Journal of Organometallic Chemistry 696 (2011) 3527–3535

Contents lists available at SciVerse ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Cationic palladacycles as catalyst precursors for phenyl acetylene polymerization

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ARTICLE INFO

Article history:
Received 7 June 2011
Received in revised form
28 July 2011
Accepted 29 July 2011

Keywords:
Cationic palladacycles
Phenyl acetylene polymerization
Polyphenylacetylene
Benzylidene–amines complexes

ABSTRACT

Novel cationic palladacycles based on benzylidene-2,6-diisopropylphenylimines were prepared via C–H activation using $Pd(CH_3CN)_2Cl_2$ as metal precursor. The complexes were fully characterized by IR and NMR spectroscopy, mass spectrometry and elemental analysis. The cationic palladacycles were found to be active catalysts for the polymerization of phenylacetylene producing largely *trans*-cisoidal PPA.

1. Introduction

The polymerization of substituted acetylene derivatives produce polymers with backbone conjugation which confer interesting and novel properties upon the polymeric material [1]. These may be further enhanced by functionalizing the polymer backbone with suitable substituents. Physical properties which these polymeric materials may display include photoconductivity [2] and liquid crystallinity [3].

The first report of the polymerization of acetylenes was by Natta and co-workers and involved a process mediated by a Ti/Al catalyst system [4]. This led to the development of early transition metal catalyst systems, particularly of group 5 and 6 metals, which demonstrated both high activity and selectivity for acetylene polymerization reactions [5]. The inherent air and moisture sensitivity of early transition metal complexes led to the development of late transition metal complexes capable of polymerizing acetylenes with polar functionality and in polar reaction media. Of all the late transition metals, rhodium complexes [6] occupy an enviable position as mediators of acetylene polymerization reactions with exceptionally high activity and selectivity [7].

Few examples of palladium-mediated acetylene polymerization reactions appear in literature. These include diphosphine-palladium(II) complexes, [8] Pd(N,N,O)Cl complexes derived from acyl hydrazone ligands, [9] and more recently bis(pyrazole)- and bis(pyrazolyl)-palladium complexes [10]. Here we report the synthesis and characterization of cationic palladacycles derived from imine ligands and their application as phenylacetylene polymerization catalysts.

2. Experimental procedure

2.1. General

All transformations were performed using standard Schlenk techniques under a nitrogen atmosphere or in a nitrogen-filled glovebox. Solvents were dried by distillation prior to use and all other reagents were employed as obtained. NMR (^{1}H: 300 and 400 MHz; ^{13}C: 75 and 100 MHz) spectra were recorded on Varian VNMRS 300 MHz; Varian Unity Inova 400 MHz spectrometers and chemical shifts are reported in ppm, referenced to the residual protons of the deuterated solvents and tetramethyl silane (TMS) as internal standard. ESI-MS (positive and negative modes) analyses were performed on either Waters API Quattro Micro or Waters API Q-TOF Ultima instruments by direct injection of sample (Capillary voltage: 3.5 kV; Cone voltage: 15 RF1:40; Source: 100 °C; Desolvation Temp: 400 °C; Desolvation gas: 500 L/h; Cone gas: 50 L/h). FT-IR analysis was performed on a Thermo Nicolet AVATAR 330 instrument, and was recorded as neat spectra (ATR) unless otherwise specified. Melting point determinations were performed on a Stuart Scientific SMP3 melting point apparatus and are reported as uncorrected. The

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doi:10.1016/j.jorganchem.2011.07.044

number-average (M_n) and weight-average molecular weights (M_w) as well as polydispersity (M_w/M_n) were determined by gel permeation chromatography (THF, 30 °C, rate - 1.0 cc/min) employing a PL mixed-C column and polystyrene standards on an Agilent 1100 series chromatograph equipped with an RI detector.

2.2. Synthesis of monofunctional imine ligands, *L1–L4*

2.2.1. Benzylidene-2,6-diisopropylphenylamine (*L1*)

To a stirring solution of 2,6-diisopropylaniline (1.8 mL, 9.423 mmol) in EtOH (10 mL) was added benzaldehyde (0.96 mL, 9.423 mmol). The resulting yellow solution was stirred for 24 h at room temperature. After the allotted time the solvent was removed, the residue obtained redissolved in dichloromethane (20 mL) and washed with H_2O (10 × 20 mL portions). The organic layer was dried over $MgSO_4$, filtered and the solvent removed. The yellow residue was recrystallized from DCM/MeOH at low temperature and was isolated as a yellow crystalline solid. Yield: 2.25 g, 90%. FT-IR (υ, C=N): 1638 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$, numbering as per Scheme 1): δ 8.22 (s, 1H, H^7); δ 7.94 (m, 2H, $H^{2,6}$); δ 7.54 (m, 3H, $H^{3,4,5}$); δ 7.17 (m, 3H, $H^{10,11}$); δ 3.00 (sept., 2H, H^{12}, $^3J_{H-H}$ 6.82 Hz); δ 1.19 (d, 12H, $H^{12,13}$, $^3J_{H-H}$ 7.02 Hz). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, numbering as per Scheme 1): δ 160.2 (*C*H=N, C^7); δ 147.5 (C_{Ar} C^8); δ 138.3 (C_{Ar}, C^9); δ 133.8 (C_{Ar}, C^1); δ 131.1 (C_{Ar}, C^4); δ 129.2 (C_{Ar}, $C^{2,6}$); δ 128.9 (C_{Ar}, $C^{3,5}$); δ 126.7 (C_{Ar}, C^{11}); δ 124.7 (C_{Ar}, C^{10}); δ 27.96 (C^{12}); δ 23.45 (C^{13}). ESI-MS (M^+, *m/z*): 266. *Anal.* Found: C, 85. 92; H, 8.70; N, 5.20. Calc. for $C_{19}H_{23}N$: C, 85.99; H, 8.74; N, 5.28.

2.2.2. 2-Chlorobenzylidene-2,6-diisopropylphenylamine (*L2*)

The same synthetic procedure as outlined above for (**L1**) was employed for the synthesis of **L2**, using 2-chlorobenzaldehyde as reagent. Yield: 2.46 g, 87%. FT-IR (υ, C=N): 1624 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, numbering as per Scheme 1): δ 8.76 (s, 1H, H^7); δ 8.37 (d, 1H, H^3, $^2J_{H-H}$ 8.58 Hz); δ 7.53 (m, 3H, $H^{4,5,6}$); δ 7.24 (m, 3H, $H^{10,11}$); δ 3.08 (sept., 2H, H^{12}, $^3J_{H-H}$ 6.82 Hz); δ 1.30 (d, 12H, $H^{12,13}$, $^3J_{H-H}$ 7.02 Hz). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, numbering as per Scheme 1): δ 159.2 (CH=N, C^7); δ 149.1 (C_{Ar}, C^8); δ 137.6 (C_{Ar}, C^9); δ 135.9 (C_{Ar}, C^2); δ 133.2 (C_{Ar}, C^1); d 132.2 (C_{Ar}, C^4); δ 129.9 (C_{Ar}, C^6); δ 128.4 (C_{Ar}, C^3); δ 127.2 (C_{Ar}, C^5); δ 124.4 (C_{Ar}, C^{11}); δ 123.1 (C_{Ar}, C^{10}); δ 27.9 (C^{12}); δ 23.5 (C^{13}). ESI-MS (M^+, *m/z*): 301. *Anal.* Found: C, 76.05; H, 7.35; N, 4.63. Calc. for $C_{19}H_{22}ClN$: C, 76.11; H, 7.40; N, 4.67.

2.2.3. 2-Bromobenzylidene-2,6-diisopropylphenylamine (*L3*)

The same synthetic procedure as outlined above for (**L1**) was employed for the synthesis of **L3**, using 2-bromobenzaldehyde as reagent. Yield: 2.98 g, 92%. FT-IR (υ, C=N):1624 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, numbering as per Scheme 1): δ 8.60 (s, 1H, H^7); δ 8.28 (dd, 1H, H^3, $^3J_{H-H}$ 7.78 Hz, $^4J_{H-H}$ 1.17 Hz); δ 7.66 (dd, 1H, H^6, $^3J_{H-H}$ 7.78 Hz, $^4J_{H-H}$ 1.17 Hz); δ 7.47 (t, 1H, H^4, $^3J_{H-H}$ 7.34 Hz); δ 7.37 (dt, 1H, H^5, $^3J_{H-H}$ 7.92 Hz, $^4J_{H-H}$ 1.91 Hz); δ 7.19 (m, 3H, $H^{10,11}$); δ 3.00 (sept., 2H, H^{12}, $^3J_{H-H}$ 6.82 Hz); δ 1.20 (d, 12H, $H^{12,13}$, $^3J_{H-H}$ 7.02 Hz). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$, numbering as per Fig. 2.3): δ 161.4 (*C*H=N, C^7); δ 148.9 (C_{Ar}, C^8); δ 137.6 (C_{Ar}, C^9); δ 134.6 (C_{Ar}, C^2); δ 133.2 (C_{Ar}, C^1); δ 132.4 (C_{Ar}, C^4); δ 128.8 (C_{Ar}, C^6); δ 127.8 (C_{Ar}, C^3); δ 125.7 (C_{Ar}, C^5); δ 124.4 (C_{Ar}, C^{11}); δ 123.1 (C_{Ar}, C^{10}); δ 27.9 (C^{12}); δ 23.5 (C^{13}). ESI-MS (M^+, *m/z*): 345. *Anal.* Found: C, 66.23; H, 6.41; N, 4.02. Calc. for $C_{19}H_{22}BrN$: C, 66.28; H, 6.44; N, 4.07.

