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Aromatic PCN pincer palladium complexes: forming and breaking C–C bonds

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Dedicated to Gerard van Koten on the occasion of his 75th birthday.

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ABSTRACT

Through a salt metathesis reaction, ($^{t-Bu}$PCN)Pd-ONO$_2$ (**2**) was prepared and used as a precursor for producing ($^{t-Bu}$PCN)Pd-OH (**3**) and ($^{t-Bu}$PCN)Pd-aryl acetylide complexes **4** (phenyl acetylide) and **5** (p-tolyl acetylide). The aryl acetylide complexes could also be prepared through another synthetic route: by condensation of **3** with the corresponding aryl acetylene. The reactivity of complexes **3** and **4** toward carbon dioxide was studied and it was found that both reactions give the hydrogen carbonate complex (**6**). The low reactivity of the Pd-acetylide bond was further confirmed by the fact that the propiolate complex undergoes decarboxylation to give **4**. PCN palladium complexes are good catalysts for the decarboxylative cross coupling reactions between acetylene carboxylic acids and aryl halides. The yield of the cross coupling product was improved by adding a catalytic amount of CuI.

1. Introduction

Transition metal pincer complexes have found great applications in catalysis due to their high thermal stability compared to other organometallic complexes as a result of the tridentate chelation of the pincer ligand [1]. The most common examples in the literature are based on symmetrical pincer architectures, *e.g.* PCP [2], NCN [3] or POCOP [4], which are all accessible through straightforward synthetic routes. Complexes of unsymmetrical pincer ligands are much less common and include *e.g.* PCN [5], PCO [6] and POCN [7] ligand frameworks. Although relatively long synthetic approaches are required to prepare these complexes they sometimes display different reactivities compared to the symmetric ones through, for example, the hemilabile character of the O/N pincer arm. One area where pincer complexes have been utilized is the stoichiometric and catalytic activation of CO_2 and it is notable that pincer ligands together with carbenes seem particularly suitable to induce a high reactivity in insertions into the metal – carbon bond to form the corresponding metal carboxylate complexes [4e,8]. However, although such insertions have been proposed in many catalytic reactions, their actual demonstration mainly include metal-alkyl bonds; there are very few examples of stoichiometric insertions of CO_2 into late metal-carbon sp^2- and sp-bonds [9]. Recently we published the first (PCN) Pd complexes [5f] and here we continue to explore their reactivity reporting the synthesis of hydroxide and acetylide derivatives and their reactivity towards CO_2 and phenyl iodide. Furthermore, the decarboxylation of (PCN)Pd phenyl propiolate complex at room temperature is reported together with a catalytic decarboxylative cross coupling reaction between the propiolic acids and aryl halides.

2. Experimental section

General Procedures and Materials. All experiments were carried out under an atmosphere of argon or nitrogen using standard Schlenk or high vacuum techniques [10] unless otherwise noted. Anhydrous solvents were obtained from a Braun SPS-800 system or distilled from sodium/benzophenone ketyl radical. NMR experiments were carried out using J. Young NMR tubes. All chemicals were purchased from Acros, Alfa Aesar or Sigma-Aldrich. ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR were recorded on a Varian Unity INOVA 500 spectrometer operating at 499.77 MHz (^{1}H) using C_6D_6 unless noted. Chemical shifts are given in ppm downfield from TMS using residual solvent peaks (^{1}H and ^{13}C{^{1}H} NMR) or H_3PO_4 as reference.

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Multiplicities are abbreviated as follows: (s) singlet, (d) doublet, (t) triplet, (q) quartet, (m) multiplet, (br) broad. Elemental analyses were performed by Mikroanalytisches Laboratorium KOLBE (Mülheim an der Ruhr, Germany). The (PCN)H ligand, the [PCN]Pd-Cl complex (**1**) and [PCN]Pd-I complex (**9**) were prepared according to previously published procedures [5f].

2-[(*N*,*N*-Dimethylamino)methyl]-6-[(di-*tert*-butylphosphino)-metyl]phenylpalladium nitrate [PCN]Pd-ONO$_2$ (2). 1 (64.0 mg, 0.150 mmol, 1.00 eq.) and $AgNO_3$ (26.8 mg, 0.158 mmol, 1.05 eq.) were stirred in 5 mL THF for 2 days. After evaporation the residue was dissolved in toluene, filtered and the filtrate was evaporated yielding 69.1 mg (99%) of the product as a pale yellow solid. Solvent vapour diffusion (benzene/hexane) at 4 °C gave single crystals suitable for X-ray analysis. ^{1}H NMR (500 MHz, C_6D_6) δ 6.94 (td, J = 7.5, 1.4 Hz, 1H), 6.77 (d, J = 7.8 Hz, 1H), 6.58 (d, J = 7.3 Hz, 1H), 3.23 (s, 2H), 2.72 (d, J = 9.4 Hz, 2H), 2.36 (d, J = 2.1 Hz, 6H), 1.12 (d, J = 14.1 Hz, 18H). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 153.1 (s), 148.1 (d, J = 15.1 Hz), 147.9 (d, J = 1.1 Hz), 124.8 (s), 122.1 (d, J = 21.1 Hz), 120.5 (s), 70.6 (d, J = 2.5 Hz), 48.8 (d, J = 2.3 Hz), 34.3 (d, J = 16.3 Hz), 32.9 (d, J = 29.1 Hz), 28.3 (d, J = 4.6 Hz). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6) δ 90.94. Anal. Found (calc. for ($C_{18}H_{31}N_2O_3PPd$) C, 46.55 (46.91); H, 6.83 (6.78); N, 5.99 (6.08).

