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N-donor 2-(Sulfonamido)benzamide ligands, their palladium(II) coordination species and C–C coupling catalysis efficiencies

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ABSTRACT

A series of synthetically accessible ligands based on new 2-(R-sulfonamido)benzamide have been prepared (R = methyl for H_3M; R = 4-toly for H_3T and T_2CN; R = 2,4,6-triisopropylphenyl for H_3iP and HiPCN). The R-substituents were selected to vary in sizes. Allowing ligand H_3iP and palladium acetate to stand in solvent leads to self-assembly of the well-defined solvent- and stoichiometry-controlled tetranuclear or hexanuclear coordination macromolecules $Pd_4(iP)_2$ and $(PdHiP)_6$, which were analysed by X-ray crystallography. It was observed that palladium active species for Suzuki coupling catalysis could be stabilized by these simple and synthetically assessable N-donor ligands as revealed by turnover frequencies reaching 5500 h^{-1}. Electronic features of these N-donors appear to be more important than the steric properties.

1. Introduction

In the last few decades, many transition metal materials have been explored for their roles as catalyst in carbon-carbon (C–C) synthetic protocols [1–7]. However, the catalytic utility and versatility of palladium species in C–C coupling is unequaled [8–10]. Consequently, molecular scientists concerned with natural products total synthesis, drug designs, supramolecular organic or organometallic chemistry and syntheses of smart materials and fine chemicals have continued to benefit from the use of palladium-mediated catalytic interventions [11–14], which has tremendously eased synthetic organic manipulations [15–17]. Among the commonly utilized palladium-catalyzed coupling methodologies such as Suzuki-Miyaura, Hiyama, Kumada, Stille, Buchwald-Hartwig, Sonogashira, Heck, Negishi, etc., Suzuki-Miyaura and Heck coupling techniques enjoy more widespread patronage because of their simplicity and substrate availability [18,19].

Different ligand designs ranging from monodentate through bidentate to polydentate have been studied as an organic backbone for active palladium centres [20–22]. Numerous highly active palladium compounds have been patented and even commercialized with trademarks [23–26]. These are mostly organometallic palladium complexes incorporating only one phosphine or N-heterocyclic carbene donor arm as the only strong base while the complementary co-ligands are usually of various weaker and easily detachable donor systems such as organometallic allylic and cyclometallated amine or halide fragments (Scheme 1, top) [26–28]. Thus, there are reasons to anticipate that the active transient species generated during catalysis are of monodentate mono-ligand compositions in nature [29–32] while coordinatively saturated palladium complexes tend to yield poor catalyst performances [33,34]. Furthermore, catalyst generation is also routinely achieved via *in situ* build-up from ligand and palladium salt or from precatalyst decomposition (Scheme 1, bottom).

However, in addition to their potential air and moisture sensitivity problems, the currently highly active phosphine or organometallic palladium precatalysts are usually expensive and synthetically inaccessible [28]. Therefore, development of inexpensive, simpler and more stable N-donor precatalysts could be

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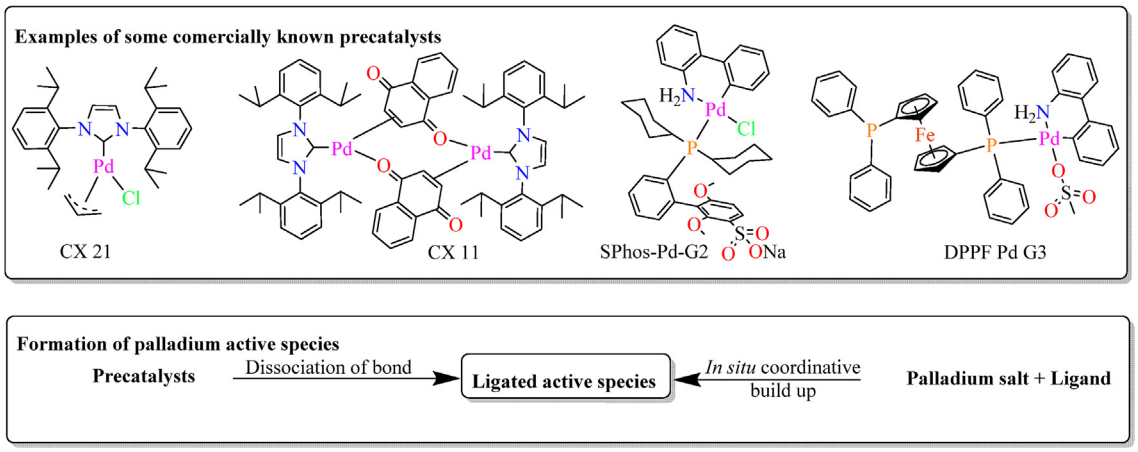


Scheme 1. (Top) Few examples of highly active and commercially available pre-catalysts [23–25,38,39] and (bottom) active catalyst formation from precatalysts decomposition or *in situ* complexation build-up.

considered necessary [35]. Furthermore, based on the conviction that hemilabile ligands could also fulfill the requirements for generating monodentate mono-ligand active species, motivation arose to design new 2-(sulfonamido)benzamide chelates derived from 2-aminobenzamide (H_4BA) and sulfonyl chloride reagents (Scheme 2). Since ligand rigidity and bulkiness is often associated with desirable catalyst efficiencies [36,37], systematic variation of substituent bulks was introduced around the sulfonamide group. Presented herein are the results for the study of the influence of electronic and structural variations of new N-donor ligands on palladium-catalyzed C–C cross coupling efficiencies.

