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Alkenylpyridine and alkenylamine complexes of palladium

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Abstract

Addition of alkenylamines and alkenylpyridines to *trans*-$[PdCl_2(coe)]_2$ *(1)* (coe = C_8H_{14}) afforded complexes of the type *trans*-$PdCl_2L_2$ (where L is a nitrogen-containing ligand). Coordination of the alkenylamine or alkenylpyridine groups occurred primarily through the nitrogen atom in all cases. Addition of aminopropylvinylether (apve = $H_2NCH_2CH_2CH_2OCH{=}CH_2$) to *(1)* gave *trans*-$PdCl_2(thmo)_2$ *(9)* (thmo = tetrahydro-2-methyl-1,3-oxazine) *via* an intramolecular hydroamination.

Introduction

Compounds containing boronic acid groups, $-B(OH)_2$, have not only found extensive application in cross-coupling reactions [1] but several examples display significant biological activity [2]. For instance, boronic acid derivatives of amino acids are effective and reversible inhibitors of the serine proteases chymotrypsin and subtilisin [3–9]. This biological activity is attributed to the boron's ability to coordinate (*via* its empty *p*-orbital) to the active hydroxyl groups of these enzymes. Boronic acid derivatives are also known to facilitate the transport of molecules across lipid bilayers [10, 11], an important attribute in the area of drug delivery. These properties prompted us to investigate the use of aminoboron compounds as ligands for biologically-active transition metals [12]. For example, palladium(II) complexes have been found to selectively cleave proteins in high yields in weakly acidic solutions [13] and palladium amine complexes have also been investigated for their potential as anti-cancer agents [14, 15]. With this in mind, we have prepared several *trans*-palladium 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 boron-containing palladium compounds. The results from the first part of our study, preparing palladium complexes containing alkenylamine and alkenylpyridine ligands, are described herein.

Experimental

Materials

Reagents and solvents used were obtained from Aldrich Chemicals. THF, hexane, and Et_2O were distilled from sodium benzophenone ketyl. CH_2Cl_2 and $CHCl_3$ were distilled from CaH_2. Na_2PdCl_4 was obtained from Johnson Matthey Ltd. *trans*-$[PdCl_2(coe)]_2$ [16], $PtI_2(cod)$ [17], $Pt(cod)Me_2$ [17], $[PtCl_2(coe)]_2$ [12], $RhCl(PPh_3)_3$ [18], $Pt(dba)_2$ [19], $[RhCl(coe)_2]_2$ [20] and $PdCl_2(NH_2CH_2Ph)_2$ [21] were prepared as described elsewhere.

Methods

N.m.r. spectra were recorded on a JEOL JNM-GSX270 FT-NMR spectrometer. ^{1}H-n.m.r. chemical shifts are reported in p.p.m. with reference to residual protons in deuteriated solvent at 270 MHz. $^{13}C\{^1H\}$-n.m.r. chemical shifts are referenced to solvent carbon resonances as internal standards at 68 MHz. Multiplicities are reported as (s) singlet, (d) doublet, (t) triplet, (m) multiplet, (br) broad, and (ov) overlapping. I.r. spectra were obtained using a Mattson Genesis II FT-IR spectrometer and are reported in cm^{-1}. M.p. were measured (uncorrected) with a Mel–Temp apparatus. Microanalyses for C, H, and N were carried out at Desert Analytics (Tucson, AZ).

trans-*$PdCl_2(2vp)_2$ (2)*

2-Vinylpyridine (137 mg, 1.30 mmol) in CH_2Cl_2 (5 cm^3) was added dropwise to *trans*-$[PdCl_2(coe)]_2$ (150 mg, 0.26 mmol) in CH_2Cl_2 (10 cm^3). After 24 h the solvent and coe were removed under vacuum and the resulting solid redissolved in CH_2Cl_2 (5 cm^3). Upon addition of hexane (5 cm^3), a yellow precipitate formed which was collected by suction filtration. Yield: 180 mg (89%); m.p. 152 °C. Spectroscopic n.m.r. data (in $CDCl_3$): ^{1}H δ: 9.00 (d, J = 5 Hz, 2H), 8.63 (br m, 2H), 7.75 (t, J = 8 Hz, 2H), 7.66 (m, 2H), 7.30 (ov m, 2H), 6.15 (d, J = 16 Hz, 2H), 5.98 (d, J = 13 Hz, 2H); $^{13}C\{^1H\}$ δ: 158.5, 152.7, 138.5, 136.9, 123.8, 122.8, 122.3. I.r. (nujol): 1602 (m), 1565 (m), 1477 (s), 1229 (w), 1165 (w),

