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Phosphorus-Containing Dendrimers and Their Transition Metal Complexes as Efficient Recoverable Multicenter Homogeneous Catalysts in Organic Synthesis

Valérie Maraval, Régis Laurent, Anne-Marie Caminade,* and Jean-Pierre Majoral*

Laboratoire de Chimie de Coordination, CNRS, 205 Route de Narbonne,
31077 Toulouse Cedex 4, France

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Metalladendrimers of generation 3 with either 24 terminal palladium or ruthenium diphosphine complexes or one ruthenium diphosphine complex located at the core have been found to be efficient, recoverable catalysts in three general organic reactions: Stille couplings, Knoevenagel condensations, and Michael additions.

Introduction

The search for an ideal catalyst that combines advantages of both homogeneous and heterogeneous catalysis is at the center of many investigations. In that sense metalladendrimers are emerging as a promising class of compounds, as predicted by Tomalia and Newkome[1] and as demonstrated in a pioneering work by van Koten et al. in 1994.[2] This interest is due to the properties of dendrimers: high solubility, high concentration of easily accessible active sites, and easy separation by nanofiltration or precipitation, to name as a few.

Some reports describe the use of nonmetalated dendrimers,[3] but the majority of the work reported in the literature is concerned with the properties of metalladendrimers as catalysts. The metal can be incorporated at the core[4] and more frequently on the surface.[5] Recently dendrimer-encapsulated metal nanoparticules were found to behave as efficient catalysts for the hydrogenation of alkenes in aqueous solution[6a] or for reactions in fluorous biphasic systems.[6b] Also, hydroformylation reactions with rhodium-complexed dendrimers grafted on silica were successfully achieved.[7]

We have previously prepared a variety of metalladendrimers from the reaction of phosphorus-containing dendrimers with various transition metal complexes. The presence of ligands such as phosphanes and diphosphanes or P=N−P=S moieties either on the surface of dendrimers or within the cascade structure allowed us to isolate dendritic complexes incorporating metals such as palladium, platinum, rhodium, ruthenium, gold, iron, tungsten, or zirconium.[8−17]

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* Corresponding authors. Fax: 33 5 61 55 30 03. E-mail: caminade@lcc-toulouse.fr or majoral@lcc-toulouse.fr.

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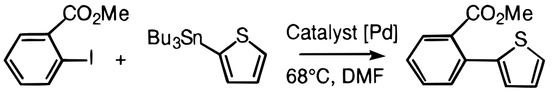
Table 1. Stille Coupling Involving Methyl-2-iodobenzoate and 2-(Tributylstannyl)thiophene



a

entry	catalyst	(mol % Pd)	*t* (h)	conversion %	ref
1	**1-[G$_3$]**	(5)	2.5	95	this work
2	**1-[G$_3$]**	(1)	12	86	this work
2′	**1-[G$_3$]** (recov)	(1)	12	80	this work
2″	**1-[G$_3$]** (recov)	(1)	12	79	this work
3	$(Ph_3P)_2PdCl_2$	(5)	20	81[b,c]	18

[a] Typical conditions: methyl-2-iodobenzoate (0.372 mL, 2.45 mmol), 2-(tributylstannyl)thiophene (0. 86 mL, 2.7 mmol), **1-[G$_3$]** (0.11 g, 0.005 mmol 5%), DMF (10 mL). [b] Pd precipitate observed. [c] The isolated product is the corresponding acid.

Here we describe our preliminary results concerning the use of palladium and ruthenium dendritic diphosphane complexes as catalysts in three general organic syntheses: cross-coupling reactions (Stille coupling), Knoevenagel condensations, and diastereoselective Michael additions.

Results and Discussion

The Stille coupling of methyl-2-iodobenzoate with 2-(tributylstannyl)thiophene is the test reaction we have chosen for evaluation of the catalytic properties of palladium complexes of dendrimers and for comparison with other catalytic systems recently reported.[18] The reaction is faster with the isolated and well-characterized dendrimer palladium complex **1-[G$_3$]** (generation 3, 24 terminal $PdCl_2$ groups) as catalyst (5 mol % Pd) (Chart 1) than with the monomer $(Ph_3P)_2PdCl_2$: 95% of conversion is observed after 2.5 h of reaction at 68 °C [to be compared with 81% of conversion after 20 h with $(Ph_3P)_2PdCl_2$ (Table 1, Figure 1)]. The same reaction performed with only 1% of **1-[G$_3$]** instead of 5% allows us to show that no significant loss of activity of the catalyst is detected after three consecutive reactions: 79−86% of conversion was observed after 12 h (Table 1, Figure 2). It can be noted that contrary to what is described with the monomer ($(Ph_3P)_2PdCl_2$) no palladium precipitate is detected with the dendrimer **1-[G$_3$]**, which is easily recovered by adding ether on the resulting mixture; dendrimer **1-[G$_3$]** precipitates as a slightly orange powder, which is reused as it stands. NMR data of a sample after removal of volatiles clearly indicate that no degradation of the dendrimer complex occurred.

