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New Building Blocks for the Noncovalent Assembly of *homo*- and *hetero*-Multinuclear Metallodendrimers

Wilhelm T. S. Huck, Bianca Snellink-Ruël, Frank C. J. M. van Veggel,* and David N. Reinhoudt*

Laboratory of Supramolecular Chemistry and Technology and MESA Research Institute, University of Twente, P.O. Box 217, NL-7500 AE Enschede, The Netherlands

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Ligands **5** and **8**, derived from the coupling of [3,5-bis[(diphenylphosphinyl)methyl]phenyl]oxy groups to bi- and trifunctional spacers, respectively, were cyclometalated with Pd[CH_3CN]$_4$(BF_4)$_2$, *cis*-[$PtCl_2(PPh_3)_2$], or $NiCl_2\cdot 6H_2O$. The cationic Pd and Pt complexes were converted into overall neutral Pd−Cl and Pt−Cl complexes. The resulting pincer complexes can be used as building blocks for the controlled assembly of both *homo*- and *hetero*-multinuclear metallodendrimers. The ^{31}P NMR spectra of the pincer complexes exhibit different shifts for chloride, H_2O, or nitrile occupying the fourth coordination site, making the ^{31}P chemical shift an excellent diagnostic tool for the assembly process.

Introduction

There is an increasing interest in the development of new strategies to synthesize well-defined nanosize structures. Noncovalent synthesis can be used to construct nanostructures in an efficient way.[1] The branched architecture and large, spherical dimensions combined with high molecular masses make dendrimers ideal model compounds to test noncovalent synthesis routes. Metallodendrimers containing transition metals in every generation have been reported in the literature.[2] In previous articles, we have described "controlled assembly" as a new approach to build metallodendrimers of nanometer dimensions.[3] The building blocks **BB−Cl** and **G$_0$** for controlled assembly contain SCS Pd−pincer complexes that are coupled via branched spacers (Chart 1).[4] The coordination of the nitrile ligand of **BB−Cl** to coordinatively unsaturated Pd centers was exploited to assemble the dendrimer building blocks via noncovalent interactions.[5]

To broaden the scope of this controlled assembly strategy, it is desirable to introduce different transition metals in such building blocks, but the SCS pincer ligands (*e.g.*, as in **G$_0$** and **BB−Cl**) cannot be used because cyclometalation is only possible with Pd(II).[6] However, with PCP instead of SCS pincer ligands, the introduction of a variety of transition metals is possible.[7] The synthesis and characterization of (metallo)dendrimers incorporating phosphorus ligands has been reported in literature.[8] The use of PCP ligands as metallodendrimer building blocks should make it possible to assemble nanosize assemblies containing a variety of (*e.g.*, catalytically active) transition metals.[9]

Results and Discussion

The synthesis leading to the pincer ligands **5** and **8** is summarized in Schemes 1 and 2. An excess of $K^{+-}PPh_2$ was added to the previously described bis(chloride) **1**[10] to give the corresponding bis(diphenylphosphine). The reaction was performed under the exclusion of air using standard Schlenk techniques. To facilitate the experimental conditions in the following steps, the diphenylphosphines were oxidized to the corresponding phosphine oxides with H_2O_2. After the deprotection of the phenol group using CsF, the phosphine oxide **2** was obtained in 60% yield. The ^1H NMR spectrum of **2** clearly shows a doublet (J = 13.8 Hz) at δ 3.49 ppm which corresponds to the $CH_2P(O)$ protons.

The synthesis of PCP pincer ligands **5** and **8** is shown in Scheme 2. Phenol **2** was coupled to spacers **3** or **6** with K_2CO_3 in CH_3CN. Compounds **4** and **7** were isolated in rather poor yields, as they slowly decomposed during column chromatography. Prior to cyclometalation, the phosphine oxide groups in **4** and **7** were reduced with trichlorosilane and triethylamine in *m*-xylene[11] to give the phosphine ligands **5** and **8**, respectively. The reduction was quantitative after 12 h, as

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[1] Philp, D.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1154.

[2] Serroni, S.; Denti, G.; Campagna, S.; Juris, A.; Ciamo, M.; Balzani, V. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1493. Campagna, S.; Denti, G.; Serroni, S.; Juris, A.; Venturi, M.; Ricevuto, V.; Balzani, V. *Chem. Eur. J.* **1995**, *1*, 211. Achar, S.; Puddephatt, R. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 847. Achar, S.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1895.

[3] Huck, W. T. S.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1213. Huck, W. T. S.; Hulst, A. J. R. L.; Timmerman, P.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1006.

[4] Similar complexes containing NCN pincer ligands have recently been reported, see: Davies, P. J.; Grove, D. M.; van Koten, G. *Organometallics* **1997**, *16*, 800.

[5] Huck, W. T. S.; van Veggel, F. C. J. M.; Kropman, B. L.; Blank, D. H. A.; Keim, E. G.; Smithers, M. M. A.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 8293. Huck, W. T. S.; Snellink-Ruël, B. A.; van Veggel, F. C. J. M.; Lichtenbelt, J. W. Th.; Reinhoudt, D. N. *Chem. Commun.* **1997**, 9.

[6] Errington, J.; McDonald, W. S.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1980**, 2313.