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948 (m), 795 (s), 765 (s). (Found: C, 43.2; H, 3.2; N, 7.1. $PdCl_2C_{14}H_{14}N_2$ calcd.: C, 43.4; H, 3.6; N, 7.2%.)

trans-*$PdCl_2(4vp)_3$ (3)*

4-Vinylpyridine (91 mg, 0.87 mmol) in CH_2Cl_2 (5 cm^3) was added to *trans*-$[PdCl_2(coe)]_2$ (100 mg, 0.17 mmol) in CH_2Cl_2 (10 cm^3) and within 5 min a yellow solid began to precipitate. After 4 h, the yellow solid was collected by suction filtration and washed with $CHCl_3$ (3 × 10 cm^3). Yield: 80 mg (59%); m.p. 252 °C (decomposition). Selected spectroscopic n.m.r. data (in DMSO-d_6): ^1H δ: 8.75 (d, J = 5 Hz, 4H), 7.69 (d, J = 5 Hz, 4H), 6.39 (q, J = 16 Hz, 2H), 5.83 (d, J = 5 Hz, 2H), 5.63 (d, J = 5 Hz, 2H). I.r. (nujol): 1611 (m), 1548 (m), 1415 (s), 1206 (m), 1071 (m), 992 (m), 937 (m), 846 (s). (Found: C, 43.4; H, 3.6; N, 7.1. $PdCl_2C_{14}H_{14}N_2$ calcd.: C, 43.4; H, 3.7; N, 7.2%.)

trans-*$PdCl_2(chp)_2$ (4)*

4-(3-Cyclohexane-1-yl)-pyridine (499 mg, 3.13 mmol) in CH_2Cl_2 (5 cm^3) was added to *trans*-$[PdCl_2(coe)]_2$ (400 mg, 0.70 mmol) in CH_2Cl_2 (20 cm^3). After 3 h, the solution was filtered and solvent removed under vacuum to give an orange solid. Recrystallization from CH_2Cl_2/hexane (10/5 cm^3) afforded an orange solid which was collected by suction filtration. Yield: 450 mg (65%); m.p. 162 °C (decomposition). Spectroscopic n.m.r. data (in $CDCl_3$): ^1H δ: 8.70 (d, J = 5 Hz, 4H), 7.20 (d, J = 5 Hz, 4H), 5.77 (s, 4H), 2.86 (m, 2H), 2.31–2.15 (ov m, 8H), 1.94 (m, 2H), 1.78 (m, 2H); $^{13}C\{^1H\}$ δ: 159.5, 152.9, 127.4, 125.6, 123.9, 39.5, 32.0, 28.6, 25.1. I.r. (nujol): 1614 (m), 1461 (m), 1432 (m), 1377 (w), 1213 (w), 1071 (w), 915 (w), 826 (m). (Found: C, 53.3; H, 5.4; N, 5.7. $PdCl_2C_{22}H_{26}N_2$ calcd.: C, 53.3; H, 5.3; N, 5.7%.)

trans-*$PdCl_2(aa)_2$ (5)*

Allylamine (100 mg, 1.78 mmol) in CH_2Cl_2 (5 cm^3) was added to *trans*-$[PdCl_2(coe)]_2$ (250 mg, 0.39 mmol) in CH_2Cl_2 (15 cm^3) at 0 °C. After 1 h, the pale yellow solution was filtered and solvent removed under vacuum to give a yellow solid. Recrystallization from CH_2Cl_2/hexane (10/5 cm^3) under an atmosphere of N_2 at 2 °C gave a yellow solid which was collected by filtration and washed with hexane (3 × 10 cm^3). Yield: 56 mg (24%); m.p. 103 °C. Spectroscopic n.m.r. data (in $CDCl_3$): ^1H δ: 5.96 (m, 2H), 5.28 (ov m, 4H), 3.42 (d, J = 5 Hz, 4H), 2.91 (br s, 4H); $^{13}C\{^1H\}$ δ: 134.2, 119.0, 47.7. I.r. (nujol): 3265 (m), 3222 (w), 3136 (w), 1640 (w), 1580 (m), 1461 (m), 1377 (w), 1337 (w), 1020 (w), 933 (w). (Found: C, 25.0; H, 4.8; N, 9.4. $PdCl_2C_6H_{14}N_2$ calcd.: C, 24.7; H, 4.8; N, 9.6%.)

