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Reactivity of palladacycles with phosphorus donor nucleophiles. The first crystal and molecular structure of a mixed-bridged acetate/phosphine dinuclear species

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ABSTRACT

Treatment of 2,4-(MeO)C_6H_3C(H)=N-[3,5-$Cl_2C_6H_3$] **1** with palladium(II) acetate in toluene at 60 °C under argon gave the dinuclear acetate-bridged palladacycle **2** as an air-stable solid. Reaction of **2** with the diphosphine $Ph_2PCH_2PPh_2$ (dppm) in 1:1 molar ratio and NH_4PF_6 yielded complex **3** where only one of the acetate ligands was exchanged by a diphosphine to give a mixed-bridged dinuclear palladacycle bearing charged and neutral linkers spanning between the metal centers, with the organic ligands in a *cis* fashion. The first crystal structure of one such complex, **3**, is now reported herein. This innovation highlights the unique ability of palladacycles to yield novel structures; more often than not, through a process of sheer serendipity. Complex **2** could be converted into the corresponding halide-bridged analogues by treatment in acetone with aqueous sodium chloride or sodium bromide to give the chloride-bridged **4**, or bromide-bridged **5**, compounds, respectively, as air-stable solids. The metallated moieties show a *trans* conformation of the Schiff base ligands, as opposed to the *cis* arrangement in **3**. Treatment of **4** and **5** with the small bite diphosphine $Ph_2PCH_2PPh_2$ in 1:1 ratio gave the dinuclear compounds **6** and **7**, likewise with two distinct bridging ligands; whereas the large bite diphosphine *trans*-$Ph_2PCH=CHPPh_2$ (*trans*-dppe) yielded **8** and **9** that are symmetric complexes across the C=C double bond as shown by the appearance of only one set of signals in the ^{1}H NMR spectrum, and by a singlet resonance in the ^{31}P-{^{1}H} spectrum for the two equivalent phosphorus nuclei. Reaction of **4** and **5** with $Ph_2PCH_2PPh_2$, $Ph_2P(CH_2)_2PPh_2$ (dppe) *cis*-$Ph_2PCH=CHPPh_2$ (*cis*-dppe), $Ph_2P(CH_2)_3PPh_2$ (dppp) or $Ph_2P(CH_2)_4PPh_2$ (dppb), and with PPh_3 in the appropriate molar ratio gave the complexes **10**-**19** as mono- or dinuclear species. All the compounds in this report were adequately characterized by microanalytical and spectroscopic measurements; the crystal molecular structures of **2**, **3**, **9** and **12** are reported.

1. Introduction

The most noticeable feature that distinguishes metallacycles is the covalent C-M bond, which was first achieved by Cope and Siekman by the reaction of aromatic azo compounds and potassium tetrachloroplatinate(II) or palladium chloride(II). [1] This milestone marked the starting point for cyclometallated compounds [2,3], which presently constitute an important branch of organometallic chemistry. In the specific case of palladium, the ensuing palladacycles [4] show considerable stability with the five- and six-membered metallacycle [5] rings being the most favoured, although studies in search for four-membered metallacycle rings [6] have recently appeared. They have numerous applications among which the following are noteworthy: metallomesogens [7,8], phosphorescent compounds [9-12], antineoplastic species [13-18], catalysts [19-23] inclusive of the Suzuki-Miyaura [24,25] and Mizoroki-Heck cross-coupling reactions [26,27], and organic synthesis intermediates [2,28]. One of the most suitable ligands for the preparation of palladacycles are the Schiff bases of variable denticity [C,N], [C,N,N], [C,N,S], [C,N:C,N] which are readily available and at times they can lead to unexpected, yet innovative reactivity. [29] The synthesis sequence usually begins with the preparation of the acetate-bridged complexes in solution, starting materials for a long series of palladacyles; notwithstanding, a ball mill mechanosynthesis method has been depicted. [30] One of the more pressing questions was to determine whether the acetate-bridged metallacycles were polymeric or dinuclear species, which was difficult to assert solely on the basis spectroscopic and microanalytical measurements, an issue that was settled with the advent of X-ray structural analysis, in favor of the dinuclear nature, at least in the solid state. [31] After a straightforward metathesis reaction with sodium chloride or bromide the subsequent halide-bridged dinuclear complexes are the starting point for a vast quantity and variety of products resulting from reactions with neutral and anionic nucleophiles, such as tertiary

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mono-, di-and triphosphines, and thallium acetylacetonate, respectively; in particular, the reactions with phosphorus donors may yield single- and dinuclear compounds with mono- or bidentate phosphines, as appropriate. Herein, we describe the synthesis, characterization and structural analysis (in part) of single and dinuclear palladacycles inclusive of mixed dinuclear μ-diphosphine/μ-acetate and μ-diphosphine/μ-halide complexes; the first molecular structural analysis of the former type is also given.

2. Materials and Methods

2.1. General procedures

Solvents were purified by standard methods. Chemicals palladium (II) acetate, 2,4-dimethoxybenzaldehyde, 3,5-dichloroaniline, ammonium hexafluorophosphate and the phosphines PPh_3, $Ph_2PCH_2PPh_2$ (dppm), $Ph_2PCH{=}CHPPh_2$ (*trans*- and *cis*-dppe), $Ph_2P(CH_2)_nPPh_2$, (n = 2, dppe, n = 3 dppp, n = 4 dppb) were used as supplied from commercial sources. Microanalyses were carried out at the Servicio de Análisis Elemental at the University of Santiago using a FISONS elemental analyzer, Model 1108. IR spectra were recorded as KBr pellets or polythene discs on ABB Bomen model MB102 (equipped with vacuum purge and with GOLDENGATE equipment for pure solid samples) and on JASCO FT/ IR-4600 (equipped with an ATR, model ATR-PRO ONE) spectrophotometers. NMR spectra were obtained as $CDCl_3$, DMSO-d_6 or Me_2CO-d_6 solutions as appropriate and referenced to $SiMe_4$ (^1H) or 85 % H_3PO_4 (^{31}P–{^1H}) and were recorded on BRUKER DPX 250 and Varian Inova 400 spectrometers. All chemical shifts, in ppm, were reported downfield from the standards.

2.2. Synthesis

Preparation of the ligand

2,4-$(MeO)_2C_6H_3C(H)$=N(3,5-$Cl_2C_6H_3$) 1. The aldehyde 2,4-dimethoxybenzaldehyde (1.0 g, 4.366 mmol) and 3,5-dichlorobenzenamine (450 mg, 4.537 mmol) were added together in chloroform (*ca.* 40 cm^3) in a round-bottom flask to give a yellow solution which was refluxed in a modified Dean-Stark apparatus for 8 h, after which the resulting solution was cooled to room temperature and the solvent was removed under reduced pressure. Yield 866.7 mg 64 %. Anal. Calc. for $C_{15}H_{13}Cl_2NO_2$ (310.18): C, 58.1, H, 4.2, N, 4.5 %. Found: C, 57.9, H, 4.4, N, 4.6 %. IR (cm^{-1}): ν(C=N): 1617 m sh. ^1H NMR ($CDCl_3$, δ ppm, J Hz): 3.87 (s, 3H, MeO); 3.88 (s, 3H, MeO); 6,46 (d, 1H, H3, ^3J(H3H5) = 2.2); 6.58 (dd, 1H, H5, ^3J(H5H6) = 8.8, ^4J(H3H5) = 2.2); 7,06 (d, 2H, H8, H12, ^4J(H8H10) = ^4J(H10H12) = 1.8); 7.16 (t, 1H, H10, ^4J(H8H10) = ^4J(H10H12) = 1.8): 8.05 (d, 1H, H6, ^{3}JH5H6) = 8.8; 8.73 (s, 1H, HC=N); ^{13}C–{^1H} NMR: 164.6 (C=N); 157.7 (C7); 161.6, 155.4 (C2, C4); 135.3 (C1); 129.5 (C6); 125.1 (C5); 120.0 (C3); 113.4 (C9, C11); 106.2 (C10); 98.2 (C8, C12); 55.8, 55.7 (MeO).

Preparation of the complexes

[Pd{2,4-$(MeO)_2C_6H_2C(H)$=N(3,5-$Cl_2C_6H_3$)}(μ-O_2CMe)]$_2$ 2. A mixture of 2,4-$(MeO)_2C_6H_3C(H)$=N(3,5-$Cl_2C_6H_3$) (552 mg, 1.778 mmol) and palladium(II) acetate (400 mg, 1.782 mmol) in toluene (40 cm^3) was stirred for 12 h at 60 ºC under argon. After cooling to room temperature, the precipitate was filtered off and the solid residue was chromatographed on a column packed with silica gel. Elution with a mixture of CH_2Cl_2:EtOH (97:3, *v/v*) afforded the final product which after concentration, was recrystallized from chloroform/n-hexane to give an orange solid. Yield 802 mg 95 %. Anal. Calc. for $C_{34}H_{30}Cl_4N_2O_8Pd_2$ (949.26): C, 43.0, H, 3.2, N, 2.9 %. Found: C, 42.9, H, 3.3, N, 2.7 % IR (cm^{-1}): ν (C=N): 1593 m sh; ν_{as} (COO): 1563 s; ν_s(COO): 1412 s. ^1H NMR ($CDCl_3$, δ ppm, J Hz): 2.06 (s, 6H, $MeCO_2$); 3.63 (s, 6H, MeO); 3.84 (s, 6H, MeO); 5.65 (d, 2H, H3, ^4J(H3H5) = 1.9); 6.05 (d, 2H, H5, ^4J(H3H5) = 1.9); 6.87 (d, 4H, H8, H12, ^4J(H8H10) = ^4J(H10H12) = 1.8); 7.09 (t, 2H, H10, ^4J(H8H10) = ^4J(H10H12) = 1.8); 7.96 (s, 2H, HC=N). ^{13}C–{^1H} NMR: 180.8 ($MeCO_2$); 168.7 (C=N); 160.3 (C7); 160.3, 160.3 (C2, C4); 134.2 (C1); 150.4 (C6); 126.2 (C5); 121.8 (C3), 126.6 (C9, C11); 108.3 (C10); 95.3 (C8, C12); 55.6, 55.4 (MeO); 24.4 ($MeCO_2$).