[7] Moulton, C. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1020. Gorla, F.; Venanzi, L. M.; Albinati, A. *Organometallics* **1994**, *13*, 1607. Weisman, A.; Gozin, M.; Kraatz, H.-B.; Milstein, D. *Inorg. Chem.* **1996**, *35*, 1792 and references cited therein.

[8] Slany, M.; Bardaji, M.; Casanove, M.-J.; Caminade, A.-M.; Majoral, J.-P.; Chaudret, B. *J. Am. Chem. Soc.* **1995**, *117*, 9764. Slany, M.; Bardaji, M.; Caminade, A.-M.; Chaudret, B.; Majoral, J.-P. *Inorg. Chem.* **1997**, *36*, 1939. Herring, A. M.; Steffey, B. D.; Miedaner, A.; Wander, S. A.; DuBois, D. L. *Inorg. Chem.* **1995**, *34*, 1100. Lange, P.; Schier, A.; Schmidbauer, H. *Inorg. Chem.* **1996**, *35*, 637.

[9] For catalytically active dendrimers, see: Knapen, J. W.; van der Made, A. W.; de Wilde, J. C.; van Leeuwen, P. W. N. M.; Wijkens, P.; Grove, D. M.; van Koten, G. *Nature* **1994**, *372*, 659.

[10] Huck, W. T. S.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *J. Mater. Chem.* **1997**, 1213.

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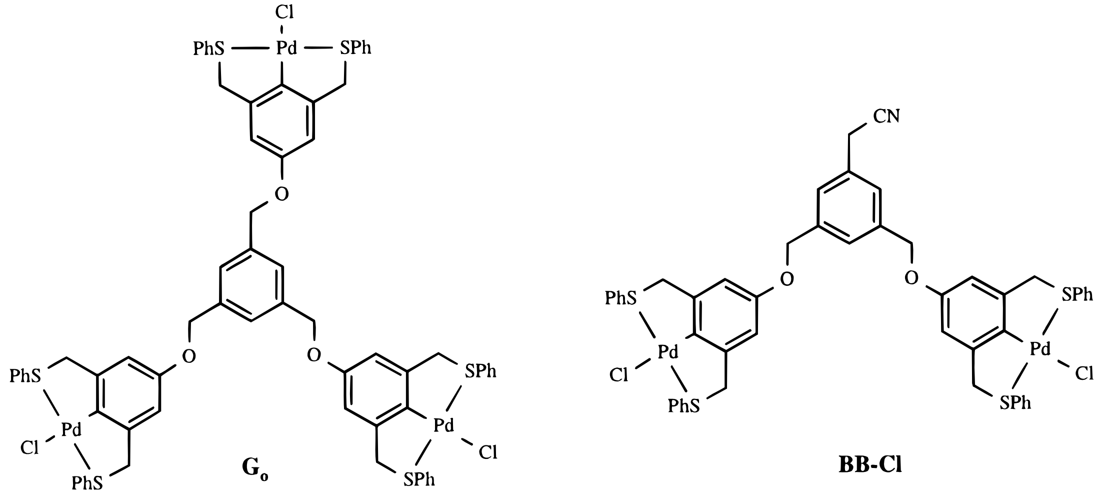
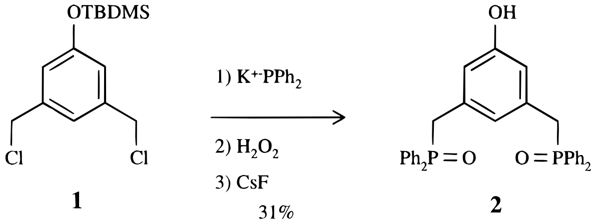
Chart 1



G$_o$

BB-Cl

Scheme 1



1 **2**

confirmed by ^{1}H NMR spectroscopy. The doublet at δ 3.49 ppm for the CH$_2$P(O) protons had disappeared, and a singlet at δ 3.21 ppm was observed for the CH$_2$P protons. The FAB-MS spectrum of **8** shows a very small signal at *m*/*z* 1587.6 (M$^+$, calcd 1587.0). Large signals are present which can be assigned to the oxidized ligand. Oxidation probably takes place inside the mass spectrometer. The ligands **5** and **8** were not purified further prior to cyclometalation.

The cyclometalation of ligands **5** and **8** using the appropriate metal complexes is summarized in Scheme 3.[12] Palladium was introduced in good yields using Pd[CH$_3$CN]$_4$(BF$_4$)$_2$ in CH$_3$CN.[13] The characteristic color change from orange to light yellow was a clear indication of cyclopalladation. The initial cationic complexes were converted to the Pd−Cl complexes by stirring with brine. The Pd complexes **G$_{0,Pd}$** and **BB$_{Pd}$−Cl** were obtained in 50−70% yield after purification by precipitation from CH$_2$Cl$_2$ with diethyl ether. The ^{1}H NMR spectrum of **BB$_{Pd}$−Cl** shows complete cyclopalladation as the signal at δ 6.49 ppm for the aryl proton between the two donor arms has disappeared completely. The signal for the CH$_2$P protons has shifted from δ 3.21 to 3.91 ppm. The absence of a doublet at δ 3.52 ppm shows that no oxidation has taken place. The ^{31}P NMR spectra for both **G$_{0,Pd}$** and **BB$_{Pd}$−Cl** show one signal at δ 33.4 ppm. This is in accordance with the chemical shifts reported for similar complexes.[14] The FAB-MS spectrum for **G$_{0,Pd}$** shows a signal at *m*/*z* 1971.3 corresponding to [**G$_{0,Pd}$** − Cl]$^+$ (calcd 1971.6). The FAB-MS spectrum of **BB$_{Pd}$−Cl** shows signals at *m*/*z* 1402.9 and 1367.2 corresponding to M$^+$ (calcd 1402.9) and [**BB$_{Pd}$−Cl** − Cl]$^+$ (calcd 1367.4), respectively.

