Synthesis, structure, and reactivity of Group 4 metallacycles incorporating a Me_2C-linked cyclopentadienyl-carboranyl ligand†‡

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Group 4 metallacycles $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti[\eta^2\text{-}N(Me)CH_2CH_2N(Me)]$ (**1a**), $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}N(Me)CH_2CH_2N(Me)](HNMe_2)$ (**1b**) and $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M[\eta^2\text{-}N(Me)CH_2CH_2CH_2N(Me)]$ (M = Ti (**2a**), Zr (**2b**), Hf (**2c**)) were synthesized by reaction of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M(NMe_2)_2$ (M = Ti, Zr, Hf) with $MeNH(CH_2)_nNHMe$ (n = 2, 3). These metal complexes reacted with unsaturated molecules such as 2,6-$Me_2C_6H_3NC$, PhNCO and PhCN to give exclusively M–N bond insertion products. The M–C_{cage} bond remained intact. Such a preference of M–N over M–C_{cage} insertion is suggested to most likely be governed by steric factors, and the mobility of the migratory groups plays no obvious role in the reactions. This work also shows that the insertion of unsaturated molecules into the metallacycles is a useful and effective method for the construction of very large ring systems.

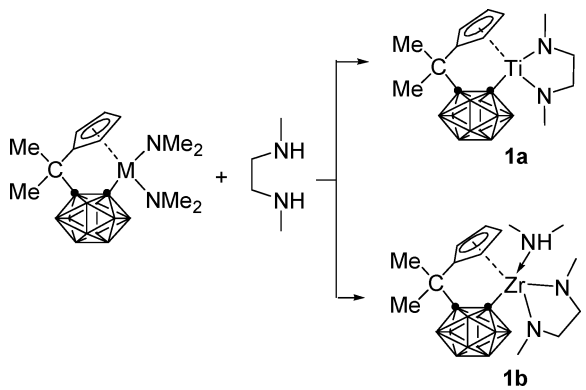
Introduction

Reactivity studies on $[\eta^5{:}\sigma\text{-}A(C_9H_6)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ (A = Me_2C,[1] Me_2Si,[1] $^iPr_2NP$[2]) and $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]$-$Ti(NMe_2)X$ (X = Cl, alkyl) complexes[3] indicate that the unsaturated molecules insert into the M–N bond only in the absence of M–C_{alkyl} bonds and the M–C_{cage} bond remains intact, *i.e.* the relative reactivity follows the trend: M–C_{alkyl} > M–N >> M–C_{cage}.[3] Since the M–C_{cage} and M–C_{alkyl} bond distances are almost identical, the preference of M–N over M–C_{cage} insertion is suggested to most likely be governed by steric factors.[1–4] On the other hand, $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]_2Zr$ is reported to catalyze the polymerization of methyl methacrylate in the absence of any cocatalyst through the action of the nucleophilic cage atom.[5] Complexes $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M(\eta^5\text{-}C_5Me_5)Cl$ (M = Ti, Zr) are active catalysts for ethylene polymerization in the presence of modified methylalumoxane. Possible involvement of the activation of the M–C_{cage} σ bond is suggested.[6] With this in mind, a question subsequently arises as to whether the mobility of the carborane cage plays a role in the migratory insertions aforementioned as the cage is tethered to the cyclopentadienyl unit in comparison to the terminal amido groups. One possible way to address this issue is to link the two terminal amido groups *via* several methylene moieties, lowering their mobility and then to investigate the reactivity patterns of the resultant metallacycles toward unsaturated molecules. We report in this article the synthesis, structure, and reactivity of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M[\eta^2$-$N(Me)(CH_2)_nN(Me)]$ (M = Ti, Zr, Hf; n = 2, 3).

Results and discussion

Synthesis of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]$-$M[\eta^2\text{-}N(Me)(CH_2)_nN(Me)]$

Salt metathesis and amine elimination are two useful methods for the preparation of metal amides.[7] Reactions of $LiN(Me)CH_2CH_2N(Me)Li$ with 0.5 equiv. of $\{[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)$-$(C_2B_{10}H_{10})]Zr(\mu\text{–}Cl)_{1.5}Cl\}_2\{Li(THF)_2\}$[8] or 1 equiv. of $[\eta^5{:}\sigma$-$Me_2C(C_5H_4)(C_2B_{10}H_{10})]ZrCl_2$[9] in THF did not afford isolable pure products. On the other hand, treatment of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)$-$(C_2B_{10}H_{10})]M(NMe_2)_2$[8] with 5 or 1.1 equiv. of $MeNHCH_2CH_2$-NHMe in toluene gave the corresponding titanium or zirconium amide complexes $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti[\eta^2$-$N(Me)CH_2CH_2N(Me)]$ (**1a**) in 68% yield, or $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)$-$(C_2B_{10}H_{10})]Zr[\eta^2\text{-}N(Me)CH_2CH_2N(Me)](HNMe_2)$ (**1b**) in 73% yield, respectively (Scheme 1). The formation of volatile Me_2NH and the chelate effect of the bidentate diamido ligand provide the driving forces for the above reactions. Both complexes were fully characterized by ^1H, ^{13}C and ^{11}B NMR as well as elemental analyses. Complex **1b** contained a coordinated Me_2NH molecule probably due to the relatively larger size of the Zr atom.



Scheme 1

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† Dedicated to Professor Ken Wade on the occasion of his 75th birthday.

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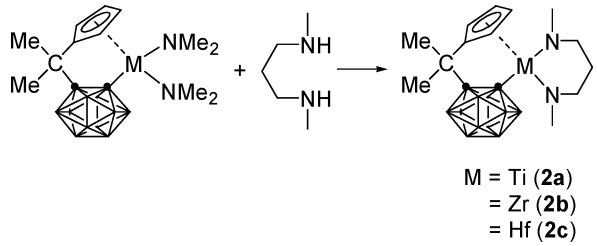
In a very similar manner, complexes [η^5:σ-$Me_2C(C_5H_4)$-$(C_2B_{10}H_{10})$]M[η^2-N(Me)$CH_2CH_2CH_2$N(Me)] (M = Ti (**2a**), Zr (**2b**) and Hf (**2c**)) were prepared in 64–82% isolated yields from the reactions of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]M$(NMe_2)_2$ with $MeNH(CH_2)_3NHMe$ in toluene (Scheme 2). They showed similar spectroscopic features and no coordination of Me_2NH, presumably owing to the formation of sterically more demanding six-membered metallacycles.



Scheme 2

The molecular structures of **1a** and **2a** were confirmed by single-crystal X-ray analyses, and are shown in Fig. 1 and 2, respectively. Key structural data are compiled in Table 1 for comparison. The Ti atom in both complexes is η^5-bound to the

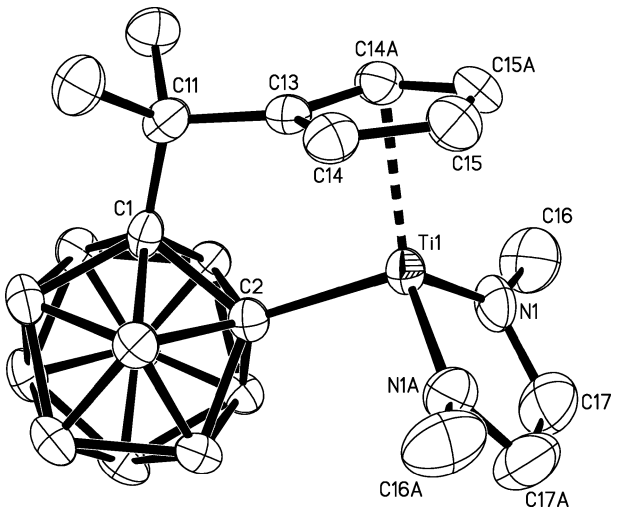


Fig. 1 Molecular structure of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti[$\eta^2$-N(Me)$CH_2CH_2$N(Me)] (**1a**).

