Specific Complexation Modes of Tripodal Polyphosphorus Ligands with Rhodium: Generating Multimetallic Compounds of Controlled Structure via Simple Coordination Chemistry

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Synthesis of structure-controlled organometallic complexes based on the chemistry of polyphosphorus ligands O═P[O(CH$_2$)$_3$PPh$_2$]$_3$ (**1**), PhP[O(CH$_2$)$_3$PPh$_2$]$_2$ (**2**), P[O(CH$_2$)$_3$PPh$_2$]$_3$ (**3**), P[O(CH$_2$)$_{10}$PPh$_2$]$_3$ (**12**), and PhP[O(CH$_2$)$_{10}$PPh$_2$]$_2$ (**13**), with [(μ-Cl)(1,5-C$_8$H$_{12}$)Rh]$_2$, in which **1**, **12**, and **13** carry out a typical bridge-splitting reaction of peripheral phosphines with the Rh-dimer, while **2** and **3** complex with rhodium through bridgehead phosphite and two terminal phosphines leading to replacement of the 1,5-cyclooctadiene ligand also, is reported.

Introduction

Metallodendrimers constitute a relatively new and promising class of highly branched macromolecules possessing a well-defined and functionalized framework that imparts novel and unusual properties.[1] Synthesis of such macromolecular transition metal complexes of controlled architecture is a fascinating area of research due to its potential in the development of active, selective, and recoverable catalysts. Catalytic dendrimers that have been investigated in this regard consist of transition metal centers placed at their core or along the periphery.[2] Many of the latter systems show a decrease in catalytic activity with an increase of surface congestion, brought on by the extensive branching of the dendritic structure.[3] In core-functionalized dendrimers, crowding around the metal center reduces accessibility of the substrate to the catalytic site.[4] Placing active transition metal centers throughout the backbone is proving to be a beneficial approach in developing efficient catalysts, since it increases the number of available active transition metal sites per dendrimer.[5] Metal centers placed within the structure of dendrimers also offer new topologies[6] that might alter reaction mechanisms and provide new pathways for affecting specific organic transformations. Thus, the effect of overall structure of the metallodendrimer on the catalytic activity and selectivity is an important and significant issue. Phosphorus-based ligands are commonly used in the design of homogeneous catalysts, especially those containing rhodium,[7] and macromolecular systems incorporating such donor sites throughout the backbone[8,9] are pivotal in heterogenizing homogeneous catalysts. We were intrigued by the possibility of constructing multimetallic complexes using tripodal polyphosphorus ligands in which the choice of the ligand at the core and in the repeating units will dictate the emerging structure and may provide an understanding of how the final dendritic structure influences the activity of transition metal centers in these dendrimers. We report herein a simple synthetic route to a variety of such ligands and examine their way of complexation with rhodium that leads to a controlled construction of multinuclear organometallic complexes in a divergent manner. An evaluation of their activity in catalytic hydrogenation of olefins is also presented.

Results and Discussion

Polyphosphorus ligands O═P[O(CH$_2$)$_3$PPh$_2$]$_3$ (**1**), PhP[O(CH$_2$)$_3$PPh$_2$]$_2$ (**2**), and P[O(CH$_2$)$_3$PPh$_2$]$_3$ (**3**) were synthesized by reacting the appropriate phosphorus chlo-

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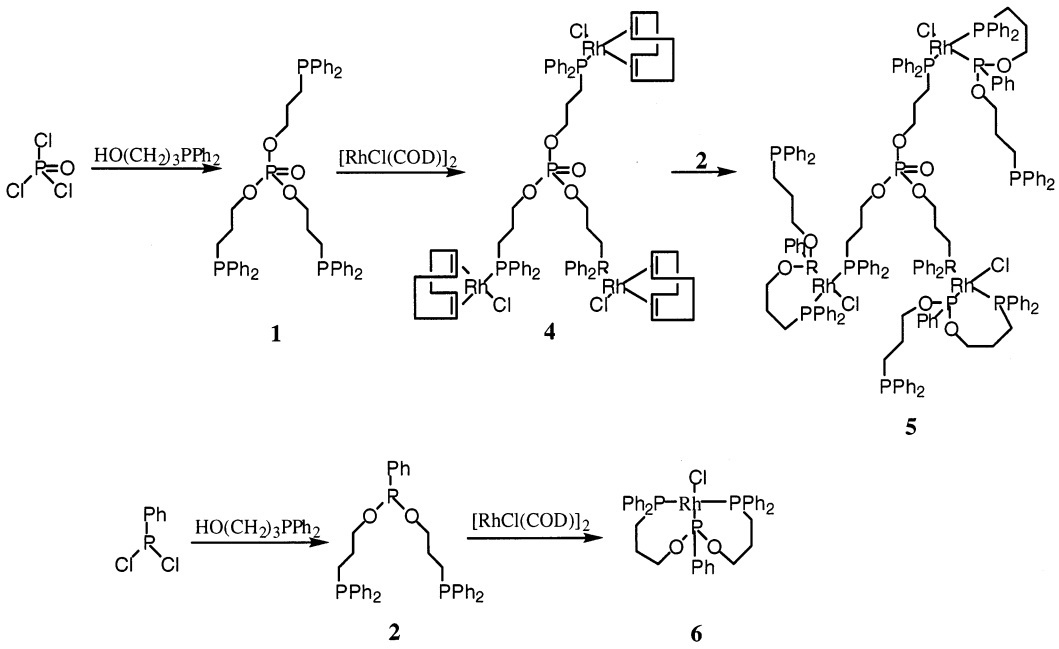
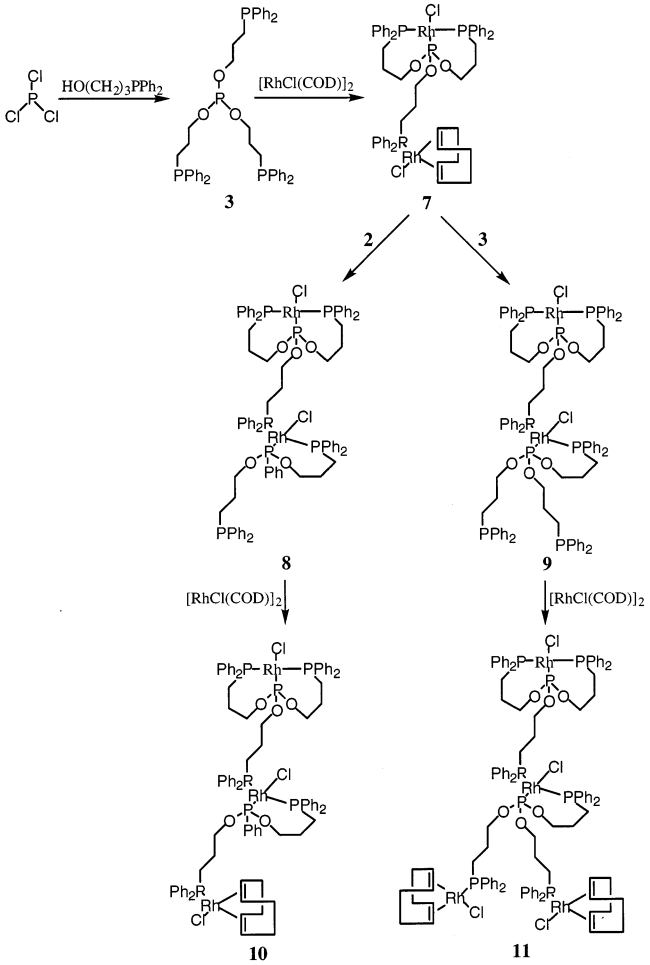
Scheme 1



