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# Dendrimers Containing Two Metallic Layers. Chloride Migration from Peripheral Gold, Palladium, or Rhodium Metals to Internal Ruthenium Atoms

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An efficient strategy for the synthesis of carbosilane dendrimers containing double metallic layers has been developed. The method consists of the attachment of the Ru(*p*-cymene)$Cl_2$ unit to the branches of a phosphino-terminated dendrimer, followed by abstraction with AgOTf of the chloride ligands from the ruthenium and selective incorporation, through the nitrogen pyridine atom, of the bifunctional 4-pyPPh$_2$ molecule. Finally, metalation of the resulting species with the complexes [(tht)AuCl], [PdCl($\eta^3$-2-MeC$_3$H$_4$)]$_2$, and [RhCl(cod)]$_2$ renders the targeted Ru/Au, Ru/Pd, and Ru/Rh dendrimers. An unexpected migration of the chloride ligand bonded to the peripheral metals to the internal ruthenium atoms was observed and discussed in terms of the results obtained from density functional calculations. In the case of the Ru/Au dendrimers, the different abilities for the ligand transfer process shown by the dendrimers in comparison with a mononuclear Ru/Au model compound are explained in terms of dendritic effects.

## Introduction

The grafting of organometallic or transition-metal fragments into the framework of dendrimers can potentially lend to the resulting species valuable properties in areas such as catalysis, electrochemistry, photochemistry, and magnetism, due to the particular environment around the metal center created by the dendrimer.[1] It is anticipated that the introduction of two or more different metals in the dendritic system can multiply these effects, so that the synthesis of heterometallic dendrimers has now become a challenge for chemists. Thus, these species are thought to be useful, for example, for the construction of nanoscale molecular architectures[2] or in catalysis.[3] Moreover, unexpected properties due to possible cooperative effects between metals should not be ruled out in these kinds of species. Although synthetic strategies for homometallodendrimers are well-known,[4] the methodology for those containing more than one metal is much less developed. With the exception of some heteronuclear cluster terminated dendrimers[5] the only examples reported up to now include heterogeneously peripherally substituted dendrimers containing cobaltocene and ferrocene units[6] and our results based on ruthenium and gold (or rhodium) dendrimers.[7] In particular, we recently reported[7a] the binding of the bifunctional ligand 4,4′-bipyridine to ruthenium atoms grafted on the periphery of a carbosilane dendrimer in the hope that, through the uncoordinated pyridyl nitrogen, new metal fragments could be added, consequently generating double-metal-layer dendrimers. By this method, bimetallic dendrimers were formed, although they were very unstable in solution. These results prompted us to employ, in this work, the (4-pyridyl)diphenylphosphine ligand, 4-pyPPh$_2$, as a bifunctional ligand. This strategy made feasible the facile synthesis of dendrimers decorated on the surface

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(1) See, for example: (a) Newkome, G. R.; Vögtle, F.; Moorefield, C. N. *Dendrimers and Dendrons*; Wiley: New York, 2001. (b) Tomalia, D. A.; Durst, H. D. In *Topics in Current Chemistry*; Weber, E., Ed.; Springer: Berlin, 1993. (c) Newkome, G. R.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689. (d) Bosman, A. W.; Janssen, H. M.; Meijer, W. *Chem. Rev.* **1999**, *99*, 1665. (e) Majoral, J. P.; Caminade, A. M. *Chem. Rev.* **1999**, *99*, 845. (f) Majoral, J. P.; Caminade, A. M.; Maraval, V. *Chem. Commun.* **2002**, 2929. (g) Fischer, M.; Vögtle, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 884. (h) Balzani, V.; Ceroni, P.; Juris, A.; Venturi, M.; Campagna, S.; Puntoriero, F.; Serroni, S. *Coord. Chem. Rev.* **2001**, *219−221*, 545. (i) Balzani, V.; Vögtle, F. *C. R. Chim.* **2003**, *6*, 867.

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(4) See, for example: (a) Stoddart, F. J.; Welton, T. *Polyhedron* **1999**, *18*, 3575. (b) Caminade, A. M.; Laurent, R.; Chaudret, B.; Majoral, J. P. *Coord. Chem. Rev.* **1998**, *178−180*, 793. (c) Dasgupta, M.; Peori, M. B.; Kakkar, A. K. *Coord. Chem. Rev.* **2002**, *233−234*, 223. (d) Rossell, O.; Seco, M.; Angurell, I. *C. R. Chim.* **2003**, *6*, 803. (e) Cuadrado, I.; Morán, M.; Losada, J.; Casado, C. M.; Pascual, C.; Alonso, B.; Lobete, F. In *Advances in Dendritic Macromolecules*; Newkome, G. R., ed.; JAI Press: Greenwich, CT, 1996; Vol. 3, pp 151−195. (f) Cuadrado, I.; Morán, M.; Casado, C. M.; Alonso, B.; Losada, J. *Coord. Chem. Rev.* **1999**, *193−195*, 395. (g) Chase, P. A.; Klein Gebbink, R. J. M.; van Koten, G. *J. Organomet. Chem.* **2004**, *689*, 4016. (h) Arévalo, S.; de Jesús, E.; de la Mata, F. J.; Flores, J. C.; Gómez, R. *Organometallics* **2001**, *20*, 2583 and references therein.

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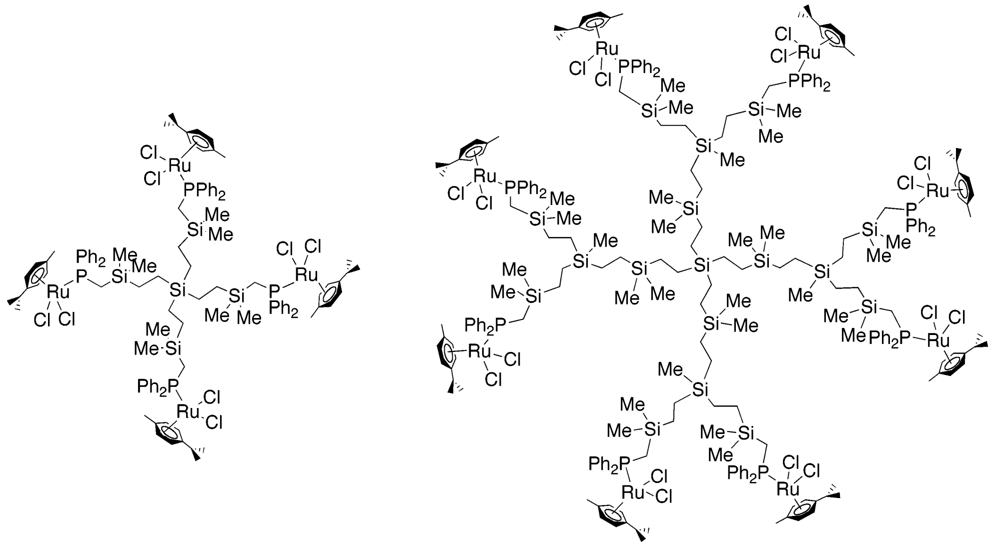
10.1021/om0504699 CCC: $30.25