2.2.4. Benzylidenepropylamine (*L4*)

The same synthetic procedure as outlined above for (**L1**) was employed for the synthesis of **L4**, using 2-bromobenzaldehyde and n-propylamine as reagent. Yield: 1.08 g, 74%. FT-IR (υ, C=N): 1645 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, numbering as per Scheme 1): δ 8.27 (s, 1H, H^7); δ 7.75 (m, 2H, $H^{2,6}$); δ 7.43 (m, 3H, $H^{3,4,5}$); δ 7.17 (m, 3H, $H^{10,11}$); δ 3.54 (t, 2H, H^8, $^3J_{H-H}$ 6.70 Hz); δ 1.68 (sext, 2H, H^9, $^3J_{H-H}$ 7.40 Hz, $^3J_{H-H}$ 7.40 Hz); δ 0.91 (t, 3H, H^{10}, $^3J_{H-H}$ 7.40 Hz). ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$, numbering as per Fig. 2.3): δ 160.6 (*C*H=N, C^7); δ 136.2 (C_{Ar}, C^1); δ 130.2 (C_{Ar}, C^4); δ 128.4 (C_{Ar}, $C^{2,6}$); δ 127.9 (C_{Ar}, $C^{3,5}$); δ 63.3 (C^8); δ 23.9 (C^9); δ 11.7 (C^{10}). ESI-MS (M^+, *m/z*): 148. *Anal.* Found: C, 81.41; H, 8.82; N, 9.43. Calc. for $C_{10}H_{13}N$: C, 81.59; H, 8.90; N, 9.51.

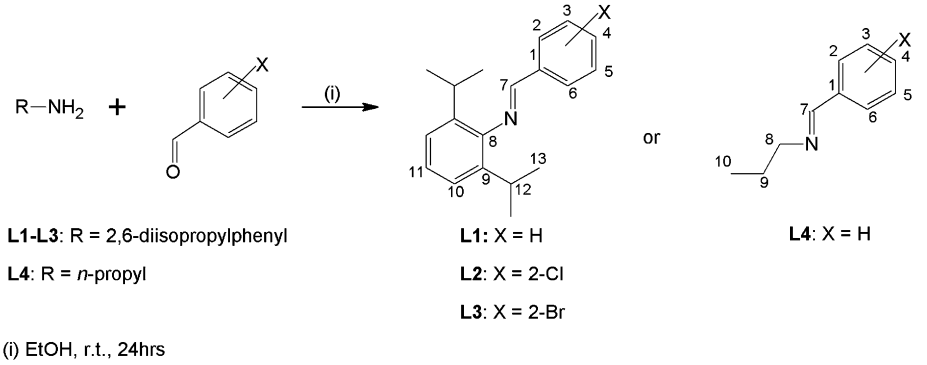
2.3. Synthesis of μ-Cl palladacycles (*C1–C4*)

2.3.1. Synthesis of [PdCl(C_6H_4)CH=N{2,6-^{i}Pr$_2$–C_6H_3}]$_2$ (*C1*)

To a stirring solution of $(MeCN)_2PdCl_2$ (100 mg, 0.386 mmol) in dichloromethane (10 mL) was added benzylidene-2,6-diisopropylphenylamine (**L1**, 102 mg, 0.386 mmol) and NaOAc (63 mg, 0.772). The reaction mixture was stirred for 18 h at room temperature, after which the solvent was removed. The yellow solid residue obtained was redissolved in dichloromethane (20 mL) and filtered through celite. The solvent was removed from the filtrate and the pale-yellow solid obtained recrystallized from dichloromethane: hexane. Yield: 120 mg, 79%. FT-IR (υ, C=N): 1599 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.75 (s, 2H, C*H*=N); δ 7.19 (m, 7H, Ar. protons); δ 7.11 (m, 7H, Ar. protons); δ 3.53 (sept., 4H, iPr-CH, $^3J_{H-H}$ 6.63 Hz); δ 1.39 (d, 6H, ^{i}Pr-*Me*, $^3J_{H-H}$ 6.04 Hz); δ 1.14 (d, 6H, ^{i}Pr-*Me*, $^3J_{H-H}$ 6.82 Hz). ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz): δ 176.21 (*C*H=N); δ 155.43 (C_1); δ 145.67 (*o*-metallated C); δ 141.48 (C_{Ar}); δ 133.90 (C_{Ar}); δ 132.56 (C_{Ar}); δ 130.86 (C_{Ar}); δ 128.29 (C_{Ar}); 127.74 (C_{Ar}); 124.68 (C_{Ar}); 123.23 (C_{Ar}); δ 28.19 (^{i}Pr-CH); δ 22.99, 24.45 (^{i}Pr-*Me*).

2.3.2. Synthesis of [PdCl(2-Cl-C_6H_3)CH=N{2,6-iPr_2–C_6H_3}]$_2$ (*C2*)

The same synthetic procedure as outlined above for (**C1**) was employed for the synthesis of **C2**, using **L2** as reagent. Yield: 145 mg, 85%. FT-IR (υ, C=N): 1585 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.14 (s, 2H, CH=N); δ 7.34 (m, 2H, Ar. protons); δ 7.20 (m, 4H, Ar.



Scheme 1. The preparation of monofunctional imine ligands, **L1–L4**.

protons); δ 7.01 (m, 6H, Ar. protons); δ 3.49 (sept., 4H, iPr-CH, $^3J_{H-H}$ 6.43 Hz); δ 1.39 (d, 6H, ^{i}Pr-*Me*, $^3J_{H-H}$ 6.43 Hz); δ 1.19 (d, 6H, ^{i}Pr-*Me*, $^3J_{H-H}$ 6.82 Hz). ^{13}C ($CDCl_3$, 75 MHz): δ 174.75 (*C*H=N); δ 156.38 (C_1); δ 142.88 (*o*-metallated C); δ 141.40 (C_{Ar}); δ 133.82 (C_{Ar}); δ 132.25 (C_{Ar}); δ 130.52 (C_{Ar}); δ 128.04 (C_{Ar}); δ 127.97 (C_{Ar}) δ 124.89 (C_{Ar}); δ 123.35 (C_{Ar}); δ 28.28 (^{i}Pr-*C*H); δ 24.48 (^{i}Pr-*Me*); δ 22.94 (^{i}Pr-*Me*).

2.3.3. Synthesis of [PdCl(2-Br-C_6H_3)CH=N{2,6-^{i}Pr$_2$–C_6H_3}]$_2$ (**C3**)

The same synthetic procedure as outlined above for (**C1**) was employed for the synthesis of **C3**, using **L3** as reagent and stirring for 6 h. Yield: 149 mg, 80%. FT-IR (υ, C=N): 1585 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.13 (s, 2H, C*H*=N); δ 7.34 (m, 2H, Ar. protons); δ 7.20 (m, 8H, Ar. protons); δ 6.87 (m, 2H, Ar. protons); δ 3.49 (sept., 4H, iPr-CH, $^3J_{H-H}$ 6.31 Hz); δ 1.38 (d, 6H, ^{i}Pr-*Me*, $^3J_{H-H}$ 6.60 Hz); δ 1.17 (d, 6H, ^{i}Pr-*Me*, $^3J_{H-H}$ 6.60 Hz). ^{13}C {^{1}H} ($CDCl_3$, 75 MHz): δ 174.15 (*C*H=N); δ 156.89 (C_1); δ 142.56 (*o*-metallated C); δ 141.35 (C_{Ar}); δ 133.85 (C_{Ar}) δ 132.45 (C_{Ar}); δ 130.62 (C_{Ar}); 128.35 (C_{Ar}); δ 127.95 (C_{Ar}); δ 124.73 (C_{Ar}); δ 123.30 (C_{Ar}); δ 28.25 (^{i}Pr-CH); δ 24.49 (^{i}Pr-*Me*); δ 22.90 (^{i}Pr-*Me*).

2.3.4. Synthesis of [PdCl(C_6H_4)CH=N{n-Pr}]$_2$ (**C4**)

The same synthetic procedure as outlined above for (**C1**) was employed for the synthesis of **C4**, using **L4** as reagent and stirring for 18 h. Yield: 140 mg, 70%. FT-IR (υ, C=N): 1638 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.79 (s, 2H, C*H*=N); δ 7.01–7.49 (m, 8H, Ar. protons); δ 3.58 (t., 4H, N–CH_2-, $^3J_{H-H}$ 6.63 Hz); δ 1.91 (sext., 4H, –CH_2–CH_2Me, $^3J_{H-H}$ 7.34 Hz); δ 0.94 (t, 6H, *n*-Pr-*Me*, $^3J_{H-H}$ 7.04 Hz). ^{13}C {^{1}H} ($CDCl_3$, 75 MHz): δ 173.69 (*C*H=N); δ 155.01 (C_1); δ 146.03 (*o*-metallated C); δ 133.30 (C_{Ar}); δ 119.83 (C_{Ar}) δ 126.96 (C_{Ar}); δ 124.68 (C_{Ar}); δ 29.69 (Pr,-NCH_2-); δ 23.33 (Pr,-*C*H_2-); δ 11.10 (Pr,-CH_3).

