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Rapid, efficient and green solid-state mechanosynthesis of palladium complexes

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Mechanochemistry has emerged as a powerful and environmentally benign alternative to conventional solution synthesis. In this study, we present a comprehensive investigation into the solid-state mechanochemical synthesis of a diverse library of palladium(II) complexes. This investigation utilized five commercially available Pd(II) precursors and twelve diene, N- and P-donor ligands. Systematic investigations have revealed that high-yielding and clean reactions can be achieved by tuning the milling frequency, reaction time, and metal-to-ligand stoichiometry, affording more than forty Pd(II) complexes. A comparison with conventional solution-based protocols is therefore indicated to underscore the operational simplicity and ecological advantage of the mechanochemical approach, as demonstrated by favorable green chemistry metrics such as low E-factors and high effective mass yields (EMYs). The validity of the methodology was established through gram-scale syntheses, which demonstrated high yields and reproducibility. These findings contribute a robust and generalizable synthetic strategy for accessing widely used palladium precursors, thus supporting the integration of mechanochemistry into green organometallic synthesis.

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1 Introduction

Palladium(II) complexes have long been recognized for their broad utility, which extends across several domains. These include catalysis,[1–10] chemotherapeutics[11,12] and luminescence.[13,14] Conventional solution protocols have historically dominated these applications, with extensive use of organic solvents, often accompanied by additives or co-catalysts, to maximize efficiency. The advent of Green Chemistry[15] has prompted researchers to explore the potential of reducing the environmental impact of palladium-mediated reactions. This has been achieved through the utilization of benign solvents, such as water,[16,17] or the removal of additives, co-catalysts and the solvent altogether.[18–20] An additional target is to perform the process under mild conditions, possibly at room temperature and without use of an inert atmosphere. However, comparatively little effort has been dedicated to enhancing the sustainability of metal complex synthesis. In practice, the majority of studies continue to utilize readily available commercial compounds, such as $Pd(OAc)_2$ or $PdCl_2$, or N- and P-ligand palladium(II) complexes that are obtained through classical multistep syntheses, which are not in accordance with the principles of Green Chemistry. It is evident that the latter routes generally entail a multitude of reaction and purification steps, the necessity of operating at elevated or low temperatures, protracted reaction times, and the requirement for repeated washings or recrystallizations.[21,22]

The need for more environmentally friendly and sustainable synthesis methods has led researchers to consider mechanochemistry as an alternative to classical solution reactions. This technique offers high yields, reduced reaction times and a lower environmental impact than traditional methods.[23–25] Although mechanochemical strategies have been successfully applied to organic synthesis, supramolecular chemistry and materials science,[26,27] their use in the synthesis of metal complexes has also begun to attract attention. Several studies have demonstrated the successful preparation of metal complexes by mechanochemical means,[28–32] including palladium(II) species.[33–38] These contributions provide a solid foundation, while at the same time highlighting the significant opportunities that remain for further exploration and advancement in this area. Recently, an increasing number of studies have focused on the mechanochemical synthesis of palladium(II) complexes with carbene ligands, particularly N-heterocyclic carbenes and palladacycles, reflecting the growing interest in this approach.[39–42]

Starting from the need for a greater number of sustainable syntheses, we investigated the mechanochemical reactivity of five commercially available palladium(II) precursors with twelve diene, N- and P-donor ligands over a range of metal-to-ligand stoichiometries. By varying milling time and frequency, we identified the key parameters that govern product formation.

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The resulting protocol offers a rapid, efficient and broadly applicable green route that requires no bulk solvents. To benchmark mechanochemistry against conventional solution methods, we provide a quantitative comparison of isolated yields, reaction times and solution temperatures *versus* milling frequencies, together with the common green metrics such as the E-factor [E-factor = (mass of waste)/(mass of product)] and the Effective Mass Yield (EMY) [EMY = (mass of product)/(total mass of material used) × 100].[43] These data highlight the sustainability and operational simplicity of the mechanochemical approach for preparing a large set of palladium(II) complexes, some of which are very widely used precursors.

2 Experimental

$PdCl_2$ and PdI_2 were purchased from Carlo Erba. $Pd(OAc)_2$, $Na_2[PdCl_4]$ and $Na_2[PdBr_4]$ were purchased from Sigma Aldrich. The ligands 1,10-phenanthroline, 2,2′;6′,2″-terpyridine, triphenylphosphine and xantphos are Sigma-Aldrich products. 1,5-Cyclooctadiene (COD) is produced by Ega-Chemie. Bis(diphenylphosphino)methane, -ethane, -propane, -butane, -ferrocene were purchased from Strem Chemicals, Inc. Bis(diisopropylphosphino)ferrocene and (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl were purchased from Alfa Aesar. Deuterated solvents chloroform ($CDCl_3$), dichloromethane (CD_2Cl_2), dimethyl sulfoxide (DMSO-d_6) and methanol (CD_3OD) used for NMR spectra were purchased from Eurisotop. Elemental analysis (C, H, and N) was carried out with a Carlo Erba 1106 elemental analyzer. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were acquired using a Bruker Avance III HD 400 MHz spectrometer equipped with a broadband 5 mm probe (1H/BBF iProbe) with a *z*-axis gradient (50 G cm^{-1}). Chemical shifts are reported in parts per million and calibrated to the solvent residue. Mechanochemical synthesis of all complexes was carried out using a Retsch Ball Mill (MM 500 Vario) with a 2 mL Eppendorf tube with zirconia balls (3 mm diameter, ~0.4 g), a 10 mL zirconia jar and zirconia balls (10 mm diameter, ~3.3 g), or a 25 mL zirconia jar and zirconia balls (15 mm diameter, ~11.4 g). In the Eppendorf tube, suitable amounts of the reactants were taken with 3 or 4 zirconia balls inside. To calculate the final mass of the products, the Eppendorf tube, or zirconia jar, and balls were appropriately calibrated. The Eppendorf tube is then closed (under argon when required to avoid oxidation by air), sealed with the help of parafilm to make it airtight and then milled under suitable milling conditions (as highlighted below for each synthesis). Approximately 5 mg of the solid sample is extracted from the Eppendorf tube (or jar) and dissolved in a suitable deuterated solvent for NMR analysis. A second portion is utilized for elemental analysis.

2.1 MC synthesis of [Pd(COD)Cl_2] (1a)

Method A: $PdCl_2$ (50.0 mg, 0.2820 mmol) and 1,5-cyclooctadiene (35 μL, 30.50 mg, 0.2820 mmol) were milled at 20 Hz for 30 min in a 10 mL zirconia jar and 1 zirconia ball (10 mm) under an air atmosphere. Yield: 98% (78.9 mg). Method B: $Na_2[PdCl_4]$ (50.00 mg, 0.1700 mmol) and 1,5-cyclooctadiene (21 μL, 18.39 mg, 0.1700 mmol) were milled at 15 Hz for 20 min in a 10 mL zirconia jar and 1 zirconia ball (10 mm) under an air atmosphere. The product was then washed with 5 mL of water and dried at low pressure. Yield: 99% (48.1 mg). Gram scale: $Na_2[PdCl_4]$ (300.00 mg, 1.0197 mmol) and 1,5-cyclooctadiene (125 μL, 110.31 mg, 1.0197 mmol) were milled at 15 Hz for 20 min in a 25 mL zirconia jar and 1 zirconia ball (15 mm) under an air atmosphere. The product was then washed with 15 mL of water and dried at low pressure. Yield: 99% (288.2 mg).

^1H NMR (400.1 MHz, $CDCl_3$, 298 K) δ 6.47–6.18 (m, 4H); 3.03–2.81 (m, 4H); 2.69–2.48 (m, 4H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K) δ 116.30 (CH of COD); 30.97 (–CH_2– of COD) (Fig. S3–S5). Elemental analysis: calculated (%) for ($C_8H_{12}Cl_2Pd$): C, 33.66; H, 4.24; Cl, 24.83; Pd, 37.27. Found (%): C, 33.97; H, 4.13.

2.2 MC synthesis of [Pd(COD)Br_2] (1b)

$Na_2[PdBr_4]$ (60.0 mg, 0.1271 mmol) and 1,5-cyclooctadiene (16 μL, 13.8 mg, 0.1271 mmol) were milled at 15 Hz for 20 min in a 10 mL zirconia jar and 1 zirconia ball (10 mm) under an air atmosphere. The product was then washed with 5 mL of water and dried at low pressure. Yield: 98% (46.6 mg).

^1H NMR (400.1 MHz, $CDCl_3$, 298 K) δ 6.56–6.26 (m, 4H); 2.96–2.69 (m, 4H); 2.60–2.40 (m, 4H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K) δ 116.53 (CH of COD); 31.15 (–CH_2– of COD) (Fig. S6 and S7). Elemental analysis: calculated (%) for ($C_8H_{12}Br_2Pd$): C, 25.66; H, 3.23; Br, 42.69; Pd, 28.42. Found (%): C, 26.04; H, 3.11.

2.3 MC synthesis of [Pd(phen)($OAc)_2$] (2a)

$Pd(OAc)_2$ (15.0 mg, 0.0668 mmol) and 1,10-phenanthroline (12.0 mg, 0.0668 mmol) were milled at 30 Hz for 90 min in a 2 mL Eppendorf tube with 3 zirconia balls (3 mm) under an air atmosphere. Yield: 94% (25.4 mg).

^1H NMR (400.1 MHz, DMSO-d_6, 298 K) δ 8.95 (dd, J_{HH} = 8.5, 1.2 Hz, 2H); 8.48 (dd, J_{HH} = 5.1, 1.1 Hz, 2H); 8.26 (s, 2H); 8.06 (dd, J_{HH} = 8.3, 5.2 Hz, 2H); 1.96 (s, 6H, –CH_3 of acetate). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K) δ 178.75 (C=O of acetate); 150.67 (CH of phen); 146.85 (quaternary C of phen); 138.54 (CH of phen); 129.76 (quaternary C of phen); 127.15 (CH of phen); 125.25 (CH of phen); 23.37 (–CH_3 of acetate) (Fig. S8 and S9). Elemental analysis: calculated (%) for ($C_{16}H_{14}N_2O_4Pd$): C, 47.49; H, 3.49; N, 6.92; O, 15.81; Pd, 26.29. Found (%): C, 47.91; H, 3.52; N, 6.95.

2.4 MC synthesis of [Pd(phen)Cl_2] (2b)

Method A: $PdCl_2$ (15.0 mg, 0.0846 mmol) and 1,10-phenanthroline (15.2 mg, 0.0846 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 3 zirconia balls (3 mm) under an air atmosphere. Yield: >99% (30.2 mg). Method B: $Na_2[PdCl_4]$ (25.0 mg, 0.0850 mmol) and 1,10-phenanthroline (15.3 mg, 0.0850 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 3 zirconia balls (3 mm) under an air atmosphere. The product was then washed with 2 mL of water and dried at low pressure. Yield: >99% (30.2 mg).

^{1}H NMR (400.1 MHz, DMSO-d_6, 298 K) δ 9.34 (dd, J_{HH} = 5.4, 1.4 Hz, 2H); 8.97 (dd, J_{HH} = 8.2, 1.3 Hz, 2H); 8.27 (s, 2H); 8.13 (dd, J_{HH} = 8.2, 5.4 Hz, 2H). ^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d_6, 298 K) δ 150.65 (CH of phen); 147.28 (quaternary C of phen); 140.54 (CH of phen); 130.87 (quaternary C of phen); 128.04 (CH of phen); 126.39 (CH of phen) (Fig. S10 and S11). Elemental analysis: calculated (%) for ($C_{12}H_8Cl_2N_2Pd$): C, 40.31; H, 2.25; Cl, 19.83; N, 7.84; Pd, 29.77. Found (%): C, 40.28; H, 2.39; N, 7.95.

2.5 MC synthesis of [Pd(phen)Br_2] (2c)

$Na_2[PdBr_4]$ (30.0 mg, 0.0636 mmol) and 1,10-phenanthroline (11.5 mg, 0.0636 mmol) were milled at 30 Hz for 90 min in a 2 mL Eppendorf tube with 3 zirconia balls (3 mm) under an air atmosphere. The product was then washed with 2 mL of water and dried at low pressure. Yield: 91% (25.8 mg).

