Trans alkenylpyridine and alkenylamine complexes of platinum

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Abstract: Addition of *cis*-cyclooctene (coe) to K_2PtCl_4 gives *trans*-$[PtCl_2(coe)]_2$ (**1**), which reacts with excess coe to give *trans*-$PtCl_2(coe)_2$ (**2**). Compound **2** was characterized by an X-ray diffraction study and crystals were found to be triclinic, a = 5.7838(5), b = 7.4347(6), c = 9.9972(9) Å, α = 83.924(1), β = 87.844(2), γ = 73.546(1)°, Z = 1, with space group $P\bar{1}$. Addition of 4-vinylpyridine (4vp) to **1** gave *trans*-$PtCl_2(4vp)_2$ (**5**) which was also characterized by an X-ray diffraction study. Crystals of **5** were monoclinic, a = 8.2255(6), b = 12.8254(10), c = 6.9624(5) Å, β = 98.8230(10)°, Z = 2, with space group $P2_1/c$. Although alkenylamines react with **1** to give a mixture of products, addition of one equivalent of apve ($H_2NCH_2CH_2CH_2OCH{=}CH_2$) to **1** cleanly afforded the organometallic product *trans*-$PtCl_2(coe)(thmo)$ (thmo = tetrahydro-2-methyl-1,3-oxazine) arising from a metal-catalyzed intramolecular hydroamination of the starting alkenylamine. Initial investigations into the functionalization of metal complexes containing pendant alkene groups have shown that catecholborane can be added in some cases, using a rhodium catalyst, to give the corresponding organoboronate ester platinum compounds.

Key words: alkenylamines, alkenylpyridines, hydroamination, hydroboration, platinum.

Résumé : L'addition du *cis*-cyclooctène (coe) au K_2PtCl_4 conduit à la formation de *trans*-$[PtCl_2(coe)]_2$ (**1**) qui réagit avec un excès de coe pour fournir le *trans*-$PtCl_2(coe)_2$ (**2**) que l'on a caractérisé par une étude de diffraction des rayons X. On a trouvé que les cristaux sont tricliniques, groupes d'espace $P\bar{1}$, *avec* a = 5,7838(5), b = 7,4347(6) et c = 9,9972(9) Å, α = 83,924(1), β = 87,844(2) et γ = 73,545(1)° et Z = 1. L'addition de 4-vinylpyridine (4vp) au composé **1** fournit le *trans*-$PtCl_2(4vp)_2$ (**5**) que l'on a aussi caractérisé par diffraction des rayons X. Les cristaux de **5** sont monocliniques, groupe d'espace $P2_1/c$, avec a = 8,2255(6), b = 12,8254(10) et c = 6,9624(5) Å, β = 98,8230(10)° et Z = 2. Même si les alcénylamines (L) réagissent avec **1** pour fournir un mélange de produits, l'addition d'un équivalent d'apve ($H_2NCH_2CH_2CH_2OCH{=}CH_2$) à **1** fournit proprement le produit organométallique *trans*-$PtCl_2(coe)(thmo)$ (thmo = tétrahydro-2-méthyl-1,3-oxazine) qui provient d'une hydroamination intramoléculaire catalysée par un métal de l'alcénylamine de départ. Des études initiales sur la fonctionnalisation de complexes métalliques contenant des groupes alcènes ont montré que sous l'influence d'un catalyseur de rhodium, on peut, dans certains cas, additionner du catécholborane pour obtenir les esters organoboronates du platine correspondants.

Mots clés : alcénylamines, alcénylpyridines, hydroamination, hydroboration, platine.

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Introduction

Cisplatin, *cis*-$PtCl_2(NH_3)_2$, is an anti-cancer agent used extensively for the treatment of testicular and ovarian tumours, and has moderate use in the treatment of neck, bladder and lung tumours (1–6). Unfortunately, widespread application of this compound has been limited by numerous drawbacks including nausea, myelosuppression of bone marrow, renal tubular necrosis leading to kidney failure, loss of high frequency hearing, and neuropathy. These side effects, coupled with the low solubility of cisplatin in water, have resulted in a large influx of research into derivatives of cisplatin in an attempt to overcome some of these limitations. With this in mind, we have prepared a number of *trans* platinum complexes containing alkenylamine and alkenylpyridine ligands and hypothesize that further hydroboration of the pendant C=C moieties in these complexes may prove to be a facile route to making novel platinum compounds containing biologically-active boronic acid groups. Platinum complexes containing alkenylamines and

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alkenylpyridines are also of interest as these ligands can coordinate to the metal centre via either the nitrogen lone pair or the alkene moiety.

Experimental

Reagents and solvents used were obtained from Aldrich Chemicals. THF, hexane, and diethyl ether were distilled from sodium benzophenone ketyl. Methylene chloride and chloroform were distilled from CaH_2. Potassium tetrachloroplatinate was obtained from Johnson Matthey Ltd. $RhCl(PPh_3)_3$ was prepared as described elsewhere (7). NMR spectra were recorded on a JEOL JNM-GSX270 FT NMR spectrometer. ^1H NMR chemical shifts are reported in ppm and referenced to residual protons in deuterated solvent at 270 MHz. $^{11}B\{^1H\}$ NMR chemical shifts are referenced to external $F_3B{\cdot}OEt_2$ at 87 MHz. $^{13}C\{^1H\}$ NMR chemical shifts are referenced to solvent carbon resonances as internal standards at 68 MHz. Multiplicities are reported as (s) singlet, (d) doublet, (t) triplet, (q) quartet, (quint) quintet, (m) multiplet, (br) broad, and (ov) overlapping. Infrared spectra were obtained using a Mattson Polaris FT-IR spectrometer and reported in cm^{-1}. Melting points were measured uncorrected with a Mel-Temp apparatus. Microanalyses for C, H, and N were carried out at Desert Analytics (Tucson, AZ).

Preparation of $[PtCl_2(coe)]_2$ (1)

$[PtCl_2(coe)]_2$ (**1**) was prepared by modification of a known procedure (8). Potassium tetrachloroplatinate (300 mg, 0.70 mmol) was dissolved in a water isopropanol mixture (10 :7 mL). A catalytic amount of tin chloride (3.8 mg, 0.02 mmol) was added to the red solution along with an excess of *cis*-cyclooctene (3.0 mL, 23.0 mmol). After 5 days, the yellow solution was decanted from a small amount of black precipitate. Compound **1** was extracted from the aqueous phase with 15 mL of methylene chloride and filtered to afford a clear yellow solution. The solvent was removed in vacuo to give a yellow solid and a small amount of yellow liquid. The liquid was dissolved in hexane (10 mL) and decanted to afford a bright yellow powder. Yield: 158 mg (58%). A yellow–orange precipitate appeared in the hexane phase after 3 days. The hexane was decanted and the solid dried. Yield: 53 mg (79% total); mp 190°C (decomposition). Spectroscopic NMR data (in $CDCl_3$): ^1H δ:1.35 (br s, 8H), 1.52 (br s, 8H), 2.18 (br d, $J_{H\text{-}H}$ = 5 Hz, 8H), 5.78 (br, 4H); $^{13}C\{^1H\}$ δ: 26.1, 27.4, 28.9, 109.2 (br). IR (nujol): 762, 817, 868, 955, 1031, 1125, 1170, 1230, 1378, 1464, 2859, 2915.

