A Trithiol Protio-Ligand and Its Fixation to the Periphery of a Carbosilane Dendrimer as Scaffolds for Polynuclear Rhodium and Iridium Complexes and Metallodendrimers

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Tris(methylenethiol)methane derivatives containing an allyl or benzyl linker ($ROCH_2C(CH_2SH)_3$; R = Bn(**6a**), $CH_2{=}CHCH_2$(**6b**)), which could allow their fixation to carbosilane dendrimers, were synthesized through a multistep synthesis. Grafting the periphery of the core dendrimer $Si[(CH_2)_3Si(Me)_2H]_4$ was achieved with the tosyl derivative $CH_2{=}CHCH_2OCH_2C(CH_2OTs)_3$ by a hydrosilylation reaction to give selectively $Si[(CH_2)_3Si(Me)_2(CH_2)_3OCH_2C(CH_2OTs)_3]_4$ (**G(0)$_{OTs-12}$**). This dendrimer was converted into the thiol-functionalized carbosilane dendrimer $Si[(CH_2)_3Si(Me)_2(CH_2)_3OCH_2C(CH_2SH)_3]_4$ (**G(0)$_{SH-12}$**) by reduction of the thiocyanate intermediate $Si[(CH_2)_3Si(Me)_2(CH_2)_3OCH_2C(CH_2SCN)_3]_4$ with $LiAlH_4$. The trithiol compounds **6a** and **6b** protonated the complexes $[Rh(\mu\text{-}OMe)(cod)]_2$ and [Rh(acac)diolefin] (M = Rh, diolefin = cod, nbd, tfb) to give the corresponding trinuclear complexes $[Rh_3\{\mu\text{-}ROCH_2c(ch_2s)_3\}(diolefin)_3]$ (**7**−**9**). Their structure can be described as an adamantane-like entity, in which the metals are held together by the thiolate arms of the ligand, with the sulfurs bridging the metal atoms in a μ_2 fashion, as shown for $[Rh_3\{\mu\text{-}BnOCH_2C(CH_2S)_3\}(nbd)_3]$ by X-ray diffraction methods. Carbonylation of **7**−**9** under atmospheric pressure gave the carbonyl complexes with the thiolate tripod ligands $[M_3\{\mu\text{-}ROCH_2C(CH_2S)_3\}(CO)_6]$ (M = Rh, Ir), which were reacted with phosphorus donor ligands ($PR_3 = PPh_3$, $P(OMe)_3$) to give $[M_3\{\mu\text{-}ROCH_2C(CH_2S)_3\}(CO)_3(PR)_3]$ as a sole isomer of averaged C_{3v} symmetry. The functional dendrimers were metalated by reaction of the core molecule $Si[(CH_2)_3Si(Me)_2(CH_2)_3OCH_2C(CH_2SH)_3]_4$ (**G(0)$_{SH-12}$**) by applying the synthetic protocols above-described for trinuclear complexes. Thus, the reactions of **G(0)$_{SH-12}$** with the complexes [M(acac)(diolefin)] (M = Rh, Ir; diolefin = cod, nbd, tfb) gave the metallodendrimers $Si[(CH_2)_3Si(Me)_2(CH_2)_3OCH_2C(CH_2S)_3\{M(diolefin)\}_3]_4$ (**G(0)$_{M(diolefin)-12}$**) as insoluble solids. Soluble metallodendrimers, $Si[(CH_2)_3Si(Me)_2(CH_2)_3OCH_2C(CH_2S)_3\{Rh(CO)_2\}_3]_4$ (**G(0)$_{Rh(CO)2-12}$**) and $Si[(CH_2)_3Si(Me)_2(CH_2)_3OCH_2C(CH_2S)_3\{M(CO)(PPh_3)\}_3]_4$ (**G(0)$_{M(CO)(PPh3)-12}$**) were obtained either by carbonylation of the diolefin compounds or by the reaction of **G(0)$_{SH-12}$** with $[M(acac)(CO)_2]$ (M = Rh, Ir), and by further reaction with PPh_3, respectively.

Introduction

Metallodendrimers are an evolving class of dendritic macromolecules that incorporate metals in their structures.[1] The main attraction about this class of architectures relies in their intrinsic properties,[2] which include a globular shape, a defined and known location of the metallic centers within the dendritic structure, a high solubility, and usually an elevated concentration of metallic sites around their peripheries. All these features make metallodendrimers valuable materials to develop a number of applications that have already been used in catalysis,[3] redox processes,[4] host−guest chemistry,[5] electronics,[6] and light-harvesting.[7]

The success of the preparation of such materials often relies on a suitable design of the ligand systems grafted to the dendritic surfaces, so that the coordination of the

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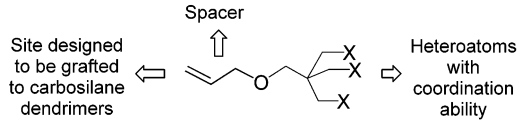
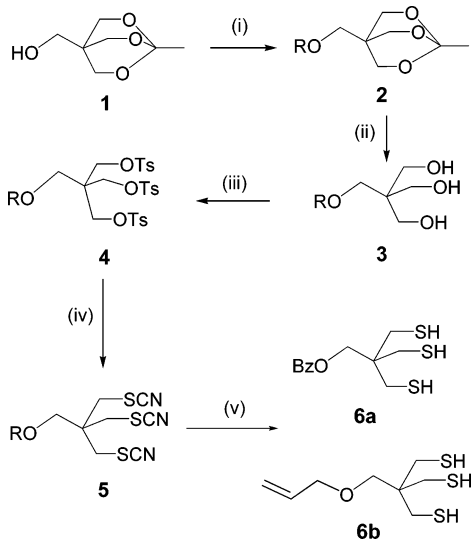
metallic fragments, which commonly is carried out in the last synthetic step, must be very efficient in order to avoid cross-linking or oligomerization processes.[8] Given the number of papers dedicated to metallodendrimers, it is surprising that there are only a few reports on dendrimers peripherally adapted with hydrosulfido groups,[9] functionalities that have the potential to stabilize complexes with virtually every metal from the periodic table.[10] Moreover, interaction of thiols with metallic nanoparticles is a topic of current interest. Recent examples are a versatile approach to stabilize gold nanoparticles of a specific size with α-functionalized thiols from a single precursor,[9a,11] and the condensation of bifunctionalized thiol-ferrocene dendrons around gold nanoparticles to form redox-active dendrimers.[12]

We have reported recently[8a] a method to prepare different generations of carbosilane dendrimers functionalized on their peripheries with hydrosulfido groups, more specifically with propanethiol chains attached to the ending silicon atoms. The goal of this project was to prepare thiolate complexes on the surface of discrete metallodendrimers with a high potential as catalytic precursors in hydroformylation of olefins.[13] However, the intrinsic architecture of these dendritic assemblies led to polymeric metallodendrimers, in which the dendritic cores remained glued to one another through the "$M(L_2)$" (M = Rh, Ir) metal fragments, forming insoluble tridimensional networks. To overcome this unwanted situation for homogeneous catalysis purposes, the architecture of the hydrosulfido periphery of the dendrimer should be designed in such a way that discrete metallodendrimers result. With this aim we have developed the synthesis of tripod-based thiol protio-ligands appropriate for their attachment to the periphery of carbosilane dendrimers. One of them incorporates an olefin side able to undergo hydrosilylation with dendrimers functionalized with Si−H peripheral bonds and also bears three arms terminated with hydrosulfido groups able to form discrete complexes of transition metals (Chart 1). A related ligand with a consequent iridium complex was reported by Maissonat and Poilblanc.[14] We also describe herein some of their rhodium and iridium complexes, the successful attachment of the ligand to preformed carbosilane dendrimers, and derived rhodium and iridium discrete metallodendrimers.

Chart 1



Scheme 1. Synthesis of the Tripod Protio-Ligands[a]



[a] i = RBr, KOH (R = $C_6H_4CH_2$, CH_2=$CHCH_2$); ii = HCl (aq); iii = TsCl, py; iv = KSCN, v = $LiAlH_4$.

Results and Discussion

Synthesis of the Tripod Protio-Ligands $ROCH_2C(CH_2SH)_3$ (R = $C_6H_5CH_2$ (Bn), 6a; CH_2=$CHCH_2$, 6b). The starting material was pentaerythol, $C(CH_2OH)_4$, an inexpensive chemical that was transformed into the known compound $HOCH_2C(CH_2O)_3CCH_3$ (**1**).[15] The apical hydroxyl group in **1** was etherified with selected benzyl (Bn) or allyl bromides to give the corresponding ether derivatives $ROCH_2C(CH_2O)_3CCH_3$ (R = Bn (**2a**), R = CH_2=$CHCH_2$ (**2b**)) in excellent yields (Scheme 1). Once the apical functionalization was achieved, the protecting orthoacetate group in **2** was hydrolyzed to the corresponding triol derivatives $ROCH_2C(CH_2OH)_3$ (R = Bn (**3a**), R = CH_2=$CHCH_2$ (**3b**)), which were isolated as analytically pure oils. Protection of the free hydroxylic functionalities with tosylate groups gave $ROCH_2C(CH_2OTs)_3$ (R = Bn (**4a**), R = CH_2=$CHCH_2$

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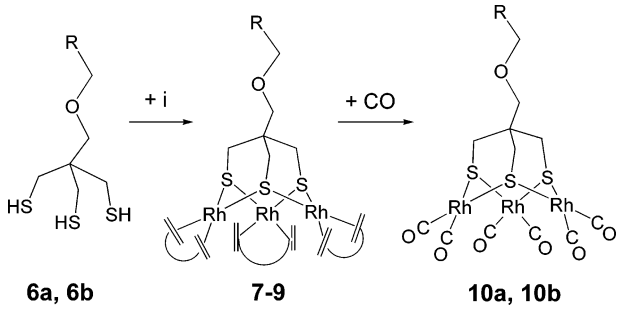
Scheme 2. Preparation and Structures of the Trinuclear Complexes[a]



[a] i = [Rh(acac)(diolefin)]; R = Bn, allyl.

(**4b**)), which were reacted with potassium thiocyanate to give the expected sulfur-containing derivatives $ROCH_2C(CH_2SCN)_3$ (R = Bn (**5a**), R = CH_2=$CHCH_2$ (**5b**)) in good yields. The final step to achieve the desired hydrosulfido tripodal systems involved the chemical reduction of the thiocyanate compounds **5** with lithium aluminum hydride in diethyl ether to give the compounds $ROCH_2C(CH_2SH)_3$ (R = Bn (**6a**), R = CH_2=$CHCH_2$ (**6b**)) as malodorous oils. All the intermediates involved in the syntheses were completely characterized by elemental analyses and multinuclear NMR and mass spectra (see Experimental Section).

