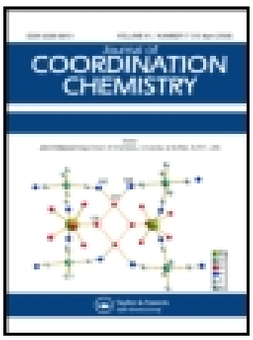

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Bicyclic N-heterocyclic carbene (NHC) ligand precursors and their palladium complexes

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Eight bicyclic amidinium precursors (**3**), prepared from *R*,*S*-tmcp (*R*,*S*-tmcp: (1*R*,3*S*)-diamino-1,2,2-trimethylcyclopentane) were described. Only five of the precursors (**3a-e**) could be converted to palladium complexes, (PdX_2(6,7-NHC)PEPPSI) (**4**) by treatment with $PdCl_2$, K_2CO_3 and pyridine (additional KBr was used for ($PdBr_2$(6,7-NHC)PEPPSI)). The salts and complexes were fully characterized by spectroscopic methods and X-ray crystallography.

Keywords: Chiral bicyclic N-heterocyclic carbine; Expanded ring *N*-heterocyclic carbine; PEPPSI-type palladium complex; Camphoric acid; X-ray diffraction

1. Introduction

N-heterocyclic carbenes (NHCs) are attractive ligands in coordination chemistry and catalysis due to their readily tunable steric and electronic nature [1-10]. Ring-expanded N-heterocyclic carbenes have become popular, as it has been established that they possess quite different properties in comparison to the more traditional five-membered derivatives [11-17]. Interest has also extended to the behavior of bicyclic NHCs, which contain two expanded rings, and

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therefore, unlike the expanded ring NHCs, where the ring is rigid, will not twist in conformation to enable coordination. These chiral ligand systems were first introduced by Wilhelm [18], Cavell [11], and Newman [19, 20], furthermore a series of bicyclic N-heterocyclic carbenes with coordination to silver [19], rhodium [19, 20], iridium [19, 20], nickel [19, 20], and copper [21] have been reported.

The ring expanded NHC complexes indicate the N-C-N angle in the NHC frame is an important factor for efficiency. However, the deprotonation step in preparation of ring expanded NHC complexes proved to be more challenging than expected and this property has been attributed to the relatively low acidity of the NC*H*N proton in the expanded ring NHC salts [22].

Chiral bicyclic PEPPSI-type palladium-NHC complexes have not been described (where PEPPSI stands for **P**yridine-**E**nhanced **P**recatalyst **P**reparation **S**tabilization and **I**nitiation). Therefore, this work focuses on coordination of chiral bicyclic NHCs to Pd(II). The complexes obtained have been characterized by elemental analysis, NMR spectroscopy, and **4a**, **4b**, **4d** and **4e** by X-ray crystallography.

2. Experimental

2.1. *General procedure*

Air sensitive experiments were carried out using standard Schlenk techniques under an atmosphere of argon. ***R,S*-tmcp** [23] and **3f** [18] were synthesized according to literature methods. Glassware was dried overnight at 120 °C and flame dried prior to use. Solvents were dried prior to use. All chemicals were obtained from commercial sources and used as received. ^{1}H and ^{13}C NMR measurements were performed using a Varian AS 400 spectrometer operating at 400 and 100 MHz, respectively. Chemical shifts were reported in ppm relative to TMS for ^{1}H and ^{13}C NMR spectra. Melting points were measured in open capillary tubes with a Stuart SMP 30 melting point apparatus. Elemental analyses were performed by ODTU Microlab (Ankara, Turkey). Optical rotations were measured using a 1 dm path length (c is given as g/100 mL) on an ADP-410 (Bellingham-Stanley) polarimeter in the reported solvent.

2.2. *Synthesis of 1*

(1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-diamine (1.0 g, 7.0 mmol) was dissolved in 10.0 mL DCM and $Et_2O{\cdot}HCl$ was added slowly until forming a white solid. The reaction mixture was

filtered. The precipitate was washed with Et_2O and dried. The product (1.25 g, 8.8 mmol) and triethyl orthoformate (10.0 mL) were refluxed for 24 h. Then, the reaction mixture was cooled; added Et_2O for precipitation of yield. The product was filtered and dried. The white solid product was recrystallized from DCM/Et_2O.

Yield: 1000 mg (92.0%) Mp > 250 °C. $[\alpha]_D^{26}$ = +50 (c = 0.06, $CHCl_3$). Anal. Calcd. for $C_9H_{17}ClN_2$ (188.69 g mol^{-}): C, 57.30; H, 9.08; N, 14.85. Found: C, 56.55; H, 8.93; N, 14.74. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.81 (s, 1H, NC*H*N); 3.37 (d, *J* = 4.3 Hz, 1H, NC(CH_2)(CH_2)C*H*N); 2.41-2.34 (m, 1H, NC(C*H*H)(CH_2)CHN); 2.12-2.05 (m, 2H, NC(CH_2)(C*H*$_2$)CHN); 2.03-1.93 (m, 1H, NC(CH*H*)(CH_2)CHN) 1.28 (s, 3H, NCC*H*$_3$); 1.06 (s, 3H, C(C*H*$_3$)(CH_3)); 0.98 (s, 3H, C(CH_3)(C*H*$_3$)]. ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 150.8 (N*C*HN); 65.3 (N*C*CH_3); 61.4 (N*C*(CH_2)(CH_2)CHN); 42.5 (*C*(CH_3)(CH_3)); 38.9 (NC(*C*H$_2$)(*C*H$_2$)CHN); 20.8 (NC*C*H_3); 16.9 (C(*C*H_3)(CH_3)); 16.3 (C(CH_3)(*C*H_3)).

2.3. *General procedure for 3a-c*

5,8,8-Trimethyl-2,4-diazabicyclo[3.2.1]oct-2-ium chloride (**2**, 2.6 mmol) was placed in a Schlenk flask and potassium carbonate (5.2 mmol), benzyl bromides (5.2 mmol), and acetonitrile (10.0 mL) were added. The reaction mixture was heated to 90 °C for 4 days. The mixture was then cooled slowly to room temperature, the acetonitrile was removed on a rotary evaporator, the remaining solid was dissolved in DCM (25.0 mL), filtered to remove the impurity, and solvent was removed in vacuum. The product was recrystallized from DCM/Et_2O.

3a: Yield: 713 mg (61%) Mp: 218-219 °C. $[\alpha]_D^{27}$ = +183.3 (c = 0.06, $CHCl_3$). Anal. Calcd. for $C_{25}H_{33}ClN_2$ (396.99 g mol^{-}): C, 75.63; H, 8.38; N, 7.06. Found: C, 75.35; H, 8.02; N, 7.53. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.03 (s, 1H, NC*H*N); 7.31 (d, *J* = 8.2 Hz, 2H, C_6H_4-*p*-(CH_3)); 7.24 (d, *J* = 8.2 Hz, 2H, C_6H_4-*p*-(CH_3)); 7.10 (d, *J* = 5.8 Hz, 2H, C_6H_4-*p*-(CH_3)); 7.08 (d, *J* = 8.2 Hz, 2H, C_6H_4-*p*-(CH_3)); 4.92 (dd, *J* = 18.4 Hz, *J* = 14.9 Hz, 2H, NC*H*$_2$$C_6H_4$-*p*-($CH_3$)); 4.62 (dd, *J* = 21.5 Hz, *J* = 14.9 Hz, 2H, NC*H*$_2$$C_6H_4$-*p*-($CH_3$)); 3.07 (d, *J* = 4.7 Hz, 1H, NC(CH_2)(CH_2)C*H*N); 2.27 (s, 3H, C_6H_4-*p*-(C*H*$_3$)); 2.25 (s, 3H, C_6H_4-*p*-(C*H*$_3$)); 2.21-2.14 (m, 1H, NC(C*H*H)(CH_2)CHN); 2.02-1.95 (m, 1H, NC(CH*H*)(CH_2)CHN); 1.92-1.85 (m, 1H, NC(CH_2)(C*H*H)CHN); 1.71-1.63 (m, 1H, NC(CH_2)(CH*H*)CHN); 1.15 (s, 3H, NCC*H*$_3$); 0.88 (s, 3H, C(C*H*$_3$)(CH_3)); 0.72 (s, 3H, C(CH_3)(C*H*$_3$)). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 138.7 (N*C*HN); 138.1 (*C*$_6$H$_4$-*p*-(CH_3)); 132.3 (*C*$_6$H$_4$-*p*-(CH_3)); 130.0 (*C*$_6$H$_4$-*p*-(CH_3)); 129.5 (*C*$_6$H$_4$-*p*-