Scheme 2



ride with HO−$(CH_2)_3$−PPh_2 at 0 °C in the presence of a strong base (NEt_3) to remove HCl formed as a byproduct, as NEt_3·HCl (Schemes 1 and 2). An alternative route to the synthesis of polyphosphorus ligands involved the coupling of HO−$(CH_2)_3$Cl with PCl_3 or $PhPCl_2$ at 0 °C in the presence of NEt_3 to afford $P[O(CH_2)_3Cl]_3$ and $PhP[O(CH_2)_3Cl]_2$, respectively. The latter were then treated with $KPPh_2$ in a THF suspension at 0 °C to give the desired products, $P[O(CH_2)_3PPh_2]_3$ and $PhP[O(CH_2)_3PPh_2]_2$. Although this second route required fewer steps, the reaction with $KPPh_2$ resulted in low yields, making the initial methodology more attractive. Polyphosphorus ligand **1** contains phosphorus oxide [P(V)] at the apical center that does not bind transition metals. In contrast, ligands **2** and **3** contain phosphite at the apex and three phosphines on the periphery, all four donor centers capable of coordinating with transition metals. Ligands **1**−**3** showed two peaks in their $^{31}P\{^1H\}$ NMR spectra (Table 1) that corresponded with the bridgehead and peripheral phosphorus centers.

To prepare multimetallic complexes, polyphosphorus ligand **1** was treated with 1.5 equiv of $[(\mu\text{-Cl})(1,5\text{-}C_8H_{12})Rh]_2$ in a bridge-splitting reaction.[10] This involved the addition of a solution of **1** to a concentrated solution of the rhodium dimer in benzene, which ensured that the rhodium dimer remained in excess, and yielded, as expected, complex **4**. The latter showed a doublet (δ 26.92 ppm, J_{Rh-P} = 149 Hz) for the terminal bound phosphines and a singlet at δ 8.35 ppm for the unbound P(V) center at the apex, in its $^{31}P\{^1H\}$ NMR spectrum. It was then reacted with 3 equiv of ligand **2**, leading to complex **5**, in which 1,5-cyclooctadiene (COD) ligand was replaced with two phosphorus centers of ligand **2** (apical phosphite and a terminal phosphine), leaving a free phosphine ligand (Scheme 1).[11] The $^{31}P\{^1H\}$ NMR spectrum of **5** depicted an AMNX type of coupling pattern at the rhodium center, leading to a doublet of doublets of doublets (δ 188.39 ppm, J_{Rh-P} = 238 Hz and J_{P-P} = 36 Hz) for the bridgehead P(III) phosphorus due to its coupling with rhodium and two cis positioned

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Table 1. $^{31}P\{^1H\}$ NMR Chemical Shifts (109 MHz, C_6D_6, δ ppm) and Coupling Constants (Hz)[a]

compd	P_A [$OP(OR)_3$]	P_A [$P(OR)_3$]	P_M [Chelating]	$P_{M'}$ [Chelating]	P_A [$PhP(OR)_2$]	P_N	other
1	s 8.39						s −14.79
2					s 156.24		s −15.96
3		s 139.21					s −16.04
4	s 8.35						d 26.92 J_{Rh-P} = 149
5	s 8.65			dd 12.39 J_{P-P} = 43 J_{Rh-P} = 129	ddd 188.39 J_{P-P} = 36 J_{Rh-P} = 238	dd 23.74 J_{P-P} = 43 J_{Rh-P} = 151	s −15.21
6				dd 12.32 J_{P-P} = 44 J_{Rh-P} = 130	ddd 187.42 J_{P-P} = 44 J_{Rh-P} = 236		
7		ddd 160.48 J_{P-P} = 52 J_{Rh-P} = 278	dd 14.03 J_{P-P} = 52 J_{Rh-P} = 130				d 26.56 J_{Rh-P} = 150
8		ddd 160.48 J_{P-P} = 54 J_{Rh-P} = 278	dd 13.94 J_{P-P} = 52 J_{Rh-P} = 129	dd 12.31 J_{P-P} = 44 J_{Rh-P} = 130	ddd 187.44 J_{P-P} = 44 J_{Rh-P} = 237	dd 26.56 J_{P-P} = 43 J_{Rh-P} = 150	s −16.13
9		ddd 161.93 J_{P-P} = 51 J_{Rh-P} = 278	dd 13.89 J_{P-P} = 51 J_{Rh-P} = 129	dd 14.97 J_{P-P} = 42 J_{Rh-P} = 132	ddd 159.41 J_{P-P} = 42 J_{Rh-P} = 278	dd 26.25 J_{P-P} = 40 J_{Rh-P} = 140	s −15.97
10		ddd 161.03 J_{P-P} = 53 J_{Rh-P} = 278	dd 14.13 J_{P-P} = 52 J_{Rh-P} = 131	dd 12.57 J_{P-P} = 45 J_{Rh-P} = 128	ddd 188.23 J_{P-P} = 45 J_{Rh-P} = 237	dd 27.01 J_{P-P} = 44 J_{Rh-P} = 151	d 24.37 J_{Rh-P} = 148
11		ddd 162.32 J_{P-P} = 52 J_{Rh-P} = 278	dd 13.79 J_{P-P} = 52 J_{Rh-P} = 130	dd 15.14 J_{P-P} = 43 J_{Rh-P} = 131	ddd 160.04 J_{P-P} = 43 J_{Rh-P} = 278	dd 25.79 J_{P-P} = 41 J_{Rh-P} = 140	d 28.98 J_{Rh-P} = 149

[a] P_A refers to the bridgehead phosphorus and P_M, $P_{M'}$, and P_N refer to bound peripheral phosphines: P_M cis to $P(OR)_3$ and $P_{M'}$ cis to $PhP(OR)_2$, except for **9** and **11**, where both P_M and $P_{M'}$ are cis to $P(OR)_3$.