2-[(*N*,*N*-Dimethylamino)methyl]-6-[(di-*tert*-butylphosphino)-metyl]phenylpalladium hydroxide [PCN]Pd-OH (3). In a Straus flask **2** (231 mg, 0.502 mmol, 1.00 eq.), KOH (560 mg, 9.98 mmol, 19.9 eq.) and 25 mL of THF were combined inside the glove box and the mixture was sonicated and then stirred for 19 h. After evaporation, swivel filtration with benzene and evaporation of the filtrate the crude product was obtained as a white powder (208 mg, 99%). Single crystals suitable for X-ray analysis were obtained from a hexane/benzene solution at −20 °C inside the glovebox. ^{1}H NMR (500 MHz, C_6D_6) δ 7.03 (td, J = 7.4, 1.2 Hz, 1H), 6.95 (d, J = 7.5 Hz, 1H), 6.76 (d, J = 7.5 Hz, 1H), 3.56 (s, 2H), 2.95 (d, J = 9.2 Hz, 2H), 2.64 (d, J = 2.0 Hz, 6H), 1.22 (d, J = 13.6 Hz, 18H), −1.32 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 154.9 (s), 148.6 (s), 147.7 (d, J = 15.3 Hz), 123.7 (s), 121.8 (d, J = 20.8 Hz), 120.0 (s), 72.9 (d, J = 2.5 Hz), 48.9 (d, J = 2.6 Hz), 35.8 (d, J = 29.0 Hz), 34.4 (d, J = 16.0 Hz), 29.2 (d, J = 5.2 Hz). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6) δ 91.44. The compound is very hygroscopic and failed to give a satisfactory elemental analysis.

2-[(*N*,*N*-Dimethylamino)methyl]-6-[(di-*tert*-butylphosphino)-metyl]phenylpalladium phenylacetylide [PCN]Pd-CC-Ph (4). *Method **A***: **2** (4.6 mg, 10.0 μmol, 1.00 eq.) and phenyl acetylene (2.2 μL, 2.0 mg, 20.0 μmol, 2.00 eq.) were stirred under nitrogen together with KOH (8.60 mg, 150 μmol, 15.0 eq.) in 0.5 mL of dry THF for 16 h. After evaporation and filtration with benzene, evaporation yielded 4.8 mg (96%) of the product. Slow solvent evaporation from a hexane solution gave single crystals suitable for X-ray diffraction. *Method **B***: **2** (138 mg, 0.3 mmol, 1.00 eq.) and phenyl acetylene (66 μL, 0.6 mmol, 2.00 eq.) were stirred under nitrogen together with K_2CO_3 (207 mg, 1.5 mmol, 5.0 eq.) in 15 mL of dry THF for 24 h. After evaporation and filtration with benzene, evaporation yielded 120 mg (80%) of the product. ^{1}H NMR (500 MHz, C_6D_6) δ 7.72 (d, J = 8.2, 2H), 7.20−7.17 (m, 2H), 7.08 (t, J = 7.0, 1H), 7.04−6.99 (m, 2H), 6.83 (d, J = 7.3 Hz, 1H), 3.57 (s, 2H), 3.13 (d, J = 9.1 Hz, 2H), 2.69 (d, J = 1.7 Hz, 6H), 1.33 (d, J = 13.9 Hz, 18H). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 171.2 (d, J = 1.9 Hz), 150.0 (s), 148.3 (d, J = 15.2 Hz), 131.5 (s), 130.6 (s), 128.8 (d, J = 15.4 Hz), 128.3 (s), 124.7 (d, J = 6.6 Hz), 121.4 (d, J = 21.0 Hz), 119.8 (s), 109.7 (s), 74.6 (d, J = 2.3 Hz), 51.1 (d, J = 2.2 Hz), 38.1 (d, J = 27.9 Hz), 34.7 (d, J = 17.3 Hz), 29.4 (d, J = 4.7 Hz). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6) δ 98.44. Anal. Found (calc. for ($C_{26}H_{36}NPPd$)) C, 62.59(62.46); H, 7.23 (7.26); N, 2.76(2.80).

2-[(*N*,*N*-Dimethylamino)methyl]-6-[(di-*tert*-butylphosphino)-metyl]phenylpalladium *p*-methylphenylacetylide [PCN]Pd-CC-Tol (5). *Method **A***: In a J. Young NMR tube **3** (4.2 mg, 10.1 μmol, 1.00 eq.) and *p*-tolylacetylene (2.3 mg, 19.8 μmol, 1.96 eq.) were dissolved in C_6D_6 inside the glove box. After less than 5 min full conversion to the product can be observed in NMR spectra. Evaporation, filtration with hexane, and evaporation yielded 5.0 mg (96%) of the product. Crystallization from a hexane solution at − 20 °C gave single crystals suitable for X-ray diffraction. *Method **B***: In a screw capped vial **2** (46.3 mg, 0.100 mmol, 1.00 eq.), K_2CO_3 (72.0 mg, 0.522 mmol, 5.22 eq.) and *p*-tolylacetylene (2.3 mg, 0.200 mmol, 2.00 eq.) were stirred for one day. The solvent was evaporated, it was filtered with benzene and evaporated again yielding 57.0 mg of a NMR-pure product as a black solid. Crystallization from hexane at − 20 °C gave the product as colourless needles (33.3 mg, 56%). ^{1}H NMR (500 MHz, C_6D_6) δ 7.66 (d, J = 8.0 Hz, 2H), 7.08 (t, J = 7.4 Hz, 1H), 7.02 (d, J = 7.0 Hz, 1H)$^{\#}$, 7.01 (d, J = 8.1 Hz, 2H)$^{\#}$, 6.83 (d, J = 7.2 Hz, 1H), 3.57 (s, 2H), 3.13 (d, J = 9.1 Hz, 2H), 2.70 (d, J = 2.1 Hz, 6H), 2.11 (s, 3H), 1.34 (d, J = 13.9 Hz, 18H), $^{\#}$signals are overlapping. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 170.9 (s), 149.6 (s), 147.9 (d, J = 15.2 Hz), 133.5 (s), 131.0 (s), 128.6 (s), 126.9 (d, J = 15.5 Hz), 124.3 (s), 121.0 (d, J = 21.0 Hz), 119.3 (s), 109.1 (s), 74.2 (d, J = 2.4 Hz), 50.7 (d, J = 2.5 Hz), 37.7 (d, J = 27.8 Hz), 34.3 (d, J = 17.3 Hz), 29.0 (d, J = 4.7 Hz), 20.9 (s) (one carbon missing/hidden under C_6D_6). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6) δ 98.40. Anal. Found (calc. for ($C_{27}H_{38}NPPd$) C, 63.21 (63.09); H, 7.46 (7.45); N, 2.70 (2.73).

