Organometallics **1997,** *16,* 3489−3497

Ruthenium Hydride and Dihydrogen Complexes with Dendrimeric Multidentate Ligands

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Received February 6, 1997[⊗]

The reaction of the ruthenium polyhydrides RuH$_2$(PPh$_3$)$_4$ and RuH$_2$(H$_2$)$_2$(PCy$_3$)$_2$ with the previously reported dendrimers G*x*-N(CH$_2$PPh$_2$)$_2$ (first, second, and third generations; G$_1$, G$_2$, and G$_3$) cleanly leads to the new complexes [G$_x$-N(CH$_2$PPh$_2$)$_2$]RuH$_2$(PPh$_3$)$_2$ (**1-G$_x$**) and [G$_x$-N(CH$_2$PPh$_2$)$_2$]RuH$_2$(H$_2$)(PCy$_3$), which exist as a mixture of isomers (**3′-G$_x$, 3″-G$_x$**, **4′-G$_x$**, and **4″-G$_x$**). Complexes **3-G$_x$/4-G$_x$** were shown to accommodate a stretched dihydrogen ligand and to display a high temperature for the minimum of the T_1 relaxation time, in agreement with their binding to the dendrimer in solution. The reactivity of these complexes with CO, leading to new dihydrido carbonyl ruthenium complexes (**2-G$_x$**, **5-G$_x$**), is described.

The search for new catalytic systems has stimulated the design of new ligands in organometallic chemistry over the past few years. In this respect, the recent development of dendrimeric molecules[1] has attracted a considerable interest as potential ligands. Examples of complexes of group 6−11 have been recently prepared[2−9] and some catalytic applications have been studied, such as the Kharash addition of polyhalogenoalkanes to carbon-carbon double bonds.[8] The expected advantage of dendrimeric ligands concerns first the catalyst recovery, which could be a valuable alternative to stabilization at the surface of a polymer or to biphasic reactions. Furthermore, the stabilization of reactive complexes at the surface of dendrimers could allow regioselectivity enhancements as a result of the blocking of conformations due to the steric crowding induced by the dendrimer.

Some of us have recently elaborated the synthesis of phosphorus-containing dendrimers up to the tenth generation.[10] The surface of these dendrimers could be functionalized with phosphine groups, hence allowing metal coordination. In particular, gold coordination allowed imaging of consecutive generations[7a] and the grafting of diphosphino groups allowed the synthesis of rhodium, palladium, and platinum complexes.[11] Some simple reactions such as CO or olefin insertion were carried out in the case of the palladium complex, but in general, the dendrimer complexes displayed a lower reactivity than their mononuclear counterparts. The origin of this phenomenon could be the steric bulk at the surface of the dendrimer, problems linked to the size of the dendrimer, namely diffusion of the reactants, or simply the stabilization of the complexes by several functions present in the dendrimers.

In order to gain a more precise knowledge of the reactivity of dendrimer/metal complexes, we chose to

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[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1997.

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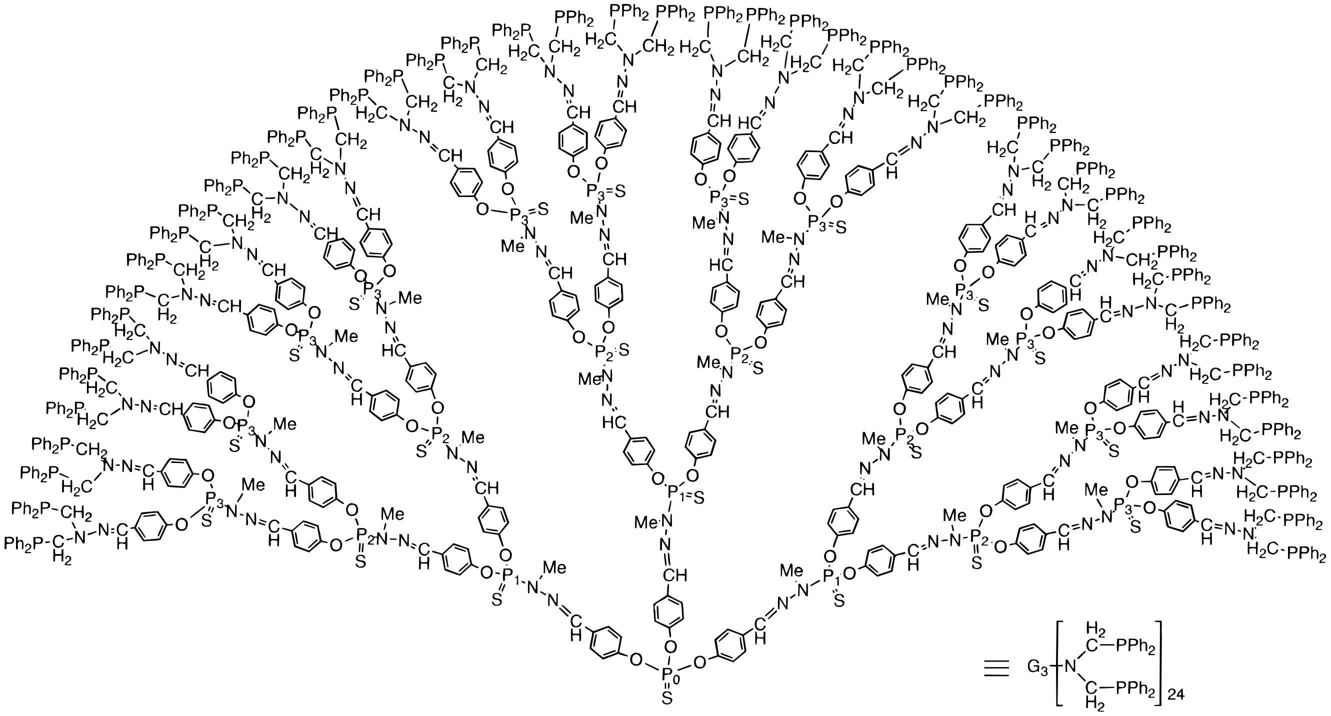
S0276-7333(97)00092-7 CCC: $14.00

Chart 1. Structure of the Dendrimer Used in This Study



study ruthenium hydride and dihydrogen derivatives. Numerous examples of both types of complexes are known, their reactivity, whether stoichiometric or catalytic, is very rich, and their spectroscopic properties, in particular for the dihydrogen complexes, is very sensitive to subtle electronic or steric modifications of their environment.[12–15] We describe in this paper the preparation of a series of new ruthenium dihydride and dihydrido dihydrogen derivatives linked to dendrimers bearing diphosphine functionalities.

The dendrimers used in this study were prepared according to a known procedure starting from a pentavalent phosphorus containing a P=S moiety. This group was repeated at each generation (see Chart 1). Addition of hydrazine to dendrimers of generation 1–3, accommodating 6–24 terminal aldehyde groups, gave rise quantitatively to new dendrimers containing $CH{=}NNH_2$ end groups. Reactions with the phosphine Ph_2PCH_2OH (2 equiv of phosphine per NH_2 group) led to dendrimeric diphosphine ligands possessing from 6 to 24 $N(CH_2PPh_2)_2$ terminal groups (G1-$N(CH_2PPh_2)_2$–G3-$N(CH_2PPh_2)_2$) (see Chart 1).

The reaction of $RuH_2(PPh_3)_4$[12] with the diphosphine dendrimers G1-$N(CH_2PPh_2)_2$ at room temperature in toluene cleanly leads within 2 h to the substitution of two triphenylphosphine ligands and formation of [G_1-$N(CH_2PPh_2)_2$]$RuH_2(PPh_3)_2$ (**1-G₁**), containing 6 ruthenium moieties linked to the dendrimer. The reaction proceeds similarly with dendrimers of higher generation to give **1-G₂** and **1-G₃** containing respectively 12 and 24 ruthenium moieties linked to each dendrimer. The spectroscopic properties of these compounds were found to be very similar. An ABMX spin system is observed in ^{31}P NMR spectroscopy for the four phosphino groups attached to ruthenium, which are observed respectively for the first generation (81 MHz, δ, C_6D_6) at 20.6 ppm (P_A, q, $^2J_{PP_{cis}} = 19.3$ Hz, PPh_2), 36.6 ppm (P_B, dt, $^2J_{PP_{trans}} = 227.4$ Hz, $^2J_{PP_{cis}} = 15.4$ Hz, PPh_2), 44.0 ppm (P_C, q, $^2J_{PP_{cis}} = 19.3$ Hz, PPh_3), and 54.3 ppm (P_D, dt, $^2J_{PP_{trans}} = 227.4$ Hz, $^2J_{PP_{cis}} = 19.3$ Hz, PPh_2). The signal for P_0, the phosphorus at the core of the dendrimer (see Chart 1), overlaps that of P_D, whereas the signal of P_1, the pentavalent phosphorus starting the first generation, is found at 63.2 ppm (s). The large J_{BD} coupling constant of 227 Hz indicates the mutual trans arrangement of P_B and P_D, whereas all $J_{PP_{cis}}$ coupling constants are found to be the same (19.3 Hz). For generations 2 and 3, the values found for the different signals are virtually identical (see Experimental Section and Figure 1). The only significant changes are for the $^2J_{PP_{cis}}$ coupling constants, which are 15.4 Hz for generation 2 and 16.9 Hz for generation 3. The signals for the pentavalent P=S groups starting generations 2 and 3 (P_2 and P_3) overlap with the signal of P_1. The ^1H NMR spectra (200 and 400 MHz, δ, C_6D_6) show, besides phenyl protons, the methylene groups attached to the phosphine end of the dendrimers between 4.0 and 4.7 ppm and the methyl groups attached to nitrogen next to the dendrimer P=S functions (see Chart 1) near 3.0 ppm. The most salient features of these spectra are the observations of hydride signals found for the first generation at −9.90 (H_a) and −8.66 (H_b) ppm. The coupling pattern of the hydride signals is complex since for H_a it consists of a doublet of doublets of quartets