^{1}H NMR (400.1 MHz, DMSO-d_6, 298 K) δ 9.63 (dd, J_{HH} = 5.4, 1.4 Hz, 2H); 8.98 (dd, J_{HH} = 8.2, 1.3 Hz, 2H); 8.28 (s, 2H); 8.14 (dd, J_{HH} = 8.2, 5.3 Hz, 2H). ^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d_6, 298 K) δ 151.89 (CH of phen); 147.37 (quaternary C of phen); 140.47 (CH of phen); 131.09 (quaternary C of phen); 128.12 (CH of phen); 126.67 (CH of phen) (Fig. S12 and S13). Elemental analysis: calculated (%) for ($C_{12}H_8Br_2N_2Pd$): C, 32.28; H, 1.81; Br, 35.79; N, 6.28; Pd, 23.84. Found (%): C, 32.21; H, 1.76; N, 5.98.

2.6 MC synthesis of [Pd(phen)I_2] (2d)

PdI_2 (20.0 mg, 0.0555 mmol) and 1,10-phenanthroline (10.0 mg, 0.0555 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 3 zirconia balls (3 mm) under an air atmosphere. Yield: >99% (29.9 mg).

^{1}H NMR (400.1 MHz, DMSO-d_6, 298 K) δ 10.02 (dd, J_{HH} = 5.4, 1.4 Hz, 2H); 8.99 (dd, J_{HH} = 8.2, 1.4 Hz, 2H); 8.27 (s, 2H); 8.16 (dd, J_{HH} = 8.2, 5.3 Hz, 2H). ^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d_6, 298 K) δ 153.44 (CH of phen); 147.32 (quaternary C of phen); 140.26 (CH of phen); 131.34 (quaternary C of phen); 128.21 (CH of phen); 126.99 (CH of phen) (Fig. S14 and S15). Elemental analysis: calculated (%) for ($C_{12}H_8I_2N_2Pd$): C, 26.67; H, 1.49; I, 46.97; N, 5.18; Pd, 19.69. Found (%): C, 26.91; H, 1.55; N, 5.24.

2.7 MC synthesis of [Pd(terpy)(OAc)]OAc (3a)

$Pd(OAc)_2$ (20.0 mg, 0.0891 mmol) and 2,2′;6′,2″-terpyridine (22.8 mg, 0.0977 mmol) were milled at 30 Hz for 120 min in a 2 mL Eppendorf tube with 3 zirconia balls (3 mm) under an air atmosphere. The product was then washed with 3 mL of diethyl ether and dried at low pressure. Yield: 98% (40.0 mg).

^{1}H NMR (400.1 MHz, DMSO-d_6, 298 K) δ 8.68–8.52 (m, 5H, terpy); 8.50–8.40 (m, 2H, terpy); 8.32 (dd, J_{HH} = 5.5, 1.5 Hz, 2H); 7.88 (ddd, J_{HH} = 7.3, 5.5, 1.4 Hz, 2H); 2.07 (s, 3H, –CH_3 of acetate); 1.60 (s, 3H, –CH_3 of acetate). ^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d_6, 298 K) δ 176.91 (C═O of acetate); 172.99 (C═O of acetate); 157.59 (quaternary C of terpy); 155.13 (quaternary C of terpy); 151.66 (CH of terpy); 143.25 (CH of terpy); 143.04 (CH of terpy); 129.17 (CH of terpy); 125.54 (CH of terpy); 124.84 (CH of terpy); 24.99 (–CH_3 of acetate); 23.80 (–CH_3 of acetate) (Fig. S16 and S17). Elemental analysis: calculated (%) for ($C_{19}H_{17}N_3O_4Pd$): C, 49.85; H, 3.74; N, 9.18; O, 13.98; Pd, 23.25. Found (%): C, 49.89; H, 3.59; N, 8.96.

2.8 MC synthesis of [Pd(terpy)Cl]Cl (3b)

Method A: $PdCl_2$ (15.0 mg, 0.0846 mmol) and 2,2′;6′,2″-terpyridine (19.7 mg, 0.0846 mmol) were milled at 30 Hz for 75 min in a 2 mL Eppendorf tube with 3 zirconia balls (3 mm) under an air atmosphere. Yield: >99% (34.6 mg). Method B: $Na_2[PdCl_4]$ (25.0 mg, 0.0850 mmol) and 2,2′;6′,2″-terpyridine (19.8 mg, 0.0850 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 3 zirconia balls (3 mm) under an air atmosphere. The product was then washed with 2 mL of water and dried at low pressure. Yield: >99% (34.6 mg).

^{1}H NMR (400.1 MHz, DMSO-d_6, 298 K) δ 8.74 (dd, J_{HH} = 5.6, 1.5 Hz, 2H); 8.70–8.56 (m, 5H, terpy); 8.46 (td, J_{HH} = 7.9, 1.6 Hz, 2H); 7.89 (ddd, J_{HH} = 7.4, 5.6, 1.4 Hz, 2H). ^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d_6, 298 K) δ 158.47 (quaternary C of terpy); 155.08 (quaternary C of terpy); 152.52 (CH of terpy); 143.27 (CH of terpy); 143.05 (CH of terpy); 129.37 (CH of terpy), 125.85 (CH of terpy); 124.90 (CH of terpy) (Fig. S18 and S19). Elemental analysis: calculated (%) for ($C_{15}H_{11}Cl_2N_3Pd$): C, 43.88; H, 2.70; Cl, 17.27; N, 10.23; Pd, 25.92. Found (%): C, 44.15; H, 3.03; N, 11.02.

2.9 MC synthesis of [Pd(terpy)Br]Br (3c)

$Na_2[PdBr_4]$ (30.0 mg, 0.0636 mmol) and 2,2′;6′,2″-terpyridine (14.8 mg, 0.0636 mmol) were milled at 30 Hz for 90 min in a 2 mL Eppendorf with 3 zirconia balls (3 mm) under an air atmosphere. The product was then washed with 2 mL of water and dried at low pressure. Yield: 94% (29.9 mg).

^{1}H NMR (400.1 MHz, DMSO-d_6, 298 K) δ 8.99 (dd, J_{HH} = 5.7, 1.4 Hz, 2H); 8.70–8.58 (m, 5H, terpy); 8.46 (td, J_{HH} = 7.9, 1.5 Hz, 2H); 7.87 (ddd, J_{HH} = 7.7, 5.6, 1.4 Hz, 2H). ^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d_6, 298 K) δ 158.64 (quaternary C of terpy); 155.05 (quaternary C of terpy); 154.45 (CH of terpy); 143.27 (CH of terpy); 142.89 (CH of terpy); 129.66 (CH of terpy); 125.96 (CH of terpy); 124.92 (CH of terpy) (Fig. S20 and S21). Elemental analysis: calculated (%) for ($C_{15}H_{11}Br_2N_3Pd$): C, 36.07; H, 2.22; Br, 31.99; N, 8.41; Pd, 21.31. Found (%): C, 36.42; H, 2.69; N, 8.31.

2.10 MC synthesis of [Pd(terpy)I]I (3d)

PdI_2 (20.0 mg, 0.0555 mmol) and 2,2′;6′,2″-terpyridine (13.0 mg, 0.0555 mmol) were milled at 30 Hz for 120 min in a 2 mL Eppendorf with 3 zirconia balls (3 mm) under an air atmosphere. Yield: 96% (31.7 mg).

^{1}H NMR (400.1 MHz, DMSO-d_6, 298 K) δ 9.34 (d, J_{HH} = 5.4 Hz, 2H); 8.69–8.57 (m, 5H, terpy); 8.43 (td, J_{HH} = 7.9, 1.5 Hz, 2H); 7.81 (t, J_{HH} = 6.4 Hz, 2H). ^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d_6, 298 K) δ 158.80 (quaternary C of terpy); 158.28 (CH of terpy); 155.00 (quaternary C of terpy); 143.17 (CH of terpy); 142.52 (CH of terpy); 130.17 (CH of terpy); 126.15 (CH of terpy); 124.88 (CH of terpy) (Fig. S22 and S23). Elemental analysis: calculated (%) for ($C_{15}H_{11}I_2N_3Pd$): C, 30.36; H, 1.87; I, 42.76; N, 7.08; Pd, 17.93. Found (%): C, 30.22; H, 1.86; N, 6.92.

2.11 MC synthesis of $[Pd(PPh_3)_2(OAc)_2]$ (4a)

$Pd(OAc)_2$ (15.0 mg, 0.0668 mmol) and triphenylphosphine (35.0 mg, 0.1336 mmol) were milled at 30 Hz for 30 min in a 2 mL Eppendorf with 4 zirconia balls (3 mm) under an argon atmosphere. Yield: 81% (yield determined by NMR in CD_2Cl_2).

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ 7.79–7.71 (m, 12H); 7.44–7.32 (m, 18H); 0.85 (s, 6H, –CH_3 of acetate). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K) δ 14.69 (s). $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, 298 K) δ 14.57 (s) (Fig. S24–S26).

2.12 MC synthesis of $[Pd(PPh_3)_2Cl_2]$ (4b)

Method A: $PdCl_2$ (15.0 mg, 0.0846 mmol) and triphenylphosphine (44.4 mg, 0.1692 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. Yield: 93% (55.2 mg). Method B: $Na_2[PdCl_4]$ (20.0 mg, 0.0680 mmol) and triphenylphosphine (35.7 mg, 0.1360 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. The product was then washed with 2 mL of water and dried at low pressure. Yield: 98% (46.8 mg).

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ 7.72 (m, 12H); 7.48–7.35 (m, 18H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K) δ 135.07 (t, $J_{PC} = 6.2$ Hz, CH of phenyl); 130.53 (s, *p*-CH of phenyl); 129.64 (t, $J_{PC} = 24.6$ Hz, quaternary C of phenyl); 128.08 (t, $J_{PC} = 5.3$ Hz, CH of phenyl). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K) δ 23.26 (s) (Fig. S27–S29). Elemental analysis: calculated (%) for ($C_{36}H_{30}Cl_2P_2Pd$): C, 61.60; H, 4.31; Cl, 10.10; P, 8.83; Pd, 15.16. Found (%): C, 61.19; H, 5.02.

2.13 MC synthesis of $[Pd(PPh_3)_2Br_2]$ (4c)

$Na_2[PdBr_4]$ (20.0 mg, 0.0424 mmol) and triphenylphosphine (22.2 mg, 0.0847 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. The product was then washed with 2 mL of water and dried at low pressure. Yield: 96% (32.2 mg).

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ 7.78–7.63 (m, 12H); 7.46–7.32 (m, 18H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K) δ 135.18 (t, $J_{PC} = 6.2$ Hz, CH of phenyl); 130.98 (quaternary C of phenyl); 130.39 (s, *p*-CH of phenyl); 127.89 (t, $J_{PC} = 5.4$ Hz, CH of phenyl). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K) δ 22.00 (s) (Fig. S30–S32). Elemental analysis: calculated (%) for ($C_{36}H_{30}Br_2P_2Pd$): C, 54.68; H, 3.82; Br, 20.21; P, 7.83; Pd, 13.46. Found (%): C, 55.12; H, 3.67.

2.14 MC synthesis of $[Pd(PPh_3)_2I_2]$ (4d)

PdI_2 (20.0 mg, 0.0555 mmol) and triphenylphosphine (29.1 mg, 0.1110 mmol) were milled at 30 Hz for 120 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. The final product is purified by dissolution in 2 mL of dichloromethane and subsequent precipitation from 2 mL of diethyl ether. Yield: 92% (45.2 mg).

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ 7.75–7.64 (m, 12H); 7.43–7.35 (m, 18H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K) δ 135.23 (t, $J_{PC} = 6.0$ Hz, CH of phenyl); 130.98 (t, $J_{PC} = 25.6$ Hz, quaternary C of phenyl); 130.25 (s, *p*-CH of phenyl); 127.66 (t, $J_{PC} = 5.4$ Hz, CH of phenyl). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K) δ 12.83 (s) (Fig. S33–S35). Elemental analysis: calculated (%) for ($C_{36}H_{30}I_2P_2Pd$): C, 48.86; H, 3.42; I, 28.69; P, 7.00; Pd, 12.03. Found (%): C, 49.12; H, 3.54.

2.15 MC synthesis of $[Pd(xantphos)(OAc)_2]$ (5a)

$Pd(OAc)_2$ (15.0 mg, 0.0668 mmol) and xantphos (38.7 mg, 0.0668 mmol) were milled at 30 Hz for 30 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. Yield: 72% (yield determined by NMR in $CDCl_3$).