Synthesis and Structural Characterization of Trinuclear Rhodium Diolefin Complexes. The compounds $ROCH_2C(CH_2SH)_3$ (R = Bn, **6a**; allyl, **6b**) bear three hydrosulfide groups acidic enough to protonate acetylacetonate (acac) and methoxo or hydroxo ligands in rhodium and iridium complexes to produce thiolate tripod-based complexes. Thus, treatment of **6a** with 3 equiv of [Rh(acac)(cod)] gave a dark red colored solution within a few seconds, from which the compound $[Rh_3\{\mu\text{-}BnOCH_2C(CH_2S)_3\}(cod)_3]$ (**7**) was isolated as a dark red microcrystalline solid in excellent yield. Alternatively, reactions of **6a** with the dinuclear complexes $[Rh(\mu\text{-}OR)(cod)]_2$ (R = H, Me) gave complex **7** in similar yield. In a different approach, compound **6a** was deprotonated with n-BuLi in THF to give the soluble lithium salt of the ligand, which afforded cleanly complex **7** upon reaction with $[Rh(\mu\text{-}Cl)(cod)]_2$. The related diolefin rhodium complexes $[Rh_3\{\mu\text{-}BnOCH_2C(CH_2S)_3\}(diolefin)_3]$ (**8a**, **9a**) and those derived from **6b**, $[Rh_3\{\mu\text{-}CH_2$=$CHCH_2\text{-}OCH_2C(CH_2S)_3\}(diolefin)_3]$ (**8b**, **9b**) (diolefin = norborna-2,5-diene (nbd) **8**, tetrafluorobenzo[5,6]bicyclo-[2.2.2]octa-2,5,7-triene (tfb) **9**), were also isolated in good yields as violet (nbd) and dark red (tfb) microcrystalline solids, respectively, by reaction of the complexes [Rh-(acac)(diolefin)] with the appropriate compounds **6a** and **6b** (Scheme 2).

Complexes **7**−**9** are trinuclear, showing the molecular ions in accordance with the calculated *m/z* values. They are very soluble in chlorinated solvents, THF, and toluene, which allowed their study by NMR methods in solution. To establish the coordination of the tridentate ligand and to obtain accurate geometrical parameters for one of them, an X-ray diffraction study on a monocrystal of the complex $[Rh_3\{\mu\text{-}BnOCH_2C(CH_2S)_3\}(nbd)_3]$ (**8a**) was carried out. Figure 1 shows the molecular structure along with the atom-labeling scheme used, and Table 1 displays selected bond distances and angles of **8a**.

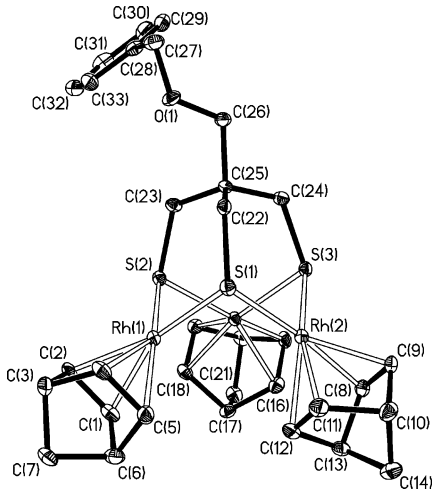


Figure 1. Molecular representation of the trinuclear complex **8a**.

Table 1. Selected Bond Distances (Å) and Angles (deg) for the Complex 8a

Rh(1)−S(1)	2.3161(8)	S(1)−Rh(2)−M(3)*	159.05(9)
Rh(1)−S(2)	2.3539(7)	S(1)−Rh(2)−M(4)*	100.41(9)
Rh(1)−M(1)* [a]	2.0498(33)	S(3)−Rh(2)−M(3)*	96.22(9)
Rh(1)−M(2)*	2.0284(33)	S(3)−Rh(2)−M(4)*	160.19(9)
Rh(2)−S(1)	2.3587(8)	S(2)−Rh(3)−S(3)	96.85(3)
Rh(2)−S(3)	2.3145(7)	S(2)−Rh(3)−M(5)*	163.78(9)
Rh(2)−M(3)*	2.0023(31)	S(2)−Rh(3)−M(6)*	93.30(10)
Rh(2)−M(4)*	2.0433(31)	S(3)−Rh(3)−M(5)*	99.33(10)
Rh(3)−S(2)	2.3222(7)	S(3)−Rh(3)−M(6)*	162.84(9)
Rh(3)−S(3)	2.3803(8)	Rh(1)−S(1)−Rh(2)	92.12(3)
Rh(3)−M(5)*	2.0538(32)	Rh(1)−S(1)−C(22)	111.43(11)
Rh(3)−M(6)*	2.0046(32)	Rh(2)−S(1)−C(22)	113.62(11)
S(1)−C(22)	1.825(3)	Rh(1)−S(2)−Rh(3)	97.68(3)
S(2)−C(23)	1.823(3)	Rh(1)−S(2)−C(23)	111.23(11)
S(3)−C(24)	1.824(3)	Rh(3)−S(2)−C(23)	111.08(11)
S(1)−Rh(1)−S(2)	94.94(3)	Rh(2)−S(3)−Rh(3)	87.59(3)
S(1)−Rh(1)−M(1)*	166.96(10)	Rh(2)−S(3)−C(24)	114.81(11)
S(1)−Rh(1)−M(2)*	96.21(9)	Rh(3)−S(3)−C(24)	110.27(11)
S(2)−Rh(1)−M(1)*	98.08(9)	S(1)−C(22)−C(25)	121.86(22)
S(2)−Rh(1)−M(2)*	164.57(9)	S(2)−C(23)−C(25)	121.79(22)
S(1)−Rh(2)−S(3)	96.61(3)	S(3)−C(24)−C(25)	122.09(22)

[a] M* represents the midpoints of the olefinic double bonds.

The structure of complex **8a** consists of three "Rh-(nbd)" fragments held together by the three thiolate arms of the ligand, with the sulfurs bridging the rhodium atoms in a μ_2 fashion. The structure can be described as an adamantane-like entity that nearly incorporates a C_3 axis passing through the C(25) and C(26) atoms. The rhodium atoms complete a typical square-planar coordination with an nbd molecule interacting through the two olefinic bonds in a η^2 mode. The separation between the adjacent rhodium centers is too long (Rh(1)···Rh(2) 3.3663(4) Å, Rh(1)···Rh(3) 3.5207(3) Å, Rh(1)···Rh(4) 3.2494(3) Å) to consider any kind of interactions between the metals.[16] The Rh−S bond distances (2.3145(7)−2.3803(8) Å) compare well with those found in some dinuclear rhodium thiolate complexes such as $[Rh_2[\mu\text{-}S(CH_2)_3S](cod)_2]$[17] or the mononuclear tripod-based complex $[(CH_3C(CH_2PPh_2)_3\text{-}Rh(CH_3C(CH_2S)_3)]$.[18] The molecular structure of com-

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plex **8a** resembles that found for the complex $[Ir_3(\mu\text{-}CH_3C(CH_2S)_3(CO)_6]$,[14] whose basic organic framework is similar to that described in this work.

The diolefin complexes **7**−**9** display in solution a structure similar to that found for **8a** in the solid state and behave in a similar way, judging from their ^1H and $^{13}C\{^1H\}$ NMR spectra. The ^1H NMR spectra showed sharp signals for the bridging ligand, while the signals for diolefin are broad at room temperature, still showing two environments for the olefinic protons as predicted for a species that possesses an effective C_{3v} symmetry. The nbd complexes **8**, however, showed a broad band for the olefin protons at room temperature. This broadening of the signals is indicative of a fluxional process that can be frozen at low temperature. Thus the ^1H NNR spectra of complexes **8** in the slow exchange showed a singlet for the three equivalent CH_2S groups and two signals for the olefin protons, as expected. Therefore, the structure in solution of complexes **7**−**9** corresponds to that found in the solid state for **8a** without the symmetry restraint imposed by the allyl or benzyl groups.

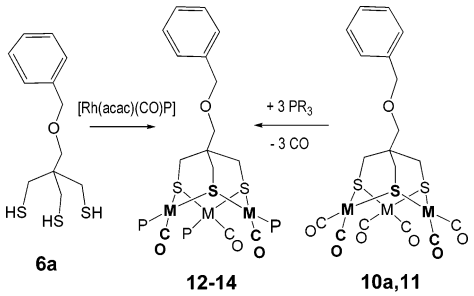
Trinuclear Rhodium and Iridium Carbonyl and Phosphine Complexes. Treatment of $ROCH_2C(CH_2SH)_3$ (R = Bn, **6a**; allyl, **6b**) with 3 molar equiv of $[Rh(acac)(CO)_2]$ gave the complexes $[Rh_3\{\mu\text{-}ROCH_2C(CH_2S)_3\}(CO)_6]$ (R = Bn, **10a**; allyl, **10b**) cleanly as black microcrystalline solids in very good yields. An alternative route to these compounds consists of the carbonylation of the diolefin complexes **7**−**9** in dichloromethane under atmospheric pressure (Scheme 2). The initial trinuclear framework is maintained in the reactions, as confirmed by the mass spectra of both complexes **10**, which showed the molecular ions along with the sequential loss of six carbonyl ligands. In addition, the IR spectra of complexes **10** in toluene showed three intense bands in the carbonyl region, which agrees with the predicted $1A_1$ and 2E active stretching modes under C_{3v} symmetry.

Complexes **10** are very soluble in diethyl ether, THF, and chlorinated solvents and insoluble in hexanes and methanol. Solutions of **10** are intensively colored and exhibit black-orange dichroism, which is indicative of intermolecular metal−metal interactions, as reported for the complex $[Ir_3\{\mu\text{-}CH_3C(CH_2S)_3\}(CO)_6]$ in the solid state.[14] The equivalence of all the carbonyl groups and of all the CH_2S moieties in the $^{13}C\{^1H\}$ NMR spectra is consistent with the structure proposed in Scheme 2.

In a similar way, reaction of $BnOCH_2C(CH_2SH)_3$ (**6a**) with 3 molar equiv of $[Ir(acac)(CO)_2]$ gave the complex $[Ir_3\{\mu\text{-}BnOCH_2C(CH_2S)_3\}(CO)_6]$ (**11**) in excellent yield as a dark blue microcrystalline solid, which in solution turns to a deep red color. The trinuclear nature of complex **11** was confirmed by the mass spectrum, and the IR spectrum in toluene showed three ν(CO) bands expected for a C_{3v} symmetry. The structure of **11** is similar to that proposed for complex $[Rh_3\{\mu\text{-}BnOCH_2C(CH_2S)_3\}(CO)_6]$ (**10a**), since their ^1H NMR spectra are virtually identical, while a singlet was observed for the carbonyl ligands in the $^{13}C\{^1H\}$ NMR spectrum of **11**.

The carbonyl complexes **10a** and **11** reacted with phosphine or phosphite donor ligands to give the product

Scheme 3



from the replacement of one sole carbonyl ligand at each metallic center (Scheme 3). In this way, the complexes $[M_3\{\mu\text{-}BnOCH_2C(CH_2S)_3\}(PR_3)_3(CO)_3]$ (M = Rh; R = Ph, **12**; OMe, **13**; M = Ir, R = Ph, **14**) were isolated as brown solids in excellent yields. While **12** and **13** can be obtained alternatively by the reactions of $[Rh(acac)(CO)(PPh_3)]$ and $[Rh(acac)(CO)(P(OMe)_3)]$ with **6a**, respectively, the reaction of $[Ir(acac)(CO)(PPh_3)]$ with **6a** gave a mixture of complexes that was not analyzed further.