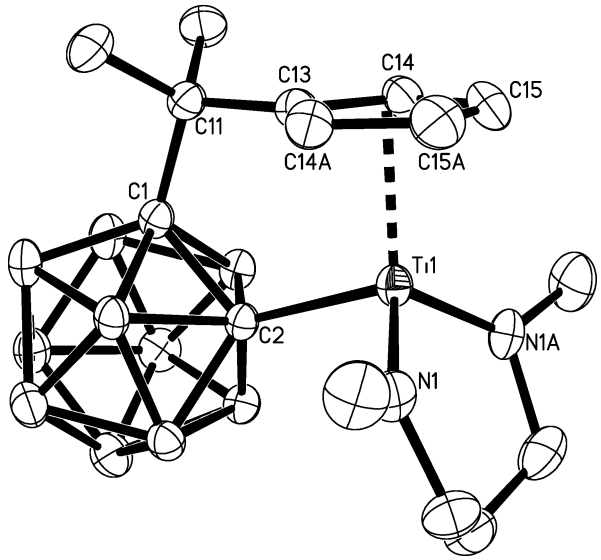


Fig. 2 Molecular structure of [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti[$\eta^2$-N(Me)$CH_2CH_2CH_2$N(Me)] (**2a**).

five-membered ring of the cyclopentadienyl group, σ-bound to a carborane cage atom, and two nitrogen atoms in a distorted-tetrahedral geometry. The average Ti–C_{ring} distances of 2.336(8) Å in **1a** and 2.367(3) Å in **2a**, the Ti–C_{cage} distances of 2.173(8) Å in **1a** and 2.199(3) Å in **2a**, the average Ti–N distances of 1.869(6) Å in **1a** and 1.882(2) Å in **2a** are very comparable to each other. These measured values are close to those of 2.369(3) Å, 2.209(2) Å, and 1.894(2) Å observed in their parent complex [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti$(NMe_2)_2$,[8] and other titanium amides.[7] The C_{ring}–C–C_{cage} angles of 109.6(7)° in **1a** and 108.4(3)° in **2a**, the Cent–Ti–C_{cage} angles of 105.9° in **1a** and 105.3° in **2a** are very similar to the corresponding values of 108.5(2)° and 105.0° found in [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti$(NMe_2)_2$.[8] The N–Ti–N angle of 96.2(4)° in **1a** is, however, significantly smaller than that of 105.6(1)° in **2a** and 106.1(2)° in [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti$(NMe_2)_2$.[8] These data suggest that the coordination geometry around the Ti atom in **2a** and [η^5:σ-$Me_2C(C_5H_4)(C_2B_{10}H_{10})$]Ti$(NMe_2)_2$ is almost identical, and no ring strain is incorporated after linking two nitrogen atoms by three methylene units.

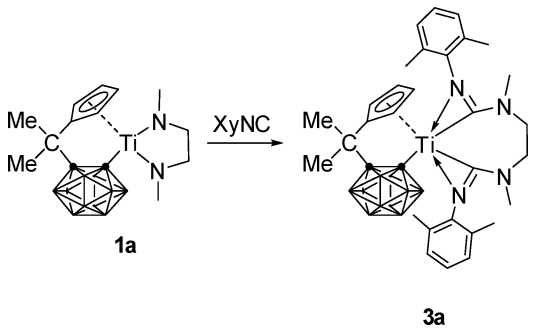
Table 1 Selected bond distances (Å) and angles (°)

Complex (M)	**1a** (Ti)	**2a** (Ti)	**3a** (Ti)	**3b** (Zr)	**4b** (Zr)	**5b** (Zr)	**6b** (Zr)	**7b** (Zr)	**8b** (Zr)[b]
av. M–C_{ring}	2.336(8)	2.367(3)	2.367(6)	2.502(4)	2.516(6)	2.542(4)	2.530(6)	2.515(3)	2.497(11)
av. M–Cent[a]	2.024	2.207	2.285	2.394	2.371	2.439	2.461	2.428	2.203
av. M–C_{cage}	2.173(8)	2.199(3)	2.285(5)	2.394(3)	2.371(5)	2.439(3)	2.461(5)	2.425(3)	2.341(9)
av. M–N_{amide}	1.869(6)	1.882(2)			2.217(5)	2.090(3)	2.075(4), 2.279(4)		
av. M–N_{amine}						2.403(3)	2.443(5)		
av. M–N_{imine}			2.112(5)	2.236(3)		2.408(3)		2.212(2)	
av. M–N_{imide}						2.265(3)			1.958(9)
av. M–$N_{nitrile}$							2.320(5)		
Cent–M–C_{cage}	105.9	105.3	103.2	100.6	98.1	96.3	96.8	100.1	99.7
C_{ring}–C–C_{cage}	109.6(7)	108.4(3)	109.1(4)	110.9(2)	109.2(5)	110.4(3)	109.9(4)	110.9(2)	110.5(8)
N–M–N	96.2(4)	105.6(1)	118.0(2)	118.6(1)	93.7(2)			116.9(1)	105.8(3)

[a] Cent: the centroid of the cyclopentadienyl ring. [b] Average values of the two crystallographically independent molecules in the unit cell.

Reactivity

Reaction of **1a**,**b** or **2b**,**c** with 2 equiv. of XyNC (2,6-$Me_2C_6H_3NC$) in toluene at room temperature gave the diinsertion products $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M[\eta^2{:}\eta^2\text{-}XyN(=C)\text{-}N(Me)(CH_2)_nN(Me)(C=)NXy]$ (**3a**, M = Ti, n = 2; **3b**, M = Zr, n = 2; **7b**, M = Zr, n = 3; **7c**, M = Hf, n = 3) in 58–70% isolated yields. Only diinsertion products were isolated in the presence of 1 or more equiv. of XyNC (Schemes 3–5). The results showed that XyNC molecules inserted exclusively into the M–N bond giving ring expansion products, and the M–C_{cage} bond remained intact regardless of the ring size of the metallacycles. They were characterized by various spectroscopic techniques and elemental analyses. The unique N–*C*=N resonance at ~205 ppm was observed in the ^{13}C NMR spectra of the insertion products. Single-crystal X-ray analyses confirmed the molecular structures of **3a**,**b** and **7b**, and showed half a molecule of benzene of solvation for both **3a**,**b**. Complexes **3a**,**b** are isostructural and isomorphous. Fig. 3 and 4 show the representative structures of **3a** and **7b**, respectively. In these structures, the central metal atom is coordinated by an η^5-cyclopentadienyl ligand, a cage carbon atom and two η^2-iminocarbamoyl ligands in a five-legged piano stool geometry. As indicated in Table 1, the key structural parameters



Scheme 3

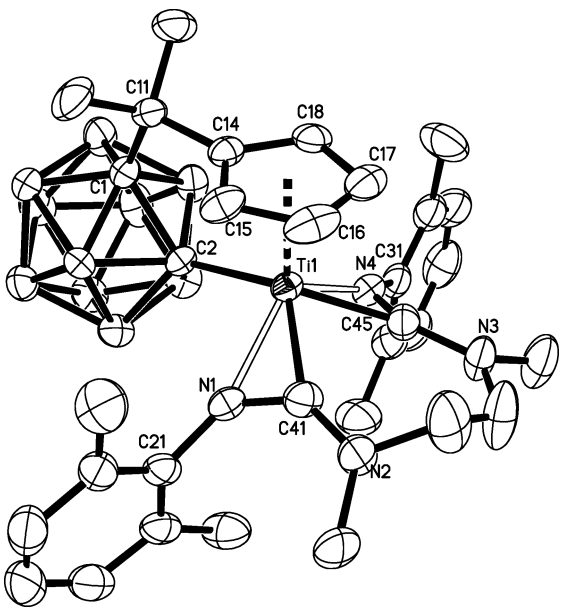


Fig. 3 Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti[\eta^2{:}\eta^2\text{-}XyN{=}CN(Me)(CH_2)_2N(Me)C{=}NXy]$ (**3a**).

