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Conjugated G_0 metallo-dendrimers, functionalized with tridentate 'pincer'-type ligands

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Abstract

1,3,5-Tris{3,5-bis[(diphenylphosphino)methyl]phenylethynyl}benzene (**1**) and hexakis{3,5-bis[(diphenylphosphino)methyl]phenylethynyl}benzene (**2**) have been synthesized and characterized. Furthermore, **1** was successfully cyclopalladated. © 2000 Elsevier Science Ltd. All rights reserved.

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

During the last decade there has been increasing interest in the development of new dendritic materials,[1] including organometallic dendrimers[2] and dendrimers containing conjugated π-systems.[3] These materials have a wide variety of applications, such as homogeneous catalysts,[2j–m] organometallic sensors[2n] or materials possessing electronic and optical properties.[2q,r]

In our research to construct nano-sized multimetallic materials based on tridentate 'pincer' type ligands, we are interested in rigid nano-size materials based on a hydrocarbon skeleton because they are potential homogeneous catalysts (the so-called cartwheel catalysts) which are expected to be suitable for separation from the reaction mixture by nanomembrane filtration.[4] The syntheses of new conjugated dendritic materials containing PCP-type ligands (Fig. 1) are reported here. These ligand systems are suitable for incorporation of transition-metals, giving rigid highly conjugated organometallic compounds.

Compounds **1** and **2** were synthesized from 1,3,5-tribromobenzene and hexabromobenzene, respectively. The aryl bromides were converted into phosphine oxides **4** and **5** via 3- and 6-fold Sonogashira coupling reactions with 3,5-bis[(diphenylphosphinoxide)methyl]phenylacetylene (**3**) (Scheme 1).[5] The cross-coupling reactions were performed in THF at reflux for 100 (for **4**) and 300 h (for **5**) affording, after purification, **4**[6] and **5**[7] in 66 and 25% yield, respectively. Unfortunately, we also observed the formation

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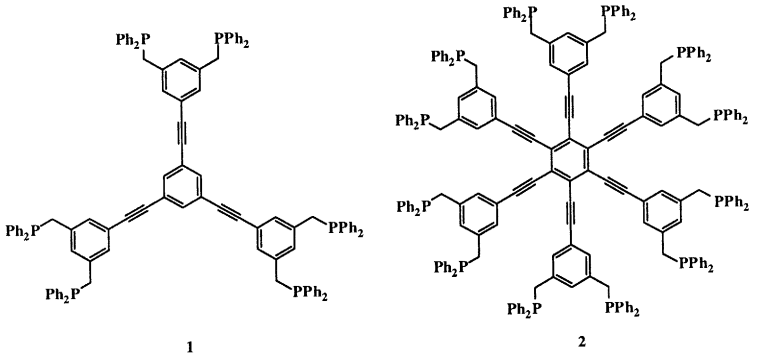
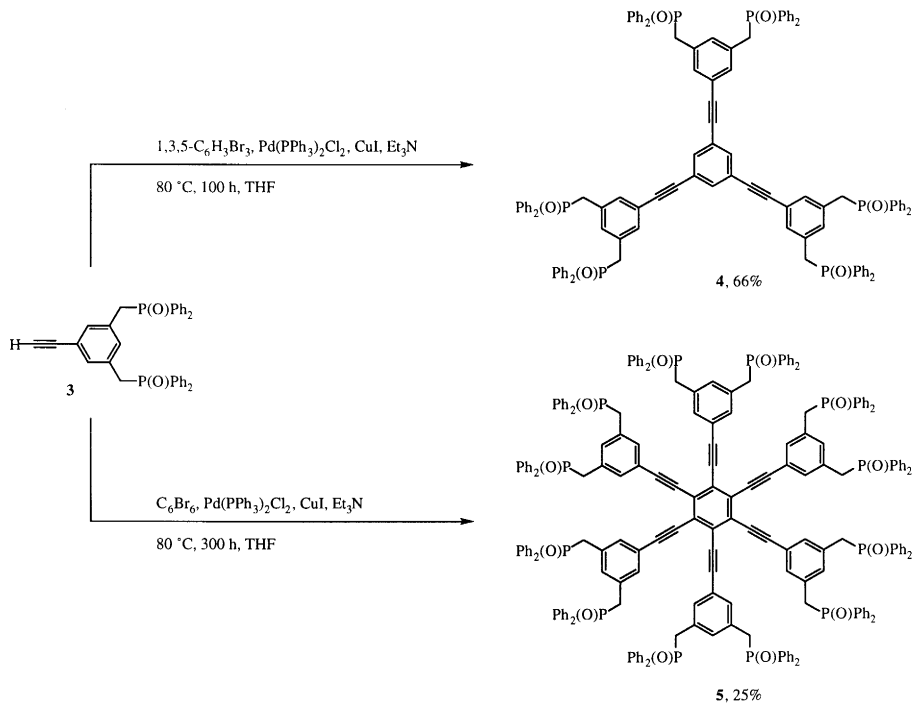