trans-*$PdCl_2(4va)_2$ (6)*

4-Vinylaniline (180 mg, 1.48 mmol) in CH_2Cl_2 (5 cm^3) was added to *trans*-$[PdCl_2(coe)]_2$ (210 mg, 0.33 mmol) in CH_2Cl_2 (20 cm^3). After 24 h, a dark yellow solid was collected by filtration and washed with CH_2Cl_2 (3 × 10 cm^3). Recrystallization from THF/hexane (25/10 cm^3) afforded an orange solid. Yield: 200 mg (76%); m.p. 214 °C (decomposition). Spectroscopic n.m.r. data (in DMSO-d_6): ^1H δ: 7.45 (d, J = 8 Hz, 4H), 7.31 (d, J = 5 Hz, 4H), 7.02 (br s, 4H), 6.75 (q, J = 27 Hz, 2H), 6.66 (q, J = 24 Hz, 2H), 5.88 (d, J = 19 Hz, 2H); $^{13}C\{^1H\}$ (in THF) δ: 141.9, 136.9, 134.4, 126.7, 122.6, 112.2. I.r. (nujol): 3237 (m), 3196 (m), 3123 (m), 1582 (m), 1508 (m), 1462 (m), 1377 (w), 1141 (m), 986 (w), 831 (m). (Found: C, 45.9; H, 4.8; N, 6.6. $PdCl_2C_{16}H_{18}N_2$ calcd.: C, 46.2; H, 4.4; N, 6.7%.)

trans-*$PdCl_2(chea)_2$ (7)*

2-(1-Cyclohexenyl)ethylamine (196 mg, 1.56 mmol) in CH_2Cl_2 (5 cm^3) was added to *trans*-$[PdCl_2(coe)]_2$ (200 mg, 0.35 mmol) in CH_2Cl_2 (20 cm^3). After 1 h, the solvent and coe were removed under vacuum and the resulting yellow solid dissolved in CH_2Cl_2 (10 cm^3). Compound *(7)* was crystallized by addition of hexane (5 cm^3) and collected by suction filtration. Yield: 195 mg (66%); m.p. 154 °C. Spectroscopic n.m.r. data (in $CDCl_3$): ^1H δ: 5.52 (s, 2H), 2.86 (m, 4H), 2.62 (br s, 4H), 2.17 (t, J = 8 Hz, 4H), 2.00 (s, 4H), 1.90 (s, 4H), 1.57 (m, 8H); $^{13}C\{^1H\}$ δ: 133.0, 125.7, 42.7, 39.8, 28.0, 25.4, 22.9, 22.5. I.r. (nujol): 3274 (w), 3215 (m), 3132 (w), 2927 (s), 1580 (w), 1462 (s), 1377 (s), 1154 (w), 1025 (w), 721 (w). (Found: C, 44.9; H, 7.0; N, 6.6. $PdCl_2C_{16}H_{30}N_2$ calcd.: C, 44.9; H, 7.1; N, 6.6%.)

trans-*$PdCl_2(aA)_2$ (8)*

N-Allylaniline (48 mg, 0.36 mmol) in CH_2Cl_2 (5 cm^3) was added to *trans*-$[PdCl_2(coe)]_2$ (51 mg, 0.08 mmol) in CH_2Cl_2 (5 cm^3). After 24 h, the solvent was removed to afford an orange–red solid. Crystallization from CH_2Cl_2/hexane (5/5 cm^3) at 2 °C afforded an orange solid which was collected by suction filtration. Yield: 20 mg (28%); m.p. 111 °C. Spectroscopic n.m.r. data (in $CDCl_3$): ^1H δ: 7.30 (m, 10H), 6.04 (m, 2H), 5.42–5.15 (ov m, 4H), 4.11 (m, 2H), 3.48 (m, 2H), 1.60 (br s, 2H); $^{13}C\{^1H\}$ δ: 144.0, 131.6, 129.6, 126.4, 121.6, 55.7. I.r. (nujol): 3166 (w), 1598 (m), 1483 (m), 1463 (m), 1378 (m), 1202 (w), 1159 (w), 1070 (m), 931 (m). (Found: C, 48.7; H, 4.9; N, 6.2. $PdCl_2C_{18}H_{22}N_2$ calcd.: C, 48.7; H, 5.0; N, 6.3%.)