The trinuclear nature of complexes **12**−**14** was confirmed by their mass spectra. These complexes exhibit one band in the IR spectra, which is in accordance with the presence of only one carbonyl ligand per metal center. A sole isomer, the most symmetrical of C_3 symmetry, resulted from these reactions, since the $^{31}P\{^1H\}$ NMR spectra of complexes **12**−**14** showed a doublet for the rhodium complexes and a singlet for the iridium one. These rhodium and iridium complexes resemble in structure and selectivity in the replacement reactions the early-late complexes $[CpTi(\mu_3\text{-}S)_3\{Rh(CO)(PR_3)\}_3]$, formed by addition of phosphine or phosphite ligands to the hexacarbonyl precursor.[19,20] However, the iridium complex does not follow the behavior of $[CpTi(\mu_3\text{-}S)_3\{Ir(CO)_2\}_3]$, for which the complexes $[CpTi(\mu_3\text{-}S)_3Ir_3(\mu\text{-}CO)(CO)_3(PR_3)_3]$ with one tetrahedral iridium center and a bridging carbonyl were isolated, probably because of the interaction of the iridium center with the early transition metal.[21]

Attachment of the Tripod System to Carbosilane Peripheries. The methodology to graft the tripod ligand to carbosilane dendrimers relies on a hydrosilylation step, in which the olefin involved is already incorporated in the ligand system and the Si−H bonds are located at specific sites on the periphery of the carbosilane dendrimer, whose preparation has been reported elsewhere.[22] However, the direct coupling of the trithiol protio-ligand or their complexes to the dendrimer by hydrosilylation was not obvious, since some functional groups were found to be incompatible with the reaction conditions used. Thus, the platinum-catalyzed hydrosilylation of the allyl-containing trinuclear complexes $[Rh_3\{\mu\text{-}CH_2{=}CHCH_2OCH_2C(CH_2S)_3\}(L{-}L)_3]$ (L−L = nbd, **8b**; tfb, **9b**; $(CO)_2$, **10b**) with the

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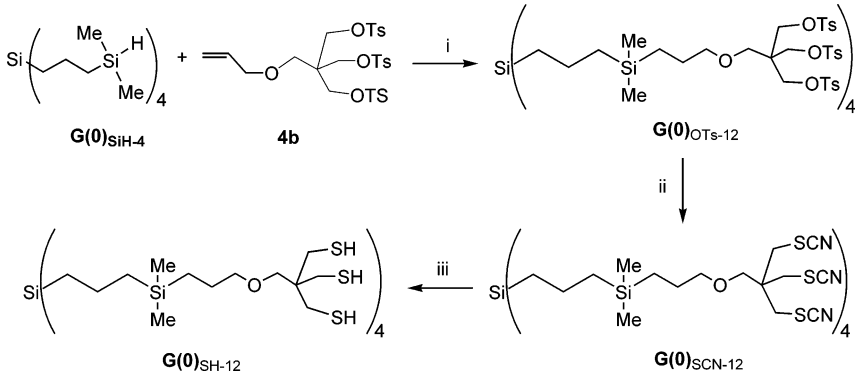
Scheme 4. Attachment of a Tripod Ligand Precursor to Carbosilane Dendrimers[a]



[a] i = Karstedt's catalyst, THF; ii = KSCN, DMF; iii = $LiAlH_4$, Et_2O.

core dendrimer $Si[(CH_2)_3Si(Me)_2H]_4$ (**G(0)$_{SiH-4}$**) did not follow the expected manifold. Instead, we observed that the allyl group of the bridging ligand underwent an isomerization process under the reaction conditions to give a mixture of the *trans*- and *cis*-1-propenyl derivatives. For example, by monitoring the reaction of the complex $[Rh_3\{\mu\text{-}CH_2{=}CHCH_2OCH_2C(CH_2S)_3\}(CO)_6]$ (**10b**) with **G(0)$_{SiH-4}$** by ^1H NMR techniques in the presence of the Karstedt's catalyst, $[\{O(SiMe_2CH{=}CH_2)_2\}_3Pt_2]$, the transformation of the allyl moiety to the corresponding mixture of isomers (*cis:trans* = 2:1) $[Rh_3\{\mu\text{-}CH_3{-}CH{=}CHOCH_2C(CH_2S)_3\}(CO)_6]$ was found to be complete in 21 h at room temperature in benzene.

It was clear at this point that the attachment of the tripod ligand to the dendrimer had to be carried out using organic-based materials. However, the hydrosilylation of the compounds $CH_2{=}CHCH_2OCH_2C(CH_2SCN)_3$ (**5b**) and $CH_2{=}CHCH_2OCH_2C(CH_2SH)_3$ (**6b**) with the dendritic core $Si[(CH_2)_3Si(Me)_2H]_4$ (**G(0)$_{SiH-4}$**) also failed, presumably because of the poisoning of the Pt^0 catalyst by the sulfur donor atoms. Nevertheless, we found that the reaction of $CH_2{=}CHCH_2OCH_2C(CH_2OTs)_3$ (**4b**) with **G(0)$_{SiH-4}$** using the Karstedt's catalyst gave cleanly the desired product of the anti-Markovnikov addition of the silane along the olefin, $Si[(CH_2)_3Si(Me)_2(CH_2)_3OCH_2C(CH_2OTs)_3]_4$ (**G(0)$_{OTs-12}$**), in quantitative yield (Scheme 4). Neither the starting material nor the Markovnikov isomer was observed in the product, which indicated that the hydrosilylation protocol to attach the tosylate derivative to the dendritic core is an excellent way to perform the coupling. Moreover, this methodology involves the formation of Si−C bonds between the core dendrimer and the precursor of the ligand, which led to very robust and thermally stable constructs. Parallel strategies[23] have been used to couple a tripod-based phosphine ligand to carbosilane dendrimers, although some of these relied on the formation of Si−O bonds,[24] which are more susceptible to the hydrolysis.

A further reaction of **G(0)$_{OTs-12}$** with potassium thiocyanate in refluxing DMF gave cleanly the dendritic derivative $Si[(CH_2)_3Si(Me)_2(CH_2)_3OCH_2C(CH_2SCN)_3]_4$ (**G(0)$_{SCN-12}$**), isolated as a heavy oil in quantitative yield. The final step involved the reduction of **G(0)$_{SCN-12}$** with $LiAlH_4$, which afforded the target dendrimer $Si[(CH_2)_3Si(Me)_2(CH_2)_3OCH_2C(CH_2SH)_3]_4$ (**G(0)$_{SH-12}$**) as an oil, which was purified by column chromatography. The purity and the identity of the target dendrimer **G(0)$_{SH-12}$** was confirmed by the MALDI-TOF spectrum, which showed a sharp signal at *m/z* 1327.5 corresponding to the molecular ion $Si[(CH_2)_3Si(Me)_2(CH_2)_3OCH_2C(CH_2SH)_3]_4^+$ minus two protons, with the expected pattern for the isotopic distribution. The dendritic intermediates involved in this multistep synthesis have been unambiguously characterized by multinuclear NMR spectroscopy and elemental analyses.

Preparation of Dodecanuclear Metallodendrimers of Rhodium and Iridium. The synthesis of metallodendrimers using the core molecule $Si[(CH_2)_3Si(Me)_2(CH_2)_3OCH_2C(CH_2SH)_3]_4$ (**G(0)$_{SH-12}$**) as support is straightforward by applying the synthetic protocols above-described for trinuclear complexes. For instance, the reactions of **G(0)$_{SH-12}$** with the complexes [Rh(acac)(diolefin)] (diolefin = cod, nbd, tfb) in a 1:12 molar ratio in THF or CH_2Cl_2 gave dark red or violet solutions from which dark solids analyzing as $Si[(CH_2)_3Si(Me)_2(CH_2)_3OCH_2C(CH_2S)_3\{Rh(diolefin)\}_3]_4$ (**G(0)$_{Rh(diolefin)-12}$**) precipitated within a few minutes. Monitoring these reactions by ^1H NMR showed clearly the release of acetylacetone, but no peaks from either the dendritic skeleton or the diolefinic ligands were observed as a consequence of the low solubility of the resulting metallodendrimers. Despite the insolubility of the above diolefin dendrimers in organic solvents, their carbonylation under atmospheric pressure gave the soluble compound $Si[(CH_2)_3Si(Me)_2(CH_2)_3OCH_2C(CH_2S)_3\{Rh(CO)_2\}_3]_4$ (**G(0)$_{Rh(CO)2-12}$**), which was fully characterized.

A direct synthesis of the carbonylmetallodendrimer **G(0)$_{Rh(CO)2-12}$** and the analogous iridium compound $Si[(CH_2)_3Si(Me)_2(CH_2)_3OCH_2C(CH_2S)_3\{Ir(CO)_2\}_3]_4$ **G(0)$_{Ir(CO)2-12}$** consisted in the reaction of **G(0)$_{SH-12}$** with $[M(acac)(CO)_2]$ (M = Rh, Ir) in a 1:12 molar ratio (Scheme 5). These compounds were isolated as black and dark red solids, respectively, in excellent yields. Both showed three ν(CO) intense bands in the IR spectrum, which agrees with a local C_{3v} symmetry. While the iridium compound is insoluble in organic solvents, **G(0)$_{Rh(CO)2-12}$** was soluble enough in $CDCl_3$ to observe the $^{13}C\{^1H\}$ NMR spectrum that is in accordance with the proposed metallodendritic structure. In particular, the carbonyl groups gave a doublet at δ 182.2 ppm ($^1J_{C-Rh}$ = 67 Hz) and the Si-Me moiety at δ −3.4 ppm, a chemical shift typical for CH_3-Si

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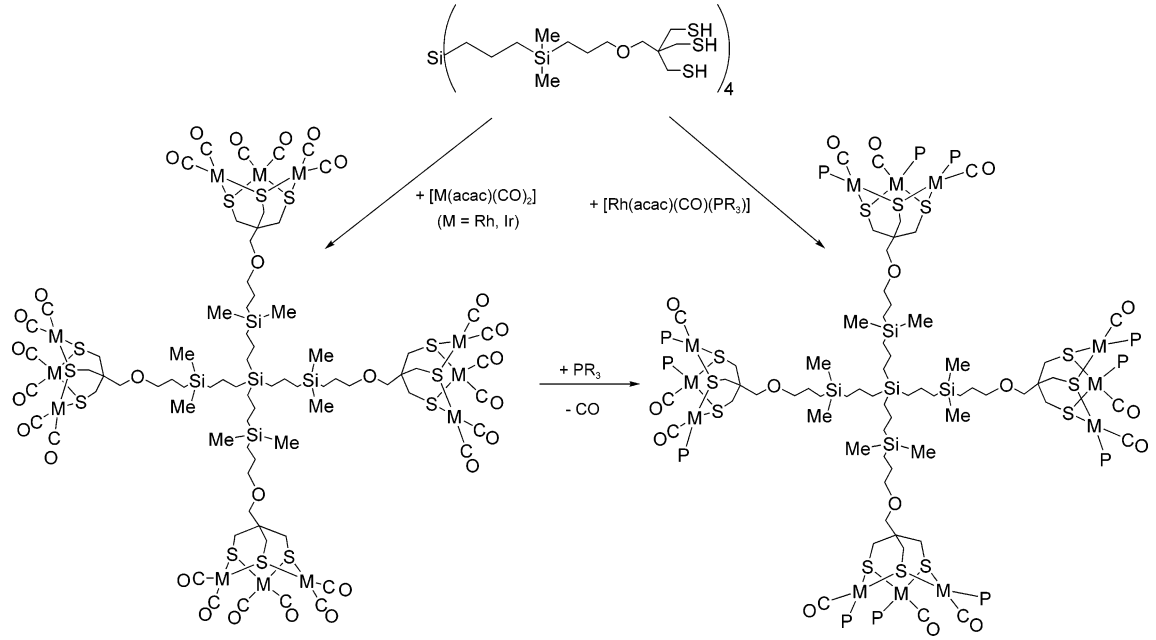
Scheme 5. Formation of Metallodendrimers of Rhodium and Iridium[a]



[a] M = Rh, Ir; P or PR_3 = PPh_3, $P(OMe)_3$.

groups. Moreover, the incorporation of the $Rh(CO)_2$ moieties to the dendrimer was indicated by the MALDI-TOF spectrum of $\mathbf{G(0)_{Rh(CO)2-12}}$, which showed peaks at *m/z* corresponding to the molecular ion minus 5, 16, and 24 carbonyl groups.