[PCN]Pd-OCO$_2$H (6). In a J. Young NMR tube, 6.0 mg (15.0 μmol) of **3** was dissolved in 0.5 ml C_6D_6 inside the glove box. The tube was degassed (three freeze-pump-thaw cycles) using the high vacuum line and the solution was pressurized with 8 atm of CO_2. The reaction was monitored by ^{1}H and ^{31}P{^{1}H} NMR and resulted in 95% of (PCN)PdOCO$_2$H and 5% of (PCN)PdONO$_2$. Single crystals suitable for X-ray analysis were obtained by slow fusion of *n*-hexane into a concentrated solution of the crude product in C_6D_6 at 5 °C. ^{1}H NMR (500 MHz, C_6D_6) δ 6.95 (t, J = 7.4 Hz, 1H), 6.81 (d, J = 7.4 Hz, 1H), 6.62 (d, J = 7.3 Hz, 1H), 3.34 (s, 2H), 2.80 (d, J = 9.2 Hz, 2H), 2.56 (s, 6H), 1.24 (d, J = 13.9 Hz, 18H). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 163.4 (s), 155.6 (s), 148.7 (s), 148.5 (d, J = 15.3 Hz), 124.7 (s), 122.2 (d, J = 21.0 Hz), 120.6 (s), 71.5 (s), 49.4 (s), 34.7 (d, J = 16.0 Hz), 33.8 (d, J = 28.7 Hz), 29.0 (d, J = 4.6 Hz). ^{31}P{^{1}H} NMR δ 89.74.

{[PCN]Pd}$_2$-(μ-CO$_3$)(7). Heating **6** to 100 °C and removing the volatiles under high vacuum or reacting **3** with 4 atm of CO_2 at room temperature gave **7**. The complex was characterised *in situ* by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy and was 77% pure (with 23% **2**). ^{1}H NMR (500 MHz, C_6D_6) δ 7.03 (t, J = 7.4 Hz, 2H), 6.92 (d, J = 7.2 Hz, 2H), 6.77 (d, J = 7.3 Hz, 2H), 3.62 (s, 4H), 2.91 (d, J = 9.4 Hz, 4H)$^{\#}$, 2.88 (br s, 12H)$^{\#}$, 1.36 (d, J = 13.7 Hz, 36H), $^{\#}$signals are overlapping. ^{31}P{^{1}H} NMR δ 88.64.

Reaction of [PCN]Pd-CC-Ph (4) with CO$_2$. In a J. Young NMR tube, 5.0 mg (10.0 μmol) of **4** was dissolved in 0.5 mL C_6D_6. The tube was degassed (three freeze-pump-thaw cycles) using the high vacuum line and the solution was pressurized with 8 atm of CO_2. The reaction was followed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. Pressurizing with CO_2 was repeated at least three times until full conversion to **6** was achieved.

Reaction of [PCN]Pd-ONO$_2$ (2) with sodium phenylpropiolate. In a J Young NMR tube, 9.22 mg (20.0 μmol, 1.00 eq.) of **2** was dissolved in 0.5 mL C_6D_6 then (3.40 mg, 20.0 μmol, 1.00 eq.) of sodium phenyl propiolate was added. The tube was sonicated and the reaction was followed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. A slight excess of sodium phenyl propiolate was added after 8 h of sonication to achieve full conversion to the product.

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Reaction of [PCN]Pd-CC-Ph (4) with aryl halide. In a J Young NMR tube, 5.0 mg (10.0 μmol, 1.00 eq.) of **4** was dissolved in 0.45 mL C_6D_6 and phenyl bromide (10.1 μL, 100 μmol, 10.0 eq.) or phenyl iodide (11.2 μL, 100 μmol, 10.0 eq.) was added. The tube was heated to 50–100 °C and the reaction was followed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. The cross coupling product, diphenylacetylene was observed in the ^{1}H NMR spectrum.

General procedures for the catalytic decarboxylative coupling reactions of phenylpropiolic acid with aryl halides. 29.2 mg (0.2 mmol) phenyl propiolic acid, 0.2 mmol aryl halide, and 276.4 mg (2.0 mmol) K_2CO_3 were mixed together in a small vial and 3 mL of the solvent was added to the vial; then the catalyst was added in 2.5% mol ratio. The reaction mixture was heated to 135 °C for 48 h. The resulting mixture was poured into 10 mL of saturated aqueous NH_4Cl solution and the organic product was extracted with 3 × 5 mL Et_2O, dried over anhydrous $MgSO_4$ and filtered over Celite.

Crystallography. Intensity data were collected with an Oxford Diffraction Excalibur 3 system, using ω-scans and MoKα (λ = 0.71073 Å) radiation [11]. The data were extracted and integrated using Crysalis RED [12]. The structures were solved by direct methods and refined by full-matrix least-squares calculations on F^2 using SHELXT [13], SHELXL [14] and OLEX^2 [15]. Molecular graphics were generated using Crystal Maker 8.7 [16].

