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METAL COMPLEXES OF FUNCTIONALIZED PHOSPHINES—I. SYNTHESIS AND CHARACTERIZATION OF 2-DIPHENYLPHOSPHINOETHYLAMINES AND SOME OF THEIR COMPLEXES WITH PLATINUM. X-RAY STRUCTURE OF $[Pt(Ph_2PCH_2CH_2NHBu^t)(Ph_2PCH_2CH_2NHBu^t \cdot HCl)Cl]Cl \cdot H_2O$

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Abstract—The new bidentate ligands $Ph_2PCH_2CH_2NHR$ [R = Bu^t, CH_2Ph, CH(Me)Ph] and $Ph_2PCH_2CH_2N(CH_2Ph)_2$ and their corresponding hydrochloride salts have been synthesized and were characterized by ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy. The ligand $Ph_2PCH_2CH_2NHBu^t$ reacts with K_2PtCl_4 or $(COD)PtCl_2$ to form $[Pt(Ph_2PCH_2CH_2NHBu^t)(Ph_2PCH_2CH_2NHBu^t \cdot HCl)Cl]Cl$, whose structure has been determined by X-ray diffraction. Treatment of this complex with HCl gas gives $[Pt(Ph_2PCH_2CH_2NHBu^t \cdot HCl)_2Cl_2]$ which can also be synthesized from $Ph_2PCH_2CH_2NHBu^t \cdot HCl$ and K_2PtCl_4.

Recently we have studied a range of amino-alkyl and hydroxy-alkyl substituted phosphines. In this paper we report the synthesis of a number of diphenylphosphinoethylamines and some of their complexes with platinum metals.

Bidentate ligands with one hard nitrogen donor and one soft phosphorus donor have been the subject of many recent reports.[1–9] These ligands can act as chelating ligands or as bridging ligands, and the enhanced stability provided by chelation has been used to examine platinum metal amides and N—H activation by these metals. Though early transition metal amides are well known, such complexes of the platinum metals are still quite rare.[10,11] However, such species have been implicated in many catalytic processes such as the rhodium catalysed synthesis of β-lactams by carbonylation of aziridines.[12] Platinum metal amides have also been proposed as key intermediates in a possible route to the catalytic amination of alkenes.[13–15] To date, most of the studies have used phosphines having a phenyl backbone connecting the phosphorus and the nitrogen centres, we are examining ligands with an alkyl backbone which should be more flexible. During the course of this work some related work using the ligand diphenylphosphinoethyl-benzylamine has been published.[16] We have synthesized this phosphine by a different route and have found some differences to the published data which were discussed below.

RESULTS AND DISCUSSION

Base-catalysed addition of amines to vinyldiphenylphosphine has been reported, using methyl lithium as the base catalyst.[17] Using primary amines the products were usually bis(diphenylphosphinoethyl)amines, though it was stated that the intermediate diphenylphosphinoethyl secondary amine could be isolated in certain cases. We have found that sodium amide is a convenient catalyst for this reaction, its low solubility in THF means that it is only present in small concentrations. Thus, refluxing vinyldiphenylphosphine with an excess of amine in THF with sodium amide as catalyst gives diphenylphosphinoethylamines $Ph_2PCH_2CH_2NHR$ [R = Bu^t, CH_2Ph, CH(Me)Ph] (**1a–c**) in good yields. The ligand **1a** is isolated as a crystalline solid, however **1b** and **1c** are oils. An excess of

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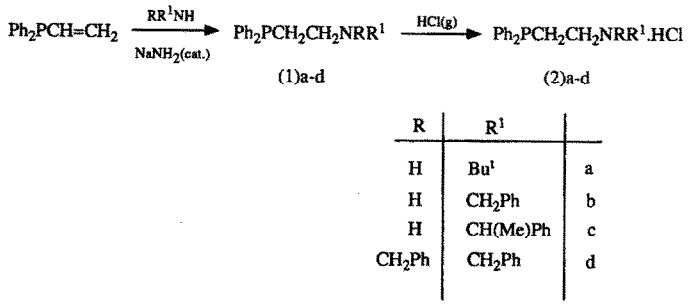


Scheme 1.

amine is used to minimize the formation of bis(diphenylphosphinoethyl)amines. If the secondary amine dibenzylamine is used instead of a primary amine, then the product is $Ph_2PCH_2CH_2N(CH_2Ph)_2$ (**1d**) (see Scheme 1).