trans-*$PdCl_2(thmo)_2$ (9)*

Tetrahydro-2-methyl-1,3-oxazine (72 mg, 0.72 mmol) in CH_2Cl_2 (5 cm^3) was added to *trans*-$[PdCl_2(coe)]_2$ (120 mg, 0.18 mmol) in CH_2Cl_2 (10 cm^3) at 0 °C. After 1 h, solvent was removed under vacuum to afford a yellow solid which was triturated with hexane (3 × 10 cm^3) to remove coe. Following extraction with Et_2O (70 cm^3), compound *(9)* was isolated upon the removal of solvent under vacuum. Yield: 65 mg (46%);

m.p. 107 °C. Spectroscopic n.m.r. data (in $CDCl_3$): ^1H δ: 4.43 (q, J = 5 Hz, 2H), 3.95 (d, J = 5 Hz, 2H), 3.67 (t, J = 11 Hz, 2H), 3.34 (m, 6H), 3.10 (m, 2H), 1.85 (d, J = 5 Hz, 6H), 1.45 (d, J = 14 Hz, 2H); $^{13}C\{^1H\}$ δ: 87.2, 67.1, 49.1, 26.5, 22.9. I.r. (nujol): 3453 (w), 3184 (w), 2935 (s), 2860 (s), 1452 (s), 1377 (s), 1138 (m), 817 (w), 722 (m). (Found: C, 31.7; H, 5.9; N, 7.2. $PdCl_2C_{10}H_{22}N_2O_2$ calcd.: C, 31.6; H, 5.9; N, 7.3%.) Alternatively, complex *(9)* could be prepared by addition of 4 equivalents of aminopropylvinylether to *trans*-$[PdCl_2(coe)]_2$ in CH_2Cl_2.

Catalytic hydroamination of apve to thmo

The catalyst (0.02 mmol) was added to excess aminopropylvinylether (40 mg, 0.40 mmol) in 1 cm^3 of $CDCl_3$. After 24 h, the reaction was analyzed by high field ^1H-n.m.r. spectroscopy. Aminopropylvinylether was then added in known amounts until it began to accumulate, indicating that no more thmo was being produced.

Results and discussion

As part of our ongoing research into making novel metal complexes containing aminoboron ligands, we initially decided to prepare unsaturated amine and pyridine palladium complexes from the monoalkene dimer *trans*-$[PdCl_2(coe)]_2$ *(1)* (coe = C_8H_{14}) [16]. This starting dimer, which is soluble in common organic solvents, was readily prepared by the addition of *cis*-cyclooctene to an aqueous solution of Na_2PdCl_4 and appears to be indefinitely stable in the solid state. Addition of neutral ligands (L) to *(1)* affords complexes of the type *trans*-$PdCl_2L_2$ [12]. 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

Although transition metal complexes [22–26] containing alkenylpyridine ligands have been reported, only a few palladium alkenylpyridine complexes are known [24–26]. For instance, reactions of Na_2PdCl_4 and 2-vinylpyridine carried out in methanol, ethanol, or isopropanol gave the corresponding di-μ-chloro-bis[alkoxy-2-(α-pyridyl)ethyl]dipalladium(II) complexes [25]. We have found that addition of 2-vinylpyridine (2vp = 2-$NC_5H_4CH{=}CH_2$, Figure 1) to *(1)* in CH_2Cl_2, however, gave exclusive formation of *trans*-$PdCl_2(2vp)_2$ *(2)* in high yields (89%). ^1H-n.m.r. data suggests that bonding occurs through the nitrogen atom [26], as the α-hydrogen of the pyridine ring shifts from 8.54 p.p.m. for the free ligand to 9.00 p.p.m. for the metal complex. Interestingly, the alkene protons also display significant deshielding in the ^1H-n.m.r. spectrum moving from 6.83 p.p.m. for the free ligand to 8.63 p.p.m. for the metal complex. A possible explanation for this observation is that the alkenyl hydrogens are oriented directly above and below the plane of the palladium atom. This type of interaction has been reported previously with $PdCl_2$(1-tetralone oxime)$_2$ [27] where one of the aromatic hydrogens shifts from 8 p.p.m. for the free ligand to almost 10 p.p.m. in the palladium complex. Likewise, a square pyramidal cyclopalladated triphosphine complex has recently been reported where a pendant imine functionality lies directly above the metal centre [28]. Attempts to grow crystals of compound *(2)* suitable for X-ray diffraction studies to confirm this arrangement proved unsuccessful. Interestingly, previous work has shown that attempts to prepare platinum complexes from 2vp resulted in the formation of several products where both the alkene and the nitrogen groups are involved in bonding to the metal centre [22, 25].