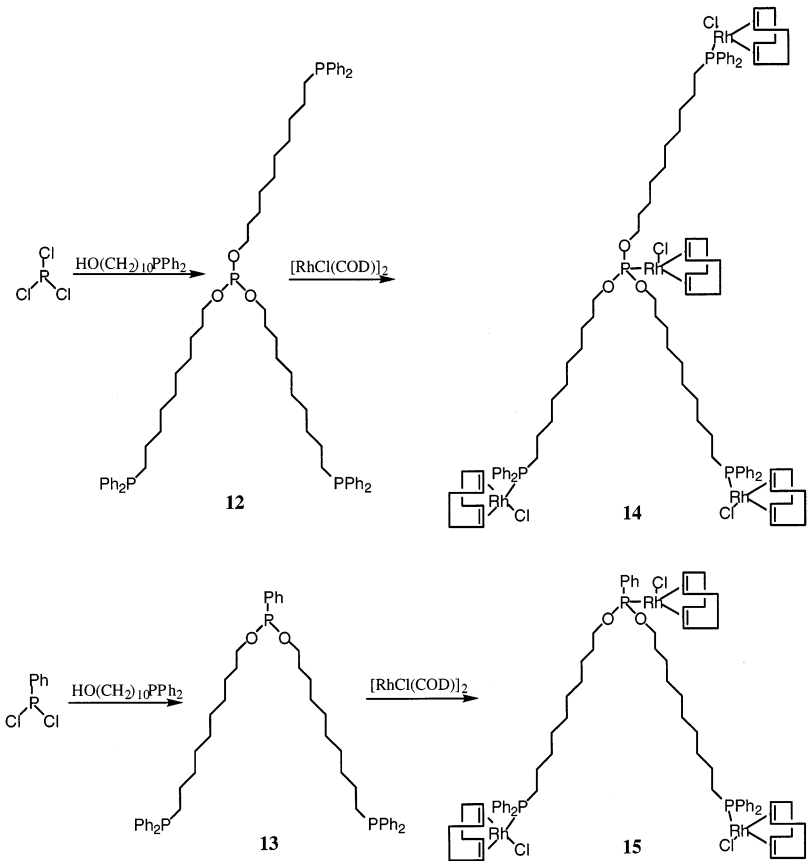
phosphine groups (Table 1). The two phosphines about the chelated rhodium center showed two doublets of doublets (δ 12.39 ppm, J_{Rh-P} = 129 Hz and J_{P-P} = 43 Hz; δ 23.74 ppm, J_{Rh-P} = 151 Hz and J_{P-P} = 43 Hz). The spectrum was consistent with a square planar arrangement of ligands at terminal rhodium centers. The P(V) bridgehead phosphorus and the free phosphine showed singlets at 8.65 and −15.21 ppm, respectively.

In a similar attempt to build multisite organometallic complexes, ligand **2** was reacted with 1.5 equiv of [(μ-Cl)(1,5-C_8H_{12})Rh]$_2$. A different reaction pattern of **2** led to the formation of complex **6**, in which, after successful bridge-splitting reaction by the phosphite ligand, two of the terminal phosphines wrapped around to replace the chelating COD ligand (Scheme 1). This complex showed an AM_2X type of coupling pattern in its $^{31}P\{^1H\}$ NMR spectrum (Table 1) that was consistent with a square planar arrangement of ligands around Rh. For example, it showed a doublet of doublets of doublets at δ 187.42 ppm (J_{Rh-P} = 236 Hz and J_{P-P} = 44 Hz) for the bridgehead phosphite due to coupling with ^{103}Rh and two phosphines and a doublet of doublets (δ 12.32 ppm, J_{Rh-P} = 130 Hz and J_{P-P} = 44 Hz) for the two trans positioned phosphines bound to rhodium. Varying the ratio and addition rates of the ligand to the rhodium dimer did not result in any change and always led to the formation of complex **6**. The treatment of the latter complex with excess PPh_3 yielded no reaction, suggesting that the polyphosphorus ligand was strongly chelated.

In a similar reaction, a solution of polyphosphorus ligand **3** was added dropwise to a concentrated solution of 2 equiv of the rhodium dimer in benzene at room temperature. As mentioned above for the reaction of **2**, it led to the formation of complex **7**, in which bridge-splitting reaction by the phosphite was followed by replacement of the 1,5-COD ligand via chelation by two of the terminal phosphines. The remaining third terminal phosphine then reacted with the rhodium dimer in a simple bridge-splitting reaction. The arrangement of the ligands at the metal center was deciphered from its $^{31}P\{^1H\}$ NMR spectrum, which was, once again, consistent with an AM_2X type of coupling pattern. The two terminal phosphines trans to each other in **7** showed a doublet of doublets (δ 14.03 ppm, J_{Rh-P} = 130 Hz and J_{P-P} = 52 Hz) due to coupling with ^{103}Rh and the bridgehead phosphite. The latter depicted a doublet of doublets of doublets (δ 160.48 ppm, J_{Rh-P} = 278 Hz and J_{P-P} = 52 Hz), due to coupling with ^{103}Rh and two phosphines. The nonchelated rhodium-bound phosphine showed a doublet at δ 26.56 ppm (J_{Rh-P} = 150 Hz). Lowering the ratio of the rhodium dimer to the polyphosphorus ligand **3** down to 0.5 equiv resulted in a similar reaction pattern of bridge-splitting by the phosphite followed by replacement of the COD ligand by the two terminal phosphines, leaving one free terminal phosphine (δ −16.13 ppm). The latter could then be reacted further with the rhodium dimer to give complex **7**.

Complex **7** was reacted with 1 equiv of **2**, which led to the replacement of the 1,5-COD ligand with the bridgehead phosphorus and one terminal phosphine, yielding complex **8** with a free phosphine center. A similar structural arrangement of ligands around Rh, as described above for **5**, **6**, and **7**, was ascertained from their $^{31}P\{^1H\}$ NMR spectra. The bridgehead phosphorus showed a doublet of doublets of doublets (δ 187.4 ppm, J_{Rh-P} = 237 Hz and J_{P-P} = 44 Hz; δ 160.48 ppm, J_{Rh-P} = 278 Hz and J_{P-P} = 54 Hz), and the bound phosphines showed a doublet of doublets each at δ 12.31 ppm, J_{Rh-P} = 130 Hz and J_{P-P} = 44 Hz; δ 13.94 ppm, J_{Rh-P} = 129 Hz and J_{P-P} = 52 Hz; δ 26.56 ppm, J_{Rh-P} = 150 Hz and J_{P-P} = 43 Hz. The free terminal phosphine in **8** showed a singlet at δ −16.13 ppm. The latter could then be

Scheme 3



reacted with 0.5 equiv of the Rh-dimer [(μ-Cl)(1,5-C_8H_{12})Rh]$_2$ in benzene, leading to a successful bridge-splitting reaction, as depicted by the appearance of a doublet for the bound terminal phosphine (complex **10**, Table 1, δ 24.37 ppm, J_{Rh-P} = 148 Hz).

