added. A cream solid immediately precipitated which was filtered, washed with Et_2O (3 × 15 mL), and dried under vacuum: yield 2.10 g (92%); mp 170–171 °C dec; IR (CH_2Cl_2) ν(NC) 2120 (s); ^1H NMR ($CDCl_3$, J in Hz) $\delta(CH_2)$ 4.44 (d, $^2J(HP)$ = 16.6), $\delta(PCH_3)$ 2.27 (d, $^2J(HP)$ = 14.4); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 85% H_3PO_4 external reference) δ(P) 30.75 (s). Anal. Calcd for $C_{11}H_{15}NPCl{\cdot}H_2O$: C, 53.77; H, 6.97; N, 5.70. Found: C, 53.16; H, 6.91; N, 5.38. PR_3 = PMe_2Ph: mp 160–161 °C; IR (CH_2Cl_2) ν(NC) 2121 (s); ^1H NMR ($CDCl_3$) $\delta(CH_2)$ 4.78 (d, $^2J(HP)$ = 16.5), $\delta(PCH_3)$ 2.60 (d, $^2J(HP)$ = 14.0); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ(P) 25.20 (s). Anal. Calcd for $C_{16}H_{17}NPCl{\cdot}H_2O$: C, 62.43; H, 6.22; N, 4.55. Found: C, 61.92; H, 6.43; N, 4.33.

***o*-$(Br^-R_3P^+-CH_2)C_6H_4NC$ (PR_3 = PPh_3, $PMePh_2$).** These ligands were prepared by the following one-pot synthesis which is described for the PPh_3 derivative. To a solution of LiBr (0.86 g, 9.90 mmol) dissolved in acetone (40 mL) were added in one portion solid *o*-$(ClCH_2)C_6H_4NC$ (0.50 g, 3.31 mmol) and PPh_3 (1.04 g, 3.97 mmol), and the reaction mixture stirred overnight at room temperature. It was then taken to dryness under reduced pressure and the solid residue taken up with CH_2Cl_2 (50 mL). After filtration, the solution was concentrated to ca. 25 mL. Addition of Et_2O (40 mL) gave a white precipitate of the product: yield 1.40 g (93%); mp 218–220 °C; IR (CH_2Cl_2) ν(NC) 2120 (s); ^1H NMR (CD_2Cl_2) $\delta(CH_2)$ 5.56 (d, $^2J(HP)$ = 14.7); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ(P) 23.10 (s). Anal. Calcd for $C_{26}H_{21}NPBr{\cdot}1.5H_2O$: C, 64.33; H, 4.98; N, 2.88. Found: C, 63.90; H, 4.47; N, 2.68. PR_3 = $PMePh_2$: IR (CH_2Cl_2) ν(NC) 2121 (s); ^1H NMR (CD_2Cl_2) $\delta(CH_2)$ 5.18 (d, $^2J(HP)$ = 16.0), δ (PCH_3) 2.80 (d, $^2J(HP)$ = 13.6); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ(P) 22.73 (s). Anal. Calcd for $C_{21}H_{19}NPBr{\cdot}H_2O$: C, 60.88; H, 5.11; N, 3.38. Found: C, 60.37; H, 4.93; N, 3.21.

***o*-$(BF_4^-R_3P^+-CH_2)C_6H_4NC$ (PR_3 = PMe_3 (L^1), PMe_2Ph (L^2), $PMePh_2$ (L^3), PPh_3 (L^4)).** The tetrafluoroborate salts of the phosphonio isocyanide ligands were obtained by metathesis of the corresponding halides with a 4–5-fold excess of $NaBF_4$ in acetone. A typical procedure is outlined for L^1. To a suspension of $NaBF_4$ (2.90 g, 26.41 mmol) in acetone (50 mL) was added in one portion solid *o*-$(Cl^-Me_3P^+-CH_2)C_6H_4NC$ (1.51 g, 6.63 mmol), and the reaction mixture was stirred at room temperature for 2 h. It was then taken to dryness, taken up with CH_2Cl_2 (50 mL), and stirred with activated charcoal. After filtration and concentration to ca. 10 mL, it was treated with Et_2O (50 mL). A cream solid precipitated which was filtered, recyrstallized from CH_2Cl_2–Et_2O, and dried under vacuum: yield 1.65 g (89%); mp 129–130 °C. Anal. Calcd for $C_{11}H_{15}NPBF_4$: C, 47.35; H, 5.42; N, 5.02. Found: C, 47.35; H, 5.93; N, 5.10. L^2: mp 98–99 °C. Anal. Calcd for $C_{16}H_{17}NPBF_4$: C, 56.34; H, 5.03; N, 4.11. Found: C, 56.03; H, 5.33; N, 3.87. L^3: mp 170–173 °C. Anal. Calcd for $C_{21}H_{19}NPBF_4$: C, 62.56; H, 4.75; N, 3.47. Found: C, 62.25; H, 5.02; N, 3.38. L^4: mp 198–200 °C. Anal. Calcd for $C_{26}H_{21}NPBF_4$: C, 67.12; H, 4.55; N, 3.01. Found: C, 66.84; H, 5.02; N, 2.91. Spectroscopic data for the ligands L^1–L^4 are listed in Table I.

Preparation of Complexes. *trans*-$[(PPh_3)_2Pt(L)Cl]BF_4$ (L = L^1 - L^4 (1 - 4)). A typical procedure is reported below for complex **1** with L^1 as the isocyanide ligand. To a solution of *cis*-$(PPh_3)_2PtCl_2$ (1.58 g, 2.00 mmol) in CH_2Cl_2 (60 mL) was added dropwise a solution of 0.985 M $AgBF_4$ (2.03 mL, 2.00 mmol) in acetone at room temperature, and the reaction mixture was stirred for 1 h. It was the filtered to remove solid AgCl, concentrated to 20 mL under reduced pressure, treated dropwise at 0 °C with a solution of L^1 (0.56 g, 2.00 mmol) in CH_2Cl_2 (30 mL) in a period of 30 min, and stirred for an additional 30 min at room temperature. The volume of the solution was reduced to 10 mL under vacuum and treated with Et_2O (50 mL) to afford a pale cream solid which was filtered, washed with Et_2O (3 × 20 mL), and dried under vacuum: yield 2.00 g (89%); mp 261–264 °C. Anal. Calcd for $C_{47}H_{45}NClP_3B_2F_8Pt$ (**1**): C, 50.36; H, 4.04; N, 1.25. Found: C, 49.94; H, 4.23; N, 1.12. Calcd for $C_{52}H_{47}NClP_3B_2F_8Pt$ (**2**): C, 52.79; H, 4.00; N, 1.18. Found: C, 52.35; H, 4.18; N, 1.05. Calcd for $C_{57}H_{49}NClP_3B_2F_8Pt$ (**3**): C, 54.98; H, 3.97; N, 1.13. Found: C, 55.29; H, 4.05; N, 1.01. Calcd for $C_{62}H_{51}NClP_3B_2F_8Pt$ (**4**): C, 56.97; H, 3.92; N, 1.07. Found: C, 56.45; H, 3.87; N, 0.95. Spectral data for **1**–**4** are reported in Table I.

***trans*-$[(PR_3)_2Pt(CH_3)(L^1)]BF_4$ (PR_3 = $PMePh_2$ (5), PMe_2Ph (6), PCy_3 (7)).** Compounds **5**–**7** were obtained by an identical procedure which is reported below for complex **5**. To a solution of *trans*-$[(PMePh_2)_2Pt(CH_3)Cl)]$ (0.32 g, 0.50 mmol) in CH_2Cl_2 (25 mL) was added dropwise a 0.985 M acetone solution of $AgBF_4$ (0.51 mL, 0.50 mmol) at 0 °C. After the addition was complete, the reaction mixture was warmed to room temperature and stirred for 30 min. It was then filtered and treated dropwise at 0 °C with a solution of L^1 (0.14 g, 0.50 mmol) in CH_2Cl_2 (10 mL) and the reaction mixture stirred for 2 h. Concentration to small volume (ca. 5 mL) and treatment with Et_2O (40 mL) gave the final product as a pale cream solid: yield 0.40 g (82%). Anal. Calcd for $C_{38}H_{44}NP_3B_2F_8Pt{\cdot}0.5CH_2Cl_2$ (**5**): C, 45.20; H, 4.43; N, 1.37. Found: C, 45.40; H, 4.80; N, 1.51. Calcd for $C_{28}H_{40}NP_3B_2F_8Pt{\cdot}0.5CH_2Cl_2$ (**6**): C, 38.26; H, 4.62; N, 1.56. Found: C, 38.63; H, 4.70; N, 1.42. Calcd for $C_{48}H_{84}NP_3B_2F_8Pt{\cdot}CH_2Cl_2$ (**7**): C, 48.16; H, 7.09; N, 1.14. Found: C, 48.24; H, 7.70; N, 1.16.

