Phosphorus-Containing Dendrimers as Multidentate Ligands: Palladium, Platinum, and Rhodium Complexes

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New dendrimers **3-[G′$_1$]**−**3-[G′$_4$]** possessing from 6 to 48 $N(CH_2PPh_2)_2$ terminal groups are described. The corresponding Pd, Pt, and Rh complexes $[N(CH_2PPh_2)_2MRR']_y$ (y from 6 to 24; generations 1−3) [M = Pd: R = R′ = Cl, Br; R = Cl, R′ = Me; R = Br, R′ = Me; R = Cl, R′ = COMe; R = Cl, R′ = norbornyl-COMe. M = Pt: R = R′ = Br, Cl, Me; R = Br, R′ = Me. M = Rh: R, R′ = acac] are prepared by reacting **3-[G′$_1$]**−**3-[G′$_3$]** with the appropriate transition metal complexes.

Introduction

The design of new ligands and the use of their corresponding complexes as effective catalysts for a variety of reactions is more than ever of current interest. Much effort has been made to enhance the regioselectivity of a number of reactions, the steric and electronic properties of the ligands having a dramatic influence on the reactivity of organometallic complexes.

Recently, attention has been focused on the use of dendrimers[1] as multidentate ligands. These macromolecules can incorporate, within the cascade structure or on the surface, metals such as ruthenium,[2] osmium,[2a,e,f,j] platinum,[3] palladium,[4] iron,[2h,5] cobalt,[6] gold,[7] tungsten,[7a] nickel,[8] copper,[9] etc.

Some of these new complexes have been shown to be luminescent,[2d] to display redox[4a,b,5e] properties, or to have been used as catalysts.[4a,b,5e,8] For example, a silane molecular tree containing 12 nickel groups exhibits catalytic activity for the Kharash addition of polyhalogenoalkanes to a carbon−carbon double bond[8] or a phosphorus-containing dendrimer in which five Pd^{II} groups bonded to tripodal phosphines catalyze the electrochemical reduction of CO_2 to CO.[4a,b]

We have reported for these last 2 years the preparation of phosphorus-containing dendrimers built to the 10th generation[7a,10] and possessing either aldehyde groups or P−Cl bonds on the surface. Reactivity of these terminal functions allowed us to prepare a large number of multi di-, tri-, or tetrafunctionalized dendrimers[11] as well as dendrimers possessing up to 3072 phosphino end groups. As a first application of these

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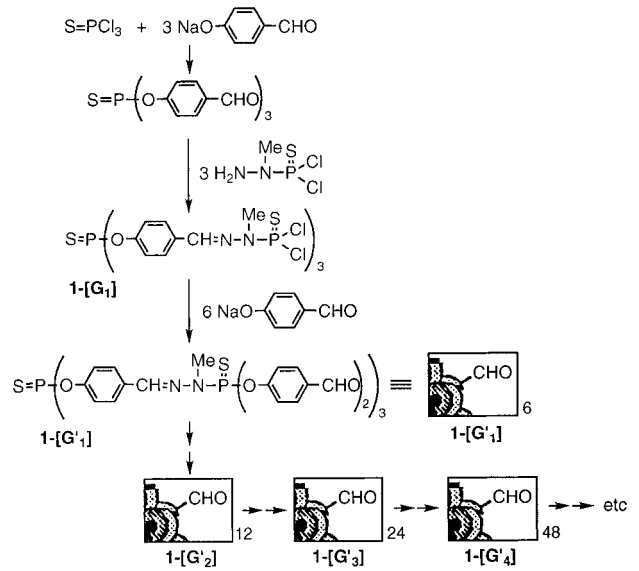
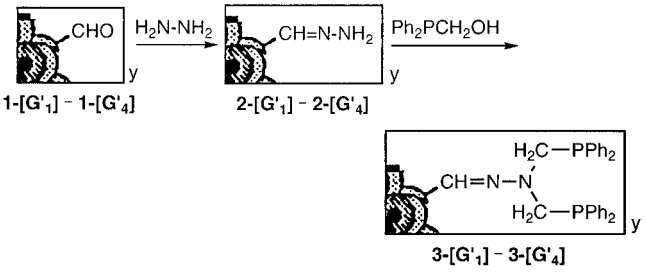
Scheme 1



Scheme 2



from y = 6 for **[G'1]** to y = 48 for **[G'4]**

dendrimers, gold complexes were prepared and were imaged by high-resolution electron microscopy in order to compare the size of consecutive generations.[7a]

We report here the grafting of diphosphino groups on the surface of some of these dendrimers and the synthesis of the corresponding Pd, Pt, and Rh complexes. It will be also demonstrated that an organometallic chemistry on the dendritic surface can be readily developed.

Results and Discussion

Dendrimers of generations 1−4 (**1-[G′1]** to **1-[G′4]**; 6−48 terminal aldehyde groups) were prepared using the strategy outlined on Scheme 1.[7a,10] Addition of hydrazine to these macromolecules gave rise quantitatively to dendrimers **2-[G′1]**−**2-[G′4]** incorporating $CH{=}NNH_2$ end groups, which were further reacted with the phosphine Ph_2PCH_2OH (2 equiv of phosphine/NH_2 group) to give the new dendrimers **3-[G′1]**−**3-[G′4]** (Scheme 2, Figure 1) possessing between 6 and 48 $N(CH_2PPh_2)_2$ terminal groups.

Palladium Complexes. The dendrimer **3-[G′1]** in solution in dichloromethane (1 equiv) was first reacted with $PdCl_2$(COD) (6 equiv). The resulting complex **4-[G′1]** obtained in 84% yield (Scheme 3) was characterized by means of ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy and elemental analysis. The ^{31}P NMR spectrum showed, for example, three singlets at 7.0 (PPh_2), 54.9 (P core), and 64.2 (P generation 1) ppm with an expected deshielding effect for the diphenylphosphino groups linked to $PdCl_2$ ($\Delta\delta$ = 32 ppm). An easy halogen

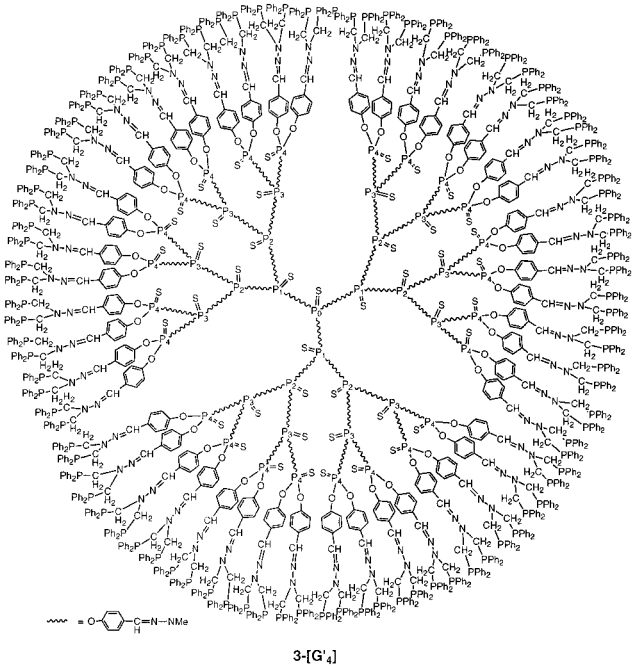


Figure 1.

exchange took place when a dichloromethane solution of **4-[G′1]** was reacted with KBr. The complex **5-[G′1]** was isolated as an orange powder in 66% yield. The same complex can be directly prepared in 80% yield by adding $PdBr_2$(COD) to **3-[G′1]**. A deshielding effect analogous to the one observed during the transformation **3-[G′1]** → **4-[G′1]** was also detected in ^{31}P NMR [$\Delta\delta$ = 28 ppm; **5-[G′1]**, singlets at 3.2 (PPh_2), 54.9 (P core), and 64.3 (P generation 1) ppm].

Treatment of **4-[G′1]** with 12 equiv of the Grignard reagent BrMgMe led to the unsymmetrical bis-substituted palladium complex **6-[G′1]**; here halogen exchange and alkylation on palladium took place simultaneously. This new complex was characterized in solution; it is slowly converted into **5-[G′1]** in a few days at room temperature.

The ^{31}P NMR spectrum of **6-[G′1]** showed for the terminal PPh_2 groups two doublets at −12.0 [$^2J_{PP}$ = 43.3 Hz, Ph_2P trans to Me−(Pd)] and 18.2 [($^2J_{PP}$ = 43.3 Hz, Ph_2P trans to Br)] ppm which were attributed by comparison with similar Pd diphosphine complexes.[12] Such an assignment was corroborated by ^{13}CO experiments. The ^{1}H NMR spectrum displayed for the methyl group bonded to Pd a doublet of doublets at 0.67 ($^2J_{PP}$ = 7.7 and 4 Hz) ppm.

On the other hand monomethylation, exclusively, can be clearly performed when **4-[G′1]** is treated with Cp_2ZrMe_2. The dendritic complex **7-[G′1]** was isolated in 65% yield (Scheme 3) and exhibited spectroscopic data similar to those of **6-[G′1]**.

Therefore, methylation of the surface metal complexes for generation 1 can be achieved either by using MeMgBr or Cp_2ZrMe_2. In the first case methylation is accompanied by halogen exchange while only methylation takes place in the second case.

7-[G′1] can be also prepared from **3-[G′1]** (1 equiv) and PdMeCl(COD) (6 equiv) (85% yield) (Scheme 3).

