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C–H and N–H activation by Pt(0) in N- and O-heteroaromatic compounds

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Abstract

The reactions of $[Pt(PEt_3)_4]$ with various azoles afforded platinum(II) hydride complexes of the type *trans*-$[PtH(1\text{-azolyl})(PEt_3)_2]$, where azolyl = indolyl (**1**), imidazolyl (**2**), benzimidazolyl (**3**), pyrazolyl (**4**) and indazolyl (**5**), by oxidative insertion of the metal centre into the N–H bonds of the respective azoles. Pyrrole was much less reactive. Complexes *trans*-$[PtH(R)(PEt_3)_2]$, where R = 2-furyl (**6**), 2-benzoxazolyl (**7**) and 2-benzothiazolyl (**8**) were prepared via C–H bond activation. For benzothiazole, insertion into the C–S bond did not occur. Analogous C–H activation products with 1-methylpyrrole and dibenzofuran could not be isolated.

Keywords: Platinum hydrides; Oxidation; C–H activation; N–H activation; NMR

1. Introduction

The removal of sulfur (as hydrogen sulfide) and nitrogen (as ammonia) by hydrotreating is practiced on a large scale in the petroleum industry in order to meet stringent environmental regulations on fuel emissions. Generally, unsaturated heterocyclic rings are the most difficult to treat and remove. While sulfur has received the most attention because of its relatively high concentration, hydrodenitrogenation and hydrodeoxygenation processes compete with hydrodesulfurization in the consumption of hydrogen gas. The importance of model systems for C-heteroatom cleavage is crucial to the understanding and subsequent development of improved processes for the removal of heteroatoms [1]. Studies into the activation of C–S bonds in aromatic thiophene and thiophene-like molecules with homogenous metal complexes have been undertaken in order to gain understanding into the role of the metal in heterogeneous systems [2]. Several examples of six-membered thiaplatinacycles, derived from C–S insertion by platinum(0) into thiophenic substrates, have been reported in the literature [3]. The activation of C–N and C–O bonds, in pyrroles and furans, respectively, is expected to be much more difficult due to their greater bond strength in comparison to the C–S bond of thiophene. A C–N bond activation of pyrrole by an iridium complex has been reported by Muller et al. [4]. The insertion of a platinum(0) fragment into the strong C–O bond of benzofuran has been achieved by Sweigart and co-workers [5] when the benzofuran is activated by coordination of a $Mn(CO)_3^+$ group to benzofuran's carbocyclic ring.

While studying C–S activations of platinum(0) with thiophenic substrates such as 2,2′-bithiophene and 2-(2-thienyl)-1-methylpyrrole, we found C–H activation to be a competing process (Scheme 1); C–S activation produced thiaplatinacycles, while C–H activation led to the formation of *trans* bisphosphine platinum(II) hydrides [6].

The activation and functionalization of C-heteroatom bonds, as well as C–H and C–C bonds in homogeneous solutions, are also of importance in organic synthesis as it could lead to the design of new processes for the utilization of hydrocarbons and other organic molecules like sulfides [7–9]. We thus became interested in extending our studies of platinum(0) oxidative addition reactions of thiophenes [6] to include other aromatic π-excessive heterocycles, such as furan and related mole-

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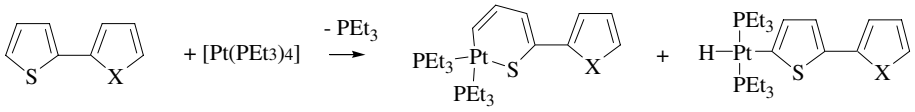


Scheme 1.

cules, to see if analogous reactions occur. As only a few examples of N–H activation of aromatic heterocycles have been reported for platinum(0) [10,11], we also wanted to do a more comprehensive and systematic study of N–H activation in pyrrole-like molecules. Therefore, the reactions of zerovalent platinum with azoles such as pyrrole, 1-methylpyrrole, indole, imidazole, benzimidazole, pyrazole and indazole were investigated. NMR spectroscopy was used to solve structures and to study compositions of complexes in solution.

2. Experimental

2.1. General

All reactions were carried out using standard Schlenk techniques under dry nitrogen. Solvents were dried and distilled before use. Pyrrole and 1-methylpyrrole were freshly distilled before use. 2-Methylbenzothiazole was prepared by adapting a method from the literature [12]. All other chemicals were used as received. $[Pt(PEt_3)_4]$ was prepared according to a previously reported procedure [13]. NMR spectra were recorded on a Bruker ARX-300 (7.0 T) operating on 1D WIN NMR and 2D WIN NMR release 6.0 Software. Chemical shifts are reported as δ values in parts per million relative to the deuterated solvent. For deuterated chloroform, the ^1H NMR spectra were calibrated at 7.240 ppm and the ^{13}C spectra at 77.00 ppm. ^{31}P NMR spectra were referenced to the deuterated lock solvent, which had been previously referenced to 85% H_3PO_4. Fast atom bombardment mass spectra (FAB-MS) were recorded on a VG 7070-E instrument (Xe beam). Melting points were determined using a Kofler hot stage microscope and are uncorrected.

2.2. Preparation of Pt(II) complexes

2.2.1. Preparation of trans-[PtH(1-indolyl)(PEt$_3$)$_2$] (1)

A solution of 1.72 mmol of $[Pt(PEt_3)_4]$ in 5 mL of toluene was added to a solution of 0.267 g (2.28 mmol) of indole in 2 mL toluene under nitrogen at room temperature. An immediate decolouration of the orange $[Pt(PEt_3)_4]$ solution occurred. The mixture was stirred for a further 10 min at room temperature, after which the solvent was removed in vacuo. The residue obtained was washed with hexane (2×1 mL) and dried in vacuo. A white waxy solid, **1**, was obtained, which slowly adopted a green/blue tinge. The compound also developed a blue colour whilst standing in $CDCl_3$. Yield: 0.8 g (85%). Calc. for $C_{20}H_{37}NP_2Pt$ (548.55): C, 43.79; H, 6.80; N, 2.55. Found: C, 43.45; H, 6.84; N, 2.53%. ^1H NMR (300.135 MHz, $CDCl_3$, 25 °C): $\delta = -15.660$ (t, $^2J_{P,H} = 15.7$ Hz, $^1J_{Pt,H} = 945$ Hz, 1 H, Pt–H), 1.006 (m, CH_3, 18 H), 1.536 (m, CH_2, 12 H), 6.501 (m, C(3)–H, 1 H), 6.850 (m, C(4)–H, 1 H), 6.910 (m, C(6)–H, 1 H), 7.155 (m, $^3J_{Pt,H} = 13.8$ Hz, C(2)–H, 1 H), 7.365 (d br, $^3J_{H,H} = 7.8$ Hz, C(7)–H, 1 H), 7.612 (m, C(5)–H, 1 H). ^{13}C NMR (121.496 MHz, $CDCl_3$, 25 °C): $\delta = 8.38$ ($^3J_{Pt,C} = 30.6$ Hz, CH_3), 17.40 (m, CH_2), 98.98 ($^3J_{Pt,C} = 26.0$ Hz, C(3)), 114.89 ($^3J_{Pt,C} = 20.5$ Hz, C(7)), 115.64 (C(6)), 116.90 (C(4)), 119.14 (C(5)), 130.36 (C(3a)), 136.48 ($^2J_{Pt,C} = 24.2$ Hz, C(2)), 145.42 (C(7a)). ^{31}P NMR (75.469 MHz, $CDCl_3$, 25 °C): $\delta = 22.62$ ($^1J_{Pt,P} = 2715$ Hz). FAB-MS: accurate mass calc. 548.2049; accurate mass found 547.1971; *m/z*: 547 ($M^+ - H$, 47%), 432 ($M^+ - C_8H_5N$, 100%), 429 ($M^+ - PEt_3$, 93%), 399 ($M^+ - PEt_3 - C_2H_6$, 36%), 371 ($M^+ - PEt_3 - 2Et$, 23%), 341 ($M^+ - PEt_3 - 2Et - C_2H_6$, 18%), 284 ($PtPEt_2^+$, 8%), 255 ($PtPEt^+$, 5%), 135 ($HOPEt_3^+$, 24%), 119 ($HPEt_3^+$, 21%); m.p.: 53–55 °C.

