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Versatile Complexation Ability of Very Large Phosphino-Terminated Dendrimers

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The synthesis of phosphino-terminated dendrimers is described up to the tenth generation, which possess more than 3000 phosphino groups (**3-[G′$_{10}$]**). Several complexation reactions of these dendrimers toward various low oxidation states transition metal derivatives have been carried out, up to generation 5 for iron (**4-[G′$_5$]**: 96 $Ph_2P{\rightarrow}Fe(CO)_4$ groups), generation 4 for tungsten (**5-[G′$_4$]**: 48 $Ph_2P{\rightarrow}W(CO)_5$ groups), generation 10 for gold (**6-[G′$_{10}$]**: 3072 $Ph_2P{\rightarrow}Au{-}Cl$ groups), and generation 6 for rhodium (**8-[G′$_6$]**: 192 $Ph_2P{\rightarrow}Rh(acac)(CO)$ groups). These reactions demonstrate that the phosphino-terminated dendrimers behave analogously to monophosphines, in spite of the nanometer size of the high generations.

Introduction

The synthesis of dendrimers, highly branched polymers of defined structure, attracts considerable attention, both from a fundamental viewpoint and for the great variety of expected applications.[1] One of the most active current areas of research is the incorporation of transition metals into such structures. For instance, transition metal complexes may serve as building blocks in the construction of dendrimers.[2] However, in this case, any wish to change the nature of the metal necessitates that the synthesis be begun again from the core. For several purposes (catalysis for example) it is not absolutely necessary to have metals included in the skeleton of the dendrimer but only localized on the periphery. This may be achieved either by grafting an organometallic fragment during the last step of the synthesis[3] or by direct complexation of alkyne-,[4] nitrogen-,[5] or phosphine-terminated dendrimers.[6] The advantage of such a procedure is that one type of dendrimer may serve to complex different types of transition metals; this behavior can be anticipated mainly for phosphino-terminated dendrimers. In a previous report, we described the synthesis of diphosphino-terminated dendrimers leading to chelate complexes of Pd, Pt, and Rh up to the third generation.[7] We report here an extension of this concept, with the study of the complexation ability of phosphino-terminated dendrimers toward Fe, W, Rh, and Au in low oxidation states, up to the fifth, the fourth, the sixth, and the tenth generations, respectively.

Such dendritic organometallic macromolecules might present some interesting properties as catalysts. Indeed a few dendrimers having metal centers as termination groups have shown such properties: arylnickel(II) dendrimers are effective as catalysts for the Karasch addition reaction of polyhaloalkanes to olefines,[5c] and P-based polypalladium complexes allowed the electrochemical reduction of CO_2 to CO.[6a,b]

Experimental Section

General. All manipulations were carried out with standard high-vacuum or dry argon atmosphere techniques. ^1H, ^{31}P, and ^{13}C NMR

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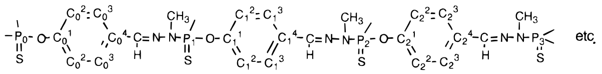
spectra were recorded on Bruker AC 80 and AC 200 spectrometers. ^{31}P NMR chemical shifts are reported in parts per million relative to 85% H_3PO_4.

The numbering used for ^{13}C and ^{31}P NMR is depicted in the following scheme:



General Procedure for the Synthesis of Dendrimers 3-[G′*n*] (Ph_2P End Groups). Neat diphenylphosphine (0.2 mL, 1.16 mmol) and paraformaldehyde (0.0348 g) are heated in a pressure Schlenk tube for 90 min at 120 °C to afford Ph_2PCH_2OH.[9] Then, a solution of **2-[G′*n*]**[8c] (***n*** = 1, 0.154 g, 0.097 mmol; ***n*** = 2, 0.196 g, 0.048 mmol; ***n*** = 3, 0.194 g, 0.024 mmol; ***n*** = 4, 0.200 g, 0.012 mmol; ***n*** = 5, 0.205 g, 0.006 mmol; ***n*** = 6, 0.206 g, 0.003 mmol; ***n*** = 10, 0.166 g, 0.15 μmol) in 5 mL of tetrahydrofuran (THF) is added. The resulting mixture is heated for 3 days at 65 °C under stirring. Then, the solvent is removed to give a yellow oil. Washings with pentane/ether (1:1) (2 × 10 mL) eliminate an excess of Ph_2PCH_2OH and give **3-[G′*n*]** as a white powder.

3-[G′$_1$]. White powder; 88% yield, mp 88 °C. ^{31}P {^{1}H} NMR ($CDCl_3$): δ −23.4 (s, PPh_2), 51.7 (s, P_0), 61.9 (s, P_1). ^{1}H NMR ($CDCl_3$): δ 3.0 (br s, 18 H, $CH_2{-}N{-}C\mathit{H}_3$), 3.4 (d, $^3J_{HP_1} = 9.8$ Hz, 9 H, $P_1{-}N{-}CH_3$), 4.2 (br s, 12 H, CH_2), 7.2−7.6 (m, 105 H, C_6H_5, C_6H_4, and $CH{=}N$). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 33.1 (d, $^2J_{CP_1} = 12.7$ Hz, $P_1{-}N{-}CH_3$), 38.9 (d, $^3J_{CP} = 6.7$ Hz, $CH_2{-}N{-}\mathit{C}H_3$), 61.0 (d, $^1J_{CP} = 10.9$ Hz, CH_2), 121.4 (d, $^3J_{CP_{0,1}} = 4.0$ Hz, C_0^2, C_1^2), 126.6 (s, C_1^3), 128.3 (s, C_0^3), 128.4 (d, $^3J_{CP} = 6.0$ Hz, *m*-C_6H_5), 128.6 (s, *p*-C_6H_5), 130.6 (s, C_1^4), 132.9 (s, C_0^4), 133.0 (d, $^2J_{CP} = 18.7$ Hz, *o*-C_6H_5), 134.2 (s, $\mathit{C}H{=}N{-}N{-}CH_2$), 137.7 (d, $^1J_{CP} = 14.0$ Hz, *i*-C_6H_5), 138.2 (d, $^3J_{CP_1} = 12.2$ Hz, $CH{=}N$), 149.6 (d, $^2J_{CP_1} = 7.9$ Hz, C_1^1), 151.1 (d, $^2J_{CP_0} = 7.7$ Hz, C_0^1). Anal. Calcd for $C_{150}H_{144}N_{18}O_9P_{10}S_4$: C, 64.79; H, 5.22; N, 9.07. Found: C, 64.48; H, 5.11; N, 8.89.

3-[G′$_2$]. White powder; 89% yield, mp 104 °C. ^{31}P {^{1}H} NMR ($CDCl_3$): δ −23.4 (s, PPh_2), 51.8 (s, P_0), 61.7 (s, P_1), 62.0 (s, P_2). ^{1}H NMR ($CDCl_3$): δ 2.9 (br s, 36 H, $CH_2{-}N{-}C\mathit{H}_3$), 3.4 (m, 27 H, $P_{1,2}{-}N{-}CH_3$), 4.2 (br s, 24 H, CH_2), 7.1−7.6 (m, 225 H, C_6H_5, C_6H_4, and $CH{=}N$). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 33.0 (d, $^2J_{CP_{1,2}} = 12.3$ Hz, $P_{1,2}{-}N{-}CH_3$), 38.9 (d, $^3J_{CP} = 6.6$ Hz, $CH_2{-}N{-}\mathit{C}H_3$), 61.0 (d, $^1J_{CP} = 10.6$ Hz, CH_2), 121.3 (d, $^3J_{CP_2} = 4.1$ Hz, C_2^2), 121.7 (m, C_0^2, C_1^2), 126.5 (s, C_2^3), 128.3 (s, C_0^3, C_1^3), 128.4 (d, $^3J_{CP} = 6.2$ Hz, *m*-C_6H_5), 128.6 (s, *p*-C_6H_5), 130.6 (s, C_2^4), 132.1 (s, C_0^4, C_1^4), 132.9 (d, $^2J_{CP} = 18.6$ Hz, *o*-C_6H_5), 134.1 (s, $\mathit{C}H{=}N{-}N{-}CH_2$), 137.6 (d, $^1J_{CP} = 13.2$ Hz, *i*-C_6H_5), 138.5 (m, $CH{=}N$), 149.5 (d, $^2J_{CP_2} = 7.9$ Hz, C_2^1), 151.2 (m, C_0^1, C_1^1). Anal. Calcd for $C_{324}H_{312}N_{42}O_{21}P_{22}S_{10}$: C, 63.46; H, 5.13; N, 9.59. Found: C, 63.09; H, 5.04; N, 9.41.

3-[G′$_3$]. White powder; 90% yield, mp 122 °C. ^{31}P {^{1}H} NMR ($CDCl_3$): δ −23.3 (s, PPh_2), 51.8 (s, P_0), 61.5 (s, P_1), 61.8 (s, P_2), 62.0 (s, P_3). ^{1}H NMR ($CDCl_3$): δ 2.9 (br s, 72 H, $CH_2{-}N{-}C\mathit{H}_3$), 3.4 (m, 63 H, $P_{1-3}{-}N{-}CH_3$), 4.2 (br s, 48 H, CH_2), 7.1−7.6 (m, 465 H, C_6H_5, C_6H_4, and $CH{=}N$). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 33.0 (d, $^2J_{CP_{1-3}} = 12.7$ Hz, $P_{1-3}{-}N{-}CH_3$), 38.8 (d, $^3J_{CP} = 6.3$ Hz, $CH_2{-}N{-}\mathit{C}H_3$), 60.9 (d, $^1J_{CP} = 10.5$ Hz, CH_2), 121.3 (d, $^3J_{CP_3} = 3.1$ Hz, C_3^2), 121.7 (m, C_0^2, C_1^2, C_2^2), 126.5 (s, C_3^3), 128.2 (s, C_0^3, C_1^3, C_2^3), 128.3 (d, $^3J_{CP} = 6.8$ Hz, *m*-C_6H_5), 128.6 (s, *p*-C_6H_5), 130.6 (s, C_3^4), 132.1 (m, C_0^4, C_1^4, C_2^4), 132.9 (d, $^2J_{CP} = 18.3$ Hz, *o*-C_6H_5), 134.1 (s, $\mathit{C}H{=}N{-}N{-}CH_2$), 137.5 (d, $^1J_{CP} = 13.2$ Hz, *i*-C_6H_5), 138.5 (m, $CH{=}N$), 149.4 (d, $^2J_{CP_3} = 7.3$ Hz, C_3^1), 151.1 (d, $^2J_{CP_{0-2}} = 6.0$ Hz, C_0^1, C_1^1, C_2^1). Anal. Calcd for $C_{672}H_{648}N_{90}O_{45}P_{46}S_{22}$: C, 62.88; H, 5.09; N, 9.82. Found: C, 62.63; H, 4.93; N, 9.70.

3-[G′$_4$]. White powder; 84% yield, mp 128 °C. ^{31}P {^{1}H} NMR ($CDCl_3$): δ −23.3 (s, PPh_2), 51.8 (s, P_0), 61.5 (s, P_1, P_2), 61.8 (s, P_3), 62.0 (s, P_4). ^{1}H NMR ($CDCl_3$): δ 2.9 (br s, 144 H, $CH_2{-}N{-}C\mathit{H}_3$), 3.4 (m, 135 H, $P_{1-4}{-}N{-}CH_3$), 4.2 (br s, 96 H, CH_2), 7.1−7.6 (m, 945 H, C_6H_5, C_6H_4, and $CH{=}N$). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 33.0 (d, $^2J_{CP_{1-4}} = 14.0$ Hz, $P_{1-4}{-}N{-}CH_3$), 38.8 (d, $^3J_{CP} = 6.2$ Hz, $CH_2{-}N{-}\mathit{C}H_3$), 60.9 (d, $^1J_{CP} = 10.2$ Hz, CH_2), 121.3 (d, $^3J_{CP_4} = 3.5$ Hz, C_4^2), 121.7 (m, C_0^2, C_1^2, C_2^2, C_3^2), 126.5 (s, C_4^3), 128.2 (s, C_0^3, C_1^3, C_2^3, C_3^3), 128.3 (d, $^3J_{CP} = 6.5$ Hz, *m*-C_6H_5), 128.5 (s, *p*-C_6H_5), 130.6 (s, C_4^4), 131.2 (m, C_0^4, C_1^4, C_2^4, C_3^4), 133.0 (d, $^2J_{CP} = 18.5$ Hz, *o*-C_6H_5), 134.1 (s, $\mathit{C}H{=}N{-}N{-}CH_2$), 137.5 (d, $^1J_{CP} = 13.5$ Hz, *i*-C_6H_5), 138.5 (m, $CH{=}N$), 149.5 (d, $^2J_{CP_4} = 7.4$ Hz, C_4^1), 151.1 (m, C_0^1, C_1^1, C_2^1, C_3^1). Anal. Calcd for $C_{1368}H_{1320}N_{186}O_{93}P_{94}S_{46}$: C, 62.61; H, 5.07; N, 9.93. Found: C, 62.40; H, 4.93; N, 9.81.