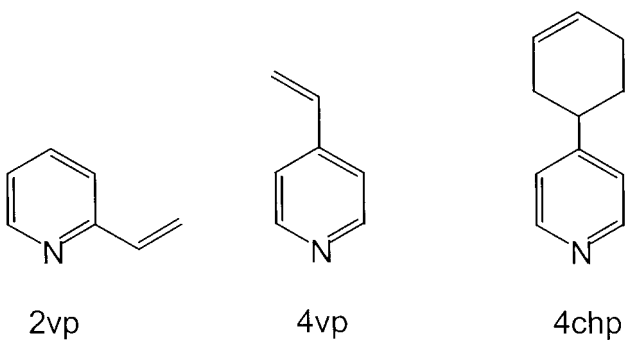

Fig. 1. Alkenylpyridines.

Similar to reactions using 2vp, the corresponding 4-vinylpyridine (4vp = 4-$NC_5H_4CH{=}CH_2$) complex, *trans*-$PdCl_2(4vp)_2$ *(3)*, was prepared by addition of 4 equivalents of 4vp to *(1)*. Unlike the 2vp compound however, complex *(3)* was insoluble in most common organic solvents and attempts to obtain spectroscopic n.m.r. data in DMSO-d_6 were complicated by displacement of the alkenylpyridine ligand. A recent X-ray diffraction study of the analogous platinum complex, *trans*-$PtCl_2(4vp)_2$, confirms that the bonding mode in these complexes occurs through the pyridine nitrogen atom [22]. The disubstituted compound *trans*-$PdCl_2(4chp)_2$ *(4)* (4chp = 4-$NC_5H_4C_6H_9$) was prepared by reacting the cyclooctene dimer *(1)* with 4 equivalents of 4chp. The resulting product has the diagnostic n.m.r. shifts for the α-hydrogens of the pyridine group from 8.48 p.p.m. for the free pyridine to 8.70 p.p.m. for the metal complex. As well, n.m.r. spectroscopy indicates that there was no significant change for the alkene resonance. The cyclohexenyl group in this complex resulted in *(4)* having increased solubility in organic solvents as compared to *(3)*.

Alkenylamines

We have found that addition of allylamine (aa = $NH_2CH_2CH{=}CH_2$, Figure 2) to *trans*-$[PdCl_2(coe)]_2$

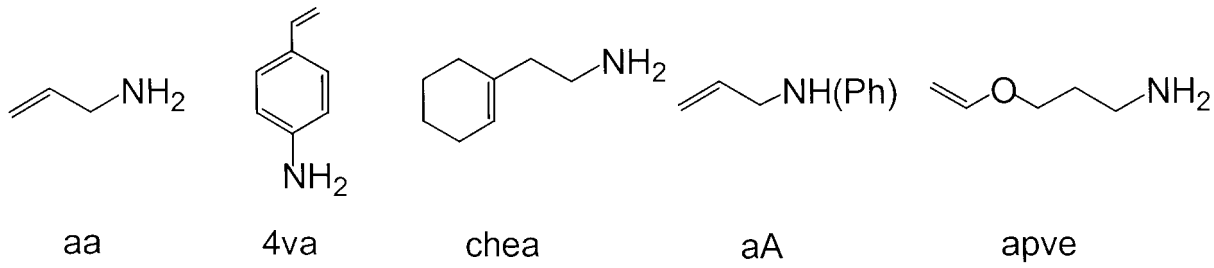

Fig. 2. Alkenylamines.

