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Heteroarylphosphorus ligands in platinum(II) complexes. The structure of *trans*-[Pt(P{2-(*N*-methylpyrrolyl)}$^{i}Pr_2)_2Cl_2$]

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Abstract

Displacement of cod from [Pt(cod)Cl_2] by 2 equiv. of heteroarylphosphorus ligand, PR_2R', in dichloromethane at ambient temperature afforded — but for one exception *trans*-[Pt(P{2-(*N*-methylpyrrolyl)}$^{i}Pr_2)_2Cl_2$] (**1**) — the expected *cis* complexes, *cis*-[Pt(P{2-(*N*-methylpyrrolyl)}$Ph_2)_2Cl_2$] (**2**), *cis*-[Pt(P{2-(5-methylthienyl)}$R_2)_2Cl_2$] (R = Ph **3**, ^{i}Pr **4**) and *cis*-[Pt(P{2-(5-bromopyridinyl)}$^{i}Pr_2)_2Cl_2$] (**5**). The complexes were fully characterised and structural assignments were based on $^{1}J(^{195}Pt–^{31}P)$ coupling constants from the NMR data. The structure of **1** was determined by X-ray crystallography, which revealed that the two pyrrolyl substituents on the phosphine ligands were oriented on opposite sides of the P–Pt–P axis. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Platinum complexes; Phosphine complexes; Aminoarene complexes

1. Introduction

The development of new ligands is becoming increasingly important to fine tune metal activity in coordination chemistry [1]. While phosphine ligands with heteroaryl substituents, such as 2-pyridinylphosphines, are widely exploited in binuclear complex formation as bridging ligands, the 2-thienyl, 2-furyl and 2-(*N*-methylpyrrolyl) substituents are less inclined to coordinate in a similar fashion through their respective heteroatoms [2]. In general, 2-thienyl and 2-furyl groups behave as moderately strong electron-withdrawing units and a comparative study of the magnitude of $^{1}J(^{77}Se–^{31}P)$ coupling constants for heteroarylphosphine selenides established an electron-withdrawing effect which follows an ordering of 2-furyl > 2-thienyl > phenyl > 2-(*N*-methylpyrrolyl) [3]. Platinum(II) complexes prepared in polar solvents from tetrachloroplatinate(II) and bis(phosphine) ligands containing 2-furyl or 2-thienyl substituents invariably afforded *cis* products, *cis*-[Pt(PR_2R')$_2Cl_2$], which did not spontaneously convert into the *trans* isomers. The mechanisms of *cis*–*trans* isomerisations have been the subject of rigorous investigations and any one of the precursor, the solvent, phosphine substituents or auxiliary ligands in the complex, may determine the structure of the final product [4]. For complexes of the type [PtL_2X_2], the *cis* isomers are generally enthalpy-driven, while the *trans* isomers are entropy-favoured. The position of 2-(*N*-alkylpyrrolyl) in the above sequence as well as the omission of phosphine ligands displaying this substituent in the literature in complexes of the type [Pt(PR_2R')$_2Cl_2$], is noteworthy. Furthermore, we observed in structural studies that 2,5-(*N*-methylpyrrolydene), in sharp contrast to 2,5-thienylene, displayed a passiveness to stabilise the carbocation centres in biscarbene complexes [5,6]. Hence, it was of some interest to us to re-investigate and compare the structures of [Pt(P{monoheteroaryl}$R_2)_2Cl_2$] (R = dialkyl and diaryl) complexes. In order to minimize variables all reactions were studied by utilising the *cis* directing precursor, dichloro-η^4-1,5-cyclooctadieneplatinum(II), as well as the same reaction conditions and solvent. The *cis* isomers were isolated as expected,

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except for the case of *trans*-[Pt(P{2-(*N*-methylpyrrolyl)}^{i}Pr$_2$)$_2$Cl$_2$], the structure of which was also confirmed by a crystal structure determination.

2. Experimental

2.1. General

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. Solvents were distilled under nitrogen from appropriate drying agents before use. The [Pt(cod)Cl$_2$] precursor was prepared from K$_2$[PtCl$_4$] according to a literature method [7]. TMEDA and *N*-methylpyrrole were distilled prior to use. All other reagents and chemicals were obtained commercially and used as received. The ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker ARX300 spectrometer operating at 300.133, 121.496 and 75.469 MHz for the respective nuclei. Chemical shifts in ^{1}H and ^{13}C{^{1}H} NMR spectra were calibrated with reference to residual proton signals of the deuterated solvent (7.24 and 77.0 ppm, respectively for CDCl$_3$). Chemical shifts of ^{31}P{^{1}H} spectra were relative to an external standard. Mass spectra (electron impact) were recorded on a Finnigan Mat 8200 instrument operating at 70 eV.

