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Unexpected alkyl-substituent exchange during the formation of a cationic bis(zirconocene) complex that contains a planar four-co-ordinate carbon atom

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Treatment of the alkyl Group 4 metallocene cation reagent $[ZrCp_2\{CH_2Si(CH_3)_3\}(THF)]^+[BPh_4]^-$ **2b** with bis(propynyl)zirconocene **1a** yielded the cationic dimetallic complex $[(ZrCp_2)_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-}CH_3CCCH_3)\{\mu\text{-}\kappa^2\text{-}C{\equiv}CCH_2Si(CH_3)_3\}]^+$ **3d** with BPh_4^- anion. Complex **3d** was characterized spectroscopically and by a crystal structure analysis. It contains a planar four-co-ordinate carbon atom, which is stabilized by the interaction with both Group 4 metal centres. Finding the $CH_2Si(CH_3)_3$ substituent, that originates from the alkylzirconocene reagent, attached at the μ-acetylide ligand in the final product is unusual. A reversible alkynyl carbometallation sequence is proposed to account for the observed selective formation of **3d**. Complex **3d** reacted with alkyl isocyanides $RN{\equiv}C$ ($R = CMe_2CH_2CMe_3$, CMe_3, or cyclohexyl) by replacement of the $\mu\text{-}\eta^1\text{:}\eta^2\text{-}CH_3CCCH_3$ ligand to form the μ-isocyanide complexes $[(ZrCp_2)_2(\mu\text{-}\eta^1\text{-}C\text{:}\eta^2\text{-}C,N\text{-}RNC)\{\mu\text{-}\kappa^2\text{-}C{\equiv}CCH_2Si(CH_3)_2\}]^+$ (with BPh_4^- anion) of which one was characterized by a crystal structure analysis.

Introduction

Dimetallic cationic metallocene complexes **3** that contain a planar four-co-ordinate carbon atom inside their bridging unsaturated hydrocarbon framework[1–4] are readily available by treatment of bis(alkynyl) Group 4 metallocene complexes (for the majority of examples the respective zirconium complexes **1** were employed) with an alkyl Group 4 metallocene cation[5] (*e.g.* "Jordan's cation" $[ZrCp_2(CH_3)(THF)]^+$ **2a**[6]). In a detailed mechanistic study[7] we had shown that this type of reaction exhibits a remarkable regioselectivity and a pronounced regiochemical "memory effect" that in most cases leads to a product formation where the respective components still have retained the essential connectivity information about their origin, even when a rapid subsequent rearrangement of the framework takes place[8] (**3a** $\rightleftharpoons$ **3a′**, as illustrated in eqn. (1) of Scheme 1).