(CH_3)); 129.3 (C_6H_4-*p*-(CH_3)); 127.9 (C_6H_4-*p*-(CH_3)); 70.7 (N*C*$H_2C_6H_4$(CH_3)); 65.2 (N*C*H_2 C_6H_4(CH_3)); 56.4 (NC(CH_2)(CH_2)*C*HN); 53.3 (N*C*(CH_2)(CH_2)CHN); 40.6 (NC(*C*H_2)(CH_2)CHN); 39.6 (NC(CH_2)(*C*H_2)CHN); 31.3 (*C*(CH_3)(CH_3)); 21.3 (C_6H_4-*p*-(*C*H_3)); 21.1 (C_6H_4-*p*-(*C*H_3)); 21.0 (NC*C*H_3); 16.9 (C(*C*H_3)(CH_3)); 14.6 (C(CH_3)(*C*H_3)).

3b: Yield: 780 mg (56%) Mp > 250 °C. $[\alpha]_D^{27}$ = +40.0 (c = 0.05, $CHCl_3$). Anal. Calcd. for $C_{31}H_{45}ClN_2$ (481.15 g mol^{-}): C, 77.38; H, 9.43; N, 5.82. Found: C, 77.95; H, 9.72; N, 6.01. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.04 (s, 1H, NC*H*N); 7.37 (d, *J* = 2.7 Hz, 4H, C_6H_4-*p*-$C(CH_3)_3$); 7.33 (d, *J* = 3.5 Hz, 4H, C_6H_4-*p*-$C(CH_3)_3$); 5.01-4.93 (m, 2H, NC$H_2C_6H_4$-*p*-$C(CH_3)_3$); 4.68 (dd, *J* = 29.0 Hz, *J* = 14.9 Hz, 2H, NC$H_2C_6H_4$-*p*-$C(CH_3)_3$); 3.09 (d, *J* = 5.1 Hz, 1H, NC(CH_2)(CH_2)C*H*N); 2.32-2.24 (m, 1H, NC(C*H*H)(CH_2)CHN); 2.12-2.04 (m, 1H, NC(CH*H*)(CH_2)CHN); 1.94-1.86 (m, 1H, NC(CH_2)(C*H*H)CHN); 1.74-1.67 (m, 1H, NC(CH_2)(CH*H*)CHN); 1.27 (s, 9H, C_6H_4-*p*-C(CH_3)$_3$); 1.26 (s, 9H, C_6H_4-*p*-C(CH_3)$_3$); 1.20 (s, 3H, NCCH_3); 0.94 (s, 3H, C(CH_3)(CH_3)); 0.79 (s, 3H, C(CH_3)(CH_3)). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 154.5 (N*C*HN); 152.0 (C_6H_4-*p*-$C(CH_3)_3$); 151.5 (C_6H_4-*p*-$C(CH_3)_3$); 132.3 (C_6H_4-*p*-$C(CH_3)_3$); 130.1 (C_6H_4-*p*-$C(CH_3)_3$); 129.1 (C_6H_4-*p*-$C(CH_3)_3$); 127.7 (C_6H_4-*p*-$C(CH_3)_3$); 125.9 (C_6H_4-*p*-$C(CH_3)_3$); 70.7 (N*C*$H_2C_6H_4$-*p*-$C(CH_3)_3$); 65.5 (N*C*$H_2C_6H_4$-*p*-$C(CH_3)_3$); 56.6 (NC(CH_2)(CH_2)*C*HN); 53.4 (N*C*(CH_2)(CH_2)CHN); 40.8 (NC(*C*H_2)(CH_2)CHN); 39.7 (NC(CH_2)(*C*H_2)CHN); 34.6 (*C*(CH_3)(CH_3)); 31.4 (C_6H_4-*p*-*C*$(CH_3)_3$); 31.2 (C_6H_4-*p*-C(*C*H_3)$_3$); 21.5 (NC*C*H_3); 17.1 (C(*C*H_3)(CH_3)); 14.8 (C(CH_3)(*C*H_3)).

3c: Yield: 980 mg (74%) Mp: 211-212 °C. $[\alpha]_D^{27}$ = +80.0 (c = 0.05, $CHCl_3$). Anal. Calcd. for $C_{29}H_{41}ClN_2$ (453.10 g mol^{-}): C, 76.87; H, 9.12; N, 6.18. Found: C, 76.38; H, 8.98; N, 6.02. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.02 (s, 1H, NC*H*N); 7.37 (d, *J* = 7.8 Hz, 2H, C_6H_4-*p*-$CH(CH_3)_2$); 7.31 (d, *J* = 8.2 Hz, 2H, C_6H_4-*p*-$CH(CH_3)_2$); 7.19 (d, *J* = 7.4, Hz 2H, C_6H_4-*p*-$CH(CH_3)_2$); 7.19 (t, *J* = 7.4, Hz, 4H, C_6H_4-*p*-$CH(CH_3)_2$); 4.97 (dd, *J* = 17.8 Hz, *J* = 14.7 Hz, 2H, NC$H_2C_6H_4$-*p*-$CH(CH_3)_2$); 4.67 (dd, *J* = 29.7 Hz, *J* = 14.9 Hz, 2H, NC$H_2C_6H_4$-*p*-$CH(CH_3)_2$); 3.09 (d, *J* = 4.7 Hz, 1H, NC(C*H*H)(CH_2)C*H*N); 2.89-2.84 (m, 2H, C_6H_4-*p*-C*H*$(CH_3)_2$); 2.30-2.22 (m, 1H, NC(CH*H*)(CH_2)CHN); 2.10-2.03 (m, 1H, NC(CH_2)(C*H*H)CHN); 1.95-1.86 (m, 1H, NC(CH_2)(CH*H*)CHN); 1.74-1.66 (m, 1H, NC(CH_2)(CH_2)CHN); 1.21 (s, 3H, C_6H_4-*p*-CH(CH_3)$_2$); 1.20 (s, 6H, C_6H_4-*p*-CH(CH_3)$_2$); 1.19 (s, 3H, C_6H_4-*p*-CH(CH_3)$_2$); 1.18 (s, 3H, NCCH_3); 0.93 (s, 3H, C(CH_3)(CH_3)); 0.78 (s, 3H, C(CH_3)(CH_3)). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 154.5 (N*C*HN); 149.8 (C_6H_4-*p*-$CH(CH_3)_2$); 149.2 (C_6H_4-*p*-$CH(CH_3)_2$); 132.7 (C_6H_4-*p*-$CH(CH_3)_2$);

130.5 (C_6H_4-*p*-$CH(CH_3)_2$); 129.4 (C_6H_4-*p*-$CH(CH_3)_2$); 128.0 (C_6H_4-*p*-$CH(CH_3)_2$); 127.0 (C_6H_4-*p*-$CH(CH_3)_2$); 70.7 ($NCH_2C_6H_4$-*p*-$CH(CH_3)_2$); 65.4 ($NCH_2C_6H_4$-*p*-$CH(CH_3)_2$); 56.7 ($NC(CH_2)(CH_2)CHN$); 53.5 ($NC(CH_2)(CH_2)CHN$); 40.8 ($NC(CH_2)(CH_2)CHN$); 39.7 ($NC(CH_2)(CH_2)CHN$); 33.8 ($C(CH_3)(CH_3)$); 33.7 (C_6H_4-*p*-$CH(CH_3)_2$); 31.4 (C_6H_4-*p*-$CH(CH_3)_2$); 23.8 (C_6H_4-*p*-$CH(CH_3)_2$); 21.5 ($NCCH_3$); 17.1 ($C(CH_3)(CH_3)$); 14.8 ($C(CH_3)(CH_3)$).