$^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K) δ 4.58 (s) (Fig. S36).

2.16 MC synthesis of $[Pd(xantphos)Cl_2]$ (5b)

Method A: $PdCl_2$ (15.0 mg, 0.0846 mmol) and xantphos (48.9 mg, 0.0846 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. The final product is purified by dissolution in 2 mL of dichloromethane and subsequent precipitation from 2 mL of diethyl ether. Yield: 78% (49.8 mg), full conversion achieved in 180 min of milling. Method B: $Na_2[PdCl_4]$ (20.0 mg, 0.0680 mmol) and xantphos (39.3 mg, 0.0680 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. The product was then washed with 2 mL of water and dried at low pressure. Yield: >99% (51.3 mg).

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ 7.64 (d, $J = 7.7$ Hz, 2H); 7.51–7.27 (m, 10H); 7.26–7.12 (m, 6H); 7.04 (td, $J = 7.8$, 2.5 Hz, 8H); 1.85 (s, 6H, –CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz $CDCl_3$, 298 K) δ 154.53 (quaternary C, arom.); 135.36 (quaternary C, arom.); 134.78 (d, $J_{PC} = 9.5$ Hz, CH of phenyl); 130.26 (CH, arom.); 130.22 (*p*-CH of phenyl); 129.51 (d, $J_{PC} = 55.7$ Hz, quaternary C of phenyl); 128.12 (d, $J_{PC} = 11.8$ Hz, CH of phenyl); 127.83 (CH, arom.); 125.29 (d, $J_{PC} = 9.1$ Hz, CH arom.); 120.03 (d, $J_{PC} = 57.4$ Hz, quaternary C, arom.); 36.99 (quaternary C, alk.); 26.83 (–CH_3). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K) δ 22.07 (s) (Fig. S37–S40). Elemental analysis: calculated (%) for ($C_{39}H_{32}Cl_2OP_2Pd$): C, 61.96; H, 4.27; Cl, 9.38; O, 2.12; P, 8.19; Pd, 14.08. Found (%): C, 62.28; H, 4.08.

2.17 MC synthesis of $[Pd(xantphos)Br_2]$ (5c)

$Na_2[PdBr_4]$ (20.0 mg, 0.0424 mmol) and xantphos (24.5 mg, 0.0424 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. The final product is purified by dissolution in 2 mL of dichloromethane and subsequent precipitation from 2 mL of diethyl ether. Yield: 92% (33.0 mg).

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ 7.79–6.88 (m, 26H); 1.84 (s, 6H, –CH_3). $^{13}C\{^1H\}$ NMR (100.6 MHz $CDCl_3$, 298 K) δ 154.73 (quaternary C, arom.); 135.26 (quaternary C, arom.); 134.81 (CH of phenyl); 130.56 (d, $J_{PC} = 53.45$ Hz, quaternary C of phenyl); 130.18 (*p*-CH of phenyl); 129.99 (CH of phenyl); 128.05 (d, $J_{PC} = 11.7$ Hz, CH of phenyl); 127.66 (CH, arom.); 125.14 (CH, arom.); 120.27 (d, $J_{PC} = 56.8$ Hz, quaternary C, arom.); 36.91 (quaternary C, alk.); 26.80 (–CH_3). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K) δ 19.90 (s) (Fig. S41–S43). Elemental analysis:

calculated (%) for ($C_{39}H_{32}Br_2OP_2Pd$): C, 55.44; H, 3.82; Br, 18.92; O, 1.89; P, 7.33; Pd, 12.60. Found (%): C, 55.42; H, 3.90.

2.18 MC synthesis of [Pd(dppm)(OAc)$_2$] (6a)

$Pd(OAc)_2$ (15.0 mg, 0.0668 mmol) and bis(diphenylphosphino) methane (25.7 mg, 0.0668 mmol) were milled at 30 Hz for 30 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. Yield: 64% (yield determined by NMR in $CDCl_3$).

$^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K) δ – 49.27 (s) (Fig. S44).

2.19 MC synthesis of [Pd(dppm)Cl$_2$] (6b)

Method A: $PdCl_2$ (15.0 mg, 0.0846 mmol) and bis(diphenylphosphino)methane (32.5 mg, 0.0846 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. Yield: >99% (47.4 mg). Method B: $Na_2[PdCl_4]$ (15.0 mg, 0.0510 mmol) and bis(diphenylphosphino)methane (19.6 mg, 0.0510 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. The product was then washed with 2 mL of water and dried at low pressure. Yield: >99% (28.5 mg).

^1H NMR (400.1 MHz, $CDCl_3$, 298 K) δ 8.11–7.86 (m, 8H, phenyl); 7.60–7.37 (m, 12H, phenyl); 4.26 (t, J_{PH} = 10.6 Hz, 2H, –CH_2–). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K) δ 133.27 (t, J_{PC} = 6.3 Hz, CH of phenyl); 132.65 (s, *p*-CH of phenyl); 129.52 (t, J_{PC} = 6.2 Hz, CH of phenyl); 126.91 (d, J_{PC} = 52.2 Hz, quaternary C of phenyl); 38.68 (t, J_{PC} = 27.3 Hz, –CH_2–). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K) δ – 54.58 (s) (Fig. S45–S47). Elemental analysis: calculated (%) for ($C_{25}H_{22}Cl_2P_2Pd$): C, 53.45; H, 3.95; Cl, 12.62; P, 11.03; Pd, 18.95. Found (%): C, 53.49; H, 3.81.

2.20 MC synthesis of [Pd(dppm)Br$_2$] (6c)

$Na_2[PdBr_4]$ (20.0 mg, 0.0424 mmol) and bis(diphenylphosphino)methane (16.3 mg, 0.0424 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. The product was then washed with 2 mL of water and dried at low pressure. Yield: >99% (30.4 mg).

^1H NMR (400.1 MHz, $CDCl_3$, 298 K) δ 8.01–7.92 (m, 8H, phenyl); 7.61–7.43 (m, 12H, phenyl); 4.30 (t, J_{PH} = 10.4 Hz, 2H, –CH_2–). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K) δ 133.40 (CH of phenyl); 132.58 (*p*-CH of phenyl); 129.44 (CH of phenyl); 40.79 (t, J_{PC} = 27.1 Hz, –CH_2–). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K) δ – 56.37 (s) (Fig. S48–S50). Elemental analysis: calculated (%) for ($C_{25}H_{22}Br_2P_2Pd$): C, 46.15; H, 3.41; Br, 24.56; P, 9.52; Pd, 16.35. Found (%): C, 46.11; H, 3.38.

2.21 MC synthesis of [Pd(dppm)I$_2$] (6d)

PdI_2 (20.0 mg, 0.0555 mmol) and bis(diphenylphosphino) methane (21.3 mg, 0.0555 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. Yield: >99% (41.1 mg).

^1H NMR (400.1 MHz, DMSO-d_6, 298 K) δ 8.00–7.81 (m, 8H, phenyl); 7.61–7.39 (m, 12H, phenyl); 4.48 (t, J_{PH} = 10.0, 2H, –CH_2–). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K) δ 133.47 (t, J_{PC} = 6.0 Hz, CH of phenyl); 132.37 (s, *p*-CH of phenyl); 129.27 (t, J_{PC} = 5.9 Hz, CH of phenyl); 127.63 (d, J_{PC} = 23.9 Hz, quaternary C of phenyl); 43.91 (t, J_{PC} = 25.4 Hz, –CH_2–). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K) δ – 63.26 (s). (Fig. S51–S53). Elemental analysis: calculated (%) for ($C_{25}H_{22}I_2P_2Pd$): C, 40.32; H, 2.98; I, 34.09; P, 8.32; Pd, 14.29. Found (%): C, 40.57; H, 2.48.

2.22 MC synthesis of [Pd(dppe)(OAc)$_2$] (7a)

$Pd(OAc)_2$ (15.0 mg, 0.0668 mmol) and bis(diphenylphosphino) ethane (26.6 mg, 0.0668 mmol) were milled at 30 Hz for 30 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. Yield: 98% (40.8 mg).

^1H NMR (400.1 MHz, $CDCl_3$, 298 K) δ 7.99–7.85 (m, 12H); 7.59–7.44 (m, 18H); 2.39–2.18 (m, 4H); 1.26 (s, 6H). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K) δ 133.86–133.17 (m, CH of phenyl); 132.08 (s, *p*-CH of phenyl); 129.51–128.80 (m, CH of phenyl); 127.82 (d, J_{PC} = 53.8 Hz, quaternary C of phenyl); 30.95 (–CH_3 of acetate); 27.33–26.49 (m, –CH_2–). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K) δ 58.21 (s) (Fig. S54–S56). Elemental analysis: calculated (%) for ($C_{30}H_{30}O_4P_2Pd$): C, 57.85; H, 4.85; O, 10.27; P, 9.94; Pd, 17.09. Found (%): C, 57.79; H, 4.91.

2.23 MC synthesis of [Pd(dppe)Cl$_2$] (7b)

Method A: $PdCl_2$ (15.0 mg, 0.0846 mmol) and bis(diphenylphosphino)ethane (33.7 mg, 0.0846 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. Yield: >99% (48.6 mg). Method B: $Na_2[PdCl_4]$ (15.0 mg, 0.0510 mmol) and bis(diphenylphosphino)ethane (20.3 mg, 0.0510 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. The product was then washed with 2 mL of water and dried at low pressure. Yield: >99% (29.3 mg).

^1H NMR (400.1 MHz, DMSO-d_6, 298 K) δ 8.01–7.79 (m, 8H, phenyl); 7.67–7.38 (m, 12H, phenyl); 2.87–2.54 (m, 4H, –CH_2–). $^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d_6, 298 K) δ 133.91 (CH of phenyl); 132.56 (*p*-CH of phenyl); 129.42 (CH of phenyl); 128.81 (d, J_{PC} = 54.87 Hz, quaternary C of phenyl); 28.26 (–CH_2–). $^{31}P\{^1H\}$ NMR (162.0 MHz, DMSO-d_6, 298 K) δ 66.60 (s) (Fig. S57–S59). Elemental analysis: calculated (%) for ($C_{26}H_{24}Cl_2P_2Pd$): C, 54.25; H, 4.20; Cl, 12.31; P, 10.76; Pd, 18.48. Found (%): C, 54.62; H, 4.13.

2.24 MC synthesis of [Pd(dppe)Br$_2$] (7c)

$Na_2[PdBr_4]$ (20.0 mg, 0.0424 mmol) and bis(diphenylphosphino)ethane (16.9 mg, 0.0424 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. The product was then washed with 2 mL of water and dried at low pressure. Yield: >99% (28.1 mg).

^1H NMR (400.1 MHz, $CDCl_3$, 298 K) δ 7.95–7.80 (m, 8H, phenyl); 7.63–7.45 (m, 12H, phenyl); 2.51–2.32 (m, 4H, –CH_2–). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K) δ 133.79 (t, J_{PC} =

5.5 Hz, CH of phenyl); 132.20 (*p*-CH of phenyl); 129.07 (t, J_{PC} = 5.7 Hz, CH of phenyl); 128.50 (d, J_{PC} = 58.2 Hz, quaternary C of phenyl); 29.05 (t, J_{PC} = 23.6 Hz, –CH_2–). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K) δ 64.49 (s) (Fig. S60–S62). Elemental analysis: calculated (%) for ($C_{26}H_{24}Br_2P_2Pd$): C, 46.99; H, 3.64; Br, 24.04; P, 9.32; Pd, 16.01. Found (%): C, 47.02; H, 3.53.

2.25 MC synthesis of [Pd(dppe)I_2] (7d)

PdI_2 (20.0 mg, 0.0555 mmol) and bis(diphenylphosphino) ethane (22.1 mg, 0.0555 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. Yield: >99% (41.9 mg).

^1H NMR (400.1 MHz, $CDCl_3$, 298 K) δ 7.90–7.77 (m, 8H, phenyl); 7.62–7.45 (m, 12H, phenyl); 2.32 (m, 4H, –CH_2–). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K) δ 133.97 (t, J_{PC} = 5.4 Hz, CH of phenyl); 132.05 (*p*-CH of phenyl); 129.67 (quaternary C of phenyl); 128.90 (t, J_{PC} = 5.3 Hz, CH of phenyl); 29.82 (–CH_2–). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K) δ 61.93 (s) (Fig. S63–S65). Elemental analysis: calculated (%) for ($C_{26}H_{24}I_2P_2Pd$): C, 41.15; H, 3.19; I, 33.46; P, 8.17; Pd, 14.03. Found (%): C, 41.48; H, 3.26.