Soluble metallodendrimers were obtained by reacting mononuclear rhodium complexes of the type [Rh(acac)(CO)(PR_3)] (R = Ph, OMe) with $\mathbf{G(0)_{SH-12}}$, which gave the compounds $Si[(CH_2)_3Si(Me)_2(CH_2)_3OCH_2C(CH_2S)_3\{Rh(CO)(PPh_3)\}_3]_4$ ($\mathbf{G(0)_{Rh(CO)(PPh3)-12}}$) and $Si[(CH_2)_3Si(Me)_2(CH_2)_3OCH_2C(CH_2S)_3\{Rh(CO)(P(OMe)_3)\}_3]_4$ ($\mathbf{G(0)_{Rh(CO)(P(OMe)3)-12}}$) (Scheme 5). The ^1H NMR spectrum of $\mathbf{G(0)_{Rh(CO)(PPh3)-12}}$ in C_6D_6 is not very significant, since broad bands were observed, suggesting a fluxional process that could not be frozen even at −90 °C in CD_2Cl_2. However the $^{13}C\{^1H\}$ NMR spectrum in CD_2Cl_2 gave signals of the tripod frameworks comparable to those shown by complex $[Rh_3\{\mu\text{-}BnOCH_2C(CH_2S)_3\}(CO)_3(PPh_3)_3]$ (**12**), and the signals from the dendritic skeleton agreed with the structure proposed for $\mathbf{G(0)_{Rh(CO)(PPh3)-12}}$. Noteworthy, the $^{31}P\{^1H\}$ NMR spectra of $\mathbf{G(0)_{Rh(CO)(PPh3)-12}}$ and ($\mathbf{G(0)_{Rh(CO)(P(OMe)3)-12}}$) showed a sole doublet, indicating the coordination of the four trinuclear tripod entities in the dendrimers is similar to the monomer version.

Treatment of $\mathbf{G(0)_{SH-12}}$ with [Ir(acac)($CO)_2$] yielded a deep red solution, which within 5 min resulted in a red insoluble solid, whose analytical data fit with those calculated for the iridium metallodendrimer $Si[(CH_2)_3Si(Me)_2(CH_2)_3OCH_2C(CH_2S)_3\{Ir(CO)_2\}_3]_4$ ($\mathbf{G(0)_{Ir(CO)2-12}}$). The ^1H NMR spectrum of the reaction in situ in $CDCl_3$ showed the release of acetylacetone, the disappearance of the SH triplet, and the shift of 0.22 ppm of the CH_2S-tripod signals of the species in solution relative to $\mathbf{G(0)_{SH-12}}$. In addition, the IR spectrum of the in situ reaction showed three bands in the carbonyl region that agree with a local C_{3v} symmetry. Despite the insolubility of $\mathbf{G(0)_{Ir(CO)2-12}}$ that precluded a further characterization, the derived metallodendrimer $Si[(CH_2)_3Si(Me)_2(CH_2)_3OCH_2C(CH_2S)_3\{Ir(CO)(PPh_3)\}_3]_4$ ($\mathbf{G(0)_{Ir(CO)(PPh3)-12}}$) resulted from the one-pot reaction of $\mathbf{G(0)_{SH-12}}$ with [Ir(acac)($CO)_2$] followed by the addition of 12 molar equiv of PPh_3. The $^{31}P\{^1H\}$ NMR spectrum of $\mathbf{G(0)_{Ir(CO)(PPh3)-12}}$ showed a sole singlet at δ −24.2 ppm, indicating that the isomer of local symmetry C_3 was formed selectively.

Experimental Section

General Procedures. All manipulations were performed under a dry argon atmosphere using Schlenk-tube techniques. Solvents were dried by standard methods and distilled under argon immediately prior to use. Standard literature procedures were used to prepare the starting materials [Rh(acac)(diolefin)] (diolefin = cod, nbd),[25] [Rh(acac)($CO)_2$],[26] [Rh(acac)(CO)(PPh_3)],[25] and [Ir(acac)(cod)].[27] The core dendrimer $Si[(CH_2)_3Si(Me)_2H]_4$ ($\mathbf{G(1)_{SiH-4}}$)[22] and the compound $HOCH_2C(CH_2O)_3CCH_3$ (**1**)[15] were synthesized according to literature procedures. All the other chemicals used in this work have been purchased from Aldrich Chemicals and used as received.

Carbon and hydrogen analyses were performed with a Perkin-Elmer 2400 microanalyzer. Mass spectra were recorded in a VG Autospec double-focusing mass spectrometer operating in the FAB^+ mode for the metal complexes and in the EI mode for the organic compounds. Ions were produced with the standard Cs^+ gun at ca. 30 kV; 3-nitrobenzyl alcohol (NBA) was used as matrix. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ spectra were recorded on Varian Unity, Bruker ARX 300, and Varian Gemini 300 spectrometers operating at 299.95, 121.42, and 75.47 MHz, 300.13, 121.49, and 75.47 MHz, and 300.08, 121.48, and 75.46 MHz, respectively. Chemical shifts are reported in ppm and referenced to Me_4Si using the residual signal of the deuterated solvent (^1H and ^{13}C) and H_3PO_4 as external reference (^{31}P). Molecular weights were determined with a Knauer osmometer using a chloroform solution of the complexes. MALDI-TOF spectra were recorded in a Reflex MALDI spectrometer operating in the linear and reflector modes.

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Synthesis of the Compounds. $BnOCH_2C(CH_2O)_3CCH_3$ (2a). Solid $HOCH_2C(CH_2O)_3CCH_3$ (**1**) (7.67 g, 47.9 mmol) was added to a stirred suspension of finely powdered KOH (12.63 g, 225.2 mmol) and benzyl bromide (9.56 g, 6.65 mL, 55.6 mmol) in DMSO (50 mL). The resulting mixture was stirred for 45 min at room temperature, and then water (100 mL) was added. The solution thus obtained was extracted with diethyl ether (3 × 50 mL). The combined organic extracts were washed with a saturated solution of NaCl, then dried over Na_2SO_4, and finally filtered through a pad of Celite. After removal of the solvent by distillation under vacuum, a heavy colorless oil was isolated (11.0 g, 92%). ^{1}H NMR ($CDCl_3$, 22 °C) δ: 7.26−7.39 (m, 5H, C_6H_5), 4.58 (s, 2H, $PhCH_2O$), 4.02 (s, 6H, $C(CH_2O)_3$), 3.20 (s, 2H, $PhCH_2OCH_2$), 1.47 (s, 3H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C) δ: 137.5 (s, C_{ipso}), 128.5 (s, C_m), 127.8 (s, C_o), 127.4 (s, C_p) (Bn), 108.4 (s, CCH_3), 73.3 (s, $PhCH_2OCH_2$), 69.3 (s, $C(CH_2O)_3$), 68.1 (s, $PhCH_2$), 34.6 (s, $C(CH_2O)_3$), 23.2 (s, CH_3). Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.24. Found: C, 67.20; H, 7.20.

CH_2=$CHCH_2OCH_2C(CH_2O)_3CCH_3$ (2b). This complex was prepared as described for **2a** starting from $HOCH_2C(CH_2O)_3CCH_3$ (2.57 g, 12.8 mmol) (**1**), KOH (3.38 g, 60.3 mmol), and allyl bromide (1.86 g, 1.33 mL, 15.4 mmol) in DMSO (15 mL) and isolated as a heavy colorless oil (2.18 g, 85%). ^{1}H NMR ($CDCl_3$, 22 °C) δ: 5.77 (m, 1H, =C*H*), 5.17 (s, 2H, =CH_2), 3.97 (m, 6H, $C(CH_2O)_3$), 3.87 (d, ^3J = 1.37 Hz, 2H, OCH_2CH=CH_2), 3.14 (s, 2H, $CH_2OCH2CH$=CH_2), 1.41 (s, 3H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C) δ: 133.9 (s, =*C*H), 117.1 (s, =*C*H_2), 108.3 (s, *C*CH_3), 72.1 (s, CH_2=$CHCH_2OCH_2$), 68.1 (s, $C(CH_2O)_3$), 42.0 (s, CH_2=$CHCH_2$), 34.5 ($C(CH_2O)_3$), 23.0 (s, CH_3). Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.98; H, 8.05. Found: C, 59.85; H, 8.01.

$BnOCH_2C(CH_2OH)_3$ (3a). Aqueous HCl (23.8 mmol, 2 mol L^{-1}, 12 mL) was added to a solution of **2a** (3.68 g, 14.7 mmol) in methanol (40 mL), and the resulting mixture was stirred for 6 h. Solid Na_2CO_3 (1.80 g, 17.0 mmol) was carefully added in small portions, and the suspension formed was vigorously stirred for an additional 3 h at room temperature. The volatiles were removed by distillation (90 °C) under reduced pressure, leaving a thick oil as residue, which was dissolved in methylene chloride and then filtered through a pad of Celite. Upon removal of the solvent under vacuum, the resulting oil was purified by column chromatography on silica gel using a mixture of CH_2Cl_2/MeOH (1:1) as eluent to yield **3a** as a colorless oil (3.08 g, 93%). ^{1}H NMR ($CDCl_3$, 22 °C) δ: 7.27−7.38 (m, 5H, C_6H_5), 4.49 (s, 2H, $PhCH_2O$), 3.69 (s, 6H, CH_2OH), 3.47 (s, 2H, $PhCH_2OCH_2$), 3.19 (br s, 3H, O*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C) δ: 137.7 (s, C_{ipso}), 128.4 (s, C_m), 127.8 (s, C_p), 127.4 (s, C_o) (Bn), 73.5 (s, $PhCH_2OCH_2$), 72.0 (s, $PhCH_2$), 63.5 (s, CH_2OH), 44.9 (s, $C(CH_2OH)_3$). MS (EI): *m/z* = 227 (M^+, 12%). Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.48; H, 7.97.

CH_2=$CHCH_2OCH_2C(CH_2OH)_3$ (3b). This complex was prepared as described for **3a** starting from aqueous HCl (56 mmol, 2 mol L^{-1}, 28.0 mL), **2b** (6.91 g, 34.5 mmol) in methanol (40 mL), and solid Na_2CO_3 (4.22 g, 39.7 mmol). The residual oil was purified by column chromatography on silica gel using a mixture of CH_2Cl_2/MeOH (1:1) as eluent to yield **3b** as a colorless oil (5.88 g, 96%). ^{1}H NMR ($CDCl_3$, 22 °C) δ: 5.82 (m, 1H, =C*H*), 5.21 (m, 2H, =CH_2), 3.96 (d, ^3J = 4.35 Hz, 2H, CH_2=$CHCH_2O$), 3.70 (s, 6H, CH_2OH), 3.48 (s, 2H, CH_2OCH_2C), 2.89 (br s, 3H, O*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C) δ: 134.1 (s, =*C*H), 117.5 (s, =*C*H_2), 72.6 (s, CH_2=$CHCH_2O$), 72.5 (s, CH_2OCH_2C), 64.3 (s, CH_2OH), 45.0 (s, $C(CH_2OH)_3$). MS (GC-MS): *m/z* = 127 (M^+ − 3OH). Anal. Calcd for $C_8H_{16}O_4$: C, 54.53; H, 9.15. Found: C, 54.19; H, 8.85.