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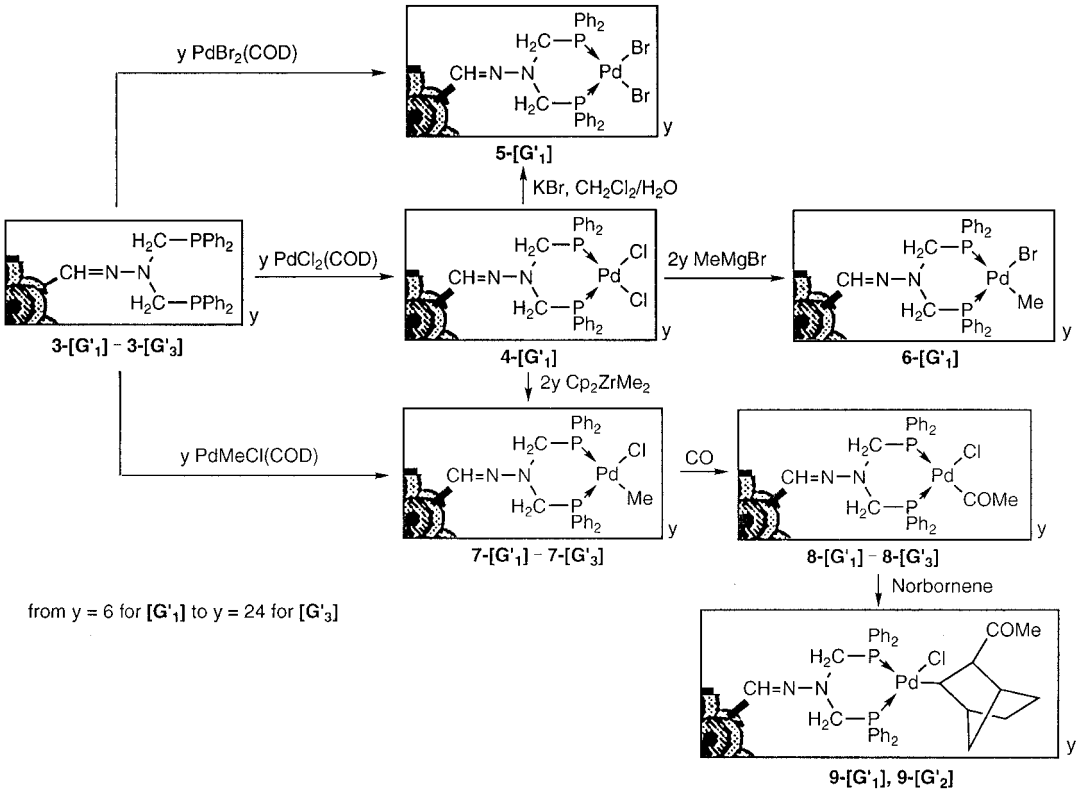
Scheme 3



A third type of reaction, namely CO insertion, was attempted on the dendritic surface. A few reports have described the carbonylation of organopalladium derivatives containing bidentate ligands with P−N,[13] N−N,[14] P−P,[12,15] or N−O[16] donor atoms. The rate of CO insertion into the Pd−Me bond in several diphosphine monomers has been recently studied[12,15] and was found to be very dependent of the nature on the ligand.

A deuteriodichloromethane solution of **7-[G′$_1$]** was pressurized to 1 bar of CO to give quantitatively **8-[G′$_1$]**. Upon carbonylation all the phosphorus resonances of the terminal diphosphino−palladium moieties were shifted to higher field: from −11.5 to −13.7 (Ph_2P trans to Me then trans to COMe) and from 21.8 to 7.4 (Ph_2P trans to Cl) ppm. The chemical shifts of the internal phosphorus atoms were unchanged, whereas, as already reported,[15a] the coupling constant $^2J_{PP}$ increased on going from the methyl complex (**7-[G′$_1$]**) to the acetyl one (**8-[G′$_1$]**): from 43.3 to 72.2 Hz. IR spectroscopy confirmed CO insertion ($\nu_{C=O}$ 1686 cm^{-1}). The ^{1}H NMR spectrum exhibited a singlet for the COMe group at 1.87 ppm (to be compared with the doublet of doublets ($^2J_{HP}$ = 7.8 and 3.5 Hz) detected at 0.58 ppm for PdMe in **7-[G′$_1$]**). ^{13}C NMR data clearly confirmed the absence of a doublet which could be attributed to the Me−Pd group. Insertion with ^{13}CO was performed in order to corroborate the proposed attribution. Indeed experiments with ^{13}CO allowed to detect the resonance of the CO group in ^{13}C NMR at 236.0 (dd, $^2J_{CPtrans}$ = 118.5 Hz, $^2J_{CPcis}$ = 13.1 Hz) (not observed with CO) and to assign unequivocally the two phosphorus resonances in the ^{31}P{^{1}H} NMR spectrum. In the ^{1}H NMR, the signal due to MeCOPd became a multiplet instead of a singlet. A similar ^{13}CO experiment has been precedently used to identify by high-pressure NMR spectroscopy a diphosphino intermediate incorporating the Pd(CO)Me moiety.[17]

8-[G′$_1$] was found to be stable more than 1 day in deuterated dichloromethane and can be stored as a solid for 3 days under argon without decomposition. Insertion of norbornene in the Pd−acetyl bond of complex **8-[G′$_1$]** took place readily with the formation of the new complex **9′-[G′$_1$]**. Resonances at −8.8 (d, $^2J_{PP}$ = 58.1 Hz, Ph_2P trans to COMe) and 23.7 (d, $^2J_{PP}$ = 58.1 Hz, Ph_2P trans to Cl) ppm were observed for the terminal diphosphino groups in **9′-[G′$_1$]**. These ^{31}P chemical shifts as well as the $^2J_{PP}$ (smaller than in the starting complex **8-[G′$_1$]**) are typical of alkyl complexes.[15a] ^{1}H NMR showed that the signal of the olefinic hydrogen at 6 ppm disappeared while that of the acyl group shifted from 1.8 to 2.2 ppm (a typical value for ketones).

The ability of dendrimers of higher generations, *i.e.* dendrimers **3-[G′$_2$]** and **3-[G′$_3$]**, to act as ligands toward PdMeCl(COD) was also investigated. The reactions were performed under the same experimental conditions as those used for **3-[G′$_1$]** and led to the formation of dendritic complexes **7-[G′$_2$]** and **7-[G′$_3$]** possessing 12 or 24 PdClMe moieties on the surface (Scheme 3). These new complexes were fairly soluble in dichloromethane

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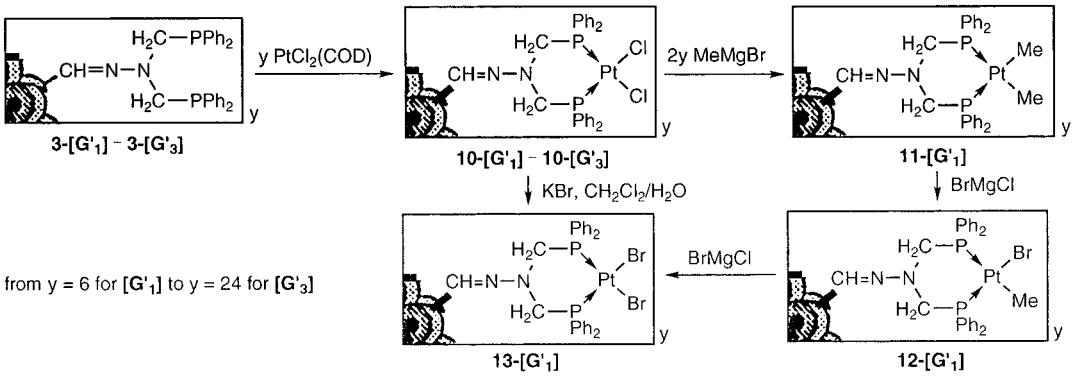
Scheme 4



as **7-[G′$_1$]** and were also fully characterized by NMR, IR, and elemental analysis. They reacted readily with CO to give the expected insertion products **8-[G′$_2$]** and **8-[G′$_3$]** showing NMR properties similar to those of **8-[G′$_1$]**. The insertion of norbornene into the Pd−acetyl bond of **8-[G′$_2$]** gave **9-[G′$_2$]**.

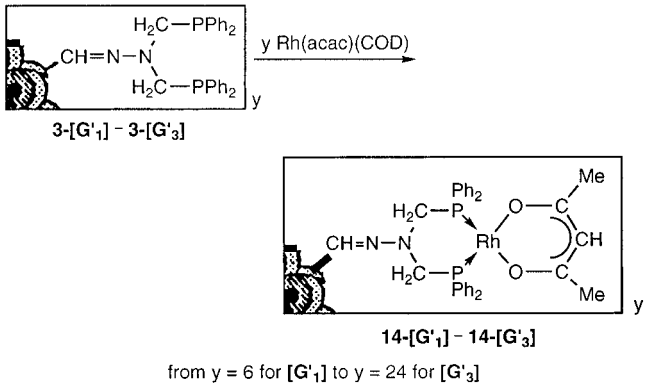
Pt Complexes. Reaction of **3-[G′$_1$]** (1 equiv) in a dichloromethane solution with $PtCl_2$(COD) (6 equiv) led to the complex **10-[G′$_1$]** obtained as a yellow powder in 95% yield.

