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# Unprecedented Hybrid Scorpionate/Phosphine Ligand Able To Be Anchored to Carbosilane Dendrimers

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The synthesis of a novel hybrid pyrazolate/phosphine anionic ligand $[CH_2{=}CHCH_2B(CH_2PPh_2)(pz)_2]^-$ is described. Coordination of this ligand to metals in a *fac* tridentate fashion occurs in the complexes $[CH_2{=}CHCH_2B(CH_2PPh_2)(pz)_2M(cod)]$, prepared by reactions of the lithium salt of the ligand with $[M(\mu\text{-Cl})(cod)]_2$ (M = Rh, Ir). They are pentacoordinated, with the rhodium complex showing a distorted trigonal-bipyramidal structure in the solid state, as determined by X-ray diffraction methods. Furthermore, the ligand has been linked to the periphery of a carbosilane dendrimer, resulting in the polyanionic dendrimer $[Li(TMED)]_4[Si\{(CH_2)_3SiMe_2(CH_2)_3B(CH_2PPh_2)(pz)_2\}_4]$, which leads further to the corresponding metallodendrimer with four rhodium atoms.

Tris(pyrazolyl)borate systems (scorpionates) have been one of the most intensely investigated ligands for decades, comprising interdisciplinary fields that range from biochemistry, materials science, to homogeneous catalysis.[1] The unique chemistry derived from the $\kappa^2$- and $\kappa^3$-coordination modes of these ligands that bind virtually any metal from the Periodic Table[2] has allowed the discovery of new properties emerging upon coordination of the scorpionate ligands to transition metals, such as C−H and C−C activation processes[3] and catalysis[4] among others.

Related anionic borate ligands shifting from hard nitrogen $\sigma$ donor to soft phosphorus $\sigma$ donor/$\pi$ acceptor atoms such as $[PhB(CH_2PR_2)_3]^-$ (R = Ph, $^iPr$) have more recently seen their genesis, creating new systems that have already provided interesting cases of C−H and Si−H bond activation.[5] However, despite the development of several generations of scorpionate ligands and the increasing interest in the synthesis and use of "heteroscorpionate" ligands derived from bis(pyrazolyl)methane,[6] there are few and old examples of boron-based hybrid pyrazolate ligands containing two pyrazolyl bridges and one dimethylamino,[7] or arylmercapto,[8] or alkoxy bridges.[9] With the aim of bringing together hard (N) and soft (P) donor atoms in pyrazolylborate systems, we have designed an efficient synthesis yielding a novel hybrid pyrazolate/phosphine anionic ligand that could lead to new reactivity patterns and provide new possibilities to the scorpionates saga.

Herein we report on the synthetic strategy leading to an allyl bis(pyrazolyl)borate ligand bifunctionalized with a phosphine group that, in addition, can be attached to the periphery of carbosilane dendrimers through the allyl linker to give polyanionic starbursts and, ultimately, neutral metallodendrimers.

Reaction of $CH_2{=}CH{-}CH_2B(O^iPr)_2$ with 1 mol equiv of $[Li(TMED)][CH_2PPh_2]$ (TMED = tetramethylethylenediamine) and 2 mol equiv of pyrazole in refluxing toluene gave the lithium salt of the anionic ligand [Li(TMED)]-

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(1) Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999.

(2) (a) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943. (b) Trofimenko, S. *Polyhedron* **2004**, *23*, 197.

(3) For example, see: (a) Paneque, M.; Poveda, M. L.; Rendón, N.; Mereiter, K. *J. Am. Chem. Soc.* **2004**, *126*, 1610. (b) Álvarez, E.; Gómez, M.; Paneque, M.; Posadas, C. M.; Poveda, M. L.; Rendón, N.; Santos, L. L.; Rojas-Lima, S.; Salazar, V.; Mereiter, K.; Ruiz, C. *J. Am. Chem. Soc.* **2003**, *125*, 1478. (c) Wiley, J. S.; Heinekey, D. M. *Inorg. Chem.* **2002**, *41*, 4961. (d) Slugov, C.; Padilla-Martínez, I.; Sirol, S.; Carmona, E. *Coord. Chem. Rev.* **2001**, *213*, 129.