2. Experimental section

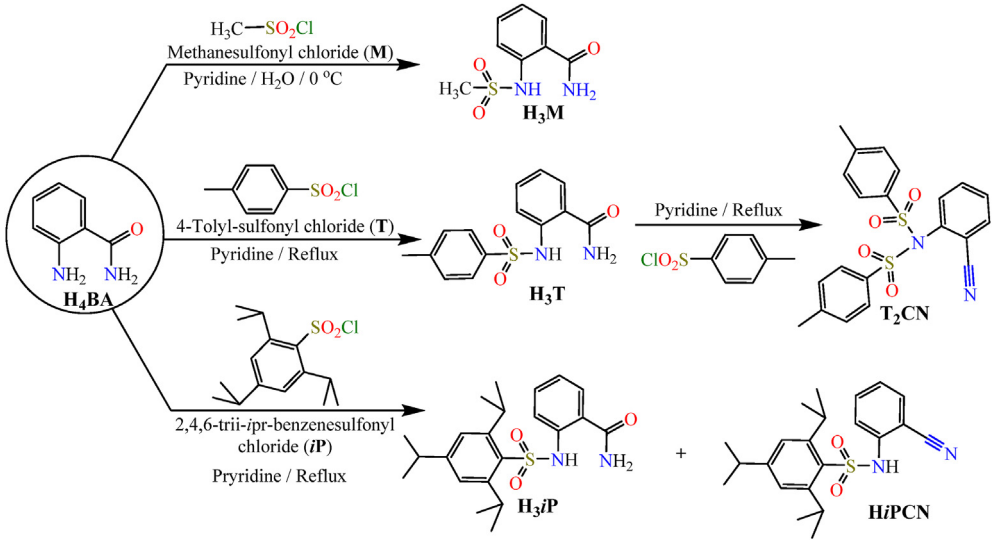
2.1. General information

All starting materials for synthesis as well as substrates for the catalytic experiments were obtained commercially as reagent and used without further purification. Microwave assisted procedures were conducted using Biotage Initiator 2.5 Microwave Reactor for ligand preparations. Impurities in all organic syntheses were excluded either by column chromatography on silica gel or recrystallization. IR spectra were measured with a Bruker Equinox FT-IR spectrometer equipped with a diamond ATR unit. Elemental analyses were carried out on Leco CHNS-932 and El Vario III elemental analysers. Mass spectrometry analyses were conducted on a Bruker MAT SSQ 710 spectrometer. ^1H and ^{13}C NMR spectra were collected on a Bruker AVANCE 400 MHz spectrometer using deuterated solvents.

2.2. Synthesis of ligands and the palladium species $Pd_4(iP)_2$ and $(PdHiP)_6$

2.2.1. 2-(methylsulfonamido)benzamide (H_3M)

To a solution of 2-aminobezamide, (2.00 g, 14.7 mmol) in a mixture of water (5 mL) and pyridine (15 mL) was added dropwise over a period of 30 min, methanesulfonyl chloride, (4.5 mL, 58.7 mmol) while stirring inside an ice bath. After 2 h, the solid was filtered and washed with methanol to give H_3M as a light yellow crystalline solid. Yield (2.52 g, 80%). M.p. = 160–161 °C. Selected IR data (ATR, cm^{-1}): *v* 3444 (m, NH), 3181 (m), 2960 (m, methyl), 1666 (s, amide), 1617 (s, C=C), 1498 (s), 1435 (s), 1382 (s), 1319 (vs), 1270



Scheme 2. Synthetic scheme and structures for the bidentate chelating amine ligands subjected to *in situ* as well as palladium precatalyst studies.

(s), 1149 (vs), 780 (vs). ^{1}H NMR (400 MHz, DMSO-d_6): δ_{ppm} 11.68 (s, 1H, NH), 8.41 (s, 1H, NH), 7.90 (d, J = 7.7 Hz, 2H, Ph), 7.56 (t, J = 4.1 Hz, 2H, Ph), 7.16 (m, J = 8.2, 5.0, 3.5 Hz, 1H, Ph), 3.13 (s, 3H, methyl). ^{13}C NMR (101 MHz, DMSO-d_6): δ 175.95, 144.95, 138.22, 134.29, 127.72, 124.25, 123.51, 21.82 (methyl). MS (EI) m/z 214 (M^+, 100%): 197, 184. Anal.: calc. for $C_8H_{10}N_2O_3S$ C, 44.85; H, 4.70; N, 13.08; S, 14.97%. Found: C, 44.95; H, 4.64; N, 13.00; S, 15.04%.

2.2.2. 2-(4-methylphenylsulfonamido)benzamide (H_3T)

2-aminobenzamide (1.00 g, 7.4 mmol) was added to toluenesulfonyl chloride (2.80 g, 14.7 mmol) in pyridine (15 mL). The reaction mixture was stirred for 15 min before it was microwaved for 4 min at 120 °C. Excess pyridine was removed by rotary evaporation. Methanol was added and the precipitates was filtered and washed with methanol which affords H_3T as a white crystalline solid. Yield (1.47 g, 70%). M.p. = 250–251 °C. Selected IR data (ATR, cm^{-1}): ν 3468 (m, NH), 3362 (m), 2960 (m, methyl), 1653 (m, amide), 1608 (m, C=C), 1493 (m), 1317 (m) 1153 (vs), 939 (s), 759 (s). ^{1}H NMR (400 MHz, DMSO-d_6): δ_{ppm} 12.19 (s, 1H, NH), 8.33 (s, 1H, NH), 7.86 (s, 1H, NH), 7.78 (d, J = 7.9 Hz, 1H, Ph), 7.66 (d, J = 7.7 Hz, 2H, Ph), 7.52 (d, J = 8.3 Hz, 1H, Ph), 7.46 (t, J = 7.7 Hz, 1H, Ph), 7.34 (d, J = 7.9 Hz, 2H, Ph), 7.09 (t, J = 7.5 Hz, 1H, Ph), 2.32 (s, 3H, methyl). ^{13}C NMR (101 MHz, DMSO-d_6): δ 171.14, 144.23, 139.71, 136.50, 133.32, 130.32, 129.41, 127.22, 123.46, 119.40, 21.41 (methyl). MS (EI) m/z 290 (M^+, 100%): 273, 209, 180, 155, 110, 91. Anal.: calc. for $C_{14}H_{14}N_2O_3S$ C, 57.92; H, 4.86; N, 9.65; S, 11.04%. Found: C, 57. 47; H, 4.77; N, 9.10; S, 11.35%.

2.2.3. N-(2-cyanophenyl)-4-methyl-N-tosylbenzenesulfonamide (T_2CN)

2-(4-methylphenylsulfonamido)benzamide, H_3T (0.50 g, 1.7 mmol) was added to *p*-toluenesulfonyl chloride (1.00 g, 5.2 mmol) in pyridine (10 mL). The mixture was refluxed for 5 h at 110 °C and then concentrated by rotary evaporation. Methanol was added to the concentrate which affords T_2CN as a white crystalline solid. Yield (0.45 g, 60%). M.p. = 193–194 °C. Selected IR data (ATR, cm^{-1}): ν 2960 (m, methyl), 2229 (m, nitrile) 1596 (s, C=C), 1446 (s) 1361 (vs), 1166 (vs), 1085 (s), 912 (vs), 860 (s), 660 (vs). ^{1}H NMR (400 MHz, DMSO-d_6): δ_{ppm} 8.00 (d, J = 7.5 Hz, 1H, Ph), 7.80 (t, J = 7.7 Hz, 1H, Ph), 7.78–7.74 (m, 1H, Ph), 7.71 (d, J = 7.9 Hz, 4H, Ph), 7.49 (d, J = 7.9 Hz, 4H, Ph), 7.14 (d, J = 7.9 Hz, 1H, Ph), 2.46 (s, 6H, methyl) ^{13}C NMR (101 MHz, *d6*- DMSO): δ 146.53, 135.21, 133.20, 131.98, 130.54, 128.99, 115.97, 21.69 (methyl). MS (EI) m/z 426 (M^+, 47%): 209, 155, 91. Anal.: calc. for $C_{21}H_{18}N_2O_4S_2$ C, 59.14; H, 4.25; N, 6.57; S, 15.03%. Found: C, 59.59; H, 4.23; N, 6.63; S, 15.26%.