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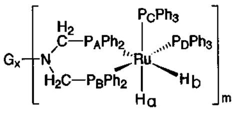

1-G$_x$

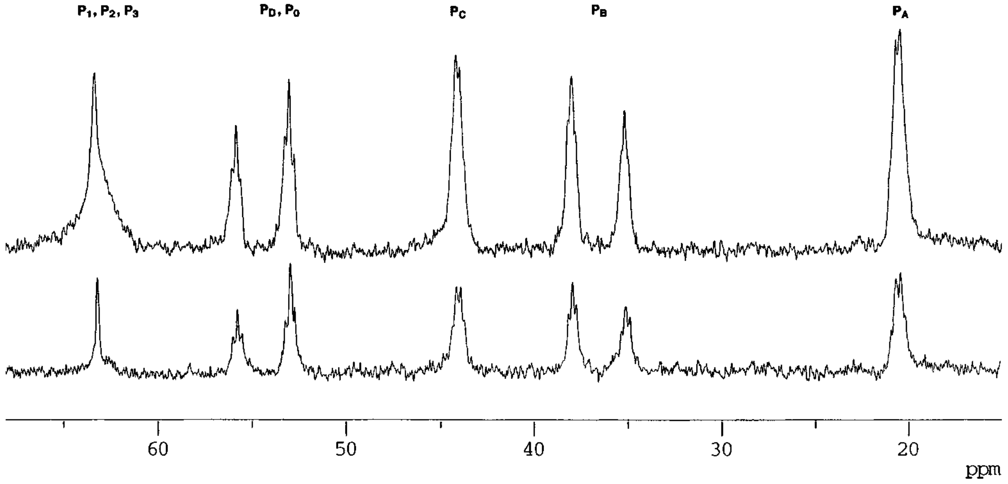

Figure 1. ^{31} P NMR spectra (161.923 MHz, C_7D_8, 293 K) of **1-[G$_1$]** (lower spectrum) and **1-[G$_3$]** (upper spectrum).

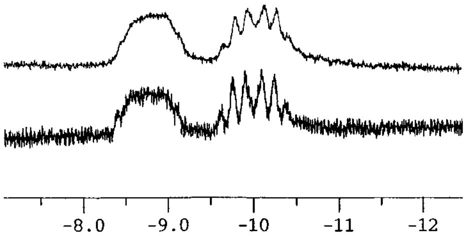

Figure 2. High-field ^{1}H NMR spectra (400 MHz, C_7D_8, 293 K) of **1-[G$_1$]** (lower spectrum) and **1-[G$_3$]** (upper spectrum).

with $^2J_{HP_{trans}} = 66.0$ Hz, $^2J_{HP_{cis}} = 30.5$ Hz and $^2J_{HH} = 4$ Hz. The signal for H_b is broader (see Figure 2) and the coupling constants were not determined with precision. As for the $^{31}P\{^1H\}$ NMR spectra, little change is observed for the ^{1}H NMR spectra according to the dendrimer generations (see experimental) except for a further broadening of the signal of H_b. In all cases, the hydrides are observed near −8.8 (br) and −10.0 ppm (dq, $J_{HP_{trans}}$ = ca. 67 Hz, $J_{HP_{cis}}$ = ca. 30 Hz). This allows us to attribute to the new complexes named hereafter **1-G$_1$**/**1-G$_3$** the all-cis structure, similar to that of $RuH_2(PPh_3)_2(dppm)$,[16] shown in Chart 1, in which P_A and P_B represent the diphenylphosphino groups linked to the dendrimer and P_C and P_D the triphenylphosphine ligands. A complete attribution of the spectra was realized by carrying out a two-dimensional GE HMQC $^1H-^{31}P\{^{31}P\}$ experiment (see Figure 3), which demonstrated the relative trans position of H_a to P_C and of H_b to P_A. Interestingly, in all cases, the Ru−H stretches are clearly visible by infrared spectroscopy near 1950 and 1860 cm^{-1}.

The reactivity of these complexes was found to be very limited. No reaction was observed with $CHCl_3$ (room temperature), which contrasts with the reactivity of the starting complex, whereas with olefin (styrene, 1-hexene, ethylene) highly insoluble compounds were formed which could not be characterized.

In order to evaluate the steric congestion of the dendrimer surface after ruthenium incorporation, molecular modeling using the Cache program was undertaken. The results are shown on Figure 4 and demonstrate that the poor reactivity of these derivatives is not due to problems related to the dendrimer but rather to steric congestion around each individual ruthenium complex and stabilization of the complex by the diphosphine ligand.

However, the three complexes reacted slowly with CO (3 bar, overnight) in toluene to give cleanly the corresponding dihydrido carbonyl derivatives **2-G$_1$**, **2-G$_2$**, and **2-G$_3$**. No intermediate or further reaction product was detected by NMR monitoring of the reaction. The incorporation of CO into the complex can be monitored by the appearance of a strong band near 1950 cm^{-1} in infrared spectroscopy. Compounds **2-G$_1$**, **2-G$_2$**, and **2-G$_3$** display in $^{31}P\{^1H\}$ NMR spectra (81 MHz, δ, C_6D_6) a characteristic AMX pattern for the phosphino groups linked to ruthenium. For the first generation, a broad triplet is observed for P_A at 25.3 ppm ($-PPh_2$), a doublet of doublets for P_B at 41.8 ppm ($^2J_{PP_{trans}} = 231.5$ Hz, $^2J_{PP_{cis}} = 22.5$ Hz, $-PPh_2$) and a doublet of doublets for P_C (PPh_3) at 58.9 ppm. In addition, the peaks of the dendrimer P=S groups are observed at 53.0 ppm (s, P_0) and 63.1 ppm (s, P_1) as in complex **1-G$_1$**. The ^{1}H NMR (200 MHz, δ, C_6D_6) shows, as previously noted, peaks attributed to the methyl group of the dendrimer skeleton near 3 ppm (P_1-N-CH_3) and the methylene groups attached to the phosphine ends between 4.0 and 4.5 ppm. In addition, the high-field spectrum at 200 MHz presents a complex structure which results from the superposition of a doublet of triplets at −7.03 ppm for a hydride located trans to a phosphine group ($^2J_{HP_{trans}}$ = 74.2 Hz, $^2J_{HP_{cis}}$ = 20.6 Hz, H_a) and a quartet at −6.69 ppm for a hydride located cis to all phosphorus atoms ($^2J_{HP_{cis}}$ = 20.8 Hz, H_b). The ^{1}H and $^{31}P\{^1H\}$ NMR spectra of the higher generation products (**2-G$_2$** and **2-G$_3$**) are virtually identical with those of **1-G$_2$**, except

