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# Synthesis of Neutral Group 4 Metal–Carboryne Complexes and Their Reactivity toward Unsaturated Molecules

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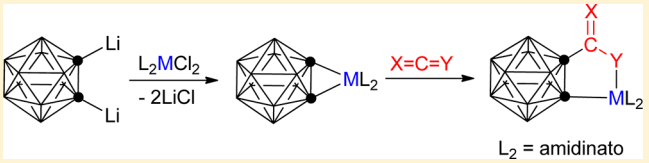
Supporting Information

**ABSTRACT:** A series of neutral group 4 metal–carboryne complexes of the general type $[\eta^2\text{-}R^2C(NR^1)_2]_2M(\eta^2\text{-}C_2B_{10}H_{10})$ were prepared via a salt metathesis reaction of $[\eta^2\text{-}R^2C(NR^1)_2]_2MCl_2$ with $Li_2C_2B_{10}H_{10}$ (M = Ti, Zr, Hf; $R^1$ = $^i$Pr, cyclohexyl, $R^2$ = Me, $^n$Bu, Ph) in high yields. Their structures were confirmed by single-crystal X-ray analyses. They reacted with ketone, nitrile, and heterocumulenes such as carbodiimide, isocyanate, thioisocyanate, carbon disulfide, and phenyl azide to give various monoinsertion products, in which the unsaturated bond inserted into one of the M–$C_{cage}$ bonds, resulting in the formation of heterocycles. However, these metal–carboryne complexes did not show any reactivity toward pyridines, alkynes, and alkenes. The results clearly indicated that $[\eta^2\text{-}R^2C(NR^1)_2]_2M(\eta^2\text{-}C_2B_{10}H_{10})$ shared some common properties with $Cp_2Zr(\eta^2\text{-}C_2B_{10}H_{10})$ in reaction with heterocumulenes; on the other hand, they showed significant differences in reaction with pyridines, alkynes, and alkenes. These may be mainly ascribed to ligand steric effects.




## INTRODUCTION

Carborynes (1,2-dehydro-*o*-carboranes) are reactive intermediates, which can undergo [4 + 2] addition, [2 + 2] addition, ene reaction, and C–H bond insertion reactions.[1] They can be stabilized by transition metals to form metal–carboryne complexes.[2] The chemical properties of these complexes depend upon the nature of the transition metals.[3] For example, Ni-carboryne can react with alkynes[4] and alkenes[5] to generate a series of cycloaddition and coupling products in both stoichimetric and catalytic manners, but does not show any activity toward other polar unsaturated molecules. In contrast, in situ generated zirconocene–carboryne $Cp_2Zr(\eta^2\text{-}C_2B_{10}H_{10})$ from $Cp_2Zr(\mu\text{-}Cl)(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ reacts readily with alkynes,[6] alkenes,[7] pyridines,[8] or polar unsaturated organic substrates[9] such as isonitrile, nitrile, and azide to give monoinsertion products. However, many attempts to isolate $Cp_2Zr(\eta^2\text{-}C_2B_{10}H_{10})$ failed.

On the other hand, it is well documented that ligands play a dominate role in both physical and chemical properties of a given metal complex.[10] We are interested in the ligand effects on the chemical properties of Zr-carboryne complexes. Our previous work focuses on the cyclopentadienyl ligand, and the proposed intermediate $Cp_2Zr(\eta^2\text{-}C_2B_{10}H_{10})$ is not isolable. To this end, we have extended our research to structurally well-defined neutral Zr-carboryne complexes and report herein the synthesis, structure, and reactivity of a series of neutral group 4 metal–carboryne complexes bearing amidinato ligands L, $(\eta^2\text{-}C_2B_{10}H_{10})M(L)_2$. Similarities and differences between $(\eta^2\text{-}C_2B_{10}H_{10})ZrCp_2$ and $(\eta^2\text{-}C_2B_{10}H_{10})Zr(L)_2$ in reactions with unsaturated molecules are also discussed.

## RESULTS AND DISCUSSION

**Synthesis.** Salt metathesis between $Li_2C_2B_{10}H_{10}$ and metal halides is a useful method for the preparation of metal–carboryne complexes.[11] The starting materials, diamidinato group 4 metal dichloride complexes $MCl_2(L)_2$ (L = $[\eta^2\text{-}R^2C(NR^1)_2]$), were prepared via reaction of $MCl_4$ with 2 equiv of lithium diamidinate that was generated in situ from the corresponding carbodiimide and $R^2Li$ in ether (see Supporting Information). Treatment of $Li_2C_2B_{10}H_{10}$ with 1 equiv of $MCl_2(L)_2$ in toluene at 0 °C gave, after workup, group 4 metal–carboryne complexes $(\eta^2\text{-}C_2B_{10}H_{10})M(L)_2$ (M = Zr, $R^1$ = Cy, $R^2$ = Me (**2a**);[12] M = Zr, $R^1$ = Cy, $R^2$ = Ph (**2b**);[12] M = Zr, $R^1$ = Cy, $R^2$ = $^n$Bu (**2c**); M = Ti, $R^1$ = Cy, $R^2$ = Ph (**2d**); M = Zr, $R^1$ = $^i$Pr, $R^2$ = Me (**2e**); M = Zr, $R^1$ = $^i$Pr, $R^2$ = Ph (**2f**); M = Zr, $R^1$ = $^i$Pr, $R^2$ = $^n$Bu (**2g**); M = Ti, $R^1$ = $^i$Pr, $R^2$ = $^n$Bu (**2h**); M = Hf, $R^1$ = $^i$Pr, $R^2$ = $^n$Bu (**2i**)) as yellow or colorless crystals in 60–72% isolated yields using the method developed in our laboratory (Scheme 1).[12]

Complexes **2a–i** are very sensitive to moisture and air, though very thermally stable. No decomposition is observed in refluxing toluene for several days. They are soluble in toluene, pyridine, and THF, but insoluble in diethyl ether and hexane.

Complexes **2a–i** were fully characterized by various spectroscopic techniques and elemental analyses. The $^1$H NMR spectra, which displayed the signals of amidinato ligands and broad peaks attributable to cage B–H, did not give much

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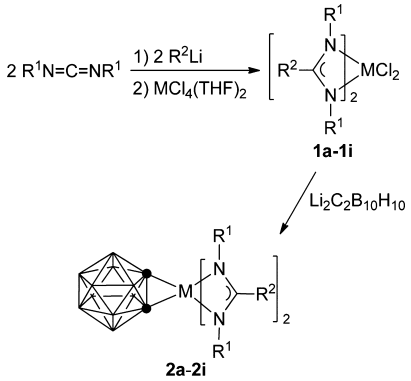
**Scheme 1. Preparation of Group 4 Metal−Carboryne Complexes**

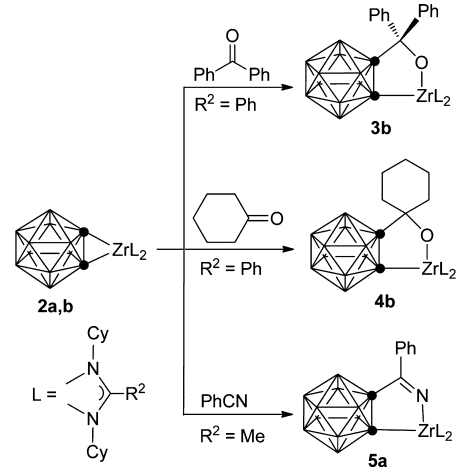



information on the solution structures. Their $^{13}C$ NMR spectra showed one peak in the region 101−116 ppm assignable to the cage carbons and one resonance in the region 177−182 ppm attributable to the quaternary carbon of the amidinato ligands, in addition to the other alkyl or aryl resonances. Their $^{11}B$ NMR spectra displayed a 4:4:2 pattern spanning a range from −3.0 to −16.0 ppm. The molecular structures of **2e**, **2g**, **2h**, and **2i** were further confirmed by single-crystal X-ray analyses (vide infra).

