ORGANOMETALLICS
Article
pubs.acs.org/Organometallics

Reactivity of Seven-Membered Azazirconacycloallenes and Four-Membered Zirconacycles toward Diphenylacetonitrile

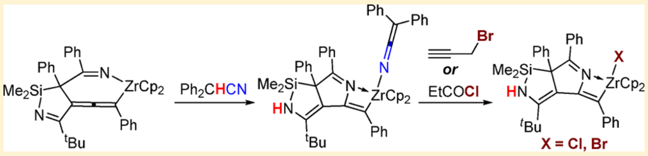
Jing Zhao,[†] Shaoguang Zhang,[‡] Wen-Xiong Zhang,[*,‡] and Zhenfeng Xi[*,‡,§]

[†]Beijing National Laboratory of Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100190, People's Republic of China

[‡]Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, People's Republic of China

[§]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China

Supporting Information

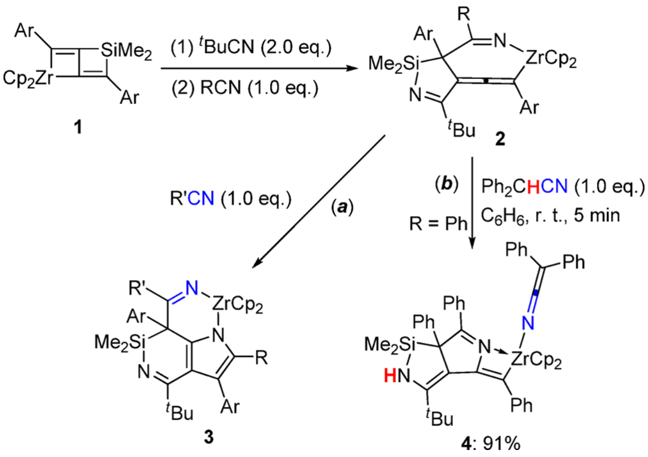


ABSTRACT: The reaction of the seven-membered azazirconacycloallene **2** with Ph_2CHCN was carried out to yield a zirconocene complex with three fused rings and a keteniminate ligand. Further reactivity toward propargyl bromide or propionyl chloride shows that the keteniminate ligand can be replaced by halogen atoms (Br or Cl). In addition, the reaction of the strained four-membered zirconacycle **1** with Ph_2CHCN gives zirconocenes possessing vinyl-imine and keteniminate species.

The synthesis and reactivity of zirconacycles have been increasingly important issues because of their broad applications in stoichiometric and catalytic transformations.[1−5] We have been interested in the isolation, structural characterization, and reaction of five-membered or strained four-membered zirconacycles since 2003.[6] Recently, we reported the reaction of zirconacyclopentene or zirconacyclopentadiene with 2 equiv of diphenylacetonitrile (Ph_2CHCN) bearing an acidic α-proton to furnish zirconocenes possessing vinyl-imine and keteniminate species.[7] Two molecules of Ph_2CHCN were found to go through a C═N insertion reaction, deprotonation, and intramolecular protonation. In contrast to the versatile chemistry of zirconacyclopentene or zirconacyclopentadiene,[2,3] the reactivity of zirconacycles containing allenyl moieties has been rarely explored.[8] In 2010, we reported the synthesis of well-defined seven-membered azazirconacycloallenes **2** by the sequential reaction of the zirconacyclobutene−silacyclobutene fused complex **1** with 2 equiv of bulky ^{t}BuCN and 1 equiv of aromatic nitrile.[9a] The preliminary insertion/rearrangement reaction of nitriles into the allenic C−Zr bond of **2** generated complexes **3** (Scheme 1, path ***a***).[9b]

Inspired by the special reactivity of five-membered zirconacycles with Ph_2CHCN, we envisioned the reactivity of azazirconacycloallene **2** and strained four-membered zirconacycle **1** toward Ph_2CHCN. Herein we report the reaction of **2** with Ph_2CHCN to yield the unexpected complex **4** (Scheme 1, path ***b***). Further reactivity of **4** with propargyl bromide or propionyl chloride is shown to provide the halogenated zirconocenes. In addition, the reaction of the strained four-membered zirconacycle **1** with Ph_2CHCN is also explored to give zirconocene complexes possessing vinyl-imine and keteniminate species.