(4) (a) Trzeciak, A. M.; Ziółkowski, J. *J. Appl. Organomet. Chem.* **2004**, *18*, 124. (b) Morilla, M. E.; Molina, M. J.; Díaz-Requejo, M. M.; Belderraín, T. R.; Nicasio, M. C.; Trofimenko, S.; Pérez, P. J. *Organometallics* **2003**, *22*, 2914. (c) Díaz-Requejo, M. M.; Belderraín, T. R.; Nicasio, M. C.; Trofimenko, S.; Pérez, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 12078. (d) Murtuza, S.; Casagrande, O. L., Jr.; Jordan, R. F. *Organometallics* **2002**, *21*, 1882. (e) Lail, M.; Bell, C. M.; Conner, D.; Cundari, T. R.; Gunnoe, T. B.; Petersen, J. L. *Organometallics* **2004**, *23*, 5007. (f) Lail, M.; Arrowood, B. N.; Gunnoe, T. B. *J. Am. Chem. Soc.* **2003**, *125*, 7506.

(5) (a) Peters, J. C.; Feldman, J. D.; Tilley, T. D. *J. Am. Chem. Soc.* **1999**, *121*, 9871. (b) Turculet, L.; Feldman, J. D.; Tilley, T. D. *Organometallics* **2004**, *23*, 2488. (c) Feldman, J. D.; Peters, J. C.; Tilley, T. D. *Organometallics* **2002**, *21*, 4050.

(6) Otero, A.; Fernández-Baeza, J.; Antiñolo, A.; Tejeda, J.; Lara-Sánchez, A.; Sánchez-Barba, L.; Rodríguez, A. M.; Maestro, M. A. *J. Am. Chem. Soc.* **2004**, *126*, 1330.

(7) Niedenzu, K.; Trofimenko, S. *Inorg. Chem.* **1985**, *24*, 4222.

(8) Thompson, J. S.; Zitzmann, J. L.; Marks, T. J.; Ibers, J. A. *Inorg. Chim. Acta* **1980**, *46*, L101.

(9) Ghosh, P.; Parkin, G. *Chem. Commun.* **1998**, 413.

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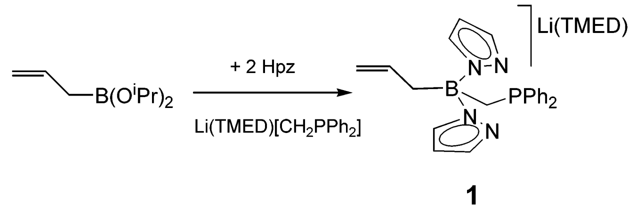
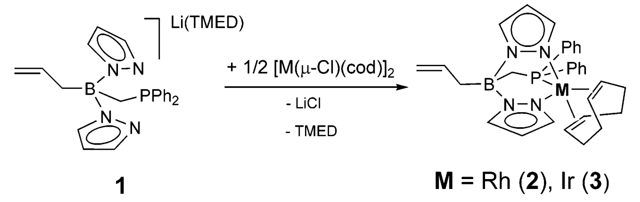
**Scheme 1.** Synthesis of Compound **1**



**Scheme 2.** Synthesis of Mononuclear Diolefin/Scorpionate Complexes



$[CH_2{=}CHCH_2B(CH_2PPh_2)(pz)_2]$ (**1**, pz = pyrazole; Scheme 1), isolated in 56% yield as a white solid.[10]

According to the proposed formula, compound **1** displayed a set of three resonances for the two equivalent pyrazolate rings and for the allyl group, along with the signals from the phosphine and TMED in the $^1H$ and $^{13}C\{^1H\}$ NMR spectra.[10] The purity of **1** was confirmed by elemental analysis, and as expected, the $^{31}P\{^1H\}$ NMR spectrum showed a sole resonance in the phosphine region.