***cis*-$[(Ph_2PCH{=}CHPPh_2)Pt(L^1)Cl]$ (8).** This compound was prepared with a procedure analogous to that described for complex **1** starting from *cis*-$(Ph_2PCH{=}CHPPh_2)PtCl_2$ (0.66 g, 1.00 mmol), 0.985 M $AgBF_4$ (1.01 mL, 1.00 mmol), and L^1 (0.28 g, 1.00 mmol): yield 0.97 g (98%). Anal. Calcd for $C_{37}H_{37}NP_3ClB_2F_8Pt{\cdot}CH_2Cl_2$: C, 42.35; H, 3.64; N, 1.30. Found: C, 42.94; H, 3.91; N, 1.20.

Cyclization Reactions of the Pt(II)-Coordinated Ligands L^1–L^4. *trans*-$\{(PPh_3)_2Pt[\overline{CN(H)\text{-}o\text{-}C_6H_4C}(PR_3)]Cl\}BF_4$ (PR_3 = PMe_3 (9), PMe_2Ph (10), $PMePh_2$ (11), PPh_3 (12)). The same

Table II. IR and ^1H NMR and $^{31}P\{^1H\}$ NMR Spectral Data for the 2-Platinum(II)-Substituted Indole Derivatives

	IR,[b] cm^{-1}		^1H NMR[c]				$^{31}P\{^1H\}$ NMR[c]				
compd[a]	ν(NH)	ν(PtCl)	δ(NH)	^3J(HPt)	^4J(HP)	$\delta(PCH_3)_{ligand}$	^2J(HP)	$\delta(P)_{ligand}$	^3J(PPt)	^4J(PP)	$\delta(P)_{metal}$	^1J(PPt)	^4J(PP)
9	3335 (w)	302 (w)	8.39 (d)	23.0	2.9	1.58 (d)	13.9	7.97 (t)	41.4	1.6	19.06 (d)	2698	1.6
10	3344 (w)	300 (w)	8.63 (d)	25.0	3.0	2.13 (d)	13.6	7.20 (t)	45.4	1.6	18.44 (d)	2700	1.6
11	3359 (w)	300 (w)	8.95 (br)	24.0	*f*	2.22 (d)	13.7	9.06 (t)	46.3	1.6	18.42	2705	1.6
12	3333 (w)	301 (w)	8.95 (d)	23.7	3.0			14.32 (t)	49.7	1.6	14.19 (d)	2793	1.6
13[d]	3361 (w)		9.37 (d)	16.0	2.6	1.59 (d)	13.7	7.35 (t)	19.5	1.8	7.35 (d)	2861	1.8
14[e]	3385 (w)		9.31 (br)	*f*	*f*	1.82 (d)	13.6	7.81 (t)	20.6	1.8	−7.88 (d)	2739	1.8
15	3389 (w)	297 (w)	8.75 (br)	20.0	*f*	1.78 (d)	14.1	9.61 (d)	33.0	3.6	55.35 (dd)[g]	2016	3.6
						1.75 (d)	14.1				44.37 (d)[g]	3709	
						1.70 (d)	13.9						

[a] See Scheme IV. [b] Nujol mull; m = medium. [c] Spectra recorded in CD_2Cl_2 at +25 °C; ^1H and ^{31}P chemical shifts were referenced to internal Me_4Si and external H_3PO_4 (85%), respectively; J in Hz; negative chemical shifts are upfield from the reference used; s = singlet; d = doublet; t = triplet; br = broad. [d] ^1H NMR: $\delta(PCH_3)_{metal}$ 1.78 (t, ^2J(HP) + ^4J(HP) = 6.5, ^3J(HPt) = 33.8), $\delta(CH_3)$ 0.08 (t, ^2J(HPt) = 52.0, ^3J(HP) = 6.7). [e] ^1H NMR: $\delta(PCH_3)_{metal}$ 1.73 (t, ^2J(HP) + ^4J(HP) = 7.5, ^3J(HPt) = 30.0), $\delta(CH_3)$ 0.20 (t, ^2J(HPt) = 53.0, ^3J(HP) = 6.9. [f] Coupling not resolved. [g] ^2J(PP) = 6.7.

procedure was followed for the preparation of complexes **9–12**, which is described for **9**. A solution of **1** (1.80 g, 1.60 mmol) in CH_2Cl_2 (50 mL) was treated with NEt_3 (2.0 mL, 1.45 g, 14.30 mmol) and the reaction mixture stirred at room temperature for 5 h. After this time, an IR spectrum of the solution in the range 2300–2000 cm^{-1} showed the absence of the ν(N≡C) absorption. The solution was taken to dryness and washed several times with H_2O (3 × 10 mL). The solid residue was taken up with CH_2Cl_2 (50 mL), dried over anhydrous Na_2SO_4, filtered off, and concentrated under reduced pressure to ca. 10 mL. On addition of Et_2O (30 mL), the product precipitated as a white solid: yield 1.28 g (78%); mp >280 °C. Anal. Calcd for $C_{47}H_{44}NClP_3BF_4Pt\cdot1.5CH_2Cl_2$ (**9**): C, 50.20; H, 4.08; N, 1.21. Found: C, 50.51; H, 4.35; N, 1.16. Calcd for $C_{53}H_{46}NClP_3BF_4Pt\cdot CH_2Cl_2$ (**10**): C, 54.40; H, 4.06; N, 1.17. Found: C, 54.01; H, 4.52; N, 1.46. Calcd for $C_{57}H_{48}NClP_3BF_4Pt\cdot CH_2Cl_2$ (**11**): C, 55.62; H, 4.83; N, 1.12. Found: C, 55.82; H, 4.33; N, 1.27. Calcd for $C_{62}H_{50}NClP_3BF_4Pt\cdot1.5CH_2Cl_2$ (**12**): C, 56.63; H, 3.96; N, 1.04. Found: C, 56.73; H, 4.31; N, 1.12.

***trans*-[(PR$_3$)$_2$Pt[$\overline{CN(H)\text{-}o\text{-}C_6H_4C(PMe_3)}$](CH$_3$)]BF$_4$ (PR$_3$ = PMePh$_2$ (13), PMe$_2$Ph (14)).** A typical preparation is reported for compound **13**. Complex **5** (0.15 g, 0.15 mmol) was dissolved in CH_2Cl_2 (10 mL) and treated with NEt_3 (0.21 mL, 1.50 mmol). The reaction mixture was stirred at room temperature until no ν(N≡C) absorption was present in the IR spectrum (ca. 2 days). It was then concentrated to ca. 3 mL and Et_2O (3 × 10 mL) added. The cream solid obtained was filtered off and dried under vacuum: yield 0.09 g (68%); mp 241–245 °C dec. Anal. Calcd for $C_{38}H_{43}NP_3BF_4Pt\cdot0.5CH_2Cl_2$ (**13**): C, 49.66; H, 4.76; N, 1.50. Found: C, 49.46; H, 5.10; N, 1.55. Calcd for $C_{28}H_{39}NP_3BF_4Pt\cdot2CH_2Cl_2$ (**14**): C, 40.18; H, 4.52; N, 1.46. Found: C, 39.88; H, 4.74; N, 1.49. The analogous reaction with the PCy_3 derivative **7** did not give the corresponding cyclization product but instead the *o*-tolyl isocyanide derivative *trans*-[$(PCy_3)_2Pt(CH_3)(CNC_6H_4\text{-}o\text{-}CH_3)$]$BF_4$, which was isolated after the CH_2Cl_2–NEt_3 reaction mixture was stirred at room temperature for 7 days by precipitation with Et_2O (30 mL). Anal. Calcd for $C_{45}H_{77}NP_2BF_4Pt$: C, 55.43; H, 7.86; N, 1.44. Found: C, 55.10; H, 8.12; N, 1.13. After filtration of the metal derivative, the solution was taken to dryness. A ^{31}P NMR spectrum of the residue revealed the presence of a sharp singlet at δ 37.08 (CD_2Cl_2) corresponding to Me_3PO, as confirmed with an authentic sample.