The same reaction done with **3-[G′$_2$]** and **3-[G′$_3$]** allowed the isolation of complexes **10-[G′$_2$]** and **10-[G′$_3$]** incorporating 12 and 24 $PtCl_2$ moieties on the dendrimer surface (Scheme 4). In addition to the singlets due to the internal phosphorus atoms, the ^{31}P NMR spectra of **10-[G′$_1$]**, **10-[G′$_2$]**, and **10-[G′$_3$]** also showed a singlet at ca. −9 ppm with ^{195}Pt satellites for the Ph_2P end groups ($^1J_{P^{195}Pt}$ from 3434 to 3440 Hz). The ^{195}Pt{^{1}H} NMR spectrum corroborated such assignment. A triplet was observed for example for **10-[G′$_1$]** at −4516 ppm. In the ^{1}H NMR spectra the complexation of platinum is revealed by the presence of $^3J_{H^{195}Pt}$ of 39.6−40.7 Hz between the CH_2 protons of the CH_2P groups and Pt.

Substitution on platinum was attempted by reacting a THF/toluene solution of MeMgBr (12 equiv) with a CD_2Cl_2 solution of **10-[G′$_1$]** (1 equiv) for 1 h at room temperature. The ^{31}P{^{1}H} NMR spectrum of the resulting solution indicated the presence of only one phosphorus compound characterized in situ; only one singlet at −1.3 ppm ($^1J_{P^{195}Pt}$ = 1795 Hz) was detected for the terminal diphenylphosphino groups. The change of the $^1J_{P^{195}Pt}$ value from 3440 Hz for **10-[G′$_1$]** to 1795 Hz for **11-[G′$_1$]** is a consequence of the well-known "trans influence" and has to be compared with the values obtained for related complexes, such as Cl_2Pt(dppe) (J = 3618 Hz) and Me_2Pt(dppe) (J = 1794 Hz).[18] The ^{1}H NMR spectrum revealed the presence of two methyl groups linked to Pt [δ(MePt) = 0.436 (br s with ^{195}Pt satellites, $^2J_{H1^{195}Pt}$ = 68.8 Hz)], and ^{13}C NMR data corroborated that a Cl−Me exchange reaction occurred.

All these NMR data were in agreement with the formation of **11-[G′$_1$]**, a compound possessing six terminal $PtMe_2$ groups. However, **11-[G′$_1$]** was found to be unstable in the presence of ClMgBr generated in the reaction. Attempts to quench ClMgBr with an aqueous solution of $NH_4^+Cl^-$ [19] did not allow its complete removal. Stirring **11-[G′$_1$]** with ClMgBr in THF/toluene/CD_2Cl_2 solution first led to the complex **12-[G′$_1$]** with Pt(Me)Br end groups and then to **13-[G′$_1$]** with $PtBr_2$ end groups.

Scheme 5



The ^{31}P NMR spectrum of compound **12-[G′$_1$]** exhibited two doublets at δ = 0.0 and δ = −3.7 ppm ($^2J_{PP}$ = 17 Hz) corresponding to two types of terminal PPh_2 groups. This indicates an unsymmetrical substitution on platinum, with one remaining methyl group, as shown by ^{1}H NMR. Furthermore, the values of $^1J_{P^{195}Pt}$ (4151 Hz for δ = 0.0 and 1673 Hz for δ = −3.7 ppm) were very different and in the range for a phosphino group trans to halogen and trans to methyl, respectively. At this step, the nature of the halogen on platinum (Cl or Br) was not clear, but compound **12-[G′$_1$]** evoluted slowly toward the symmetrical complex **13-[G′$_1$]**. This compound was fully halogenated as shown by the value of $^1J_{P^{195}Pt}$ (3363 Hz). This value is slightly different from that of the chlorine derivative **10-[G′$_1$]** (3440 Hz) and indicated the formation of the $PtBr_2$ complex **13-[G′$_1$]** rather than that of the starting $PtCl_2$ complex **10-[G′$_1$]**. This assignment was corroborated by the reaction of KBr with **10-[G′$_1$]** in CH_2Cl_2 which gave the same compound **13-[G′$_1$]**, isolated and fully characterized. The main difference between compounds **10-[G′$_1$]** and **13-[G′$_1$]** is observed on the ^{195}Pt NMR spectra which gave a triplet at δ = −4516 and δ = −4789 ppm, respectively.

Rhodium Complexes. The reaction of the rhodium complex Rh(acac)(COD) (6, 12, or 24 equiv) with **3-[G′$_1$]**, **3-[G′$_2$]**, or **3-[G′$_3$]** (1 equiv), respectively, yielded after workup yellow orange powders characterized as the expected diphosphino−rhodium complexes **14-[G′$_1$]**, **14-[G′$_2$]**, or **14-[G′$_3$]** (Scheme 5). ^{31}P NMR spectra exhibited for the terminal diphosphino groups doublets ($^1J_{P-Rh}$ from 130.8 to 131.2 Hz) at 21.8−23.5 ppm, besides the singlets due to the internal phosphorus

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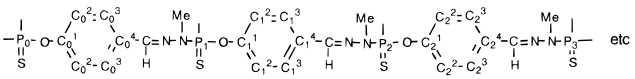
groups. ^{1}H NMR did not show any resonance which could be attributed to COD and showed characteristic data for acac moieties. Moreover ^{13}C NMR spectra also exhibited the acac resonances.

Conclusion

It has been demonstrated that a number of diphosphino groups (up to 48) can be anchored on the surface of dendrimers and that these diphosphino end groups remained perfectly available for further complexation reactions. Indeed, a variety of Pd, Pt, and Rh complexes were prepared, the surface of dendrimers being covered by up to 24 metal atoms. Preliminary experiments showed that it was possible to do some clear organometallic chemistry on the surface suggesting that these new metallic dendrimers might be of use as catalysts. Such an assumption is under investigation.

Experimental Section

General Methods. 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, relative to 85% H_3PO_4 for ^{31}P, and relative to H_2PtCl_6 for ^{195}Pt. The numbering of the dendrimer skeleton used for ^{1}H, ^{13}C, and ^{31}P NMR is depicted on the following scheme:



Note: Signals of the CH_2 groups are partially overlapped by the solvent for all complexes whose ^{13}C{^{1}H} NMR spectra are run in CD_2Cl_2.

Compounds **2-[G′1]**−**2-[G′4]**,[11a] $PdCl_2$(COD), $PdBr_2$(COD), and $PtCl_2$(COD),[20] PdMeCl(COD),[21] Rh(acac)(COD),[22] and Ph_2PCH_2OH[23] were prepared according to literature procedures.

General procedure for the Synthesis of Compounds 3-[G′$_n$]. A solution of **2-[G′$_n$]** (***n*** = 1, 0.146 g, 0.097 mmol; ***n*** = 2, 0.18 g, 0.05 mmol; ***n*** = 3, 0.31 g, 0.04 mmol; ***n*** = 4, 0.16 g, 0.01 mmol) in THF (5 mL) was added at room temperature to a mixture of Ph_2PH (***n*** = 1, 0.21 mL, 1.2 mmol; ***n*** = 2, 0.23 mL, 1.3 mmol; ***n*** = 3, 0.36 mL, 2.1 mmol; ***n*** = 4, 0.18 mL, 1.05 mmol) and $(CH_2O)_x$ (***n*** = 1, 0.036 g; ***n*** = 2, 0.039 g, ***n*** = 3, 0.063 g; ***n*** = 4, 0.032 g), which was heated without solvent in a pressure Schlenk tube for 90 min at 120 °C. The resulting mixture was stirred for 12 h at room temperature. The solvent was removed to give a yellow oil. After the oil was washed with 2 × 10 mL of pentane/ether (1:1), **3-[G′$_n$]** was obtained as a white powder.

3-[G′$_1$]: White powder, mp 91 °C; 88% yield. ^{31}P{^{1}H} NMR (δ, $CDCl_3$): −25.5 (s, PPh_2), 51.8 (s, P_0), 62.0 (s, P_1) ppm. ^{1}H NMR (δ, $CDCl_3$): 3.3 (d, $^3J_{HP1}$ = 10.2 Hz, 9H, P_1−N−CH_3), 4.2 (s, 24H, CH_2−P), 7.1−7.8 (m, 165H, C_6H_5, C_6H_4 and CH=N) ppm. ^{13}C{^{1}H} NMR (δ, $CDCl_3$): 33.2 (d, $^2J_{CP1}$ = 13.1 Hz, P_1−N−CH_3), 56.8 (d, $^1J_{CP}$ = 7.0 Hz, CH_2−P), 121.4 (br s, C_1^2), 121.6 (s, C_0^2), 126.7 (s, C_0^3 and C_1^3), 128.6 (d, $^3J_{CP}$ = 3.4 Hz, *m*-C_6H_5), 128.9 (s, *p*-C_6H_5), 130.0 (s, C_0^4), 131.1 (s, C_1^4), 133.1 (d, $^2J_{CP}$ = 19.9 Hz, *o*-C_6H_5), 133.1 (s, *C*H=NNCH$_2$), 137.3 (d, $^1J_{CP}$ = 14.2 Hz, *i*-C_6H_5), 138.2 (d, $^3J_{CP1}$ = 11.9 Hz, $(CH{=}N)_0$), 149.6 (d, $^2J_{CP1}$ = 7.7 Hz, C_1^1), 151.1 (d, $^2J_{CP0}$ = 7.8 Hz, C_0^1) ppm. Anal. Calc for $C_{222}H_{198}N_{18}O_9P_{16}S_4$: C, 68.62; H, 5.14; N, 6.49. Found: C, 68.31; H, 4.95; N, 6.18.