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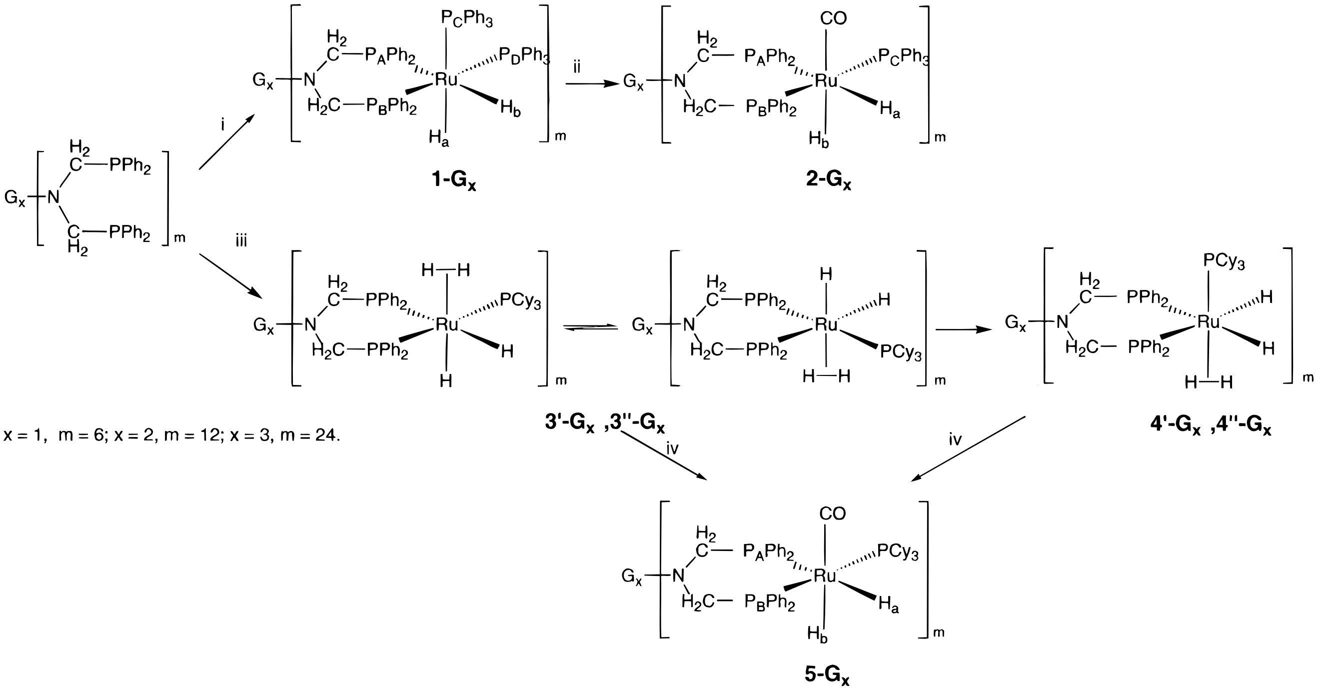
[16] Chaudret, B.; Commenges, G.; Poilblanc, R. *J. Chem. Soc., Dalton Trans.* **1984**, 1635.

Scheme 1. Reaction of $RuH_2(PPh_3)_4$ and of $RuH_2(H_2)_2(PCy_3)_2$ with Dendrimer Diphosphines[a]



[a] Reactants: (i) $RuH_2(PPh_3)_4$; (ii) CO; (iii) $RuH_2(H_2)_2(PCy_3)_2$; (iv) CO.

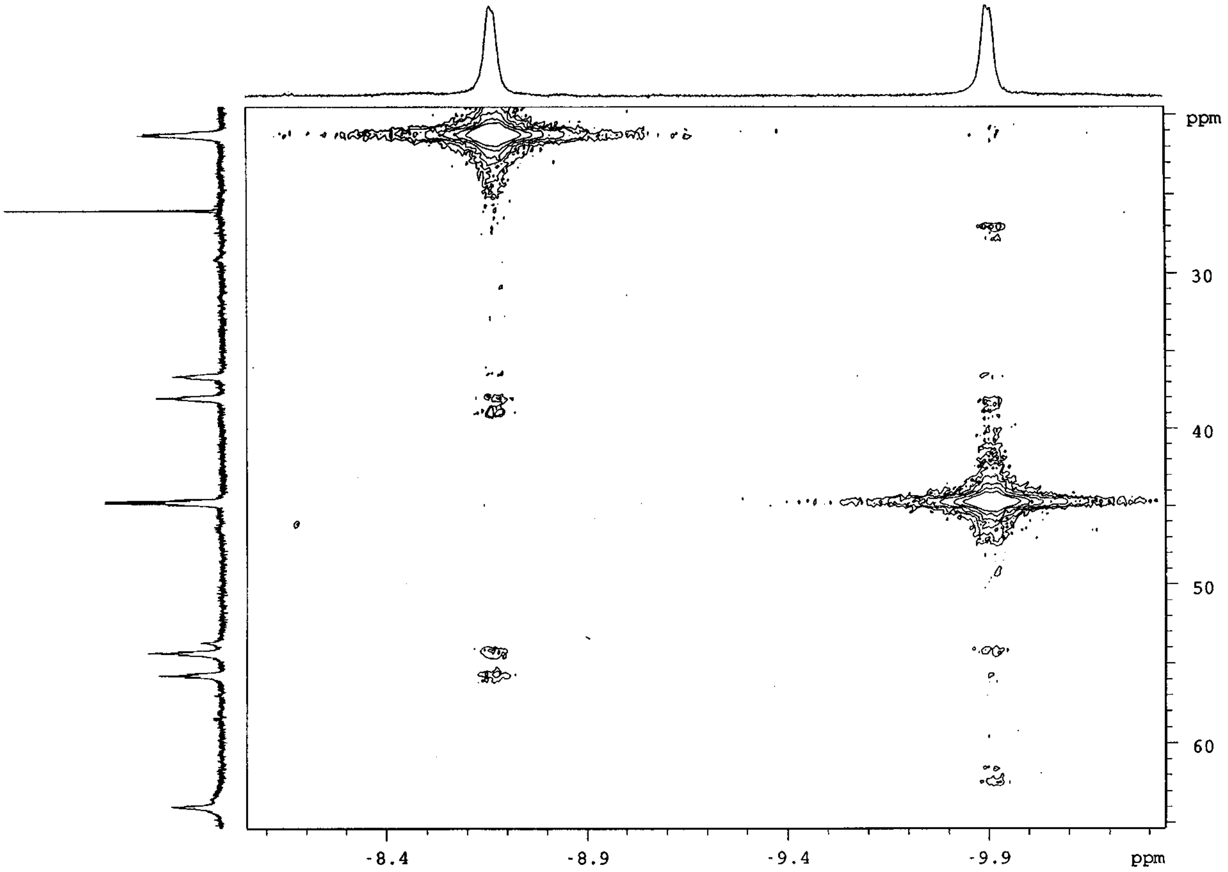


Figure 3. GE HMQC $^{1}H-^{31}P\{^{31}P\}$ spectrum of **1-[G$_1$]** showing the coupling of H_a to P_C and of H_b to P_A (the sharp peak at 26 ppm is due to triphenylphosphine oxide formed by oxidation of PPh_3 liberated in the reaction mixture).

for a broadening probably originating in the longer correlation time of the dendrimeric complex.

These complexes adopt the geometry shown in Scheme 1, in which the triphenylphosphine ligand is located trans to one arm of the dendrimer diphosphine and the CO group is trans to a hydride, as demonstrated above by ^{1}H and ^{31}P NMR spectroscopy. This structure is similar to that of the known mononuclear complex $RuH_2(CO)(PPh_3)(L_2)$.[17]

In order to have access to a more reactive ruthenium

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[17] Jung, C. W.; Garrou, P. E. *Organometallics* **1982**, *1*, 658.

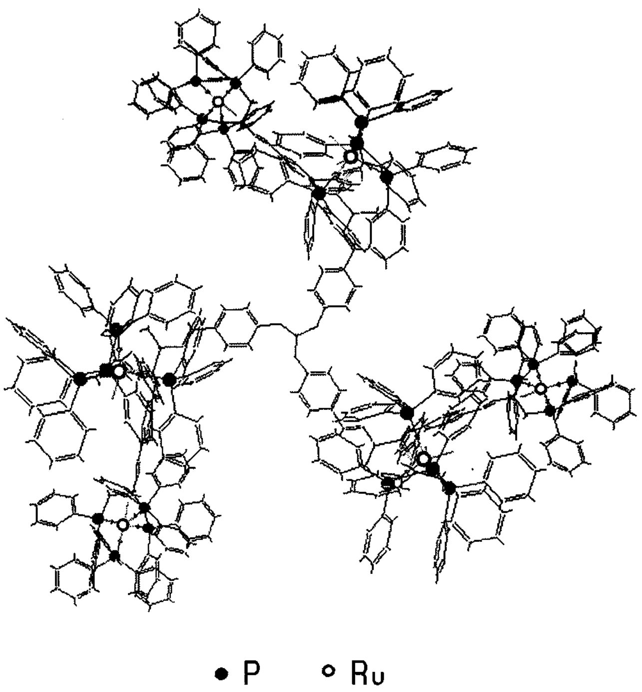

Figure 4. Calculated molecular model of **1-[G$_1$]**.

site, the dendrimer diphosphines were reacted with the bis(dihydrogen) complex $RuH_2(H_2)_2(PCy_3)_2$.[15a,b] In this case, the reaction sequence was more complex. When the reaction was performed at −50 °C in the absence of stirring in d_8-toluene, the first complex **3′-G$_1$** forms rapidly. It shows a broad hydride signal at −7.38 ppm in ^1H NMR and an AX_2 pattern in ^{31}P NMR (67.3 ppm, t, PCy_3; 38.7 ppm, d, $-PPh_2$; $^2J_{PP} = 105.3$ Hz). In addition, the pentavalent phosphorus sulfide groups of the dendrimer backbone (respectively P_0 and P_1, see Chart 1) are observed at 53.0 and 63.1 ppm. When the reaction mixture is left at room temperature and the reaction monitored by NMR spectroscopy, new compounds are detected, namely first **3″-G$_1$**, which disappeared together with **3′-G$_1$** after a few hours. Compound **3″-G$_1$** shows a broad hydride signal at −7.66 ppm and a ^{31}P NMR pattern similar to that of **3′-G$_1$** (43.0 ppm, d, $^2J_{PP} = 102.1$ Hz, $-PPh_2$; 53.0 ppm, s, P_0; 63.2 ppm, s, P_1; 66.9 ppm,t, $^2J_{PP} = 102.1$ Hz, PCy_3).