3-[G′$_5$]. White powder; 87% yield, mp 136 °C. ^{31}P {^{1}H} NMR ($CDCl_3$): δ −23.3 (s, PPh_2), 51.8 (s, P_0), 61.5 (s, P_1, P_2), 61.6 (s, P_3), 61.8 (s, P_4), 62.0 (s, P_5). ^{1}H NMR ($CDCl_3$): δ 2.9 (br s, 288 H, $CH_2{-}N{-}C\mathit{H}_3$), 3.4 (m, 279 H, $P_{1-5}{-}N{-}CH_3$), 4.2 (br s, 192 H, CH_2), 7.1−7.6 (m, 1905 H, C_6H_5, C_6H_4, and $CH{=}N$). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 33.0 (d, $^2J_{CP_{1-5}} = 13.9$ Hz, $P_{1-5}{-}N{-}CH_3$), 38.8 (d, $^3J_{CP} = 6.3$ Hz, $CH_2{-}N{-}\mathit{C}H_3$), 60.9 (d, $^1J_{CP} = 10.4$ Hz, CH_2), 121.2 (br s, C_5^2), 121.7 (m, C_0^2, C_1^2, C_2^2, C_3^2, C_4^2), 126.4 (s, C_5^3), 128.2 (s, C_0^3, C_1^3, C_2^3, C_3^3, C_4^3), 128.3 (d, $^3J_{CP} = 6.9$ Hz, *m*-C_6H_5), 128.5 (s, *p*-C_6H_5), 130.6 (s, C_5^4), 131.1 (m, C_0^4, C_1^4, C_2^4, C_3^4, C_4^4), 132.9 (d, $^2J_{CP} = 18.6$ Hz, *o*-C_6H_5), 134.1 (s, $\mathit{C}H{=}N{-}N{-}CH_2$), 137.5 (d, $^1J_{CP} = 13.9$ Hz, *i*-C_6H_5), 138.3 (m, $CH{=}N$), 149.4 (d, $^2J_{CP_5} = 7.3$Hz, C_5^1), 151.1 (m, C_0^1, C_1^1, C_2^1, C_3^1, C_4^1). Anal. Calcd for $C_{2760}H_{2664}N_{378}O_{189}P_{190}S_{94}$: C, 62.48; H, 5.06; N, 9.98. Found: C, 62.08; H, 4.97; N, 9.81.

3-[G′$_6$]. White powder; 88% yield, mp 138 °C. ^{31}P {^{1}H} NMR ($CDCl_3$): δ −23.3 (s, PPh_2), 51.8 (s, P_0), 61.5 (s, P_1, P_2), 61.6 (s, P_3, P_4), 61.8 (s, P_5), 62.0 (s, P_6). ^{1}H NMR ($CDCl_3$): δ 2.9 (br s, 576 H, $CH_2{-}N{-}C\mathit{H}_3$), 3.4 (m, 567 H, $P_{1-6}{-}N{-}CH_3$), 4.2 (br s, 384 H, CH_2), 7.1−7.6 (m, 3825 H, C_6H_5, C_6H_4, and $CH{=}N$). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 33.0 (d, $^2J_{CP_{1-6}} = 13.0$ Hz, $P_{1-6}{-}N{-}CH_3$), 38.8 (d, $^3J_{CP} = 6.3$ Hz, $CH_2{-}N{-}\mathit{C}H_3$), 60.8 (d, $^1J_{CP} = 11.6$ Hz, CH_2), 121.2 (br s, C_6^2), 121.7 (m, C_0^2, C_1^2, C_2^2, C_3^2, C_4^2, C_5^2), 126.4 (s, C_6^3), 128.2 (s, C_0^3, C_1^3, C_2^3, C_3^3, C_4^3, C_5^3), 128.3 (d, $^3J_{CP} = 6.9$ Hz, *m*-C_6H_5), 128.5 (s, *p*-C_6H_5), 130.6 (s, C_6^4), 131.1 (m, C_0^4, C_1^4, C_2^4, C_3^4, C_4^4, C_5^4), 132.9 (d, $^2J_{CP} = 18.6$ Hz, *o*-C_6H_5), 134.1 (s, $\mathit{C}H{=}N{-}N{-}CH_2$), 137.5 (d, $^1J_{CP} = 13.4$ Hz, *i*-C_6H_5), 138.4 (m, $CH{=}N$), 149.4 (d, $^2J_{CP_6} = 7.3$ Hz, C_6^1), 151.1 (m, C_0^1, C_1^1, C_2^1, C_3^1, C_4^1, C_5^1). Anal. Calcd for $C_{5544}H_{5352}N_{762}O_{381}P_{382}S_{190}$: C, 62.42; H, 5.05; N, 10.00. Found: C, 62.15; H, 4.94; N, 9.87.

3-[G′$_{10}$]. White powder; 92% yield. ^{31}P {^{1}H} NMR ($CDCl_3$): δ −22.8 (s, PPh_2), 61.5−62.0 (br s, $P_1{-}P_{10}$). ^{1}H NMR ($CDCl_3$): δ 2.8 (s, 9216 H, $CH_2{-}N{-}C\mathit{H}_3$), 3.3 (m, 9207 H, $P_{1-10}{-}N{-}CH_3$), 4.1 (br s, 6144 H, CH_2), 7.2−7.7 (m, 58353 H, C_6H_5, C_6H_4, and $CH{=}N$). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 32.8 (d, $^2J_{CP_{1-10}} = 13.1$ Hz, $P_{1-10}{-}N{-}CH_3$), 39.0 (d, $^3J_{CP} = 6.5$ Hz, $CH_2{-}N{-}\mathit{C}H_3$), 60.8 (d, $^1J_{CP} = 11$ Hz, CH_2), 121.2 (br s, C_{10}^2), 121.7 (br s, C_0^2, C_1^2, C_2^2, C_3^2, C_4^2, C_5^2, C_6^2, C_7^2, C_8^2, C_9^2), 126.4 (s, C_{10}^3), 128.2 (s, C_0^3, C_1^3, C_2^3, C_3^3, C_4^3, C_5^3, C_6^3, C_7^3, C_8^3, C_9^3), 128.3 (d, $^3J_{CP} = 6.5$ Hz, *m*-C_6H_5), 128.6 (s, *p*-C_6H_5), 130.5 (s, C_{10}^4), 131.3 (s, C_0^4, C_1^4, C_2^4, C_3^4, C_4^4, C_5^4, C_6^4, C_7^4, C_8^4, C_9^4), 132.9 (d, $^2J_{CP} = 18$ Hz, *o*-C_6H_5), 134.0 (s, $\mathit{C}H{=}N{-}N{-}CH_2$), 137.4 (d, $^1J_{CP} = 13$ Hz, *i*-C_6H_5), 139.0 (m, $CH{=}N$), 150.1 (d, $^2J_{CP_{10}} = 7$ Hz, C_{10}^1), 151.4 (m, C_0^1, C_1^1, C_2^1, C_3^1, C_4^1, C_5^1, C_6^1, C_7^1, C_8^1, C_9^1, C_{10}^1).

General Procedure for the Synthesis of Dendrimers 4-[G′*n*] ($Ph_2P{\rightarrow}Fe(CO)_4$ End Groups). To a solution of 0.1 g of dendrimer **3-[G′*n*]** (***n*** = 1, 0.036 mmol; ***n*** = 2, 0.0163 mmol; ***n*** = 3, 0.0078 mmol; ***n*** = 4, 0.0038 mmol; ***n*** = 5, 0.0019 mmol) in 5 mL of THF is added $Fe_2(CO)_9$ (***n*** = 1, 0.086 g, 0.24 mmol; ***n*** = 2, 0.080 g, 0.22 mmol; ***n*** = 3, 0.076 g, 0.21 mmol; ***n*** = 4, 0.073 g, 0.20 mmol; ***n*** = 5, 0.073 g, 0.20 mmol). The resulting mixture is stirred for 12 h at room temperature and then filtered. The solvent is removed under vacuum to give a brown oil which is washed with ether (2 × 10 mL) to give the iron complex **4-[G′*n*]** as a brown powder.

4-[G′$_1$]. Brown powder; 85% yield, mp 118 °C. ^{31}P {^{1}H} NMR ($CDCl_3$): δ 51.8 (s, P_0), 61.7 (s, P_1), 67.1 (s, PPh_2). ^{1}H NMR ($CDCl_3$): δ 2.8 (s, 18 H, $CH_2{-}N{-}C\mathit{H}_3$), 3.4 (br s, 9 H, $P_1{-}N{-}CH_3$), 4.6 (s, 12 H, CH_2), 7.0−7.7 (m, 105 H, C_6H_5, C_6H_4, and $CH{=}N$). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 32.9 (d, $^2J_{CP_1} = 12.8$ Hz, $P_1{-}N{-}CH_3$), 39.0 (s, $CH_2{-}N{-}\mathit{C}H_3$), 62.5 (d, $^1J_{CP} = 34.8$ Hz, CH_2), 121.3 (br s, C_0^2, C_1^2), 126.5 (s, C_1^3), 128.4 (s, C_0^3), 128.5 (d, $^3J_{CP} = 9.8$ Hz, *m*-C_6H_5), 130.1 (s, C_1^4), 130.7 (s, *p*-C_6H_5), 131.8 (s, C_0^4), 132.8 (d, $^2J_{CP} = 9.8$ Hz, *o*-C_6H_5), 133.1 (d, $^1J_{CP} = 38.6$ Hz, *i*-C_6H_5), 133.7 (s, $\mathit{C}H{=}N{-}N{-}CH_2$), 137.8 (d, $^3J_{CP_1} = 12.4$ Hz, $CH{=}N$), 149.6 (d, $^2J_{CP_1} = 7.5$ Hz, C_1^1), 151.1 (d, $^2J_{CP_0} = 7.6$ Hz, C_0^1), 213.1 (d, $^2J_{CP} = 18.5$ Hz, CO). IR (KBr): 2046, 1971, 1923 ($\nu_{C=O}$) cm^{-1}. Anal. Calcd for $C_{174}H_{144}N_{18}Fe_6O_{33}P_{10}S_4$: C, 55.17; H, 3.83; N, 6.66. Found: C, 54.88; H, 3.71; N, 6.51.

4-[G′$_2$]. Brown powder; 87% yield, mp 121 °C. ^{31}P {^{1}H} NMR ($CDCl_3$): δ 51.9 (s, P_0), 61.3 (s, P_1), 61.8 (s, P_2), 67.0 (s, PPh_2). ^{1}H NMR ($CDCl_3$): δ 2.8 (s, 36 H, $CH_2{-}N{-}C\mathit{H}_3$), 3.3 (br s, 27 H, $P_{1,2}{-}$

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(9) Hellmann, H.; Bader, J.; Birkner, H.; Schumacher, O. *Liebigs Ann. Chem.* **1962**, *659*, 49.