2.2. Crystal structure determination

The intensity data for **1** was collected on a Nonius Kappa CCD diffractometer, using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz, polarisation and absorption effects [8]. The structure was solved by direct methods and refined by full-matrix least-squares techniques against F_o^2 [9,10]. The hydrogen atoms of the compound were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically [10]. XP (Siemens Analytical X-ray Instruments) was used for structure representations. Crystal data for **1**: $C_{22}H_{40}Cl_2N_2P_2Pt$, $M_r = 660.49$ g mol^{-1}, colourless prism, size $0.14 \times 0.12 \times 0.10$ mm^3, monoclinic, space group $P2_1/n$, $a = 8.1993(3)$, $b = 8.2423(3)$, $c = 19.4461(6)$ Å, $\beta = 94.303(2)°$, $V = 1310.48(8)$ Å^3, $T = -90$°C, $Z = 2$, $D_{calc} = 1.674$ g cm^{-3}, μ(Mo Kα) = 56.92 cm^{-1}, ω-scan, transmin: 0.553, transmax: 0.968, $F(000) = 656$, 6702 reflections in $h(-10/10)$, $k(-10/8)$, $l(-24/23)$, measured in the range $3.51° \leq \theta \leq 26.32°$, completeness $\theta_{max} = 99\%$, 2638 independent reflections, $R_{int} = 0.041$, 2173 reflections with $F_o > 4\sigma(F_o)$, 133 parameters, 0 restraints, $R_{1(obs)} = 0.032$, $wR_{2(obs)} = 0.072$, $R_{1(all)} = 0.042$, $wR_{2(all)} = 0.076$, Goodness-of-fit on $F^2 = 1.120$, largest difference peak and hole: 1.246/−1.779 e Å^{-3}.

2.3. Preparation of the phosphine ligands

2.3.1. Preparation of diisopropyl-2-(5-methylthienyl)phosphine

A solution of n-BuLi (14.2 cm^3 of 1.6 M in hexane, 22.7 mmol) was added dropwise to a solution of 2-methylthiophene (2.00 cm^3, 20.7 mmol) in THF (10 cm^3) at room temperature (r.t.). No external cooling was applied and the resultant mixture was stirred for 1 h. The reaction mixture was then cooled to 0°C over an ice-bath before P^{i}Pr$_2$Cl (3.30 cm^3, 20.7 mmol) was introduced. After allowing the reaction to proceed for 1 additional h at r.t., the solvents were removed under reduced pressure. Et$_2$O was added, the mixture filtered through silica gel (layered with anhydrous Na$_2$SO$_4$) and the filtrate vacuum-evaporated to dryness. The orange coloured oil obtained was distilled under reduced pressure to give a colourless liquid. Yield 3.4 g (76%). ^{1}H NMR δ (CDCl$_3$): 7.07 (SC$_4$*H*$_2$, 1H, dd, $^{3}J_{HH} = 3.2$, $^{3}J_{PH} = 6.6$ Hz), 6.71 (SC$_4$*H*$_2$, 1H, m), 2.47 (SC$_4$H$_2$–C*H*$_3$, 3H, s), 2.00 (P(C*H*Me$_2$)$_2$, 2H, heptet of d, $^{3}J_{HH} = 7.0$, $^{2}J_{PH} = 1.1$ Hz), 1.09–0.96 (P(CH*Me*$_2$)$_2$, 12H, m) ppm. ^{31}P{^{1}H} δ (CDCl$_3$): 1.2 ppm.

2.3.2. Preparation of 2-(5-methylthienyl)diphenylphosphine

A procedure similar to that described above was followed, using PPh$_2$Cl (3.80 cm^3, 20.6 mmol) instead of P^{i}Pr$_2$Cl. Yield 4.9 g (84%). ^{1}H NMR δ (CDCl$_3$): 7.35 (Ph, 10H, m), 7.13 (SC$_4$*H*$_2$, 1H, dd, $^{3}J_{HH} = 3.4$, $^{3}J_{PH} = 6.6$ Hz), 6.75 (SC$_4$*H*$_2$, 1H, m), 2.45 (C*H*$_3$, 3H, s) ppm. ^{31}P{^{1}H} δ (CDCl$_3$): −18.7 ppm.