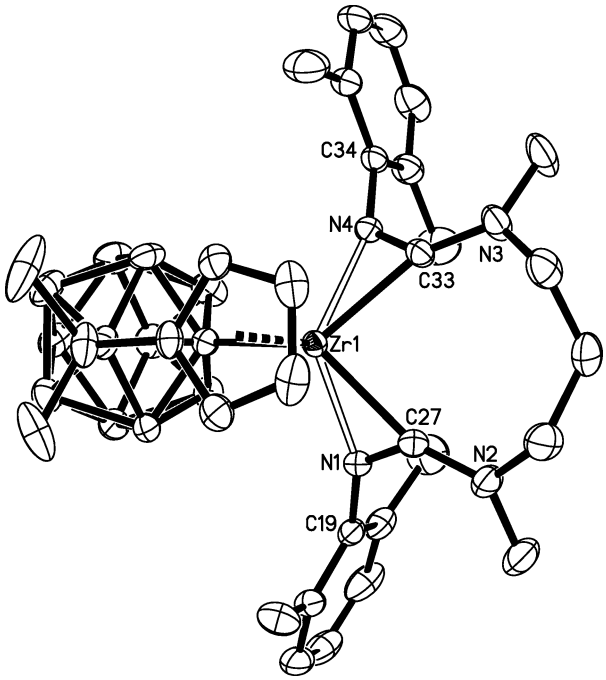
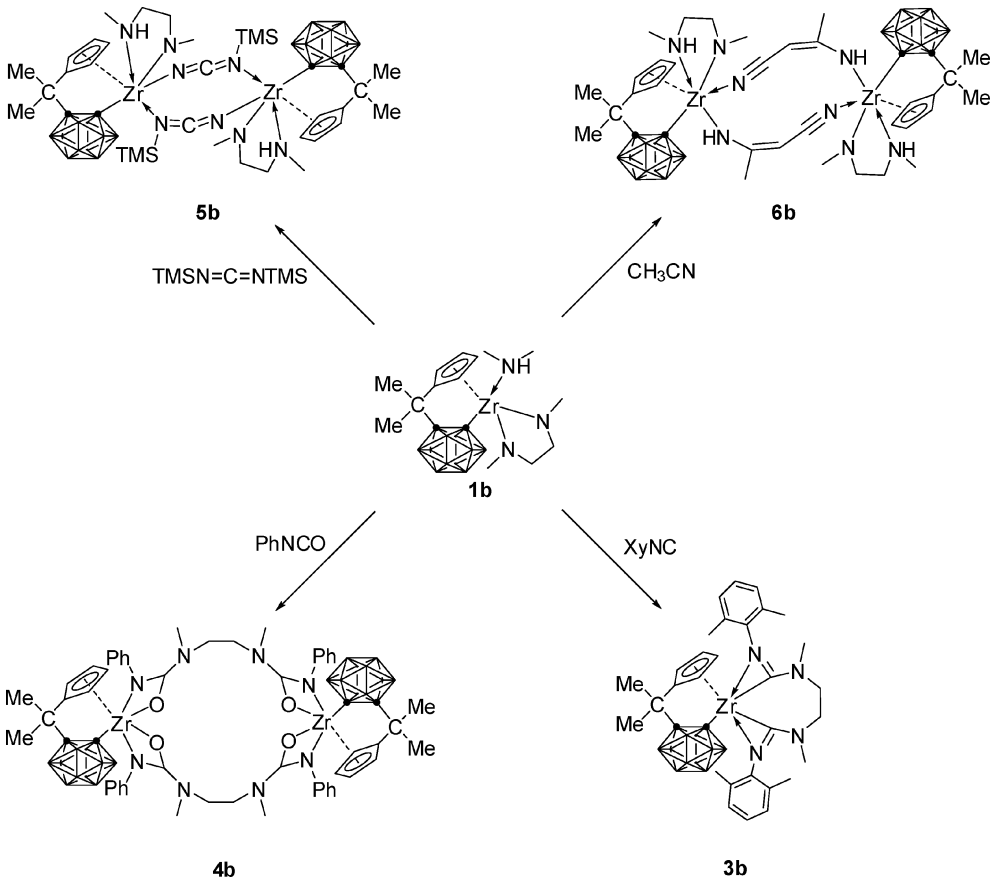


Fig. 4 Molecular structure of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2{:}\eta^2\text{-}XyN{=}CN(Me)(CH_2)_3N(Me)C{=}NXy]$ (**7b**).

in **3b** and **7b** are very similar, and are agreeably comparable with the literature data.[7] The average Zr–C(sp^2) distances [2.162(3) Å in **3b** and 2.190(3) Å in **7b**] and Zr–N(sp^2) distances [2.236(3) Å in **3b** and 2.212(2) Å in **7b**] are close to the corresponding values of 2.259(4) Å and 2.221(3) Å in $Zr(NMeCyc)_2[C(NAr)NMeCyc]_2$ (Cyc = cyclohexyl, Ar = 2,6-dimethylphenyl),[10a] 2.209(8) Å and 2.143(6) Å in $(\eta^5\text{-}C_9H_6)Zr[C(NMe_2){=}N(2,6\text{-}Me_2C_6H_3)]_2Cl$.[10b] The average Ti–C($sp^2$) (2.033(6) Å) and Ti–N($sp^2$) (2.111(5) Å) distances are close to the corresponding values of 2.061(5) and 1.955(4) Å in $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(Cl)[\eta^2\text{-}C(NMe_2){=}N(C_6H_3Me_2\text{-}2,6)]$,[3] 2.032(5) Å and 1.982(4) Å in $(\eta^5\text{-}C_9H_6)Ti[C(NMe_2){=}N(2,6\text{-}Me_2Ph)]Cl_2$.[10b]

Treatment of **1b** with 1 or 2 equiv. of PhNCO in DME (dimethoxyethane) at room temperature afforded a diinsertion product $\{[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\mu\text{-}\eta^2{:}\eta^2\text{-}OCN(Ph)\text{-}N(Me)CH_2CH_2(Me)N(Ph)NCO]\}_2$ (**4b**) in 69% isolated yield (Scheme 4). A characteristic N–*C*=O resonance at 156.1 ppm was observed in the ^{13}C NMR spectrum of **4b**. Unlike $[\eta^5{:}\sigma\text{-}Me_2A(C_9H_6)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}N(Ph)C(NMe_2)O]_2$ (A = Me_2C,[1] Me_2Si,[1] $^iPr_2NP$[2]), **4b** did not show any activity toward PhNCO. The reasons are presumably owing to the steric effects imposed by the very crowded coordination environments around the Zr atom in **4b**, which may also lead to the formation of the dinuclear complex bearing an 18-membered metallacyclic ring. Such a dimeric structure was confirmed by a single-crystal diffraction study. Each Zr atom is η^5-bound to a cyclopentadienyl ring, η^2-bound to each of two OC(NMeR)NPh moieties and σ-bound to a cage carbon atom in a five-legged piano stool geometry (Fig. 5). The average Zr–C_{ring} distance of 2.516(6) Å and Zr–C_{cage} distance of 2.371(5) Å are very close to the corresponding values found in **3b**. The average Zr–N/O distance of 2.217(5)/2.196(4) Å compare well with the 2.242(3)Å/2.165(3) Å observed in $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}N(Ph)C(NMe_2)O]_2$[1]



Scheme 4

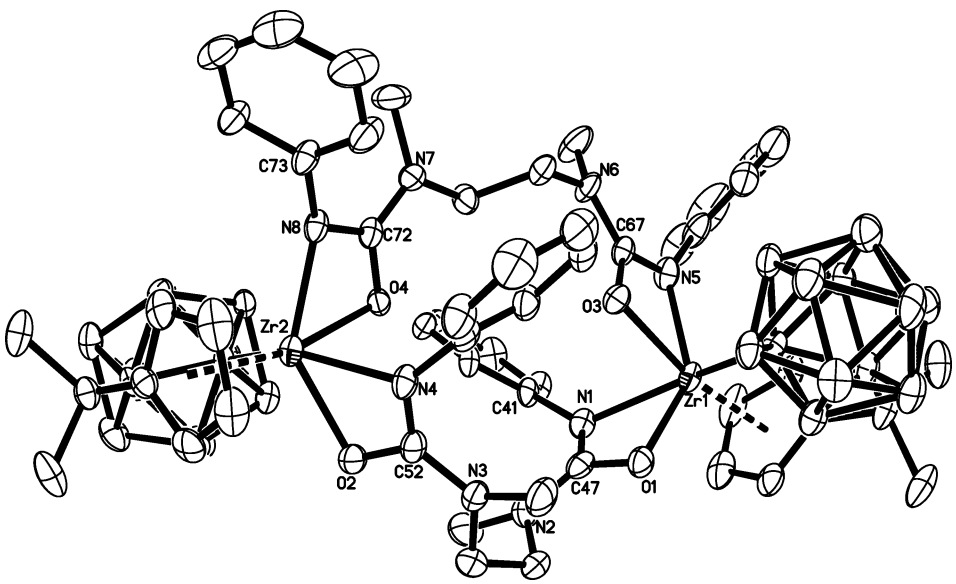


Fig. 5 Molecular structure of $\{[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\mu\text{-}\eta^2{:}\eta^2\text{-}OCN(Ph)N(Me)CH_2CH_2(Me)N(Ph)NCO]\}_2$ (**4b**).

and 2.186(4)/2.161(3) in $[\eta^5{:}\sigma\text{-}{}^iPr_2NP(C_9H_6)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}OCN(Ph)][\eta^2\text{-}OC(NMe_2)N(Ph)C{=}(NPh)O]$.[2]

Reaction of **2b** with 2 equiv. of PhCN in DME at room temperature generated a diinsertion dimeric complex $\{[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\mu\text{-}N{=}C(Ph)N(Me)(CH_2)_3N(Me)(Ph)\text{-}C{=}N]\}_2$ (**8b**) in 64% isolated yield (Scheme 5). Such a ring expansion reaction led to the formation of a 20-membered metallacyclic ring. Its ^{13}C NMR spectrum exhibited a unique N=*C*–N resonance at 163.4 ppm. As shown in Fig. 6, each Zr atom is coordinated by an η^5-cyclopentadienyl ring, a cage carbon atom and two nitrogen atoms in a four-legged piano stool geometry. The average Zr–N distance of 1.958(9) Å is