**Chart 1. Starting Ruthenium Dendrimers Used in This Work**



**1** **8**

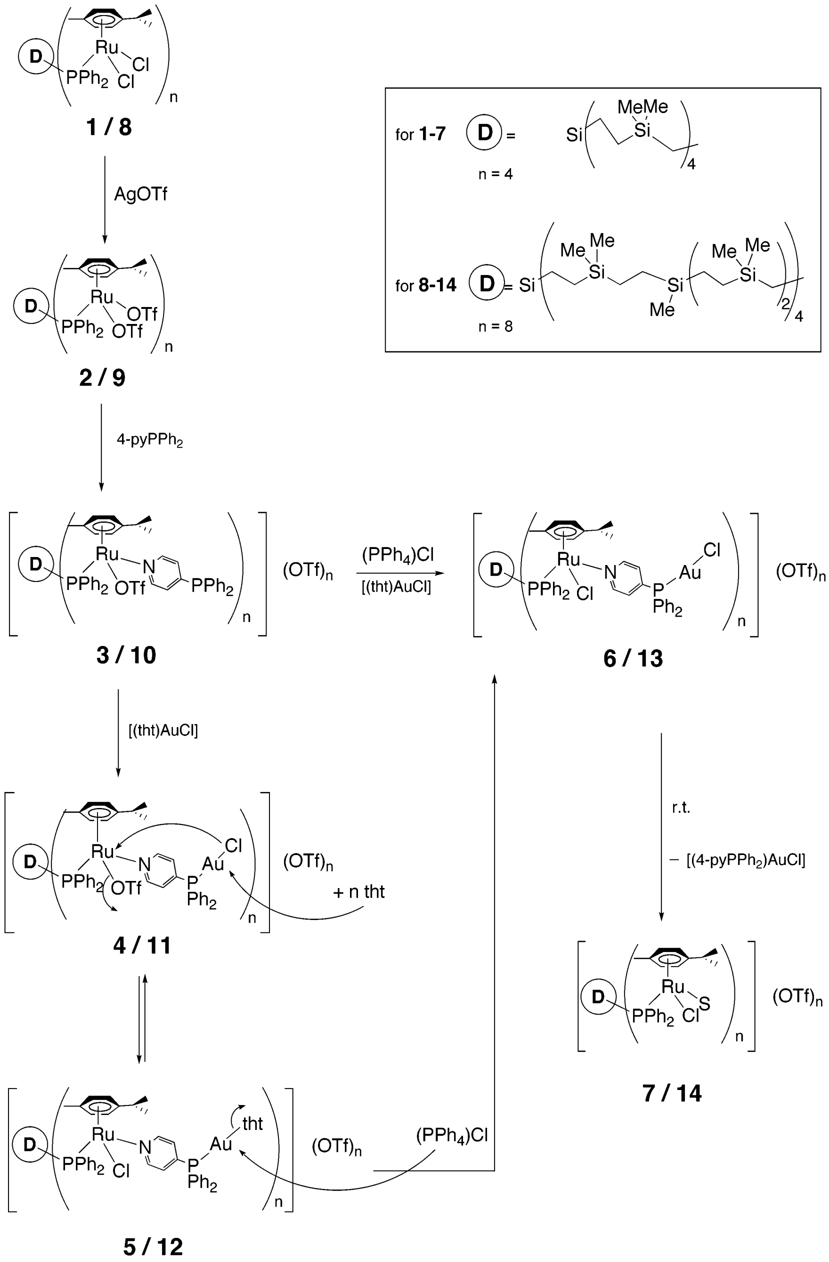
with gold, palladium, or rhodium metals containing, in addition, an internal layer of ruthenium atoms. Interestingly, an unprecedented migration of the chloride ligand bonded to the peripheral metal atoms (Au, Pd, or Rh) toward the ruthenium centers has been observed, and it has been interpreted by means of a theoretical study employing methods based on density functional theory.

## Results and Discussion

**Synthesis and Characterization of Ru/Au Double-Metallic-Layer Dendritic Systems.** Dendrimer **1**[7b] (Chart 1) was chosen as the starting material for the synthesis of bimetallic ruthenium- and gold-containing dendrimers, and the corresponding reactions are represented in Scheme 1. First, **1** was reacted in $CH_2Cl_2$ with 8 equiv of AgOTf for the abstraction of the chloride ligands. After filtration of AgCl, the $^{31}P$ NMR spectrum of the resulting red solution showed the dendrimer **2** as a unique product, which was not isolated. The addition of 4 equiv of 4-$pyPPh_2$ rapidly turned the solution yellow and rendered **3**, which showed one 4-$pyPPh_2$ ligand per ruthenium atom. The addition of a further 4 equiv of the ligand did not provide the bis(4-pyridyldiphenylphosphine) derivative, probably because of peripheral steric congestion.

**3** was isolated as a yellow powder and characterized by elemental analyses and $^1H$, $^{13}C$, $^{29}Si$, and $^{31}P$ NMR spectroscopy. It is remarkable that, despite the bifunctional character of 4-$pyPPh_2$, the Ru atom appears in all cases selectively attached to the ligand via the N atom and no traces of product containing a Ru−P bond were detected. Unfortunately, FAB and MALDI-TOF mass spectroscopy gave extensive fragmentation and they could not be used for the structural elucidation of **3** or any of the other species reported in this paper. The $^1H$ NMR spectrum of **3** contained two methyl resonances of the isopropyl group of *p*-cymene at $\delta$ 1.09 and 0.97 ppm as a result of the presence of the chiral ruthenium center. Note that, after the entry of one pyridine ligand, the symmetry plane containing the ruthenium atom is lost and that the high congestion on the metal precludes the free rotation of both *p*-cymene and the 4-pyridyldiphenylphosphine ligands. Moreover, the α-protons of the pyridine ring shifted, after coordination, to low field and they can be used as a diagnostic tool for the coordination of the 4-pyridylphosphine ligand. The $^{31}P$ NMR spectrum exhibited only two signals at $\delta$ 31.3 ($PPh_2Ru-$) and −4.2 ppm ($PPh_2py$), evidencing complete metalation of the dendrimer. The $^{19}F$ NMR spectrum showed two signals for the triflate anion: one corresponding to the free triflate at $\delta$ −79.0 ppm and the other at around $\delta$ −78.2 ppm (broad), belonging to the coordinated anion. Dendrimer **3** features the appropriate requirements for the formation of double metallic layers: ruthenium atoms occupying internal sites and uncoordinated phosphine ligands in the periphery. For this reason, **3** has been used as the starting material throughout this paper. Our first attempts in this field were centered on the grafting of gold atoms at the surface of **3** by the use of [(tht)AuCl] (tht = tetrahydrothiophene). Clear evidence for the formation of bimetallic **4** was given by its $^{31}P$ NMR spectroscopy. Thus, the free phosphine signal of $\delta$ −4.2 ppm disappeared and a new signal at $\delta$ 32.3 ppm emerged, indicative of the presence of the $PPh_2AuCl$ entity. The resonance of the $PPh_2Ru$ group did not move significantly from that in **3**. On the other hand, the presence of the AuCl moiety induced chemical shifting of the resonance signals of the α-protons of the pyridine ring to low fields. The proton integration ratio for the rest of the signals confirmed the structure proposed. The ratio between free and coordinated triflate remained as observed in **3**. The most striking feature of this reaction was observed when the reaction solution of **4** was left at room temperature. After several minutes, the chloride ligand spontaneously migrated from gold to ruthenium atoms to give **5** (see Scheme 1). This was substantiated by the $^{31}P$ NMR spectrum, which showed the appearance of a new signal for the $PPh_2Ru$ fragment at $\delta$ 26.1 ppm, while the signal for $PPh_2Au$ underwent low-field shifting to $\delta$ 34.4 ppm. This was accompanied by remarkable displacements in the $^1H$ NMR spectrum of the signals of the free tht (from $\delta$ 2.79, 1.91 ppm to $\delta$ 3.21, 2.09 ppm), revealing the

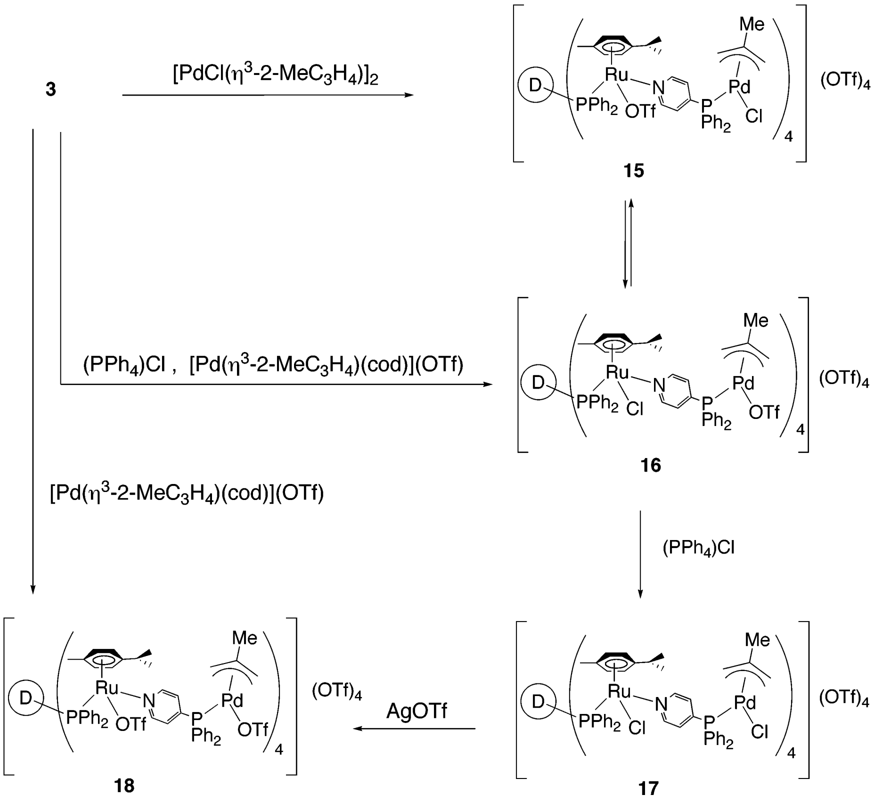
**Scheme 1. Synthesis of Bimetallic Ruthenium/Gold Dendrimers**