[{Pd[2,4-$(MeO)_2C_6H_2C(H)$=N-(3,5-$Cl_2C_6H_3$)]}$_2$(μ-$Ph_2PCH_2PPh_2$)(μ-O_2CMe)][PF_6] 3. $Ph_2PCH_2PPh_2$ (dppm) (8.7 mg, 0.023 mmol) was added to a suspension of **2** (22.0 mg, 0.023 mmol) in acetone (*ca*. 25 cm^3). The mixture was stirred for 2 h at room temperature and then NH_4PF_6 (3.8 mg, 0.023 mmol) was added. The mixture was stirred for a further 24 h at room temperature after which the solution was filtered off and after concentration the residue was chromatographed on a column packed with silica gel. Elution with a mixture of CH_2Cl_2:EtOH (97:2, *v/v*) afforded the final product which after concentration, was recrystallized from chloroform/n-hexane to give a brown solid. Yield 31.9 mg 97.8 %. Anal. Calc. for $C_{57}H_{49}Cl_4F_6N_2O_6P_3Pd_2$ (1419.53): C, 48.2, H, 3.5, N, 2.0 %. Found: C, 48.1, H, 3.7, N, 1.7 %. IR (cm^{-1}): ν(C=N): 1586 m, ν_{as}(COO), 1561 s; ν_s(COO), 1424 s; ν_{as}(PF) = 834 vs, ν_{as}(PF2) = 556 m. ^1H NMR ($CDCl_3$, δ ppm, J Hz): 2.18 (s, 3H, $MeCO_2$); 3.00 (s, 6H, MeO); 3.76 (s, 6H, MeO); 5.32 (m, 2H, PCH_2P); 5.39 (dd, 2H, H5, ^4J(H3H5) = 1.9, ^4J(H5P) = 7.2); 5.96 (d, 2H, H3, ^4J(H3H5) = 1.9; 6.98 (d, 4H, H8, H12, ^4J(H8H10) = ^4J(H10H12) = 1.8); 7.25 (t, 2H, H10, ^4J(H8H10) = ^4J(H10H12) = 1.8); 8.64 (s, 2H, HC=N). ^{31}P-{^1H} NMR (CDCl3, δ ppm, J Hz): 30.81 (s, 2P). Specific molar conductivity Λ_M = 176 Ω^{-1} cm^2 mol^{-1}.

[Pd{2,4-$(MeO)_2C_6H_2C(H)$=N(3,5-$Cl_2C_6H_3$)}(μ-Cl)]$_2$ 4. An aqueous solution of NaCl (*ca.* 10^{-2} M) was added dropwise to a solution of **2** (670 mg, 0.723 mmol) in acetone (25 cm^3) and the mixture was stirred for 24 h at 40 ºC, after which time complex **4** precipitated out as an orange solid, which was filtered off and dried *in vacuo* over P_2O_5. Yield 442.8 mg 67,89 %. Anal. Calc. for $C_{30}H_{24}Cl_6N_2O_4Pd_2$ (902.08): C, 39.9, H, 2.7, N, 3.1 %. Found: C, 39.7, H, 2.9, N, 3.3 %. IR (cm^{-1}): ν(C=N): 1591 m; ν(Pd-Cl): 312, 268 m. ^1H NMR (d_6-DMSO, d ppm, J Hz): 3.88 (s, 6H, MeO); 3.91 (s, 6H, MeO); 6.25 (d, 2H, H3); 7.01 (d, 2H, H5); 1.8); 8.30 (s, 2H, HC=N).

[Pd{2,4-$(MeO)_2C_6H_2C(H)$=N(3,5-$Cl_2C_6H_3$)}(μ-Br)]$_2$ 5. An aqueous solution of NaBr (*ca.* 10^{-2} M) was added dropwise to a solution of **2** (165 mg, 0.174 mmol) in acetone (25 cm^3) and the mixture was stirred for 24 h at 40 ºC, after which time complex **5**

precipitated out as an orange solid, which was filtered off and dried *in vacuo* over P_2O_5. Yield 163.8 mg 95 %. Anal. Calc. for $C_{30}H_{24}Br_2Cl_4N_2O_4Pd_2$ (990.97): C, 36.4, H, 2.4, N, 2.8 %. Found: C, 36.6, H, 2.4, N, 2.6 %. IR (cm^{-1}): ν(C=N): 1590 m; ν(Pd-Br): 183, 172 m. ^{1}H NMR (d_6-DMSO, δ ppm, J Hz): 3.77 (s, 6H, MeO); 3.78 (s, 6H, MeO); 6.46 (d, 2H, H3, ^{3}J(H3H5) = 1.4); 7.09 (d, 2H, H5, ^{4}J (H3H5) = 1.4); 7.38 (d, 4H, H8, H12, ^{4}J(H8H10) = ^{4}J(H10H12) = 1.8); 7.47 (t, 2H, H10, ^{4}J(H8H10) = ^{4}J(H10H12) = 1.8); 8.30 (s, 2H, HC=N).

[{Pd[2,4-(MeO)$_2$C$_6$H$_2$C(H)=N-(3,5-Cl$_2$C$_6$H$_3$)]}$_2$(μ-Cl)(μ-Ph$_2$PCH$_2$PPh$_2$)]Cl 6. To a stirred suspension of compound **4** (50.0 mg, 0.053 mmol) in acetone (*ca.* 25 cm^3), $Ph_2PCH_2PPh_2$ (dppm) (21.0 mg, 0.053 mmol) was added. The mixture was stirred for 24 h at room temperature. The resulting yellow precipitate was filtered off and dried *in vacuo*. Yield 58.4 mg 85.6 %. Anal. Calc. for $C_{55}H_{46}Cl_6N_2O_4P_2Pd_2$ (1286.47): C, 51.4, H, 3.6, N 2.2 %. Found: C, 50.9, H 3.3, N, 2.6 %. IR (cm^{-1}): ν(C=N): 1586 m; ν(Pd-Cl): 291 m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 2,98 (s, 6H, MeO); 3.73 (s, 6H, MeO); 4.30 (t, 2H, PCH_2P, ^{2}J(PH) =11.5; 5,35 (dd, 2H, H5, ^{4}J (H3H5) = 1.9, ^{4}J(H5P) = 6.6); 5,91 (d, 2H, H3, ^{4}J(H3H5) = 1.9); 7,00 (d, 4H, H8, H12, ^{4}J(H8H10) = ^{4}J(H10H12) = 1.8); 7,21 (t, 2H, H10); 8.45 (d, 2H, HC=N, ^{4}J(H5P) = 7.1). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ ppm, J Hz): 31,9 (s, 2P). Specific molar conductivity Λ_M = 146 Ω^{-1} cm^2 mol^{-1}.

[{Pd[2,4-(MeO)$_2$C$_6$H$_2$C(H)=N-(3,5-Cl$_2$C$_6$H$_3$)]}(μ-Br)(μ-Ph$_2$PCH$_2$PPh$_2$)]Br 7. To a stirred suspension of compound **5** (60.0 mg, 0.062 mmol) in acetone (*ca.* 25 cm^3), $Ph_2PCH_2PPh_2$ (dppm) (24.0 mg, 0.062 mmol) was added. The mixture was stirred for 24 h at room temperature. The resulting yellow precipitate was filtered off and dried *in vacuo*. Yield 69.7 mg 81.7 %. Anal. Calc. for $C_{55}H_{46}Br_2Cl_4N_2O_4P_2Pd_2$ (1375.37): C, 48.0, H, 3.4, N, 2.0 %. Found: C, 48.0, H, 2.3, N, 3.5 %. IR (cm^{-1}): ν(C=N): 1588 m; ν(Pd-Br): 177 m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 2,98 (s, 6H, MeO); 3.73 (s, 6H, MeO); 5.03 (t, 2H, PCH_2P, ^{2}J(PH)=11.5; 5,38 (dd, 2H, H5, ^{4}J(H3H5) = 1.8, ^{4}J(H5P) = 7.1); 5,91 (d, 2H, H3, ^{4}J(H3H5) = 1.8); 7,00 (d, 4H, H8, H12, ^{4}J(H8H10) = ^{4}J(H10H12) = 1.8); 7,24 (t, 2H, H10); 8.14 (d, 2H, HC=N, ^{4}J(H5P) = 6.6). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ ppm, J Hz): 26,0 (s, 2P). Specific molar conductivity Λ_M = 170 Ω^{-1} cm^2 mol^{-1}.