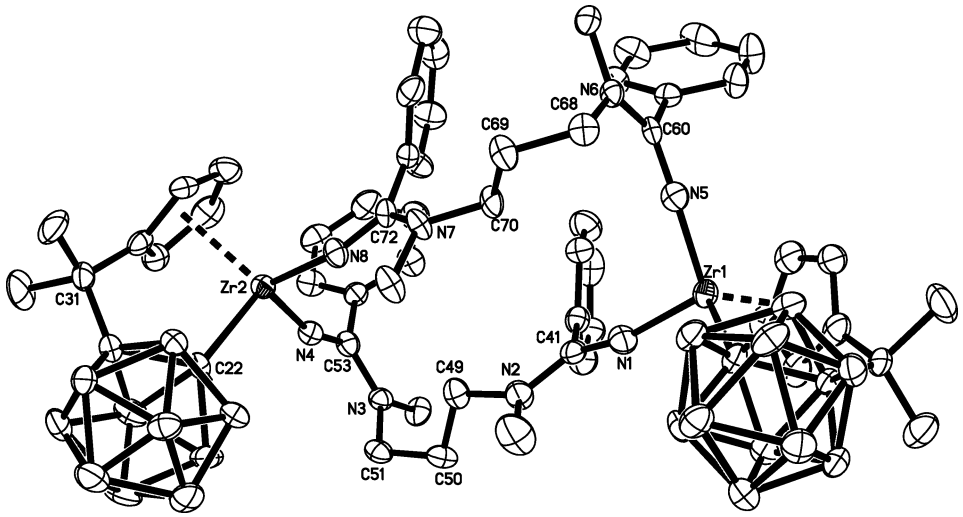
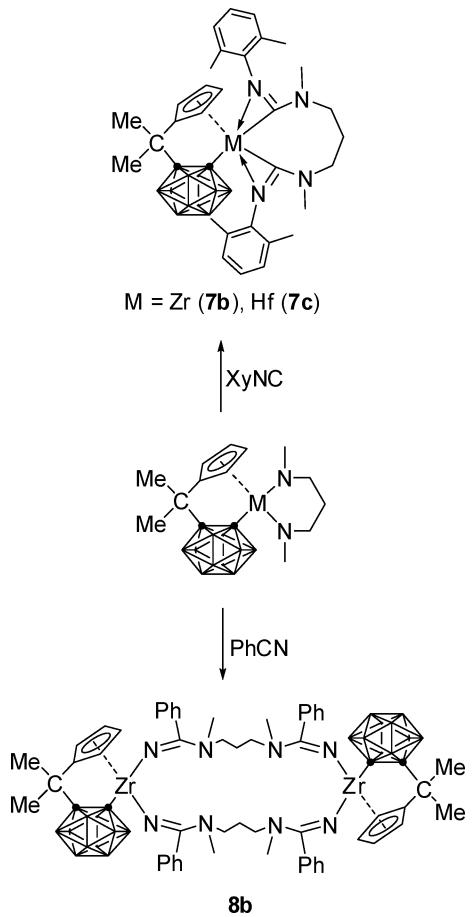


Fig. 6 Molecular structure of $\{[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\mu\text{-}N{=}C(Ph)N(Me)(CH_2)_3N(Me)(Ph)C{=}N]\}_2$ (**8b**), showing one of the two crystallographically independent molecules in the unit cell.



Scheme 5

close to the corresponding value of 1.972(2) Å observed in $[\eta^5{:}\sigma\text{-}Me_2C(C_9H_6)(C_2B_{10}H_{10})]Zr[N{=}C(Ph)NMe_2]_2$.[1]

On the other hand, interaction of **1b** with 2 equiv. of CH_3CN in DME at room temperature gave an unexpected product $\{[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}N(Me)(CH_2)_2NH(Me)][\mu\text{-}NHC(CH_3){=}CHC{\equiv}N]\}_2$ (**6b**) in 42% isolated yield (Scheme 4). The NMR data were not obtainable due to the insolubility of **6b** in organic solvents. Its composition and molecular structure were unambiguously confirmed by elemental analyses and single-crystal X-ray analyses. As shown in Fig. 7, each Zr atom is coordinated to an η^5-cyclopentadienyl ring, a cage carbon atom and four nitrogen atoms in a five-legged piano stool geometry. A much shorter Zr–N(1) distance of 2.075(4) Å over the Zr–N(2) distance of 2.443(5) Å and the planar geometry of N(1) suggest that N(1) is the amido nitrogen and N(2) is the amino nitrogen. The Zr–N(3)/N(4) distances of 2.279(4)/2.320(5) Å, C(28)–N(4)/C(27) distances of 1.149(7)/1.387(8) Å and C(25)–N(3)/C(27) distances of 1.316(7)/1.392(7) Å as well as the planarity of the N(4)–C(28)–C(27A)–C(25A)–N(3A) fragment indicated some electron delocalization over such a unit. These structural data imply that the N(3) atom is best described as an amido nitrogen formed *via* a 1,3-proton shift. Scheme 6 shows a possible reaction pathway for the formation of **6b**. Acid–base reaction between **1b** and CH_3CN gives the intermediate **A** which contains Zr–C_{alkyl}, Zr–C_{cage} and Zr–N bonds. The second equivalent of CH_3CN inserts into the Zr–C_{alkyl} bond to afford the monoinsertion species **B**/**B′**, which dimerizes to form the final product **6b**. This result suggests that the reactivity follows the order: Zr–C_{alkyl} > Zr–N >> Zr–C_{cage}.

Complex **1b** reacted with TMS–N=C=N–TMS in toluene at room temperature to afford a desilylation product $\{[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}N(Me)(CH_2)_2NH(Me)][\mu\text{-}TMSN{=}C{=}N]\}_2$ (**5b**) in 53% isolated yield (Scheme 4). This complex was fully characterized by various spectroscopic techniques. A unique N=*C*=N resonance at 125.1 ppm was observed in its ^{13}C NMR spectrum. As shown in Fig. 8, the coordination environment of the Zr atom in **5b** is very similar to that observed in **6b**. The C(26)–N(4)/N(3) distances of 1.167(4)/1.286(4) Å and the linearity of the N(3)–C(26)–N(4) unit suggest that the N=C=N moiety remains in the product, which is consistent with the NMR results. The Zr–N(1)/N(2) distances of 2.403(3)/2.090(3) Å and the planarity of N(1) indicate that N(1) is the amido nitrogen and N(2) is the amino nitrogen.

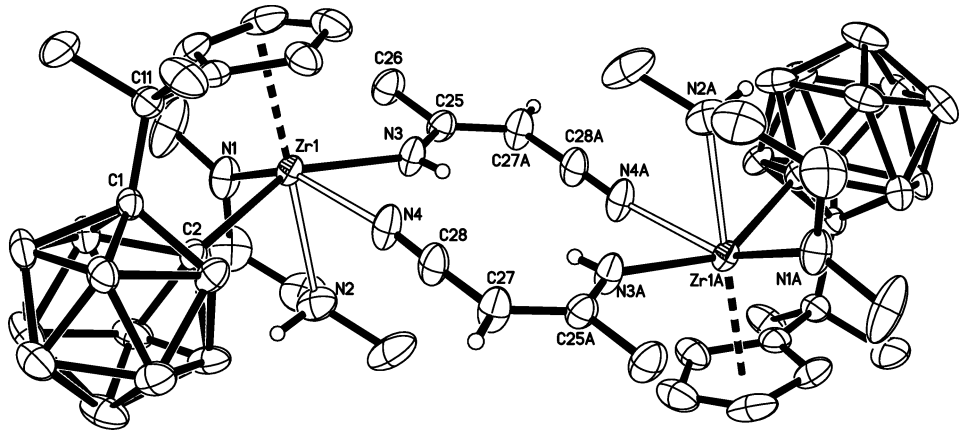
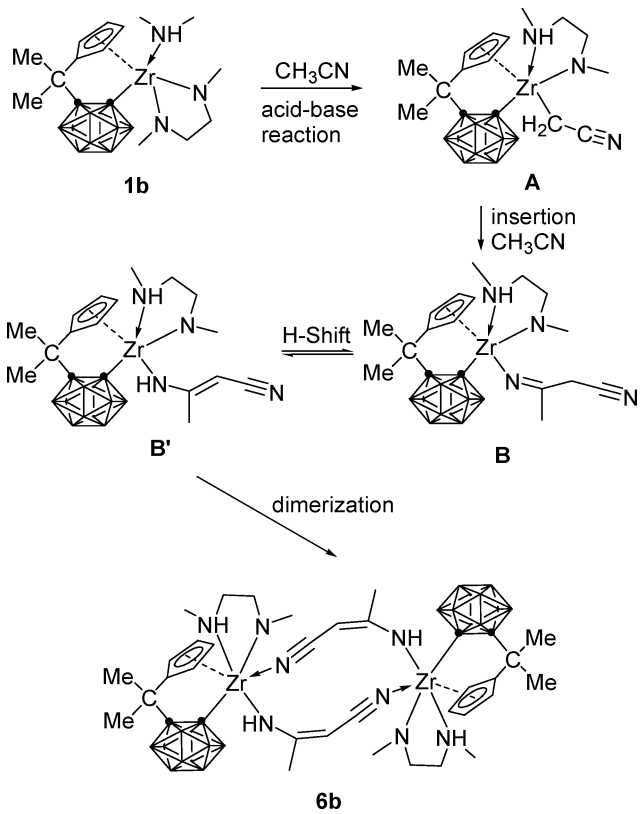
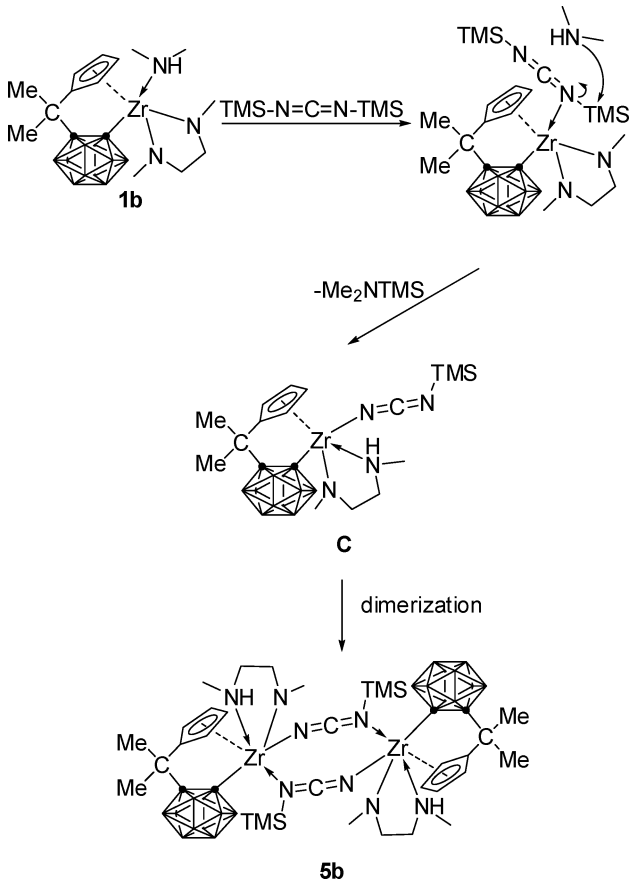