2.4. *General procedure for 3d,e*

Derivatives of benzaldehyde (6.0 mmol) and 1,2,2-trimethylcyclopentane-1,3-diamine (**1**, 3.0 mmol) were refluxed in degassed EtOH (15.0 mL) for 2 h under argon. After cooling, the solution was concentrated to small volume *in vacuo* giving a white solid. This was filtered under argon, washed sparingly with cold EtOH and dried under vacuum. To a solution of diimine (3.0 mmol) in MeOH was added portionwise $NaBH_4$ (8.1 mmol). The mixture was stirred overnight at RT and then hydrolyzed by careful addition of conc. HCl (1.0 mL). The methanol was removed under reduced pressure and the residue dissolved in water (50.0 mL). The aqueous solution was made basic by the addition of 6 M NaOH solution and extracted into Et_2O (3×20.0 mL). After drying over $MgSO_4$ and removal of volatiles, the product was obtained. Synthesized product (3.0 mmol) and NH_4BF_4 (3.0 mmol) were heated in triethyl orthoformate (5.0 mL) at 100 °C under argon for 2 h. After cooling, the white precipitate was filtered and recrystallized from DCM/Et_2O.

3d: Yield: 352 mg (52%) Mp: 155-156 °C. $[\alpha]_D^{27}$ = +166.7 (c = 0.06, $CHCl_3$). Anal. Calcd. for $C_{25}H_{33}ClN_2O_2$ (428.99 g mol^{-}): C, 69.99; H, 7.75; N, 6.53. Found: C, 69.67; H, 7.29; N, 6.79. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.28 (s, 1H, NC*H*N); 7.28 (d, *J* = 8.6 Hz, 2H, C_6H_4-*p*-(OCH_3)); 7.24 (d, *J* = 9.0 Hz, 2H, C_6H_4-*p*-(OCH_3)); 6.86 (d, *J* = 2.0 Hz, 2H, C_6H_4-*p*-(OCH_3)); 6.84 (d, *J* = 2.0 Hz, 2H, C_6H_4-*p*-(OCH_3)); 4.68-4.63 (m, 2H, $NCH_2C_6H_4$-*p*-(OCH_3)); 4.54-4.44 (m, 2H, $NCH_2C_6H_4$-*p*-(OCH_3)); 3.77 (s, 3H, C_6H_4-*p*-(OCH_3)); 3.76 (s, 3H, C_6H_4-*p*-(OCH_3)); 3.11 (d, *J* = 5.1 Hz, 1H, $NC(CH_2)(CH_2)CHN$); 2.31-2.24 (m, 1H, $NC(CHH)(CH_2)CHN$); 2.13-2.06 (m, 1H, $NC(CHH)(CH_2)CHN$); 1.96-1.87 (m, 1H, $NC(CH_2)(CHH)CHN$); 1.75-1.67 (m, 1H, $NC(CH_2)(CHH)CHN$); 1.20 (s, 3H, $NCCH_3$); 0.93 (s, 3H, $C(CH_3)(CH_3)$); 0.77 (s, 3H, $C(CH_3)(CH_3)$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.0 (N*C*HN); 159.6 (C_6H_4-*p*-(OCH_3)); 153.6 (C_6H_4-*p*-(OCH_3)); 131.0 (C_6H_4-*p*-(OCH_3)); 129.5 (C_6H_4-*p*-(OCH_3)); 127.0 (C_6H_4-*p*-(OCH_3)); 124.9 (C_6H_4-*p*-(OCH_3)); 114.5 (C_6H_4-*p*-(OCH_3));

114.4 (C_6H_4-*p*-(OCH_3)); 71.0 (N*C*$H_2C_6H_4$-*p*-(OCH_3)); 65.3 (N*C*$H_2C_6H_4(OCH_3)$); 56.9 (NC(CH_2)(CH_2)*C*HN); 55.2 (C_6H_4-*p*-(O*C*H_3)); 53.7 (N*C*(CH_2)(CH_2)CHN); 40.6 (NC(*C*H_2)(CH_2)CHN); 39.8 (NC(CH_2)(*C*H_2)CHN); 31.3 (*C*(CH_3)(CH_3)); 21.4 (NC*C*H_3); 16.9 (C(*C*H_3)(CH_3)); 14.7 (C(CH_3)(*C*H_3)).

3e: Yield: 972 mg (60%) Mp: 162-163 °C. $[\alpha]_D^{27}$ = +220.0 (c = 0.06, $CHCl_3$). Anal. Calcd. for $C_{27}H_{37}ClN_2O_2$ (457.04 g mol^{-}): C, 70.95; H, 8.16; N, 6.13. Found: C, 70.57; H, 8.48; N, 6.42. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.27 (s, 1H, NC*H*N); 7.26 (d, *J* = 8.6 Hz, 2H, C_6H_4-*p*-(OCH_2CH_3)); 7.21 (d, *J* = 8.6 Hz, 2H, C_6H_4-*p*-(OCH_2CH_3)); 6.84 (d, *J* = 1.2 Hz, 2H, C_6H_4-*p*-(OCH_2CH_3)); 6.82 (d, *J* = 1.6 Hz, 2H, C_6H_4-*p*-(OCH_2CH_3)); 4.65-4.61 (m, 2H, NC$H_2C_6H_4$-*p*-(OCH_2CH_3)); 4.52-4.42 (m, 2H, NC$H_2C_6H_4$-*p*-(OCH_2CH_3)); 4.00-3.93 (m, 4H, C_6H_4-*p*-(OCH_2CH_3)); 3.11 (d, *J* = 4.7 Hz, 1H, NC(CH_2)(CH_2)C*H*N); 2.27-2.20 (m, 1H, NC(C*H*H)(CH_2)CHN); 2.08-2.01 (m, 1H, NC(CH*H*)(CH_2)CHN); 1.95-1.87 (m, 1H, NC(CH_2)(C*H*H)CHN); 1.73-1.65 (m, 1H, NC(CH_2)(CH*H*)CHN); 1.37 (m, 6H, C_6H_4-*p*-(OCH_2CH_3)); 1.19 (s, 3H, NCC*H*$_3$); 0.91 (s, 3H, C(C*H*$_3$)(CH_3)); 0.75 (s, 3H, C(CH_3)(C*H*$_3$)). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 159.4 (N*C*HN); 159.0 (C_6H_4-*p*-(OCH_2CH_3)); 153.4 (C_6H_4-*p*-(OCH_2CH_3)); 130.9 (C_6H_4-*p*-(OCH_2CH_3)); 129.4(C_6H_4-*p*-(OCH_2CH_3)); 126.8 (C_6H_4-*p*-(OCH_2CH_3)); 124.7 (C_6H_4-*p*-(OCH_2CH_3)); 114.9 (C_6H_4-*p*-(OCH_2CH_3)); 114.8 (C_6H_4-*p*-(OCH_2CH_3)); 71.0 (N*C*$H_2C_6H_4(OCH_2CH_3)$); 65.2 (N*C*$H_2C_6H_4(OCH_2CH_3)$); 63.4 (NC(CH_2)(CH_2)*C*HN); 56.8 ($C_6H_4(OCH_2CH_3)$); 53.6 (N*C*(CH_2)(CH_2)CHN); 53.7(NC(*C*H_2)(CH_2)CHN); 40.5 (NC(*C*H_2)(*C*H_2)CHN); 39.7 (C_6H_4-*p*-(OCH_2CH_3)); 31.3 (*C*(CH_3)(CH_3)); 21.3 (NC*C*H_3); 16.8 (C(*C*H_3)(CH_3)); 14.7 (C(CH_3)(*C*H_3)).