The ligands have been characterized by their ^1H, ^{13}C-$\{^1H\}$ and ^{31}P-$\{^1H\}$ NMR spectra (Table 1). All the ligands show a single resonance in the ^{31}P-$\{^1H\}$ NMR spectrum at around δ −20. The ^{13}C-$\{^1H\}$ NMR spectra each show two doublets between δ 29 and 46 due to the C_2H_4 backbone, as well as signals due to the phenyl groups and the R substituent on the nitrogen. There is some confusion in the literature about the assignment of these signals

Table 1. ^1H, ^{13}C-$\{^1H\}$ and ^{31}P-$\{^1H\}$ NMR data for new ligands[a]

Compound	$\delta(^{31}P)$[b]	$\delta(^1H)$	$\delta(^{13}C)$[c]
1a	−20.6	1.25 (s, 9H, But), 2.24 [t, 2H, CH_2, *J*(HH) 7.5], 2.70 [td, 2H, CH_2, *J*(HH) 7.5, *J*(PH) 8.5], 7.35 (m, 10H, Ph)	28.9 (CMe_3), 29.9 [d, C_1, ^1J(PC) 12], 39.4 [d, C_2, ^2J(PC) 21], 50.4 (CMe_3), 128–139 (Ph)
2a	−19.9	1.25 (s, 9H, But), 2.84 (m, 2H, CH_2), 2.94 (m, 2H, CH_2), 7.55 (m, 10H, Ph), 9.4 (br, 2H, NH_2)	24.9 [d, C_1, ^1J(PC) 14], 26.0 (CMe_3), 39.4 [d, C_2, ^2J(PC) 28], 128–136 (Ph)
1b	−20.6	1.60 (br, 1H, NH), 2.29 [t, 2H, CH_2, *J*(HH) 7.5], 2.78 [td, 2H, CH_2, *J*(HH) 7.5, *J*(PH) 8.5], 3.7 (s, 2H, CH_2Ph), 7.3 (m, 15H, Ph)	29.0 [d, C_1, ^1J(PC) 12], 46.0 [d, C_2, ^2J(PC) 20], 53.6 (CH_2Ph), 125–140 (Ph)
2b	−20.4	2.62 (m, 2H, CH_2), 2.85 (m, 2H, CH_2), 3.95 (s, 2H, CH_2Ph), 7.35 (m, 15H, Ph), 10.1 (br, 2H, NH_2)	24.1 [d, C_1, ^1J(PC) 16], 43.2 [d, C_2, ^2J(PC) 26], 50.1 (CH_2Ph), 128–136 (Ph)
1c	−20.8	1.28 [d, 3H, Me, *J*(HH) 6.5], 2.22 (m, 2H, CH_2), 2.61 (m, 2H, CH_2), 3.70 [q, 1H, CH, *J*(HH) 6.5], 7.3 (m, 15H, Ph)	24.2 (Me), 29.1 [d, C_1, ^1J(PC) 12], 44.1 [d, C_2, ^2J(PC) 19.6], 57.8 (CH), 126–145 (Ph)
2c	−20.8	1.69 [d, 3H, Me, *J*(HH) 6.6], 2.75 (m, 4H, CH_2), 4.13 (m, 1H, CH), 7.3 (m, 15H, Ph), 9.99 (Br, 1H, NH), 10.38 (br, 1H, NH)	20.7 (Me), 24.2 (br, C_1) 43.0 [d, C_2, ^2J(PC) 22], 58.5 (CH), 127–136 (Ph)
1d	−20.4	2.25 (m, 2H, CH_2), 2.61 (m, 2H, CH_2), 3.55 (s, 4H, CH_2Ph), 7.29 (m, 20H, Ph)	25.6 [d, C_1, ^1J(PC) 13], 49.7 [d, C_2, ^2J(PC) 22], 57.8 (CH_2Ph), 126–140 (Ph)
2d	−19.8	1.70 (br, 1H, MeO*H*), 2.65 (m, 2H, CH_2), 2.94 (m, 2H, CH_2), 3.46 (s, 3H, *M*eOH), 4.05 [dd, 2H, CH, *J*(HH) 5, 13], 4.30 [dd, 2H, CH, *J*(HH) 2, 13], 7.4 (m, 20H, Ph), 12.5 (br, 1H, NH)	22.5 [d, C_1, ^1J(PC) 17], 47.4 [d, C_2, ^2J(PC) 29], 50.6 (MeOH), 56.7 (CH_2Ph), 128–136 (Ph)

[a] Chemical shifts (δ) in ppm, coupling constants in Hz. Measurements at room temperature in $CDCl_3$.
[b] Chemical shifts are positive to high frequency of 85% H_3PO_4 (external) (0.0 ppm).
[c] The carbon atoms of the ethyl backbone of the ligands are numbered as follows $Ph_2PC_1C_2NRR^1$.