3-[G′$_2$]: White powder, mp 96 °C; 89% yield. ^{31}P{^{1}H} NMR (δ, $CDCl_3$): −25.5 (s, PPh_2), 51.8 (s, P_0), 62.1 (s, P_1, P_2) ppm. ^{1}H NMR (δ, $CDCl_3$): 3.4 (d, $^3J_{HP1}$ = 8.2 Hz, 27H, P_{1-2}−N−CH_3), 4.2 (s, 48H, CH_2−P), 7.0−7.8 (m, 345H, C_6H_5, C_6H_4 and CH=N) ppm. ^{13}C{^{1}H} NMR (δ, $CDCl_3$): 33.0 (d, $^2J_{CP1-2}$ = 13.1 Hz, P_{1-2}−N−CH_3), 56.6 (d, $^1J_{CP}$ = 9.1 Hz, CH_2−P), 121.3 (br s, C_2^2), 121.8 (m, C_0^2 and C_1^2), 126.5 (s, C_0^3, C_1^3 and C_2^3), 128.4 (d, $^3J_{CP}$ = 5.3 Hz, *m*-C_6H_5), 128.7 (s, *p*-C_6H_5), 129.8 (s, C_0^4 and C_1^4), 131.0 (s, C_2^4), 132.9 (d, $^2J_{CP}$ = 19.1 Hz, *o*-C_6H_5), 133.0 (s, *C*H=NNCH$_2$), 137.2 (d, $^1J_{CP}$ = 14.0 Hz, *i*-C_6H_5), 138.6 (m, $(CH{=}N)_{0-1}$), 149.4 (d, $^2J_{CP2}$ = 8.5 Hz, C_2^1), 151.2 (m, C_0^1 and C_1^1) ppm. Anal. Calc for $C_{468}H_{420}N_{42}O_{21}P_{34}S_{10}$: C, 67.38; H, 5.07; N, 7.05. Found: C, 67.25; H, 4.92; N, 6.93.

3-[G′$_3$]: White powder, mp 108 °C; 87% yield. ^{31}P{^{1}H} NMR (δ, $CDCl_3$): −25.5 (s, PPh_2), 51.8 (s, P_0), 61.9 (s, P_1, P_2), 62.1 (s, P_3) ppm. ^{1}H NMR (δ, $CDCl_3$): 3.4 (m, 63H, P_{1-2-3}−N−CH_3), 4.1 (s, 96H, CH_2−P), 7.1−7.8 (m, 705H, C_6H_5, C_6H_4, and CH=N) ppm. ^{13}C{^{1}H} NMR (δ, $CDCl_3$): 33.0 (d, $^2J_{CP1-2-3}$ = 13.0 Hz, P_{1-2-3}−N−CH_3), 56.7 (d, $^1J_{CP}$ = 9.8 Hz, CH_2−P), 121.2 (d, $^3J_{CP2}$ = 3.3 Hz, C_3^2), 121.7 (m, C_0^2, C_1^2, and C_2^2), 126.5 (s, C_0^3, C_1^3, C_2^3, and C_3^3), 128.4 (d, $^3J_{CP}$ = 5.1 Hz, *m*-C_6H_5), 128.7 (s, *p*-C_6H_5), 129.9 (m, C_0^4, C_1^4, and C_2^4), 130.9 (s, C_3^4), 132.9 (d, $^2J_{CP}$ = 19.3 Hz, *o*-C_6H_5), 132.9 (s, *C*H=NNCH$_2$), 137.1 (d, $^1J_{CP}$ = 14.0 Hz, *i*-C_6H_5), 138.3 (m, $(CH{=}N)_{0-1-2}$), 149.4 (d, $^2J_{CP3}$ = 7.4 Hz, C_3^1), 151.1 (m, C_0^1, C_1^1, and C_2^1) ppm. Anal. Calc for $C_{960}H_{864}N_{90}O_{45}P_{70}S_{22}$: C, 66.82; H, 5.05; N, 7.31. Found: C, 66.69; H, 4.88; N, 7.15.

3-[G′$_4$]: White powder, mp 119 °C; 91% yield. ^{31}P{^{1}H} NMR (δ, $CDCl_3$): −25.5 (s, PPh_2), 61.9 (s, P_1, P_2, P_3), 62.1 (s, P_4) ppm. ^{1}H NMR (δ, $CDCl_3$): 3.2 (m, 135H, $P_{1-2-3-4}$−N−CH_3), 4.1 (br s, 96H, CH_2−P), 7.1−7.7 (m, 1425H, C_6H_5, C_6H_4 and CH=N) ppm. ^{13}C{^{1}H} NMR (δ, $CDCl_3$): 33.0 (d, $^2J_{CP1-2-3-4}$ = 12.9 Hz, $P_{1-2-3-4}$−N−CH_3), 56.2 (br s, CH_2−P), 121.2 (br s, C_4^2), 121.7 (m, C_0^2, C_1^2, C_2^2, and C_3^2), 126.5 (s, C_0^3, C_1^3, C_2^3, C_3^3, and C_4^3), 128.4 (d, $^3J_{CP}$ = 3.9 Hz, *m*-C_6H_5), 128.7 (s, *p*-C_6H_5), 130.9 (m, C_0^4, C_1^4, C_2^4, and C_3^4), 132.1 (s, C_4^4), 132.9 (d, $^2J_{CP}$ = 19.8 Hz, *o*-C_6H_5), 132.9 (s, *C*H=NNCH$_2$), 137.1 (d, $^1J_{CP}$ = 14.4 Hz, *i*-C_6H_5), 138.5 (m, $(CH{=}N)_{0-1-2-3}$), 149.4 (d, $^2J_{CP4}$ = 6.9 Hz, C_4^1), 151.2 (m, C_0^1, C_1^1, C_2^1, and C_3^1) ppm. Anal. Calc for $C_{1944}H_{1752}N_{186}O_{93}P_{142}S_{46}$: C, 66.56; H, 5.03; N, 7.43. Found: C, 66.40; H, 4.94; N, 7.23.

Synthesis of Compound 4-[G′$_1$]. To a solution of $PdCl_2$(COD) (0.044 g; 0.154 mmol or 0.088 g; 0.309 mmol) in CH_2Cl_2 (20 or 30 mL) was added slowly a dichloromethane solution (20 or 35 mL) containing **3-[G′$_1$]** (0.1 g; 25.7 μmol or 0.2 g; 51.5 μmol). The mixture was stirred for 1 h, and then the solvent was removed under vacuum. The yellow residue was washed with 1:1 diethyl ether/tetrahydrofuran (2 × 10 mL) and then with diethyl ether (10 mL).

4-[G′$_1$]: Yellow powder, mp 240 °C; 84% yield. ^{31}P{^{1}H} NMR (δ, CD_2Cl_2): 5.8 (s, PPh_2), 52.7 (s, P_0), 62.0 (s, P_1) ppm. ^{1}H NMR (δ, CD_2Cl_2): 3.32 (d, $^3J_{HP1}$ = 10.7 Hz, 9H, P_1−N−CH_3), 4.27 (s, 24H, CH_2−P), 7.1−7.9 (m, 165H, C_6H_5, C_6H_4, and CH=N) ppm. ^{13}C{^{1}H} NMR (δ, CD_2Cl_2): 33.3 (d, $^2J_{CP1}$ = 10.1 Hz, P_1−N−CH_3), 52.3 (m, CH_2−P), 121.4 (br s, C_1^2), 121.8 (s, C_0^2), 127.5 (s, C_0^3 and C_1^3), 128.7 (d, *i*-C_6H_5, overlapped with *m*-C_6H_5), 129.0 (d, $^3J_{CP}$ = 11.4 Hz, *m*-C_6H_5), 132.0 (s, *p*-C_6H_5, C_0^4 and C_1^4), 134.1 (d, $^2J_{CP}$ = 10.4 Hz, *o*-C_6H_5), 137.1 (br s, *C*H=NNCH$_2$), 139.0 (br s $(CH{=}N)_0$), 150.8 (d, $^2J_{CP1}$ = 7.7 Hz, C_1^1), 151.4 (d, $^2J_{CP0}$ = 5.8 Hz, C_0^1) ppm. IR (KBr): 290 (ν_{Pd-Cl}) cm^{-1}. Anal. Calc for $C_{222}H_{198}N_{18}Cl_{12}O_9P_{16}S_4Pd_6$: C, 53.87; H, 4.03; N, 5.09. Found: C, 53.4; H, 4.45; N, 4.7.

Synthesis of Compound 5-[G′$_1$]. First Method. To a solution of $PdBr_2$(COD) (0.058 g; 0.154 mmol) in CH_2Cl_2 (20 mL) was added slowly a dichloromethane solution (20 mL) containing **3-[G′$_1$]** (0.1 g; 25.7 μmol). The mixture was stirred for 1 h, and then the solvent was removed under vacuum. The orange residue was washed with 1:1 diethyl ether/tetrahydrofuran (2 × 10 mL) and then with diethyl ether (10 mL). Yield: 80%.

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Second Method. To a solution of complex **4-[G′$_1$]** (0.06 g; 12.1 μmol) in CH_2Cl_2 (20 mL) was added a water solution (10 mL) containing 0.04 g (0.336 mmol) of KBr. The mixture was stirred for 2 h, and then the organic layer was extracted and washed with water (2 × 5 mL). Anhydrous $MgSO_4$ was added, the solution filtered, and the solvent removed to give an orange powder which was washed with diethyl ether (10 mL). Yield: 66%.