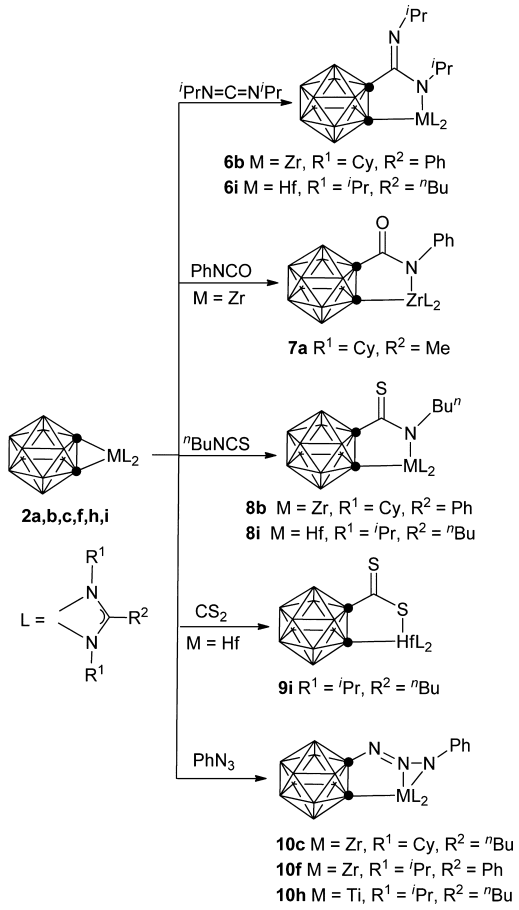
**Reactivity.** The reactivity of the above group 4 metal−carboryne complexes toward various kinds of unsaturated molecules was examined. Complex **2b** reacted with 1 equiv of diphenyl ketone or cyclohexanone in toluene at room temperature to give the monoinsertion products, five-membered heterocycle $[\eta^2\text{-CyNC(Ph)NCy}]_2\text{Zr}[\sigma{:}\sigma\text{-}\{\text{OC(Ph)}_2\text{C}_2\text{B}_{10}\text{H}_{10}\}]$ (**3b**) or $[\eta^2\text{-CyNC(Ph)NCy}]_2\text{Zr}[\sigma{:}\sigma\text{-}\{\text{OC}[\text{-(CH}_2)_5\text{-}]\text{-C}_2\text{B}_{10}\text{H}_{10}\}]$ (**4b**) in >87% isolated yield. Reaction of **2a** with 1 equiv of PhCN in toluene at room temperature afforded $[\eta^2\text{-CyNC(Me)NCy}]_2\text{Zr}[\sigma{:}\sigma\text{-}\{[\text{N=C(Ph)C}_2\text{B}_{10}\text{H}_{10}\}]$ (**5a**) in 76% yield (Scheme 2). They were inert toward an excess amount of substrates, and no multi-insertion products were observed.

Reaction of **2b** or **2i** with 1 equiv of carbodiimide $^i$PrN=C=NPr$^i$ in toluene at room temperature generated the monoinsertion products $[\eta^2\text{-CyNC(Ph)NCy}]_2\text{M}[\sigma{:}\sigma\text{-}\{[^i\text{PrNC(=NPr}^i\text{)C}_2\text{B}_{10}\text{H}_{10}\}]$ (M = Zr (**6a**), Hf (**6i**)) in >90% yields (Scheme 3). Interaction of **2a** with 1 equiv of PhNCO in toluene at room temperature gave the C=N insertion rather than the C=O insertion product, $[\eta^2\text{-CyNC(Me)NCy}]_2\text{Zr}[\sigma{:}\sigma\text{-}\{[\text{PhNC(=O)C}_2\text{B}_{10}\text{H}_{10}\}]$ (**7a**), in 93% yield. This is different from the literature reports, in which the C=O inserts into M−C/M−N bonds.[13] It was noted that **7a** did not react further with PhNCO. Treatment of **2b** or **2i** with 1 equiv of $^n$BuNCS in toluene at room temperature yielded again the C=N insertion products $[\eta^2\text{-CyNC(Ph)NCy}]_2\text{Zr}[\sigma{:}\sigma\text{-}\{[^n\text{BuNC(=S)-C}_2\text{B}_{10}\text{H}_{10}\}]$ (**8b**) and $[\eta^{2\text{-}i}\text{PrNC(}^n\text{Bu)N}^i\text{Pr}]_2\text{Hf}[\sigma{:}\sigma\text{-}\{[^n\text{BuNC-(=S)C}_2\text{B}_{10}\text{H}_{10}\}]$ (**8i**) in ∼80% yields. These results may be ascribed to the stability of the insertion products since the C=O or C=S insertion species bearing an exocyclic imino group are less stable than the C=N insertion ones **7a**, **8b**, and **8i**.

**Scheme 2. Reaction of Zr-Carboryne Complexes with Ketone and Nitrile**




**Scheme 3. Reaction of Group 4 Metal−Carboryne Complexes with Heterocumulenes**




Reaction of **2i** with an excessive amount of $CS_2$ in refluxing toluene in a closed vessel gave the monoinsertion product $[\eta^{2\text{-}i}\text{PrNC(Bu}^n\text{)NPr}^i]_2\text{Hf}[\sigma{:}\sigma\text{-}\{[\text{SC(=S)C}_2\text{B}_{10}\text{H}_{10}\}]$ (**9i**) in 60% yield, whereas no reaction was observed at room temperature according to the $^{11}B$ NMR spectrum (Scheme 3). Reaction of **2c**, **2f**, or **2h** with excessive $PhN_3$ afforded the monoinsertion products $[\eta^2\text{-CyNC(}^n\text{Bu)NCy}]_2\text{Zr}[\eta^2{:}\sigma\text{-1-PhN=N-N-1,2-C}_2\text{B}_{10}\text{H}_{10}]$ (**10c**), $[\eta^{2\text{-}i}\text{PrNC(Ph)NPr}^i]_2\text{Zr-}[\eta^2{:}\sigma\text{-1-PhN=N-N-1,2-C}_2\text{B}_{10}\text{H}_{10}]$ (**10f**), or $[\eta^{2\text{-}i}\text{PrNC(}^n\text{Bu)-}$


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**Table 1. Selected Bond Lengths (Å) and Angles (deg) for Metal−Carboryne Complexes 2**

| compd (M) | av M−$C_{cage}$ | $C_{cage}$−$C_{cage}$ | av M−N | $C_{cage}$−M−$C_{cage}$ | av N−M−N |
|---|---|---|---|---|---|
| **2e** (Zr) | 2.324(3) | 1.668(6) | 2.233(2) | 42.1(1) | 59.8(1) |
| **2g** (Zr) | 2.271(2) | 1.685(4) | 2.201(1) | 43.6(1) | 60.3(1) |
| **2h** (Ti) | 2.137(4) | 1.625(9) | 2.067(2) | 44.7(2) | 63.3(1) |
| **2i** (Hf) | 2.258(2) | 1.696(6) | 2.187(2) | 44.1(2) | 60.7(1) |

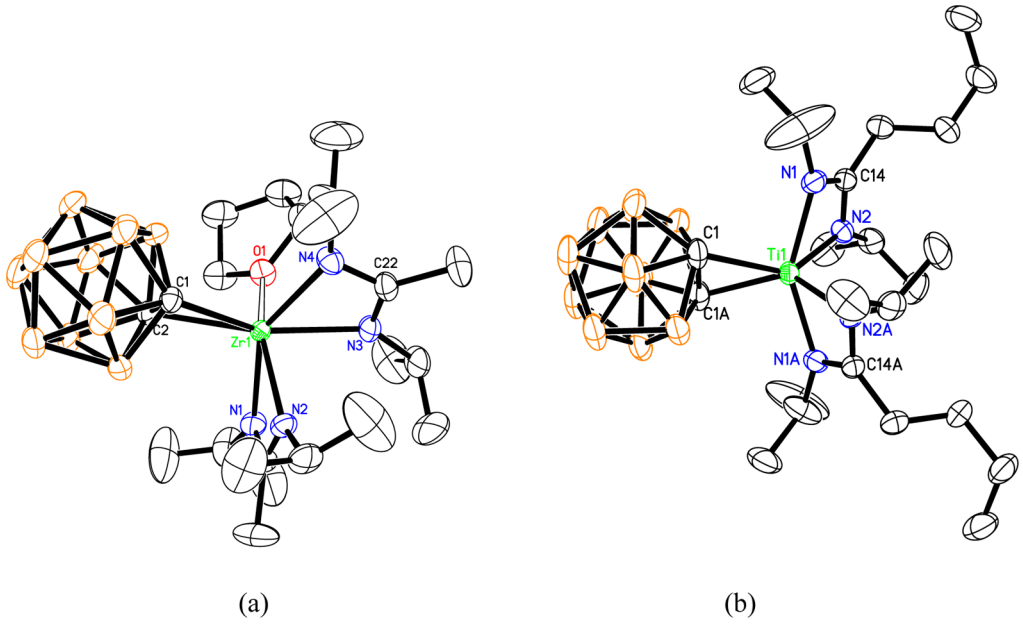


**Figure 1.** Molecular structures of (a) **2e** and (b) **2h**.

$NPr^i]_2Ti[\eta^2{:}\sigma$-1-PhN═N-N-1,2-$C_2B_{10}H_{10}]$ (**10h**) in ∼80% yields, which is similar to that of $Cp_2Zr(\mu$-Cl)$(\mu$-$C_2B_{10}H_{10})$Li-$(OEt_2)_2$.[9]

The insertion products **3**−**10** are moisture sensitive. They are soluble in toluene, pyridine, and THF, but insoluble in diethyl ether and hexane.

The aforementioned results clearly show that the polar unsaturated molecules can insert into the group 4 metal−carbon(cage) bond in **2** to form the monoinsertion products regardless of the nature of group 4 metals. No double insertion products are observed even under forced reaction conditions in the presence of an excess amount of substrates. Significantly different from in situ generated $Cp_2Zr(\eta^2$-$C_2B_{10}H_{10})$, these amidinato-ligated neutral group 4 metal−carboryne complexes show no reactivity toward internal alkynes, alkenes, and pyridine derivatives even under forced reaction conditions, suggesting that co-ligands play a crucial role in the chemical properties of metal−carboryne complexes.