$BnOCH_2C(CH_2OTs)_3$ (4a). To a solution of **3a** (13.47 g, 59.52 mmol) in pyridine (60 mL) cooled at −5 °C was added *p*-toluenesulfonyl chloride (43.59 g, 238.1 mmol) in small portions to keep the reaction temperature below 0 °C. After stirring at 0 °C for 2 h and then at room temperature for 24 h, the pink-colored reaction mixture was poured into crushed-iced water. The precipitate thus obtained was filtered off, washed with cold diethyl ether, and dried under vacuum to yield **4a** as a white solid (29.61 g, 72%). ^{1}H NMR ($CDCl_3$, 22 °C) δ: 7.86 (d, ^3J = 8.24 Hz, 6H, $C_6H_4CH_3$), 7.46 (m, 11H, C_6H_5 + $C_6H_4CH_3$), 4.43 (s, 2H, $PhCH_2O$), 4.08 (s, 6H, CCH_2OTs), 3.47 (s, 2H, $PhCH_2OCH_2$), 2.60 (s, 9H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C) δ: 145.3 (s, C_{ipso} Ts), 131.7 (s, C_{ipso} Bn), 130.0 (s, C_m+C_p Ts), 128.3 (s, C_m Bn), 127.9 (s, C_o Ts), 127.7 (s, C_p Bn), 127.2 (s, C_o Bn), 73.2 (s, $PhCH_2OCH_2$), 66.6 (s, CH_2OTs), 66.2 (s, $PhCH_2$), 43.6 (s, $C(CH_2OTs)_3$), 21.4 (s, CH_3). MS (EI): *m/z* = 517 (M^+ − 2 OTs, 15%). Anal. Calcd for $C_{33}H_{36}O_{10}S_3$: C, 57.54; H, 5.27. Found: C, 57.78; H, 5.13.

CH_2=$CHCH_2OCH_2C(CH_2OTs)_3$ (4b). This complex was prepared as described for **4a** starting from **3b** (3.96 g, 22.5 mmol) in pyridine (20 mL) and *p*-toluenesulfonyl chloride (17.15 g, 89.9 mmol) to yield **4b** as a white solid (10.3 g, 72%). ^{1}H NMR ($CDCl_3$, 22 °C) δ: 7.69 (d, ^3J = 8.2 Hz, 6H), 7.36 (d, ^3J = 8.0 Hz 6H) ($C_6H_4CH_3$), 5.59 (m, 1H, =C*H*), 5.05 (m, 2H, =CH_2), 3.88 (s, 6H, CH_2OTs), 3.69 (d, ^3J = 1.4 Hz, 2H, CH_2=$CHCH_2O$), 3.28 (s, 2H, CH_2OCH_2C), 2.44 (s, 9H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C) δ: 140.9 (s, C_{ipso} Ts), 129.3 (s, =CH), 127.4 (s, C_p Ts), 125.6 (s, C_m Ts), 123.5 (s, C_o Ts), 112.8 (s, =CH_2), 67.6 (s, CH_2=$CHCH_2O$), 62.3 (s, CH_2OTs), 61.5 (s, CH_2OCH_2C), 39.1 (s, $C(CH_2OTs)_3$), 17.0 (s, CH_3). MS (EI): *m/z* = 366 (M^+ − 3 $C_6H_5CH_3$), 309 (M^+ − 3 $C_6H_5CH_3$ − OCH_2CH=CH_2). Anal. Calcd for $C_{29}H_{34}O_{10}S_3$: C, 54.53; H, 5.37. Found: C, 55.05; H, 5.57.

$BnOCH_2C(CH_2SCN)_3$ (5a). A mixture of **4a** (2.02 g, 2.93 mmol) and KSCN (3.70 g, 38.1 mmol) in dry DMF (15 mL) was stirred at 140 °C for 6 h. The resulting dark solution was poured into cold water and left overnight at 5 °C. The tan precipitate formed was separated by decantation, washed with water, and then dissolved in methylene chloride (3 × 20 mL). The combined organic fractions were washed with a saturated NaCl solution, dried over Na_2SO_4, filtered, and then vacuum-dried, yielding a brownish oil (870 mg, 85%). ^{1}H NMR ($CDCl_3$, 22 °C) δ: 7.31−7.35 (m, 5H, C_6H_5), 4.55 (s, 2H, $PhCH_2O$), 3.60 (s, 2H, $PhCH_2OCH_2$), 3.29 (s, 6H, CH_2SCN). ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C) δ: 136.3 (s, C_{ipso}), 128.6 (s, C_m), 128.5 (s, C_o), 128.2 (s, C_p) (Bn), 111.4 (s, SCN), 73.4 (s, $PhCH_2OCH_2$), 69.1 (s, $PhCH_2$), 45.8 (s, $C(CH_2SCN)_3$), 35.8 (s, CH_2SCN). Anal. Calcd for $C_{15}H_{15}N_3OS_3$: C, 51.55; H, 4.33. Found: C, 51.23; H, 4.21.

CH_2=$CHCH_2OCH_2C(CH_2SCN)_3$ (5b). This complex was prepared as described for **5a** starting from **4b** (6.96 g, 10.90 mmol), KSCN (13.77 g, 141.7 mmol), and dry DMF (30 mL) to give a brownish oil (2.21 g, 68%). ^{1}H NMR ($CDCl_3$, 22 °C) δ: 5.81 (m, 1H, =C*H*), 5.19 (m, 2H, =CH_2), 4.02 (d, ^3J = 5.0 Hz, 2H, CH_2=$CHCH_2O$), 3.55 (s, 2H, CH_2OCH_2C), 3.30 (s, 6H, CH_2SCN). ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C) δ: 133.8 (s, =*C*H), 118.6 (s, =*C*H_2), 112.6 (s, S*C*N), 72.0, 71.8 (s, CH_2O), 55.8 (s, $C(CH_2SCN)_3$), 45.8 (s, CH_2SCN). Anal. Calcd for $C_{11}H_{13}N_3OS_3$: C, 44.12; H, 4.38. Found: C, 44.38; H, 4.35.

$BnOCH_2C(CH_2SH)_3$ (6a). A solution of **5a** (2.10 g, 6.01 mmol) in a mixture of diethyl ether/THF (1:1, 10 mL) was added to a stirred suspension of $LiAlH_4$ (0.46 g, 12.0 mmol) in diethyl ether (15 mL) under an argon atmosphere. The resulting suspension was stirred for 3 h and then carefully hydrolyzed with a saturated solution of NH_4Cl until two phases were clearly separated. The aqueous layer was extracted with diethyl ether (3 × 50 mL), and then the combined organic factions were dried over Na_2SO_4 and filtered. After removal of volatiles under reduced pressure the residual pale yellow oil was purified by column chromatography on silica gel eluting with a mixture of hexanes/ethyl acetate, 9:1 (1.30 g, 79%). ^{1}H NMR ($CDCl_3$, 22 °C) δ: 7.35−7.29 (m, 5H, C_6H_5), 4.48 (s, 2H, $PhCH_2O$), 3.34 (s, 2H, $PhCH_2OCH_2$), 2.62 (d, ^3J = 8.5 Hz, 6H, CH_2SH), 1.14 (t, ^3J = 8.93 Hz, 3H, S*H*). ^{13}C{^{1}H} NMR (C_6D_6, 22 °C) δ: 138.9 (s, C_{ipso}), 129.0 (s, C_m), 128.3 (s, C_o), 128.2 (s, C_p) (Bn), 73.6 (s, $PhCH_2OCH_2$), 70.0 (s, $PhCH_2$), 27.4 (s, CH_2-

SH), 43.6 (s, $C(CH_2SH)_3$). MS (EI): m/z = 272 (M^+ − 2 H). Anal. Calcd for $C_{12}H_{18}OS_3$: C, 52.51; H, 6.61. Found: C, 52.75; H, 6.71.

CH_2=CH$CH_2OCH_2C(CH_2SH)_3$ (6b). This complex was prepared as described for **6a**, starting from **5b** (2.34 g, 7.81 mmol) in THF (50 mL) and $LiAlH_4$ (0.22 g, 5.72 mmol) in diethyl ether (75 mL). The resulting pale yellow oil was purified by column chromatography on silica gel eluting with a mixture of hexanes/ethyl acetate, 9:1 (1.40 g, 80%). ^{1}H NMR ($CDCl_3$, 22 °C) δ: 5.83 (m, 1H, =C*H*), 5.19 (m, 2H, =CH_2), 4.02 (d, ^3J = 1.1 Hz, 2H, CH_2=CHCH_2O), 3.32 (s, 2H, CH_2OCH_2C), 2.61 (s, 6H, CH_2SH), 1.23 (br s, 3H, S*H*). ^{13}C{^{1}H} NMR (C_6D_6, 22 °C) δ: 134.5 (s, =*C*H), 117.1 (s, =*C*H_2), 72.1 (s, CH_2=CH*C*H_2O), 69.3 (s,CH_2OCH_2C), 43.1 (s, *C*$(CH_2SH)_3$), 26.8 (s, *C*H_2SH). MS (GC-MS): m/z = 222 (M^+ − 2 H). Anal. Calcd for $C_8H_{16}OS_3$: C, 42.82; H, 7.19. Found: C, 42.78; H, 7.15.

[Rh_3{μ-BnOCH_2C$(CH_2S)_3$}(cod)$_3$] (7). *Method A*: To a solution of [Rh(μ-OH)(cod)]$_2$ (0.19 g, 0.41 mmol) in THF (6 mL) at 0 °C was added a solution of **6a** (0.074 g, 0.27 mmol) in THF (4 mL) to give a dark red solution within a few seconds. The solution was stirred for 30 min, allowing it to reach room temperature. After evaporation of the solvent under reduced pressure, the oily residue was washed repeatedly with cold methanol to give a dark red solid (0.23 g, 84%). *Method B*: To a solution of [Rh(acac)(cod)] (0.30 g, 0.96 mmol) in THF (6 mL) was added a solution of **6a** (87 mg, 0.32 mmol) in THF (4 mL) to give a dark red solution within a few seconds. The solution was stirred for 30 min and then filtered via cannula to a Shlenk tube. After evaporation of the solvent under reduced pressure, the oily residue was washed repeatedly with cold methanol to give a dark red solid (0.25 g, 86%). *Method C*: To a solution of **6a** (52 mg, 0.19 mmol) in THF (4 mL) at −78 °C was added n-BuLi (0.36 mL, 1.6 mol L^{-1}, 0.57 mmol) via syringe to render a yellow solution, which was stirred for 10 min. Solid [Rh(μ-Cl)(cod)]$_2$ (0.14 g, 0.28 mmol) was then added to the resulting mixture at −78 °C to give a dark red solution, which was allowed to gradually reach room temperature. The solvent was evaporated under vacuum, and the residue was extracted with toluene (10 mL) and filtered through a pad of Celite under argon. After removal of volatiles a red solid was isolated (0.15 g, 88%). ^{1}H NMR (C_6D_6, 22 °C) δ: 7.62−7.14 (m, 5H, C_6H_5), 4.87 (m, 6H, =C*H*), 4.45 (m, 6H, =C*H*) (cod), 3.75 (s, 2H, PhCH_2O), 2.62 (s, 2H, $PhCH_2OCH_2$), 2.58 (s, 6H, CH_2S), 2.49 (m, 6H), 2.32 (m, 6H), 2.07 (m, 6H), 1.86 (m, 6H) (CH_2, cod). ^{13}C{^{1}H} NMR (C_6D_6, 22 °C) δ: 140.0 (s, C_{ipso}), 129.0 (s, C_m), 128.1 (s, C_p), 127.8 (s, C_o) (Bn), 82.4 (d, $^1J_{C-Rh}$ = 11 Hz, =*C*H) (cod), 81.8 (s, $PhCH_2OCH_2$), 80.0 (d, $^1J_{C-Rh}$ = 10 Hz, =*C*H) (cod), 74.1 (s, Ph*C*H_2O), 46.5 (s, *C*$(CH_2S)_3$), 32.0 (s, *C*H_2S), 31.9, 31.8 (s, *C*H_2, cod). MS (FAB+): m/z = 904 (M^+, 87), 578 (M^+ − 3 cod, 69%). Anal. Calcd for $C_{36}H_{51}ORh_3S_3$: C, 47.79; H, 5.68. Found: C, 47.80; H, 5.21.