Nickel was introduced by stirring ligands **5** and **8** with NiCl$_2$·6H$_2$O and (*i*-Pr)$_2$EtN (Hünig's base). Initially, a red complex is formed which led to the light yellow PCPNi−Cl complex after the addition of base. This was isolated in fairly low and variable yields because the complex is rather sensitive toward oxidation in solution. The complexes were purified by repeated precipitation from a solution in CH$_2$Cl$_2$ with diethyl ether. The ^{1}H NMR spectra of **G$_{0,Ni}$** and **BB$_{Ni}$−Cl** were similar to the spectra of the analogous Pd compounds. The ^{31}P NMR spectra for both **G$_{0,Ni}$** and **BB$_{Ni}$−Cl** show one signal at δ 34.6 ppm. The FAB-MS spectra confirmed the formation of the Ni complexes. The spectrum of **G$_{0,Ni}$** shows signals at *m*/*z* 1864.4 and 1828.3 corresponding to M$^+$ (calcd 1864.2) and [**G$_{Ni}$−Cl** − Cl]$^+$ (calcd 1828.3), respectively. The FAB-MS spectrum of **BB$_{Ni}$−Cl** shows a signal at *m*/*z* 1272.7 corresponding to [**BB$_{Ni}$−Cl** − Cl]$^+$ (calcd 1272.2).

Cycloplatination was achieved by reaction of the phosphine ligands **5** and **8** with *cis*-[PtCl$_2$(PPh$_3$)$_2$].[15] The initial complex contained one molecule of coordinated PPh$_3$ at the fourth coordination site and was in equilibrium with the desired chloride adduct. To obtain the Pt−Cl complex, the PPh$_3$ was removed by stirring with elemental sulfur and KCl. Subsequently, the complexes were triturated with MeOH and toluene to remove any residual PPh$_3$.[16] The Pt complexes were characterized by ^{1}H and ^{31}P NMR spectroscopy and FAB-MS. The ^{1}H NMR spectra of **G$_{0,Pt}$** and **BB$_{Pt}$−Cl** do not differ significantly from the analogous Ni and Pd complexes. The signal for the proton between the two donor arms at δ 6.49 has disappeared completely, indicating complete cyclometalation. The signal for the CH$_2$P protons

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(11) Hattori, T.; Sakamoto, J.; Hayashizaka, N.; Miyano, S. *Synthesis* **1994**, 199.

(12) It should be possible to introduce Rh(I) and Ir(I) in PCP ligands. See ref 7 and Gupta, M.; Hagen, C.; Flesher, R. J.; Kaska, W. C.; Jensen, C. M. *J. Chem. Soc., Chem. Commun.* **1996**, 2083. However, reaction of **5** with HRh(PPh$_3$)$_4$ or [RhCl(cod)]$_2$ (cod = 1,5-cyclooctadiene) did not give any cyclometalated products. The only difference with the ligands used in the literature is that ligands **5** and **8** all have *para* ether functions. Apparently, the electron-donating properties of this substituent deactivate the C−H bond toward insertion by the transition metal.

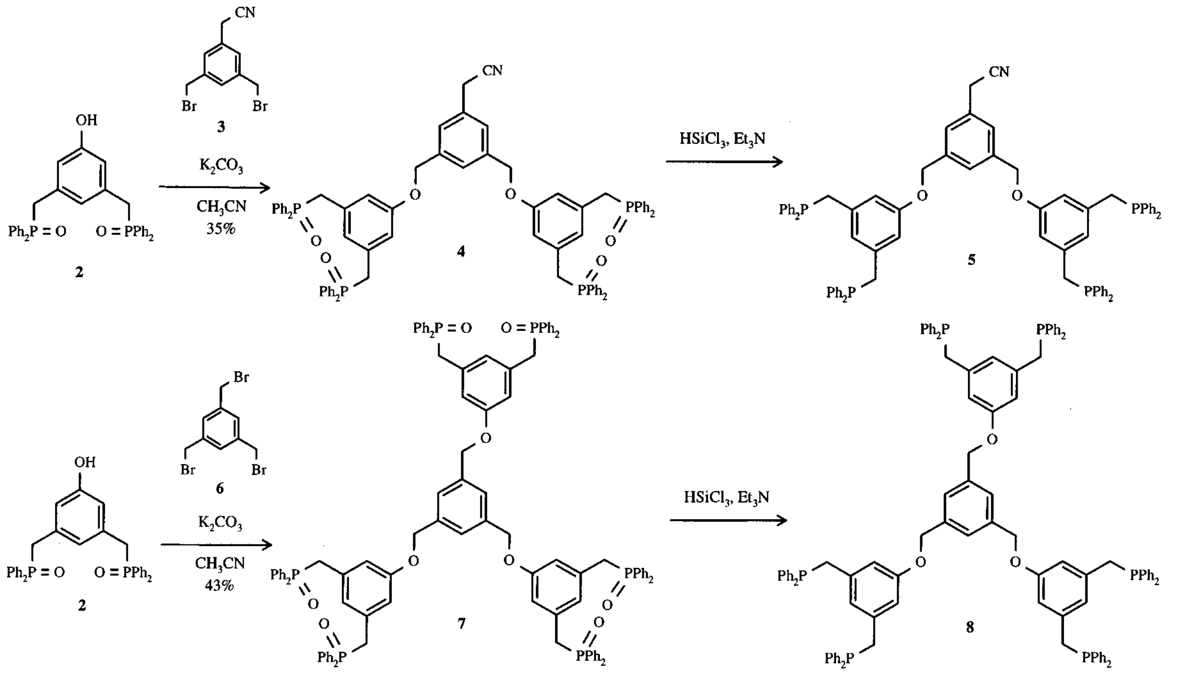
(13) Loeb, S. J.; Shimizu, G. K. H. *J. Chem. Soc., Chem. Commun.* **1993**, 1395.