2.3.3. Preparation of diisopropyl-2-(*N*-methylpyrrolyl)phosphine

N-Methylpyrrole (2.50 cm^3, 28.2 mmol) was reacted with n-BuLi (16.0 cm^3 of a 1.6 M hexane solution, 25.6 mmol) in the presence of TMEDA (3.84 cm^3, 25.6 mmol). The reaction mixture was heated for 20 min at 50°C, and then allowed to cool to r.t. before the temperature was decreased to −60°C (acetone–dry ice), before P^{i}Pr$_2$Cl (4.07 cm^3, 25.6 mmol) was added. The product was filtered through silica gel. Yield 2.5 g (50%). ^{1}H NMR δ (CDCl$_3$): 6.72 (NC$_4$*H*$_3$, 1H, m), 6.26 (NC$_4$*H*$_3$, 1H, m), 6.14 (NC$_4$*H*$_3$, 1H, dd, $^{3}J_{HH} = 3.7$, $^{3}J_{PH} = 2.5$ Hz), 3.70 (NC*H*$_3$, 3H, s), 1.96 (P(C*H*Me$_2$)$_2$, 2H, heptet of d, $^{3}J_{HH} = 6.90$, $^{2}J_{PH} = 0.9$ Hz), 0.99 (PCH*Me*$_2$, dd, 6H, $^{3}J_{HH} = 7.1$, $^{3}J_{PH} = 16.3$ Hz), 0.90 (PCH*Me*$_2$, dd, 6H, $^{3}J_{HH} = 7.0$, $^{3}J_{PH} = 11.7$) ppm. ^{31}P{^{1}H}?δ (CDCl$_3$): −18.8 ppm.

2.3.4. Preparation of 2-(*N*-methylpyrrolyl)diphenylphosphine

The phosphine ligand was prepared as described above, adding PPh$_2$Cl (4.60 cm^3, 25.6 mmol) instead of P^{i}Pr$_2$Cl. The product was purified as described above.

Yield 5.6 g (82%). ^{1}H NMR δ ($CDCl_3$): 6.84 (NC_4H_3, 1H, m), 6.15 (NC_4H_3, 1H, m), 5.88 (NC_4H_3, 1H, dd, $^3J_{HH} = 3.62$, $^3J_{PH} = 1.81$ Hz), 3.62 (NCH_3, 3H, s). $^{31}P\{^1H\}$ δ ($CDCl_3$): -29.3 ppm.

2.3.5. Preparation of 2-(6-bromopyridinyl)diisopropylphosphine

2,6-Dibromopyridine (1.137 g, 4.80 mmol) was reacted with n-BuLi (3.30 cm^3 of a 1.6 M hexane solution, 5.28 mmol) in CH_2Cl_2 at -78°C for 20 min. Thereafter, P^iPr_2Cl (0.76 cm^3, 4.8 mmol) was added and after 30 min the reaction mixture was allowed to equilibrate to r.t. Water was added and the aqueous layer extracted with Et_2O. The combined organic fractions were dried (Na_2SO_4), filtered, and the solvents were removed by rotary evaporation at reduced pressure. The ligand was purified by column chromatography (silica gel with Et_2O–hexane mixtures as eluant). Yield 0.79 g (60.0%). ^{1}H NMR δ ($CDCl_3$): 7.42 (NC_5H_3, 1H, d, $^3J_{HH} = 3.0$ Hz), 7.40 (NC_5H_3, d, 1H, $^3J_{HH} = 2.4$ Hz), 7.35 (NC_5H_3, 1H, m), 2.25 ($P(CHMe_2)_2$, 2H, heptet of d, $^3J_{HH} = 7.1$, $^2J_{PH} = 2.6$ Hz), 1.09 ($PCMe_2$, dd, 6H, $^3J_{HH} = 7.1$, $^3J_{PH} = 14.7$ Hz) and 0.92 ($PCMe_2$, dd, 6H, $^3J_{HH} = 7.0$, $^3J_{PH} = 12.1$ Hz) ppm. $^{31}P\{^1H\}$ δ ($CDCl_3$): 16.4 ppm.

