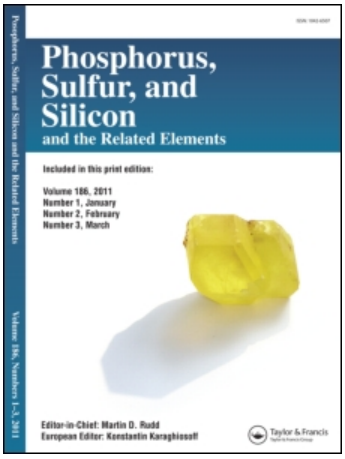

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Synthesis and Characterization of Controlled Dendritic Architectures by Association of Two Phosphorus Dendrons Through a Metallic Center

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The reactions of $RuCl_2(PPh_3)_3$ with either a small amino diphosphine or a first-generation phosphorus-containing dendron possessing an aminodiphosphine as the core induce the formation of complexes in which two amino diphosphines are associated through the metallic center. Determination of the structure of the smallest complex by X-ray diffraction shows that the metal is surrounded by a square-based bi-pyramid defined by the four phosphorus atoms of both diphosphines in a single plane, with the chlorine atoms at both summits. The first generation dendrons behave in the same way as the small compound, and allow us to isolate an original bis dendron, associated through the ruthenium atom.

Keywords Crystal structure; dendrimers; dendrons; diphosphine; ruthenium

INTRODUCTION

Dendritic architectures have been strongly stirring up the imagination of the scientific community for more than 20 years, due to the numerous unique properties they possess, in particular in the fields of catalysis, materials, and biology. Most of these compounds have a regular multibranched architecture emanating from a central core, and are named dendrimers.[1] In contrast with all the other types of artificial polymers, dendrimers are not synthesized by polymerization reactions but step-by-step. The synthesis of dendrimers is of particular interest, because it constitutes one of the rare examples of perfectly controlled

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Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

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and highly reproducible processes able to afford nano-objects. However, more complex dendritic architectures can be also developed, thanks to the step-by-step syntheses; they generally employ the use of "dendrons. " Dendrons are reminiscent of dendrimers, but in contrast to dendrimers, they possess one reactive function at the level of the core. Most dendrons are obtained by a convergent strategy introduced by Hawker and Fréchet,[2] and are generally synthesized only up to generation 2, 3, or 4 in order to avoid the steric crowding of the core function. Depending on the type of function, several dendrons can be associated by their core in a spontaneous self-assembly,[3] around a metal,[4] or by reaction with a multifunctional core.[5]

Since 1994, we have synthesized dendrimers[6] and special dendritic architectures[7] possessing phosphorus atoms as branching points. Figure 1 illustrates the various types of dendritic architectures that we have already prepared thanks to the versatility of the chemistry of phosphorus: layered dendrimers,[8] "multiplurifunctionalized" dendrimers,[9] layer-block dendrimers,[10] surface-block dendrimers,[11] star polymers,[12] and even highly sophisticated architectures in which dendrons are linked to the interior of a dendrimer.[13]