***cis*-[(Ph$_2$PCH=CHPPh$_2$)Pt[$\overline{CN(H)\text{-}o\text{-}C_6H_4C(PMe_3)}$]Cl]BF$_4$ (15).** To a solution of **8** (0.33 g, 0.33 mmol) in CH_2Cl_2 (20 mL) was added NEt_3 (0.46 mL, 3.30 mmol), and the mixture was stirred at room temperature for 1 h. The solution was concentrated to 5 mL under reduced pressure and Et_2O (30 mL) added. The pale yellow solid formed was filtered off, washed with H_2O (3 × 10 mL) and Et_2O (3 × 10 mL), and recrystallized from CH_2Cl_2–Et_2O: yield 0.27 g (82%); mp 173–175 °C. Anal. Calcd for $C_{37}H_{36}NClP_3BF_4Pt\cdot CH_2Cl_2$: C, 46.10; H, 3.87; N, 1.42. Found: C, 46.54; H, 4.29; N, 1.75.

Cyclization Reaction of Free L^4. Synthesis of $\overline{N(o\text{-}C_6H_4)C(PPh_3)C(H)}$ (L^5). A suspension of L^4 (0.46 g, 1.00 mmol) in THF (25 mL) was reacted with a 5-fold excess of $NaNH_2$ at room temperature for 2 h. The dark orange reaction mixture was taken to dryness and Et_2O (40 mL) added and filtered off. The yellow solution was taken to dryness to give a yellow solid which did not show any presence of the starting ν(NC) aborption in the IR spectrum: yield 0.27 g (71%); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ(P) 10.93 (s); the mass spectrum showed M$^+$ at *m/e* 377. Anal. Calcd for $C_{26}H_{20}NP$: C, 82.77; H, 5.34; N, 3.71. Found: C, 82.32; H, 5.47; N, 3.27.

Pt(II) Complexes of L^5. *cis*-[(PPh$_3$)$_2$Pt[$\overline{N(o\text{-}C_6H_4)C(PPh_3)C(H)}$]Cl]BF$_4$. To a solution of *cis*-$[(PPh_3)_2PtCl]_2(BF_4)_2$ (0.15 g, 0.09 mmol), prepared as described above for **1**, in CH_2Cl_2 (10 mL) was quickly added dropwise a solution of L^5 (0.07 g, 0.18 mmol) in CH_2Cl_2 (5 mL) at room temperature. The reaction mixture was stirred for an additional 1.5 h and then concentrated to a small volume and Et_2O (30 mL) added. The white solid formed was filtered off and dried under vacuum: yield 0.19 g (85%); IR (Nujol) ν(PtCl) 307 (w); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) $\delta(P_{metal})_{trans\ to\ Cl}$ 15.82 (d, ^2J(PP) = 18.0, ^1J(PPt) = 3765), δ-

Table III. Crystal Data and Intensity Collection Parameters for *trans*-{$(PPh_3)_2Pt[\overline{CN(H)\text{-}o\text{-}C_6H_4C(PMe_3)}]Cl$}$BF_4 \cdot C_2H_4Cl_2$ (9)

formula	$C_{49}H_{48}BCl_3F_4NP_3Pt$
M_r	1132.11
cryst system	monoclinic
space group	$P2_1/m$
a, Å	10.434 (1)
b, Å	23.465 (2)
c, Å	11.725 (1)
β, deg	112.88 (2)
U, Å^3	2644.9
Z	2
D(calcd), g cm^{-3}	1.42
μ(Mo Kα), cm^{-1}	29.7
min transmissn factor	0.708
cryst dimens, mm	0.25 × 0.5 × 0.25
scan mode	$\omega/2\theta$
θ range, deg	2.5–25
octants of rec space explored	$\pm h,k,l$
measd refltns	5010
obsd unique refltns with $I > 2.5\sigma(I)$	3964
final R and R_w indices	0.040, 0.045
ω scan width, deg	0.8 + 0.35 tan θ
prescan speed, deg min^{-1}	10
prescan acceptance $\sigma(I)/I$	0.5
max scan time, s	120
requested $\sigma(I)/I$	0.01
parameters refined	310

(P_{metal})$_{cis\ to\ Cl}$ 5.72 (d, ^2J(PP) = 18.0, ^1J(PPt) = 3062), δ(P_{ligand}) 11.63 (s, ^4J(PPt) 11.7), δ(P_{ligand}) 11.54 (s, ^4J(PPt) = 10.8). Anal. Calcd for $C_{62}H_{50}NClP_3BF_4Pt \cdot 1.5CH_2Cl_2$: C, 56.63; H, 3.96; N, 1.04. Found: C, 56.95; H, 4.00; N, 0.84.

***trans*-$(PPh_3)Pt[\overline{N(o\text{-}C_6H_4)C(PPh_3)}C(H)]Cl_2$.** This compound was prepared by an analogous procedure to that described above starting from L[5] (0.08 g, 0.21 mmol) and *cis*-$[(PPh_3)PtCl_2]_2$[21] (0.11 g, 0.21 mmol) in CH_2Cl_2: yield 0.12 g (66%); IR (Nujol) ν(PtCl) 340 (w); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ(P_{metal}) 3.76 (s, ^1J(PPt) = 3421), δ(P_{ligand}) 11.73 (s, ^4J(PPt) = 11.1. Anal. Calcd for $C_{44}H_{35}NCl_2P_2Pt \cdot 1.5CH_2Cl_2$: C, 54.58; H, 3.76; N, 1.41. Found: C, 54.24; H, 3.51; N, 1.41.

X-ray Structural Determination. Crystal data for **9** are summarized in Table III together with some experimental details. Crystals suitable for X-ray analysis were obtained by slow diffusion of Et_2O into a solution of complex **9** in 1,2-dichloroethane kept at room temperature. Diffraction intensities were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation (λ = 0.71069 Å), reduced to F_o values and corrected for crystal decay. An empirical absorption correction was applied by measuring scans at intervals of 10° around the diffraction vectors of eight selected reflections near χ = 90° (transmission range = 71–100%). The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least squares, the minimized function being $\sum w(|F_o| - |F_c|)^2$. The weighting scheme employed was $w = k/[\sigma^2(F_o) + |g|F^2]$, where k and g were refined (0.3 and 0.07, respectively). The SHELX76 package of crystallographic programs[22] was used for all computations with the analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, taken from ref 22b. Thermal vibrations were treated anisotropically for all non-hydrogen atoms of the cation. H atoms were added in a calculated position (C–H = 1.08 Å) and not refined, although their contribution to the structure factors were taken into account. Both the BF_4^- anion and the $C_2H_4Cl_2$ solvent molecules were 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 two positions for the Cl atoms were detected and partial occupancies could be refined (0.6 for the main image). A final difference Fourier map showed residual peaks lower than 1.5 e Å^{-3} in the vicinity of the Pt atom. The atomic coordinates are