coordination of this ligand to the gold atom. The chloride migration was not complete, and after several hours equilibrium between **4** and **5** was achieved with a 2:3 molar ratio. As we will discuss later, theoretical calculations have shown that the Au−S(tht) bond seems to be the driving force for the migratory process. As a confirmation of this fact, when **4** was rapidly precipitated from the solution after its formation and then redissolved in $CH_2Cl_2$ (in absence of tht), it did not show the migration of the halide. The addition of an equimolar amount of $(PPh_4)Cl$ to the solution of **5** yielded **6**, which could be isolated as a yellow solid and characterized by NMR spectroscopy, confirming the presence of the $PPh_2AuCl$ and $PPh_2Ru$ groups. After several hours in solution, **6** underwent partial decoordination of [(4-pyPPh$_2$)AuCl] to give **7** ($^{31}$P NMR $\delta$ 22.1 ppm). This behavior is in contrast with that shown by **3**, which is stable after several days in solution. The lability of the metalloligand in **6** can be attributed to the presence of the chloride ligand, which reduces the positive charge on the ruthenium so that it facilitates the release of the metalloligand. The calculated NBO charges (see Computational Details) indicated a significant reduction of the ruthenium atomic charge: +0.25 for the ruthenium atoms coordinated to the triflate while only +0.09 for those coordinated to the chloride anions.

Given that the migration between two metals carried out by the chloride has no precedent, we became interested in knowing whether this process also occurs with the use of a third-generation carbosilane dendrimer peripherally functionalized with Ru($p$-cymene)$Cl_2$ groups. With this aim, we performed the reactions represented in Scheme 1 employing **8** (Chart 1) instead of **3** as starting dendrimer. **9** and **10** were easily prepared, as indicated in Scheme 1. **10** incorporated the AuCl fragment after reaction with [(tht)AuCl] to give **11**, which rapidly showed the migration of the chloride toward the ruthenium, rendering **12**. The $^{31}$P and $^{1}$H NMR data are practically identical with those found for **4** and **5**, confirming the reproducibility of the process. Further-

**Scheme 2. Synthesis of Bimetallic Ruthenium/Palladium Dendrimers**



more, the addition of $(PPh_4)Cl$ to a solution of **12** allowed the isolation of **13**, with $(PPh_4)OTf$ as an impurity, showing Ru−Cl and Au−Cl bonds. Like **6**, **13** releases the gold complex gradually in solution to afford **14**. Figure 1 illustrates through $^{31}P$ NMR spectra the formation of **11**, the chloride migration to yield a mixture of **11** and **12**, and the synthesis of **13**, with **14** and the gold ligand as impurities.

That the same behavior concerning the chloride migration is shown by both the first- and third-generation dendrimers is not surprising, given that both of these compounds should reasonably follow the same mechanism, since the dendrimer peripheries are basically identical.

The use of the model compound $[Ru(OTf)(p\text{-cymene})(PMePh_2)(pyPPh_2)][OTf]$ (**M**) instead of the dendrimer molecules gave similar results. Thus, the reaction of **M** with [(tht)AuCl] yielded the bimetallic Ru/Au species $[Ru(OTf)(p\text{-cymene})(PMePh_2)(pyPPh_2AuCl)][OTf]$, which underwent chloride transfer from the gold to the ruthenium center. However, it is remarkable that, in this case, the chloride migration takes place less extensively (the mixture composition was about 1:10 after 12 h in solution, in contrast with the 2:3 composition found using **3** or **10**). Given that the electronic environments on the ruthenium atoms are practically the same for **3**, **10**, and **M**, steric effects should be invoked for explaining their different capabilities for the ligand transfer process. Hence, this is really a dendritic effect on the basis of steric congestion.

Given the singularity of the chloride migratory reaction, it seemed interesting to synthesize new dendrimers containing metals other than gold on the surface, to examine the scope of this process. On the other hand, due to the interest of metallodendrimers for use in catalysis, we were interested in the construction of species containing not only ruthenium but also other metals with proven catalytical activity, such as palladium and rhodium.

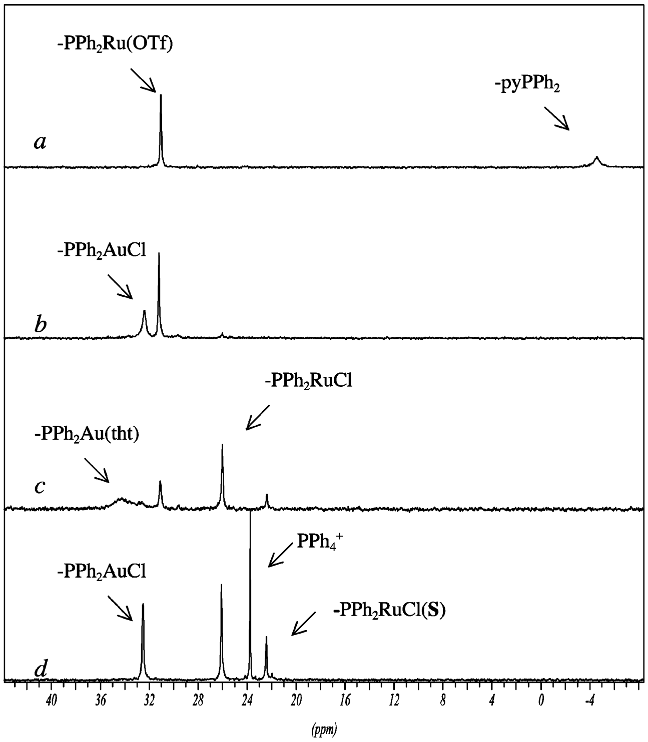
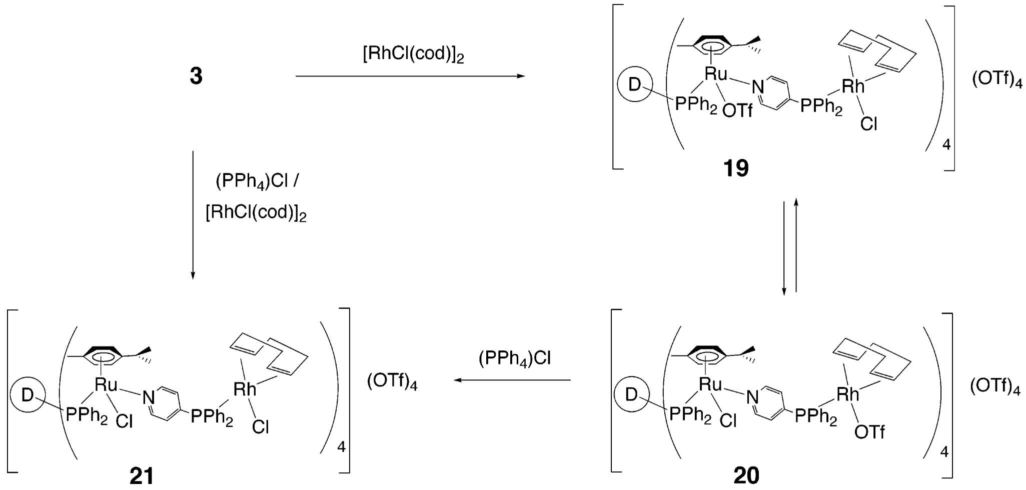


**Figure 1.** $^{31}P$ NMR spectra: (a) spectrum of a $CH_2Cl_2$ solution of **10**; (b) spectrum of **11** (taken after 5 min of the addition of [(tht)AuCl] to **10**); (c) spectrum taken after 7 h at room temperature (mixture of **11** and **12**); (d) spectrum after addition of $PPh_4Cl$ to yield **13**.