2.4. Preparation of Pt(II) complexes

2.4.1. Dichlorobis[diisopropyl-2-(N-methylpyrrolyl)phosphine]platinum(II) (1)

A solution of diisopropyl(*N*-methylpyrrolyl)-phosphine (0.274 g, 1.39 mmol) in 5 cm^3 of CH_2Cl_2 was slowly added to a suspension of [Pt(cod)Cl_2] (0.260 g, 0.695 mmol) in 5 cm^3 CH_2Cl_2. The resulting mixture was stirred at r.t. for 14 h. After removal of the solvent, a solid was obtained, which was washed with hexane and with Et_2O. Yield 0.42 g (89.0%). X-ray quality crystals were grown from a solution of **1** in CH_2Cl_2, layered with hexane at -20°C over several days. *Anal.* Calc. for $C_{22}H_{40}Cl_2N_2P_2Pt$: C, 40.01; H, 6.10; N, 4.24. Found: C, 39.9; H, 6.00; N, 4.36%. ^{1}H NMR δ ($CDCl_3$): 6.84 (NC_4H_3, 2H, m), 6.34 (NC_4H_3, 2H, dd, $^3J_{HH} = 1.3$, $^3J_{PH} = 8.8$ Hz), 6.22 (NC_4H_3, 2H, m), 4.16 (NCH_3, 6H, s), 2.79 ($P(CHMe_2)_2$, 4H, m), 1.22 ($P(CMe_2)_2$, 24H, m) ppm. $^{13}C\{^1H\}$ δ ($CDCl_3$): 128.2 (NCHCH), 119.1 (NC*C*H), 114.7 (*ipso*-*C*P), 108.1 (NC*C*H), 37.4 (N*Me*), 22.3 ($P(CMe_2)$, 18.6 ($P(CMe_2)$, 17.7 ($P(CMe_2)$ ppm. $^{31}P\{^1H\}$ δ ($CDCl_3$): 14.4 (Pt satellites $^1J_{PtP} = 2430.0$ Hz) ppm. EI MS (70 eV): *m*/*z* no M^+ was observed.

2.4.2. Dichlorobis[2-(N-methylpyrrolyl)-diphenylphosphine]platinum(II) (2)

A solution of (*N*-methylpyrrolyl)diphenyl phosphine (0.56 g, 2.11 mmol) in 10 cm^3 CH_2Cl_2 was slowly added to a suspension of [Pt(cod)Cl_2] (0.376 g, 1.00 mmol) in 5 cm^3 CH_2Cl_2. Yield 0.66 g (83%). *Anal.* Calc. for $C_{34}H_{32}Cl_2N_2P_2Pt$: C, 51.27; H, 4.05; N, 3.52. Found: C, 51.48; H, 4.31; N, 3.38%. ^{1}H NMR δ ($CDCl_3$): 7.44 (Ph *o*-H, 8H, m), 7.32 (Ph *p*-H, 4H, m), 7.13 *m*-H, 8H, m), 6.74 (NC_4H_3, 2H, m), 5.99 (NC_4H_3, 2H, m), 5.96 (NC_4H_3, 2H, m), 3.48 (NCH_3, 6H, s) ppm. $^{13}C\{^1H\}$ δ ($CDCl_3$): 134.4 (*o*-*C*), 130.9 (*p*-*C*), 129.7 (*ipso*-C_6H_5), 128.7 (NC*C*H), 128.1 (*m*-*C*), 122.7 (NC*C*H) 108.2 (NC*C*H), 37.5 (N*Me*) ppm, (*ipso*-NC_4H_3) not observed. $^{31}P\{^1H\}$ δ ($CDCl_3$): -3.5 (Pt satellites $^1J_{PtP} = 3644.3$ Hz) ppm.

2.4.3. Dichlorobis[2-(5-methylthienyl)-diphenylphosphine]platinum(II) (3)

Complex **3** was isolated as a white solid from 2-(5-methylthienyl)diphenylphosphine (0.700 g, 2.48 mmol) and [Pt(cod)Cl_2] (0.464 g, 1.24 mmol) under the same reaction conditions as for **1**. Yield 0.94 g (91%). *Anal.* Calc. for $C_{34}H_{30}Cl_2P_2S_2Pt$: C, 49.16; H, 3.64. Found: C, 49.6; H, 3.91%. ^{1}H NMR δ ($CDCl_3$): 7.46 (Ph *o*-*H*, 8H, m), 7.30 (Ph *p*-*H*, 4H, t, $^3J_{HH} = 7.6$ Hz), 7.15 (Ph *m*-*H*, 8H, td, $^3J_{HH} = 7.6$, $^3J_{HH} = 2.0$ Hz), 6.77 (SC_4H_2, 4H, m), 2.42 (CH_3, 6H, s) ppm. $^{13}C\{^1H\}$ δ ($CDCl_3$): 149.6 (*ipso*-*C*CH_3), 141.0 (SC_4H_2), 125.7 (SC_4H_2), 134.2 (*o*-*C*), 130.6 (*p*-*C*), 130.0 (*ipso*-C_6H_5), 128.4 (*ipso*-SC_4H_2), 127.6 (*m*-*C*), 30.9 ($PCPh_2$), 15.0 (CH_3) ppm. $^{31}P\{^1H\}$ δ ($CDCl_3$): 5.1 (Pt satellites $^1J_{PtP} = 3695.8$ Hz) ppm. EI MS (70 eV): *m*/*z* 835 [M^+, 5%], 797 [$M^+ - Cl$, 3%], 759 [$M^+ - 2Cl$, 1%], 476 [$Pt(MeSC_4H_2PPh_2)^+$, 0.6%], 282 [$MeSC_4H_2PPh_2^+$, 100%], 205 [$MeSC_4H_2PPh^+$, 42%], 97 [$MeSC_4H_2^+$, 12%].