[{Pd[2,4-(MeO)$_2$C$_6$H$_2$C(H)=N-(3,5-Cl$_2$C$_6$H$_3$)]}$_2$(μ-*trans*-Ph$_2$PCH=CHPPh$_2$)(Cl$_2$)] 8. To a stirred suspension of **4** (27.0 mg, 0.020 mmol) in acetone (*ca.* 25 cm^3), *trans*-$Ph_2PCH=CHPPh_2$ (*trans*-dppe) (8.1 mg, 0.020 mmol) was added. The mixture was stirred for 24 h at room temperature. The resulting yellow precipitate was filtered off and dried *in vacuo*. Yield 20.1 mg 77.3 %. Anal. Calc. for $C_{56}H_{46}Cl_6N_2O_4P_2Pd_2$ (1298.48): C, 51.8, H, 3.6, N, 2.2. Found: C, 48.5, H, 3.2, N, 2.2. IR (cm^{-1}): ν(C=N): 1611 m; ν(Pd-Cl): 291 m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 2.88 (s, 6H, MeO); 3.73 (s, 6H, MeO); 5,59 (br, 2H, H5); 5,93 (d, 2H, H3, ^{4}J(H3H5) = 1.8); 6.51 (m, 2H, PCH=CHP); 7,20 (s, 4H, H8, H12); 8.50 (d, 2H, HC=N); ^{4}J (H5P) = 7.0). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ ppm, J Hz): 37,5 (s, 2P).

[{Pd[2,4-(MeO)$_2$C$_6$H$_2$C(H)=N-(3,5-Cl$_2$C$_6$H$_3$)]}$_2$(μ-*trans*-Ph$_2$PCH=CHPPh$_2$)(Br$_2$)] 9. To a stirred suspension of **4** (27.0 mg, 0.027 mmol) in acetone (*ca.* 25 cm^3), *trans*-$Ph_2PCH=CHPPh_2$ (*trans*-dppe) (11 mg, 0.028 mmol) was added. The mixture was stirred for 24 h at room temperature. The resulting yellow precipitate was filtered off and dried *in vacuo*. Yield 34.7 mg 89.4 %. Anal. Calc. for $C_{56}H_{46}Br_2Cl_4N_2O_4P_2Pd_2$ (1387.38): C, 48.5, H, 3.3, N, 2.0. Found: C, 48.5, H, 3.2, N, 2.2. IR (cm^{-1}): ν(C=N): 1612 m; ν(Pd-Br): 176 m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 2.89 (s, 6H, MeO); 3.73 (s, 6H, MeO); 5,61 (br, 2H, H5); 5,93 (d, 2H, H3, ^{4}J(H3H5) = 1.7); 6.54 (m, 2H, PCH=CHP); 7,24 (s, 4H, H8, H12); 8.48 (br, 2H, HC=N). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ ppm, J Hz): 39,3 (s, 2P).

[Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(3,5-Cl$_2$C$_6$H$_3$)}(Cl)(PPh$_3$)] 10. To a stirred suspension of **4** (50.0 mg, 0.055 mmol) in acetone (*ca.* 25 cm^3), PPh_3 (29.0 mg, 0.111 mmol) was added. The mixture was stirred for 24 h at room temperature and after which the solution was filtered off and after concentration afforded the final product which was recrystallized from chloroform/n-hexane. The resulting orange precipitate was filtered off and dried *in vacuo*. Yield 42.7 mg 54 %. Anal. Calc. for $C_{33}H_{27}Cl_3NO_2PPd$ (713.33): C, 55.6, H, 3.8, N, 2.0 %. Found: C, 55.6, H, 3.5, N, 2.2 %. IR (cm^{-1}): ν(C=N): 1585 m sh; ν(Pd-Cl): 294 m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 3.76 (s, 3H, MeO); 2.94 (s, 3H, MeO); 5,67 (dd, ^{1}H, H5, ^{4}J(H3H5) = 1.8, ^{4}J(H5P) = 6.7); 5,96 (d, 1H, H3, ^{4}J(H3H5) = 1.8); 7,18 (t, 1H, H10, ^{4}J (H8H10) = ^{4}J(H10H12) = 1.9); 7,27 (d, 2H, H8, H12, ^{4}J(H8H10) = ^{4}J(H10H12) = 1.9); 8.52 (d, 1H, HC=N, ^{4}J(HP) = 7.0); ^{31}P-{^{1}H} NMR ($CDCl_3$, δ ppm, J Hz): 23.78 (s, 1P).

[Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(3,5-Cl$_2$C$_6$H$_3$)}(Br)(PPh$_3$)] 11. To a stirred suspension of **5** (29.0 mg, 0.029 mmol) in acetone (*ca.* 25 cm^3), PPh_3 (15.0 mg, 0.057 mmol) was added. The mixture was stirred for 24 h at room temperature and after which the solution was filtered off and after concentration afforded the final product which was recrystallized from chloroform/n-hexane. The resulting orange precipitate was filtered off and dried *in vacuo*. Yield 40.9 mg 93 %. Anal. Calc. for $C_{33}H_{27}BrCl_2NO_2PPd$ (757.78): C, 52.3, H, 3.6, N, 1.8 %. Found: C, 52.1, H, 3.6, N, 1.8 %. IR (cm^{-1}): ν(C=N): 1584 m sh; ν(Pd-Br): 204 m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 3.76 (s, 3H, MeO); 2.94 (s, 3H, MeO); 5,64 (dd, 1H, H5, ^{4}J(H3H5) = 2.0, ^{4}J (H5P) = 6.9); 5,96 (d, 1H, H3, ^{4}J(H3H5) = 2.0); 7,18 (t, 1H, H10, ^{4}J (H8H10) = ^{4}J(H10H12) = 1.8); 7,25 (d, 2H, H8, H12, ^{4}J(H8H10) = ^{4}J(H10H12) = 1.8); 8.53 (d, 1H, HC=N, ^{4}J(HP) = 7.0). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ ppm, J Hz): 44.57 (s, 1P).

[Pd{2,4-(MeO)$_2$C$_6$H$_2$C(H)=N(3,5-Cl$_2$C$_6$H$_3$)}(Br)(PPh$_3$)$_2$] 12. Compound **12** was prepared analogously from **5** (30.0 mg, 0.031 mmol) and PPh_3 (40.0 mg, 0.124 mmol). Yield 65.9 mg 52.1 %. Anal. Calc. for $C_{51}H_{42}BrCl_2NO_2P_2Pd$ (1020.06): C, 60.1, H, 4.2, N, 1.4. Found: C, 60.1, H, 4.3, N, 1.4 %. IR (cm^{-1}): ν(C=N): 1556 m; ν (Pd-Br) 203 m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 3.76 (s, 3H, MeO); 2.94 (s, 3H, MeO); 5,65 (d, 1H, H5, ^{4}J(H3H5) = 1.9); 5,96 (d, 1H, H3, ^{4}J(H3H5) = 1.9); 8.53 (s, 1H, HC=N); 7,25 (d, 2H, H8, H12, ^{4}J (H8H10) = ^{4}J(H10H12) = 1.8); 7,18 (t, 1H, H10, ^{4}J(H8H10) = ^{4}J (H10H12) = 1.9);. ^{31}P-{^{1}H} NMR ($CDCl_3$, δ ppm, J Hz): 23.66 (s, P).

[{Pd[2,4-(MeO)$_2$C$_6$H$_2$C(H)=N-(3,5-Cl$_2$C$_6$H$_3$)]}$_2$(μ-Ph$_2$P(CH$_2$)$_3$PPh$_2$)(Cl$_2$)] 13. To a stirred suspension of **4** (39.0 mg, 0.045 mmol)

in acetone (*ca.* 25 cm^3), $Ph_2P(CH_2)_3PPh_2$ (dppp) (22 mg, 0.045 mmol) was added. The mixture was stirred for 24 h at room temperature. The resulting orange precipitate was filtered off and dried *in vacuo*. Yield 20.1 mg 78.3 %. Anal. Calc. for $C_{57}H_{50}Cl_6N_2O_4P_2Pd_2$ (1314.52): C, 52.1, H, 3.8, N, 2.1 %. Found: C, 52.5, H, 3.7, N, 2.2 %. IR (cm^{-1}): ν(C=N): 1585 m sh; u(Pd-Cl) 287 m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 3.00 (s, 6H, MeO); 3.75 (s, 6H, MeO); 5,68 (dd, 2H, H5, ^{4}J(H3H5) = 1.9, ^{4}J(H5P) = 6.7); 5,66 (d, 2H, H3, ^{4}J(H3H5) = 1.9); 7,27 (br, 4H, H8, H12); 8.45 (d, 2H, HC=N); ^{4}J(H5P) = 6.8). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ ppm, J Hz): 36,5 (s, 2P).

[{Pd[2,4-$(MeO)_2C_6H_2C(H)$=N-(3,5-$Cl_2C_6H_3$)]}$_2$(μ-$Ph_2P(CH_2)_3PPh_2$)(Br_2)] 14. The diphosphine dppp (7.0 mg, 0.017 mmol) was added to a suspension of **5** (17.0 mg, 0.017 mmol) in acetone (*ca.* 25 cm^3). The mixture was stirred for 24 h at room temperature after which the solution was filtered off and after concentration was recrystallized from acetone/n-hexane to give a yellow solid witch was filtered off and dried *in vacuo*. Yield 20.1 mg 84.1 %Anal. Calc. for $C_{57}H_{50}Br_2Cl_4N_2O_4P_2Pd_2$ (1403.42): C, 48.8, H, 3.6, N, 2.0. Found: C, 49.1, H, 3.3, N, 2.0 %. IR (cm^{-1}): ν(C=N): 1588 m; ν(Pd-Br): 201 m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 3.74 (s, 6H, MeO); 2.98 (s, 6H, MeO) 5,65 (dd, 2H, H5, ^{4}J(H3H5) = 1.9, ^{4}J(H5P) = 6.3); 5,94 (d, 2H, H3, ^{4}J(H3H5) = 1.9); 7,18 (d, 4H, H8, H12, ^{4}J(H8H10) = ^{4}J(H10H12) = 1.9); 7,25 (t, 2H, H10, ^{4}J(H8H10) = ^{4}J(H10H12) = 1.9); 8.44 (d, 2H, HC=N, ^{4}J(H5P) = 6.7). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ ppm, J Hz): 35,9 (s, 2P).