Table IV. Fractional Atomic Coordinates and Thermal Parameters of *trans*-{$(PPh_3)_2Pt[\overline{CN(H)\text{-}o\text{-}C_6H_4C(PMe_3)}]Cl$}$BF_4 \cdot C_2H_4Cl_2$ (9)

atom	x	y	z	U_{iso} or U_{eq}
Pt	0.05816 (2)	0.25	0.07026 (2)	0.0340 (2)
Cl	−0.18558 (19)	0.25	−0.04394 (21)	0.0530 (10)
P(1)	0.42965 (20)	0.25	0.04764 (19)	0.0483 (10)
P(2)	0.04914 (11)	0.34914 (6)	0.06254 (10)	0.0380 (7)
N	0.2819 (7)	0.25	0.3106 (6)	0.049 (3)
C(1)	0.2572 (7)	0.25	0.1847 (6)	0.038 (2)
C(2)	0.3892 (7)	0.25	0.1773 (6)	0.040 (2)
C(3)	0.4934 (7)	0.25	0.3031 (7)	0.048 (3)
C(4)	0.6393 (8)	0.25	0.3522 (9)	0.058 (3)
C(5)	0.7079 (10)	0.25	0.4805 (9)	0.067 (3)
C(6)	0.6355 (10)	0.25	0.5587 (8)	0.064 (3)
C(7)	0.4947 (10)	0.25	0.5115 (8)	0.060 (3)
C(8)	0.4232 (7)	0.25	0.3814 (7)	0.040 (3)
C(9)	0.2811 (11)	0.25	−0.0913 (8)	0.091 (3)
C(10)	0.5323 (8)	0.3114 (3)	0.0466 (7)	0.077 (3)
C(11)	−0.0169 (5)	0.3813 (2)	0.1694 (5)	0.048 (2)
C(12)	0.0029 (7)	0.4390 (2)	0.1955 (6)	0.065 (2)
C(13)	−0.0494 (9)	0.4646 (3)	0.2752 (7)	0.083 (3)
C(14)	−0.1203 (8)	0.4321 (3)	0.3315 (7)	0.080 (3)
C(15)	−0.1348 (7)	0.3752 (3)	0.3077 (6)	0.080 (3)
C(16)	−0.0843 (7)	0.3493 (3)	0.2282 (6)	0.063 (2)
C(17)	0.2118 (5)	0.3883 (2)	0.0978 (5)	0.046 (2)
C(18)	0.2297 (6)	0.4260 (2)	0.0120 (6)	0.057 (2)
C(19)	0.3531 (7)	0.4575 (3)	0.0475 (7)	0.076 (3)
C(20)	0.4537 (8)	0.4521 (3)	0.1593 (8)	0.080 (3)
C(21)	0.4402 (6)	0.4146 (3)	0.2456 (6)	0.061 (2)
C(22)	0.3171 (6)	0.3822 (2)	0.2144 (5)	0.054 (2)
C(23)	−0.0616 (5)	0.3738 (2)	−0.0894 (4)	0.045 (2)
C(24)	−0.0438 (7)	0.3523 (3)	−0.1908 (5)	0.064 (2)
C(25)	−0.1251 (8)	0.3697 (3)	−0.3125 (6)	0.067 (3)
C(26)	−0.2215 (8)	0.4103 (3)	−0.3274 (6)	0.071 (3)
C(27)	−0.2458 (9)	0.4325 (4)	−0.2289 (7)	0.085 (3)
C(28)	−0.1644 (7)	0.4164 (3)	−0.1090 (7)	0.072 (3)
B	0.1158 (10)	0.25	0.5564 (9)	0.066 (2)
F(1)	0.2618 (11)	0.25	0.6228 (12)	0.174 (2)
F(2)	0.0630 (9)	0.2029 (4)	0.5903 (8)	0.174 (2)
F(3)	0.0970 (14)	0.25	0.4329 (9)	0.174 (2)
Cl(1)	0.3837 (5)	0.0421 (2)	0.5226 (5)	0.107 (1)
Cl(2)	0.3085 (5)	0.0887 (2)	0.7578 (4)	0.107 (1)
Cl(3)	0.3381 (7)	0.0340 (3)	0.5213 (7)	0.107 (1)
Cl(4)	0.3877 (8)	0.0963 (3)	0.7888 (6)	0.107 (1)
C(48)	0.2804 (14)	0.1002 (4)	0.5253 (12)	0.167 (3)
C(49)	0.3566 (15)	0.1271 (6)	0.6531 (9)	0.167 (3)

Table V. Relevant Bond Distances (Å) and Angles (deg) of *trans*-{$(PPh_3)_2Pt[\overline{CN(H)\text{-}o\text{-}C_6H_4C(PMe_3)}]Cl$}$BF_4 \cdot C_2H_4Cl_2$ (9)

Bond Distances

Pt–Cl	2.369 (2)	C(5)–C(6)	1.40 (1)
Pt–P(2)	2.329 (1)	C(6)–C(7)	1.35 (1)
Pt–C(1)	1.987 (6)	C(7)–C(8)	1.41 (1)
P(2)–C(11)	1.81 (1)	C(8)–N	1.38 (1)
P(2)–C(17)	1.83 (1)	N–C(1)	1.40 (1)
P(2)–C(23)	1.80 (1)	C(3)–C(8)	1.38 (1)
C(1)–C(2)	1.41 (1)	P(1)–C(2)	1.73 (1)
C(2)–C(3)	1.45 (1)	P(1)–C(9)	1.76 (1)
C(3)–C(4)	1.40 (1)	P(1)–C(10)	1.80 (1)
C(4)–C(5)	1.39 (1)		

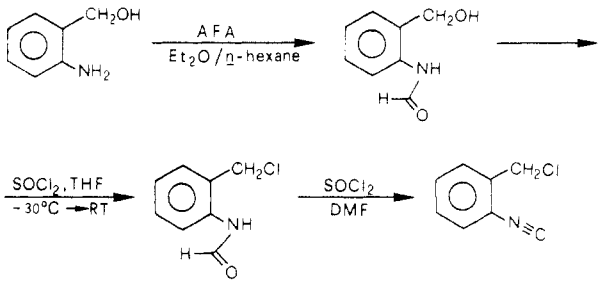
Bond Angles

C(1)–Pt–Cl	172.9 (2)	P(1)–C(2)–C(3)	123.5 (6)
C(1)–Pt–P(2)	92.4 (1)	C(2)–C(3)–C(4)	132.9 (9)
Cl–Pt–P(2)	87.7 (1)	C(2)–C(3)–C(8)	107.2 (7)
Pt–P(2)–C(11)	114.2 (2)	C(3)–C(4)–C(5)	117.6 (9)
Pt–P(2)–C(17)	118.2 (2)	C(4)–C(5)–C(6)	121.8 (9)
Pt–P(2)–C(23)	111.1 (2)	C(5)–C(6)–C(7)	120.6 (8)
C(2)–P(1)–C(9)	112.7 (5)	C(6)–C(7)–C(8)	118.4 (9)
C(2)–P(1)–C(10)	110.8 (3)	C(7)–C(8)–C(3)	121.6 (8)
Pt–C(1)–N	115.4 (6)	C(7)–C(8)–N	129.8 (9)
Pt–C(1)–C(2)	138.3 (6)	C(8)–N–C(1)	110.5 (7)
C(1)–C(2)–P(1)	129.1 (5)	P(2)–Pt–P(2′)	175.0 (2)

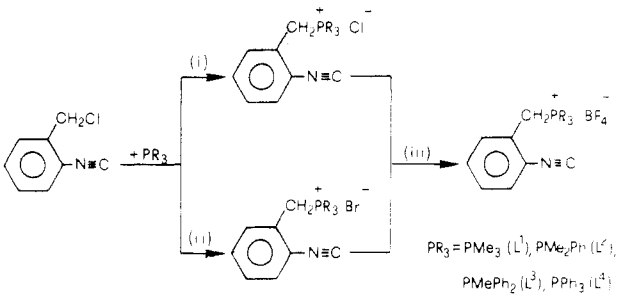
(21) Smithies, A. C.; Schmidt, P.; Orchin, M. *Inorg. Synth.* **1970**, *12*, 240.

(22) (a) SHELX76, by Sheldrick, G. M., University of Cambridge, 1976. (b) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, pp 99, 149.

Scheme I



Scheme II



(i) CH_2Cl_2, RT; + PR_3 = PMe_3, PMe_2Ph. (ii) Acetone, RT; + PR_3 = $PMePh_2$, PPh_3; + LiBr(exc). (iii) Acetone, RT; + $NaBF_4$ (exc), -NaX (X = Cl, Br).