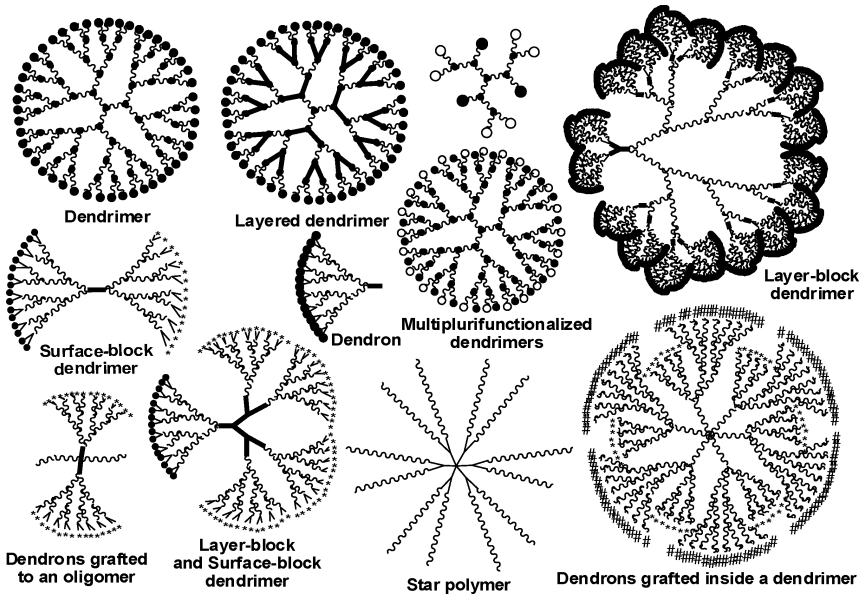


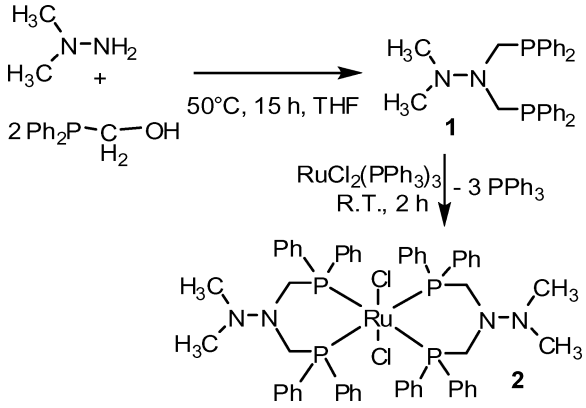
FIGURE 1 Various types of phosphorus-containing dendritic architectures built with one phosphorus at each branching point.

In this article, we report our attempts to synthesize new phosphorus-containing dendritic architectures by associating two dendrons by their core around a metal.

RESULTS AND DISCUSSION

As indicated in the Introduction, associating two dendrons through a metallic center has some precedents.[4] The type of metal used includes in several cases transition metals (often with the aim of performing catalysis experiments), but to the best of our knowledge, such an experiment has not been attempted previously with ruthenium derivatives. We have already grafted ruthenium to the core of dendrons to perform diastereoselective Michael additions.[14] We will show here that the same metal is able to accommodate two dendrons.

Pincer diphosphino derivatives are generally stable ligands for ruthenium, thus the dendrons that will be used should possess such a ligand at the core. The first experiment is conducted with two equivalents of a small model of the dendron that is the diphosphine **1** (obtained by reaction of Ph_2PCH_2OH with 1,1′-dimethylhydrazine[14]), and $RuCl_2(PPh_3)_3$,[15] chosen because it was previously shown to be able to accommodate two diphosphines.[16] The complexation reaction, monitored by ^{31}P NMR, displays the disappearance of the signal at $\delta\ ^{31}P = -24$ ppm corresponding to compound **1**, on behalf of a new singlet at $\delta\ ^{31}P = 0.2$ ppm corresponding to the complex **2**, together with a singlet at -7 ppm, corresponding to free PPh_3 (Scheme 1). After workup, only the signals corresponding to **2** are detected by ^{31}P NMR. This compound is also characterized by ^1H NMR, which displays in particular



SCHEME 1

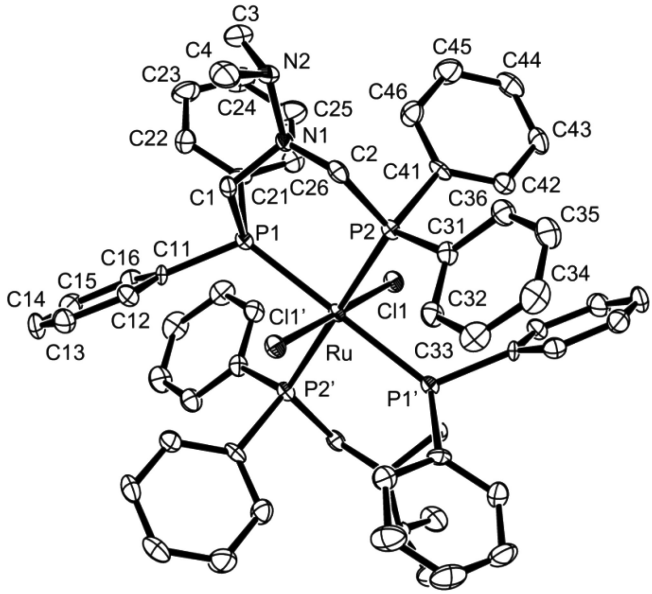
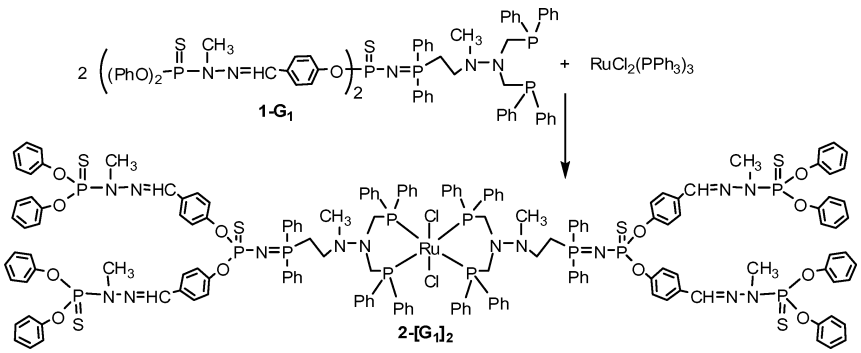


