

Tris(pyrazolyl)borate carbosilane dendrimers and metallodendrimers†

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A modified tris(pyrazolylborate) ligand has been prepared in two steps. First, reaction of triisopropylborate with allylmagnesium bromide and further treatment with benzoyl chloride gave $\text{CH}_2 = \text{CHCH}_2\text{B}(\text{O}^i\text{Pr})_2$ (**1**), which was then reacted with potassium pyrazolate and pyrazole to give the compound $\text{K}[\text{CH}_2 = \text{CHCH}_2\text{Bpz}_3]$ (**2**). The new allyl-containing scorpionate anion of **2** acts as a bi- or tri-dentate ligand, as shown by the mononuclear complexes $[\text{CH}_2 = \text{CHCH}_2\text{Bpz}_3\text{M}(\text{LL})]$ ($\text{M} = \text{Rh}$, $\text{LL} = \text{nbd}$, **3**; $\text{LL} = \text{tfb}$, **4**; $\text{LL} = (\text{CO})(\text{PPh}_3)$, **5**; $\text{M} = \text{Ir}$, $\text{LL} = \text{cod}$, **6**), obtained from reactions of the chlorido-bridged dinuclear complexes $[\{\text{M}(\mu\text{-Cl})(\text{LL})\}_2]$ with **2**. Furthermore, the borate **1** represents a key material to achieve the attachment of tris(pyrazolyl)borate groups to the peripheries of carbosilane dendrimers. Thus, the platinum-catalyzed hydrosilylation reactions of compound **1** with the dendritic cores $\text{Si}[(\text{CH}_2)_3\text{SiMe}_2\text{H}]_4$ (**G(0)**–(**SiH**)₄), (**G(1)**–(**SiH**)₈), and (**G(2)**–(**SiH**)₁₆) gave the corresponding borate-containing dendrimers $\text{Si}[(\text{CH}_2)_3\text{SiMe}_2(\text{CH}_2)_3\text{B}(\text{O}^i\text{Pr})_2]_4$ (**G(0)**–**B**₄), $\text{Si}[(\text{CH}_2)_3\text{SiMe}_2\{(\text{CH}_2)_3\text{SiMe}_2(\text{CH}_2)_3\text{B}(\text{O}^i\text{Pr})_2\}]_4$ (**G(1)**–**B**₈), and $\text{Si}[(\text{CH}_2)_3\text{SiMe}_2\{(\text{CH}_2)_3\text{SiMe}_2\{(\text{CH}_2)_3\text{SiMe}_2(\text{CH}_2)_3\text{B}(\text{O}^i\text{Pr})_2\}\}]_4$ (**G(2)**–**B**₁₆) selectively in the anti-Markovnikov direction. Further reactions of **G(0)**–**B**₄, **G(1)**–**B**₈ and **G(2)**–**B**₁₆ with potassium pyrazolate and pyrazole rendered the corresponding polyanionic dendrimers $\text{K}_4[\text{Si}\{(\text{CH}_2)_3\text{SiMe}_2(\text{CH}_2)_3\text{Bpz}_3\}]_4$ (**G(0)**–(**Bpz**)₄), **G(1)**–(**Bpz**)₈, and **G(2)**–(**Bpz**)₁₆, respectively, which contain 4, 8, and 16 tris(pyrazolyl)borate groups symmetrically located around the dendritic peripheries. These unusual polyanionic dendrimers are excellent scaffolds to support metal centres, as shown by the reactions of **G(0)**–(**Bpz**)₄, **G(1)**–(**Bpz**)₈, and **G(2)**–(**Bpz**)₁₆ with $[\{\text{Rh}(\mu\text{-Cl})(\text{nbd})\}_2]$ to give the neutral rhodadendrimers $[\text{Si}\{(\text{CH}_2)_3\text{SiMe}_2(\text{CH}_2)_3\text{Bpz}_3\text{Rh}(\text{nbd})\}]_4$ **G(0)**–(**Bpz**,Rh)₄, **G(1)**–(**Bpz**,Rh)₈ and **G(2)**–(**Bpz**,Rh)₁₆ as stable solids in excellent yields. Following this protocol, mixed rhodium/iridium metallodendrimers can be prepared.

Introduction

Polypyrazolylborates (scorpionates) have been one of the most intensely investigated ligands in inorganic chemistry during the last decades. After more than 2000 papers on the subject,¹ they have found a wide range of uses that cover from modelling the active site of metallo-enzymes² to catalysis³ and materials science.⁴ Given the versatile properties, high stability and rich chemistry associated to the scorpionates and their complexes, it would be very convenient to graft these systems on dendritic peripheries. Moreover, the hypothetical situation of having these nitrogen-donor ligands and complexes strategically located at specific sites around a core dendrimer is itself very attractive to develop materials with new properties to be discovered. Furthermore, given that the catalytic activity of some complexes based on scorpionates is known for a variety of processes and metals,³ the use of catalysts on a dendritic level could be, among others, an issue of special

interest. The use of metallodendrimers as the active homogeneous catalytic species is a topic currently pursued and developed by a number of research groups.⁵ The main attraction about these catalysts relies in their large size, a property that has allowed in many cases the clean separation from the organic reaction products by applying simple nanofiltration techniques.⁶

All these considerations prompted us to envisage a way to functionalise carbosilane dendritic peripheries with tris(pyrazolyl)borate ligands focusing on the ultimate goal of preparing stable metallodendrimers. Although the related neutral tris(pyrazolyl)methane systems have been recently coupled to the first generation of a carbosilane dendrimer through reactive O–Si linkages,⁷ we have found no references concerning the incorporation of the anionic borate counterparts. In addition the idea of grafting the surface of dendrimers with tripod ligands to avoid the leaching of the corresponding metallodendrimers when used for catalysis has been scarcely exploited, although some examples of carbosilane dendrimers with N-donor, P-donor and S-donor tripod ligands have been reported.⁸ We describe herein an efficient synthetic route for grafting specifically designed tris(pyrazolyl)borates (RTp) to carbosilane dendrimers to generate unusual anionic dendrimers with very robust constructs (through Si–C bond formation) in high yield, and further, able to form neutral metallodendrimers (rhodadendrimers).

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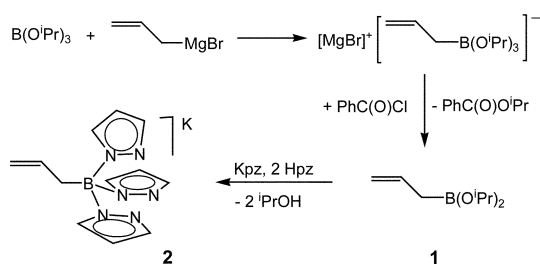
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† Dedicated to Prof. Dr Victor Riera on occasion of his 70th birthday.