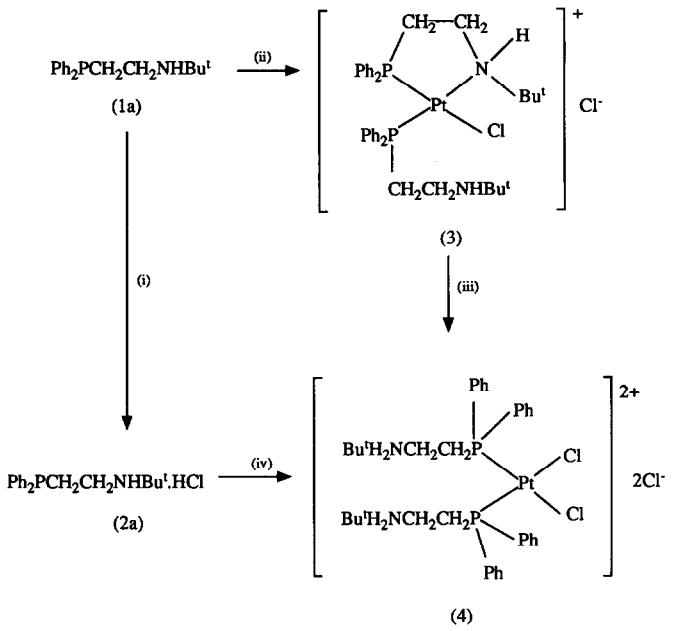
which has been based on the relative magnitudes of ^1J(PC) and ^2J(PC).[9,16] Since we have made a series of these ligands which vary only in the nature of the groups attached to nitrogen we have been able to base our assignments on chemical shift arguments as well as on coupling constants. The signal at δ 29 does not vary by more than 1 ppm for each different R group, whereas the other doublet at around δ 40 varies by about 7 ppm depending on the nature of R thus, we assign the signals at approx. δ 29 to the CH_2 next to the phosphorus atom and those at approx. δ 40 to the CH_2 next to the nitrogen. The greater electronegativity of nitrogen compared to phosphorus leads to the signal being more down field. With these assignments we find that ^2J(PC) is bigger than ^1J(PC) for all these phosphines, as was suggested for $Ph_2PCH_2CH_2NMe_2$.[9] A previous study of tertiary phosphines concluded that ^1J(PC) and ^2J(PC) for alkyl side chains are approximately equal in magnitude.[18] This contrasts with the assignment made recently for the ligand $Ph_2PCH_2CH_2NHR \cdot HCl$ (R = CH_2Ph) where the assignments were made on the basis that ^1J(PC) is larger than ^2J(PC).[16] The ^{1}H NMR spectra show two multiplets in the region δ 2–3 due to the CH_2CH_2 backbone, as well as signals due to the phenyl groups and the R substituent attached to nitrogen. We assume the multiplet to lower field is due to the CH_2 next to nitrogen, with that to higher field being the one next to phosphorus as suggested for the $^{13}C\{^1H\}$ spectra.