The lithium compound is a new class of tridentate ligand that was used to prepare new rhodium and iridium complexes. Thus, **1** was reacted with the chloro-bridged dinuclear complexes $[M(\mu\text{-}Cl)(cod)]_2$ (cod = 1,5-cyclooctadiene) in toluene to give the compounds $[CH_2{=}CHCH_2B(CH_2PPh_2)(pz)_2M(cod)]$ [M = Rh (**2**), M = Ir (**3**)], isolated as bright yellow and white crystals, respectively, in good yields (Scheme 2).[11]

The mononuclear formulation of **2** and **3** was indicated by the mass spectrum (fast atom bombarment, FAB), which was corroborated by an X-ray crystal structure determination for **2** (Figure 1).[12]

The geometry around the rhodium atom is best described as a slightly distorted trigonal bipyramid where the nitrogen of a pyrazole ring occupies the axial position while the P-donor atom and the nitrogen of the other pyrazole are placed in the equatorial plane. Then, the new ligand adopts the *fac* disposition often found in rhodium diolefin complexes with the classical tris(pyrazolyl)borate ligands in a $\kappa^3$-coordination mode.[13] However, it differs from the situation found in the complex $[PhB(CH_2P^iPr_2)_3]Rh(CO)_2$, in which the coordination geometry of the rhodium atom is better described as a distorted square-based pyramid.[5b] The novel complexes **2** and **3** feature a hybrid situation between a zwitterionic borate counteranion, partially bound to the metallic center by the

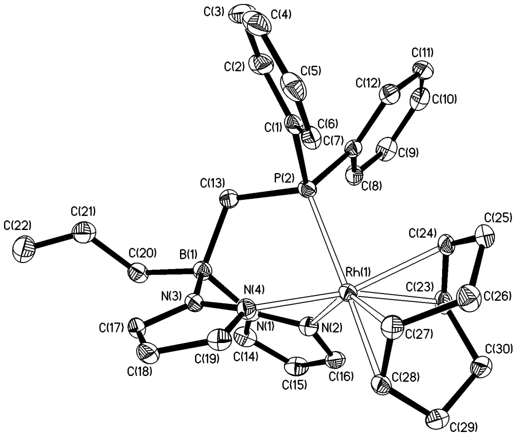


**Figure 1.** ORTEP diagram of **2** with 30% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Rh(1)−N(4) 2.1113(19), Rh(1)−N(2) 2.2650(19), Rh(1)−P(2) 2.3590(7), Rh(1)−M(1) 2.0323(23), Rh(1)−M(2) 1.9982(24), P(2)−C(13) 1.828(2), B(1)−N(1) 1.572(3), B(1)−N(3) 1.563(3), B(1)−C(13) 1.619(3), B(1)−C(20) 1.621(4), C(20)−C(21) 1.491(4), C(21)−C(22) 1.310(4); P(2)−Rh(1)−N(4) 84.41(6), P(2)−Rh(1)−N(2) 85.16(5), P(2)−Rh(1)−M(1) 96.01(8), P(2)−Rh(1)−M(2) 149.27(7), N(2)−Rh(1)−N(4) 84.09(7), N(2)−Rh(1)−M(1) 102.32(9), N(2)−Rh(1)−M(2) 124.49(9), N(4)−Rh(1)−M(1) 173.59(8), N(4)−Rh(1)−M(2) 90.42(9), M(1)−Rh(1)−M(2) 85.97(10), where M(1) and M(2) are the midpoints of the olefinic bonds C(23)−C(24) and C(27)−C(28), respectively.