Results and discussion

Synthesis of allyl-functionalised boron compounds and their rhodium and iridium complexes

The synthesis of the potassium salt of allyltris(pyrazolyl)borate was achieved in two separate steps (Scheme 1). First, the compound $\text{CH}_2=\text{CHCH}_2\text{B}(\text{O}^i\text{Pr})_2$ (**1**) was prepared by reaction of triisopropyl borate, with allylmagnesium bromide in diethyl ether at low temperature to give a copious white suspension, of presumably magnesium allyltris(isopropyl)borate bromide. A further treatment of this suspension with benzoyl chloride released compound **1**, which was isolated as a colorless liquid in reasonable yield. The characterization and purity of **1** was assessed by the ^1H NMR spectrum, which showed the typical allylic resonances and two signals for the protons of the isopropoxy groups attached to boron.

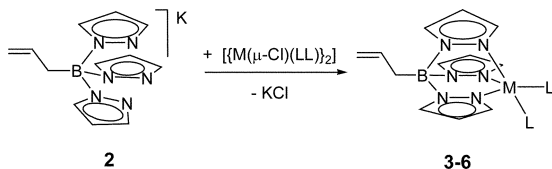


Scheme 1 Synthetic strategy for the allyl-functionalised trispyrazolylborate ligand **2**.

In a second step, compound **1** was reacted with one molar-equiv. of potassium pyrazolate and two molar-equiv. of pyrazole in refluxing toluene to afford $\text{K}[\text{CH}_2=\text{CHCH}_2\text{Bpz}_3]$ (**2**), which was isolated as a white powder in good yield.

In accordance with the structure shown in Scheme 1, the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **2** displayed a set of three resonances for the equivalent pyrazolate rings in the anion, and those for the allyl group. Thus, the synthesis of **2** follows a facile and original procedure, outlined by Venanzi *et al.*,⁹ which is distinct from the described methods leading to modified pyrazolylborate ligands containing organic groups directly attached to the boron center.¹⁰

As expected, the salt **2** is the source of the new scorpionate ligand on reaction with transition metal chlorocomplexes. Thus, reactions of **2** with $[\{\text{M}(\mu\text{-Cl})(\text{LL})\}_2]$ (Scheme 2) gave the mononuclear complexes $[\text{CH}_2=\text{CHCH}_2\text{Bpz}_3\text{M}(\text{LL})]$ ($\text{M} = \text{Rh}$, $\text{LL} = \text{nbd}$, **3**; $\text{LL} = \text{tfb}$, **4**; $\text{LL} = (\text{CO})(\text{PPh}_3)$, **5**; $\text{M} = \text{Ir}$, $\text{LL} = \text{cod}$, **6**), which were isolated as bright yellow (Rh) or pink (Ir) microcrystalline solids in excellent yields (Scheme 2).



Scheme 2 $\text{M} = \text{Rh}$, $\text{LL} = \text{nbd}$, **3**; $\text{LL} = \text{tfb}$, **4**; $\text{LL} = (\text{CO})(\text{PPh}_3)$, **5**; $\text{M} = \text{Ir}$, $\text{LL} = \text{cod}$, **6**.

The new complexes **3–6** showed spectroscopic features similar to those reported for related tris(pyrazolyl)borate ligands.¹¹ For example, the ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the complex

$[\text{CH}_2=\text{CHCH}_2\text{Bpz}_3\text{Rh}(\text{nbd})]$ (**3**) at r. t. showed three signals for the equivalent pyrazolate rings, three resonances for the allyl group, and one distinct resonance for each one of the CH , $=\text{CH}$ and CH_2 groups from the diolefin ligand. These features are consistent with a fluxional molecule containing a penta-coordinated rhodium atom or a square-planar structure with fast exchange between free and coordinated pyrazolyl rings, as previously observed.¹² Furthermore, the mononuclear nature of complexes **3–6** was confirmed by FAB(+) spectrometry.

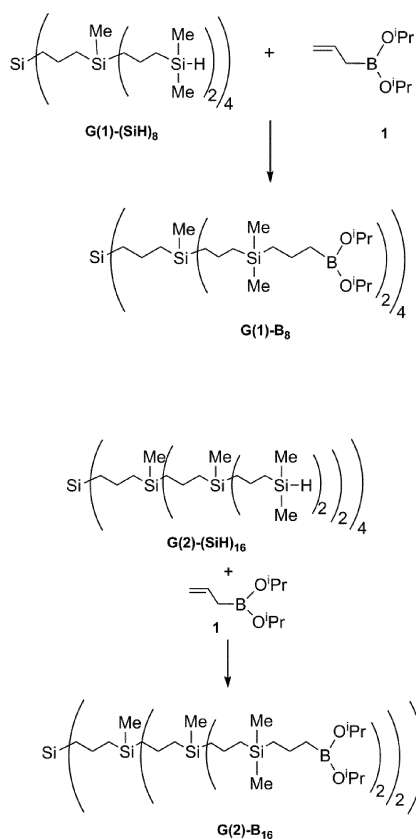
Attachment of tris(pyrazolyl)borate groups to carbosilane dendrimers

Once the ability of the allyl-containing scorpionate salt $\text{K}[\text{CH}_2=\text{CHCH}_2\text{Bpz}_3]$ (**2**) to form stable mononuclear complexes was established, we focused our attention on the grafting of tris(pyrazolyl)borate groups to carbosilane dendritic peripheries with the ultimate goal of preparing stable, neutral metallodendrimers. In this context, the allyl-containing compound **1** proved to be a key material to attach borate groups to the periphery of carbosilane dendrimers bearing Si–H peripheral functional groups.

We have recently communicated on the covalent attachment of this moiety to a first-generation carbosilane dendrimer bearing four Si–H groups, and the further functionalisation at boron.¹³ The extension of this approach to the chemistry of tris(pyrazolyl)borate systems has allowed the preparation of stable dendritic polyanionic assemblies up to the third generation, as described herein. The procedure consists of platinum-catalyzed hydrosilylation reactions involving the borate compound **1** and carbosilane dendritic cores adapted with terminal Si–H functionalities, whose preparation have been reported elsewhere,¹⁴ using the Karstedts catalyst, $[\{\text{O}(\text{SiMe}_2\text{CH}=\text{CH}_2)_3\text{Pt}_2]$ to give selectively the anti-Markovnikov addition products. In this way, reaction of **1** with the core dendrimer $\text{Si}[(\text{CH}_2)_3\text{SiMe}_2\text{H}]_4$ ($\text{G}(\mathbf{0})\text{-(SiH)}_4$) gave the addition product $\text{Si}[(\text{CH}_2)_3\text{SiMe}_2(\text{CH}_2)_3\text{B}(\text{O}^i\text{Pr})_2]_4$ ($\text{G}(\mathbf{0})\text{-B}_4$) cleanly in quantitative yield. In the same way, the first and second generations of these borate-containing dendrimers were prepared by reacting $\text{Si}[(\text{CH}_2)_3\text{SiMe}\{(\text{CH}_2)_3\text{SiMe}_2\text{H}\}_2]_4$ ($\text{G}(\mathbf{1})\text{-(SiH)}_8$) and $\text{Si}[(\text{CH}_2)_3\text{SiMe}\{(\text{CH}_2)_3\text{SiMe}\{(\text{CH}_2)_3\text{SiMe}_2\text{H}\}_2\}_2]_4$ ($\text{G}(\mathbf{2})\text{-(SiH)}_{16}$) with **1**, in the appropriate molar ratio, to afford the dendrimers $\text{Si}[(\text{CH}_2)_3\text{SiMe}\{(\text{CH}_2)_3\text{SiMe}_2(\text{CH}_2)_3\text{B}(\text{O}^i\text{Pr})_2\}_2]_4$ ($\text{G}(\mathbf{1})\text{-B}_8$) and $\text{Si}[(\text{CH}_2)_3\text{SiMe}\{(\text{CH}_2)_3\text{SiMe}\{(\text{CH}_2)_3\text{SiMe}_2(\text{CH}_2)_3\text{B}(\text{O}^i\text{Pr})_2\}_2\}_2]_4$ ($\text{G}(\mathbf{2})\text{-B}_{16}$) (Scheme 3), respectively, in quantitative yields.