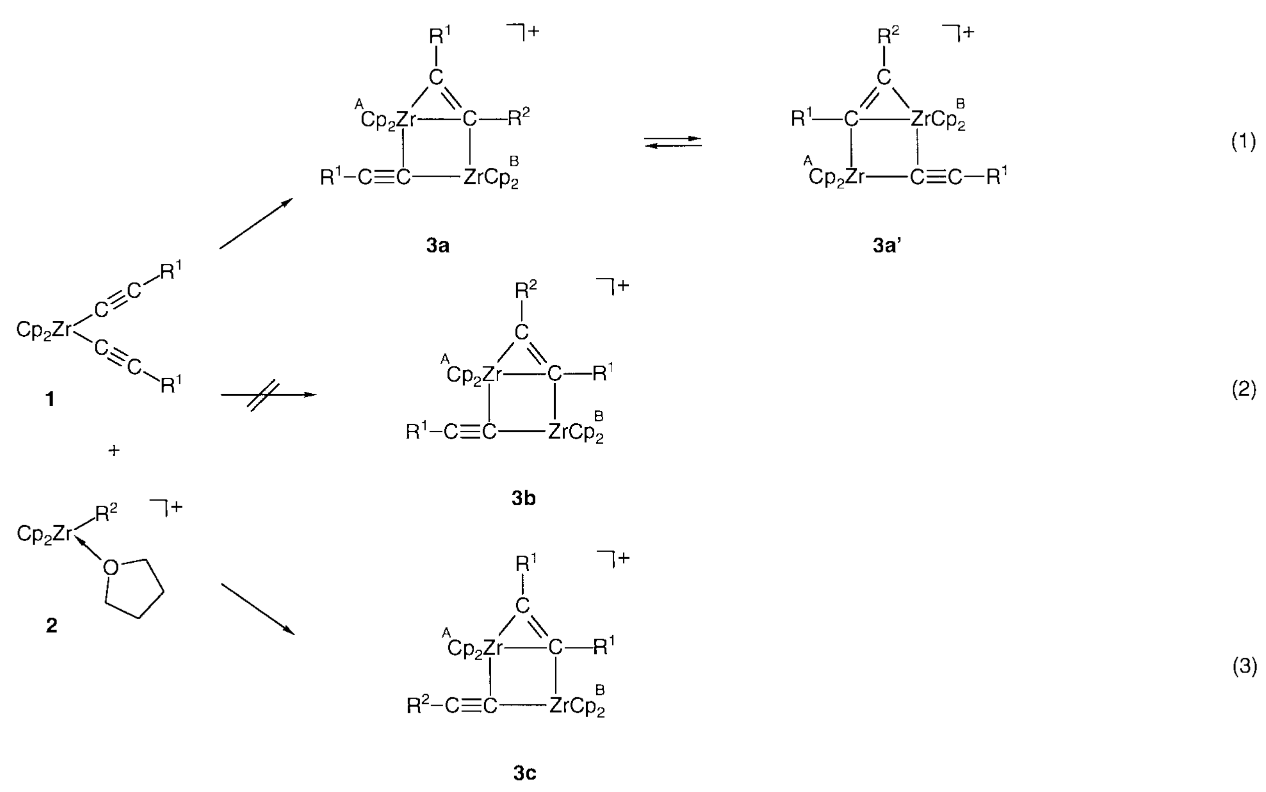
The "wrong" regioisomers **3b** (see eqn. (2) of Scheme 1) were not found, but we have now, to our knowledge for the first time, observed the clean formation of the alternative regioisomer **3c** (see eqn. (3) of Scheme 1) where a substituent R^1 at one of the σ-alkynyl ligands has become exchanged with the σ-alkyl group R^2 introduced by the alkylmetallocene cation reagent $[ZrCp_2R]^+$ **2**. The synthetic example showing this unusual behaviour is described in this article, and we have tried to offer an explanation.

Results and discussion

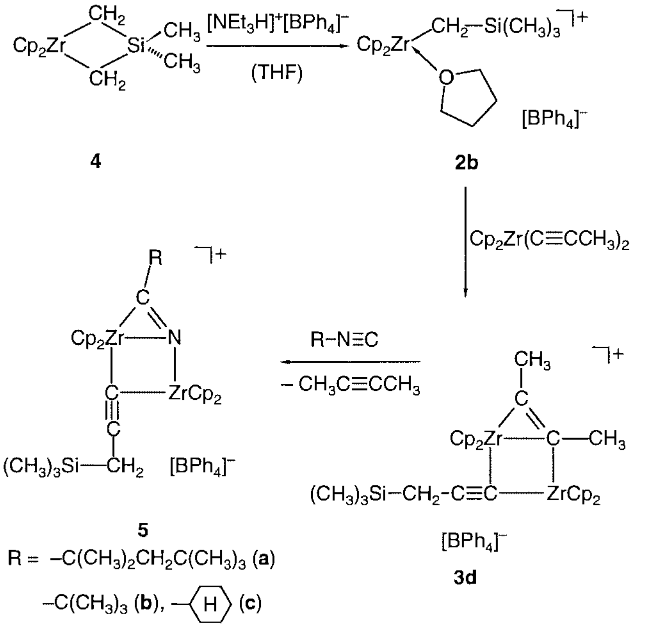
For this study we have employed the cation $[ZrCp_2\{CH_2Si(CH_3)_3\}(THF)]^+$ **2b**, with BPh_4^- anion. It was prepared, as described by Petersen and co-workers,[9] by treatment of the silazirconacyclobutane reagent[10] **4** with triethylammonium tetraphenylborate in tetrahydrofuran. The cation **2b** was then treated with bis(propynyl)zirconocene **1a** in a 1 : 1 stoichiometry. At ambient temperature in bromobenzene solution a slow reaction ensues (5 d), leading to a single organometallic product **3d** that was isolated as a solid material in 47% yield (Scheme 2). Single crystals of **3d** were obtained from dichloromethane–diethyl ether. The crystal structure analysis shows well separated anion and cation moieties of **3d** in the crystal (Fig. 1). The cation exhibits the typical planar dimetallabicyclic framework that is characteristic for this class of compounds.[2,3] The two zirconocene units are inequivalent. They are bridged by a $\mu\text{-}\eta^1\text{:}\eta^2$-2-butyne ligand. Carbon atom C2 of this ligand system is planar four-co-ordinate. The sum of bonding angles at C2 is 360.2°. It has four close bonding contacts to its neighbouring atoms (C2–C1 1.540(4), C2–C3 1.315(5), C2–Zr1 2.314(4), and C2–Zr2 2.514(3) Å). These bonding parameters are unexceptional for this class of compounds. Many examples of this anti-van't Hoff/LeBel complex type have shown similar bonding features.[2,3] Also, the C3–Zr2 linkage is very short at 2.179(3) Å, as is often observed in such types of frameworks. In addition, the zirconium atoms in **3d** are connected in plane by a $\mu\text{-}\kappa^2\text{-}C{\equiv}CCH_2Si(CH_3)_3$ bridging ligand. The corresponding metal–carbon σ-bond lengths are 2.263(3) (Zr1–C5) and 2.452(3) Å (Zr2–C5). This acetylide ligand is strongly leaning over toward the metal centre Zr2, but the corresponding Zr2–C6 interaction (2.824(3) Å) is probably rather weak.