[Pd{2,4-$(MeO)_2C_6H_2C(H)$=N-(3,5-$Cl_2C_6H_3$)}$_2$(μ-$Ph_2P(CH_2)_4PPh_2$)(Cl_2)] 15. To a stirred suspension of **4** (50.0 mg, 0.055 mmol) in acetone (*ca.* 25 cm^3), $Ph_2P(CH_2)_3PPh_2$ (dppb) (24 mg, 0.056 mmol) was added. The mixture was stirred for 24 h at room temperature. The resulting yellow precipitate was filtered off and dried *in vacuo*. Yield 49.6 mg 67.0 %. Anal. Calc. for $C_{58}H_{52}Cl_6N_2O_4P_2Pd_2$ (1328.55): C, 52.4, H, 4.0, N, 2.1 %. Found: C, 52.1, H, 3.7, N, 2.1 %. IR (cm^{-1}): ν(C=N): 1611 w; ν(Pd-Cl) 293: m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 3.00 (s, 6H, MeO); 3.74 (s, 6H, MeO); 5,69 (br, 2H, H5); 5,95 (br, 2H, H3); 6,55 (d, 4H, H8, H12, ^{4}J(H8H10) = ^{4}J(H10H12) = 1.8); 6,73 (t, 2H, H10, ^{4}J(H8H10) = ^{4}J(H10H12) = 1.9); 8.47 (br, 2H, HC=N); ^{31}P-{^{1}H} NMR ($CDCl_3$, d ppm, J Hz): 33,1 (s, 2P).

[Pd{2,4-$(MeO)_2C_6H_2C(H)$=N-(3,5-$Cl_2C_6H_3$)}($Ph_2PCH_2CH_2$)PPh_2-P,P)][PF_6] 16. $Ph_2PCH_2CH_2PPh_2$ (dppe) (45.0 mg, 0.112 mmol) was added to a suspension of **4** (50.0 mg, 0.055 mmol) in acetone (*ca.* 25 cm^3). The mixture was stirred for 2 h at room temperature and then NH_4PF_6 (6.9 mg, 0.042 mmol) was added. The mixture was stirred for a further 20 h at room temperature after which the solution was filtered off and after concentration was recrystallized from chloroform/n-hexane to give a yellow solid witch was filtered off and dried *in vacuo*. Yield 80.0 mg 81.2 %. Anal. Calc. for $C_{41}H_{36}Cl_2F_6NO_2P_3Pd$ (958.97): C, 51.4, H, 3.8, N, 1.5 %. Found: C, 51.7, H, 3.6, N, 1.4 %. IR (cm^{-1}): ν(C=N): 1585 m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 3.20 (s, 3H, MeO); 3.78 (s, 3H, MeO); 5,88 (ddd, 1H, H5, ^{4}J(H3H5) = 2.0, ^{4}J(H5Pc) = 5.8, ^{4}J(H5Pt) = 8.2); 6,08 (d, 1H, H3, ^{4}J(H3H5) = 2.0); 6,61 (d, 2H, H8, H12, ^{4}J(H8H10) = ^{4}J(H10H12) = 1.8); 6,86 (t, 1H, H10, ^{4}J(H8H10) = ^{4}J(H10H12) = 1.8); 8.36 (dd, 1H, HC=N, ^{4}J(HPc) = 1.8, ^{4}J(H5Pt) = 6.9). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ ppm, J Hz): 45.6 (d, 1P, J(PP) = 27.6); 63.1 (d, 1P, J(PP) = 27.6). Specific molar conductivity Λ_M = 230 Ω^{-1} cm^2 mol^{-1}.

[Pd{2,4-$(MeO)_2C_6H_2C(H)$=N-(3,5-$Cl_2C_6H_3$)}($Ph_2P(CH_2)_4PPh_2$-*P,P*)][PF_6] 17. Compound **17** was prepared similarly from **4** (50.0 mg, 0.055 mmol) and dppb (48.0 mg, 0.112 mmol). Yield 97.0 mg 81.2 %. Anal. Calc. for $C_{43}H_{40}Cl_2F_6NO_2P_3Pd$ (987.02): C, 52.3, H, 4.1, N, 1.4 %. Found: C, 51.9, H, 4.3, N, 1.6 %. IR (cm^{-1}): ν(C=N): 1591 d. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 3.11 (s, 3H, MeO); 3.75 (s, 3H, MeO); 5,80 (ddd, 1H, H5, ^{4}J(H3H5) = 1.9, ^{4}J(H5Pc) = 6.2, ^{4}J(H5Pt) = 8.9); 6,02 (d, 1H, H3, ^{4}J(H3H5) = 1.9); 6,29 (d, 2H, H8, H12, ^{4}J(H8H10) = ^{4}J(H10H12) = 1.8); 6,83 (t, 1H, H10, ^{4}J(H8H10) = ^{4}J(H10H12) = 1.8; 8.23 (dd, 1H, HC=N, ^{4}J(HPc) = 1.1, ^{4}J(H5Pt) = 6.6)). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ ppm, J Hz): 0.5 (d, 1P, J(PP) = 57.2); 27.3 (d, 1P, J(PP) = 57.2). Specific molar conductivity Λ_M = 176 Ω^{-1} cm^2 mol^{-1}.

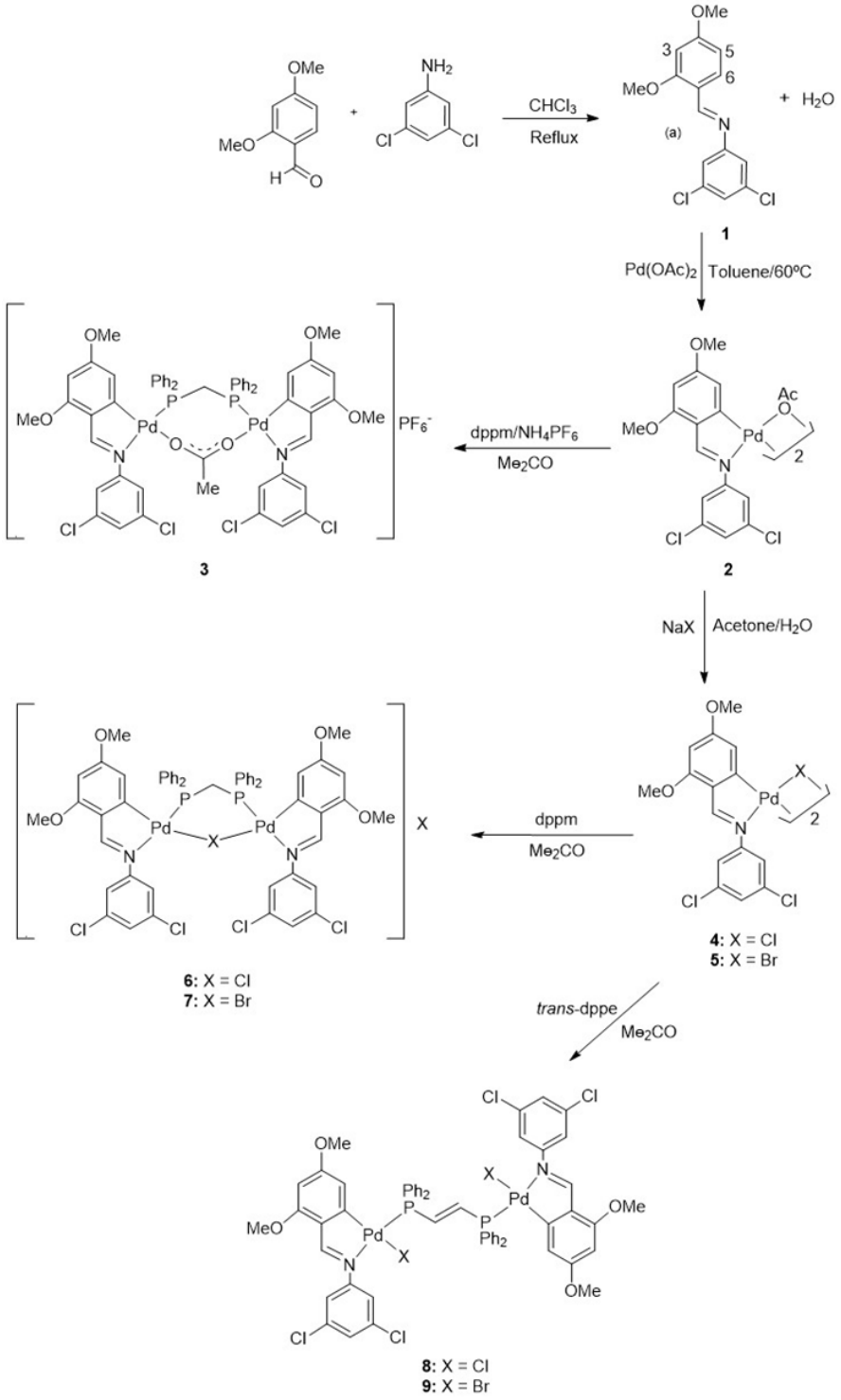
[Pd{2,4-$(MeO)_2C_6H_2C(H)$=N-(3,5-$Cl_2C_6H_3$)}($Ph_2PCH_2PPh_2$-*P,P*)][PF_6] 18. Compound **18** was prepared similarly to from $Ph_2PCH_2PPh_2$ (32.0 mg, 0.083 mmol) and **5** (42.0 mg, 0.042 mmol). Yield 39.2 mg 97.5 %. Anal. Calc. for $C_{40}H_{34}Cl_2F_6NO_2P_3Pd$ (944.94): C, 50.8, H, 3.6, N, 1.5 %. Found: C, 50.9, H, 3.3, N, 1.8 %. IR (cm^{-1}): ν(C=N): 1591 m. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 3.22 (s, 3H, MeO); 3.76 (s, 3H, MeO); 4.18 (dd, 2H, PCH_2P, ^{2}J(HP) = 11.3, ^{2}J(HP) = 8.7); 5,79 (ddd, 1H, H5, ^{4}J(H3H5) = 2.0, ^{4}J(H5Pc) = 8.3, ^{4}J(H5Pt) = 9.9); 6,03 (d, 1H, H3, ^{4}J(H3H5) = 2.0); 8.38 (d, 1H, HC=N, ^{4}J(HP) = 5.5); 6,91 (d, 2H, H8, H12, ^{4}J(H8H10) = ^{4}J(H10H12) = 1.9); 7,01 (t, 1H, H10, ^{4}J(H8H10) = ^{4}J(H10H12) = 1.9). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ ppm, J Hz): -8.4 (d, 1P, J(PP) = 68.3); -32.5 (d, 1P, J(PP) = 68.3). Specific molar conductivity Λ_M = 123 Ω^{-1} cm^2 mol^{-1}.