The reaction of complex **7** with 1 equiv of **3** led to the formation of complex **9** via replacement of the bound COD ligand in **7** with the chelating bridgehead phosphorus and one terminal phosphine of **3** and leaving two free terminal phosphines. Complex **9** showed a doublet of doublets of doublets for each bridgehead phosphorus unit (δ 161.93 ppm, J_{Rh-P} = 278 Hz and J_{P-P} = 51 Hz; δ 159.41 ppm, J_{Rh-P} = 278 Hz and J_{P-P} = 42 Hz), a doublet of doublets for the trans positioned phosphines on the first rhodium center (δ 13.89 ppm, J_{Rh-P} = 129 Hz and J_{P-P} = 51 Hz), and a doublet of doublets for the bound phosphines on the second rhodium center (δ 26.25 ppm, J_{Rh-P} = 140 Hz and J_{P-P} = 40 Hz; δ 14.97 ppm, J_{Rh-P} = 132 Hz and J_{P-P} = 42 Hz). The two free phosphine centers showed a singlet at δ −15.97 ppm. A solution of complex **9** was then added to a benzene solution of 1 equiv of the rhodium dimer, leading to the formation of complex **11** by a bridge-splitting reaction of the terminal phosphines in **9** with [(μ-Cl)(1,5-C_8H_{12})-Rh]$_2$. The formation of this complex was indicated by the appearance of a doublet for the terminal (bound) phosphines (δ 28.98 ppm, J_{Rh-P} = 149 Hz).

It was postulated that the reaction pattern of polyphosphorus ligands **2** and **3** may be due to the short length of the alkane chain in HO−$(CH_2)_3$−PPh_2 that brings the terminal phosphines in close proximity to the bridgehead phosphorus, leading to the formation of a stable seven-membered chelate ring in these complexes.

Table 2. $^{31}P\{^1H\}$ NMR Chemical Shifts (109 MHz, C_6D_6, δ ppm) and Coupling Constants (Hz)

compd	P_A [$P(OR)_3$]	P_A [$PhP(OR)_2$]	P_M
12	s 136.25		s −15.95
13		s 155.36	s −16.02
14	d 112.34		d 26.92
	J_{Rh-P} = 253		J_{Rh-P} = 149
15		d 128.34	d 26.90
		J_{Rh-P} = 247	J_{Rh-P} = 147

To test this hypothesis, the monophosphine reagent HO−$(CH_2)_{10}$−PPh_2 required for the synthesis of longer alkane chain tripodal phosphines was prepared from 1-chloro-10-decanol by first protecting its hydroxyl group by reacting it with Et_2NSiMe_3 in benzene to give Me_3-SiO−$(CH_2)_{10}$−Cl. The latter was reacted with $KPPh_2$, followed by deprotection with a methanol/citric acid mixture, to give the monophosphine HO−$(CH_2)_{10}$−PPh_2. It was then reacted with PCl_3 or $PhPCl_2$ to give the desired polyphosphorus ligands **12** and **13**, respectively. These ligands showed two peaks in their $^{31}P\{^1H\}$ NMR spectra (Table 2) that were assigned to their bridgehead and peripheral phosphorus centers. The polyphosphorus ligand **12** was reacted with 2 equiv of the rhodium dimer [(μ-Cl)(1,5-C_8H_{12})Rh]$_2$ in benzene. The bridge-splitting reaction of the phosphorus center led to the exclusive formation of complex **14** (Scheme 3). The $^{31}P\{^1H\}$ NMR spectrum of the latter complex showed a doublet at δ 112.34 ppm for the bridgehead phosphite bound to rhodium (J_{Rh-P} = 253 Hz) and a doublet for the three terminal phosphines bound to rhodium at δ 26.92 ppm (J_{Rh-P} = 149 Hz, Table 2). The lengthened arms of the terminal phosphines placed the P(III) donor centers at

a sufficient distance that prevented their concerted interaction with the bridgehead phosphorus to form a chelating ring, to displace the bound COD ligand on rhodium. A similar reaction of the tripodal ligand **13** with 1.5 equiv of $[(\mu\text{-Cl})(1,5\text{-}C_8H_{12})Rh]_2$ yielded complex **15** via a simple bridge-splitting reaction without any chelating ring formation by the terminal phosphines (Scheme 3, Table 2).

The results presented above suggest that the tripodal phosphorus ligands play an important and useful role in tailoring the structure of their corresponding organometallic complexes. For example, by starting with ligand **1** at the core in which the apical phosphorus is unable to carry out a bridge-splitting reaction with $[(\mu\text{-Cl})(1,5\text{-}C_8H_{12})Rh]_2$, or with ligands **12** and **13**, where the length of the alkane chain arm prevents the formation of a chelate ring, multimetallic complexes with a typical spherical structure are obtained. In contrast, placing polyphosphorus ligand **2** or **3** at the core or using them as repeat units leads to nonspherical structures. Such a structural control in the design of multimetallic complexes such as organometallic dendrimers will be extremely useful in tailoring their properties, leading to efficient transition metal based catalysts.

We attempted an evaluation of the catalytic activity of some of these complexes for olefin hydrogenation that is typically catalyzed by Wilkinson type ($ClRh(PPh_3)_3$) complexes.[12] Hydrogenation of decene in a 1:200 metal-to-substrate ratio was carried out at 25 °C under 20 bar H_2 pressure for 1 h in benzene with metal complexes **5**, **6**, **8**, and **9**. Complex **6** represents a model rhodium center that becomes a part of the multimetallic complexes **5** (with a typical spherical structure) and **8** and **9** (with a nonspherical structure). After a catalytic run, the organic product was extracted into hexanes, and the conversion to decane was determined using mass spectrometry, GC analysis, and ^1H NMR spectroscopy. The catalyst was recovered by precipitation using hexanes and purified using a mixture of benzene and hexanes. Complexes **5**, **6**, **8**, and **9** were found to be active catalysts for olefin hydrogenation. Complexes **8** and **9** showed turnover numbers (mol_{prod}/mol_{cat} = 196 and 194, respectively) and percent conversions (98 and 97%, respectively) that were very similar to the model complex **6** (turnover number of 196, and percent conversion 98), while complex **5** showed a turnover number (188) and percent conversion (90%) that were lower. A detailed evaluation of this difference in activity and its interpretation in larger multimetallic systems with varied spherical and nonspherical structures constitute our ongoing efforts in this area.