Fig. 1.

of a considerable amount of unidentified, poorly soluble side-products. The side-products most probably originate from competitive metal-catalyzed polymerization reactions of the triple bond in **3**. Moreover, metal-catalyzed ring-closure and subsequent polymerization reactions of the products **4** and **5** as well as of their intermediates can be expected to occur, cf. the low yield of **5** which may be connected to the much longer reaction time required.

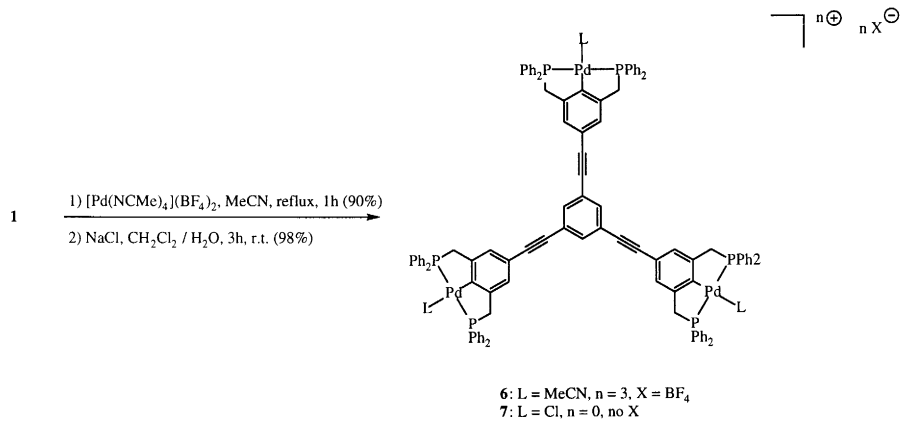


Scheme 1.

The phosphine oxides **4** and **5** were then reduced by trichlorosilane affording the corresponding G_0 dendritic hexa-(**1**)[8] and dodecaphosphine (**2**)[9] in quantitative yield.

Cyclopalladation of **1** using $[Pd(NCMe)_4](BF_4)_2$ in acetonitrile gave ionic palladium(II) complex **6**[10] in 90% yield. Subsequent treatment of **6** with NaCl in a CH_2Cl_2/H_2O mixture generated quantitatively the neutral chloro complex **7**[11] (Scheme 2).

The full-cyclopalladation of **2** is currently under investigation. So far, using the same reaction



Scheme 2.

conditions as were successful for the quantitative formation of **6** did not give the corresponding hexapalladated product. Only partial cyclopalladation occurred which most likely is due to the fact that the intermediate semi-palladated products (**2**·Pd_n) have decreased solubility when *n* approaches 6.

All new compounds were characterized by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy, MALDI-TOF and elemental analysis.