FIGURE 2 ORTEP drawing of compound **2**. Selected bond lengths (Å) and bond angles (°): Ru—P1 2.4317(13); Ru—P2 2.3752(12); Ru—Cl 2.4294(10); P1—Ru—P1' 180.00(5); P2—Ru—P2′ 180.0; P1—Ru—P2′ 92.55(4); P1—Ru—P2 87.45(4); P1—Ru—Cl1 100.56(4); P1—Ru—Cl1′ 79.44(4); P2—Ru—Cl1 91.73(4); P2—Ru—Cl1′ 88.27(4).

a deshielding of the signal corresponding to the P-CH_2-N groups, from 3.6 ppm in **1** to 3.9 ppm in **2**.

To further characterize compound **2**, and in particular the arrangement around the metallic center, orange single crystals of compound **2** were grown in dichloromethane from a concentrated solution. The ORTEP drawing of compound **2** is shown in Figure 2. It is worth noting that both Cl are in the trans position, and that they constitute the summits of a square-based bi-pyramid defined by the four phosphorus atoms around Ru.

Having demonstrated the viability of our method with a small compound, we decided to apply the same methodology to a real dendron. For this purpose, the first generation dendron **1-G**$_1$ possessing a diphosphine as core was synthesized as indicated previously.[17] Reaction of two equivalents of **1-G**$_1$ with one equivalent of $RuCl_2(PPh_3)_3$ affords as expected the bis-dendron **2-[G**$_1$**]**$_2$ (Scheme 2). ^{31}P NMR is again the best method to characterize this compound, which displays two singlets and two doublets. The most characteristic signal is the singlet at δ



SCHEME 2

$^{31}P = 1.1$ ppm, corresponding to the complexed diphosphine, whereas the other singlet at 62.9 ppm corresponds to the $P(S)(OPh)_2$ end groups. It is worth noting that the two doublets characteristic of the P=N–P=S linkages in **2-[G$_1$]$_2$** ($\delta\,^{31}P = 18.7$ and 51.6 ppm, respectively with $^2J_{PP} = 31.8$ Hz) are identical to those found for **2-G$_1$,** thus this linkage is not implied in the complexation. Indeed, we have previously shown that complexation of P=N–P=S linkages (for instance by gold), induces a significant shielding of the doublet corresponding to the P=S group ($\Delta\delta = 17$ ppm).[18] ^{1}H NMR is also useful to characterize the bis dendron **2-[G$_1$]$_2$**; it displays also the same deshielding than the one observed in the reaction **1** → **2** for the P-CH_2-N groups from 3.5 ppm for **2-G$_1$** to 3.9 ppm for **2-[G$_1$]$_2$**. In view of these data, we can deduce that the structure of the bis dendron **2-[G$_1$]$_2$** at the level of the core is the same than that of compound **2**.

CONCLUSION

We have shown in this article our preliminary results for the synthesis of original bis dendrons, coupled by their core through a ruthenium center. The coupling occurs as easily with the first generation dendron as with a very simple model, thus such methodology should be usable for the coupling of larger dendrons. Furthermore, ^{31}P NMR appears again as a very valuable and sensitive tool to characterize sophisticated macromolecules.

EXPERIMENTAL

All manipulations were carried out using standard high vacuum and dry-argon techniques. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with Bruker AC 200, AC 250, or DPX 300 spectrometers. References for NMR chemical shifts are 85% H_3PO_4 for ^{31}P and $SiMe_4$ for ^{1}H. Solvents

were dried and distilled prior to use (THF over sodium/benzophenone, CH_2Cl_2 over phosphorus pentoxide) and degassed when phosphines are used. Compounds **1**,[14] **1-G$_1$**,[17] and $RuCl_2(PPh_3)_3$[15] were synthesized as previously published.

Synthesis and Characterization of Compound 2

0.190 g (0.417 mmol) of compound **1** in solution in dichloromethane (5 mL) was added to 0.200 g (0.208 mmol) of dichloro tris-(triphenylphosphine) ruthenium (II) in solution in dichloromethane (15 mL). The resulting mixture was stirred for 2 h at room temperature, then evaporated to dryness to afford an orange powder. This powder was washed twice with ether, then twice with pentane, to afford compound **2** as an orange powder in 76% yield. Single crystals suitable for X-ray characterization were grown at room temperature from a concentrated solution of **2** in dichloromethane.