Yellow crystals of **2** could be isolated from solutions of **1** in the presence of excess coe. The mp was found to be 178°C (decomposition). Spectroscopic NMR data (in $CDCl_3$): ^1H δ: 1.45 (br s, 8H), 1.62 (br s, 8H), 2.29 (br d, $J_{H\text{-}H}$ = 5 Hz, 8H), 5.94 (br, 4H); $^{13}C\{^1H\}$ δ: 26.3, 27.6, 29.2, 113.3 (br). IR (nujol): 762, 818, 953, 1125, 1170, 1233, 1317, 1354, 1380, 1427, 1467, 1529, 2845, 2884, 2972. The formation of this monomer has been reported previously (8). Interestingly, C and H elemental analyses from this previous study varied over time, suggesting loss of the second coe ligand to give **1** is facile even in the solid state.

Preparation of *trans*-$PtCl_2$(coe)(2vp) (3)

2-Vinylpyridine (14 mg, 0.13 mmol) in 3 mL of CH_2Cl_2 was added dropwise at 0°C to a solution of *trans*-$[PtCl_2(coe)]_2$ (50 mg, 0.07 mmol) in 15 mL of CH_2Cl_2. The reaction was stirred for 4 h at which point solvent was removed under vacuum to afford a yellow solid which was washed with ether (2 × 2 mL) and hexane (3 × 5 mL). Yield: 26 mg (40%); mp 187°C (decomposition). Spectroscopic NMR data (in $CDCl_3$): ^1H δ: 1.43 (s, 4H), 1.80 (br s, 4H), 2.22–2.49 (ov m, 4H), 5.53 (m, $J_{H\text{-}Pt}$ = 70 Hz, 2H), 5.83 (d, $J_{H\text{-}H}$ = 8 Hz, 1H), 6.06 (d, $J_{H\text{-}H}$ = 15 Hz, 1H), 7.31 (t, $J_{H\text{-}H}$ = 5 Hz, 1H), 7.72 (m, 2H), 8.12 (d of d, $J_{H\text{-}H}$ = 15, 5 Hz, 1H), 8.68 (d, $J_{H\text{-}H}$ = 5 Hz, $J_{H\text{-}Pt}$ = 35 Hz, 1H); $^{13}C\{^1H\}$ δ: 26.1, 27.9, 29.0, 94.5 ($J_{C\text{-}Pt}$ = 153 Hz), 121.7, 123.2, 124.0, 135.2, 138.7, 150.3, 156.7. IR (nujol): 761, 793, 939, 957, 1108, 1127, 1163, 1229, 1377, 1465, 1562, 1602, 2857, 2897, 2941, 2966. Elemental analysis calcd. for $PtCl_2C_{15}H_{21}N$: C 37.42, H 4.41, N 2.91; found: C 37.68, H 4.50, N 3.01.

Preparation of *trans*-$PtCl_2$(coe)(4vp) (4)

4-Vinylpyridine (60 mg, 0.56 mmol) in 5 mL of CH_2Cl_2 was added dropwise to a stirred solution of **1** (200 mg, 0.27 mmol) in 15 mL of CH_2Cl_2 at 0°C. The solvent was removed under vacuum after 4 h to afford a yellow solid which was washed with hexane (3 × 5 mL). Spectroscopic NMR data (in $CDCl_3$): ^1H δ: 1.47 (s, 6H), 1.83 (br s, 2H), 2.36 (br s, 2H), 2.54 (br s, 2H), 5.55 (br d, $J_{H\text{-}H}$ = 11 Hz, $J_{H\text{-}Pt}$ = 64 Hz, 2H), 5.61 (d, $J_{H\text{-}H}$ = 11 Hz, 1H), 6.06 (d, $J_{H\text{-}H}$ = 19 Hz, 1H), 6.68 (d of d, $J_{H\text{-}H}$ = 11, 5 Hz, 1H), 7.40 (d, $J_{H\text{-}H}$ = 5 Hz, 2H), 8.78 (d, $J_{H\text{-}H}$ = 5 Hz, $J_{H\text{-}Pt}$ = 27 Hz, 2H); $^{13}C\{^1H\}$ δ: 26.4, 28.3, 29.4, 94.4 ($J_{C\text{-}Pt}$ = 158 Hz), 122.3, 122.9, 133.3, 148.3, 151.7. Attempts to isolate **4** for elemental analysis were complicated by disproportionation in solution to give **1** and **5**.

Preparation of *trans*-$PtCl_2(4vp)_2$ (5)

4-Vinylpyridine (25 mg, 0.24 mmol) in 1 mL of CH_2Cl_2 was added dropwise to a stirred solution of **1** (45 mg, 0.06 mmol) in 7 mL of CH_2Cl_2. The mixture was cooled to 0°C for 2 days and the resultant off-white precipitate was filtered and dried under vacuum. Yield: 43 mg (75%); mp 264°C (decomposition). Spectroscopic NMR data (in $CDCl_3$): ^1H δ: 5.60 (d, $J_{H\text{-}H}$ = 11 Hz, 2H), 6.02 (d, $J_{H\text{-}H}$ = 19 Hz, 2H), 6.58 (d of d, $J_{H\text{-}H}$ = 19, 11 Hz, 2H), 7.18 (d, $J_{H\text{-}H}$ = 8 Hz, 4H), 8.84 (br d, $J_{H\text{-}H}$ = 6 Hz, $J_{H\text{-}Pt}$ = 30 Hz, 4H); $^{13}C\{^1H\}$ δ: 121, 122, 133, 147, 155. IR (nujol): 666, 846, 991, 1206, 1417, 1435, 1499, 1546, 1616, 2943. Elemental analysis calcd. for $PtCl_2C_{14}H_{14}N_2$: C 35.29, H 2.97, N 5.88; found: C 34.72, H 2.99, N 5.69.

Preparation of *trans*-$PtCl_2$(coe)(4chp) (6)

4-(3-Cyclohexen-1-yl)pyridine (89 mg, 0.56 mmol) in 5 mL of CH_2Cl_2 was added dropwise to a stirred solution of **1** (200 mg, 0.27 mmol) in 15 mL of CH_2Cl_2 at 0°C. The reaction was allowed to proceed for 4 h at which point the solvent was removed under vacuum. The resultant orange oil was dissolved in 1 mL of CH_2Cl_2 after which 5 mL of hexane was added and the reaction mixture stored at 0°C for 18 h. The precipitate was collected and determined to be **7** by NMR spectroscopic data. The solvent was removed from the filtrate to afford a bright yellow solid. Spectroscopic

NMR data (in $CDCl_3$) for **6**: ^{1}H δ: 1.46 (m, 6H), 1.76 (ov m, 4H), 2.15 (s, 2H), 2.32 (m, 4H), 2.53 (m, 2H), 2.89 (s, 1H), 5.66 (d, $J_{H\text{-}H}$ = 8 Hz, $J_{H\text{-}Pt}$ = 72 Hz, 2H), 5.72 (s, 2H), 7.29 (d, $J_{H\text{-}H}$ = 5 Hz, 2H), 8.73 (br d, $J_{H\text{-}H}$ = 5 Hz, $J_{H\text{-}Pt}$ = 32 Hz, 2H); ^{13}C{^{1}H}δ: 25.0, 26.3, 28.1, 28.5, 29.3, 31.8, 39.5, 94.1 ($J_{C\text{-}Pt}$ = 156 Hz), 124.0, 125.4, 127.3, 151.2, 153.2. Attempts to isolate **6** were complicated by disproportionation in solution to give **1** and **7**.