2.4. Synthesis of mononuclear palladacycles

2.4.1. Synthesis of [Pd(PPh_3)(C_6H_4)CH=N{2,6-^{i}Pr$_2$–C_6H_3}Cl] (**C5**)

To a stirring solution of [PdCl(C_6H_4)CH=N{2,6-^{i}Pr$_2$–C_6H_3}]$_2$ (**C1**, 128 mg, 0.158 mmol) in dichloromethane (5 mL) was added triphenylphosphine (83 mg, 0.316 mmol). The reaction mixture was stirred under an inert atmosphere and at room temperature for 1 h, after which the solvent was removed. The yellow solid residue obtained was recrystallized from dichloromethane:Et_2O. Yield: 162 mg, 77%. FT-IR (υ, C=N): 1604 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.11 (d, 1H, $^4J_{H-P}$ 7.78 Hz); δ 7.71–7.78 (m, 6H, Ar. protons); δ 7.33–7.43 (m, 9H, Ar. protons); δ 7.14–7.23 (m, 3H, Ar. protons); δ 7.02 (t, 1H, $^3J_{H-H}$ 7.34 Hz); δ 6.70 (t, 1H, $^3J_{H-H}$ 7.34 Hz); δ 6.50 (t, 1H, $^3J_{H-H}$ 7.04 Hz); δ 3.42–3.53 (sept., 2H, ^{i}Pr-C*H*, $^3J_{H-H}$ 6.75 Hz); δ 1.37 (d, 6H, ^{i}Pr-*Me*, $^3J_{H-H}$ 6.90 Hz); δ 1.21 (d, 6H, ^{i}Pr-*Me*, $^3J_{H-H}$ 6.90 Hz). ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz): δ 177.03 (*C*H=N); δ 159.54 (C_1); δ 145.15 (*o*-metallated C); δ 141.48 (C_{Ar}); δ 140.80 (C_{Ar}); δ 138.20 (C_{Ar}); δ 135.41 (C_{Ar}); δ 135.04 (C_{Ar}); δ 131.68 (C_{Ar}); δ 130.83 (C_{Ar}); δ 130.56 (C_{Ar}); δ 128.84 (C_{Ar}); δ 127.92 (C_{Ar}); δ 126.88 (C_{Ar}); δ 124.09 (C_{Ar}); δ 122.77 (C_{Ar}); δ 28.64 (^{i}Pr-CH); δ 24.51 (^{i}Pr-*Me*); δ 23.02 (^{i}Pr-*Me*). ^{31}P{^{1}H} NMR: δ 42.41. ESI-MS (+, *m/z*): 633 [M – Cl]$^+$. *Anal.* Found: C, 66.42; H, 5.54; N, 2.04. Calc for $C_{37}H_{37}ClNPPd$: C, 66.47; H, 5.58; N, 2.10.

2.4.2. Synthesis of [Pd(PPh_3)(2-Cl-C_6H_3)CH=N{2,6-^{i}Pr$_2$–C_6H_3}Cl] (**C6**)

The same synthetic procedure as outlined above for (**C5**) was employed for the synthesis of **C6**, using [PdCl(2-Cl-C_6H_3)CH=N{2,6-^{i}Pr$_2$–C_6H_3}]$_2$ (**C2**) as reagent. Yield: 182 mg, 83%. FT-IR (υ, C=N): 1605 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.61 (d, 1H, $^4J_{H-P}$ 7.92 Hz); δ 7.69–7.77 (m, 6H, Ar. protons); δ 7.33–7.44 (m, 9H, Ar. protons); δ 7.15–7.23 (m, 3H, Ar. protons); δ 6.92 (d, 1H, $^3J_{H-H}$ 7.92 Hz); δ 6.61 (t, 1H, $^3J_{H-H}$ 7.78 Hz); δ 6.38 (t, 1H, $^3J_{H-H}$ 7.04 Hz); δ 3.40–3.49 (sept., 2H, ^{i}Pr-C*H*, $^3J_{H-H}$ 6.90 Hz); δ 1.37 (d, 6H, ^{i}Pr-*Me*, $^3J_{H-H}$ 6.43 Hz); δ 1.23 (d, 6H, ^{i}Pr-*Me*, $^3J_{H-H}$ 6.90 Hz). ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz): δ 175.58 (*C*H=N); δ 160.21 (C_1); δ 145.81 (*o*-metallated C); δ 141.05 (C_{Ar}); δ 140.38 (C_{Ar}); δ 138.14 (C_{Ar}); δ 135.04 (C_{Ar}); 134.96 (C_{Ar}); δ 130.76 (C_{Ar}); δ 130.71 (C_{Ar}); δ 128.22 (C_{Ar}); δ 128.03 (C_{Ar}); δ 127.19 (C_{Ar}); δ 124.12 (C_{Ar}); δ 122.86 (C_{Ar}); δ 28.64 (^{i}Pr–CH); δ 24.56 (^{i}Pr-*Me*); δ 22.97 (^{i}Pr-*Me*). ^{31}P{^{1}H} NMR: δ 41.76. ESI-MS (+, *m/z*): 667 [M – Cl]$^+$. *Anal.* Found: C, 63.18; H, 5.11; N, 1.92. Calc for $C_{37}H_{36}Cl_2NPPd$: C, 63.22; H, 5.16; N, 1.99.

2.4.3. Synthesis of [Pd(PPh_3)(2-Br-C_6H_3)CH=N{2,6-^{i}Pr$_2$–C_6H_3}Cl] (**C7**)

The same synthetic procedure as outlined above for (**C5**) was employed for the synthesis of **C7**, using [PdCl(2-Br-C_6H_3)CH=N{2,6-^{i}Pr$_2$–C_6H_3}]$_2$ (**C3**) as reagent. Yield = 184 mg, 78%. FT-IR (υ, C=N): 1606 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.61 (d, 1H, $^4J_{H-P}$ 7.78 Hz); δ 7.69–7.76 (m, 6H, Ar. protons); δ 7.33–7.44 (m, 9H, Ar. protons); δ 7.15–7.24 (m, 3H, Ar. protons); δ 7.10 (d, 1H, $^3J_{H-H}$ 6.90 Hz); δ 6.51 (t, 1H, $^3J_{H-H}$ 7.19 Hz); δ 6.42 (t, 1H, $^3J_{H-H}$ 6.90 Hz); δ 3.40–3.49 (sept., 2H, ^{i}Pr-C*H*, $^3J_{H-H}$ 6.90 Hz); δ 1.37 (d, 6H, ^{i}Pr-*Me*, $^3J_{H-H}$ 6.90 Hz); δ 1.23 (d, 6H, ^{i}Pr-*Me*, $^3J_{H-H}$ 6.90 Hz). ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz): δ 177.70 (*C*H=N); δ 160.69 (C_1); δ 145.92 (*o*-metallated C); δ 141.23 (C_{Ar}); δ 140.74 (C_{Ar}); δ 137.27 (C_{Ar}); δ 135.04 (C_{Ar}); 134.96 (C_{Ar}); δ 130.84 (C_{Ar}); δ 130.49 (C_{Ar}); δ 128.29 (C_{Ar}); δ 128.01 (C_{Ar}); δ 127.13 (C_{Ar}); δ 124.38 (C_{Ar}); δ 122.13 (C_{Ar}); δ 28.65 (^{i}Pr-*C*H); δ 24.58 (^{i}Pr-*Me*); δ 22.96 (^{i}Pr-*Me*). ^{31}P{^{1}H} NMR: 41.53. ESI-MS (+, *m/z*): 711 [M – Cl]$^+$. *Anal.* Found: C, 59.40; H, 4.82; N, 1.80. Calc for $C_{37}H_{36}BrClNPPd$: C, 59.46; H, 4.85; N, 1.87.

2.4.4. Synthesis of [Pd(PPh_3)(C_6H_4)CH=N{n-Pr}Cl] (**C8**)

The same synthetic procedure as outlined above for (**C5**) was employed for the synthesis of **C8**, using [PdCl(C_6H_4)CH=N{*n*-Pr}]$_2$ (**C4**) as reagent. Yield = 156 mg, 89%. FT-IR (υ, C=N): 1626 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.07 (d, 1H, $^4J_{H-P}$ 7.78 Hz); δ 7.73–7.79 (m, 6H, Ar. protons); δ 7.33–7.39 (m, 9H, Ar. protons); δ 7.16 (m, 1H, Ar. proton); δ 6.90 (t, 1H, $^3J_{H-H}$ 7.34 Hz); δ 6.53 (t, 1H, $^3J_{H-H}$ 7.34 Hz); δ 6.39 (t, 1H, $^3J_{H-H}$ 6.82 Hz); δ 3.90 (t., 2H, N-CH_2-, $^3J_{H-H}$ 6.75 Hz); δ 1.88 (sext., 2H,-CH_2–*Me*, $^3J_{H-H}$ 7.14 Hz); δ 0.91 (t, 3H, *n*-Pr-*Me*, $^3J_{H-H}$ 6.96 Hz). ^{13}C {^{1}H} NMR ($CDCl_3$, 75 MHz): δ 174.72 (*C*H=N); δ 158.46 (C_1); δ 144.17 (*o*-metallated C); δ 138.34 (C_{Ar}); δ 138.14 (C_{Ar}); δ 135.60 (C_{Ar}); δ 135.36 (C_{Ar}); δ 135.04 (C_{Ar}); δ 134.92 (C_{Ar}); δ 130.70 (C_{Ar}); δ 130.65 (C_{Ar}); δ 129.50 (C_{Ar}); δ 29.69 (-NCH_2-); δ 24.09 (*n*-Pr-*C*H_2-); δ 11.26 (*n*-Pr-*Me*). ^{31}P{^{1}H} NMR: δ 42.79. ESI-MS (+, *m/z*): 514 [M – Cl]$^+$. *Anal.* Found: C, 60.42; H, 4.32; N, 2.01. Calc for $C_{28}H_{27}ClNPPd$: C, 61.10; H, 4.94; N, 2.54.

