A New Divergent Route to the Synthesis of Organophosphine and Metallodendrimers via Simple Acid−Base Hydrolytic Chemistry

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Metallodendrimers are emerging as a promising class of new materials for a variety of applications including heterogenizing homogeneous catalysis.[1] They offer a unique set of properties such as solubility, precise molecular architecture, predetermined chemical composition, and the ability, due to their nanoscopic size and relative rigidity, to be removed from solvent streams by crystallization or ultrafiltration methods for recycling. The introduction of transition metals into dendrimers has been a recent trend and can be achieved either by surface modification in which the mode of attachment is at the periphery of the arboreal or incorporation of the transition metal within the dendritic infrastructure, a much more arduous task.[2−6] In this paper, we report a new divergent synthesis of tri-branched phosphorus-containing dendrimers and their metal-containing counterparts based on simple acid−base hydrolytic chemistry and starting from commercially available reagents. The flexibility and versatility of the new route allows the build-up of dendritic materials by molecular design, and the organophosphine moieties are linked together by dimethylsiloxane bridges, adding to their thermal stability and chain flexibility. The Rh(I) bound pseudospheres were found to be active catalysts for the efficient hydrogenation of decene, and at the completion of the reaction, the metallodendrimer was easily separated from the reaction products and recycled.

The divergent synthetic methodology used to prepare organophosphine and metallodendrimers is based on the acid−base hydrolysis of aminosilanes with molecules containing terminal OH groups.[7,8] For example, $(CH_3)_3SiNEt_2$ reacts at ambient temperature with molecules such as $P\{(CH_2)_3OH\}_3$ ($\mathbf{P_1}$), to give $P\{(CH_2)_3OSi(CH_3)_3\}_3$ and diethylamine. The reaction sequence based on this chemistry but employing a bifunctional silane, bis-(dimethylamino)dimethylsilane, $(CH_3)_2Si(NMe_2)_2$, leads to the organophosphine dendrimers as shown in Scheme 1. The synthesis involves the dropwise addition of tri(hydroxypropyl)phosphine ($\mathbf{P_1}$) to a THF solution of 3 equiv of $(CH_3)_2Si(NMe_2)_2$, which results in the formation of the silylamine adduct ($\mathbf{P_1Si_1}$) in 91% isolated yield. The latter is subsequently added dropwise to a solution of 3 equiv of $\mathbf{P_1}$ resulting in the formation of $\mathbf{P_4}$. The pendant groups on $\mathbf{P_4}$ are hydroxyls which are used to continue the dendrimer growth. In the second growth cycle, tetranuclear $\mathbf{P_4}$ reacts cleanly with 6 molar equiv of $(CH_3)_2Si(NMe_2)_2$ and $\mathbf{P_1}$, in sequence, to result in the formation of $\mathbf{P_{10}}$.[9] Repetition of these reactions using 12 and 24 equiv of $(CH_3)_2Si(NMe_2)_2$ and $\mathbf{P_1}$ affords the third ($\mathbf{P_{22}}$) and fourth ($\mathbf{P_{46}}$) generation of dendrimers in excellent yields. $\mathbf{P_4}$, $\mathbf{P_{10}}$, $\mathbf{P_{22}}$, and $\mathbf{P_{46}}$ are clear, colorless liquids whose viscosity increases with an increase in generation number.

The organophosphine dendrimers were characterized by ^1H NMR, $^{31}P\{^1H\}$ NMR, $^{29}Si\{^1H\}$ NMR, FT-IR, MALDI-TOF mass spectrometry, and elemental analysis. The peaks in the ^1H NMR spectra show broadening with increasing size, suggesting restricted motion of the inner generations. In their $^{31}P\{^1H\}$ NMR spectra, the phosphines in each generation are chemical shift distinct. For example, the $^{31}P\{^1H\}$ NMR spectrum of $\mathbf{P_{10}}$ shows three different phosphorus resonances integrating at 6:3:1: P^6 (δ −31.11), P^3 (δ −31.33), P^1 (δ −31.59 ppm), corresponding to the phosphorus centers at the outer surface, middle, and in the inner core, respectively. $^{29}Si\{^1H\}$ NMR spectra of organophosphine dendrimers show a single resonance at around −3.70 ppm corresponding to $(CH_3)_2Si−(OCH_2CH_2)_2$ linkages.