(14) Kraatz, H.-B.; Milstein, D. *J. Organomet. Chem.* **1995**, *488*, 223.

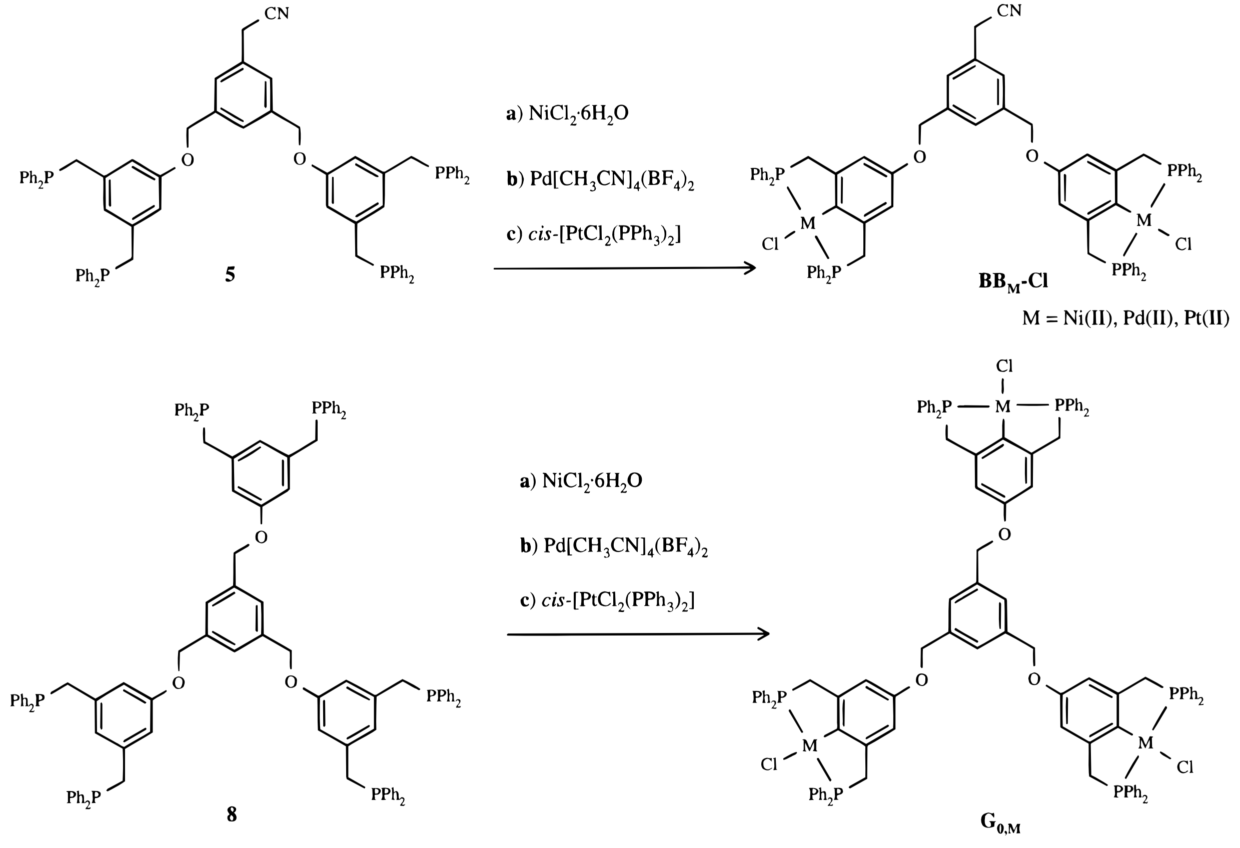
(15) Gorla, F.; Venanzi, L. M.; Albinati, A. *Organometallics* **1994**, *13*, 43.

(16) According to the literature procedures, reaction with [Pt$_2$(μ-Cl)$_2$(η^3-CH$_2$C(CH$_3$)CH$_2$)$_2$] should lead in one step to the desired Pt−Cl complex. However, no reaction took place even after refluxing for 48 h. Anklin, C. G.; Pregosin, P. S.; Wombacher, F. J.; Rüegg, H. J. *Organometallics* **1990**, *9*, 1953.