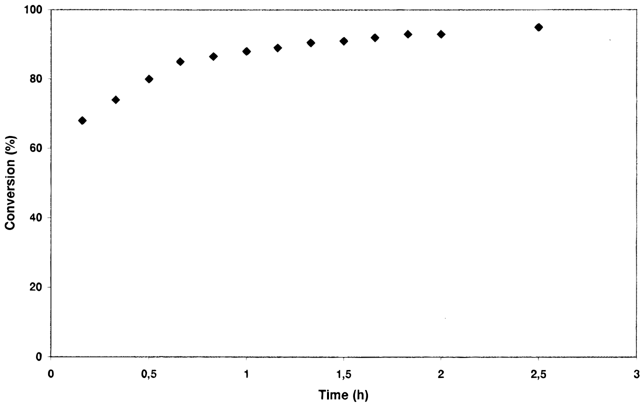


Figure 1. Stille coupling of methyl-2-iodobenzoate with 2-(tributylstannyl)thiophene at 68 °C in the presence of 5% mol Pd of catalyst **1-[G$_3$]**.

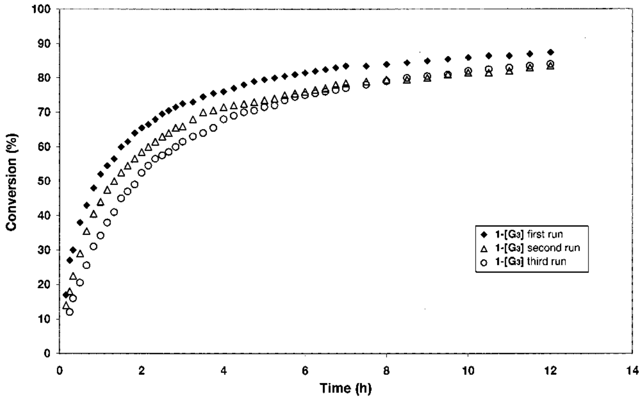


Figure 2. Stille coupling of methyl-2-iodobenzoate with 2-(tributylstannyl)thiophene at 68 °C in the presence of 1% mol Pd of catalyst **1-[G$_3$]**.

Similarly **1-[G$_3$]** exhibits catalytic activity for other Stille couplings such as the reaction of iodobenzene with tributylvinyltin. Indeed three types of catalysts were used. The first one, i.e., complex **2-[G$_3$]**, was prepared “in situ” by mixing a dendrimer of generation 3 with $Pd(OAc)_2$ (P/Pd: 4/1). Isolated complexes **1-[G$_3$]** and **1-[G$_1$]** incorporating respectively 24 and 6 terminal $[N(CH_2PPh_2)_2PdCl_2]$ units were also tested. The results together with reaction conditions are collected in Table 2. Dendrimer **2-[G$_3$]** appears to be an efficient catalyst under mild conditions like the “monomer” $[(Fu_3P)_4/Pd(OAc)_2]$, **3**,[19] but in contrast to **3**, it can be recycled several times without loss of activity (Table 2, entries 1, 1′, 1″). Note that a tetraphosphole/$Pd(OAc)_2$ complex **4**[19] although slightly less efficient (Table 2, entry 4) can also be recycled. Complex **1-[G$_3$]** was also found to be effective with a slightly decreasing activity when reused (Table 2, entries 7, 7′, 8, 8′).

The catalytic properties of phosphorus-containing dendrimer complexes were also investigated toward another general reaction in organic synthesis, the Knoevenagel reaction. The reaction involving malonitrile and cyclohexanone and leading to the corresponding unsaturated nitrile was chosen as a test reaction, to compare the properties of the dendritic diphosphane ruthenium complexes **5-[G$_3$]** (generation 3, 24 terminal $[(-PPh_2)_2RuH_2(PPh_3)_2]$) and **5-[G$_1$]** (generation 1, 6