After 4 h in solution the compounds "**3**" (**3′-G$_1$** and **3″-G$_1$**) have disappeared at the benefit of a new family of compounds "**4**" (**4′-G$_1$** and **4″-G$_1$**). **4′-G$_1$** appears first and shows a quartet pattern in ^1H NMR at −8.53 ppm ($J_{PH} = 13$ Hz) and an AX_2 pattern in ^{31}P NMR but with a reduced P−P coupling constant compared to complexes **3** (65.6 ppm, d [$-PPh_2$]; 57.9 ppm, t [PCy_3], $J_{PP} = 15.4$ Hz; 53.0 ppm, s, P_0; 63.2 ppm, s, P_1). Finally, **4″-G$_1$**, displaying a geometry similar to that of **4′-G$_1$** forms (^1H NMR [200 MHz, C_6D_6], −8.06 ppm, q, $^2J_{HP} = 11.8$ Hz; $^{31}P\{^1H\}$ NMR [81 MHz, C_6D_6], 26.6 ppm, t, $^2J_{PP_{cis}} = 21.1$ Hz, PCy_3; 53.0 ppm, s, P_0; 63.2 ppm, s, P_1; 69.2 ppm, d, $-PPh_2$). In benzene, the reaction carried out at room temperature leads first to a mixture of **3′-G$_1$** and **4′-G$_1$**, which after 1 h transforms almost exclusively into **4′-G$_1$**.

The difference between compounds **3** and compounds **4** originates in the geometrical conformation of the phosphine ligands around ruthenium (see Scheme 1). Thus, in the former case the AX_2 pattern in ^{31}P NMR displaying a large P/P coupling constant indicates both the fluxionality of the molecule and the trans position of the PCy_3 ligand toward the dendrimer diphosphine; 106.1 Hz is approximately the mean value between typical trans (200 Hz) and typical cis (10−20 Hz) P−P coupling constants. However, compounds **3**, in which the bulky tricyclohexylphosphine ligand is located far from the dendrimer are surprisingly not the stable isomers and rearrange into compounds **4**, which adopt an "all cis" configuration. All complexes are fluxional, which is apparent in ^{31}P NMR for **3** and in ^1H NMR in all cases. The exact number of hydrides present is at first sight difficult to ascertain from these data. However, the relaxation time of the signals of **4′-G$_1$** and **4″-G$_1$** measured at variable temperatures shows a minimum value of respectively 58 and 48 ms at 293 K (400 MHz). These values are relatively long but are in agreement with the presence of dihydrogen ligands and are comparable to or shorter than the values found by Crabtree et al. for $RuH_2(H_2)(PPh_3)_3$ (38 ms at 205 K, 250 MHz).[13a] Furthermore, the hydride signal found for compounds **4** is very similar to that found for $RuH_2(H_2)(PCy_3)_3$[15a] and we have shown that addition of CO (3 bar) to the **3**−**4** mixture led specifically to the unique new dihydrido carbonyl complex **5-G$_1$**, similar to **2-G$_1$** but accommodating a PCy_3 instead of a PPh_3 ligand (vide infra). We therefore propose that we have synthesized a new series of dihydrido dihydrogen complexes. The minimum of the relaxation time T_1 is found around 50 ms (400 MHz), which is high for a dihydrogen complex and indicates a stretching of the H−H bond as a result of the electronic density of ruthenium, as in $RuH_2(H_2)(PPh_3)_3$ itself (H−H distances have been calculated in the case of third-generation complexes; *vide infra*). The temperature of the minimum is found around 293 K, very different from that observed for mononuclear derivatives, which is close to 240−250 K for such PCy_3 complexes[15] and even lower with less bulky ligands. Polymers usually have longer rotational correlation times than small molecules and so a shift of the temperature of the T_1 minimum to higher values is expected. The observation of a minimum of T_1 at high temperature therefore demonstrates that the ruthenium moiety is bound firmly to the bulky dendrimer, the correlation time of which is very long.

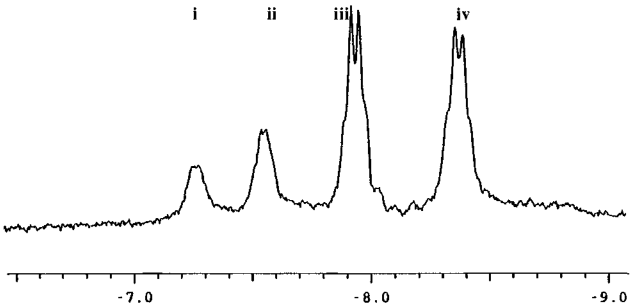

Figure 5. High-field ^1H NMR spectrum (400 MHz, C_7D_8, 313 K) of the mixture **3′-[G$_3$]** (**i**), **3″-[G$_3$]** (**ii**), **4′-[G$_3$]** (**iv**), and **4″-[G$_3$]** (**iii**).

The same chemistry was possible when using a third-generation dendrimer. The reaction with $RuH_2(H_2)_2(PCy_3)_2$ yielded rapidly a mixture of four isomers (**3′-G$_3$**, **3″-G$_3$**, **4′-G$_3$**, and **4″-G$_3$**), comparable to the first-generation system (see Figure 5). The isomerization reactions were, however, slower, which allowed the determination of the relaxation time of the hydride ligands of each isomer. Interestingly, the temperature of the T_1 minimum was found near 273 K, i.e. smaller than that of the first generation, despite the much larger steric bulk induced by the dendrimer. This is probably due to the fact that, as in polymers, relaxation modes other than simple tumbling of the molecule occur in solution: group rotational motion, for example. The minimum T_1 values (400 MHz) were found to be 39 ms for **3′-G$_3$**, 39 ms for **3″-G$_3$**, 43 ms for **4′-G$_3$**, and 49 ms for **4″-G$_3$**. Again these values are relatively long but are in the usual range for stretched dihydrogen complexes. In order to confirm the presence of dihydrogen in complexes **3** and **4** and rule out any effect of the dendrimer, we measured under the same conditions the relaxation time T_1 of the analogous dihydrido carbonyl third-generation derivative (**5-G$_3$**, *vide infra*) and found a minimum value of 460 ms (400 MHz, room temperature). Upon neglecting the effect on relaxation of the presence of two cis-hydride ligands, we could calculate the H−H distance within the coordinated dihydrogen molecules of **3′-G$_3$**, **3″-G$_3$**, **4′-G$_3$**, and **4″-G$_3$** using the value found for **5-G$_3$** as a reference value for all relaxation effects other than those due to the H−H interaction within the coordinated dihydrogen molecule and the methodology developed by Halpern and by Morris.[18] The calculations give respectively 0.89, 0.89, 0.91, and 0.93 Å, assuming a rapid rotation of the dihydrogen ligand, or 1.13, 1.13, 1.15, and 1.18 Å assuming a slow rotation of the dihydrogen ligand. These values are totally comparable to those found for similar mononuclear ruthenium complexes, which suggests that the presence of the large dendrimeric ligand has no effect on the bonding of dihydrogen.

In contrast to mononuclear complexes such as $RuH_2(H_2)(PPh_3)_3$, the dendrimer derivatives exist as a mixture of four isomers, the stable ones adopting an all-cis configuration. The isomerization of compounds **3** into compounds **4** is understandable. The presence of the isomers **3′-G$_x$** and **3″-G$_x$** on one side and **4′-G$_x$** and **4″-G$_x$** on the other (x = 1, 3) is more surprising and cannot be due to the relative position of the phosphine groups, as described above. Furthermore, their presence cannot result from a different arrangement of the hydride and dihydrogen ligands around ruthenium, since like all ruthenium complexes of this type i.e. accommodating both hydride and dihydrogen ligands, complexes **3** and **4** are fluxional down to the lowest temperature we could reach. It is noteworthy that $RuH_2(H_2)_2(PCy_3)_2$ is fluxional down to 130 K in Freons.[19] The only possibility is, therefore, that these isomers reflect the presence of different conformations of dendrimer functions located near the complex (the amino group for example). The reason this isomerization is only observed with hydrides and dihydrogen ligand may be steric (all other possible ligands, including CO, beeing more bulky) or electronic (hydrogen bonding between the nitrogen lone pair and the relatively acidic dihydrogen ligand beeing a possible driving force). Another possibility could be the existence of a dissociative equilibrium between a dihydrido dihydrogen species and a dihydride. However, this can be ruled out on the basis of the NMR and optical properties of our reaction mixture. The only isolated 16-electron complex of this type, $RuH_2[P(tol)_3]_3$ (tol = p-CH_3-C_6H_4), is red and shows a sharp high-field quartet in ^{1}H NMR with large J_{PH} coupling constants.[20]

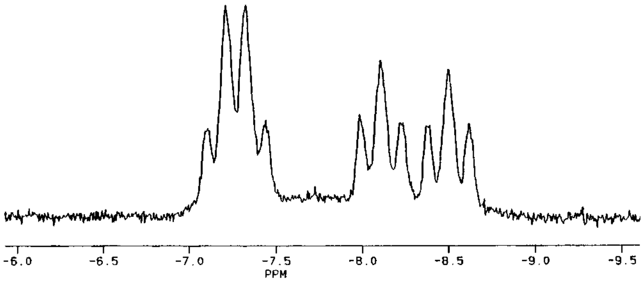

Figure 6. High-field ^{1}H NMR spectrum (200 MHz, C_6D_6, 303 K) of **5-[G$_2$]**.