(1) afforded the novel diamine complex *trans*-$PdCl_2(aa)_2$ *(5)* in low yield (24%). Although complex *(5)* is soluble in CH_2Cl_2, degradation occurs over time ($t_{1/2} \simeq 1$ h) to give a mixture of unidentified products along with palladium metal. This observation is not surprising as several allylamine complexes of platinum have been reported where the alkene moiety competes for binding with the metal centre [22]. The amine hydrogens in *(5)* appear as a broad peak in the ^{1}H-n.m.r. spectrum and shift downfield from 1.23 for free allylamine to 2.91 p.p.m. upon coordination to palladium. The peaks attributed to the alkenyl hydrogens, however, remain relatively unchanged shifting from 5.90 and 5.20 p.p.m. for free allylamine to 5.96 and 5.28 p.p.m., respectively, for the metal complex. This suggests that coordination of the allylamine ligand again occurs solely through the nitrogen atom. I.r. data supports this hypothesis as the C=C π stretch for free allylamine at 1637 cm^{-1} only shifts to 1580 cm^{-1} for the palladium complex. The C=C π stretch for *trans*-$[PdCl_2(coe)]_2$, where the alkene is directly bound to the metal centre, appears at 1513 cm^{-1}. Likewise, *trans*-$PdCl_2(4va)_2$ *(6)* was synthesized in moderate yield (76%) by addition of 4-vinylaniline (4va = $H_2NC_6H_4CH{=}CH_2$) to *(1)*. ^{1}H-n.m.r. and i.r. data indicate that coordination of the ligand again occurs through the amine nitrogen. For example, the C=C π stretch shifts only slightly from 1620 cm^{-1} for free 4-vinylaniline to 1582 cm^{-1} for the metal complex in the solid state. The expected diamine complex *trans*-$PdCl_2(chea)_2$ *(7)* (chea = 2-$H_2NCH_2CH_2C_6H_9$) was also prepared by addition of chea to dimer *(1)*. Complex *(7)* is soluble in common organic solvents and stable indefinitely in solution. Not surprisingly, coordination in this case again appears to be through the nitrogen atom as no appreciable change in the alkenyl proton was observed in the ^{1}H-n.m.r. spectrum. Remarkably, addition of the bulky secondary amine *N*-allylaniline (aA = $NH(Ph)CH_2CH{=}CH_2$) to *(1)* afforded the diamine *trans*-$PdCl_2(aA)_2$ *(8)*, albeit in low yield (28%). This result is surprising as the analogous platinum complex could not be generated from *trans*-$[PtCl_2(coe)]_2$ [29]. The weak nucleophilic nature of aA presumably precludes substitution of the coe group in *trans*-$[PtCl_2(coe)]_2$ where the alkene is held more strongly to the metal centre, due to increased π-backbonding, than in the case for the less electron rich palladium compound *(1)* [24].

Interestingly, attempts to prepare the diamine complex derived from addition of aminopropylvinylether (apve = $H_2NCH_2CH_2CH_2OCH{=}CH_2$) to *(1)* led to the formation of *trans*-$PdCl_2(thmo)_2$ *(9)* (thmo = tetrahydro-2-methyl-1,3-oxazine) [30], which presumably arises from a palladium mediated intramolecular hydroamination of the starting amine (Figure 3). This reaction probably proceeds *via* initial coordination of the amine group to the metal centre with subsequent isomerization to give a transient palladium alkene intermediate. The alkene is now activated towards nucleophilic attack by the amine group [31–41] and selective attack at the carbon alpha to the ether oxygen affords a six-membered ring alkylpalladium species. Subsequent hydrogen abstraction of the amino group by the metal yields an alkylmetal hydride which undergoes reductive elimination to produce free thmo and the coordinatively unsaturated fragment '$PdCl_2(coe)$' [42]. This intermediate, or unreacted *(1)*, rapidly traps free thmo as *trans*-$PdCl_2(coe)(thmo)$, which rapidly converts another molecule of apve to thmo, and with loss of coe, affords the diamine complex *(9)*.

We have found that several palladium and platinum complexes effectively catalyse the intramolecular hydroamination of apve in high turnover numbers (Table 1). For instance, PdI_2 (entry 1) catalyses the hydroamination of apve to thmo with a turnover number of 1500. $PdI_2(thmo)_2$ (entry 2), generated *in situ* by addition of thmo to PdI_2, shows comparable catalytic activity to PdI_2, suggesting that the diamine complex may be a resting state in the catalytic cycle. Iodides appear to be better catalysts than the corresponding chlorides, as clearly seen for PdI_2 (entry 1) and $PdCl_2$ (entry 12) which have turnover numbers of 1500 and 2, respectively. The preformed dichloride complex $PdCl_2(thmo)_2$ (entry 8) showed greater catalytic activity than $PdCl_2$ did (entry 12), presumably due to the increased solubility of complex *(9)* in organic solvents. High turnover numbers were also achieved with several platinum complexes, which showed comparable activity to their palladium analogues (entries 6 and 7). Surprisingly, rhodium complexes (entries 13 and 14) failed to affect this transformation [43]. We have also found that attempts to catalyse these reactions in aqueous solvents were complicated by cleavage of the O—Csp^2 bond of apve to give complex product distributions. This reaction is highly specific for apve as efforts to catalyse the intermolecular hydroamination of ethylvinylether