2.4.5. Synthesis of [Pd(PMe_3)(2-Cl-C_6H_3)CH=N{2,6-^{i}Pr$_2$–C_6H_3}Cl] (**C9**)

The same synthetic procedure as outlined above for (**C5**) was employed for the synthesis of **C9**, using [PdCl(2-Cl-C_6H_3)CH=N{2,6-^{i}Pr$_2$–C_6H_3}]$_2$ (**C2**) and trimethylphosphine as reagent. Yield: 131 mg, 80%. FT-IR (υ, C=N): 1609 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.51 (d, 1H, $^4J_{H-P}$ 7.81 Hz); δ 7.24–7.28 (m, 2H, Ar. protons); δ 7.18–7.21 (m, 3H, Ar. protons); δ 7.11 (d, 1H, $^3J_{H-H}$ 7.03 Hz); δ 3.23–3.70 (sept., 2H, ^{i}Pr-C*H*, $^3J_{H-H}$ 6.64 Hz); δ 1.69 (d, 9H,P(*Me*)$_3$, $^2J_{H-P}$ 10.74 Hz); δ 1.34 (d, 6H, ^{i}Pr-*Me*, $^3J_{H-H}$ 7.03 Hz); δ 1.16 (d, 6H, ^{i}Pr-*Me*, $^3J_{H-H}$ 7.23 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 174.92 (*C*H=N); δ 160.54 (C_1); δ 145.32 (*o*-metallated); δ 141.71 (C_{Ar}); δ 140.79 (C_{Ar}); δ 138.65 (C_{Ar}); δ 135.21 (C_{Ar}); δ 129.79 (C_{Ar}); δ 125.47 (C_{Ar}); δ 123.36 (C_{Ar}); δ 122.89 (C_{Ar}); δ 28.40 (^{i}Pr-*C*H); δ 22.90 (P*Me*$_3$); δ 16.99 (^{i}Pr-*Me*); δ 16.33 (^{i}Pr-*Me*). ^{31}P{^{1}H} NMR: - 4.60. ESI-MS (+, *m/z*): 481 [M – Cl]$^+$. *Anal.* Found: C, 51.05; H, 5.76; N, 2.68. Calc for $C_{22}H_{30}Cl_2NPPd$: C, 51.13; H, 5.85; N, 2.71.

2.5. Synthesis of cationic mononuclear palladacycles

2.5.1. Synthesis of [Pd(MeCN)(PPh_3)(C_6H_4)CH=N{2,6-^{i}Pr$_2$–C_6H_3}]$^+$[B(Ar)$_4$]$^-$ [Ar = 3,5- (CF_3)$_2$–C_6H_3] (**C10**)

To a stirring solution of [Pd(PPh_3)(C_6H_4)CH=N{2,6-^{i}Pr$_2$–C_6H_3}Cl] (C5, 50 mg, 0.075 mmol) in dichloromethane (7 mL) was added

a solution of $NaB(Ar)_4$ (66 mg, 0.075 mmol) in acetonitrile (3 mL). The onset of a white precipitate was observed immediately, and the reaction mixture was stirred at room temperature for 2 h. After the allotted time the reaction mixture was filtered and the solvent removed. The resulting pale yellow solid residue was recrystallized from dichloromethane:pentane and a pale yellow solid was isolated. Yield: 101 mg, 88%. FT-IR (υ, C═N): 1616 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.09 (d, 1H, $^4J_{H-P}$ 7.60 Hz); δ 7.64–7.71 (m, 12H, Ar. protons, B(*Ar*)$_4$); δ 7.41–7.56 (m, 15H, Ar. protons, P*Ph*$_3$); δ 7.19–7.28 (m, 4H, Ar. protons); δ 7.12 (t, 1H, $^3J_{H-H}$ 7.48 Hz); δ 6.78 (t, 1H, $^3J_{H-H}$ 7.92 Hz); δ 6.48 (t, 1H, $^3J_{H-H}$ 7.34 Hz); δ 3.35 (sept., 2H, ^{i}Pr-C*H*, $^3J_{H-H}$ 6.90 Hz); δ 1.28 (d, 6H, ^{i}Pr-*Me*, $^3J_{H-H}$ 6.75 Hz); δ 1.25 (d, 6H, ^{i}Pr-*Me*, $^3J_{H-H}$ 6.75 Hz); δ 1.06 (s, 3H, *Me*CN). ^{13}C {^1H} NMR ($CDCl_3$, 75 MHz): δ 178.15 (*C*H═N); δ 162.66 (C_{Ar}, B*Ar*$_4$); δ 162.00 (C_{Ar}, B*Ar*$_4$); δ 161.33 (C_{Ar}, B*Ar*$_4$); δ 160.67 (C_{Ar}, B*Ar*$_4$); δ 153.99 (C_1); δ 147.67 (*o*-metallated C); δ 143.76 (C_{Ar}); δ 140.40 (C_{Ar}); δ 138.83 (C_{Ar}); δ 134.75 (C_{Ar}); δ 134.59 (C_{Ar}); δ 132.24 (C_{Ar}); δ 130.73 (C_{Ar}); δ 129.18 (C_{Ar}); δ 128.63 (C_{Ar}); δ 128.18 (C_{Ar}); δ 126.32 (C_{Ar}); δ 123.67 (C_{Ar}); δ 122.71 (C_{Ar}); δ 117.43 (*C*≡N); δ 28.59 (^{i}Pr-*C*H); δ 24.10 (^{i}Pr-*Me*); δ 22.62 (^{i}Pr-*Me*); δ 0.13 (CN–*C*H$_3$). ^{31}P{^1H} NMR: δ 41.24. ESI-MS (+, *m/z*): 674 [M-B(Ar)$_4$]$^+$. ESI-MS (-, *m/z*): 863 [B(Ar)$_4$]$^-$. *Anal.* Found: C, 55.01; H, 3.14; N, 1.43. Calc for $C_{71}H_{52}BF_{24}N_2PPd$: C, 55.47; H, 3.41; N, 1.82.

2.5.2. Synthesis of [Pd(MeCN)(PPh$_3$)(2-Cl-C$_6$H$_3$)CH═N{2,6-^{i}Pr$_2$–C$_6$H$_3$}]$^+$[B(Ar)$_4$]$^-$ [Ar = 3,5–(CF$_3$)$_2$–C$_6$H$_3$] (**C11**)

The same synthetic procedure as outlined above (**C10**) was employed for the synthesis of **C11**, using [Pd(PPh$_3$)(2-Cl-C$_6$H$_3$)CH═N{2,6-^{i}Pr$_2$–C$_6$H$_3$}Cl] (**C6**) as reagent. Yield: 107 mg, 91%. FT-IR (υ, C═N): 1611 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.59 (d, 1H, $^4J_{H-P}$ 7.60 Hz); δ 7.63–7.70 (m, 12H, Ar. protons, B(*Ar*)$_4$); δ 7.43–7.54 (m, 15H, Ar. protons, P*Ph*$_3$); δ 7.21–7.30 (m, 3H, Ar. protons); δ 7.06 (d, 1H, $^3J_{H-H}$ 8.19 Hz); δ 6.70 (t, 1H, $^3J_{H-H}$ 7.99 Hz); δ 6.35 (t, 1H, $^3J_{H-H}$ 7.02 Hz); δ 3.34 (sept., 2H, ^{i}Pr-CH, $^3J_{H-H}$ 6.82 Hz); δ 1.30 (d, 6H, ^{i}Pr-*Me*, $^3J_{H-H}$ 6.63 Hz); δ 1.29 (d, 6H, ^{i}Pr-*Me*, $^3J_{H-H}$ 6.82 Hz); δ 1.05 (s, 3H, *Me*CN). ^{13}C {^1H} NMR ($CDCl_3$, 75 MHz): δ 178.95 (*C*H═N); δ 162.66 (C_{Ar}, BAr$_4$); δ 162.02 (C_{Ar}, B*Ar*$_4$); δ 161.32 (C_{Ar}, B*Ar*$_4$); δ 160.66 (C_{Ar}, B*Ar*$_4$); δ 155.56 (C_1); δ 146.13 (*o*-metallated C); δ 143.84 (C_{Ar}); δ 140.28 (C_{Ar}); δ 137.99 (C_{Ar}); δ 134.77 (C_{Ar}); δ 133.88 (C_{Ar}); δ 132.39 (C_{Ar}); δ 130.70 (C_{Ar}); δ 129.26 (C_{Ar}); δ 128.54 (C_{Ar}); δ 127.91 (C_{Ar}); δ 126.37 (C_{Ar}); δ 123.77 (C_{Ar}); δ 122.71 (C_{Ar}); δ 117.45 (*C*≡N); δ 28.69 (^{i}Pr-*C*H); δ 24.21 (^{i}Pr-*Me*); δ 22.57 (^{i}Pr-*Me*); δ 0.11 (CN–*C*H$_3$). ^{31}P{^1H} NMR: δ 40.97. ESI-MS (+, *m/z*): 709 [M-B(Ar)$_4$]$^+$. ESI-MS (-, *m/z*): 863 [B(Ar)$_4$]$^-$. *Anal.* Found: C, 53.89; H, 2.94; N, 1.42. Calc for $C_{71}H_{51}BClF_{24}N_2PPd$: C, 54.25; H, 3.27; N, 1.78.