As mentioned above, the reaction of the mixture of dihydrido dihydrogen isomers with CO leads in the case of the first two generations to only one complex **5-G$_x$**, similar to **2-G$_x$** (x = 1, 2). In the case of the third generation, the reaction produces first a mixture of two dihydrido carbonyl isomers, which rapidly rearrange into only one isomer **5-G$_3$**, displaying the same geometry as **5-G$_1$**, i.e. a geometry in which the PCy_3 ligand is located trans to the dendrimer diphosphine (see Scheme 1). This can be deduced from the observation of a single C−O stretch in infrared spectroscopy near 1940 cm^{-1} and from NMR data. The ^{1}H NMR (200 MHz, C_6D_6) spectra display high-field signals at −8.3 ppm (dt, $^2J_{HP_{trans}}$ = 78.5 Hz, $^2J_{HP_{cis}}$ = 21 Hz, H$_a$,) and −7.3 ppm (q, $^2J_{HP_{cis}}$ = 21 Hz, H$_b$); in contrast to the hydride signals of complexes **2** we do not observe an overlap of the hydride resonances (see Figure 6). The $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6) shows a triplet for P$_A$ at 25.0 ppm (t, $^2J_{PP_{cis}}$ = 21.3 Hz, $-PPh_2$) and two doublets of doublets respectively at 42.2 ppm for P$_B$ ($^2J_{PP_{trans}}$ = 220.0 Hz, $^2J_{PP_{cis}}$ = 21.3 Hz, $-PPh_2$), 53.0 (s, P$_0$), 63.2 (s, P$_1$) and 66.2 ppm for P$_C$ (PCy_3). In addition, the dendrimer phosphorus groups P$_0$ and P$_1$ are observed respectively at 53.0 and 63.2 ppm in the case of the first generation. As stated above, the minimum of the relaxation time T_1 was measured in the case of **5-G$_3$** to be 460 ms at room temperature (400 MHz). This is a normal value for such hydride derivatives, which confirms that, apart from the temperature of the minimum shifted to high temperature, no effect of the dendrimer can be observed on the relaxation of metal-bound hydrides.

In conclusion, we report in this paper the synthesis of a new series of ruthenium complexes linked to dendrimers. They are to the best of our knowledge the first hydride derivatives linked to dendrimers and are therefore good candidates to explore the catalytic properties of these new species. The very characteristic spectroscopic properties of these complexes, in particular the ^{31}P and the high-field ^{1}H NMR spectra, which in mononuclear complexes are very sensitive to subtle changes of their environment, are invariant as a function of the dendrimer generation used as a ligand. This is particularly clear in Figures 1, 2, and 6 but is also true for all compounds prepared in this study. This, in our opinion, is a good indication that, as already

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[18] (a) Desrosiers, P. J.; Cai, P.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173. (b) Bautista, M. T.; Capellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 4876. (c) Moreno, B.; Sabo-Etienne, S.; Chaudret, B.; Rodriguez, A.; Jalon, F.; Trofimenko, S. *J. Am. Chem. Soc.* **1995**, *117*, 7441.

[19] Rodriguez, V.; Sabo-Etienne, S.; Chaudret, B.; Thoburn, J.; Ulrich, S.; Limbach, H.-H.; Eckert, J. Unpublished results.

[20] Arliguie, T.; Chaudret, B.; Morris, R. H. *Polyhedron* **1988**, *7*, 2031.

Table 1. Analyses of Dendrimers

1-[G$_1$]: Anal. Calcd for $C_{438}H_{390}N_{18}O_9P_{28}S_4Ru_6$: C, 68.75; H, 5.15; N, 3.3. Found: C, 67.35; H, 4.8; N, 3.0.
1-[G$_2$]: Anal. Calcd for $C_{900}H_{804}N_{42}O_{21}P_{58}S_{10}Ru_{12}$: C, 68.1; H, 5.1; N, 3.7. Found: C, 65.4; H, 4.75; N, 3.8.
1-[G$_3$]: Anal. Calcd for $C_{1824}H_{1632}N_{90}O_{45}P_{118}S_{22}Ru_{24}$: C, 67.8; H, 5.1; N, 3.9. Found: C, 65.5; H, 4.7; N, 3.95.
2-[G$_1$]: Anal. Calcd for $C_{336}H_{300}N_{18}O_{15}P_{22}S_4Ru_6$: C, 64.6; H, 4.85; N, 4.05. Found: C, 63.15; H, 4.9; N, 4.15.
2-[G$_2$]: Anal. Calcd for $C_{696}H_{624}N_{42}O_{33}P_{46}S_{10}Ru_{12}$: C, 64.0; H, 4.8; N, 4.5. Found: C, 62.25; H, 4.7; N, 4.75.
2-[G$_3$]: Anal. Calcd for $C_{1416}H_{1272}N_{90}O_{69}P_{94}S_{22}Ru_{24}$: C, 63.7; H, 4.8; N, 4.7. Found: C, 62.1; H, 4.8; N, 5.4.
3′-[G$_1$]: Anal. Calcd for $C_{330}H_{420}N_{18}O_9P_{22}S_4Ru_6$: C, 63.95; H, 6.45; N, 4.05. Found: C, 60.7; H, 5.3; N, 4.25.
4′-[G$_1$] + 4″-[G$_1$]: Anal. Calcd for $C_{330}H_{420}N_{18}O_9P_{22}S_4Ru_6$: C, 63.95; H, 6.45; N, 4.05. Found: C, 59.9; H, 5.45; N, 4.25.
5-[G$_1$]: Anal. Calcd for $C_{336}H_{408}N_{18}O_{15}P_{22}S_4Ru_6$: C, 63.5; H, 6.45; N, 3.95. Found: C, 62.85; H, 6.3; N, 4.2.
5-[G$_2$]: Anal. Calcd for $C_{696}H_{840}N_{42}O_{33}P_{46}S_{10}Ru_{12}$: C, 62.95; H, 6.4; N, 4.45. Found: C, 61.95; H, 6.0; N, 5.0.
5-[G$_3$]: Anal. Calcd for $C_{1416}H_{1704}N_{90}O_{69}P_{94}S_{22}Ru_{24}$: C, 62.7; H, 6.35; N, 4.65. Found: C, 61.3; H, 5.75; N, 5.35.

claimed, the growth of the dendrimers does not alter their electronic and steric properties up to a size which is not reached in the relatively small dendrimers used here. The most interesting derivatives contain dihydrogen ligands for which we have calculated in the case of the third generation a H−H distance (ca. 0.9 Å, rapid rotation; ca. 1.15 Å, slow rotation) similar to those calculated for mononuclear ruthenium dihydrogen complexes. The temperature of the T_1 minimum can be used to definitely demonstrate the firm binding of the ruthenium complexes to the dendrimer in solution. The observation of several isomers of the dendrimer dihydrogen complexes is unusual and has to be due to slight modifications of the dendrimer backbone geometry. The presence or absence of some hydrogen bonding between the acidic dihydrogen ligand and the nitrogen lone pair could be at the origin of this phenomenon. Preliminary experiments have demonstrated the relative inertness of the dendrimer complexes **1-G$_x$** and **2-G$_x$** ($x = 1-3$) but this is likely to be due to a steric protection of the ligands around ruthenium, for example the $-N(CH_2PPh_2)_2$ moiety, rather than to a steric hindrance of the dendrimer core. Only substitution of PPh_3 by CO was found to be clean. In contrast, the dendrimer dihydrogen derivatives are reactive. For example the mixture of isomers **3′-G$_1$**, **3″-G$_1$**, **4′-G$_1$**, and **4″-G$_1$**, whatever the relative concentration of each species, reacts cleanly with thiols (RSH) to give a single species which displays spectroscopic properties similar to $RuH(SR)(PPh_3)_3$[21] as well as with silanes and olefins. Furthermore, preliminary catalytic tests indicate a good activity of these compounds for ketone hydrogenation. We are therefore exploring now the reactivity of these new dihydrogen dendrimer complexes.

Experimental Section

General Considerations. All manipulations were carried out with standard high-vacuum or dry argon atmosphere techniques. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AC 200, AC 250, or AMX 400 spectrometer. The NMR chemical shifts are reported in ppm, relative to Me_4Si for ^{1}H and ^{13}C and relative to 85% H_3PO_4 for ^{31}P.