[Pd{2,4-$(MeO)_2C_6H_2C(H)$=N-(3,5-$Cl_2C_6H_3$)}$_2$(*cis*-Ph_2PCH=$CHPPh_2$-*P,P*)][Br] 19. *cis*-Ph_2PCH=$CHPPh_2$ (40.0 mg, 0.101 mmol) was added to a suspension of **5** (50.0 mg, 0.050 mmol) in acetone (*ca.* 25 cm^3). The mixture was stirred for 22 h at room temperature after which the solution was filtered off and after concentration was recrystallized from chloroform/n-hexane to give a yellow solid witch was filtered off and dried *in vacuo*. Yield 68.3 mg 76.6 %. Anal. Calc. for $C_{41}H_{34}BrCl_2NO_2P_2Pd$ (891.89): C, 55.2, H, 3.8, N, 1.6 %. Found: C, 55.6, H, 3.5, N, 1.5 %. IR (cm^{-1}): ν(C=N): 1608 w. ^{1}H NMR ($CDCl_3$, δ ppm, J Hz): 3.41 (s, 3H, MeO); 3.71 (s, 3H, MeO); 6,50 (ddd, 1H, H5, ^{4}J(H3H5) = 2.0, ^{4}J(H5Pc) = 4.7, ^{4}J(H5Pt) = 7.9); 6,03 (d, 1H, H3, ^{4}J(H3H5) = 2.0); 6,29 (d, 2H, H8, H12, ^{4}J(H8H10) = ^{4}J(H10H12) = 1.8); 6,90 (t, 1H, H10, ^{4}J(H8H10) = ^{4}J(H10H12) = 1.8); 8.13 (d, 1H, HC=N, ^{4}J(HP) = 1.4). ^{31}P-{^{1}H} NMR ($CDCl_3$, δ ppm, J Hz): 51.2 (d, 1P, J(PP) = 16.7); 59.5 (d,1P, J (PP) = 16.7) Specific molar conductivity Λ_M = 163 Ω^{-1} cm^2 mol^{-1}.

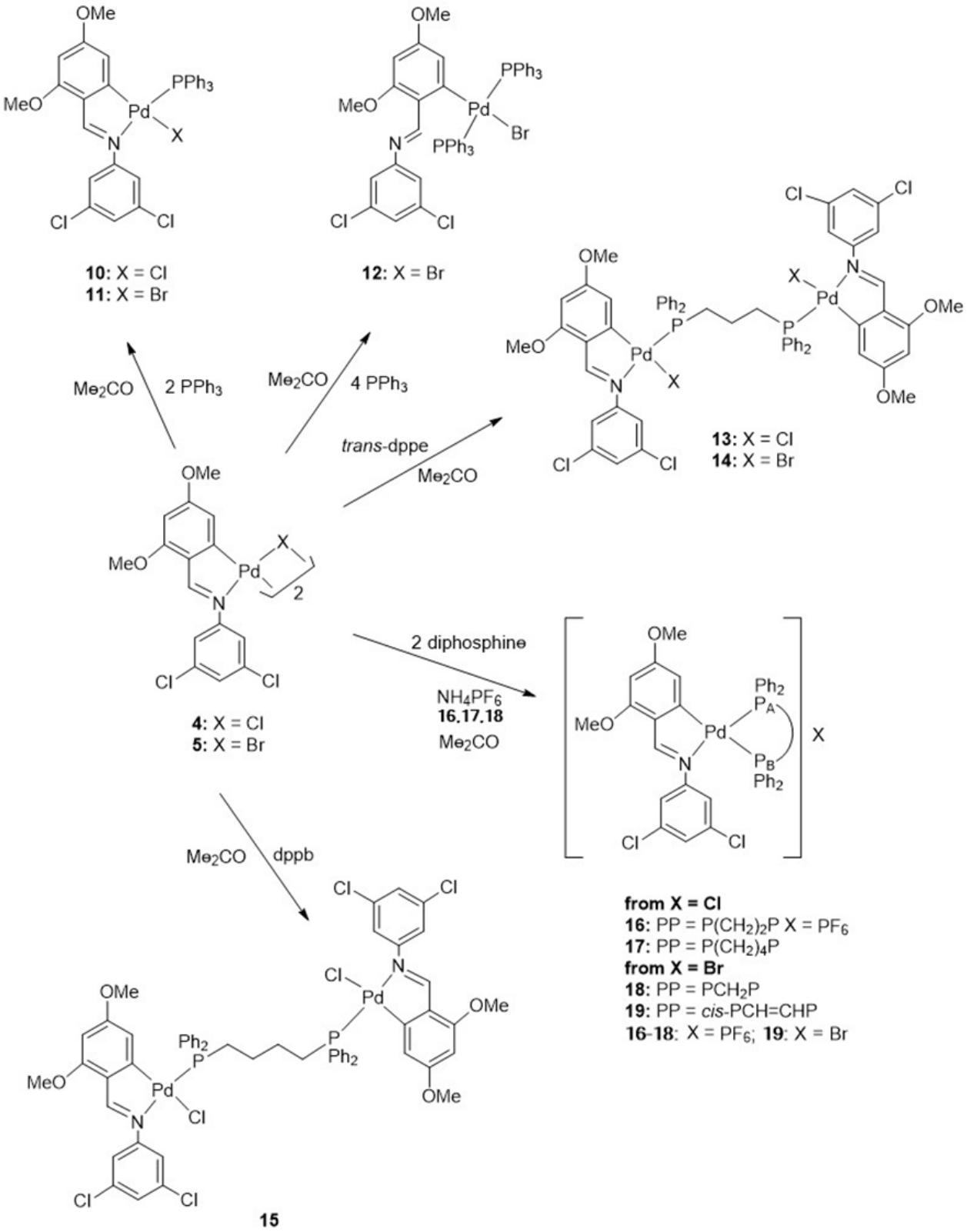
3. Results and Discussion

The complexes and reaction patterns are shown in **Schemes 1** and **2**. The compounds described in this paper were characterized by microanalytical measurements (C, H, N; the error being an absolute

0.3 %) by IR and by ^{1}H and ^{31}P-{^{1}H} NMR spectroscopy, and (in part) by X-ray diffraction analysis; crystallographic data are in **Table 1**. Treatment of the ligand **1** with palladium(II) acetate in toluene at 60 °C for 12 h and work up of the mixture gave complex **2** as an orange solid (see Experimental). The IR spectrum showed the band for the ν (C=N) stretch at lower frequency than in the ligand spectrum [32] and an up-field shift of the *H*C=N the resonance in the ^{1}H NMR spectrum; these data concur with Pd-N bond formation. [33] The ν_{as}(COO) and ν_{s}(COO) values were in agreement with bridging acetate groups; [34] the proton NMR spectrum showed a singlet resonance *ca.* 2.00 ppm (6H) which was ascribed to the equivalent methyl acetate protons, reflecting a *trans* geometry of the cyclometallated moieties, and absence of the H6 resonance consequent upon metallation of the ligand.



Scheme 1 | Reaction sequence leading to the syntheses of the compounds **2-9**.



Scheme 2 | Reactivity of the dinuclear halide-bridged complexes.

Table 1 | Crystallographic data for **2**, **3**, **9** and **12**.