2.5. *General procedure for 3f-h*

Derivatives of benzyl chloride (4.0 mmol) in dry acetonitrile (15 mL) were added to the stirred solution of diamine (*R*,*S*-tmcp, 2.0 mmol) and triethylamine (4.0 mmol, 2 eq.) at RT. The resulting mixture was heated at reflux for 20 h. Triethylamine hydrochloride was filtered off and the solvent was removed under vacuum. Excess derivatives of benzyl chloride separated from the product by FCC on silica gel with CH_2Cl_2 as eluent and the product was eluted with 10% EtOAc/CH_2Cl_2. Evaporation of the solvent gave the product. Product (1.0 mmol), triethyl orthoformate (1.2 mmol) and ammonium tetrafluoroborate (1.0 mmol) were heated in dry

toluene (5.0 mL) for 5 h at 100 °C in a Schlenk flask. The product was filtered and then washed twice with Et_2O to give a solid. The product was recrystallized from DCM/Et_2O.

3g: Yield: 260 mg (48%) Mp: 199-200 °C. $[\alpha]_D^{28}$ = +33.1 (c = 0.05, $CHCl_3$). Anal. Calcd. for $C_{31}H_{45}ClN_2$ (481.15 g mol^{-}): C, 77.38; H, 9.43; N, 5.82. Found: C, 77.75; H, 9.62; N, 6.13. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.82 (d, *J* = 6.5 Hz, 2H, $C_6H(CH_3)_4$); 5.76 (s, 1H, NC*H*N); 4.59-4.46 (m, 2H, $NCH_2C_6H(CH_3)_4$); 4.44-4.27 (m, 2H, $NCH_2C_6H(CH_3)_4$); 3.78 (d, *J* = 4.7 Hz, 1H, $NC(CH_2)(CH_2)CHN$); 2.58-2.49 (m, 1H, $NC(CHH)(CH_2)CHN$); 2.47-2.35 (m, 1H, $NC(CHH)(CH_2)CHN$); 2.31-2.25 (m, 1H, $NC(CH_2)(CHH)CHN$); 2.23-2.12 (m, 1H, $NC(CH_2)(CHH)CHN$); 2.07 (s, 6H, $C_6H(CH_3)_4$-*m*-CH_3); 2.06 (s, 6H, $C_6H(CH_3)_4$-*m*-CH_3); 1.86 (s, 12H, $C_6H(CH_3)_4$-*o*-CH_3); 1.54 (s, 3H, $NCCH_3$); 1.26 (s, 3H, $C(CH_3)(CH_3)$); 1.14 (s, 3H, $C(CH_3)(CH_3)$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 147.3 (NCHN); 134.9 ($C_6H(CH_3)_4$); 134.5 ($C_6H(CH_3)_4$); 133.2 ($C_6H(CH_3)_4$); 133.0 ($C_6H(CH_3)_4$); 126.5 ($C_6H(CH_3)_4$); 71.5 ($NCH_2C_6H(CH_3)_4$); 67.9 ($NCH_2C_6H(CH_3)_4$); 51.6 ($NC(CH_2)(CH_2)CHN$); 47.0 ($NC(CH_2)(CH_2)CHN$); 41.0 ($C(CH_3)(CH_3)$); 39.6 ($C(CH_2)(CH_2)CH$); 32.0 ($NC(CH_2)(CH_2)CHN$); 21.3 ($NCCH_3$); 20.3 ($C_6H(CH_3)_4$-*m*-CH_3); 16.9($C_6H(CH_3)_4$-*o*-CH_3); 14.9 ($C(CH_3)(CH_3)$); 14.0 ($C(CH_3)(CH_3)$).

3h: Yield: 280 mg (44%) Mp: 222-223 °C. $[\alpha]_D^{28}$ = +83.8 (c = 0.05, $CHCl_3$). Anal. Calcd. for $C_{33}H_{49}ClN_2$ (509.20 g mol^{-}): C, 77.84; H, 9.70; N, 5.50. Found: C, 77.96; H, 9.93; N, 5.71. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.93 (s, 1H, NC*H*N); 4.52-4.27 (m, 4H, $NCH_2C_6(CH_3)_5$); 3.78 (d, *J* = 4.7 Hz, 1H, $NC(CH_2)(CH_2)CHN$); 2.59-2.20 (m, 4H, $NC(CH_2)(CH_2)CHN$); 2.15 (s, 6H, $C_6(CH_3)_5$-*p*-CH_3); 2.02 (s, 12H, $C_6(CH_3)_5$-*m*-CH_3); 1.89 (s, 12H, $C_6(CH_3)_5$-*o*-CH_3); 1.53 (s, 3H, $NCCH_3$); 1.26 (s, 3H, $C(CH_3)(CH_3)$); 1.16 (s, 3H, $C(CH_3)(CH_3)$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 147.5 (NCHN); 136.5 ($C_6(CH_3)_5$); 133.5 ($C_6(CH_3)_5$); 133.4 ($C_6(CH_3)_5$); 132.7 ($C_6(CH_3)_5$); 123.6 ($C_6(CH_3)_5$); 71.9 ($NCH_2C_6(CH_3)_5$); 67.9 ($NCH_2C_6(CH_3)_5$); 52.1 ($NC(CH_2)(CH_2)CHN$); 47.6 ($NC(CH_2)(CH_2)CHN$); 41.0 ($C(CH_3)(CH_3)$); 39.6 ($NC(CH_2)(CH_2)CHN$); 32.0 ($NC(CH_2)(CH_2)CHN$); 25.0 ($NCCH_3$); 21.4 ($C_6(CH_3)_5$-*p*-CH_3); 16.8 ($C_6(CH_3)_5$-*m*-CH_3); 16.7 ($C_6(CH_3)_5$-*o*-CH_3); 16.0 ($C(CH_3)(CH_3)$); 14.0 ($C(CH_3)(CH_3)$).

2.6. *General procedure for 4a-e*

A mixture of amidinium salt (**3a-e**, 1.0 mmol), $PdCl_2$ (1.1 mmol), K_2CO_3 (5.0 mmol) and excess KBr (only necessary to synthesize **4a-c**) was heated in pyridine (5.0 mL) at 110 °C for 18 h

(unless excess KBr is added to the reaction media a mixture of dibromo, dichloro and bromo-chloro complexes were obtained [24]). The pyridine was then removed in vacuum. The residue was washed with saturated aqueous $CuSO_4$ solution and extracted in DCM (2×20.0 mL). The organic layer was separated and dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated under vacuum and then pumped dried to give the crude product as a yellow solid. The products were recrystallized from THF/hexane.