The important result from this crystal structure analysis is the observation that the acetylide substituents are in unexpected positions. In the product obtained one of the methyl groups originally attached to the acetylide ligand, that has eventually become the $\mu\text{-}\kappa^2\text{-}C{\equiv}CR$ moiety, has exchanged with the $CH_2Si(CH_3)_3$ group that was introduced with the Cp_2ZrR^+ cation reagent.

The $^1H/^{13}C$ NMR spectra of complex **3d** are as expected at low temperature (^1H, 203 K, ^{13}C, 223 K in CD_2Cl_2). Two separate pairs of Cp signals (^1H δ 5.85, 5.69; ^{13}C δ 109.7, 108.1) are observed. There are the resonances of two different CH_3 groups at the $\mu\text{-}\eta^1\text{:}\eta^2\text{-}Me_2C_2$-bridging ligand ($^1H$ δ 2.47, −0.13; ^{13}C δ 28.8, −25.5); the resonances at negative δ values belong to the methyl substituent at the planar four-co-ordinate carbon centre C2. The C2 ^{13}C NMR resonance appears in the olefinic region (δ 124.4) as expected. The adjacent C3 resonance is at δ 211.8, which is also very typical for this type of complex. The μ-κ²-acetylide ^{13}C NMR resonances were found at δ 133.0 and 110.1 (C5, C6), and the $^1H/^{13}C$ NMR