Reaction of the ligands **1a–d**, as a solution in diethyl ether, with HCl gas readily yields the hydrochloride salts, **2a–d**, which may be recrystallized from methanol, in certain cases with incorporation of methanol into the crystal. It is this presence of methanol of crystallization which we feel confused previous workers in their reported isolation of $Ph_2PCH_2CH_2NHCH_2Ph \cdot HCl$ (**2b**). The ^{1}H NMR spectrum of this salt (Table 1) shows two multiplets at δ 2.6 and 2.85 assigned to the PCH_2CH_2N backbone, as well as a singlet δ 3.95 due to the CH_2 of the benzyl. This contrasts with the reported values of multiplets at δ 4.2 and 2.7 assigned to the PCH_2CH_2N backbone, and a singlet at δ 3.5 due to the CH_2 of the benzyl. We believe that the ligand previously formulated as $Ph_2PCH_2CH_2NHCH_2Ph \cdot HCl$[16] (**2b**) is in fact $Ph_2PCH_2CH_2N(CH_2Ph)_2 \cdot HCl \cdot (MeOH)$ (**2d**), which we have prepared independently from vinyldiphenylphosphine and dibenzylamine followed by treatment with gaseous HCl as described above. On examining the ^{1}H NMR spectrum of $Ph_2PCH_2CH_2N(CH_2Ph)_2 \cdot HCl \cdot (MeOH)$ (**2d**) at high field (300 MHz) (Table 1), the signal at δ 2.7 can be seen to consist of two multiplets at δ 2.65 and 2.95 which we assign to the PCH_2CH_2N backbone, while the multiplet at δ 4.2 is actually two doublets of doublets at δ 4.3 and 4.15 which we now assign to the CH_2 of the benzyl groups, each CH_2 consisting of two diastereotopic protons which couple to each other and to the hydrogen on the nitrogen. The singlet at δ 3.5 is due to methanol of crystallization and can be observed in the $^{13}C\{^1H\}$ NMR spectrum at δ 50.

We have attempted to repeat the synthesis of $Ph_2PCH_2CH_2NHCH_2Ph$ as reported by Khan and Reddy[16] starting from 2-aminoethanol and benzyl chloride. However, we find that this gives dibenzylaminoethanol as the major product even when only one equivalent of benzyl chloride is used. This could explain their isolation of $Ph_2PCH_2CH_2N(CH_2Ph)_2$ which, as explained above, we believe to be their final product.

The ligand **1a** (R = Bu^t) reacts with K_2PtCl_4 or with $(COD)PtCl_2$ to give the salt **3** (Scheme 2) in which one ligand coordinates through just the phosphorus atom while the other forms a five-membered ring coordinating through both the phosphorus and nitrogen atoms. This is easily seen in the $^{31}P\{^1H\}$ NMR spectrum which shows two inequivalent phosphorus atoms at δ +32.67 and −2.22, respectively. The signal to lower field being the phosphorus in the five-membered ring.[19] The P—Pt coupling constants are 3765 and 3203 Hz as expected for phosphorus *trans* to chloride and amine, respectively. Similar complexes have been obtained from $Ph_2PCH_2CH_2NMe_2$[9] and $Ph_2PCH_2CH_2NHR$ (R = CH_2Ph),[16] though as discussed above the latter actually contains $Ph_2PCH_2CH_2N(CH_2Ph)_2$. Using the related hydroxyalkylphosphine, $Ph_2PCH_2CH_2OH$, Pringle *et al.* showed that the species formed was solvent dependent.[20] We observe some broadness in the $^{31}P\{^1H\}$ NMR spectrum of **3** in $CDCl_3$ which may be indicative of an exchange process, but do not observe the species with both chlorides coordinated and the ligands coordinated only through the phosphorus. This is consistent with an amine being a better donor than an alcohol and thus competing more effectively with chloride for one coordination site.

We have carried out an X-ray crystal structure determination of complex **3** which actually crystallized as the hydrochloride salt, i.e. the uncoordinated nitrogen had been protonated by traces of acid possibly from the dichloromethane solvent, and with a molecule of water of crystallization. The structure of the cation and the principal bond lengths and angles are shown in Fig. 1. The structure clearly shows the presence of one monodentate phosphine and one bidentate ligand. The chelating ligand spans an angle of 85.9(3)° and has Pt—P and



Scheme 2. (i) HCl(g); (ii) K_2PtCl_4 or $(COD)PtCl_2$; (iii) HCl(g); (iv) K_2PtCl_4.

Pt—N bond lengths of 2.226(3) and 2.139(8) Å, respectively, which are similar to those of 86.4°, 2.245 and 2.12 Å, respectively, found for the *o*-diphenylphosphinoaniline ligand in the dication *cis*-$[Pt(o\text{-}Ph_2PC_6H_4NH_2)_2]^{2+}$.[4b]

Treatment of complex **3** with HCl gas gives complex **4** (Scheme 2) in which both the ligands are coordinated through the phosphorus atom only, the amine substituents having been protonated to the hydrochloride salts. This complex may be prepared independently from the ligand hydrochloride salt and K_2PtCl_4. Complex **4** shows the expected $^{31}P\{^1H\}$ NMR spectrum (δ +3.63) with platinum satellites [J(Pt—P) = 3623 Hz] consistent with phosphorus coordinated *trans* to chloride.