Fig. 7 Molecular structure of $\{[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}N(Me)(CH_2)_2NH(Me)][\mu\text{-}NHC(CH_3){=}CHC{\equiv}N]\}_2$ (**6b**).



Scheme 6



Scheme 7

It is noteworthy that **2b** did not react with TMS–N=C=N–TMS even in refluxing toluene, indicating that the coordinated Me_2NH in **1b** played a role in the desilylation process. Scheme 7 shows a proposed mechanism for the formation of **5b**.

Conclusion

Group 4 metallacycles can be conveniently prepared *via* amine exchange reaction of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M(NMe_2)_2$ with diamines $HN(Me)(CH_2)_nN(Me)H$ (n = 2, 3) in toluene. The formation of volatile Me_2NH and the chelate effect of the diamido ligands are the driving forces of the reactions. Reactivity studies show that unsaturated molecules insert exclusively into the M–N bonds to give the ring expansion products, and the M–C_{cage} bond remains intact. These results suggest that the inertness of the M–C_{cage} bond toward unsaturated molecules is best ascribed to the steric effect of the cage, and the mobility of the migratory groups may not play a role in the insertion reactions. This work also shows that insertion of unsaturated molecules into the M–N bonds in metallacycles is a useful and effective method for the construction of large ring systems.

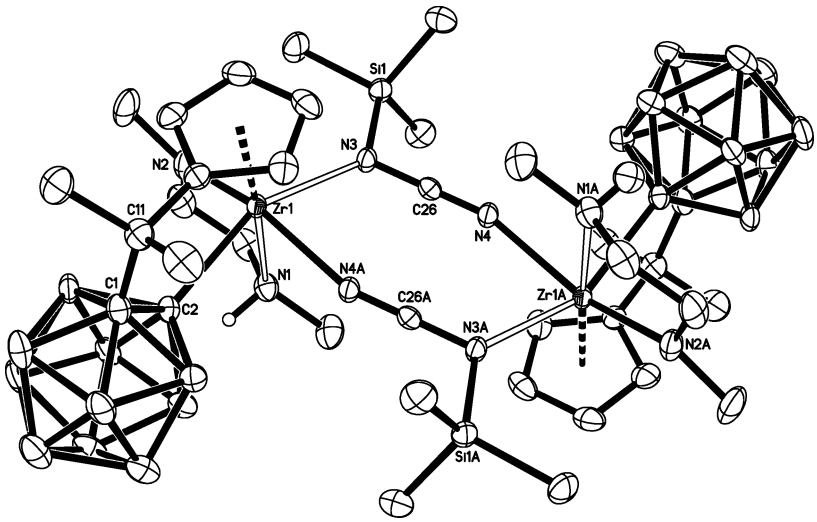


Fig. 8 Molecular structure of $\{[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}N(Me)(CH_2)_2NH(Me)][\mu\text{-}TMSN{=}C{=}N]\}_2$ (**5b**).

Experimental

General procedures

All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. All organic solvents were heated to reflux over sodium benzophenone for several days and freshly distilled prior to use. $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]M(NMe_2)_2$ (M = Ti, Zr, Hf) were prepared according to the literature method.[8] All chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise noted. IR spectra were obtained from KBr pellets prepared in the glovebox on a Perkin-Elmer 1600 Fourier transform spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300 and 75 MHz, respectively. ^{11}B NMR spectra were recorded on a Varian Inova 400 spectrometer at 128 MHz. All chemical shifts were reported in δ units with reference to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, and to external $BF_3{\cdot}OEt_2$ (δ = 0.00 ppm) for boron chemical shifts. Elemental analyses were performed by Shanghai Institute of Organic Chemistry, The Chinese Academy of Sciences, China.

Syntheses

Prepartion of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti[\eta^2\text{-}N(Me)CH_2CH_2N(Me)]$ (1a). To a toluene (15 mL) solution of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(NMe_2)_2$ (191 mg, 0.5 mmol) was added dropwise a toluene (8 mL) solution of $MeNHCH_2CH_2NHMe$ (220 mg, 2.5 mmol) at 0 °C with stirring. The mixture was warmed to room temperature and then heated at 60 °C for 2 d. After filtration, the resulting red solution was concentrated under vacuum to about 5 mL. Complex **1a** was isolated as red crystals after this solution had stood at room temperature for 1 d (129 mg, 68%). ^{1}H NMR (300 MHz, C_6D_6): δ 5.55 (brs, 2H), 5.43 (brs, 2H) (C_5H_4), 3.49 (d, J = 9.0 Hz, 2H), 3.25 (d, J = 9.0 Hz, 2H) (NCH_2), 2.62 (s, 6H) ($N(CH_3)$), 1.44 (s, 6H) ($C(CH_3)_2$). ^{13}C NMR (75 MHz, C_6D_6): δ 135.4, 112.2, 109.2 (C_5H_4), 57.6 (NCH_2), 50.4 ($N(CH_3)$), 42.4 ($C(CH_3)_2$), 31.9 ($C(CH_3)_2$), the cage carbons were not observed. ^{11}B NMR (128 MHz, C_6D_6): δ −3.2 (2B), −6.2 (2B), −9.7 (4B), −12.3 (2B). IR (KBr, cm^{-1}): ν 2576 (vs) (B–H). Anal. calcd for $C_{14}H_{30}B_{10}N_2Ti$: C, 43.97; H, 7.91; N, 7.33. Found: C, 43.88; H, 8.34; N, 7.10%.

Preparation of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr[\eta^2\text{-}N(Me)CH_2CH_2N(Me)](HNMe_2)$ (1b). To a toluene (15 mL) solution of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Zr(NMe_2)_2$ (214 mg, 0.5 mmol) was added dropwise a toluene (8 mL) solution of $MeNHCH_2CH_2NHMe$ (49 mg, 0.6 mmol) at −30 °C with stirring. The mixture was warmed to room temperature and stirred for 20 min. After filtration, the resulting orange-red solution was concentrated under vacuum to about 5 mL, to which was added 5 mL of *n*-hexane. Complex **1b** was isolated as an orange solid after this solution had stood at −30 °C for 2 d (173 mg, 73%). ^{1}H NMR (300 MHz, C_6D_6): δ 5.98 (d, J = 1.8 Hz, 1H), 5.59 (brs, 1H), 5.44 (brs, 1H), 5.34 (brs, 1H) (C_5H_4), 2.88 (s, 6H) ($N(CH_3)$), 2.67 (m, 4H) (NCH_2), 1.73 (d, J = 6.0 Hz, 6H) ($NH(CH_3)_2$), 1.44 (s, 3H), 1.42 (s, 3H) ($C(CH_3)_2$). ^{13}C NMR (75 MHz, C_6D_6): δ 146.2, 113.4, 110.4, 107.5 (C_5H_4), 56.4, 52.4 (NCH_2), 46.9, 42.8 ($N(CH_3)$), 41.7 ($C(CH_3)_2$), 37.9, 32.2 ($C(CH_3)_2$), 33.4 ($NH(CH_3)_2$), the cage carbons were not observed. ^{11}B NMR (128 MHz, C_6D_6): δ −2.1 (1B), −3.1 (1B), −4.6 (1B), −5.2 (1B), −9.0 (3B), −11.1 (3B). IR (KBr, cm^{-1}): ν 2552 (vs) (B–H). Anal. calcd for $C_{14}H_{30}B_{10}N_2Zr$ [**1b**–Me_2NH]: C, 39.50; H, 7.10; N, 6.58. Found: C, 39.76; H, 7.62; N, 6.68%.