2.5.3. Synthesis of [Pd(MeCN)(PPh$_3$)(2-Br-C$_6$H$_3$)CH═N{2,6-^{i}Pr$_2$–C$_6$H$_3$}]$^+$[B(Ar)$_4$]$^-$ [Ar = 3,5–(CF$_3$)$_2$–C$_6$H$_3$] (**C12**)

The same synthetic procedure as outlined above (**C10**) was employed for the synthesis of **C12**, using [Pd(PPh$_3$)(2-Br-C$_6$H$_3$)CH═N{2,6-^{i}Pr$_2$–C$_6$H$_3$}Cl] (**C7**) as reagent. Yield: 87 mg, 72%. FT-IR (υ, C═N): 1615 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.56 (d, 1H, $^4J_{H-P}$ 7.60 Hz); δ 7.64–7.71 (m, 12H, Ar. protons, B(*Ar*)$_4$); δ 7.41–7.52 (m, 15H, Ar. protons, P*Ph*$_3$); δ 7.18–7.27 (m, 3H, Ar. protons); δ 7.05 (d, 1H, $^3J_{H-H}$ 8.12 Hz); δ 6.70 (t, 1H, $^3J_{H-H}$ 7.94 Hz); δ 6.37 (t, 1H, $^3J_{H-H}$ 6.89 Hz); δ 3.33 (sept., 2H, ^{i}Pr-CH, $^3J_{H-H}$ 7.04 Hz); δ 1.31 (d, 6H, ^{i}Pr-*Me*, $^3J_{H-H}$ 6.63 Hz); δ 1.30 (d, 6H, ^{i}Pr-*Me*, $^3J_{H-H}$ 6.82 Hz); δ 1.09 (s, 3H, *Me*CN). ^{13}C {^1H} NMR ($CDCl_3$, 75 MHz): δ 178.89 (*C*H═N); δ 162.66 (C_{Ar}, BAr$_4$); δ 162.01 (C_{Ar}, B*Ar*$_4$); δ 161.34 (C_{Ar}, B*Ar*$_4$); δ 160.68 (C_{Ar}, B*Ar*$_4$); δ 155.34 (C_1); δ 146.06 (*o*-metallated C); δ 143.94 (C_{Ar}); δ 140.33 (C_{Ar}); δ 137.83 (C_{Ar}); δ 134.69 (C_{Ar}); δ 133.79 (C_{Ar}); δ 132.36 (C_{Ar}); δ 130.62 (C_{Ar}); δ 129.11 (C_{Ar}); δ 128.49 (C_{Ar}); δ 127.79 (C_{Ar}); δ 126.33 (C_{Ar}); δ 123.77 (C_{Ar}); δ 122.71 (C_{Ar}); δ 117.39 (C≡N); δ 28.63 (^{i}Pr-*C*H); δ 24.56 (^{i}Pr-*Me*); δ 22.94 (^{i}Pr-*Me*); δ 0.08 (CN–CH$_3$). ^{31}P{^1H} NMR: δ 40.56. ESI-MS (+, *m/z*): 753 [M-B(Ar)$_4$]$^+$. ESI-MS (-, *m/z*): 863 [B(Ar)$_4$]$^-$. *Anal.* Found: C, 52.59; H, 2.85; N, 1.39. Calc for $C_{71}H_{51}BBrF_{24}N_2PPd$: C, 52.76; H, 3.18; N, 1.73.

2.5.4. Synthesis of [Pd(MeCN)(PPh$_3$)(C$_6$H$_4$)CH═N{n-Pr}]$^+$[B(Ar)$_4$]$^-$ [Ar = 3,5–(CF$_3$)$_2$–C$_6$H$_3$] (**C13**)

The same synthetic procedure as outlined above for (**C10**) was employed for the synthesis of **C13**, using [Pd(PPh$_3$)(C$_6$H$_4$)CH═N{*n*-Pr}Cl] (**C8**) as reagent. Yield: 77 mg, 73%. FT-IR (υ, C═N): 1618 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.99 (d, 1H, $^4J_{H-P}$ 7.48 Hz); δ 7.63–7.69 (m, 12H, Ar. protons, BAr$_4$); δ 7.44–7.51 (m, 15H, Ar. protons, P*Ph*$_3$); δ 7.28 (m, 1H, Ar. protons); δ 7.00 (t, 1H, $^3J_{H-H}$ 7.36 Hz); δ 6.59 (t, 1H, $^3J_{H-H}$ 7.99 Hz); δ 6.34 (t, 1H, $^3J_{H-H}$ 6.82 Hz); δ 3.52 (t., 2H, N–CH$_2$-, $^3J_{H-H}$ 6.75 Hz); δ 1.51 (sext., 2H,-CH$_2$–*Me*, $^3J_{H-H}$ 7.14 Hz); δ 1.22 (s, 3H, *Me*CN); δ 0.86 (t, 3H, *n*-Pr-*Me*, $^3J_{H-H}$ 6.96 Hz). ^{13}C {^1H} NMR ($CDCl_3$, 75 MHz): δ 177.94 (*C*H═N); δ 162.32 (C_{Ar}, BAr$_4$); 161.95 (C_{Ar}, B*Ar*$_4$); δ 161.02 (C_{Ar}, B*Ar*$_4$); δ 160.29 (C_{Ar}, B*Ar*$_4$); δ 153.94 (C_1); δ 147.29 (*o*-metallated C); δ 134.34 (C_{Ar}); δ 132.14 (C_{Ar}); δ 130.60 (C_{Ar}); δ 129.29 (C_{Ar}); δ 127.74 (C_{Ar}); δ 126.32 (C_{Ar}); δ 123.70 (C_{Ar}); δ 122.64 (C_{Ar}); δ 117.20 (*C*≡N); δ 29.49 (-NCH$_2$-); δ 24.19 (*n*-Pr-*C*H$_2$-); δ 11.34 (*n*-Pr-*Me*); δ 0.11 (CN–*C*H$_3$). ^{31}P{^1H} NMR: 40.97. ESI-MS (+, *m/z*): 556 [M-B(Ar)$_4$]$^+$. ESI-MS (-, *m/z*): 863 [B(Ar)$_4$]$^-$. *Anal.* Found: C, 52.14; H, 2.62; N, 1.71. Calc for $C_{62}H_{42}BF_{24}N_2PPd$: C, 52.47; H, 2.98; N, 1.97.

2.5.5. Synthesis of [Pd(MeCN)(PMe$_3$)(2-Cl-C$_6$H$_3$)CH═N{2,6-^{i}Pr$_2$–C$_6$H$_3$}]$^+$[B(Ar)$_4$]$^-$ [Ar = 3,5–(CF$_3$)$_2$–C$_6$H$_3$] (**C14**)

The same synthetic procedure as outlined above (**C10**) was employed for the synthesis of **C14**, using [Pd(PMe$_3$)(2-Cl-C$_6$H$_3$)CH═N{2,6-^{i}Pr$_2$–C$_6$H$_3$}Cl] (**C9**) as reagent. Yield: 94 mg, 90%. FT-IR (υ, C═N): 1613 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.40 (d, 1H, $^4J_{H-P}$ 7.80 Hz); δ 7.64–7.71 (m, 12H, Ar. protons, B(*Ar*)$_4$); δ 6.94–7.10 (m, 3H, Ar. protons); δ 7.06 (d, 1H, $^3J_{H-H}$ 8.01 Hz); δ 6.95 (t, 1H, $^3J_{H-H}$ 7.94 Hz); δ 6.62 (t, 1H, $^3J_{H-H}$ 7.00 Hz); δ 2.89 (sept., 2H, ^{i}Pr-C*H*, $^3J_{H-H}$ 6.99 Hz); δ 1.13 (s, 3H, *Me*CN); δ 0.98 (d, 6H, ^{i}Pr-*Me*, $^3J_{H-H}$ 6.82 Hz); δ 0.91 (d, 6H, ^{i}Pr-*Me*, $^3J_{H-H}$ 6.62 Hz). ^{13}C {^1H} NMR ($CDCl_3$, 75 MHz): δ 178.90 (*C*H═N); δ 162.86 (C_{Ar}, BAr$_4$); δ 162.42 (C_{Ar}, B*Ar*$_4$); δ 161.02 (C_{Ar}, B*Ar*$_4$); δ 160.59 (C_{Ar}, B*Ar*$_4$); δ 155.65 (C_1); δ 146.19 (*o*-metallated C); δ 133.62 (C_{Ar}); δ 132.40 (C_{Ar}); δ 130.71 (C_{Ar}); δ 129.28 (C_{Ar}); δ 128.57 (C_{Ar}); δ 127.95 (C_{Ar}); δ 126.33 (C_{Ar}); δ 123.71 (C_{Ar}); δ 122.75 (C_{Ar}); δ 117.49 (*C*≡N); δ 28.69 (^{i}Pr-CH); δ 24.21 (^{i}Pr-*Me*); δ 22.57 (^{i}Pr-*Me*); δ 21.93 (P*Me*$_3$); δ 0.07 (CN–*C*H$_3$). ^{31}P{^1H} NMR: δ - 3.98. ESI-MS (+, *m/z*): 522 [M-B(Ar)$_4$]$^+$. ESI-MS (-, *m/z*): 863 [B(Ar)$_4$]$^-$. *Anal.* Found: C, 48.13; H, 2.91; N, 1.62. Calc for $C_{56}H_{45}BClF_{24}N_2PPd$: C, 48.54; H, 3.27; N, 2.02.