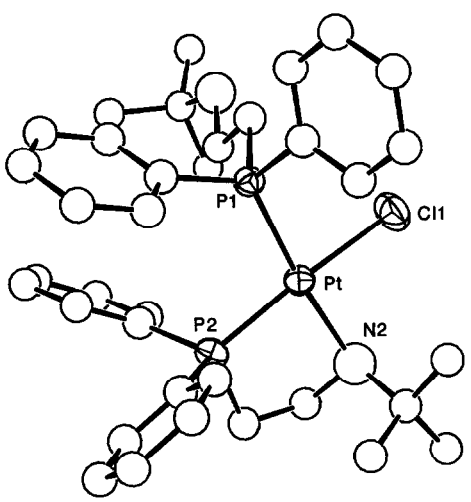


Fig. 1. Molecular structures of the cation $[Pt(Ph_2PCH_2CH_2NHBu^t)(Ph_2PCH_2CH_2NH_2Bu^t)Cl]^{2+}$. Selected bond lengths (Å) and bond angles (°): P(1)—Pt 2.260(2), Pt—Cl(1) 2.367(3), P(2)—Pt 2.226(3), N(2)—Pt 2.139(8); P(2)—Pt—P(1) 100.4(1), P(2)—Pt—N(2) 85.9(3), P(1)—Pt—Cl(1) 87.0(1), N(2)—Pt—Cl(1) 86.6(3).

In conclusion, we have shown that sodium amide-catalysed addition of amines to vinyldiphenylphosphine can be used to produce a series of ligands $Ph_2PCH_2CH_2NHR$. Our evidence suggests that a previous report[16] of $Ph_2PCH_2CH_2NH(CH_2Ph)$ and some of its complexes is wrong, and that they should be reformulated as containing $Ph_2PCH_2CH_2N(CH_2Ph)_2$. The ligand $Ph_2PCH_2CH_2NHBu^t$ reacts with K_2PtCl_4 or $(COD)PtCl_2$ to form a complex in which one ligand is chelated and the other is bound only through phosphorus. Further studies to examine the reactivity of this complex and the effect of changing the Bu^t group are in progress.

EXPERIMENTAL

Petroleum ether, diethyl ether, toluene and THF were all dried by refluxing over purple sodium/benzophenone in a nitrogen atmosphere. Dichloromethane was purified by refluxing over calcium hydride. The compounds vinyldiphenylphosphine[21] and $(COD)PtCl_2$[22] were prepared by the literature methods. Chlorodiphenylphosphine and L-(−)-1-phenylethylamine (Lancaster Synthesis), t-butylamine, benzylamine and sodium amide suspension in toluene (Aldrich) were all used as

supplied. The syntheses of phosphorus-containing compounds were carried out in deoxygenated solvents under a nitrogen atmosphere. Once isolated as pure solids, all new phosphine compounds are relatively air-stable and precautions for their storage are unnecessary.

^1H and ^{13}C-$\{^1H\}$ NMR spectra were recorded on a Bruker AM300 spectrometer as $CDCl_3$ solutions with internal $SiMe_4$ as reference. ^{31}P-$\{^1H\}$ NMR spectra were recorded on a Jeol FX60 instrument at 24.15 MHz in $CDCl_3$ solution and were referenced to external 85% H_3PO_4 with shifts to high frequency being positive. Microanalyses were performed by Butterworth Laboratories Ltd, Middlesex.

Preparation of $Ph_2PCH_2CH_2NHBu^t$ (**1a**)

An excess of t-butylamine (3.38 g, 46.12 mmol) and sodium amide (two spatulas full from a suspension in toluene) were added to a solution of vinyldiphenylphosphine (2.46 g, 11.53 mmol) in THF (30 cm^3). The solution was refluxed under a nitrogen atmosphere for 1.5 h. The sodium amide was destroyed by addition of aqueous ammonium chloride solution (15 cm^3 of a 10% solution). The phosphine was extracted from the aqueous layer with dichloromethane and dried with anhydrous magnesium sulphate. The dichloromethane was removed under reduced pressure and the product was dissolved in petroleum ether and filtered to remove any insoluble impurities. Recrystallization from petroleum ether gave $Ph_2PCH_2CH_2NHBu^t$ as a cream solid (2.80 g, 85%). Found: C, 75.2; H, 8.3; N, 4.3. $C_{18}H_{24}NP$ requires: C, 75.8; H, 8.5; N, 4.9%.