Scheme 1



Scheme 2

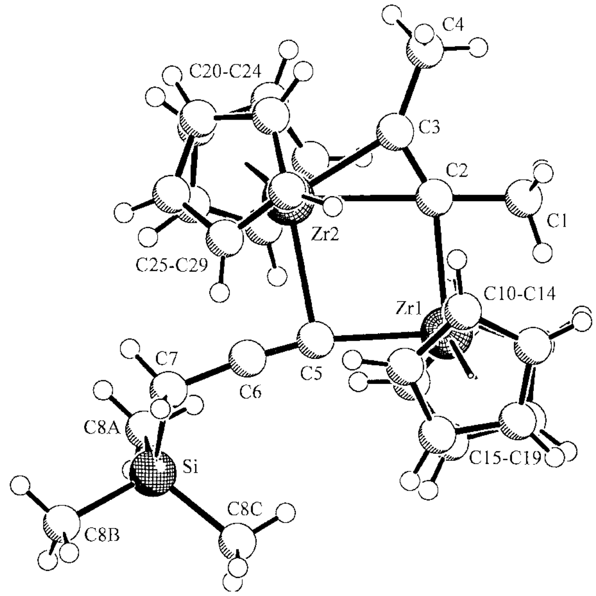


Fig. 1 Molecular structure of compound **3d** (cation only). Selected bond lengths (Å) and angles (°): Zr1–C5 2.263(3), Zr1–C2 2.314(4), Zr1···Zr2 3.5467(4), Zr2–C3 2.179(3), Zr2–C5 2.452(3), Zr2–C2 2.514(3), Zr2–C6 2.824(3), C1–C2 1.540(4), C2–C3 1.315(5), C3–C4 1.497(5), C5–C6 1.217(4), C6–C7 1.469(4) and C7–Si 1.903(4), C5–Zr1–C2 88.22(11), C5–Zr1–Zr2 43.27(8), C3–Zr2–C5 111.25(12), C3–Zr2–C2 31.52(12), C5–Zr2–C2 79.82(10), C3–C2–C1 121.0(3), C3–C2–Zr1 154.2(2), C1–C2–Zr1 84.6(2), C3–C2–Zr2 60.06(18), C1–C2–Zr2 177.5(3), Zr1–C2–Zr2 94.46(11), C2–C3–C4 129.1(3), C2–C3–Zr2 88.4(2), C4–C3–Zr2 142.5(3), C6–C5–Zr1 166.9(3), C6–C5–Zr2 94.6(2), Zr1–C5–Zr2 97.50(12), C5–C6–C7 173.3(3) and C6–C7–Si 111.1(2).

signals of the corresponding $CH_2Si(CH_3)_3$ substituent, that is attached at the acetylide carbon centre C6 (atom numbering as in Fig. 1), appear at δ 1.99/14.3 (CH_2) and 0.27/−2.1 ($Si(CH_3)_3$).

Complex **3d** shows temperature-dependent dynamic NMR spectra, like many examples of this class of organometallic planar four-co-ordinate carbon complexes.[8] Raising the monitoring temperature rapidly results in a broadening of the NMR resonances of the methyl groups C2–CH_3 and C3–CH_3, of the carbon atoms C2 and C3 and both metallocene moieties Cp_2Zr1 and Cp_2Zr2, and eventually to pairwise coalescence. The NMR features of the bridging $C{\equiv}CCH_2Si(CH_3)_3$ ligand remain unaffected by this dynamic exchange process (see eqn. (1) in Scheme 1); they are temperature invariant in the applied temperature range. From the ^1H NMR Cp coalescence the Gibbs activation barrier for the automerization process of complex **3d** was obtained as $\Delta G^{\ddagger}_{autom.}$ (250 K) = 11.5 ± 0.5 kcal mol^{-1}.

The uncommon substitution pattern of complex **3d** (*i.e.* with both propynyl derived methyl groups eventually appearing in the μ-η^1:η^2-2-butyne ligand and the trimethylsilylmethyl

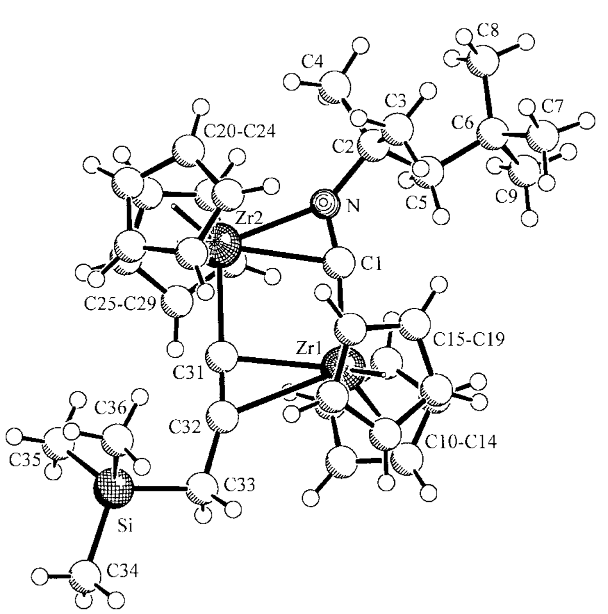


Fig. 2 A view of the molecular structure of complex **5a** (cation only)

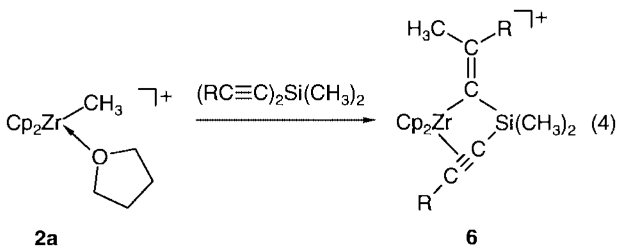
substituent from the $[ZrCp_2\{CH_2Si(CH_3)_3\}]^+$ reagent ending up as a new alkynyl substituent) is thus apparent from the crystal structure analysis and the very characteristic spectroscopic behaviour of this product. A few subsequent reactions were carried out that give derivatives of this organometallic system which principally showed that this substitution pattern was retained.