**Scheme 3. Synthesis of Bimetallic Ruthenium/Rhodium Dendrimers**



**Ruthenium/Palladium Dendrimers.** Scheme 2 outlines the synthesis of ruthenium- and palladium-containing dendrimers.

Dendrimer **3** was used as starting material. The reaction of **3** with [PdCl($\eta^3$-2-MeC$_3$H$_4$)]$_2$ in CH$_2$Cl$_2$ resulted in the rapid formation of **15** according to the $^1$H and $^{31}$P NMR parameters, close to those described for similar palladium-containing dendrimers.[8]

After 1 h in solution, a yellow solid precipitated which was only soluble in nitromethane and whose $^{31}$P NMR spectrum showed the presence of two products, **15** and **16**, in an approximately 1:1 molar ratio. **16** is the result of the chloride migration in **15** from the palladium to the ruthenium. The phosphorus nucleus of the *P*Ph$_2$Ru unit resonated at $\delta$ 27.9 ppm for **15** and $\delta$ 23.4 ppm for **16** and is illustrative of the chloride migration. The mixture of **15** and **16** in equilibrium fits well with our calculations in that the difference in energy between both dendrimers is only about 1.8 kcal/mol (see the next section). The addition of an equimolar amount of (PPh$_4$)Cl to the solution containing **15** and **16** gave **17**, which displays Ru−Cl and Pd−Cl bonds. **17** is soluble in common solvents but, as observed for **6**, the presence of the chloride bonded directly to the ruthenium facilitates the decoordination of the palladium unit. Thus, for example, after a short time, a CH$_2$Cl$_2$ solution of **17** evidenced the presence of [PdCl($\eta^3$-2-MeC$_3$H$_4$)(4-pyPPh$_2$)]. On the other hand, the abstraction of the chloride ligands from **17** with AgTfO gave **18**, which displayed vacancies on both metal centers. **18** was isolated as a pure compound and characterized by $^1$H, $^{13}$C, $^{29}$Si, and $^{31}$P NMR spectroscopy. A simpler way to synthesize this dendrimer was by the reaction of **3** with [Pd($\eta^3$-2-MeC$_3$H$_4$)(cod)](OTf) in dichloromethane. Note that Scheme 2 shows the formation of the four possible Ru/Pd isomer dendrimers (**15**−**18**) on the basis of the presence or absence of triflate (or vacancies) on the metal centers. **18** was anticipated to be a precursor for triple-metallic-layered dendrimers due to the vacancy on the palladium, which could facilitate the entry of a new metal fragment on the periphery. Moreover, the vacancy on the ruthenium could avoid the decoordination of the palladium ligand. However, treatment of **18** in nitromethane with [(4-pyPPh$_2$)AuCl] yielded a complex mixture of products which foiled our efforts to understand the reactions involved in such a process. Despite these unsuccessful results, we believe that the use of other metalloligands could afford triple-metallic-layered dendrimers in the future.

**Ruthenium/Rhodium Dendrimers.** The synthesis of the bimetallic ruthenium and rhodium-containing dendrimers is represented in Scheme 3.

The bimetallic Ru/Rh dendrimer **19** was obtained by the reaction of **3** with the dinuclear rhodium complex [RhCl(cod)]$_2$. The *P*Ph$_2$RhCl signal appeared at $\delta$ 31.8 ppm ($J_{\mathrm{PRh}}$ = 150 Hz), and that of the *P*Ph$_2$Ru ($\delta$ 31.0 ppm) did not shift, as expected. **19** behaves in the same way as **4** and **15**, and after several minutes at room temperature new signals at $\delta$ 26.4 ppm (*P*Ph$_2$RuCl) and $\delta$ 23.1 ppm (*P*Ph$_2$Rh, $J_{\mathrm{PRh}}$ = 148 Hz) began to emerge, indicating once again the migration of the chloride from rhodium to ruthenium to provide **20**. Equilibrium was achieved after 10 h. Likewise, the addition of PPh$_4$Cl generated a bimetallic dendrimer showing chloride ligands on both metal centers, **21**. The reaction was clean, and no other signals were present. In contrast with the behavior reported for **6** and **17**, **21** is quite stable in solution and only traces derived from decoordination were detected after 24 h. In summary, the synthesis and behavior of the bimetallic ruthenium/rhodium dendrimers follows the pattern described above for the gold and palladium species.

The presence of the cyclooctadiene ligand, which is known to undergo easy replacement by phosphine ligands,[9] made **21** a promising precursor for the construction of triple-metallic-layer dendrimers. However, our attempts to substitute the cyclooctadiene ligand for 1,1′-bis(diphenylphosphino)ferrocene (dppf) turned out to be unsuccessful. Whatever the reaction conditions, the cleavage of the phosphorus−rhodium bond was the predominant process, precluding the isolation of the expected Ru/Rh/Fe trimetallic dendrimer.

**Theoretical Study of the Ligand Migration.** To understand the relative stabilities of the species involved in the ligand migration process, we have carried out density functional calculations (see Computational

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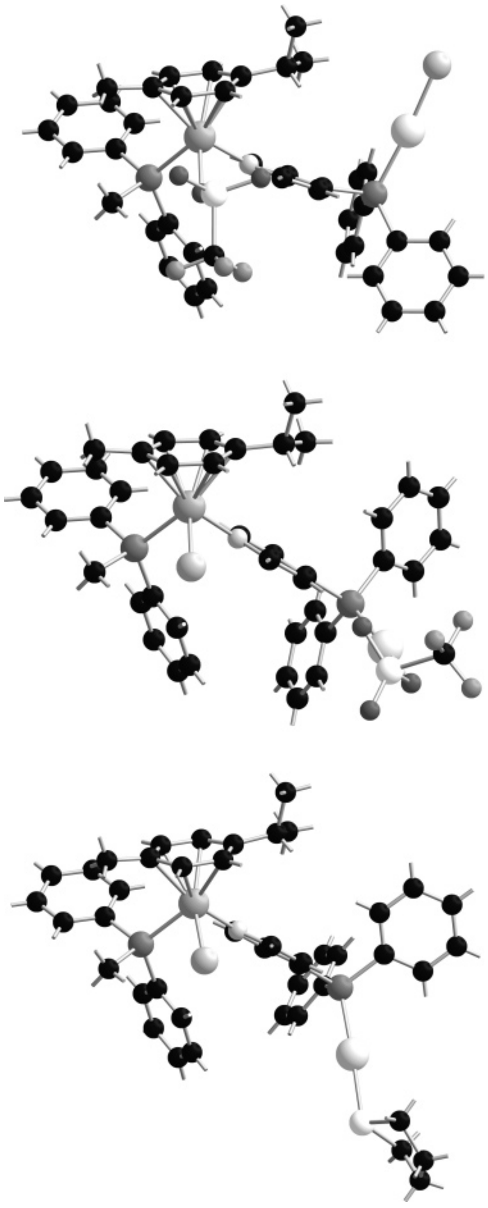

**Figure 2.** Representation of the three optimized model structures using the B3LYP functional corresponding to the ruthenium/gold dendrimers Ru(OTf)−AuCl (**4**), RuCl−Au(OTf), and RuCl−Au(tht) (**5**) (from top to bottom).

Details). In the case of the ruthenium/gold compounds, we have optimized the geometry for three model structures corresponding to the Ru(OTf)−AuCl (4), RuCl−Au(OTf), and RuCl−Au(tht) (**5**) systems, while for the ruthenium/palladium system the two models Ru(OTf)−PdCl (**15**) and RuCl−Pd(OTf) (**16**) were optimized. The Cartesian coordinates corresponding to such optimized models are included as Supporting Information, and the structures are represented in Figures 2 and 3.