2.2.2. Preparation of trans-[PtH(1-imidazolyl)(PEt$_3$)$_2$] (2)

Compound **2**, a white solid, was prepared by combining 1.95 mmol of $[Pt(PEt_3)_4]$ in 5 mL of toluene and 0.174 g (2.28 mmol) of imidazole in 2 mL toluene in the same manner as described for **1**. Yield: 0.7 g (72 %). calc for $C_{15}H_{34}N_2P_2Pt$ (499.48): C, 36.07; H, 6.86; N, 5.61. Found: C, 36.08; H, 6.80; N, 5.43%. ^1H NMR (300.135 MHz, $CDCl_3$, 25 °C): $\delta = -16.326$ (t, $^2J_{P,H} = 15.5$ Hz, $^1J_{Pt,H} = 966$ Hz, 1 H, Pt–H), 1.018 (m, CH_3, 18 H), 1.615 (m, CH_2, 12 H), 6.721 (br, $^3J_{Pt,H} = 11.5$ Hz, C(5)–H, 1 H), 7.133 (s br, C(2)–H, 1 H), 7.213 (br, $^3J_{Pt,H}$ unresolved, C(4)–H, 1 H). ^{13}C NMR (121.496 MHz, $CDCl_3$, 25 °C): $\delta = 8.36$ ($^3J_{Pt,C} = 30.5$ Hz, CH_3), 17.65 (m, CH_2), 125.10 ($^2J_{Pt,C} = 21.5$ Hz, C(5)), 127.45 ($^3J_{Pt,C} = 30.6$ Hz, C(4)), 143.26 ($^2J_{Pt,C} = 26.9$ Hz, C(2)). ^{31}P NMR (75.469 MHz, $CDCl_3$, 25 °C): $\delta = 21.65$ ($^1J_{Pt,P} = 2705$ Hz). FAB-MS: accurate mass calc.: 499.1845; accurate mass found: 498.1766; *m/z*: 498 ($M^+ - H$, 58%), 432 ($M^+ - C_4H_4N$, 88%), 403 ($HPt(PEt_3)_2^+ - Et$, 31%), 374 ($HPt(PEt_3)_2^+ - 2Et$, 29%), 345 ($HPt(PEt_3)_2^+ - 3Et$, 24%), 313 ($PtPEt_3^+$, 25%), 284 ($(PtPEt_2)^+$, 13%), 256 ($PtPEt_2^+ - C_2H_4$, 9%), 135 ($(HOPEt_3)^+$, 100%), 119 ($HPEt_3^+$, 34%); m.p.: 47–50 °C.

*2.2.3. Preparation of trans-[PtH(1-benzimidazolyl)(PEt$_3$)$_2$] (**3**)*

By a procedure similar to that described for **2**, complex **3** was obtained from 1.25 mmol of [Pt(PEt$_3$)$_4$] and 0.154 g (1.30 mmol) benzimidazole. Yield: 0.6 g (87%). Calc. for $C_{19}H_{36}N_2P_2Pt$ (549.54): C, 41.53; H, 6.60; N, 5.10. Found: C, 41.44; H, 6.52; N, 4.99. ^{1}H NMR (300.135 MHz, $CDCl_3$, 25 °C): $\delta = -15.831$ (t, $^2J_{P,H} = 15.3$ Hz, $^1J_{Pt,H} = 989$ Hz, 1 H, Pt–H), 0.992 (m, CH_3, 18 H), 1.546 (m, CH_2, 12 H), 7.025 (m, C(4)–H, C(7)–H, 2 H), 7.455 (m, C(5)–H or C(6)–H, 1 H), 7.710 (m, C(5)–H or C(6)–H, 1 H), 7.710 (m, C(2)–H, 1 H). ^{13}C NMR (121.496 MHz, $CDCl_3$, 25 °C): $\delta = 8.33$ ($^3J_{Pt,C} = 30.5$ Hz, CH_3), 17.66 (m, CH_2), 114.49 ($^4J_{Pt,C} = 17.1$ Hz, C(6)), 118.21 (C(5)), 119.06 (C(4), C(7)), 145.34 (C(3a)), 148.18 (C(7a)), 150.51 ($^2J_{Pt,C} = 26.4$ Hz, C(2)). ^{31}P NMR (75.469 MHz, $CDCl_3$, 25 °C): $\delta = 22.03$ ($^1J_{Pt,P} = 2691$ Hz). FAB-MS: accurate mass calc.: 549.2002; accurate mass found: 550.2079; *m/z*: 550 ($M^+ + H$, 40%), 432 ($M^+ + H - PEt_3$, 100%), 375 ($M^+ + H - PEt_3 - Et - C_2H_4$, 18%), 347 ($M^+ + H - PEt_3 - Et - 2C_2H_4$, 16%), 314 ($HPtPEt_3^+$, 11%), 283 ($PtPEt_3^+ - C_2H_6$, 7%), 255 ($PtPEt_3^+$, 4%), 119 ($HPEt_3^+$, 27%); m.p.: 82–85 °C.