Complex **3d** was treated with a *ca.* 4-fold excess of 1,1,3,3-tetramethylbutyl isocyanide in dichloromethane at room temperature. During several hours the 2-butyne moiety of **3d** became substituted by the isocyanide unit with formation of the new complex **5a** (see Scheme 2).[11] Complex **5a** has retained the μ-$C{\equiv}CCH_2Si(CH_3)_2$ ligand (^{13}C NMR acetylide signals at δ 150.3 and 129.4, ^1H NMR resonances of the $CH_2Si(CH_3)_3$ group at δ 2.04 and 0.32) which is bridging between the two chemically inequivalent Cp_2Zr moieties ($^1H/^{13}C$ NMR signals at δ 5.68, 5.66/106.4, 106.0). The ^{13}C NMR resonance of the former isonitrile $N{\equiv}C$ atom occurs at δ 279.6 for the complex **5a**.

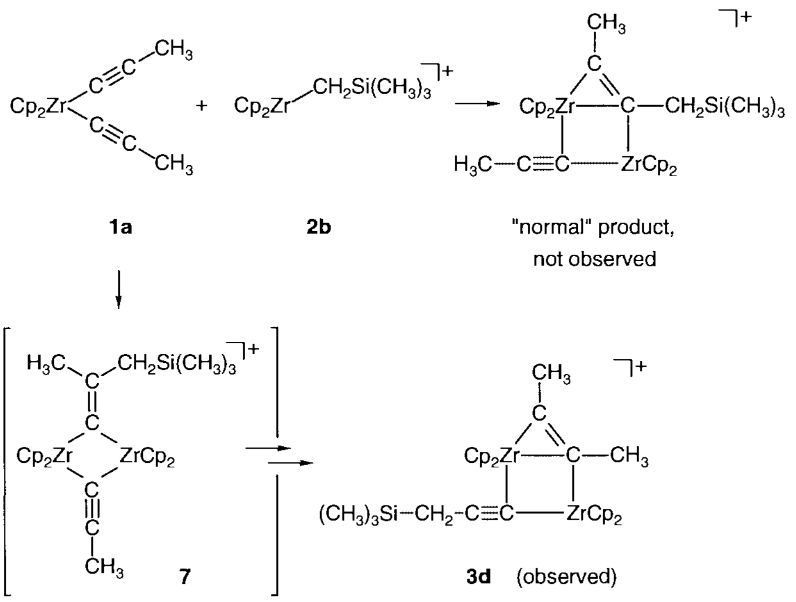
Single crystals of complex **5a** were obtained from dichloromethane–ether. The crystal structure analysis (see Fig. 2) shows well separated cations and anions in the crystal. Complex **5a** contains a planar central framework with a μ-η^1-C : η^2-C,N-isocyanide ligand and a μ-η^1-C : η^2-C_2-acetylide ligand bridging between two zirconocene units. It is one of the rare examples of a (μ-isocyanide)M_2 complex of an early transition metal,[12] but its overall structural type is not unprecedented.[11] The C1–N bond of **5a** is rather short at 1.221(5) Å. The corresponding Zr1–C1 and Zr2–N bond lengths are 2.150(4) and 2.282(3) Å, respectively. The remaining Zr2–C1 distance amounts to 2.416(5) Å. The pertinent bonding parameters at the (μ-acetylide)Zr_2 unit in **5a** are 2.261(4) (Zr2–C31), 1.211(5) (C31–C32), 2.430(5) (C31–Zr1), and 2.600(4) Å (C32–Zr1). The Zr1 ··· Zr2 separation is 3.515(1) Å. The Zr2 acetylide unit is close to linear (bond angles Zr2–C31–C32 178.9(4), C31–C32–C33 163.5(5)°), whereas the Zr1–C1–N unit is strongly bent at nitrogen (angles Zr1–C1–N 169.4(4), C1–N–C2 128.0(4)°).