2.2.4. 2-(2,4,6-triisopropylphenylsulfonamido)benzamide (H_3iP) and N-(2-cyanophenyl)-2,4,6-triisopropylbenzenesulfonamide (HiPCN)

A mixture of 2- aminobenzamide (0.30 g, 2.2 mmol) and 2, 4, 6-triiso-propylbezenesulfonyl chloride (2.00 g, 6.6 mmol) in 15 mL pyridine was refluxed overnight at 120 °C. Pyridine was removed under reduced pressure while the residue was purified on silica gel column with THF/n-hexane (3:7). H_3iP was obtained as off-white crystalline solid. Yield (0.13 g, 9%). M.p. = 217–218 °C. Selected IR data (ATR, cm^{-1}): ν 3436 (m, NH), 3183 (m), 2958 (m, methyl), 1673 (s, amide), 1622 (m, C=C), 1601 (m, C=C), 1493 (m), 1423 (m), 1333 (m), 1266 (m), 1150 (vs), 921 (s), 752 (vs). ^{1}H NMR (400 MHz, DMSO-d_6): δ_{ppm} 10.43 (s, 1H, NH), 7.84 (d, J = 7.6 Hz, 1H, Ph), 7.64 (t, J = 7.8 Hz, 1H, Ph), 7.42 (t, J = 7.4 Hz, 1H, Ph), 7.22 (s, 2H, Ph), 7.12 (d, J = 8.1 Hz, 1H, Ph), 3.83 (dd, J = 12.9, 6.4 Hz, 2H, *i*-Pr), 2.92 (dt, J = 13.6, 6.8 Hz, 1H, *i*-Pr), 1.20 (d, J = 6.8 Hz, 6H, methyl), 1.09 (d, J = 6.6 Hz, 12H, methyl). ^{13}C NMR (101 MHz, *d6*- DMSO): δ 153.11, 150.35, 134.53, 127.98, 124.21, 33.73 (alkyl), 29.70 (alkyl), 25.00 (alkyl), 22.76 (alkyl). MS (EI) m/z 385 (M^+, 20%): 343, 267, 251, 202, 117. Anal.: calc. for $C_{22}H_{30}N_2O_3S$ C, 65.64; H, 7.51; N, 6.96; S, 7.96%. Found: C, 65.40; H, 7.52; N, 6.86; S, 7.82%.

Ligand H*i*PCN was eluted after H_3iP as off-white powder. Yield (1.23 g, 68%). M.p. = 146–147 °C. Selected IR data (ATR, cm^{-1}): ν 3223 (m, NH), 2961 (s, *i*-Pr), 2234 (m, nitrile), 1599 (s, C=C), 1489 (s), 1427 (m), 1364 (m), 1162 (vs), 901 (s), 759 (vs). ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.31 (s, 1H, NH), 8.36 (s, 1H, Ph), 7.86 (s, 1H, Ph), 7.82 (d, J = 7.9 Hz, 1H, Ph), 7.42 (t, J = 7.7 Hz, 1H, Ph), 7.29 (d, J = 8.3 Hz, 1H, Ph), 7.24 (s, 2H, Ph), 7.06 (t, J = 7.5 Hz, 1H, Ph), 4.17 (m, J = 13.1, 6.5 Hz, 2H, *i*-Pr), 2.90 (m, J = 13.7, 6.8 Hz, 1H, *i*-Pr), 1.17 (m, 18H, methyl). ^{13}C NMR (101 MHz, *d6*- DMSO): δ 171.24, 153.43, 150.39, 140.02, 132.99, 129.51, 124.43, 122.77, 118.79, 118.00, 49.06 (alkyl), 33.72 (alkyl), 29.64 (alkyl), 24.97 (alkyl), 23.75 (alkyl). MS (EI) m/z 403 (M^+, 10%): 383, 368, 267, 251, 203, 187, 136, 119. Anal. calc. for $C_{22}H_{28}N_2O_2S$ C, 68.72; H, 7.34; N, 7.29; S, 8.34%. Found: C, 68.71; H, 7.36; N, 6.75; S, 7.87%.

2.2.5. $Pd_4(iP)_2$ and $(PdHiP)_6$

A mixture of H_3iP (10 mg, 0.025 mmol) and two equivalent of palladium(II) acetate (10 mg, 0.05 mmol) were stirred in acetonitrile for 3 h. The clear orange solution was allowed to stand at room temperature under slow evaporation and the tetranuclear complex $Pd_4(iP)_2$ was obtained as orange crystals suitable for x-ray measurement after standing overnight. Yield (0.02 g, 64%) M.p. = 282–283 °C. Selected IR data (ATR cm^{-1}): ν 2962 (m), 2322 (m), 1678 (s), 1532 (s), 1465 (vs), 1412 (vs), 1286 (s), 1190 (vs), 1129 (vs), 832 (vs). Anal. Calc. for $C_{54}H_{69}N_9O_{10}Pd_4S_2.(H_2O)$ C, 42.90; H, 4.73; N, 8.34; S, 4.24 Found: C, 43.04; H, 4.72; N, 8.01; S, 4.09. Hexanuclear greenish-yellow crystals of the palladium species $(PdHiP)_6$ suitable for x-ray analyses were also isolated from a solution of H_3iP (10 mg, 0.025 mmol) and one equivalent of palladium(II) acetate (6 mg, 0.025 mmol) in acetonitrile, which was layered with diethyl ether and allowed to stand at room temperature for 3 weeks under slow evaporation. NMR analyses of both palladium species were considered not useful since there are non-equivalent corresponding protons from multiple ligands, which leads to complicated spectra.

2.3. Catalysis experiments

2.3.1. Suzuki-Miyaura

In a typical Suzuki-Miyaura coupling reaction, (4-bromophenyl) methanol (0.19 g, 1.0 mmol), (4-acetylphenyl)boronic acid (0.23 g, 1.2 mmol), K_3PO_4 (0.26 g, 1.4 mmol), $Pd(AcO)_2$ (0.2 mol % relative to the aryl bromide) and a given ligand (0.7 mol %) were weighed into a 10 mL round-bottom flask equipped with magnetic stirrer bar. These were then refluxed for the desired reaction time using 3:1 ethanol/water mixture (4 mL) as reaction media. In the case of preformed palladium(II) complex, 0.05 mol % equivalent relative to the aryl bromide was used. After the desired reflux duration, an aliquot of the reaction mixture was transferred into a clean conical flask and the solvents was largely removed under vacuum. The residue was then collected in deuterated DMSO and its ^{1}H NMR analysed. The yields were evaluated by comparing integration values for NMR signal of the methylene $-CH_2-$ protons of (4-bromophenyl)methanol at $\delta \approx 4.4$ ppm with that of the corresponding biphenyl products at $\delta \approx 4.7$ ppm [31]. The various biphenyl products have been characterized in our previous studies [20,31,34].

