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Acetylene-bridged *P,C,P′*-ligands and corresponding cyclopalladated compounds

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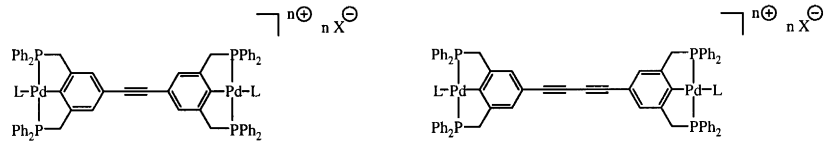
Abstract

Bis-'pincer'-cyclopalladates **1** and **2** containing an ethynediyl- or a butadiynediyl-bridge have been synthesized, characterized and used as precatalysts in the Heck reaction.

Keywords: alkynes; coupling reactions; phosphines; palladium compounds.

Metallocycles containing a tridentate *P,C,P′*-coordination mode have been investigated extensively during the last decade.[1] It was found that these systems can perform some interesting new types of transformations.[2]

We have synthesized binuclear palladium complexes of a new type, in which two cyclopalladated 'pincer' groups are connected via an ethynediyl- (**1**) or a butadiynediyl-bridge (**2**) (Fig. 1). Such polynuclear conjugated organometallic compounds have attracted considerable attention due to their possible applications as building blocks for new conjugated organometallic oligomers and polymers, new types of catalysts and materials with magnetic, nonlinear optical or liquid crystalline properties.[3]



1a: L = MeCN, n = 2, X = BF_4
1b: L = Cl, n = 0, no X

2a: L = MeCN, n = 2, X = BF_4
2b: L = Cl, n = 0, no X

Fig. 1.

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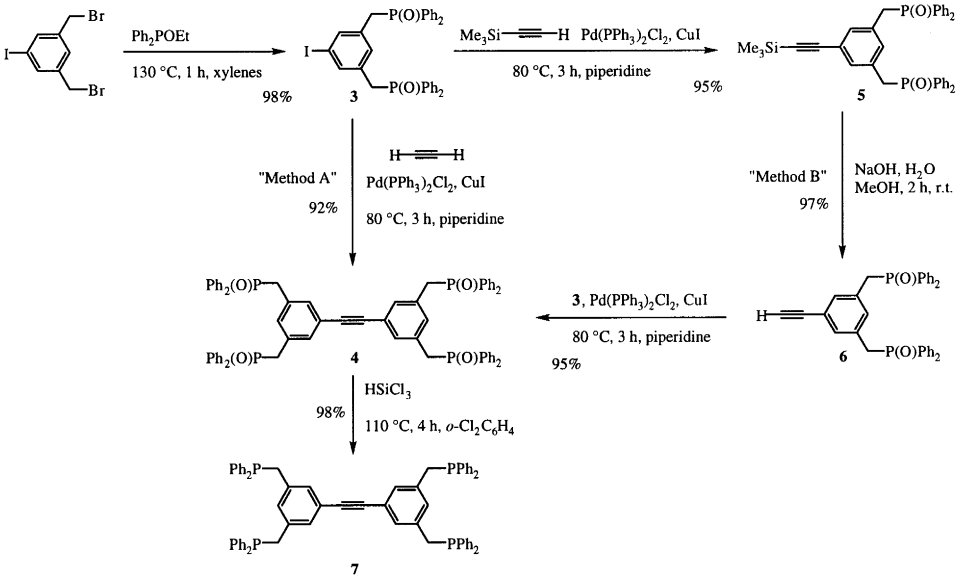
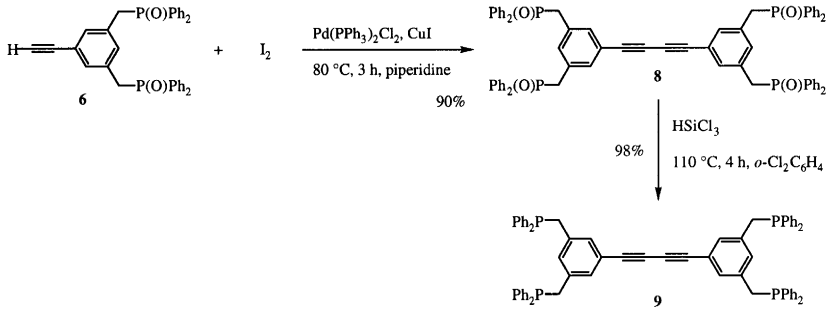
Multidentate tetraphosphine ligand **7** was prepared in two different ways, as shown in Scheme 1. First, 3,5-bis(bromomethyl)iodobenzene[4] was converted into phosphine oxide **3** with ethyl diphenylphosphinite using Arbuzov reaction conditions.[5] When compound **3** was used in a cross-coupling reaction with acetylene gas using the Sonogashira reaction conditions, tetraphosphine oxide **4** was obtained in 92% yield (Method A, Scheme 1).[6] Second, compound **4** could also be obtained by cross-coupling of **3** with (trimethylsilyl)acetylene (Sonogashira conditions),[7] followed by the basic removal of the trimethylsilyl substituent[8] and subsequent cross-coupling of the obtained monoarylacetylene **6** with another equivalent of **3**;[9] overall yield 88% (Method B, Scheme 1). In the last step, **4** was reduced with trichlorosilane to the desired 3,3′,5,5′-tetra[(diphenylphosphino)methyl]tolane (**7**) in quantitative yield.[10]