2.4.4. Dichlorobis[diisopropyl-2-(5-methylthienyl)phosphine]platinum(II) (4)

Complex **4** was formed from diisopropyl-2-(5-methylthienyl)phosphine (0.520 g, 2.4 mmol) and [Pt(cod)Cl_2] (0.425 g, 1.14 mmol) using the same procedure as for **3**. A white powder was obtained. Yield 0.75 g (95%). *Anal.* Calc. for $C_{22}H_{38}Cl_2P_2S_2Pt$: C, 38.04; H, 5.51. Found: C, 38.23; H, 5.31%. ^{1}H NMR δ ($CDCl_3$): 6.72 (SC_4H_2, 2H, dd, $^3J_{HH} = 3.5$, $^3J_{PH} = 6.1$ Hz), 6.42 (SC_4H_2, 2H, d, $^3J_{HH} = 3.5$ Hz), 3.08 ($P(CHMe_2)_2$, 4H, m), 2.41 (SC_4H_2–CH_3, 6H, s), 1.49 ($P(CHMe_2)$, 12H, dd, $^3J_{HH} = 7.1$, $^3J_{PH} = 17.1$ Hz), 1.11 ($P(CHMe_2)$, 12H, dd, $^3J_{HH} = 6.9$, $^3J_{PH} = 16.3$ Hz) ppm. $^{13}C\{^1H\}$ δ ($CDCl_3$): 145.4 (*ipso*-*C*CH_3), 135.9 (SC*C*H), 126.3 (SC*C*H), 121.3 (*ipso*-*C*P, d, $^1J_{PC} = 46.4$ Hz), 27.7 ($P(CMe_2)$, d, $^1J_{PC} = 39.7$ Hz, $^3J_{PtC}$ unresolved), 19.6 ($P(CMe_2)$, d, $^2J_{PC} = 12.2$ Hz, $^3J_{PtC}$ unresolved), 15.0 (SC_4H_2–*C*H_3) ppm. $^{31}P\{^1H\}$ δ ($CDCl_3$): 19.2 (Pt satellites $^1J_{PtP} = 3763.4$ Hz) ppm. EI MS (70 eV): *m*/*z* 694 [M^+, 8%], 659 [$M^+ - Cl$, 2%], 624 [$M^+ - 2Cl$, 2%], 581 [$M^+ - 2Cl - {}^iPr$, 1%], 538 [$M^+ - 2Cl - 2{}^iPr$, 1%], 410 [$Pt(MeSC_4H_2P^iPr_2)^+$, 0.2%], 367 [$Pt(MeSC_4H_2P^iPr)^+$, 1%], 323 [$Pt(MeSC_4H_2)^+$, 4%], 214 [$MeSC_4H_2P^iPr_2^+$,

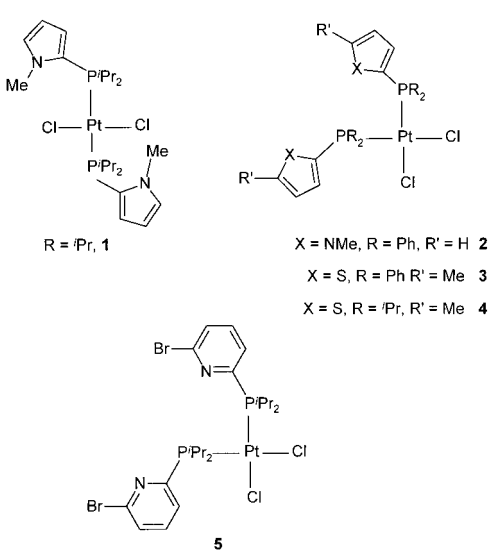
100%], 129 [$MeSC_4H_2P^+$, 72%] and 97 [$MeSC_4H_2^+$, 4%].