4a: Yield: 140 mg (27%) Mp: 240-241 °C. $[\alpha]_D^{27}$ = +120.0 (c = 0.05, $CHCl_3$). Anal. Calcd. for $C_{30}H_{37}Br_2N_3Pd$ (705.86 g mol$^-$): C, 51.05; H, 5.28; N, 5.95. Found: C, 52.00; H, 5.64; N, 5.83. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.86 (d, *J* = 6.3 Hz, 2H, C_5H_5N); 7.69-7.61 (m, 3H, C_5H_5N); 7.22-7.16 (m, 8H, C_6H_4-*p*-(CH_3)); 6.71 (d, *J* = 14.5 Hz, 1H, NC*H*HC$_6$H$_4$-*p*-(CH_3)); 6.41 (d, *J* = 16.4 Hz, 1H, NCH*H*C$_6$H$_4$-*p*-(CH_3)); 5.56 (d, *J* = 16.4 Hz, 1H, NC*H*HC$_6$H$_4$-*p*-(CH_3)); 4.98 (d, *J* = 14.9 Hz, 1H, NCH*H*C$_6$H$_4$-*p*-(CH_3)); 2.91 (d, *J* = 4.7 Hz, 1H, NC(CH_2)(CH_2)C*H*N); 2.57-2.51 (m, 1H, NC(C*H*H)(CH_2)CHN); 2.37 (s, 3H, C$_6$H$_4$-*p*-(C*H*$_3$)); 2.34 (s, 3H, C$_6$H$_4$-*p*-(C*H*$_3$)); 2.24-2.17 (m, 1H, NC(CH*H*)(CH_2)CHN); 1.86-1.75 (m, 1H, NC(CH_2)(C*H*H)CHN); 1.68-1.61 (m, 1H, NC(CH_2)(CH*H*)CHN); 1.15 (s, 3H, NCC*H*$_3$); 1.00 (s, 3H, C(C*H*$_3$)(CH_3)); 0.78 (s, 3H, C(CH_3)(C*H*$_3$)). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 175.4 (Pd-*C*$_{carbene}$); 152.5 (*C*$_5$H$_5$N); 137.7 (*C*$_6$H$_4$-*p*-(CH_3)); 137.5 (*C*$_6$H$_4$-*p*-(CH_3)); 136.5 (*C*$_5$H$_5$N); 136.1 (*C*$_6$H$_4$-*p*-(CH_3)); 132.7 (*C*$_6$H$_4$-*p*-(CH_3)); 129.8 (*C*$_6$H$_4$-*p*-(CH_3)); 129.2 (*C*$_6$H$_4$-*p*-(CH_3)); 129.0 (*C*$_6$H$_4$-*p*-(CH_3)); 127.7 (*C*$_6$H$_4$-*p*-(CH_3)); 124.3 (*C*$_5$H$_5$N); 72.1 (N*C*H$_2$C$_6$H$_4$-*p*-(CH_3)); 65.3 (N*C*H$_2$C$_6$H$_4$-*p*-(CH_3)); 60.8 (N*C*(CH_2)(CH_2)CHN); 58.8 (NC(CH_2)(CH_2)*C*HN); 41.8 (NC(*C*H$_2$)(CH_2)CHN); 38.6 (NC(CH_2)(*C*H$_2$)CHN); 30.3 (*C*(CH_3)(CH_3)); 22.2 (C$_6$H$_4$-*p*-(*C*H$_3$)); 21.3 (C$_6$H$_4$-*p*-(*C*H$_3$)); 21.2 (NC*C*H$_3$); 18.2 (C(*C*H$_3$)(CH_3)); 17.2 (C(CH_3)(*C*H$_3$)).

4b: Yield: 226 mg (41%) Mp: 265-266 °C (decomposition). $[\alpha]_D^{27}$ = +80.0 (c = 0.05, $CHCl_3$). Anal. Calcd. for $C_{36}H_{49}Br_2N_3Pd$ (790.02 g mol$^-$): C, 54.73; H, 6.25; N, 5.32. Found: C, 54.23; H, 6.42; N, 5.15. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.88 (d, *J* = 5.1 Hz, 2H, C_5H_5N); 7.73-7.64 (m, 3H, C_5H_5N); 7.42-7.37 (m, 4H, C$_6$H$_4$-*p*-C(CH_3)$_3$); 7.22-7.18 (m, 4H, C$_6$H$_4$-*p*-C(CH_3)$_3$); 6.71 (d, *J* = 14.5 Hz, 1H, NC*H*HC$_6$H$_4$-*p*-C(CH_3)$_3$); 6.35 (d, *J* = 16.8 Hz, 1H, NCH*H*C$_6$H$_4$-*p*-C(CH_3)$_3$); 5.63 (d, *J* = 16.4 Hz, 1H, NC*H*HC$_6$H$_4$-*p*-C(CH_3)$_3$); 5.02 (d, *J* = 14.5 Hz, 1H, NCH*H*C$_6$H$_4$-*p*-C(CH_3)$_3$); 2.94 (d, *J* = 4.7 Hz, 1H, NC(CH_2)(CH_2)C*H*N); 2.57-2.50 (m, 1H, NC(C*H*H)(CH_2)CHN); 2.26-2.17 (m, 1H, NC(CH*H*)(CH_2)CHN); 1.85-1.75 (m, 1H, NC(CH_2)(C*H*H)CHN); 1.68-1.60 (m, 1H, NC(CH_2)(CH*H*)CHN); 1.34 (s, 9H, C$_6$H$_4$-*p*-C(C*H*$_3$)$_3$);

1.32 (s, 9H, C_6H_4-*p*-C(CH_3)$_3$); 1.18 (s, 3H, NCCH_3); 1.01 (s, 3H, C(CH_3)(CH_3)); 0.79 (s, 3H, C(CH_3)(CH_3)). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 175.2 (Pd-$C_{carbene}$); 152.6 (C_6H_4-*p*-C(CH_3)$_3$); 150.9 (C_6H_4-*p*-C(CH_3)$_3$); 149.8 (C_5H_5N); 137.4 (C_5H_5N); 136.0 (C_6H_4-*p*-C(CH_3)$_3$); 132.7 (C_6H_4-*p*-C(CH_3)$_3$); 129.4 (C_6H_4-*p*-C(CH_3)$_3$); 127.6 (C_6H_4-*p*-C(CH_3)$_3$); 125.4 (C_6H_4-*p*-C(CH_3)$_3$); 125.2 (C_6H_4-*p*-C(CH_3)$_3$); 124.3 (C_5H_5N); 72.1 (NCH$_2$C$_6$H$_4$-*p*-C(CH_3)$_3$); 65.4 (NCH$_2$C$_6$H$_4$-*p*-C(CH_3)$_3$); 60.8 (NC(CH_2)(CH_2)CHN); 58.9 (NC(CH_2)(CH_2)CHN); 41.8 (NC(CH$_2$)(CH_2)CHN); 38.9 (NC(CH_2)(CH$_2$)CHN); 34.6 (C_6H_4-*p*-C(CH_3)$_3$); 34.5 (C_6H_4-*p*-C(CH_3)$_3$); 31.4 (C_6H_4-*p*-C(CH$_3$)$_3$); 31.3 (C_6H_4-*p*-C(CH_3)$_3$); 30.3 (C(CH_3)(CH_3)); 22.3 (NCCH_3); 18.2 (C(CH_3)(CH$_3$)); 17.3 (C(CH$_3$)(CH_3)).

4c: Yield: 248 mg (45%) Mp: 208-209 °C (decomposition). $[\alpha]_D^{27}$ = +120.0 (c = 0.05, $CHCl_3$). Anal. Calcd. for $C_{34}H_{45}Br_2N_3Pd$ (761.97 g mol^{-}): C, 53.59; H, 5.95; N, 5.51. Found: C, 53.45; H, 6.20; N, 5.36. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.88 (dd, 2H, C_5H_5N); 7.71 (d, *J* = 8.2 Hz, 3H, C_5H_5N); 7.65 (d, *J* = 7.8 Hz, 2H, C_6H_4-*p*-CH(CH_3)$_2$); 7.26-7.19 (m, 6H, C_6H_4-*p*-CH(CH_3)$_2$); 6.72 (d, *J* = 14.5 Hz, 1H, NCHHC$_6$H$_4$-*p*-CH(CH_3)$_2$); 6.37 (d, *J* = 16.4 Hz, 1H, NCHHC$_6$H$_4$-*p*-CH(CH_3)$_2$); 5.61 (d, *J* = 16.4 Hz, 1H, NCHHC$_6$H$_4$-*p*-CH(CH_3)$_2$); 5.01 (d, *J* = 14.5 Hz, 1H, NCHHC$_6$H$_4$-*p*-CH(CH_3)$_2$); 2.93 (d, *J* = 4.7 Hz, 1H, NC(CH_2)(CH_2)CHN); 2.90-2.87 (m, 2H, C_6H_4-*p*-CH(CH_3)$_2$); 2.61-2.51 (m, 1H, NC(CHH)(CH_2)CHN); 2.25-2.19 (m, 1H, NC(CHH)(CH_2)CHN); 1.84-1.76 (m, 1H, NC(CH_2)(CHH)CHN); 1.67-1.60 (m, 1H, NC(CH_2)(CHH)CHN); 1.27 (d, *J* = 3.9 Hz, 6H, C_6H_4-*p*-CH(CH_3)$_2$); 1.25 (d, *J* = 3.9 Hz, 6H, C_6H_4-*p*-CH(CH_3)$_2$); 1.17 (s, 3H, NCCH_3); 1.00 (s, 3H, C(CH_3)(CH_3)); 0.79 (s, 3H, C(CH_3)(CH_3)). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 175.3 (Pd-$C_{carbene}$); 152.6 (C_5H_5N); 148.6 (C_6H_4-*p*-CH(CH_3)$_2$); 147.5 (C_6H_4-*p*-CH(CH_3)$_2$); 137.4 (C_5H_5N); 136.4 (C_6H_4-*p*-CH(CH_3)$_2$); 133.1 (C_6H_4-*p*-CH(CH_3)$_2$); 129.8 (C_6H_4-*p*-CH(CH_3)$_2$); 127.8 (C_6H_4-*p*-CH(CH_3)$_2$); 126.6 (C_6H_4-*p*-CH(CH_3)$_2$); 126.3 (C_6H_4-*p*-CH(CH_3)$_2$); 124.2 (C_5H_5N); 72.1 (NCH$_2$C$_6$H$_4$-*p*-CH(CH_3)$_2$); 65.4 (NCH$_2$C$_6$H$_4$-*p*-CH(CH_3)$_2$); 60.8 (NC(CH_2)(CH_2)CHN); 58.9 (NC(CH_2)(CH_2)CHN); 41.8 (NC(CH$_2$)(CH_2)CHN); 38.9 (NC(CH_2)(CH$_2$)CHN); 33.8 (C_6H_4-*p*-CH(CH_3)$_2$); 33.7 (C_6H_4-*p*-CH(CH_3)$_2$); 30.3 (C(CH_3)(CH_3)); 24.0 (C_6H_4-*p*-CH(CH$_3$)$_2$); 23.9 (C_6H_4-*p*-CH(CH$_3$)$_2$); 22.3 (NCCH_3); 18.2 (C(CH$_3$)(CH_3)); 17.3 (C(CH_3)(CH$_3$)).