The new route to preparing organophosphine dendrimers is attractive since it produces, in a limited number of steps, dendrimers that are not easily accessible via conventional routes. In addition, it offers flexibility in binding a variety of transition metals to the phosphorus based donor centers. The organophosphine dendrimers were functionalized with Rh(I) complexes using bridge-splitting[10] reactions of the rhodium(I) dimer, $[(\mu-Cl)(1,5-C_8H_{12})Rh]_2$. For example, the reaction of $\mathbf{P_{10}}$ with 5 molar equiv of $[(\mu-Cl)(1,5-C_8H_{12})Rh]_2$ at 25 °C gave $\mathbf{P_{10}Rh_{10}}$.[11] The ligation of Rh to phosphines is evidenced by the presence of doublets (due to P−Rh coupling) in the $^{31}P\{^1H\}$ NMR spectra and by a downfield shift of the cyclooctadiene proton resonances in their ^1H NMR spectra. No peaks for any residual unbound phosphine were observed in the $^{31}P\{^1H\}$ NMR spectra, suggesting high efficiency of metal loading in these organophosphine dendrimers.

The organometallic dendrimers can also be prepared directly starting with the complex, $Rh(1,5-C_8H_{12})(Cl)P\{(CH_2)_3OH\}_3$, $\mathbf{Rh_1}$ (Scheme 1). The core ($\mathbf{Rh_1}$, $Rh(1,5-C_8H_{12})(Cl)P\{(CH_2)_3OH\}_3$) for the construction of a three-directional organometallic cascade was first treated carefully with 3 equiv of $(CH_3)_2Si(NMe_2)_2$, resulting in the formation of $(COD)ClRhP[(CH_2)_3OSi(CH_3)_2N(CH_3)_2]_3$ ($\mathbf{Rh_1Si_1}$). The latter was then added to 3 equiv of $\mathbf{Rh_1}$. The $\mathbf{Rh_4}$ complex thus obtained was subsequently used to continue the dendrimer growth up to 46 rhodium centers (Figure 1). The ^{31}P-

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(9) $\mathbf{P_{10}}$: 95% yield. ^1H NMR (270 MHz, C_6D_6) δ 0.05 (54H, s, $(CH_3)_2Si$), 1.33−1.59 (60H, m, CH_2), 3.39 (60H, br t, J_{H-H} = 4.6 Hz, PCH_2), 3.64 (60H, t, J_{H-H} = 5.9 Hz, CH_2O), 4.43 (12H, br s, OH) ppm. $^{13}C\{^1H\}$ NMR (67.9 MHz, C_6D_6) δ −2.74 (s, CH_3Si), 29.31 (d, J_{C-C} = 11.8 Hz, CH_2), 39.72 (m, J_{C-C} = 21 Hz, PCH_2), 62.49 (d, J_{C-C} = 12 Hz, CH_2O) ppm. $^{31}P\{^1H\}$ NMR (109 MHz, C_6D_6) δ −31.1 (s), −31.33 (s), −31.59 (s) ppm. $^{29}Si\{^1H\}$ NMR (53.7 MHz, C_6D_6) δ −3.60 ppm. FT-IR (KBr) ν 709, 799, 845, 938, 1088, 1257, 1435, 2870, 2934, 3355 cm^{-1}. MALDI-TOF MS (LiBr/dldronel) *m/z* 2586.2. Anal. Calcd for $C_{108}H_{246}O_{30}Si_9P_{10}$ (2587.65) C, 50.13%; H, 9.58%. Found C, 50.53%; H, 9.40%.