*2.2.4. Preparation of trans-[PtH(1-pyrazolyl)(PEt$_3$)$_2$] (**4**)*

A toluene solution of 1.55 mmol of [Pt(PEt$_3$)$_4$] and 0.107 g (1.57 mmol) of pyrazole was used to prepare compound **4**, a yellow oil. Yield: 0.5 g (65%). Calc. for $C_{15}H_{34}N_2P_2Pt$ (499.48): C, 36.07; H, 6.86; N, 5.61. Found: C, 36.37; H, 7.00; N, 5.42%. ^{1}H NMR (300.135 MHz, $CDCl_3$, 25 °C): $\delta = -17.011$ (t, $^2J_{P,H} = 15.6$ Hz, $^1J_{Pt,H} = 942$ Hz, 1 H, Pt–H), 0.945 (m, CH_3, 18 H), 1.536 (m, CH_2, 12 H), 5.835 (m, C(4)–H, 1 H), 6.764 (d, $^3J_{H,H} = 1.9$ Hz, $^3J_{Pt,H}$ unresolved, C(5)–H, 1 H), 7.338 (m, C(3)–H, 1 H). ^{13}C NMR (121.496 MHz, $CDCl_3$, 25C): $\delta = 7.74$ (CH_3), 17.11 (m, CH_2), 102.30 ($^3J_{Pt,C} = 25.2$ Hz, C(4)), 135.36 ($^2J_{Pt,C} = 50.3$ Hz, C(5)), 137.44 ($^3J_{Pt,C} = 46.7$ Hz, C(3)). ^{31}P NMR (75.469 MHz, $CDCl_3$, 25C): $\delta = 22.41$ ($^1J_{Pt,P} = 2744$ Hz). FAB-MS: accurate mass calc.: 499.1845; accurate mass found: 499.1853; *m/z*: 499 (M^+, 18%), 430 ($M^+ - C_3H_4N_2H$, 100%), 402 ($M^+ - C_3H_4N_2H - Et$, 28%), 374 ($M^+ - C_3H_4N_2H - 2C_2H_4$, 28%), 347 ($M^+ - C_3H_4N_2H - 2C_2H_4 - C_2H_3$, 25%), 314 ($HPtPEt_3^+$, 20%), 283 ($PtPEt_3^+ - C_2H_6$, 13%), 255 ($PtPEt^+$, 9%), 135 ($HOPEt_3^+$, 15%), 119 ($HPEt_3^+$, 20%).

*2.2.5. Preparation of trans-[PtH(1-indazolyl)(PEt$_3$)$_2$] (**5**)*

A solution of 1.60 mmol of [Pt(PEt$_3$)$_4$] was added to a suspension of 0.188 g (1.59 mmol) of indazole in 5 mL of toluene. The solution decolourized and was stirred at room temperature for 1 h, after which the solvent was removed in vacuo. The resultant white solid, **5**, was washed with hexane and dried in vacuo. Yield: 0.5 g (61%). Calc. for $C_{19}H_{36}N_2P_2Pt$ (549.54): C, 41.53; H, 6.60; N, 5.10. Found: C, 41.80; H, 6.54; N, 5.15%. **5a** ^{1}H NMR (300.135 MHz, $CDCl_3$, 25 °C): $\delta = -16.163$ (t, $^2J_{P,H} = 15.3$ Hz, $^1J_{Pt,H} = 958$ Hz, 1 H, Pt–H), 0.966 (m, CH_3), 1.532 (m, CH_2), 6.837 (t, $^3J_{H,H} = 7.1$ Hz, C(5)–H, 1 H), 7.040 (t, $^3J_{H,H} = 7.6$ Hz, C(6)–H, 1 H), 7.500 (d, $^3J_{H,H} = 8.1$ Hz, C(7)–H, 1 H), 7.663 (d, $^3J_{H,H} = 8.1$ Hz, C(4)–H, 1 H), 8.125 (s, C(3)–H, 1 H). ^{13}C NMR (121.496 MHz, $CDCl_3$, 25 °C): $\delta = 8.35$ ($^3J_{Pt,C} = 30.5$ Hz, CH_3), 17.84 (m, CH_2), 113.44 ($^3J_{Pt,C} = 17.1$ Hz, C(7)), 116.99 (C(5)), 119.89 (C(4)), 121.51 (C(6)), 125.95 (C(3a)), 132.73 ($^3J_{Pt,C} = 34.1$ Hz, C(3)), 148.86 (C(7a)). ^{31}P NMR (75.469 MHz, $CDCl_3$, 25 °C): $\delta = 22.98$ ($^1J_{Pt,P} = 2729$ Hz). **5b** ^{1}H NMR (300.135 MHz, $CDCl_3$, 25 °C): $\delta = -16.821$ (t, $^2J_{P,H} = 15.3$ Hz, $^1J_{Pt,H} = 958$ Hz, 1 H, Pt–H), 0.966 (m, CH_3), 1.532 (m, CH_2), 6.616 (t, $^3J_{H,H} = 7.1$ Hz, CH, 1 H), 6.813 (t, $^3J_{H,H} = 7.1$ Hz, CH, 1 H), 7.365 (d, $^3J_{H,H} = 8.2$ Hz, CH, 1 H), 7.470 (d, $^3J_{H,H} = 8.1$ Hz, CH, 1 H), 8.125 (s, C(3)–H, 1 H). ^{13}C NMR (121.496 MHz, $CDCl_3$, 25 °C): $\delta = 8.28$ ($^3J_{Pt,C}$ unresolved, CH_3), 17.84 (m, CH_2), 113.65 (CH), 117.61 (CH), 119.18 (CH), 122.42 (CH), 132.48 (CH), *ipso*-C unresolved. ^{31}P NMR (75.469 MHz, $CDCl_3$, 25C): $\delta = 21.80$ ($^1J_{Pt,P} = 2733$ Hz). FAB-MS: accurate mass calc.: 549.2002; accurate mass found: 549.2002; *m/z*: 549 (M^+, 62%), 518 ($M^+ - H - C_2H_6$, 10%), 491 ($M^+ - C_2H_6 - Et$, 5%), 462 ($M^+ - C_2H_6 - 2Et$, 9%), 431 ($M^+ - PEt_3$ or $M^+ - C_7H_6N_2$, 24%), 428 ($M^+ - 3H - C_7H_6N_2$, 98%), 399 ($M^+ - 3H - C_7H_6N_2 - Et$, 50%), 370 ($M^+ - 3H - C_7H_6N_2 - 2Et$, 41%), 313 ($PtPEt_3^+$, 28%), 283 ($PtPEt_3^+ - C_2H_6$, 21%), 255 ($PtPEt^+$, 11%), 135 ($HOPEt_3^+$, 100%), 119 ($HPEt_3^+$, 43%); m.p.: 192–194 °C.

*2.2.6. Preparation of trans-[PtH(2-furyl)(PEt$_3$)$_2$] (**6**)*

To a solution of 0.155 g (2.23 mmol) of furan in 10 mL of toluene was added a solution of 1.13 mmol of [Pt(PEt$_3$)$_4$] in 5 mL of toluene. The mixture was heated to reflux for 16 h. The resulting dark brown solution was placed under vacuum and the solvent removed to give **6** as a brown oil. Yield: 0.4 g (71%). Calc. for $C_{16}H_{34}OP_2Pt$ (499.47): C, 38.48; H, 6.86. Found: C, 38.24; H, 7.00%. ^{1}H NMR (300.135 MHz, $CDCl_3$, 25 °C): $\delta = -7.059$ (t, $^2J_{P,H} = 17.8$ Hz, $^1J_{Pt,H} = 666$ Hz, 1 H, Pt–H), 1.012 (m, CH_3, 18 H), 1.655 (m, CH_2, 12 H), 5.794 (d, $^3J_{H,H} = 3.2$ Hz, C(3)–H, 1 H), 6.268 (m, C(4)–H, 1 H), 7.651 (m, C(5)–H, 1 H). ^{13}C NMR (121.496 MHz, $CDCl_3$, 25 °C): $\delta = 8.40$ ($^3J_{Pt,C} = 31.4$ Hz, CH_3), 17.90 (m, CH_2), 110.65 (C(4)), 111.42 (C(3)), 142.22 (C(5)), C(2) not resolved. ^{31}P NMR (75.469 MHz, $CDCl_3$, 25 °C): $\delta = 20.27$ ($^1J_{Pt,P} = 2695$ Hz). FAB-MS: accurate mass calc.: 499.1945; accurate mass found: 498.1767; *m/z*: 498 ($M^+ - H$, 16%), 467 ($M^+ - H - C_2H_6$, 5%), 431 ($M^+ - H - C_4H_3O$ or $Pt(PEt_3)_2^+$, 39%), 402 ($Pt(PEt_3)_2^+ - Et$, 27%), 373 ($Pt(PEt_3)_2^+ - 2Et$, 19%), 344