Preparation of *trans*-$PtCl_2(4chp)_2$ (7)

4-(3-Cyclohexen-1-yl)pyridine (45 mg, 0.29 mmol) in 1 mL of CH_2Cl_2 was added dropwise to a stirred solution of **1** (50 mg, 0.07 mmol) in 15 mL of CH_2Cl_2. The solvent was removed under vacuum after the reaction was allowed to proceed for 5 h. The resultant yellow oil was dissolved in 1 mL of CH_2Cl_2 after which addition of hexane (3 mL) to the solution produced an off-white precipitate. Yield: 53 mg (68%); mp 272°C (decomposition). Spectroscopic NMR data (in $CDCl_3$): ^{1}H δ 1.60 (m, 4H), 1.93 (m, 4H), 2.25 (m, 4H), 2.87 (br s, 2H), 5.77 (s, 4H), 7.16 (d, $J_{H\text{-}H}$ = 5 Hz, 4H), 8.75 (d, $J_{H\text{-}H}$ = 5 Hz, $J_{H\text{-}Pt}$ = 32 Hz, 4H); ^{13}C{^{1}H} δ 25.1, 28.6, 32.0, 39.5, 123.9, 125.6, 127.4, 153.1, 159.2. IR (nujol): 719, 829, 1069, 1212, 1244, 1422, 1616, 2936. Elemental analysis calcd. for $PtCl_2C_{22}H_{26}N_2$: C 45.21, H 4.49, N 4.79; found: C 44.83, H 4.26, N 4.62.

Preparation of *trans*-$PtCl_2(aa)_2$ (8)

Allylamine (18 mg, 0.32 mmol) in 3 mL of CH_2Cl_2 was added to a stirred solution of **1** (50 mg, 0.07 mmol) in 10 mL of CH_2Cl_2 at 0°C. Within 30 min a yellow precipitate had formed and was collected by suction filtration. Yield: 37 mg (72%); mp 214°C (decomposition). Spectroscopic NMR data (in $CDCl_3$): ^{1}H δ: 3.49 (d, $J_{H\text{-}H}$ = 5 Hz, 4H), 5.37 (d of d, $J_{H\text{-}H}$ = 11, 5 Hz, 2H), 5.97 (m, 4H), 8.18 (br s, 4H); ^{13}C{^{1}H} δ: 44.2, 123.7, 131.9. IR (nujol): 722, 1018, 1108, 1566, 1603, 2928. Elemental analysis calcd. for $PtCl_2C_6H_{14}N_2$: C 18.95, H 3.72, N 7.37; found: C 18.95, H 3.97, N 7.23. Complex **8** eventually decomposes in solution to give a number of unidentified products.

Preparation of *trans*-$PtCl_2$(coe)(chea) (9)

2-(1-Cyclohexenyl)ethylamine (35 mg, 0.28 mmol) in 15 mL of CH_2Cl_2 was added to a solution of **1** (100 mg, 0.13 mmol) in 10 mL of CH_2Cl_2 at 0°C. The reaction was allowed to proceed for 3 h at which point solvent was removed under vacuum to afford an orange oil. The oil was dissolved in 1 mL of CH_2Cl_2 after which hexane (10 mL) was added and the reaction mixture cooled to 0°C. After 18 h, a pale yellow precipitate was collected by suction filtration and found to be a mixture of products by NMR spectroscopy. The solvent was allowed to evaporate from the filtrate over 48 h to afford bright yellow needles which were collected and dried under vacuum. Yield: 70 mg (52%); mp 122°C. Spectroscopic NMR data (in $CDCl_3$): ^{1}H δ: 1.43 (m, 6H), 1.59 (ov m, 4H), 1.78 (br s, 2H), 1.92 (br s, 2H), 2.01 (br s, 2H), 2.24 (br m, 4H), 2.39 (ov m, 2H), 3.09 (m, $J_{H\text{-}H}$ = 8 Hz, 2H), 3.72 (br s, $J_{H\text{-}Pt}$ = 59 Hz, 2H), 5.30 (d, $J_{H\text{-}H}$ = 11 Hz, $J_{H\text{-}Pt}$ = 81 Hz, 2H), 5.55 (s, 1H); ^{13}C{^{1}H} δ: 22.4, 22.8, 25.5, 26.4, 27.9, 28.1, 29.5 ($J_{C\text{-}Pt}$ = 41 Hz), 39.7, 42.7, 93.6 ($J_{C\text{-}Pt}$ = 158 Hz), 126.5, 132.8. IR (nujol): 722, 1001, 1231, 1377, 1461, 1579, 2841, 2968. Elemental analysis calcd. for $PtCl_2C_{16}H_{29}N$: C 38.31, H 5.84, N 2.79; found: C 38.72, H 5.92, N 2.86.

Preparation of *trans*-$PtCl_2$(coe)(thmo) (10)

Tetrahydro-2-methyl-1,3-oxazine (14 mg, 0.14 mmol) in 3 mL of CH_2Cl_2 was added dropwise to a solution of **1** (50 mg, 0.07 mmol) in 10 mL of CH_2Cl_2 at 0°C. Solvent was removed after 4 h to afford a yellow oil which was triturated with hexane (3 × 5 mL) and dried under vacuum to afford a yellow solid. Yield: 25 mg (40%); mp 98°C. Spectroscopic NMR data (in $CDCl_3$): ^{1}H δ: 1.37 (br s, 6H), 1.70 (ov m, 6H), 2.13 (br s, 2H), 2.29 (br s, 2H), 3.39 (m, 2H), 3.70 (t, $J_{H\text{-}H}$ = 16 Hz, 1H), 3.92 (m, 1H), 4.45 (br s, 1H), 4.60 (m, 2H), 5.27 (m, 2H); ^{13}C{^{1}H} δ: 22.3, 25.6, 25.9, 27.4, 27.6, 28.9, 48.4, 86.5, 92.9 ($J_{C\text{-}Pt}$ = 140 Hz). IR (nujol): 815, 846, 963, 1017, 1059, 1099, 1139, 1230, 1378, 1461, 2889, 3216, 3433. Elemental analysis calcd. for $PtCl_2C_{13}H_{25}NO$: C 32.71, H 5.28, N 2.93; found: C 33.10, H 5.23, N 2.90.

Catalyzed hydroboration of *trans*-$PtCl_2(4vp)_2$ (5) with catecholborane

Under an atmosphere of dinitrogen, *trans*-$PtCl_2(4vp)_2$ (25 mg, 0.05 mmol) was suspended in 1 mL of $CDCl_3$ with 7 mol% of Wilkinson's catalyst, $RhCl(PPh_3)_3$. Catecholborane (14 mg, 0.12 mmol) in 0.5 mL of $CDCl_3$ was added dropwise to the stirred suspension and the reaction mixture was allowed to stand for 48 h and then analyzed by NMR spectroscopy. Spectroscopic NMR data (in $CDCl_3$): ^{1}H δ: 1.22 (t, $J_{H\text{-}H}$ = 8 Hz), 1.50 (d, $J_{H\text{-}H}$ = 8 Hz), 1.64 (t, $J_{H\text{-}H}$ = 8 Hz), 2.12 (s), 2.69 (q, $J_{H\text{-}H}$ = 8 Hz), 3.03 (ov), 5.29 (s), 5.38 (s), 5.63 (m), 7.0 (m), 8.74 (d, $J_{H\text{-}H}$ = 5 Hz); ^{11}B{^{1}H} δ: 7.0 (s), 7.8 (s), 12.3 (s), 29.0 (s), 23.2 (br), 35.0 (br).