Compound	**2**	**3**	**9**	**12**
Empirical formula	$C_{68}H_{60}Cl_8N_4O_{16}Pd_4$	$C_{58.25}H_{50.25}Cl_{7.75}F_6N_2O_6P_3Pd_2$	$C_{60}H_{50}Br_2Cl_{16}N_2O_4P_2Pd_2$	$C_{52}H_{43}BrCl_5NO_2P_2Pd$
Formula weight	1898.40	1568.70	1864.78	1139.3
Temperature/K	100(2)	100.0	293(2)	293(2)
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	P-1	c2/c	P-1	P2(1)/C
a/Å	9.5409(13)	21.057(2)	9.125(5)	13.0621(4)
b/Å	14.8059(18)	20.817(2)	12.412(5)	35.3990(12)
c/Å	26.074(3)	32.852(3)	16.598(5)	12.3864(4)
α/°	97.798(2)	90	96.758(5)	90
β/°	92.009(2)	97.016(2)	96.150(5)	117.9930(10)
γ/°	93.866(2)	90	94.181(5)	90
Volume/Å^3	3637.3(8)	14292(3)	1849.1(14)	5057.2(3)
Z	2	8	1	4
ρ_{calc}g/cm^3	1.733	1.458	1.675	1.496
μ/mm^{-1}	1.335	0.921	2.232	1.525
F(000)	1888	6276	920	2296
Crystal size/mm^3	0.28 × 0.14 × 0.08	0.32 x 0.19 x 0.15	0.33 x 0.15 x 0.10	0.44 x 0.30 x 0.21
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2θ /°	1.69 to 28.28	1.25 to 28.30	1.24 to 28.29	1.15 to 28.29
Index ranges	-12 ≤ h ≤ 12, -19 ≤ k ≤ 19, -34 ≤ l ≤ 34	-28 ≤ h ≤ 26, -23 ≤ k ≤ 27, -43 ≤ l ≤ 23	-12 ≤ h ≤ 10, -16 ≤ k ≤ 16, -22 ≤ l ≤ 22	-17 ≤ h ≤ 10, -46 ≤ k ≤ 47, -16 ≤ l ≤ 16
Reflections collected	66916	52294	18238	49417
Independent reflections	17756 [R_{int} = 0.0351]	17676 [R_{int} = 0.1983]	8920 [R(int) = 0.0227]	12517 [R(int) = 0.0357]
Data/restraints/parameters	17756 / 0 / 901	17676 / 30 / 826	8920 / 48 / 455	12517 / 48 / 607
Goodness-of-fit on F^2	1.076	0.990	1.140	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0561, wR_2 = 0.1328	R_1 = 0.0634, wR_2 = 0.1682	R_1 = 0.0338, wR_2 = 0.0902	R_1 = 0.0391, wR_2 = 0.1075
Final R indexes [all data]	R_1 = 0.1033, wR_2 = 0.1650	R_1 = 0.1436, wR_2 = 0.2059	R_1 = 0.0542, wR_2 = 0.1234	R_1 = 0.0645, wR_2 = 0.1368
Largest diff. peak/hole/e Å^{-3}	2.667/-1.463	1.262/-0660	0.643/-0.744	1.63/-1.91

Crystal structure of 2

Appropriate crystals of **2** were precipitated by recrystallization from a dichloromethane-*n*-hexane solution. The structure of **2** is given in **Figure 1** and the caption contains selected interatomic distances and angles for **2**. Crystallographic data are given in **Table 1**. The crystals consist of discrete molecules separated by normal van der Waals distances. The asymmetric unit comprises two molecules of **2**. The molecular configuration is a dinuclear anti isomer with the cyclopalladated moieties in an open book geometry supported by two acetate-bridging ligands linking the palladium atoms. [35] The Pd-Pd distances of 2.8937(7) and 2.9050(7) may be regarded as nonbonding given the covalent radius of square-planar Pd(II) of 1.31 Å. [36] Nevertheless, in view of the palladium van der Waals radius of 1.61 Å some interaction may exist. [37] The geometry around palladium is slightly distorted square-planar with coordination to a nitrogen atom of the imine group, an *ortho* carbon of the phenyl ring, and two oxygen atoms, one from each of the bridging acetates. The two [C,N] metallacycles are in an open book disposition with the close-to-parallel ligands lying above one another consequent on the geometry of the two mutually *cis* acetate ligands. The ensuing ligand repulsions on the *trans* side of each molecule originates tilting of the palladium coordination planes at angles of 26.0 and 25.5°.

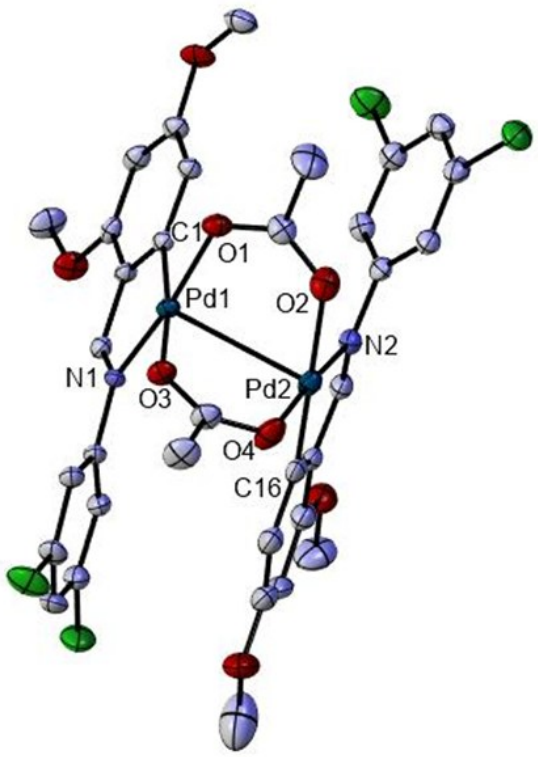


Figure 1 | ORTEP drawing of compound **2** with thermal ellipsoid plot shown at 50 % probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)-Pd(1) 1.971(5); N(1)-Pd(1) 2.055(4); O(1)-Pd(1) 2.033(4); O(3)-Pd(1) 2.162(4); C(16)-Pd(2) 1.928(6); N(2)-Pd(2) 2.018(5); O(2)-Pd(2) 2.138(4); O(4)-Pd(2) 2.042(4). C(1)-Pd(1)-N(1) 81.1(2); C(1)-Pd(1)-O(5) 164.6(2); N(1)-Pd(1)-O(5) 88.91(17); C(1)-Pd(1)-P(1) 102.23(17); N(1)-Pd(1)-P(1) 166.07(13); O(5)-Pd(1)-P(1) 90.27(12); C(16)-Pd(2)-O(6) 172.79(19); C(16)-Pd(2)-N(2) 81.2(2); O(6)-Pd(2)-N(2) 92.07(16); C(16)-Pd(2)-P(2) 94.42(16); O(6)-Pd(2)-P(2) 92.51(12); N(2)-Pd(2)-P(2) 173.27(13).

The palladium-nitrogen bonds of Pd(1)-N(1) 2.055(4), Pd(2)-N(2) 2.018, Pd(3)-N(3) 2.027(5) and Pd(4)-N(4) 2.046(4) Å, concur with the value based on the covalent radii for both atoms, 1.31 Å and 0.701 Å, respectively, whilst the palladium-carbon bonds Pd(1)-C(1) 1.971(5), Pd(2)-C(16) 1.928(6), Pd(3)-C(35) 1.072(6) and Pd(4)-C(50) 1.972(5) show lower values than expected 2.081 Å [C(sp^2) 0.771 Å], pointing to an important amount of multiple bonding. As for the bonds to oxygen each metal atom shows two distinct Pd-O distances consequent on the differing *trans* influence of the aromatic carbon atom and the imine nitrogen giving lengthening of the Pd-O band *trans* to carbon; *e.g.*, Pd(1)-O(1) 2.033(4) Å and Pd(1)-O(3) 2.162(4) Å, the latter *trans* to carbon. The sum of angles at each palladium is *ca.* 360°, with moderate divergence form the ideal square-planar environment in the aftermath of chelation by the metallacycle, as shown by the diminished N-Pd-C bond angles, *e.g.*, C(1)-Pd(1)-N(1) 81.05(19) Å. Treatment of compound **2** with the diphosphine $Ph_2PCH_2PPh_2$ (dppm) in 1:1 molar ratio and NH_4PF_6 yielded complex **3**. Two different ligands, *i.e.*, an acetate anion and a tertiary diphosphine span across the two metal centers with the oxygen and phosphorus donors *trans* to the aryl carbon and imine nitrogen atoms, respectively. The values for the ν_{as}(COO) and ν_s(COO) bands in the IR spectrum concur with its bridging coordination. Only one collection of signals was observed in the ^{1}H and ^{31}P NMR (a singlet resonance) spectra in compliance with the symmetric nature of the compound. The resonances at 3.76 and 3.00 ppm were assigned to the MeO groups, the latter high-field shifted due to the shielding effect of the phosphine phenyl rings; this concurs with a phosphorus trans to nitrogen geometry. The signal at 5.32 ppm was assigned as a multiplet to the PCH_2P protons owing to the AA´XX´ spin system. The conductivity measurement in dry acetonitrile, Λ_M = 176 W^{-1} cm^2 mol^{-1}, indicates a 1:1 electrolyte species. [38]

Crystal structure of 3

Suitable crystals of **3** were grown from a chloroform solution. The crystal structure of **3** and selected interatomic distances and angles for **3** are depicted in **Figure 2**. The asymmetric unit comprises one molecule of **3**, and the structure consists of discrete molecules with the palladium(II) atoms bonded in a slightly distorted square-planar environment to two mutually perpendicular pairs of [O,O] and [P,P] donors, pertaining to bridging acetate and bis (diphenylphosphino)methane ligands, respectively; the former are both *trans* to the phenyl carbons and the latter to the imine nitrogens, with an angle between the [Pd(1)Pd(2)O(5)O(6)] and [Pd(1) Pd(2)P(1)P(2)] planes of 89.91°. The bond distances and angles are within the predicted values (*vide supra*); but it should be noted that as opposed to the structure of **2** the two oxygen donors are *trans* to