($Pt(PEt_3)_2^+ - 3Et$, 13%), 314 ($HPtPEt_3^+$, 11%), 284 ($PtPEt_2^+$, 10%), 255 ($PtPEt^+$, 7%), 135 ($HOPEt_3^+$, 100%), 119 ($HPEt_3^+$, 33%).

2.2.7. Preparation of trans-[PtH(2-benzoxazolyl)(PEt_3)$_2$] (7)

A solution of 0.196 g (1.65 mmol) benzoxazole and 1.62 mmol [$Pt(PEt_3)_4$] was refluxed in toluene for 40 h. The colour of the solution changed gradually from yellow to red. After removal of the solvent in vacuo, a red oil, **7**, was isolated. Yield: 0.8 g (90%). Calc. for $C_{19}H_{35}NOP_2Pt$ (550.52): C, 41.45; H, 6.41; N, 2.54. Found: C, 41.33; H, 6.24; N, 2.48%. ^{1}H NMR (300.135 MHz, $CDCl_3$, 25 °C): $\delta = -7.490$ (t, $^2J_{P,H} = 17.3$ Hz, $^1J_{Pt,H} = 682$ Hz, 1 H, Pt–H), 1.000 (m, CH_3, 18 H), 1.654 (m, CH_2, 12 H), 6.982 (t, $^3J_{H,H} = 6.1$ Hz, C(6)–H, 1 H), 7.050 (t, $^3J_{H,H} = 7.1$ Hz, C(5)–H, 1 H), 7.321 (d, $^3J_{H,H} = 6.1$ Hz, C(4)–H, 1 H), 7.506 (d, $^3J_{H,H} = 7.1$ Hz, C(7)–H, 1 H). ^{13}C NMR (121.496 MHz, $CDCl_3$, 25 °C): $\delta = 8.51$ ($^3J_{Pt,C} = 29.4$ Hz, CH_3), 19.21 (m, CH_2), 108.62 ($^4J_{Pt,C} = 55.7$ Hz, C(4)), 116.99 (C(7)), 120.46 (C(6)), 121.33 (C(5)), 144.2 ($J_{Pt,C} = 44.9$ Hz, *ipso*-C), 152.81 ($J_{Pt,C} = 24.2$ Hz, *ipso*-C). ^{31}P NMR (75.469 MHz, $CDCl_3$, 25 °C): $\delta = 20.34$ ($^1J_{Pt,P} = 2650$ Hz). FAB-MS: accurate mass calc.: 550.1842; accurate mass found: 551.1920; *m/z*: 551 ($M^+ + H$, 76%), 428 ($M^+ - 3H - C_7H_5NO$, 58%), 402 ($M^+ - C_7H_5NO - C_2H_6$, 44%), 398 ($M^+ - 4H - C_7H_5NO - C_2H_6$, 40%), 374 ($M^+ - C_7H_5NO - 2Et$ or $HPt(PEt_3)^+$, 34%), 370 ($M^+ - 4H - C_7H_5NO - 2Et$, 40%), 344 ($Pt(PEt_3)_2^+ - 3Et$, 19%), 314 ($HPtPEt_3^+$, 17%), 284 ($PtPEt_2^+$, 10%), 135 ($OPEt_3^+$, 100%), 120 ($C_7H_5NOH^+$, 13%), 119 ($HPEt_3^+$, 36%).

2.2.8. Preparation of trans-[PtH(2-benzothiazolyl)(PEt_3)$_2$] (8)

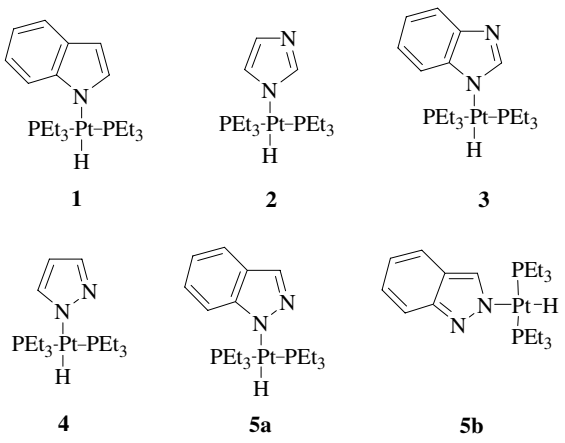
Benzothiazole (0.70 mL, 6.4 mmol) was added to a solution of 3 mmol of [$Pt(PEt_3)_4$] in 20 mL toluene. The mixture was refluxed for 4 1/2 h and then stirred at room temperature overnight. After work-up, a red oil, **8**, was obtained. Yield: 1.3 g (76 %). Calc. for $C_{19}H_{35}NP_2SPt$ (566.59): C, 40.28; H, 6.23; N, 2.47. Found: C, 40.15; H, 6.13; N, 2.39%. ^{1}H NMR (300.135 MHz, $CDCl_3$, 25 °C): $\delta = -7.916$ (t, $^2J_{P,H} = 17.7$ Hz, $^1J_{Pt,H} = 694$ Hz, 1 H, Pt–H), 0.959 (m, CH_3, 18 H), 1.521 (m, CH_2, 12 H), 7.119 (dt, $^3J_{H,H} = 7.6$ Hz, $^4J_{H,H} = 1.1$ Hz C(5)–H, 1 H), 7.590 (d, $^3J_{H,H} = 7.6$ Hz, C(7)–H, 1 H), 7.700 (dt, $^3J_{H,H} = 7.5$ Hz, $^4J_{H,H} = 1.1$ Hz C(6)–H, 1 H), 7.748 (d, $^3J_{H,H} = 7.8$ Hz, C(4)–H, 1 H). ^{13}C NMR (121.496 MHz, $CDCl_3$, 25 °C): $\delta = 8.14$ ($^3J_{Pt,C} = 28.3$ Hz, CH_3), 18.41 (m, CH_2), 117.27 (C(2)), 120.04 (C(7)), 120.23 (C(4)), 121.67 (C(6)), 123.92 (C(5)), 137.19 (C(7a)), 155.41 (C(3a)). ^{31}P NMR (75.469 MHz, $CDCl_3$, 25 °C): $\delta = 15.32$ ($^1J_{Pt,P} = 2585$ Hz). FAB-MS: accurate mass calc.: 566.1613; accurate mass found: 566.1614; *m/z*: 566 (M^+, 62%), 429 ($M^+ - 2H - C_7H_5NS$, 39%), 401 ($M^+ - H - C_7H_5NO - Et$, 22%), 398 ($M^+ - 4H - C_7H_5NS - C_2H_6$, 40%), 374 ($M^+ - C_7H_5NS - 2Et$ or $HPt(PEt_3)^+$, 34%), 371 ($M^+ - H - C_7H_5NS - Et - C_2H_6$, 16%), 314 ($HPtPEt_3^+$, 13%), 285 ($HPtPEt_2^+$, 7%), 255 ($PtPEt^+$, 5%), 135 ($OPEt_3^+$ or $C_7H_5NS^+$, 100%), 119 ($HPEt_3^+$, 51%).