$\mathrm{N{-}CH_3}$), 4.5 (s, 24 H, $\mathrm{CH_2}$), 7.0−7.7 (m, 225 H, $\mathrm{C_6H_5}$, $\mathrm{C_6H_4}$, and CH=N). ^{13}C {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 32.9 (d, $^2J_{\mathrm{CP}_{1,2}}$ = 12.8 Hz, $\mathrm{P_{1,2}{-}N{-}CH_3}$), 39.0 (s, $\mathrm{CH_2{-}N{-}}C\mathrm{H_3}$), 62.5 (d, $^1J_{\mathrm{CP}}$ = 34.5 Hz, $\mathrm{CH_2}$), 121.2 (br s, $\mathrm{C_2}^2$), 121.7 (m, $\mathrm{C_0}^2$, $\mathrm{C_1}^2$), 126.4 (s, $\mathrm{C_2}^3$), 128.2 (s, $\mathrm{C_0}^3$, $\mathrm{C_1}^3$), 128.4 (d, $^3J_{\mathrm{CP}}$ = 9.6 Hz, *m*-$\mathrm{C_6H_5}$), 130.1 (s, $\mathrm{C_2}^4$), 130.7 (s, *p*-$\mathrm{C_6H_5}$), 131.1 (s, $\mathrm{C_0}^4$, $\mathrm{C_1}^4$), 132.8 (d, $^2J_{\mathrm{CP}}$ = 9.2 Hz, *o*-$\mathrm{C_6H_5}$), 133.0 (d, $^1J_{\mathrm{CP}}$ = 38.6 Hz, *i*-$\mathrm{C_6H_5}$), 133.7 (s, *C*H=N−N−$\mathrm{CH_2}$), 138.0 (m, CH=N), 149.5 (d, $^2J_{\mathrm{CP}_2}$ = 7.3 Hz, $\mathrm{C_2}^1$), 151.2 (m, $\mathrm{C_0}^1$, $\mathrm{C_1}^1$), 213.0 (d, $^2J_{\mathrm{CP}}$ = 18.3 Hz, CO). IR (KBr): 2047, 1972, 1922 ($\nu_{\mathrm{C=O}}$) cm^{-1}. Anal. Calcd for $\mathrm{C_{372}H_{312}N_{42}Fe_{12}O_{69}P_{22}S_{10}}$: C, 54.84; H, 3.86; N, 7.22. Found: C, 54.61; H, 3.71; N, 7.09.

4-[G′$_3$]. Brown powder; 91% yield, mp 123 °C. ^{31}P {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 51.9 (s, $\mathrm{P_0}$), 61.3 (s, $\mathrm{P_1}$), 61.5 (s, $\mathrm{P_2}$), 61.7 (s, $\mathrm{P_3}$), 67.0 (s, $\mathrm{PPh_2}$). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 2.7 (s, 72 H, $\mathrm{CH_2{-}N{-}C}H_3$), 3.4 (br s, 63 H, $\mathrm{P_{1-3}{-}N{-}CH_3}$), 4.5 (s, 48 H, $\mathrm{CH_2}$), 7.0−7.7 (m, 465 H, $\mathrm{C_6H_5}$, $\mathrm{C_6H_4}$, and CH=N). ^{13}C {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 33.0 (d, $^2J_{\mathrm{CP}_{1-3}}$ = 13.0 Hz, $\mathrm{P_{1-3}{-}N{-}CH_3}$), 39.0 (s, $\mathrm{CH_2{-}N{-}}C\mathrm{H_3}$), 62.5 (d, $^1J_{\mathrm{CP}}$ = 34.7 Hz, $\mathrm{CH_2}$), 121.2 (br s, $^3J_{\mathrm{CP}_3}$ = 3.1 Hz, $\mathrm{C_3}^2$), 121.7 (m, $\mathrm{C_0}^2$, $\mathrm{C_1}^2$, $\mathrm{C_2}^2$), 126.4 (s, $\mathrm{C_3}^3$), 128.4 (br d, $^3J_{\mathrm{CP}}$ = 7.6 Hz, *m*-$\mathrm{C_6H_5}$ and $\mathrm{C_0}^3$, $\mathrm{C_1}^3$, $\mathrm{C_2}^3$), 130.0 (s, $\mathrm{C_3}^4$), 130.7 (s, *p*-$\mathrm{C_6H_5}$), 131.8 (m, $\mathrm{C_0}^4$, $\mathrm{C_1}^4$, $\mathrm{C_2}^4$), 132.7 (d, $^2J_{\mathrm{CP}}$ = 8.5 Hz, *o*-$\mathrm{C_6H_5}$), 133.0 (d, $^1J_{\mathrm{CP}}$ = 37.7 Hz, *i*-$\mathrm{C_6H_5}$), 134.7 (s, *C*H=N−N−$\mathrm{CH_2}$), 138.6 (m, CH=N), 149.5 (d, $^2J_{\mathrm{CP}_3}$ = 7.7 Hz, $\mathrm{C_3}^1$), 151.1 (d, $^2J_{\mathrm{CP}_{0-2}}$ = 6.0 Hz, $\mathrm{C_0}^1$, $\mathrm{C_1}^1$, $\mathrm{C_2}^1$) 213.0 (d, $^2J_{\mathrm{CP}}$ = 17.4 Hz, CO). IR (KBr): 2046, 1970, 1923 ($\nu_{\mathrm{C=O}}$) cm^{-1}. Anal. Calcd for $\mathrm{C_{768}H_{648}N_{90}Fe_{24}O_{141}P_{46}S_{22}}$: C, 54.70; H, 3.87; N, 7.47. Found: C, 54.57; H, 3.80; N, 7.29.

4-[G′$_4$]. Brown powder; 90% yield, mp 131 °C. ^{31}P {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 51.9 (s, $\mathrm{P_0}$), 61.3 (s, $\mathrm{P_1}$), 61.5 (s, $\mathrm{P_2}$), 61.5 (s, $\mathrm{P_3}$), 61.7 (s, $\mathrm{P_4}$), 67.0 (s, $\mathrm{PPh_2}$). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 2.8 (s, 144 H, $\mathrm{CH_2{-}N{-}C}H_3$), 3.3 (br s, 135 H, $\mathrm{P_{1-4}{-}N{-}CH_3}$), 4.5 (s, 96 H, $\mathrm{CH_2}$), 7.1−7.6 (m, 945 H, $\mathrm{C_6H_5}$, $\mathrm{C_6H_4}$, and CH=N). ^{13}C {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 33.0 (d, $^2J_{\mathrm{CP}_{1-4}}$ = 12.1 Hz, $\mathrm{P_{1-4}{-}N{-}CH_3}$), 38.9 (s, $\mathrm{CH_2{-}N{-}}C\mathrm{H_3}$), 62.4 (d, $^1J_{\mathrm{CP}}$ = 30.2 Hz, $\mathrm{CH_2}$), 121.2 (d, $^3J_{\mathrm{CP}_4}$ = 3.5 Hz, $\mathrm{C_4}^2$), 121.6 (m, $\mathrm{C_0}^2$, $\mathrm{C_1}^2$, $\mathrm{C_2}^2$, $\mathrm{C_3}^2$), 126.4 (s, $\mathrm{C_4}^3$), 128.4 (br d, $^3J_{\mathrm{CP}}$ = 8.4 Hz, *m*-$\mathrm{C_6H_5}$ and $\mathrm{C_0}^3$, $\mathrm{C_1}^3$, $\mathrm{C_2}^3$, $\mathrm{C_3}^3$), 130.1 (s, $\mathrm{C_4}^4$), 130.7 (s, *p*-$\mathrm{C_6H_5}$), 131.1 (m, $\mathrm{C_0}^4$, $\mathrm{C_1}^4$, $\mathrm{C_2}^4$, $\mathrm{C_3}^4$), 132.8 (d, $^2J_{\mathrm{CP}}$ = 9.3 Hz, *o*-$\mathrm{C_6H_5}$), 133.1 (d, $^1J_{\mathrm{CP}}$ = 39.1 Hz, *i*-$\mathrm{C_6H_5}$), 133.7 (s, *C*H=N−N−$\mathrm{CH_2}$), 138.6 (m, CH=N), 149.5 (d, $^2J_{\mathrm{CP}_4}$ = 7.3 Hz, $\mathrm{C_4}^1$), 151.2 (m, $\mathrm{C_0}^1$, $\mathrm{C_1}^1$, $\mathrm{C_2}^1$, $\mathrm{C_3}^1$), 213.0 (d, $^2J_{\mathrm{CP}}$ = 18.8 Hz, CO). IR (KBr): 2046, 1969, 1924 ($\nu_{\mathrm{C=O}}$) cm^{-1}. Anal. Calcd for $\mathrm{C_{1560}H_{1320}N_{186}Fe_{48}O_{285}P_{94}S_{46}}$: C, 54.63; H, 3.88; N, 7.60. Found: C, 54.45; H, 3.71; N, 7.48.

4-[G′$_5$]. Brown powder; 89% yield, mp 141 °C. ^{31}P {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 51.9 (s, $\mathrm{P_0}$), 61.3 (s, $\mathrm{P_1}$, $\mathrm{P_2}$), 61.4 (s, $\mathrm{P_3}$), 61.5 (s, $\mathrm{P_4}$), 62.0 (s, $\mathrm{P_5}$), 67.0 (s, $\mathrm{PPh_2}$). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 2.8 (s, 288 H, $\mathrm{CH_2{-}N{-}C}H_3$), 3.3 (br s, 279 H, $\mathrm{P_{1-5}{-}N{-}CH_3}$), 4.4 (s, 192 H, $\mathrm{CH_2}$), 7.1−7.6 (m, 1905 H, $\mathrm{C_6H_5}$, $\mathrm{C_6H_4}$, and CH=N). ^{13}C {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 33.0 (d, $^2J_{\mathrm{CP}_{1-5}}$ = 13.4 Hz, $\mathrm{P_{1-5}{-}N{-}CH_3}$), 39.1 (s, $\mathrm{CH_2{-}N{-}}C\mathrm{H_3}$), 62.7 (d, $^1J_{\mathrm{CP}}$ = 32.6 Hz, $\mathrm{CH_2}$), 121.3 (s, $\mathrm{C_5}^2$), 121.8 (m, $\mathrm{C_0}^2$, $\mathrm{C_1}^2$, $\mathrm{C_2}^2$, $\mathrm{C_3}^2$, $\mathrm{C_4}^2$), 126.6 (s, $\mathrm{C_5}^3$), 128.5 (d, $^3J_{\mathrm{CP}}$ = 7.9 Hz, *m*-$\mathrm{C_6H_5}$ and $\mathrm{C_0}^3$, $\mathrm{C_1}^3$, $\mathrm{C_2}^3$, $\mathrm{C_3}^3$, $\mathrm{C_4}^3$), 130.2 (s, $\mathrm{C_5}^4$), 130.8 (s, *p*-$\mathrm{C_6H_5}$), 131.1 (m, $\mathrm{C_0}^4$, $\mathrm{C_1}^4$, $\mathrm{C_2}^4$, $\mathrm{C_3}^4$, $\mathrm{C_4}^4$), 132.9 (d, $^2J_{\mathrm{CP}}$ = 7.0 Hz, *o*-$\mathrm{C_6H_5}$), 133.1 (d, $^1J_{\mathrm{CP}}$ = 38.5 Hz, *i*-$\mathrm{C_6H_5}$), 133.8 (s, *C*H=N−N−$\mathrm{CH_2}$), 137.9 (m, CH=N), 149.6 (d, $^2J_{\mathrm{CP}_5}$ = 7.7 Hz, $\mathrm{C_5}^1$), 151.4 (m, $\mathrm{C_0}^1$, $\mathrm{C_1}^1$, $\mathrm{C_2}^1$, $\mathrm{C_3}^1$, $\mathrm{C_4}^1$), 213.0 (d, $^2J_{\mathrm{CP}}$ = 17.9 Hz, CO). IR (KBr): 2045, 1969, 1920 ($\nu_{\mathrm{C=O}}$) cm^{-1}. Anal. Calcd for $\mathrm{C_{3144}H_{2664}N_{378}Fe_{96}O_{573}P_{190}S_{94}}$: C, 54.60; H, 3.88; N, 7.65. Found: C, 54.35; H, 3.73; N, 7.43.

General Procedure for the Synthesis of Dendrimers 5-[G′$_n$] ($\mathbf{Ph_2P{\rightarrow}W(CO)_5}$ End Groups). A solution of 0.1 g of dendrimer **3-[G′$_n$]** (***n*** = 1, 0.036 mmol; ***n*** = 2, 0.0163 mmol; ***n*** = 3, 0.0078 mmol; ***n*** = 4, 0.0038 mmol) in 10 mL of THF is added to a solution of $\mathrm{W(CO)_5(THF)}$, obtained by irradiation of $\mathrm{W(CO)_6}$ (***n*** = 1, 0.1 g, 0.28 mmol; ***n*** = 2, 0.088 g, 0.25 mmol; ***n*** = 3, 0.085 g, 0.243 mmol; ***n*** = 4, 0.084 g, 0.24 mmol) in THF (30 mL). The resulting mixture is stirred for 6 h at room temperature, and then the solvent is removed under vacuum to give a brown oil which is washed with ether (2 × 10 mL) to give the tungsten complex **5-[G′$_n$]** as a yellow powder.