A question arises whether electronic or steric factors dominate the differences in the above reactions. It is documented that Cp is a $6e^-$ donor, whereas amidinato anions are $4e^-$ donors. The latter ligands are expected to have polarized M−N bonds, leading to more electrophilic metal centers. However, their group 4 metal complexes $[R^1NC(R^2)NR^1]_2MCl_2$ and $[R^1NC(R^2)NR^1]_2MMe_2$ (M = Ti, Zr, and Hf; $R^1$, $R^2$ = alkyls) show lower catalytic activities than the metallocene analogues $Cp_2MCl_2/Cp_2MMe_2$ in ethylene polymerization. This unexpected result has been ascribed to the larger steric effect of bis(amidinate) ligands than that of biscyclopentadienyls.[14] In this regard, the differences in reactivities between $(\eta^2$-$C_2B_{10}H_{10})ZrCp_2$ and $(\eta^2$-$C_2B_{10}H_{10})$-$Zr[R^1NC(R^2)NR^1]_2$ may be best ascribed to steric effects of co-ligands, as $\pi$-coordination of alkenes/alkynes to group 4 metals requires a larger vacant side.

Complexes **3**−**10** were fully characterized by $^1H$, $^{13}C$, and $^{11}B$ NMR and IR spectroscopy as well as elemental analyses. The $^{11}B$ NMR spectra showed different patterns from their parent metal−carboryne complexes due to the changes in the molecular symmetry of the insertion products. The characteristic cage carbon atoms were observed in a range from 73.2 to 111.4 ppm as two peaks, which were also very different from their parent carboryne complexes.

**Structure.** Complexes **2e**, **2g**, **2h**, and **2i** were further confirmed by single-crystal X-ray analyses. Their key structural parameters are compiled in Table 1. They share a similar core structure in which the group 4 metal atom is $\eta^2$-bound to two amidinato ligands and one carboryne moiety. An additional THF coordination is observed in the solid-state structure of **2e**. The representative structures of **2e** and **2h** are shown in Figure 1. As the recrystallization conditions for all complexes are identical, the coordination of THF to the Zr atom in **2e** might be simply ascribed to the crystal packing requirements. On the other hand, the structure of **2e** could be viewed as a model complex of the reaction intermediates for the insertion of unsaturated molecules into the M−C bond in M-carboryne complexes.

The M−C(cage)/C(cage)−C(cage)/M−N distances and C(cage)−M−C(cage)/N−M−N angles found in **2** (Table 1) are similar to each other if the differences in ionic radii of group 4 metals are taken into consideration. These measured values are very close to those reported for Zr-carboryne complexes.[12]

The molecular structures of monoinsertion products **3**−**9** contain a common structural motif of a five-membered heterocycle and adopt a similar geometry, in which the group 4


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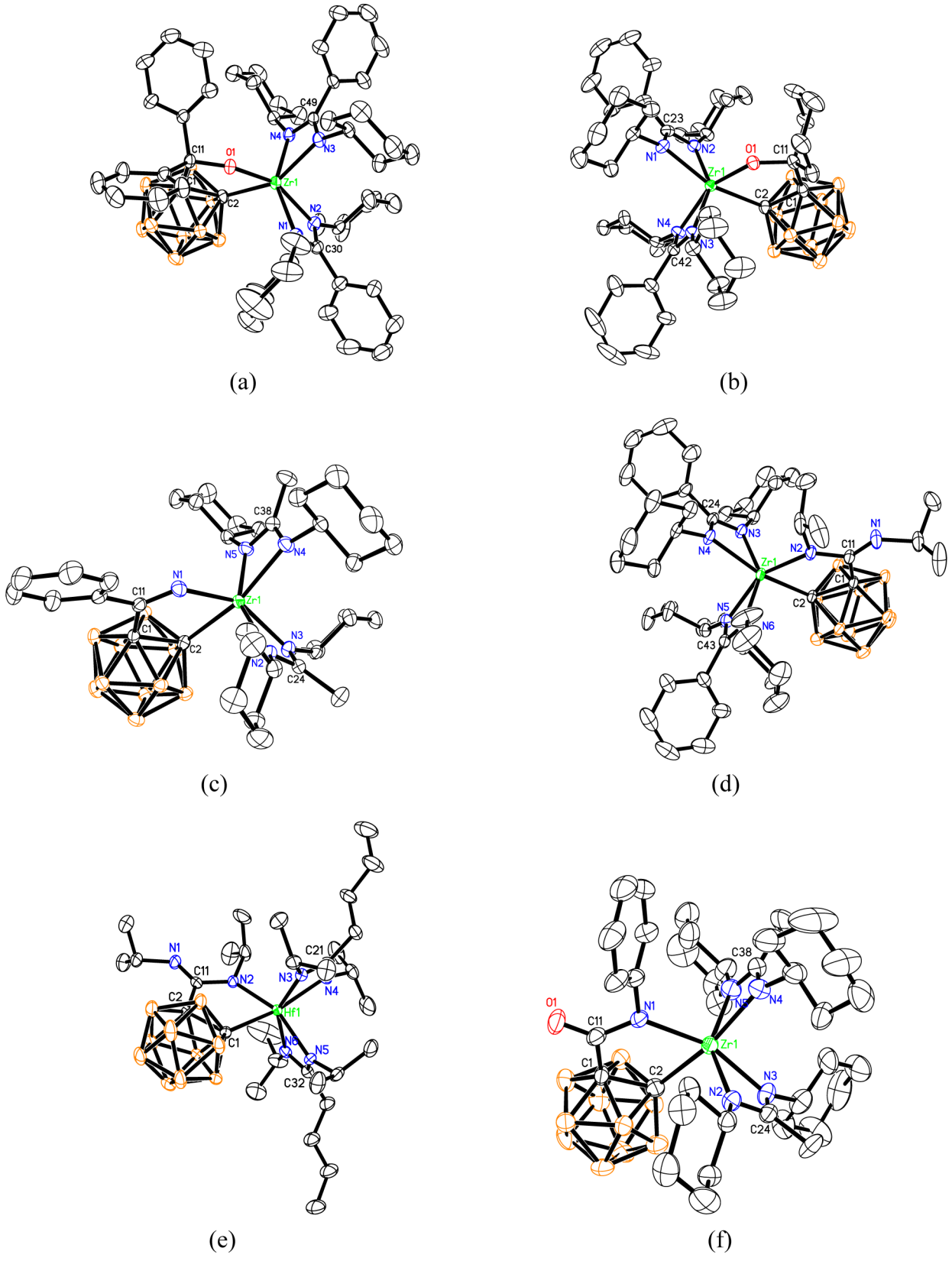


**Figure 2.** continued


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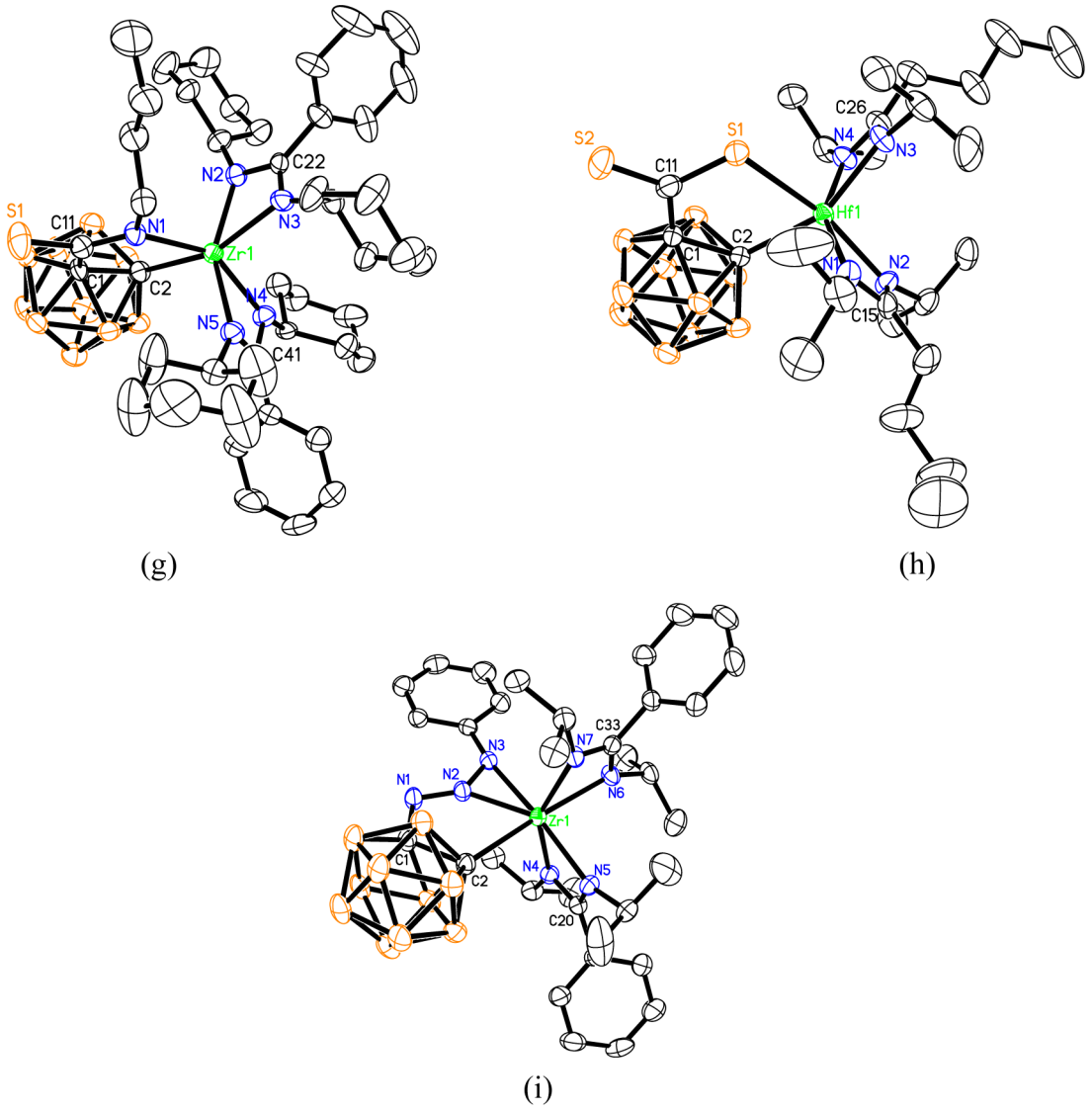
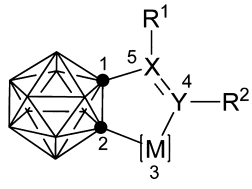