Scheme 2



Scheme 3



M = Ni(II), Pd(II), Pt(II)

is broad and slightly shifted to δ 3.86 ppm. The ^{31}P NMR spectra of both **G$_{0,Pt}$** and **BB$_{Pt}$–Cl** show one singlet at δ 32.3 ppm with two corresponding ^{195}Pt satellites. The P–Pt coupling constant is 1481 Hz, close to the value obtained from the ^{195}Pt NMR (1467 Hz) results. One singlet with two satellites is visible in the ^{195}Pt NMR of **G$_{0,Pt}$** at δ −4286.1 ppm, which confirms the formation of a PCP Pt–Cl complex. The FAB-MS spectra of **G$_{0,Pt}$** and **BB$_{Pt}$–Cl** show signals at m/z 2237.0 and 1545.8 corresponding to [**G$_{0,Pt}$** − Cl]$^+$ (calcd 2237.8), and [**BB$_{Pt}$–Cl** − Cl]$^+$ (calcd 1545.3), respectively.

^{31}P NMR spectroscopy can be a powerful tool in characterizing the internal structure of *homo*- and *hetero*-nuclear metallodendrimers. Small changes in the chemical shifts caused by a shielding of the inner generation by the outer layers might be visible in the ^{31}P spectrum as the chemical shift values are very

Table 1. ^{31}P NMR Chemical Shift Values[a] for BB_M−Cl and $G_{0,M}$[b]

	Ni	Pd	Pt
−Cl	34.6	33.4; 31.8[c]	32.3
$-BF_4^-/H_2O$	37.0	36.1[c]	39.6
$-BF_4^-/CH_3CN$	45.0	39.1; 38.6[c]	*d*

[a] Samples measured in $CDCl_3$; except *c*. [b] Identical values for **BB_M−Cl** and **$G_{0,M}$**. [c] CD_3NO_2/CD_2Cl_2 (1:1). [d] Not measured.

sensitive toward small changes in the microenvironment around the metal center.[17] A series of ^{31}P NMR measurements were conducted to determine the chemical shift of the P atoms in the various complexes. As discussed above, all **BB_M−Cl** and **$G_{0,M}$** complexes (M = Pd, Pt, Ni) gave one single signal in $CDCl_3$ (Table 1). As expected, the signals exhibit solvent dependence, as demonstrated by the shift from δ 33.4 ppm in $CDCl_3$ to δ 31.8 ppm in CD_3NO_2/CD_2Cl_2 (1:1) for the Pd complexes (Table 1).

When a solution of $AgBF_4$ in water was added to a solution of **$G_{0,Ni}$** in $CDCl_3$, an immediate and complete shift from δ 34.6 to 37.0 ppm was observed, which was assigned to the cationic aqua complex. The shift was not caused by changes in solvent polarity, as a drop of water without $AgBF_4$ did not result in any significant change in the ^{31}P NMR spectrum. Subsequent addition of a small amount of CD_3CN resulted in the instantaneous formation of the acetonitrile complex, which was clear from the shift of the ^{31}P NMR signal to δ 45.0 ppm. The results concerning the other metal centers are also summarized in Table 1. These model experiments gave a qualitative idea about the controlled assembly strategy.[3] It indicates that activation of the M−Cl complexes and coordination of the nitrile ligands are very fast and quantitative reactions. The equilibrium between the different complexes is completely shifted to the complex with the strongest coordinating ligand occupying the fourth coordination site.

The use of the building blocks described above in the controlled assembly of both *homo*- and *hetero*-multinuclear metallodendrimers is in progress.[18]

Conclusions

To broaden the scope of the controlled assembly process, a number of building blocks containing Ni(II), Pd(II), and Pt(II) centers have been synthesized. ^{31}P NMR spectroscopy was used to study the reactions which are needed in the controlled assembly process at the fourth coordination site. The exchange of the chloride ligands with neutral solvent molecules *via* reaction with $AgBF_4$ is a fast and quantitative reaction.

Experimental Section

Syntheses were carried out using standard Schlenk techniques under an atmosphere of argon. Melting points were determined with a Reichert melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ (unless indicated otherwise) with Me_4Si as the internal standard on a Bruker AC 250 spectrometer. ^{31}P NMR spectra were recorded on a Varian 400WB spectrometer with H_3PO_4 as the internal standard. Both ^{13}C and ^{31}P NMR spectra were recorded in the ^{1}H-decoupled mode. FAB-MS spectra were recorded with a Finnigan MAT 90 spectrometer using *m*-NBA as a matrix. THF was freshly distilled from Na/benzophenone and CH_2Cl_2 from K_2CO_3. Other chemicals were of reagent grade and used as received. Column chromatography was performed with silica gel 60H (0.005−0.040 mm) from Merck. $Pd[CH_3CN](BF_4)_2$,[19] *cis*-$[PtCl_2(PPh_3)_2]$,[16] α,α′,α″-tribromomesitylene,[20] and compounds **1**[10] and **3**[10] were prepared according to literature procedures.