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(10) Synthesis of **1**. A Schlenk tube was charged with $[Li(TMED)][CH_2PPh_2]$ (1.83 g, 5.69 mmol), toluene (20 mL), and $CH_2CHCH_2B(O^iPr)_2$ (0.97 g, 5.69 mmol) under argon. The mixture was stirred for 15 min, and then pyrazole (0.77 g, 11.34 mmol) was added. The resulting solution was refluxed for 12 h under a vigorous stirring and then evaporated to dryness under vacuum to give a white oily material, which was washed with cold hexanes (2 × 10 mL) to afford a white solid. Yield: 1.81 g (56%). $^1H$ NMR ($C_6D_6$, 300 MHz) $\delta$: 8.00 (d, $J$ = 2.1 Hz, 2H, pz), 7.48 (m, 4H, $H_o$ Ph), 7.16 (d, $J$ = 2.1 Hz, 2H, pz), 7.04 (m, 6H, $H_m + H_p$ Ph), 6.30 (m, 1H, CH allyl), 6.23 (t, $J$ = 2.1 Hz, 2H, pz), 5.13 (d, $J$ = 17.1 Hz, 1H, ${=}CH_2$), 5.03 (d, $J$ = 10.2 Hz, 1H, $=CH_2$), 2.33 (d, 2H, $J$ = 6.9 Hz, $CH_2$), 1.84 (s, 4H, $CH_2$ TMED), 1.83 (s, 14 H, TMED + $CH_2P$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz) $\delta$: 143.2 (d, $^1J_{CP}$ = 14 Hz, $C_{ipso}$ Ph), 141.8 (CH allyl), 138.7, 133.5 (pz), 132.9 (d, $^2J_{CP}$ = 19 Hz, $C_o$ Ph) 127.6 (d, $^3J_{CP}$ = 7 Hz, $C_m$ Ph), 127.3 ($C_p$, Ph), 112.7 ($=CH_2$ allyl), 102.7 (pz), 57.2 ($CH_2$ TMED), 46.0 ($CH_3$ TMED), 29 (br s, $CH_2$ allyl), 24 (br s, $CH_2P$). $^{31}P\{^1H\}$ NMR ($C_6D_6$, 121 MHz) $\delta$: −15.4 (s). Anal. Calcd for $C_{28}H_{39}BLiN_6P$: C, 66.15; H, 7.73; N, 16.53. Found: C, 66.05; H, 7.85; N, 16.49.

(11) Selected spectroscopic and analytical data. Data for complex **2**. $^1H$ NMR ($C_6D_6$, 300 MHz) $\delta$: 7.95 (d, $J$ = 1.8 Hz, 2H), 7.73 (d, $J$ = 2.4 Hz, 2H) (pz), 7.34 (m, 4H, $C_o$ Ph), 6.94 (m, 6H, $H_m + H_p$ Ph), 6.20 (m, 1H, CH allyl), 6.16 (t, $J$ = 2.1 Hz, 2H, pz), 5.18 (dd, $J$ = 17.1 and 2.4 Hz, 1H, $=CH_2$), 5.05 (dd, $J$ = 9.9 and 2.4 Hz, 1H, $=CH_2$) (allyl), 3.58 (m, 4H, =CH cod), 2.41 (m, 4H, $CH_2$ cod), 2.17 (d, $J$ = 6.6 Hz, 2H, $CH_2$ allyl), 1.82 (m, 4H, $CH_2$ cod), 1.31 (d, $^2J_{HP}$ = 13.8 Hz, 2H, $CH_2P$). $^{31}P\{^1H\}$ NMR ($C_6D_6$, 121 MHz) $\delta$: 27.0 (d, $^1J_{PRh}$ = 120.6 Hz). $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75 MHz) $\delta$: 142.0 (pz), 141.5 (CH allyl), 137.0 (d, $^1J_{CP}$ = 37 Hz, $C_{ipso}$ Ph), 133.9 (pz), 133.6 (d, $^2J_{CP}$ = 10 Hz, $C_o$ Ph), 129.6 ($C_p$ Ph), 128.5 ($C_m$ Ph), 114.4 ($=CH_2$ allyl), 105.3 (pz), 77.8 (br s, =CH), 32.3 ($CH_2$ cod), 30.9 (br s, $CH_2$ allyl), 23.2 (br s, $CH_2P$). FAB(+): *m*/*z* (%) 596 ($M^+$, 85), 555 ($M^+$ − allyl, 100), 529 ($M^+$ − pz, 75), 488 ($M^+$ − allyl − pz, 80). Anal. Calcd for $C_{30}H_{35}BN_4PRh$: C, 60.42; H, 5.91; N, 9.40. Found: C, 60.35; H. 5.87; N, 9.23. Data for complex **3**. $^1H$ NMR ($C_6D_6$, 300 MHz) $\delta$: 7.69 (s, 4H, pz), 7.32 (m, 4H, $C_o$ Ph), 6.98 (m, 6H, $H_m + H_p$ Ph), 6.21 (m, 1H, CH allyl), 5.99 (s, 2H, pz), 5.19 (d, $J$ = 16.5 Hz, 1H, $=CH_2$), 5.07 (d, $J$ = 10.2 Hz, 1H, $=CH_2$ allyl), 3.19 (m, 4H, =CH), 2.47 (m, 4H, $CH_2$ cod), 2.13 (d, $J$ = 6.9 Hz, 2H, $CH_2$ allyl), 1.83 (m, 4H, $CH_2$ cod), 1.50 (d, $^2J_{HP}$ = 12.6 Hz, 2H, $CH_2P$). $^{31}P\{^1H\}$ NMR ($C_6D_6$, 121 MHz) $\delta$: −0.75. $^{13}C\{^1H\}$ NMR ($C_6D_6$, 75 MHz) $\delta$: 136.1 (CH allyl), 135.2 (pz), 132.4 (d, $^1J_{CP}$ = 38 Hz, $C_{ipso}$ Ph), 128.8 (pz), 128.5 (d, $^2J_{CP}$ = 11 Hz, $C_o$ Ph), 124.5 ($C_p$ Ph), 109.5 ($=CH_2$ allyl), 100.5 (pz), 54.1 (br s, =CH), 28.2, 25.1 ($CH_2$ cod), 24.0 (br s, $CH_2$ allyl), 15.5 (br s, $CH_2P$). FAB(+): *m*/*z* (%) 685 ($M^+$, 90), 644 ($M^+$ − allyl, 80), 618 ($M^+$ − pz, 100). Anal. Calcd for $C_{30}H_{35}BIrN_4P$: C, 52.55; H, 5.15; N, 8.17. Found: C, 52.41; H. 5.05; N, 8.22.