**Figure 2.** Molecular structures of (a) **3b**, (b) **4b**, (c) **5a**, (d) **6b**, (e) **6i**, (f) **7a**, (g) **8b**, (h) **9i**, and (i) **10f**.

**Table 2. Selected Bond Lengths (Å) and Angles (deg) for Monoinsertion Products**




| compd (M) | M−C(2) | C(1)−C(2) | C(1)−X(5) | Y(4)−X(5) | M−Y(4) | av M−$N_{amidinato}$ | C(2)−M−Y(4) | av $N_{amidinato}$−M−$N_{amidinato}$ |
|---|---|---|---|---|---|---|---|---|
| **3b** (Zr) | 2.371(6) | 1.710(7) | 1.595(7) | 1.413(6) | 1.954(3) | 2.223(5) | 73.7(2) | 60.0(2) |
| **4b** (Zr) | 2.402(3) | 1.711(5) | 1.556(5) | 1.421(4) | 1.931(2) | 2.223(3) | 74.1(1) | 60.0(1) |
| **5a** (Zr) | 2.413(4) | 1.679(5) | 1.508(6) | 1.383(5) | 2.089(3) | 2.220(5) | 74.3(1) | 59.8(1) |
| **6b** (Zr) | 2.396(4) | 1.695(6) | 1.519(7) | 1.389(6) | 2.077(4) | 2.241(5) | 72.7(2) | 59.5(2) |
| **6i** (Hf) | 2.349(4) | 1.703(6) | 1.534(6) | 1.387(6) | 2.099(4) | 2.208(4) | 73.9(2) | 60.5(1) |
| **7a** (Zr) | 2.389(9) | 1.658(12) | 1.509(11) | 1.380(11) | 2.208(7) | 2.207(7) | 74.3(3) | 60.4(3) |
| **8b** (Zr) | 2.383(7) | 1.680(10) | 1.522(10) | 1.330(9) | 2.383(7) | 2.207(7) | 74.3(2) | 60.9(3) |
| **9i** (Hf) | 2.340(5) | 1.669(6) | 1.514(7) | 1.725(6) | 2.572(1) | 2.168(4) | 77.4(1) | 61.3(2) |
| **10f** (Zr) | 2.506(3) | 1.728(5) | 1.449(4) | 1.285(4) | 2.137 (3) | 2.218(3) | 66.2(1) | 60.3(1) |

metal atom is $\eta^2$-bound to two amidinato ligands and $\sigma$-bound to one cage carbon atom and one heteroatom in a propeller-like geometry, as shown in Figure 2. For complex **10f**, an additional intramolecular coordination of an exo-nitrogen atom to the Zr atom at a distance of 2.330(3) Å is observed, which is similar to that found in $Cp_2Zr[\eta^2{:}\sigma\text{-}(PhNN{=}N)(C_2B_{10}H_{10})]$.[9] This extra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coordination bond leads to the elongated bond distances around the Zr atom.

Table 2 lists the key structural parameters of **3**−**10**. It is noted that the five atoms of the heterocycle in these insertion products are almost coplanar, with a sum of the five interior angles of ca. 537°. They have very comparable structural parameters around the group 4 metals. The observed M−C(cage) and cage C−C distances are longer than the corresponding values of their parent complexes, but are similar to those found in group 4 metal−carboranyl complexes.[12,15]

## CONCLUSION

A series of neutral group 4 metal−carboryne complexes were synthesized via a salt metathesis reaction of (amidinato)$_2$MCl$_2$ with $Li_2C_2B_{10}H_{10}$. Single-crystal X-ray analyses show that they have similar structures to $\eta^2$-carboryne coordination regardless of the metal size. They reacted with polar unsaturated molecules such as ketone, nitrile, carbodiimide, isocyanate, thioisocyanate, carbon disulfide, and azide to give monoinsertion products. No double-insertion products were observed. However, they did not show any activities toward pyridines, alkynes, and alkenes. These results indicated that complexes **2** exhibited a similar reactivity pattern to that of $Cp_2Zr(\mu\text{-Cl})(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ in reaction with polar unsaturated molecules;[9] on the other hand, **2** demonstrated significantly different properties from $Cp_2Zr(\mu\text{-Cl})(\mu\text{-}C_2B_{10}H_{10})Li(OEt_2)_2$ in reaction with pyridines, alkenes, and alkynes.[6−8] These differences may be best ascribed to steric effects imposed by amidonato ligands.

## EXPERIMENTAL SECTION

**General Procedures.** $^n$BuLi was added under an atmosphere of dry nitrogen with the rigid exclusion of air and moisture using standard Schlenk techniques. Other experiments were performed in a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. $^1$H NMR spectra were recorded on either a Bruker DPX 300 spectrometer at 300 MHz or a Bruker DPX 400 spectrometer at 400 MHz. $^{13}$C{$^1$H} NMR spectra were recorded on either a Bruker DPX 300 spectrometer at 75 MHz or a Bruker DPX 400 spectrometer at 100 MHz. $^{11}$B{$^1$H} NMR spectra were recorded on either a Bruker DPX 300 spectrometer at 96 MHz or a Varian Inova 400 spectrometer at 128 MHz. All chemical shifts were reported in $\delta$ units with reference to the residual protons and carbons of the deuterated solvents for proton and carbon chemical shifts and to external $BF_3{\cdot}OEt_2$ (0.00 ppm) for boron chemical shifts. Infrared spectra were obtained from KBr pellets prepared in the glovebox on a Perkin-Elmer 1600 Fourier transform spectrometer. Elemental analyses were performed by the Analytical Laboratory of the Shanghai Institute of Organic Chemistry, CAS, China. Complexes **2a**,[12] **2b**,[12] and [$\eta^2$-R$^1$NC(R$^2$)-NR$^1$]$_2$MCl$_2$ were prepared according to literature methods[16,17] or modified methods. All other chemicals were purchased from either Sigma-Aldrich or Acros Chemical Co. and used as received unless otherwise specified.

*Preparation of [$\eta^2$-CyNC(Bu$^n$)NCy]$_2$Zr($\eta^2$-$C_2B_{10}H_{10}$) (**2c**).* To a stirring solution of *o*-$C_2B_{10}H_{12}$ (0.72 g, 5.00 mmol) in diethyl ether (30 mL) was slowly added $^n$BuLi (6.3 mL, 10.00 mmol, 1.6 M in hexane) at 0 °C, and the mixture was stirred at room temperature for 1 h. After removal of the solvent under vacuum, the residue was suspended in toluene (30 mL), to which was slowly added a toluene solution (20 mL) of [$\eta^2$-CyNC(Bu$^n$)NCy]$_2$ZrCl$_2$ (3.45 g, 5.00 mmol) at 0 °C. The reaction mixture was then stirred at room temperature for 24 h. After filtration, the precipitate was washed with hot toluene (3 × 10 mL). Removal of the solvent from the combined toluene solutions gave a crude product. Recrystallization from THF/hexane (30 mL, 1/5 in v/v) at room temperature afforded **2c** as yellow crystals (3.31 g, 87%). $^1$H NMR (benzene-$d_6$): $\delta$ 3.27 (m, 4H, NC*H*), 2.18 (m, 4H, C$H_2$), 1.81 (m, 24H, C$H_2$), 1.53 (m, 4H, C$H_2$), 1.45 (m, 4H, C$H_2$), 1.26 (m, 16H, C$H_2$), 0.80 (t, $J$ = 7.2 Hz, 6H, C$H_3$). $^{13}$C{$^1$H} NMR (benzene-$d_6$): $\delta$ 182.0 (NCN), 104.2 (cage *C*), 57.8 (NCH), 35.3, 35.0, 29.4, 26.3, 26.2, 25.4, 23.2, 13.6 (CH$_2$ and CH$_3$). $^{11}$B{$^1$H} NMR (benzene-$d_6$): $\delta$ −0.1 (4B), −6.5 (4B), −14.2 (2B). IR (KBr, cm$^{-1}$): $\nu$ 2564 (BH). Anal. Calcd for $C_{36}H_{72}B_{10}N_4Zr$ (**2c**): C, 56.87; H, 9.54; N, 7.37. Found: C, 56.74; H, 9.26; N, 7.28.