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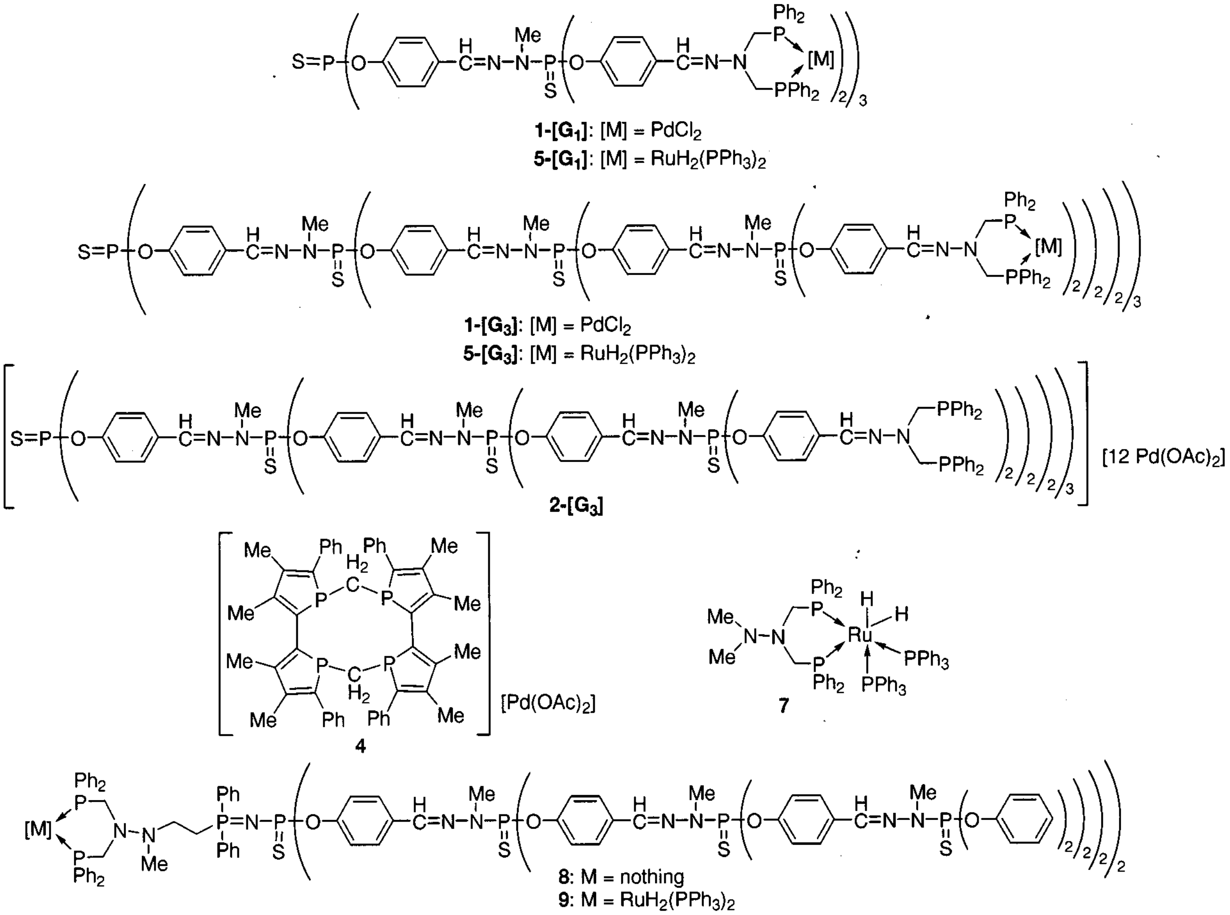
Chart 1



1-[G$_1$]: [M] = $PdCl_2$
5-[G$_1$]: [M] = $RuH_2(PPh_3)_2$

1-[G$_3$]: [M] = $PdCl_2$
5-[G$_3$]: [M] = $RuH_2(PPh_3)_2$

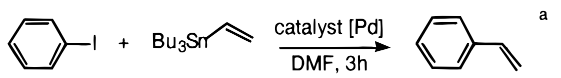
2-[G$_3$]

4

7

8: M = nothing
9: M = $RuH_2(PPh_3)_2$

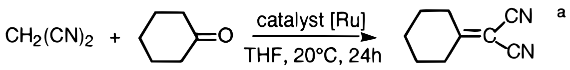
Table 2. Stille Coupling Involving Iodobenzene and Tributylvinyltin



entry	catalyst	(mol % Pd)	T °C (bath)	conversion %	ref
1	**2-[G$_3$]**	(5)	50	100	this work
1′	**2-[G$_3$]** (recov)	(5)	50	100	this work
1″	**2-[G$_3$]** (recov)	(5)	50	100	this work
2	**2-[G$_3$]**	(1)	80	100^b	this work
3	**3**	(5)	50	100	19
4	**4**	(5)	50	85	19
5	**1-[G$_1$]**	(1)	90	100^b	this work
6	**1-[G$_3$]**	(1)	90	100^b	this work
7	**1-[G$_3$]**	(5)	50	100	this work
7′	**1-[G$_3$]** (recov)	(5)	50	95	this work
8	**1-[G$_3$]**	(2)	50	100	this work
8′	**1-[G$_3$]** (recov)	(2)	50	92	this work