2.26 MC synthesis of [Pd(dppp)$(OAc)_2$] (8a)

$Pd(OAc)_2$ (15.0 mg, 0.0668 mmol) and bis(diphenylphosphino) propane (27.6 mg, 0.0668 mmol) were milled at 30 Hz for 30 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. Yield: 73% (yield determined by NMR in $CDCl_3$).

$^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K) δ 9.22 (s) (Fig. S66).

2.27 MC synthesis of [Pd(dppp)Cl_2] (8b)

Method A: $PdCl_2$ (15.0 mg, 0.0846 mmol) and bis(diphenylphosphino)propane (34.9 mg, 0.0846 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. Yield: >99% (49.8 mg). Method B: $Na_2[PdCl_4]$ (15.0 mg, 0.0510 mmol) and bis(diphenylphosphino)propane (21.0 mg, 0.0510 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. Yield: >99% (30.0 mg).

^1H NMR (400.1 MHz, DMSO-d_6, 298 K) δ 7.90–7.69 (m, 8H, phenyl); 7.56–7.40 (m, 12H, phenyl); 2.77–2.60 (m, 4H, P–CH_2–); 1.85–1.57 (m, 2H, –CH_2–). $^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d_6, 298 K) δ 134.14 (CH of phenyl); 131.62 (*p*-CH of phenyl); 130.05 (d, J_{PC} = 57.3 Hz, quaternary C of phenyl); 128.79 (CH of phenyl); 24.64 (P–CH_2–); 18.39 (–CH_2–). $^{31}P\{^1H\}$ NMR (162.0 MHz, DMSO-d_6, 298 K) δ 12.56 (s) (Fig. S67–S69). Elemental analysis: calculated (%) for ($C_{27}H_{26}Cl_2P_2Pd$): C, 55.00; H, 4.44; Cl, 12.02; P, 10.50; Pd, 18.04. Found (%): C, 55.06; H, 4.39.

2.28 MC synthesis of [Pd(dppp)Br_2] (8c)

$Na_2[PdBr_4]$ (20.0 mg, 0.0424 mmol) and bis(diphenylphosphino)propane (17.5 mg, 0.0424 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. The product was then washed with 2 mL of water and dried at low pressure. Yield: >99% (28.7 mg).

^1H NMR (400.1 MHz, $CDCl_3$, 298 K) δ 7.88–7.72 (m, 8H, phenyl); 7.54–7.38 (m, 12H, phenyl); 2.50–2.32 (m, 4H, P–CH_2–); 2.16–1.94 (m, 2H, –CH_2–). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K) δ 133.69 (CH of phenyl); 131.39 (*p*-CH of phenyl); 129.99 (d, J_{PC} = 59.0 Hz, quaternary C of phenyl); 128.63 (CH of phenyl); 26.05 (t, J_{PC} = 19.2 Hz, P–CH_2–); 18.56 (–CH_2–). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K) δ 7.56 (s) (Fig. S70–S72). Elemental analysis: calculated (%) for ($C_{27}H_{26}Br_2P_2Pd$): C, 47.78; H, 3.86; Br, 23.55; P, 9.13; Pd, 15.68. Found (%): C, 48.02; H, 3.91.

2.29 MC synthesis of [Pd(dppp)I_2] (8d)

PdI_2 (20.0 mg, 0.0555 mmol) and bis(diphenylphosphino) propane (22.9 mg, 0.0555 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. Yield: >99% (42.8 mg).

^1H NMR (400.1 MHz, $CDCl_3$, 298 K) δ 7.84–7.70 (m, 8H, phenyl); 7.52–7.37 (m, 12H, phenyl); 2.48–2.30 (m, 4H, P–CH_2–); 2.14–1.93 (m, 2H, –CH_2–). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K) δ 133.79 (CH of phenyl); 131.29 (*p*-CH of phenyl); 128.53 (CH of phenyl); 25.39 (t, J_{PC} = 19.9 Hz, P–CH_2–); 18.39 (–CH_2–). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K) δ – 0.18 (s) (Fig. S73–S75). Elemental analysis: calculated (%) for ($C_{27}H_{26}I_2P_2Pd$): C, 41.97; H, 3.39; I, 32.85; P, 8.02; Pd, 13.77. Found (%): C, 42.04; H, 3.27.

2.30 MC synthesis of [Pd(dppb)$(OAc)_2$] (9a)

$Pd(OAc)_2$ (15.0 mg, 0.0668 mmol) and bis(diphenylphosphino) butane (28.5 mg, 0.0668 mmol) were milled at 30 Hz for 30 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. Yield: 88% (yield determined by NMR in $CDCl_3$).

$^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K) δ 25.46 (s) (Fig. S76).

2.31 MC synthesis of [Pd(dppb)Cl_2] (9b)

Method A: $PdCl_2$ (15.0 mg, 0.0846 mmol) and bis(diphenylphosphino)butane (36.1 mg, 0.0846 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. Yield: >99% (51.0 mg). Method B: $Na_2[PdCl_4]$ (15.0 mg, 0.0510 mmol) and bis(diphenylphosphino)butane (21.7 mg, 0.0510 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. The product was then washed with 2 mL of water and dried at low pressure. Yield: >99% (30.7 mg).

^1H NMR (400.1 MHZ, $CDCl_3$, 298 K) δ 7.88–7.32 (m, 20H, phenyl); 2.46 (s, 4H, P–CH_2–); 1.88 (d, J_{HH} = 22.6 Hz, 4H, –CH_2–). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$, 298 K) δ 133.66 (CH of phenyl); 131.27 (*p*-CH of phenyl); 128.57 (CH of phenyl); 27.59 (P–CH_2–); 23.44 (–CH_2–). $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 298 K) δ 28.71 (s) (Fig. S77–S79). Elemental analysis: calculated (%) for ($C_{28}H_{28}Cl_2P_2Pd$): C, 55.70; H, 4.67; Cl, 11.74; P, 10.26; Pd, 17.63. Found (%): C, 55.75; H, 4.54.

2.32 MC synthesis of [Pd(dppb)Br_2] (9c)

$Na_2[PdBr_4]$ (20.0 mg, 0.0424 mmol) and bis(diphenylphosphino)butane (18.1 mg, 0.0424 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. The product was then washed with 2 mL of water and dried at low pressure. Yield: >99% (29.3 mg).

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ 7.89–7.33 (m, 20H, phenyl); 2.47 (s, 4H, P–CH_2–); 1.85 (d, J_{HH} = 22.8 Hz, 4H, –CH_2–). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 298 K) δ 133.94; 133.77; 131.17; 130.86; 128.87; 128.51; 34.17 (–CH_2–); 29.13 (–CH_2–). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$, 298 K) δ 25.64 (s) (Fig. S80–S82). Elemental analysis: calculated (%) for ($C_{28}H_{28}Br_2P_2Pd$): C, 48.54; H, 4.08; Br, 23.07; P, 8.95; Pd, 15.37. Found (%): C, 48.47; H, 4.00.

2.33 MC synthesis of [Pd(dppf)Cl_2] (10b)

Method A: $PdCl_2$ (15.0 mg, 0.0846 mmol) and bis(diphenylphosphino)ferrocene (46.9 mg, 0.0846 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. Yield: >99% (61.4 mg). Method B: $Na_2[PdCl_4]$ (15.0 mg, 0.0510 mmol) and bis(diphenylphosphino)ferrocene (28.3 mg, 0.0510 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. The product was then washed with 2 mL of water and dried at low pressure. Yield: >99% (37.2 mg).

^{1}H NMR (400.1 MHz, CD_3OD, 298 K) δ 7.95–7.83 (m, 8H, phenyl); 7.61–7.41 (m, 12H, phenyl); 4.56 (s, 4H, Cp^-); 4.30 (s, 4H, Cp^-). ^{13}C{^{1}H} NMR (100.6 MHz, CD_3OD, 298 K) δ 134.67 (CH of phenyl); 131.32 (*p*-CH of phenyl); 127.95 (CH of phenyl); 127.37 (t, J_{PC} = 32.3 Hz, quaternary C of Cp^-); 76.64 (CH of Cp^-); 74.24 (CH of Cp^-). ^{31}P{^{1}H} NMR (162.0 MHz, CD_3OD, 298 K) δ 35.74 (s) (Fig. S83–S85). Elemental analysis: calculated (%) for ($C_{34}H_{28}Cl_2FeP_2Pd$): C, 55.81; H, 3.86; Cl, 9.69; Fe, 7.63; P, 8.47; Pd, 14.54. Found (%): C, 56.04; H, 3.79.

2.34 MC synthesis of [Pd(dppf)Br_2] (10c)

$Na_2[PdBr_4]$ (20.0 mg, 0.0424 mmol) and bis(diphenylphosphino)ferrocene (23.5 mg, 0.0424 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. The product was then washed with 2 mL of water and dried at low pressure. Yield: >99% (34.7 mg).

^{1}H NMR (400.1 MHz, CD_3OD, 298 K) δ 7.94–7.85 (m, 8H, phenyl); 7.48–7.38 (m, 12H, phenyl); 4.52 (s, 4H, Cp^-); 4.26 (s, 4H, Cp^-). ^{13}C{^{1}H} NMR (100.6 MHz, CD_3OD, 298 K) δ 134.80 (CH of phenyl); 131.08 (*p*-CH of phenyl); 127.73 (CH of phenyl); 76.47 (CH of Cp^-); 73.98 (CH of Cp^-). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$, 298 K) δ 30.60 (s) (Fig. S86–S88). Elemental analysis: calculated (%) for ($C_{34}H_{28}Br_2FeP_2Pd$): C, 49.76; H, 3.44; Br, 19.47; Fe, 6.81; P, 7.55; Pd, 12.97. Found (%): C, 49.08; H, 3.32.

2.35 MC synthesis of [Pd(dppf)I_2] (10d)

PdI_2 (20.0 mg, 0.0555 mmol) and bis(diphenylphosphino) ferrocene (30.8 mg, 0.0555 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. Yield: >99% (50.7 mg).

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ 8.07–7.77 (m, br, 8H, phenyl); 7.63–7.33 (m, br, 12H, phenyl); 4.35 (s, br, 4H, Cp^-); 4.15 (s, br, 4H, Cp^-). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 298 K) δ 135.21 (d, J_{PC} = 11.5 Hz, CH of phenyl); 134.12 (d, J_{PC} = 54.0 Hz, quaternary C of phenyl); 131.06 (*p*-CH of phenyl); 127.86 (d, J_{PC} = 11.5 Hz, CH of phenyl); 76.19 (d, J_{PC} = 10.1 Hz, CH of Cp^-); 73.48 (d, J_{PC} = 6.5 Hz, CH of Cp^-). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$, 298 K) δ 24.23 (s) (Fig. S89–S91). Elemental analysis: calculated (%) for ($C_{34}H_{28}I_2FeP_2Pd$): C, 44.64; H, 3.09; I, 27.75; Fe, 6.11; P, 6.77; Pd, 11.64. Found (%): C, 45.01; H, 2.99.

2.36 MC synthesis of [Pd(dippf)Cl_2] (11b)

Method A: $PdCl_2$ (15.0 mg, 0.0846 mmol) and bis(diisopropylphosphino)ferrocene (35.4 mg, 0.0846 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. Yield: 82% (41.3 mg). Method B: $Na_2[PdCl_4]$ (15.0 mg, 0.0510 mmol) and bis(diisopropylphosphino)ferrocene (21.3 mg, 0.0510 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. The product was then washed with 2 mL of water and dried at low pressure. Yield: >99% (30.2 mg).

^{1}H NMR (400.1 MHz, CD_3OD, 298 K) δ 4.76 (s, 4H, Cp^-); 4.60 (s, 4H, Cp^-); 2.96 (p, J_{HH} = 7.0 Hz, 4H, –CH–); 1.66–1.53 (m, 12H, –CH_3); 1.34–1.21 (m, 12H, –CH_3). ^{13}C{^{1}H} NMR (100.6 MHz, CD_3OD, 298 K) δ 74.28; 72.42; 19.66; 18.33. ^{31}P{^{1}H} NMR (162.0 MHz, CD_3OD, 298 K) δ 65.84 (s) (Fig. S92–S94). Elemental analysis: calculated (%) for ($C_{22}H_{36}Cl_2FeP_2Pd$): C, 44.35; H, 6.09; Cl, 11.91; Fe, 9.38; P, 10.40; Pd, 17.87. Found (%): C, 44.96; H, 6.16.