2.3.2. Heck-mizoroki

In a typical Heck coupling experiment, (4-bromophenyl)methanol (0.19 g, 1.0 mmol), styrene (0.17 mL, 1.5 mmol), potassium carbonate (0.17 g, 1.5 mmol) and precatalyst **$Pd_4(iP)_2$** (0.8 mg, 0.05 mol % relative to the aryl bromide) were weighed into a 10 mL

round-bottom flask equipped with magnetic stirrer bar. Using 3:1 DMF/water mixture (4 mL) as media, the mixture was then refluxed at a given temperature and for the desired duration. An aliquot of the reaction mixture was taken directly into NMR tube while deuterated DMSO was added for ^{1}H NMR measurement. The determination of yields was achieved by comparing the methoxy $-OCH_3$ protons of 4-methoxystyrene at $\delta \approx 3.74$ ppm with that of the corresponding Heck product at $\delta \approx 3.76$ ppm. The produced Heck coupling product (4-styrylphenyl)methanol was isolated, purified and characterized: M.P = 173 °C. Selected IR data (ATR, cm^{-1}): *v* 3290 (m), 3052 (w), 3022 (w), 2860 (w, methylene CH) 1593 (m, C=C), 1576 (m), 1507 (m), 1488 (w), 1446 (s), 998 (s), 970 (s), 802 (s), 687 (s). ^{1}H NMR (400 MHz, DMSO-d_6) δ_{ppm} 7.59 (dd, J = 12.4, 7.7 Hz, 4H), 7.32 (m, 7H), 5.22 (s, 1H), 4.51 (s, 2H). 13C NMR (101 MHz, DMSO-d_6) δ_{ppm} 142.59, 137.58, 135.94, 129.16, 128.77, 128.27, 127.99, 127.26, 126.86, 126.71, 63.16. EI MS: 210 (M^+, 100%): 193 ($M^+ - OH$), 178 (($M^+ - CH_2OH$), 165, 152, 31 (CH_2OH), 27. Anal. calc. for $C_{15}H_{14}O$, C, 85.60; H, 6.71% found: C, 85.11; H, 6.65%.

2.4. Structure determinations

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects; absorption was taken into account on a semi-empirical basis using multiple-scans [40–43]. The structures were solved by direct methods (SHELXS) and refined by full-matrix least squares techniques against Fo^2 (SHELXL-97 and SHELXL-2014) [43]. The hydrogen atoms bonded to the amine-groups of H_3M and $(PdHiP)_6$ were located by difference Fourier synthesis and refined isotropically. All other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen, non-disordered atoms were refined anisotropically [43]. The crystal of $(PdHiP)_6$ and $Pd_4(iP)_2$ contain large voids, filled with disordered solvent molecules. The size of the voids are 576 and 770 Å^3/unit cell, respectively. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the program PLATON [44] resulting in 152 and 207 electrons/unit cell, respectively. The crystal of H_3M was a non-merohedral twin. The twin law was determined by PLATON [44] to (−0.002 0.000−0.998) (0.000−1.000 0.000) (−1.002 0.000 0.002). The contribution of the main component were refined to 0.615(1). Crystallographic data as well as structure solution and refinement details are summarized in Table 1. XP (SIEMENS Analytical X-ray Instruments, Inc.1994) [45] was used for structure representations.

3. Results and discussion

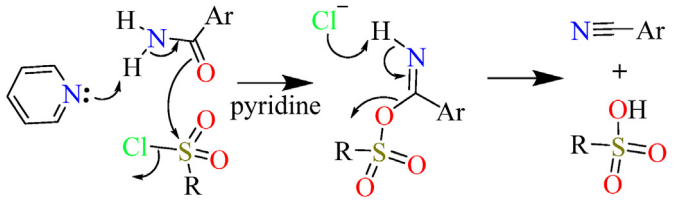
3.1. Synthesis and characterization

Elemental analysis and spectroscopic data gave good agreement with the identities of the series of synthesized ligands H_3M – H*i*PCN. In all cases of syntheses, between 2 and 4 equivalents of the sulfonyl chloride reagents were deployed. However, reactions at low temperatures and/or shorter reaction times as for both H_3M and H_3T yielded only mono-sulfonyl condensation products as the main products (Scheme 2). Attempting prolonged reflux at high temperature enabled condensation of a second sulfonyl chloride reagent on the same aromatic NH_2 function and/or an unexpected reduction of the amide NH_2 group to nitrile, which produced T_2CN and H*i*PN (Scheme 2) as the predominant products. Under this condition, the amide NH_2 function reacts with the excess sulphonyl chloride by dehydration of the amide as illustrated in Scheme 3 [46,47]. Perhaps this may mark another new aspect of sulfonyl chloride utility as well as novel pathway to the conversion of primary amide to nitrile due to its operational simplicity. Several efforts were made under various reaction conditions to obtain palladium(II) complexes from the isolated N-donors ligands.

Table 1
Crystal and structural refinement data for ligands H_3M and T_2CN as well as palladium complexes $(PdHiP)_6$ and $Pd_4(iP)_2$.

Compound	H_3M	T_2CN	$(PdHiP)_6$	$Pd_4(iP)_2$
formula	$C_8H_{10}N_2O_3S$	$C_{21}H_{18}N_2O_4S_2$	$C_{156}H_{204}N_{24}O_{18}Pd_6S_6$*	$C_{56}H_{69}N_{10}O_{10}Pd_4S_2$*
fw (g·mol^{-1})	214.24	426.49	3534.18[*]	1531.93[*]
°C	20(2)	−140(2)	−140(2)	−140(2)
crystal system	monoclinic	triclinic	triclinic	triclinic
space group	P 2$_1$/n	P ī	P ī	P ī
a/Å	19.733(4)	7.4591(4)	16.5121(4)	10.7928(3)
b/Å	5.2950(11)	8.1714(4)	17.8664(4)	18.2590(4)
c/Å	19.791(4)	16.7248(9)	18.6882(5)	20.7825(5)
α/°	90	85.057(3)	110.329(1)	112.833(1)
β/°	116.84(3)	86.259(3)	108.604(1)	100.598(1)
γ/°	90	74.408(3)	100.765(1)	92.204(1)
V/Å^3	1845.1(6)	977.29(9)	4616.8(2)	3682.84(16)
Z	8	2	1	2
ρ (g·cm^{-3})	1.542	1.449	1.271[*]	1.381[*]
μ (cm^{-1})	3.33	3.04	0.7[*]	10.7[*]
measured data	24108	9349	55920	40584
data with I > 2σ(I)	4171	3781	15740	14329
unique data (R_{int})	4223/0.0350	4404/0.0377	20818/0.0539	16656/0.0291
wR_2 (all data, on F^2)[a]	0.1070	0.1640	0.1383	0.0938
R_1 ($I > 2\sigma(I)$)[a)]	0.0397	0.0616	0.0574	0.0415
S[b]	1.104	1.137	1.086	1.055
Res. dens./e·Å^{-3}	1.228/-0.442	0.748/-0.656	1.040/-0.641	2.375/-1.470
absorpt method	multi-scan	multi-scan	multi-scan	multi-scan
absorpt corr $T_{min/max}$	0.6793/0.7456	0.5925/0.7456	0.5527/0.7455	0.6399/0.7456
CCDC No.	1878808	1878809	1878810	1878811

* The derived parameters do not contain the contribution of the disordered solvent.
[a] Definition of the *R* indices: $R_1 = (\Sigma||F_o|-|F_c||)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$+bP; $P = [2F_c^2 + \mathrm{Max}(F_o^2]/3$.
[b] $s = \{\Sigma[w(F_o^2-F_c^2)^2]/(N_o-N_p)\}^{1/2}$.