[a] Typical conditions: iodobenzene (0.60 mL, 5.34 mmol), tributylvinyltin (1.56 mL, 5.34 mmol), and **2-[G$_3$]** (prepared by stirring $Pd(OAc)_2$ (0.060 g, 0.267 mmol) and the dendrimer of generation 3 (0.380 g, 0. 022 mmol) in DMF (20 mL) at 50 °C for 15 min.), or iodobenzene (0.92 mL, 8.2 mmol), tributylvinyltin (2.40 mL, 8.20 mmol), and **1-[G$_3$]** (0.37 g, 0. 017 mmol) in DMF (25 mL). [b] Pd precipitate observed.

Table 3. Knoevenagel Condensation Involving Malonitrile and Cyclohexanone



entry	catalyst	(mol % Ru)	conversion %	ref
1	**5-[G$_3$]**	(1)	100^b	this work
1′	**5-[G$_3$]** (recov)	(1)	100	this work
1″	**5-[G$_3$]** (recov)	(1)	95	this work
2	**5-[G$_1$]**	(1)	100	this work
2′	**5-[G$_1$]**	(1)	100	this work
2″	**5-[G$_1$]**	(1)	83	this work
3	**6**	(3)	100^c	20
4	**7**	(1)	80	this work

[a] Typical conditions: malonitrile (0.736 g, 11.139 mmol), cyclohexanone (1.270 mL, 12.253 mmol), **5-[G$_3$]** (0.150 g, 0.0046 mmol). [b] 85% isolated yield after distillation. [c] 79% isolated yield after distillation.

terminal $[(-PPh_2)_2RuH_2(PPh_3)_2]$) with that of the "monomer" $RuH_2(PPh_3)_4$, **6**, which was found to be very efficient for such reactions in neutral conditions (3 mol % Ru in dry THF at room temperature).[20] Under similar conditions, 1 mol % metal of **5-[G$_3$]** (0.04 mol % of **5-[G$_3$]**) allows the total conversion of malonitrile into the corresponding unsaturated nitrile. Complex **5-[G$_3$]** can be recovered by precipitation with ether and reused without significant loss of catalytic activity (Table 3, entries 1, 1′, 1″, Figure 3). The same observations were done with **5-[G$_1$]**, but in this case the reaction is slower in the earliest stages (Figure 3). Interestingly, the reaction was also performed using the monomer $[Me_2N-N(CH_2PPh_2)_2RuH_2(PPh_3)_2]$, **7** (same ligand system as dendrimer **5-[G$_3$]**), as catalyst; only 80% of conversion is observed after 24 h of reaction with 1% of **7** (Table 3, entry 4, Figure 3). Moreover the complex **7** cannot be recovered and therefore cannot be efficiently recycled

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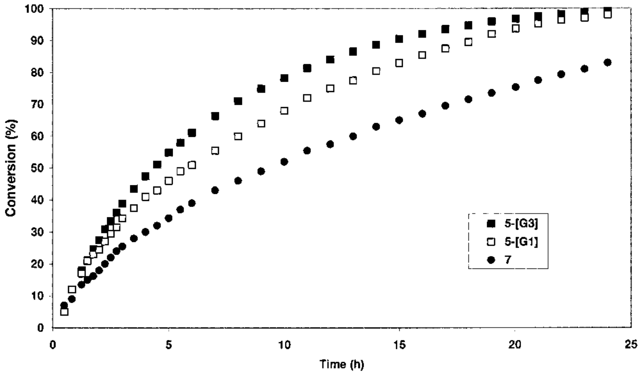
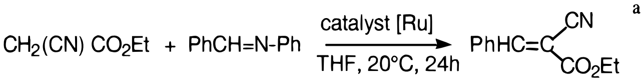


Figure 3. Knoevenagel condensation involving malonitrile and cyclohexanone with dendrimer **5-[G$_1$]** or **5-[G$_1$]** or with monomer **7** as catalyst.