[Rh_3{μ-BnOCH_2C$(CH_2S)_3$}(nbd)$_3$] (8a). To a solution of [Rh(acac)(nbd)] (0.24 g, 0.82 mmol) in toluene (7 mL) was added a solution of **6a** (75 mg, 0.27 mmol) in toluene (4 mL) to give a dark violet solution within a few seconds. The solution was stirred for 30 min, and the volatiles were evaporated under reduced pressure to give a violet solid, which was washed with methanol and vacuum-dried (0.21 g, 87%). ^{1}H NMR ($CDCl_3$, −60 °C) δ: 7.16−6.94 (m, 5H, C_6H_5), 4.50 (m, 6H, =C*H*), 3.97 (m, 6H, =C*H*), 3.77 (m, 3H, C*H*) (nbd), 3.68 (s, 2H, PhCH_2OCH_2), 3.52 (m, 3H, C*H*) (nbd), 2.60 (s, 6H, CH_2S), 2.22 (s, 2H, $PhCH_2OCH_2$), 1.33 (m, 6H, CH_2 nbd). ^{13}C{^{1}H} NMR (C_7D_8, 22 °C) δ: 130.0−128.0 (all s, Ph), 84.2 (s, $PhCH_2OCH_2$), 73.2 (s, Ph*C*H_2), 63.9, 63.8 (s, *C*H), 62.3, 56.6 (br s, =*C*H) (nbd), 50.9 (s, *C*H_2 nbd), 46.1 (s, *C*$(CH_2S)_3$, 29.9 (s, *C*H_2S). MS (FAB+): m/z = 674 (M^+ − 2 nbd, 25), 579 (M^+ − 3 nbd, 35%). Anal. Calcd for $C_{33}H_{39}ORh_3S_3$: C, 46.27; H, 4.59. Found: C, 46.78; H, 4.11.

[Rh_3{μ-CH_2=CH$CH_2OCH_2C(CH_2S)_3$}(nbd)$_3$] (8b). Complex **8b** was isolated as a violet microcrystalline solid following the procedure described for **8a**, starting from **6b** (0.14 g, 0.63 mmol) and [Rh(acac)(nbd)] (0.56 g, 1.89 mmol) (0.47 g, 92%). ^{1}H NMR (C_6D_6, 22 °C) δ: 5.52 (m, 1H, C*H*), 4.88 (m, 2H, =CH_2) (allyl), 4.21 (m, 12H, =C*H*), 3.73 (m, 6H, C*H*) (nbd), 3.41 (dm, 2H, CH_2 allyl), 2.53 (s, 6H, CH_2S), 2.39 (s, 2H, OCH_2), 1.37 (s, 12H, CH_2 nbd). ^{13}C{^{1}H} NMR (C_6D_6, 22 °C) δ: 130.2 (s, *C*H), 111.3 (s, =*C*H) (allyl), 84.2 (s, OCH_2), 79.3 (s, *C*H_2, allyl), 59.0, 58.9 (s, *C*H nbd), 58.0, 52.5 (br s, =*C*H nbd), 46.0 (s, *C*H_2 nbd), 41.2 (s, *C*$(CH_2S)_3$, 24.9 (s, *C*H_2S). MS (FAB+): m/z = 806 (M^+, 5), 613 (M^+ − Rh − nbd, 35%). Anal. Calcd for $C_{29}H_{37}ORh_3S_3$: C, 43.19; H, 4.61. Found: C, 43.36; H, 4.81.

[Rh_3{μ-BnOCH_2C$(CH_2S)_3$}(tfb)$_3$] (9a). To a solution of [Rh(acac)(tfb)] (0.24 g, 0.33 mmol) in THF (10 mL) at 0 °C was added a solution of **6a** (60 mg, 0.22 mmol) in THF (4 mL), giving a dark red solution within a few seconds. The solution was stirred for 30 min. After evaporation of the solvent under reduced pressure, the oily residue was washed repeatedly with cold methanol to give a dark red solid (0.26 g, 93%). ^{1}H NMR ($CDCl_3$, 22 °C) δ: 7.21−7.14 (m, 5H, C_6H_5), 5.68 (m, 3H, C*H*), 5.22 (m, 3H, C*H*) (tfb), 4.07 (s, 2H, PhCH_2OCH_2), 4.00 (m, 6H, =C*H*), 3.46 (m, 6H, =C*H*) (tfb), 2.55 (s, 2H, $PhCH_2OCH_2$), 2.52 (s, 6H, CH_2S). ^{13}C{^{1}H} NMR (C_7D_8, 22 °C) δ: 139.7 (dm, $^1J_{C-F}$ = 265 Hz), 138.6 (dm, $^1J_{C-F}$ = 252 Hz) (*C*F tfb), 140.1 (s, C_{ipso} Bn), 138.0, 136.8 (m, *C*F tfb), 128.4 (s, C_m), 127.6 (s, C_p), 127.4 (s, C_o) (Bn), 83.2 (s, $PhCH_2OCH_2$), 73.2 (s, Ph*C*H_2), 63.9, 57.6 (br s, =*C*H) (tfb), 41.4 (s, *C*$(CH_2S)_3$), 41.0, 40.2 (br s, *C*H) (tfb), 29.9 (s, *C*H_2S). Anal. Calcd for $C_{48}H_{33}OF_{12}Rh_3S_3$: C, 45.74; H, 2.64. Found: C, 45.50; H, 2.64.

[Rh_3{μ-CH_2=CH$CH_2OCH_2C(CH_2S)_3$}(tfb)$_3$] (9b). Complex **9b** was isolated as a red microcrystalline solid following the procedure described for **9a** starting from **6b** (51 mg, 0.23 mmol) and [Rh(acac)(tfb)] (0.25 g, 0.34 mmol) (0.27 g, 99%). ^{1}H NMR ($CDCl_3$, 22 °C) δ: 5.63 (m, 4H, C*H* allyl + C*H* tfb), 5.16 (m, 3H, C*H*, tfb), 4.99 (m, 2H, =CH_2 allyl), 3.96 (m, 6H, =C*H*), 3.46 (d, 2H, CH_2 allyl), 3.41 (m, 6H, =C*H*) (tfb), 2.47 (s, 6H, CH_2S), 2.44 (s, 2H, $PhCH_2OCH_2$). MS (FAB+): m/z = 1208 (M^+, 30%). Anal. Calcd for $C_{44}H_{31}OF_{12}Rh_3S_3$: C, 43.73; H, 2.59. Found: C, 43.89; H, 2.66.

[Rh_3{μ-BnOCH_2C$(CH_2S)_3$}(CO)$_6$] (10a). To a solution of [Rh(acac)(CO)$_2$] (0.42 g, 1.64 mmol) in diethyl ether (30 mL) at −78 °C was added a solution of **6a** (0.10 g, 0.55 mmol) in diethyl ether (4 mL) to give a dark blue solution within a few seconds. The solution was stirred for 30 min, filtered under argon via cannula, and then evaporated to dryness to yield a dark blue, microcrystalline solid (0.36 g, 89%). ^{1}H NMR (C_6D_6, 22 °C) δ: 7.13−6.94 (m, 5H, C_6H_5), 3.87 (s, 2H, PhCH_2O), 2.07 (s, 2H, $PhCH_2OCH_2$), 1.67 (s, 6H, CH_2S). ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C) δ: 183.8 (d, $^1J_{C-Rh}$ = 66 Hz, *C*O), 138.2 (s, C_{ipso}), 129.1 (s, C_m), 128.2 (s, C_P), 128.2 (s, C_O) (Bn), 82.9 (s, $PhCH_2OCH_2$), 73.4 (s, Ph*C*H_2) 41.2 (s, *C*$(CH_2S)_3$), 21.3 (s, *C*H_2S). MS (FAB+): m/z = 748 (M^+, 35), 720 (M^+ − 1 CO, 100), 692 (M^+ − 2 CO, 60), 664 (M^+ − 3 CO, 40), 636 (M^+ − 4 CO, 35), 608 (M^+ − 5 CO, 70), 578 (M^+ − 6 CO, 60%). IR (toluene, cm^{-1}): ν(CO), 2085 (s), 2058 (s), 2015 (s). Anal. Calcd for $C_{18}H_{15}O_7Rh_3S_3$: C, 28.89; H, 2.02. Found: C, 29.10; H, 1.92.

[Rh_3{μ-CH_2=CH$CH_2OCH_2C(CH_2S)_3$}(CO)$_6$] (10b). Complex **11b** was isolated as a black, microcrystalline solid following the procedure described for **10a** starting from **6b** (0.15 g, 0.67 mmol) and [Rh(acac)(CO)$_2$] (0.52 g, 2.00 mmol) (0.44 g, 94%). ^{1}H NMR ($CDCl_3$, 22 °C) δ: 5.63 (m, 1H, C*H*), 4.94 (m, 2H, =CH_2), 3.33 (dm, 2H, =C*H*) (allyl), 2.05 (s, 2H, OCH_2), 1.68 (s, 6H, CH_2S). ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C) δ: 183.7 (d, $^1J_{C-Rh}$ = 66 Hz, *C*O), 134.7 (s, *C*H), 117.4 (s, =*C*H) (allyl), 83.3 (s, OCH_2), 72.5 (s, *C*H_2 allyl), 41.5 (s, *C*$(CH_2S)_3$), 21.7 (s, *C*H_2S). MS (FAB+): m/z = 698 (M^+, 20), 670 (M^+ − 1 CO, 70), 642 (M^+ − 2 CO, 35), 614 (M^+ − 3 CO, 25), 586 (M^+ − 4 CO, 15), 558 (M^+ − 5 CO, 10), 530 (M^+ − 6 CO, 16%). IR (toluene, cm^{-1}): ν(CO), 2084 (s), 2056 (s), 2015 (s). Anal. Calcd for $C_{14}H_{13}O_7Rh_3S_3$: C, 24.09; H, 1.87. Found: C, 24.05; H, 1.77.

[Ir_3{μ-BnOCH_2C$(CH_2S)_3$}(CO)$_6$] (11). To a solution of [Ir(acac)(CO)$_2$] (0.57 g, 1.64 mmol) in THF (6 mL) at −78 °C was

added a solution of **6a** (0.15 g, 0.55 mmol) in diethyl ether (4 mL) to give a dark blue solution within a few seconds. The solution was stirred for 30 min and then concentrated to ca. 3 mL. Upon addition of hexanes, a black solid precipitated. The supernatant solution was decanted, and the dark blue solid was vacuum-dried (0.36 g, 89%). ^{1}H NMR ($CDCl_3$, 22 °C) δ: 7.22−7.00 (m, 5H, C_6H_5), 3.94 (s, 2H, PhCH_2O), 1.95 (s, 2H, PhCH$_2$OCH_2), 1.90 (s, 6H, CH_2S). ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C) δ: 173.1 (s, *C*O), 129.1 (s, C_{ipso}), 129.1 (s, C_m), 128.7 (s, C_p), 128.4 (s, C_o) (Bn), 83.5 (s, PhCH$_2$OCH$_2$), 73.4 (s, Ph*C*H$_2$), 42.3 (s, *C*(CH$_2$S)$_3$), 20.3 (s, *C*H$_2$S). MS (FAB+): *m/z* = 1017 (M$^+$, 87), 989 (M$^+$ − 1 CO, 100), 961 (M$^+$ − 2 CO, 34), 933 (M$^+$ − 3 CO, 29), 905 (M$^+$ − 4 CO, 34), 876 (M$^+$ − 5 CO, 60), 849 (M$^+$ − 6 CO, 22%). IR (toluene, cm^{-1}): ν(CO), 2080 (s), 2049 (s), 2004 (s). Anal. Calcd for $C_{18}H_{15}O_7Ir_3S_3$: C, 21.27; H, 1.49. Found: C, 21.51; H, 1.52.