3. Results and discussion

3.1. Reactions of tetrakis(triethylphosphine)platinum(0) resulting in N–H activation

Under mild conditions tetrakis(triethylphosphine)platinum(0), [$Pt(PEt_3)_4$], reacted with indole, imidazole, benzimidazole, pyrazole and indazole, respectively, by oxidatively inserting a $Pt(PEt_3)_2$ moiety into their respective N–H bonds. Platinum(II) hydride complexes of the type *trans*-[PtH(1-azolyl)(PEt_3)$_2$] (**1**–**5**) were obtained (Scheme 2). These oxidative addition reactions were complete within minutes at room temperature; decolouration of the orange/yellow [$Pt(PEt_3)_4$] solutions occurred immediately upon addition of the azole.

Hydridoamido complexes of the platinum group metals have previously been prepared and characterized [14], but the syntheses of these complexes generally followed various routes that did not involve oxidative insertion of a metal centre into the N–H bond. Some examples are: the ligand replacement between *trans*-[$PtH(NO_2)(PEt_3)_2$] and NaNHPh [15], the reaction of *trans*-[$PtH(NH_3)(PCy_3)_2$]ClO_4 with amide [16], the reduction reaction of *cis*-[$PtCl_2(PPh_3)_2$] and five-substituted tetrazoles in the presence of hydrazine [17]. Intramolecular oxidative addition of an N–H bond to rhodium(I) and iridium(I) has been reported [18], but a chelating ligand was required to facilitate the insertion [19]. Milstein and co-workers [20] oxidatively inserted an iridium(I) moiety into an N–H bond of ammonia. A similar reaction with aniline [21] gave a stable *cis*-hydride complex capable of catalyzing the amination of



Scheme 2.

norbornylene. The analogous platinum(II) and palladium(II) complexes could not be prepared. Oxidative addition of N–H groups to the [Ru(dmpe)$_2$] fragment, where dmpe = 1,2-bis(dimethylphosphino)ethane, has been found to occur with various azoles. [RuH(naphthyl)(dmpe)$_2$] reacts under heating with pyrrole, but at room temperature with pyrazole, to yield octahedral ruthenium(II) hydride complexes [22]. Reactions at the N–H bonds of imides (e.g. succinimide) with zerovalent platinum or palladium precursors gave platinum(II) imide hydride complexes [23]. Merola and Ladipo [24] later reported the activation of heterocyclic amine N–H bonds of pyrrole and indole by [Ir(η^4-cod)(PMe$_3$)$_3$]Cl. Indeed, only a couple of examples of N–H bond activation for aromatic heterocycles by platinum(0) have been reported in the literature. Maitlis et al. [11] reported that tris(trialkylphosphine)platinum(0), where alkyl = Me or Et, reacts with carbazole to form a platinum(II) hydride with the phosphines in *trans* positions. The only other example we could find of N–H bond activation by platinum(0) is attributed to Stone and coworkers [10], who reacted bis(tricyclohexylphosphine)platinum(0) with pyrrole.

The amount of structural information obtained as a result of characteristic domains and informative coupling constants for multinuclear NMR resonances of [Pt(H)(R′) (PEt$_3$)$_2$] systems (R′ = N- or C-bound heteroaryl ligand) cannot be over emphasized. The high-field region of the ^{1}H NMR spectrum was particularly useful, as it is a region free of resonance signals other than those arising from hydride protons. The hydride ^{1}H NMR data and the ^{31}P NMR data for the complexes are summarized in Table 1. In each case the hydride proton gives rise to a triplet pattern with accompanying satellites due to coupling to ^{195}Pt, indicative of a *trans* bisphosphine geometry [25].

The chemical shifts of the hydride proton in the N-bound complexes [Pt(H)(R′)(PR$_3$)$_2$], where R′ = pyrrolyl, R = Cy [10] and R′ = 5-phenyltetrazolato, 5-bromotetrazolato and 5-chlorotetrazolato and R = Ph [17] lie between −15.6 and −16.6 ppm. When the R′ group is derived from succinimide, phthalimide, saccharin and parabanic acid and R = Ph, the hydride proton resonates at approximately −14.0 to −15.7 [23]. The complex *trans*-[PtH(1-carbazolyl)(PEt$_3$)$_2$], which is analogous to complexes **1**–**5**, has similar NMR data reported [11], viz. $\delta_H = -14.4$, $^1J_{Pt,H} = 940$ Hz, $^2J_{P,H} = 17$ Hz. The chemical shifts of the hydride protons in complexes **1**–**5** vary from −15.6 to −17.0 ppm (Table 1) and clearly fall into the range where the ligand *trans* to the hydride is N-bound. The hydride coupling constants for **1**–**5** also correspond to the literature values of $^2J_{P,H}$ and $^1J_{Pt,H}$ for N-bound [Pt(H)(R)(PR$_3$)$_2$] complexes, which are in the range of 10.2–17.0 and 940–970 Hz, respectively [11,17,23]. The ^{31}P NMR spectrum for each of complexes **1**–**5** consists of a single resonance peak accompained by satellites, indicating equivalent phosphine moieties in mutually *trans* positions. The magnitude of the $^1J_{Pt,P}$ coupling constants for complexes **1**–**5** (∼2690–2750 Hz) further supports the *trans* geometry, and compares favourably with the value of 2693 Hz reported for *trans*-[PtH(1-carbazolyl)(PEt$_3$)$_2$] [11]. The chemical shift of 22.6 ppm also corresponds to that of complexes **1**–**5** (21.6–23.0).