Scheme 1.

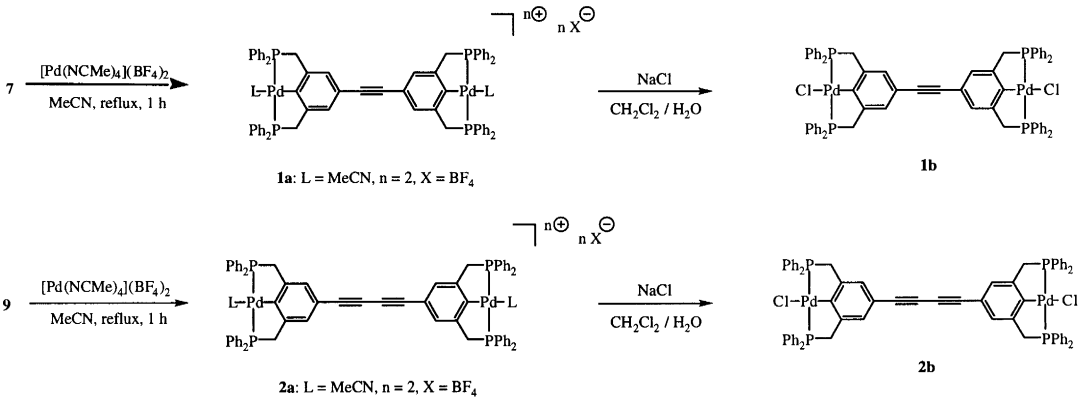
3,3′,5,5′-Tetra[(diphenylphosphinoxide)methyl]diphenylbutadiyne (**8**) was prepared in 90% yield from **6** via an oxidative coupling reaction using iodine (Scheme 2).[11] Reduction of **8** using trichlorosilane, afforded the desired tetraphosphine **9** in quantitative yield.[10]



Scheme 2.

Cyclopalladated products **1a** and **2a** were obtained via a direct electrophilic palladation with $[Pd(NCMe)_4](BF_4)_2$ in refluxing acetonitrile in 51 and 21% yield, respectively (Scheme 3).[12,13]

When these ionic complexes were treated with NaCl in a CH_2Cl_2/H_2O mixture, the corresponding neutral palladium chloride complexes **1b** and **2b** were obtained in quantitative yields (Scheme 3).[14,15]



Scheme 3.

The somewhat low yields of **1a** and **2a** were probably caused by competitive palladium-catalyzed polymerization of the triple bonds during the aromatic palladation reaction. The side products were highly soluble in acetonitrile and formed dark-colored solutions whereas **1a** and **2a** were white crystals, poorly soluble in cold acetonitrile. The nature of these side products is currently under investigation.

All new compounds were characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, and elemental analysis. Compound **1a** was also characterized by crystal structure determination.

Furthermore, initial experiments have shown that **1a** and **2a** are highly active catalyst precursors for the Heck reaction of iodobenzene with styrene or methyl acrylate.

Acknowledgements

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5. A modification of a literature procedure[3a] was used: 3,5-Bis(bromomethyl)iodobenzene (14.0 g, 35.9 mmol) and ethyl diphenylphosphinite (16.6 g, 72 mmol) were mixed in *m*-xylene (20 mL) and stirred at 130°C for 1 h. The reaction mixture

was cooled to room temperature and concentrated in vacuo. Benzene (70 mL) was added to the residue and the solution was heated, filtered and cooled to room temperature. Upon cooling, **3**·benzene was obtained as white crystals. The product was washed with C_6H_6 and dried, giving 25 g (98%) of **3**, m.p. 91°C. Anal. calcd for $C_{38}H_{33}P_2O_2I$: C, 64.21; H, 4.73; P, 8.71. Found: C, 64.14; H, 4.75; P, 8.80. Compound **3** can be obtained as a white amorphous powder by removal of the solvent in vacuo. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.43 (d, 4H, *J*=13.8 Hz), 6.95 (t, 1H, *J*=1.8 Hz), 7.15, (d, 2H, *J*=1.8 Hz), 7.3–7.7 (m, 20H).