Complex **3d** undergoes analogous exchange reactions with extrusion of the newly formed 2-butyne moiety upon treatment with *tert*-butyl isocyanide or cyclohexyl isocyanide. The resulting products **5b** and **5c** show similar spectral properties as **5a** (for details see the Experimental section).

The "memory effect" in the formation of the planar four-coordinate carbon complexes **3** (see Scheme 1) indicates a reaction pathway that involves alkynyl group transfer and subsequent formal reductive elimination (to form *e.g.* the μ-2-butyne ligand) at the stage of a sequence of dimetallic intermediates (see Scheme 3). The now observed complete alkyl group transfer is formally the result of a σ-bond exchange process. In view of substantial literature precedence (see below) it is likely that the observed CH_3 *vs.* $CH_2Si(CH_3)_3$ exchange may have taken place by a stepwise addition/elimination process, probably proceeding by means of an intermediate carbometallation product[13] **7** (see Scheme 3). A few related cases of such addition reactions of Cp_2ZrR^+ systems have previously been observed; the reaction depicted in eqn. (4) is a typical example.[14]

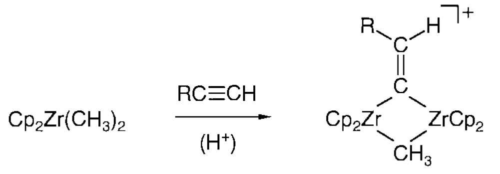


2a **6**



Scheme 3

Horton and Orpen[15] had observed the formation of examples of the carbometallation products **7a** upon treatment of mixtures of dimethylzirconocene and 1-alkynes, bearing small alkyl substituents, with dimethylanilinium tetraphenylborate (see eqn. (5)). We had spectroscopically



7a

(5)

detected the blue isomers **7** in a few selected cases during the formation of examples of the anti van't Hoff/LeBel systems **3**, but never separated or isolated them from these mixtures so far.[16]

Reversal of the alkynyl carbometallation by means of cleavage of the C(sp^2)–CH$_3$ bond[17] provides a simple mechanistic pathway that would lead to the here observed exchange of the substituents and ultimately to the selective formation of the unprecedented isomer **3d**. The fact that this product is formed so selectively without the admixture of intermolecular cross-over products seems to indicate that intramolecular sequences at the stage of the dimetallic systems might dominate this chemistry.

Experimental

All reactions were carried out in an inert atmosphere (argon) using Schlenk-type glassware or in a glove-box. Solvents were dried and distilled under argon prior to use. The starting materials [ZrCp$_2${CH$_2$Si(CH$_2$)$_3$}(THF)]$^+$[BPh$_4$]$^-$ **2b**[9] and ZrCp$_2$(C≡CCH$_3$)$_2$ **1a**[18] were prepared according to literature procedures. For additional general information see ref. 7.

Reaction of bis(propynyl)zirconocene 1a with [ZrCp$_2${CH$_2$Si(CH$_2$)$_3$}(THF)]$^+$[BPh$_4$]$^-$: synthesis of complex 3d