*Preparation of [$\eta^2$-CyNC(Ph)NCy]$_2$Ti($\eta^2$-$C_2B_{10}H_{10}$) (**2d**).* This complex was prepared as purple crystals from $Li_2C_2B_{10}H_{10}$ [prepared in situ from *o*-$C_2B_{10}H_{12}$ (0.72 g, 5.00 mmol) and $^n$BuLi (6.3 mL, 10.00 mmol, 1.6 M in hexane)] and [$\eta^2$-CyNC(Ph)NCy]$_2$TiCl$_2$ (3.43 g, 5.00 mmol) in toluene (40 mL) using the same procedure reported for **2c**: yield 2.73 g (72%). $^1$H NMR (benzene-$d_6$): $\delta$ 7.28 (m, 2H), 7.08 (m, 8H), 3.48 (m, 4H, NC*H*), 2.04 (m, 4H), 1.90 (m, 4H), 1.59 (m, 16H), 1.37 (m, 4H), 0.99 (m, 12H) (Cy). $^{13}$C{$^1$H} NMR (benzene-$d_6$): $\delta$ 177.6 (NCN), 132.0, 129.9, 128.9, 127.3, 127.0 (phenyl *C*), 107.0 (cage *C*), 61.4 (NCH), 34.8, 34.7, 26.2, 25.5 (CH$_2$). $^{11}$B{$^1$H} NMR (benzene-$d_6$): $\delta$ −2.4 (4B), −7.2 (4B), −14.9 (2B). IR (KBr, cm$^{-1}$): $\nu$ 2568 (BH). Anal. Calcd for $C_{40}H_{64}B_{10}N_4Ti$ (**2d**): C, 63.47; H, 8.52; N, 7.40. Found: C, 63.50; H, 8.60; N, 7.19.

*Preparation of [$\eta^2$-$^i$PrNC(Me)NPr$^i$]$_2$Zr($\eta^2$-$C_2B_{10}H_{10}$)(THF) (**2e**).* This complex was prepared as yellow crystals from $Li_2C_2B_{10}H_{10}$ [prepared in situ from *o*-$C_2B_{10}H_{12}$ (0.72 g, 5.00 mmol) and $^n$BuLi (6.3 mL, 10.00 mmol, 1.6 M in hexane)] and [$\eta^2$-$^i$PrNC(Me)NPr$^i$]$_2$ZrCl$_2$ (2.22 g, 5.00 mmol) in toluene (30 mL) using the same procedure reported for **2c**: yield 2.06 g (70%). $^1$H NMR (benzene-$d_6$): $\delta$ 3.68 (m, 4H, THF), 3.49 (m, 4H, NC*H*), 1.46 (s, 6H, C$H_3$), 1.37 (m, 4H, THF), 1.13 (d, $J$ = 6.3 Hz, 12H, C$H_3$), 1.00 (d, $J$ = 6.6 Hz, 12H, C$H_3$). $^{13}$C{$^1$H} NMR (benzene-$d_6$): $\delta$ 177.3 (NCN), 104.2 (cage *C*), 71.6 (THF), 48.9 (NCH), 25.1, 24.5, 24.2, 12.9 ($^i$Pr + THF). $^{11}$B{$^1$H} NMR (benzene-$d_6$): $\delta$ −1.4 (4B), −6.9 (4B), −13.8 (2B). IR (KBr, cm$^{-1}$): $\nu$ 2556 (BH). Anal. Calcd for $C_{18}H_{52}B_{10}N_4Zr$ (**2e** − THF): C, 41.91; H, 8.60; N, 10.86. Found: C, 42.21; H, 8.82; N, 10.67.

*Preparation of [$\eta^2$-$^i$PrNC(Ph)NPr$^i$]$_2$Zr($\eta^2$-$C_2B_{10}H_{10}$)(THF) (**2f**).* This complex was prepared as yellow crystals from $Li_2C_2B_{10}H_{10}$ [prepared in situ from *o*-$C_2B_{10}H_{12}$ (0.72 g, 5.00 mmol) and $^n$BuLi (6.3 mL, 10.00 mmol, 1.6 M in hexane)] and [$\eta^2$-$^i$PrNC(Ph)NPr$^i$]$_2$ZrCl$_2$ (2.85 g, 5.00 mmol) in toluene (30 mL) using the same procedure reported for **2c**: yield 3.24 g (91%). $^1$H NMR (benzene-$d_6$): $\delta$ 7.29 (m, 2H), 7.17 (m, 8H) (phenyl *H*), 4.06 (m, 4H, THF), 3.56 (m, 4H, NC*H*), 1.54 (m, 4H, THF), 1.23 (d, $J$ = 6.6 Hz, 12H, C$H_3$), 1.22 (d, $J$ = 6.3 Hz, 12H, C$H_3$). $^{13}$C{$^1$H} NMR (benzene-$d_6$): $\delta$ 178.7 (NCN), 133.0, 129.3, 129.1, 128.7, 126.2, 125.8 (phenyl *C*), 104.6 (cage *C*), 72.7 (THF), 50.5 (NCH), 25.2, 24.8 ($^i$Pr + THF). $^{11}$B{$^1$H} NMR (benzene-$d_6$): $\delta$ −0.7 (4B), −6.5 (4B), −13.9 (2B). IR (KBr, cm$^{-1}$): $\nu$ 2567 (BH). Anal. Calcd for $C_{32}H_{56}B_{10}N_4OZr$ (**2f**): C, 53.97; H, 7.93; N, 7.87. Found: C, 53.66; H, 7.93; N, 7.62.

*Preparation of [$\eta^2$-$^i$PrNC(Bu$^n$)NPr$^i$]$_2$Zr($\eta^2$-$C_2B_{10}H_{10}$) (**2g**).* This complex was prepared as light yellow crystals from $Li_2C_2B_{10}H_{10}$ [prepared in situ from *o*-$C_2B_{10}H_{12}$ (0.72 g, 5.00 mmol) and $^n$BuLi (6.3 mL, 10.00 mmol, 1.6 M in hexane)] and [$\eta^2$-$^i$PrNC(Bu$^n$)NPr$^i$]$_2$ZrCl$_2$ (2.64 g, 5.00 mmol) in toluene (30 mL) using the same procedure reported for **2c**: yield 2.79 g (93%). $^1$H NMR (benzene-$d_6$): 3.47 (m, 4H, NC*H*), 2.01 (t, $J$ = 8.1 Hz, 4H, C$H_2$), 1.32 (m, 4H, C$H_2$), 1.19 (d, $J$ = 6.6 Hz, 12H, C$H_3$), 1.13 (d, $J$ = 6.3 Hz, 12H, C$H_3$), 1.11 (m, 4H, C$H_2$), 0.77 (t, $J$ = 7.2 Hz, 6H, C$H_3$). $^{13}$C{$^1$H} NMR (benzene-$d_6$): $\delta$ 181.7 (NCN), 103.8 (cage *C*), 48.7 (NCH), 29.1, 26.2, 25.2, 24.9, 23.3, 13.6 (CH$_2$ and CH$_3$). $^{11}$B{$^1$H} NMR (benzene-$d_6$): $\delta$ −0.4 (4B), −6.8 (4B), −14.4 (2B). IR (KBr, cm$^{-1}$): $\nu$ 2561 (BH). Anal. Calcd for $C_{24}H_{56}B_{10}N_4Zr$ (**2g**): C, 48.04; H, 9.41; N, 9.34. Found: C, 47.73; H, 9.00; N, 9.28.

*Preparation of [$\eta^2$-$^i$PrNC(Bu$^n$)NPr$^i$]$_2$Ti($\eta^2$-$C_2B_{10}H_{10}$) (**2h**).* This complex was prepared as purple crystals from $Li_2C_2B_{10}H_{10}$ [prepared in situ from *o*-$C_2B_{10}H_{12}$ (0.72 g, 5.00 mmol) and $^n$BuLi (6.3 mL, 10.00 mmol, 1.6 M in hexane)] and [$\eta^2$-$^i$PrNC(Bu$^n$)NPr$^i$]$_2$TiCl$_2$ (2.43 g, 5.00 mmol) in toluene (30 mL) using the same procedure reported for **2c**: yield 2.64 g (95%). $^1$H NMR (benzene-$d_6$): $\delta$ 3.77 (m, 4H, NC*H*), 2.09 (m, 4H, C$H_2$), 1.39 (m, 4H, C$H_2$), 1.20 (d, $J$ = 6.6 Hz, 12H, C$H_3$), 1.16 (d, $J$ = 6.6 Hz, 12H, C$H_3$), 1.13 (m, 4H, C$H_2$), 0.79 (t, $J$ = 7.2 Hz, 6H, C$H_3$). $^{13}$C{$^1$H} NMR (benzene-$d_6$): $\delta$ 179.1 (NCN), 105.9 (cage *C*), 51.2 (NCH), 28.7, 27.4, 24.8, 24.5, 23.4, 13.6 (CH$_2$ and CH$_3$). $^{11}$B{$^1$H}


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NMR (benzene-$d_6$): $\delta$ −2.7 (4B), −7.5 (4B), −15.2 (2B). IR (KBr, $cm^{-1}$): $\nu$ 2559 (BH). Anal. Calcd for $C_{24}H_{56}B_{10}N_4Ti$ (**2h**): C, 51.78; H, 10.14; N, 10.06. Found: C, 52.24; H, 10.34; N, 10.06.