Scheme 1. Reactions of Complex 2 with Different Nitriles



When azazirconacycloallene **2** was treated with Ph_2CHCN, the analogous **3** was not observed. Interestingly, the unexpected complex **4** was obtained. Single crystals of **4** suitable for X-ray analysis were grown in benzene/THF (1/1) mixed solvents at room temperature. X-ray analysis of **4** reveals that it consists of three fused rings: one five-membered azasilacyclopentene, one five-membered azacyclopentene, and one four-membered ring which contains a neutral N-donor ligand (Figure 1). The zirconium center in **4** adopts a nine-coordinated environment bonded with two Cp, one nitrogen from the keteniminate ligand, and one chelating vinyl-imine fragment. The amino

Received: October 9, 2012
Published: November 29, 2012

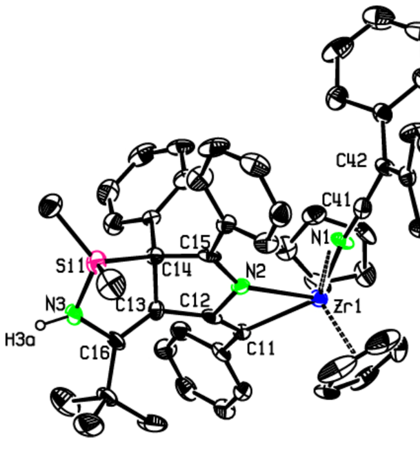


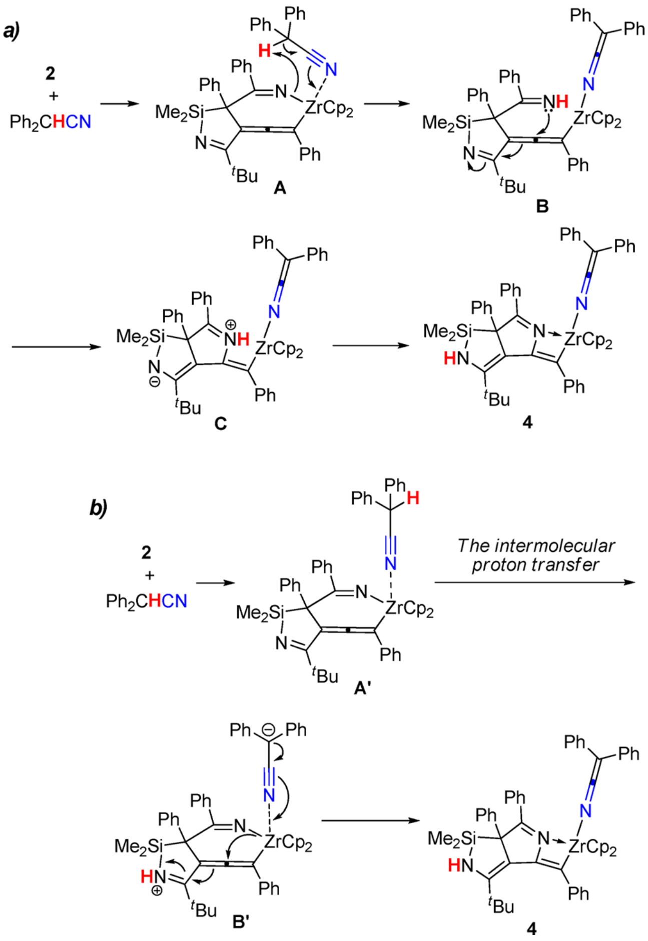
Figure 1. ORTEP drawing of **4** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity, except for H3a on the N3 atom. Selected bond lengths (Å) and angle (deg): Zr1−N1 = 2.222(5), N1−C41 = 1.175(6), C41−C42 = 1.395(7), Zr1−C11 = 2.339(5), Zr1−N2 = 2.465(4), N2−C15 = 1.297(6), N2−C12 = 1.458(6), C11−C12 = 1.384(7), C12−C13 = 1.532(7), C13−C16 = 1.341(6), N3−H3a = 0.91(5), N3−C16 = 1.429(7), Si1−N3 = 1.738(5); N1−C41−C42 177.2(7).

hydrogen neighboring the silicon atom in the azasilacyclopentene ring displayed a singlet at δ 2.48 ppm in the ^{1}H NMR spectrum. In ^{13}C NMR spectroscopy, two singlets at δ 180.49 and 57.29 ppm were unambiguously assigned to the C(sp) and C(sp^2) atoms in the keteniminate unit, respectively.