5-[G′$_1$]: Orange powder, mp 215 °C. $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2): 1.0 (s, PPh_2), 52.7 (s, P_0), 62.1 (s, P_1) ppm. ^1H NMR (δ, CD_2Cl_2): 3.32 (d, $^3J_{HP1}$ = 10.4 Hz, 9H, P_1-N-CH_3), 4.27 (s, 24H, CH_2-P), 6.9−7.9 (m, 165H, C_6H_5, C_6H_4, and CH=N) ppm. $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2): 33.2 (d, $^2J_{CP1}$ = 12.6 Hz, P_1-N-CH_3), 52.1 (m, CH_2-P), 121.4 (br s, C_1^2), 121.7 (s, C_0^2), 127.4 (s, C_0^3 and C_1^3), 128.3 (d, *i*-C_6H_5, overlapped with *m*-C_6H_5), 128.9 (d, $^3J_{CP}$ = 11.3 Hz, *m*-C_6H_5), 132.0 (s, *p*-C_6H_5), 132.1 (s, C_0^4 and C_1^4), 134.2 (d, $^2J_{CP}$ = 9.8 Hz, *o*-C_6H_5), 136.3 (br s, *C*H=NNCH$_2$), 138.9 (br s, (CH=N)$_0$), 150.7 (d, $^2J_{CP1}$ = 6.3 Hz, C_1^1), 151.2 (d, $^2J_{CP0}$ = 8.7 Hz, C_0^1) ppm. Anal. Calc for $C_{222}H_{198}N_{18}Br_{12}O_9P_{16}S_4Pd_6$: C, 48.63; H, 3.64; N, 4.60. Found: C, 48.5; H, 3.7; N, 4.15.

"In Situ" Synthesis of Compound 6-[G′$_1$]. To a deuteriodichloromethane (0.5 mL) solution of complex **4-[G′$_1$]** (0.015 g, 3.03 μmol) was added MgBrMe (0.4 mmol, 28 μL of a 1.4 M THF/toluene solution). The yellow solution became orange.

6-[G′$_1$]. $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2): −14.2 (d, $^2J_{PP}$ = 43.3 Hz, PPh_2 trans Me), 16.0 (d, $^2J_{PP}$ = 43.3 Hz, PPh_2 trans Br), 52.8 (s, P_0), 62.3 (s, P_1) ppm. ^1H NMR (δ, CD_2Cl_2): 0.67 (dd, $^2J_{HP}$ = 7.7 and 4.0 Hz, 18H, Me−Pd), 3.32 (d, $^3J_{HP1}$ = 10.6 Hz, 9H, P_1-N-CH_3), 4.36 (s, 12H, CH_2-P), 4.43 (s, 12H, CH_2-P), 6.6−7.9 (m, 165H, C_6H_5, C_6H_4, and CH=N) ppm.

Synthesis of Compound 7-[G′$_1$]. First Method. To a solution of complex **4-[G′$_1$]** (0.05 g; 10.1 μmol) in CH_2Cl_2 (20 mL) at 0 °C and protected from light was added Cp_2ZrMe_2 (0.03 g; 0.12 mmol). The mixture was stirred for 3 h, leaving the temperature to increase. Then the solvent was removed under vacuum to give a yellow powder which was washed with diethyl ether (2 × 5 mL) and then with tetrahydrofuran (2 × 5 mL) to eliminate unreacted $ZrCp_2Me_2$. Yield: 65%.

General Procedure for the Synthesis of Compounds 7-[G′$_n$]. A solution of dendrimer **3-[G′$_n$]** (***n*** = 1, 0.200 g, 51.5 μmol; ***n*** = 2, 0.050 g, 6.0 μmol; ***n*** = 3, 0.055 g, 3.19 μmol) in dichloromethane (10 mL) was slowly added to a solution of PdMeCl(COD) (***n*** = 1, 0.082 g, 0.309 mmol; ***n*** = 2, 0.019 g, 0.072 mmol, ***n*** = 3, 0.020 g, 0.077 mmol) in dichloromethane (10 mL). The mixture was stirred for 2 h, and then the solvent was removed under vacuum. The yellow residue was washed with 1/1 diethyl ether/tetrahydrofuran (2 × 5 mL) and then with diethyl ether (5 mL).

7-[G′$_1$]: Yellow powder, mp 203 °C; 85% yield. $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2): −13.7 (d, $^2J_{PP}$ = 43.3 Hz, PPh_2 trans Me), 19.6 (d, $^2J_{PP}$ = 43.3 Hz, PPh_2 trans Cl), 52.7 (s, P_0), 62.2 (s, P_1) ppm. ^1H NMR (δ, CD_2Cl_2): 0.58 (dd, $^2J_{HP}$ = 7.8 and 3.5 Hz, 18H, Me−Pd), 3.33 (d, $^3J_{HP1}$ = 10.1 Hz, 9H, P_1-N-CH_3), 4.38 (s, 12H, CH_2-P), 4.42 (s, 12H, CH_2-P), 6.5−7.9 (m, 165H, C_6H_5, C_6H_4, and CH=N) ppm. $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2): 13.7 (d, $^2J_{CP}$ = 100.3 Hz, Pd−CH_3), 33.1 (d, $^2J_{CP1}$ = 12.4 Hz, P_1-N-CH_3), 55.6 (m, CH_2-P), 56.2 (m, CH_2-P), 121.2 (s, C_1^2), 121.7 (s, C_0^2), 126.8 (s, C_0^3 and C_1^3), 128.7 (m, *m*-C_6H_5), 129.8 (d, $^1J_{CP}$ = 49.4 Hz, *i*-C_6H_5), 130.5 (s, *p*-C_6H_5), 131.1 (s, *p*-C_6H_5), 132.1 (d, $^1J_{CP}$ = 55.2 Hz, *i*-C_6H_5), 132.2 (s, C_0^4 and C_1^4), 133.9 (m, *o*-C_6H_5), 134.8 (s, *C*H=NNCH$_2$), 138.5 (br s, (CH=N)$_0$), 150.1 (d, $^2J_{CP1}$ = 7.3 Hz, C_1^1), 151.1 (d, $^2J_{CP0}$ = 7.3 Hz, C_0^1) ppm. IR (KBr): 289 (ν_{Pd-Cl}) cm^{-1}. Anal. Calc for $C_{228}H_{216}N_{18}Cl_6O_9P_{16}S_4Pd_6$: C, 56.73; H, 4.51; N, 5.22. Found: C, 56.1; H, 4.5; N, 4.85.

7-[G′$_2$]: Yellow powder, mp 205 °C; 80% yield. $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2): −13.9 (d, $^2J_{PP}$ = 42.7 Hz, PPh_2 trans Me), 19.5 (d, $^2J_{PP}$ = 42.7 Hz, PPh_2 trans Cl), 52.7 (s, P_0), 62.3 (s, P_1, P_2) ppm. ^1H NMR (δ, CD_2Cl_2): 0.58 (m, 36H, Me−Pd), 3.29 (d, $^3J_{HP1-2}$ = 7.8 Hz, 27H, $P_{1-2}-N-CH_3$), 4.37 (s, 24H, CH_2-P), 4.40 (s, 24H, CH_2-P), 6.6−8.0 (m, 345H, C_6H_5, C_6H_4, and CH=N) ppm. $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2): 13.9 (d, $^2J_{CP}$ = 100.6 Hz, Pd−CH_3), 33.1 (d, $^2J_{CP1-2}$ = 11.6 Hz, $P_{1-2}-N-CH_3$), 55.6 (m, CH_2-P), 56.3 (m, CH_2-P), 121.2 (s, C_2^2), 122.0 (s, C_0^2 and C_1^2), 126.9 (s, C_0^3, C_1^3, and C_2^3), 128.9 (m, *m*-C_6H_5), 129.9 (d, $^1J_{CP}$ = 49.3 Hz, *i*-C_6H_5), 130.6 (s, *p*-C_6H_5), 131.2 (s, *p*-C_6H_5), 132.2 (d, $^1J_{CP}$ = 53.7 Hz, *i*-C_6H_5), 132.3 (s, C_0^4, C_1^4, and C_2^4), 134.1 (m, *o*-C_6H_5), 134.9 (s, *C*H=NNCH$_2$), 138.1 (m, (CH=N)$_{0-1}$), 150.3 (br s, C_2^1), 151.6 (m, C_0^1 and C_1^1) ppm. IR (KBr): 287 (ν_{Pd-Cl}) cm^{-1}. Anal. Calc for $C_{480}H_{456}N_{42}Cl_{12}O_{21}P_{34}S_{10}Pd_{12}$: C, 56.38; H, 4.49; N, 5.75. Found: C, 55.15; H, 4.6; N, 4.95.

7-[G′$_3$]: Yellow powder, mp 195 °C; 75% yield. $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2): −13.9 (d, $^2J_{PP}$ = 40.5 Hz, PPh_2 trans Me), 19.5 (d, $^2J_{PP}$ = 40.5 Hz, PPh_2 trans Cl), 52.7 (s, P_0), 62.2 (s, P_1, P_2, P_3) ppm. ^1H NMR (δ, CD_2Cl_2): 0.58 (m, 72H, Me−Pd), 3.28 (br s, 63H, $P_{1-2-3}-N-CH_3$), 4.37 (br s, 96H, CH_2-P), 6.5−8.0 (m, 705H, C_6H_5, C_6H_4, and CH=N) ppm. $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2): 13.9 (d, $^2J_{CP}$ = 100.6 Hz, Pd−CH_3), 33.2 (d, $^2J_{CP1-2-3}$ = 11.6 Hz, $P_{1-2-3}-N-CH_3$), 55.7 (m, CH_2-P), 56.3 (m, CH_2-P), 121.2 (s, C_3^2), 122.0 (s, C_0^2, C_1^2, and C_2^2), 126.9 (s, C_0^3, C_1^3, C_2^3, and C_3^3), 128.9 (m, *m*-C_6H_5), 129.9 (d, $^1J_{CP}$ = 50.9 Hz, *i*-C_6H_5), 130.6 (s, *p*-C_6H_5), 131.2 (s, *p*-C_6H_5), 132.2 (d, $^1J_{CP}$ = 55.2 Hz, *i*-C_6H_5), 132.3 (s, C_0^4, C_1^4, C_2^4, and C_3^4), 134.1 (m, *o*-C_6H_5), 134.9 (s, *C*H=NNCH$_2$), 139.4 (m, (CH=N)$_{0-1-2}$), 150.2 (m, C_3^1), 151.5 (m, C_0^1, C_1^1, and C_2^1) ppm. IR (KBr): 289 (ν_{Pd-Cl}) cm^{-1}. Anal. Calc for $C_{984}H_{936}N_{90}Cl_{24}O_{45}P_{70}S_{22}Pd_{24}$: C, 56.22; N, 4.49; N, 6.00. Found: C, 54.0; H, 4.15; N, 5.65.