*Preparation of [$\eta^2$-$^i$PrNC(Bu$^n$)NPr$^i$]$_2$Hf($\eta^2$-$C_2B_{10}H_{10}$) (**2i**).* This complex was prepared as colorless crystals from $Li_2C_2B_{10}H_{10}$ [prepared in situ from *o*-$C_2B_{10}H_{12}$ (0.72 g, 5.00 mmol) and $^n$BuLi (6.3 mL, 10.00 mmol, 1.6 M in hexane)] and [$\eta^2$-$^i$PrNC(Bu$^n$)NPr$^i$]$_2$HfCl$_2$ (3.08 g, 5.00 mmol) in toluene (40 mL) using the same procedure reported for **2c**: yield 2.85 g (83%). $^1$H NMR (benzene-$d_6$): 3.67 (m, 4H, NC*H*), 2.05 (t, *J* = 7.8 Hz, 4H, C$H_2$), 1.34 (m, 4H, C$H_2$), 1.20 (d, *J* = 6.3 Hz, 12H, C$H_3$), 1.16 (d, *J* = 6.3 Hz, 12H, C$H_3$), 1.11 (m, 4H, C$H_2$), 0.78 (t, *J* = 7.2 Hz, 6H, C$H_3$). $^{13}$C{$^1$H} NMR (benzene-$d_6$): $\delta$ 181.4 (NCN), 116.0 (cage *C*), 48.5 (NCH), 29.1, 26.6, 25.1, 24.8, 23.3, 13.6 (C$H_2$ and C$H_3$). $^{11}$B{$^1$H} NMR (benzene-$d_6$): $\delta$ −0.8 (2B), −0.7 (2B), −7.5 (4B), −15.2 (2B). IR (KBr, $cm^{-1}$): $\nu$ 2559 (BH). Anal. Calcd for $C_{24}H_{56}B_{10}N_4Hf$ (**2i**): C, 41.94; H, 8.21; N, 8.15. Found: C, 41.87; H, 8.30; N, 7.98.

*Preparation of [$\eta^2$-CyNC(Ph)NCy]$_2$Zr[σ:σ:σ-{(Ph)$_2$C(O)$C_2B_{10}H_{10}$}] (**3b**).* To a stirring suspension of **2b** (174 mg, 0.2 mmol) in toluene (10 mL) at room temperature was added benzophenone (36 mg, 0.2 mmol), and the mixture was stirred at room temperature for 48 h. A clear colorless solution was formed. After concentration of the solution to ca. 3 mL, the resulting solution stood at room temperature overnight to yield **3b** as colorless crystals (200 mg, 95%). $^1$H NMR (pyridine-$d_5$): $\delta$ 8.31 (m, 4H), 7.65 (m, 6H), 7.55 (m, 2H), 7.49 (m, 4H), 7.42 (m, 2H), 7.31 (m, 2H) (phenyl *H*), 2.13 (m, 3H), 1.97 (m, 6H), 1.85 (m, 3H), 1.61 (m, 12H), 1.38 (m, 4H), 1.15 (m, 6H), 1.05 (m, 6H), 0.96 (m, 4H) (Cy). $^{13}$C{$^1$H} NMR (pyridine-$d_5$): $\delta$ 182.5 (NCN), 129.3, 128.7, 128.3, 128.0, 127.2, 126.9, 126.8, 126.6, 125.9, 125.1, 122.3 (phenyl *C*), 107.7, 100.3 (cage *C*), 91.6 (*C*-O), 57.8 (NCH), 34.9, 25.1, 25.0, 24.8 (*C*H$_2$). $^{11}$B{$^1$H} NMR (pyridine-$d_5$): $\delta$ −2.1 (4B), −7.5 (6B). IR (KBr, $cm^{-1}$): $\nu$ 2563 (BH). Anal. Calcd for $C_{61}H_{90}B_{10}N_4O_3Zr$ (**3b** + 2THF): C, 64.79; H, 7.59; N, 5.70. Found: C, 64.95; H, 7.12; N, 5.69.

*Preparation of [$\eta^2$-CyNC(Ph)NCy]$_2$Zr[σ:σ:σ-{[-(CH$_2$)$_5$-]C(O)-$C_2B_{10}H_{10}$}] (**4b**).* To a stirring suspension of **2b** (174 mg, 0.20 mmol) in toluene (10 mL) at room temperature was added cyclohexanone (20 mg, 0.20 mmol), and the mixture was stirred at room temperature for 48 h. A clear colorless solution was formed. After concentration of the solution to ca. 3 mL, the resulting solution stood at room temperature overnight to yield **4b** as colorless crystals (156 mg, 87%). $^1$H NMR (pyridine-$d_5$): $\delta$ 7.56 (m, 4H), 7.50 (m, 4H), 7.42 (m, 2H) (phenyl *H*), 3.36 (m, 2H, NC*H*), 2.99 (m, 2H, NC*H*), 2.42 (m, 2H, C$H_2$), 1.99 (m, 4H, C$H_2$), 1.72 (m, 24H, C$H_2$), 1.46 (m, 6H, C$H_2$), 1.06 (m, 14H, C$H_2$). $^{13}$C{$^1$H} NMR (pyridine-$d_5$): $\delta$ 181.2 (NCN), 132.1, 129.2, 128.3, 128.0, 127.4, 126.9, 125.9, 122.3 (phenyl *C*), 106.1, 100.7 (cage *C*), 84.9 (*C*-O), 57.1 (NCH), 39.5, 34.9, 34.4, 25.3, 25.0, 22.6, 13.1 (CH$_2$). $^{11}$B{$^1$H} NMR (pyridine-$d_5$): $\delta$ −5.5 (6B), −10.0 (4B). IR (KBr, $cm^{-1}$): $\nu$ 2570 (BH). Anal. Calcd for $C_{46}H_{74}B_{10}N_4OZr$ (**4b**): C, 61.50; H, 8.30; N, 6.24. Found: C, 61.38; H, 8.36; N, 6.03.

*Preparation of [$\eta^2$-CyNC(Me)NCy]$_2$Zr[σ:σ:σ-{[N=C(Ph)$C_2B_{10}H_{10}$}] (**5a**).* This complex was prepared as yellow crystals from **2a** (270 mg, 0.4 mmol) and benzonitrile (51 mg, 0.5 mmol) in toluene (20 mL) using the same procedure reported for **3b**: yield 237 mg (76%). $^1$H NMR (benzene-$d_6$): $\delta$ 8.21 (m, 2H), 7.02 (m, 3H) (phenyl *H*), 3.31 (m, 4H, NC*H*), 1.87 (m, 8H, C$H_2$), 1.69 (s, 6H, C$H_3$), 1.65 (m, 8H), 1.55 (m, 12H), 1.29 (m, 8H), 1.12 (m, 4H) (C$H_2$). $^{13}$C{$^1$H} NMR (benzene-$d_6$): $\delta$ 179.4 (NCN), 172.3 (CN), 135.4, 131.0, 129.8, 128.1 (phenyl *C*), 104.1, 99.2 (cage *C*), 56.9 (NCH), 35.1, 26.0, 13.8 (CH$_2$). $^{11}$B{$^1$H} NMR (benzene-$d_6$): $\delta$ −1.5 (3B), −5.0 (3B), −8.9 (4B). IR (KBr, $cm^{-1}$): $\nu$ 2585 (BH). Anal. Calcd for $C_{37}H_{65}B_{10}N_5Zr$ (**5**): C, 57.03; H, 8.41; N, 8.99. Found: C, 56.91; H, 8.20; N, 9.01.