$^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 0.2$ (s) ppm. ^1H NMR ($CDCl_3$): $\delta = 2.3$ (s, 12H, CH_3), 3.9 (d, $^2J_{HP} = 10.0$ Hz, 8H, CH_2), 6.8–7.7 (m, 40H, CHarom) ppm. Anal. Calcd for $C_{56}H_{60}N_4P_4Cl_2Ru$: C, 61.99; H, 5.57; N, 5.16. Found: C, 61.93; H, 5.50; N, 5,09.

Synthesis and Characterization of the Bis Dendron 2-[G$_1$]$_2$

0.318 g (0.208 mmol) of dendron **1-G$_1$** in solution in dichloromethane (5 mL) was added to 0.100 g (0.104 mmol) of dichloro tris-(triphenylphosphine) ruthenium (II) in solution in dichloromethane (10 mL). The resulting mixture was stirred for 2 h at room temperature, then evaporated to dryness to afford an orange powder. This powder was washed three times with a mixture ether/pentane, to afford the bis dendron **2-[G$_1$]$_2$** as an orange powder in 88% yield.

$^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 1.1$ (s, PPh_2), 18.7 (d, $^2J_{PP} = 31.8$ Hz, P=N–P=S), 51.6 (d, $^2J_{PP} = 31.8$ Hz, P=N–P=S), 62.9 (s, NNP=S) ppm. ^1H NMR ($CDCl_3$): $\delta = 2.3$ (br s, 6H, C$\underline{H}_3$–N–CH_2), 2.9 (m, 8H, CH_2–CH_2–P), 3.3 (d, $^3J_{HP} = 10.4$ Hz, 12H, CH_3–N–P), 3.9 (d, $^2J_{HP} = 10.8$ Hz, 8H, N–C$\underline{H}_2$–PPh_2), 6.8–7.8 (m, 120H, CHarom, CH=N) ppm. Anal. Calcd for $C_{162}H_{154}N_{14}O_{12}P_{12}S_6Cl_2Ru$: C, 60.33; H, 4.81; N, 6.08. Found: C, 60.28; H, 4.75; N, 5.98.

X-Ray Structure Determination for Compound 2

Measurement was carried out on a one circle IPDS STOE X-ray diffractometer system (Mo-radiation, $\lambda = 0.71073$ Å, 50KV/30mA power), at low temperature (T = 160(2) K). Frames were integrated with the aid

of STOE, X-RED, Data Reduction for STADI4 and IPDS, Revision 1.08. Stoe software.[19]

A total of 167 frames were collected for a hemisphere of reflections. Based on a triclinic crystal system (P -1), the integrated frames yielded a total of 12053 reflections at a maximum 2θ angle of 45.98 degrees, of which 4428 were independent reflections ($R_{int} = 0.0486$, $R_{sig} = 0.0695$, completeness = 94.8%) and 3134 (70.8%) reflections were greater than 2σ (I). The unit cell parameters were $\mathbf{a} = 12.0173(15)$ Å, $\mathbf{b} = 12.4932(16)$ Å, $\mathbf{c} = 13.2869(17)$ Å, $\alpha = 87.307(16)^\circ$, $\beta = 66.722(14)^\circ$, $\gamma = 67.290(15)^\circ$, V =1677.2(4) Å^3, Z = 1, calculated density $D_c = 1.553$ g/cm^3. Absorption corrections were applied (absorption coefficient $\mu = 0.929$ mm^{-1} max/min transmission 0.691 and −0.626) using the Difabs program.[20]

Structure was solved by using direct methods, with the aid of SIR92[20] and refined by least-squares procedures on F^2 using SHELXL-97[21] included in the WinGX programs.[22] Direct methods of phase determination followed by some Fourier cycles of refinement led to an electron density map, from which most of the non-hydrogen atoms were identified. With subsequent isotropic refinement, all of the non-hydrogen atoms were identified, atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms were refined by means of a full matrix least-squares procedure on F^2. The hydrogen atoms were included in the refinement in calculated positions, riding on the carbon atoms to which they were connected. Drawing of molecule was realized with the aid of ORTEP32.[23] Atomic scattering factors were taken from International Tables for X-Ray Crystallography.[24]

The refinement converged at R1 = 0.0359, wR2 = 0.0752, with intensity $I > 2\sigma$ (I). The largest peak/hole in the final difference map was 0.691 and -0.626 e.Å^{-3}. Further details on the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ UK, by quoting the full journal citation.

Supplementary Data

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC (**2**). Copies of the data can be obtained free of charge via www.ccdc.cam.uk/data_request/cif.

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