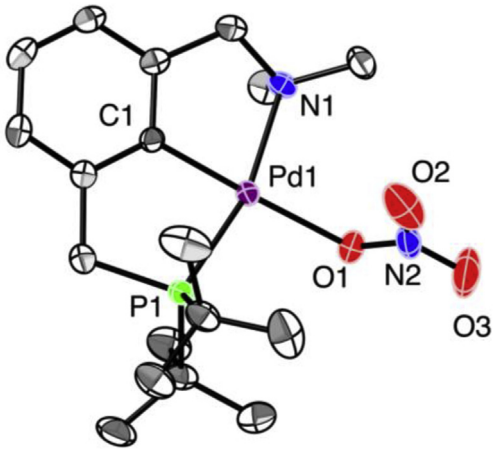


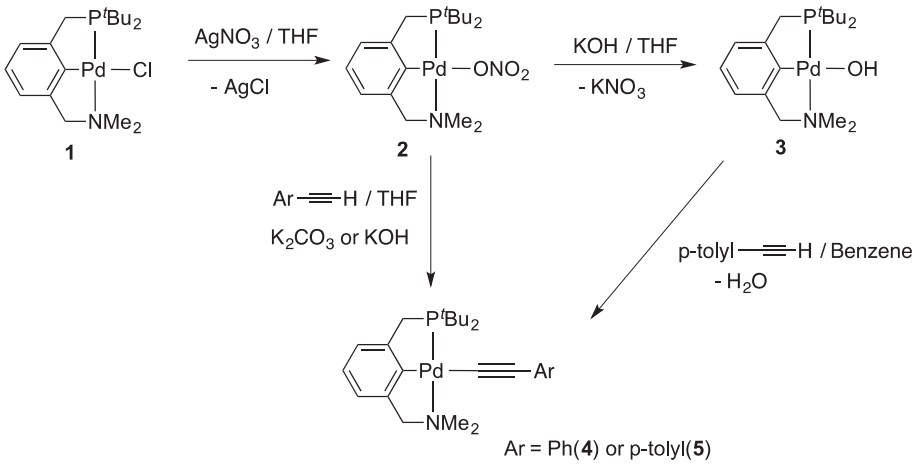
Fig. 1. Molecular structure of **2** at the 30% probability level. Hydrogen atoms and the benzene solvent are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Pd1-C1 = 1.976(4), Pd1-P1 = 2.2702(11), Pd1-N1 = 2.192(3), Pd1-O1 = 2.167(3), O1-N2 = 1.260(6), O2-N2 = 1.253(7), O3-N2 = 1.229(7), C1- Pd1-P1 = 82.97 (12), N1-Pd1-P1 = 164.97 (10), O1- Pd1-P1 = 101.28 (10), O1- Pd1-N1 = 92.68 (14), C1- Pd1-O1 = 172.48 (16).

3. Results and discussions

3.1. Synthesis of (PCN)Pd complexes

The (PCN)Pd-Cl(**1**) complex was synthesized through cyclometallation of the (PCN)H pincer preligand with $(PhCN)_2PdCl_2$ using our previously published procedure [5f]. A salt metathesis reaction with $AgNO_3$ produced the complex ($^{t-Bu}$PCN)Pd-ONO_2(**2**) in 99% yield and this was used as a precursor for preparing the hydroxide and the aryl acetylide complexes as illustrated in Scheme 1. The molecular structure of **2** is given in Fig. 1. The hydroxide complex (**3**) was synthesized by a procedure analogous to the one used for (PCP)Pd-OH [17a]. Sonication of **2** with an excess of KOH in THF under an inert atmosphere offered complex **3**, which shows a single ^{31}P NMR peak at 91.44 ppm and a ^{1}H NMR spectrum with an upfield singlet at −1.32 ppm, which agrees well with the few palladium hydroxide complexes based on pincer ligands that have been reported [5g,6b,17–18]. Complex **3** was further characterised by ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectroscopy and the molecular structure was determined by X-ray diffraction analysis showing a monomeric hydroxide complex (Fig. 2). The complex is very hygroscopic and therefore failed to give a proper elemental analysis; it crystallised with three molecules of water. The hydroxide complex showed no tendency, neither in solution nor in the solid state, to form bridging dinuclear complexes as was recently reported by Goldberg for the analogous $^{t-Bu}$PCO pincer palladium hydroxide complex and the pyrazole-based PCN pincer palladium hydroxide complex which, however, were prepared using a different synthetic route [5g,6b]. The Pd-O bond distance of 2.115(4) Å in **3** is slightly longer than the corresponding distance in the pyrazole-based PCN pincer palladium hydroxide complex (2.078(7) and 2.080(7) Å for the two molecules in the asymmetric unit) [5g]. As previously observed [5g,17–18] the water molecules in the structure of **3** form a hydrogen bonded network connecting two terminal hydroxide complexes.

There are only a few previous examples of palladium pincer acetylide complexes and they were synthesized either through base assisted ligand substitution [2a] or metathesis of free acetylene with hydride or alkyl complexes [18b,19]. Here, we obtained



Scheme 1. Synthesis of (PCN)Pd-hydroxide and arylacetylide complexes.

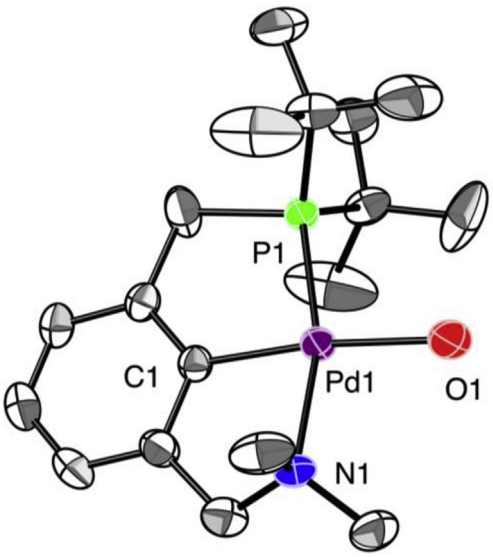


Fig. 2. Molecular structure of **3** at the 30% probability level. Hydrogen atoms and three water molecules are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Pd1-C1 = 1.980(4), Pd1-P1 = 2.2539(11), Pd1-N1 = 2.174(4), Pd1-O1 = 2.115(4), C1-Pd1-P1 = 82.82 (13), N1- Pd1-P1 = 164.47 (12), O1- Pd1-P1 = 103.93 (11), O1- Pd1-N1 = 91.31 (15), C1- Pd1-O1 = 173.02 (16).