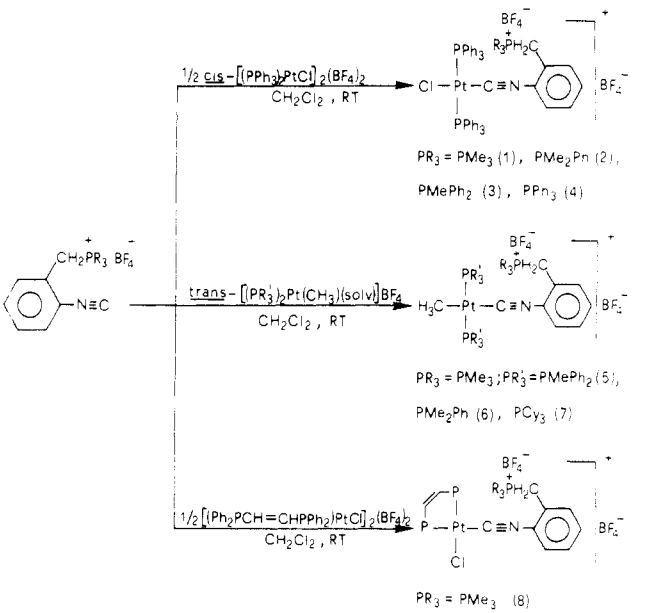
reported in Table IV and relevant bond distances and angles in Table V.

Results and Discussion

Synthesis of the Ligands. Scheme I reports an alternative synthesis from that previously reported[8] for the *o*-(chloromethyl)phenyl isocyanide ligand which is subsequently used in the preparation of the phosphonium-substituted isocyanides. The first stage involves conversion of the amino group of the *o*-aminobenzyl alcohol to the corresponding formamide with acetic formic anhydride.[15] Subsequent reaction with $SOCl_2$ in THF at −30 °C converts the *o*-CH_2OH group of the formamide into the corresponding *o*-CH_2Cl moiety.[23] The resulting (*o*-(chloromethyl)phenyl)formamide is then dehydrated with $SOCl_2$/DMF[24] to give the isocyanide *o*-$(ClCH_2)C_6H_4NC$ with an overall yield of ca. 30%.

The phosphonium-substituted isocyanides *o*-$(X^-R_3P^+-CH_2)C_6H_4NC$ (X = Cl, Br; PR_3 = PMe_3, PMe_2Ph, $PMePh_2$, PPh_3) are obtained in nearly quantitative yield by reacting the chloromethyl function of the isocyanide with a ca. 30% molar excess of the tertiary monophosphines PR_3, as shown in Scheme II. The phosphines PMe_3 and PMe_2Ph are nucleophilic enough to react directly with *o*-$(ClCH_2)C_6H_4NC$ in CH_2Cl_2 at room temperature (route i) to give the corresponding phosphonium chloride salts, while the phosphines $PMePh_2$ and PPh_3 give better yields of the phosphonium products when they are reacted with *o*-(chloromethyl)phenyl isocyanide in acetone at room temperature in the presence of 3–5-fold excess of LiBr (route ii). In this latter case the phosphonium products are isolated as their bromide salts, suggesting that the more reactive bromo intermediate *o*-$(BrCH_2)C_6H_4NC$ is likely to be involved during the reaction. The analogous reaction of *o*-$(ClCH_2)C_6H_4NC$ with excess of NaI in acetone has been shown[8] to produce the corresponding iodo derivative *o*-$(ICH_2)C_6H_4NC$. However, chloride–bromide exchange between the phosphonium and lithium salts is a possible alternative. Finally, the phosphonium halide salts are more conveniently converted (route iii) into the less hygroscopic tetrafluoroborate salts L^1–L^4 by reaction with excess $NaBF_4$ in acetone with a maximum yield of 80%.

Scheme III



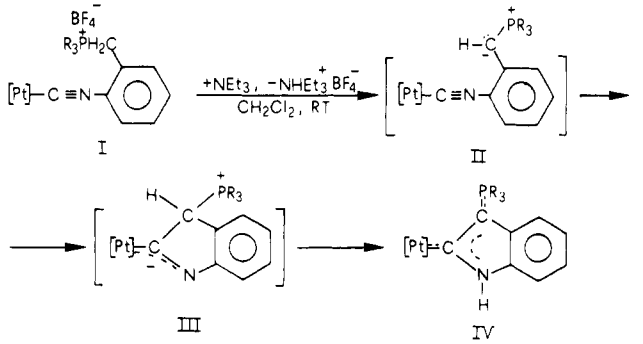
Ligands L^1–L^4 are crystalline, pale cream, odorless solids which are stable in the solid state and in solution. No decomposition is observed upon exposure to light over a period of months. They are very soluble in chlorinated as well as alcoholic solvents, but only slightly soluble in acetone, and insoluble in diethyl ether. All the ligands gave satisfactory elemental analyses. Diagnostic spectral features (Table I) are the ν(N≡C) stretching frequency (2120–2122 cm^{-1} (CH_2Cl_2)), the methylene resonance of the R_3P^+–CH_2– moiety which shows up in the ^1H NMR spectra as a doublet in the range δ 3.85–4.96 (^2J(HP) = 14.3–16.1 Hz), and the ^{31}P signal of the phosphonium group which is observed in the range δ 22.42–30.18 as a sharp singlet (a normal range for the resonances of these groups).[10]

Platinum(II) Complexes of L^1–L^4. The coordinating ability of the isocyanide ligands L^1–L^4 has been tested in a series of reactions with some cationic Pt(II) species which have been appropriately chosen in order to investigate more deeply the subsequent reaction chemistry of these metal–ligand systems as related also to the electronic and steric effects of the metal substituents. These reactions are outlined in Scheme III. Complexes 1–8 are easily obtained in 60–80% yield from the precursors *cis*-P_2PtCl_2 (P = PPh_3, $^1/_2$ *cis*-$Ph_2PCH{=}CHPPh_2$) and *trans*-$P_2Pt(CH_3)Cl$ (P = $PMePh_2$, PMe_2Ph, PCy_3) by initial halide abstraction with equivalent amounts of $AgBF_4$ in CH_2Cl_2 and subsequent treatment of the resultant cationic intermediates with stoichiometric amounts of the required phosphonium isocyanide ligand. Their structures have been assigned on the basis of IR and ^1H and $^{31}P\{^1H\}$ NMR data (Table I).

Complexes 1–4 display the ν(NC) absorption in the range 2186–2191 cm^{-1} in CH_2Cl_2 with a maximum shift to lower frequency of 17 cm^{-1} with respect to the parent *o*-(chloromethyl)phenyl isocyanide derivative *trans*-$[(PPh_3)_2Pt(CNC_6H_4$-*o*-$CH_2Cl)Cl]BF_4$[25] (ν(NC) 2203 cm^{-1} (CH_2Cl_2)),

(23) March, J. *Advanced Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1977; pp 392–394.
(24) Wolborsky, H. M.; Niznik, G. E. *J. Org. Chem.* **1972**, *37*, 187.

Scheme IV



[Pt] = trans-[(PPh$_3$)$_2$PtCl]BF$_4$, PR$_3$ = PMe$_3$ (9), PMe$_2$Ph (10), PMePh$_2$ (11), PPh$_3$ (12)

[Pt] = trans-[(PMePh$_2$)$_2$Pt(CH$_3$)]BF$_4$, PR$_3$ = PMe$_3$ (13)

[Pt] = trans-[(PMe$_2$Ph)$_2$Pt(CH$_3$)]BF$_4$, PR$_3$ = PMe$_3$ (14)

[Pt] = cis-[(Ph$_2$CH=CHPPh$_2$)PtCl]BF$_4$, PR$_3$ = PMe$_3$ (15)

indicating that the observed decrease in the stretching frequency is essentially due to the bulkier *o*-$CH_2PR_3^+$ group, which somewhat sterically hinders the coordination of the isocyanide. Release of some steric strain as in compound **8** where the PPh_3 ligand is replaced by a smaller Cl ligand shifts the ν(N≡C) to higher frequency (2209 cm^{-1}).