The dendrimeric ligands were synthesized as previously reported.[11]

Reproducibly, problems were observed with the characterization of the new compounds by elemental analysis. They were attributed to the great insolubility of the dendrimer hydride derivatives, which precluded their satisfactory purification, even though the NMR spectra only indicated the presence of a single species in solution. Only **5-[G$_1$]** and **5-[G$_2$]**, which were found to be more soluble and could be redissolved and reprecipitated, gave rise to acceptable analyses. Typical analytical results are given in Table 1. NMR spectra were recorded either on the isolated solids or after performing the reaction in the NMR tube.

Synthesis of 1-[G$_1$]. A 0.112 g (29 μmol) amount of $G_1(PPh_2)_2$ was added to a solution of 0.2 g (0.174 mmol) of $RuH_2(PPh_3)_4$ in 20 mL of toluene. 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 once with diethyl ether (10 mL) and twice with pentane (2 × 10 mL) and then dried under vacuum. Yield: 87%.

1-[G$_1$]: light yellow powder. $^{31}P\{^1H\}$ NMR (81 MHz, δ, C_6D_6): 20.6 (q, $^2J_{PP_{cis}} = 19.3$ Hz, PPh_2 *cis* PPh_3), 36.6 (dt, $^2J_{PP_{trans}} = 227.4$ Hz, PPh_2 *trans* PPh_3), 44.0 (q, PPh_3 *cis* PPh_2), 54.3 (dt, PPh_3 *trans* PPh_2, P_0 overlapped), 63.2 (s, P_1) ppm. ^{1}H NMR (200 MHz, δ, C_6D_6): −9.97 (dq, $^2J_{HP_{trans}} = 66.0$ Hz, $^2J_{HP_{cis}} = 30.5$ Hz, 6H, H^- *trans* PPh_3), −8.75 (br m, 6H, H^- *trans* PPh_2), 2.96 (d, $^3J_{HP_1} = 9.9$ Hz, 9H, P_1-N-CH_3), 4.02 (d, $^2J_{HH} = 8.9$ Hz, 6H, CH_2-P), 4.26 (d, $^2J_{HH} = 12.8$ Hz, 6H, CH_2-P), 4.47 (d, $^2J_{HH} = 12.8$ Hz, 6H, CH_2-P), 4.58 (br s, 6H, CH_2-P), 6.8−8.0 (m, 345H, C_6H_5, C_6H_4, and CH=N) ppm. $^1H\{^{31}P\}$ NMR (400 MHz, δ, C_6D_6): −9.90 (d, $^2J_{HH} = 4$ Hz, H^- *trans* PPh_3), −8.66 (d, H^- *trans* PPh_2), 3.03 (s, P_1-N-CH_3), 4.09 (d, $^2J_{HH} = 13.2$ Hz, CH_2-P), 4.34 (d, $^2J_{HH} = 14.3$ Hz, CH_2-P), 4.55 (d, $^2J_{HH} = 13.3$ Hz, CH_2-P), 4.71 (d, $^2J_{HH} = 10.4$ Hz, CH_2-P), 6.7−8.1 (m, C_6H_5, C_6H_4, and CH=N) ppm. IR (KBr): ν(Ru−H) 1950 (w, br), 1859 (m, br) cm^{-1}.

Synthesis of 1-[G$_2$]. A 0.121 g (15 μmol) amount of $G_2(PPh_2)_2$ was added to a solution of 0.2 g (0.174 mmol) of $RuH_2(PPh_3)_4$ in 20 mL of toluene. 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 once with diethyl ether (10 mL) and two times with pentane (2 × 10 mL) and then dried under vacuum. Yield: 83%.

1-[G$_2$]: light yellow powder. $^{31}P\{^1H\}$ NMR (81 MHz, δ, C_6D_6): 20.3 (q, $^2J_{PP_{cis}} = 15.4$ Hz, PPh_2 *cis* PPh_3), 36.6 (dt, $^2J_{PP_{trans}} = 227.4$ Hz, PPh_2 *trans* PPh_3), 44.1 (q, PPh_3 *cis* PPh_2), 54.3 (dt, PPh_3 *trans* PPh_2, P_0 overlapped), 63.4 (s, P_1, P_2) ppm. ^{1}H NMR (200 MHz, δ, C_6D_6): −10.03 (d, $^2J_{HP_{trans}} = 66.7$ Hz, $^2J_{HP_{cis}} = 28.3$ Hz, 12H, H^- *trans* PPh_3), −8.82 (br m, 12H, H^- *trans* PPh_2), 2.90 (d, $^3J_{HP_{1-2}} = 10.0$ Hz, 27H, $P_{1-2}-N-CH_3$), 3.99 (d, $^2J_{HH} = 8.9$ Hz, 12H, CH_2-P), 4.23 (d, $^2J_{HH} = 12.8$ Hz, 12H, CH_2-P), 4.44 (d, $^2J_{HH} = 12.8$ Hz, 12H, CH_2-P), 4.58 (br s, 12H, CH_2-P), 6.7−8.1 (m, 705H, C_6H_5, C_6H_4, and CH=N) ppm. IR (KBr): ν(Ru−H) 1955 (w, br), 1859 (m, br) cm^{-1}.

Synthesis of 1-[G$_3$]. A 0.062 g (3.6 μmol) amount of $G_3(PPh_2)_2$ was added to a solution of 0.1 g (0.087 mmol) of $RuH_2(PPh_3)_4$ in 10 mL of toluene. 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 once with diethyl ether (10 mL) and two times with pentane (2 × 10 mL) and then dried under vacuum. Yield: 90%.

1-[G$_3$]: light yellow powder. $^{31}P\{^1H\}$ NMR (81 MHz, δ, C_6D_6): 20.7 (q, $^2J_{PP_{cis}} = 16.9$ Hz, PPh_2 *cis* PPh_3), 36.6 (dt, $^2J_{PP_{trans}} = 225.5$ Hz, PPh_2 *trans* PPh_3), 44.2 (q, PPh_3 *cis* PPh_2), 54.3 (dt, PPh_3 *trans* PPh_2, P_0 overlapped), 63.3 (s, P_1, P_2, P_3) ppm. ^{1}H NMR (200 MHz, δ, C_6D_6): −9.97 (dq, $^2J_{HP_{trans}} = 67.0$ Hz, $^2J_{HP_{cis}} = 26.6$ Hz, 24H, H^- *trans* PPh_3), −8.78 (br m, 24H, H^-

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(21) Chaudret, B.; Poilblanc, R. *Inorg. Chim. Acta* **1979**, *L209*, 34.

trans PPh_2), 2.92 (br s, 63H, $P_{1-2-3}-N-CH_3$), 4.02 (br s, 24H, CH_2-P), 4.22 (br s, CH_2-P), 4.45 (br s, 24H, CH_2-P), 4.60 (br s, 24H, CH_2-P), 6.7−8.1 (m, 1425H, C_6H_5, C_6H_4, and CH=N) ppm. IR (KBr): ν(Ru−H) 1951 (w, br), 1858 (m, br) cm^{-1}.

Synthesis of 2-[G$_1$]. A toluene (8 mL) solution of 0.06 g (7.8 μmol) of complex **1-[G$_1$]** in a Fisher−Porter bottle was carefully evacuated and pressurized three times to 3 bar of CO. The solution was stirred overnight, after which the bottle was depressurized and the clear solution was transferred and evaporated to dryness. The off-white residue was washed with pentane (3 × 5 mL) and then dried under vacuum. Yield: 96%.

2-[G$_1$]: off-white powder. $^{31}P\{^1H\}$ NMR (81 MHz, δ, C_6D_6): 25.3 (br t, PPh_2 *cis* PPh_3), 41.8 (dd, $^2J_{PP_{trans}} = 231.5$ Hz, $^2J_{PP_{cis}} = 22.5$ Hz, PPh_2 *trans* PPh_3), 53.0 (s, P_0), 58.9 (dd, PPh_3 *trans* PPh_2), 63.1 (s, P_1) ppm. ^1H NMR (200 MHz, δ, C_6D_6): −7.03 (dt, $^2J_{HP_{trans}} = 74.2$ Hz, $^2J_{HP_{cis}} = 20.6$ Hz, 6H, H^- *trans* PPh_2), −6.69 (q, $^2J_{HP_{cis}} = 20.8$ Hz, 6H, H^- *trans* CO), 2.96 (d, $^3J_{HP_1} = 9.8$ Hz, 9H, P_1-N-CH_3), 4.1−4.4 (m, 24H, CH_2-P), 6.4−8.3 (m, 255H, C_6H_5, C_6H_4, and CH=N) ppm. IR (KBr): ν(Ru−CO) 1947 (s) and ν(Ru−H) 1900 (sh) cm^{-1}. IR (toluene): ν(Ru−CO) 1951 (s) and ν(Ru−H) 1902 (w, br) cm^{-1}.

Synthesis of 2-[G$_2$]: as for **2-[G$_1$]** using 0.06 g (3.8 μmol) of complex **1-[G$_2$]**. Yield: 93%.