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6. 1,3,5-Tribromobenzene (1.0 g, 3.17 mmol), 3,5-bis[(diphenylphosphinoxide)methyl]phenylacetylene (8.0 g, 13.16 mmol), bis(triphenylphosphine)palladium dichloride (0.19 g, 0.27 mmol), triphenylphosphine (35 mg, 0.14 mmol), triethylamine (5.0 mL, 36.0 mmol) and CuI (20 mg, 0.11 mmol) were subsequently dissolved in THF (50 mL) and stirred for 100 h at 80°C. Next, all volatiles were evaporated in vacuo and the solid residue was washed with C_6H_6, dissolved in CH_2Cl_2 (100 mL), washed with H_2O (4×100 mL) and dried ($MgSO_4$). All volatiles were evaporated and the crude product was crystallized from C_6H_6 and dried in vacuo at 100°C. Yield: 3.5 g (66%), m.p. 158–159°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.55 (d, 12H, *J*=13.6 Hz), 7.10 (s, 9H), 7.36–7.76 (m, 63H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 38.0 (d, *J*=65.8 Hz), 88.2, 90.3, 123.1, 124.1, 128.8 (d, *J*=12.0 Hz), 131.3 (d, *J*=9.2 Hz), 132.0, 132.1, 132.6, 133.3, 134.1. ^{31}P NMR (80.96 MHz, $CDCl_3$): δ 30.2. MALDI-TOF MS (3,5-dihydroxybenzoic acid matrix) *m/z* 1770.10 ([M+Ag]+) (calcd mass $C_{108}H_{84}O_6P_6Ag$: 1771.65).
7. Hexabromobenzene (1.0 g, 1.81 mmol), 3,5-bis[(diphenylphosphinoxide)methyl]phenylacetylene (8.0 g, 13.16 mmol), bis(triphenylphosphine)palladium dichloride (0.19 g, 0.27 mmol), triphenylphosphine (35 mg, 0.14 mmol), triethylamine (5.0 mL, 36.0 mmol) and CuI (20 mg, 0.11 mmol) were subsequently dissolved in THF (50 mL) and stirred for 300 h at 80°C. Next, all volatiles were evaporated in vacuo and the solid residue was washed with C_6H_6, dissolved in CH_2Cl_2 (100 mL), washed with H_2O (4×100 mL) and dried ($MgSO_4$). All volatiles were evaporated and the crude product was extracted into MeOH (5 mL), filtered and MeOH was evaporated again. The product was crystallized from C_6H_6 and isopropanol and dried in vacuo at 100°C. Yield: 1.5 g (25%) as a yellow solid, m.p. 169°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.40 (d, 24H, *J*=13.6 Hz), 6.91 (s, 6H), 7.08 (s, 12H), 7.18–7.68 (m, 120H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 37.6 (d, *J*=65.9 Hz), 87.4, 123.3, 127.5, 128.7 (d, *J*=12.0 Hz), 131.3 (d, *J*=9.7 Hz), 131.5, 132.0, 132.2 (d, *J*=10.6 Hz), 133.1, 133.4. ^{31}P NMR (80.96 MHz, $CDCl_3$): δ 30.1. MALDI-TOF MS (3,5-dihydroxybenzoic acid matrix) *m/z* 3355.94 ([M+Ag]+) (calcd mass $C_{210}H_{162}O_{12}P_{12}Ag$: 3357.31).
8. 1,3,5-Tris{3,5-bis[(diphenylphosphinoxide)methyl]phenylethynyl}benzene (**4**) (1.7 g, 1.0 mmol) was suspended in C_6H_6 (30 mL) and trichlorosilane (1.8 mL, 18.0 mmol) was added via syringe. The reaction mixture was stirred at reflux for 16 h, then cooled to room temperature and excess of trichlorosilane was evaporated in vacuo. Next, a degassed solution of NaOH (3.0 g, 75 mmol) in H_2O (15 mL) was added and this mixture was stirred for 15 min. The organic layer was separated, dried ($MgSO_4$) and evaporated. Yield: 1.05 g (98%), m.p. 74–75°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.32 (s, 12H), 6.85 (s, 3H), 7.04 (s, 6H), 7.30–7.50 (m, 60H), 7.52 (d, 3H, *J*=0.80 Hz). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 36.0 (d, *J*=16.1 Hz), 87.6, 90.2, 122.8, 124.3, 128.7 (d, *J*=6.9 Hz), 129.1, 130.5 (d, *J*=4.6 Hz), 131.2 (t, *J*=6.9 Hz), 133.1 (d, *J*=18.4 Hz), 134.1, 137.9 (d, *J*=6.4 Hz), 138.1 (d, *J*=13.4 Hz). ^{31}P NMR (80.96 MHz, CDCl3): δ −9.0.