Scheme 3. Probable mechanism for sulfonyl chloride-mediated dehydration of the amide function to form the nitrile product.

However, only ligand H_3iP formed well-defined complexation products $Pd_4(iP)_2$ and $(PdHiP)_6$, which respectively assembled as tetranuclear and hexanuclear complexes from the same starting materials, but in the presence of slight solvent media variation (Scheme 4). It is noteworthy that one of the ligands in $Pd_4(iP)_2$ was covalently modified by probable incorporation of acetonitrile moiety ($CH_3C{=}N$) at the amide oxygen. Furthermore, a strange appearance of a bridging NO_2 group was also observed in the structure of $Pd_4(iP)_2$, which is uncommon. However, in the course of our studies of palladium structures, this surprise appearance of coordinated NO_2 group has been encountered a number of times in different styles (see Supplementary Information Fig. S1) and attempt to explain its origin has been reported by Raithby and Fairlamb [48].

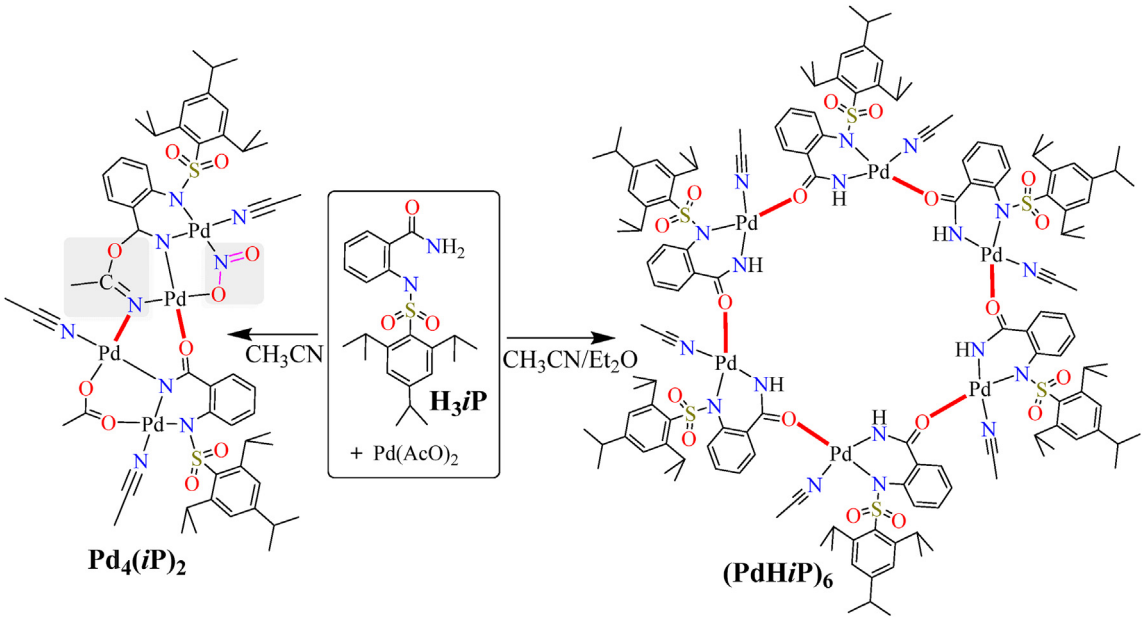
3.2. Structural characterization

Single crystals of H_3M, T_2CN and $Pd_4(iP)_2$ suitable for X-ray measurement were obtained by slow solvent evaporation from their acetonitrile solution. Single crystals of $(PdHiP)_6$ were obtained by slow diffusion of diethylether into a previously stirred acetonitrile solution of ligand H_3iP and $Pd(AcO)_2$. Data for their structural refinement and processing parameters are collected in Table 1 and their crystal structures are presented in Fig. 1 – 3. Compounds H_3M and T_2CN crystallize in the monoclinic P21/n and triclinic P$\bar{1}$ space groups respectively (Fig. 1). Complexes $(PdHiP)_6$ and $Pd_4(iP)_2$ both crystallize in the triclinic P$\bar{1}$ space group (Figs. 2 and 3). Selected bond lengths around the coordination centre for the structures of $(PdHiP)_6$ and $Pd_4(iP)_2$ are collected in the Supplementary Information Table S2 and they are within expected values [49]. The Pd–O bonds are generally in the range from 2.041 Å to 2.071 Å while the Pd–N bonds generally range from 1.942 to 2.025 Å, which suggests that the nitrogen donor atoms are stronger donors than the oxygen donor atoms.

The assembly of six units of square planar palladium centres into the hexanuclear macromolecular $(PdHiP)_6$ can be considered as networking between the palladium ion of one complex unit and the amide carbonyl oxygen of another complex unit. On the other hand, the structure of $Pd_4(iP)_2$ consist of two ligands and four palladium centres. Each palladium centre is different from one another. In general, the hemilability of the studied ligands could be implied from the consistently longer Pd–N bond lengths for the anilinyl N-donor than for the amide N-donor. Furthermore, the incorporation of coordinated acetonitrile suggests that the palladium complexes would easily generate coordinatively non-saturated active catalyst centres, which presents hope of forming desirable monodentate mono-ligand active catalyst species. These structural features also suggest how the ligands may possibly assemble during *in situ* '$Pd(AcO)_2$ + ligand' catalysis situations. For comparative reasons, $Pd_4(iP)_2$ has been tested as precatalyst in C–C coupling reactions.

3.3. Determining suitable reaction parameters for Suzuki-Miyaura C–C coupling

In order to determine reaction settings under which the various ligands would be compared, ligands H_3M and H_3T were used as representatives of the ligand series to test for suitable reaction time, base additive, boronic acid loading and $Pd(AcO)_2$: ligand ratio. The typical coupling reaction consisted of (4-bromophenyl)methanol and (4-acetylphenyl)boronic acid and the decision to use (4-bromophenyl)methanol arose from the need to use ^1H NMR signal of its methylene ($-CH_2-$) function for yield determination [31]. The results of the various parameters tested are summarized in Table 2.