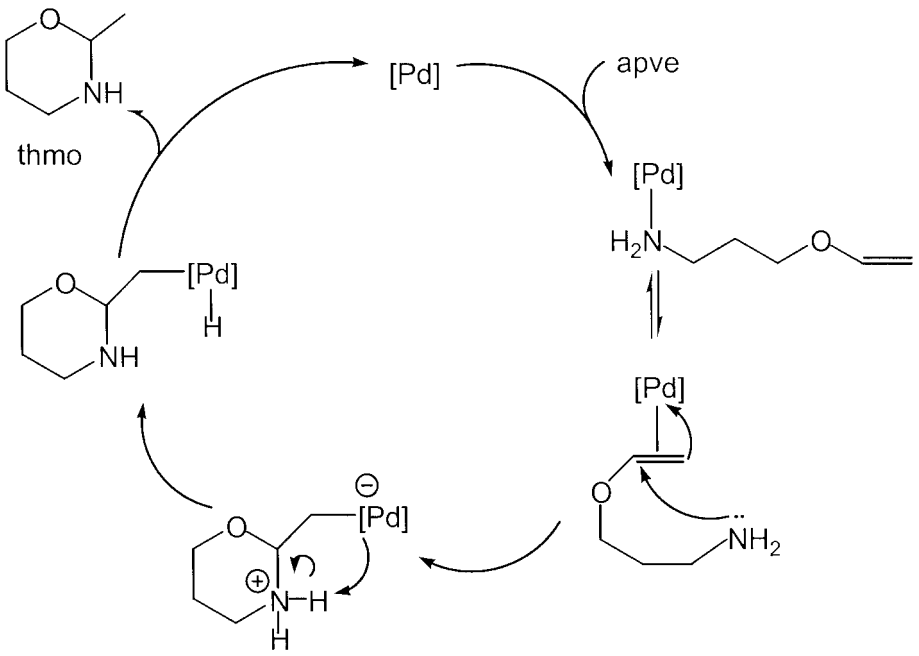

Fig. 3. Intramolecular hydroamination of aminopropylvinylether.

and propylamine using these palladium complexes proved unsuccessful. Likewise, hydroamination was not observed when *(1)* was treated with 2-(1-cyclohexenyl)ethylamine. This latter result was not unexpected as 2-(1-cyclohexenyl)ethylamine is a bulky trisubstituted alkene and lacks a heteroatom α to the double bond. It appears that the ether oxygen in apve also plays a role in the activation of the alkene towards intramolecular nucleophilic attack.

In summary, we have prepared several *trans* alkenylpyridine and alkenylamine palladium complexes from the organometallic dimer *trans*-$[PdCl_2(coe)]_2$. Coordination in all cases appears to proceed primarily through the nitrogen atom. Further investigations will be conducted on the hydroboration of the pendant alkene groups in these complexes, the results of which will be reported in due course. We have also found that palladium and platinum complexes effectively catalyse the intramolecular hydroamination of apve in high turnover numbers. Studies of an asymmetric variant of the hydroamination chemistry, as well as expanding the scope of the reaction, are currently under investigation.

Table 1. Metal catalysed hydroamination of apve

Entry	Catalyst	TON[a]
1	PdI_2	1500
2	$PdI_2(thmo)_2$	1500
3	$PdI_2(chea)_2$	1000
4	$PdI_2(NH_2CH_2Ph)_2$	500
5	$Pt(cod)Me_2$[b]	300
6	$[PtCl_2(coe)]_2$	200
7	$[PdCl_2(coe)]_2$	200
8	$PdCl_2(thmo)_2$	200
9	$PtI_2(cod)$[b]	100
10	$Pt(dba)_2$[c]	25
11	$PdCl_2(chea)_2$	20
12	$PdCl_2$	2
13	$[RhCl(coe)_2]_2$	2
14	$RhCl(PPh_3)_3$	0

[a] TON = turnover number = number of molecules of thmo produced per molecule of catalyst; [b] cod = *cis*-cycloocta-1-5-diene; [c] dba = dibenzylideneacetone.

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TMCH 4769