arylacetylide complexes **4** and **5** either via the former pathway or through a new synthetic route involving C—H activation of the free acetylene where the hydroxide ligand acts as an internal base. Both reactions take place at room temperature, which is advantageous to the metathesis pathways which generally suffer from using thermally unstable complexes as starting materials and which require high temperatures in case of the alkyl metal complexes. Moreover, formation of byproducts such as styrene was observed in the metathesis reactions. The new arylacetylide complexes **4** and **5** were fully characterised with ^{1}H, $^{31}P\{^{1}H\}$, and $^{13}C\{^{1}H\}$ NMR spectroscopy, elemental analysis and X-ray diffraction analysis, cf. Fig. 3.

3.2. Reaction of CO_2 with **3**

The reactivity of the hydroxide complex with carbon dioxide was investigated. Compound **3** was pressurized with approximately 8 atm of CO_2 using C_6D_6 as a solvent. In the ^{31}P NMR spectrum, two new signals at 89.74 ppm (95%) and 90.93 ppm (5%) appeared within minutes. The ^{13}C NMR spectrum displays a sharp singlet for the major product at 163.4 ppm which is consistent with formation of the expected hydrogen carbonate pincer complex (**6**), cf. Scheme 2. Free CO_2 was observed as well in the ^{13}C NMR spectrum at 124.8 ppm [20]. Heating up to 100 °C had no effect on the product distribution. The ^{1}H, ^{31}P and ^{13}C NMR spectra of the minor product confirm its identity as complex **2**, which is probably formed due to presence of trace amounts of an NMR silent inorganic nitrate salt in the hydroxide complex; the nitrate anion displaces the weakly bound hydrogen carbonate anion producing complex **2**. The structure of complex **6** was further confirmed by an X-ray diffraction analysis (Fig. 4). Single crystals were obtained by slow diffusion of *n*-hexane into a concentrated benzene-d_6 solution of the crude product, and the recrystallization also allowed for a separation of **6** and **2**. When a lower pressure of CO_2 (4 atm) was used complex **6** was not observed, and instead the ^{31}P NMR spectrum displayed a new broad signal at 88.63 ppm in addition to the signal for complex **2** at 90.93 ppm. Similarly to above reaction, heating had no effect on the product distribution.

Crystallization by slow diffusion of *n*-hexane into the crude benzene-d_6 solution led to the formation of small crystals, which were not suitable for X-ray diffraction. However, the ^{31}P NMR spectrum of the crystals displayed a sharp signal corresponding to complex **6** at 89.74 ppm with trace amount of the original complex. To confirm the identity of the second insertion product, **7**, and study its relation with the hydrogen carbonate complex, **6** was synthesized as we described above and the solution was heated at 100 °C under vacuum. The solid residue was kept for drying on the high vacuum line for approximately 5 h and redissolved in C_6D_6. The $^{31}P\{^{1}H\}$ NMR spectrum showed a broad signal at 88.63 ppm as observed above. This indicates that the insertion of CO_2 into the hydroxide complex is reversible and that **7** can be formulated as a dimeric compound with a bridging carbonate; this was confirmed

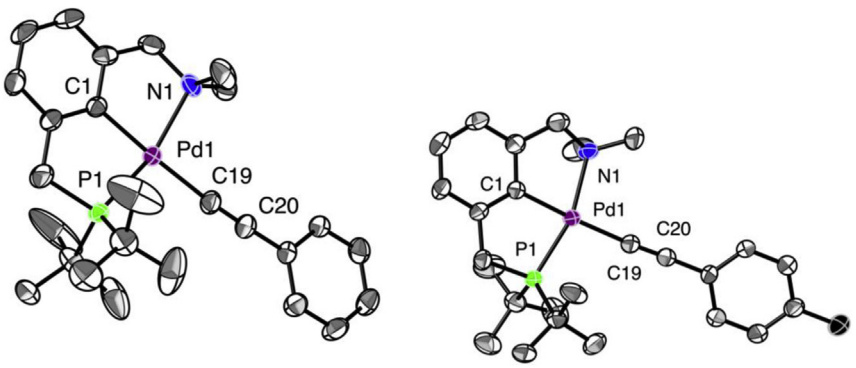
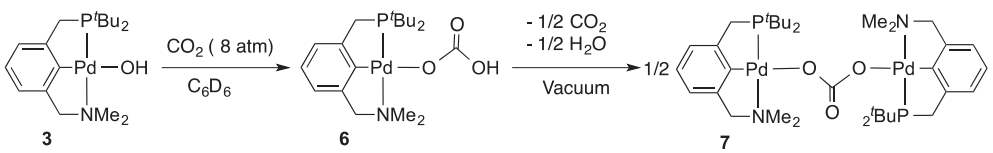


Fig. 3. Molecular structures of **4** and **5** at the 30% probability level. Hydrogen atoms are omitted for clarity.



Scheme 2. Insertion of CO_2 into (PCN)Pd-hydroxide complex (**3**).