3,5-Bis[(diphenylphosphinyl)methyl]phenol (2). Dichloride **1** (4 g, 13.1 mmol) was dissolved in THF (150 mL), and the solution was put under an argon atmosphere using a freeze−thaw cycle. Subsequently, potassium diphenylphosphide (79 mL, 39.3 mmol, 0.5 N solution in THF) was added *via* a syringe at room temperature. The reaction mixture was refluxed for 1 h, during which the color of the reaction mixture changed from bright red to dark yellow. After the reaction mixture was cooled to room temperature, the solvent was evaporated *in vacuo* and the residue dissolved in CH_2Cl_2. To this solution a 10% aqueous solution of H_2O_2 (100 mL) was added, and the mixture was stirred vigorously for 1 h. After separation of the layers, the organic phase was washed with brine (250 mL) and H_2O (100 mL) and dried over Na_2SO_4. After evaporation of the solvent, the residue was dissolved in THF (200 mL) and solid CsF (2.19 g, 14.4 mmol) was added. After the reaction mixture was heated to reflux and stirred overnight at room temperature, the THF was evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2 (200 mL), washed with water (200 mL), and dried over Na_2SO_4. After purification by column chromatography (silica, eluent CH_2Cl_2/MeOH 99:1 to 97:3), **2** was obtained pure as a white solid. Yield: 2.1 g (31%). Mp: 118−120 °C. ^{1}H NMR: δ 7.83−7.21 (m, 20H, PPh_2), 6.72 (s, 2H, ArH), 6.43 (s, 1H, ArH), 3.49 (d, 4H, $J = 13.8$ Hz, CH_2P). FAB-MS: *m/z* 523.2 ($(M + H)^+$, calcd 523.2). Anal. Calcd for $C_{32}H_{28}O_3P_2$: C, 73.56; H, 5.40. Found: C, 73.90; H, 5.42.

α,α′-Bis[[3,5-bis[(diphenylphosphinyl)methyl]phenyl]oxy]-α″-cyanomesitylene (4). Pincer ligand **2** (2.00 g, 3.90 mmol) and K_2CO_3 (0.54 g, 3.90 mmol) were stirred in CH_3CN (50 mL) for 1 h at room temperature. Subsequently, α,α′-dibromo-α″-cyanomesitylene (0.42 g, 1.18 mmol) was added, and the reaction mixture was stirred for 4 days at 40 °C. TLC showed complete conversion, and the solvent was evaporated. The residue was dissolved in CH_2Cl_2 (100 mL) and washed with brine (100 mL) and water (100 mL), and the organic phase was dried over Na_2SO_4. After concentration under reduced pressure, the crude product was purified by column chromatography (SiO_2, CH_2Cl_2/Et_3N 95:5). Et_3N was removed by washing the column fraction with 1 N HCl (100 mL) and brine (100 mL), and after drying over Na_2SO_4, pure **4** was obtained as a white solid. Yield: 0.70 g (35%). Mp: 120−122 °C. ^{1}H NMR: δ 7.68−5.59 (m, 16H, PPh_2), 7.51−7.37 (m, 24H, PPh_2), 7.23 (s, 2H, ArH), 7.19 (s, 1H, ArH), 6.66 (s, 2H, ArH), 6.58 (s, 4H, ArH), 4.72 (s, 4H, CH_2O), 3.76 (s, 2H, CH_2-CN), 3.52 (d, 8H, $J = 13.7$ Hz, CH_2P). ^{13}C NMR: δ 158.2, 138.3, 133.0, 132.7, 131.8−125.9, 115.2, 69.0, 46.1, 37.4. ^{31}P NMR: δ 29.5. FAB-MS: *m/z* 1186.3 (M^+, calcd 1186.2), 1208.5 ($(M + Na)^+$, calcd 1209.2). Anal. Calcd for $C_{74}H_{63}NO_6P_4{\cdot}NaCl$: C, 71.41; H, 5.10; N, 1.12. Found: C, 71.90; H, 5.36; N, 1.09.[21]

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(17) Launay, N.; Caminade, A.-M.; Lahana, R.; Majoral, J.-P. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1589. Galliot, C.; Prévoté, D.; Caminade, A.-M.; Majoral, J.-P. *J. Am. Chem. Soc.* **1995**, *117*, 5470.

(18) Preliminary MALDI-TOF MS experiments revealed that it is possible to synthesize metallodendrimers containing either Pd or Ni. In addition to the signals for the (oxidized) building block, the MALDI-TOF mass spectrum of **$G_{1,PdPd}$** shows a signal at *m/z* 6115 corresponding to $[M - 3BF_4]^+$ (calcd 6111). A signal at *m/z* 5687 corresponding to $[M - 3BF_4]^+$ (calcd 5682) is present in the MALDI-TOF mass spectrum of **$G_{1,NiNi}$**. The complexes are sensitive toward oxidation in solution, and future experiments will be carried out under rigorous exclusion of air during the assembly process.

(19) Sen, A.; Ta-Wang, L. *J. Am. Chem. Soc.* **1981**, *103*, 4627.

(20) Vögtle, F.; Zuber, M.; Lichtenhaler, R. *Chem. Ber.* **1973**, *106*, 717.

(21) The phosphine oxide ligands easily complex NaCl, which can also be seen in the FAB-MS spectrum $(M + Na)^+$. Apparently, the ligand was not washed sufficiently with water to remove all of the NaCl. However, this did not hamper further reactions.