Catalyzed hydroboration of *trans*-$PtCl_2(4chp)_2$ (7) with catecholborane

Under an atmosphere of dinitrogen, *trans*-$PtCl_2(4chp)_2$ (52 mg, 0.09 mmol) was dissolved in 1 mL of $CDCl_3$ with 7 mol% catalyst. Catecholborane (24 mg, 0.20 mmol) in 0.5 mL of $CDCl_3$ was added dropwise to the stirred solution and the reaction was allowed to proceed for 48 h and then analyzed by NMR spectroscopy. Spectroscopic NMR data (in $CDCl_3$): ^{1}H δ: 1.45–1.59 (ov m), 2.00–2.18 (ov m), 2.66 (m), 6.92–7.39 (ov m), 8.75 (d, $J_{H\text{-}H}$ = 5 Hz), 8.88 (d, $J_{H\text{-}H}$ = 5 Hz); ^{11}B{^{1}H} δ: 12.3 (s), 23.0 (s), 36.3 (br); ^{13}C{^{1}H} δ 21.2 (br, C-B), 21.8 (br, C-B), 27.1, 27.2, 27.7, 33.3, 33.7, 34.1, 43.6, 44.4, 112.6, 112.8, 121.6, 122.9, 124.0, 148.2, 148.3, 153.5, 159.4.

The platinum aminoboronate ester was formed in situ as described in the previous procedure and removed from the dinitrogen atmosphere. Addition of 0.5 mL of D_2O to this product resulted in a convincing change in the solution's appearance from brown to orange in colour. Spectroscopic NMR data (in $CDCl_3$): ^{1}H δ: 1.48–1.58 (ov m), 1.99 (m), 2.18 (m), 2.65 (m), 6.70 (d, $J_{H\text{-}H}$ = 5 Hz), 6.88 (d, $J_{H\text{-}H}$ = 5 Hz), 7.09–7.21 (ov m), 7.39 (m), 8.73 (d, $J_{H\text{-}H}$ = 5 Hz); ^{11}B{^{1}H} δ: 19.6 (s, $B(OH)_3$), 36.9 (br); ^{13}C{^{1}H} δ 21.2 (br, C-B), 22 (br, C-B), 27.1, 27.2, 27.6, 33.0, 33.6, 33.7, 43.6, 44.3, 115.6, 120.9, 124.0, 148.2, 153.2, 159.5.

Table 1. Crystallographic data collection parameters for *trans*-$PtCl_2(coe)_2$ (**2**) and *trans*-$PtCl_2(4vp)_2$ (**5**).

Complex	**2**	**5**
Formula	$C_{16}H_{28}Cl_2Pt$	$C_{14}H_{14}Cl_2N_2Pt$
fw	486.37	476.26
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	5.7838 (5)	8.2255 (6)
b (Å)	7.4347 (6)	12.8254 (10)
c (Å)	9.9972 (9)	6.9624 (5)
α (°)	83.924 (1)	—
β (°)	87.844 (2)	98.8230 (10)
γ (°)	73.546 (1)	—
V (Å^3)	409.95 (6)	725.81 (9)
Z	1	2
ρ_{calcd} (g cm^{-3})	1.970	2.179
Crystal size (mm)	0.15 × 0.20 × 0.20	0.15 × 0.20 × 0.20
Temperature (K)	183 (2)	193 (2)
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
μ, (mm^{-1})	8.869	10.021
Total reflections[a]	2602	4464
Total unique relections	1807	1689
No. of variables	88	88
Largest difference peak/hole (e Å^{-3})	1.061/–1.889	0.624/–1.177
R^b	0.0232	0.0188
R_w	0.0606	0.0480
GoF[c]	0.575	1.093

[a] $I_o > 3\sigma(I_o)$.
[b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma(w(|F_o| - |F_c|)^2/\Sigma(w|F_o|)^2]^{1/2}$.
[c] $[\Sigma(w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$.

X-ray crystallographic data for 2 and 5

Crystals of **2** and **5** suitable for X-ray diffraction studies were obtained by crystallization from solutions of methylene chloride at 5°C. A summary of the crystal data and parameters for data collection is given in Table 1. Data were collected at 183 K (for **2**) and 193 K (for **5**) on a Siemens SMART/CCD diffractometer equipped with an LT-II low temperature device. Diffracted data were corrected for absorption using the SADABS[4] program. SHELXTL was used for structure solution and refinement was based on F^2.[5] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at calculated positions and refined isotropically on the basis of the corresponding carbon atoms [*U*(H) = 1.2*U*eq(C)]. Selected bond distances and angles are given in Tables 2 and 4 and final atomic coordinates in Tables 3 and 5. Complete tables of bond distances and angles, final atomic coordinates, and anisotropic displacement parameters have been deposited as supporting material.[6]

Results and discussion

As part of our ongoing research into making novel aminoboron platinum complexes, we decided to initially prepare a number of unsaturated *trans* amine and pyridine complexes from the monoalkene dimer *trans*-$[PtCl_2(coe)]_2$ (**1**) (coe = η^2 – C_8H_{14}) (8). The starting organometallic dimer, which is soluble in common organic solvents, was readily prepared by the addition of *cis*-cyclooctene to aqueous solutions of K_2PtCl_4, and appears to be indefinitely stable in the solid state. A recent paper examining reaction mechanisms for alkene exchange with *trans*-$[PtCl_2(C_2H_4)]_2$ suggests that a two-step process incorporating *trans*-$PtCl_2(C_2H_4)_2$ might be occurring in the steady state (9). Indeed, the analogous disubstituted alkene complex *trans*-$PtCl_2(coe)_2$ (**2**) could be crystallized in minor amounts (<10%) by addition of excess coe to **1** (10).

We have carried out an X-ray diffraction study on **2** which shows the platinum metal centre in a square plane with the cyclooctene ligands lying *trans* to one another. The structure of **2** is shown in Fig. 1, summary of the crystallographic data presented in Table 1, pertinent bond distances and angles given in Table 2, and atomic coordinates provided in Table 3. Platinum–carbon bond distances of 2.258(4) and 2.278(4) Å are somewhat longer than analogous Pt(II) complexes where a chloride ligand lies *trans* to the alkene group. For instance, average bond lengths of 2.128(19), 2.13(2),

[4] G.M. Sheldrick. SADABS Univ. Gottingen (1996).
[5] G.M. Sheldrick. SHELXTL Release 5.03; Siemens Analytical X-ray Instruments Inc., Madison, Wis. (1994).
[6] A complete set of data may be purchased from: The Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, Ontario, Canada, K1A 0S2. Tables of coordinates, bond distances and angles, and alternative views of **2** and **5** have also been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, 12 Union Road, Cambridge, CB2 1EZ, U.K.

Table 2. Selected bond distances (Å) and angles (°) for *trans*-$PtCl_2(coe)_2$ (**2**).[a]

Bond distances	
Pt(1)—C(2)#1	2.258(4)
Pt(1)—C(2)	2.258(4)
Pt(1)—C(1)#1	2.278(4)
Pt(1)—C(1)	2.278(4)
Pt(1)—Cl(1)	2.3107(10)
Pt(1)—Cl(1)#1	2.3107(10)
C(1)—C(2)	1.389(5)
C(1)—C(8)	1.499(6)
C(2)—C(3)	1.492(6)
C(3)—C(4)	1.543(6)
C(4)—C(5)	1.532(6)
C(5)—C(6)	1.550(6)
C(6)—C(7)	1.536(6)
C(7)—C(8)	1.547(6)
Bond angles	
C(2)-C(1)-C(8)	125.2(4)
C(1)-C(2)-C(3)	123.8(4)
C(2)-C(3)-C(4)	109.5(3)
C(5)-C(4)-C(3)	114.6(3)
C(4)-C(5)-C(6)	116.4(4)
C(7)-C(6)-C(5)	115.2(4)
C(6)-C(7)-C(8)	115.4(4)
C(1)-C(8)-C(7)	112.2(4)
Cm-Pt1-Cl(1)[b]	85.7

[a]Symmetry transformations used to generate equivalent atoms: #1 –x, –y, –z.