Scheme 4. Isolated palladium complexes $Pd_4(iP)_2$ and $(PdHiP)_6$. Shaded parts of complex $Pd_4(iP)_2$ respectively indicate covalently incorporated acetonitrile on the ligand H_3iP and NO_2 moiety coordinatively bridging between two Pd centres.

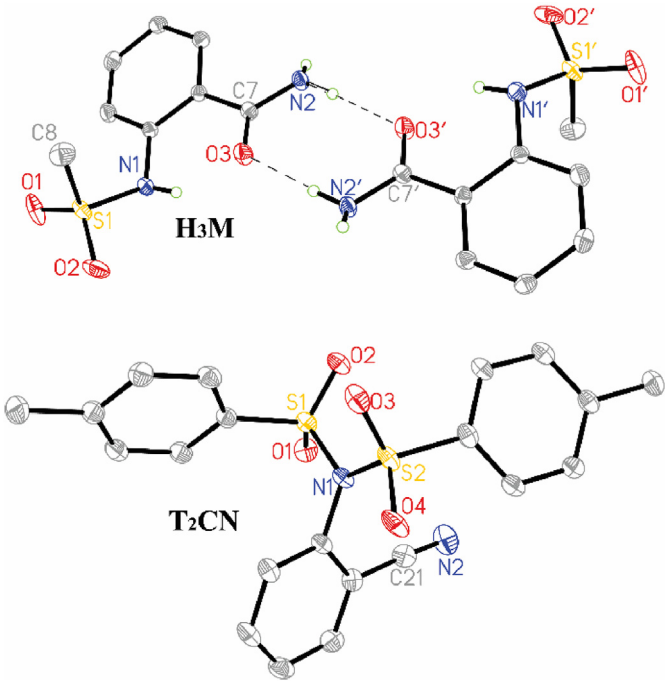


Fig. 1. X-ray structure of ligands H_3M (top) and T_2CN (bottom). Protons and solvent molecules have been omitted for clarity.

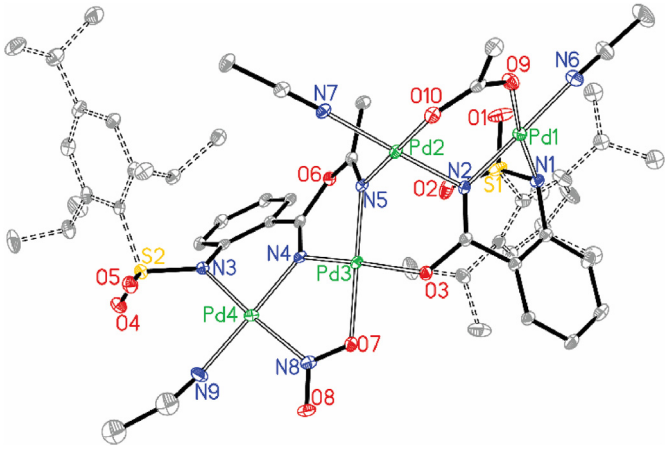


Fig. 2. X-ray structure of complex $Pd_4(iP)_2$. The bonds in the triisopropylphenyl substituents are displayed as dashes to improve clarity. Protons and solvent molecules have also been omitted for clarity and ellipsoids are drawn at the 20% probability level.

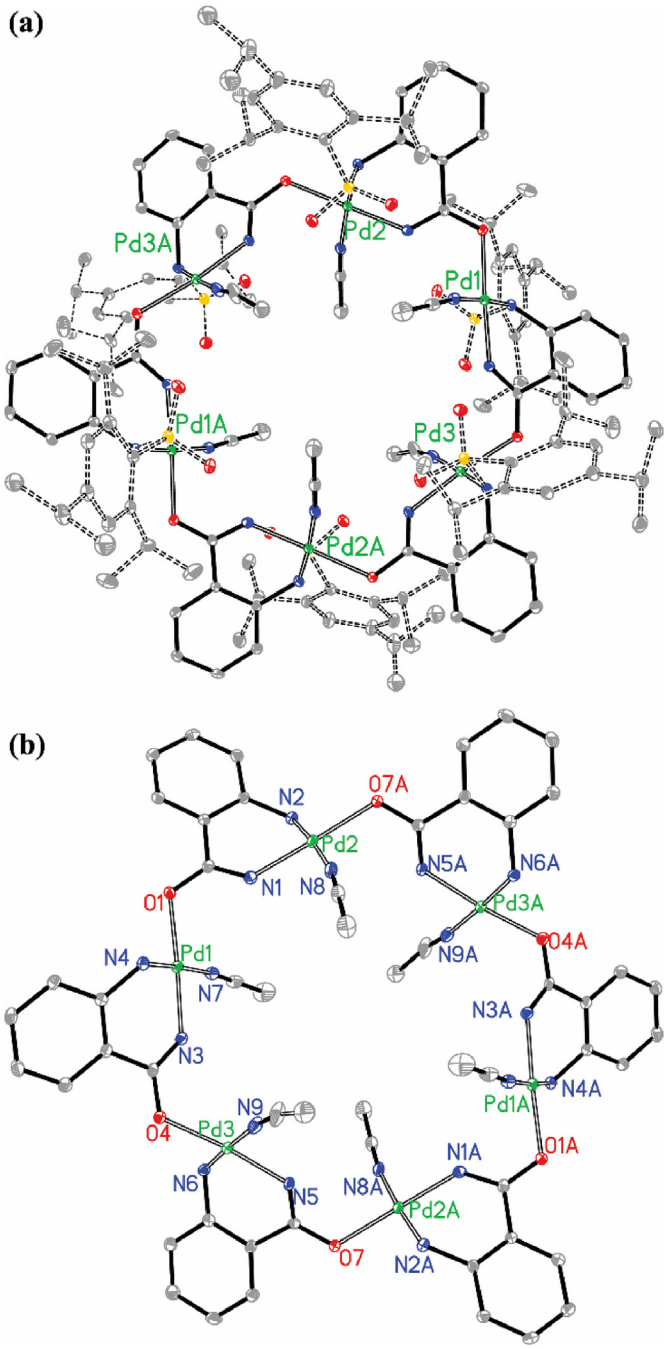


Fig. 3. X-ray structure of complex $(PdHiP)_6$ showing (a) the complete molecule where the bonds of the triisopropylphenyl substituents are displayed as dashes for clarity and (b) the molecule where all substituents sulfonyl fragments have been omitted for clarity. Protons and solvent molecules have been omitted for clarity and ellipsoids are drawn at the 20% probability leve.