*Preparation of [$\eta^2$-CyNC(Ph)NCy]$_2$Zr[σ:σ:σ-{[$^i$PrNC(=N$^i$Pr)-$C_2B_{10}H_{10}$}] (**6b**).* This complex was prepared as colorless crystals from **2b** (174 mg, 0.2 mmol) and *N*,*N*′-diisopropylcarbodiimide (25 mg, 0.2 mmol) in toluene (10 mL) using the same procedure reported for **3b**: yield 176 mg (95%). $^1$H NMR (pyridine-$d_5$): $\delta$ 7.73 (m, 2H), 7.67 (m, 4H), 7.52 (m, 4H) (phenyl *H*), 4.82 (m, 2H, NC*H*), 3.77 (m, 2H, THF), 3.35 (m, 2H, NC*H*), 2.99 (m, 2H, NC*H*), 2.45 (m, 2H, C$H_2$), 2.15 (m, 2H, C$H_2$), 2.05 (m, 8H, C$H_2$), 1.95 (d, *J* = 6.0 Hz, 3H, C$H_3$), 1.88 (d, *J* = 6.0 Hz, 3H, C$H_3$), 1.79 (m, 12H, C$H_2$), 1.63 (m, 2H, THF), 1.45 (m, 6H, C$H_2$), 1.23 (d, *J* = 6.0 Hz, 3H, C$H_3$), 1.20 (d, *J* = 6.0 Hz, 3H, C$H_3$), 1.09 (m, 4H, C$H_2$), 0.96 (m, 6H, C$H_2$). $^{13}$C{$^1$H} NMR (pyridine-$d_5$): $\delta$ 181.8, 180.0, 178.9 (NCN), 129.4, 129.3, 128.8, 128.5, 128.3, 126.5, 126.2, 125.9, 125.7, 122.9, 122.7, (phenyl *C*), 99.8, 80.7 (cage *C*), 59.1, 58.0, 57.3, (NCH), 46.3, 44.6, 36.7, 35.0, 34.8, 34.7, 34.4, 25.9, 25.3, 25.1, 24.9, 24.8, 24.3, 22.6, 21.6 (CH$_2$ and C$H_3$). $^{11}$B{$^1$H} NMR (pyridine-$d_5$): $\delta$ −2.1 (3B), −6.7 (7B). IR (KBr, $cm^{-1}$): $\nu$ 2582 (BH). Anal. Calcd for $C_{49}H_{82}B_{10}N_6O_{0.5}Zr$ (**6b** + 0.5 THF): C, 61.14; H, 8.59; N, 8.73. Found: C, 61.28; H, 8.92; N, 8.38.

*Preparation of [$\eta^2$-$^i$PrNC($^n$Bu)NPr$^i$]$_2$Hf[σ:σ:σ-{[$^i$PrNC(=NPr$^i$)-$C_2B_{10}H_{10}$}] (**6i**).* This complex was prepared as a colorless solid from **2i** (206 mg, 0.3 mmol) and *N*,*N*′-diisopropylcarbodiimide (76 mg, 0.6 mmol) in toluene (20 mL) using the same procedure reported for **3b**: yield 223 mg (91%). $^1$H NMR (benzene-$d_6$): $\delta$ 4.91 (m, 1H), 4.39 (m, 1H), 4.22 (m, 1H) 3.69 (m, 2H), 3.54 (m, 1H) (NC*H*), 2.09 (m, 4H, C$H_2$), 1.83 (d, *J* = 8.4 Hz, 3H, C$H_3$), 1.58 (d, *J* = 8.4 Hz, 6H, C$H_3$), 1.40 (d, *J* = 8.4 Hz, 3H, C$H_3$), 1.35 (d, *J* = 8.4 Hz, 3H, C$H_3$), 1.31 (m, 8H, C$H_2$), 1.25 (m, 9H) (C$H_3$), 1.17 (d, *J* = 8.4 Hz, 3H, C$H_3$), 1.06 (d, *J* = 8.4 Hz, 3H, C$H_3$), 0.90 (d, *J* = 8.4 Hz, 3H, C$H_3$), 0.86 (d, *J* = 8.4 Hz, 3H, C$H_3$), 0.83 (m, 6H, C$H_3$). $^{13}$C{$^1$H} NMR (benzene-$d_6$): $\delta$ 183.8, 181.6, 151.6 (NCN), 106.7, 81.6 (cage *C*), 49.0, 48.2, 47.7, 47.3, 46.7 (NCH), 29.2, 29.0, 28.7, 27.2, 27.1, 25.9, 25.4, 25.3, 25.0, 24.7, 24.6, 24.3, 23.6, 23.5, 23.4, 21.9, 13.6 (*C*H$_2$ and CH$_3$). $^{11}$B{$^1$H} NMR (benzene-$d_6$): $\delta$ −2.09 (3B), −7.0 (3B), −10.0 (3B), −11.5 (1B). IR (KBr, $cm^{-1}$): $\nu$ 2580, 2550 (BH). Anal. Calcd for $C_{31}H_{70}B_{10}HfN_6$ (**6i**): C, 45.77; H, 8.67; N, 10.33. Found: C, 45.77; H, 8.57; N, 10.16.

*Preparation of [$\eta^2$-CyNC(Me)NCy]$_2$Zr[σ:σ:σ-{[PhN(CO)$C_2B_{10}H_{10}$}] (**7a**).* This complex was prepared as colorless crystals from **2a** (135 mg, 0.2 mmol) and PhNCO (24 mg, 0.2 mmol) in toluene (10 mL) using the same procedure reported for **3b**: yield 148 mg (93%). $^1$H NMR (pyridine-$d_5$): $\delta$ 7.43 (m, 2H), 7.33 (m, 2H), 7.25 (m, 1H) (phenyl *H*), 4.10 (m, 2H, NC*H*), 3.59 (m, 2H, THF), 2.91 (m, 2H, NC*H*), 2.30 (s, 3H), 2.27 (s, 3H) (C$H_3$), 1.99 (m, 2H), 1.76 (m, 18H), 1.59 (m, 4H), 1.43 (m, 2H), 1.27 (m, 14H), 0.92 (m, 2H) (C$H_2$+THF). $^{13}$C{$^1$H} NMR (pyridine-$d_5$): $\delta$ 183.5, 180.6, 171.8 (NCN and CO), 143.7, 128.0, 127.4, 125.7 (phenyl *C*), 88.6, 81.6 (cage *C*), 57.9, 56.0 (NCH), 35.5, 34.0, 32.8, 31.0, 25.7, 24.9, 15.1, 13.5 (CH$_2$ and CH$_3$). $^{11}$B{$^1$H} NMR (pyridine-$d_5$): $\delta$ −2.7 (4B), −6.9 (6B). IR (KBr, $cm^{-1}$): $\nu$ 2596, 2564 (BH). Anal. Calcd for $C_{37}H_{65}B_{10}N_5OZr$ (**7a**): C, 55.81; H, 8.23; N, 8.80. Found: C, 55.79; H, 8.29; N, 8.43.

*Preparation of [$\eta^2$-CyNC(Ph)NCy]$_2$Zr[σ:σ:σ-{[$^n$BuNC(=S)$C_2B_{10}H_{10}$}] (**8b**).* This complex was prepared as yellow crystals from **2b** (174 mg, 0.2 mmol) and $^n$BuNCS (46 mg, 0.4 mmol) in toluene (10 mL) using the same procedure reported for **3b**. Recrystallization from a mixed solvent of hexane and ether (1/2 in v/v) afforded **8b** (144 mg, 79%). $^1$H NMR (benzene-$d_6$): $\delta$ 7.77 (d, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.23 (m, 1H), 7.12 (m, 7H) (phenyl *H*), 4.83 (m, 1H), 4.24 (m, 1H), 4.01 (m, 1H), 3.30 (m, 1H) (NC*H*), 2.91 (m, 1H), 2.64 (m, 1H), 2.06 (m, 2H), 1.86 (m, 8H), 1.69 (m, 18H), 1.44 (m, 6H) (C$H_2$), 1.04 (t, *J* = 7.2 Hz, 3H, C$H_3$), 1.01 (m, 4H), 0.90 (m, 6H) (C$H_2$). $^{13}$C{$^1$H} NMR (benzene-$d_6$): $\delta$ 204.4, 186.1, 180.2 (NCN and CS), 133.0, 130.9, 130.2, 130.1, 129.8, 128.9, 126.5, 126.4, 126.3 (phenyl *C*), 95.4, 92.3 (cage *C*), 60.3, 59.1, 58.2, 58.1, 50.4 (NCH and NCH$_2$), 44.3, 38.0, 36.9, 36.1, 35.8, 35.4, 35.3, 34.1, 33.8, 31.7, 31.5, 26.7, 26.5, 26.2, 25.8, 25.5, 25.3, 25.2, 21.4, 19.6, 14.5, 13.1 (CH$_2$ and CH$_3$). $^{11}$B{$^1$H} NMR (benzene-$d_6$): $\delta$ −2.5 (4B), −6.8 (6B). IR (KBr, $cm^{-1}$): $\nu$ 2563 (BH). Anal. Calcd for $C_{45}H_{73}B_{10}N_5SZr$ (**8b**): C, 59.04; H, 8.04; N, 7.65. Found: C, 59.07; H, 7.98; N, 7.82.

*Preparation of [$\eta^2$-$^i$PrNC(Bu$^n$)NPr$^i$]$_2$Hf[σ:σ:σ-{[$^n$BuNC(=S)-$C_2B_{10}H_{10}$}] (**8i**).* This complex was prepared as a light yellow solid from **2i** (206 mg, 0.3 mmol) and $^n$BuNCS (69 mg, 0.6 mmol) in toluene (10 mL) using the same procedure reported for **3b**: yield 209 mg (87%). $^1$H NMR (benzene-$d_6$): $\delta$ 4.65 (m, 2H, NC*H*), 3.58 (m, 4H, NC*H* +C$H_2$), 2.10 (q, *J* = 7.2, 4H, C$H_2$), 1.61 (m, 2H, C*H*), 1.41 (m, 6H), 1.18 (m, 19H), 0.98 (m, 6H), 0.87 (m, 12H) (C$H_2$ and C$H_3$). $^{13}$C{$^1$H} NMR (benzene-$d_6$): $\delta$ 205.3, 187.8, 183.0 (NCN and CS), 102.7, 91.5 (cage *C*), 51.0, 49.5, 48.2, 47.9, 47.6 (NCH and NCH$_2$), 30.6, 29.7, 29.5, 28.2, 27.2, 26.8, 26.6, 25.1, 25.0, 24.5, 24.3, 24.0, 23.6, 23.4, 23.3, 21.2, 14.3, 13.6, 13.5 (CH$_2$ and CH$_3$). $^{11}$B{$^1$H} NMR (benzene-$d_6$): $\delta$ −3.3 (3B), −7.0 (4B), −8.7 (2B), −12.8 (1B). IR (KBr, $cm^{-1}$): $\nu$ 2594, 2564 (BH).