3.1.1. Reactions of tetrakis(triethylphosphine)platinum(0) with indole and pyrrole

Although we were able to prepare, purify and analyse the platinum(II) indolyl hydride complex, **1**, and the analogous carbazolyl complex has been reported previously [11], the corresponding pyrrolyl complex could not be obtained. Despite prolonged reflux of a toluene solution containing the zerovalent platinum precursor and pyrrole, the oxidative addition reaction did not proceed to any appreciable extent. Samples of the reaction mixture were periodically removed and analysed by NMR spectroscopy. An extremely low intensity triplet at −16.285 ppm, with coupling constants $^1J_{Pt,H} = 922$ Hz and $^2J_{P,H} = 15.7$ Hz, was observed in the ^{1}H NMR spectrum, while a singlet peak at 22.3 ppm with coupling constant $^1J_{Pt,P} = 2734$ Hz was obtained in the ^{31}P NMR spectrum. These data are comparable to NMR data

Table 1
Summary of pertinent NMR data for *trans*-[PtH(R)(PEt$_3$)$_2$] complexes[a]

Complex	R	High field ^{1}H NMR			^{31}P NMR	
		δ (ppm)	$^2J_{P,H}$ (Hz)	$^1J_{Pt,H}$ (Hz)	δ (ppm)	$^1J_{Pt,P}$ (Hz)
1	1-Indolyl	−15.660	15.7	945	22.62	2715
2	1-Imidazolyl	−16.326	15.5	966	21.65	2705
3	1-Benzimidazolyl	−15.831	15.3	989	22.03	2691
4	1-Pyrazolyl	−17.011	15.6	942	22.41	2744
5a	1-Indazoyl	−16.163	15.3	958	22.98	2729
5b	2-Indazoyl	−16.821	15.3	958	21.80	2733
6	2-Furyl	−7.059	17.8	666	20.27	2695
7	2-Benzoxazolyl	−7.490	17.3	682	20.34	2650
8	2-Benzothiazolyl	−7.916	17.7	694	15.32	2585

[a] Recorded in $CDCl_3$.

recorded for complexes **1**–**5** (Table 1) and seem to indicate the presence of a very small amount of a N-bound platinum(II) hydride, possibly *trans*-[PtH(1-pyrrolyl)(PEt_3)$_2$]. However, it was not possible to isolate this small amount of hydride product from the reaction mixture containing excess reactants and without direct evidence of the pyrrolyl group, the identity of this hydride remains speculative.

The remarkably different reactivity of pyrrole with [$Pt(PEt_3)_4$] as opposed to indole and carbazole is not readily explained. Structurally, pyrrole and its mono- and di-annelated counterparts, indole and carbazole, appear to be extremely similar; all three contain a five-membered π-excessive aromatic ring with a N–H functional group [26]. The presence of the additional fused benzene rings in indole and carbazole does not sterically prevent the approach of the metal centre, indeed, the reactivity is enhanced rather than diminished. The pK_a value for the NH acid dissociation of carbazole is 17.06, similar to the pK_a of indole (16.97). Pyrrole is only slightly less acidic with a pK_a of 17.5 [27]. On comparing the computed charge on each atom, as determined by a PM3 semi-empirical calculation method and a Polak–Ribiere (conjugate gradient) algorithm [28], the nitrogen atom of pyrrole carries a larger positive value than for indole or carbazole (Fig. 1). The overall charge on each nitrogen atom results from the contribution of a resonance hybrid in which a positive charge resides on the nitrogen atom. In contrast, the NH-hydrogen carries a smaller positive charge in pyrrole than in either indole or carbazole. Hence, there is greater polarization of the N–H bond in pyrrole, and this decreases for indole and carbazole. The charge and NH acidity indicate that the N–H bond is stronger in pyrrole than in carbazole and indole. This partially explains the poorer reactivity with platinum(0) for pyrrole than indole or carbazole. Comparison of the hydride ^{1}H NMR chemical shifts for *trans*-[PtH(R)(PEt_3)$_2$], where R = 1-indolyl (**1**), 1-carbazolyl shows a downfield shift from indolyl to carbazolyl as the degree of annelation increases in the same order.

Stone and co-workers [10] reported that the reaction of bis(tricyclohexylphosphine)platinum(0) with pyrrole at room temperature resulted in the isolation of *trans*-[PtH(1-pyrrolyl)(PCy_3)$_2$] after 40 h. The reactivity of tertiary phosphine complexes of platinum(0), i.e., [$Pt(PR_3)_n$], is determined by the steric and electronic properties of the phosphine, as well as the coordination number, *n*. The two-coordinate [$Pt(PCy_3)_2$] precursor is stabilized by the bulky tricyclohexylphosphine groups, and this 14-valence electron species exhibits enhanced reactivity towards oxidative addition [29]. In contrast, [$Pt(PEt_3)_4$] readily loses one phosphine to yield [$Pt(PEt_3)_3$] (a 16-electron species), but no evidence of the dissociation of a second phosphine to yield [$Pt(PEt_3)_2$] has yet been observed spectroscopically. Two-coordinate [$Pt(PEt_3)_2$] can be generated in situ by the photolysis of the platinum(II) oxalate compound, [$Pt(C_2O_4)(PEt_3)_2$], and subsequent oxidative addition reactions can occur under mild conditions [30].

3.1.2. Reactions of tetrakis(triethylphosphine)platinum(0) with imidazole, benzimidazole, pyrazole and indazole

Azoles with an additional nitrogen atom in the ring, such as imidazole and benzimidazole, are relatively stronger acids (pK_a 14.17 and 12.75, respectively [31]) than pyrrole and indole. The introduction of a pyridinic nitrogen atom increases the heteroaromatic ring's capacity to accept electronic charge. Imidazole and benzimidazole react with [$Pt(PEt_3)_4$] to give hydrides **2** and **3**, respectively. The free azoles both display annular tautomerism in solution, where a proton is rapidly transferred between the two nitrogen atoms. This results in an average NMR signal for protons C(4)–H and C(5)–H of imidazole. Certain imidazole and imidazolyl metal complexes exhibit a similar type of fluxional behaviour (metallotropy) [32]. Complex **2** was found, however, not to be fluxional.

In a similar manner to imidazole and benzimidazole, pyrazole and indazole reacted with [$Pt(PEt_3)_4$] to generate **4** and **5a**, respectively. Pyrazole also exhibits annular tautomerism; the protons at C(3)–H and C(5)–H give rise to a single ^{1}H NMR resonance. Certain metal complexes containing anionic 1-pyrazolyl or neutral monodentate pyrazole ligands also have the 3- and 5-positions equalized by a 1,2-metal shift [33]. Like **2**, complex **4** was not fluxional.

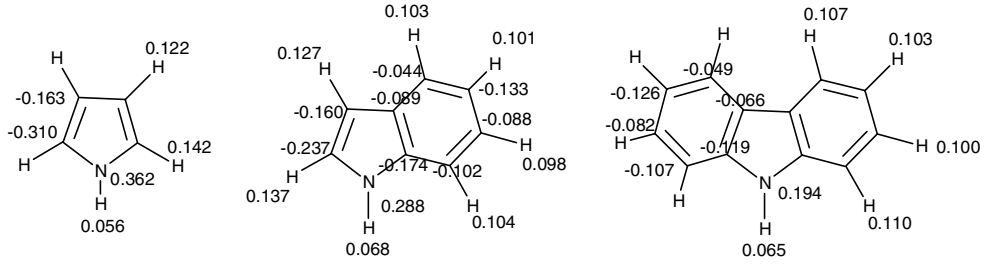


Fig. 1.