*2.4.5. Preparation of dichlorobis[5-(2-bromopyridinyl)-diisopropylphosphine]platinum(II) (**5**)*

A similar procedure was followed as described above. [Pt(cod)Cl_2] (0.386 g, 1.03 mmol) was reacted with 2-(6-bromopyridinyl)diisopropylphosphine (0.565 g, 2.06 mmol). The complex was isolated as white, crystalline flat needles. Yield 0.797 g (95%). *Anal*. Calc. for $C_{22}H_{34}Br_2Cl_2N_2P_2Pt$: C, 32.45; H, 4.21; N, 3.44. Found: C, 32.81; H, 4.11%. ^{1}H NMR δ ($CDCl_3$): 7.13 (NC_5H_3, 6H, m), 3.06 ($P(CHMe_2)_2$, 4H, m), 1.55 and 1.07 ($P(CMe_2)_2$, dd, $^3J_{HH} = 7.2$, $^3J_{PH}$ 16.3 Hz and m, 24H) ppm. $^{13}C\{^1H\}$ δ ($CDCl_3$): 141.7 (*ipso-C*P), 139.75 (*ipso-C*Br), 137.3 (*p-C*), 128.4 (*m-C*), 125.6 (*m-C*), 25.6 ($P(CHCH_3)_2$), 19.5 and 19.0 ($P(CHCH_3)_2$) ppm. $^{31}P\{^1H\}$ δ ($CDCl_3$): 28.2 (Pt satellites $^1J_{PtP} = 3711.7$ Hz) ppm. EI MS (70 eV): m/z 817 [M^+, 63%], 310 [$PtBrCl^+$, 100%], 232 [$BrpyP^iPr^+$, 84%], 230 [$PtCl^+$, 100%].

3. Results and discussion

The phosphine ligands were prepared by utilising standard synthetic organic methods which involved the monolithiation of *N*-methylpyrrole, 2-methylthiophene, and 2,6-dibromopyridine [11], followed by quenching with the chlorodiphenylphosphine or chlorodiisopropylphosphine electrophile. The platinum(II) complexes were obtained by the displacement of 1,5-cyclooctadiene from dichloro(η^4-1,5-cyclooctadiene)platinum(II) by 2 equiv. of the appropriate phosphine ligand at ambient temperature in dichloromethane. All the complexes were isolated as white solids and purified by washing with various solvents. *cis* Products were expected to form from the direct replacement of a 1,5-cyclooctadiene ligand in the metal precursor by two phosphine ligands. This was indeed the case in all the reactions with the exception of dichlorobis[diisopropyl-2-(*N*-methylpyrrolyl)phosphine]platinum(II) (**1**) (Scheme 1).



Scheme 1.

Grim and co-workers showed that aryl substituents promote, to an extent, the stabilisation of the *cis* isomers [12]. The synthesis of bis(phosphine)platinum(II) complexes under analogous reaction conditions, with 2-(5-methylthienyl)diphenylphosphine and 2-(*N*-methylpyrrolyl)diphenylphosphine, respectively, led to the isolation of dichlorobis[2-(*N*-methylpyrrolyl)-diphenylphosphine]platinum(II) (**2**), and dichlorobis[2-(5-methylthienyl)diphenylphosphine]platinum(II) (**3**). The magnitude of the $^1J(^{195}Pt–^{31}P)$ coupling constants of 3644.3 and 3695.8 Hz for **2** and **3**, respectively, fit into the range of ^1J ($^{195}Pt–^{31}P$) values reported for other *cis*-dichlorobis(phosphine)platinum(II) complexes [13]. A heteroaryl substituent with strong coordinating power via the N-heteroatom, such as a pyridinyl derivative [14] also yields a *cis* product, bis(2-{6-bromopyridinyl}diphenylphosphine)dichloroplatinum(II), **5** ($^1J(^{195}Pt–^{31}P) = 3711.7$ Hz). It is interesting to note that in **5** there is evidence (the resonance is broadened and shifted upfield) from the ^{1}H NMR spectrum that hydrogen bonding occurs between methyl hydrogen atoms of the isopropyl group and the nitrogen atom of the pyridine ring. On comparison with related complexes reported in the literature, the $^1J(^{195}Pt–^{31}P)$ coupling constants for **3** and for **5** correspond favourably with the 3681 Hz for *cis*-bis(diphenyl-2-thienylphosphine)dichloroplatinum(II) [15] and 3675.6 Hz for *cis*-bis(diphenyl-2-pyridinylphosphine)dichloroplatinum(II), respectively (dichloromethane-d_2) [16]. Incomplete spectroscopic data were reported for the former complex. On replacing the two phenyl groups on the heteroarylphosphine ligands with isopropyl groups, *cis*-dichlorobis(2-{5-methylthienyl}diisopropylphosphine)-platinum(II) (**4**), was obtained. Its $^1J(^{195}Pt–^{31}P)$ coupling constant of 3763.4 Hz is once again indicative of a *cis* configuration. However, replacement of phenyl groups of the 2-(*N*-methylpyrrolyl)phosphine ligand by isopropyl groups results in a platinum(II) complex, **1**, displaying a significantly smaller $^1J(^{195}Pt–^{31}P)$ coupling constant of 2430.0 Hz. This value is characteristic of *trans*-dichlorobis(phosphine)platinum(II) complexes [13].