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Anal. Calcd for $C_{45}H_{73}B_{10}N_5SZr$ (**8i**): C, 59.04; H, 8.04; N, 7.65. Found: C, 59.07; H, 7.98; N, 7.82.

*Preparation of [$\eta^2$-$^i$PrNC(Bu$^n$)NPr$^i$]$_2$Hf[σ:σ:σ-{SC(=S)C$_2$B$_{10}$H$_{10}$}] (**9i**).* This complex was prepared as light purple crystals from **2i** (206 mg, 0.3 mmol) and $CS_2$ (76 mg, 1.0 mmol) in toluene (20 mL) in a closed flask at 100 °C for 3 days using the same procedure reported for **3b**: yield 137 mg (60%). $^1$H NMR (benzene-$d_6$): δ 2.07 (m, 4H, C$H_2$), 1.33 (m, 4H, C$H_2$), 1.22 (q, $J$ = 6.4, 12H, C$H_3$), 1.16 (m, 6H, C$H_2$), 1.04 (m, 10H, C$H_2$), 0.79 (t, $J$ = 7.2, 6H, C$H_3$). $^{13}$C{$^1$H} NMR (benzene-$d_6$): δ 185.2 (*C*S), 110.5, 99.5 (cage *C*), 48.6 (NCH), 28.9, 28.1, 25.0, 24.7, 23.4, 13.5 ($CH_2$ and $CH_3$). $^{11}$B{$^1$H} NMR (benzene-$d_6$): δ −1.2 (1B), −3.4 (2B), −6.7 (4B), −8.7 (3B). IR (KBr, cm$^{-1}$): ν 2564 (BH). Anal. Calcd for $C_{25}H_{56}B_{10}HfN_4S_2$ (**9i**): C, 39.33; H, 7.39; N, 7.34. Found: C, 39.53; H, 7.40; N, 6.97.

*Preparation of [$\eta^2$-CyNC($^n$Bu)NCy]$_2$Zr[σ:σ:σ-(PhN-N=N)-C$_2$B$_{10}$H$_{10}$] (**10c**).* This complex was prepared as yellow crystals from **2c** (380 mg, 0.5 mmol) and $PhN_3$ (179 mg, 1.5 mmol) in toluene (20 mL) using the same procedure reported for **3b**: yield 320 mg (76%). $^1$H NMR (benzene-$d_6$): δ 8.13 (d, $J$ = 7.6 Hz, 2H), 7.19 (dd, $J$ = 7.6 and 8.0 Hz, 2H), 6.92 (dd, $J$ = 7.6 Hz, 1H) (phenyl H), 3.44 (m, 4H, NC*H*), 2.68 (m, 1H), 2.26 (m, 4H), 2.10 (m, 1H), 1.84 (m, 16H), 1.60 (m, 10H), 1.40 (m, 4H), 1.28 (m, 10H), 1.18 (m, 6H), 1.04 (m, 2H, C$H_2$), 0.85 (t, $J$ = 7.2 Hz, 6H). $^{13}$C{$^1$H} NMR (benzene-$d_6$): δ 181.1, 180.0 (NCN), 143.6, 129.2, 127.5, 122.9 (phenyl *C*), 111.2, 108.2 (cage *C*), 58.3, 57.4, 57.2, 56.8 (NCH), 37.5, 36.8, 36.5, 35.9, 35.3, 34.9, 33.7, 33.6, 29.9, 28.9, 26.8, 26.6, 26.2, 26.1, 26.0, 25.9, 25.7, 25.4, 25.3, 23.6, 23.2 ($CH_2$ and $CH_3$). $^{11}$B{$^1$H} NMR (benzene-$d_6$): δ −0.9 (2B), −6.0 (8B). IR (KBr, cm$^{-1}$): ν 2580 (BH). Anal. Calcd for $C_{42}H_{77}B_{10}N_7Zr$ (**10c**): C, 57.36; H, 8.83; N, 11.15. Found: C, 57.61; H, 8.79; N, 11.32.

*Preparation of [$\eta^2$-$^i$PrNC(Ph)NPr$^i$]$_2$Zr[σ:σ:σ-(PhN-N=N)-C$_2$B$_{10}$H$_{10}$] (**10f**).* This complex was prepared as yellow crystals from **2f** (357 mg, 0.5 mmol) and $PhN_3$ (179 mg, 1.5 mmol) in toluene (20 mL) using the same procedure reported for **3b**: yield 338 mg (89%). $^1$H NMR (benzene-$d_6$): δ 8.26 (d, $J$ = 8.1 Hz, 2H), 7.66 (brs, 1H), 7.38 (m, 12H) (phenyl H), 3.56 (m, 1H), 3.45 (m, 1H), 3.29 (m, 2H), (NC*H*), 2.11 (s, C$H_3$ of toluene), 1.41 (m, 3H), 1.29 (m, 3H), 1.13 (d, $J$ = 5.4 Hz, 12H, C$H_3$), 0.66 (m, 6H). $^{13}$C{$^1$H} NMR (benzene-$d_6$): δ 179.6, 177.9 (NCN), 143.4, 137.8, 132.5, 131.4, 129.5, 129.3, 129.2, 128.5, 127.5, 126.2, 125.6, 122.6 (phenyl *C*), 111.4, 108.5 (cage *C*), 49.8 (NCH), 26.1, 25.4, 25.0, 23.0, 21.4 (C$H_3$). $^{11}$B{$^1$H} NMR (benzene-$d_6$): δ −1.0 (2B), −6.2 (8B). IR (KBr, cm$^{-1}$): ν 2555 (BH). Anal. Calcd for $C_{41}H_{61}B_{10}N_7Zr$ (**10f** + toluene): C, 57.85; H, 7.22; N, 11.52. Found: C, 57.98; H, 7.27; N, 11.40.

*Preparation of [$\eta^2$-$^i$PrNC(Bu$^n$)NPr$^i$]$_2$Ti[σ:σ:σ-(PhN-N=N)-C$_2$B$_{10}$H$_{10}$] (**10h**).* This complex was prepared as yellow crystals from **2h** (279 mg, 0.5 mmol) and $PhN_3$ (179 mg, 1.5 mmol) in toluene (20 mL) using the same procedure reported for **3b**: yield 301 mg (89%). $^1$H NMR (benzene-$d_6$): δ 8.30 (d, $J$ = 7.6 Hz, 2H), 7.26 (dd, $J$ = 7.6 and 8.1 Hz, 2H), 7.08 (dd, $J$ = 7.6 Hz, 1H) (phenyl H), 3.76 (m, 2H), 3.68 (m, 2H) (NC*H*), 2.05 (m, 4H, C$H_2$), 1.42 (m, 4H, C$H_2$), 1.25 (d, $J$ = 6.6 Hz, 12H, C$H_3$), 1.18 (d, $J$ = 6.6 Hz, 12H, C$H_3$), 1.12 (m, 4H, C$H_2$), 0.76 (d, $J$ = 7.1 Hz, 6H, C$H_3$). $^{13}$C{$^1$H} NMR (benzene-$d_6$): δ 179.5, 178.1 (NCN), 143.2, 130.5, 128.3, 125.0 (phenyl *C*), 110.8, 107.3 (cage *C*), 50.8 (NCH), 28.2, 27.0, 25.3, 25.0, 22.3, 15.1 ($CH_2$ and $CH_3$). $^{11}$B{$^1$H} NMR (benzene-$d_6$): δ −1.6 (2B), −6.9 (8B). IR (KBr, cm$^{-1}$): ν 2562 (BH). Anal. Calcd for $C_{30}H_{61}B_{10}N_7Ti$ (**10h**): C, 53.32; H, 9.10; N, 14.51. Found: C, 53.58; H, 9.25; N, 14.33.

**X-ray Structure Determination.** All single crystals were immersed in Paratone-N oil and sealed under nitrogen in thin-walled glass capillaries. Data were collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation. An empirical absorption correction was applied using the SADABS program.[18] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares on $F^2$ using the SHELXTL program package.[19] All hydrogen atoms were geometrically fixed using the riding model. Details of the crystal structures were included in the Supporting Information.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Synthesis and characterization of new complexes [$\eta^2$-R$^2$C-(NR$^1$)$_2$]$_2$MCl$_2$, crystal data and details of data collection and structure refinements, as well as crystallographic data in CIF format for **1b**, **1d**, **1e**, **1f**, **1h**, **2e**, **2g**, **2h**, **2i**, and **3**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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