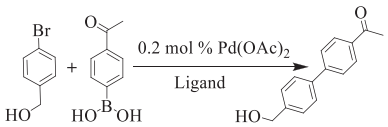
At oil bath temperature of 100 °C and 10 min reflux in the presence of K_2CO_3 (1 mmol), $Pd(AcO)_2$ (0.2 mol %) and in 4 mL of 3:1 EtOH/H_2O mixture, changing the amount of ligand H_3T from 0.4 mol % through 0.7 mol % to 1.0 mol % produced marginal yield increase from 16% through 24%–29% respectively. Thus, further reactions were continued with 0.7 mol % ligand. Conducting the same reaction with ligand H_3M at 10 min and 30 min respectively yielded 38% and 40% of the coupling product. Therefore, necessity for longer reflux times was not supported and the results indicate that the generated active species are probably short-lived under the reflux condition.

Continuing with 0.7 mol % of H_3M at 10 min reflux and keeping other parameters constant, the test of various base additives revealed that K_3PO_4 is favoured in the coupling reaction (yield = 57% with 1.0 mmol K_3PO_4). Furthermore, as the amount of K_3PO_4 was increased to 1.2 mmol the yield increased to 74% even under reflux time of 5 min, which further suggests that the original 10 min is probably much more than the effective duration of the catalyst's life under the reflux situation.

3.4. Comparing ligand frameworks in relation to catalysis outcomes

Eventually, the optimized catalytic reaction setting consisting of 4 mL of 3:1 EtOH/H_2O, 1.2 mmol K_3PO_4, 0.7 mol % ligand +0.2 mol % $Pd(AcO)_2$, 1 mmol 4-bromophenylmethanol, 1.2 mmol 4-

Table 2
Optimization of reaction parameters for Suzuki-Miyaura coupling[a].



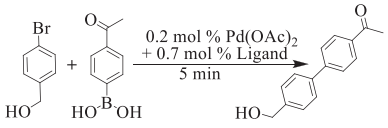
Ligand (mol %)[b]	Time (min)	Base (mmol)	Yield (%)
H_3T (0.4)	10	K_2CO_3 (1.0)	16
H_3T (0.7)	10	K_2CO_3 (1.0)	24
H_3T (1.0)	10	K_2CO_3 (1.0)	29
H_3M (0.7)	10	K_2CO_3 (1.0)	38
H_3M (0.7)	30	K_2CO_3 (1.0)	40
H_3M (0.7)	10	Na_2CO_3 (1.0)	41
H_3M (0.7)	10	Et_3N (1.0)	21
H_3M (0.7)	10	KOH (1.0)	29
H_3M (0.7)	10	K_3PO_4 (1.0)	57
H_3M (0.7)	5	K_3PO_4 (1.2)	74

[a] Reaction conditions: (4-acetylphenyl)boronic acid (1.2 mmol); (4-bromophenyl)methanol (1 mmol); $Pd(AcO)_2$ (0.2 mol % relative to (4-bromophenyl)methanol); ligand amount (0.4–1.0 mol % relative to); solvent 3:1 EtOH/H_2O (4 mL); base (1.0–1.2 mmol); oil bath temperature set at 100 °C; Yield was determined by ^1H NMR and reported to the nearest whole number.
[b] The amount of ligand in mol % is relative to (4-bromophenyl)methanol (1 mmol).

acetylphenylboronic acid, oil bath temperature of 100 °C and 5 min' reflux duration was applied in the presence of differing N-donor ligand frameworks. The results for the *in situ* catalyst generation experiments are presented in Table 3, which generally shows that changing the ligands has some influence on the activity of the palladium active centres.

In general, the methyl-substituted H_3M ligand performed better than the triisopropylphenyl- and tolyl-substituted ligands. Therefore, it may be concluded that N-donor active palladium centres are better stabilized by ligand H_3M, which may can be attributed to stronger N-donor strength enabled by the methyl fragment on the sulfonyl S-atom. Comparing ligands H_3M, H_3T and H_3iP, the ligands varied only at the S-atom with the substituents of methyl, tolyl and triisopropyl respectively. It is therefore noteworthy that the observed trend appears to follow the $+I$ contribution from these substituents; i.e. methyl for H_3M (TOF = 4500 h^{-1}) > triisopropylphenyl for H_3iP (TOF = 3780 h^{-1}) > tolyl for H_3T (TOF = 3300 h^{-1}). Consequently, the role of electronic character of the N-donors overrides the influence of steric features of the substituents around the N-donor atom. Furthermore, similar N-supported palladium complexes require higher catalyst loadings and hours of reflux to attain high catalyst yields [50–52].

Table 3
Catalytic performance for the series of ligands investigated[a].3



Catalyst system	Yield (%)	TOF (h^{-1})
$Pd(AcO)_2$	39	2340
H_3M + $Pd(AcO)_2$	74	4500
H_3T + $Pd(AcO)_2$	55	3300
T_2CN + $Pd(AcO)_2$	53	3180
H_3iP + $Pd(AcO)_2$	63	3780
$HiPCN$ + $Pd(AcO)_2$	59	3540
$Pd_4(iP)_2$[b]	75	4500

[a] Reaction conditions: (4-Acetylphenyl)boronic acid (1.2 mmol), (4-bromophenyl)methanol (1 mmol), solvent: EtOH/H_2O (3 mL + 1 mL), Base (K_3PO_4, 1.2 mmol), time (5 min reflux), temperature (100 °C), ligand amount (0.7 mol % relative to (4-bromophenyl)methanol), $Pd(AcO)_2$ (0.2 mol % relative to (4-bromophenyl)methanol); Yield was determined by ^1H NMR and reported to the nearest whole number.
[b] $Pd_4(iP)_2$ (0.05 mol % relative to (4-bromophenyl)methanol).

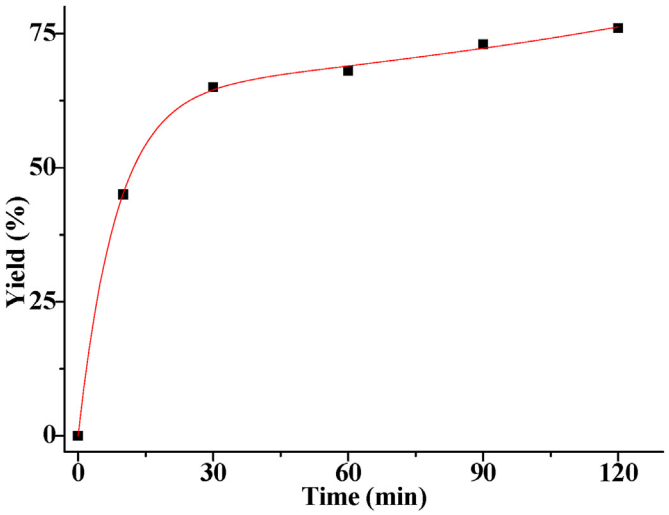
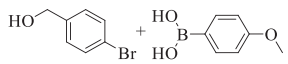
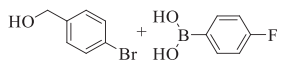
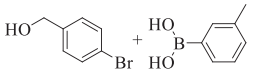
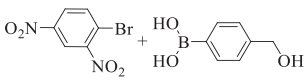
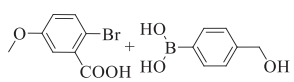
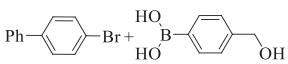
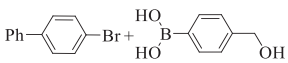


Fig. 4. *In situ* catalytic performance of ligand H_3M at 50 °C at varying times.