It is known[26] that ν(N≡C) for metal-coordinated isocyanides is sensitive to the nature of the trans ligand X and decreases with increasing electron donation by X. Such electronic trans influence is clearly observed in complexes **5–7** where a strong σ-donor group such as CH_3 is trans to the isocyanide. Thus, the ν(N≡C) frequency in complexes **5** and **6** decreases by ca. 30–35 cm^{-1} with respect to the chloro derivatives **1–4**. Such a frequency decrease is even more marked in compound **7** where the combined contribution of steric effects due to the presence of the two highly sterically demanding metal-coordinated PCy_3 phosphines and the electronic effect due to the trans CH_3 group causes the ν(N≡C) to drop by ca. 60 cm^{-1} (i.e., 2129 cm^{-1}), approaching the value of the free isocyanide L^1 (2122 cm^{-1}).

In the ^{1}H NMR spectra (Table I) the methylene signal of the $-CH_2PR_3^+$ group is a doublet by coupling with the adjacent phosphorus atom and is shifted in compounds **1–6** to higher fields with respect to the free ligands L^1–L^4. This shielding effect probably arises by the presence of the aryl substituents on the metal-coordinated phosphines which are mutally trans and cis to the ligand in **1–6**. Such effect, which has been noticed for other Pt(II) species,[27] is not present in compounds **7** and **8**.

Cyclization Reactions. 2-Pt(II)-Substituted Indole Derivatives. As we have already communicated for complex **2**,[14] all the trans complexes (except **7**) and the cis complex **8** of Scheme III are found to react with a 10-fold excess of a mild base such as NEt_3 in CH_2Cl_2 at room temperature to afford in good yield (ca. 70%) the C-2 metal-bonded indole derivatives **9–15** according to the mechanism proposed in Scheme IV. In the first step, NEt_3 attacks the activated methylene group of the $-CH_2PR_3^+$ phosphonium moiety of I, producing the highly reactive ylide–isocyanide–metal intermediate II, which shows the ylide function in the 1,2-zwitterionic structure. Subsequently, the nucleophilic ylidic carbanion of II intramolecularly adds to the adjacent coordinated isocyanide giving the intermediate 3-hydro-3-phosphonio-3*H*-indole (III) which eventually converts to the final stable indole derivative IV by proton shift. The intermediates II and III could not be isolated or identified, probably owing to their enhanced reactivity toward the highly reactive isocyanide, but we expect that a forthcoming kinetic study will reveal their role in the overall process.[28] However, it is likely that the conversion from III to IV takes place either intramolecularly or by the assistance of the NEt_3–$NHEt_3^+$ system acting as a proton-transfer agent. A similar mechanism of proton transfer was observed for the analogous step in the formation of aminocarbene complexes by nucleophilic attack of amines on Pd(II)-coordinated isocyanides.[29]

Carbanion attack on the isocyano function has also been described for the synthesis of indole derivatives by Cu_2O-catalyzed cyclization[5-7] or selective ortho-lithiation of *o*-alkylphenyl isocyanides[30] and subsequent intramolecular ring closure.

The "ylide–carbene" compounds **9–15** are quite stable in the solid state and in solution. They are fairly soluble in CH_2Cl_2 and insoluble in Et_2O. Their structures have been fully established by IR and ^{1}H and ^{31}P{^{1}H} NMR spectroscopy (Table II) and by a single-crystal X-ray structure determination carried out for **9** (see below). All these complexes generally include various amounts of crystallization CH_2Cl_2, as shown by elemental analysis data and confirmed by ^{1}H NMR spectra.

Their spectral features are as follows. The ^{31}P NMR resonance of the ylidic phosphorus of the "carbene" unit shows different multiplicities depending on the stereochemistry around the platinum fragment. Thus, in the *trans* complexes **9–14**, it appears as a triplet flanked by ^{195}Pt satellites ($I = {}^1/_2$, 34% abundance) owing to coupling with the two magnetically equivalent metal-coordinated phosphines (^4J(PP) = 1.6–1.8 Hz), which, in turn, show up as a doublet with ^{195}Pt satellites. On the other hand, in the case of the cis compound **15**, the ^{31}P-ylide signal appears as a doublet (with ^{195}Pt satellites) arising from coupling with only the phosphorus atom of the chelated diphosphine trans to the carbene carbon (^4J(PP) = 3.6 Hz). In this derivative the central signal of the phosphorus nucleus trans to the carbenoid ligand is observed as a doublet of doublets by coupling with the phosphonium ylide atom and with the cis phosphorus atom (^2J(PP) = 6.7 Hz), which displays the expected doublet.

The magnitude of the $^3J(^{31}P(ylide)–^{195}Pt)$ coupling constant is markedly sensitive to the nature of the ligand trans to the carbene carbon. Thus, the ^3J(PPt) coupling for **9–12** with chloride as the trans ligand is in the range 41.4–49.7 Hz. These values are lowered to 33 Hz in **15** with a trans P donor, dropping finally to ca. 20 Hz in **13** and **14** which have the strong σ-carbon donor CH_3 group. The order of increasing ^3J(PPt) coupling with changes in the trans ligand is then $CH_3 < P < Cl$, which reflects the expected relative trans influence of these groups, i.e., $CH_3 > P > Cl$.[26]

(25) This compound was prepared as described for compounds **1–4** (see Experimental Section): IR ν(NC) 2203 (s) cm^{-1} (CH_2Cl_2), ν(PtCl) 341 (w) cm^{-1} (Nujol); ^{1}H NMR (CD_2Cl_2) $\delta(CH_2)$ 3.58 (s); ^{31}P{^{1}H} NMR (CD_2Cl_2) δ(P) 18.84 (s, ^1J(PPt) = 2168 Hz).

(26) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

(27) Strukul, G.; Michelin, R. A.; Orbell, J. D.; Randaccio, L. *Inorg. Chem.* **1983**, *22*, 3706.

(28) Michelin, R. A., et al., work in progress.

(29) Belluco, U.; Michelin, R. A.; Uguagliati, P.; Crociani, B. *J. Organomet. Chem.* **1983**, *250*, 565.

(30) Ito, Y.; Kobayashi, K.; Saegusa, T. *J. Am. Chem. Soc.* **1977**, *99*, 3532.

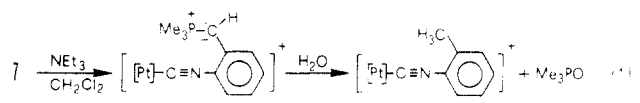
The ^{31}P chemical shifts of the ylidic phosphorus in **9–15** fall in the range 7.20–14.32 ppm with an upfield shift of 8–23 ppm with respect to the free and Pt(II)-coordinated phosphonium precursors, analogously to what was observed for other P-ylide systems.[10]

In the ^1H NMR spectra of complexes **9–13** the N–H signal is observed as a doublet (δ 8.3–9.3) flanked by ^{195}Pt satellites owing to coupling with the ylide phosphorus atom ($^4J(PP)$ = 2.6–3.0 Hz) rather than with the metal-coordinated phosphines which eventually would give rise to a triplet in the trans complexes **9–14**. The magnitude of the $^3J(HPt)$ coupling constant (16–25 Hz) is consistent with a cis Pt–C(carbene)–N–H arrangement.[31]

All of the complexes **9–15** display the ν(NH) and ν(PtCl) stretchings in the IR as weak absorptions (Nujol) at 3389–3333 cm^{-1} and 297–302 cm^{-1}, respectively.

Qualitative observations of the reaction times for the cyclization reactions depicted in Scheme IV, based on monitoring the $\nu(N{\equiv}C)$ disappearance in the IR of the precursors **1–8**, lead to the following order of reactivity **8** > **1–4** > **5–7** (Table I). This order parallels also the values of the corresponding $\Delta\nu = \nu(N{\equiv}C)_{coord} - \nu(N{\equiv}C)_{free}$ shifts,[32] which reflect the electrophilic character[33] of the isocyanide carbon and therefore its ability to react with nucleophiles to form carbene complexes.[29] Within the homologous series of compounds **1–4** (Table I and Scheme III), the order of reactivity is **4** > **3** > **2** > **1**. Such order cannot be explained in terms of $\Delta\nu$ shifts which are almost the same for the four complexes but rather as a result of a faster formation of the carbanion intermediate II (Scheme IV) when R = Ph. The greater acidity of the methylene protons in the triphenylphosphonium derivative **4** is also reflected in their lowest field proton resonance (Table I).[10]

Compound **7**, which shows the lowest $\Delta\nu$ (7 cm^{-1}), does not form the final "ylide–carbene" complex of type **IV** (Scheme IV) but instead the *o*-tolyl isocyanide derivative *trans*-$[(PCy_3)_2Pt(CNC_6H_4\text{-}o\text{-}CH_3)Cl]BF_4$ and the phosphine oxide Me_3PO (see Experimental Section). The ylide intermediate (eq 1) preferentially undergoes hydrolysis by



traces of H_2O present in the solvent instead of interacting with the unactivated isocyano ligand in the sterically hindered environment due to the presence of the two mutually trans bulky tricyclohexylphosphines.