5-[G′$_1$]. Yellow powder; 90% yield, mp 131 °C. ^{31}P {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 16.1 (s, $^1J_{\mathrm{PW}}$ = 241.9 Hz, $\mathrm{PPh_2}$), 52.0 (s, $\mathrm{P_0}$), 61.8 (s, $\mathrm{P_1}$). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 2.7 (s, 18 H, $\mathrm{CH_2{-}N{-}C}H_3$), 3.3 (br s, 9 H, $\mathrm{P_1{-}N{-}CH_3}$), 4.5 (s, 12 H, $\mathrm{CH_2}$), 7.0−7.7 (m, 105 H, $\mathrm{C_6H_5}$, $\mathrm{C_6H_4}$, and CH=N). ^{13}C {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 33.0 (d, $^2J_{\mathrm{CP}_1}$ = 12.9 Hz, $\mathrm{P_1{-}N{-}CH_3}$), 38.9 (s, $\mathrm{CH_2{-}N{-}}C\mathrm{H_3}$), 63.2 (d, $^1J_{\mathrm{CP}}$ = 30.6 Hz, $\mathrm{CH_2}$), 121.3 (br s, $\mathrm{C_0}^2$, $\mathrm{C_1}^2$), 126.6 (s, $\mathrm{C_1}^3$), 128.6 (d, $^3J_{\mathrm{CP}}$ = 9.2 Hz, *m*-$\mathrm{C_6H_5}$ and $\mathrm{C_0}^3$), 130.2 (s, *p*-$\mathrm{C_6H_5}$), 130.9 (s, $\mathrm{C_1}^4$), 132.4 (s, $\mathrm{C_0}^4$), 132.5 (d, $^2J_{\mathrm{CP}}$ = 10.7 Hz, *o*-$\mathrm{C_6H_5}$), 133.7 (s, *C*H=N−N−$\mathrm{CH_2}$), 134.9 (d, $^1J_{\mathrm{CP}}$ = 39.0 Hz, *i*-$\mathrm{C_6H_5}$), 138.6 (d, $^3J_{\mathrm{CP}_0}$ = 12.3 Hz, CH=N), 149.7 (d, $^2J_{\mathrm{CP}_1}$ = 7.3 Hz, $\mathrm{C_1}^1$), 151.1 (d, $^2J_{\mathrm{CP}_0}$ = 7.7 Hz, $\mathrm{C_0}^1$), 196.7 (d, $^2J_{\mathrm{CP}}$ = 6.8 Hz, $^1J_{\mathrm{CW}}$ = 119.3 Hz, *cis*-CO), 199.4 (d, $^2J_{\mathrm{CP}}$ = 21.8 Hz, *trans*-CO). IR (KBr): 2069, 1981, 1918 ($\nu_{\mathrm{C=O}}$) cm^{-1}. Anal. Calcd for $\mathrm{C_{180}H_{144}N_{18}O_{39}P_{10}S_4W_6}$: C, 45.76; H, 3.07; N, 5.34. Found: C, 45.51; H, 2.93; N, 5.22.

5-[G′$_2$]. Yellow powder; 91% yield, mp 138 °C. ^{31}P {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 16.1 (s, $^1J_{\mathrm{PW}}$ = 241.1 Hz, $\mathrm{PPh_2}$), 52.0 (s, $\mathrm{P_0}$), 61.6 (s, $\mathrm{P_1}$), 62.0 (s, $\mathrm{P_2}$). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 2.7 (s, 36 H, $\mathrm{CH_2{-}N{-}C}H_3$), 3.3 (br s, 27 H, $\mathrm{P_{1,2}{-}N{-}CH_3}$), 4.5 (s, 24 H, $\mathrm{CH_2}$), 7.0−7.7 (m, 225 H, $\mathrm{C_6H_5}$, $\mathrm{C_6H_4}$, and CH=N). ^{13}C {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 33.0 (d, $^2J_{\mathrm{CP}_{1,2}}$ = 13.1 Hz, $\mathrm{P_{1,2}{-}N{-}CH_3}$), 38.9 (s, $\mathrm{CH_2{-}N{-}}C\mathrm{H_3}$), 63.2 (d, $^1J_{\mathrm{CP}}$ = 30.8 Hz, $\mathrm{CH_2}$), 121.2 (d, $^3J_{\mathrm{CP}_2}$ = 4.1 Hz, $\mathrm{C_2}^2$), 122.1 (m, $\mathrm{C_0}^2$, $\mathrm{C_1}^2$) 126.6 (s, $\mathrm{C_2}^3$), 128.6 (d, $^3J_{\mathrm{CP}}$ = 8.9 Hz, *m*-$\mathrm{C_6H_5}$ and $\mathrm{C_0}^3$, $\mathrm{C_1}^3$), 130.1 (s, *p*-$\mathrm{C_6H_5}$), 130.8 (s, $\mathrm{C_2}^4$), 131.1 (s, $\mathrm{C_0}^4$, $\mathrm{C_1}^4$), 132.4 (d, $^2J_{\mathrm{CP}}$ = 10.7 Hz, *o*-$\mathrm{C_6H_5}$), 133.7 (s, *C*H=N−N−$\mathrm{CH_2}$), 134.9 (d, $^1J_{\mathrm{CP}}$ = 38.8 Hz, *i*-$\mathrm{C_6H_5}$), 138.6 (m, CH=N), 149.6 (d, $^2J_{\mathrm{CP}_2}$ = 6.9 Hz, $\mathrm{C_2}^1$), 151.3 (m, $\mathrm{C_0}^1$, $\mathrm{C_1}^1$), 196.7 (d, $^2J_{\mathrm{CP}}$ = 7.0 Hz, $^1J_{\mathrm{CW}}$ = 120.5 Hz, *cis*-CO), 199.4 (d, $^2J_{\mathrm{CP}}$ = 21.6 Hz, *trans*-CO). IR (KBr): 2069, 1981, 1914 ($\nu_{\mathrm{C=O}}$) cm^{-1}. Anal. Calcd for $\mathrm{C_{384}H_{312}N_{42}O_{81}P_{22}S_{10}W_{12}}$: C, 46.03; H, 3.14; N, 5.87. Found: C, 45.78; H, 3.06; N, 5.69.

5-[G′$_3$]. Yellow powder; 90% yield, mp 139 °C. ^{31}P {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 16.1 (s, $^1J_{\mathrm{PW}}$ = 240.7 Hz, $\mathrm{PPh_2}$), 52.0 (s, $\mathrm{P_0}$), 61.2 (s, $\mathrm{P_1}$), 61.6 (s, $\mathrm{P_2}$), 62.0 (s, $\mathrm{P_3}$). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 2.6 (s, 72 H, $\mathrm{CH_2{-}N{-}C}H_3$), 3.3 (br s, 63 H, $\mathrm{P_{1-3}{-}N{-}CH_3}$), 4.4 (s, 48 H, $\mathrm{CH_2}$), 7.0−7.6 (m, 465 H, $\mathrm{C_6H_5}$, $\mathrm{C_6H_4}$, and CH=N). ^{13}C {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 33.0 (d, $^2J_{\mathrm{CP}_{1-3}}$ = 12.9 Hz, $\mathrm{P_{1-3}{-}N{-}CH_3}$), 38.9 (s, $\mathrm{CH_2{-}N{-}}C\mathrm{H_3}$), 63.3 (d, $^1J_{\mathrm{CP}}$ = 32.0 Hz, $\mathrm{CH_2}$), 121.2 (br s, $\mathrm{C_3}^2$), 121.8 (m, $\mathrm{C_0}^2$, $\mathrm{C_1}^2$, $\mathrm{C_2}^2$) 126.5 (s, $\mathrm{C_3}^3$), 128.5 (d, $^3J_{\mathrm{CP}}$ = 8.9 Hz, *m*-$\mathrm{C_6H_5}$ and $\mathrm{C_0}^3$, $\mathrm{C_1}^3$, $\mathrm{C_2}^3$), 130.1 (s, *p*-$\mathrm{C_6H_5}$), 130.8 (s, $\mathrm{C_3}^4$), 132.1 (s, $\mathrm{C_0}^4$, $\mathrm{C_1}^4$, $\mathrm{C_2}^4$), 132.4 (d, $^2J_{\mathrm{CP}}$ = 10.5 Hz, *o*-$\mathrm{C_6H_5}$), 133.6 (s, *C*H=N−N−$\mathrm{CH_2}$), 134.9 (d, $^1J_{\mathrm{CP}}$ = 38.7 Hz, *i*-$\mathrm{C_6H_5}$), 138.6 (m, CH=N), 149.6 (d, $^2J_{\mathrm{CP}_3}$ = 7.3 Hz, $\mathrm{C_3}^1$), 151.1 (m, $\mathrm{C_0}^1$, $\mathrm{C_1}^1$, $\mathrm{C_2}^1$), 196.7 (d, $^2J_{\mathrm{CP}}$ = 6.4 Hz, $^1J_{\mathrm{CW}}$ = 122.3 Hz, *cis*-CO), 199.4 (d, $^2J_{\mathrm{CP}}$ = 23.1 Hz, *trans*-CO). IR (KBr): 2069, 1981, 1923 ($\nu_{\mathrm{C=O}}$) cm^{-1}. Anal. Calcd for $\mathrm{C_{792}H_{648}N_{90}O_{165}P_{46}S_{22}W_{24}}$: C, 46.16; H, 3.17; N, 6.12. Found: C, 46.00; H, 3.08; N, 5.98.

5-[G′$_4$]. Yellow powder; 88% yield, mp 145 °C. ^{31}P {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 16.1 (s, $^1J_{\mathrm{PW}}$ = 237.6 Hz, $\mathrm{PPh_2}$), 52.0 (s, $\mathrm{P_0}$), 61.2 (s, $\mathrm{P_1}$, $\mathrm{P_2}$), 61.6 (s, $\mathrm{P_3}$), 62.0 (s, $\mathrm{P_4}$). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 2.5 (s, 144 H, $\mathrm{CH_2{-}N{-}C}H_3$), 3.3 (br s, 135 H, $\mathrm{P_{1-4}{-}N{-}CH_3}$), 4.4 (s, 96 H, $\mathrm{CH_2}$), 7.0−7.7 (m, 945 H, $\mathrm{C_6H_5}$, $\mathrm{C_6H_4}$, and CH=N). ^{13}C {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 32.9 (d, $^2J_{\mathrm{CP}_{1-4}}$ = 13.1 Hz, $\mathrm{P_{1-4}{-}N{-}CH_3}$), 38.8 (s, $\mathrm{CH_2{-}N{-}}C\mathrm{H_3}$), 63.2 (d, $^1J_{\mathrm{CP}}$ = 33.2 Hz, $\mathrm{CH_2}$), 121.1 (br s, $\mathrm{C_4}^2$), 121.7 (m, $\mathrm{C_0}^2$, $\mathrm{C_1}^2$, $\mathrm{C_2}^2$, $\mathrm{C_3}^2$) 126.5 (s, $\mathrm{C_4}^3$), 128.5 (d, $^3J_{\mathrm{CP}}$ = 8.7 Hz, *m*-$\mathrm{C_6H_5}$ and $\mathrm{C_0}^3$, $\mathrm{C_1}^3$, $\mathrm{C_2}^3$, $\mathrm{C_3}^3$), 130.0 (s, *p*-$\mathrm{C_6H_5}$), 130.8 (s, $\mathrm{C_4}^4$), 131.2 (m, $\mathrm{C_0}^4$, $\mathrm{C_1}^4$, $\mathrm{C_2}^4$, $\mathrm{C_3}^4$), 132.3 (d, $^2J_{\mathrm{CP}}$ = 10.7 Hz, *o*-$\mathrm{C_6H_5}$), 133.6 (s, *C*H=N−N−$\mathrm{CH_2}$), 134.9 (d, $^1J_{\mathrm{CP}}$ = 38.7 Hz, *i*-$\mathrm{C_6H_5}$), 138.5 (m, CH=N), 149.6 (d, $^2J_{\mathrm{CP}_4}$ = 7.1 Hz, $\mathrm{C_4}^1$), 151.1 (m, $\mathrm{C_0}^1$, $\mathrm{C_1}^1$, $\mathrm{C_2}^1$, $\mathrm{C_3}^1$), 196.6 (d, $^2J_{\mathrm{CP}}$ = 6.8 Hz, $^1J_{\mathrm{CW}}$ = 123.9 Hz, *cis*-CO), 199.4 (d, $^2J_{\mathrm{CP}}$ = 23.4 Hz, *trans*-CO). IR (KBr): 2069, 1981, 1920 ($\nu_{\mathrm{C=O}}$) cm^{-1}. Anal. Calcd for $\mathrm{C_{1608}H_{1320}N_{186}O_{333}P_{94}S_{46}W_{48}}$: C, 46.22; H, 3.18; N, 6.23. Found: C, 45.98; H, 3.06; N, 6.10.