2.6. X-ray crystallography

Single crystals of complex **C2** were mounted on nylon loops and centred in a stream of cold nitrogen at 100(2) K. Crystal evaluation and data collection was performed on a Bruker-Nonius SMART Apex-CCD diffractometer with Mo K_α radiation (λ = 0.71073 Å). Data collection were recorded using ω scans. Data reduction and absorption corrections were performed using SAINT [11] and SADABS [11,12], which forms part of the APEX II software package. The structure was solved by direct methods and refined by using SHELXS-97 [13] and SHELXL-97 [13] within the X-Seed graphical user interface [14]. All non-hydrogen atoms were refined anisotropically by full matrix least squares calculations on F^2 and all hydrogen atoms were placed in calculated positions using riding models.

2.7. Phenylacetylene polymerization

The cationic palladium complex (0.03 mmol) was dissolved in dichloromethane (10 mL). Thereafter phenylacetylene (in molar

ratio 1:50; 1:100 or 1:200 Pd:PA) was added. The reaction mixture was stirred under an inert atmosphere at 60 °C for the required time. A colour-change from light yellow to orange was observed. After the allotted time the solvent was removed and MeOH (20 mL) added to precipitate the polymer, followed by stirring overnight. The brown solid which had formed was filtered and dried *in vauo*. The filtrate was collected, the solvent removed and the brown residue which was obtained was dried *in vacuo*.

3. Results and discussion

3.1. Synthesis of cationic palladacycles

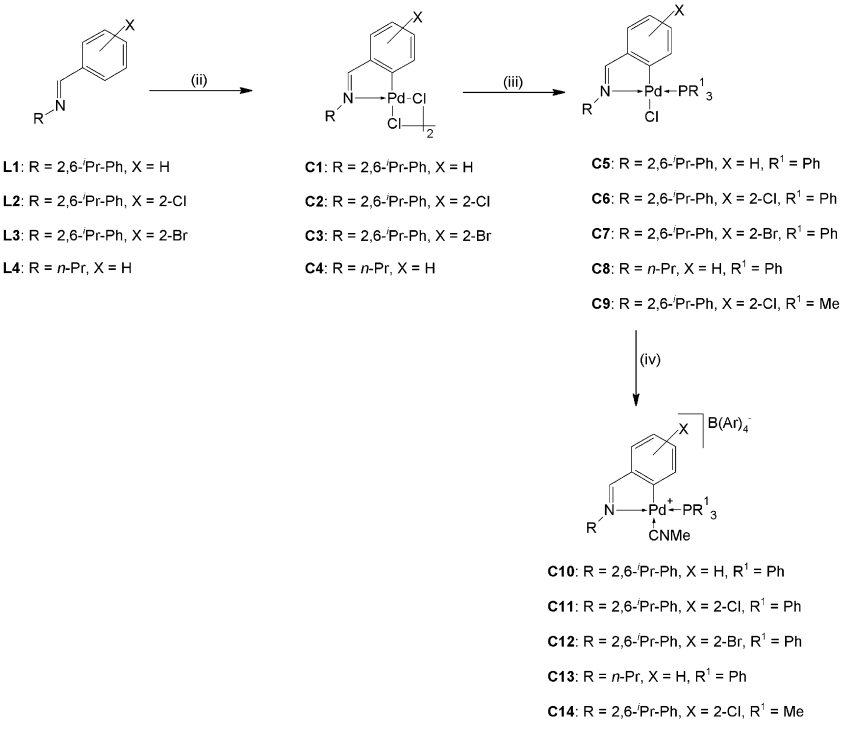
For the benefit of the reader, all syntheses and characterization data are outlined in Section 2. Monofunctional imine ligands, **L1**–**L4**, were prepared by Schiff base condensation of 2,6-diisopropylaniline and *n*-propylamine with various mono-substituted aldehydes (Scheme 1). Ligands **L1**–**L3** was isolated as pale-yellow crystalline solids whereas ligand **L4** was isolated as a bright-yellow oil, in high yields in all cases. The ligands displayed solubility in polar organic solvents as well as stability both in solution and in the solid state. Ligands **L1**, **L3**–**L4** have been reported previously [15], whereas ligand **L2** is novel. FT-IR analysis indicated the formation of the desired condensation product as evidenced by the absence of characteristic $\upsilon_{C=O}$ bands of the aldehyde starting material and the formation of absorption bands corresponding to the $\upsilon_{C=N}$ of the imine products in the range 1620–1650 cm^{-1}.

The imine proton resonances in the ^1H NMR spectra of the ligands were observed in the range δ 8.20–8.80 ppm. For ligands **L2** and **L3** (halide substituents) the imine resonances are shifted more downfield in comparison to **L1** and **L4**. This difference may be attributed to the inductive effect of the halogen substituents [16]. The aromatic region of the ^1H NMR spectra showed resonances typical of either 1,2- or 1,4-disubstitution. In the aliphatic region we observed the equivalence of the ^{i}Pr groups (for ligands **L1**–**L3**), observed as a doublet integrating for twelve protons, due to free rotation about the C–N single bond. For ligand **L4** the aliphatic region showed resonances due to the *n*-propyl chain. In the ^{13}C NMR spectra of the ligands the imine carbon resonances were observed in the range 158–162 ppm.

The chloro-bridged palladacycles, **C1**–**C4**, were prepared by the reaction of the palladium precursor bis(acetonitrile) palladium dichloride, $(MeCN)_2PdCl_2$, with **L1**–**L4**, in the presence of excess NaOAc as a base at room temperature (Scheme 2) and the reaction proceeded via electrophilic C–H activation. The palladacycles were isolated as yellow air-stable solids in 70–90% yield. Complexes **C1** and **C4** were found to be soluble in chlorinated organic solvents whereas **C2** and in particular **C3** displayed only partial solubility in chlorinated organic solvents.

In the FT-IR spectra of the complexes the imine absorption band was observed to shift to lower wavenumbers in the range 1580–1638 cm^{-1}, in comparison to that of the free ligands. This was indicative of the coordination of the N-atom of the imine moiety to the metal centre which resulted in a decrease in the double bond character of the imine functionality [17].

The ^1H NMR spectra of the complexes showed an upfield shift of the imine proton resonances in the range of δ 7.75–8.14 ppm, in comparison to that of the free ligands. Furthermore, in the aromatic region the resonance of the *ortho*-H atom of the benzylidene ring disappeared and a complicated series of multiplets were observed integrating for eight (as is the case for **C4**), twelve (as is the case for **C2** and **C3**) and fourteen protons (as is the case for **C1**) respectively. This was indicative of the fact that cyclopalladation took place preferentially via C–H bond activation [18]. In the aliphatic region the methine proton resonances of the isopropyl substituents (for



Scheme 2. The preparation of neutral and cationic phosphine-substituted palladacycles.

C1–**C3**) and the methylene protons of the *n*-propyl chain (for **C4**) were observed to shift downfield as a result of complexation of the ligand to the metal centre and the *Me*-groups of the ^{i}Pr unit was split into two doublets integrating for a total of six protons each.

Analogous resonance shifts to those observed in the ^{1}H NMR spectra were observed when subjecting the μ-Cl complexes to ^{13}C NMR analysis. The imine carbon atom resonances shifted to the high field region upon complexation and was observed in the range δ 173–177 ppm. Also, the carbon atom bound to palladium was observed to resonate in the range δ 142–146 ppm and provided further evidence for cyclopalladation occurring [15,19].

Suitable crystals of complex **C2** for single crytal X-ray diffraction analysis were obtained by the slow evaporation of a dichloromethane: hexane mixture. The complex crystallised as a discrete molecule with one half of the molecule in the asymmetric unit. Crystallographic data (Table 1) as well as selected bond lengths and angles are tabulated (Table 2). The molecule consists of two palladium centres bridged by two chloride atoms. The remainder of the coordination sphere of the metal is occupied by the Schiff base ligand, coordinated through the benzylidene carbon and imine nitrogen atom to form the five-membered chelate ring (Fig. 1).