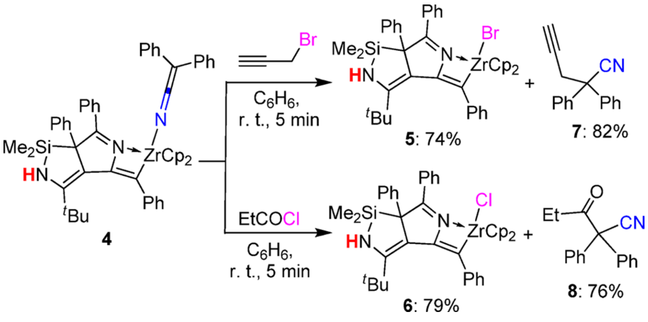
Two possible mechanisms for the formation of **4** are proposed (Scheme 2). The coordination of the CN group of Ph$_2$CHCN to the zirconium center would give rise to the intermediate **A**. **A** goes through intramolecular proton transfer to yield the intermediate **B**. Then the intramolecular hydroamination of N−H across the allenyl moiety in **B** should generate the zwitterionic complex **C**.[10] Further intramolecular proton transfer gives the final product **4** (path ***a***). Another possible mechanism for the formation of **4** cannot be ruled out (pathway ***b***). The coordination of the CN group of Ph$_2$CHCN to the zirconium center would give rise to the intermediate **A′**. **A′** goes through intermolecular proton transfer to yield the zwitterionic intermediate **B′**, which should generate the final product **4**.

The reactivity of **4** toward propargyl bromide and propionyl chloride was investigated. Interestingly, the keteniminate ligand was replaced by halogen atoms to provide zirconocene complexes **5** and **6** in high yield, respectively (Scheme 3). Compounds **7** and **8** were isolated and characterized by combining the ^{1}H NMR, ^{13}C NMR, and HRMS data. The single-crystal structures of **5** and **6** confirmed their zirconium−halogen bonds (Figure 2). The zirconium center in **5** and **6** also adopts a nine-coordinated environment bonded with two Cp, one halogen ligand (Br or Cl), and one chelating vinyl-imine fragment. The lengths of the Zr−Br bond in **5** and Zr−Cl bond in **6** are 2.7741(8) and 2.573(1) Å, respectively. The bond lengths Zr1−N1 (2.414(3) Å) in **5** and Zr1−N1 (2.438(4) Å) in **6** are slightly shorter than that found in **4** (Zr1−N2 = 2.465(4) Å). The Zr1−C15 distance (2.319(3) Å) in **5** and Zr1−C1 distance (2.314(5) Å) in **6** are also comparable with Zr1−C11 distance (2.339(5) Å) in **4**.

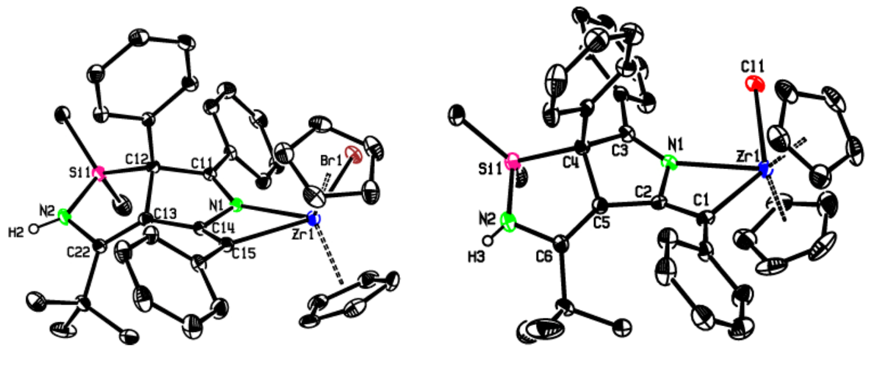
Scheme 2. Two Possible Mechanisms for the Formation of 4



Scheme 3. Formation of Zirconocene Complexes 5 and 6 by Reaction of 4 with Propargyl Bromide or Propionyl Chloride



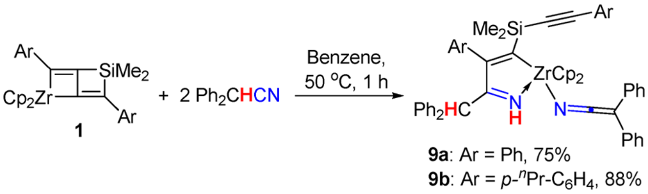
In addition, the zirconacyclobutene−silacyclobutene fused complex **1**, first reported by Takahashi and co-workers,[11] was allowed to react with 2.0 equiv of diphenylacetonitrile to give zirconocene species **9**, which contains vinyl-imine and keteniminate species (Scheme 4). An X-ray analysis of **9a** unambiguously revealed the structure of the keteniminate unit and one chelating vinyl-imine fragment (Figure 3). The bond lengths N2−C38 (1.288(3) Å), Zr1−N2 (2.2629(18) Å), and Zr1−N1 (2.267(2) Å) are comparable with those found in [Cp$_2$Zr{η^2(C,N)-C(TMS)C(CH$_3$)C(Ph$_2$CH)NH}{NCC(C$_6$H$_5$)$_2$}] (1.290(5), 2.265(4), and 2.290(4) Å).[7a] The terminal keteniminate Ph$_2$C═C═N unit has a nearly linear N1−C11−C12 angle (178.6(3)°). This Ph$_2$C═C═N unit was also confirmed by comparing the bond lengths N1−C11 (1.176(3) Å) and C11−C12 (1.370(3) Å) with those in [Cp$_2$Zr{η^2(C,N)-C(TMS)C(CH$_3$)C(Ph$_2$CH)NH}{NCC(C$_6$H$_5$)$_2$}] (1.159(5) and 1.386(6) Å).[7a]