2.37 MC synthesis of [Pd(dippf)Br_2] (11c)

$Na_2[PdBr_4]$ (20.0 mg, 0.0424 mmol) and bis(diisopropylphosphino)ferrocene (17.72 mg, 0.0424 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. The product was then washed with 2 mL of water and dried at low pressure. Yield: >99% (28.8 mg).

^{1}H NMR (400.1 MHz, DMSO-d_6, 298 K) δ 4.69 (s, 4H, Cp^-); 4.59 (s, 4H, Cp^-); 1.52–1.42 (m, 12H). ^{31}P{^{1}H} NMR (162.0 MHz, DMSO-d_6, 298 K) δ 64.20 (s) (Fig. S95 and S96). Elemental analysis: calculated (%) for ($C_{22}H_{36}Br_2FeP_2Pd$): C, 38.60; H, 5.30; Br, 23.35; Fe, 8.16; P, 9.05; Pd, 15.54. Found (%): C, 38.92; H, 5.41.

2.38 MC synthesis of [Pd(dippf)I_2] (11d)

PdI_2 (20.0 mg, 0.0555 mmol) and bis(diisopropylphosphino) ferrocene (23.2 mg, 0.0555 mmol) were milled at 30 Hz for 60 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. Yield: >99% (43.2 mg).

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ 4.65–4.36 (m, br, 8H, Cp^-); 3.49–3.21 (m, 4H, –CH–); 1.36–1.00 (m, 24H, –CH_3). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 298 K) δ 73.85; 72.07; 31.58–30.42 (m); 21.50; 19.98. ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$, 298 K)

δ 56.98 (s) (Fig. S97–S99). Elemental analysis: calculated (%) for ($C_{22}H_{36}I_2FeP_2Pd$): C, 33.95; H, 4.66; I, 32.60; Fe, 7.17; P, 7.96; Pd, 13.66. Found (%): C, 33.03; H, 4.72.

2.39 MC synthesis of [Pd((*R*)-BINAP)Cl_2] (12b)

$Na_2[PdCl_4]$ (15.0 mg, 0.0510 mmol) and (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (31.7 mg, 0.0510 mmol) were milled at 30 Hz for 90 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. The product was then washed with 2 mL of water and dried at low pressure. Yield: >99% (40.4 mg).

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ 7.91–7.79 (m, 8H); 7.77–7.28 (m, 18H); 7.19–7.11 (m, 2H); 6.94–6.61 (m, 8H). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 298 K) δ 138.75 (quaternary C); 135.34; 135.24; 134.09; 131.04; 130.54; 129.16; 129.05; 128.45; 128.34; 128.18; 127.88; 127.75; 127.59; 127.40; 126.60; 122.62 (quaternary C); 122.07 (quaternary C). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$, 298 K) δ 28.56 (s) (Fig. S100–S102). Elemental analysis: calculated (%) for ($C_{44}H_{32}Cl_2P_2Pd$): C, 66.07; H, 4.03; Cl, 8.86; P, 7.74; Pd, 13.30. Found (%): C, 66.08; H, 4.07.

2.40 MC synthesis of [Pd((*R*)-BINAP)Br_2] (12c)

$Na_2[PdBr_4]$ (20.0 mg, 0.0424 mmol) and (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (26.4 mg, 0.0424 mmol) were milled at 30 Hz for 120 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. The product was then washed with 2 mL of water and dried at low pressure. Yield: >99% (37.4 mg).

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ 7.92–7.33 (m); 7.17–7.07 (m); 6.92–6.81 (m); 6.80–6.62 (m). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 298 K) δ 138.76 (quaternary C); 135.30; 134.04 (quaternary C); 133.03 (quaternary C); 132.10; 130.97; 130.43; 128.97; 128.16; 127.83; 127.64; 127.41; 126.73; 122.71 (quaternary C); 122.15 (quaternary C). ^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$, 298 K) δ 25.30 (s) (Fig. S103–S105). Elemental analysis: calculated (%) for ($C_{44}H_{32}Br_2P_2Pd$): C, 59.46; H, 3.63; Br, 17.97; P, 6.97; Pd, 11.97. Found (%): C, 59.49; H, 3.72.

2.41 MC synthesis of [Pd((*R*)-BINAP)I_2] (12d)

PdI_2 (15.0 mg, 0.0416 mmol) and (*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (25.9 mg, 0.0416 mmol) were milled at 30 Hz for 120 min in a 2 mL Eppendorf tube with 4 zirconia balls (3 mm) under an argon atmosphere. Yield: >99% (40.5 mg).

^{1}H NMR (400.1 MHz, $CDCl_3$, 298 K) δ 8.09–7.30 (m); 7.19–6.58 (m). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 298 K) δ 138.79 (quaternary C); 135.38; 135.28; 133.90 (quaternary C); 133.07; 132.98; 130.88; 130.64; 1230.17; 128.74; 128.64; 128.46; 128.36; 128.10; 127.65; 127.58; 127.53; 127.46; 126.56; 123.10 (quaternary C); 122.59 (quaternary C). ^{31}P{^{1}H} NMR (162.0 MHz $CDCl_3$, 298 K) δ 16.52 (s) (Fig. S106–S108). Elemental analysis: calculated (%) for ($C_{44}H_{32}I_2P_2Pd$): C, 53.77; H, 3.28; I, 25.82; P, 6.30; Pd, 10.83. Found (%): C, 54.00; H, 3.55.

The acquired NMR spectra, detailed experimental procedures, and additional experimental data are included in the SI.

3 Results and discussion

3.1 Mechanochemical synthesis of palladium(II) diene complexes

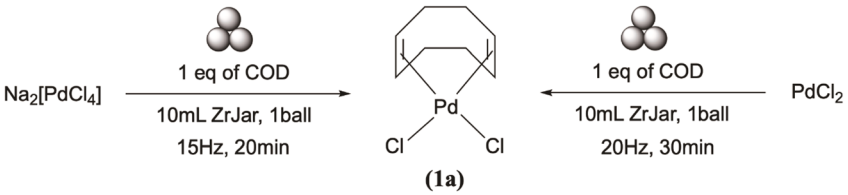
The primary objective of the present study was the synthesis of palladium(II) diene complexes with 1,5-cyclooctadiene (COD) as a ligand. The complexes [Pd(COD)Cl_2] and [Pd(COD)Br_2] have been recognized in the scientific literature for a considerable period and are extensively utilized as precursors for additional syntheses.[21]

Synthesis of [Pd(COD)Cl_2] (**1a**) in solution is achieved through the reaction of $K_2[PdCl_4]$ for a duration of one hour, followed by purification through recrystallization and filtration. In any case, it is feasible to synthesize **1a** at 15 Hz milling for 20 minutes by employing a mechanochemical approach, with a yield of 99%. It is also noteworthy that the reaction will occur in five minutes of milling at 30 Hz. In this instance, the formation of a powder is observed, which undergoes a transition from yellow to light grey, thereby indicating the onset of degradation. Therefore, it can be concluded that 15 Hz is the optimal choice. It has been demonstrated that the degradation of the compound is started at a milling time that exceeds 30 minutes. The complex was characterized by ^{1}H NMR and ^{13}C{^{1}H} NMR after its synthesis. The characterization data are consistent with those reported in the existing literature.[21] In order to corroborate the scalability of the reaction, a gram-scale reaction was additionally tested, yielding analogous results to those previously reported. The removal of NaCl as a reaction co-product was achieved through two washing steps with water, followed by a drying process conducted at low pressure. Subsequently, $PdCl_2$ was utilized as a precursor for the synthesis of **1a**, with the objective of circumventing the necessity for subsequent purification. In consideration of the reduced reactivity of $PdCl_2$, the reaction is expected to occur at a frequency of 20 Hz over a duration of 30 minutes of milling, yielding a product yield of 98%. The final methodology under consideration is not present in the extant literature (Scheme 1).

Subsequently, the bromide analogue of complex **1a** was synthesized. The reaction was initiated with $Na_2[PdBr_4]$ at a frequency of 15 Hz, employing a milling process that lasted for 20 minutes. The resultant yield was found to be 98%. The complex [Pd(COD)Br_2] (**1b**) was synthesized and characterized, and its properties aligned with those reported in the literature.[44]

The synthesis of the iodine analogue complex was unsuccessful, with conversion rates no higher than 30% being reported under optimal conditions of Hz and time. Regarding the tests using $Pd(OAc)_2$, no reaction occurred. Attempts have been made to synthesize the [PdMe(COD)Cl] complex mechanochemically from $SnMe_4$, following the solution procedure known in the literature.[22] Dry milling conditions and liquid assisted milling (LAG) conditions with dichloromethane were tried, and none were successful.

To verify that the reaction occurs mechanochemically and is not an in-tube reaction, precursors of chlorine and bromine were placed into an NMR tube in $CDCl_3$ together with 1,5-cyclooctadiene. After the insertion of the reagents, the tube was



Scheme 1 Formation of **1a** from $Na_2[PdCl_4]$ and $PdCl_2$.

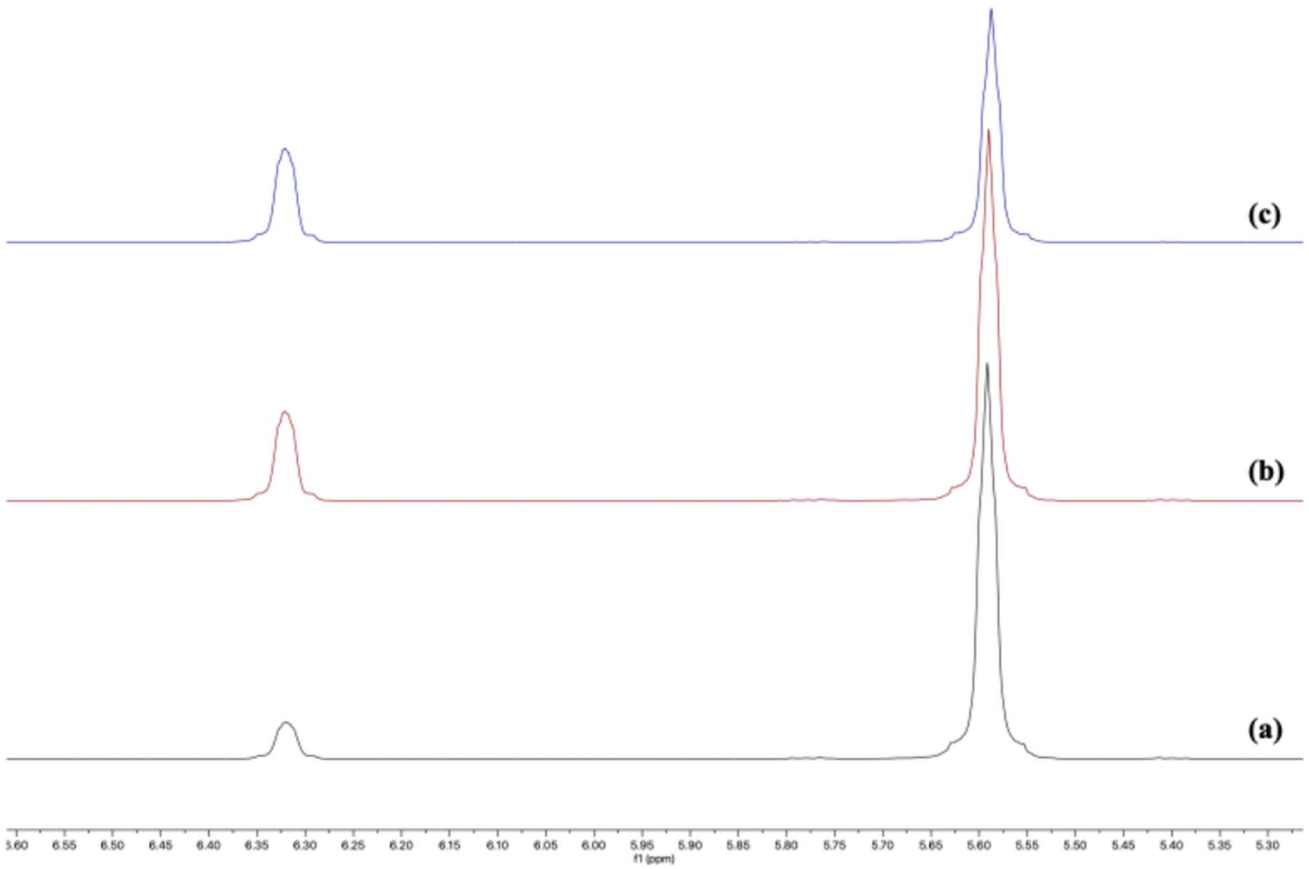


Fig. 1 ^{1}H NMR spectra of the in-tube reaction of **1a** (400.1 MHz, $CDCl_3$, 298 K) after (a) 20 min, 10%; (b) 28 hours, 23%; (c) 1 week, 33%.