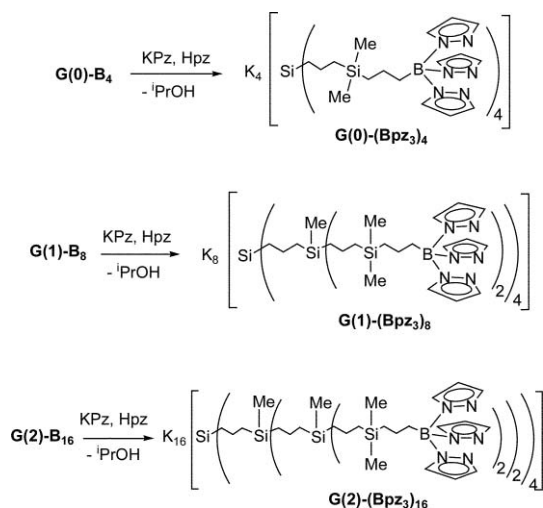
All these dendritic intermediates isolated as pure heavy oils were unambiguously characterized by multinuclear NMR techniques. The ^1H NMR spectra of $\text{G}(\mathbf{n})\text{-B}_m$ ($n = 0, m = 4$; $n = 1, m = 8$; $n = 2, m = 16$) in CDCl_3 showed signals for the carbosilane skeletons along with septuplets at δ 4.3 ppm and doublets at δ 1.1 ppm, characteristic of the isopropoxy groups attached to boron, whose integrations fitted with the proposed structures, a fact confirmed by their $^{13}\text{C}\{^1\text{H}\}$ NMR spectra.

Then, the dendritic intermediate $\text{Si}[(\text{CH}_2)_3\text{SiMe}_2(\text{CH}_2)_3\text{B}(\text{O}^i\text{Pr})_2]_4$ ($\text{G}(\mathbf{0})\text{-B}_4$) was reacted with four molar equiv. of potassium pyrazolate and pyrazole in excess in refluxing toluene to give the tetraanionic dendrimer $\text{K}_4[\text{Si}\{(\text{CH}_2)_3\text{SiMe}_2(\text{CH}_2)_3\text{B}(\text{pz})_3\}_4]$ ($\text{G}(\mathbf{0})\text{-(Bpz}_3)_4$), peripherally functionalised with four tris(pyrazolyl)borate groups.



Scheme 3 Hydrosilylation of the compound $\text{CH}_2=\text{CHCH}_2\text{B}(\text{O}^i\text{Pr})_2$ (**1**) with the dendritic cores **G(1)-(SiH)₈** and **G(2)-(SiH)₁₆**, adapted with Si-H termini.

Following this synthetic protocol, the anionic dendrimers $\text{K}_8[\text{Si}\{(\text{CH}_2)_3\text{SiMe}\{(\text{CH}_2)_3\text{SiMe}_2(\text{CH}_2)_3\text{Bpz}_3\}\}_2]_4$ (**G(1)-(Bpz₃)₈**) and $\text{K}_{16}[\text{Si}\{(\text{CH}_2)_3\text{SiMe}\{(\text{CH}_2)_3\text{SiMe}\{(\text{CH}_2)_3\text{SiMe}_2(\text{CH}_2)_3\text{Bpz}_3\}\}_2]_4$] (**G(2)-(Bpz₃)₁₆**) (Scheme 4), containing tris(pyrazolyl)borate on their peripheries were straightforwardly obtained by reaction of the dendritic borates **G(1)-B₈** and **G(2)-B₁₆** with potassium pyrazolate and pyrazole under the appropriate molar ratio.



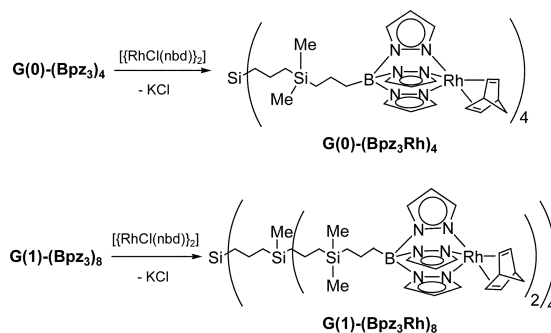
Scheme 4 Syntheses of the three generations of polyanionic tris(pyrazolyl)borate-containing carbosilane dendrimers.

The novel family of polyanionic dendrimers **G(n)-(Bpz₃)_m** ($n = 0, m = 4; n = 1, m = 8; n = 2, m = 16$) are very soluble in organic polar solvents and water, and they were characterized by multinuclear NMR spectroscopy (^1H , ^{13}C , ^{11}B) and elemental analyses. For instance, the ^1H NMR spectrum of **G(0)-(Bpz₃)₄** in deuterated acetone showed the expected three resonances for the equivalent pyrazolyl rings along with the resonances assigned to the carbosilane skeleton. Moreover, the pyrazolate carbons of **G(0)-(Bpz₃)₄** were observed as three singlets at low field in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, together with the signals corresponding to the methylene carbons and a singlet at $\delta -3.3$ ppm from the Me-Si group. Interestingly, the methyl-silicon resonances in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of these compounds are a diagnostic for the dendritic generation.

Thus, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **G(1)-(Bpz₃)₈** showed two singlets at $\delta -3.2$ and -4.9 ppm, while that for **G(2)-(Bpz₃)₁₆** showed three signals at $\delta -3.3, -5.0$ and -5.2 ppm. Furthermore, the ^{11}B NMR spectrum of **G(0)-(Bpz₃)₄** showed a sole singlet, which is accordance with an identical environment for the four boron atoms linked to the dendritic skeleton.

Preparation and characterization of neutral tris(pyrazolyl)borate rhodium metallodendrimers

These new compounds, **G(n)-B_m** ($n = 0, m = 4; n = 1, m = 8; n = 2, m = 16$), belong to a new class of polyanionic dendrimers with tridentate N-donor ligands on their surfaces. They were used for the synthesis of new metallodendrimers of rhodium by reacting them with the appropriate chloro-complexes. The metathesis reactions were carried out in acetonitrile and the resulting rhodadendrimers were conveniently extracted with hexanes and isolated as analytically pure light yellow solids in very good yields. Thus, reaction of **G(0)-(Bpz₃)₄** with two molar-equiv. of $[\{\text{Rh}(\mu\text{-Cl})(\text{nbd})\}_2]$ gave straightforwardly the metallodendrimer $\text{Si}\{(\text{CH}_2)_3\text{SiMe}_2(\text{CH}_2)_3\text{B}(\text{pz})_3\text{Rh}(\text{nbd})\}_4$ (**G(0)-(Bpz₃Rh)₄**) (Scheme 5).