6. Compound **3**·benzene (11.2 g, 15.6 mmol), $PdCl_2(PPh_3)_2$ (100 mg, 0.14 mmol) and CuI (30 mg, 0.18 mmol) were dissolved in degassed piperidine (60 mL) and heated to 80°C. Acetylene gas was then bubbled slowly through this mixture at the same temperature for 3 h. The solvent was removed in vacuo and the residue was washed with benzene, dissolved in CH_2Cl_2 (150 mL). The organic layer was washed with water (3×150 mL) and dried ($MgSO_4$). Next, the solvent was evaporated and the crude product was suspended in benzene, boiled for 30 min, cooled to room temperature, collected and dried in vacuo at 100°C, giving 7.5 g (92%) of **4**. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.47 (d, 8H, *J*=13.6 Hz), 7.00 (s, 6H), 7.30–7.70 (m, 40H).
7. Compound **3**·benzene (11.2 g, 15.6 mmol), (trimethylsilyl)acetylene (1.8 g, 19.0 mmol), $PdCl_2(PPh_3)_2$ (100 mg, 0.14 mmol) and CuI (30 mg, 0.18 mmol) were dissolved in degassed piperidine (60 mL) and heated to 80°C for 3 h. The solvent was removed in vacuo and the residue was dissolved in CH_2Cl_2 (150 mL). The organic layer was washed with water (5×200 mL) and dried ($MgSO_4$). The solvent was evaporated and the product was crystallized from benzene, giving 9.0 g (95%) of **5**. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.12 (s, 9H), 3.48 (d, 4H, *J*=13.2 Hz), 6.94 (t, 1H, *J*=1.4 Hz), 7.04 (d, 2H, *J*=1.4 Hz), 7.30–7.70 (m, 20H).
8. To a solution of **5** (9.0 g, 15.0 mmol) in methanol (100 mL) was added 5 M NaOH-solution in water (3.5 mL) and this mixture was stirred at room temperature for 2 h. The solution was diluted with water (100 mL) and the product was extracted into CH_2Cl_2 (100 mL). The organic layer was collected, washed with water (2×200 mL) and dried ($MgSO_4$). After removal of the solvent, white crystals of **6**·benzene were obtained by crystallization from benzene. Yield 8.9 g (97%). M.p. 110°C. Anal. calcd for $C_{40}H_{34}P_2O_2$: C, 78.93; H, 5.63; P, 10.18. Found: C, 78.85; H, 5.75; P, 10.16. Compound **6** could be obtained as a white amorphous solid by removal of the solvent in vacuo at 110°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.89 (s, 1H), 3.48 (d, 4H, *J*=13.6 Hz), 7.00 (s, 3H) 7.30–7.70 (m, 20H).
9. Reaction conditions as mentioned in Ref. 7. Same work-up as mentioned in Ref. 6.
10. The procedure described in the literature[3a] was used. Compound **7**: m.p. 187°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.34 (s, 4H), 6.86 (t, 2H, *J*=1.2 Hz), 7.05 (d, 4H, *J*=1.2 Hz), 7.30–7.50 (m, 40H). Compound **9**: m.p. 195°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.32 (s, 8H), 6.93 (t, 2H, *J*=1.5 Hz), 7.03 (d, 4H, *J*=1.5 Hz), 7.30–7.50 (m, 40H).
11. Lio, Q.; Burton, D. J. *Tetrahedron Lett.* **1997**, *38*, 4371–4374. A modification of a literature procedure was used: **6**·benzene (1.15 g, 1.90 mmol), iodine (0.30 g, 1.20 mmol), $PdCl_2(PPh_3)_2$ (13 mg, 18 μmol) and CuI (3 mg, 16 μmol) were dissolved in piperidine (12 mL) and stirred at 80°C for 4 h. The solvent was then removed in vacuo, the residue washed with benzene and dissolved in CH_2Cl_2 (20 mL). The organic layer was washed with water (3×20 mL) and dried ($MgSO_4$). After evaporation of the solvent, the crude product was suspended in benzene (15 mL), heated to reflux for 30 min, cooled to room temperature, collected and dried in vacuo at 100°C, yielding 0.90 g (90%) of **8**, m.p. 287°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.46 (d, 8H, *J*=13.6 Hz), 6.97 (d, 4H, *J*=1.8 Hz), 7.00 (t, 2H, *J*=1.8 Hz), 7.30–7.70 (m, 40H).