[b]Cm is in the middle of the C(1)—C(2) bond.

and 2.12(2) Å have been reported for $K[PtCl_3(C_2H_4)]$ (11), $PtCl(C_6H_2Me_3)(\eta^4\text{-}C_8H_{12})$ (12), and $[PtCl_2(C_7H_{12})]_2$ (13), respectively. However, the Pt—C bond distance in **2** is similar to that reported for the double bond *trans* to the mesityl group ($C_6H_2Me_3$) in the previous example (cf. 2.30(2) Å). The carbon–carbon bond distance of 1.389(5) Å shows the expected weakening of the double bond due to π-backbonding from the metal to the empty π^* orbital of the alkene (14).

Addition of neutral ligands (L) to either **1** or **2** will give complexes of the type *trans*-$PtCl_2(coe)L$ and, upon addition of a second equivalent of ligand, the disubstituted species *trans*-$PtCl_2L_2$ (15). Reactions with alkenylpyridine and alkenylamine ligands are of special interest because coordination of these ligands to a transition metal can occur via either the alkene moiety and (or) the nitrogen lone pair.

Alkenylpyridines

A number of transition metal complexes (16–23) containing alkenylpyridine ligands have been reported. For example, addition of 2-vinylpyridine (2vp = 2-$NC_5H_4CH{=}CH_2$) to $[Cu(NCCH_3)_4][ClO_4]$ gave the binuclear complex $[Cu_2(\mu\text{-}2vp)_2(2vp)_2][ClO_4]_2$ where two of the alkenylpyridine ligands use the nitrogen and the alkene to bond to two respective metal centres (16). For this study we decided to prepare *trans* complexes from three commercially available alkenylpyridines (Fig. 2).

Table 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients for *trans*-$PtCl_2(coe)_2$ (**2**). *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	*U*(eq)
Pt(1)	0	0	0	16(1)
Cl(1)	3265(2)	–1340(1)	1394(1)	24(1)
C(1)	2409(7)	–1393(6)	–1674(4)	19(1)
C(2)	1241(7)	–2656(5)	–1051(4)	18(1)
C(3)	–681(8)	–3230(6)	–1703(4)	22(1)
C(4)	464(9)	–5041(6)	–2393(5)	26(1)
C(5)	2532(9)	–4921(6)	–3369(5)	26(1)
C(6)	2023(9)	–3197(7)	–4444(4)	27(1)
C(7)	3150(9)	–1635(6)	–4166(4)	26(1)
C(8)	1883(8)	–391(6)	–3057(4)	23(1)

Table 4. Selected bond distances (Å) and angles (°) for *trans*-$PtCl_2(4vp)_2$ (**5**).[a]

Bond distances	
Pt(1)—N(1)	2.020(3)
Pt(1)—N(1)#1	2.020(3)
Pt(1)—Cl(1)	2.2996(8)
Pt(1)—Cl(1)#1	2.2996(8)
N(1)—C(5)	1.350(4)
N(1)—C(1)	1.352(4)
C(1)—C(2)	1.373(5)
C(2)—C(3)	1.398(5)
C(3)—C(4)	1.403(5)
C(3)—C(6)	1.473(5)
C(4)—C(5)	1.368(5)
C(6)—C(7)	1.330(6)
Bond Angles	
N(1)-Pt(1)-N(1)#1	180.0
N(1)-Pt(1)-Cl(1)	89.92(8)
N(1)#1-Pt(1)-Cl(1)	90.08(8)
N(1)-Pt(1)-Cl(1)#1	90.08(8)
N(1)#1-Pt(1)-Cl(1)#1	89.92(8)
Cl(1)-Pt(1)-Cl(1)#1	180.0
C(5)-N(1)-C(1)	117.9(3)
C(5)-N(1)-Pt(1)	120.0(2)
C(1)-N(1)-Pt(1)	122.1(2)
N(1)-C(1)-C(2)	122.2(3)
C(1)-C(2)-C(3)	120.3(3)
C(2)-C(3)-C(4)	116.8(3)
C(2)-C(3)-C(6)	120.4(3)
C(4)-C(3)-C(6)	122.8(3)
C(5)-C(4)-C(3)	119.9(3)
N(1)-C(5)-C(4)	122.8(3)
C(7)-C(6)-C(3)	125.0(4)

[a]Symmetry transformations used to generate equivalent atoms: #1 (–x + 1), (–y + 1), –z.

Previous work has shown that attempts to prepare *cis*-$PtCl_2(2vp)_2$ (20) from K_2PtCl_4 resulted in the formation of several products where both the alkene and nitrogen groups are involved in bonding to platinum. Likewise, efforts to generate the *trans* derivative from *trans*-$PtCl_2(NCCH_3)_2$ have also proven unsuccessful (23). Although we were also unable to generate *trans*-$PtCl_2(2vp)_2$ from addition of 2vp to

Table 5. Atomic coordinates (× 10^4) and equivalent isotropic displacement coefficients for *trans*-$PtCl_2(4vp)_2$ (**5**). *U*(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	*U*(eq)
Pt(1)	5000	5000	0	20(1)
Cl(1)	3695(1)	5692(1)	2403(1)	31(1)
N(1)	6632(3)	6188(2)	343(4)	21(1)
C(1)	6151(4)	7197(3)	253(5)	24(1)
C(2)	7255(4)	8005(3)	531(5)	25(1)
C(3)	8945(4)	7804(3)	909(5)	25(1)
C(4)	9427(4)	6754(3)	1009(5)	25(1)
C(5)	8261(4)	5985(3)	711(5)	24(1)
C(6)	10133(5)	8671(3)	1204(6)	33(1)
C(7)	11757(5)	8568(4)	1365(6)	44(1)

trans-$[PtCl_2(coe)]_2$ (**1**), the novel organometallic complex *trans*-$PtCl_2(coe)(2vp)$ (**3**), which is soluble in common organic solvents such as methylene chloride, could be isolated in moderate yield (40%). Steric congestion around the nitrogen atom in 2-vinylpyridine presumably inhibits addition of a second equivalent of this ligand to the metal centre. The ^{1}H NMR spectrum for **3** shows a shift for the pyridine ring's α-carbon proton from 8.54 ppm for free 2vp to 8.68 ppm in the complex. Coupling ($J_{H\text{-}Pt}$ = 35 Hz) to the ^{195}Pt nucleus (14) is also observed for this resonance. Shifts for the alkenyl peaks are also observed by ^{1}H NMR spectroscopy for this complex, suggesting that the alkenyl group may lie directly above the plane of the platinum atom (15).