Description of the Structure of 9. The crystal contains *trans*-$\{(PPh_3)_2Pt[\overline{CN(H)\text{-}o\text{-}C_6H_4C(PMe_3)}]Cl\}^+$ cations and BF_4^- anions, together with partially disordered $C_2H_4Cl_2$ molecules. Both cation and anion possess crystallographic C_s—*m* symmetry, with the carbenoid ligand, the Pt atom, and the Cl atom of the cation lying on the mirror plane, which also relates the two trans PPh_3 ligands and one Me group of the PMe_3 ligand. In such a way only half of the molecular structure is crystallographically independent (hereafter a prime label will refer to symmetry-related atoms). In the anion case the mirror plane contains two F atoms and the B atom, while the two remaining F atoms are related by the mirror plane. The solvent molecule lies in general position, a discussion of the observed disorder is reported in the Experimental Section.

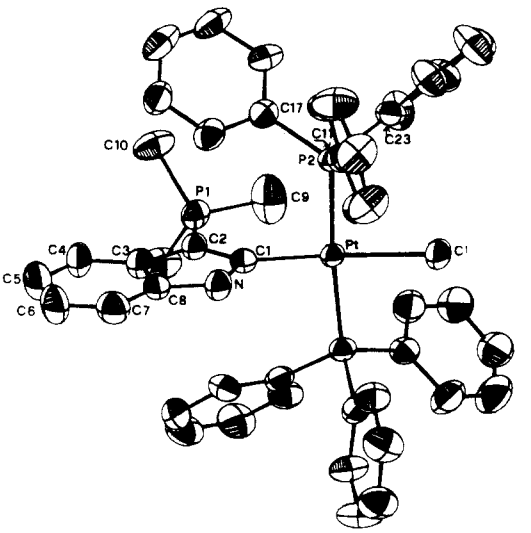


Figure 1. ORTEP drawing of the molecule *trans*-$\{(PPh_3)_2Pt[\overline{CN(H)\text{-}o\text{-}C_6H_4C(PMe_3)}]Cl\}BF_4\cdot C_2H_4Cl_2$ (**9**) showing the atom labeling (unlabeled atoms are referred by the mirror plane).

The coordination geometry about the Pt(II) center is almost square-planar with maximum deviation from the C(1)–P(2)–Pt–P(2′)–Cl plane of 0.09 Å. However, the angular values for the cis ligands, C(1)–Pt–P(2) = 92.4 (1)° and Cl–Pt–P(2) = 87.7 (1)°, indicate that a slight distortion of the Pt atom stereogeometry takes place. This effect is determined by the steric interaction between the carbenoid system and the bulky PPh_3 ligands, which are "pushed" toward the Cl atom with consequent deviation from linearity of the P(2)–Pt–P(2′) angle (175.0 (2)°). This deformation is accompanied by an out of plane bending of the C(1)–Pt–Cl angle (172.9 (2)°).

Although the Pt–P bond lengths depend on the nature of both the phosphine ligands and the other ligands in the inner platinum coordination sphere, the observed value of 2.329 (1) Å is in good agreement with those reported for other square-planar Pt(II) complexes such as *trans*-$\{(PMe_2Ph)_2Pt[C(NMe_2)CH_2CH_2OH]Cl\}^+$ (2.312 (3) Å)[34] or $[(PPh_3)\overline{PtCH_2N(Me)_2CH_2N(Me)_2}(Cl)]^+$ (2.223 (2) Å).[35]

The Pt–Cl bond length of 2.369 (2) Å is of comparable magnitude to those found in some neutral and cationic Pt(II)–carbene complexes such as *cis*-$Cl_2(Et_3P)PtC(NPhCH_2)_2$ (Pt–Cl(trans to carbene) = 2.362 (3) Å),[36] *cis*-$Cl_2(Et_3P)PtC(OEt)NHPh$ (Pt–Cl(trans to carbene) = 2.361 (5) Å),[36] and *trans*-$[Cl(Me_2PhP)_2PtC(NMe_2)CH_2CH_2OH]PF_6$ (Pt–Cl = 2.356 (4) Å)[34] but is shorter than that found in *trans*-$(PPh_3)_2Pt(Me)Cl$ (Pt–Cl = 2.431 (3) Å)[37] where the stronger σ-donor methyl group is trans to chloride. As pointed out by Muir and Muir,[36] the multiple-bond character of the Pt–C interaction and the trans Pt–Cl bond length are highly related. In our case, the value of the Pt–Cl distance confirms the good σ-donor but poor π-acceptor properties of carbenes[38] when compared with more efficient π-ligands such as isocyanides or carbon monoxide where the shorter Pt–Cl bond lengths are always observed.[36] On the other hand, the value of 1.99 (1) Å for

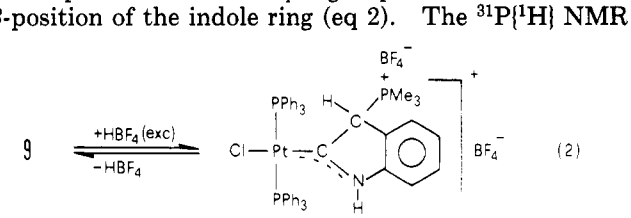
(31) Crociani, B.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1974**, *693*.
(32) Badley, E. M.; Chatt, J.; Richards, R. L. *J. Chem. Soc. A* **1971**, *21*.
(33) Crociani, B.; Boschi, T.; Belluco, U. *Inorg. Chem.* **1970**, *9*, 2021.
(34) Stepaniak, R. F.; Payne, N. C. *Can. J. Chem.* **1978**, *56*, 1602.
(35) Barefield, E. K.; Carrier, A. M.; Sepelak, D. J.; Van Derveer, D. G. *Organometallics* **1982**, *1*, 103.
(36) Manojlović-Muir, L. J.; Muir, K. W. *Inorg. Chim. Acta* **1974**, *10*, 47.
(37) Bardi, R.; Piazzesi, A. M. *Inorg. Chim. Acta* **1981**, *47*, 249.
(38) Schubert, U. *Coord. Chem. Rev.* **1984**, *55*, 261.

the Pt–C distance indicates a strong σ-interaction and a weak trans influence of Cl. This value can be compared with other Pt–C(carbene) bond lengths for square-planar Pt(II) systems which generally occur in the range 1.82–2.01 Å when chloride is *trans* to the carbene ligand.[39]

The main outcome of the structural analysis is the geometry of the PMe_3-substituted indole moiety which constitutes the carbenoid ligand. The indole plane is strictly perpendicular to the Pt(II) coordination square. Bond lengths within the condensed system indicate extensive electronic delocalization (C–C values range from 1.38 (1) to 1.45 (1) Å, average 1.40 (2) Å; C–N, average 1.38 (1) Å). The C—N values are, in fact, longer than those expected for a C=N double bond in Pt(II)-bonded aminocarbene systems (C–N = 1.27–1.33 Å)[39] and are well in agreement with those observed for other indole or indole-like systems (1.37 (1) Å in $\{(PEt_3)_2Pt[C(Cl\cdot C_6H_3NH)(NHMe)]Cl_2\}^+$;[40] 1.38 (1) Å in $Rh_2(O_2CC_2H_5)_4$(7-azaindole)$_2$[41]). Also the C(1)–C(2) bond distance of 1.41 (1) Å is longer than those found for C(carbene)–C(ylide) bond lengths in related ylide–carbene complexes of the type $(CO)_5Cr(OSiMe_3)CHPMe_3$ (1.332 (9) Å),[42] $Cp(CO)_2Mn(CO_2Me)CHPPh_3$ (1.361 (4) Å),[43] and $Cp(CO)_2MnC(OMe)C(Me)PMe_3$ (1.386 (14) Å)[44] for which the vinyl-like form A has been shown to predominate over the ylide–carbene structure B on the basis of structural data.

