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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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