The corresponding 4-vinylpyridine (4vp = 4-$NC_5H_4CH{=}CH_2$) complex, *trans*-$PtCl_2(coe)(4vp)$ (**4**), was prepared by addition of 2 equivalents of 4vp to **1**, along with minor amounts of the disubstituted product *trans*-$PtCl_2(4vp)_2$ (**5**) and unreacted **1**. For complex **4**, the diagnostic shift from 8.56 ppm for free 4vp to 8.78 ppm is observed in the ^{1}H NMR spectrum, along with coupling to platinum ($J_{H\text{-}Pt}$ = 27 Hz), for the pyridine ring's α-carbon protons. Complex **5** could be readily prepared by the addition of excess 4vp to **1**. Although NMR spectroscopic data show similar trends upon complexation to platinum, unambiguous assignment of **5** is based upon an X-ray diffraction study. The molecular structure of **5** is shown in Fig. 3, relevant bond angles and distances in Table 4, and atomic coordinates in Table 5. The platinum atom lies in a distorted square plane with two Cl atoms and two 4vp N atoms coordinated to the metal centre in a *trans* geometry. The Pt—Cl and Pt—N bond distances of 2.2996(8) and 2.020(3) Å, respectively, are similar to those reported for *cis*-$PtCl_2(4vp)_2$ (21). Bond lengths of 1.330(6) Å are typical for uncomplexed C—C double bonds. The alkenylpyridines are planar with bond distances and angles similar to those observed in other transition metal pyridine derivatives (21).

The organometallic complex *trans*-$PtCl_2(coe)(4chp)$ (**6**) (4chp = 4-(3-cyclohexen-1-yl)pyridine) and the disubstituted compound *trans*-$PtCl_2(4chp)_2$ (**7**) were readily prepared from reaction of the cyclooctene dimer **1** with 2 and 4 equivalents of 4chp, respectively, (24). Complex **6** has the diagnostic shift for the α-hydrogens of the pyridine group in the ^{1}H NMR spectrum (8.49 ppm for free 4chp to 8.73 ppm for **6**) along with coupling to the ^{195}Pt nucleus ($J_{H\text{-}Pt}$ = 72 Hz). The cyclohexenyl groups in **7** resulted in this complex having increased solubility in common organic solvents as compared to **5**.

Fig. 1. Molecular structure of *trans*-$PtCl_2(coe)_2$ (**2**).

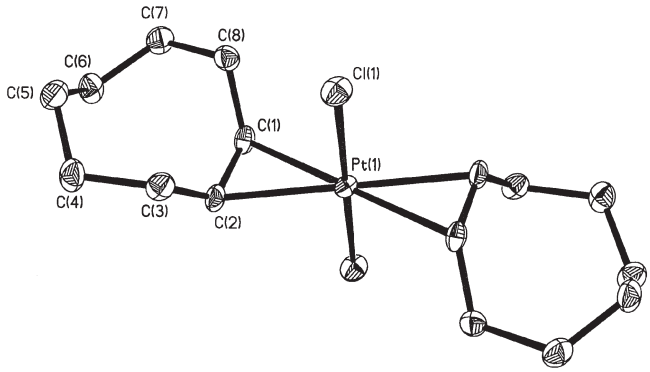
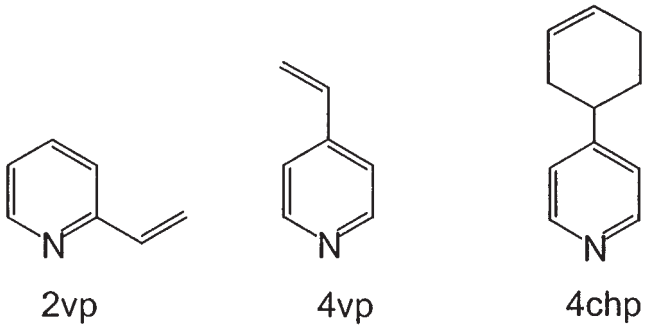


Fig. 2. Alkenylpyridines.



Alkenylamines

The synthesis of platinum complexes containing neutral and protonated alkenylamines has been reported previously (25–28). For example, addition of allylamine (aa = $NH_2CH_2CH{=}CH_2$) to acidic solutions of $[PtCl_4]^{2-}$ are known to give zwitterionic $PtCl_3(CH_2{=}CHCH_2NH_3)$ where only the C=C group of the alkenylamine is coordinated to the platinum centre (14, 25). In the absence of protonation, or by treatment with NaOH, the above complex can be transformed into a neutral alkenylamine species where the ligand is capable of coordinating in a chelating bidentate manner through both the alkene moiety and the nitrogen lone pair (26). Another allylamine complex has been reported in which the ligand bridges two metal centres by binding to one metal via the nitrogen atom and to the other platinum using the alkene group (29). We have found that addition of aa to *trans*-$[PtCl_2(coe)]_2$ (**1**) afforded the novel diamine complex *trans*-$PtCl_2(aa)_2$ (**8**) in high yield (72%). Complex **8** is only sparingly soluble in common organic solvents such as methylene chloride. The amine hydrogens appear as a broad peak in the ^{1}H NMR spectrum and shift from 1.23 for free allylamine to 8.18 ppm in **8**. Likewise, the broad methylene peak shifts from 3.36 to 3.49 ppm upon complexation. The vinyl peaks, however, remain relatively unchanged suggesting that coordination of the allylamine ligand occurs through the nitrogen atom only. IR data supports this hypothesis as the C=C π stretch found in free allylamine at 1637 cm^{-1} only shifts to 1603 cm^{-1} when the ligand coordinates to Pt(II). For metal complexes containing the

Fig. 3. Molecular structure of *trans*-$PtCl_2(4vp)_2$ (**5**).

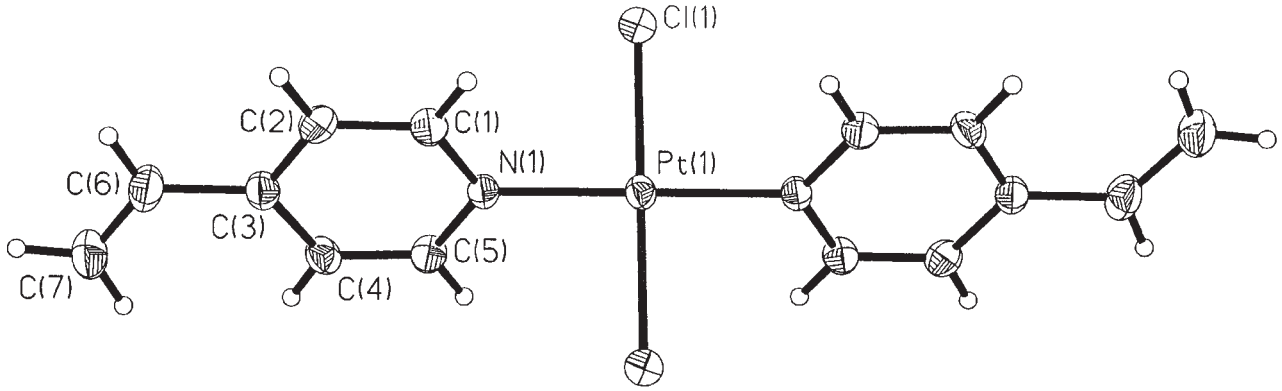
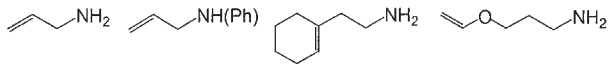


Fig. 4. Alkenylamines.



protonated alkenylamine ligands, where the alkene is directly bound to the metal centre, this band appears near 1500 cm^{-1} (26). Efforts to prepare the monoamine complex *trans*-$PtCl_2$(coe)(aa) have proven unsuccessful.