Preparation of $Ph_2PCH_2CH_2NHCH_2Ph$ (**1b**)

This was prepared in a similar manner to $Ph_2PCH_2CH_2NBu^t$ above from vinyldiphenylphosphine (5.34 g, 25.2 mmol), though after refluxing for 1.5 h the solution had become purple. Excess benzylamine was removed from the product by heating at 60°C *in vacuo*. The product, $Ph_2PCH_2CH_2NHCH_2Ph$ (5.84 g, 73%), was isolated as a yellow oil.

Preparation of $Ph_2PCH_2CH_2NHCH(Me)Ph$ (**1c**)

$Ph_2PCH_2CH_2NHCH(Me)Ph$ was prepared as above, and was isolated as a colourless oil in 84% yield.

Preparation of $Ph_2PCH_2CH_2N(CH_2Ph)_2$ (**1d**)

This was prepared in a similar way except that only a slight excess of dibenzylamine was used (1.1 equiv.). Excess amine was removed by heating at 150°C *in vacuo* and $Ph_2PCH_2CH_2N(CH_2Ph)_2$ was isolated as a pale yellow oil in 79% yield.

Preparation of $Ph_2PCH_2CH_2NHBu^t \cdot HCl$ (**2a**)

Hydrogen chloride gas was bubbled through a solution of $Ph_2PCH_2CH_2NHBu^t$ (3.0 g, 10.51 mmol) in diethyl ether (50 cm^3). After a few seconds a white solid precipitated, the diethyl ether was removed *in vacuo* and the product was recrystallized from methanol giving $Ph_2PCH_2CH_2NHBu^t \cdot HCl$ (2.78 g, 82%) as white crystals. Found: C, 66.0; H, 7.4; N, 4.4. $C_{18}H_{25}ClNP$ requires: C, 67.2; H; 7.8; N, 4.3%.

The other hydrochloride salts were prepared in the same way; $Ph_2PCH_2CH_2NH(CH_2Ph) \cdot HCl$ (**2b**) (80%); Found: C, 69.6; H, 6.7; N, 4.0. $C_{21}H_{23}ClNP$ requires: C, 70.9; H, 6.5; N, 3.9%. $Ph_2PCH_2CH_2NHCH(Me)Ph \cdot HCl$ (**2c**) (75%); Found: C, 70.1; H, 7.0; N, 3.9. $C_{22}H_{25}ClNP$ requires: C, 71.4; H, 6.8; N, 3.8%. $Ph_2PCH_2CH_2N(CH_2Ph)_2 \cdot HCl \cdot (MeOH)$ (**2d**) (64%); Found: C, 72.6; H, 6.9; N, 3.1. $C_{29}H_{33}ClNOP$ requires: C, 72.9; H, 7.0; N, 2.9%.

Reaction of K_2PtCl_4 *with* $Ph_2PCH_2CH_2NHBu^t$

A solution of $Ph_2PCH_2CH_2NHBu^t$ (700 mg, 2.45 mmol) in acetone (25 cm^3) was added to a solution of K_2PtCl_4 (500 mg, 1.2 mmol) in water (8 cm^3). The solution changed from red to yellow on addition of the phosphine and was stirred for 0.5 h at room temperature. The solvent was removed *in vacuo* and the residue was dissolved in dichloromethane and filtered to remove potassium chloride. Evaporation of the dichloromethane gave $[\overline{Pt(Ph_2PCH_2CH_2NHBu^t)}(Ph_2PCH_2CH_2NHBu^t)Cl]Cl$ (**3**) as a yellow solid (915 mg, 91%). Recrystallization gave the hydrochloride salt with one molecule of water of crystallization. Found: C, 47.9; H, 5.9; N, 2.6. $C_{36}H_{51}Cl_3N_2OP_2Pt$ requires: C, 48.5; H, 5.8; N, 3.1%. ^1H NMR: δ 1.35 (s, 9H, Bu^t), 1.45 (s, 9H, Bu^t), 2.6–3.5 (br m, 8H, CH_2), 7.5 (m, 20H, Ph). ^{31}P-$\{^1H\}$ NMR: δ −2.2 [d, J(PP) 20, J(PtP) 3203 Hz], +32.7 [d, J(PP) 20, J(PtP) 3765 Hz].