The geometry around the metal centre is distorted square planar as evidenced by the sum of the angles about the palladium centre. The most noticeable distortion is found for the C(6)–Pd–N(1) angle of the cyclometallated ring of 81.5(2)° which is as a result of chelation of the ligand to the metal centre. The Pd–C bond length of 1.979(6) Å is somewhat shorter than the expected value based on the sum of the covalent radii whereas the Pd–N bond length of 2.028(5) Å is longer than the expected value for the sum of the van der Waals radii [20]. This difference is due to the differing *trans* influence of the two coordinating atoms. This is further demonstrated by the difference in the Pd–Cl bond lengths. The Pd–Cl(1) bond *trans* to the N-atom of 2.329(2) Å is shorter than the Pd–Cl bond *trans* to the C-atom, which has a length of 2.447(2) Å. The Pd–Pd interatomic distance of 3.477 Å precludes any Pd–Pd interaction. All bond lengths and angles fall within the range observed for analogous μ-Cl palladacycles [15].

The chloro-bridged palladacycles, **C1**–**C4**, were reacted with tertiary phosphines, varying in their steric and electronic properties (Scheme 2). The phosphine-substituted palladacycles (**C5** to **C9**) were isolated as pale-yellow air- and moisture-stable solids in high yields and displayed solubility in chlorinated organic solvents but were found to be insoluble in alkanes, ethers and alcohols.

Table 1
Crystallographic data for complexes **C2**.

Complex	**C2**
Empirical Formula	$C_{38}H_{42}Cl_4N_2Pd_2$
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal System	monoclinic
Space Group	$P_{21/n}$
a [Å]	9.8189(18)
b [Å]	10.0246(18)
c [Å]	18.797(3)
α [°]	90.00
β [°]	91.899(2)
γ [°]	90.00
volume [Å^3]	1849.2(6)
Z	2
calc density [Mg/m^3]	1.583
μ (Mo K)[mm^{-1}]	1.291
F(000)	888
crystal dimensions (mm)	0.14 × 0.10 × 0.04
goodness-of-fit on F^2	1.171
Final R indices [I > 2σ(I)]	R_1 = 0.0591
	wR_2 = 0.1322

Table 2
Selected bond lengths (Å) and angles (°) of complexes **C2**.

Complex	**C2**
Pd(1)-N(1)	2.028(5)
Pd(1)-C(6)	1.979(6)
C(7)-N(1)	1.288(8)
Pd(1)-Cl(1)	2.447(2)
Pd(1)-Cl(A)	2.329(2)
Pd(1)••Pd	3.477
N(1)-Pd(1)-C(6)	178.2(2)
N(1)-Pd(1)-Cl(1)	176.3(2)
N(1)-Pd(1)-Cl(A)	96.9(2)
C(6)-Pd(1)-Cl(1)	94.9(2)
C(6)-Pd-Cl(A)	178.2(2)
Cl(1)-Pd(1)-Cl(A)	86.59(6)

In the FT-IR spectrum of the mononuclear complexes, a slight shift to higher wavenumbers of the imine absorption band was observed, in comparison to the μ-Cl palladacycles. This was due to the relative increase in σ-donor ability of the phosphine ligand, when compared to Cl^- and resulted in an increase in the double bond character of the C=N bond. Also, strong absorption bands in the range 1430–1440 cm^{-1} and 680–690 cm^{-1} were observed in the FT-IR spectra of the complexes which were attributed to the υ(C–P) and C–H out of plane bending vibrations respectively. These observations provided further evidence that coordination of the ligand to the metal centre had occurred [21].

In the ^{1}H NMR spectra of the mononuclear cyclometallated complexes, **C5**–**C11**, the imine proton resonance was observed to shift upfield in comparison to the μ-Cl complexes, with the triphenylphosphine complexes shifting more downfield than their trimethylphosphine analogues. This was attributed to an increase in the basicity of the trimethylphosphine ligand, which resulted in an increase in electron density on the palladium centre. This in turn resulted in back-donation of excess electron density onto the imine functional group thereby shielding the imine proton from the effect of the externally applied magnetic field [16]. Also, the imine proton resonance was observed to be split into a doublet integrating for one proton in the range δ 8.00–8.70 ppm as a result of four-bond coupling ($^{4}J_{H-P}$) of the imine proton to the phosphorus atom of the tertiary phosphine ligand.

The bridge-splitting reaction was noted to have a remarkable effect on the proton resonances associated with the ligand backbone. The H-atom *ortho* to the metallated carbon atom was observed to be the most shielded, as a result of the coordination of

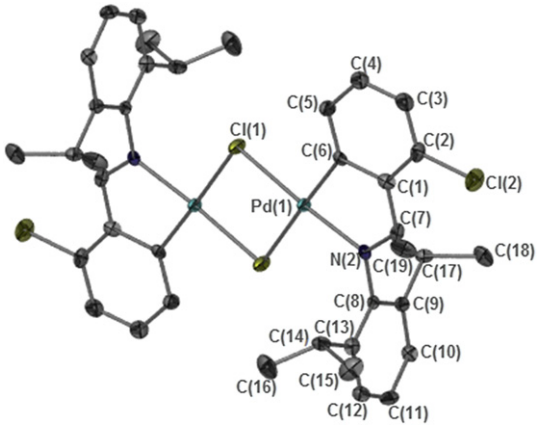


Fig. 1. Molecular structure of complex **C2**, drawn with 50% probability ellipsoids. Hydrogen atoms omitted for clarity.

the triphenylphosphine ligand in a *cis* fashion relative to the metallated carbon atom. The phenyl protons experience anisotropic shielding by the aromatic rings, resulting in an upfield shift of these resonances [16,21b]. The *ortho* H-atom also exhibited $^4J_{H-P}$ coupling to the P-atom of the tertiary phosphine which provided further evidence to the *cis* geometry of the phosphine ligand. The methine protons of the ^{i}Pr groups of complexes **C5**–**C7**, **C9** as well as the methylene protons of the *n*-propyl chain (**C8**) were observed to resonate in the same region as observed for complexes **C1**–**C4** and confirmed coordination of the imine N-atom to the palladium centre.

Analogous resonances to those of complexes **C1**–**C4** were observed in the ^{13}C NMR spectra of the cleaved complexes (**C5**-**C9**) with the imine carbon resonance observed in the range δ 174–178 ppm, while the *o*-metallated carbon resonance was observed in the range δ 145–146 ppm.

In the ^{31}P{^{1}H} NMR spectra of complexes **C5**–**C9** only a single resonance was observed in the range δ 41–43 ppm for the PPh_3-cleaved (**C5**–**C8**) complexes and in the range δ −4 to −5 ppm for the PMe_3-cleaved complex (**C9**). The coordinated tertiary phosphine was observed to be high field shifted when compared to the free phosphine ligand. This provided further confirmation that the phosphine was in fact coordinated to the metal centre [22].

The phosphine-substituted palladacycles were also characterized by ESI-MS. The major fragment observed in the positive ion ESI-MS spectra of the phosphine-cleaved complexes corresponded to the fragment, $[M - Cl]^+$, in which the Cl− ion was abstracted as a result of the ionization process [23].

The neutral mononuclear palladacycles (**C5**–**C9**) were reacted with $NaB(Ar)_4$ [Ar = 3,5-bistrifluoromethylphenyl] in the presence of acetonitrile as coordinating solvent to generate cationic palladacycles (**C10**–**C14**, Scheme 2). The cationic palladacycles were isolated in high yields as pale-yellow air- and moisture-stable solids. The complexes displayed solubility in common organic solvents but were insoluble in unsatutared hydrocarbons.

^{1}H NMR analysis of the cationic palladacycles showed analogous resonances to that observed for the neutral palladacycles, with the addition of a multiplet in the range δ 7.60–7.80 ppm which integrated for a total of twelve protons as a result of the counter-ion. Also, a singlet was observed in the aliphatic region in the range δ 1–1.30 ppm integrating for three protons and was ascribed to the coordinating acetonitrile molecule.

In the ^{13}C NMR spectrum of the cationic complexes four resonances were observed in the range δ 160–163 ppm which was assigned the $B(Ar)_4$− ion. The *Me*-carbon of the acetonitrile was observed in the range δ 0–1 ppm.

No significant shift of the phosphorus resonance was observed in the ^{31}P{^{1}H} NMR spectrum of the cationic complexes in comparison to the neutral complexes which confirmed that the tertiary phosphine remained coordinated in the same fashion in the cationic palladacycles.

ESI-MS analysis (positive and negative mode) showed peaks corresponding to the cationic fragment as well as the anionic fragment of which the molecule was comprised and elemental analysis was in agreement with the proposed molecular composition.

3.2. Phenylacetylene oligo-/polymerization

The cationic palladacycles (**C10**–**C14**) were evaluated as catalysts in the oligo-/poly-merization of phenylacetylene (PA). A series of optimization catalytic runs were performed employing complex**C10** as catalyst (Fig. 2). An increase in the ratio of monomer to catalyst resulted in a decrease in activity, thus a monomer/catalyst ratio of 50:1 was employed for all subsequent catalytic runs.

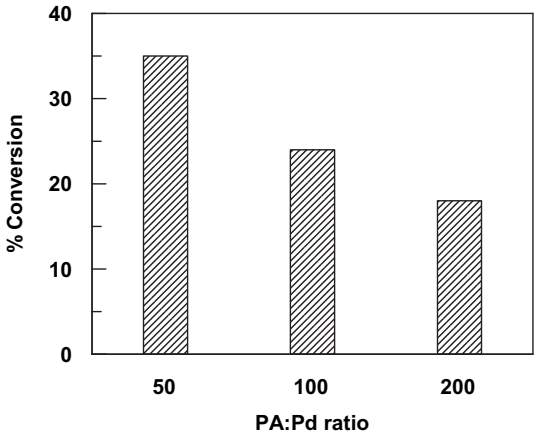


Fig. 2. Effect of monomer concentration of PA conversion, employing catalyst **C10**.