2-[G$_2$]: white powder. $^{31}P\{^1H\}$ NMR (81 MHz, δ, C_6D_6): 25.4 (br t, PPh_2 *cis* PPh_3), 41.8 (dd, $^2J_{PP_{trans}} = 231.3$ Hz, $^2J_{PP_{cis}} = 23.1$ Hz, PPh_2 *trans* PPh_3), 53.1 (s, P_0), 58.9 (dd, PPh_3 *trans* PPh_2), 63.2 (s, P_1, P_2) ppm. ^1H NMR (200 MHz, δ, C_6D_6): −7.04 (dt, $^2J_{HP_{trans}} = 76.1$ Hz, $^2J_{HP_{cis}} = 22.7$ Hz, 12H, H^- *trans* PPh_2), −6.69 (q, $^2J_{HP_{cis}} = 21.8$ Hz, 12H, H^- *trans* CO), 2.94 (d, $^3J_{HP_{1-2}} = 8.3$ Hz, 27H, $P_{1-2}-N-CH_3$), 4.1−4.4 (m, 48H, CH_2-P), 6.4−8.3 (m, 525H, C_6H_5, C_6H_4, and CH=N) ppm. ^1H NMR (200 MHz, δ, CD_2Cl_2): −7.71 (dt, $^2J_{HP_{trans}} = 74.8$ Hz, $^2J_{HP_{cis}} = 24.1$ Hz, H^- *trans* PPh_2), −7.15 (q, $^2J_{HP_{cis}} = 24.0$ Hz, H^- *trans* CO), 3.29 (br s, $P_{1-2}-N-CH_3$), 4.1−4.4 (m, CH_2-P), 6.5−8.2 (m, C_6H_5, C_6H_4, and CH=N) ppm. IR (KBr): ν(Ru−CO) 1948 (s) and ν(Ru−H) 1900 (sh) cm^{-1}. IR (toluene): ν(Ru−CO) 1951 (s) cm^{-1}.

Synthesis of 2-[G$_3$]: as for **2-[G$_1$]** using 10 mL of toluene and 0.08 g (2.5 μmol) of complex **1-[G$_3$]**. Yield: 97%.

2-[G$_3$]: off-white powder. $^{31}P\{^1H\}$ NMR (81 MHz, δ, C_6D_6): 25.3 (br t, PPh_2 *cis* PPh_3), 41.8 (dd, $^2J_{PP_{trans}} = 231.3$ Hz, $^2J_{PP_{cis}} = 22.5$ Hz, PPh_2 *trans* PPh_3), 53.0 (s, P_0), 58.8 (dd, PPh_3 *trans* PPh_2), 63.3 (s, P_1, P_2, P_3) ppm. ^1H NMR (200 MHz, δ, C_6D_6): −7.05 (dt, $^2J_{HP_{trans}} = 73.8$ Hz, $^2J_{HP_{cis}} = 21.4$ Hz, 24H, H^- *trans* PPh_2), −6.69 (q, $^2J_{HP_{cis}} = 21.8$ Hz, 24H, H^- *trans* CO), 2.92 (br s, 63H, $P_{1-2-3}-N-CH_3$), 4.1−4.4 (m, 96H, CH_2-P), 6.4−8.3 (m, 1065H, C_6H_5, C_6H_4, and CH=N) ppm. IR (KBr): ν(Ru−CO) 1947 (s) and ν(Ru−H) 1900 (sh) cm^{-1}. IR (toluene): ν(Ru−CO) 1950 (s) and ν(Ru−H) 1902 (w, br) cm^{-1}.

Synthesis of 3′-[G$_1$], 3″-[G$_1$], 4′-[G$_1$], and 4″-[G$_1$]. A 0.019 g (28 μmol) amount of $RuH_2(H_2)_2(PCy_3)_2$ and 0.018 g (4.6 μmol) of $G_1(PPh_2)_2$ were placed in a NMR tube. Addition of 0.5 mL of d_8-toluene led to gas evolution and formation of an orange solution, which was quickly frozen at −50 °C. The NMR spectra recorded at room temperature showed mainly the presence of **3′-[G$_1$]**. The course of the reaction was monitored by NMR every 1 h. **3′-[G$_1$]** transformed after 2 h into a mixture of the four products **3′-[G$_1$], 3″-[G$_1$]**, **4′-[G$_1$]**, and **4″-[G$_1$]** and finally after 4 h into a mixture of **4′-[G$_1$]** and **4″-[G$_1$]**.

The same experiment carried out in C_6D_6 at room temperature led initially to two products (**3′-[G$_1$]** and **4′-[G$_1$]**) as observed by NMR. They transformed after 1 h into a mixture of the four products and after 4 h into **4′-[G$_1$]**.

The same experiments carried out with stirring showed the same processes but were faster.

Synthesis. A 2 mL amount of toluene was added over a mixture of 0.038 g (57 μmol) of $RuH_2(H_2)_2(PCy_3)_2$ and 0.037 g (9.5 μmol) of $G_1(PPh_2)_2$ at −30 °C and stirred for 30 min. Addition of pentane (15 mL) afforded **3′-[G$_1$]** as an orange solid, which was washed with pentane (2 × 10 mL).

A 2 mL amount of toluene was added over a mixture of 0.038 g (57 μmol) of $RuH_2(H_2)_2(PCy_3)_2$ and 0.037 g (9.5 μmol) of $G_1(PPh_2)_2$ at room temperature and stirred for 30 min. Addition of pentane (15 mL) afforded an orange solid, which was washed with pentane (2 × 10 mL).

3′-[G$_1$]: $^{31}P\{^1H\}$ NMR (81 MHz, δ, C_6D_6): 38.7 (d, $^2J_{PP_{trans}} = 105.3$ Hz, PPh_2), 52.7 (s, P_0), 63.0 (s, P_1), 67.3 (t, PCy_3) ppm. ^1H NMR (200 MHz, δ, C_6D_6): −7.38 (br s), 1.1−2.0 (m, Cy), 2.96 (d, $^3J_{HP_1} = 9.8$ Hz, P_1-N-CH_3), 4.20 (s, CH_2-P), 6.6−8.0 (m, C_6H_5, C_6H_4, and CH=N) ppm. IR (KBr): ν(Ru−H) 1906 (m, br), 1958 (sh) cm^{-1}.

3″-[G$_1$]: $^{31}P\{^1H\}$ NMR (81 MHz, δ, C_6D_6): 43.0 (d, $^2J_{PP_{trans}} = 102.1$ Hz, PPh_2), 53.0 (s, P_0), 63.2 (s, P_1), 66.9 (t, PCy_3) ppm. ^1H NMR (200 MHz, δ, C_6D_6): −7.66 (br s), 1.1−2.0 (m, Cy), 3.02 (br s, P_1-N-CH_3), 3.70 (m, CH_2-P), 6.6−8.0 (m, C_6H_5, C_6H_4, and CH=N) ppm.

4′-[G$_1$]: $^{31}P\{^1H\}$ NMR (81 MHz, δ, C_6D_6): 53.0 (s, P_0), 57.9 (t, $^2J_{PP_{cis}} = 15.4$ Hz, PCy_3), 63.2 (s, P_1), 65.6 (d, PPh_2) ppm. ^1H NMR (200 MHz, δ, C_6D_6): −8.53 (q, $^2J_{HP} = 13.0$ Hz), 1.1−2.0 (m, Cy), 3.02 (br s, P_1-N-CH_3), 3.30 (br m, CH_2-P), 6.6−8.0 (m, C_6H_5, C_6H_4, and CH=N) ppm.

4″-[G$_1$]: $^{31}P\{^1H\}$ NMR (81 MHz, δ, C_6D_6): 26.6 (t, $^2J_{PP_{cis}} = 21.1$ Hz, PCy_3), 53.0 (s, P_0), 63.2 (s, P_1), 69.2 (d, PPh_2) ppm. ^1H NMR (200 MHz, δ, C_6D_6): −8.06 (q, $^2J_{HP} = 11.8$ Hz), 1.1−2.0 (m, Cy), 3.02 (br s, P_1-N-CH_3), 3.60 (br m, CH_2-P), 6.6−8.0 (m, C_6H_5, C_6H_4 and CH=N) ppm. IR (KBr) final solid in toluene: ν(Ru−H) 1919 (m, br), 1958 (sh) cm^{-1}.

Synthesis of 3′-[G$_3$], 3″-[G$_3$], 4′-[G$_3$], and 4″-[G$_3$]. A 0.020 g (30 μmol) amount of $RuH_2(H_2)_2(PCy_3)_2$ and 0.022 g (1.3 μmol) of $G_3(PPh_2)_2$ were introduced into an NMR tube. Addition of 0.5 mL of d_8-toluene or C_6D_6 led to gas evolution (dihydrogen) and to an orange solution which was characterized by NMR as containing **3′-[G$_3$]**. After 1 h in solution, a mixture of **3′-[G$_3$]** and **3″-[G$_3$]** was observed and after 4 h, four products were observed which eventually all transformed into **4′-[G$_3$]** after 15 h. The same processes were observed when the reaction was repeated in a Schlenk tube with stirring. The reactions were slower for generation 3 than for generation 1, probably because of lack of solubility.