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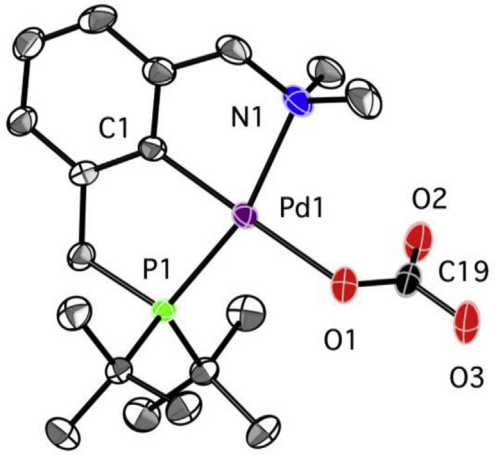
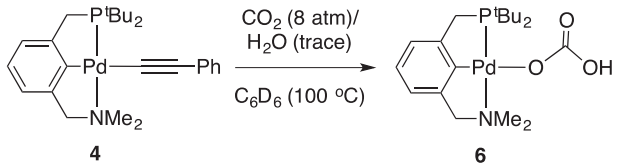


Fig. 4. Molecular structure of **6** at the 30% probability level. Hydrogen atoms and the benzene solvent are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Pd1-C1 = 1.970(2), Pd1-P1 = 2.2398(12), Pd1-N1 = 2.174(4), Pd1-O1 = 2.133(3), C1-Pd1-P1 = 82.94 (9), N1- Pd1-P1 = 162.74 (12), O1- Pd1-P1 = 99.29 (10), O1- Pd1-N1 = 97.44 (15), C1- Pd1-O1 = 174.70 (13).



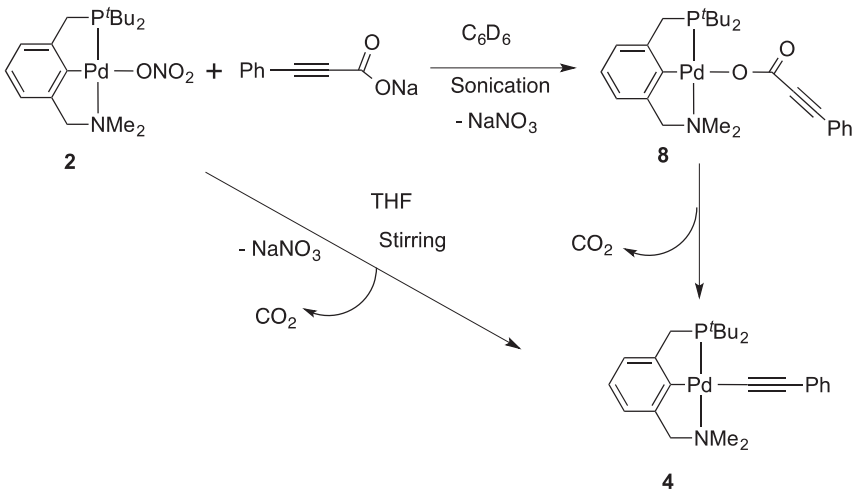
Scheme 3. Carboxylation reaction of (PCN)Pd-phenyl acetylide complex.

through an independent experiment, see below (Scheme 2). Formation of bridging carbonates have previously been reported for the (PCP^{i-Pr})Pd-OCO$_2$H complex [17b] and the hemilabile (PCO)Pd-OCO$_2$H complex during carboxylation [6b]. In the PCO-case the hemilability was clearly shown in that one of the oxygen arms is displaced by the carbonate. However, in the present PCN system, there is no apparent hemi-lability in the pincer fragments and the bridging carbonate ligand is η^1-bound to both of the palladium atoms.

The reactivity of **3** towards carbon monoxide was also investigated, where the corresponding (PCP) system gives a hydroxycarbonyl complex [18b]. For **3** we instead observed palladium black and a number of molecular products the distribution of which was not reproducible and probably very sensitive to conditions and impurities. In one of the experiment, however, we isolated X-ray quality crystals to give the structure of **7** (see Supporting information). Its NMR spectra coincide with complex **7** isolated above and form the basis for our structural assignment.

3.3. Reaction of CO_2 with aryl acetylide complexes

Metal acetylide complexes have been proposed as the active species in the catalytic cycle for carboxylation of terminal alkynes to form the corresponding propiolic acids [21], but there are no examples of stoichiometric insertions of CO_2 into late metal-acetylide bonds. On the contrary, it has been shown that the insertion of CO_2 into late metal-carbon bonds with sp- and sp^2-hybridization is usually not possible [4e,18b,22] with a few exceptions [9]. We therefore decided to study the carboxylation reaction of complex **4**, to probe the effect of hemilability in this respect. Thus, **4** was pressurized with approximately 8 atm of CO_2 in a J. Young NMR tube using C_6D_6 as a solvent. The reaction was monitored by recording ^{31}P and ^{1}H NMR spectra periodically. No reaction took place at room temperature but by increasing the temperature to 100 °C, a new signal was observed in the ^{31}P NMR spectrum at 89.73 ppm. The reaction is very sluggish and only 30% conversion was achieved after one month. The tube was repeatedly pressurized with CO_2 and the reaction was monitored for ca. six months to get full conversion of the starting material. Traces of the chloride complex and other unknown complexes were observed, but the major insertion product was identified by NMR spectroscopy as the hydrogen carbonate complex **6**, cf. Scheme 3. When the carboxylation reaction was carried out in presence of water (two droplets), full conversion to **6** was achieved in 10 days under the same reaction conditions. No hydroxide complex was observed as an intermediate during this reaction, and, furthermore, when a solution of **4** in C_6D_6 was heated to 100 °C in the presence of water there was no detectable formation of **3**. Therefore, we favour a mechanism involving reaction between carbonic acid (generated from the carbon dioxide and water) and **4** where the acetylide ligand is protonolysed and the hydrogen carbonate coordinated to the



Scheme 4. Reaction of (PCN)Pd-ONO$_2$ complex with sodium phenyl propiolate.