Scheme 5 Preparation of rhodadendrimers **G(0)-(Bpz₃Rh)₄** and **G(1)-(Bpz₃Rh)₈** through metathesis reactions.

Analogously, the rhodium metallodendrimers $\text{Si}\{(\text{CH}_2)_3\text{SiMe}\{(\text{CH}_2)_3\text{SiMe}_2(\text{CH}_2)_3\text{Bpz}_3\text{Rh}(\text{nbd})\}\}_2]_4$ (**G(1)-(Bpz₃Rh)₈**) and $\text{Si}\{(\text{CH}_2)_3\text{SiMe}\{(\text{CH}_2)_3\text{SiMe}\{(\text{CH}_2)_3\text{SiMe}_2(\text{CH}_2)_3\text{B}(\text{pz})_3\text{Rh}(\text{nbd})\}\}_2]_4$] (**G(2)-(Bpz₃Rh)₁₆**) (Fig. 1) containing 8 and 16 “Rh(nbd)” peripheral organometallic fragments, respectively, were prepared by reactions of **G(1)-(Bpz₃)₈** and **G(2)-(Bpz₃)₁₆** with $[\{\text{Rh}(\mu\text{-Cl})(\text{nbd})\}_2]$, respectively.

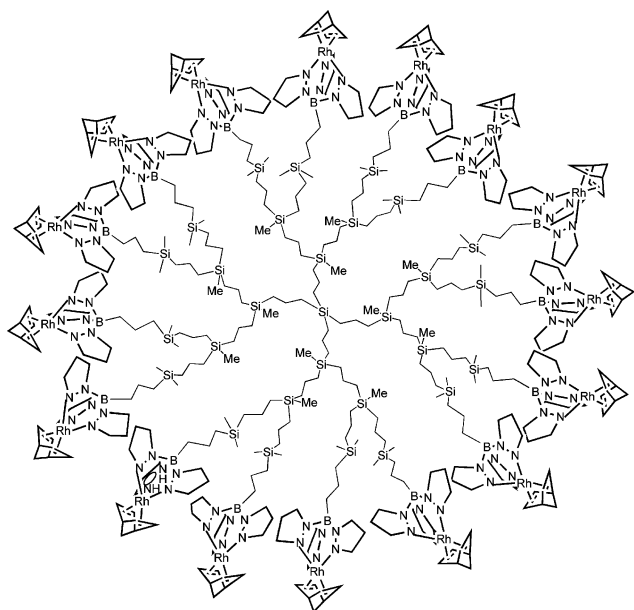


Fig. 1 Drawing of the metallo dendrimer $G(2)-(Bpz_3Rh)_{16}$.

The rhodium metallo dendrimers were found to be moisture and air-stable solids, for which their analytical and spectroscopic data were in agreement with their proposed structures. For instance, the 1H NMR spectrum of the rhodadendrimer of the highest generation, $G(2)-(Bpz_3Rh)_{16}$, showed three expected resonances in the aromatic region for the pyrazolate protons, resembling the situation observed for the complex $[CH_2=CHCH_2Bpz_3Rh(nbd)]$ (3). In a similar way, the olefinic and bridgehead protons of the diolefin ligands gave signals at δ 3.71 and 3.26 ppm, respectively, while broad bands for the methylenic chains and a sharp singlet at δ -0.03 ppm for the methyl groups attached to silicon were observed. The $^{13}C\{^1H\}$ NMR spectrum of $G(2)-(Bpz_3Rh)_{16}$ was indicative of the purity of this metallo dendrimer, since all the resonances observable were unambiguously assigned (see Experimental). Furthermore, the ^{11}B NMR spectrum of this rhodadendrimer showed a sole singlet at δ -0.98 ppm. In addition, MALDI-TOF spectrometric measurements gave mass values corresponding to the expected ones for all generations of metallo dendrimers.

Unfortunately, all attempts to grow-up monocrystals from both the potassium and thallium salts of the polyanionic tris(pyrazolyl)borate-containing carbosilane dendrimers and the rhodadendrimers were unsuccessful.

Molecular modeling was then performed on the $G(n)$ ($n = 0, 1, 2$) rhodadendrimers using the modeling program contained in the Accelerlys software package,¹⁵ to estimate their gas-phase three-dimensional structure. For $G(0)-(Bpz_3Rh)_4$ a molecular diameter of ca. 34 Å was calculated, while for the $G(1)-(Bpz_3Rh)_8$ and $G(2)-(Bpz_3Rh)_{16}$ metallo dendrimers the diameters extended to ca. 46 Å and 53 Å, respectively. Although these data only give information about the volume of the fully stretched dendrimers, the values suggest these macromolecules are large enough to be used for nanofiltration purposes.⁵ The size and shape of $G(2)-(Bpz_3Rh)_{16}$ is shown in Fig. 2, where a densely packed system is observable.

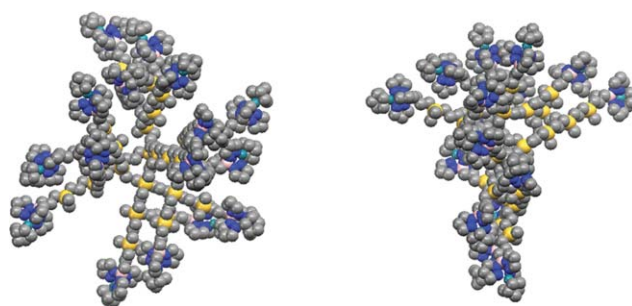


Fig. 2 Space filling model of the "front" (right) and "side" (left) view of the calculated structure of $G(2)-(Bpz_3Rh)_{16}$.

Preparation of tris(pyrazolyl)borate heterometallic rhodium/iridium metallo dendrimers

The polyanionic dendrimers described herein provide the possibility of specific complexation for a variety of metals. In an attempt to prepare heterometallic rhodium and iridium metallo dendrimers, we carried out the reaction of $G(0)-(Bpz_3)_4$ with an equimolar mixture of $[Rh(\mu-Cl)(nbd)]_2$ and $[Ir(\mu-Cl)(cod)]_2$, in which the iridium complex incorporates a different diolefin (1,5-cyclooctadiene) in order to distinguish between the different metallic fragments by NMR spectra. A pink solid was isolated from this reaction in good yield, whose analytical data were in accordance with the formation of a metallo dendrimer containing exactly half loading of both metals of formula $Si[(CH_2)_3Si(Me)_2(CH_2)_3Bpz_3\{Rh(nbd)\}]_2[(CH_2)_3Si(Me)_2(CH_2)_3-Bpz_3\{Ir(cod)\}]_2$ ($G(0)-(Bpz_3Rh_{0.5}Ir_{0.5})_4$). As a statistical distribution of the metals can be anticipated, the formation of a single defined product, such as the one shown for the zeroth generation $G(0)-(Bpz_3Rh_{0.5}Ir_{0.5})_4$ (Fig. 3), is unlikely.