Conclusions

We have developed a simple route to a variety of easily accessible tripodal polyphosphorus ligands. The reaction of the latter with $[RhCl(COD)]_2$ and the structural arrangement of ligands around rhodium in the resulting compounds are dependent on the type of polyphosphorus ligand employed for the reaction. When the central and terminal phosphorus units can act in concert with each other, the chelate effect leads to replacement of the COD ligand after a successful bridge-splitting reaction by the apical phosphorus. The synthetic elaboration of this methodology to construct hyperbranched organometallic complexes and the influence of their structure on the catalytic efficiency are currently being pursued.

Experimental Section

General Procedures. All manipulations were performed under a nitrogen atmosphere either using standard Schlenk line techniques or in an Innovative Technology (Braun) Labmaster MB-150-M drybox. Solvents were distilled over appropriate drying agents and stored under nitrogen. The following were purchased and used as received: 1-chloro-3-propanol (Aldrich), 1-chloro-10-decanol (Aldrich), phosphorus trichloride (Aldrich), dichlorophenylphosphine (Aldrich), chlorodiphenylphosphine (Aldrich), 3-hydroxypropyldiphenylphosphine (Organometallics), and $[RhCl(1,5\text{-cyclooctadiene})]_2$ (Pressure Chemicals). NMR spectra were recorded on a JEOL 270 MHz spectrometer at ambient temperature, and the chemical shifts in ppm are relative to tetramethylsilane as an internal standard for ^1H and ^{13}C NMR spectra and H_3PO_4 for $^{31}P\{^1H\}$ NMR spectra. Coupling constants (J) are given in Hz. Mass spectra were obtained using a low-resolution KRATOS MS25RSA spectrometer. MALDI-TOF mass spectra were obtained on a Kratos Kompact Maldi 3 v 4.0 spectrometer using LiBr/didronel or Li/gentistic acid as a matrix. Elemental analyses were performed by Guelph Chemical Labortories, Guelph, Ontario.

$O{=}P[O(CH_2)_3PPh_2]_3$ (1). Phosphorus oxychloride (253 mg, 1.65 mmol) was combined with 3 equiv of $HO(CH_2)_3PPh_2$ (1.21 g, 4.95 mmol) in a solution mixture of 30 mL of THF and 15 mL of triethylamine cooled to 0 °C. During the addition, the formation of a white solid (NEt_3HCl) was observed. Once the addition was complete, the reaction mixture was allowed to warm to room temperature and stirred overnight. The white solid was removed via vacuum filtration, and THF and triethylamine were removed via static vacuum distillation to afford a clear viscous liquid. Yield: 872 mg, 68%. Anal. Calcd for $C_{45}H_{48}O_4P_4$: C, 69.58; H, 6.23. Found: C, 69.71; H, 5.97. ^1H NMR (270 MHz, C_6D_6): δ (ppm) 1.61 (6H, m, $-CH_2-$), 2.11 (6H, t,, J_{H-H} = 6.1 Hz, $-CH_2P-$), 3.77 (6H, t, J_{H-H} = 5.9 Hz, $-CH_2O-$), 7.43, 7.73 (30H, m, $-C_6H_5-$). EI-MS: m/z 775.

$PhP[O(CH_2)_3PPh_2]_2$ (2). Dichlorophenylphosphine (523 mg, 2.92 mmol) was dissolved in 25 mL of THF and added dropwise to a solution of 2 equiv of $HO(CH_2)_3PPh_2$ (1.43 g, 5.84 mmol) in 30 mL of THF and 15 mL of triethylamine, cooled to 0 °C. The formation of a white solid was observed during the addition. The reaction mixture was warmed to room temperature and stirred overnight. The white precipitate was removed by filtration, and THF and triethylamine were removed via static vacuum distillation to afford a clear viscous liquid. Yield: 1.37 g, 79%. Anal. Calcd for $C_{36}H_{37}O_2P_3$: C, 72.79; H, 6.27. Found: C, 72.22; H, 6.52. ^1H NMR (270 MHz, C_6D_6): δ (ppm) 1.71 (4H, m, $-CH_2-$), 2.06 (4H, t, J_{H-H} = 6.1 Hz, $-CH_2P-$), 3.72 (4H, t, J_{H-H} = 5.9 Hz, $-CH_2O-$), 7.09, 7.64 (20H, m, $-P(C_6H_5)_2-$), 7.89, 8.26 (5H, m, $-O_2P(C_6H_5)-$). EI-MS: m/z 594.

$P[O(CH_2)_3PPh_2]_3$ (3). Phosphorus trichloride (1.012 g, 7.37 mmol) was dissolved in 25 mL of THF and added dropwise to a solution of 3 equiv of $HO(CH_2)_3PPh_2$ (5.437 g, 22.3 mmol) in 30 mL of THF and 15 mL of triethylamine, cooled to 0 °C. The formation of a white solid was observed during the addition. The reaction mixture was warmed to room temperature and

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stirred overnight. The white precipitate was removed by filtration, and THF and triethylamine were removed via static vacuum distillation to afford a clear viscous liquid. Yield: 3.609 g, 64%. Anal. Calcd for $C_{45}H_{48}O_3P_4$: C, 71.04; H, 6.36. Found: C, 71.58; H, 6.70. ^{1}H NMR (270 MHz, C_6D_6): δ (ppm) 1.70 (6H, m, $-CH_2-$), 2.08 (6H, t, $J_{H-H} = 6.1$ Hz, $-CH_2P-$), 3.70 (6H, t, $J_{H-H} = 5.9$ Hz, $-CH_2O-$), 7.43, 7.73 (30H, m, $-C_6H_5-$). EI-MS: *m*/*z* 760.

O=P[O(CH$_2$)$_3$PPh$_2$RhCl(1,5-C$_8$H$_{12}$)]$_3$ (4). O=P[O(CH$_2$)$_3$PPh$_2$]$_3$ (154 mg, 0.198 mmol) was dissolved in 10 mL of benzene and added dropwise to a solution of 1.5 equiv of [(μ-Cl)(1,5-C_8H_{12})Rh]$_2$ (147 mg, 0.297 mmol) in 10 mL of benzene. The mixture was stirred for 2 h at ambient temperature, after which the solvent was removed under vacuum. The orange residue was precipitated using benzene and hexanes to give a yellow powder. Yield: 287 mg, 97%. Anal. Calcd for $C_{69}H_{84}O_4P_4Rh_3Cl_3$: C, 54.65; H, 5.58. Found: C, 54.22; H, 6.01. ^{1}H NMR (270 MHz, C_6D_6): δ (ppm) 1.71 (6H, m, $-CH_2-$), 2.20 (30H, m, $-CH_2-$), 3.91 (6H, t, $J_{H-H} = 5.9$ Hz, $-CH_2O-$), 4.17, 5.86 (12H, s br, CH=CH), 7.43, 7.73 (30H, m, $-C_6H_5-$). EI-MS: *m*/*z* 1520.