A suspension of 200 mg (28.5 mmol) of complex **2b** and 86 mg (28.5 mmol) of **1a** in 20 mL of bromobenzene was stirred for 5 d at room temperature. Diethyl ether (50 mL) was added. The precipitated solid was collected by filtration and washed with 20 mL of ether to yield 123 mg (47%) **3d**, mp 170 °C (decomp.) (Found: C, 69.34; H, 6.28. C$_{54}$H$_{57}$BSiZr$_2$ requires C, 69.94; H, 6.19). Single crystals were obtained by diffusion of ether vapor into a solution of **3d** in dichloromethane at −36 °C. δ_H (dichloromethane-*d*$_2$, 599.99 MHz, 203 K, atom numbering as used in Fig. 1) 5.85, 5.69 (s, each 10 H, Cp), 2.47 (s, 3 H, 3-CH$_3$), 1.99 (s, 2 H, CH$_2$[Si]), 0.27 (s, 9 H, Si(CH$_3$)$_3$), −0.13 (s, 3 H, 2-CH$_3$); BPh$_4^-$ 7.30 (m, 8 H), 7.05 (m, 8 H) and 6.90 (m, 4 H). Dynamic ^{1}H NMR spectra: T_c of the Cp resonances at 250 K, $\Delta\nu = 106$ Hz, $\Delta G^{\ddagger}_{\text{autom}}(250\ \text{K}) = 11.5 \pm 0.5$ kcal mol^{-1} (calculated according to the Gutowsky–Holm approximation)[19] δ_C (dichloromethane-*d*$_2$, 150.84 MHz, 223 K) 211.8 (C3), 133.0, 110.1 (C5, C6), 124.4 (C2), 109.7, 108.1 (Cp), 28.8 (C4), 14.3 (C7), −2.1 (C8) and −25.5 (C1); BPh$_4^-$ 164.5 ($^1J_{CB} = 50$ Hz), 136.3, 126.0, 122.0. Gradient enhanced heteronuclear single quantum coherence[20] (GHSQC): δ_C/δ_H (dichloromethane-*d*$_2$, 150.84/599.99 MHz, 223 K) 109.7/5.85 (CCp/CpH), 108.1/5.69 (CCp/CpH), 28.8/2.47 (C4/4-H), 14.3/1.99 (C7/7-H), −2.1/0.27 (C8/8-H), −25.5/-0.13 (C1/1-H). Gradient enhanced heteronuclear multiple bond correlation[20] (GHMBC): δ_C/δ_H (dichloromethane-*d*$_2$, 150.84/599.99 MHz, 223 K) 211.8/2.47 (C3/4-H), 211.8/−0.13 (C3/1-H), 133.0/1.99, 110.1/1.99 (C5/7-H, C6/7-H), 124.4/2.47 (C2/4-H), 124.4/−0.13 (C2/1-H), 14.3/0.27 (C7/8-H) and −2.1/1.99 (C8/7-H). IR (KBr) $\tilde{\nu}$/cm^{-1} 2038 (C≡C).

Crystallography

Crystal data for compound 3d. C$_{54}$H$_{57}$BSiZr$_2$, $M = 927.34$, orthorhombic, space group *Pna*2$_1$, (no. 33), $a = 25.643(1)$, $b = 18.965(1)$, $c = 9.398(1)$ Å, $V = 4570.4(6)$ Å^3, $T = 198$ K, $Z = 4$, μ(Mo-Kα) = 0.518 mm^{-1}, 28027 reflections measured, 8364 unique ($R_{\text{int}} = 0.044$), which were used in all calculations. The final $wR(F^2)$ was 0.070, $R1 = 0.032$. Nonius KappaCCD diffractometer with rotating anode generator Nonius FR591. Programs used: data collection Collect, data reduction Denzo-SMN, absorption correction SORTAV, structure solution SHELXS 97, structure refinement SHELXL 97, graphics SCHAKAL 92.[21]

Crystal data for compound 5a. C$_{59}$H$_{68}$BNSiZr$_2$, $M = 1012.48$, orthorhombic, space group *Pna*$_1$ (no. 33), $a = 18.999(1)$, $b = 27.303(1)$, $c = 9.902(1)$ Å, $V = 5136.5(6)$ Å^3, $T = 198$ K, $Z = 4$, μ(Mo-Kα) = 0.467 mm^{-1}, 40566 reflections measured, 9960 unique ($R_{\text{int}} = 0.062$), which were used in all calculations. The final $wR(F^2)$ was 0.081, $R1 = 0.038$.

CCDC reference number 186/1512.

See http://www.rsc.org/suppdata/dt/1999/2551/ for crystallographic files in .cif format.