Polymerization data showing the effect of reaction temperature and reaction time on catalyst performance are tabulated in Table 3. Under optimized reaction conditions cationic palladacycles **C10**–**C14** were efficient catalysts for the PA oligo-/poly-merization (Entries 1–5).

At room temperature oligo-/poly-mers with low molecular weights and relatively narrow polydispersity indices were obtained. A mixture of *cis*-transoidal (65%) and *trans*-cisoidal (35%) isomers was observed as determined by FT-IR and ^{1}H NMR spectroscopy. ^{1}H NMR analysis of the oligo-/polymers showed a singlet at δ 5.84 ppm indicative of the vinyl protons of the polymer backbone being in a *cis* configuration. Additionally, broad resonances at δ 6.64 ppm (*o*-aromatic protons) and δ 6.95 ppm (*m*- and *p*-aromatic protons) were observed which is indicative of an oligo-/polymer with a regular head-to-tail structure of *cis*-transoidal oligo-/poly-phenylacetylene [7a,8]. Broad resonances were also observed in the range 7.00–7.20 ppm which can be ascribed to the aromatic protons of the *trans*-cisoidal isomer [10].

Strong absorption bands at 756 and 895 cm^{-1} were observed in the FT-IR spectrum of the oligo-/polymers which are characteristic of *cis*-transoidal oligo-/poly-phenylacetylene [24]. Furthermore, the IR spectrum showed an additional strong absorption band at 1278 cm^{-1} which is characteristic of the *trans*-cisoidal isomeric structure. These results confirmed the formation of both

Table 3
Data for PA oligo-/polymerization catalyzed by cationic palladacycles, **C10**–**C14**.[a]

Entry	Cat.	Temp (°C)	Time (h)	Conversion %	Activity[b]	M_w	PDI
1	**C10**	25	24	35	1767	801	1.30
2	**C11**	25	24	52	2667	1034	1.46
3	**C12**	25	24	44	2233	929	1.47
4	**C13**	25	24	36	1833	705	1.25
5	**C14**	25	24	16	810	45,222	1.78
6	**C10**	60	24	84	4300	638	1.16
7	**C11**	60	24	99	5067	675	1.12
8	**C12**	60	24	90	4600	712	1.17
9	**C13**	60	24	71	3633	577	1.08
10	**C14**	60	24	37	1890	59,863	1.54
11	**C10**	25	48	56	2867	2162	1.01
12	**C11**	25	48	55	2833	2226	1.01
13	**C12**	25	48	53	2733	2189	1.00
14	**C13**	25	48	64	3267	2196	1.01
15	**C14**	25	48	34	1737	55,963	1.36

[a] Reaction conditions: CH_2Cl_2 (10 mL), PA:Pd = 50:1 unless otherwise specified, catalyst concentration 3 $\times 10^{-3}$ M.
[b] Activity = g PPA/mol Pd.

cis-transoidal and *trans*-cisoidal oligo-/polyphenylacetylene at room temperature. From the analytical data obtained it would appear that an insertion mechanism predominates at room temperature for our catalyst system as had been observed for Rh catalyst systems [25].

The catalytic activity, (g PPA/mol Pd) ranged between 700 and 2800, with the highest activity observed for **C11** (Fig. 3). The order of catalytic activity may be arranged as follows: **C11** > **C12** > **C13** > **C10** > **C14**.

This result indicated that the substituent on the imino-N atom does not have a significant effect on catalytic activity whereas electron-withdrawing substituents at the 2-position on the cyclometallated ring resulted in an increase in catalytic activity. This is as a result of the fact that electron-withdrawing groups enhanced the electrophilicity of the palladium centre thereby promoting monomer coordination. The nature of the phosphine also seems to have a marked effect on the efficiency of the catalyst. The precursor containing the more basic tertiary phosphine, PMe_3 (**C14**) showed a much lower catalyst activity (Table 3, entries 2 and 5). This again can be attributed to the fact that the more basic phosphine increased the electron density on the metal thus reducing the electrophilicity of the metal centre. This would reduce the rate of monomer coordination and insertion. The net result is that the PMe_3 based catalyst, **C14**, has an activity which is about half of that of the PPh_3 analogue, **C11** (entries 1 and 5, Table 3). It is also possible that phosphine dissociation plays a role in the catalytic process. In this case PPh_3 is more likely to dissociate more easily than PMe_3. Phosphine dissociation will facilitate the coordination of the monomer thus enhancing the rate of the reaction. This could also explain the higher activity of the PPh_3 based catalyst.

In addition to affecting the catalyst activity, the decrease in steric bulk of the tertiary phosphine impacts on the molecular weight as well as on the polydispersity of the formed polymer. The PMe_3 based catalyst gives a polymer with higher molecular weight as well as higher PDI values.

From these results it is clear that the rate of chain propagation exceeds the rate of chain transfer when considering catalyst **C14** in comparison to catalyst **C11**. This is most probably due to the fact that β-hydride transfer will be slower for a metal centre which has a higher electron density (PMe_3 complex) compared to that of a metal centre with lower electron density (PPh_3 complex). The catalyst system $[Rh(OMe)(nbd)]_2/PMePh_2$ (nbd = 2,5-norbornadiene) has been shown to polymerize PA to high molecular weight and slightly broader PDI values, consistent with our results with catalyst **C14** [7c].

Polymerization experiments were also performed at an elevated temperature (60 °C, Table 3, entries 6–10) to study the effect of temperature on the catalytic activity and stereoselectivity. An increase in reaction temperature resulted in a dramatic increase in catalytic activity with activities ranging between 1900 and 5100 while following the same trend in catalytic activity for the different catalysts observed at room temperature. The oligo-/poly-phenylacetylenes produced had slightly lower molecular weights than those obtained at room temperature. This may be attributed to an increase in the rate of chain termination relative to propagation at elevated temperature. The FT-IR spectrum of the oligo-/polyphenylacetylene showed strong absorption bands at 1278, 980 and 915 cm^{-1} which are characteristic of *trans*-cisoidal PPA [24]. ^1H NMR analysis showed broad resonances in the range δ 6.40–7.60 ppm as well as the absence of any vinylic proton resonances which confirmed the selective formation of *trans*-cisoidal oligo-PPA at higher temperature [26]. It has been proposed previously that higher reaction temperatures lead to selective *trans* monomer insertion [27].

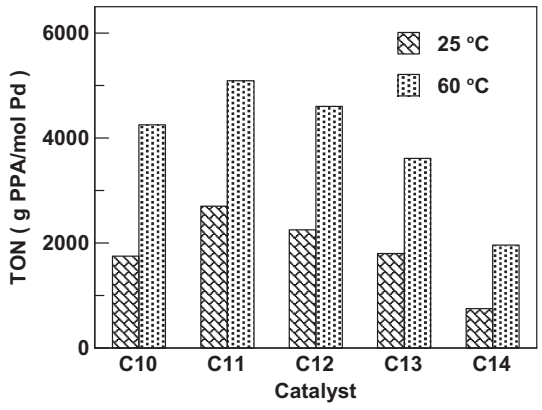


Fig. 3. Catalyst activity for catalyst **C10**–**C14**.

Interestingly the PMe_3 catalysts behaved differently when compared to the PPh_3 based catalysts. The former did not show a decrease in molecular weight of the polymer obtained at elevated temperature. Instead it shows a 30% increase in molecular weight of the polymer at elevated temperature. It would thus appear that even at 60 °C, the rate of chain propagation still exceeds that of chain transfer for the PMe_3 catalysts.

Increasing reaction time while performing the polymerization runs at room temperature resulted in a slight increase in catalytic activity while significantly increasing the molecular weight of the produced oligo-/PPA (Table 3, entry 11–15). A further improvement in the PDI values was also observed under these reaction conditions. The polyphenylacetylene produced showed IR absorption bands and ^1H NMR resonances characteristic of head-to-tail *cis*-transoidal PPA.

4. Conclusions

We have prepared and characterized air- and moisture-stable cationic palladacycles which were active catalysts of the oligo-/polymerization of PA. At room temperature moderate activities were observed with a mixture of *cis*-transoidal and *trans*-cisoidal oligo-/PPA produced, the *cis*-transoidal oligo-/PPA being the major product. At higher temperature a marked increase in catalytic activity was observed with the selective formation of *trans*-cisoidal PPA. The presence of electron-withdrawing groups on the cyclometallated ring served to enhance the catalytic activity of the palladacycles. Reaction time had a marked effect on polymer molecular weight, with high molecular weight polymers being formed at longer reaction time. Even though the PPA produced by the cationic palladacycles had low molecular weights in all cases polymers with narrow PDI's were obtained.

Acknowledgements

Acknowledgements go to National Research Foundation (South Africa) and the DST/NRF COE in Catalysis (c*change) as well as the NRF/SIDA for financial support. This work was also supported by Research Committees of the University of the Western Cape and Stellenbosch University.

Appendix A. Supplementary material

Crystallographic Data Centre. Copies of the data [CCDC 82836] can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (international) + 44(1223)336 033, E-mail: deposit@ccdc.cam.ac.uk].

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