(12) Crystal data for $C_{30}H_{35}BN_4PRh$: $M$ = 596.31, monoclinic, space group $C2/c$, $a$ = 15.2487(9) Å, $b$ = 10.7799(6) Å, $c$ = 32.9759(19) Å, $\beta$ = 101.6490(10)°, $V$ = 5308.9(5) Å$^3$, $T$ = 100(2) K, $Z$ = 8, $\mu$(Mo K$\alpha$) = 0.710 73 mm$^{-1}$, 16 590 reflections measured, 5784 unique reflections. Final $R_1$ value = 0.0309; $R_w(F^2)$ = 0.0620 for $I \geq 2\sigma(I)$. The corresponding values for all data are $R_1$ = 0.0398 and $R_w(F^2)$ = 0.0640.

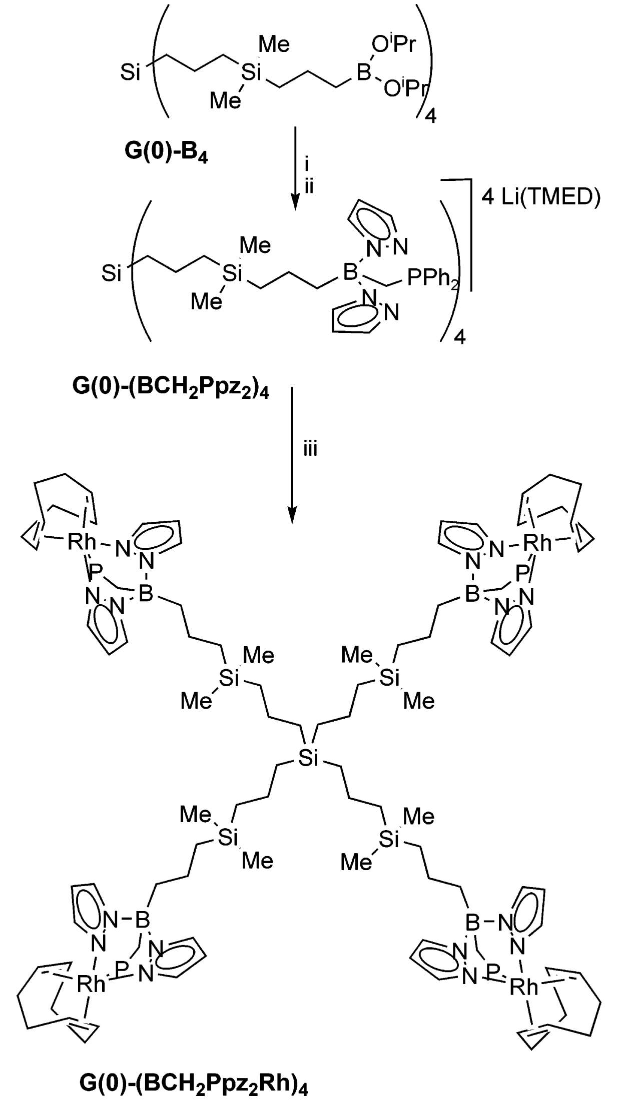
(13) (a) Akita, M.; Ohta, K.; Takahashi, Y.; Hikichi, S.; Moro-oka, Y. *Organometallics* **1997**, *16*, 4121 (b) Bucher, U. E.; Currao, A.; Nesper, R.; Rüegger, H.; Venanzi, L. M.; Younger, E. *Inorg. Chem.* **1995**, *34*, 66.