General Procedure for the "in Situ" Synthesis of Compounds 8-[G′$_n$]. A 1 mL volume of a CD_2Cl_2 solution of complex **7-[G′$_n$]** (***n*** = 1, 0.02 g, 4.14 μmol; ***n*** = 2, 0.02 g, 1.96 μmol; ***n*** = 3, 0.02 g, 0.95 μmol) in a 10 mL Fisher Porter bottle was carefully evacuated and pressurized 3 times to 1 bar of CO. The solution became darker and was stirred for 6 h. It was then transferred to an NMR tube. The same experiment was performed with ^{13}CO for **7-[G′$_1$]** and afforded compound **8-[G′$_1$](^{13}CO)**.

8-[G′$_1$]. $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2): −15.9 (d, $^2J_{PP}$ = 72.2 Hz, PPh_2 trans COMe), 5.2 (d, $^2J_{PP}$ = 72.2 Hz, PPh_2 trans Cl), 52.7 (s, P_0), 62.3 (s, P_1) ppm. ^1H NMR (δ, CD_2Cl_2): 1.87 (s, 18H, Me−COPd), 3.34 (d, $^3J_{HP1}$ = 10.1 Hz, 9H, P_1-N-CH_3), 4.35 (s, 12H, CH_2-P), 4.51 (s, 12H, CH_2-P), 6.5−7.9 (m, 165H, C_6H_5, C_6H_4, and CH=N) ppm. $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2): 33.1 (d, $^2J_{CP1}$ = 10.6 Hz, P_1-N-CH_3), 36.7 (dd, $^3J_{CP}$ = 38.3, $^3J_{CP}$ = 22.7 Hz, *C*H_3−CO−Pd), 55.6 (m, CH_2-P), 56.2 (m, CH_2-P), 121.3 (s, C_1^2), 121.7 (s, C_0^2), 126.9 (s, C_0^3 and C_1^3), 129.0 (m, *m*-C_6H_5), 130.0 (d, $^1J_{CP}$ = 42.3 Hz, *i*-C_6H_5), 130.6 (s, *p*-C_6H_5), 131.1 (s, C_0^4 and C_1^4), 131.3 (s, *p*-C_6H_5), 132.7 (d, $^1J_{CP}$ = 57.9 Hz, *i*-C_6H_5), 133.9 (m, *o*-C_6H_5), 134.1 (s, *C*H=NNCH$_2$), 138.8 (br s, (CH=N)$_0$), 150.2 (d, $^2J_{CP1}$ = 6.9 Hz, C_1^1), 151.2 (d, $^2J_{CP0}$ = 8.7 Hz, C_0^1) ppm. IR (CD_2Cl_2): 1686 ($\nu_{C=O}$) cm^{-1}.

8-[G′$_1$](^{13}CO). $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2): −15.9 (dd, $^2J_{PC}$ = 118.5 Hz, $^2J_{PP}$ = 72.2 Hz, PPh_2 trans COMe), 5.2 (dd, $^2J_{PC}$ = 13.1 Hz, $^2J_{PP}$ = 72.2 Hz, PPh_2 trans Cl), 52.7 (s, P_0), 62.3 (s, P_1) ppm. ^1H NMR (δ, CD_2Cl_2): 1.87 (m, 18H, Me−COPd), 3.34 (d, $^3J_{HP1}$ = 10.5 Hz, 9H, P_1-N-CH_3), 4.35 (s, 12H, CH_2-P), 4.51 (s, 12H, CH_2-P), 6.5−7.9 (m, 165H, C_6H_5, C_6H_4, and CH=N) ppm. $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2): 236.0 (dd, $^2J_{CPtrans}$ = 118.5 Hz, $^2J_{CPcis}$ = 13.1 Hz, *C*OMe).

8-[G′$_2$]. $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2): −16.1 (d, $^2J_{PP}$ = 71.3 Hz, PPh_2 trans COMe), 5.1 (d, $^2J_{PP}$ = 71.3 Hz, PPh_2 trans Cl), 52.6 (s, P_0), 62.3 (s, P_1, P_2) ppm. ^1H NMR (δ, CD_2Cl_2): 1.86 (s, 36H, Me−COPd), 3.30 (d, $^3J_{HP1}$ = 9.0 Hz, 27H, $P_{1-2}-N-CH_3$), 4.35 (s, 24H, CH_2-P), 4.51 (s, 24H, CH_2-P), 6.5−7.9 (m, 345 H, C_6H_5, C_6H_4, and CH=N) ppm. $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2): 33.6 (s, $P_{1-2}-N-CH_3$), 36.3 (m, *C*H_3−CO−Pd), 55.6 (m, CH_2-P), 56.2 (m, CH_2-P), 121.3 (s, C_2^2), 121.7 (s, C_0^2 and C_1^2), 126.9 (s, C_0^3, C_1^3 and C_2^3), 129.0 (m, *m*-C_6H_5), 130.1 (d, $^1J_{CP}$ = 44.0 Hz, *i*-C_6H_5), 130.7 (s, *p*-C_6H_5), 131.3 (s, *p*-C_6H_5), 132.2 (d, $^1J_{CP}$ = 55.9 Hz, *i*-C_6H_5), 132.5 (s, C_0^4, C_1^4, and C_2^4), 133.9 (m, *o*-C_6H_5), 134.1 (s, *C*H=NNCH$_2$), 139.1 (m, (CH=N)$_{0-1}$), 150.3 (br s, C_2^1), 151.5 (m, C_0^1 and C_1^1) ppm. IR (CD_2Cl_2): 1686 ($\nu_{C=O}$) cm^{-1}.

8-[G′$_3$]. $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2): −16.0 (d, $^2J_{PP}$ = 73.9 Hz, PPh_2 trans COMe), 5.2 (d, $^2J_{PP}$ = 73.9 Hz, PPh_2 trans Cl), 52.7 (s, P_0), 62.2 (s, P_1, P_2, P_3) ppm. ^1H NMR (δ, CD_2Cl_2): 1.86 (s, 72H, Me−COPd), 3.30 (br s, 63H, P_{1-2-3}−N−CH_3), 4.34 (br s, 48H, CH_2−P), 4.50 (br s, 48H, CH_2−P), 6.5−8.0 (m, 705H, C_6H_5, C_6H_4, and CH═N) ppm. $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2): 33.2 (s, P_{1-2-3}−N−CH_3), 36.5 (m, *C*H_3−CO−Pd), 55.6 (m, CH_2−P), 56.2 (m, CH_2−P), 121.3 (s, C_3^2), 122.0 (s, C_0^2, C_1^2, and C_2^2), 126.9 (s, C_0^3, C_1^3, C_2^3, and C_3^3), 129.0 (m, *m*-C_6H_5), 130.2 (d, $^1J_{CP}$ = 50.0 Hz, *i*-C_6H_5), 130.7 (s, *p*-C_6H_5), 131.2 (s, C_0^4, C_1^4, C_2^4, and C_3^4), 131.4 (s, *p*-C_6H_5), 132.4 (d, $^1J_{CP}$ = 40.1 Hz, *i*-C_6H_5), 133.9 (m, *o*-C_6H_5), 134.1 (s, *C*H═NNCH_2), 138.4 (br s, $(CH═N)_{0-1-2}$), 150.2 (s, C_3^1), 151.5 (m, C_0^1, C_1^1, and C_2^1). IR (CD_2Cl_2): 1685 ($\nu_{C=O}$) cm^{-1}.

General Procedure for the "in Situ" Synthesis of 9-[G′$_n$]. To a deuteriodichloromethane (0.5 mL) solution of **8-[G′$_n$]** (***n*** = 1, 4.14 μmol; ***n*** = 2, 1.96 μmol) prepared *in situ* as described above and transferred to a NMR tube was added norbornene (***n*** = 1, 2.4 mg, 24.8 μmol; ***n*** = 2, 2.2 mg, 23.5 μmol). Then proton and phosphorus NMR spectra were run.

9-[G′$_1$]. $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2): −11.0 (d, $^2J_{PP}$ = 58.1 Hz, PPh_2 trans COMe), 21.5 (d, $^2J_{PP}$ = 58.1 Hz, PPh_2 trans Cl), 52.6 (s, P_0), 62.2 (s, P_1) ppm. ^1H NMR (δ, CD_2Cl_2): 0.7−2.6 (m, 60H, inserted norbornane), 2.20 (s, 18H, Me−CO), 3.28 (d, $^3J_{HP1}$ = 9.0 Hz, 9H, P_1−N−CH_3), 4.42 (br s, 12H, CH_2−P), 4.55 (br s, 12H, CH_2−P), 6.9−8.0 (m, 165H, C_6H_5, C_6H_4, and CH═N) ppm.