Preparation of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti[\eta^2\text{-}N(Me)CH_2CH_2CH_2N(Me)]$ (2a). To a toluene (15 mL) solution of $[\eta^5{:}\sigma\text{-}Me_2C(C_5H_4)(C_2B_{10}H_{10})]Ti(NMe_2)_2$ (191 mg, 0.5 mmol) was added dropwise a toluene (8 mL) solution of $MeNH(CH_2)_3NHMe$ (153 mg, 1.5 mmol) at 0 °C with stirring. The mixture was warmed to room temperature and heated at 90 °C for 2 d. After filtration, the resulting red solution was concentrated under vacuum to about 8 mL. Complex **2a** was isolated as orange-red crystals after this solution had stood at room temperature for 3 d (124 mg, 64%). ^{1}H NMR (300 MHz, C_6D_6): δ 5.47 (m, 4H) (C_5H_4), 3.12 (m, 2H), 2.86 (m, 2H) (NCH_2), 2.69 (s, 6H) ($N(CH_3)$), 1.59 (m, 2H) ($CH_2CH_2CH_2$), 1.43 (s, 6H) ($C(CH_3)_2$). ^{13}C NMR (75 MHz,

C_6D_6): δ 149.5, 112.4, 110.0 (C_5H_4), 62.6 (NCH_2), 48.7 (N(CH_3)), 42.0 ($C(CH_3)_2$), 31.9 (C(CH_3)$_2$), 31.2 ($CH_2CH_2CH_2$), the cage carbons were not observed. ^{11}B NMR (128 MHz, C_6D_6): δ −2.6 (2B), −5.6 (2B), −8.9 (4B), −11.7 (2B). IR (KBr, cm^{-1}): ν 2598 (vs), 2565 (vs), 2540 (vs) (B–H). Anal. calcd for $C_{15}H_{32}B_{10}N_2Ti$: C, 45.45; H, 8.14; N, 7.07. Found: C, 44.92; H, 7.95; N, 7.26%.

Preparation of [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Zr[η^2-N(Me)-CH$_2$CH$_2$CH$_2$N(Me)] (2b). To a toluene (15 mL) solution of [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Zr(NMe$_2$)$_2$ (214 mg, 0.5 mmol) was added dropwise a toluene (8 mL) solution of MeNH(CH$_2$)$_3$NHMe (56 mg, 0.55 mmol) at 0 °C with stirring. The mixture was warmed to room temperature and stirred overnight. After filtration, the resulting yellow solution was concentrated under vacuum to about 8 mL. Complex **2b** was isolated as yellow crystals after this solution had stood at room temperature for 2 d (179 mg, 82%). ^{1}H NMR (300 MHz, C_6D_6): δ 5.66 (d, J = 2.7 Hz, 2H), 5.61 (d, J = 2.7 Hz, 2H) (C_5H_4), 2.90 (m, 4H) (NCH_2), 2.66 (s, 6H) (N(CH_3)), 1.97 (m, 2H), ($CH_2CH_2CH_2$), 1.40 (s, 6H) (C(CH_3)$_2$). ^{13}C NMR (75 MHz, C_6D_6): δ 146.4, 113.0, 109.3 (C_5H_4), 57.3 (NCH_2), 46.0 (N(CH_3)), 42.5 ($C(CH_3)_2$), 32.6 (C(CH_3)$_2$), 27.4 ($CH_2CH_2CH_2$), the cage carbons were not observed. ^{11}B NMR (128 MHz, C_6D_6): δ −2.3 (2B), −5.1 (2B), −8.6 (2B), −9.2 (2B), −11.9 (2B). IR (KBr, cm^{-1}): ν 2562 (vs) (B–H). Anal. calcd for $C_{15}H_{32}B_{10}N_2Zr$: C, 40.97; H, 7.33; N, 6.37. Found: C, 40.99; H, 7.74; N, 6.13%.

Preparation of [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Hf[η^2-N(Me)-CH$_2$CH$_2$CH$_2$N(Me)] (2c). This complex was prepared as yellow crystals from [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Hf(NMe$_2$)$_2$ (258 mg, 0.5 mmol) and MeNH(CH$_2$)$_3$NHMe (56 mg, 0.55 mmol) in toluene using an identical procedure to that reported for **2b**: yield 214 mg (82%). ^{1}H NMR (300 MHz, C_6D_6): δ 5.59 (d, J = 2.1 Hz, 2H), 5.57 (d, J = 2.1 Hz, 2H) (C_5H_4), 3.01 (m, 4H) (NCH_2), 2.75 (s, 6H) (N(CH_3)), 1.78 (m, 2H) ($CH_2CH_2CH_2$), 1.38 (s, 6H) (C(CH_3)$_2$). ^{13}C NMR (75 MHz, C_6D_6): δ 145.8, 112.0, 108.7 (C_5H_4), 57.8 (NCH_2), 45.1 (N(CH_3)), 42.0 ($C(CH_3)_2$), 32.5 (C(CH_3)$_2$), 28.2 ($CH_2CH_2CH_2$), the cage carbons were not observed. ^{11}B NMR (128 MHz, C_6D_6): δ −1.4 (1B), −2.1 (1B), −4.9 (2B), −8.9 (4B), −12.0 (2B). IR (KBr, cm^{-1}): ν 2566 (vs) (B–H). Anal. calcd for $C_{15}H_{32}B_{10}N_2Hf$: C, 34.18; H, 6.12; N, 5.32. Found: C, 34.11; H, 6.57; N, 4.78%.

Preparation of [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Ti[η^2:η^2-XyN=CN(Me)(CH$_2$)$_2$N(Me)C=NXy] (3a). To a toluene (15 mL) solution of **1a** (190 mg, 0.5 mmol) was added dropwise a toluene (8 mL) solution of XyNC (2,6-Me$_2$C$_6$H$_3$NC) (131 mg, 1.0 mmol) at −30 °C with stirring. The mixture was warmed to room temperature and stirred overnight. After filtration, the white solid was collected and redissolved in THF (20 mL). The resulting pale-yellow solution was concentrated to about 8 mL. Complex **3a** was isolated as yellow crystals after this solution had stood at room temperature for 2 d (225 mg, 66%). Crystals suitable for X-ray analyses were grown from a benzene–THF solution at room temperature. ^{1}H NMR (300 MHz, pyridine-d_5): δ 7.09 (m, 6H) (C_6H_3), 5.85 (d, J = 2.4 Hz, 2H), 5.83 (d, J = 2.4 Hz, 2H) (C_5H_4), 3.81 (dd, J = 8.4 and 7.2 Hz, 2H), 3.38 (m, 2H) (NCH_2), 2.53 (s, 6H) (N(CH_3)), 2.27 (s, 6H), 1.94 (s, 6H) ($C_6H_3(CH_3)_2$), 1.72 (s, 6H) (C(CH_3)$_2$). ^{13}C NMR (75 MHz, pyridine-d_5): δ 203.9 (C=N), 148.2, 147.5, 133.0, 132.6, 129.0, 128.4, 125.4 (aryl C), 105.4, 103.0 (C_5H_4), 53.7 (NCH_2), 42.3 ($C(CH_3)_2$), 36.8 (NCH_3), 33.2 (C(CH_3)$_2$), 21.3, 20.5 ($C_6H_3(CH_3)_2$), the cage carbons were not observed. ^{11}B NMR (128 MHz, pyridine-d_5): δ −3.9 (2B), −5.9 (2B), −9.2 (3B), −10.3 (2B), −13.4 (1B). IR (KBr, cm^{-1}): ν 2598 (vs), 2538 (vs) (B–H). Anal. calcd for $C_{32}H_{48}B_{10}N_4Ti$: C, 59.61; H, 7.50; N, 8.69. Found: C, 59.88; H, 7.65; N, 8.40%.