3′-[G$_3$]: $^{31}P\{^1H\}$ NMR (81 MHz, δ, C_6D_6): 38.7 (d, $^2J_{PP_{trans}} = 106.1$ Hz, PPh_2), 53.1 (s, P_0), 63.4 (s, P_1, P_2, P_3), 67.3 (t, PCy_3). ^1H NMR (200 MHz, δ, C_6D_6): −7.38 (br s), 1.1−1.9 (m, Cy), 2.93 (br s, $P_{1-2-3}-N-CH_3$), 4.20 (s, CH_2-P), 6.5−8.4 (m, C_6H_5, C_6H_4, and CH=N) ppm.

3″-[G$_3$]: $^{31}P\{^1H\}$ NMR (81 MHz, δ, C_6D_6): 43.0 (d, $^2J_{PP_{trans}} = 102.0$ Hz, PPh_2), 53.1 (s, P_0), 63.4 (s, P_1, P_2, P_3), 66.9 (t, PCy_3 *trans* PPh_2) ppm. ^1H NMR (200 MHz, δ, C_6D_6): −7.71 (br s), 1.1−1.9 (m, Cy), 2.98 (br s, $P_{1-2-3}-N-CH_3$), 3.70 (m, CH_2-P), 6.5−8.4 (m, C_6H_5, C_6H_4, and CH=N) ppm.

4′-[G$_3$]: $^{31}P\{^1H\}$ NMR (81 MHz, δ, C_6D_6): 53.1 (s, P_0), 57.8 (t, $^2J_{PP_{cis}} = 14.7$ Hz, PCy_3), 63.4 (s, P_1, P_2, P_3), 65.6 (d, PPh_2 *trans* PCy_3), ^1H NMR (200 MHz, δ, C_6D_6): −8.55 (q, $^2J_{HP} = 12.8$ Hz), 1.1−1.9 (m, Cy), 2.98 (br s, $P_{1-2-3}-N-CH_3$), 3.30 (br m, CH_2-P), 6.5−8.4 (m, C_6H_5, C_6H_4, and CH=N) ppm.

4″-[G$_3$]: $^{31}P\{^1H\}$ NMR (81 MHz, δ, C_6D_6): 26.6 (t, $^2J_{PP_{cis}} = 21.1$ Hz, PCy_3), 53.1 (s, P_0), 63.4 (s, P_1, P_2, P_3), 69.2 (d, PPh_2 *trans* PCy_3). ^1H NMR (200 MHz, δ, C_6D_6): −8.11 (br m), 1.1−1.9 (m, Cy), 2.98 (br s, $P_{1-2-3}-N-CH_3$), 3.60 (br m, CH_2-P), 6.5−8.4 (m, C_6H_5, C_6H_4, and CH=N) ppm.

Synthesis of 5-[G$_1$]. A 0.052 g (78 μmol) amount of $RuH_2(H_2)_2(PCy_3)_2$ and 0.05 g (13 μmol) of $G_1(PPh_2)_2$ were introduced into a Fisher−Porter bottle. After addition of 10 mL of toluene the solution was stirred for 5 min; then the bottle was carefully evacuated and pressurized three times with 3 bar of CO. After the mixture was stirred overnight, the bottle was depressurized and the clear solution was transferred into a Schlenk tube and evaporated to ca. 1 mL. Addition of pentane (15 mL) afforded **5-[G$_1$]** as a white solid, which was washed with pentane (2 × 5 mL) and dried under vacuum. Yield: 90%.

5-[G$_1$]: white powder. $^{31}P\{^1H\}$ NMR (81 MHz, δ, C_6D_6): 25.0 (t, $^2J_{PP_{cis}} = 21.3$ Hz, PPh_2 *cis* PCy_3), 42.2 (dd, $^2J_{PP_{trans}} = 220.0$ Hz, PPh_2 *trans* PCy_3), 53.0 (s, P_0), 63.2 (s, P_1), 66.2 (dd,

PCy_3 *trans* PPh_2) ppm. ^{1}H NMR (200 MHz, δ, C_6D_6): −8.31 (dt, $^2J_{HP_{trans}} = 78.5$ Hz, $^2J_{HP_{cis}} = 21.6$ Hz, 6H, H^- *trans* PPh_2), −7.28 (q, $^2J_{HP_{cis}} = 21.1$ Hz, 6H, H^- *trans* CO), 1.1−2.0 (m, 198H, Cy), 2.98 (d, $^3J_{HP_1} = 10.0$ Hz, 9H, $P_1{-}N{-}CH_3$), 3.9−4.5 (m, 24H, $CH_2{-}P$), 6.5−8.3 (m, 165H, C_6H_5, C_6H_4, and CH═N) ppm. IR (KBr): ν(Ru−CO) 1936 (s) and ν(Ru−H) 2032 (vw), 1895 (sh) cm^{-1}. IR (toluene): ν(Ru−CO) 1939 (s) cm^{-1}. Anal. Calcd for $C_{336}H_{408}N_{18}O_{15}P_{22}S_4Ru_6$: C, 63.5; H, 6.45; N, 3.95. Found: C, 62.85; H, 6.3; N, 4.2.

Synthesis of 5-[G2]: as for **5-[G$_1$]** using 0.048 g (72 μmol) of $RuH_2(H_2)_2(PCy_3)_2$ and 0.05 g (6.0 μmol) of $G_2(PPh_2)_2$. Yield: 65%.

5-[G$_2$]: off-white powder. $^{31}P\{^1H\}$ NMR (81 MHz, δ, C_6D_6): 24.9 (m, PPh_2 *cis* PCy_3), 42.2 (dd, $^2J_{PP_{trans}} = 219.1$ Hz, $^2J_{PP_{cis}} = 21.3$ Hz, PPh_2 *trans* PCy_3), 53.3 (s, P_0), 63.4 (s, P_1, P_2), 66.0 (dd, PCy_3 *trans* PPh_2) ppm. ^{1}H NMR (200 MHz, δ, C_6D_6): −8.31 (dt, $^2J_{HP_{trans}} = 78.6$ Hz, $^2J_{HP_{cis}} = 23.3$ Hz, 12H, H^- *trans* PPh_2), −7.27 (q, $^2J_{HP_{cis}} = 22.2$ Hz, 12H, H^- *trans* CO), 1.1−2.0 (m, 396H, Cy), 2.94 (br s, 27H, $P_{1-2}{-}N{-}CH_3$), 3.9−4.5 (m, 48H, $CH_2{-}P$), 6.5−8.3 (m, 345H, C_6H_5, C_6H_4, and CH═N) ppm. IR (KBr): ν(Ru−CO) 1936 (s) and ν(Ru−H) 2030 (vw), 1884 (m, br) cm^{-1}. IR (toluene): ν(Ru−CO) 1933 (s) cm^{-1}. Anal. Calcd for $C_{696}H_{840}N_{42}O_{33}P_4S_{10}Ru_{12}$: C, 62.95; H, 6.4; N, 4.45. Found: C, 61.95; H, 6.0; N, 5.0.

Synthesis of 5-[G$_3$]: as for **5-[G$_1$]** using 0.047 g (70 μmol) of $RuH_2(H_2)_2(PCy_3)_2$ and 0.05 g (2.9 μmol) of $G_3(PPh_2)_2$. Yield: 95%.

5-[G$_3$]: off-white powder. $^{31}P\{^1H\}$ NMR (81 MHz, δ, C_6D_6): 24.9 (m, PPh_2 *cis* PCy_3), 42.3 (dd, $^2J_{PP_{trans}} = 220.0$ Hz, $^2J_{PP_{cis}} = 21.5$ Hz, PPh_2 *trans* PCy_3), 53.3 (s, P_0), 63.4 (s, P_1, P_2, P_3), 66.0 (dd, PCy_3 *trans* PPh_2) ppm. ^{1}H NMR (200 MHz, δ, C_6D_6): −8.30 (dt, $^2J_{HP_{trans}} = 80.4$ Hz, $^2J_{HP_{cis}} = 24.1$ Hz, 24H, H^- *trans* PPh_2), −7.28 (q, $^2J_{HP_{cis}} = 21.4$ Hz, 24H, H^- *trans* CO), 1.1−2.0 (m, 792H, Cy), 2.94 (br s, 63H, $P_{1-2-3}{-}N{-}CH_3$), 3.9−4.5 (m, 96H, $CH_2{-}P$), 6.4−8.3 (m, 705H, C_6H_5, C_6H_4, and CH═N) ppm. IR (KBr): ν(Ru−CO) 1936 (s) and ν(Ru−H) 2030 (vw), 1886 (m, lr) cm^{-1}. IR (toluene): ν(Ru−CO) 1939 (s) cm^{-1}.

T_1 Data (ms) Measured at 400 MHz (d_8-Toluene):

derivative	253 K	273 K	293 K	313 K
4′-[G$_1$]	62	52	48	62
4″-[G$_1$]	72	69	58	75
4′-[G$_3$]	48	43	50	54
4″-[G$_3$]	50	49	60	67
3′-[G$_3$]	39	39	48	58
3″-[G$_3$]	42	39	48	54

Acknowledgment. We thank the CNRS for support. M.B. thanks the Ministerio de Educación y Cultura (Madrid, Spain) for a grant.

OM970092+