4d: Yield: 193 mg (46%) Mp: 203-204 °C. $[\alpha]_D^{27}$ = +140 (c = 0.05, $CHCl_3$). Anal. Calcd. for $C_{30}H_{37}Cl_2N_3O_2Pd$ (648.96 g mol^{-}): C, 55.52; H, 5.75; N, 6.48. Found: C, 55.85; H, 6.68; N, 5.96. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.87-8.85 (m, 2H, C_5H_5N); 7.71 (d, *J* = 8.6 Hz, 2H,

C_5H_5N); 7.66 (d, J = 8.6 Hz, 1H, C_5H_5N); 7.24-7.21 (m, 4H, C_6H_4-p-OCH_3); 6.90 (dd, J = 8.8 Hz, J = 2.2 Hz, 4H, C_6H_4-p-(OCH_3)); 6.57 (d, J = 14.9 Hz, 1H, NCHHC$_6$H$_4$-p-(OCH_3)); 6.06-5.96 (m, 2H, NCH_2C$_6$H$_4$-p-(OCH_3)); 5.20 (d, J = 14.5 Hz, 1H, NCHHC$_6$H$_4$-p-(OCH_3)); 3.81 (s, 3H, C_6H_4-p-(OCH_3)); 3.79 (s, 3H, C_6H_4-p-(OCH_3)); 2.90 (d, J = 4.7 Hz, 1H, NC(CH_2)(CH_2)CHN); 2.42-2.35 (m, 1H, NC(CHH)(CH_2)CHN); 2.10-2.03 (m, 1H, NC(CHH)(CH_2)CHN); 1.80-1.72 (m, 1H, NC(CH_2)(CHH)CHN); 1.62-1.55 (m, 1H, NC(CH_2)(CHH)CHN); 1.06 (s, 3H, NCCH_3); 1.05 (s, 3H, C(CH_3)(CH_3)); 0.78 (s, 3H, C(CH_3)(CH_3)). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 174.7 (Pd-$C_{carbene}$); 159.4 (C_6H_4-p-(OCH_3)); 158.7 (C_6H_4-p-(OCH_3)); 151.2 (C_5H_5N); 137.6 (C_5H_5N); 131.2 (C_6H_4-p-(OCH_3)); 131.1 (C_6H_4-p-(OCH_3)); 129.1 (C_6H_4-p-(OCH_3)); 127.9 (C_5H_5N); 124.3 (C_6H_4-p-(OCH_3)); 113.9 (C_6H_4-p-(OCH_3)); 113.7 (C_6H_4-p-(OCH_3)); 71.7 (NCH$_2$C$_6$H$_4$-p-(OCH_3)); 65.3 (NCH$_2$C$_6$H$_4$-p-(OCH_3)); 60.0 (NC(CH_2)(CH_2)CHN); 57.7 (NC(CH_2)(CH_2)CHN); 55.2 (C_6H_4-p-(OCH$_3$)); 41.4 (NC(CH$_2$)(CH_2)CHN); 39.1 (NC(CH_2)(CH$_2$)CHN); 30.6 (C(CH_3)(CH_3)); 22.2 (NCCH_3); 17.8 (C(CH$_3$)(CH_3)); 16.7 (C(CH_3)(CH$_3$)).