12. A solution of $[Pd(NCMe)_4](BF_4)_2$ (1.83 g, 4.12 mmol) in MeCN (150 mL) was added to **5** (2.0 g, 2.06 mmol) and heated to reflux for 2 h. The reaction mixture was cooled to room temperature and the solvent evaporated in vacuo. The crude product was recrystallized from MeCN giving 1.5 g (51%) of white crystals. Compound **1a**: ^{1}H NMR (200 MHz, CD_3CN): δ 4.21 (t, 8H, *J*=4.8 Hz, CH2), 7.34 (s, 4H, ArH), 7.6–8.0 (m, 40H, PPh_2). ^{13}C NMR (50.3 MHz, CD_3CN): δ 40.5 (t, *J*=15.2 Hz), 132.2, 133.2 (t, *J*=6.9 Hz), 148.7 (t, *J*=10.4 Hz), 156.9 Hz. ^{31}P NMR (80.96 MHz, CD_3CN): δ 48.03. Anal. calcd for $C_{70}H_{58}P_4N_2B_2F_8Pd_2$: C, 58.48; H, 4.07; N, 1.95. Found: C, 58.31; H, 4.01; N, 1.81.
13. A solution of $[Pd(NCMe)_4](BF_4)_2$ (1.15 g, 2.59 mmol) in MeCN (100 mL) was added to **9** (1.3 g, 1.31 mmol) and heated to reflux for 1 h. The reaction mixture was cooled to room temperature and the solvent evaporated in vacuo. The crude product was recrystallized from MeCN giving 0.4 g (21%) of white crystals. Compound **2a**: ^{1}H NMR (400 MHz, CD_3CN): δ 4.21 (t, 8H, *J*=4.8 Hz, CH2), 7.38 (s, 4H, ArH), 7.6–7.9 (m, 40H, PPh_2). ^{31}P NMR (161.9 MHz, CD_3CN): δ 46.8. Anal. calcd for $C_{72}H_{58}P_4N_2B_2F_8Pd_2$: C, 59.17; H, 4.00; N, 1.92. Found: C, 59.32; H, 4.08; N, 1.83.
14. To a suspension of **1a** (0.35 g, 0.24 mmol) in CH_2Cl_2 (40 mL) was added brine (40 mL) and this mixture was stirred overnight. The organic layer was separated, dried ($MgSO_4$), filtered and evaporated to dryness. Compound **1b**: yield 0.3 g (98%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.92 (t, 8H, *J*=4.6 Hz, CH_2), 7.26 (s, 4H, ArH), 7.3–8.0 (m, 40 H, PPh_2). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 42.7 (t, *J*=14.5 Hz), 89.8, 120.8, 126.1 (t, *J*=11.2 Hz), 129.1 (t, *J*=5.3 Hz), 130.9, 131.9 (t, *J*=21.7 Hz), 133.2 (t, *J*=6.7 Hz), 148.3 (t, *J*=10.8 Hz), 161.6. ^{31}P NMR (80.96 MHz, $CDCl_3$): δ 34.3. Anal. calcd for $C_{66}H_{52}P_4Cl_2Pd_2$: C, 63.28; H, 4.18. Found: C, 63.10; H, 4.05.

15. To a suspension of **2a** (0.20 g, 0.14 mmol) in CH_2Cl_2 (20 mL) was added brine (20 mL) and this mixture was stirred overnight. The organic layer was separated, dried ($MgSO_4$), filtered and evaporated to dryness. **2b**: yield 0.2 g (97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.96 (t, 8H, J=4.2 Hz, CH_2), 7.29 (s, 4H, ArH), 7.3–8.0 (m, 40 H, PPh_2). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 42.40 (t, J=14.5 Hz), 73.95, 81.89, 118.94, 126.64 (t, J=11.4 Hz), 128.81 (t, J=5.4 Hz), 130.71, 131.50 (t, J=21.4 Hz), 132.91 (t, J=6.8 Hz), 148.17 (t, J=11.2 Hz), 163.05. ^{31}P NMR (161.9 MHz, $CDCl_3$): δ 32.8. Anal. calcd for $C_{68}H_{52}P_4Cl_2Pd_2$: C, 63.97; H, 4.10. Found: C, 63.78; H, 4.01.