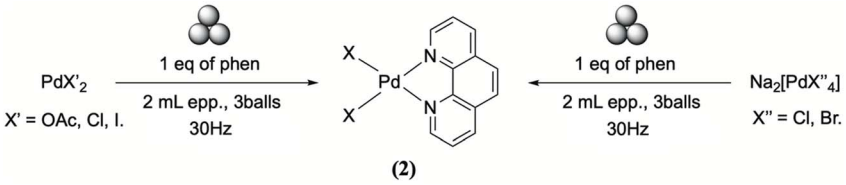
monitored after a period of 20 minutes, which revealed a conversion of 10% for **1a** and 2% for **1b**. As illustrated in Fig. 1, there was a marginal increase in conversions, to 33% for **1a** to 14% for **1b**, following a one-week period.

3.2 Mechanochemical synthesis of palladium(II) N-ligand complexes

Following the synthesis of diene complexes, research shifted towards complexes with N-donor ligands. Considering our preceding research, conducted by us,[36] which pertained also to the synthesis of complexes of palladium(II) with 2,2′-bipyridine, the present study is focused on 1,10-phenanthroline (phen) as the primary ligand under investigation. The synthesis of these complexes utilized all five Pd(II) precursors available (Scheme 2).

The mechanochemical synthesis of $[Pd(phen)(OAc)_2]$ (**2a**) was achieved at a frequency of 30 Hz over a duration of 90 minutes, with a reaction yield of 94%. The presence of a single acetate signal at ^{1}H NMR, in conjunction with a single $-CH_3$ and C═O signal at $^{13}C\{^1H\}$ NMR, indicates that both acetates are directly bound to palladium (see Fig. S8 and S9 in the SI for further details). Quantitative yields were observed from both precursors in the analogous complex with chlorine $[Pd(phen)Cl_2]$ (**2b**), for which the same reaction conditions were employed. To verify that the reaction in the case of **2b** proceeds quantitatively, a test was performed by adding a 10% excess of ligand (1.1 eq.). The ground powder was then analyzed by ^{1}H NMR and an excess of free ligand was observed (see Fig. 2).

For the complexes $[Pd(phen)Br_2]$ (**2c**) and $[Pd(phen)I_2]$ (**2d**), the application of very similar reaction conditions resulted in yield values of 91% and >99%, respectively. All the complexes mentioned above were obtained in sufficient purity for complete NMR characterization and elemental analysis (see the



Scheme 2 Formation of [Pd(phen)X_2] (**2**).

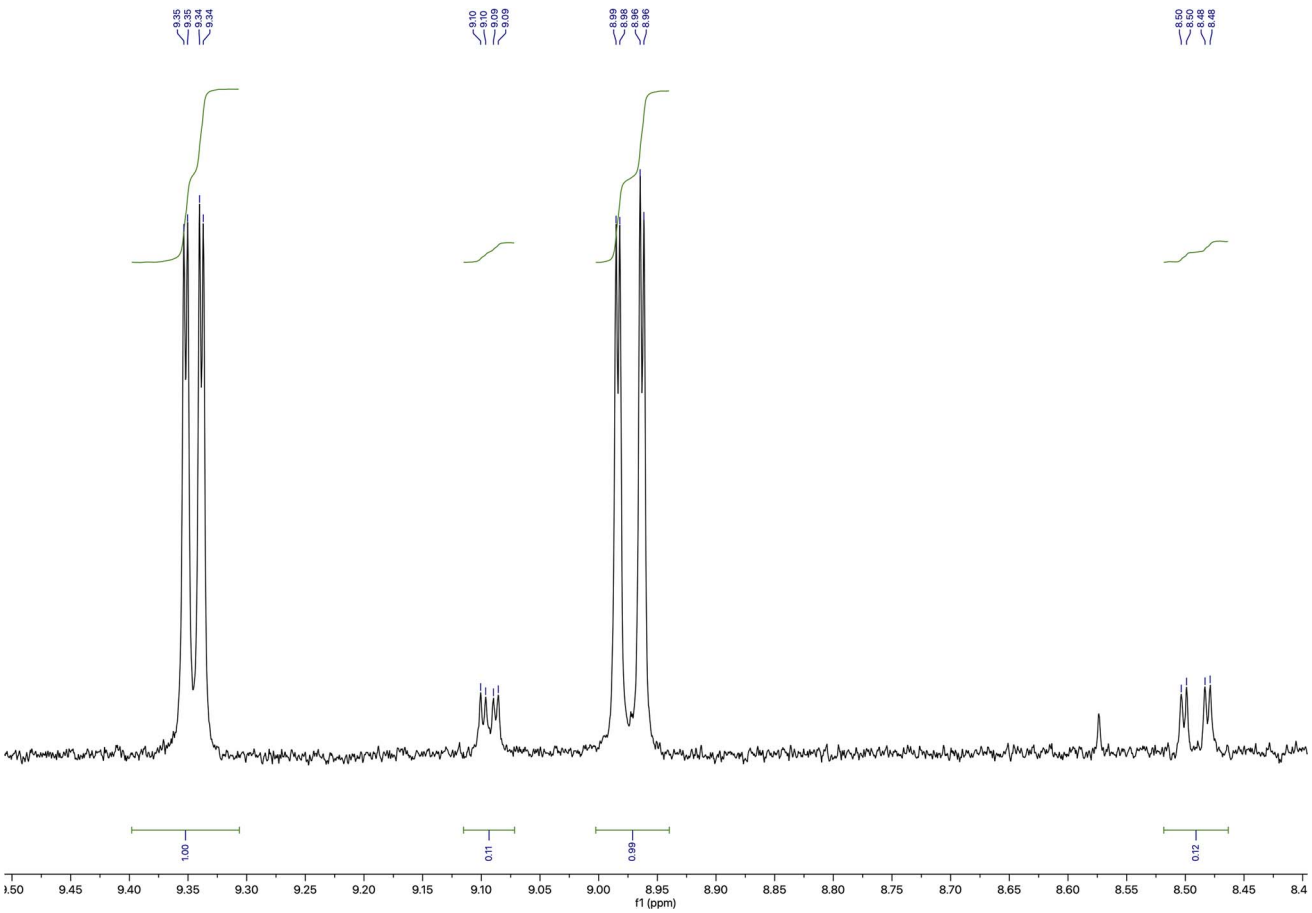
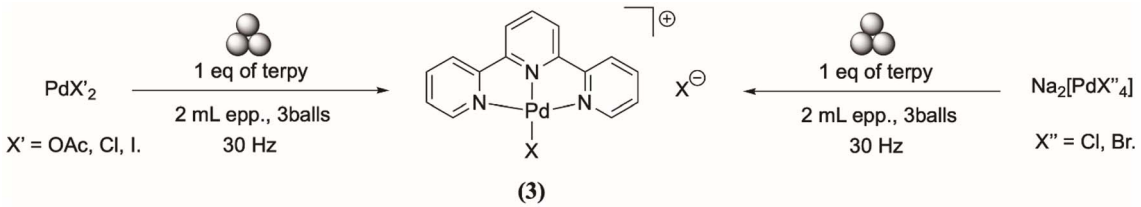


Fig. 2 ^{1}H NMR spectra of **2b** (400.1 MHz, DMSO-d_6, 298 K) with 10% of free ligand.



Scheme 3 Formation of [Pd(terpy)X]X (**3**).

Experimental section). The data obtained are consistent with those documented in the literature.[45,46] It has been demonstrated that utilizing twice the ligand equivalents in comparison to the precursor does not result in the formation of the biscationic species.

Mechanochemical synthesis of palladium(II) complexes with N-donor ligands was later extended to 2,2′;6′,2″-terpyridine (terpy) (Scheme 3). The synthesis of [Pd(terpy)(OAc)](OAc) (**3a**) in an Eppendorf tube was completed with 1.1 eq. of terpy, in 2 hours, with a yield of 98%, after three washes with diethyl ether.

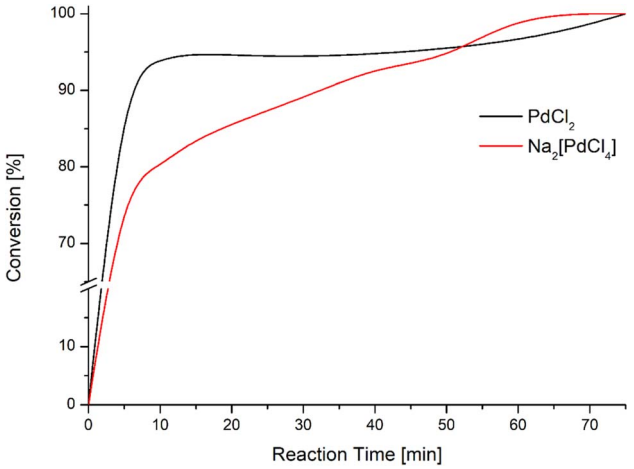


Fig. 3 Formation of [Pd(terpy)Cl]Cl (**3b**) with milling time from both precursors.

The NMR characterization is in agreement with the formation of the desired species. Furthermore, the $^{13}C\{^1H\}$ NMR spectrum shows the presence of two different acetates, one in the first sphere and the other in the second coordination sphere (see Fig. S17 in the SI for details). As for the synthesis of the analogous terpyridine complexes with chlorine (**3b**), the reaction proceeds with quantitative yields, in 60 minutes for $Na_2[PdCl_4]$ and 75 minutes for $PdCl_2$. The synthesis of the analogous species of bromine (**3c**) and iodine (**3d**) proceeds cleanly with yields of 94% and 96%, respectively. For all these complexes, the products were obtained without further purification (see the Experimental section).[47]

For complex **3b**, an in-tube reaction was performed, with conversion over time monitored by ^1H NMR. After six hours, no complex formation was observed, with only free terpyridine present (see Fig. S121 in the SI for details).

A conversion test was also performed for this complex. The test was carried out in an Eppendorf tube, with both metal precursors and terpyridine in quantities of exactly one equivalent. The test results, summarized in Fig. 3, showed that for both precursors, the conversion in the early stages of the reaction is very rapid, especially in the case of $PdCl_2$. The completion of the reaction, however, is not so rapid, probably due to the lack of diffusive phenomena, absent in solid-state reactions.

Other pyridine-like ligands have also been employed in the mechanochemical synthesis of Pd(II) complexes. Unfortunately, attempts to use 2-benzoylpyridine and 2-acetylpyridine have met with negative results.