5 **6**

Figure 2. ORTEP drawings of **5** and **6** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity except for H2 in **5** and H3 in **6**. Selected bond lengths (Å): **5**, Zr1−Br1 = 2.7741(8), Zr1−C15 = 2.319(3), Zr1−N1 = 2.414(3), N1−C11 = 1.310(4), N1−C14 = 1.448(4), C13−C14 = 1.480(5), C13−C22 = 1.361(5), N2−H2 = 0.8601, N2−C22 = 1.409(5), Si1−N2 = 1.742(3); **6**, Zr1−Cl1 = 2.573(1), Zr1−N1 = 2.438(4), Zr1−C1 = 2.314(5), N1−C3 = 1.306(6), N1−C2 = 1.444(6), C2−C5 = 1.473(6), C5−C6 = 1.341(7), N2−H3 = 0.69(5), N2−C6 = 1.420(7), N2−Si1 = 1.729(6).

Scheme 4. Reaction of Complex 1 with Ph_2CHCN to Yield Zirconocene Species 9



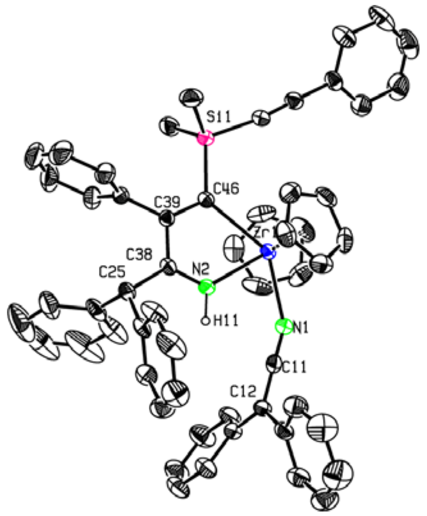
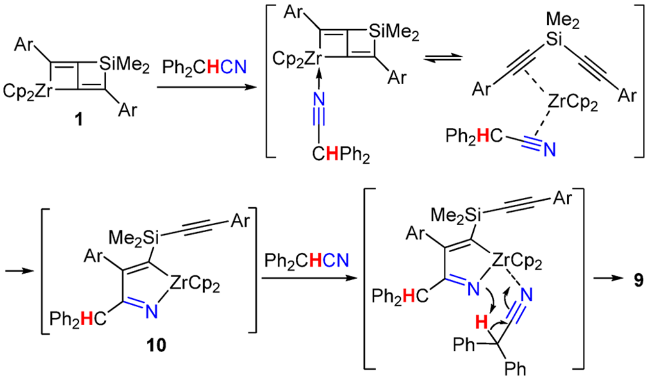


Figure 3. ORTEP drawing of **9a** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity, except for H11 on the azazirconacycle. Selected bond lengths (Å) and angle (deg): Zr1−C46 = 2.403(2), Zr1−N2 = 2.2629(18), N2−C38 = 1.288(3), Zr1−N1 = 2.267(2), N1−C11 = 1.176(3), C11−C12 = 1.370(3); N1−C11−C12 = 178.6(3).

Formation of **9** takes place through a nitrile-induced skeletal rearrangement to generate the azazirconacyclopentadiene **10**. The successive coordination of the second nitrile to **10** and intramolecular proton transfer gives the final product **9** (Scheme 5).

Scheme 5. Proposed Mechanism for the Formation of 9



In summary, we report the reaction of the seven-membered azazirconacycloallene **2** with Ph_2CHCN to yield a zirconocene complex with three fused rings and a keteniminate ligand. Further reactivity of **2** toward propargyl bromide or propionyl chloride shows that the keteniminate ligand can be replaced by halogen atoms (Br or Cl). Moreover, the four-membered zirconacycles **1** have been found to react with 2 equiv of Ph_2CHCN to yield the unexpected keteniminate species **9**. Studies of the further reactivity of these new complexes are in progress.