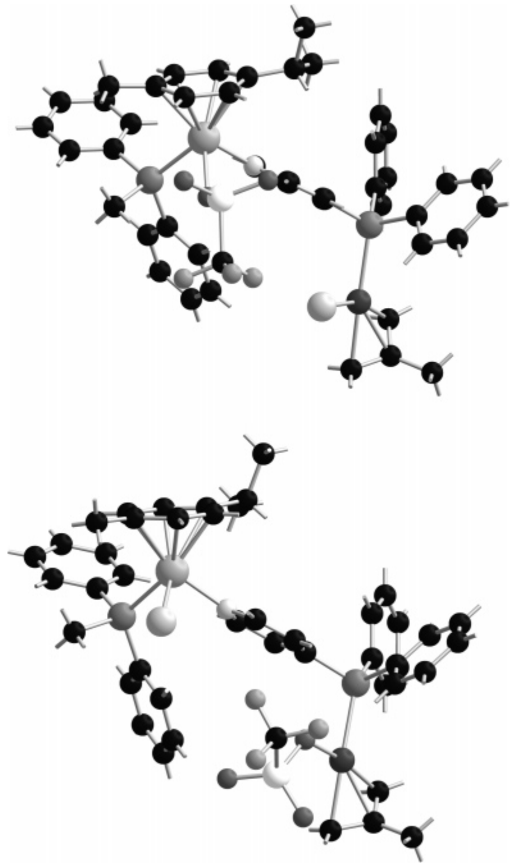

**Figure 3.** Representation of the two optimized model structures using the B3LYP functional corresponding to the ruthenium/palladium dendrimers (top) Ru(OTf)−PdCl (**15**) and (bottom) RuCl−Pd(OTf) (**16**).

The calculated energy differences for the ligand migration of the chloride and triflate ligands show different behaviors for the ruthenium/gold and ruthenium/palladium systems. Thus, in both cases the coordination of the triflate to the internal ruthenium atom is the more stable isomer; however, the energy difference is 12.4 kcal/mol in the case of the gold compound, while it is only 1.8 kcal/mol for the palladium complex. Hence, this result agrees well with the experimental behavior that the **15** and **16** dendrimers are identified in the proportion 1:1. In addition, the largest energy difference in the case of the gold compound justifies the possibility of isolating the Ru(OTf)−AuCl dendrimer (**4**) without ligand migration, as was observed experimentally. The calculated Ru−O bond energy is only 4.4 kcal/mol larger than the equivalent Ru−Cl value, in agreement with the equilibrium found experimentally from the NMR data. However, this difference seems to compensate for the steric effects due to the larger volume of the triflate ligand, as is shown for the faster and larger ligand migration found experimentally for the dendritic complex than for the model compound **M**.

A simple explanation for this different behavior between the gold and palladium dendrimers could be attributed to the greater softness of the gold atom in comparison with the palladium atom and, consequently, its preference for the coordination with the chloride anion over that with the triflate ligand. From the geometrical point of view, the analysis of Figures 2 and 3 also indicates that a greater proximity between the Cl and OTf ligands in the case of the palladium complexes would also facilite ligand migration in the palladium dendrimers.

In the case of gold dendrimers, a partial migration of the chloride anions only is probably induced mainly by the presence of the tht ligand and the steric effects. The Au−S bond is especially strong, and it can compete in the coordination of the heavy atoms with anionic ligands, such triflate. However, the Au−Cl bond energy is slightly larger. The calculated Au−S bond energy is

35.1 kcal/mol larger than the equivalent value for the Au−O bond of the triflate ligand. Hence, this is the driving force to produce the ligand migration to obtain the RuCl−Au(tht) (**5**) dendrimer. However, the most stable system, RuCl−AuCl (**6**), as was shown experimentally, is obtained in the presence of $PPh_4Cl$ by confirming the strength of the Au−Cl bond.

## Concluding Remarks

Bimetallic carbosilane dendrimers containing an internal ruthenium-based layer and a surface decorated with gold, palladium, or rhodium units have been synthesized. The route involves the selective binding of the bifunctional 4-pyPPh$_2$ ligand to the ruthenium atoms via the N donor atom as the key step. Thus, the reaction of the terminal phosphine with [(tht)AuCl], $[PdCl(\eta^3\text{-}2\text{-}MeC_3H_4)]_2$, or $[RhCl(cod)]_2$ enables metalation of the periphery of the dendrimer. A surprising chloride migration induced mainly for a dendritic effect from the peripheral metals to the ruthenium atoms was observed in all cases. Theoretical calculations based on density functional theory show a preference for the coordination of the ruthenium atoms with the triflate ligands. However, in the case of the palladium compounds the energy difference with the isomer resulting from the chloride migration is very small, in agreement with the simultaneous presence of both isomers detected by NMR, while in the case of the gold compounds only the presence of the tht ligand induces a partial chloride migration, due to the great stability of the Au−S bonds.

## Experimental Section

**General Considerations.** All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were distilled from sodium/benzophenone ketyl ($Et_2O$), dried with $CaCl_2$, and stored over molecular sieves (acetone) or dried with $CaCl_2$ and distilled from $CaH_2$ ($CH_2Cl_2$) under $N_2$ prior to use. Elemental analyses (C, H) were performed at the Servicio de Microanálisis del Centro de Investigación y Desarrollo del Consejo Superior de Investigaciones Científicas (CSIC). $^1H$, $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$, $^{31}P\{^1H\}$, and $^{19}F\{^1H\}$ NMR spectra were recorded at 25 °C on Bruker 250 and Mercury 400 spectrometers. Chemical shifts are reported in ppm relative to external standards ($SiMe_4$ for $^1H$, $^{13}C$, and $^{29}Si$, 85% $H_3PO_4$ for $^{31}P$, $CF_3COOH$ for $^{19}F$), and coupling constants are given in Hz.

The starting materials $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(cod)][OTf]$,[10] $[PdCl(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)]_2$,[11] $[RhCl(cod)]_2$,[12] [(tht)AuCl],[13] 4-pyridyldiphenylphosphine,[14] and dendrimers **1** and **8**[7b] were prepared by following published procedures. Other reagents were purchased from commercial suppliers.

**General Method for the Preparation of Gold- and Ruthenium-Containing Dendrimers. Dendrimer 3.** To a solution of **1** (148 mg, 0.062 mmol) in 20 mL of $CH_2Cl_2$ was added AgOTf (190 mg, 0.740 mmol). The mixture was stirred for 2 h, and the AgCl that formed was removed by filtration through Celite. This solution was added to another of 4-pyridyldiphenylphosphine (130 mg, 0.49 mmol) in $CH_2Cl_2$ (10 mL). The mixture was stirred for 1 h, and the solvent was evaporated to dryness. The residue was washed with ether, and the product was recrystallized with dichloromethane/ether. The complex was obtained as a yellow solid (203 mg, 75% yield). $^1H$ NMR (400 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 8.28 ($s_{br}$, 8H; py $H_\alpha$), 7.80−7.70 (m, 88H; $C_6H_5$, py $H_\beta$), 5.87, 5.81, 5.58, 5.35 (m, 16H; $C_6H_4$), 2.11 (m, 4H; $CH(CH_3)_2$), 1.8 (m, 20H; $CH_2P$, $CH_3$), 1.09, 0.97 (m, 24H; $CH(CH_3)_2$), 0.04 to −0.59 (m, 40H; $CH_2Si$, $CH_3Si$). $^{13}C$ NMR (100 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 153.6 ($s_{br}$; py $C_\alpha$), 134.3 (d, $^2J_{CP}$ = 8.3 Hz; o-$C_6H_5$), 134.3−127.5 (m, $C_6H_5$; py $C_\beta$), 120.7 (q, $^1J_{CF}$ = 321 Hz; $CF_3SO_3$), 118.0 (q, $^1J_{CF}$ = 321 Hz, $CF_3SO_3$), 114.1 (s; $C-CH(CH_3)_2$), 103.3 (s; $C-CH_3$), 90.4, 89.0, 83.9, 80.8 ($s_{br}$; $C_6H_4$), 30.5 (s; $CH(CH_3)_2$), 21.8, 21.1 (s; $CH(CH_3)_2$), 17.6 (s; $CH_3$), 10 (m; $CH_2P$), 8.8 (s; $C^2H_2Si^1$), 1.8 (s; $C^1H_2Si^0$), −2.5, −3.0 (s; $CH_3Si^1$). $^{29}Si$ NMR (49.66 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 8.3 (s; $Si^0$), 4.3 (d; $^2J_{SiP}$ = 14.8 Hz; $Si^1$). $^{31}P$ NMR (101 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 31.3 (s; Ru−$PPh_2$), −4.2 ($s_{br}$; py$PPh_2$). $^{19}F$ NMR (376.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ −78.2 ($s_{br}$), −79.0 (s) ($CF_3SO_3$). Anal. Calcd for $C_{184}H_{200}F_{24}N_4O_{24}P_8Ru_4S_8Si_5$ (4356.6): C, 50.73; H, 4.63. Found: C, 50.36; H, 4.80.