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(11) $\mathbf{P_{10}Rh_{10}}$: 94% yield. ^1H NMR (270 MHz, C_6D_6) δ 0.28 (54H, s, $(CH_3)_2$-Si), 1.21−1.32 (60H, m, CH_2), 1.42 (60H, tt, J_{H-H} = 6.6 Hz, CH_2P), 2.07 (80H, m, $20CH_2CH_2$), 3.56 (60H, tt, J_{H-H} = 5.9 Hz, OCH_2), 4.30 (12H, br s, OH), 5.57 (40H, br s, $CH=CH$) ppm. $^{31}P\{^1H\}$ NMR (109 MHz, C_6D_6) δ 8.94 (d, J_{Rh-P} = 142.9 Hz), 11.73 (d, J_{Rh-P} = 144.2 Hz), 17.32 (d, J_{Rh-P} = 145.5 Hz) ppm. FT-IR (KBr) ν 498, 798, 848, 938, 1088, 1258, 1332, 1426, 1602, 2833, 2871, 2928, 3414 cm^{-1}. MALDI-TOF MS (LiBr/dldronel) *m/z* 5054.8. Anal. Calcd for $C_{188}H_{366}O_{30}Si_9P_{10}Rh_{10}Cl_{10}$ (5053.05) C, 44.68%; H, 7.30%. Found C, 45.00%; H, 7.38%.

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Scheme 1
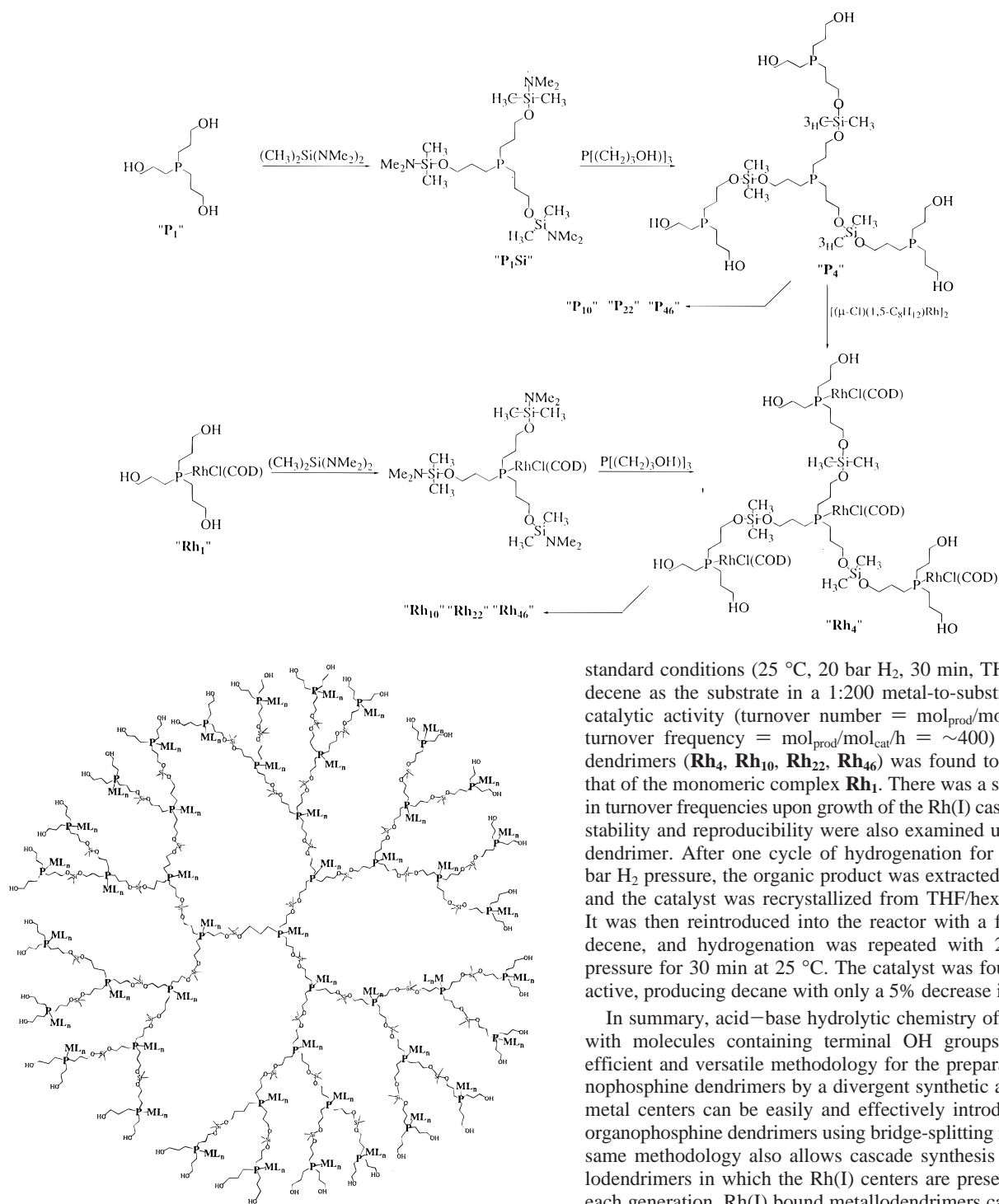
Figure 1.