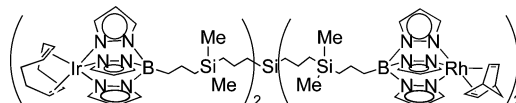


Fig. 3 Proposed averaged structure of $G(0)-(Bpz_3Rh_{0.5}Ir_{0.5})_4$.

Nevertheless, the 1H NMR spectrum of this solid $G(0)-(Bpz_3Rh_{0.5}Ir_{0.5})_4$, suggests the formation of a well-defined material that resembles the averaged C_{2v} symmetry. Thus, the spectrum displayed six distinct resonances for the pyrazolate protons along with signals from both diolefins in a 1 : 1 ratio, whose assignment was carried out unambiguously by a COSY- 1H , 1H experiment. Two sharp resonances of the Si-Me protons were observed at δ 0.22 and 0.24 ppm and at δ -3.1 and -3.2 ppm in the 1H and $^{13}C\{^1H\}$ NMR spectra, respectively, which is a remarkable diagnostic of the proposed symmetry. This symmetrical dendrimer is the main one, as confirmed by the MALDI-TOF spectrum of $G(0)-(Bpz_3Rh_{0.5}Ir_{0.5})_4$ which showed a sharp peak at m/z : 2435 for the compound with the $[Rh_2Ir_2]$ core; minor peaks at m/z : 2331, 2225, 2543 and 2646, corresponding to metallo dendrimers of the cores $[Rh_3Ir]$, $[Rh_4]$, $[Ir_3Rh]$, and $[Ir_4]$, respectively, were also observed.

In conclusion, we describe here a simple and efficient synthesis of a modified scorpionate ligand with an allyl group attached to boron. This ligand is able to coordinate metals, as expected. Moreover, the allyl group allows the peripheral attachment of

this tris(pyrazolyl)borate ligand to carbosilane dendrimers to give unusual polyanionic dendrimers. Furthermore, they are excellent systems for the incorporation of transition metals, as confirmed by the preparation of metallodendrimers that contain up to sixteen rhodium centers.

Experimental

All manipulations were performed under a dry argon atmosphere using Schlenk 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 [$\{M(\mu\text{-Cl})(\text{diolofin})\}_2$] ($M = \text{Rh}$, diolofin = cod,¹⁶ nbd,¹⁷ tfbb;¹⁸ $M = \text{Ir}$, diolofin = cod¹⁹) and $[\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$.²⁰ All the other chemicals used in this work were purchased from Aldrich 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. Ions were produced with the standard C^{s+} gun at *ca.* 30 kV; 3-nitrobenzyl alcohol (NBA) was used as matrix. ¹H and ¹³C{¹H} and ³¹P{¹H} spectra were recorded on Varian UNITY, Bruker ARX 300, and Varian Gemini 300 spectrometers operating at 299.95, 75.47, and 121.42 MHz, 300.13, 75.47, and 121.49 MHz, and 300.08, 75.46, and 121.48 MHz, respectively. Chemical shifts are reported in ppm and referenced to Me₄Si using the residual signal of the deuterated solvent (¹H and ¹³C), and H₃PO₄ as external reference (³¹P). MALDI-TOF spectra were recorded in a REFLEX MALDI spectrometer operating in the linear and reflector modes.

Synthesis of the compounds

CH₂CH=CH₂B(OⁱPr)₂ (1). To a solution of triisopropyl borate (10.00 g, 12.3 cm³, 53.17 mmol) in diethyl ether (150 cm³) a solution of allyl magnesium bromide (1.22 mol L⁻¹, 45.0 cm³, 55.00 mmol) in diethyl ether was added dropwise at -78 °C to give a copious white suspension. The mixture was stirred for 3 h at -78 °C and then allowed to warm gradually. Benzoyl chloride (7.73 g, 6.4 cm³, 55.00 mmol) was then added with a dropping funnel and the resulting yellow solution was stirred at room temperature for 8 h. The volatiles were removed by distillation at 60 °C and the product **1** was isolated as a colorless liquid by distillation of the residue under reduced pressure. (4.86 g, 55%). (Found: C, 63.45; H, 11.22. C₉H₁₉BO₂ requires C, 63.57; H, 11.26). ¹H NMR (CDCl₃, δ): 5.87 (m, 1H, CH), 4.87 (m, 2H, =CH₂) (allyl), 4.37 (sept, 2H, CH OⁱPr), 1.67 (d, 2H, CH₂ allyl), 1.13 (d, 12H, Me OⁱPr). ¹³C{¹H} NMR (CDCl₃, δ): 135.8 (CH), 113.8 (=CH₂) (allyl), 65.1 (CH), 24.2 (Me) (OⁱPr), 20.0 (br, CH₂B).

K[CH₂=CHCH₂Bpz₃] (2). A Schlenk tube equipped with a Dean-Stark trap was charged with **1** (0.66 g, 3.91 mmol), potassium pyrazolate (0.42 g, 4.00 mmol), pyrazole (1.06 g, 15.64 mmol) and toluene (20 cm³) under an argon atmosphere. The mixture was refluxed for 12 h and then evaporated to dryness. The resulting white residue was washed several times with diethyl ether to afford **2** as a white solid. (0.85 g, 75%). (Found: C, 49.31; H, 4.81; N, 28.82. C₁₂H₁₄BKN₆ requires C, 49.33; H, 4.83; N, 28.76). ¹H NMR (acetone-d₆, δ): 7.54 (d, 2.1 Hz, 3H), 7.51 (d, 2.1 Hz, 3H), 6.15 (t, 2.1 Hz, 3H) (CH pz), 5.81 (m, 1H, CH), 4.92

(dm, 1H, =CH₂), 4.72 (dm, 1H, =CH₂), 2.43 (d, 7.1 Hz, CH₂) (allyl). ¹³C{¹H} NMR (CDCl₃, δ): 142.4 (CH allyl), 138.9, 133.3 (pz), 111.3 (=CH₂ allyl), 102.9 (pz), 20.1 (br, CH₂B).