**Dendrimer 4.** To a solution of dendrimer **3** (22 mg, 0.005 mmol) in 3 mL of $CD_2Cl_2$ was added 6.5 mg (0.020 mmol) of [(tht)AuCl], and the solution evolution was controlled by NMR. $^1H$ NMR (400 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 8.64 ($s_{br}$, 8H; py $H_\alpha$), 7.87−6.88 (m, 88H; $C_6H_5$, py $H_\beta$), 5.93, 5.82, 5.68, 5.37 (m, 16H; $C_6H_4$), 2.95 (m, 16H; tht), 2.25 (sep, $^3J_{HH}$ = 6.8 Hz, 16H; $CH(CH_3)_2$), 2.06−1.60 (m, 36H; $CH_2P$, $CH_3$, tht), 1.14, 0.97 (d, $^3J_{HH}$ = 6.8 Hz, 24H; $CH(CH_3)_2$), −0.03 (m, 16H; $CH_2Si$), −0.24, −0.56 (m, 24H; $CH_3Si$). $^{31}P$ NMR (101 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 32.3 (s; Au−$PPh_2$), 31.2 (s; Ru−$PPh_2$). $^{19}F$ NMR (376.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ −78.1 ($s_{br}$), −79.0 (s) ($CF_3SO_3$).

**Dendrimer 6.** To a solution of dendrimer **3** (22 mg, 0.005 mmol) in 3 mL of $CH_2Cl_2$ was added 7.6 mg (0.020 mmol) of $(PPh_4)Cl$ and 6.5 mg (0.020 mmol) of [(tht)AuCl]. The solvent was evaporated to dryness, and the residue was washed with ether. $^1H$ NMR (400 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 8.84 ($s_{br}$, 8H; py $H_\alpha$), 7.93−7.03 (m, 88H; $C_6H_5$, py $H_\beta$), 5.50, 5.43, 5.28 (m, 16H; $C_6H_4$), 2.79 (m, 16H; tht), 2.38 (m, 4H; $CH(CH_3)_2$), 1.91−1.74 (m, 36H; $CH_2P$, $CH_3$, tht), 1.15, 1.00 (m, 24H; $CH(CH_3)_2$), −0.01 to −0.65 (m, 40H; $CH_2Si$, $CH_3Si$). $^{31}P$ NMR (101 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 31.8 ($s_{br}$; Au−$PPh_2$), 26.2 (s; Ru−$PPh_2$), 23.7 (s; $PPh_4$). $^{19}F$ NMR (376.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ −79.2 (s; $CF_3SO_3$).

**Dendrimer 10.** Experimental conditions and workup were identical with those of the preparation of **3** (120 mg, 71% yield). $^1H$ NMR (400 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 8.28 ($s_{br}$, 16H; py $H_\alpha$), 7.89−6.90 (m, 176H; $C_6H_5$, py $H_\beta$), 5.81, 5.70, 5.37 (m, 32H; $C_6H_4$), 2.11 (m, 8H; $CH(CH_3)_2$), 1.75 (m, 40H; $CH_2P$, $CH_3$), 1.07, 0.92 (m, 48H; $CH(CH_3)_2$), 0.21 to −0.53 (m, 148H; $CH_2Si$, $CH_3Si$). $^{13}C$ NMR (100 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 154.4 ($s_{br}$; py $C_\alpha$), 134.3−128.9 (m; $C_6H_5$, py $C_\beta$), 121.0 (q, $^1J_{CF}$ = 319 Hz; $CF_3SO_3$), 118.3 (q, $^1J_{CF}$ = 317 Hz; $CF_3SO_3$), 91.0, 83.1, 81.3 ($s_{br}$; $C_6H_4$), 30.7 (s; $CH(CH_3)_2$), 21.8 ($s_{br}$; $CH(CH_3)_2$), 17.9 (s; $CH_3$), 10 (m; $CH_2P$), 9.0 (s; $C^6H_2Si^3$), 6.9, 6.6, 4.2, 2.6 (s; $CH_2Si$), −1.9, −2.5, −4.7 (s; $CH_3Si$). $^{29}Si$ NMR (49.66 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 9.22 (s; $Si^0$), 8.06 (s; $Si^2$), 5.30 (s; $Si^1$), 5.60 ($s_{br}$; $Si^3$). $^{31}P$ NMR (101 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 31.0 (s; Ru−$PPh_2$), −4.6 ($s_{br}$; py$PPh_2$). $^{19}F$ NMR (376.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ −77.9 ($s_{br}$), −78.5 (s) ($CF_3SO_3$). Anal. Calcd for $C_{396}H_{468}F_{48}N_8O_{48}P_{16}Ru_8S_{16}Si_{17}$ (9314.6): C, 51.06; H, 5.06. Found: C, 50.92; H, 5.15.

**Dendrimer 11.** Experimental conditions and workup were identical with those of the preparation of **4**, using dendrimer **10** as starting material. $^1H$ NMR (400 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 8.63 ($s_{br}$, 16H; py $H_\alpha$), 7.88−6.84 (m, 176H; $C_6H_5$, py $H_\beta$), 5.87, 5.60, 5.36 (m, 32H; $C_6H_4$), 3.02 (m, 32H; tht), 2.34 (sep, $^3J_{HH}$ = 6.8 Hz, 8H; $CH(CH_3)_2$), 2.08−1.85 (m, 72H; $CH_2P$, $CH_3$, tht), 1.12, 0.95 (d, $^3J_{HH}$ = 6.8 Hz, 48H; $CH(CH_3)_2$), 0.29 to −0.48 (m, 148H; $CH_2Si$, $CH_3Si$). $^{31}P$ NMR (101 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 32.4 (s; Au−$PPh_2$), 31.2 (s; Ru−$PPh_2$). $^{19}F$ NMR (376.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ −78.1 ($s_{br}$), −79.0 (s) ($CF_3SO_3$).

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**Dendrimer 13.** Experimental conditions and workup were identical with those of the preparation of **6**. $^1$H NMR (400 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 8.83 ($s_{br}$, 16H; py $H_\alpha$), 7.92−7.01 (m, 176H; $C_6H_5$; py $H_\beta$), 5.48, 5.20, (s, 32H; $C_6H_4$), 2.80 (m, 32H; tht), 2.34 (sep, $^3J_{HH} = 6.8$ Hz, 8H; $\mathit{CH}(CH_3)_2$), 2.08−1.85 (m, 72H; $CH_2P$, $CH_3$, tht), 1.12, 0.95 (d, $^3J_{HH} = 6.8$ Hz, 48H; $CH(\mathit{CH_3})_2$), 0.29 to −0.48 (m, 148H; $CH_2Si$, $CH_3Si$). $^{31}$P NMR (101 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 32.5 (s; Au−$PPh_2$), 26.1 (s; Ru−$PPh_2$), 23.7 (s; $PPh_4$). $^{19}$F NMR (376.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ −79.1 (s; $CF_3SO_3$).

**General Method for the Preparation of Palladium- and Ruthenium-Containing Dendrimers. Dendrimer 15.** To a solution of 25 mg (0.0057 mmol) of dendrimer **3** in $CH_2Cl_2$ was added 4.5 mg (0.011 mmol) of $[PdCl(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)]_2$. The solution was stirred for 15 min, after which $^{31}$P NMR solution spectra showed dendrimer **15** as the unique product. $^1$H NMR (400 MHz, $[D_3]$nitromethane, 25 °C): $\delta$ 8.60 ($s_{br}$; py $H_\alpha$). $^{31}$P NMR (101 MHz, $[D_3]$nitromethane, 25 °C): $\delta$ 27.9 ($s_{br}$; Ru−$PPh_2$), 21.6 ($s_{br}$; Pd−$PPh_2$). After 1 h in solution a yellow solid was isolated by filtration as a mixture of **15** and **16**.