O=P{O(CH$_2$)$_3$PPh$_2$(RhCl)PhP[O(CH$_2$)$_3$PPh$_2$]$_2$}$_3$ (5). O=P[O(CH$_2$)$_3$PPh$_2$RhCl(1,5-C_8H_{12})]$_3$ (157 mg, 0.104 mmol) was dissolved in 10 mL of benzene and added dropwise to a solution of 3 equiv of PhP[O(CH$_2$)$_3$PPh$_2$]$_2$ (186 mg, 0.311 mmol) in 10 mL of benzene. The mixture was stirred for 2 h at ambient temperature, after which the solvent was removed in vacuo. The orange residue was precipitated using benzene and hexanes to give a yellow powder. Yield: 271 mg, 88%. Anal. Calcd for $C_{153}H_{159}Cl_3O_{10}P_{13}Rh_3$: C, 61.75; H, 5.38. Found: C, 61.29; H, 5.13. ^{1}H NMR (270 MHz, C_6D_6): δ (ppm) 1.64−1.71 (18H, m, $-CH_2-$), 2.23−2.61 (18H, m, $-CH_2P-$), 3.87−3.91 (18H, m, $-CH_2O-$), 7.12, 7.73 (90H, m, P(C_6H_5)), 7.85, 8.31 (15H, m, $-O_2PC_6H_5$)). MALDI-TOF (LiBr/gentistic acid): 2970.

PhP[O(CH$_2$)$_3$PPh$_2$]$_2$[RhCl] (6). PhP[O(CH$_2$)$_3$PPh$_2$]$_2$ (129 mg, 0.220 mmol) was dissolved in 10 mL of benzene and added dropwise to a solution of 1.5 equiv of [(μ-Cl)(1,5-C_8H_{12})Rh]$_2$ (161 mg, 0.328 mmol) in 10 mL of benzene. The mixture was stirred for 3 h at ambient temperature, after which the solvent was removed in vacuo. The orange residue was precipitated using benzene and hexanes to give a yellow powder. Yield: 147 mg, 97%. Anal. Calcd for $C_{36}H_{37}ClO_2P_3Rh$: C, 58.99; H, 5.08. Found: C, 58.54; H, 5.36. ^{1}H NMR (270 MHz, C_6D_6): δ (ppm) 1.71 (4H, m, $-CH_2-$), 2.04 (4H, m, $-CH_2P-$), 3.87 (4H, m, $-CH_2O-$), 7.12, 7.74 (20H, m, P(C_6H_5)), 8.07, 8.34 (5H, m, $-O_2PC_6H_5$)). EI-MS: *m*/*z* 702.

{**RhCl**}**P[O(CH$_2$)$_3$PPh$_2$]$_3$[RhCl(1,5-C$_8$H$_{12}$] (7).** P[O(CH$_2$)$_3$PPh$_2$]$_3$ (257 mg, 0.338 mmol) was dissolved in 10 mL of benzene and added dropwise to a solution of 2 equiv of [(μ-Cl)(1,5-C_8H_{12})Rh]$_2$ (334 mg, 0.676 mmol) in 10 mL of benzene. The mixture was stirred for 2 h at ambient temperature, after which the solvent was removed in vacuo. The orange residue was precipitated using benzene and hexanes to give a yellow powder. Yield: 379 mg, 98%. Anal. Calcd for $C_{53}H_{60}Cl_2O_3P_4Rh_2$: C, 55.56; H, 5.28. Found: C, 55.47; H, 5.49. ^{1}H NMR (270 MHz, C_6D_6): δ (ppm) 1.40 (6H, m, $-CH_2-$), 2.13 (8H, s, br, $-CH_2-$), 2.20 (6H, m, $-CH_2P-$), 3.57 (6H, m, $-CH_2O-$), 4.30, 5.83 (4H, s, br, $-CH=CH-$) 7.11, 7.76 (30H, m, P(C_6H_5)). EI-MS: *m*/*z* 1144.

{**RhCl**}**P[O(CH$_2$)$_3$PPh$_2$]$_3$[RhCl]PPh[O(CH$_2$)$_3$PPh$_2$]$_2$} (8).** PhP[O(CH$_2$)$_3$PPh$_2$]$_2$ (68 mg, 0.113 mmol) was dissolved in 10 mL of benzene and added dropwise to a solution of ClRhP[(OCH$_2$)$_3$PPh$_2$]$_3$RhCl(1,5-C_8H_{12})] (**7**) (129 mg, 0.113 mmol) in 10 mL of benzene. The mixture was stirred for 3 h at ambient temperature, after which the solvent was removed under vacuum. The orange residue was precipitated using benzene and hexanes to give a yellow powder. Yield: 177 mg, 96%. Anal. Calcd for $C_{81}H_{85}O_5P_7Rh_2Cl_2$: C, 62.78; H, 5.84. Found: C, 62.59; H, 5.67. ^{1}H NMR (270 MHz, C_6D_6): δ (ppm) 1.10−1.41 (10H, m, $-CH_2-$), 2.21−2.61 (10H, m, $-CH_2P-$), 3.57−3.85 (10H, m, $-CH_2O-$), 7.11, 7.75 (50H, m, P(C_6H_5)), 7.98, 8.30 (5H, m, P(C_6H_5)). EI-MS: *m*/*z* 1634.

{**RhCl**}**P[O(CH$_2$)$_3$PPh$_2$]$_3$[RhCl]P[O(CH$_2$)$_3$PPh$_2$]$_3$ (9).** P[O(CH$_2$)$_3$PPh$_2$]$_3$ (93 mg, 0.12 mmol) was dissolved in 10 mL of benzene and added dropwise to a solution of ClRhP[(OCH$_2$)$_3$PPh$_2$]$_3$RhCl(1,5-C_8H_{12})] (**7**) (138 mg, 0.120 mmol) in 10 mL of benzene. The mixture was stirred for 2 h at ambient temperature, after which the solvent was removed under vacuum. The orange residue was precipitated using benzene and hexanes to give a yellow powder. Yield: 209 mg, 97%. Anal. Calcd for $C_{90}H_{96}O_6P_4Rh_2Cl_2$: C, 55.11; H, 5.38. Found: C, 54.75; H, 5.32. ^{1}H NMR (270 MHz, C_6D_6): δ (ppm) 1.07−1.46 (12H, m, $-CH_2-$), 2.21−2.61 (12H, m, $-CH_2P-$), 3.67−3.87 (12H, m, $-CH_2O-$), 7.14, 7.85 (60H, m, P(C_6H_5)), 7.98, 8.30 (5H, m, P(C_6H_5)). EI-MS: *m*/*z* 1799.