α,α′,α″-Tris[[3,5-bis[(diphenylphosphinyl)methyl]phenyl]oxy]mesitylene (7). The experimental conditions are similar to those described for **4**; white solid. Yield: 0.45 g (43%). Mp: 135−138 °C. ^{1}H NMR: δ 7.68−7.61 (m, 24H, PPh_2), 7.47−7.40 (m, 36H, PPh_2), 7.18 (s, 3H, ArH), 6.69 (s, 3H, ArH), 6.57 (s, 6H, ArH), 4.69 (s, 6H, CH_2), 3.52 (d, 12H, *J* = 13.8 Hz, CH_2P). ^{13}C NMR: δ 158.9, 137.7, 133.6, 131.8, 130.0, 129.4, 128.5, 115.3, 69.4, 38.4. ^{31}P NMR: δ 29.5. FAB-MS: *m/z* 1681.8 (M^+, calcd 1681.7). Anal. Calcd for $C_{105}H_{90}O_9P_6$: C, 74.99; H, 5.39. Found: C, 74.71; H, 5.20.

α,α′-Bis[[3,5-bis[(diphenylphosphino)methyl]phenyl]oxy]-α″-cyanomesitylene (5). Phosphine oxide **4** (0.1 g, 0.06 mmol) was suspended in *m*-xylene, which was flushed with argon. $HSiCl_3$ (0.14 mL, 1.43 mmol) and degassed Et_3N were added *via* a syringe. The reaction flask was closed, heated to 120 °C, and stirred overnight. After the mixture was cooled to room temperature, the clear solution was poured into degassed 2 N NaOH (100 mL). The white suspension which formed was extracted with toluene (2 × 50 mL) and concentrated *in vacuo*. ^{1}H NMR spectroscopy of the crude product showed complete reduction of the phosphine oxide groups. The colorless oil was used directly for the cyclometalation. ^{1}H NMR: δ 7.28−7.15 (m, 43H, ArH), 6.45 (s, 2H, ArH), 6.32 (s, 4H, ArH), 4.66 (s, 4H, CH_2O), 3.67 (s, 2H, CH_2CN), 3.18 (s, 8H, CH_2P).

α,α′,α″-Tris[[3,5-bis[(diphenylphosphinyl)methyl]phenyl]oxy]mesitylene (8). The experimental conditions are similar to those described for the reduction of **7**; colorless oil. ^{1}H NMR: δ 7.35−7.10 (m, 63H, ArH), 6.49 (s, 3H, ArH), 6.33 (s, 6H, ArH), 4.62 (s, 6H, CH_2O), 3.21 (s, 12H, CH_2P). FAB-MS: *m/z* 1587.6 (M^+, calcd for $C_{105}H_{90}O_3P_6$ 1587.0).

$G_{0,Pd}$. The freshly reduced ligand **8** (95.1 mg, 0.060 mmol) was dissolved in CH_3CN (25 mL), and $Pd[CH_3CN]_4(BF_4)_2$ (80.0 mg, 0.18 mmol) was added in one portion. After 15 min of stirring at room temperature, the pale yellow solution was evaporated to dryness. The residue was dissolved in CH_2Cl_2 (25 mL) and stirred overnight with brine (25 mL). The layers were separated, and the organic solvent was evaporated under reduced pressure. After crystallization from CH_2Cl_2/diethyl ether, pure $G_{0,Pd}$ was obtained as a pale yellow solid. Yield: 80 mg (67%). Mp: 137−138 °C. ^{1}H NMR: δ 7.78−7.70 (m, 24H, PPh_2), 7.38−7.31 (m, 39H, PPh_2 + ArH), 6.72 (s, 6H, $Ar_{Pd}H$), 5.22 (s, 4H, CH_2Cl_2), 4.93 (s, 6H, CH_2O), 3.84 (bs, 12H, CH_2P). ^{31}P NMR: δ 33.0. FAB-MS: *m/z* 1971.3 ($(M - Cl)^+$, calcd 1972.6). Anal. Calcd for $C_{105}H_{87}O_3P_6Pd_3Cl_3 \cdot 2.25CH_2Cl_2$: C, 58.57; H, 4.19. Found: C, 58.05; H, 4.09.

$BB_{Pd}-Cl$. The experimental conditions are similar to those described for $G_{0,Pd}$; pale yellow solid. Yield: 72 mg (55%). Mp: 157−158 °C. ^{1}H NMR: δ 7.90−7.78 (m, 16H, PPh_2), 7.42−7.36 (m, 24H, PPh_2), 7.35 (s, 1H, ArH), 7.32 (s, 2H, ArH), 6.68 (s, 4H, $Ar_{Pd}H$), 5.22 (s, 3H, CH_2Cl_2), 4.95 (s, 4H, CH_2O), 3.91 (bs, 8H, CH_2P), 3.75 (s, 2H, CH_2CN). ^{31}P NMR: δ 33.4. FAB-MS: *m/z* 1369.0 ($[M - Cl]^+$, calcd 1368.4). Anal. Calcd for $C_{74}H_{61}P_4NO_2Pd_2Cl_2 \cdot 1.5CH_2Cl_2$: C, 59.69; H, 4.16; N, 0.90. Found: C, 59.41; H, 4.15; N, 0.99.