Preparation of [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Zr[η^2:η^2-XyN=CN(Me)(CH$_2$)$_2$N(Me)C=NXy] (3b). This complex was prepared as colorless crystals from **1b** (235 mg, 0.5 mmol) and XyNC (131 mg, 1.0 mmol) in toluene using an identical procedure to that reported for **3a**: yield 247 mg (68%). Crystals suitable for X-ray analyses were grown from a benzene–THF solution at room temperature. ^{1}H NMR (300 MHz, pyridine-d_5): δ 7.08 (m, 6H) (C_6H_3), 6.05 (m, 4H) (C_5H_4), 3.87 (dd, J = 8.4 and 7.2 Hz, 2H), 3.36 (m, 2H) (NCH_2), 2.51 (s, 6H) (NCH_3), 2.29 (s, 6H), 1.91 (s, 6H) ($C_6H_3(CH_3)_2$), 1.71 (s, 6H) (C(CH_3)$_2$). ^{13}C NMR (75 MHz, pyridine-d_5): δ 207.4 (C=N), 146.8, 146.7, 130.9, 130.7, 128.9, 127.5, 127.3, 124.0, 121.4 (aryl C), 105.5, 102.4 (C_5H_4), 54.7 (NCH_2), 42.0 (C(CH_3)$_2$), 35.1 (NCH_3), 32.6 (C(CH_3)$_2$), 19.6, 18.8 ($C_6H_3(CH_3)_2$), the cage carbons were not observed. ^{11}B NMR (128 MHz, pyridine-d_5): δ −3.3 (2B), −5.3 (2B), −9.1 (5B), −13.3 (1B). IR (KBr, cm^{-1}): ν 2554 (vs) (B–H). Anal. calcd for $C_{32}H_{48}B_{10}N_4Zr$: C, 55.86; H, 7.03; N, 8.14. Found: C, 55.40; H, 7.39; N, 7.86%.

Preparation of {[η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Zr[μ-η^2:η^2-OCN(Ph)N(Me)CH$_2$CH$_2$(Me)N(Ph)NCO]}$_2$ (4b). To a DME (30 mL) solution of **1b** (235 mg, 0.5 mmol) was added dropwise a DME (10 mL) solution of PhNCO (112 mg, 1.0 mmol) at −30 °C with stirring. The mixture was warmed to room temperature and stirred for 10 min. After filtration, the resulting pale yellow solution was concentrated under vacuum to about 30 mL. Complex **4b** was isolated as colorless crystals after this solution had stood at room temperature for 2 d (228 mg, 69%). ^{1}H NMR (300 MHz, pyridine-d_5): δ 9.13 (brs, 2H), 7.98 (d, J = 7.8 Hz, 6H), 7.64 (dd, J = 7.8 and 6.9 Hz, 8H), 7.03 (dd, J = 7.8 and 6.9 Hz, 4H) (C_6H_5), 6.62–6.17 (m, 8H) (C_5H_4), 3.57 (brs, 8H) (NCH_2), 3.06 (s, 12H) (N(CH_3)), 1.44 (s, 12H) (C(CH_3)$_2$). ^{13}C NMR (75 MHz, pyridine-d_5): δ 156.1 (N–C=O), 140.9, 132.0, 129.1, 128.7, 128.3, 128.0, 121.9, 120.1 (aryl C + C_5H_4), 57.9 (NCH_2), 46.9 (NCH_3), 40.7 ($C(CH_3)_2$), 34.9, 29.9 (C(CH_3)$_2$), the cage carbons were not observed. ^{11}B NMR (128 MHz, pyridine-d_5): δ −3.7 (6B), −9.0 (4B), −11.2 (4B), −13.3 (6B). IR (KBr, cm^{-1}): ν 2549 (vs) (B–H). Anal. calcd for $C_{56}H_{80}B_{20}N_8O_2Zr_2$: C, 50.65; H, 6.07; N, 8.44. Found: C, 50.42; H, 6.40; N, 8.24%.

Preparation of {[η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Zr[η^2-N(Me)-(CH$_2$)$_2$NH(Me)][μ-TMSN=C=N]}$_2$ (5b). To a toluene (15 mL) solution of **1b** (235 mg, 0.5 mmol) was added dropwise a toluene (8 mL) solution of TMSN=C=NTMS (170 mg, 1.0 mmol) at −30 °C with stirring, and the mixture was warmed to room temperature and stirred overnight. After filtration, the resulting clear orange solution was concentrated under vacuum to about 10 mL. Complex **5b** was isolated as yellow crystals after this solution had stood at room temperature for 5 d (142 mg, 53%). ^{1}H NMR (300 MHz, pyridine-d_5): δ 6.65 (d, J = 2.7 Hz, 1H), 6.46 (d, J = 2.7 Hz, 1H), 5.88 (d, J = 2.7 Hz, 1H), 5.18 (d, J = 2.7 Hz, 1H) (C_5H_4), 3.61 (m, 2H), 3.18 (m, 2H) (CH_3NCH_2),

3.40 (s, 6H) (N(CH_3)), 2.64 (m, 4H) (CH_3NHCH_2), 2.33 (d, J = 5.7 Hz, 6H) (NHCH_3), 1.59 (s, 6H), 1.45 (s, 6H) (C(CH_3)$_2$), 0.44 (s, 18H) (Si(CH_3)$_3$). ^{13}C NMR (75 MHz, pyridine-d_5): δ 144.1 (C_5H_4), 125.1 (N=C=N), 117.6, 113.0, 112.1, 110.0 (C_5H_4), 103.8, 102.4 (cage C), 59.6 (CH_3NCH_2), 51.9 (CH_3NHCH_2), 50.6 (N(CH$_3$)), 39.5 (NH(CH$_3$)), 40.7 (C(CH$_3$)$_2$), 27.6, 26.3 (C(CH$_3$)$_2$), 2.0 (Si(CH$_3$)$_3$). ^{11}B NMR (128 MHz, pyridine-d_5): δ −3.4 (6B), −6.3 (6B), −9.2 (8B). IR (KBr, cm^{-1}): ν 2556 (vs) (B–H). Anal. calcd for $C_{32}H_{68}B_{20}N_6Si_2Zr_2$ (**5b**–$C_4H_{12}N_2$): C, 38.75; H, 6.91; N, 8.47. Found: C, 39.18; H, 6.94; N, 7.95%.

Preparation of {[η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Zr[η^2-N(Me)-(CH$_2$)$_2$NH(Me)][μ-NHC(CH$_3$)=CHC≡N]}$_2$ (6b). This complex was prepared as yellow crystals from **1b** (235 mg, 0.5 mmol) and CH_3CN (62 mg, 1.5 mmol) in DME using an identical procedure to that reported for **4b**: yield 106 mg (42%). NMR data were not obtainable since the crystals were not soluble in any organic solvents. IR (KBr, cm^{-1}): ν 3788 (w), 3719 (w), 3272 (w), 2903 (m), 2550 (vs) (B–H), 2328 (w), 2166 (s), 1625 (w), 1521 (s), 1048 (m), 1005 (m), 803 (m). Anal. calcd for $C_{36}H_{72}B_{20}N_8Zr_2$: C, 42.57; H, 7.15; N, 11.03. Found: C, 42.95; H, 7.32; N, 10.61%.

Preparation of [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Zr[η^2:η^2-XyN=CN(Me)(CH$_2$)$_3$N(Me)C=NXy] (7b). This complex was prepared as colorless crystals from **2b** (220 mg, 0.5 mmol) and XyNC (131 mg, 1.0 mmol) in toluene solution using an identical procedure to that reported for **3a**: yield 222 mg (63%). ^{1}H NMR (300 MHz, pyridine-d_5): δ 7.08 (m, 6H) (C_6H_3), 6.25 (brs, 2H), 6.01 (brs, 2H) (C_5H_4), 3.80 (m, 2H), 3.20 (m, 2H) (NCH_2), 2.47 (s, 6H) (N(CH_3)), 2.24 (s, 6H), 2.18 (m, 2H) ($CH_2CH_2CH_2$), 1.99 (s, 6H) (C_6H_3(CH_3)$_2$), 1.68 (s, 6H) (C(CH_3)$_2$). The ^{13}C NMR was not obtainable due to very poor solubility. ^{11}B NMR (128 MHz, pyridine-d_5): δ −3.2 (2B), −5.4 (2B), −9.0 (6B). IR (KBr, cm^{-1}): ν 2593 (vs), 2547 (vs) (B–H). Anal. calcd for $C_{33}H_{50}B_{10}N_4Zr$: C, 56.45; H, 7.18; N, 7.98. Found: C, 56.71; H, 6.96; N, 7.62%.