General Procedure for the Synthesis of Dendrimers 6-[G′$_n$] ($\mathbf{Ph_2P{\rightarrow}Au{-}Cl}$ End Groups). To a solution of dendrimer **3-[G′$_n$]** (***n*** = 1, 0.1 g, 0.036 mmol; ***n*** = 4, 0.1 g, 3.8 μmol; ***n*** = 5, 0.1 g, 1.88 μmol; ***n*** = 6, 0.083 g, 0.78 μmol; ***n*** = 10, 0.03 g, 0.017 μmol) in $\mathrm{CH_2Cl_2}$ (20 mL) was added AuCl(tht) (***n*** = 1, 0.069 g, 0.22 mmol; ***n*** = 4, 0.059 g, 0.18 mmol; ***n*** = 5, 0.058 g, 0.18 mmol; ***n*** = 6, 0.048 g, 0.15 mmol; ***n*** = 10, 0.017 g, 53.7 μmol) at room temperature. This solution was stirred for 2 h, and then the solvent was concentrated to *ca.* 2 mL. Addition of diethyl ether (15 mL) afforded the gold complex **6-[G′$_n$]** as a white solid, which was washed with diethyl ether (2 × 10 mL).

6-[G′$_1$]. White powder; 70% yield, mp 152 °C (dec). ^{31}P {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 21.0 (s, $\mathrm{PPh_2}$), 52.5 (s, $\mathrm{P_0}$), 62.5 (s, $\mathrm{P_1}$). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 3.0 (s, 18H, $\mathrm{CH_2{-}N{-}C}H_3$), 3.3 (d, $^3J_{\mathrm{HP}_1}$ = 10.6 Hz, 9 H, $\mathrm{P_1{-}N{-}CH_3}$), 4.5 (s, 12 H, $\mathrm{CH_2}$), 7.1−7.7 (m, 105 H, $\mathrm{C_6H_5}$, $\mathrm{C_6H_4}$, and CH=N). ^{13}C {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 33.3 (d, $^2J_{\mathrm{CP}_1}$ = 13.0 Hz, $\mathrm{P_1{-}N{-}CH_3}$), 39.0 (d, $^3J_{\mathrm{CP}}$ = 4.4 Hz, $\mathrm{CH_2{-}N{-}}C\mathrm{H_3}$), 59.4 (d, $^1J_{\mathrm{CP}}$ = 38.6 Hz, $\mathrm{CH_2}$), 121.2 (m, $\mathrm{C_0}^2$, $\mathrm{C_1}^2$), 126.8 (s, $\mathrm{C_1}^3$), 128.2 (d, $^1J_{\mathrm{CP}}$ = 57.7 Hz, *i*-$\mathrm{C_6H_5}$), 128.4 (s, $\mathrm{C_0}^3$), 129.0 (d, $^3J_{\mathrm{CP}}$ = 11.4 Hz, *m*-$\mathrm{C_6H_5}$), 131.8 (s,

p-$\mathrm{C_6H_5}$ and $\mathrm{C_0}^4$), 132.9 (s, $\mathrm{C_1}^4$ and $C\mathrm{H{=}N{-}N{-}CH_2}$), 133.6 (d, $^2J_{\mathrm{CP}} = 12.8$ Hz, o-$\mathrm{C_6H_5}$), 138.4 (br s, $\mathrm{CH{=}N}$), 149.8 (d, $^2J_{\mathrm{CP_1}} = 7.6$ Hz, $\mathrm{C_1}^1$), 150.8 (d, $^2J_{\mathrm{CP_0}} = 7.6$ Hz, $\mathrm{C_0}^1$). IR (KBr): 328 (m, $\nu_{\mathrm{Au-Cl}}$) cm^{-1}. Anal. Calcd for $\mathrm{C_{150}H_{144}N_{18}Cl_6O_9P_{10}S_4Au_6}$: C, 43.15; H, 3.48; N, 6.04. Found: C, 43.2; H, 3.25; N, 5.8.

6-[G′$_4$]. White powder; 75% yield, mp 160 °C (dec). ^{31}P {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 21.2 (s, $\mathrm{PPh_2}$), 62.6 (s, $\mathrm{P_1, P_2, P_3, P_4}$). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 2.9 (s, 144H, $\mathrm{CH_2{-}N{-}C}H_3$), 3.5 (br s, 135 H, $\mathrm{P_{1-4}{-}N{-}CH_3}$), 4.4 (s, 96 H, $\mathrm{CH_2}$), 7.0−7.6 (m, 945 H, $\mathrm{C_6H_5}$, $\mathrm{C_6H_4}$, and $\mathrm{CH{=}N}$). ^{13}C {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 33.0 (d, $^2J_{\mathrm{CP_{1-4}}} = 17.1$ Hz, $\mathrm{P_{1-4}{-}N{-}CH_3}$), 39.0 (s, $\mathrm{CH_2{-}N{-}}C\mathrm{H_3}$), 59.0 (d, $^1J_{\mathrm{CP}} = 36.5$ Hz, $\mathrm{CH_2}$), 121.2 (br s, $\mathrm{C_4}^2$), 121.7 (m, $\mathrm{C_0}^2$, $\mathrm{C_1}^2$, $\mathrm{C_2}^2$, $\mathrm{C_3}^2$), 126.9 (s, $\mathrm{C_4}^3$), 128.3 (d, $^1J_{\mathrm{CP}} = 58$ Hz, i-$\mathrm{C_6H_5}$), 128.5 (s, $\mathrm{C_0}^3$, $\mathrm{C_1}^3$, $\mathrm{C_2}^3$, $\mathrm{C_3}^3$), 129.0 (d, $^3J_{\mathrm{CP}} = 11.4$ Hz, m-$\mathrm{C_6H_5}$), 131.8 (s, p-$\mathrm{C_6H_5}$ and $\mathrm{C_4}^4$), 132.3 (m, $\mathrm{C_0}^4$, $\mathrm{C_1}^4$, $\mathrm{C_2}^4$, $\mathrm{C_3}^4$, $C\mathrm{H{=}N{-}N{-}CH_2}$), 133.5 (d, $^3J_{\mathrm{CP}} = 12.6$ Hz, o-$\mathrm{C_6H_5}$), 138.6 (m, $\mathrm{CH{=}N}$), 149.8 (d, $^2J_{\mathrm{CP_2}} = 7.3$ Hz, $\mathrm{C_4}^1$), 151.0 (m, $\mathrm{C_0}^1$, $\mathrm{C_1}^1$, $\mathrm{C_2}^1$, $\mathrm{C_3}^1$). IR (KBr): 327 (m, $\nu_{\mathrm{Au-Cl}}$) cm^{-1}. Anal. Calcd for $\mathrm{C_{1368}H_{1320}N_{186}Cl_{48}O_{93}P_{94}S_{46}Au_{48}}$: C, 43.94; H, 3.56; N, 6.97. Found: C, 43.45; H, 3.55; N, 6.45.

6-[G′$_5$]. White powder; 76% yield, mp 160 °C (dec). ^{31}P {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 21.1 (s, $\mathrm{PPh_2}$), 62.2 (s, $\mathrm{P_1, P_2, P_3, P_4, P_5}$). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 2.9 (s, 288H, $\mathrm{CH_2{-}N{-}C}H_3$), 3.3 (br s, 279 H, $\mathrm{P_{1-5}{-}N{-}CH_3}$), 4.5 (s, 192 H, $\mathrm{CH_2}$), 7.1−7.7 (m, 1905 H, $\mathrm{C_6H_5}$, $\mathrm{C_6H_4}$, and $\mathrm{CH{=}N}$). ^{13}C {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 33.3 (d, $^2J_{\mathrm{CP_{1-5}}} = 13.2$ Hz, $\mathrm{P_{1-5}{-}N{-}CH_3}$), 39.3 (s, $\mathrm{CH_2{-}N{-}}C\mathrm{H_3}$), 59.1 (d, $^1J_{\mathrm{CP}} = 39.7$ Hz, $\mathrm{CH_2}$), 121.3 (s, $\mathrm{C_5}^2$), 121.8 (m, $\mathrm{C_0}^2$, $\mathrm{C_1}^2$, $\mathrm{C_2}^2$, $\mathrm{C_3}^2$, $\mathrm{C_4}^2$), 127.2 (s, $\mathrm{C_5}^3$), 128.4 (d, $^1J_{\mathrm{CP}} = 58$ Hz, i-$\mathrm{C_6H_5}$), 128.6 (m, $\mathrm{C_0}^3$, $\mathrm{C_1}^3$, $\mathrm{C_2}^3$, $\mathrm{C_3}^3$, $\mathrm{C_4}^3$), 129.1 (d, $^3J_{\mathrm{CP}} = 11.0$ Hz, m-$\mathrm{C_6H_5}$), 132.0 (s, p-$\mathrm{C_6H_5}$ and $\mathrm{C_5}^4$), 132.5 (m, $\mathrm{C_0}^4$, $\mathrm{C_1}^4$, $\mathrm{C_2}^4$, $\mathrm{C_3}^4$, $\mathrm{C_4}^4$ and $C\mathrm{H{=}N{-}N{-}CH_2}$), 133.7 (d, $^2J_{\mathrm{CP}} = 11.0$ Hz, o-$\mathrm{C_6H_5}$), 138.5 (m, $\mathrm{CH{=}N}$), 149.9 (m, $\mathrm{C_5}^1$), 151.5 (m, $\mathrm{C_0}^1$, $\mathrm{C_1}^1$, $\mathrm{C_2}^1$, $\mathrm{C_3}^1$, $\mathrm{C_4}^1$). IR (KBr): 330 (m, $\nu_{\mathrm{Au-Cl}}$) cm^{-1}. Anal. Calcd for **6-[G′$_5$]** ($\mathrm{C_{2760}H_{2664}N_{378}Cl_{96}O_{189}P_{190}S_{94}Au_{96}}$): C, 43.99; H, 3.56; N, 7.03. Found: C, 43.0; H, 3.4; N, 6.4. Anal. Calcd for **6-[G′$_5$]**·21$\mathrm{CH_2Cl_2}$ ($\mathrm{C_{2781}H_{2706}N_{378}Cl_{138}O_{189}P_{190}S_{94}Au_{96}}$): C, 43.39; H, 3.54; N, 6.86.

6-[G′$_6$]. White powder; 65% yield, mp 142 °C (dec). ^{31}P {^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 21.1 (s, $\mathrm{PPh_2}$), 62.9 (s, $\mathrm{P_1, P_2, P_3, P_4, P_5, P_6}$). ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 2.9 (s, 576 H, $\mathrm{CH_2{-}N{-}C}H_3$), 3.4 (m, 567H, $\mathrm{P_{1-6}{-}N{-}CH_3}$), 4.5 (s, 384 H, $\mathrm{CH_2}$), 7.1−7.7 (m, 3825 H, $\mathrm{C_6H_5}$, $\mathrm{C_6H_4}$, and $\mathrm{CH{=}N}$). ^{13}C {^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 33.3 (d, $^2J_{\mathrm{CP_{1-6}}} = 12.0$ Hz, $\mathrm{P_{1-6}{-}N{-}CH_3}$), 39.3 (s, $\mathrm{CH_2{-}N{-}}C\mathrm{H_3}$), 59.3 (d, $^1J_{\mathrm{CP}} = 40.7$ Hz, $\mathrm{CH_2{-}P}$), 121.4 (s, $\mathrm{C_6}^2$), 121.9 (m, $\mathrm{C_0}^2$, $\mathrm{C_1}^2$, $\mathrm{C_2}^2$, $\mathrm{C_3}^2$, $\mathrm{C_4}^2$, $\mathrm{C_5}^2$), 127.1 (s, $\mathrm{C_6}^3$), 128.4 (d, $^1J_{\mathrm{CP}} = 58$ Hz, i-$\mathrm{C_6H_5}$), 128.6 (s, $\mathrm{C_0}^3$, $\mathrm{C_1}^3$, $\mathrm{C_2}^3$, $\mathrm{C_3}^3$, $\mathrm{C_4}^3$, $\mathrm{C_5}^3$), 129.3 (d, $^3J_{\mathrm{CP}} = 10.6$ Hz, m-$\mathrm{C_6H_5}$), 132.0 (s, p-$\mathrm{C_6H_5}$ and $\mathrm{C_6}^4$), 132.4 (m, $\mathrm{C_0}^4$, $\mathrm{C_1}^4$, $\mathrm{C_2}^4$, $\mathrm{C_3}^4$, $\mathrm{C_4}^4$, $\mathrm{C_5}^4$ and $C\mathrm{H{=}N{-}N{-}CH_2}$), 133.8 (d, $^2J_{\mathrm{CP}} = 12.3$ Hz, o-$\mathrm{C_6H_5}$), 139.4 (m, $\mathrm{CH{=}N}$), 150.0 (m, $\mathrm{C_6}^1$), 151.5 (m, $\mathrm{C_0}^1$, $\mathrm{C_1}^1$, $\mathrm{C_2}^1$, $\mathrm{C_3}^1$, $\mathrm{C_4}^1$, $\mathrm{C_5}^1$). IR (KBr): 328 (m, $\nu_{\mathrm{Au-Cl}}$) cm^{-1}. Anal. Calcd for **6-[G′$_6$]** ($\mathrm{C_{5544}H_{5352}N_{762}Cl_{192}O_{381}P_{382}S_{190}Au_{192}}$): C, 44.01; H, 3.57; N, 7.05. Found: C, 42.7; H, 3.55; N, 6.65. Anal. Calcd for **6-[G′$_6$]**·62$\mathrm{CH_2Cl_2}$ ($\mathrm{C_{5606}H_{5476}N_{762}Cl_{316}O_{381}P_{382}S_{190}Au_{192}}$): C, 43.01; H, 3.53; N, 6.82.