The tautomerism of indazole is somewhat different to that of pyrazole, imidazole and benzimidazole (Scheme 3). The equilibrium lies in favour of the 1*H*-indazole structure, although the energy difference between the tautomers is quite small [26]. When indazole is alkylated in the presence of base, a mixture of 1- and 2-alkylindazole is obtained. This type of reactivity is mirrored in the reaction of indazole with $[Pt(PEt_3)_4]$. A small amount of **5b** was obtained in addition to **5a**, in a ratio of 1:8 based on ^1H NMR data.

The ^1H NMR chemical shifts for the hydride protons and the ^{31}P NMR chemical shifts for the imidazolyl (**2**) and pyrazolyl (**4**) complexes are both more upfield than their annelated counterparts, the benzimidazolyl (**3**) and indazolyl (**5a/5b**) complexes, respectively. This follows the same trend found for analogous indolyl, **1**, and carbazolyl [11] complexes and reflects the electron-withdrawing effect of the fused benzene ring. The $^1J_{Pt,H}$ values are smaller for the imidazolyl and pyrazolyl complexes than the corresponding benzimidazolyl and indazolyl complexes, while the $^1J_{Pt,P}$ and $^2J_{P,H}$ values are slightly larger in the same order.

3.1.3. Reactions of tetrakis(triethylphosphine)platinum(0) with 1-methylpyrrole

In the absence of relatively reactive N–H sites, 1-methylpyrrole was expected to undergo C–H activation, rather than C–N insertion. The complex $[Rh(C_5Me_5)(H)Ph(PMe_3)]$ has previously been reported to react with 1-methylpyrrole by C–H activation at the α-carbon to form $[Rh(C_5Me_5)(H)(2\text{-}\{1\text{-methylpyrrolyl}\})(PMe_3)]$ [34]. However, despite heating a mixture of 1-methylpyrrole and $[Pt(PEt_3)_4]$ in toluene for prolonged periods, no oxidative addition product could be isolated.

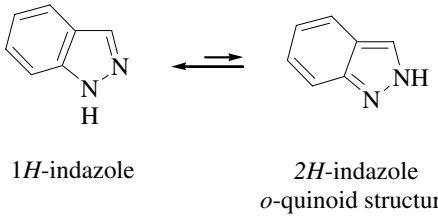
3.1.4. Reactions of tris(triphenylphosphine)platinum(0) with selected azoles

Since N–H activation for the azoles described above was achieved relatively easily by $[Pt(PEt_3)_4]$, it was thought that it would be possible to obtain the analogous triphenylphosphine platinum(II) complexes by employing harsher reaction conditions and longer reaction times, as triphenylphosphine is a weaker base than triethylphosphine. Solutions of tris(triphenylphosphine)platinum(0), $[Pt(PPh_3)_3]$, with imidazole and pyrazole, respectively, were heated in toluene at 60 °C for a week without a platinum(II) hydride azolyl complex being detected by NMR spectroscopy. While $[Pt(PPh_3)_3]$ is not basic enough to effect facile oxidative addition into a N–H bond of an heteraromatic compound, it has been shown to activate the N–H bonds of succinimide, phthalimide (by refluxing for 24 h), saccharin (within minutes at room temperature) and parabanic acid (after several hours at room temperature) [23]. These substrates are stronger nitrogen-donor bases and considerably stronger NH acids (pK_a succinimide = 9.5, pK_a phthalimide = 8.3) [35].

3.2. Reactions of tetrakis(triethylphosphine)platinum(0) resulting in C–H activation

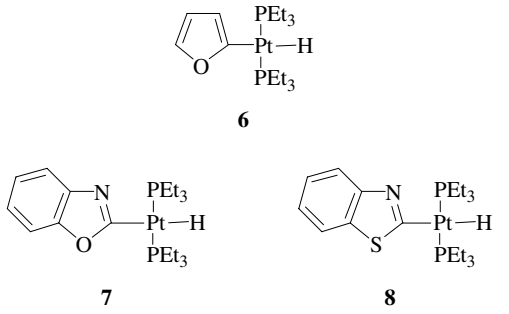
Pre-coordination of a $Mn(CO)_3^+$ metal fragment to the benzene ring of benzofuran activates the C–O bond towards cleavage by a weak nucleophile such as $[Pt(PPh_3)_2(C_2H_4)]$ [5]. In the absence of this "remote activation" of a coordinated metal centre, C–O bond insertion is considerably less favourable than C–S bond cleavage due to the high C–O bond strength, and to the fact that late transition metals prefer bonding to sulfur than to oxygen atoms. The bonds more accessible to oxidative addition by a platinum(0) centre would more likely be the C–H and C–C bonds of the oxygen heterocycle. Generally, both thermodynamic and kinetic factors lead to C–H bonds being more amenable to oxidative addition than C–C bonds [8a,36], the latter usually requiring an additional driving force such as the relief of steric strain [37] or an energy gain from aromatization [38].

When $[Pt(PEt_3)_4]$ was reacted with excess furan under heating, the NMR data of the resultant hydride complex, as for complexes **1**–**5**, indicated a structure of the type *trans*-$[PtH(R')(PEt_3)_2]$. The position of attachment of the platinum to the furyl ring is mostly likely at C(2), to give **6** (Scheme 4), as aromatic heterocycles tend to undergo C–H activation at the α-position with respect to the heteroatom. This position is also the site for lithiation by butyllithium, where the butylate base essentially abstracts the proton from C(2). C–H activation at C(2) of furan was reported for the thermolysis of



1*H*-indazole 2*H*-indazole
o-quinoid structure

Scheme 3.



6 **7** **8**

Scheme 4.

[$Rh(C_5Me_5)(H)Ph(PMe_3)$] in the presence of excess furan [34], With the α-positions blocked in 2,5-dimethylfuran, C–H activation was forced to occur at the β-position. The catalytic C–C coupling of furan to acrylate by palladium(II) has been found to occur via a C–H activation at C(2) although this intermediate was not isolated [39]. Similarly, gold(III) chloride catalyses the coupling of 2-methylfuran to methyl vinyl ketone at C(5) [40]. The π-excessive nature of furan, and the fact that furan has a lower resonance energy than benzene allows for the metal to attach at C(2), whilst benzene does not undergo an analogous reaction under similar conditions. In fact, benzene or toluene is used as the solvent in oxidative addition reactions of this type.

A compound similar to **6** has been reported in the literature, viz. [PtH(2-{5-OOCPh}furyl)(PEt_3)$_2$] [15], prepared from phenyl 2-furoate and *trans*-[PtH(NHPh)(PEt_3)$_2$]. The authors regard this reaction as a C–H activation rather than a process involving deprotonation of the phenyl 2-furoate by the anilide anion followed by coordination of the resultant furyl carbanion to the platinum centre; the driving force probably being the formation of a stronger Pt–C bond which has been shown to be thermodynamically more stable than a Pt–N bond [41]. The ^{1}H hydride and ^{31}P NMR data for this compound ($\delta_H = -6.80$ ppm, t, $^1J_{Pt,H} = 663$ Hz, $^2J_{P,H} = 18$ Hz; $\delta_P = 20.4$, s, $^1J_{Pt,P} = 2690$ Hz) closely resembles that of **6** (Table 1).

In contrast to furan, dibenzofuran, like 1-methylpyrrole, is practically inert towards C–H activation by [$Pt(PEt_3)_4$].