Reaction of $(COD)PtCl_2$ *with* $Ph_2PCH_2CH_2NHBu^t$

A solution of $(COD)PtCl_2$ (300 mg, 0.80 mmol) and $Ph_2PCH_2CH_2NHBu^t$ (480 mg, 1.68 mmol) in dichloromethane (50 cm^3) was stirred for 30 min,

the solution was reduced in volume and petroleum ether was added to precipitate [Pt($Ph_2PCH_2CH_2NHBu^t$)($Ph_2PCH_2CH_2NHBu^t$)Cl]Cl (**3**) (506 mg, 75%) as a yellow solid.

Reaction of K_2PtCl_4 *with* $Ph_2PCH_2CH_2NHBu^t \cdot HCl$

A solution of $Ph_2PCH_2CH_2NHBu^t \cdot HCl$ (404 mg, 1.26 mmol) in methanol (30 cm^3) was added to a solution of K_2PtCl_4 (260 mg, 0.63 mmol) in water (5 cm^3). The solution was stirred for 2 h after which time the solvent was removed and the residue was dissolved in dichloromethane and filtered. Evaporation of the dichloromethane gave [Pt($Ph_2PCH_2CH_2NHBu^t \cdot HCl)_2Cl_2$] (**4**) as a white solid (360 mg, 68%). Found: C; 46.9; H, 6.0; N, 2.8. $C_{36}H_{50}Cl_4N_2P_2Pt$ requires: C, 47.5; H, 5.5; N, 3.1%. ^1H NMR: δ 1.40 (s, 18H, Bu^t), 3.40 (br, 8H, CH_2), 7.30 (br m, 20H, Ph), 9.50 (br, 4H, NH_2). ^{31}P-{^1H} NMR: δ 3.63 [J(PtP) 3623 Hz].

Reaction of [Pt($Ph_2PCH_2CH_2NHBu^t$)($Ph_2PCH_2CH_2NHBu^t$)Cl]Cl (**3**) *with* HCl

Hydrogen chloride gas was bubbled through a solution of [Pt($Ph_2PCH_2CH_2NHBu^t$)($Ph_2PCH_2CH_2NHBu^t$)Cl]Cl in methanol for 5 min, after which time the ^{31}P-{^1H} NMR spectrum showed complete conversion to [Pt($Ph_2PCH_2CH_2NHBu^t \cdot HCl)_2Cl_2$] (**4**).

Crystal structure determination

Crystals of complex **3** were obtained from methanol–dichloromethane. The unit cell parameters were determined by least squares refinement of ω-measurements of different layers.[23] Data were collected on a Stoë STADI-2 diffractometer with an ω-scan technique in the range $7 < 2\theta < 50°$. The intensities of 8135 reflections were measured and these data were corrected for Lorentz and polarization effects to give 4958 unique reflections with $I > 3\sigma(I)$. Subsequent calculations were carried out with the computer program SHELX-76.[24]

Crystal data for [$C_{36}H_{51}Cl_3N_2OP_2Pt$] (**3**): M = 891.16, monoclinic, a = 11.430(14), b = 14.726(9), c = 24.129(6) Å, β = 104.46(4)°, U = 3932.69 $Å^3$, Z = 4, D_c = 1.50 g cm^{-3}, $F(000)$ = 1792. Space group $P2_1/c$, λ(Mo-K_α) = 0.71069 Å, μ(Mo-K_α) = 36.41 cm^{-1}.

The molecular structure was solved by conventional Patterson and Fourier difference techniques. Scattering factors were taken from ref. 25. An absorption correction[23] was applied to the data with the maximum and minimum transmission factors of 0.712 and 0.604, respectively. Phenyl rings were included as rigid groups with D_{6h} symmetry and C—C distances of 1.395 Å. The hydrogen atoms of the phenyl and the CH_2 groups were included in calculated positions (C—H = 1.08 Å). All non-hydrogen atoms were refined anisotropically. Final cycles of refinement employed a weighting factor w calculated from $w = k/(\sigma^2F + gF^2)$, where k = 1.6096 and g = 0.000826, and gave final values of R = 0.0534 and R_w = 0.0535.

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