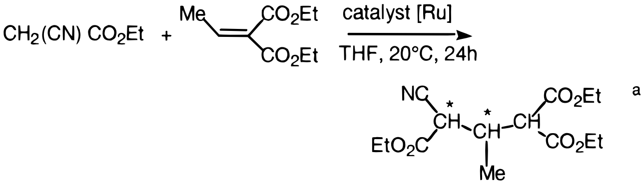
Table 4. Knoevenagel Condensation Involving Ethyl Cyanoacetate and *N*-Benzylideneaniline



entry	catalyst	(mol % Ru)	conversion %	ref
1	**5-[G$_3$]**	(1)	100	this work
1′	**5-[G$_3$]** (recov)	(1)	100	this work
1″	**5-[G$_3$]** (recov)	(1)	99	this work
2	**6**	(3)	82[b]	20

[a] Typical conditions: ethyl cyanoacetate (1.660 mL, 15.594 mmol), *N*-benzylideneaniline (3.109 g, 17.154 mmol), **5-[G$_3$]** (0.210 g, 0.0065 mmol). [b] Isolated yield after distillation.

Table 5. Diasteroselective Michael Addition Involving Ethyl Cyanoacetate and Diethyl Ethylidenemalonate



entry	catalyst	(mol % Ru)	conversion %	diast ratio[b]	ref
1	**6**	(3)	100[c]	69/31	20
2	**5-[G$_3$]**	(1)	100	73/27	this work
2′	**5-[G$_3$]** (recov)	(1)	100	73/27	this work
2″	**5-[G$_3$]** (recov)	(1)	90	73/27	this work
3	**9**	(1)	100	72/28	this work
3′	**9** (recov)	(1)	100	72/28	this work
3″	**9** (recov)	(1)	89	72/28	this work

[a] Typical conditions: NCCH$_2$CO$_2$Et (1.976 mL, 18.565 mmol), CH$_3$CH=C(CO$_2$Et)$_2$ (3.732 mL, 20.421 mmol), **5-[G$_3$]** (0.250 g, 0.0077 mmol), THF (20 mL); or NCCH$_2$CO$_2$Et (0.990 mL, 9.30 mmol), CH$_3$CH=C(CO$_2$Et)$_2$ (1.869 mL, 10.23 mmol), **9** (0.540 g, 0.093 mmol), THF (20 mL). [b] Determined by ^{1}H NMR (Bruker AMX 400). [c] 90% isolated yield.

as dendrimer **5-[G$_3$]**. Complex **5-[G$_3$]** was also found to be an efficient recoverable multicenter catalyst in the reaction of ethyl cyanoacetate with *N*-benzylideneaniline with high yield of ethyl benzylidenecyanoacetate (Table 4, entries 1, 1′, 1″).

The low-valent ruthenium hydride complex **6** also catalyzed the Michael addition of activated methylene compounds to activated olefins. In the example reported in Table 5, the use of 3 mol % of **6** allowed Murahashi et al.[20] to obtain the Michael adduct (100% conversion) with a diastereoisomer ratio of 69/31 (Table 5, entry 1). Under the same experimental conditions (THF, room temperature, 24 h) 100% conversion was obtained using 1 mol % metal of **5-[G$_3$]** (instead of 3 mol % of **6**), without significant change in the diastereoisomeric ratio. Recycling the catalyst by precipitation with ether is possible without loss of activity and selectivity (Table 5 entries 2, 2′, 2″).

Complex **9**, composed of a dendrimer of generation 3 bearing only one metallic center located at the core, was prepared by reacting the dendrimer **8**[21] with RuH$_2$(PPh$_3$)$_4$. It was expected that steric hindrance around the metallic center due to the dendrimer shell might change significantly the diastereoselectivity of such a reaction. Indeed **9** (1 mol %) appeared to be as effective as **5-[G$_3$]** and can be recycled several times without loss of activity but unfortunately did not exhibit higher substrate selectivity (Table 5, entries 3, 3′, 3″).

In conclusion, the efficiency of several metalladendrimers as catalysts in three general organic syntheses has been fully demonstrated. Activity can be compared with that of classical monomer complexes and is often higher, but in marked contrast with these monomers, recycling is possible without significant loss of activity. Investigations are underway in order to have a better insight into these catalytic processes and to extend the use of these dendrimers for reactions of industrial interest.

Experimental Section

All manipulations were carried out with standard high-vacuum and dry-argon techniques. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded with Bruker AC200, AC250, DPX300, or AMX 400 spectrometers. References for NMR chemical shifts are 85% H$_3$PO$_4$ for ^{31}P NMR and SiMe$_4$ for ^{1}H and ^{13}C NMR. The attribution of ^{13}C NMR signals has been done using Jmod, two-dimensional HMBC and HMQC, broad band, or CW ^{31}P decoupling experiments when necessary. The numbering used for NMR is shown Figure 4. Compounds **1-[G$_1$]**,[10] **1-[G$_3$]**,[10] **5-[G$_3$]**,[12] and **8**[21] were prepared according to published procedures.