phosphine group, and a neutral molecule in which there is an efficient resonance delocalization of the borate charge in the pyrazolate rings.

The boron compound $CH_2{=}CH{-}CH_2B(O^iPr)_2$, prepared as described by Venanzi et al.,[14] is a highly versatile reagent, whose allyl group provides the linking to carbosilane dendrimers through a platinum-catalyzed hydrosilylation process. Thus, the core dendrimer $[Si[(CH_2)_3SiMe_2(CH_2)_3B(O^iPr)_2]_4$ (**G(0)-B**$_4$) was prepared quantitatively by reacting the boron compound with $Si[(CH_2)_3SiMe_2H]_4$[15] in the presence of Karstedt's catalyst in toluene. Following the protocol used to prepare **1**, **G(0)-B**$_4$ was reacted with $[Li(TMED)][CH_2PPh_2]$[16] and then with pyrazole in toluene to give the dendrimer $[Li(TMED)]_4[Si\{(CH_2)_3SiMe_2(CH_2)_3B(CH_2PPh_2)(pz)_2\}_4]$ [**G(0)-(BCH$_2$Ppz$_2$)$_4$**; Scheme 3]. This polyanionic dendrimer was found to be very soluble in benzene and polar solvents, and it was characterized by multinuclear NMR spectroscopy ($^1H$ and $^{31}P$) and elemental analysis.[17]

Metallodendrimers resulting from **G(0)-(BCH$_2$Ppz$_2$)$_4$** are easily accessible by treatment with chloro-containing complexes. As an example, **G(0)-(BCH$_2$Ppz$_2$)$_4$** was reacted with 2 mol equiv of the chloro-bridged complex $[Rh(\mu\text{-}Cl)(cod)]_2$ in toluene to give the neutral compound $Si[(CH_2)_3SiMe_2(CH_2)_3B(CH_2PPh_2)(pz)_2Rh(cod)]_4$ [**G(0)-(BCH$_2$Ppz$_2$Rh)$_4$**], isolated as a bright yellow solid in good yield (Scheme 3). This metallodendrimer is a moisture- and air-stable solid, for which analytical, NMR spectroscopic data, and MALDI-TOF spectrometric measurements were found to be in agreement with the proposed structure.[18]

**Scheme 3.** Synthesis of the Polyanionic Hybrid Scorpionate Dendrimer **G(0)-(BCH$_2$Ppz$_2$)$_4$** and the Rhodium Metallodendrimer **G(0)-(BCH$_2$Ppz$_2$Rh)$_4$**[a]



[a] (i) $[Li(TMED)][CH_2PPh_2]$, toluene; (ii) pzH, toluene, reflux. (iii) $[Rh(\mu\text{-}Cl)(cod)]_2$.

In conclusion, we describe here a simple and efficient synthesis for an unprecedented hybrid pyrazolate/phosphine tridentate anionic ligand that may be applied for the preparation of related scorpionate systems. Additionally, this novel ligand bears an allyl group that serves as the linker between the ligand and carbosilane dendrimers. This connection leads eventually to an unusual polyanionic dendrimer, which is an excellent scaffold for the incorporation of transition metals, as confirmed by the preparation of the zeroth generation of a rhodadendrimer.

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**Supporting Information Available:** Crystallographic data in CIF format for complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Bucher, U. E.; Fässler, T. F.; Hunziker, M.; Nesper, R.; Rüegger, H.; Venanzi, L. M. *Gazz. Chim. Ital.* **1995**, *125*, 181.