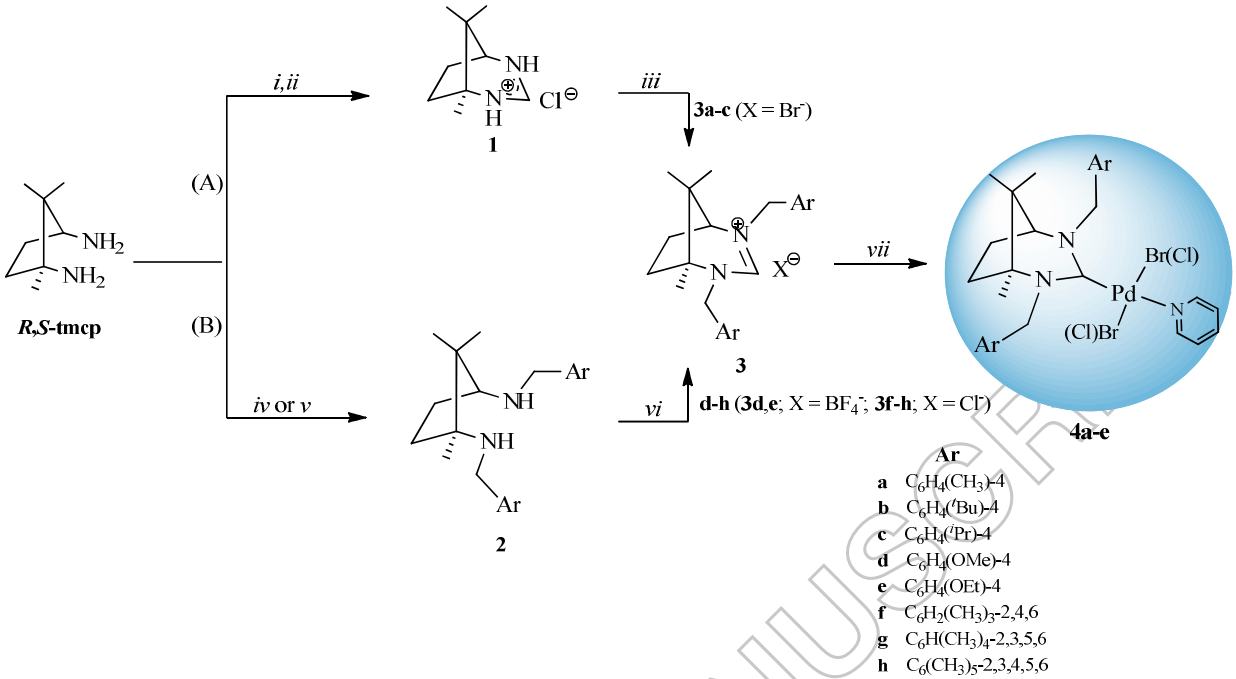
4e: Yield: 163 mg (47%) Mp: 203-204 °C. $[\alpha]_D^{27}$ = +26.0 (c = 0.04, $CHCl_3$). Anal. Calcd. for $C_{32}H_{41}Cl_2N_3O_2Pd$ (677.01 g mol^{-}): C, 56.77; H, 6.10; N, 6.21. Found: C, 56.53; H, 6.34; N, 5.81. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.85 (dd, J = 6.7 Hz, J = 1.6 Hz, 1H, C_5H_5N); 7.69 (d, J = 9.0 Hz, 2H, C_5H_5N); 7.63 (d, J = 8.6 Hz, 1H, C_5H_5N); 7.24-7.20 (m, 4H, C_6H_4-p-(OCH_2CH_3)); 6.88 (dd, J = 8.6 Hz, J = 2.4 Hz, 4H, C_6H_4-p-(OCH_2CH_3)); 6.56 (d, J= 14.5 Hz, 1H, NCHHC$_6$H$_4$-p-(OCH_2CH_3)); 6.00 (s, 2H, NCH_2C$_6$H$_4$-p-(OCH_2CH_3)); 5.18 (d, J= 14.5 Hz, 1H, NCHHC$_6$H$_4$-p-(OCH_2CH_3)); 4.05-3.98 (m, 4H, C_6H_4-p-(OCH_2CH$_3$)); 2.89 (d, J= 4.7 Hz, 1H, NC(CH_2)(CH_2)CHN); 2.41-2.34 (m, 1H, NC(CHH)(CH_2)CHN); 2.09-2.02 (m, 1H, NC(CHH)(CH_2)CHN); 1.79-1.70 (m, 1H, NC(CH_2)(CHH)CHN); 1.61-1.53 (m, 1H, NC(CH_2)(CHH)CHN); 1.39 (q, J = 6.8 Hz, 6H, C_6H_4-p-(OCH_2CH_3)); 1.04 (s, 3H, NCCH_3); 1.03 (s, 3H, C(CH_3)(CH_3)); 0.76 (s, 3H, C(CH_3)(CH_3)). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 174.5 (Pd-$C_{carbene}$); 158.7 (C_6H_4-p-(OCH_2CH_3)); 158.0 (C_6H_4-p-(OCH_2CH_3)); 153.3 (C_6H_4-p-(OCH_2CH_3)); 151.1 (C_5H_5N); 137.6 (C_5H_5N); 131.1 (C_6H_4-p-(OCH_2CH_3)); 130.9 (C_6H_4-p-(OCH_2CH_3)); 129.1 (C_6H_4-p-(OCH_2CH_3)); 127.6 (C_6H_4-p-(OCH_2CH_3)); 124.9 (C_6H_4-p-(OCH_2CH_3)); 124.2 (C_5H_5N); 114.3 (C_6H_4-p-(OCH_2CH_3)); 114.2 (C_6H_4-p-(OCH_2CH_3)); 71.7 (NCH$_2$C$_6$H$_4$-p-(OCH_2CH_3)); 65.2 (NCH$_2$C$_6$H$_4$-p-(OCH_2CH_3)); 63.3 (C_6H_4-p-(OCH$_2$CH$_3$)); 63.2 (C_6H_4-p-(OCH$_2$CH$_3$)); 60.0 (NC(CH_2)(CH_2)CHN); 57.7 (NC(CH_2)(CH_2)CHN); 41.3

(NC(CH$_2$)(CH$_2$)CHN); 39.0 (NC(CH$_2$)(CH$_2$)CHN); 30.6 (C(CH$_3$)(CH$_3$)); 22.1 (NCCH_3); 17.8 (C(CH$_3$)(CH$_3$)); 16.7 (C(CH$_3$)(CH$_3$)); 14.8 (C$_6$H$_4$-*p*-(OCH$_2$$CH_3$)); 14.7 (C$_6H_4$-*p*-(OCH$_2$$CH_3$)).

3. Results and discussion

3.1. *Synthesis of the chiral bicyclic amidinium precursors (3a-h)*

A limited number of chiral (NHC)Pd(II) complexes have been reported [25]. For us the use of readily available camphoric acid derivative *R*,*S*-tmcp was appealing [11, 18]. Camphoric acid was converted to *R*,*S*-tmcp ((1*R*,3*S*)-diamino-1,2,2-trimethylcyclopentane) [23] as described *via* a Schmidt reaction using concentrated sulfuric acid and sodium azide [18, 26, 27]. For synthesis of amidinium precursors, two different routes (A and B) were employed as shown in scheme 1. Route (A) involves the initial ring closure and subsequent introduction of the exo N-substituents, whereas route (B) [18, 19] involves the initial modification of the diamine through alkylation of the nitrogen prior to ring closure, as shown in scheme 1.



Reagent and conditions: (*i*) $Et_2O.HCl$; (*ii*) $HC(OEt)_3$, reflux; (*iii*) K_2CO_3, R-X (**3a-c**), CH_3CN, 80 °C, 4 days; (*iv*) a) EtOH, RCHO (**3d,e**), reflux, b) $NaBH_4$, MeOH, RT; (*v*) NEt_3, R-X (**3f-h**), CH_3CN, 80 °C, 24 h; (*vi*) NH_4BF_4, $HC(OEt)_3$, reflux; (*vii*) K_2CO_3, $PdCl_2$, C_5H_5N, KBr (for **4a-c**), 110 °C, 18 h.

Scheme 1. Synthesis of bicyclic NHC precursors and their PEPPSI-type (NHC)Pd(II) complexes.

First, diamine derivative was converted to diamine hydrochloride by ether hydrochloride. This is followed by ring closure with triethyl orthoformate to form **1** (Route A). The ring closure was successful as shown by appearance of the NCHN peak in both the ^{13}C NMR and ^{1}H NMR at 150.8 ppm and 7.81 ppm, respectively. Single crystals of **1** were obtained from vapor diffusion of DCM and diethyl ether. The alkyl derivatives were synthesized by deprotonation of the nitrogens using potassium carbonate, followed by reaction with benzyl bromides to form **3a-c**. In Route (B) the alkylation reaction was performed either by treating the diamine with an aromatic aldehyde followed by reduction of the imine or directly with an arylmethylene bromide. The diamine obtained was converted to the amidinium precursors as a white solid by cyclization with triethyl orthoformate in the presence of NH_4BF_4 (**3d-h**).

Compounds **3a-h** were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy. In the ^{1}H NMR spectra of the salts the characteristic NC*H*N proton shifts were 5.93-10.04 ppm and in

^{13}C NMR the NC*H*N shifts were 138.7-160.0 ppm. The NC*H*N of **3f-h**, having BF_4^-, moved upfield to 5.89, 5.76 and 5.93 ppm, respectively. In **3f-h** a restricted rotation was observed by the ^{1}H NMR signal of the NC*H*N. It is likely that the large upfield shifts of the protons of **3f-h** are due to proximity to the middle of the arene rings next to C9 (figure 1) methyl group of the camphor skeleton [18].

3.2. *Synthesis of the chiral PEPPSI-type bicyclic 6,7-NHC palladium complexes (4a-e)*

All attempts to react **4a** with the standard palladium precursors $Pd(OAc)_2$ and $PdCl_2$ in PhMe in the presence of conventional bases did not lead to the target complexes. We therefore decided to react the amidinium salts with $PdCl_2/K_2CO_3$ in pyridine as a base and supporting ligand and obtained the expected complexes as yellow solids. This procedure is suitable for deprotonation and coordination of acidic ring-expanded NHC precursors [28]. Attempts to coordinate the bulkier NHC precursors (**3f-h**) to palladium were unsuccessful; after heating $PdCl_2$/**3f**/K_2CO_3 and KBr in pyridine for several days, only unreacted material was recovered.

Incorporation of the chiral bicyclic NHC to **4a-e** was evident from the NMR spectra showing the conspicuous absence of the NC*H*N resonance of the reacting NHC precursors while a new Pd-$C_{carbene}$ resonance appeared at 174.2-175.4 ppm in ^{13}C{^{1}H}NMR spectra.