**Dendrimer 16.** A mixture of dendrimer **3** (26 mg, 0.006 mmol), $(PPh_4)Cl$ (9 mg, 0.024 mmol), and $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(cod)][OTf]$ (10 mg, 0.024 mmol) in $CH_2Cl_2$ (5 mL) was stirred for 15 min. $^1$H NMR (400 MHz, $[D_3]$nitromethane, 25 °C): $\delta$ 8.81 ($s_{br}$; py $H_\alpha$). $^{31}$P NMR (101 MHz, $[D_3]$nitromethane, 25 °C): $\delta$ 23.4 ($s_{br}$; Ru−$PPh_2$), 20.8 ($s_{br}$; Pd−$PPh_2$).

**Dendrimer 17.** A solution of 20 mg (0.0045 mmol) of dendrimer **3**, $(PPh_4)Cl$ (7 mg, 0.018 mmol), and $[PdCl(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)]_2$ (3.6 mg, 0.009 mmol) in 5 mL of $CH_2Cl_2$ was stirred for 15 min. Dendrimer **17** was obtained as a yellow solid with $(PPh_4)(OTf)$ as an impurity. Dendrimer **17** could also be obtained by adding 7 mg (0.018 mmol) of $(PPh_4)Cl$ to a solution of dendrimers **15** and **16** (23 mg, 0.0045 mmol) in nitromethane. $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ 8.72 ($s_{br}$, 8H; py $H_\alpha$), 8.00−7.00 (m, 168H; $C_6H_5$, py $H_\beta$, $PPh_4$), 5.49, 5.38, 5.26 (m, 16H; $C_6H_4$), 4.57, 3.55, 3.16, 2.89 ($s_{br}$, 16H; $CH_2$), 2.49 (vt, $^3J_{HP} = 14.5$ Hz, 8H; $CH_2P$), 2.26 (m, 4H; $\mathit{CH}(CH_3)_2$), 1.98 (s, 12H; $CH_3$), 1.71 (m, 12H; $CH_3$), 1.07, 0.93 (d, $^3J_{HH} = 6.7$ Hz, 24H; $CH(\mathit{CH_3})_2$), −0.06 (m, 16H; $CH_2Si$), −0.38, −0.65 (s, 24H; $CH_3Si$). $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta$ 155.6 ($s_{br}$; py $C_\alpha$), 138.8−116.9 (m; $C_6H_5$), 121.1 (q, $^1J_{CF} = 321$ Hz; $CF_3SO_3$), 110.2 (s; $\mathit{C}-CH(CH_3)_2$), 101.2 (s; $\mathit{C}-CH_3$), 90.6, 88.2, 78.3 ($s_{br}$; $C_6H_4$), 62.1 ($s_{br}$, $CH_2$), 30.6 (s; $\mathit{CH}(CH_3)_2$), 23.0 (s; $CH_3$), 22.1, 21.8 (s; $CH(\mathit{CH_3})_2$), 17.4 (s; $CH_3$), 12.7 (m; $CH_2P$), 8.7 (s; $C^2H_2Si^1$), 2.3 (s; $C^1H_2Si^0$), −2.1, −2.6 (s; $CH_3Si^1$). $^{31}$P NMR (101 MHz, $CDCl_3$, 25 °C): $\delta$ 26.6 (s; Ru−$PPh_2$), 24.6 (s; Pd−$PPh_2$), 23.6 (s; $PPh_4$). $^{19}$F NMR (376.5 MHz, $CDCl_3$, 25 °C): $\delta$ −79.6 (s; $CF_3SO_3$).

**Dendrimer 18.** A solution of **3** (52 mg, 0.012 mmol) in 5 mL of $CH_2Cl_2$ was added to another of $[Pd(\eta^3\text{-}2\text{-}Me\text{-}C_3H_4)(cod)][OTf]$ (20 mg, 0.048 mmol) in 5 mL of $CH_2Cl_2$. After 1 h of stirring the yellow solid was isolated by filtration (42 mg, 63%). $^1$H NMR (400 MHz, $[D_3]$nitromethane, 25 °C): $\delta$ 8.60 ($s_{br}$, 8H; py($H_\alpha$)), 8.00−7.02 (m, 88H; $C_6H_5$, py $H_\beta$), 5.7−5.44 (m, 16H; $C_6H_4$), 4.2−3.4 (m, 16H; $CH_2$), 2.26−1.88 (m, 36H; $\mathit{CH}(CH_3)_2$, $CH_3$, $CH_2P$, $CH_3$), 1.16, 0.99 ($s_{br}$, 24H; $CH(\mathit{CH_3})_2$), 0.1 to −0.43 (m, 40H; $CH_2Si$, $CH_3Si$). $^{13}$C NMR (63 MHz, $[D_3]$nitromethane, 25 °C): $\delta$ 155.3 (br; py $C_\alpha$), 134.9−128.7 (m; $C_6H_5$), 121.2 (q, $^1J_{CF} = 321$ Hz; $CF_3SO_3$), 118.3 (q, $^1J_{CF} = 320$ Hz; $CF_3SO_3$), 112.1 ($s_{br}$; $C-CH(CH_3)_2$), 104.5 ($s_{br}$; $\mathit{C}-CH_3$), 91.0, 81.7 ($m_{br}$; $C_6H_4$), 30.7 (s; $\mathit{CH}(CH_3)_2$), 22.6 (s; $CH_3$), 21.6 ($s_{br}$; $CH(CH_3)_2$), 17.3 (s; $CH_3$), 10.7 (m; $CH_2P$), 8.5 ($s_{br}$; $C^2H_2Si^1$), 1.8 ($s_{br}$; $C^1H_2Si^0$), −2.7, −3.0 ($s_{br}$; $CH_3Si^1$). $^{31}$P NMR (101 MHz, $[D_3]$nitromethane, 25 °C): $\delta$ 27.5 ($s_{br}$; Ru−$PPh_2$), 21.0 (s; Pd−$PPh_2$). $^{19}$F NMR (376.5 MHz, $[D_3]$nitromethane, 25 °C): $\delta$ −78.9 ($s_{br}$), −79.6 (s) ($CF_3SO_3$).

**General Method for the Preparation of Rhodium- and Ruthenium-Containing Dendrimers. Dendrimer 19.** A solution of dendrimer **3** (30 mg, 0.007 mmol) and $[RhCl(cod)]_2$ (7 mg, 0.014 mmol) in 3 mL of $CDCl_3$ was stirred for 15 min, and the solution evolution was controlled by NMR. $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ 8.45 ($s_{br}$, 8H; py($H_\alpha$)), 8.00−6.93 (m, 88H; $C_6H_5$, py($H_\beta$)), 5.92, 5.80, 5.72, 5.60, 5.34, (m, 24H; $C_6H_4$, cod CH=CH), 3.08 ($s_{br}$, 8H; cod CH=CH), 2.43 (m, 16H; cod $CH_2$), 2.09−1.65 (m, 40H; $\mathit{CH}(CH_3)_2$, $CH_2P$, $CH_3$, cod $CH_2$), 1.07, 0.94 (d, $^3J_{HH} \approx 6$ Hz, 24H; $CH(\mathit{CH_3})_2$), −0.01 (m, 16H; $CH_2Si$), −0.33, −0.65 (m, 24H; $CH_3Si$). $^{31}$P NMR (101 MHz, $CDCl_3$, 25 °C): $\delta$ 31.8 (d, $^1J_{PRh} \approx 150$ Hz; Rh−$PPh_2$), 31.0 (s; Ru−$PPh_2$).