[Rh$_3$(μ-BnOCH$_2$C(CH$_2$S)$_3$)(CO)$_3$(PPh$_3$)$_3$] (12). To a solution of [Rh$_3$(μ-BnOCH$_2$C(CH$_2$S)$_3$)(CO)$_6$] (**10a**) (0.20 g, 0.27 mmol) in THF (10 mL) at 0 °C was added a solution of PPh_3 (0.21 g, 0.81 mmol) in THF (3 mL). A color change was observed along with the evolution of carbon monoxide. After stirring for 30 min, the solvent was evaporated under vacuum, affording a brown solid, which was washed with methanol and then vacuum-dried (0.37 g, 95%). ^{1}H NMR ($CDCl_3$, 22 °C) δ: 7.99−7.05 (m, 50H, C_6H_5), 3.87 (s, 2H, PhCH_2O), 2.36 (s, 2H, PhCH$_2$OCH_2), 2.32 (s, 6H, CH_2S). ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C) δ: 189.2 (dd, $^1J_{C-Rh}$ = 70 Hz, $^2J_{C-P}$ = 19 Hz, *C*O), 140.7−122.3 (C_6H_5), 83.9 (s, PhCH$_2$O*C*H$_2$), 73.7 (s, Ph*C*H$_2$), 43.6 (s, *C*(CH$_2$S)$_3$), 20.1 (s, *C*H$_2$S). ^{31}P{^{1}H} NMR ($CDCl_3$, 22 °C) δ: 36.3 (d, $^1J_{P-Rh}$ = 154 Hz). MS (FAB+): *m/z* = 1424 (M$^+$ − CO, 5), 1104 (M$^+$ − 3 CO−PPh$_3$, 7%). IR (toluene, cm^{-1}): ν(CO), 1976 (s). Anal. Calcd for $C_{69}H_{60}O_4P_3Rh_3S_3$: C, 57.11; H, 4.17. Found: C, 56.94; H, 4.63.

[Rh$_3$(μ-BnOCH$_2$C(CH$_2$S)$_3$)(CO)$_3$(P(OMe)$_3$)$_3$] (13). To a solution of [Rh$_3$(μ-BnOCH$_2$C(CH$_2$S)$_3$)(CO)$_6$] (**10a**) (0.79 g, 0.11 mmol) in THF (6 mL) at 0 °C was added a solution of P(OMe)$_3$ (0.39 g, 0.32 mmol, 37 μL) in THF (3 mL). A color change to brown was observed together with the evolution of carbon monoxide. After stirring for 30 min, the solvent was evaporated under vacuum, affording a brown solid, which was washed with methanol and then vacuum-dried (950 mg, 87%). ^{1}H NMR ($CDCl_3$, 22 °C) δ: 7.48−7.10 (m, 5H, C_6H_5), 4.07 (s, 2H, PhCH_2O), 3.77 (d, $^3J_{H-P}$ = 12 Hz, 27H, P(OMe)$_3$), 3.70 (s, 2H, PhCH$_2$OCH_2), 2.52 (s, 6H, CH_2S). ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C) δ: 187.5 (dd, $^1J_{C-Rh}$ = 69 Hz, $^2J_{C-P}$ = 25 Hz, *C*O), 139.0 (s, C_{ipso}), 128.9 (s, C_m), 128.6 (s, C_p), 128.0 (s, C_o) (Bn), 84.5 (s, PhCH$_2$O*C*H$_2$), 73.6 (s, Ph*C*H$_2$), 52.5 (s, (P(OMe)$_3$)), 42.5 (s, *C*(CH$_2$S)$_3$), 26.5 (s, *C*H$_2$S). ^{31}P{^{1}H} NMR ($CDCl_3$, 22 °C) δ: 135.7 (d, $^1J_{P-Rh}$ = 240.3 Hz). MS (FAB+): *m/z* = 1036 (M$^+$, 17), 1008 (M$^+$ − CO, 38), 980 (M$^+$ − 2 CO, 38), 952 (M$^+$ − 3 CO, 100%). IR (toluene, cm^{-1}): ν(CO), 1982 (s). Anal. Calcd for $C_{24}H_{42}O_{13}P_3Rh_3S_3$: C, 27.81; H, 4.08. Found: C, 27.67; H, 4.13.

[Ir$_3$(μ-BnOCH$_2$C(CH$_2$S)$_3$)(CO)$_3$(PPh$_3$)$_3$] (14). To a solution of [Ir$_3$(μ-BnOCH$_2$C(CH$_2$S)$_3$)(CO)$_6$] (**11**) (0.16 g, 0.16 mmol) in THF (6 mL) at 0 °C was added a solution of PPh_3 (0.12 g, 0.47 mmol) in THF (3 mL). A color change to brown was observed together with the evolution of carbon monoxide. After stirring for 30 min, the solvent was evaporated to ca. 2 mL, and after addition of hexanes a brown solid precipitated. The remaining solution was cannulated off, and the solid was washed with hexanes and then vacuum-dried (0.23 g, 86%). ^{1}H NMR ($CDCl_3$, 22 °C) δ: 7.87−7.68 (m, 18H, PPh_3), 7.13−6.89 (m, 32H, C_6H_5), 3.82 (s, 2H, PhCH_2O), 1.90 (s, 2H, PhCH$_2$OCH_2), 0.99 (s, 6H, CH_2S). ^{31}P{^{1}H} NMR ($CDCl_3$, 22 °C) δ: −8.1 (s). MS (FAB+): *m/z* = 1718 (M$^+$, 35). IR (toluene, cm^{-1}): ν(CO), 2009 (s). Anal. Calcd for $C_{69}H_{60}Ir_3O_4P_3S_3$: C, 48.21; H, 3.52. Found: C, 48.11; H, 3.47.

Si[(CH$_2$)$_3$Si(Me)$_2$(CH$_2$)$_3$OCH$_2$C(CH$_2$OTs)$_3$]$_4$ (G(0)$_{OTs-12}$). To a mixture of Si[(CH$_2$)$_3$Si(Me)$_2$H]$_4$ (2.05 g, 4.72 mmol) and CH$_2$=CHCH$_2$OCH$_2$C(CH$_2$OTs)$_3$ (**4b**) (12.07 g, 18.9 mmol) in THF (10 mL) was added 8 drops of a 2.1−2.3% solution of Karstedt's catalyst in xylene. The reaction mixture was stirred for 48 h at room temperature, and then the volatiles were removed under reduced pressure to give a thick oil. This was purified by column chromatography on silica gel (hexanes/ethyl acetate, 9:1) and then eluted with methylene chloride to afford a thick, colorless oil (14.05 g, 99%). ^{1}H NMR ($CDCl_3$, 22 °C) δ: 7.73 (d, ^3J = 7.8 Hz, 24H, $C_6H_4CH_3$), 7.29 (d, ^3J = 7.4 Hz, 24H, $C_6H_4CH_3$), 3.88 (s, 24H, CH_2OTs), 3.22 (s, 8H, OCH_2), 3.11 (t, $^3J_{H-H}$ = 6.9 Hz, 8H, CH_2O), 2.44 (s, 36H, $C_6H_4CH_3$), 1.30 (m, 16H, CH_2), 0.55 (m, 16H, CH_2), 0.31 (m, 8H, CH_2), −0.07 (s, 24 H, SiCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C) δ: 145.3 (s, C_{ipso}), 132.0 (s, C_p), 130.0 (s, C_o), 127.9 (s, C_m) (Ts), 74.4 (s, OCH$_2$), 66.8 (s, *C*H$_2$OTs), 66.5 (s, *C*H$_2$O), 43.6 (s, *C*(CH$_2$)$_3$), 23.4 (s, *C*H$_2$), 21.5 ($C_6H_4CH_3$), 19.9, 18.3, 17.3, 10.9 (s, *C*H$_2$), −3.7 (s, SiCH_3). Anal. Calcd for $C_{136}H_{188}O_{40}S_{12}Si_5$: C, 54.67; H, 6.34. Found: C, 54.92; H, 5.95.

Si[(CH$_2$)$_3$Si(Me)$_2$(CH$_2$)$_3$OCH$_2$C(CH$_2$SCN)$_3$]$_4$ (G(0)$_{SCN-12}$). A mixture of **G(0)$_{OTs-12}$** (14.05 g, 4.71 mmol) and KSCN (68.80 g, 708 mmol) in dry DMF (125 mL) was heated at 150 °C in an oil bath for 24 h. The resulting cool solution was poured into ice and then left at 5 °C overnight. The tan precipitate formed was separated by decantation, washed with water, and extracted with methylene chloride (3 × 20 mL). The combined organic fractions were washed with a saturated solution of NaCl, dried over Na_2SO_4, and then filtered. Upon removal the volatiles under reduced pressure, a thick brownish oil was obtained (7.56 g, 98%). ^{1}H NMR ($CDCl_3$, 22 °C) δ: 3.26 (s, 24H, CH_2SCN), 3.23 (s, 8H, OCH_2), 3.06 (m, 8H, CH_2O), 1.53 (m, 8H, CH_2), 1.29 (m, 8H, CH_2), 0.53 (m, 16H, CH_2), 0.46 (m, 8H, CH_2), −0.24 (s, 24 H, SiCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C) δ: 111.1 (s, SCN), 74.4 (s, OCH$_2$), 72.6 (s, *C*H$_2$O), 46.0 (s, *C*H$_2$-SCN), 37.2 (s, *C*(CH$_2$)$_3$), 23.7, 19.4, 18.4, 17.4, 11.2 (s, *C*H$_2$), −3.5 (s, SiCH_3). Anal. Calcd for $C_{64}H_{104}N_{12}O_4S_{12}Si_5$: C, 47.14; H, 6.43. Found: C, 47.25; H, 5.91.

Si[(CH$_2$)$_3$Si(Me)$_2$(CH$_2$)$_3$OCH$_2$C(CH$_2$SH)$_3$]$_4$ (G(0)$_{SH-12}$). To a well-stirred suspension of $LiAlH_4$ (2.02 g, 53.2 mmol) in diethyl ether (20 mL) was added dropwise a solution of **G(0)$_{SCN-12}$** (10.84 g, 6.65 mmol) in a mixture (1:1) of diethyl ether and THF (40 mL). The reaction mixture was stirred for 15 h and then was carefully hydrolyzed with a saturated NH_4-Cl solution until two layers separated. The aqueous phase was extracted with diethyl ether (3 × 50 mL), and the combined organic fractions were dried over Na_2SO_4 and filtered. Then the volatiles were removed under reduced pressure to afford a brown oil. This was purified by chromatography on silica gel using a mixture of hexanes/ethyl acetate (9:1), obtaining a clear, malodorous oil (7.05 g, 65%). ^{1}H NMR ($CDCl_3$, 22 °C) δ: 3.47 (m, 8H, CH_2O), 3.33 (s, 8H, OCH_2), 2.64 (s, 24H, CH_2-SH), 1.54 (m, 8H, CH_2), 1.30 (m, 8H, CH_2), 1.22 (t, ^3J = 7.1 Hz, 12H, CH$_2$S*H*), 0.54 (m, 16H, CH_2), 0.47 (m, 8H, CH_2), −0.02 (s, 24 H, SiCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C) δ: 74.5 (s, OCH$_2$), 70.2 (s, *C*H$_2$O), 46.0 (s, *C*(CH$_2$)$_3$), 27.1 (s, *C*H$_2$SH), 30.0, 20.1, 18.5, 15.3, 11.4 (s, *C*H$_2$), −3.4 (s, SiCH_3). MALDI-TOF: calcd 1330; found, 1327.5. Anal. Calcd for $C_{52}H_{116}O_4S_{12}$-Si_5: C, 46.94; H, 8.79. Found: C, 47.09; H, 8.43.