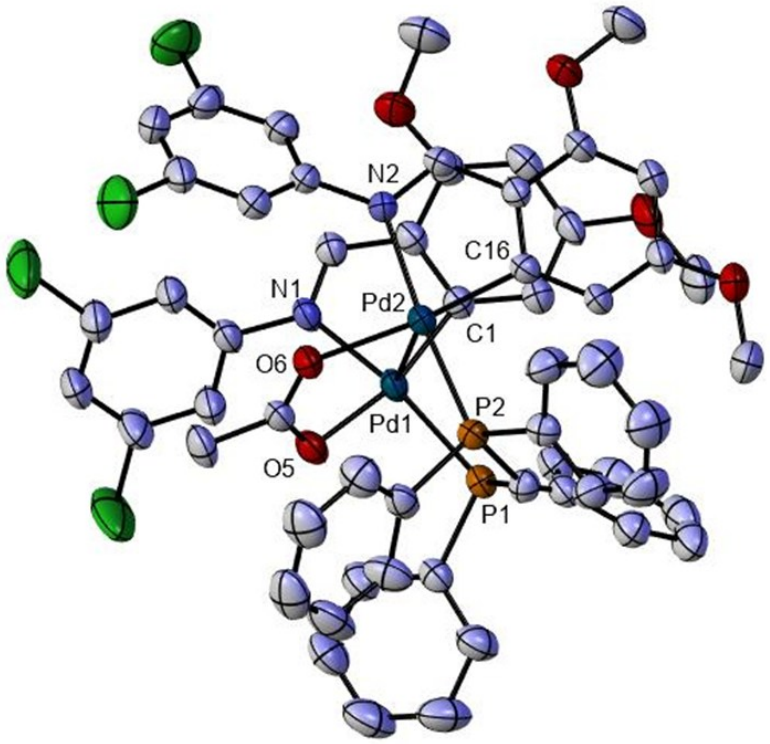


Figure 2 | ORTEP drawing of compound **3** with thermal ellipsoid plot shown at 50 % probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)-Pd(1) 2.006(5); N(1)-Pd(1) 2.054(5); O(5)-Pd(1) 2.131(4); P(1)-Pd(1) 2.2724(17); C(16)-Pd(2) 2.023(5); N(2)-Pd(2) 2.119(4); O(6)-Pd(2) 2.108(4); P(2)-Pd(2) 2.2595(15). C(1)-Pd(1)-O(1) 89.82(19); C(1)-Pd(1)-N(1) 81.05(19); O(1)-Pd(1)-O(3) 88.32(15); N(1)-Pd(1)-O(3) 100.46(16); O(1)-Pd(1)-N(1) 170.62(16); C(1)-Pd(1)-O(3) 172.60(18); C(16)-Pd(2)-N(2) 82.2(2); C(16)-Pd(2)-(4) 92.8(2); N(2)-Pd(2)-O(2) 96.80(17); O(4)-Pd(2)-O(2) 88.21(18); N(2)-Pd(2)-O(4) 174.83(18; C(16)-Pd(2)-O(2) 178.9(2).

phenyl carbons, hence the lengthening of both Pd-O linkages Pd(1) -O(5) and Pd(2)-O(6) of 2.131(4) and 2.108(4) Å, respectively. Likewise, similar elongated Pd-N distances should be assumed from the theoretical value of 2.011 Å (*vide supra*), yet only one is significantly longer, *i.e.*, Pd(2)-N(2) of 2.119(4) Å. We trust this to be due to the somewhat reduced N-Pd-N angle at Pd(1) which hinders the phosphorus *trans* influence sufficiently so as to diminish the Pd(1)-N(1) length to only a minor extent of 2.054(5) Å; *cf.* N(1) -Pd(1)-P(1) 166.07(13)° and N(2)-Pd(2)-P(2) 173.27°. Furthermore, the bonding assembly of the bridging ligands sets the Schiff base ligands in a "*cis*" nature, *i.e.*, with the metallated rings pointing in the same direction; in contrast to the structure of **2** with a '*trans*' arrangement of the palladated ligands. Reaction of **2** in acetone with aqueous sodium chloride or bromide readily gave *via* metathesis the ensuing halide-bridged compounds **4** and **5**, respectively, which were fully characterized. The spectroscopic data are like the parent compound **1**, save for the Pd-X bonds resulting from exchange of the bridging units, and they are in agreement with the absence of the acetate ligands (see Experimental). The IR spectra showed two ν(Pd-X) bands, consistent with an asymmetric Pd_2X_2 bridging unit: υ(Pd-Cl) 312, 268 cm^{-1}, 4; υ(Pd-Br) 183, 172 cm^{-1}, **5**; the higher frequency stretch was assigned to the Pd-X bond *trans* to the nitrogen atom because of the disparate *trans* influence of the C (aryl) and N(imine) atoms consistent with an asymmetric Pd_2X_2 bridging unit. Reaction of dppm or with (*trans*-dppe) in 1:1 molar ratios gave **6** and **7**, on the one hand (**Scheme 1**), and **8** and **9**, on the other (**Scheme 1**), respectively. Likewise, treatment of **4** and **5** with $Ph_2P(CH_2)_3PPh_2$ (dppp) or $Ph_2P(CH_2)_4PPh_2$ (dppb), gave compounds **13-14** and **15** (X = Cl) (**Scheme 2**), also respectively; all compounds were fully characterized. The ^{31}P NMR showed a singlet resonance for the two equivalent phosphorus nuclei; accordingly, for symmetry reasons only one set of signals for the proton resonances was present. The phosphorus donors are *trans* to the nitrogen atoms (*vide supra*). The *H*C=N resonance was a doublet (except for **9** and **15**) due to coupling to the nucleus with $^4J(PH)$ *ca.* 6-7 ppm. The PCH=CHP signals were assigned as multiplets for the AA´XX´ spin systems in both cases. The IR spectra showed the υ (Pd-X) stretches at slightly lower frequencies due to the *trans* influence of the aryl carbon atom, υ(Pd-Cl) 291 cm^{-1}, **6**; υ(Pd-Br) 177 cm^{-1}, **7**; υ(Pd-Cl) 291 cm^{-1}, **8**; υ(Pd-Br) 176 cm^{-1}, **9**; υ(Pd-Cl) 287 cm^{-1}, **13**; υ(Pd-Br) 201 cm^{-1}, **14**; υ(Pd-Cl) 293 cm^{-1}, **15**. The conductivity measurement in dry acetonitrile Λ_M = 146 and 170 Ω^{-1} cm^2 mol^{-1}, for **6** and **7**, respectively, suggest 1:1 electrolyte species. Treatment of **4** and **5** with triphenylphosphine in 1:2 or 1:4 ratio in acetone yielded the mononuclear complexes compounds **10-11** and **12**, respectively as air-stable solids, characterized accordingly. The spectroscopic data for **10-11** point towards a *trans* arrangement of the nitrogen and phosphorus atoms giving a $^4J(PH)$ of 7 Hz; the C

(4)-MeO resonance was shifted to higher field in a similar fashion as for the compounds with the diphosphine ligands (*vide supra*). As for complex **12** the incoming second phosphine ligand cleaves the Pd-N bond with opening of the metallacycle ring, but keeping the halide ligand bonded to the metal, in non-electrolyte species, shown by the presence of the corresponding υ(Pd-X) stretches in the IR spectra. The phosphorus resonance in the ^{31}P NMR spectrum was a singlet resonance in accordance with a *trans* P-Pd-P geometry and in the ^{1}H NMR the *H*C=N resonance was also a singlet. It has been argued that in such compounds some interaction between the nitrogen and palladium atoms may exist (*vide infra*, structure of **12**); nevertheless, absence of any ^{4}J(PH) coupling seems to preclude this possibility. This coincides with the angle between the metallated phenyl ring plane and the palladium coordination plane close to 90° and may be tentatively taken as an extension of the Karplus correlation relative to the influence of the dihedral angle on the coupling constant. [39] Yet, the phosphorus NMR indicates the phosphine phenyl rings still exert some shielding influence on the phenyl protons, their resonances and that of the C(4)-methoxy group being high-field shifted.

Crystal structure of 9

Satisfactory crystals of **9** were obtained by recrystallization from a dichloromethane-hexane solution. The structure of **9** is given in **Figure 3** inclusive of the caption containing selected interatomic distances and angles. The molecule is a centrosymmetric dinuclear complex, incorporating two square-planar palladium(II) atoms related by an inversion center, both being linked to a bromide ligand, a bidentate N-(2,4-dimethoxybenzylidene)-3,5-dichloroaniline-*C,N* (C *trans* to bromide), and finally a centrosymmetric *trans*-1,2-bis(diphenylphosphino)ethene which bridges the two palladium centers; thus, the asymmetric unit consists of half of the molecule of **9**. The observed bond dsistances and angles are within the predicted values (*vide supra*), displaying somewhat larger values for the elongated Pd-Br and Pd-N bond distances caused by the *trans* influence of the phenyl carbon and phosphorus atoms, respectively.

Unlike the previous structures the phenyl ring on nitrogen is quite tilted away from the metallacycle plane with an angle between the [Pd(1)C(1)C(6)C(7)N(1)] and [C(8)C(9)C(10)C(11)C(12)C(13)] planes of 73.58°; *cf.* complexes **2** and **3** where the analogous angles are at 40.90 and 56.51°, respectively. Treatment of **4** and **5** with diphosphines in 1:1 ratio and NH_4PF_6 gave complexes where the two phosphorus donors were linked by a carbon chain, as opposed to the monophosphine situation in compound **12**, with removal of the halide-ligand from the palladium coordination sphere, but preserving the metallacycle ring, yielding 1:1 electrolytes; therefore, only compounds **16-19** are obtained regardless of the starting dinuclear compound. The corresponding metallacycle ring has a varied number of links depending on the number of carbons joining the phosphorus atoms. The H5 resonance in the ^{1}H NMR was a *ddd* coupled to H3 and to the two phosphorus nuclei with ^{4}J(HP_B), *pseudo-trans*, greater than ^{4}J(HP_A), *pseudo-cis*. The phosphorus nuclei resonances were doublets; the higher field doublet was ascribed to the nucleus *trans* to the aryl carbon, P_B, whilst the lower field one to the nucleus *trans* to the imine nitrogen, P_A.