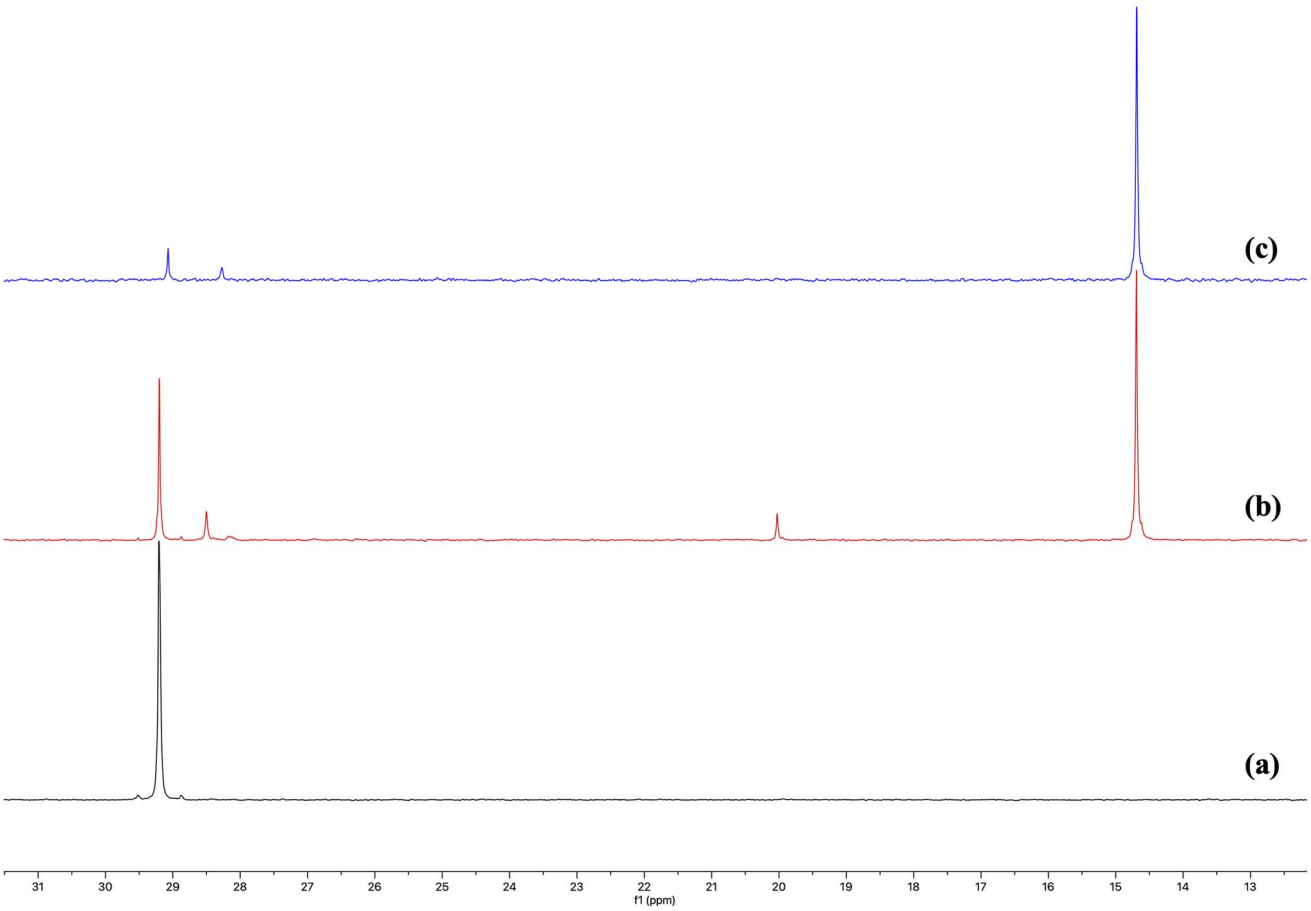


Fig. 4 $^{31}P\{^1H\}$ NMR spectra (162.0 MHz, $CDCl_3$, 298 K) of (a) $Pd(OAc)_2$ with $2PPh_3$ milled for 2 hours with the formation of PPh_3O; (b) $Pd(OAc)_2$ with $2PPh_3$ milled for 30 minutes with the formation of PPh_3O and **4a**; (c) $Pd(OAc)_2$ with $2PPh_3$ milled for 30 minutes in an Ar atmosphere with the formation of **4a** with high selectivity.

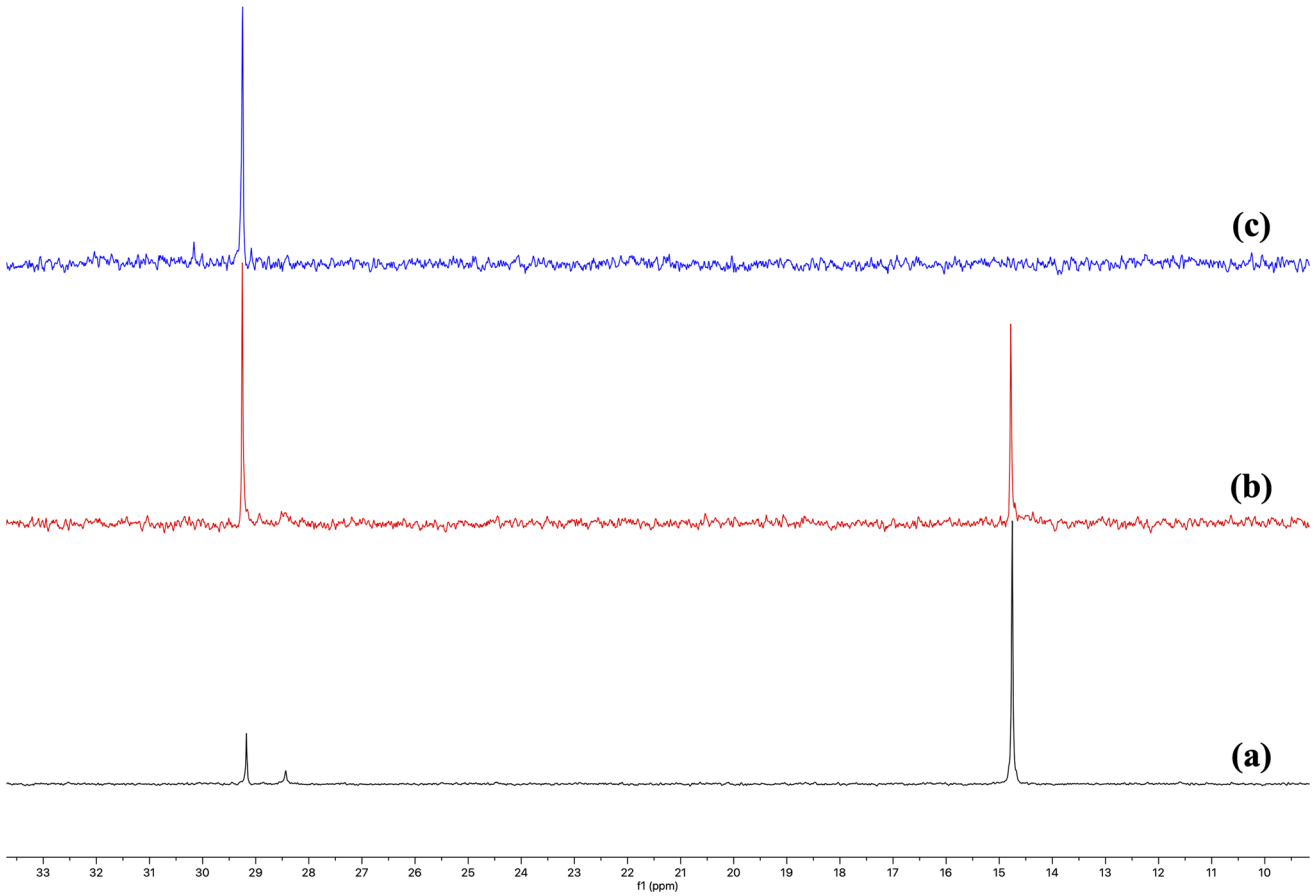


Fig. 5 $^{31}P\{^{1}H\}$ NMR spectra (162.0 MHz, $CDCl_3$, 298 K) of (a) **4a** immediately; (b) **4a** after 2 hours; (c) **4a** after 1 day.

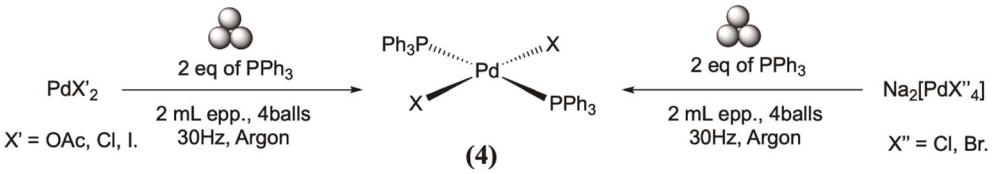
3.3 Mechanochemical synthesis of palladium(II) P-ligand complexes

Subsequent to the synthesis of the complexes described above, our research shifted to the synthesis of complexes with P-donor ligands, with the first ligand studied being triphenylphosphine (PPh_3). The initial synthetic trial was initiated with commercial palladium(II) precursors, employing milling of $Pd(OAc)_2$ with 2 equivalents of PPh_3 for 2 hours. The $^{31}P\{^{1}H\}$ NMR spectrum of this reaction (see Fig. 4a) demonstrated the quantitative formation of triphenylphosphine oxide (PPh_3O) at 29.30 ppm. Following the results of the test, it was determined that the reaction time should be reduced to 30 minutes to observe the formation of the complex. This reduction in reaction time would result in a decrease in mechanical energy. In this instance, the $^{31}P\{^{1}H\}$ NMR spectrum (Fig. 4b) indicates the formation of the compound $[Pd(PPh_3)_2(OAc)_2]$ (**4a**) at 14.69 ppm, thereby corroborating the data reported in the literature.[48] Lowering the mill frequency from 30 Hz to 15 Hz leads to a decrease in selectivity of the complex.

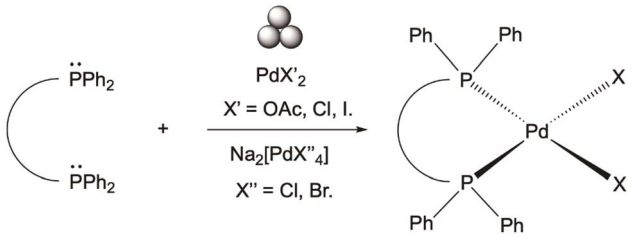
In view of the foregoing result, it was hypothesized that the synthesis of these phosphine compounds is contingent on the control of the atmosphere. The subsequent test was performed in a closed Eppendorf tube, with parafilm, previously charged in an argon atmosphere. The $^{31}P\{^{1}H\}$ NMR spectrum revealed a high conversion (94%) in CD_2Cl_2 (see Fig. S26 in the SI), accompanied by an equally high selectivity (81%). The values of conversion and selectivity were obtained in CD_2Cl_2, since this solvent was found to be less reactive towards the species under investigation. Furthermore, the tube was freshly prepared and immediately analyzed. Indeed, the same spectrum was repeated after a few minutes, at which point it was evident that the species of interest was no longer present in solution, with the appearance of new species. Subsequently, an investigation was conducted into the degradation of compound **4a**. The resulting spectra are presented in Fig. 5. $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR characterization studies at 233.15 K were attempted but were unsuccessful, as reactivity occurred immediately upon preparation of the NMR tube.

Very similar reaction conditions were used for the subsequent synthesis of analogous complexes $[Pd(PPh_3)_2Cl_2]$ (**4b**), $[Pd(PPh_3)_2Br_2]$ (**4c**) and $[Pd(PPh_3)_2I_2]$ (**4d**) (Scheme 4), with yields of 98%, 96% and 92% respectively (see the Experimental section). These complexes did not show reactivity in $CDCl_3$ during NMR characterization.

The first bidentate ligand employed was xantphos. In the case of the precursor $Pd(OAc)_2$, the reaction produces four products. The conversion was high (94%), but the selectivity towards the desired product [Pd(xantphos)$(OAc)_2$] (**5a**) was low



Scheme 4 Reaction scheme for the formation of *trans*-[Pd(PPh$_3$)$_2$X$_2$] (**4**).



Scheme 5 Formation of [Pd(P∩P)X$_2$].

(72%) and its behavior in solution during the NMR characterization is similar to that of **4a**.

In the synthesis of [Pd(xantphos)Cl$_2$] (**5b**), the reaction proceeds efficiently if Na$_2$[PdCl$_4$] is employed, yielding products in quantitative amounts. Conversely, when PdCl$_2$ is utilized, the conversion stops at 78%, exhibiting complete selectivity. Regarding [Pd(xantphos)Br$_2$] (**5c**), the reaction was executed over a period of 60 minutes of milling, producing a pure product with a yield of 91%. In contrast, the iodide analogue has not been observed, despite various synthetic attempts.

Furthermore, a reaction was conducted for the P-ligand complexes within an NMR tube, which was subsequently monitored *via* ^{31}P{^{1}H} NMR spectroscopy. The complex selected was **5b**, and the conversion detected was 8% after 15 minutes, 22% after 1.15 hours, and 31% after 24 hours (see the SI for details).

The synthesis and characterization of the complexes with Pd(OAc)$_2$ and diphosphines (Scheme 5) proved to be more complicated, particularly due to the reduced stability in solution as previously observed with compounds **4a** and **5a**. Additionally, the formation of various unidentified species was noted, along with the desired product and the corresponding phosphine oxide. Removal of PPh$_3$O was attempted through washing the complex with diethyl ether and pentane. However, degradation of the compound was observed, as in NMR tubes. It was found that only the [Pd(dppe)(OAc)$_2$] (**7a**) complex was stable in solution, thus allowing full characterization to be performed.