Confirmation of the *trans* configuration of phosphine ligands in **1** was obtained from a single crystal X-ray structure determination. X-ray quality crystals of **1** were grown from a dichloromethane solution layered with hexane. The molecular structure of **1** is given in Fig. 1 and selected bond lengths and angles are listed in Table 1. A square planar structure is adopted with two molecules of phosphine ligands occupying *trans* posi-

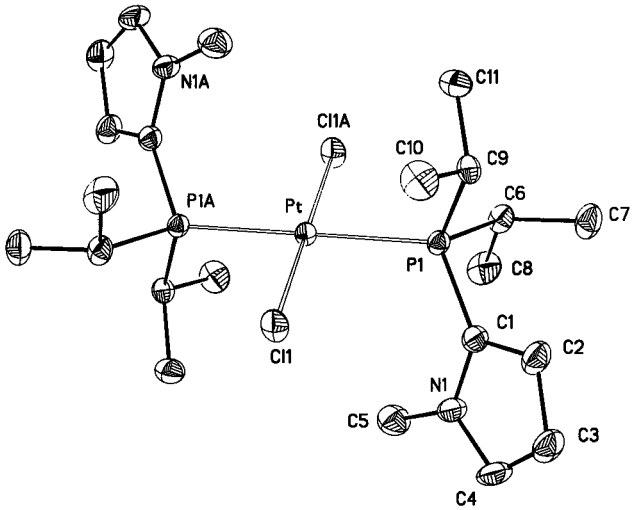


Fig. 1. Molecular structure of *trans*-[Pt(P{2-(*N*-methylpyrrolyl)}-$^{i}Pr_2)_2Cl_2$] (**1**).

Table 1
Selected bond lengths (Å) and angles (°) for **1** [a]

Pt–Cl(1)	2.321(1)
Pt–P(1)	2.334(1)
P(1)–C(1)	1.808(6)
P(1)–C(9)	1.855(6)
P(1)–C(6)	1.858(6)
N(1)–C(1)	1.385(8)
N(1)–C(4)	1.380(7)
N(1)–C(5)	1.467(7)
Cl(1A)–Pt–Cl(1)	180.0
Cl(1A)–Pt–P(1)	89.49(5)
Cl(1)–Pt–P(1)	90.52(5)
C(1)–P(1)–Pt	116.2(2)
C(9)–P(1)–Pt	109.7(2)
C(6)–P(1)–Pt	116.5(2)
C(8)–C(6)–P(1)	111.3(4)
C(7)–C(6)–P(1)	112.0(4)
C(10)–C(9)–P(1)	112.1(4)
C(11)–C(9)–P(1)	109.3(4)

[a] Symmetry transformations used to generate equivalent atoms: A: $-x, -y, -z$.

tions. Deviations of the bond angles at platinum from 90° are minimal and the P–Pt–Cl atoms are almost co-planar. The Pt–Cl and Pt–P bond lengths are 2.321(2) and 2.334(1) Å, respectively. Both bond lengths are in the normal range for *trans*-Pt–Cl and *trans*-Pt–P bonds [17]. In the analogous compound *trans*-dichlorobis(triethylphosphine)platinum(II) the Pt–Cl bond length is also reported to be slightly shorter than the Pt–P bond length [18]. The average P–C(isopropyl) bond distance is 1.857(6), which is 0.049 Å longer than the P–C(pyrrolyl) bond length of 1.808(6) Å. This feature has been observed in other alkyl–aryl phosphines [19]. The two isopropyl groups attached to a phosphorus atom display slightly different orientations. One methyne group has a C–P–Pt angle of 116.2(2)° while the other is 109.7(2)°. Furthermore, while the C7–C6–P and C10–C9–P angles are identical at 112.1(4)°, the other methyl group of each isopropyl substituent gives different angles viz. 109.3(4)° for C11–C9–P and 111.3(4)° for C8–C6–P. The *N*-methyl group is slightly tilted away from the phosphorus and inclined to the far side of the pyrrole ring (C1–N–C5 = 128.8(5), and C4–N–C5 = 122.2(5)°).