[CH₂=CHCH₂Bpz₃Rh(nbd)] (3). To a solution of [$\{\text{Rh}(\mu\text{-Cl})(\text{nbd})\}_2$] (0.33 g, 0.71 mmol) in acetonitrile (8 cm³), solid **2** (0.41 g, 1.42 mmol) was added, and the resulting yellow mixture was stirred at room temperature for 1 h. The volatiles were removed under reduced pressure and the residue was extracted with hexanes (20 cm³). Evaporation of the solvent afforded complex **3** as a pale yellow solid. (0.42 g, 66%). (Found: C, 50.94; H, 5.01; N, 18.48. C₁₉H₂₂BN₆Rh requires C, 50.92; H, 4.95; N, 18.75). ¹H NMR (CDCl₃, δ): 7.66 (d, 2.1 Hz, 3H), 7.64 (d, 2.1 Hz, 3H), 6.15 (t, 2.1 Hz, 3H) (CH pz), 6.13 (m, 1H, CH allyl), 5.30 (d, 17.0 Hz, 1H), 5.17 (d, 10.1 Hz, 1H) (=CH₂ allyl), 3.82 (m, 2H, CH nbd), 3.34 (m, 4H, =CH nbd), 2.53 (d, 6.0 Hz, 2H, CH₂ allyl), 1.30 (m, 2H, CH₂ nbd). ¹³C{¹H} NMR (CDCl₃, δ): 139.7 (pz), 138.1 (CH allyl), 132.9 (pz), 116.4 (=CH₂), 104.3 (pz), 58.3 (d, ³J_{CRh} = 6.4 Hz, CH₂ nbd), 47.7 (d, ²J_{CRh} = 2.7 Hz, CH nbd), 38.4 (d, ¹J_{CRh} = 10.4 Hz, =CH nbd). FAB(+): *m/z* 448 (M⁺, 65%), 407 (90, M-allyl), 381 (100, M-pz).

[CH₂=CHCH₂Bpz₃Rh(tfb)] (4). To a solution of [$\{\text{Rh}(\mu\text{-Cl})(\text{tfb})\}_2$] (50 mg, 0.07 mmol) in acetonitrile (8 cm³), solid **2** (40 mg, 0.14 mmol) was added, and the resulting mixture was stirred at room temperature for 1 h. The volatiles were removed under reduced pressure and then the residue was extracted with diethyl ether (20 cm³). Evaporation of the solvent afforded the compound **4** as a yellow solid. (70 mg, 89%). (Found: C, 49.69; H, 3.43; N, 14.49. C₂₄H₂₀BF₄N₆Rh requires C, 49.51; H, 3.46; N, 14.44). ¹H NMR (CDCl₃, δ): 7.74 (d, 2.1 Hz, 3H), 7.66 (d, 2.0 Hz, 3H), 6.20 (t, 2.1 Hz, 3H) (CH pz), 6.16 (m, 1H, CH allyl), 5.41 (m, 2H, CH tfb), 5.32 (d, 16.8 Hz, 1H), 5.18 (d, 9.9 Hz, 1H) (=CH₂ allyl), 3.12 (m, 4H, =CH tfb), 2.52 (d, 6.6 Hz, 2H, CH₂ allyl). FAB(+): *m/z* 581 (M⁺, 85%), 541 (100, M-allyl), 515 (95, M-pz).

[CH₂=CHCH₂Bpz₃Rh(CO)(PPh₃)] (5). To a solution of $[\text{Rh}(\text{CO})(\text{PPh}_3)_2\text{Cl}]$ (0.24 g, 0.34 mmol) in CH₂Cl₂ (15 cm³), solid **2** (0.10 g, 0.34 mmol) was added to give a yellow suspension, which was stirred at room temperature for 30 min. The volatiles were removed under reduced pressure, and the residue was extracted with hexanes (20 cm³). Evaporation of the solvent afforded **5** as a pale yellow solid. (0.20 g, 91%). (Found: C, 57.81; H, 4.30; N, 12.95. C₃₁H₂₉BN₆OPRh requires C, 57.61; H, 4.52; N, 13.00). ¹H NMR (CDCl₃, δ): 7.46 (set of m, 21H, PPh₃ + CH pz), 6.10 (t, 2.1 Hz, 3H, CH pz), 5.62 (m, 1H, CH), 5.03 (d, 17.2 Hz, 1H, =CH₂), 4.87 (d, 10.1 Hz, 1H, =CH₂), 2.71 (d, 6.4 Hz, 2H, CH₂) (allyl). ³¹P{¹H} NMR (CDCl₃, δ): 43.8 (d, ¹J_{PRh} = 157.8 Hz). FAB(+): *m/z* 646 (M⁺, 15%), 605 (30, M-allyl), 579 (35, M-pz), 356 (35, M-PPh₃-CO).

[CH₂=CHCH₂Bpz₃Ir(cod)] (6). To a solution of [$\{\text{Ir}(\mu\text{-Cl})(\text{cod})\}_2$] (86 mg, 0.13 mmol) in acetonitrile (15 cm³), solid **2** (75 mg, 0.26 mmol) was added, and the resulting red mixture was stirred at room temperature for 1 h. The volatiles were removed under reduced pressure, and the residue was extracted with hexanes (20 cm³). Evaporation of the solvent afforded **6** as a pink microcrystalline solid. (0.15 g, 94%). (Found: C, 43.28; H, 4.58; N, 15.02. C₂₀H₂₆BIrN₆ requires C, 43.40; H, 4.73; N, 15.18). ¹H NMR (C₆D₆, δ): 7.72 (d, 1.50 Hz, 3H), 7.55 (d, 2.4 Hz, 3H) (CH pz), 6.02 (m, 1H, CH allyl), 5.88 (t, 2.4 Hz, 3H, CH pz), 5.05

(m, 2H, =CH₂ allyl), 3.57 (m, 4H, =CH cod), 2.45 (m, 4H, CH₂ cod), 2.27 (d, 6.6, 2H, CH₂ allyl), 1.78 (m, 4H, CH₂ cod). ¹³C{¹H} NMR (C₆D₆, δ): 140.0 (s, CH pz), 134.0 (br s, =CH allyl), 133.5 (s, CH pz), 114.5 (br s, =CH₂ allyl), 105.6 (s, CH pz), 55.7 (s, =CH cod), 33.5 (s, CH₂ cod), 22.3 (br s, CH₂ allyl). FAB(+): *m/z* 554 (M⁺, 100%), 487 (70, M-pz).

Si[(CH₂)₃SiMe₂(CH₂)₃B(OⁱPr)₂]₄ (G(0)–B₄). A thick-glassed tube was charged with G(0)–(SiH)₄ (0.61 g, 1.40 mmol), **1** (1.00 g, 5.88 mmol), four drops of a solution of the Karstedts catalyst in xylene, and hexanes (5 cm³). The mixture was degassed and stirred at 60 °C for 12 h. Upon cooling the resulting dark brown solution was transferred *via* cannula to a Schlenk flask and then evaporated under reduced pressure affording G(0)–B₄ as a viscous brownish oil in quantitative yield. ¹H NMR (CDCl₃, δ): 4.35 (sept, 8H, CH), 1.23 (m, 16H, CH₂), 1.12 (d, 48H, CH₃ ⁱPr), 1.05 (m, 8H, CH₂), 0.50 (m, 24H, CH₂), –0.07 (m, 24H, Me).

Si[(CH₂)₃SiMe{(CH₂)₃SiMe₂(CH₂)₃B(OⁱPr)₂}]₂]₄ (G(1)–B₈). The compound was isolated as a thick brownish oil in quantitative yield following the procedure described for G(0)–B₄, by reacting G(1)–(SiH)₈ (0.89 g, 0.75 mmol) with **1** (1.15 g, 6.78 mmol). ¹H NMR (CDCl₃, δ): 4.30 (sept, 16H, CH), 1.30 (m, 42H, CH₂), 1.07 (d, 96H, CH₃ ⁱPr), 0.71 (m, 14H, CH₂), 0.45 (m, 64H, CH₂), –0.12 (s, 48H, Me), –0.15 (s, 12H, Me). ¹³C{¹H} NMR (CDCl₃, δ): 64.8 (CH), 24.6 (CH₃) (ⁱPr), 20.4 (br, CH₂B), 20.3, 19.2, 18.8, 18.6, 18.5 (CH₂), –3.3, –4.8 (Me).