9-[G′$_2$]. $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2): −11.4 (d, $^2J_{PP}$ = 56.8 Hz, PPh_2 trans COMe), 21.2 (d, $^2J_{PP}$ = 56.8 Hz, PPh_2 trans Cl), 52.3 (s, P_0), 62.4 (s, P_1, P_2) ppm. ^1H NMR (δ, CD_2Cl_2): 0.7−2.7 (m, 120H, inserted norbornane), 2.18 (s, 36H, Me−CO), 3.30 (d, $^3J_{HP1}$ = 9.0 Hz, 27H, P_{1-2}−N−CH_3), 4.43 (br s, 24H, CH_2−P), 4.56 (br s, 24H, CH_2−P), 6.8−8.0 (m, 345 H, C_6H_5, C_6H_4, and CH═N) ppm.

General Procedure for the Synthesis of Compounds 10-[G′$_n$]. A solution of **3-[G′$_n$]** (***n*** = 1, 99.5 mg, 0.0256 mmol; ***n*** = 2, 96 mg, 0.011 mmol, ***n*** = 3, 161.5 mg, 0.0095 mmol) in CH_2Cl_2 (5 mL) was slowly added within 1 h at room temperature to a solution of (COD)$PtCl_2$ (***n*** = 1, 57.7 mg, 0.154 mmol; ***n*** = 2, 50 mg, 0.134 mmol; ***n*** = 3, 85.4 mg, 0.228 mmol) in CH_2Cl_2 (5 mL). The solution was stirred overnight, and then the solvent was evaporated and the yellow powder obtained washed with $CHCl_3$ (2 × 10 mL).

10-[G′$_1$]: Yellow powder, mp 235 °C; 95% yield. $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2): −8.9 (s, $^1J_{P^{195}Pt}$ = 3440 Hz, PPh_2), 52.5 (s, P_0), 62.0 (s, P_1) ppm. ^1H NMR (δ, CD_2Cl_2): 3.31 (br d, $^3J_{HP}$ = 10.7 Hz, 9H, P_1−N−CH_3), 4.34 (m, 24H, CH_2−P), 6.9−8.0 (m, 165H, C_6H_5, C_6H_4, and CH═N) ppm. $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2): 33.4 (d, $^2J_{CP}$ = 12 Hz, P_1−N−CH_3), 51.3 (m, CH_2P), 121.6 (s, C_1^2), 121.9 (s, C_0^2), 127.2 (br d, $^1J_{CP}$ = 65 Hz, *i*-C_6H_5), 127.5 (s, C_0^3, C_1^3), 129.1 (m, *m*-C_6H_5), 130.2 (s, C_0^4), 132.2 (s, *p*-C_6H_5), 132.6 (s, C_1^4), 134.2 (m, *o*-C_6H_5), 135.6 (s, CH═NN), 138.3 (d, $^3J_{CP}$ = 10 Hz, $(CH═N)_0$), 150.9 (d, $^2J_{CP}$ = 7 Hz, C_1^1), 151.4 (d, $^2J_{CP}$ = 8 Hz, C_0^1) ppm. $^{195}Pt\{^1H\}$ NMR (δ, CD_2Cl_2): −4516 (t, $^1J_{^{195}PtP}$ = 3438 Hz) ppm. Anal. Calc for $C_{222}H_{198}N_{18}Cl_{12}O_9P_{16}S_4Pt_6$: C, 48.64; H, 3.64; N, 4.60. Found: C, 48.23; H, 3.75; N, 4.48.

10-[G′$_2$]: Yellow powder, mp 260 °C (dec); 90% yield. $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2): −9 (s, $^1J_{P^{195}Pt}$ = 3438 Hz, PPh_2), 52.3 (s, P_0), 61.9 (s, P_2), 62.5 (s, P_1) ppm. ^1H NMR (δ, CD_2Cl_2): 3.31 (br s, 27H, P_{1-2}−N−CH_3), 4.35 (m, 48H, CH_2−P), 6.9−7.9 (m, 345H, C_6H_5, C_6H_4, and CH═N) ppm. $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2): 33.5 (br s, P_{1-2}−N−CH_3), 50.3 (m, CH_2P), 120.7 (s, C_2^2), 121.6 (br s, C_0^2, C_1^2), 126.2 (br d, $^1J_{CP}$ = 71 Hz, *i*-C_6H_5), 126.6 (br s, C_0^3, C_1^3, C_2^3), 128.2 (m, *m*-C_6H_5), 130.6 (s, C_0^4, C_1^4), 131.3 (s, *p*-C_6H_5), 131.6 (s, C_2^4), 133.3 (m, *o*-C_6H_5), 134.9 (s, CH═NN), 138.6 $(CH═N)_{0-1}$), 149.9 (br s, C_2^1), 150.7 (m, C_0^1, C_1^1) ppm. Anal. Calc for $C_{468}H_{420}N_{42}Cl_{24}O_{21}P_{34}S_{10}Pt_{12}$: C, 48.73; H, 3.67; N, 5.10. Found: C, 48.19; H, 3.80; N, 4.62.

10-[G′$_3$]: Yellow powder, mp 251 °C (dec); 91% yield. $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2): −9 (br s, $^1J_{P^{195}Pt}$ = 3434 Hz, PPh_2), 52.3 (s, P_0), 61.9 (s, P_3), 62.4 (s, P_2), 62.5 (s, P_1) ppm. ^1H NMR (δ, CD_2Cl_2): 3.35 (br s, 63H, P_{1-2-3}−N−CH_3), 4.30 (m, 48H, CH_2−P), 7.0−7.9 (m, 705H, C_6H_5, C_6H_4, and CH═N) ppm. $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2): 32.5 (br s, P_{1-2-3}−N−CH_3), 50.3 (m, CH_2P), 120.7 (s, C_3^2), 121.3 (br s, C_0^2, C_1^2, C_2^2, C_3^2), 126.2 (br d, $^1J_{CP}$ = 62 Hz, *i*-C_6H_5), 127.3 (br s, C_0^3, C_1^3, C_2^3, C_3^3), 128.2 (m, *m*-C_6H_5), 130.7 (s, C_0^4, C_1^4, C_2^4), 131.3 (s, *p*-C_6H_5), 131.6 (s, C_3^4), 133.3 (m, *o*-C_6H_5), 134.9 (s, CH═NN), 138.5 (m, $(CH═N)_{0-1-2}$), 150.0 (br s, C_3^1), 150.7 (m, C_0^1, C_1^1, C_2^1) ppm. Anal. Calc for $C_{960}H_{864}N_{90}Cl_{48}O_{45}P_{70}S_{22}Pt_{24}$: C, 48.78; H, 3.68; N, 5.33. Found: C, 48.02; H, 3.87; N, 4.67.

"In Situ" Synthesis of Compound 11-[G′$_1$]. A solution of MeMgBr in 3/1 thf/toluene (0.080 mL, 0.112 mmol, c = 1.4 M) was added slowly at room temperature to a solution of **10-[G′$_1$]** (43.4 mg, 0.0079 mmol) in 2 mL of CD_2Cl_2. The solution, which was heterogeneous at the beginning of the addition, cleared up within 5 min. The NMR spectra, performed after stirring the solution for 1 h, showed the presence of only one phosphorus compound, **11-[G′$_1$]**.

11-[G′$_1$]. $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2): −1.3 (s, $^1J_{P^{195}Pt}$ = 1795 Hz, PPh_2), 52.4 (s, P_0), 62.2 (s, P_1) ppm. ^1H NMR (δ, CD_2Cl_2): 0.44 (br s, $^2J_{H^{195}Pt}$ = 68.8 Hz, 36H, CH_3−Pt), 3.38 (br d, $^3J_{HP}$ = 10.0 Hz, 9H, P_1−N−CH_3), 4.47 (m, 24H, CH_2−P), 6.9−8.0 (m, 165H, C_6H_5, C_6H_4, and CH═N) ppm. $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2): 4.1 (dd, $^2J_{CPtrans}$ = 100 Hz, $^2J_{CPcis}$ = 10 Hz, $^1J_{C^{195}Pt}$ = 605 Hz, CH_3−Pt), 33.6 (d, $^2J_{CP}$ = 12 Hz, P_1−N−CH_3), 52.0 (m, CH_2P), 121.4 (s, C_1^2), 121.9 (s, C_0^2), 126.7 (s, C_0^3, C_1^3), 128.4 (m, *m*-C_6H_5), 130.3 (s, *p*-C_6H_5), 131.8 (s, C_0^4), 132.6 (br d, $^1J_{CP}$ = 57 Hz, *i*-C_6H_5), 132.8 (s, C_1^4), 134.0 (m, *o*-C_6H_5), 134.8 (s, CH═NN), 138.8 (br s, $(CH═N)_0$), 150.1 (d, $^2J_{CP}$ = 8 Hz, C_1^1), 151.4 (d, $^2J_{CP}$ = 9 Hz, C_0^1) ppm.

Synthesis of Compound 12-[G′$_1$]. The slow evolution of **11-[G′$_1$]** in solution at room temperature resulted in a new compound, **12-[G′$_1$]**, which was isolated after evaporation of the solvent and washings with ether (3 × 5 mL).