For the purpose of comparison, the precatalyst $Pd_4(iP)_2$ at 0.05 mol % loading was also subjected to same catalytic condition as for the ligands and it could be concluded that preformed complexes possess advantage over the *in situ* approach; i.e. TOF = 4500 h^{-1} for $Pd_4(iP)_2$ compared to TOF = 3780 h^{-1} for H_3iP. In calculating the TOF values, the tetranuclear nature of $Pd_4(iP)_2$ was taken into consideration, which is why 0.05 mol % (i.e. 0.2 mol % ÷ 4) of the complex was deployed.

Table 4
Substrate scope by $Pd_4(iP)_2$ as precatalyst.[a].

Substrates	Yield(%)	TOF (h^{-1})
	84	5290
	70	4000
	92	5520
	80	4800
	74	4440
	19	1140
	56	3360

[a] Reaction conditions: Solvent: EtOH/H_2O (3 mL + 1 mL), Base (K_3PO_4, 1.2 mmol), time (5 min reflux), temperature of oil bath (100 °C), $Pd_4(iP)_2$ (0.05 mol%) (4-acetylphenyl)boronic acid (1.2 mmol), (4-bromophenyl)methanol (1 mmol), Yield was determined by ^1H NMR and reported to the nearest whole number.

In order to investigate the observed early termination of catalyst activities during the reflux experiments, the determined reaction conditions except for reaction temperature of 50 °C was applied for ligand H_3M, and yields were determined as a function of time. Interestingly, the catalyst generated *in situ* at ambient temperature proved to be living as illustrated in Fig. 4.

In an attempt to elucidate the substrate profile of the precatalyst $Pd_4(iP)_2$ at 0.05 mol % loading, the catalytic activity of the complex was investigated towards other substrates according to the already established reaction settings above. The results are presented in Table 4. One important observation is that the pre-catalyst generally displayed favourable catalytic activity towards various aryl halides and arylboronic acids within the 5 min' reaction duration. However, presence of carboxy group ortho to the bromo atom proved to hinder the coupling reaction.

3.5. Heck C–C coupling performance in the presence of $Pd_4(iP)_4$

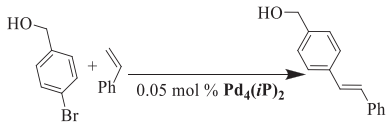
Test for the Heck coupling potential was carried using the preformed complex $Pd_4(iP)_2$ in the coupling of (4-bromophenyl) methanol and styrene. Due to the volatile nature of styrene (S), 1.5 mmol was used. The catalysis outcomes are summarized in Table 5. While varying reaction media and base additives under 60-min reflux and oil bath temperature set to 100 °C, the catalytic yields remained low in the range of 8%–31%. However, if higher temperatures would be explored, only the DMF/H_2O (3:1) provides the possibility despite its lower yield at 100 °C than for acetonitrile/water, ethanol/water or only water. Thus, exploring 140 °C in DMF/H_2O (3:1), a yield of 8% at 100 °C relative to the 73% recorded at 140 °C indicated the preference for high temperature catalyst productivity by $Pd_4(iP)_4$. Furthermore, there is a gradual increase in yields when reflux durations of 1 and 3 h are compared, which suggests that, in the Heck case, the catalyst species formed in DMF/H_2O and at the operational temperatures remained active.

4. Conclusion

2-Aminobenzamide was condensed with the sulfonyl chloride reagents (methylsulfonyl chloride, *p*-toluenesulfonyl chloride or 2,4,6-triisopropylbenzenesulfonyl chloride), which yielded well characterized, simple, N-donor ligand derivatives H_3M, H_3T, T_2CN, H_3iP and H*i*PCN. The complexation experiments revealed that the ligands potentially possess variable coordination possibilities as well as possible accompanying ligand and/solvent oxidative reactivities. Defined solvent-controlled tetranuclear and hexanuclear coordination products $Pd_4(iP)_2$ and $(PdHiP)_6$ were self-assembled by allowing palladium acetate and ligand H_3iP to stand in solvent. Single crystal analyses confirmed the structures of ligands H_3M and T_2CN as well as for the complexes $Pd_4(iP)_2$ and $(PdHiP)_6$.

Testing the N-donors as support ligands in palladium-catalyzed Suzuki coupling revealed high performances either by *in situ* '$Pd(AcO)_2$ + ligand' approach or by deployment of the precatalyst. That such simple and synthetically assessable N-donor ligands could couple aryl bromides and arylboronic acids with turn over frequencies attaining 5500 h^{-1} within 5 min of reflux enables the conclusion that palladium active species could also be stabilized by N-donor ligand frameworks. It was also concluded that, under similar reaction conditions, preformed coordination precatalyst $Pd_4(iP)_2$ offered better catalytic benefit relative to the corresponding *in situ* catalyst generation. Heck coupling activities by $Pd_4(iP)_2$ were also observed. While the active species formed during the Suzuki coupling showed stability at ambient temperatures in ethanol/water media, catalyst activity in the Heck coupling only produced high yields at high temperatures. In general, the overall catalytic results present motivation for further study of N-donor-stabilized palladium catalysts and optimism that affordable and efficient phosphine-free catalysts can be attained.

Table 5
Heck coupling reaction by the precatalyst $Pd_4(iP)_2$[a].



Solvent	Base	Temp.(°C)	Time (min)	Yield (%)
H_2O	K_2CO_3	100	60	9
CH_3CN/H_2O (1:1)	K_2CO_3	100	60	18
EtOH/H_2O (1:1)	K_2CO_3	100	60	22
EtOH/H_2O (1:1)	K_3PO_4	100	60	31
EtOH/H_2O (1:1)	NaOH	100	60	27
EtOH/H_2O (1:1)	KOH	100	60	27
DMF/H_2O (3:1)	K_2CO_3	100	60	8
DMF/H_2O (3:1)	K_2CO_3	140	60	73
DMF/H_2O (3:1)	K_2CO_3	140	180	84
DMF/H_2O (3:1)	K_3PO_4	140	60	46
DMF/H_2O (3:1)	K_3PO_4	140	180	48

[a] Reaction conditions: Solvent (4 mL), Base (1.5 mmol), time (60, 180 min reflux), $Pd_4(iP)_2$ pre-catalyst (0.05 mol%), styrene, (1.5 mmol), (4-bromophenyl)methanol, (1 mmol). Yield was determined by ^1H NMR and reported to the nearest whole number.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molstruc.2019.07.054.

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