We have attempted to prepare platinum complexes with other alkenylamines (Fig. 4) in an effort to confirm the bonding modes in these unique ligands. Unfortunately, no reaction was observed between dimer **1** and secondary amine *N*-allylaniline (aA = $NH(Ph)CH_2CH{=}CH_2$). The increased steric bulk of this amine, as compared with allylamine, presumably precludes coordination to the metal centre. Conversely, *trans*-$PtCl_2$(coe)(chea) (**9**) was prepared by addition of 2-(1-cyclohexenyl)ethylamine (chea) to dimer **1**. As with the other monoamine complexes, the $^{13}C\{^1H\}$ NMR spectrum for **9** exhibits a singlet for the sp^2 carbons of the coe ligand at 93.6 ppm with diagnostic ^{195}Pt satellites ($J_{C\text{-}Pt}$ = 158 Hz). Unfortunately, treatment of **1** with four equivalents of chea led to a complex mixture of products, even at low temperatures.

Addition of aminopropylvinylether (apve = $H_2NCH_2CH_2CH_2OCH{=}CH_2$) to *trans*-$[PtCl_2(coe)]_2$ (**1**) gave the unexpected product *trans*-$PtCl_2$(coe)(thmo) (**10**) (thmo = tetrahydro-2-methyl-1,3-oxazine) in moderate yields (40%). The formation of thmo presumably arises from a platinum mediated intramolecular hydroamination of the starting apve group (30). A proposed mechanism for this reaction is shown in Fig. 5 (31). Coordination of the alkene group to the metal centre activates it towards nucleophilic attack by the amine group. Selective attack at the carbon α to the ether oxygen affords an alkylplatinum intermediate. Subsequent hydrogen abstraction from the ammonium group yields an alkylmetal hydride intermediate which undergoes reductive elimination to produce free thmo and the coordinatively unsaturated metal species '$PtCl_2$(coe)'. This complex, or unreacted **1**, rapidly traps free thmo to give *trans*-$PtCl_2$(coe)(thmo). This reaction is specific for the hydroamination product as no other apve derivatives were observed. Further work in this area will concentrate on examining the hydroamination of *N*-substituted apve derivatives, the results of which will be reported in due course.

Hydroboration of Metal Complexes

We hypothesize that hydroboration of pendant alkenyl groups in the above mentioned alkenylamine and alkenylpyridine compounds, followed by aqueous workup, should give novel platinum complexes containing boronic acids, $-B(OH)_2$ (32). Compounds containing boronic acids have extensive biological activity (33) as well as facilitate the transport of molecules across lipid bilayers (34, 35). As hydroborations of the starting alkenylamines and alkenylpyridines are known to give a number of unwanted products (36, footnote 7), this present methodology is advantageous in that coordination of the ligand to the metal centre deactivates the lone pair of nitrogen.

Initial work was conducted on the monoalkene complexes **3**, **4**, **6**, and **9**. Not surprisingly, however, hydroborations of these complexes always gave complex product distributions arising from attack of the borane at the metal centre following initial loss of the labile cyclooctene ligand. We therefore decided to concentrate our efforts on functionalizing the disubstituted analogues and proceeded by using the fully characterized pyridine complex *trans*-$PtCl_2(4vp)_2$ (**5**). Reactions of **5** with catecholborane (HBcat, cat = $O_2C_6H_4$), using 7 mol% of $RhCl(PPh_3)_3$ (37), gave mixtures of *anti*-Markovnikov (45% by ^1H NMR spectroscopy) and Markovnikov (45%) hydroboration products, products derived from a dehydrogenative borylation/hydrogenation (5% each) pathway, as well as some decomposition to platinum metal. Dehydrogenative borylation is basically a mechanism that replaces one of the alkene hydrogens with a Bcat group while generating H_2; this latter species accounts for the observation of products containing hydrogenated 4-ethylpyridine. The complex product distributions observed in these reactions is somewhat surprising in light of the fact that hydroborations of styrene derivatives ($ArCH{=}CH_2$) using HBcat can give exclusive formation of either the Markovnikov ($ArCH(Bcat)CH_3$) or *anti*-Markovnikov ($ArCH_2CH_2Bcat$) products depending upon the choice of catalyst (37, 38).

It is plausible that the numerous products observed in hydroborations of **5** may be arising from the low solubility

[7] C.M. Vogels, P.E. O'Connor, M.P. Shaver, T.E. Phillips, K.J. Watson, and S.A. Westcott. unpublished results.

Fig. 5. Intramolecular hydroamination of aminopropylvinylether.

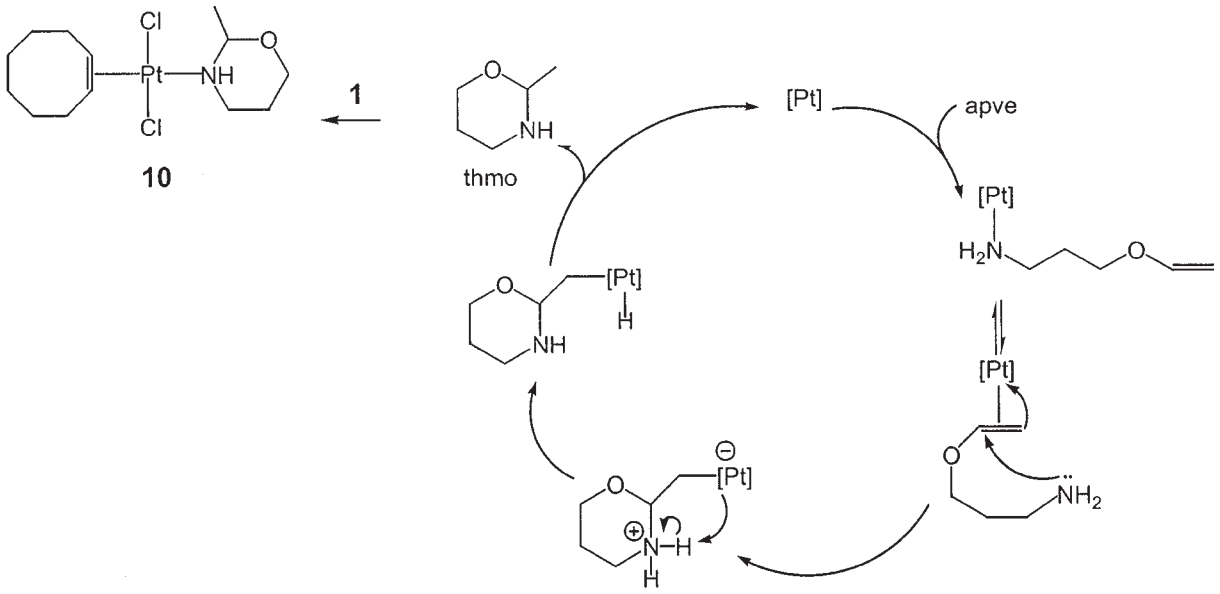
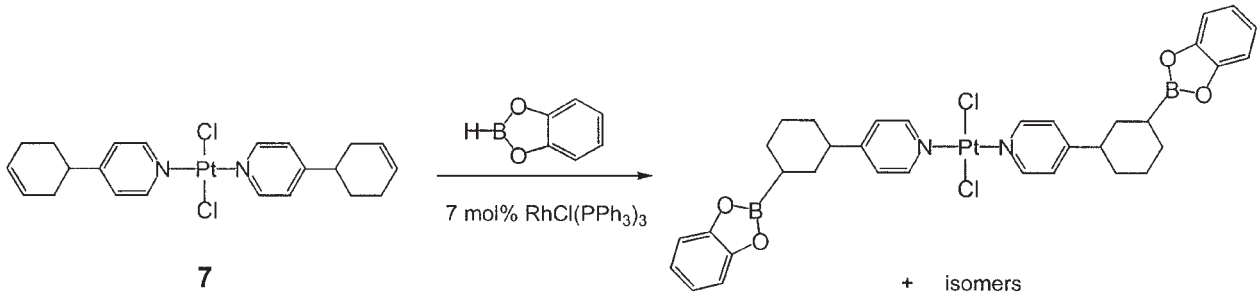