Si[(CH₂)₃SiMe{(CH₂)₃SiMe₂(CH₂)₃B(OⁱPr)₂}]₂]₄ (G(2)–B₁₆). The compound was isolated as a thick brownish oil in quantitative yield following the procedure described for G(0)–B₄, by reacting G(2)–(SiH)₁₆ (1.00 g, 0.37 mmol) with **1** (1.27 g, 7.49 mmol). ¹H NMR (CDCl₃, δ): 4.34 (sept, 32H, CH), 1.31 (m, 90H, CH₂), 1.11 (d, 192H, CH₃ ⁱPr), 0.76 (m, 30H, CH₂), 0.45 (m, 144H, CH₂), –0.08 (m, 108 H), –0.10 (m, 24H) (Me). ¹³C{¹H} NMR (CDCl₃, δ): 64.9 (CH), 24.4 (CH₃) (ⁱPr), 20.3 (br s, CH₂B), 21.5, 20.3, 19.3, 19.1, 19.0, 18.8, 18.5, 17.9, 17.5 (CH₂), –3.2, –4.9, –5.1 (Me).

K₄[Si{(CH₂)₃SiMe₂(CH₂)₃Bpz₃}]₄ (G(0)–(Bpz₃)₄). A Schlenk tube equipped with a Dean–Stark trap was charged with G(0)–B₄ (1.56 g, 1.40 mmol), potassium pyrazolate (0.61 g, 5.74 mmol), pyrazole (1.14 g, 16.80 mmol) and toluene (20 cm³) under an argon atmosphere. The mixture was refluxed for 12 h and then allowed to cool at r. t. affording a brownish oil. The supernatant solution was decanted off and the residue was washed repeatedly with diethyl ether to give G(0)–(Bpz₃)₄ as a white solid. (1.75 g, 78%). (Found: C, 50.61; H, 6.57; N, 19.85. C₆₈H₁₀₈B₄K₄N₂₄Si₅ requires C, 50.99; H, 6.80; N, 20.99). ¹H NMR (acetone-d₆, δ): 7.57 (d, 12H, CH), 7.51 (d, 12H, CH), 6.18 (t, 12H, CH) (pz), 1.48 (m, 16H, CH₂), 1.26 (m, 8H, CH₂), 0.66 (m, 24H, CH₂), 0.01 (s, 24H, Me). ¹³C{¹H} NMR (acetone-d₆, δ): 138.7, 132.9, 102.9 (pz), 20.6, 19.7, 18.7, 17.7 (CH₂), –3.3 (Me). ¹¹B{¹H} NMR (acetone-d₆, δ): 2.56 (br s).

K₈[Si[(CH₂)₃SiMe{(CH₂)₃SiMe₂(CH₂)₃Bpz₃}]₂]₄ (G(1)–(Bpz₃)₈). The compound was isolated as a white off solid following the procedure described for G(0)–(Bpz₃)₄, by reacting G(1)–B₈ (1.91 g, 0.75 mmol), potassium pyrazolate (0.66 g, 6.17 mmol) and pyrazole (1.13 g, 16.57 mmol). Yield: 2.43 g (92%). (Found: C, 51.97; H, 7.19; N, 19.12. C₁₅₂H₂₅₂B₈K₈N₄₈Si₁₃ requires C, 51.92; H, 7.22; N, 19.12). ¹H NMR (acetone-d₆, δ): 7.58 (s, 24H), 7.52 (s,

24H), 6.19 (s, 24H) (CH pz), 1.51 (m, 42H, CH₂), 1.26 (m, 14H, CH₂), 0.68 (m, 64H, CH₂), 0.08 (s, 12H, Me), 0.02 (s, 48H, Me). ¹³C{¹H} NMR (acetone-d₆, δ): 138.7, 132.9, 102.9 (pz), 20.5, 19.7, 19.0, 18.8, 18.6 (CH₂), –3.2 (Me), –4.9 (Me).

K₁₆[Si[(CH₂)₃SiMe{(CH₂)₃SiMe₂(CH₂)₃Bpz₃}]₂]₄ (G(2)–(Bpz₃)₁₆). The compound was isolated as a white off solid following the procedure described for G(0)–(Bpz₃)₄, by reacting G(2)–B₁₆ (2.00 g, 0.37 mmol), potassium pyrazolate (0.66 g, 6.20 mmol), pyrazole (1.53 g, 22.47 mmol). Yield: 2.36 g (87%). (Found: C, 52.02; H, 7.35; N, 18.36. C₃₂₀H₅₄₀B₁₆K₁₆N₉₆Si₂₉ requires C, 52.33; H, 7.41; N, 18.31). ¹H NMR (acetone-d₆, δ): 7.58 (s, 48H), 7.51 (s, 48H), 6.18 (s, 48H) (CH pz), 1.51 (m, 90H, CH₂), 1.31 (m, 30H, CH₂), 0.66 (m, 144H, CH₂), 0.15 (s, 24H, Me), 0.02 (s, 108H, Me). ¹³C{¹H} NMR (CD₃OD, δ): 138.5, 132.7, 102.7 (pz), 20.3, 19.5, 18.9, 18.6, 18.5 (CH₂), –3.3, –5.0, –5.2 (Me).

Si[(CH₂)₃SiMe₂(CH₂)₃Bpz₃Rh(nbd)]₄ (G(0)–(Bpz₃Rh)₄). To a solution of [{Rh(μ-Cl)(nbd)}₂] (0.17 g, 0.37 mmol) in acetonitrile (10 cm³), solid G(0)–(Bpz₃)₄ (0.30 g, 0.19 mmol) was added, and the resulting mixture was stirred at room temperature for 1 h. The volatiles were pumped off under reduced pressure and the residue was extracted with hexanes (20 cm³). Evaporation of the solvent afforded G(0)–(Bpz₃Rh)₄ as a pale yellow solid. (0.36 g, 88%). (Found: C, 51.89; H, 6.51; N, 15.01. C₉₆H₁₄₀B₄N₂₄Rh₄Si₅ requires C, 51.81; H, 6.34; N, 15.10). ¹H NMR (CDCl₃, δ): 7.62 (s, 12H, CH), 7.54 (s, 12H, CH), 6.18 (s, 12H, CH) (pz), 3.79 (m, 8H, CH nbd), 3.32 (m, 16H, =CH nbd), 1.60 (m, 12H, CH₂), 1.40 (m, 10H, CH₂), 1.27 (m, 8H, CH₂ nbd), 0.82 (m, 10H, CH₂), 0.64 (m, 16H, CH₂), –0.03 (s, 24H, Me). ¹³C{¹H} NMR (CDCl₃, δ): 139.7, 132.6, 104.3 (pz), 58.5 (d, ³J_{CRh} = 6.4 Hz, CH₂), 47.8 (d, ²J_{CRh} = 2.7 Hz, CH), 38.9 (d, ¹J_{CRh} = 10.4 Hz, =CH) (nbd), 22.5 (br, CH₂B), 20.5, 20.4, 19.9, 18.6, 17.6 (CH₂), –3.2 (Me). MALDI-TOF: *m/z* 2224.7 (calcd. 2225.6).