9. Hexakis{3,5-bis[(diphenylphosphinoxide)methyl]phenylethynyl}benzene (**5**) (1.2 g, 0.37 mmol) was suspended in 1,2-dichlorobenzene (30 mL) and trichlorosilane (1.4 mL, 13.4 mmol) was added via syringe. The reaction mixture was stirred at reflux at 110°C for 5 h, then cooled to room temperature and excess of trichlorosilane was evaporated in vacuo. Next, a degassed solution of NaOH (2.5 g, 62.5 mmol) in H_2O (15 mL) was added and this mixture was stirred for 15 min. The organic layer was separated, dried ($MgSO_4$) and evaporated. The solid residue was washed with hexanes and dried in vacuo. Yield: 1.10 g (98%) as a yellow amorphous powder. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.14 (s, 24H), 6.67 (s, 6H), 7.04 (s, 12H), 7.10–7.40 (m, 120H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 36.1 (d, *J*=16.5 Hz), 87.2, 99.7, 123.2, 127.6, 128.6 (d, *J*=6.4 Hz), 129.0, 130.7 (d, *J*=5.1 Hz), 131.4 (t, *J*=7.1 Hz), 133.0 (d, *J*=18.4 Hz), 134.1, 137.8 (d, *J*=7.8 Hz), 138.2 (d, *J*=15.6 Hz). ^{31}P NMR (80.96 MHz, $CDCl_3$): δ −9.1.
10. $PdCl_2$ (0.39 g, 2.2 mmol) was suspended in refluxing MeCN (50 mL) and a solution of silver tetrafluoroborate (0.86 g, 4.4 mmol) in MeCN (20 mL) was added. The resulting mixture was stirred for 5 min at the same temperature, then cooled to room temperature, filtered, degassed and added under an inert atmosphere to **1** (1.15 g, 0.73 mmol). The reaction mixture was refluxed for 1 h, cooled to room temperature and all volatiles were evaporated. The solid was dissolved in CH_2Cl_2 (50 mL), filtered and the solvent was evaporated. The crude product was crystallized from MeCN/MeOH, giving 1.50 g (90%) of **6** as white crystals. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.20 (t, 12H, *J*=4.7 Hz), 7.38 (s, 6H), 7.60–8.00 (m, 63H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 38.7 (t, *J*=15.2 Hz), 86.2, 88.7, 119.7, 122.5, 125.3 (t, *J*=12.0 Hz), 127.9 (t, *J*=5.1 Hz), 128.3 (t, *J*=22.6 Hz), 130.4, 131.3 (t, *J*=6.9 Hz), 132.2, 146.9 (t, *J*=9.9 Hz), 155.7. ^{31}P NMR (80.96 MHz, $CDCl_3$): δ 46.1; MALDI-TOF MS (9-nitroanthracene matrix) *m/z* 1921.73 ([M−3NCMe−2BF_3−BF_4]+) (calcd mass $C_{108}H_{81}P_6Pd_3F_2$: 1921.95).

11. To a suspension of **6** (0.2 g, 90 μmol) in CH_2Cl_2 (20 mL) was added brine (20 mL) and this mixture was stirred at room temperature for 3 h. The organic layer was separated, dried ($MgSO_4$) and all volatiles were evaporated. Yield: 0.17 g (98%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.92 (t, 12H, J=4.4 Hz), 7.28 (s, 6H), 7.30–7.46 (m, 36H), 7.54 (s, 3H), 7.76–7.96 (m, 24H). ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 42.7 (t, J=14.7 Hz), 88.1, 91.2, 120.2, 124.4, 126.3 (t, J=11.5 Hz), 129.1 (t, J=5.1 Hz), 131.0, 131.9 (t, J=21.9 Hz), 133.2 (t, J=6.7 Hz), 148.4 (t, J=10.8 Hz), 162.3. ^{31}P NMR (80.96 MHz, $CDCl_3$): δ 34.2. MALDI-TOF MS (9-nitroanthracene matrix) *m/z* 1954.79 ([M−Cl]+) (calcd. mass $C_{108}H_{81}P_6Pd_3Cl_2$: 1954.86).