Synthesis of the Ligand Me$_2$N−N(CH$_2$PPh$_2$)$_2$. Neat diphenylphosphine (4 mL, 23.032 mmol) and paraformaldehyde (0.691 g, 23.032 mmol) are heated for 2 h at 120 °C in a Schlenk tube to give Ph$_2$PCH$_2$OH. Then a solution of 1,1-dimethylhydrazine (0.700 mL, 9.213 mmol) in THF (5 mL) was added, and the resulting mixture was heated at 50 °C for 12 h under stirring. The solvent was removed under vacuum, and the excess of diphenylphosphine was removed by distillation, to give Me$_2$N−N(CH$_2$PPh$_2$)$_2$ as a white powder in 97% yield. ^{31}P{^{1}H}NMR (CDCl$_3$): δ −24.3 (s) ppm. ^{1}H NMR (CDCl$_3$): δ 2.2 (s, 6H, CH$_3$), 3.6 (d, $^2J_{HP} = 4.5$ Hz, 4H, CH$_2$); 7.0−7.3 (m, 20H, CHarom) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 38.8 (s, CH$_3$), 53.3 (d, $^1J_{CP} = 5.0$ Hz, CH$_2$) 128.2 (d, $^3J_{CP} = 7.5$ Hz, *m*-C$_6$H$_5$), 128.5 (s, *p*-C$_6$H$_5$), 133.3 (d, $^2J_{CP} = 17.9$ Hz, *o*-C$_6$H$_5$), 138.4 (d, $^1J_{CP} = 13.8$ Hz, *i*-C$_6$H$_5$) ppm. Anal. Calcd for C$_{28}$H$_{30}$N$_2$P$_2$ (456.5): C, 73.67; H, 6.62; N, 6.13. Found: C, 73.54; H, 6.50; N, 6.26.

Synthesis of the Ruthenium Monomer Complex 7. To a solution of RuH$_2$(PPh$_3$)$_4$ (1 g; 0.87 mmol) in THF (80 mL) was added a THF solution (20 mL) of Me$_2$N−N(CH$_2$PPh$_2$)$_2$ (0.4 g; 0.87 mmol). The mixture was stirred for 2 h in the dark, after which the solution was filtered and evaporated to dryness under vacuum. The light yellow residue was washed several times with pentane and dried under vacuum. Yield: 56%.

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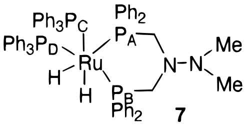
(21) Maraval, V.; Laurent, R.; Caminade, A. M.; Majoral, J. P. *J. Am. Chem. Soc.* **2000**, *122*, 2499.



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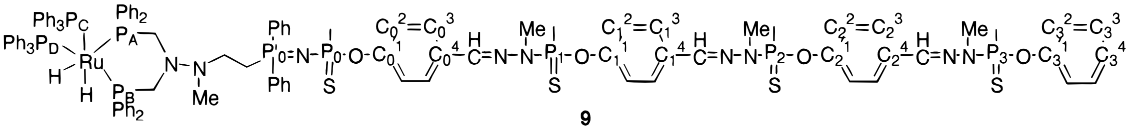

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Figure 4. Numbering used for NMR for complexes **7** and **9**.