Si[(CH₂)₃Si(Me)₂(CH₂)₃Bpz₃{Rh(nbd)}]₂[(CH₂)₃Si(Me)₂(CH₂)₃–Bpz₃{Ir(cod)}]₂ (G(0)–(Bpz₃Rh_{0.5}Ir_{0.5})₄). To a solution of G(0)–(Bpz₃)₄ (0.10 g, 0.062 mmol) in acetonitrile (15 cm³), a mixture of [{Rh(μ-Cl)(nbd)}₂] (28 mg, 0.062 mmol) and [{Ir(μ-Cl)(cod)}₂] (41 mg, 0.062 mmol) was added all at once, and the resulting mixture was stirred at room temperature for 3 h. The volatiles were removed under reduced pressure and the residue was extracted with hexanes (20 cm³) and then with diethyl ether (20 cm³). Evaporation of the combined extracts afforded a bright red solid. (0.14 g, 92%). (Found: C, 48.27; H, 6.05; N, 13.67. C₉₈H₁₄₈B₄Ir₂N₂₄Rh₂Si₅ requires C, 48.31; H, 6.12; N, 13.80). ¹H NMR (C₆D₆, δ): 7.84 (s, 6H, CH), 7.72 (s, 12H, CH), 7.59 (s, 6H, CH), 6.10 (s, 6H, CH), 6.00 (s, 6H, CH) (pz), 3.69 (m, 12H, =CH cod + CH nbd), 3.23 (m, 8H, =CH nbd), 2.55 (m, 8H, CH₂ cod), 1.92 (m, 8H, CH₂ cod), 1.85 (m, 24H, CH₂), 1.27 (s, 4H, CH₂ nbd), 1.03 (m, 16H, CH₂), 0.98 (m, 8H, CH₂), 0.24 (s, 12H, Me), 0.22 (s, 12H, Me). ¹³C{¹H} NMR (CDCl₃, 293 K) δ: 139.7, 139.4, 132.5, 132.4, 105.0, 104.4 (pz), 58.1 (d, ³J_{CRh} = 5.0 Hz, CH₂ nbd), 54.5 (=CH cod), 47.9 (CH nbd), 37.5 (m, =CH nbd), 32.9 (CH₂ cod), 24.3, 23.3 (br s, CH₂B), 21.0, 20.8, 20.6, 20.5, 20.4, 19.2, 18.1 (CH₂), –3.2, –3.1 (Me). MALDI-TOF: *m/z* 2435.0 (calcd. 2436.3).

Si[(CH₂)₃SiMe{(CH₂)₃SiMe₂(CH₂)₃Bpz₃Rh(nbd)}]₂]₄ (G(1)–(Bpz₃Rh)₈). To a solution of [{Rh(μ-Cl)(nbd)}₂] (0.13 g, 0.28 mmol) in acetonitrile (10 cm³), solid G(1)–(Bpz₃)₈ (0.25 g,

0.07 mmol) was added, and the resulting mixture was stirred at room temperature for 1 h. The volatiles were removed under reduced pressure and the resulting residue was extracted with hexanes (20 cm³). Evaporation of the solvent afforded **G(1)**–(**Bpz**₃Rh)₈ as a pale yellow solid. (0.29 g, 86%). (Found: C, 52.73; H, 6.60; N, 13.94. C₂₀₈H₃₁₆B₈N₄₈Rh₈Si₁₃ requires C, 52.44; H, 6.69; N, 14.11). ¹H NMR (CDCl₃, δ): 7.62 (s, 24H), 7.54 (s, 24H), 6.16 (s, 24H) (CH pz), 3.78 (m, 16H, CH nbd), 3.31 (m, 32H, =CH nbd), 1.60 (m, 28H, CH₂), 1.35 (m, 14H, CH₂), 1.26 (m, 16H, CH₂ nbd), 0.82 (m, 14H), 0.60 (m, 64H) (CH₂), 0.00 (s, 48H, Me), –0.03 (s, 12H, Me). ¹³C{¹H} NMR (CDCl₃, δ): 139.8, 132.7, 104.4 (pz), 58.5 (d, ³J_{CRh} = 6.4 Hz, CH₂), 47.8 (d, ³J_{CRh} = 2.7 Hz, CH), 38.9 (d, ¹J_{CRh} = 10.4 Hz, =CH) (nbd), 22.5 (br, CH₂B), 20.5, 20.4, 19.9, 18.6, 17.6 (CH₂), –3.2 (Me). MALDI-TOF: *m/z* 4763.7 (calcd. 4763.9).

Si[(CH₂)₃SiMe{(CH₂)₃SiMe{(CH₂)₃SiMe₂(CH₂)₃Bpz₃Rh–(nbd)}₂}]₂]₄ (**G(2)**–(**Bpz**₃Rh)₁₆). To a solution of [{Rh(μ-Cl)(nbd)}₂] (79 mg, 0.18 mmol) in acetonitrile (10 cm³), solid **G(2)**–(**Bpz**₃)₁₆ (0.16 g, 0.02 mmol) was added, and the resulting mixture was stirred at room temperature for 1 h. The volatiles were removed by reduced pressure and the residue was extracted with hexanes (20 cm³). Evaporation of the solvent afforded a pale yellow solid. Yield: 0.18 g (85%). (Found: C, 52.63; H, 6.83; N, 13.56. C₄₃₂H₆₆₈B₁₆N₉₆Rh₁₆Si₂₉ requires C, 52.73; H, 6.84; N, 13.66). ¹H NMR (C₆D₆, δ): 7.70 (s, 48H), 7.63 (s, 48H), 6.13 (s, 48H) (CH pz), 3.71 (m, 32H, CH nbd), 3.26 (m, 64H, =CH nbd), 1.92 (m, 32H, CH₂), 1.79 (m, 84H, CH₂), 1.30 (m, 32H, CH₂ nbd), 0.98 (m, 148H, CH₂), 0.41 (s, 108H, Me), –0.03 (s, 24H, Me). ¹³C{¹H} NMR (C₆D₆, δ): 140.3, 133.0, 105.1 (pz), 58.8 (d, ³J_{CRh} = 5.9 Hz, CH₂), 47.6 (CH), 38.2 (d, ¹J_{CRh} = 10.8 Hz, =CH) (nbd), 23.3 (br, CH₂B), 21.5, 21.2, 21.0, 20.1, 19.9, 19.6, (CH₂), –2.4, –4.0 (Me). ¹¹B{¹H} NMR (C₆D₆, δ): –0.98 (br s). MALDI-TOF: *m/z* 9839 (calcd. 9840.6).

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