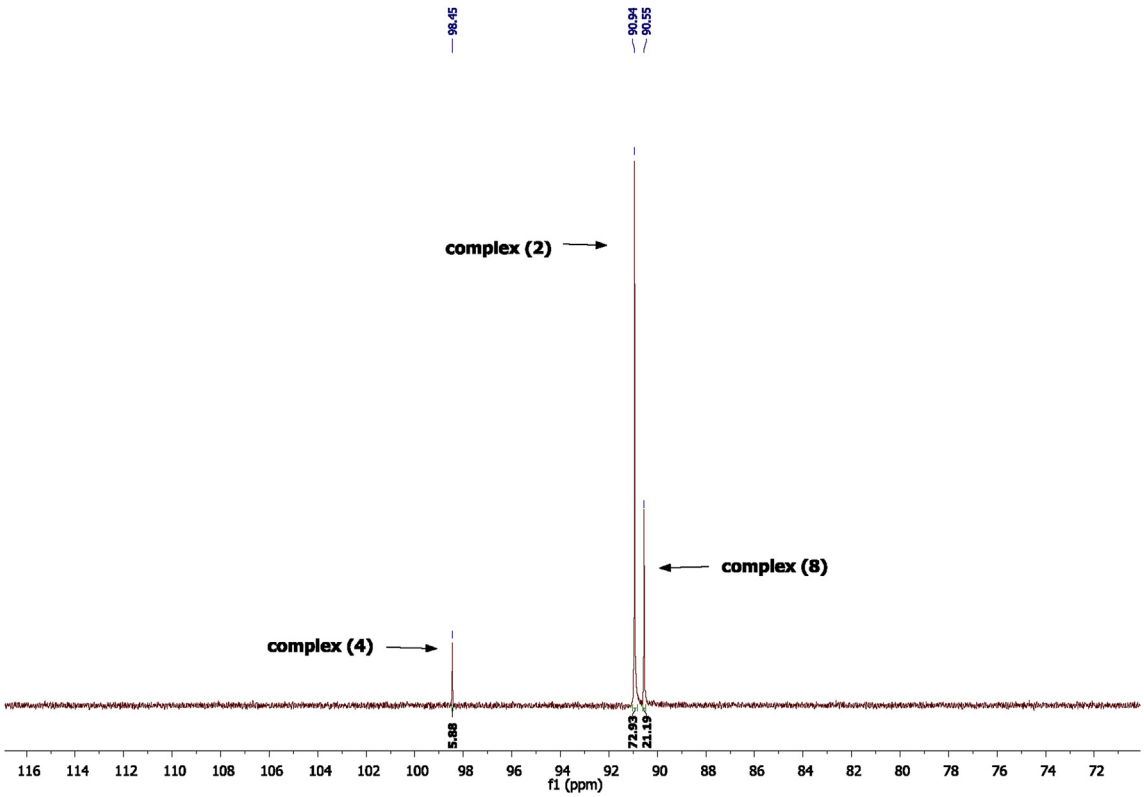
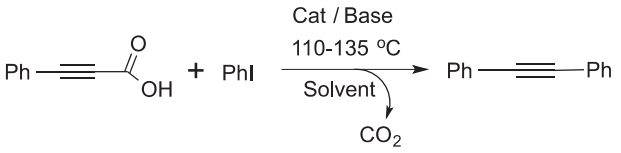
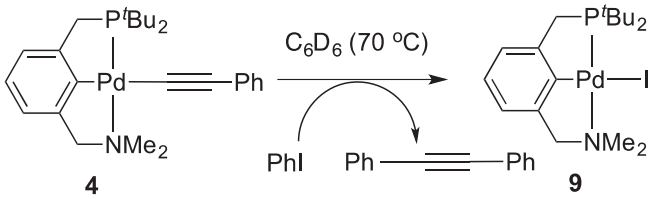


Fig. 5. ^{31}P NMR spectrum for the reaction of **2** with sodium phenyl propiolate after 5 min sonication.



Scheme 5. Catalytic decarboxylative cross coupling reaction of phenylpropiolic acid and phenyl iodide.



Scheme 6. Reaction of (PCN)Pd-phenyl acetylide complex (**4**) with phenyl iodide.

vacated coordination site. This mechanism has been previously proposed for a similar reaction of carbon dioxide with the Pd-Me bond of L_2PdMe_2 complexes (where L_2 = tmeda, dppe or MDC^{Mes}) giving $L_2PdMe(O_2COH)$ as the main product in the presence of moisture [23].

To verify that the phenyl propiolate complex (**8**) was not formed we decided to synthesise it independently. Thus, complex **2** was reacted with sodium phenyl propiolate in THF but instead of the expected complex **8** complex **4** was exclusively formed (Scheme 4).

Table 1
Screening optimal conditions for the decarboxylative cross coupling reaction of phenyl propiolic acid with PhI.

Entry	Catalyst	Catalyst loading/mol%	Solvent	Base	Base (equiv)	T/°C	t/h	Yield/%[c]
1	–	0	MeCN	Cs_2CO_3	1.2	110	14	0
2	(PCN)Pd-Cl	0.5	THF	K_2CO_3	1.2	110	14	4
3	(PCN)Pd-Cl	1	THF	Cs_2CO_3	1.2	110	14	2.7
4	(PCN)Pd-Cl	2.5	MeCN	LiO^tBu	1.2	135	48	3.3
5	(PCN)Pd-Cl	2.5	MeCN	TMEDA	1.2	135	48	4.9
6	(PCN)Pd-Cl	2.5	MeCN	K_2CO_3	1.2	135	30	9.5
7	(PCN)Pd-Br	2.5	MeCN	K_2CO_3	1.2	135	30	0
8	(PCN)Pd-ONO_2	2.5	MeCN	K_2CO_3	1.2	135	30	9.1
9	(PCN)Pd-Cl	2.5	MeCN	K_2CO_3	3	135	48	15.8
10	(PCN)Pd-Cl	2.5	MeCN	K_2CO_3	10	135	48	23.2
11[a]	(PCN)Pd-Cl	2.5	MeCN	K_2CO_3	10	135	48	54.4
12[b]	–	0	MeCN	K_2CO_3	10	135	48	3.3

Reaction conditions: Phenylpropiolic acid (0.2 mmol), ArI (0.2 mmol), and solvent (3 mL).
[a] CuI (7.5 mol %) was used.
[b] CuI (7.5 mol %) was used without the palladium catalyst.
[c] The yield was determined as an average of two runs by GC using decane as internal standard.