Benzoxazole is similar to the anellated furan, benzo[*b*]furan, but with a pyridine-like nitrogen atom at position 3. It can also be compared to benzimidazole, where an NH group takes the place of the oxygen atom. In a similar manner to that of furan, benzoxazole undergoes a C–H activation with [$Pt(PEt_3)_4$] at the α-position to generate the complex *trans*-[PtH(2-benzoxazolyl)(PEt_3)$_2$], **7** (Scheme 4). Upon coordination of the platinum centre to C(2), the ^{1}H NMR resonance of H(2) in free benzoxazole disappears and a triplet hydride signal is observed at −7.490 ppm. The resonances of the fused benzene ring shift approximately ~0.24 ppm upfield relative to the free ligand. The hydride ^{1}H and ^{31}P NMR data are similar to that of **6**.

The benzothiazole molecule has two possible reactive sites. The C(vinyl)–S bond could be attacked to generate a thiaplatinacycle analogous to that obtained with benzothiophene, where the C(vinyl)–S rather than the C(aryl)–S bond is the preferred site of C–S activation [3a]. Alternatively, a C–H bond activation at C(2) would lead to a hydride complex analogous to that obtained with benzoxazole (**7**). For benzothiazole it was found that the C–H activation is preferred, and the complex *trans*-[PtH(2-benzothiazolyl)(PEt_3)$_2$], **8**, was isolated (Scheme 4). Once again the position of attack was at C(2). When a methyl group was attached at C(2), no evidence of a hydride species could be detected. With the C–H activation site blocked, it was hoped that insertion into the C(vinyl)–S bond could be achieved. It has been shown that, despite the crowding of the α-carbon in 2-methyldibenzothiophene, insertion into the C(vinyl)–S bond has been reported to occur [3d]. However, after heating a solution of [$Pt(PEt_3)_4$] and 2-methylbenzothiazole in toluene at 60 °C for 3 days, no evidence of a thiaplatinacycle was observed. Decomposition of the metal precursor occurred with neither C–S nor C–H activation taking place.

Column chromatography of **8** caused the complex to undergo a change to form a bimetallic bridging hydride species [42] which could not be unambiguously characterized. However, an indication of the nature of the bridging hydride could be gleaned from the NMR data. The ^{1}H NMR spectrum displayed a doublet of doublet of doublet pattern centred at −5.455 ppm and flanked by two sets of ^{195}Pt-satellites. This pattern of three superimposed subspectra arises from the three different isotopomeric combinations of platinum nuclei having different nuclear spins (Pt/Pt 43.8%, ^{195}Pt/Pt 22.4%, Pt/^{195}Pt 22.4% and ^{195}Pt/^{195}Pt 11.4%), and results in a pseudo quintet structure of 1:8:18:8:1. The $^1J_{Pt,H}$ coupling constants of 533 Hz and 432 Hz fall within the range previously found for other $Pt_2(\mu\text{-H})$ complexes [43]. The hydride proton is coupled to three nonequivalent phosphines: $^2J_{P(trans),H}$ 74.5, $^2J_{P(cis),H}$ 19.1 and 12.9 Hz (*J trans* > *J cis* [44]). Three phosphine resonances were also present in the ^{31}P NMR spectrum: δ_1 23.63 ppm, d, $J_{P,P} = 33.1$ Hz, $J_{P,P} = 2.5$ Hz; $^2J_{Pt,P} = 488$ Hz, $^1J_{Pt,P} = 4705$ Hz; δ_2 3.40 ppm, $J_{P,P} = 24.2$ Hz, $J_{P,P} = 2.5$ Hz, $^2J_{Pt,P} = 96$ Hz, $^1J_{Pt,P} = 2458$ Hz; δ_3 1.95, $J_{P,P} = 24.2$ Hz, $J_{P,P} = 33.1$ Hz, $^2J_{Pt,P} = 120$ Hz, $^1J_{Pt,P} = 2411$ Hz ($^2J_{Pt,P}$ values are generally considerably smaller than $^1J_{Pt,P}$ values [45]). These data indicate that a bridging phosphido group is not present as such groups resonate far downfield (>100 ppm) [46].

By comparison of the ^{31}P NMR data for complexes **6**–**8**, it can be seen that the chemical shifts for the phosphine phosphorus atoms are very similar for **6** and **7**, i.e., 20.27 and 20.34 ppm, respectively. However, when a sulfur atom rather than a more electronegative oxygen atom is found in the heterocycle, the phosphorus atoms in the benzothiazolyl complex, **8**, are more shielded and the resonance peak shifts upfield to 15.32 ppm. The hydride proton resonance is also more upfield for **8** than for **6** and **7**.

The hydride protons for complexes **6**–**8** (C–Pt–H type systems) resonate at ca. −7.5 ppm in the ^{1}H NMR spectra. This is approximately 8–10 ppm more downfield than for the hydride protons of complexes **1**–**5** (N–Pt–H type systems). The $^2J_{P,H}$ coupling constants are ca. 2 Hz larger for the Pt–C complexes (**6**–**8**) than the Pt–N hydrides (**1**–**5**). In contrast, the $^1J_{Pt,H}$ couplings are smaller

by ca. 270 Hz. Smaller $^{1}J_{Pt,H}$ coupling constants are associated with stronger *trans* influence ligands [47]. Therefore, the C-bound heteroaryl groups have a stronger *trans* influence than the N-bound azoles. The ^{31}P NMR data for these platinum(II) hydride complexes show little variation between the two types of hydrides. The chemical shifts of the Pt–C hydrides (**6**–**8**) are slightly more upfield than the Pt–N complexes (**1**–**5**). On average the $^{1}J_{Pt,P}$ coupling constants are smaller for the Pt–C (**6**–**8**) than the Pt–N complexes (**1**–**5**).

4. Conclusion

Oxidative insertion into the N–H bonds of nitrogen heteroaromatic compounds (viz. indole, imidazole, pyrazole, benzimidazole and indazole) occurred readily with $[Pt(PEt_3)_4]$. The reactivity of pyrrole was appreciably poorer. Activation of the relatively weaker N–H bonds occurs more readily than at C–S or C–H bonds. In thiophene-like molecules, the $Pt(PEt_3)_2$ fragment inserts into the C(vinyl)–S bonds [3], although C–H activation can also occur in certain cases [6]. Oxygen-containing heteroaromatic compounds reacted via C–H activation at the α-carbon atoms, as was found for furan, benzoxazole and benzothiazole. The reactivity of benzothiazole resembles that of benzoxazole rather than that of benzothiophene; the α-C–H bond rather than C(vinyl)–S bond was the preferred site of attack by the zerovalent metal. Both C–H and N–H bond activation led to the isolation of *trans*-$[PtHR(PEt_3)_2]$ complexes, where R = 1-indolyl, 1-imidazolyl, 1-pyrazolyl, 1-benzimidazolyl, 1-indazolyl, 2-furyl, 2-benzoxazoyl and 2-benzothiazolyl; the *trans* isomers being thermodynamically favoured.

Acknowledgements

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