The *cis* complexes did not afford crystals suitable for single-crystal X-ray diffraction studies. We ascribe this to better packing of the molecules resulting from the centrosymmetric *trans* complex compared to the *cis* complexes.

The reason for **1** assuming a *trans* conformation while **2**–**5** are *cis* isomers, we believe, lies in electronic rather than steric effects. Even large bulky phosphines can stabilise the *cis* isomer. For example, the intermeshing ability of the phosphine ligand in *cis*-dichlorobis(di-*tert*-butylphenylphosphine)platinum(II) alleviates steric hindrance and allows for the *cis* configuration to be adopted [19]. An example of a case where electronic interactions lead to quite different properties in pyrrole- or thiophene-like molecules is given by the comparison of the 2,2′-diaryl molecules. A twisted conformation is observed for 2,2′-bi(*N*-methylpyrrole) in the biscarbene complex $[(CO)_5WC(OEt)C_5H_5N–C_5H_5NC(OEt)W(CO)_5]$, where the two pyrrole rings are twisted away from each other [5]. By contrast, the analogous biscarbene complex with a 2,2′-biphenyl spacer [20] and 5,5′-substituted 2,2-bithiophene compounds [21] have planar structures with rotation about the 2,2′-linkage bond severely restricted. This implies that the π-orbitals of the sulfur atom are involved in delocalization of electron density over the two thiophene rings, whereas this is not the case for dipyrroles. The difference in the electronic properties between the 5-membered heterocycles of 2-methylthiophene and *N*-methylpyrrole determines the bonding properties of these phosphine ligands and plays a role in the reasons for **1** adopting a *trans* configuration.

The *cis* complexes do not spontaneously undergo *cis*–*trans* isomerisation to the thermodynamically more stable *trans* isomer. It is difficult to establish a trend amongst the various interrelating factors that affect the isomerisation equilibrium, although the effect of the substituent at phosphorus is marked. As discussed below, the diisopropyl-2-(*N*-methylpyrrolyl)phosphine ligand is the most shielded of the series of phosphines in this investigation, suggesting that the phosphine ligand is a relatively stronger electron-donor. This may affect the reaction kinetics leading to the *trans* rather than the *cis* isomer. The presence of a trace amount of free phosphine is known to catalyse the isomerisation [4]. It can thus be argued that platinum(II), being a relatively electron-rich metal centre, could have a greater tendency to labilise the stronger donor phosphine ligand.

Chemical shifts of phosphines in the ^{31}P NMR spectra are affected by the electronegativity of the group attached to phosphorus. The increased shielding of the phosphorus centre in the order triphenylphosphine (−4.7 ppm [3]), 2-{5-methylthienyl}diphenylphosphine (−18.7 ppm) and 2-{*N*-methylpyrrolyl}diphenylphosphine (−29.3 ppm) suggests that the electron donor ability of the aryl substituents increases from phenyl, to 5-methylthienyl, to *N*-methylpyrrolyl. From the view of group electronegativities of the heteroatom of thienyl and pyrrolyl compared to phenyl, the observed trend is in apparent contradiction. Studies of quarterization kinetics by Allen et al. has shown that diphenyl-2-thienylphosphine reacts half as fast as does triphenylphosphine, indicating that the thienyl substituent behaves as a stronger electron withdrawing substituent than phenyl [22]. However, as thienyl, and pyrrolyl, are classified as 'π-excessive' systems, these studies suggest that electron density is returned to phosphorus via the π-system by pπ–dπ interactions. Electron-withdrawing or -donating abilities of aryl and heteroaryl sustituents involves both σ (inductive) and π (resonance) properties [22]. Cone angles also affect ^{31}P NMR chemical shifts [13b]. For example, the phenyl groups in triphenylphosphine are more electron-withdrawing than the isopropyl groups in triisopropylphosphine, yet the phosphorus centre in the latter is more deshielded than in the former. This is due to the increase in cone angle from 145° in triphenylphosphine to 160° in triisopropylphosphine [23]. An analogous type of effect is presumed to account for the differences in ^{31}P chemicals shifts for 2-{5-methylthienyl}diphenylphosphine (−18.7 ppm) and 2-{5-methylthienyl}-diisopropylphosphine (1.2 ppm); and 2-{*N*-methylpyrrolyl}diisopropylphosphine) (−18.3 ppm) and 2-{*N*-methylpyrrolyl}diphenylphosphine (−29.3 ppm). Upon coordination with platinum, the phosphorus is deshielded in each of the complexes.

4. Supplementary material

Further details of the crystal structure investigations are available on request from The Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, on quoting the depository number CCDC-136338 (**1**), the names of the authors, and the journal citation.

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