6-[G′$_{10}$]. White powder; 70% yield. ^{31}P {^{1}H} NMR ($\mathrm{CD_2Cl_2}$): δ 21.1 (s, $\mathrm{PPh_2}$), 62.7 (s, $\mathrm{P_1, P_2, P_3, P_4, P_5, P_6, P_7, P_8, P_9, P_{10}}$). IR (KBr): 328 (m, $\nu_{\mathrm{Au-Cl}}$) cm^{-1}.

Synthesis of Dendrimers 7-[G′$_4$] ($\mathbf{Ph_2P{\rightarrow}Au{-}Me}$ End Groups). To a solution of **6-[G′$_4$]** (0.05 g, 1.34 μmol) in dichloromethane (10 mL) was added $\mathrm{ZrCp_2Me_2}$ (0.032 g, 0.128 mmol) at room temperature. The mixture was stirred for 2 h and then evaporated to dryness. The white solid was washed with diethyl ether. This product is contaminated by zirconium derivatives.

7-[G′$_4$]. White powder. ^{31}P {^{1}H} NMR ($\mathrm{CDCl_3}$): 38.2 (s, $\mathrm{PPh_2}$), 62.7 (s, $\mathrm{P_1, P_2, P_3, P_4}$) ppm. ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.4 (d, $^3J_{\mathrm{HP}} = 8.1$ Hz, 144 H, $\mathrm{Au{-}CH_3}$), 3.0 (s, 144 H, $\mathrm{CH_2{-}N{-}C}H_3$), 3.2 (br s, 135 H, $\mathrm{P_{1-4}{-}N{-}CH_3}$), 4.4 (s, 96H, $\mathrm{CH_2{-}P}$), 7.0−7.6 (m, 945 H, $\mathrm{C_6H_5}$, $\mathrm{C_6H_4}$, and $\mathrm{CH{=}N}$).

General Procedure for the Synthesis of Dendrimers 8-[G′$_n$] ($\mathbf{Ph_2P{\rightarrow}Rh(acac)(CO)}$ End Groups). To a solution of 0.1 g of **3-[G′$_n$]** ($\boldsymbol{n} = 1$, 0.036 mmol; $\boldsymbol{n} = 5$, 1.88 μmol; $\boldsymbol{n} = 6$, 0.94 μmol) in $\mathrm{CH_2Cl_2}$ (20 mL) was added $\mathrm{Rh(acac)(CO)_2}$ ($\boldsymbol{n} = 1$, 0.056 g, 0.22 mmol; $\boldsymbol{n} = 5$, 0.047 g, 0.18 mmol; $\boldsymbol{n} = 6$, 0.046 g, 0.18 mmol) at room temperature and stirred for 1 h. The solvent was removed under vacuum and the yellow residue washed with diethyl ether (3 × 10 mL).

8-[G′$_1$]. Yellow powder; 80% yield, mp 110 °C (dec). ^{31}P {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 41.5 (d, $^1J_{\mathrm{PRh}} = 172.0$ Hz, $\mathrm{PPh_2}$), 52.7 (s, $\mathrm{P_0}$), 62.8 (s, $\mathrm{P_1}$). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.75 (s, 18 H, $\mathrm{CH_3}$ acac), 2.06 (s, 18 H, $\mathrm{CH_3}$ acac), 2.77 (s, 18 H, $\mathrm{CH_2{-}N{-}C}H_3$), 3.3 (d, $^3J_{\mathrm{HP_1}} = 10.2$ Hz, 9 H, $\mathrm{P_1{-}N{-}CH_3}$), 4.67 (s, 12 H, $\mathrm{CH_2}$), 5.45 (s, 6 H, CH acac), 7.1−7.8 (m, 105 H, $\mathrm{C_6H_5}$, $\mathrm{C_6H_4}$, and $\mathrm{CH{=}N}$). ^{13}C {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 26.9 (s, $\mathrm{CH_3}$ acac), 27.5 (d, $^4J_{\mathrm{CP}} = 5.5$ Hz, $\mathrm{CH_3}$ acac), 33.0 (d, $^2J_{\mathrm{CP_1}} = 12.9$ Hz, $\mathrm{P_1{-}N{-}CH_3}$), 39.0 (s, $\mathrm{CH_2{-}N{-}}C\mathrm{H_3}$), 57.2 (d, $^1J_{\mathrm{CP}} = 29.5$ Hz, $\mathrm{CH_2}$), 100.6 (s, CH acac), 121.3 (d, $^3J_{\mathrm{CP_1}} = 4.8$ Hz, $\mathrm{C_1}^2$), 121.5 (d, $^3J_{\mathrm{CP_0}} = 4.8$ Hz, $\mathrm{C_0}^2$), 126.2 (s, $\mathrm{C_1}^3$),127.9 (d, $^3J_{\mathrm{CP}} = 10.1$ Hz, m-$\mathrm{C_6H_5}$), 128.3 (s, $\mathrm{C_0}^3$), 128.9 (s, $C\mathrm{H{=}N{-}N{-}CH_2}$), 130.1 (s, p-$\mathrm{C_6H_5}$ and $\mathrm{C_1}^4$), 131.8 (d, $^1J_{\mathrm{CP}} = 48.7$ Hz, i-$\mathrm{C_6H_5}$), 132.7 (s, $\mathrm{C_0}^4$), 133.9 (d, $^2J_{\mathrm{CP}} = 10.8$ Hz, o-$\mathrm{C_6H_5}$), 137.9 (s, $\mathrm{CH{=}N}$), 149.2 (d, $^2J_{\mathrm{CP_1}} = 7.5$ Hz, $\mathrm{C_1}^1$), 150.9 (d, $^2J_{\mathrm{CP_0}} = 7.6$ Hz, $\mathrm{C_0}^1$), 184.9 (s, $\mathrm{C{=}O}$ acac), 187.6 (s, $\mathrm{C{=}O}$ acac), 188.8 (dd, $^1J_{\mathrm{CRh}} = 76.2$ Hz, $^2J_{\mathrm{CP}} = 24.2$ Hz, CO). IR ($\mathrm{CH_2Cl_2}$): 1977 (s, ν_{CO}) cm^{-1}. Anal. Calcd for $\mathrm{C_{186}H_{186}N_{18}O_{27}P_{10}S_4Rh_6}$: C, 53.69; H, 4.51; N, 6.06. Found: C, 53.85; H, 4.45; N, 5.85.

8-[G′$_5$]. Yellow powder; 78% yield, mp 125 °C (dec). ^{31}P {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 41.5 (d, $^1J_{\mathrm{PRh}} = 178.7$ Hz, $\mathrm{PPh_2}$), 62.8 (s, $\mathrm{P_1, P_2, P_3, P_4, P_5}$). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.70 (s, 288 H, $\mathrm{CH_3}$ acac), 2.00 (s, 288 H, $\mathrm{CH_3}$ acac), 2.72 (s, 288 H, $\mathrm{CH_2{-}N{-}C}H_3$), 3.21 (br s, 279 H, $\mathrm{P_{1-5}{-}N{-}CH_3}$), 4.64 (s, 192 H, $\mathrm{CH_2}$), 5.40 (s, 96 H, CH acac), 7.1−7.8 (m, 1905 H, $\mathrm{C_6H_5}$, $\mathrm{C_6H_4}$, and $\mathrm{CH{=}N}$). IR ($\mathrm{CH_2Cl_2}$): 1976 (s, ν_{CO}) cm^{-1}.

8-[G′$_6$]. Yellow powder; 75% yield, mp 140 °C (dec). ^{31}P {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 41.4 (d, $^1J_{\mathrm{PRh}} = 171.3$ Hz, $\mathrm{PPh_2}$), 62.8 (s, $\mathrm{P_1, P_2, P_3, P_4, P_5, P_6}$). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.69 (s, 576 H, $\mathrm{CH_3}$ acac), 1.99 (s, 576 H, $\mathrm{CH_3}$ acac), 2.71 (s, 576 H, $\mathrm{CH_2{-}N{-}C}H_3$), 3.21 (br s, 567 H, $\mathrm{P_{1-6}{-}N{-}CH_3}$), 4.64 (s, 384 H, $\mathrm{CH_2}$), 5.39 (s, 192 H, CH acac), 7.1−7.8 (m, 3825 H, $\mathrm{C_6H_5}$, $\mathrm{C_6H_4}$, and $\mathrm{CH{=}N}$). IR ($\mathrm{CH_2Cl_2}$): 1976 (s, ν_{CO}) cm^{-1}.

General Procedure for the Synthesis of Dendrimers 9-[G′$_n$] ($\mathbf{Ph_2P{\rightarrow}Rh(Cl)(COD)}$ End Groups). To a solution of 0.2 g of **3-[G′$_n$]** ($\boldsymbol{n} = 1$, 0.072 mmol; $\boldsymbol{n} = 4$, 7.6 μmol) in 20 mL of $\mathrm{CH_2Cl_2}$ was added the $[\mathrm{Rh}(\mu\text{-}\mathrm{Cl})(\mathrm{COD})]_2$ ($\boldsymbol{n} = 1$, 0.106 g, 0.216 mmol; $\boldsymbol{n} = 4$, 0.09 g, 0.0183 mmol) at room temperature. The resulting mixture was stirred for 1 h. The solvent was removed under vacuum and the yellow residue washed three times with diethyl ether (10 mL).