{^{1}H} NMR spectrum of **Rh$_4$** exhibits two doublets at δ 15.4 (J_{Rh-P} = 144.9 Hz) and 18.72 (J_{Rh-P} = 143.9 Hz) ppm, corresponding to the central **Rh$_1$** and the outer three Rh centers of the second generation, respectively. This suggests that the rhodium–phosphorus groups from each generation are chemical shift distinct. With the growth of each generation, a new Rh–P doublet emerges, suggesting dendrimer rather than polymer growth.

The Rh(I) bound metallodendrimers were successfully employed as efficient catalysts for olefin hydrogenation. Under standard conditions (25 °C, 20 bar H$_2$, 30 min, THF) and using decene as the substrate in a 1:200 metal-to-substrate ratio, the catalytic activity (turnover number = mol$_{prod}$/mol$_{cat}$ = ~200, turnover frequency = mol$_{prod}$/mol$_{cat}$/h = ~400) of the Rh(I) dendrimers (**Rh$_4$**, **Rh$_{10}$**, **Rh$_{22}$**, **Rh$_{46}$**) was found to be similar to that of the monomeric complex **Rh$_1$**. There was a slight decrease in turnover frequencies upon growth of the Rh(I) cascade. Catalyst stability and reproducibility were also examined using the **Rh$_{46}$** dendrimer. After one cycle of hydrogenation for 30 min at 20 bar H$_2$ pressure, the organic product was extracted into pentane, and the catalyst was recrystallized from THF/hexanes mixture. It was then reintroduced into the reactor with a fresh batch of decene, and hydrogenation was repeated with 20 bar of H$_2$ pressure for 30 min at 25 °C. The catalyst was found to be still active, producing decane with only a 5% decrease in conversion.

In summary, acid–base hydrolytic chemistry of aminosilanes with molecules containing terminal OH groups provides an efficient and versatile methodology for the preparation of organophosphine dendrimers by a divergent synthetic approach. The metal centers can be easily and effectively introduced into the organophosphine dendrimers using bridge-splitting reactions. The same methodology also allows cascade synthesis of the metallodendrimers in which the Rh(I) centers are present throughout each generation. Rh(I) bound metallodendrimers catalyze hydrogenation of decene with activities similar to their monomeric adduct, and the catalytic dendrimer can be easily separated and recycled. Further elaboration of this synthetic approach and the catalytic exploration of the organometallic dendrimers are currently being pursued.