■ EXPERIMENTAL SECTION

Synthesis of Complex 4. In a 20 mL Schlenk tube, diphenylacetonitrile (39 mg, 0.2 mmol) and **2** (134 mg, 0.2 mmol) were added into the benzene solvent (5 mL). After the reaction mixture was stirred at room temperature for 5 min, it was dried under vacuum and the residue was washed with hexane. After filtering, the solid was dried under vacuum to give **4** as a red solid (156 mg, 91% based on 0.2 mmol scale). ^1H NMR (400 MHz, C_6D_6): δ −0.43 (s, 3H, $SiMe_2$), 0.12 (s, 3H, $SiMe_2$), 0.84 (s, 9H, CMe_3), 2.48 (br s, 1H, NH), 5.51 (s, 5H, C_5H_5), 6.08 (s, 5H, C_5H_5), 6.91−7.06 (m, 8H, C_6H_5), 7.18−7.26 (m, 5H, C_6H_5), 7.30 (t, J = 7.8 Hz, 4H, C_6H_5), 7.50 (d, J = 7.2 Hz, 4H, C_6H_5), 7.60 (d, J = 7.2 Hz, 2H, C_6H_5), 7.77 (d, J = 7.2 Hz, 2H, C_6H_5); ^{13}C NMR (100 MHz, C_6D_6): δ −3.77 (s, 1 CH_3), −2.26 (s, 1 CH_3), 28.42 (s, 3 CH_3), 35.02 (s, 1 quat C), 57.29 (s, 1 quat C), 61.77 (s, 1 quat C), 109.90 (s, 5 CH), 111.55 (s, 5 CH), 118.73 (s, 1 quat C), 120.28 (s, 2 CH), 124.19 (s, 4 CH), 125.18 (s, 1 CH), 126.64 (s, 1 CH), 127.08 (s, 2 CH), 127.29 (s, 2 CH), 128.40 (s, 2 CH), 128.53 (s, 2 CH), 128.61 (s, 2 CH), 128.80 (s, 4 CH), 130.05 (s, 2 CH), 131.51 (s, 1 CH), 134.48 (s, 1 quat C), 142.30 (s, 2 quat

C), 144.36 (s, 1 quat C), 145.90 (s, 1 quat C), 149.35 (s, 1 quat C), 149.86 (s, 1 quat C), 159.55 (s, 1 quat C), 177.58 (s, 1 quat C), 180.49 (s, 1 quat C). Anal. Calcd for $C_{54}H_{51}N_3SiZr$: C, 75.30; H, 5.97; N, 4.88. Found: C, 75.36; H, 5.96; N, 4.89. Recrystallization of **4** from benzene/THF (1/1) mixed solvents at room temperature gave single crystals suitable for X-ray analysis.

Formation of Complex 5 and Compound 7. In a 20 mL Schlenk tube, propargyl bromide (17 μL, 0.2 mmol) and **4** (172 mg, 0.2 mmol) were added into the benzene solvent (5 mL). After the reaction mixture was stirred at room temperature for 5 min, it was dried under vacuum and the residue was washed with hexane. Filtration gave an orange solid and a clear filtrate. The filtrate was reduced under vacuum and was subjected to SiO_2 column chromatography with petroleum ether/ethyl acetate (100/5) as the eluent to give compound **7** as a colorless oil (see the Supporting Information). The orange solid was dried under vacuum to give **5** (111 mg, 74% based on a 0.2 mmol scale). ^1H NMR (400 MHz, C_6D_6): δ −0.46 (s, 3H, $SiMe_2$), 0.13 (s, 3H, $SiMe_2$), 0.83 (s, 9H, CMe_3), 2.45 (br s, 1H, NH), 5.69 (s, 5H, C_5H_5), 6.20 (s, 5H, C_5H_5), 6.81 (d, J = 7.2 Hz, 2H, C_6H_5), 6.92−6.94 (m, 1H, C_6H_5), 7.01 (t, J = 7.7 Hz, 3H, C_6H_5), 7.17−7.22 (m, 5H, C_6H_5), 7.62 (d, J = 7.6 Hz, 2H, C_6H_5), 7.91 (d, J = 7.2 Hz, 2H, C_6H_5); ^{13}C NMR data were not collected because of the poor solubility of **5** in C_6D_6, THF-d_8, toluene-d_8, etc. Anal. Calcd for $C_{40}H_{41}BrN_2SiZr$: C, 64.14; H, 5.52; N, 3.74. Found: C, 64.31; H, 5.63; N, 3.81. Recrystallization of **5** from benzene/THF (1/1) mixed solvents at room temperature gave single crystals suitable for X-ray analysis.