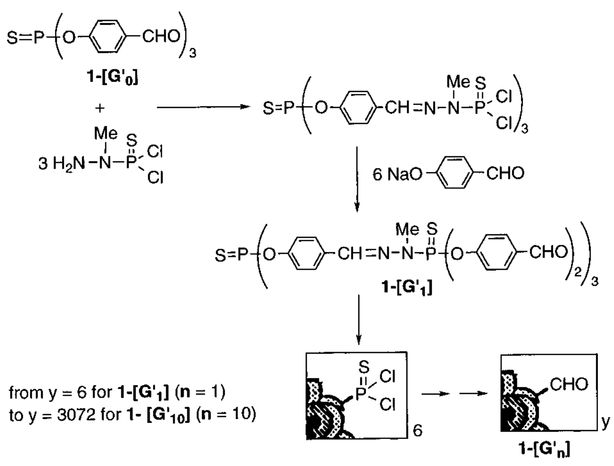
9-[G′$_1$]. Yellow powder; 92% yield, mp 88 °C. ^{31}P {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 23.1 (d, $^1J_{\mathrm{PRh}} = 149.9$ Hz, $\mathrm{PPh_2}$), 52.4 (s, $\mathrm{P_0}$), 62.5 (s, $\mathrm{P_1}$). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.8−2.3 (m, 48 H, $\mathrm{CH_2}$), 3.0 (s, 12 H, $\mathrm{HC{=}CH}$), 3.1 (s, 18 H, $\mathrm{CH_2{-}N{-}C}H_3$), 3.3 (d, $^3J_{\mathrm{HP_1}} = 10.2$ Hz, 9 H, $\mathrm{P_1{-}N{-}CH_3}$), 4.7 (s, 12 H, $\mathrm{CH_2{-}P}$), 5.5 (br s, 12 H, $\mathrm{HC{=}CH}$), 7.1−7.8 (m, 105 H, $\mathrm{C_6H_5}$, $\mathrm{C_6H_4}$, and $\mathrm{CH{=}N}$). ^{13}C {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 28.6 (s, $\mathrm{CH_2}$), 32.7 (s, $\mathrm{CH_2}$), 33.1 (s, $\mathrm{P_1{-}N{-}CH_3}$), 39.8 (s, $\mathrm{CH_2{-}N{-}}C\mathrm{H_3}$), 58.2 (d, $^1J_{\mathrm{CP}} = 23.7$ Hz, $\mathrm{CH_2{-}P}$), 70.5 (d, $^1J_{\mathrm{CRh}} = 14.4$ Hz, $\mathrm{HC{=}CH}$), 104.7 (m, $\mathrm{HC{=}CH}$), 121.3 (d, $^3J_{\mathrm{CP_{0,1}}} = 5.8$ Hz, $\mathrm{C_0}^2$, $\mathrm{C_1}^2$), 126.2 (s, $\mathrm{C_1}^3$), 127.9 (d, $^3J_{\mathrm{CP}} = 9.5$ Hz, m-$\mathrm{C_6H_5}$), 128.3 (s, $\mathrm{C_0}^3$), 128.7 (s, $C\mathrm{H{=}N{-}N{-}CH_2}$), 130.0 (s, p-$\mathrm{C_6H_5}$ and $\mathrm{C_1}^4$), 131.1 (d, $^1J_{\mathrm{CP}} = 39.3$ Hz, i-$\mathrm{C_6H_5}$), 132.7 (s, $\mathrm{C_0}^4$), 134.4 (d, $^2J_{\mathrm{CP}} = 10.3$ Hz, o-$\mathrm{C_6H_5}$), 137.9 (d, $^3J_{\mathrm{CP_1}} = 11.9$ Hz, $\mathrm{CH{=}N}$), 149.2 (d, $^2J_{\mathrm{CP_1}} = 7.1$ Hz, $\mathrm{C_1}^1$), 150.9 (d, $^2J_{\mathrm{CP_0}} = 8.8$ Hz, $\mathrm{C_0}^1$). Anal. Calcd for $\mathrm{C_{198}H_{216}N_{18}Cl_6O_9P_{10}S_4Rh_6}$: C, 55.8; H, 5.1; N, 5.9. Found: C, 55.05; H, 5.15; N, 5.65.

9-[G′$_4$]. Yellow powder; 91% yield, mp 112 °C (dec). ^{31}P {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 23.2 (d, $^1J_{\mathrm{PRh}} = 148.6$ Hz, $\mathrm{PPh_2}$), 62.5 (s, $\mathrm{P_1, P_2, P_3, P_4}$). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 1.8−2.4 (m, 384 H, $\mathrm{CH_2}$), 3.0 (s, 96 H, $\mathrm{HC{=}CH}$), 3.1 (s, 144 H, $\mathrm{CH_2{-}N{-}C}H_3$), 3.3 (m, 135 H, $\mathrm{P_{1-4}{-}N{-}CH_3}$), 4.7 (s, 96 H, $\mathrm{CH_2{-}P}$), 5.4 (br s, 96 H, $\mathrm{HC{=}CH}$), 7.0−7.8 (m, 945 H, $\mathrm{C_6H_5}$, $\mathrm{C_6H_4}$, and $\mathrm{CH{=}N}$). ^{13}C {^{1}H} NMR ($\mathrm{CDCl_3}$): δ 28.6 (s, $\mathrm{CH_2}$), 32.7 (s, $\mathrm{CH_2}$), 33.0 (s, $\mathrm{P_{1-4}{-}N{-}CH_3}$), 39.8 (s, $\mathrm{CH_2{-}N{-}}C\mathrm{H_3}$), 58.1 (d, $^1J_{\mathrm{CP}} = 22.8$ Hz, $\mathrm{CH_2}$), 70.5 (d, $^1J_{\mathrm{CRh}} = 12.6$ Hz, $\mathrm{HC{=}CH}$), 104.4 (m, $\mathrm{HC{=}CH}$), 121.2 (br s, $\mathrm{C_4}^2$), 121.7 (br s, $\mathrm{C_0}^2$, $\mathrm{C_1}^2$, $\mathrm{C_2}^2$, $\mathrm{C_3}^2$), 126.2 (s, $\mathrm{C_4}^3$), 127.8 (d, $^3J_{\mathrm{CP}} = 9.1$ Hz, m-$\mathrm{C_6H_5}$), 128.4 (s, $\mathrm{C_0}^3$, $\mathrm{C_1}^3$, $\mathrm{C_2}^3$, $\mathrm{C_3}^3$), 128.7 (s, $C\mathrm{H{=}N{-}N{-}CH_2}$), 130.0 (s, p-$\mathrm{C_6H_5}$ and $\mathrm{C_4}^4$), 131.5 (d, $^1J_{\mathrm{CP}} = 36.7$ Hz, i-$\mathrm{C_6H_5}$), 132.0 (s, $\mathrm{C_0}^4$, $\mathrm{C_1}^4$, $\mathrm{C_2}^4$, $\mathrm{C_3}^4$), 134.4 (d, $^2J_{\mathrm{CP}} = 10.1$ Hz, o-$\mathrm{C_6H_5}$), 137.1 (m, $\mathrm{CH{=}N}$), 149.2 (d, $^2J_{\mathrm{CP_4}} = 7.7$ Hz, $\mathrm{C_4}^1$), 150.9 (m, $\mathrm{C_0}^1$, $\mathrm{C_1}^1$, $\mathrm{C_2}^1$, $\mathrm{C_3}^1$).

Results and Discussion

Among the various methods of synthesis of phosphorus dendrimers we already reported,[6c,8] we decided to choose the two step procedure which gives alternatively chlorine and aldehydes on the periphery, depending upon the step considered (Scheme 1).[8a−d] The strategy we used to graft phosphines starting from aldehyde-terminated dendrimers **1-[G′*n*]** implies

Scheme 1



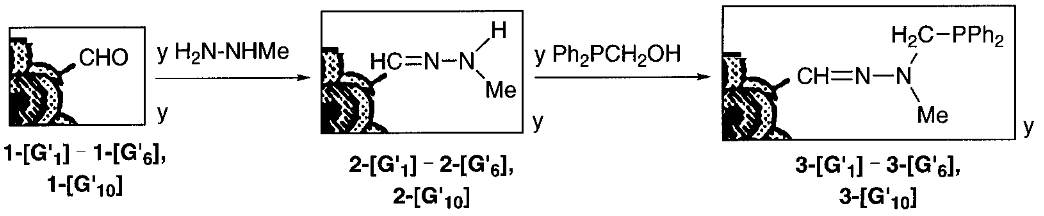
first condensation of the aldehydes with methylhydrazine, leading to compounds **2-[G′$_n$]** (*n* = 1−6,10).[8c] Then a Mannich type reaction with Ph_2PCH_2OH[9] affords diphenylphosphino-terminated dendrimers **3-[G′*n*]** in nearly quantitative yield (Scheme 2). This reaction needs 3 days at 65 °C to go to completion for all the generations, including the tenth generation **3-[G′$_{10}$]** that we already briefly described.[6c] To the best of our knowledge, this compound which possesses more than 3000 phosphino groups is the largest polyphosphine of defined structure ever synthesized. Compounds **3-[G′*n*]** (as well as their complexes) are fully characterized by ^{31}P, ^{1}H, and ^{13}C NMR and elemental analysis. For instance, ^{31}P NMR spectra of compounds **3-[G′$_n$]** show, besides the signals corresponding to the skeleton of the dendrimer, the presence of one singlet at $\delta = -23.4$ ppm corresponding to the PPh_2 groups grafted on the surface of the dendrimer.

In order to verify the complexation ability of all of the diphenylphosphino groups of dendrimers **3-[G′$_n$]**, we tested first the reactivity of very common transition metal derivatives, $Fe_2(CO)_9$ and $W(CO)_5(THF)$. In all cases, the complexation occurs in a few hours at room temperature, to give the iron(0) and tungsten(0) derivatives, **4-[G′*n*]** and **5-[G′*n*]**, respectively (Scheme 3, Figure 1). The reaction is monitored by ^{31}P NMR, which shows for all of the generations the total disappearance of the signal corresponding to the [Ph_2P:] groups on behalf of a singlet at $\delta = 51.9$ ppm for the [$Ph_2P \rightarrow Fe(CO)_4$] groups of **4-[G′*n*]** (*n* = 1−5) or at $\delta = 16.1$ ppm (with satellites $^1J_{PW} = 241$ Hz) for the [$Ph_2P \rightarrow W(CO)_5$] groups of **5-[G′$_n$]** (*n* = 1−4). The expected increase of the *i*-C−P coupling constant of the phenyl groups ($^1J_{i-CP} = 14$ Hz for **3-[G′$_n$]**; $^1J_{i-CP} = 39$ Hz for **4-[G′$_n$]** and **5-[G′$_n$]**) is an indication for the complexation, as is the appearance of doublets for the CO groups in ^{13}C NMR with characteristic coupling constants (**4-[G′$_n$]**, $\delta = 213$ ppm, $^2J_{CP} = 18$ Hz; **5-[G′$_n$]**, $\delta = 196.7$ ppm, $^2J_{CP} = 7$ Hz (*cis*-CO) and $\delta = 199.4$, $^2J_{CP} = 22$ Hz (*trans*-CO)).

These first experiments with M(0) derivatives have been extended to the complexation of M(I) derivatives. For instance, the reaction of AuCl(tht) (tht = tetrahydrothiophene) with **3-[G′$_n$]** (*n* = 1, 4−6, 10) proceeds readily at room temperature in CH_2Cl_2, even for the tenth generation (Scheme 4, Figure 1). The formation of complexes **6-[G′$_n$]** induces the expected downfield shift in ^{31}P NMR spectra for the signal of the PPh_2 groups (from $\delta = -23.4$ ppm for **3-[G′$_n$]** to $\delta = 21$ ppm for **6-[G′$_n$]**). The absence of any trace of free phosphine in ^{31}P NMR spectra confirms the complete complexation of all of the terminal groups in the limit of NMR precision (2%). However, even after several washings and drying under vacuum, ^{1}H NMR spectra show the presence of an important proportion of dichloromethane, which is extremely difficult to eliminate for high generations, and give poor quality elemental analysis for these derivatives.

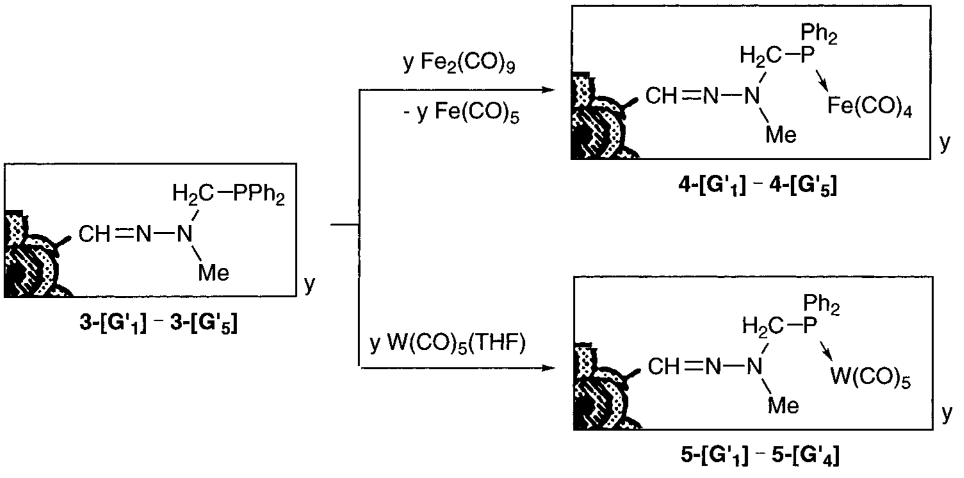
The presence of more than 3000 gold atoms on the surface of dendrimer **6-[G′$_{10}$]** allows the visualization of this molecule