Preparation of [η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Hf[η^2:η^2-XyN=CN(Me)(CH$_2$)$_3$N(Me)C=NXy] (7c). This complex was prepared as colorless crystals from **2c** (257 mg, 0.5 mmol) and XyNC (131 mg, 1.0 mmol) in toluene solution using an identical procedure to that reported for **3a**: yield 231 mg (58%). ^{1}H NMR (300 MHz, pyridine-d_5): δ 7.04 (m, 6H) (C_6H_3), 6.21 (brs, 2H), 5.96 (brs, 2H) (C_5H_4), 3.76 (brs, 2H), 3.18 (brs, 2H) (NCH_2), 2.45 (s, 6H) (NCH_3), 2.15 (m, 2H) ($CH_2CH_2CH_2$), 2.03 (s, 6H), 1.58 (s, 6H) (C_6H_3(CH_3)$_2$), 1.68 (s, 6H) (C(CH_3)$_2$). The ^{13}C NMR was not obtainable due to very poor solubility. ^{11}B NMR (128 MHz, pyridine-d_5): δ −3.0 (2B), −5.2 (2B), −8.9 (4B), −10.2 (2B). IR (KBr, cm^{-1}): ν 2598 (vs), 2544 (vs) (B–H). Anal. calcd for $C_{33}H_{50}B_{10}N_4Hf$: C, 50.21; H, 6.38; N, 7.10. Found: C, 50.55; H, 6.32; N, 6.59%.

Preparation of {[η^5:σ-Me$_2$C(C$_5$H$_4$)(C$_2$B$_{10}$H$_{10}$)]Zr[μ-N=C(Ph)-N(Me)(CH$_2$)$_3$N(Me)(Ph)C=N]}$_2$ (8b). This complex was prepared as pale-yellow crystals from **2b** (220 mg, 0.5 mmol) and PhCN (104 mg, 1.0 mmol) in DME using an identical procedure to that reported for **4b**: yield 206 mg (64%). Crystals suitable for X-ray analyses were grown from a THF solution at room temperature. ^{1}H NMR (300 MHz, pyridine-d_5): δ 7.42 (m, 12H), 6.82 (brs, 8H) (C_6H_5), 6.16 (brs, 4H), 4.92 (brs, 4H) (C_5H_4), 2.98 (m, 8H) (NCH_2), 2.77 (s, 12H) (NCH_3), 1.98 (m, 2H) ($CH_2CH_2CH_2$), 1.56 (s, 12H) (C(CH_3)$_2$). ^{13}C NMR (75 MHz, pyridine-d_5): δ 163.4 (N–C=N), 144.5, 140.6, 140.4, 127.9, 126.4, 110.1, 109.2, 108.8, 106.5 (aryl C + C_5H_4), 103.2, 100.6 (cage C), 71.4 (NCH$_2$), 57.9 (N(CH$_3$)), 41.6 (C(CH$_3$)$_2$), 32.5 (C(CH$_3$)$_2$), 26.6 ($CH_2CH_2CH_2$). ^{11}B NMR (128 MHz, pyridine-d_5): δ −3.2 (6B), −5.5 (6B), −9.2 (8B). IR (KBr, cm^{-1}): ν 2558 (vs) (B–H). Anal. calcd for $C_{61}H_{90}B_{20}N_8O_{0.75}Zr_2$ [**8b** + 0.75THF]: C, 54.43; H, 6.74; N, 8.32. Found: C, 54.75; H, 6.62; N, 8.14%.

Table 2 Crystal data and summary of data collection and refinement for **1a**, **2a**, **3a**·0.5C$_6$H$_6$ and **3b**·0.5C$_6$H$_6$

	1a	**2a**	**3a**·0.5C$_6$H$_6$	**3b**·0.5C$_6$H$_6$
Formula	$C_{14}H_{30}B_{10}N_2Ti$	$C_{15}H_{32}B_{10}N_2Ti$	$C_{35}H_{51}B_{10}N_4Ti$	$C_{35}H_{51}B_{10}N_4Zr$
Crystal size/mm	0.50 × 0.50 × 0.40	0.40 × 0.30 × 0.20	0.40 × 0.30 × 0.20	0.40 × 0.30 × 0.20
M_r	382.4	396.4	683.8	727.1
Crystal system	Trigonal	Trigonal	Monoclinic	Monoclinic
Space group	$R3m$	$R3m$	$P2_1/n$	$P2_1/n$
a/Å	25.806(4)	26.045(1)	10.500(2)	10.472(1)
b/Å	25.806(4)	26.045(1)	17.092(3)	17.389(2)
c/Å	9.888(2)	9.844(1)	21.352(4)	21.659(3)
α/°	90	90	90	90
β/°	90	90	98.56(3)	98.68(3)
γ/°	120	120	90	90
V/Å^3	5702.7(16)	5782.8(7)	3789.5(13)	3898.8(9)
Z	9	9	4	4
D_c/Mg m^{-3}	1.002	1.025	1.199	1.239
Radiation (λ(Mo-Kα))/Å	0.71073	0.71073	0.71073	0.71073
$2\theta_{max}$/°	50.0	56.0	50.0	56.6
μ/mm^{-1}	0.339	0.336	0.257	0.313
F(000)	1800	1872	1444	1516
Measured reflections	3637	13291	7069	26972
Observed reflections [$I > 2\sigma(I)$]	1271	2843	6681	9663
Parameters	133	139	451	451
Goodness of fit on F^2	0.956	0.973	0.968	1.014
R(int)	0.058	0.045	0.072	0.045
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.054$, $wR_2 = 0.131$	$R_1 = 0.043$, $wR_2 = 0.105$	$R_1 = 0.071$, $wR_2 = 0.174$	$R_1 = 0.049$, $wR_2 = 0.119$

Table 3 Crystal data and summary of data collection and refinement for **4b**, **5b**, **6b**, **7b** and **8b**·0.75THF

	4b	**5b**	**6b**	**7b**	**8b**·0.75THF
Formula	$C_{56}H_{80}B_{20}N_8O_4Zr_2$	$C_{36}H_{80}B_{20}N_8Si_2Zr_2$	$C_{36}H_{72}B_{20}N_8Zr_2$	$C_{33}H_{50}B_{10}N_4Zr$	$C_{61}H_{90}B_{20}N_8O_{0.75}Zr_2$
Crystal size/mm	0.50 × 0.30 × 0.10	0.30 × 0.20 × 0.20	0.40 × 0.30 × 0.20	0.50 × 0.40 × 0.30	0.40 × 0.20 × 0.20
M_r	1327.9	1079.9	1015.7	702.1	1346.1
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a/Å	10.896(2)	15.741(2)	14.933(2)	10.696(2)	19.677(2)
b/Å	17.104(2)	10.721(1)	9.927(1)	17.369(3)	24.137(3)
c/Å	20.437(3)	16.257(2)	17.170(2)	21.358(2)	34.482(4)
α/°	73.67(1)	90	90	90	90
β/°	80.77(1)	101.21(1)	93.55(1)	96.45(1)	98.69(1)
γ/°	74.87(1)	90	90	90	90
V/Å^3	3512.7(8)	2691.0(5)	2540.3(4)	3942.7(10)	16189(3)
Z	2	2	2	4	8
D_c/Mg m^{-3}	1.255	1.333	1.328	1.183	1.105
Radiation (λ(Mo-Kα))/Å	0.71073	0.71073	0.71073	0.71073	0.71073
$2\theta_{max}$/°	50.0	56.0	50.0	50.0	50.0
μ/mm^{-1}	0.345	0.469	0.448	0.307	0.297
F(000)	1368	1120	1048	1464	5584
Measured reflections	19247	17992	13447	20935	86960
Observed reflections [$I > 2\sigma(I)$]	12298	6500	4479	6939	28466
Parameters	811	307	310	433	1721
Goodness of fit on F^2	0.841	1.003	1.045	1.070	0.817
R(int)	0.0640	0.051	0.045	0.036	0.167
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.062$, $wR_2 = 0.126$	$R_1 = 0.048$, $wR_2 = 0.117$	$R_1 = 0.054$, $wR_2 = 0.136$	$R_1 = 0.036$, $wR_2 = 0.093$	$R_1 = 0.086$, $wR_2 = 0.211$

X-Ray structure determination

All single crystals were immersed in Paraton-N oil and sealed under N_2 in thin-walled glass capillaries. Data were collected at 293 K on a Brucker SMART 1000 CCD diffractometer using Mo-Kα radiation. An empirical absorption correction was applied using the SADABS program.[11] 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 calculations on F^2 using the SHELXTL program package.[12] All hydrogen atoms except for the disordered solvent molecules were geometrically fixed using the riding model. Molecular structures of **3a**,**b** showed half benzene of solvation. There were two crystallographyically independent molecules in the unit cell of **8b** and three highly disordered THF molecules with a site occupancy of 0.5, resulting in a relatively high R value. The THF molecules were refined by means of a 'similarity restraint'. Crystal data and details of data collection and structure refinements were given in Tables 2 and 3.

CCDC reference numbers 665266–665274 for **1a**, **2a**, **3a**, **3b**, **4b**, **5b**, **6b**, **7b** and **8b**, respectively.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b716929a

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