Formation of Complex 6 and Compound 8. In a 20 mL Schlenk tube, propionyl chloride (17 μL, 0.2 mmol) and **4** (171 mg, 0.2 mmol) were added into the benzene solvent (5 mL). After the reaction mixture was stirred at room temperature for 5 min, it was dried under vacuum and the residue was washed with hexane. Filtration gave a yellow solid and a clear filtrate. The filtrate was reduced under vacuum and was subjected to SiO_2 column chromatography with petroleum ether/ethyl acetate (100/10) as the eluent to give compound **8** as a colorless oil (see the Supporting Information). The yellow solid was dried under vacuum to give **6** (111 mg, 79% based on 0.2 mmol scale). ^1H NMR (400 MHz, C_6D_6): δ −0.43 (s, 3H, $SiMe_2$), 0.16 (s, 3H, $SiMe_2$), 0.84 (s, 9H, CMe_3), 2.46 (br s, 1H, NH), 5.66 (s, 5H, C_5H_5), 6.21 (s, 5H, C_5H_5), 6.81 (d, J = 7.2 Hz, 2H, C_6H_5), 6.95−7.03 (m, 3H, C_6H_5), 7.12−7.22 (m, 6H, C_6H_5), 7.62 (d, J = 7.2 Hz, 2H, C_6H_5), 7.96 (d, J = 7.2 Hz, 2H, C_6H_5); ^{13}C NMR data were not collected because of the poor solubility of **6** in C_6D_6, THF-d_8, toluene-d_8, etc. Anal. Calcd for $C_{40}H_{41}ClN_2SiZr$: C, 68.19; H, 5.87; N, 3.98. Found: C, 68.39; H, 5.94; N, 3.99. Recrystallization of **6** from THF/toluene (1/1) mixed solvents at −20 °C gave single crystals suitable for X-ray analysis.

Formation of Complexes 9a,b. In a 20 mL Schlenk tube, diphenylacetonitrile (77 mg, 0.4 mmol) and **1a** (96 mg, 0.2 mmol) were added into the benzene solvent (5 mL). After the reaction mixture was stirred at 50 °C for 1 h, it was dried under vacuum and the residue was washed with hexane. After filtering, the solid was dried under vacuum to give **9a** as a green solid (130 mg, 75% based on 0.2 mmol scale). ^1H NMR (300 MHz, C_6D_6): δ 0.17 (s, 6H, $SiMe_2$), 4.90 (s, 1H, CH), 6.12 (s, 10H, 2 C_5H_5), 6.65 (d, J = 6.9 Hz, 2H, C_6H_5), 6.76 (d, J = 6.9 Hz, 4H, C_6H_5), 6.90−7.01 (m, 14H, C_6H_5), 7.30 (t, J = 7.5 Hz, 4H, C_6H_5), 7.44−7.47 (m, 2H, C_6H_5), 7.58 (d, J = 7.5 Hz, 4H, C_6H_5), 8.59 (br s, 1H, NH); ^{13}C NMR (75 MHz, C_4D_8O): δ 4.28 (s, 2 CH_3), 57.60 (s, 1 quat C), 59.30 (s, 1 CH), 98.87 (s, 1 quat C), 107.10 (s, 1 quat C), 111.37 (s, 10 CH), 120.06 (s, 2 CH), 124.01 (s, 4 CH), 127.82 (s, 2 CH), 128.21 (s, 2 CH), 128.37 (s, 4 CH), 128.40 (s, 1 CH), 128.75 (s, 4 CH), 129.28 (s, 2 CH), 129.44 (s, 1 CH), 129.63 (s, 4 CH), 129.70 (s, 1 quat C), 131.92 (s, 2 CH), 132.36 (s, 2 CH), 138.28 (s, 2 quat C), 142.41 (s, 1 quat C), 142.47 (s, 2 quat C), 155.02 (s, 1 quat C), 155.08 (s, 1 quat C), 192.56 (s, 1 quat C), 233.79 (s, 1 quat C). Anal. Calcd for $C_{56}H_{48}N_2SiZr$: C, 77.46; H, 5.57; N, 3.23. Found: C, 77.62; H, 5.65; N, 3.31. Recrystallization of **9a** from benzene at room temperature gave single crystals suitable for X-ray analysis.