{**RhCl**}**P[O(CH$_2$)$_3$PPh$_2$]$_3$[RhCl]PhP[O(CH$_2$)$_3$PPh$_2$]$_2$[RhCl(1,5-C$_8$H$_{12}$)] (10).** {RhCl}P[O(CH$_2$)$_3$PPh$_2$]$_3$[RhCl]PPh[O(CH$_2$)$_3$PPh$_2$]$_2$} (**8**) (68 mg, 0.042 mmol) was dissolved in 15 mL of benzene and added dropwise to a solution of 0.5 equiv of [(μ-Cl)(1,5-C_8H_{12})Rh]$_2$ (10 mg, 0.021 mmol) in 10 mL of benzene. The mixture was stirred for 3 h at ambient temperature, after which the solvent was removed under vacuum. The orange residue was precipitated using benzene and hexanes to give a yellow powder. Yield: 73 mg, 93%. Anal. Calcd for $C_{89}H_{97}O_5P_7Rh_3Cl_3$: C, 56.90; H, 5.20. Found: C, 55.70; H, 5.35. ^{1}H NMR (270 MHz, C_6D_6): δ (ppm) 1.08−1.40 (10H, m, $-CH_2-$), 2.20 (8H, s, br), 2.37−2.63 (10H, m, $-CH_2P-$), 4.17, 5.86 (4H, s, br, $-CH=CH-$), 7.15, 7.76 (50H, m, P(C_6H_5)), 7.97, 8.25 (5H, m, P(C_6H_5)). EI-MS: *m*/*z* 1874.

{**RhCl**}**P[O(CH$_2$)$_3$PPh$_2$]$_3$[RhCl]P[O(CH$_2$)$_3$PPh$_2$]$_3$[RhCl(1,5-C$_8$H$_{12}$)]$_2$ (11).** {RhCl}P[O(CH$_2$)$_3$PPh$_2$]$_3$[RhCl]P[O(CH$_2$)$_3$PPh$_2$]$_3$ (**9**) (78 mg, 0.043 mmol) was dissolved in 15 mL of benzene and added dropwise to a solution of 1 equiv of [(μ-Cl)(1,5-C_8H_{12})Rh]$_2$ (20 mg, 0.043 mmol) in 10 mL of benzene. The mixture was stirred for 3 h at ambient temperature, after which the solvent was removed under vacuum. The orange residue was precipitated using benzene and hexanes to give a yellow powder. Yield: 93 mg, 94%. Anal. Calcd for $C_{106}H_{120}O_6P_8Rh_4Cl_4$: C, 55.56; H, 5.28. Found: C, 55.06; H, 5.05. ^{1}H NMR (270 MHz, C_6D_6): δ (ppm) 1.12−1.53 (12H, m, $-CH_2-$), 2.13 (16H, s, br), 2.33−2.64 (12H, m, $-CH_2P-$), 4.25, 5.85 (8H, s, br, $-CH=CH-$), 7.06, 7.94 (60H, m, P(C_6H_5)), 7.98, 8.30 (5H, m, P(C_6H_5)). MALDI-TOF (LiBr/gentistic acid): 2295.

P[OCH$_2$)$_{10}$PPh$_2$]$_3$ (12). *HO(CH$_2$)$_{10}$PPh$_2$, (CH$_3$)$_3$SiO(CH$_2$)$_{10}$Cl:* A solution of 1-chloro-10-decanol (3.57 g, 0.018 mol) in 20 mL of benzene was added to *N*,*N*′-diethyltrimethylsilylamine (2.69 g, 0.018 mol). The cloudy mixture was stirred at 55 °C for 14 h. The pale yellow liquid was centrifuged and the liquid decanted off in order to remove trace amounts of solid white precipitate. Benzene and diethylamine were removed via static vacuum distillation to afford a pale yellow liquid. Yield: 4.62 g, 97%. Anal. Calcd for $C_{13}H_{29}OSiCl$: C, 58.94; H, 11.03. Found: C, 58.95; H, 10.95. ^{1}H NMR (270 MHz, C_6D_6): δ (ppm) 0.11 (9H, s, $-CH_3$, 0.97−1.56 (16H, m, $-CH_2-$), 3.13 (2H, t, $J_{H-H} = 6.9$ Hz, $-CH_2Cl$), 3.54 (2H, t, $J_{H-H} = 6.3$ Hz, $-CH_2O-$). CI-MS: *m*/*z* 265. *(CH$_3$)$_3$SiO(CH$_2$)$_{10}$PPh$_2$*: A solution of potassium diphenylphosphide (29.22 mL, 0.015 mol) in THF was added dropwise to a solution of $(CH_3)_3SiO(CH_2)_{10}Cl$ (3.87 g, 0.015 mol) in 15 mL of THF at 0 °C over a period of 4 h. The yellowish orange solution was allowed to warm to room temperature overnight. The solid white KCl salt produced was removed via static vacuum distillation. Benzene was added to extract the product, and after vacuum distillation afforded a pale yellow liquid. Yield: 5.91 g, 95%. ^{1}H NMR (270 MHz, C_6D_6): δ (ppm) 0.13 (9H, s, $-CH_3$), 1.13−1.62 (16H, m, $-CH_2-$), 1.98 (2H, t, $J_{H-H} = 7.6$ Hz, $-CH_2P-$), 3.55 (2H, t, $J_{H-H} = 6.3$ Hz, $-CH_2O-$), 7.08, 7.47 (10H, m, $-C_6H_5$). ^{31}P{^{1}H} NMR (109 MHz, C_6D_6): δ (ppm) −15.75 (s). CI-MS: *m*/*z* 415. *HO(CH$_2$)$_{10}$PPh$_2$*: Anhydrous citric acid (1.38 g, 7.16 mmol) was dissolved in 15 mL of methanol, and the solution was transferred via syringe into a Schlenk flask containing $(CH_3)_3SiO-$