Scheme 2

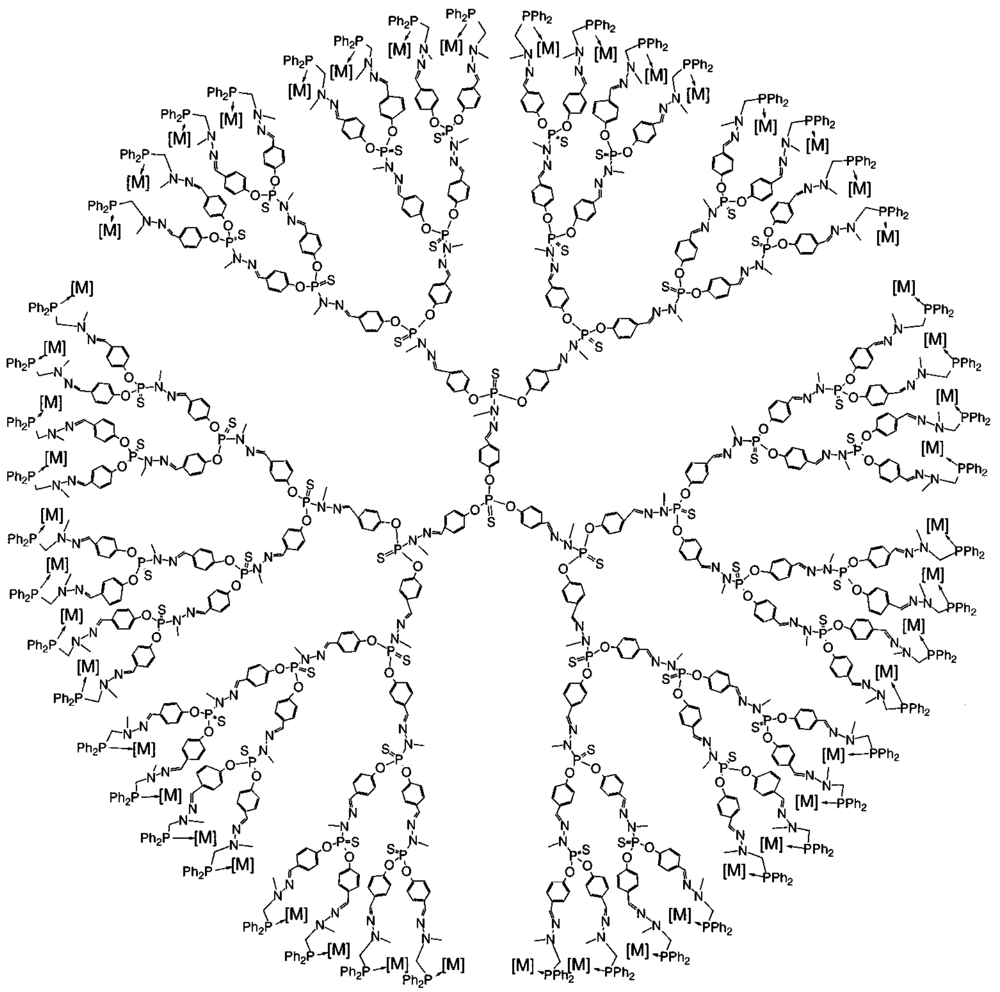


from y = 6 for [G'1] to y = 3072 for [G'10]

Scheme 3



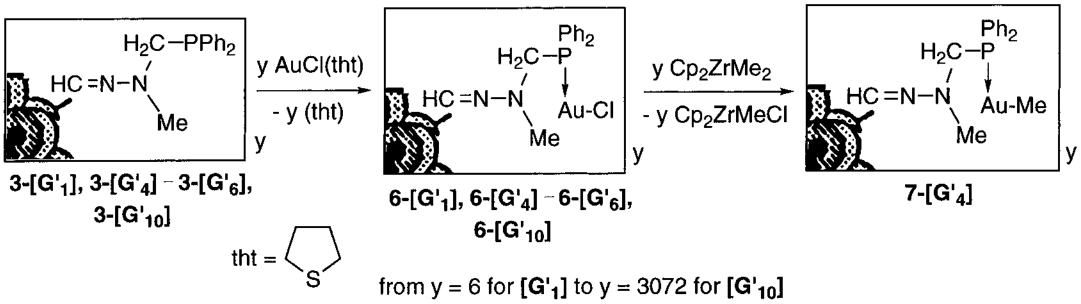
from y = 6 for [G'1] to y = 96 for [G'5]



	4-[G′4]	**5-[G′4]**	**6-[G′4]**	**7-[G′4]**	**8-[G′4]**	**9-[G′4]**
[M] =	$Fe(CO)_4$	$W(CO)_5$	Au-Cl	Au-Me	Rh(acac)(CO)	RhCl(COD)

Figure 1. Representation of dendrimers of generation 4 with 48 terminal $Fe(CO)_4$ (**4-[G′4]**), $W(CO)_5$ (**5-[G′4]**), Au−Cl (**6-[G′4]**), Au−Me (**7-[G′4]**), Rh(acac)(CO)(**8-[G′4]**), and RhCl(COD) (**9-[G′4]**) groups.

Scheme 4



by high-resolution electron microscopy.[6c] Figure 2 is a micrograph of an isolated molecule of **6-[G′10]**. This compound is bowl-shaped, and its diameter is $d = 155$ Å. This value is much larger than the one reported for the 10th generation of PAMAM dendrimers ($d = 107$ Å), also measured by electron microscopy.[1a] The larger diameter of our dendritic system at the same generation level is certainly the main factor which explains our recent isolation of the highest generation ever known in dendrimer chemistry.[10]

The presence of one chlorine atom bonded to each gold atom of the surface prompted us to test the reactivity of complexes

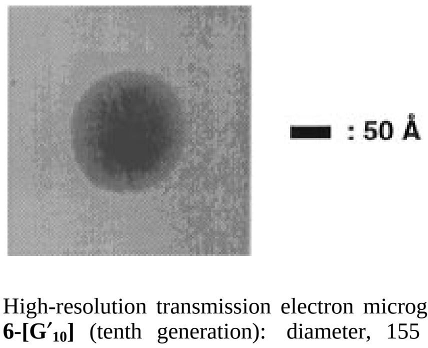


Figure 2. High-resolution transmission electron micrograph of the dendrimer **6-[G′10]** (tenth generation): diameter, 155 Å; 1900K magnification (reproduced at 60% of original size); 300 KV accelerating voltage.

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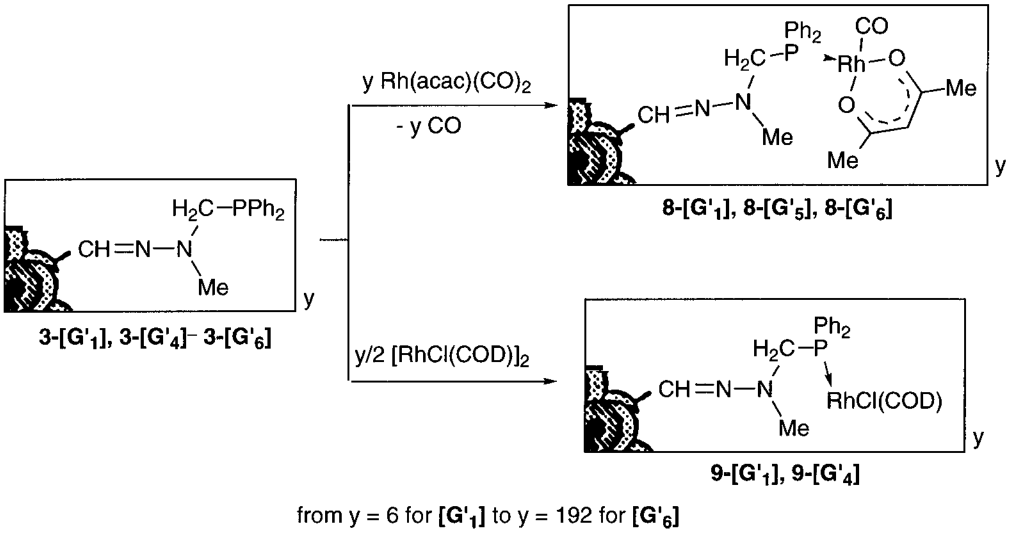
(10) Construction of phosphorus containing dendrimers has been conducted up to generation 12: Lartigue, M.-L.; Fayet, J.-P.; Donnadieu, B.; Galliot, C.; Caminade, A. M.; Majoral, J. P. Submitted for publication.

Scheme 5



6-[G′$_n$]. Indeed, it is well-known that LAu−Cl complexes display a versatile reactivity (for instance, they react easily with RLi or Grignard reagents to afford the corresponding LAu−R complexes). We carried out only one experiment between dendrimer **6-[G′$_4$]** and Cp_2ZrMe_2 as alkylating agent.[11] The exchange reaction occurs readily at room temperature to afford dendrimer **7-[G′$_4$]** (Scheme 4). The exchange is characterized by the deshielding of the signal corresponding to the PPh_2 group (δ ^{31}P = 38.2 ppm for **7-[G′$_4$]**) and the presence of a doublet for the Me−Au groups in ^{1}H NMR spectra (δ = 0.4 ppm, $^3J_{HP}$ = 8.1 Hz). However, ^{1}H NMR spectra also indicate the presence of residual zirconium derivatives. Several attempts to purify dendrimer **7-[G′$_4$]** by washings or column chromatography were unsuccessful. Despite the presence of impurities, this reaction demonstrates that the grafting of Au−Cl groups on the dendrimer does not hinder their reactivity.

The reaction of Rh(I) derivatives such as $Rh(acac)(CO)_2$ (acac = acetylacetonate) with dendrimer **3-[G′$_n$]** (***n*** = 1, 5, 6) also proceeds readily at room temperature (Scheme 5). The complexation is unambiguously characterized in all cases by the appearance of a doublet at δ = 41.5 ppm ($^1H_{PRh} \cong 175$ Hz) in the ^{31}P NMR spectra of compounds **8-[G′$_n$]**. The structure is confirmed in ^{1}H NMR spectra by the presence of two singlets corresponding to two different CH_3 groups for the acac moieties, due to the decrease of symmetry of rhodium in complexes **8-[G′$_n$]**. The poor solubility of complexes **8-[G′$_5$]** and **8-[G′$_6$]** precludes their characterization by ^{13}C NMR; however, the spectrum of the first generation **8-[G′$_1$]** confirms the presence of two types of CH_3 acac groups (δ = 26.9 and 27.5 ppm) and three carbonyl groups (δ = 184.9 and 187.6 ppm, CO acetyl; δ = 188.8 ppm, $^1J_{CRh}$ = 76.2 Hz, $^2J_{CP}$ = 24.2 Hz, RhCO).

This problem of poor solubility is not encountered starting from another Rh(I) derivative, $[Rh(\mu\text{-}Cl)(COD)]_2$, at least up to the fourth generation. Indeed, the reaction of this dimer with **3-[G′$_1$]** and **3-[G′$_4$]** proceeds rapidly at room temperature to afford the corresponding complexes **9-[G′$_1$]** and **9-[G′$_4$]** (Scheme 5, Figure 1). These dendrimers are fully characterized by NMR; for instance, a doublet at δ = 23.1 ppm ($^1J_{PRh}$ = 149 Hz) corresponding to the PPh_2 groups appears in the ^{31}P NMR spectra, and signals characteristic of complexed cyclooctadiene are detected in ^{1}H and ^{13}C NMR spectra.

Conclusion

We have demonstrated that phosphino-terminated dendrimers, from generation one (six phosphino groups) to generation ten (3072 phosphino groups), are extremely powerful and highly versatile reagents for the complexation of various low oxydation state (0 and I) transition metals. Indeed, the total and easy complexation of iron, tungsten, gold, and rhodium derivatives (group 6, 8, 9, or 11 and row 4, 5, or 6 elements), starting from only one family of dendrimers, illustrates the potential of these nanosized compounds to be used in most of the reactions described for monophosphines. The exchange reaction of 48 chlorine atoms with 48 methyl groups in the transformation **6-[G′$_4$]** → **7-[G′$_4$]** can be compared to those already described for monophosphine−gold complexes and confirms the easy access to the metal and its availability for further reactions, despite its linkage to the huge dendrimer. This property should open large perspectives for the design of new catalysts.

Acknowledgment. The authors thank CNRS for support and Dr. Marie-José Casanove for HREM micrographs. M.B. thanks Ministerio de Educacion y Cultura (Spain) for a grant.

IC961258M

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[11] See for example: (a) Igau, A.; Dufour, N.; Mahieu, A.; Majoral, J. P. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 95. (b) Mahieu, A.; Igau, A.; Jaud, J.; Majoral, J. P. *Organometallics* **1995**, *14*, 944.