(15) (a) Chai, M.; Pi, Z.; Tessier, C.; Rinaldi, P. L. *J. Am. Chem. Soc.* **1999**, *121*, 273. (b) Cuadrado, I.; Morán, M.; Losada, J.; Casado, M. C.; Pascual, C.; Alonso, B.; Lobete, F. *Adv. Dendritic Macromol.* **1996**, *3*, 151. (c) Seyferth, D.; Son, D. Y. *Organometallics* **1994**, *13*, 2682.

(16) Fraenkel, G.; Winchester, W. R.; Williard, P. G. *Organometallics* **1989**, *8*, 2308.

(17) **G(0)-(BCH$_2$Ppz$_2$)$_4$**. A Schlenk tube was charged with $[Li(TMED)][CH_2PPh_2]$ (0.96 g, 2.99 mmol) and toluene (10 mL) under argon. A solution of **G(0)-B**$_4$ (0.83 g, 0.75 mmol) in toluene (5 mL) was then added via cannula to give a yellowish solution within 5 min. After stirring for 90 min, solid pyrazole (0.43 g, 6.35 mmol) was added to the reaction vessel, and the resulting mixture was refluxed for 12 h. The volatiles were removed under vacuum, and the oily residue was washed with cold hexanes to afford a off-white solid, which was dried under vacuum. Yield: 1.57 g (85%). $^1H$ NMR ($C_6D_6$, 300 MHz) $\delta$: 7.98 (s, 8H, CH), 7.52 (m, 16H, $C_o$ Ph), 7.38 (s, 8H, CH) (pz), 7.10 (m, 24H, $C_m + C_p$ Ph), 6.31 (s, 8H, CH pz), 1.89 (s, 72H, TMED + $CH_2P$), 1.60 (m, 12H), 0.84 (m, 12H), 0.73 (m, 24H, $CH_2$), 0.04 (s, 24H, $CH_3$). $^{31}P\{^1H\}$ NMR ($C_6D_6$, 121 MHz) $\delta$: −14.7. Anal. Calcd for $C_{132}H_{208}B_4Li_4N_{24}P_4Si_5$: C, 64.28; H, 8.50; N, 13.63. Found: C, 64.13; H, 8.41; N, 13.49.

(18) **G(0)-(BCH$_2$Ppz$_2$Rh)$_4$.** $^1H$ NMR ($C_6D_6$, 300 MHz) $\delta$: 8.11 (s, 8H), 7.89 (s, 8H, pz), 7.54 (m, 16H, $H_o$ Ph), 7.09 (m, 24H, $C_m + C_p$ Ph), 6.36 (s, 8H, pz), 3.74 (m, 16H, ═CH), 2.56 (m, 16H), 1.96 (m, 16H, $CH_2$ cod), 1.76 (m, 16H, $CH_2$), 1.52 (d, $^2J_{HP} = 13.8$ Hz, 8H, $CH_2P$), 0.98 (m, 32H, $CH_2$), 0.24 (s, 24H, $CH_3$). $^{31}P\{^1H\}$ NMR ($C_6D_6$, 121 MHz) $\delta$: 27.7 (d, $^1J_{PRh} = 119.2$ Hz).$^{13}C\{^1H\}$ NMR ($C_6D_6$, 75 MHz) $\delta$: 141.4 (pz), 136.4 (d, $^1J_{CP} = 37$ Hz, $C_{ipso}$ Ph), 133.1 (pz), 132.9, 128.9, 127.8 (Ph), 104.8 (pz), 77.3 (br s, ═CH), 31.9 ($CH_2$, cod), 28.1 (br s, $CH_2$), 21.3 (br s, $CH_2P$), 21.1, 20.8, 20.5, 19.1, 18.0 ($CH_2$), −2.9 ($CH_3$). MALDI-TOF: *m*/*z* 2819.0 (calcd 2818.4). Anal. Calcd for $C_{140}H_{192}B_4N_{16}P_4Rh_4Si_5$: C, 59.66; H, 6.87; N, 7.95. Found: C, 59.45; H, 6.65; N, 7.86