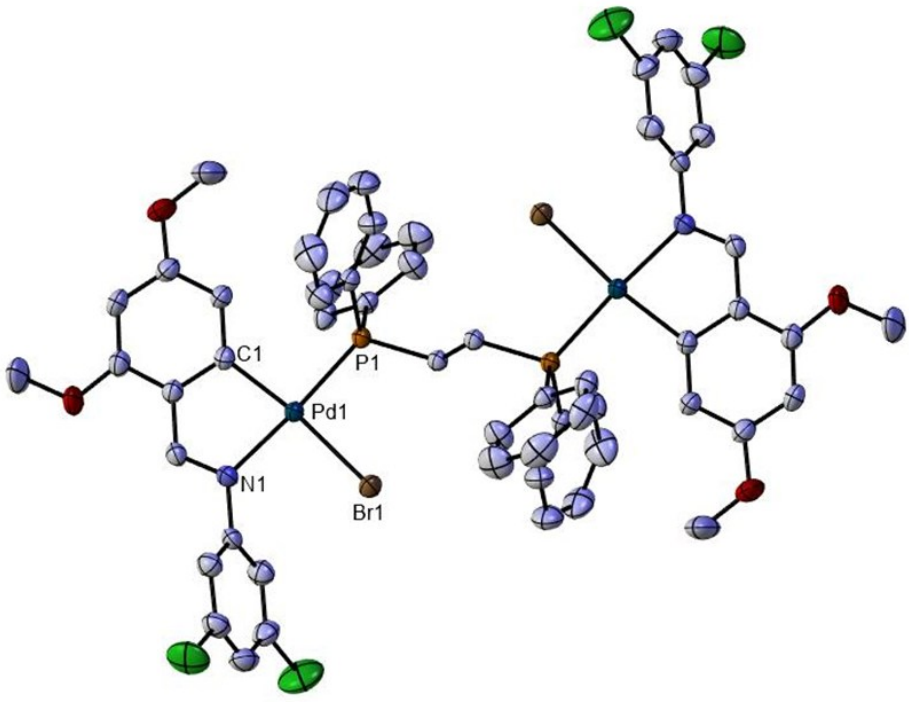


Figure 3 | ORTEP drawing of compound **9** with thermal ellipsoid plot shown at 50 % probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)-Pd(1) 2.025(3); N(1)-Pd(1) 2.097(3); Br(1)-Pd(1) 2.5074(9); P(1)-Pd(1) 2.2553(10). C(1)-Pd(1) 2.025(3); N(1)-Pd(1) 2.097(3); Br(1)-Pd(1) 2.5074(9); Pd(1)-P(1) 2.2553(10). C(1)-Pd(1)-N(1) 80.99(12); C(1)-Pd(1)-P(1) 93.88(10); N(1)-Pd(1)-Br(1) 92.63 (8); P(1)-Pd(1)-Br(1) 92.94(3); N(1)-Pd(1)-P(1) 172.43(8); C(1)-Pd(1)-Br(1) 171.91(10).

This is inferred on the premise that a ligand of greater *trans* influence shifts the phosphorus resonance trans to itself to higher field. [40-42] Coupling of the imine resonance to phosphorus was detected in all cases, albeit only for **16** and **17** could coupling to both ^{31}P nuclei be disclosed. The PCH=CHP proton resonances could not be clearly assigned (compound **19**); we suggest they were shifted to lower field due to shielding of the phosphine phenyls and hence occluded by them.

Structure of complex 12

Proper crystals of **12** were obtained by recrystallization from a dichloromethane-*n*-hexane solution. The structure of **12** is given in **Figure 4** together with selected interatomic distances and angles. The crystal structure consists of discrete molecules. The palladium atom is in a square-planar environment bonded to the aryl carbon, the bromide and the two phosphorus atoms. The angles between adjacent atoms in the coordination sphere lie in the range 86.35(8)º [C(1)-Pd(1)-P(1)] to 95.24(2)º [P(2)-Pd(1)-Br(2)]. The distances at palladium are similar to previous reported values (*vide supra*). The dihedral angles between the metalated ring and the coordination and aniline ring plane are 85.05° and 44.93°, respectively. Pd(II) complexes, with trimethyl-, triethyl-, and triphenylphosphine, as well as with bis(diphenylphosphino)methane (dppm), showing Pd···N weak interactions in the range 2.576(4)-2.805(5) have been reported suggesting five-coordinate complexes; [43,44] and we have shown even shorter distances of 2.359 Å and 2.338 Å for complexes with $(Ph_2PCH_2CH_2)_2PPh$ (triphos), the latter being the shortest one reported to date. [45] In the present case the Pd-N distance, 2.785 Å, certainly precludes any covalent interaction, albeit given the palladium van der Waals radius of 1.61 Å (*vide supra*) some interaction may be predicted pointing towards an occupied apical site of the square planar palladium coordination plane by the imine nitrogen atom.

4. Conclusions

In this work, we have shown that the reaction of a particular Schiff base with palladium acetate produces a dinuclear palladium complex with bridging acetate ligands; these may be easily replaced by a diphosphine or halide ions. In the first case, compounds with mixed bridging ligands are produced, and in the second, the corresponding metathesis reaction gives rise to the ensuing dinuclear complexes with bridging chloride or bromide ligands. The latter are excellent starting reagents for treatment with nucleophiles, such as tertiary phosphines literally giving rise to a huge score of derivatives, some of which are presented here. Thus, depending on the number of phosphorus donor atoms, dinuclear and mononuclear

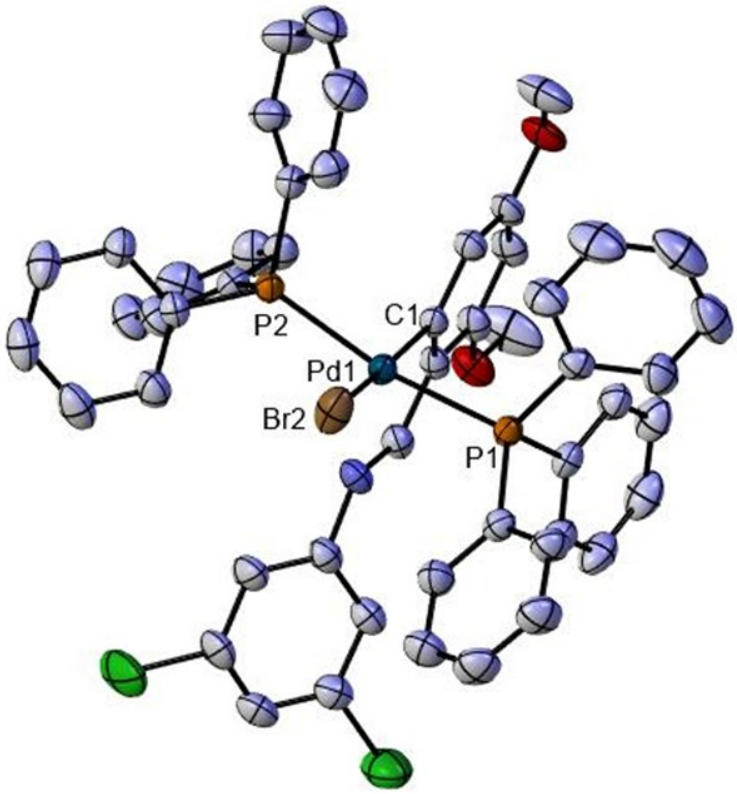


Figure 4 | ORTEP drawing of compound **12** with thermal ellipsoid plot shown at 50 % probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)-Pd(1) 1.996(3); Br(2)-Pd(1) 2.5131(4); P(1)-Pd(1) 2.3353(7); P(2)-Pd(1) 2.3464(7). C(1)-Pd(1)-P(1) 86.35(8); C(1)-Pd(1)-P(2) 86.54(8); P(1)-Pd(1)-P(2) 170.17(3); C(1)-Pd(1)-Br(2) 169.30(9); P(1)-Pd(1)-Br(2) 90.53(2); P(2)-Pd(1)-Br(2) 95.24(2).

complexes can be obtained. In the former case, the metal centers are joined by a) two distinct bridging ligands, diphosphine and halide; b) two identical halide ions; c) only one bridging diphosphine. In the latter case the metal is bonded, a) to one phosphorus donor and a terminal halide; b) to two phosphines, inducing cleavage of the Pd-N and thus losing its palladacycle character; c) to a chelating diphosphine and absence of the halide ion. Four crystal structures have been described, that for compound **3** being the first crystal and molecular structure depicting a dinuclear palladacycle with mixed diphosphine and acetate linkers, whose arrangement seems to resemble that of the parent compound **2**; notwithstanding, the orientation of the metallated ligands adopt a *cisoid* geometry, as opposed to the *transoid* fashion in the structure of **2**.

Supplementary Materials

ACESION Codes: CCDC 2529548 (**2**), CCDC 2529549 (**3**), CCDC 25295550 (**9**), and CCDC 2530054 (**12**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_ request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Author Contributions

Conceptualization, J.M.V. and J.M.O.; methodology, J.M.O.; software, F.L.M.; validation, J.M.V., J.M.O. and M.D.; formal analysis, J.M.O.; investigation J.M.V. and J.M.O.; resources, J.M.O.; data curation, F.L.M. and M.D.; writing—original draft preparation, J.M.V. and J.M.O.; writing—review and editing, J.M.V.; visualization, J.M.V., J.M.O. and F.L.M.; supervision, J.M.V. and M.D.; project administration, J.M.O.; funding acquisition, J.M.O. All authors have read and agreed to the published version of the manuscript.

Conflict of Interests

The authors declare no conflict of interest.

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