**Dendrimer 21.** A solution of dendrimer **3** (30 mg, 0.007 mmol), $[RhCl(cod)]_2$ (7 mg, 0.014 mmol), and $(PPh_4)Cl$ (10 mg, 0.028 mmol) in 5 mL of $CH_2Cl_2$ was stirred for 5 min. The solvent was evaporated to dryness and the residue washed with ether to obtain a yellow solid. $^1$H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta$ 8.70 ($s_{br}$, 8H; py($H_\alpha$)), 7.89−6.98 (m, 168H; $C_6H_5$, py($H_\beta$), $PPh_4$), 5.56, 5.42, 5.27 (m, 24H; $C_6H_4$, cod CH=CH), 3.10 ($s_{br}$, 8H; cod CH=CH), 2.4−1.68 (m, 56H; $\mathit{CH}(CH_3)_2$, $CH_2P$, $CH_3$, cod $CH_2$), 1.08, 0.89 ($s_{br}$, 24H; $CH(\mathit{CH_3})_2$), −0.09 (m, 16H; $CH_2Si$), −0.39, −0.65 ($s_{br}$, 24H; $CH_3Si$). $^{13}$C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta$ 155.1 ($s_{br}$; py $C_\alpha$), 135.8−128.7 ($C_6H_5$; py $C_\beta$), 121.2 (q; $^1J_{CF} = 321$ Hz; $CF_3SO_3$), 108−103 (m; cod CH=CH), 90.4, 89.0 ($s_{br}$; $C_6H_4$), 73 (m; cod CH=CH), 32.9 ($s_{br}$; cod $CH_2$), 30.7 (s; $\mathit{CH}(CH_3)_2$), 29.0 ($s_{br}$; cod $CH_2$), 21.9 (s; $CH(\mathit{CH_3})_2$), 17.4 (s; $CH_3$), 10 (m; $CH_2P$), 8.7 (s; $C^2H_2Si^1$), 1.8 (s; $C^1H_2Si^0$), −2.1, −2.6 (s; $CH_3Si^1$). $^{31}$P NMR (101 MHz, $CDCl_3$, 25 °C): $\delta$ 29.8 (d, $^1J_{PRh} = 155$ Hz; Rh−$PPh_2$), 25.0 (s; Ru−$PPh_2$), 22.3 (s; $PPh_4$).

**Synthesis of [Ru(OTf)(*p*-cymene)($PMePh_2$)(pyP$Ph_2$)][OTf] (M).** Experimental conditions and workup were identical with those of the preparation of **3** (103 mg, 91% yield). $^1$H NMR (400 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 8.20 (d, $^3J_{HH} = 5$ Hz; 2H; py $H_\alpha$), 7.40−7.14 (m, 20H; $C_6H_5$), 6.88 (pt, $^3J_{HH} = {}^3J_{HP} = 5$ Hz; 2H, py $H_\beta$), 6.34 (d, $^3J_{HH} = 6$ Hz; 1H, $C_6H_4$), 5.90 (d, $^3J_{HH} = 6$ Hz; 1H, $C_6H_4$), 5.80 (dd, $^3J_{HH} = 6.2$ Hz; $^3J_{HP} = 1.2$ Hz;1H, $C_6H_4$), 5.70 (dd, $^3J_{HH} = 6.2$ Hz; $^3J_{HP} \approx 1.5$ Hz; 1H, $C_6H_4$), 2.38 (d, $^2J_{HP} = 9.9$ Hz; 3H, $CH_3P$), 2.13 (sep, $^3J_{HH} = 6.9$ Hz; 1H; $\mathit{CH}(CH_3)_2$), 1.83 (s, 3H; $CH_3$), 1.01, 1.00 (d + d, $^3J_{HH} = 6.9$ Hz; 6H; $CH(\mathit{CH_3})_2$). $^{13}$C NMR (62.9 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 153.2 (s; py $C_\alpha$), 134.7−128.7 (m, $C_6H_5$; py $C_\beta$, 121.0 (q, $^1J_{CF} = 320$ Hz; $CF_3SO_3$), 118.1 (q, $^1J_{CF} = 318$ Hz, $CF_3SO_3$), 117.4 (d; $^2J_{CP} = 5.8$ Hz; $\mathit{C}-CH(CH_3)_2$), 103.9 (s; $\mathit{C}-CH_3$), 91.4 (d, $^2J_{CP} = 6.5$ Hz; $C_6H_4$), 84.3 (s; $C_6H_4$), 83.5 (s; $C_6H_4$), 31.3 (s; $\mathit{CH}(CH_3)_2$), 22.6, 20.9 (s; $CH(\mathit{CH_3})_2$), 18.7 (s; $CH_3$), 13.6 (d; $^1J_{CP} = 33$ Hz; $CH_3P$). $^{31}$P NMR (101 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 20.4 (s; Ru−$PPh_2$), −4.2 ($s_{br}$; pyP$Ph_2$). $^{19}$F NMR (376.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ −78.3 (s), −79.2 (s) ($CF_3SO_3$). Anal. Calcd for $C_{42}H_{41}F_6NO_6P_2RuS_2$ (996.9): C, 50.60; H, 4.15. Found: C, 50.78; H, 4.26; MS (ES$^+$): *m*/*z* 848.3 [M − OTf]$^+$.

**Synthesis of [Ru(OTf)(*p*-cymene)($PMePh_2$)(pyP$Ph_2$-AuCl)][OTf].** To a solution of complex **M** (30 mg, 0.030 mmol) in 3 mL of $CH_2Cl_2$ was added 9.6 mg (0.03 mmol) of [(tht)AuCl]. The mixture was stirred for 15 min, and the solvent was evaporated to dryness. The residue was washed with ether and dried under vacuum (31 mg, 85% yield). $^1$H NMR (400 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 8.53 ($s_{br}$; 2H; py $H_\alpha$), 7.49−7.10 (m, 22H; $C_6H_5$, py $H_\beta$), 6.37 (d, $^3J_{HH} = 6$ Hz; 1H, $C_6H_4$), 5.94 (d, $^3J_{HH} = 6$ Hz; 1H, $C_6H_4$), 5.91 (d, $^3J_{HH} = 6$ Hz; 1H, $C_6H_4$), 5.68 ($d_{br}$, $^3J_{HH} = 6$ Hz; 1H, $C_6H_4$), 2.39 (d, $^2J_{HP} = 10.0$ Hz; 3H, $CH_3P$), 2.22 (sep, $^3J_{HH} = 6.9$ Hz; 1H; $\mathit{CH}(CH_3)_2$), 1.87 (s, 3H; $CH_3$), 1.03, 1.02 (d + d, $^3J_{HH} = 6.9$ Hz; 6H; $CH(\mathit{CH_3})_2$). $^{13}$C NMR (100 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 155.1 ($s_{br}$; py $C_\alpha$), 134.8−128.4 (m, $C_6H_5$; py $C_\beta$), 121.0 (q, $^1J_{CF} = 321$ Hz; $CF_3SO_3$), 118.0 (q, $^1J_{CF} = 318$ Hz, $CF_3SO_3$), 117.3 (d; $^2J_{CP} = 6.6$ Hz; $\mathit{C}-CH(CH_3)_2$), 104.2 (s; $\mathit{C}-CH_3$), 91.9 (d, $^2J_{CP} = 5.9$ Hz; $C_6H_4$), 84.7 (s; $C_6H_4$), 83.9 (s; $C_6H_4$), 83.8 (s; $C_6H_4$), 31.4 (s; $\mathit{CH}(CH_3)_2$), 22.5, 21.1 (s; $CH(\mathit{CH_3})_2$), 18.7 (s; $CH_3$), 13.4 (d; $^1J_{CP} = 33.4$ Hz; $CH_3P$). $^{31}$P NMR (101 MHz, $CD_2Cl_2$, 25 °C): $\delta$ 20.5 (s; Ru−$PPh_2$), 32.2 (s; Au−$PPh_2$). $^{19}$F NMR (376.5 MHz, $CD_2Cl_2$, 25 °C): $\delta$ −78.2 (s), −79.1 (s) ($CF_3SO_3$);. Anal. Calcd for $C_{42}H_{41}AuClF_6NO_6P_2RuS_2$ (1229.4): C, 41.03; H, 3.36. Found: C, 41.36; H, 3.26; MS (ES$^+$): *m*/*z* 1080.3 [M − OTf]$^+$.

**Computational Details.** The calculations were performed using the Gaussian03 C01 version[15] with the hybrid B3LYP functional[16−18] and the Stoll-Preuss pseudopotentials for the metal atoms,[19] while the Dunning−Huzinaga double-$\zeta$ basis[20] set was employed for the main-group elements. The atomic charges were calculated using the natural bond orbital approach.[21]

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**Supporting Information Available:** Tables giving Cartesian coordinates corresponding to the optimized models using the B3LYP functional. This material is available free of charge via the Internet at http://pubs.acs.org.

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