Si[(CH$_2$)$_3$Si(Me)$_2$(CH$_2$)$_3$OCH$_2$C(CH$_2$S)$_3${Rh(CO)$_2$}$_3$]$_4$ (G(0)$_{Rh(CO)2-12}$). To a solution of **G(0)$_{SH-12}$** (71 mg, 0.053 mmol) in dichloromethane (10 mL) was added solid [Rh(acac)(CO)$_2$] (0.16 g, 0.635 mmol) to give a black solution, which was stirred for 30 min. The solution was evaporated to ca. 2 mL, and after addition of hexanes a black solid precipitated. The solid was filtered, washed with hexanes, and then vacuum-dried (0.16 g, 94%). ^{1}H NMR ($CDCl_3$, 22 °C) δ: 3.25 (t, ^3J = 6.63 Hz, 8H, CH_2O), 2.89 (s, 8H, OCH_2C), 2.22 (s, 24H, CH$_2$S), 1.45 (m, 8H), 1.27 (m, 8H), 0.50 (m, 16H), 0.35 (m, 8H) (CH_2), −0.16 (s, 24H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 22 °C) δ: 182.2 (d, $^1J_{C-Rh}$ = 67 Hz, *C*O), 84.0 (s, OCH$_2$), 74.6 (s, *C*H$_2$O) 41.5 (s, *C*(CH$_2$S)$_3$), 23.7 (s, CH$_2$), 21.6 (s, *C*H$_2$S), 20.0, 18.5, 17.5, 11.3 (s, *C*H$_2$), −3.4 (s, *C*H$_3$). IR (toluene, cm^{-1}): ν(CO), 2085 (s), 2060 (s), 2014 (s). Anal. Calcd for $C_{76}H_{104}O_{28}S_{12}Si_5Rh_{12}$: C, 28.30; H, 3.25.

Found: C, 28.13; H, 3.69. MALDI-TOF: 3085 ($M^+ - 5CO$), 2778 ($M^+ - 16CO$), 2554 ($M^+ - 24CO$).

$Si[(CH_2)_3Si(Me)_2(CH_2)_3OCH_2C(CH_2S)_3\{Ir(CO)_2\}_3]_4$ ($G(0)_{Ir(CO)2-12}$). An NMR tube was charged with $G(0)_{SH-12}$ (10 mg, 0.007 mmol), $[Ir(acac)(CO)_2]$ (31 mg, 0.090 mmol), and $CDCl_3$ (0.5 mL). The mixture was shaken for 5 min, and the resulting deep red solution was analyzed by IR and NMR techniques. After 10 min a red solid precipitated, and this was collected and subjected to elemental analysis. ^1H NMR ($CDCl_3$, 22 °C) δ: 3.24 (t, ^3J = 6.61 Hz, 8H, CH_2O), 2.77 (s, 8H, OCH_2C), 2.49 (s, 24H, CH_2S), 1.44 (m, 8H), 1.23 (m, 8H), 0.55 (m, 16H), 0.33 (m, 8H) (CH_2), −0.25 (s, 24H, CH_3). IR (toluene, cm^{-1}): ν(CO), 2065 (s), 2053 (s), 2002 (s). Anal. Calcd for $C_{76}H_{104}Ir_{12}O_{28}S_{12}Si_5$: C, 21.24; H, 2.44. Found: C, 21.12; H, 2.36.

$Si[(CH_2)_3Si(Me)_2(CH_2)_3OCH_2C(CH_2S)_3\{Rh(CO)(PPh_3)\}_3]_4$ ($G(0)_{Rh(CO)(PPh3)-12}$). To a solution of $G(0)_{SH-12}$ (0.17 g, 0.13 mmol) in toluene (10 mL) at −78 °C was added a solution of $[Rh(acac)(CO)(PPh_3)]$ (0.77 g, 1.55 mmol) in toluene (10 mL) via cannula under argon. A slight color change to deep yellow was observed, and upon reaching room temperature, the color turned to dark red gradually. After stirring for 30 min at room temperature, the solvent was evaporated under vacuum to give a dark red oil, which was washed with diethyl ether to afford a red solid, which was dried under vacuum (0.69 g, 89%). ^1H NMR (CD_2Cl_2, −90 °C) δ: 7.25−7.63 (set of m, 180H, C_6H_5), 3.11 (br s, 8H, CH_2O), 2.72 (br s, 8H, OCH_2), 2.15 (br s, 24H, CH_2S), 1.45−0.50 (set of m, 40H, CH_2), −0.11 (br s, 24H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C) δ: 189.0 (dd, $^1J_{C-Rh}$ = 71 Hz, $^2J_{C-P}$ = 19 Hz, *C*O), 136.5−130.1 (C_6H_5), 84.7 (s, O*C*H_2), 75.2 (s, *C*H_2O), 43.6 (s, *C*$(CH_2S)_3$), 30.1 (s, *C*H_2S), 27.5, 21.0, 19.6, 18.6, 12.0 (s, *C*H_2), −2.7 (s, *C*H_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −90 °C) δ: 36.1 (d, $^1J_{P-Rh}$ = 152.9 Hz). IR (toluene, cm^{-1}): ν(CO), 1967 (s). Anal. Calcd for $C_{280}H_{284}O_{16}P_{12}Rh_{12}S_{12}Si_5$: C, 55.70; H, 4.74. Found: C, 55.53; H, 5.00.

$Si[(CH_2)_3Si(Me)_2(CH_2)_3OCH_2C(CH_2S)_3\{Rh(CO)(P(OMe)_3)\}_3]_4$ ($G(0)_{Rh(CO)(P(OMe)3)-12}$). To a solution of $G(0)_{SH-12}$ (0.13 g, 0.10 mmol) in toluene (10 mL) at −78 °C was added a solution of $[Rh(acac)(CO)(P(OMe)_3)]$ (0.42 g, 1.20 mmol) in toluene (10 mL) via cannula under argon. A drastic color change from pale yellow to a dark-colored solution was observed upon reaching room temperature. After stirring for 2 h at room temperature, the solvent was evaporated under vacuum to give a black oil, which was washed with cold diethyl ether, affording a black solid, which was dried under vacuum (0.33 g, 84%). ^1H NMR (CD_2Cl_2, 22 °C) δ: 3.61 (m, 108H, $P(OCH_3)_3$), 2.94 (br s, 8H, CH_2O), 2.43 (br s, 24H, CH_2S), 2.40 (br s, 8H, OCH_2), 1.53−0.60 (set of m, 40H, CH_2), 0.00 (br s, 24H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C) δ: 185.6 (m, *C*O), 83.6 (s, O*C*H_2), 73.4 (s, *C*H_2O), 50.5 (s, $(P(OMe)_3)$), 40.6 (s, *C*$(CH_2S)_3$), 24.7 (s, *C*H_2S), 22.8, 19.1, 17.9, 16.7, 10.4 (s, *C*H_2), −4.5 (s, *C*H_3). $^{31}P\{^1H\}$ NMR (C_6D_6, 22 °C) δ: 133.7 (d, $^1J_{P-Rh}$ = 179.4 Hz). IR: ν(CO), 1996 (s). Anal. Calcd for $C_{100}H_{212}O_{28}P_{12}Rh_{12}S_{12}Si_5$: C, 27.43; H, 4.88. Found: C, 27.32; H, 4.72.

Synthesis of $Si[(CH_2)_3Si(Me)_2(CH_2)_3OCH_2C(CH_2S)_3\{Ir(CO)(PPh_3)\}_3]_4$ ($G(0)_{Ir(CO)(PPh3)-12}$). To a solution of $G(0)_{SH-12}$ (13 mg, 0.01 mmol) in dichloromethane (10 mL) was added a solution of $[Ir(acac)(CO)_2]$ (41 mg, 0.12 mmol) in dichloromethane (5 mL) via cannula under argon, to give a deep red solution within a few seconds. Then PPh_3 (31 mg, 0.12 mmol) was added to give a red solution with evolution of carbon monoxide. After stirring for 10 min the solution was evaporated to ca. 1 mL, and addition of hexanes gave an orange solid, which was washed with hexanes and then vacuum-dried (59 mg, 85%). ^1H NMR ($CDCl_3$, 22 °C) δ: 7.25−7.62 (set of m, 180H, C_6H_5), 2.92 (t, ^3J = 6.60 Hz, 8H, CH_2O), 2.23 (s, 8H, OCH_2), 1.86 (br s, 24H, CH_2S), 1.45 (m, 8H), 1.22 (m, 8H), 0.53 (m, 16H), 0.27 (m, 8H) (CH_2), −0.06 (s, 24H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 22 °C) δ: 177.4 (s, *C*O), 136.0−130.9 (C_6H_5), 84.1 (s, O*C*H_2), 74.9 (s, *C*H_2O), 53.6 (s, *C*$(CH_2S)_3$), 25.1 (s, *C*H_2S), 21.0, 19.6, 18.5, 15.9, 12.0 (s, *C*H_2), −2.7 (s, *C*H_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 22 °C) δ: −24.2 (s). IR ν(CO), 2010.0 (s). Anal. Calcd for $C_{280}H_{284}Ir_{12}O_{16}P_{12}S_{12}Si_5$: C, 47.31; H, 4.03. Found: C, 47.17; H, 4.24.

X-ray Structural Determination of Compound 8a. Suitable crystals for the X-ray diffraction experiments were obtained by slow evaporation of hexane into a concentrated toluene solution of **8a** at 5 °C. Intensity data were collected at low temperature (100(2) K) on a CCD Bruker SMART APEX diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) by using ω rotations (0.3°). Instrument and crystal stability were evaluated by measuring equivalent reflections at different times; no significant decay was observed. Data were corrected for Lorentz and polarization effects, and a semiempirical absorption correction was applied.[28] The structure was solved by Patterson and difference Fourier methods.[29] Anisotropic displacement parameters were applied for all non-hydrogen atoms. Hydrogen atoms were found in subsequent difference Fourier maps and included as free isotropic atoms; five of them were refined with a riding thermal parameter. Refinements were carried out by full-matrix least-squares on F^2 (SHELXL-97).[29] The highest residuals were found in the proximity of metal centers and have no chemical sense.

Crystal data for 8a: $C_{33}H_{39}ORh_3S_3$, M = 856.55; crystal size 0.235 × 0.130 × 0.109 mm^3; orthorhombic, $P2_12_12_1$; a = 13.6332(7) Å, b = 14.4891(7) Å, c = 14.9966(8) Å; Z = 4; V = 2962.3(3) $Å^3$; D_c = 1.921 g/cm^3; μ = 1.891 mm^{-1}, minimum and maximum transmission factors 0.665 and 0.820; $2\theta_{max}$ = 56.4°; 19 394 reflections collected, 6769 unique [R(int) = 0.0251]; number of data/restraints/parameters 6769/0/512; final GoF 1.053, R_1 = 0.0224 [6594 reflns $I > 2\sigma(I)$], wR_2 = 0.0502 for all data; largest diff peak 0.68 e·$Å^{-3}$.

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Supporting Information Available: Details of the X-ray crystallographic study of **8a** (as a crystallographic information file). This material is available free of charge via the Internet at http://pubs.acs.org.

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