^{31}P{^{1}H} NMR (THF-d_8): δ 23.4 (“q”, $^2J_{PPcis} = 21$ Hz, P$_A$), 39.8 (ddd, $^2J_{PPtrans} = 224$ Hz, $^2J_{PBPA} = 21$ Hz, $^2J_{PBPC} = 15$ Hz, P$_B$), 47.1 (“t”d, $^2J_{PPcis} = 21$ Hz,$^2J_{PCPB}$= 15 Hz, P$_C$), 57.1 (d“t”, $^2J_{PPtrans} = 224$ Hz, $^2J_{PPcis} = 21$ Hz, P$_D$). ^{1}H NMR (THF-d_8): δ −10.4 (“dqd”, $^2J_{HPtrans} = 67$ Hz, $^2J_{HPcis} = 31$ Hz,$^2J_{H-H} = 6.5$ Hz, 1 H, H_{trans}-Ru−PPh$_3$), −9.3 (ddddd, $^2J_{HPtrans} = 71$ Hz, $^2J_{HPcis} = 39$ Hz,$^2J_{HPcis} = 23$ Hz, $^2J_{HPcis} = 15$ Hz, $^2J_{H-H} = 6.5$ Hz, 1H, H_{trans}-Ru−PPh$_2$), 2.1 (s, 6 H, CH$_3$−N−), 3.0 (t, $^2J_{HP} = {}^2J_{HH} = 11$ Hz, 1H, N−CH_2−P$_A$Ph$_2$), 3.2 (t, $^2J_{HP} = {}^2J_{HH} = 11$ Hz, 1H, N-CH_2−P$_B$Ph$_2$), 3.7 (t, $^2J_{HP} = {}^2J_{HH} = 11$ Hz, 1H, N−CH_2−P$_A$-Ph$_2$), 3.9 (t, $^2J_{HP} = {}^2J_{HH} = 11$ Hz, 1 H, N−CH_2−P$_B$Ph$_2$), 6.7−7.4 (m, 50 H, CH arom.). ^{13}C{^{1}H} NMR (THF-d_8): δ 38.4 (s, CH$_3$−N), 53.6 (d, $^1J_{CP} = 27$ Hz, CH$_2$−P$_B$), 60.5 (br d, $^1J_{CP} = 27$ Hz, CH$_2$−P$_A$), 126.5 (d, $^3J_{CP} = 7.5$ Hz, m-C$_6$H$_5$−P$_A$), 126.6 (d, $^3J_{CP} = 7.5$ Hz, m-C$_6$H$_5$−P$_B$), 126.9 (d, $^3J_{CP} = 7.5$ Hz, m-C$_6$H$_5$−P$_D$), 127.3 (d, $^3J_{CP} = 7.5$ Hz, m-C$_6$H$_5$−P$_C$), 127.35 (d, $^3J_{CP} = 7.5$ Hz, m-C$_6$H$_5$−P$_B$), 127.6 (d, $^3J_{CP} = 7.5$ Hz, m-C$_6$H$_5$−P$_A$), 127.6, 127.8, 127.9, 128.1 (4s, p-C$_6$H$_5$−P$_{A,B,C,D}$), 132.1 (d, $^2J_{CP} = 9$ Hz, o-C$_6$H$_5$−P$_B$), 132.7 (d, $^2J_{CP} = 9$ Hz, o-C$_6$H$_5$−P$_A$), 134.4 (d, $^2J_{CP} = 11$ Hz, o-C$_6$H$_5$−P$_B$ and o-C$_6$H$_5$−P$_D$), 134.6 (d, $^2J_{CP} = 15$ Hz, o-C$_6$H$_5$−P$_C$), 134.9 (d, $^2J_{CP} = 15$ Hz, o-C$_6$H$_5$−P$_A$), 141.1 (dd, $^1J_{CP} = 15$ Hz, $^3J_{CP} = 6$ Hz, i-C$_6$H$_5$−P$_A$), 142.6 (br d, $^1J_{CP} = 23$ Hz, i-C$_6$H$_5$−P$_C$), 143.4 (br d, $^1J_{CP} = 31$ Hz, i-C$_6$H$_5$−P$_B$), 143.6 (dd, $^1J_{CP} = 38$ Hz, $^3J_{CP} = 4$ Hz, i-C$_6$H$_5$−P$_D$), 145.6 (dd, $^1J_{CP} = 53$ Hz, $^3J_{CP} = 6$ Hz, i-C$_6$H$_5$−P$_B$), 149.1 (dd, $^1J_{CP} = 38$ Hz, $^3J_{CP} = 6$ Hz, i-C$_6$H$_5$−P$_A$). Anal. Calcd for $C_{64}H_{62}N_2P_4Ru$ (1084): C, 70.90; H, 5.76; N, 2.58. Found: C, 71.12; H, 5.55; N, 2.76.

Synthesis of the Ruthenium Dendrimer Complex 9. To a solution of RuH$_2$(PPh$_3$)$_4$ (0,1 g; 0.087 mmol) in THF (20 mL) was added a THF solution (10 mL) of the dendron **8** (0.45 g; 0.0087 mmol). The mixture was stirred for 2 h in the dark, after which the solution was filtered and evaporated to dryness under vacuum. The light yellow residue was washed several times with pentane and dried under vacuum. Yield: 88%.