$G_{0,Ni}$. The freshly reduced ligand **8** (95.1 mg, 0.060 mmol) was dissolved in a mixture of CH_2Cl_2/EtOH 3:1 (50 mL), and 6 equiv of $NiCl_2 \cdot 6H_2O$ (0.09 g, 0.36 mmol) was added in one portion. The reaction mixture was stirred for 1 h at 60 °C, and a red solution formed. To this red solution Hünig's base (0.07, 0.42 mmol) was added, and the reaction mixture was heated to reflux. The color changed to light yellow in 0.5 h, and the mixture was stirred at room temperature overnight. The solvent was evaporated under reduced pressure, and the residue was dissolved in CH_2Cl_2 (50 mL). The excess amount of $NiCl_2$ was filtered off. The organic phase was washed with water, and G_0Ni was obtained as a pale yellow solid by precipitation with diethyl ether. Yield: 40 mg (24%). Mp: 167−170 °C. ^{1}H NMR: δ 7.80−7.76 (m, 24H, PPh_2), 7.42−7.29 (m, 39H, PPh_2 + ArH), 6.63 (s, 6H, $Ar_{Ni}H$), 4.90 (s, 6H, CH_2O), 3.73 (bs, 12H, CH_2P). ^{31}P NMR: δ 34.2. FAB-MS: *m/z* 1864.2 (M^+, calcd 1864.2), 1828.3 ($(M - Cl)^+$, calcd 1828.7). Anal. Calcd for $C_{105}H_{87}O_3P_6Ni_3Cl_3 \cdot 2.25NiCl_2$: C, 58.47; H, 4.16. Found: C, 58.20; H, 4.00.

$BB_{Ni}-Cl$. The experimental conditions are similar to those described for $G_{0,Ni}$; pale yellow solid. Yield: 24 mg (14%). Mp: 162−164 °C. ^{1}H NMR: δ 7.91−7.85 (m, 16H, PPh_2), 7.45−7.35 (m, 25H, PPh_2 + ArH), 7.32 (s, 2H, ArH), 6.77 (s, 4H, $Ar_{Ni}H$), 5.22 (s, 1H, CH_2Cl_2), 4.98 (s, 4H, CH_2O), 3.85 (bs, 8H, CH_2P), 3.72 (s, 2H, CH_2CN). ^{31}P NMR: δ 34.6. FAB-MS: *m/z* 1272.7 ($(M - Cl)^+$, calcd 1272.2). Anal. Calcd for $C_{74}H_{61}NO_2P_4Ni_2Cl_2 \cdot 0.5CH_2Cl_2$: C, 66.24; H, 4.63; N, 1.04. Found: C, 66.37; H, 4.45; N, 1.21.

$G_{0,Pt}$. Reduced ligand **5** (0.084 mmol) was dissolved in degassed $CHCl_3$ (25 mL), and 2 equiv of *cis*-$[PtCl_2(PPh_3)_2]$ (0.13 g, 0.168 mmol) was added. The mixture was heated to reflux and stirred for 20 h, during which a white precipitate formed. After the reaction mixture was cooled to room temperature, the volume was reduced *in vacuo* to 10 mL and elemental sulfur (0.04 g, 0.164 mmol), KCl (0.01 g, 0.164 mmol), and acetone (4 mL) were added. The resulting suspension was stirred for 5 h at 50 °C, whereupon the reaction mixture was evaporated to dryness. Repeated crystallization from CH_2Cl_2/diethyl ether and washing with cold toluene (10 mL) gave $G_{0,Pt}$ as a white solid. Yield: 80 mg (60%). Mp: 181−183 °C. ^{1}H NMR: δ 7.89−7.82 (m, 24H, PPh_2), 7.40−7.31 (m, 39H, PPh_2 + ArH), 6.77 (s, 6H, $Ar_{Pt}H$), 4.98 (s, 6H, CH_2O), 3.84 (bs, 12H, CH_2P). ^{31}P NMR: δ 32.3 (J_{PPt} = 1481 Hz). ^{195}Pt NMR: δ −4286 (J_{PtP} = 1467 Hz). FAB-MS: *m/z* 2237.0 ($(M - Cl)^+$, calcd 2237.8). Anal. Calcd for $C_{105}H_{87}O_3P_6Pt_3Cl_3 \cdot 0.5S_8 \cdot 2C_7H_8$: C, 55.68; H, 4.40; S, 4.44. Found C, 55.25; H, 4.01; S, 4.96.

$BB_{Pt}-Cl$. The experimental conditions are similar to those described for $G_{0,Pt}$; white solid. Yield: 0.06 g (40%). Mp: 178−179 °C. ^{1}H NMR: δ 7.95−7.81 (m, 16H, ArH), 7.49−7.39 (m, 25H, ArH), 7.33 (s, 2H, ArH), 6.77 (s, 4H, $Ar_{Pt}H$), 4.99 (s, 4H, CH_2O), 3.86 (bs, 8H, CH_2P), 3.84 (s, 2H, CH_2CN). ^{31}P NMR: δ 32.3 (J_{PPt} = 1467 Hz). ^{195}Pt NMR: δ −4286 (J_{PtP} = 1467 Hz). FAB-MS: *m/z* 1546.2 ($(M - Cl)^+$, calcd 1545.8). Anal. Calcd for $C_{74}H_{61}NO_2P_4Pt_2Cl_2$: C, 56.21; H, 3.89; N, 0.89. Found: C, 56.44; H, 3.92; N, 0.94.

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