The preparation of **9b** was similar to that of **9a**. Green solid, isolated yield 88%. ^1H NMR (300 MHz, C_6D_6): δ 0.24 (s, 6H, $SiMe_2$), 0.75 (t, J = 7.4 Hz, 3H, $CH_2CH_2CH_3$), 0.84 (t, J = 7.2 Hz, 3H, $CH_2CH_2CH_3$), 1.35−1.42 (m, 2H, $CH_2CH_2CH_3$), 1.45−1.53 (m, 2H, $CH_2CH_2CH_3$), 2.28 (t, J = 7.7 Hz, 2H, $CH_2CH_2CH_3$), 2.40 (t, J = 7.4 Hz, 2H, $CH_2CH_2CH_3$), 4.99 (s, 1H, CH), 6.16 (s, 10H, 2 C_5H_5), 6.65 (d, J = 7.8 Hz, 2H, C_6H_4), 6.78−6.98 (m, 16H, C_6H_5 and C_6H_4), 7.31 (t, J = 7.8 Hz, 4H, C_6H_5), 7.48 (d, J = 8.1 Hz, 2H, C_6H_4), 7.59 (d, J = 7.5 Hz, 4H, C_6H_5), 8.59 (br s, 1H, NH). ^{13}C NMR (75 MHz, C_4D_8O): δ 4.33 (s, 2 CH_3), 14.02 (s, 1 CH_3), 14.16 (s, 1 CH_3), 25.32 (s, 1 CH_2), 25.57 (s, 1 CH_2), 38.47 (s, 1 CH_2), 38.73 (s, 1 CH_2), 57.56 (s, 1 quat C), 59.32 (s, 1 CH), 98.22 (s, 1 quat C), 107.33 (s, 1 quat C), 111.38 (s, 10 CH), 120.05 (s, 2 CH), 124.05 (s, 4 CH), 128.45 (s, 2 CH), 128.76 (s, 4 CH), 129.41 (s, 2 CH), 129.62 (s, 4 CH), 129.68 (s, 4 CH), 129.74 (s, 2 CH), 131.88 (s, 2 CH), 132.34 (s, 2 CH), 137.93 (s, 1 quat C), 138.42 (s, 2 quat C), 139.84 (s, 1 quat C), 142.28 (s, 1 quat C), 142.57 (s, 2 quat C), 144.37 (s, 1 quat C), 155.00 (s, 1 quat C), 155.18 (s, 1 quat C), 192.87 (s, 1 quat C), 234.23 (s, 1 quat C). Anal. Calcd for $C_{62}H_{60}N_2SiZr$: C, 78.18; H, 6.35; N, 2.94. Found: C, 78.31; H, 6.37; N, 2.93.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and CIF files giving crystallographic data for **4**−**6** and **9a**, NMR data, further experimental details, and spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: wx_zhang@pku.edu.cn (W.-X.Z.); zfxi@pku.edu.cn (Z.X.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Natural Science Foundation of China, and the "973" program from the National Basic Research Program of China (2012CB821600).

■ REFERENCES

(1) For reviews of zirconacycles, see: (a) Broene, R. D.; Buchwald, S. L. *Science* **1993**, *261*, 1696−1701. (b) Negishi, E.; Takahashi, T. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 755−769. (c) Takahashi, T.; Xi, Z.; Kotora, M. *Rec. Res. Dev. Pure Appl. Chem.* **1998**, *2*, 515−525. (d) Takahashi, T.; Kotora, M.; Hara, R.; Xi, Z. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2591−2602. (e) Takahashi, T.; Li, Y. In *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; Wiley-VCH: Weinhein, Germany, 2002; pp 50−85. (f) Erker, G.; Kehr, G.; Fröhlich, R. *J. Organomet. Chem.* **2004**, *689*, 4305−4318. (g) Negishi, E. *Dalton Trans.* **2005**, 827−848. (h) Rosenthal, U.; Burlakov, V. V.; Bach, M. A.; Beweries, T. *Chem. Soc. Rev.* **2007**, *36*, 719−728. (i) Suzuki, N.; Hashizume, D. *Coord. Chem. Rev.* **2010**, *254*, 1307−1326. (j) Chen, C.; Xi, C. *Chin. Sci. Bull.* **2010**, *55*, 3235−3247.