^{31}P{^{1}H} NMR (THF-d_8): δ 21.6 (d, $^2J_{PP} = 34$ Hz, P′$_0$), 25.2 (br s, P$_A$), 40 (br d, $^2J_{PPtrans}$= 225 Hz, P$_B$), 46.7 (“q”, $^2J_{PPcis} = 18$ Hz, P$_C$), 55.1 (d, $^2J_{PP} = 34$ Hz, P$_0$), 56.9 (d“t”, $^2J_{PPtrans} = 225$ Hz, $^2J_{PPcis} = 21$ Hz, P$_D$), 65.6 (s, P$_1$, P$_2$, P$_3$). ^{1}H NMR (THF-d_8): δ −10.4 (dq, $^2J_{HPtrans} = 60$ Hz, $^2J_{HPcis} = 30$ Hz, 1H, H_{trans}-Ru−PPh$_3$, −9.3 (m, 1H, H_{trans}-Ru−PPh$_2$), 2.1 (s, 3 H, CH_3−N−CH$_2$−), 2.4 (m, 2H, CH$_2$−P′$_0$), 2.6 (m, 2H, CH_2−CH$_2$−P′$_0$), 2.9 (br s, 1H, N-CH_2−P$_A$Ph$_2$), 3.2 (br s, 1H, N−CH_2−P$_B$Ph$_2$), 3.4 (br d,$^3J_{HP} = 10.2$ Hz, 42 H, CH$_3$−N−P$_{1,2,3}$), 3.6 (br s, 1H, N-CH_2−P$_A$Ph$_2$), 3.9 (br s, 1H, N−CH_2−P$_B$Ph$_2$), 6.6−7.9 (m, 210H, CH arom and CH═N). ^{13}C{^{1}H} NMR (THF-d_8): δ 29.5 (d, $^1J_{CP} = 57$ Hz, CH$_2$−P′$_0$), 32.7 (d, $^2J_{CP} = 12.7$ Hz, CH$_3$−N−P$_{1,2,3}$), 34.5 (s, CH_3−N−CH$_2$), 44.7 (s, N−CH_2−CH$_2$−P′$_0$), 51.4 (d, $^1J_{CP} = 25$ Hz, CH$_2$−P$_B$), 59 (d, $^1J_{CP} = 25$ Hz, CH$_2$−P$_A$), 121.7 (d, $^3J_{CP} = 4.5$ Hz, C$_3$2), 122 (d, $^3J_{CP} = 4.5$ Hz, C$_0$2, C$_1$2, C$_2$2), 125.4 (s, C$_3$4), 126.5 (br d, $^3J_{CP} = 7$ Hz, m-C$_6$H$_5$−P$_{A,B}$), 127 (br d, $^3J_{CP} = 7$ Hz, m-C$_6$H$_5$−P$_D$), 127.3 (br d, $^3J_{CP} = 7$ Hz, m-C$_6$H$_5$−P$_C$), 128.2 (br s, p-C$_6$H$_5$−P$_{A,B,C,D}$), 128.4 (s, C$_2$3), 128.5 (s, C$_1$3, C$_0$3), 128.8 (d, $^3J_{CP} = 12$ Hz, m-C$_6$H$_5$−P′$_0$), 129.7 (s, C_3^3), 132 (s, C_0^4), 132.4 (d, $^2J_{CP} = 9.5$ Hz, o-C$_6$H$_5$−P′$_0$), 133 (s, C_1^4), 133.1 (s, C_2^4), 133.4 (s, p-C$_6$H$_5$−P′$_0$), 134.4 (d, $^2J_{CP} = 15$ Hz, o-C$_6$H$_5$−P$_{B,D}$), 134.7 (br d, $^2J_{CP} = 15$ Hz, o-C$_6$H$_5$−P$_{A,C}$), 139.4 (d, $^3J_{CP} = 13.4$ Hz, CH═N−N−P$_3$), 140 (d, $^3J_{CP} = 13.3$ Hz, CH═N−N−P$_2$), 140.5 (d, $^3J_{CP} = 10.8$ Hz, CH═N−N−P$_1$), 151.4 (d, $^2J_{CP} = 7$ Hz, C_3^1), 151.9 (d, $^2J_{CP} = 6.8$ Hz, C_2^1, C_1^1), 153.8 (d, $^2J_{CP} = 8$ Hz, C_0^1). Anal. Calcd for $C_{285}H_{265}N_{31}O_{30}P_{20}S_{15}Ru$ (5806): C, 58.95; H, 4.61; N, 7.47. Found: C, 58.82; H, 4.52; N, 7.36.

General Conditions for Catalysis Experiments. For the procedure, see Tables 1−5. Degassed and distilled ether (100 mL) was added to the THF or DMF solution to precipitate the catalyst when the reaction has gone to completion. After filtration, the dendrimer complex was washed with ether (15 mL) and dried under vacuum. For reuse the resulting powder was solubilized in THF or DMF and the starting reagents were added to the resulting solution.

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