A B

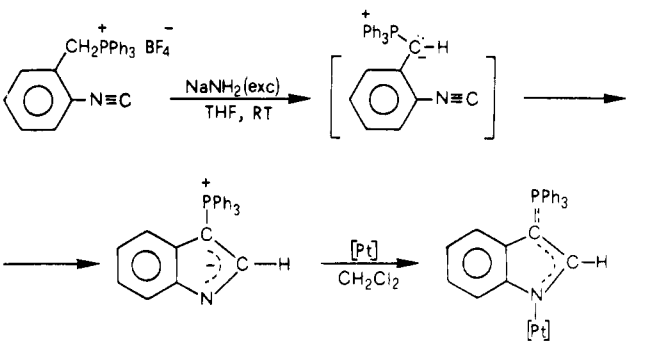
The above-reported C—N and C(1)—C(2) bond distances for the carbenoid ligand in **9** account also for the absence in the IR spectra of complexes **9**–**14** of the C=N and C=C vibrations which usually show up as strong to medium absorptions between 1500 and 1600 cm^{-1} in aminocarbene[3,45] or vinyl-like ylide–carbene–metal[42] complexes, respectively. Furthermore, as a consequence of the electronic delocalization, the carbenoid ligand in complex **9** shows the typical reactivity of indoles[46] reacting with electrophiles such as HBF_4 to give proton addition at the β-position of the indole ring (eq 2). The $^{31}P\{^1H\}$ NMR



(2)

spectrum (CD_2Cl_2) of **9** recorded in the presence of excess HBF_4(Et_2O solvent) shows resonances due to the metal-coordinated PPh_3 ligands (δ 17.29 (s, ^1J(PPt) = 2493 Hz) and to the Me_3P^+– phosphonium group at δ 29.02 (see for comparison purposes the δ values of Me_3P^+– in compounds L^1 and **1**, Table I). The resulting 3*H*-indolium cation is stable in solution in the presence of excess acid, but it rapidly restores the indole ring of **9** by liberating HBF_4 in an attempted precipitation with Et_2O and subsequent dissolution in CH_2Cl_2.

Scheme V



[Pt] = cis-$[(PPh_3)_2PtCl]BF_4$; trans-$[(PPh_3)_2PtCl]$

Finally, inspection of the P–C interaction in the Me_3P–indole system indicates that a certain degree of multiple-bond character can be inferred for the P(1)–C(2) bond which appears to be shorter (1.73 (1) Å) than the other P(1)–C distances (mean 1.78 (1) Å) and close to the values of partially double P–C bonds in free phosphonium ylides (1.66–1.75 Å).[47] Further, the P(1)–C(2) bond length is also shorter than the corresponding P–C distances reported for the aforementioned ylide–carbene complexes.[42–44] In other words, a participation of P(1) in a largely delocalized system comprised of the carbenoid ligand and the Pt atom can be envisaged.

1-Pt(II)-Substituted Indole Derivatives. In an attempt to isolate the free ylide–isocyanide ligands *o*-$(R_3P^+–\ddot{C}H^-)C_6H_4NC$, we reacted *o*-$(BF_4^-Ph_3P^+–CH_2)C_6H_4NC$ with a base. While no reaction occurs with excess NEt_3 after being stirred for several days at room temperature in CH_2Cl_2 (as monitored also by ^{31}P NMR spectroscopy), a fast reaction takes place in THF at room temperature in the presence of excess of a stronger base such as $NaNH_2$ (Scheme V). The above reaction sequence, which is analogous to that reported in Scheme IV for the Pt(II)-coordinated isocyanides and similar also to that described for the intramolecular cyclization of *o*-alkylphenyl isocyanides, leads instead to the formation to the 3-(triphenylphosphonio)indolyl ligand L^5. The structure of L^5 is based on elemental analysis, mass spectral and ^{31}P NMR data (see Experimental Section), and its IR spectrum which does not show ν(NH), ν(NC), and $\nu(BF_4)$ stretchings. Its structure is further confirmed by its metal coordination chemistry resulting in the formation of Pt(II)–indole derivatives (see Experimental Section) of the type *cis*-$\{(PPh_3)_2Pt[\overline{N(o\text{-}C_6H_4)C(PPh_3)C(H)}]Cl\}BF_4$ and *trans*-$\{(PPh_3)Pt[\overline{N(o\text{-}C_6H_4)C(PPh_3)C(H)}]Cl_2\}$, in which the Pt atom is bound to the N(1) position of the indole ring. A diagnostic feature in these derivatives is in fact the ^4J(PPt) coupling of the phosphorus ylide atom (δ ca. 11.7) with the ^{195}Pt nucleus of ca. 11 Hz.

It is worthwhile to mention that the synthesis and the transition-metal chemistry of the first ylide–isocyanide ligand $Ph_3P^+—\ddot{C}H^-—N\equiv C$ has been recently reported.[48]

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Conclusion

In this paper we have reported the synthetic, spectroscopic, and structural investigations of several Pt(II)-substituted indole derivatives. These species were obtained by intramolecular cyclization reactions of an electrophilic isocyanide carbon with the adjacent carbanion of an ylide group generated by nucleophilic attack of a base on the acidic methylene protons of either the free or metal-coordinated isocyanides o-($BF_4^-R_3P^+$–CH_2)C_6H_4NC. When such ligands are coordinated to Pt(II), these reactions are also metal-promoted since Pt acts as an activating agent for the isocyano function, thus making possible the subsequent action of the otherwise uneffective mild base NEt_3. Furthermore, the Pt(II) fragment can be selectively placed in the 1- or 2-position of the indole ring depending on whether the nucleophilic attack of the base on the $-CH_2PR_3^+$ group precedes or follows, respectively, the coordination of the isocyano function to the metal. The heterodifunctional ligands o-(XCH_2)C_6H_4NC (X = organic or organometallic functionality) are being currently investigated with the aim of effecting intramolecular attack at the coordinated isocyanide by changing X or the isocyanide-bound metal. In particular, when X is a metal fragment,[9] such reactions should lead to novel homo- or heterobinuclear systems with the two metal centers lying in close proximity via base-promoted generation of the metal-substituted carbanion $X\ddot{C}H^-$–, which subsequently attacks the appropriately activated metal-coordinated isocyanide. The possibility of generating a transition-metal-substituted carbanion has been recently demonstrated.[49]

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Supplementary Material Available: Listings of hydrogen atom coordinates, bond distances and angles, and thermal parameters (17 pages); a list of observed and calculated structural factors (23 pages). Ordering information is given on any current masthead page.

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Preparation and Reactions of (*E*)-α-Lithio-α-(methyldiphenylsilyl)alkenes†

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Alkylation of (dibromomethyl)methyldiphenylsilane and thermolysis of the resulting (α,α-dibromoalkyl)silanes in DMF provides the (*Z*)-1-bromo-1-(methyldiphenylsilyl)alkenes in good yield. These have been converted to their corresponding lithium reagents by metal–halogen exchange. The stereointegrity of these vinyllithium reagents was found to be excellent at temperatures below 0 °C. These lithium reagents were reacted with alkyl halides, group IV (14) chlorides, aldehydes, benzoyl chloride, and acetic anhydride. The synthetic potential of these systems was demonstrated by the preparation of (*Z*)-heneicosene, the pheromone of the house fly (musca domestica), and of 1-phenyl-1,2-butadiene. The Grignard reagents of the vinyl bromides were also studied, but to a lesser extent.

Introduction

In conjuction with an interest in investigating the potential of organosilicons optically active at silicon in enantioselective synthesis, studies which currently involve the 1-naphthylphenylmethylsilyl group,[2] we have been carrying out several studies with the diphenylmethylsilyl group, which serves as a reasonable, readily available model for the 1-naphthylphenylmethylsilyl group. We wish to report herein on the preparation of and some of the

† Dedicated to Dr. George Zweifel on the occasion of his 60th birthday.

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