These chemical shifts of **4** are similar to that observed for ring-expanded (Pd(NHC)(3-ClPy)Cl_2) [24] but are at lower field (by ~4 ppm for six-membered and/or 14 ppm for seven-membered rings compared to related expanded ring NHC complexes) [13]. In order to confirm the proposed structures of the complexes unequivocally, **4a**, **4b**, **4d** and **4e** have been further characterized by single crystal X-ray diffraction.

3.3. *Crystal structure determination of 1, 4a, 4b, 4d and 4e*

The perspective ORTEP-3 [29] views of the compounds are depicted in figures 1 and 2, while the key bond lengths and angles are given in table S1. All the compounds are chiral and crystallize in noncentrosymmetric space groups, except **4a**, which is racemic and crystallizes in the centrosymmetric space group $P\bar{1}$ [30, 31].

1 crystallizes as a salt in which the charge of the NHC cation is balanced by a chloride. The C—N bond lengths compared to amidinium carbon are almost equal (1.290(3) and 1.302(3) Å) with the C—N—C angle of 121.64(17)°. These geometric parameters are

comparable with those reported for similar compounds [19, 20, 32]. In the crystal structure, the NHC cation is connected to the anion by a N1—H1···Cl1 hydrogen bond with D—H, H···A, D···A and D—H···A values being 0.83(4) Å, 2.31(4) Å, 3.127(2) Å and 168(4)°, respectively.

In **4a**, **4b**, **4d** and **4e**, Pd(II) has a *trans*-square-planar coordination geometry from one carbene C of NHC ligand, one pyridine N and two halides (Br or Cl). The Pd—Br, Pd—Cl, Pd—N and Pd—C bond lengths are from 2.367(4) to 2.4094(14) Å, 2.301(6) to 2.331(6) Å, 2.086(12) to 2.16(2) Å and 1.909(15) to 2.00(2) Å, respectively. From *cis* angles, which vary from 85.0(6) to 93.8(5)°, and the *trans* angles, which vary from 172.72(15) to 178.73(6)° (table S1), the coordination around the Pd(II) is distorted. When the C—N bond lengths in the complexes are compared with those in **1**, coordination elongates the N1—C1 and N2—C1 bonds. The C—N—C angles contract except for that in **4e**. In the coordination plane, the r.m.s. deviation through these five atoms is 0.0274 Å, 0.0376 Å (0.0197 Å), 0.0169 Å (0.0360 Å) and 0.0113 Å, while the coordination plane makes dihedral angles of 51.32(5)°, 27.60(9)° (15.39(11)°), 47.89(5)° (48.22(5)°) and 43.98(7)° with the pyridine ring for **4a**, **4b**, **4d** and **4e**, respectively. In **4b** and **4d**, there are two molecules in the asymmetric unit. For the sake of clarity, only one of the two molecules is shown in figure 2. In the foregoing discussion, parameters belonging to the second molecule are quoted in square brackets.

3.4. *X-ray crystallography*

Intensity data of the compounds were collected on a STOE IPDS II diffractometer at room temperature (296 K) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) by applying the ω-scan method. Data collection and cell refinements were carried out using X-AREA [33]. Data reduction was applied using X-RED32 [33]. The structures were solved by direct methods using SHELXS-2013 [34] and refined with full-matrix least-squares calculations on F^2 using SHELXL-2014 [34] implemented in the WinGX [29] program suite. All carbon bound hydrogens were placed geometrically and treated using a riding model, fixing the bond lengths at 0.93, 0.98, 0.97 and 0.96 Å for aromatic CH, methine CH, CH_2 and CH_3, respectively. The nitrogen bound hydrogens in **1** were located in a difference Fourier map and refined isotropically. The displacement parameters of the carbon bound hydrogens were fixed at U_{iso}(H) = 1.2U_{eq} (1.5U_{eq} for methyl) of their parent atoms. C3, C4, C6, C7 and C8 of bicyclic NHC ring in **4a** and *tert*-butyl groups in **4b** show positional disorder, so geometric and atomic displacement

parameter (ADP) restraints were applied to the disordered atoms to stop distortion. The details of the data collection and structure solution are collected in table S2.

4. Conclusion

A series of cyclic amidinium precursors (**3a-h**) derived from camphoric acid have been synthesized in good yields. The amidinium precursors (**3a-e**) having relatively acidic NC*H*N protons ($\delta > 7$ ppm) were converted to the corresponding PEPPSI-type Pd-NHC complexes [(6,7-NHC)PdX_2(pyridine)] *via* reaction of $PdCl_2$, K_2CO_3 in boiling pyridine in the presence of KBr. To the best of our knowledge, they represent the only structurally characterized chiral bicyclic PEPPSI-type Pd-NHC complexes. The change of the N-substituents on the precursors has a pronounced influence on the complex formation; Ar rings with *o*-substituents are resistant to complexation.

Supplementary material

CCDC 1041983, 1041984, 1041985, 1041986 and 1041987 contain the supplementary crystallographic data for **1**, **4a**, **4b**, **4d** and **4e**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

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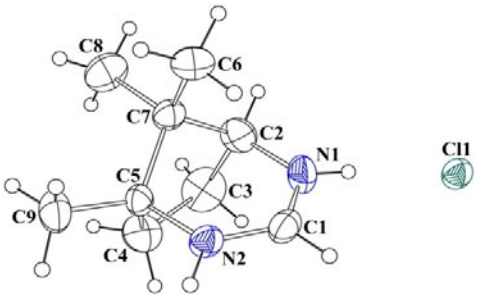
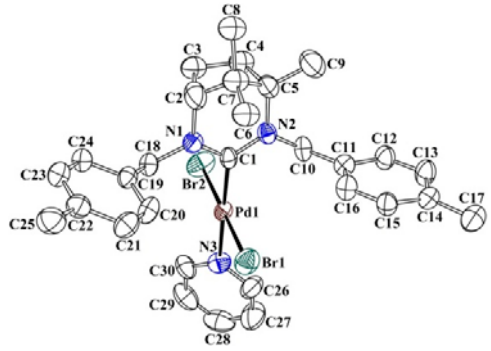
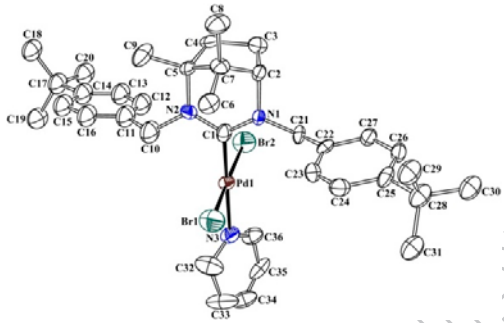


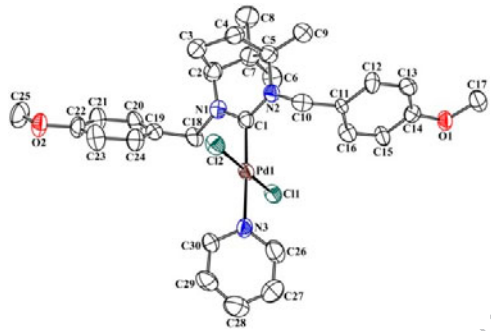
Figure 1. A view of **1** showing the atom-numbering scheme. Thermal ellipsoids are drawn at 30% probability and hydrogens are shown as small spheres of arbitrary radii.



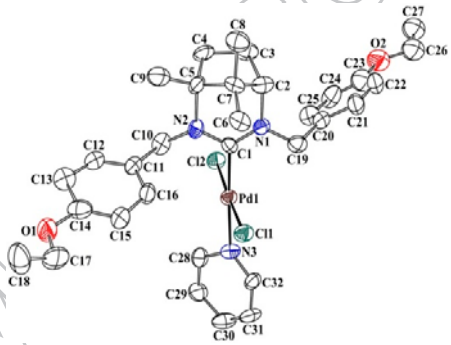
4a



4b



4d



4e

Figure 2. A view of **4a**, **4b**, **4d** and **4e** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Hydrogens are omitted for clarity and only the major parts of disordered fragment are drawn for **4a** and **4b**.

Graphical abstract