12-[G′$_1$]. $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2): −3.7 (d, $^2J_{PP}$ = 17 Hz, $^1J_{P^{195}Pt}$ = 1673 Hz, PPh_2 trans Me), 0.0 (d, $^2J_{PP}$ = 17 Hz, $^1J_{P^{195}Pt}$ = 4151 Hz, PPh_2 trans Br), 52.4 (s, P_0), 62.2 (s, P_1) ppm. ^1H NMR (δ, CD_2Cl_2): 0.52 (dd, $^3J_{HP}$ = 6.8 Hz, $^3J_{HP}$ = 4.7 Hz, $^2J_{H^{195}Pt}$ = 59.2 Hz, 18H, CH_3−Pt), 3.32 (br d, $^3J_{HP}$ = 10.2 Hz, 9H, P_1−N−CH_3), 4.44 (m, 12H, CH_2−P), 4.46 (m, 12H, CH_2−P), 6.7−7.8 (m, 165H, C_6H_5, C_6H_4, and CH═N) ppm. $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2): 6.9 (dd, $^2J_{CPtrans}$ = 95 Hz, $^2J_{CPcis}$ = 6 Hz, $^1J_{C^{195}Pt}$ = 680 Hz, CH_3−Pt), 33.2 (d, $^2J_{CP}$ = 12 Hz, P_1−N−CH_3), 51.2 (m, CH_2P), 121.2 (br s, C_1^2), 121.7 (s, C_0^2), 126.9 (s, C_0^3, C_1^3), 127.7 (br d, $^1J_{CP}$ = 48 Hz, *i*-C_6H_5), 128.7 (m, *m*-C_6H_5), 130.0 (s, C_0^4), 130.7 (s, *p*-C_6H_5), 131.1 (s, C_1^4), 131.4 (s, *p*-C_6H_5), 132.5 (br d, $^1J_{CP}$ = 47 Hz, *i*-C_6H_5), 134.1 (m, *o*-C_6H_5), 134.5 (s, CH═NN), 138.8 (d, $^3J_{CP}$ = 16 Hz $(CH═N)_0$), 150.3 (d, $^2J_{CP}$ = 7 Hz, C_1^1), 151.3 (d, $^2J_{CP}$ = 8 Hz, C_0^1) ppm.

Synthesis of Compound 13-[G′$_1$]. A solution of **10-[G′$_1$]** (57 mg, 0.0104 mmol) in 25 mL of CH_2Cl_2 was added to a solution of KBr (47 mg, 0.154 mmol) in 10 mL of water, at room temperature. After the solution was stirred for 3 h, the two phases were separated and the organic phase was dried over $MgSO_4$ and evaporated.

13-[G′$_1$]: Yellow powder, mp 270 °C (dec); 90% yield. $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2): −9.9 (s, $^1J_{P^{195}Pt}$ = 3363 Hz, PPh_2), 52.4 (s, P_0), 61.9 (s, P_1) ppm. ^1H NMR (δ, CD_2Cl_2): 3.32 (br d, $^3J_{HP}$ = 10.2 Hz, 9H, P_1−N−CH_3), 4.33 (m, 24H, CH_2−P), 6.9−7.9 (m, 165H, C_6H_5, C_6H_4, and CH═N) ppm. $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2): 33.3 (d, $^2J_{CP}$ = 11 Hz, P_1−N−CH_3), 50.9 (m, CH_2P), 121.4 (br s, C_1^2), 121.7 (br s, C_0^2), 127.3 (s, C_0^3, C_1^3), 127.5 (br d, $^1J_{CP}$ = 69 Hz, *i*-C_6H_5), 128.8 (m, *m*-C_6H_5), 130.0 (s, C_0^4), 132.0 (s, *p*-C_6H_5), 132.5 (s, C_1^4), 134.1 (m, *o*-C_6H_5), 134.9 (s, CH═NN), 139.0 (d, $^3J_{CP}$ = 13 Hz, $(CH═N)_0$), 150.7 (d, $^2J_{CP}$ = 7 Hz, C_1^1), 151.2 (d, $^2J_{CP}$ = 8 Hz, C_0^1) ppm. $^{195}Pt\{^1H\}$ NMR (δ, CD_2Cl_2): −4789 (t, $^1J_{^{195}PtP}$ = 3485 Hz) ppm. Anal. Calc for $C_{222}H_{198}N_{18}Br_{12}O_9P_{16}S_4Pt_6$: C, 44.33; H, 3.32; N, 4.19. Found: C, 43.96; H, 3.45; N, 3.98.

General Procedure for the Synthesis of Compounds 14-[G′$_n$]. A solution of **3-[G′$_n$]** (***n*** = 1, 100 mg, 25.7 μmol; ***n*** =

2, 100 mg, 12.0 μmol; ***n*** = 3, 60 mg, 3.48 μmol) in dichloromethane (15 mL) was added slowly to a solution of Rh(acac)(COD) (***n*** = 1, 48 mg, 0.154 mmol; ***n*** = 2, 45 mg, 0.144 mmol; ***n*** = 3, 26 mg, 0.083 mmol) in dichloromethane (15 mL). The mixture was stirred for 2 h, and then the solvent was removed under vacuum and the yellow-orange residue washed three times with diethyl ether (10 mL).

14-[G′$_1$]: Yellow-orange powder, mp 245 °C; 76% yield. ^{31}P{^{1}H} NMR (δ, $CDCl_3$): 21.8 (d, $^1J_{PRh}$ = 130.8 Hz, PPh_2), 52.8 (s, P_0), 62.6 (s, P_1) ppm. ^{1}H NMR (δ, $CDCl_3$): 1.84 (s, 36H, CH_3 acac), 3.33 (br s, 9H, P_1-N-CH_3), 4.61 (m, 24H, CH_2-P), 5.41 (s, 6H, CH acac), 6.7−8.2 (m, 165H, C_6H_5, C_6H_4, and CH=N) ppm. ^{13}C{^{1}H} NMR (δ, $CDCl_3$): 27.7 (s, CH_3 acac), 33.1 (d, $^2J_{CP1}$ = 9.9 Hz, P_1-N-CH_3), 52.3 (m, CH_2-P), 98.7 (s, CH acac), 121.6 (br s, C_1^2 and C_0^2), 127.5−135.8 (m, C_0^3, C_1^3, C_0^4, C_1^4, *i*-C_6H_5, *m*-C_6H_5, *p*-C_6H_5, *o*-C_6H_5, and *C*H=NNCH$_2$), 139.6 (s, $(CH=N)_0$), 150.6 (d, $^2J_{CP1}$ = 7.9 Hz, C_1^1), 151.1 (d, $^2J_{CP0}$ = 7.9 Hz, C_0^1), 184.9 (s, CO acac) ppm. Anal. Calc for $C_{252}H_{240}N_{18}O_{21}P_{16}S_4Rh_6$: C, 59.37; H, 4.74; N, 4.95. Found: C, 55.6; H, 4.45; N, 4.4. Anal. Calc for **14-[G′$_1$]**·6CH_2Cl_2: C, 55.26; H, 4.53; N, 4.49.

14-[G′$_2$]: Yellow-orange powder, mp 250 °C; 80% yield. ^{31}P{^{1}H} NMR (δ, $CDCl_3$): 22.0 (d, $^1J_{PRh}$ = 130.8 Hz, PPh_2), 62.6 (s, P_1, P_2) ppm. ^{1}H NMR (δ, $CDCl_3$): 1.84 (s, 72H, CH_3 acac), 3.28 (br s, 27H, $P_{1-2}-N-CH_3$), 4.61 (m, 48H, CH_2-P), 5.40 (s, 12H, CH acac), 6.6−8.1 (m, 345H, C_6H_5, C_6H_4, and CH=N) ppm. ^{13}C{^{1}H} NMR (δ, $CDCl_3$): 27.6 (s, CH_3 acac), 32.9 (s, $P_{1-2}-N-CH_3$), 51.8 (m, CH_2-P), 98.6 (s, CH acac), 121.6 (br s, C_0^2, C_1^2, and C_2^2), 127.5−135.8 (m, C_0^3, C_1^3, C_2^3, C_0^4, C_1^4, C_2^4, *i*-C_6H_5, *m*-C_6H_5, *p*-C_6H_5, *o*-C_6H_5, and *C*H=NNCH$_2$), 139.3 (m, $(CH=N)_{0-1}$), 150.5 (br s, C_2^1), 151.4 (m, C_0^1 and C_1^1), 184.9 (s, CO acac) ppm.

14-[G′$_3$]: Orange powder, mp 256 °C; 75% yield. ^{31}P{^{1}H} NMR (δ, CD_2Cl_2): 23.5 (d, $^1J_{PRh}$ = 131.2 Hz, PPh_2), 64.7 (s, P_1, P_2, P_3) ppm. ^{1}H NMR (δ, CD_2Cl_2): 1.86 (s, 144H, CH_3 acac), 3.33 (br s, 63H, $P_{1-2-3}-N-CH_3$), 4.61 (m, 96 H, CH_2-P), 5.44 (s, 24H, CH acac), 6.8−8.1 (m, 705H, C_6H_5, C_6H_4, and CH=N) ppm. ^{13}C{^{1}H} NMR (δ, CD_2Cl_2): 27.5 (s, CH_3 acac), 33.0 (d, $^2J_{CP1-2-3}$ = 10.2 Hz, $P_{1-2-3}-N-CH_3$), 51.4 (m, CH_2-P), 98.4 (s, CH acac), 121.6 (br s, C_0^2, C_1^2, C_2^2, and C_3^2), 127.4−135.8 (m, C_0^3, C_1^3, C_2^3, C_3^3, C_0^4, C_1^4, C_2^4, C_3^4, *i*-C_6H_5, *m*-C_6H_5, *p*-C_6H_5, *o*-C_6H_5, and *C*H=NNCH$_2$), 139.4 (m, $(CH=N)_{0-1-2}$), 150.5 (m, C_3^1), 151.3 (m, C_0^1, C_1^1, and C_2), 184.9 (s, CO acac) ppm.

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Supporting Information Available: NMR spectra (6 pages). Ordering information is given on any current masthead page.

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