Fig. 6. Hydroboration of *trans*-$PtCl_2(4chp)_2$ (**7**) with catecholborane.



of the starting platinum material in organic solvents. We therefore decided to investigate the catalyzed hydroboration of organic soluble *trans*-$PtCl_2(4chp)_2$ (**7**). Addition of HBcat to **7** employing 7 mol% $RhCl(PPh_3)_3$ as a catalyst gave the desired hydroborated product (Fig. 6) as ascertained by multinuclear NMR spectroscopy. The diagnostic peak at 36 ppm in the $^{11}B\{^1H\}$ NMR spectrum suggests the formation of an organoboronate ester (38). Further evidence that the 1,2-disubstituted alkene is being reduced is indicated by the disappearance of the vinylic peak in the ^1H NMR spectrum. Preliminary results attempting to convert the hydroborated product to the corresponding boronic acid compound have also proven successful. However, because of the disubstituted nature of the alkene, it appears that this reaction is not selective as regioisomers are present as observed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. We are currently examining the full scope of this reaction in an effort to improve selectivities and will report our results in due course.

Conclusions

We have prepared a number of *trans* platinum alkenylpyridine and alkenylamine complexes from the organometallic dimer *trans*-$[PtCl_2(coe)]_2$ (coe = *cis*-cyclooctene). Coordination in all cases appears to proceed through the nitrogen lone pair and not the alkene moiety. Several novel organometallic complexes of the type *trans*-[PtCl(coe)L] (L = alkenylpyridine or alkenylamine) have also been prepared and characterized. Initial investigations into the functionalization of the pendant alkene groups have shown that catecholborane can be added to these complexes, using a rhodium catalyst, to give the corresponding organoboronate ester platinum compounds.

Acknowledgements

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References

1. R. Young, B. Chabner, S. Hubbard, R. Fischer, R. Bender, T. Anderson, and V. de Vita. Proc. Am. Soc. Clin. Oncol. **19**, 378 (1978).
2. E. Wong and C.M. Giandomenico. Chem. Rev. **99**, 2451 (1999).
3. E.R. Jamieson and S.J. Lippard. Chem. Rev. **99**, 2467 (1999).
4. J. Reedijk. Chem. Rev. **99**, 2499 (1999).
5. H. Kawai, Y. Kitano, M. Mutoh, and G. Hata. Chem. Pharm. Bull. **41**, 357 (1993).
6. U. Bierbach and N. Farrell. J. Biol. Inorg. Chem. **3**, 570 (1998), and refs. therein.
7. J.A. Osborn and G. Wilkinson. Inorg. Synth. **28**, 77 (1990).
8. E. Kuljian and H. Frye. Z. Naturforsch. B: Anorg. Chem. Org. Chem. Biochem. Biophys. Biol. **20b**, 204 (1965).
9. M.R. Plutino, S. Otto, A. Roodt, and L.I. Elding. Inorg. Chem. **38**, 1233 (1999).
10. J.F. Harrod. Inorg. Chem. **4**, 428 (1965).
11. J.A.J. Jarvis, B.T. Kilbourn, and P.G. Owston. Acta. Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem. **B27**, 366 (1971).
12. K.A. Fallis, G.K. Anderson, and N.P. Rath. Organometallics, **12**, 2435 (1993).
13. J. Bordner and D.W. Wertz. Inorg. Chem. **13**, 1639 (1974).
14. F.R. Hartley. The chemistry of platinum and palladium. John Wiley & Sons, New York. 1973.
15. C.M. Vogels, H.L. Wellwood, K. Biradha, M.J. Zaworotko, S.A. Westcott. Can. J. Chem. **77**, 1196 (1999).
16. M. Munakata, S. Kitagawa, H. Simono, T. Emori, and H. Masuda. J. Chem. Soc. Chem. Commun. 1798 (1987).
17. L.M. Engelhardt, P.C. Healy, J.D. Kildea, and A.H. White. Aust. J. Chem. **42**, 185 (1989).
18. R. Settambolo, S. Scamuzzi, A. Caiazzo, and R. Lazzaroni. Organometallics, **17**, 2127 (1998).
19. D. Thomas, W. Baumann, A. Spannenberg, R. Kempe, and U. Rosenthal. Organometallics, **17**, 2096 (1998).
20. A. Kasahara, K. Tanaka, and T. Izumi. Bull. Chem. Soc. Jpn. **42**, 1702 (1969).
21. M. Kubiak and J. Kuduk-Jaworska. Acta. Crystallogr. Sect. C: Cryst. Struct. Commun. **C42**, 1703 (1986).
22. J. Kuduk-Jaworska. Pol. J. Chem. **59**, 705 (1985).
23. A.G.M.M. Hossain and K. Ogura. Indian. J. Chem. **35A**, 373 (1996).
24. M.J. Bloemink, R.J. Heetebrij, J. Ireland, G.B. Deacon, and J. Reedijk. JBIC J. Biol. Inorg. Chem. **1**, 278 (1996).
25. R.G. Denning, F.R. Hartley, and L.M. Venanzi. J. Chem. Soc. A 324 (1967), and refs. therein.
26. D.B. Brown, A.R. Khokhar, M.P. Hacker, J.J. McCormack, and W.M. Stalick. Inorg. Chim. Acta. **67**, 45 (1982).
27. J. Viljanen, K.D. Klika, R. Sillanpää, and J. Arpalahti. Inorg. Chem. **38**, 4924 (1999).
28. E.I. Montero, S. Díaz, A.M. González-Vadillo, J.M. Pérez, C. Alonso, and C. Navarro-Ranninger. J. Med. Chem. **42**, 4264 (1999).
29. A.V. Kotov and L.N. Essen. Zh. Neorg. Khim. **15**, 2188 (1970).
30. C.M. Vogels, P.G. Hayes, M.P. Shaver, S.A. Westcott. Chem. Commun. (Cambridge), 51 (2000).
31. T.E. Muller and M. Beller. Chem. Rev. **98**, 675 (1998).
32. H.C. Brown. Hydroboration. Wiley–Interscience, New York. 1962.
33. C. Morin. Tetrahedron, **50**, 12521 (1994).
34. P.R. Westmark, S.J. Gardiner, and B.D. Smith. J. Am. Chem. Soc. **118**, 11093 (1996).
35. M. Takeuchi, T. Imada, S. Shinkai. J. Am. Chem. Soc. **118**, 10658 (1996).
36. A. Dicko, M. Montury, and M. Baboulene. Tetrahedron Lett. **28**, 6041 (1987).
37. I. Beletskaya and A. Pelter. Tetrahedron, **53**, 4957 (1997).
38. S.A. Westcott, H.P. Blom, T.B. Marder, and R.T. Baker. J. Am. Chem. Soc. **114**, 8863 (1992).