$(CH_2)_{10}PPh_2$ (2.97 g, 7.16 mmol), resulting in a cloudy mixture. The latter was stirred at ambient temperature until a clear solution was formed. Methanol was then removed via static vacuum distillation, and benzene was added to extract the product. Benzene was removed via static vacuum distillation to afford a pale yellow viscous liquid. Yield: 2.23 g, 91%. Anal. Calcd for $C_{22}H_{31}OP$: C, 77.26; H, 9.14. Found: C, 76.70; H, 8.78. ^{1}H NMR (270 MHz, C_6D_6): δ (ppm) 1.11−1.55 (16H, m, $-CH_2-$), 1.99 (2H, t, J_{H-H} = 7.6 Hz, $-CH_2P-$), 3.46 (2H, t, J_{H-H} = 6.3 Hz, $-CH_2O-$), 7.09, 7.47 (10H, m, C_6H_5). ^{31}P{^{1}H} NMR (109 MHz, C_6D_6): δ (ppm) −15.75 (s). EI-MS: *m*/*z* 342. Phosphorus trichloride (0.505 g, 3.68 mmol) was dissolved in 25 mL of THF and added dropwise using a dropping funnel to a solution of 3 equiv of $HO(CH_2)_{10}PPh_2$ (3.78 g, 11.1 mmol) in 30 mL of THF and 15 mL of triethylamine that was cooled to 0 °C. Once the addition was complete, the reaction mixture was allowed to warm to room temperature and left stirring overnight. A white precipitate that was formed during the reaction was removed via vacuum filtration, and THF/triethylamine was removed via extensive static vacuum distillation to afford a viscous liquid. Yield: 2.39 g, 62%. ^{1}H NMR (270 MHz, C_6D_6): δ (ppm) 1.15−1.58 (48H, m, $-CH_2-$), 2.02 (6H, t, J_{H-H} = 7.6 Hz, $-CH_2P-$), 3.68 (6H, t, J_{H-H} = 6.3 Hz, $-CH_2O-$), 7.09, 7.47 (30H, m, C_6H_5). EI-MS: *m*/*z* 1055.

$PhP[O(CH_2)_{10}PPh_2]_2$ (13). $PhPCl_2$ (489 mg, 2.73 mmol) was dissolved in 25 mL of THF and added dropwise using a dropping funnel to a solution of 2 equiv of $HO(CH_2)_{10}PPh_2$ (1.87 g, 5.46 mmol) in 30 mL of THF and 15 mL of triethylamine that was cooled to 0 °C. Once the addition was complete, the reaction mixture was allowed to warm to room temperature and left stirring overnight. A white precipitate that was formed during the reaction was removed via vacuum filtration, and THF/triethylamine was removed via extensive static vacuum distillation to afford a viscous liquid. Yield: 1.52 g, 71%. Anal. Calcd for $C_{50}H_{65}O_2P_3$: C, 75.92; H, 6.28. Found: C, 75.10; H, 6.33. ^{1}H NMR (270 MHz, C_6D_6): δ (ppm) 1.14−1.57 (32H, m, $-CH_2-$), 2.03 (4H, t, J_{H-H} = 7.6 Hz, $-CH_2P-$), 3.69 (4H, t, J_{H-H} = 6.3 Hz, $-CH_2O-$), 7.10, 7.49 (20H, m, C_6H_5), 7.87, 8.28 (5H, m, C_6H_5). EI-MS: *m*/*z* 792.

$[1,5\text{-}C_8H_{12})ClRh]P[O(CH_2)_{10}PPh_2RhCl(1,5\text{-}C_8H_{12})]_3$ (14). $P[OCH_2)_3PPh_2]_3$ (**12**) (134 mg, 0.126 mmol) was dissolved in 15 mL of benzene and added dropwise to a solution of 2 equiv of $[(\mu\text{-}Cl)(1,5\text{-}C_8H_{12})Rh]_2$ (109 mg, 0.253 mmol) in 15 mL of benzene. The mixture was stirred for 1 h at ambient temperature, after which the solvent was removed under vacuum. The orange residue was precipitated using benzene and hexanes to give a yellow powder. Yield: 229 mg, 89%. Anal. Calcd for $C_{58}H_{138}O_3P_4Rh_4Cl_4$: C, 57.66; H, 6.81. Found: C, 57.40; H, 6.82. ^{1}H NMR (270 MHz, C_6D_6): δ (ppm) 0.86−1.61 (48H, m, $-CH_2-$), 2.17 (32H, s, b, $-CH_2CH_2-$), 2.57 (6H, m, $-CH_2P-$), 3.57 (6H, m, $-CH_2O-$), 4.34, 5.78 (16H, s, b, $-CH{=}CH-$), 7.10, 7.49 (30H, m, C_6H_5). MALDI-TOF (LiBr/gentistic acid): 2045.

$[1,5\text{-}C_8H_{12})ClRh]PhP[O(CH_2)_{10}PPh_2RhCl(1,5\text{-}C_8H_{12})]_2$ (15). $PhP[OCH_2)_3PPh_2]_2$ (**12**) (154 mg, 0.195 mmol) was dissolved in 10 mL of benzene and added dropwise to a solution of 1.5 equiv of $[(\mu\text{-}Cl)(1,5\text{-}C_8H_{12})Rh]_2$ (144 mg, 0.292 mmol) in 15 mL of benzene. The mixture was stirred for 3 h at ambient temperature, after which the solvent was removed under vacuum. The orange residue was precipitated using benzene and hexanes to give a yellow powder. Yield: 268 mg, 90%. ^{1}H NMR (270 MHz, C_6D_6): δ (ppm) 1.14−1.57 (32H, m, $-CH_2-$), 2.03 (4H, m, $-CH_2P-$), 3.69 (4H, m, $-CH_2O-$), 4.34, 5.78 (16H, s, b, $-CH{=}CH-$), 7.10, 7.49 (20H, m, C_6H_5), 7.87, 8.28 (5H, m, C_6H_5). EI-MS: *m*/*z* 1529.

Hydrogenation of Decene. A typical run for the hydrogenation of decene using complex **6** is described here. A solution of 25 mg (0.035 mmol) of **6** and 1 g of decene (7.13 mmol) in 10 mL of benzene was placed in a hydrogen bomb, pressurized with H_2 (20 bar), and left to react for 1 h at room temperature. Hexane (5 mL) was then added to precipitate the catalyst, which was removed by filtration. The hexane and benzene were removed from the filtrate by static vacuum distillation to afford 998 mg of decane. It was characterized by GC, MS, and ^{1}H NMR. Turnover number (mol_{sub}/mol_{cat}) = 196. ^{1}H NMR (270 MHz, C_6D_6): δ 0.93 (6H, t, J_{H-H} = 5.9 Hz, $-CH_3$), 1.44 (16H, s, $-CH_2-$). GC retention time 11.29 min (90 °C, He carrier gas, 14 psi, flame ionization detector, Ph-Me siloxane capillary column). EI-MS: *m*/*z* 142.

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