For all complexes with palladium(II) precursors with halogens, the syntheses of the complexes with diphosphines proceed well and in quantitative yields (Table 1 and Scheme 5). However, just the species [Pd(dppb)I$_2$] was not observed.

Concerning the synthesis of compounds with (*R*)-BINAP, the complexes were obtained with quantitative yields starting from Na$_2$[PdCl$_4$], Na$_2$[PdBr$_4$] and PdI$_2$, as precursors. The synthesis of complex **12b** from PdCl$_2$ showed low conversions (17%) after 120 min of reaction, thus excluding this precursor.

Table 1 Products obtained in the mechanochemical synthesis described above

	Precursor, yield (%)			
Ligand	Pd(OAc)$_2$	PdCl$_2$† or Na$_2$[PdCl$_4$]‡	Na$_2$[PdBr$_4$]	PdI$_2$
dppm	**6a**, 64%	**6b**, >99%†	**6c**, >99%	**6d**, >99%
dppe	**7a**, 98%	**7b**, >99%†	**7c**, >99%	**7d**, >99%
dppp	**8a**, 73%	**8b**, >99%†	**8c**, >99%	**8d**, >99%
dppb	**9a**, 88%	**9b**, >99%†	**9c**, >99%	No formation
dppf	—	**10b**, >99%†	**10c**, >99%	**10d**, >99%
dippf	—	**11b**, >99%‡	**11c**, >99%	**11d**, >99%
(*R*)-BINAP	—	**12b**, >99%‡	**12c**, >99%	**12d**, >99%

3.4 Green metrics: mechano- *vs.* solution-synthesis

A comparative assessment of green metrics between the mechanochemical synthesis developed in this study and established solvothermal methods is provided in Table 2.

The transformation of palladium(II) precursors was successfully carried out, with reaction durations ranging from 20 minutes to 2 hours. In comparison with conventional solution methodologies, this mechanochemical approach is notably less complex, thus eliminating the need for precipitation, solvent washing and drying steps.

The omission of bulk solvents from the reaction protocol is a pivotal step in the pursuit of a more sustainable synthetic strategy, chiefly by virtue of the reduction in chemical waste. In contradistinction to conventional solution reactions, which frequently depend on stoichiometric excesses to achieve complete conversion, the mechanochemical method generally permits the utilization of equimolar reactant ratios. This phenomenon is attributed to the enhanced reactivity and thorough mixing facilitated by mechanical grinding, which usually promotes complete consumption of the starting materials. Consequently, this approach not only reduces reagent excess but also simplifies downstream purification steps.

A comparison was made between mechanochemical synthesis and its solution-based counterparts, with the use of two key indicators. The E-factor and the Effective Mass Yield (EMY) are both important factors to consider. These metrics offer insight into the environmental impact of the process. However, it is important to note that many solution procedures, as documented in the relevant literature, lack the detailed experimental data needed for accurate assessments of green metrics. The data collected and calculated may not accurately

Table 2 Green metrics comparison between mechano- and solution-synthesis[a]

	Mechanochemical synthesis (this work)			Solution synthesis				
Complex	E-factor	EMY	Time [min]	E-factor	EMY	Time [min]	Temp. [°C]	Ref.
[Pd(COD)Cl_2] (**1a**)	0.02 (A)[b]	98 (A)[b]	30 (A)[b]	194	0.51	60	r.t.	21
[Pd(COD)Br_2] (**1b**)	108	0.92	20	236	0.42	60	r.t.	21
[Pd(phen)$(OAc)_2$] (**2a**)	0.06	94	90	204	0.49	30	r.t.	49
[Pd(phen)Cl_2] (**2b**)	0 (A)	100 (A)	60 (A)	79	1.25	180	r.t.	50
[Pd(phen)Br_2] (**2c**)	78	1.26	90	261	0.38	180	100	51
[Pd(phen)I_2] (**2d**)	0	100	60	630	0.16	30	r.t.	52
[Pd(terpy)(OAc)](OAc) (**3a**)	54	1.83	120	—	—	—	—	—
[Pd(terpy)Cl]Cl (**3b**)	0 (A)	100 (A)	75 (A)	111	0.89	15	50	53 [c]
[Pd(terpy)Br]Br (**3c**)	67	1.46	90	—	—	—	—	—
[Pd(terpy)I]I (**3d**)	0.04	96	120	—	—	—	—	—
[Pd$(PPh_3)_2Cl_2$] (**4b**)	0.08 (A)	93	60 (A)	2.76	26	120	80	54
[Pd$(PPh_3)_2Br_2$] (**4c**)	62	1.58	60	21	4.45	240	180	55
[Pd$(PPh_3)_2I_2$] (**4d**)	90	1.09	120	20	4.78	240	180	54
[Pd(xantphos)Cl_2] (**5b**)	28 (B)	3.45 (B)	60 (B)	74	1.33	2880	110	56
[Pd(xantphos)Br_2] (**5c**)	124	0.80	60	2585	0.04	2400	r.t.	57
[Pd(dppm)Cl_2] (**6b**)	0 (A)	100 (A)	60 (A)	33	2.95	30	r.t.	58
[Pd(dppm)Br_2] (**6c**)	66	1.49	60	65	1.61	1440	r.t.	59
[Pd(dppm)I_2] (**6d**)	0	100	60	587	0.15	60	r.t.	60
[Pd(dppe)$(OAc)_2$] (**7a**)	0.02	98	30	46	2.12	—	r.t.	61
[Pd(dppe)Cl_2] (**7b**)	0 (A)	100 (A)	60 (A)	32	3.00	30	r.t.	58
[Pd(dppe)Br_2] (**7c**)	71	1.38	60	81	1.21	360	r.t.	62
[Pd(dppe)I_2] (**7d**)	0	100	60	471	0.21	—	r.t.	63
[Pd(dppp)Cl_2] (**8b**)	0 (A)	100 (A)	60 (A)	29	3.37	30	r.t.	58
[Pd(dppp)Br_2] (**8c**)	143	0.70	60	86	1.14	720	r.t.	64
[Pd(dppp)I_2] (**8d**)	0	100	60	362	0.28	30 + 60	40 + r.t.	65
[Pd(dppb)Cl_2] (**9b**)	0 (A)	100 (A)	60 (A)	89	1.11	120	70	66
[Pd(dppb)Br_2] (**9c**)	69	1.44	60	367	0.28	180	r.t.	67
[Pd(dppf)Cl_2] (**10b**)	0 (A)	100 (A)	60 (A)	23	4.21	60	r.t.	68
[Pd(dppf)Br_2] (**10c**)	58	1.70	60	20	4.70	60	r.t.	68
[Pd(dppf)I_2] (**10d**)	0	100	60	32	2.94	30	r.t.	68
[Pd(dippf)Cl_2] (**11b**)	66 (B)	1.41 (B)	60 (B)	4706	0.02	30 + 10 + 10	50, 20, −35	69
[Pd(dippf)Br_2] (**11c**)	69	1.48	60	—	—	—	—	—
[Pd(dippf)I_2] (**11d**)	0	100	60	—	—	—	—	—
[Pd((*R*)-BINAP)Cl_2] (**12b**)	50	1.97	90	77	1.29	600	r.t.	70
[Pd((*R*)-BINAP)Br_2] (**12c**)	54	1.83	90	77	1.29	960	r.t.	71
[Pd((*R*)-BINAP)I_2] (**12d**)	0	100	120	—	—	—	—	—

[a] Only the complexes obtained with good selectivity or that can be obtained pure with a few purification steps were evaluated. [b] (A) and (B) refer to the synthetic methods of chloride complexes, present in the experimental part. [c] The synthesis reported refers to the Pt(II) species. However, it is reported in many articles as a protocol also valid for the synthesis of the Pd(II) species.

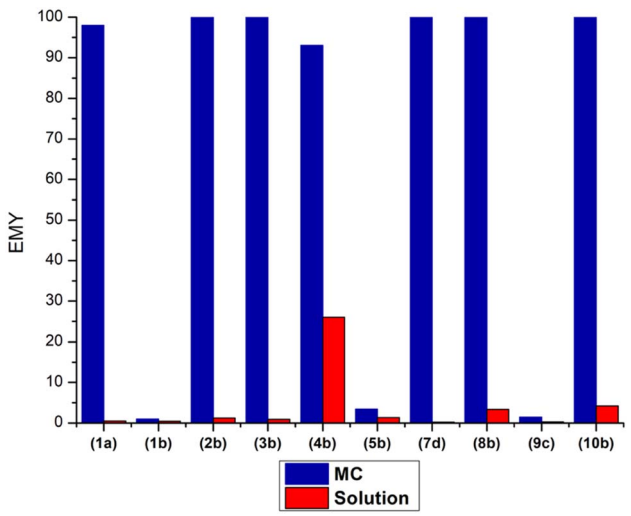


Fig. 6 Comparison of EMY in mechanochemistry and solution.

reflect the reality of solution-based procedures. The graph in Fig. 6 reports the EMY values of some palladium(II) complexes described above, showing how the mechanochemical approach is, where applied, more efficient in sustainability and efficiency. The selected and analyzed complexes are compounds that are predominantly recurring in scientific publications, with uses as precursors or catalysts.

The findings of this study suggest that, in most synthesized compounds, the mechanochemical method yielded optimal values. Conversely, solution processes documented in the extant literature yielded higher E-factors and lower EMY values. The findings demonstrate the enhanced sustainability of the mechanochemical approach in comparison to solution-phase methodologies. However, it should be noted that mechanochemistry cannot replace the solvothermal approach for all compounds, thus resulting in a complementary synthetic method to those already known in the literature, with

characteristics of efficiency and sustainability. In addition to the ecological benefits, mechanochemistry also offers certain practical advantages, such as the simplification of synthesis protocols. While solution protocols rarely achieve complete product yields, largely due to solvent management and purification losses, our mechanochemical protocols demonstrated complete conversions with short milling times in several cases. While the technique is not universally applicable, it has been demonstrated to be highly effective for a wide range of palladium(II) complexes.

4 Conclusion

A simple mechanochemical protocol was demonstrated, which enables highly efficient and rapid solid-state synthesis of several palladium(II) complexes. This is achieved without the use of bulk solvents, longer reaction times or reaction setups for synthesis under inert conditions.

It is possible to ascertain the optimal conditions for the Pd(II) precursors utilized by accurately adjusting the ligand/Pd precursor ratio, as well as the milling time and frequency. It is worth noting that most palladium complexes were obtained within 30 to 60 minutes, in good to high yields. In the majority of cases, the conversion was quantitative, and purification was not necessary (or, at the very least, a simple washing of a slight excess of ligand or a salt as a reaction co-product).

A gram-scale reaction under mechanochemical conditions was also demonstrated for the compound [Pd(COD)Cl_2] (**1a**), from Na_2[$PdCl_4$], thereby indicating that the mechanochemical approach can be a valuable addition to the commonly employed solvothermal method. The possibility of synthesizing widely used precursors, such as [Pd(COD)Cl_2] (**1a**) and [Pd(COD)Br_2] (**1b**), increases the potential that mechanochemistry offers to palladium(II) chemistry.

Palladium(II) complexes with phosphines as ligands and acetate as the anion have proven to be more difficult to characterize, despite a clean and almost quantitative reaction occurring in the solid state.

To provide a more comprehensive assessment of mechanochemistry with other solution-based approaches, a range of metrics were analyzed for the synthesized and isolated palladium(II) complexes. The parameters considered encompassed yield, reaction time, temperature for the solution approach and frequency for the mechanochemical way. In addition, two common green metrics were considered: the E-factor and the Effective Mass Yield (EMY) of conventional methodologies and mechanochemical synthesis. A comparison of the parameters clearly indicates that the mechanochemical approach is more sustainable, prompt and energy-efficient in the synthesis of palladium(II) compounds.

These findings imply that the present mechanochemistry method has the potential for wide application as an efficient, cost-effective, and sustainable synthesis technique for palladium(II) compounds, and it is reasonable to predict that rapid development will be observed in the coming years. These results open the prospect of an expansion of the mechanochemical syntheses of palladium(II) complexes, implementing new N- and P-donor ligands and carbenes.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: **https://doi.org/10.1039/d5mr00107b**.

Conflicts of interest

There are no conflicts to declare.

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