Reaction of complex 3d

With C≡NC(CH$_3$)$_2$CH$_2$(CH$_3$)$_3$: preparation of complex 5a. The isocyanide C≡NC(CH$_3$)$_2$CH$_2$(CH$_3$)$_2$ (0.3 mL, 1.69 mmol) was added to a solution of 350 mg (0.38 mmol) of complex **3d** in 20 mL of dichloromethane at room temperature. The mixture was stirred at ambient temperature overnight, then reduced to *ca.* one half of its volume *in vacuo*. The product was precipitated by the addition of pentane (20 mL). The resulting yellow solid was collected by filtration and washed with 20 mL of pentane, then dried *in vacuo*. Yield of **5a**: 246 mg (64%), mp 200 °C (decomp. at 256 °C) (Found: C, 69.18; H, 7.24; N, 1.38. C$_{59}$H$_{68}$BNSiZr$_2$ requires C, 69.99; H, 6.77; N, 1.38). δ_H (dichloromethane-*d*$_2$, 200.13 MHz) 5.68, 5.66 (s, each 10 H, Cp), 2.04 (s, 2 H, ≡CCH$_2$), 1.94 (s, 2 H, CH$_2$), 1.73 (s, 6 H, C(CH$_3$)$_2$), 1.20 (s, 9 H, C(CH$_3$)$_3$) and 0.32 (s, 9 H, Si(CH$_3$)$_3$); BPh$_4^-$ 7.3 (m, 8 H), 7.1 (ps t, 8 H) and 6.9 (ps t, 4 H). δ_C (dichloromethane-*d*$_2$, 50.32 MHz) 279.6 (N=C), 150.3, 129.4 (C≡C), 106.4, 106.0 (Cp), 72.4 (*C*Me$_2$), 58.2 (CH$_2$), 32.5 (*C*Me$_3$), 31.9 (C(*C*H$_3$)$_3$), 30.2 (NC(*C*H$_3$)$_2$), 19.0 (CH$_2$[Si]) and −1.6 (Si(CH$_3$)$_3$); BPh$_4^-$: 164.5 (^{1}J$_{CB}$ = 50 Hz), 136.3, 126.0 and 122.1. IR (KBr) $\tilde{\nu}$/cm^{-1} 1694 (C=C).

With *tert*-butyl isocyanide: preparation of complex 5b. *tert*-Butyl isocyanide (0.3 mL, 2.70 mmol) was added to a solution of 500 mg (0.54 mmol) of complex **3d** in 20 mL of dichloromethane. The mixture was stirred for 24 h at ambient temperature. The product was precipitated by the addition of pentane (30 mL), collected by filtration, washed with pentane (10 mL), and dried *in vacuo* to yield 251 mg (49%) of **5b**, mp 241 °C (decomp. at 254 °C) (Found: C, 68.34; H, 6.57; N, 1.41. C$_{55}$H$_{60}$BNSiZr$_2$ requires C, 69.07; H, 6.32; N, 1.46). δ_H (dichloromethane-*d*$_2$, 200.13 MHz) 5.67 (s, 20 H, Cp), 2.04 (s, 2 H, ≡CCH$_2$), 1.65 (s, 2 H, C(CH$_3$)$_3$) and 0.32 (s, 9 H, Si(CH$_3$)$_3$); BPh$_4^-$ signals as for **5a**. δ_C (dichloromethane-*d*$_2$, 50.32 MHz) 280.2 (C=N), 150.2, 129.3 (C≡C), 106.4, 106.0 (Cp), 67.3 (*C*(CH$_3$)$_3$), 31.1 (C(*C*H$_3$)$_3$), 19.0 (≡C*C*H$_2$) and −1.7 (Si(CH$_3$)$_3$); BPh$_4^-$ signals as for **5a**. IR (KBr) $\tilde{\nu}$/cm^{-1} 1705, 1682 (C=C, C=N).

With cyclohexyl isocyanide: preparation of complex 5c. Analogously as described above, 500 mg (0.54 mmol) of complex **3d** were treated with 0.3 mL (2.70 mmol) of cyclohexyl isocyanide in 20 mL of dichloromethane (12 h, ambient temperature). Work-up with pentane gave 421 mg (79%) of **5c**, mp 207 °C (decomp. at 253 °C) (Found: C, 69.70; H, 6.95; N, 2.24. C$_{57}$H$_{62}$BNSiZr$_2$ requires C, 69.68; H, 6.36; N, 1.43%).

δ_H (dichloromethane-d_2, 200.13 MHz) 5.66, 5.64 (s, each 10 H, Cp), 3.88 (m, 1 H, cyclohexyl CH), 2.04 (s, 2 H, $\equiv CCH_2$), 2.50–1.25 (m, 10 H, cyclohexyl CH_2) and 0.32 (s, 9 H, $Si(CH_3)_3$); BPh_4^- signals as for **5a**. δ_C (dichloromethane-d_2, 50.32 MHz) 278.5 (C=N), 150.4, 129.2 (C≡C), 106.4, 105.8 (Cp), 70.3 (cyclohexyl CH), 35.2, 25.7, 25.6 (cyclohexyl CH_2), 19.0 ($\equiv C\mathit{C}H_2$) and −1.7 ($Si(CH_3)_3$); BPh_4^- signals as for **5a**. IR (KBr) $\tilde{\nu}/cm^{-1}$ 1697 (C=N).

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