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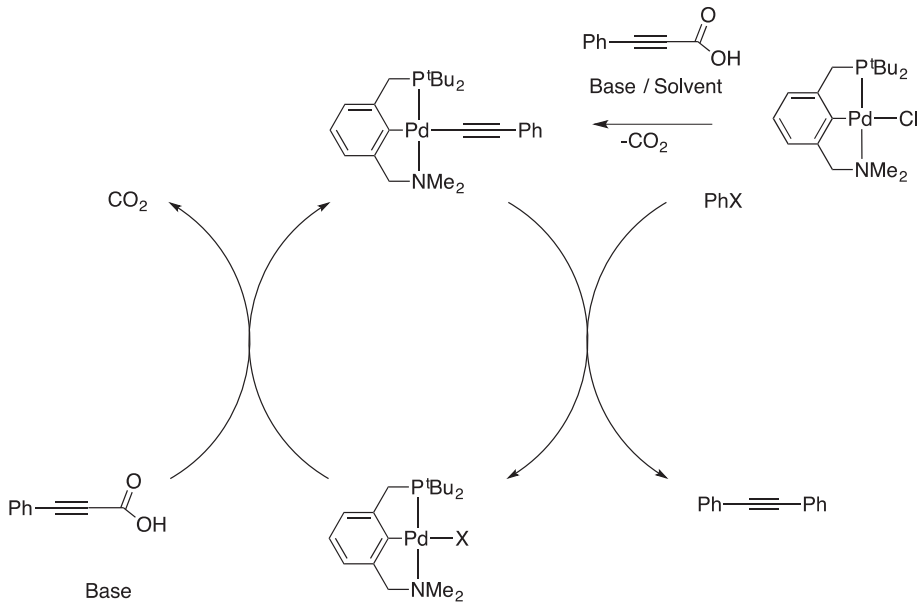

Scheme 7. The suggested mechanism for catalytic decarboxylative cross coupling reaction.

To further investigate this reaction, complex **2** was reacted with sodium phenyl propiolate also in C_6D_6 and the reaction was monitored by ^1H and ^{31}P NMR spectroscopy. After five minutes of sonication, two new products in addition to the starting material (**2**) were formed based on the ^{31}P NMR spectrum (Fig. 5).

The more downfield signal was assigned to complex **4** (based on the isolated compound) and the more upfield signal to the expected complex **8** (Fig. 5). The latter disappeared during the course of the reaction and **4** was the only product indicating that the carboxylation of phenyl acetylide complex is not thermodynamically favourable, whereas the reverse decarboxylation is. This again underlines the fact that strong late metal-carbon bonds are unlikely intermediates in carboxylation reactions [22a].

The facile decarboxylation reaction of the phenyl propiolic salt at room temperature with the nitrate complex suggests that PCN pincer palladium complexes could be competent catalysts for decarboxylative cross coupling reactions of propiolic acids and aryl halides.

3.4. Catalytic decarboxylative cross coupling

The reaction between phenyl propiolic acid and iodobenzene (Scheme 5) was selected as a benchmark reaction in decarboxylative cross coupling reactions. The optimized reaction conditions using (PCN) palladium complexes as catalysts are shown in Table 1.

No product was formed in absence of catalyst (Entry 1). Only 4% was obtained when 0.5% catalyst loading was used and different PCN palladium catalysts gave similar results. Increasing the catalyst loading led to a slight improvement in the yield and K_2CO_3 was found to be the best base for the reaction. Increasing the amount of base and adding a catalytic amount of CuI to the reaction mixture finally gave a fair yield of diphenylacetylene of 54% (Entries 9 and 10). CuI has been reported to mediate the Sonogashira coupling [26]. However, a blank experiment using CuI without the palladium catalyst did not show any catalytic activity under our conditions (Entry 12).

To probe the mechanism of the reaction, we reacted complex **4** with phenyl iodide in C_6D_6 (Scheme 6) and monitored the reaction with ^1H and ^{31}P NMR spectroscopy.

Complete conversion of **4** to the corresponding iodide complex (**9**) was achieved at 70 °C (see Supporting Information). At the same time the C–C coupled product was observed in the ^1H NMR spectrum and its structure was confirmed by comparison with an authentic sample and through a GC-MS analysis. The mild reaction condition probably rule out the formation of the cross coupling product through a mechanism involving *in situ* generation of Pd(0) as a result of decomposition of the PCN palladium phenyl acetylide complex, as previously observed for high temperature pincer palladium based cross-coupling reactions [2c,24]. Indeed, no complexes other than the starting phenyl acetylide complex and the produced iodide complex were observed during the reaction in Scheme 6. Thus, we suggest the catalytic cycle depicted below to explain the decarboxylative cross coupling reaction, where both steps have been demonstrated stoichiometrically (Scheme 7). It is clear that the C-C bond forming step is very facile and the reason for the sluggish catalysis most probably lies in the poor nucleophilicity of the propiolate; its substitution of fairly strongly coordinated iodide is likely slow and thermodynamically disfavoured. With the addition of CuI the mechanism changes in that the propiolate can be decarboxylated on copper [25] and the acetylide can be transmetallated from copper to palladium.

4. Conclusion

PCN palladium arylacetylide complexes were synthesized using two new routes: one based on internal base assisted C–H activation and one based on decarboxylation of the propiolate complex. Thus, it was found that the insertion of CO_2 into the palladium-acetylide bond is thermodynamically unfavourable and that there, furthermore, instead is a slow hydrolysis of the Pd–C bond by the *in situ* formed carbonic acid (from CO_2 and adventitious water) giving the corresponding hydrogen carbonate complex. The latter was obtained also as product of CO_2 insertion into the hydroxide complex. The aryl acetylide complexes react with aryl iodide to give C–C coupling and this together with fact that the acetylide complexes can be formed from the propiolate formed the basis for a (PCN)Pd mediated decarboxylative cross coupling.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2017.04.025.

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