(2) For selected examples of zirconacyclopentenes, see: (a) Takahashi, T.; Xi, Z.; Kotora, M.; Xi, C.; Nakajima, K. *Tetrahedron Lett.* **1996**, *37*, 7521−7524. (b) Liu, Y.; Sun, W.-H.; Nakajima, K.; Takahashi, T. *Chem. Commum.* **1998**, 1133−1134. (c) Dumond, Y.; Negishi, E. *J. Am. Chem. Soc.* **1999**, *121*, 11223−11224. (d) Zhao, C.; Lu, J.; Yan, J.; Xi, Z. *Tetrahedron Lett.* **2003**, *44*, 6895−6898. (e) Norton, D.; Whitby, R. J.; Griffen, E. *Chem. Commun.* **2004**, 1214−1215. (f) Liu, Y.; Gao, H. *Org. Lett.* **2006**, *8*, 309−311. (g) Chen, J.; Li, Y.; Gao, H.; Liu, Y. *Organometallics* **2008**, *27*, 5619−5623. (h) Chen, C.; Liu, Y.; Xi, C. *Tetrahedron Lett.* **2009**, *50*, 5434−5436. (i) Zheng, W.; Wu, Y.; Zheng, F.; Hu, L.; Hong, Y. *Tetrahedron Lett.* **2010**, *51*, 4702−4704.

(3) For selected examples of zirconacyclopentadienes, see: (a) Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.*

1986, *27*, 2829−2832. (b) Erker, G.; Zwettler, R.; Krüger, C.; Hyla-Kryspin, I.; Gleiter. *Organometallics* **1990**, *9*, 524−530. (c) Ruwwe, J.; Erker, G.; Fröhlich, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 80−82. (d) Mahieu, A.; Miquel, Y.; Igau, A.; Donnadieu, B.; Majoral, J.-P. *Organometallics* **1997**, *16*, 3086−3088. (e) Takahashi, T.; Sun, W.-H.; Xi, C.; Kotora, M. *Chem. Commun.* **1997**, 2069−2070. (f) Nakamoto, M.; Tilley, T. D. *Organometallics* **2001**, *20*, 5515−5517. (g) Xi, Z.; Fan, H.-T.; Mito, S.; Takahashi, T. *J. Organomet. Chem.* **2003**, *682*, 108−112. (h) Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Organometallics* **2004**, *23*, 4160−4165. (i) Chen, C.; Xi, C.; Jiang, Y.; Hong, X. *J. Am. Chem. Soc.* **2005**, *127*, 8024−8025. (j) Liu, Y.; Liu, M.; Song, Z. *J. Am. Chem. Soc.* **2005**, *127*, 3662−3663. (k) Yan, X.; Zhou, Y.; Xi, C. *Chem. Commun.* **2010**, *46*, 7801−7803. (l) Gessner, V. H.; Tannacl, J. F.; Miller, A. D.; Tilley, T. D. *Acc. Chem. Res.* **2011**, *44*, 435−446.

(4) For selected examples of azazirconacycles, see: (a) Negishi, E.; Holms, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336−3346. (b) Takahashi, T.; Kageyama, M.; Denisov, V.; Hara, R.; Negishi, E. *Tetrahedron Lett.* **1993**, *34*, 687−690. (c) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1993**, *12*, 3705−3723. (d) Binger, P.; Sandmeyer, F.; Krüger, C. *Organometallics* **1995**, *14*, 2969−2976. (e) Zippel, T.; Arndt, P.; Ohff, A.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Organometallics* **1998**, *17*, 4429−4437. (f) Takahashi, T.; Xi, C.; Xi, Z.; Kageyama, M.; Fischer, R.; Nakajima, K.; Negishi, E. *J. Org. Chem.* **1998**, *63*, 6802−6806. (g) Takahashi, T.; Tsai, F.-Y.; Li, Y.; Wang, H.; Kondo, Y.; Yamanaka, M.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **2002**, *124*, 5059−5067. (h) Liu, Y.; Shen, B.; Kotora, M.; Nakajima, K.; Takahashi, T. *J. Org. Chem.* **2002**, *67*, 7019−7028. (i) Ruck, R. T.; Zuckerman, R. L.; Krska, S. W.; Bergman, R. G. *Angew. Chem., Int. Ed.* **2004**, *43*, 5372−5374. (j) Liu, Y.; Yan, B. *Organometallics* **2006**, *25*, 544−547. (k) Bach, M. A.; Beweries, T.; Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Organometallics* **2007**, *26*, 4592−4597.

(5) For selected examples of zirconacyclocumulenes, see: (a) Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Organometallics* **2004**, *23*, 5188−5192. (b) Bredeau, S.; Ortega, E.; Delmas, G.; Richard, P.; Fröhlich, R.; Donnadieu, B.; Kehr, G.; Pirio, N.; Erker, G.; Meunier, P. *Organometallics* **2009**, *28*, 181−187. (c) Fu, X.; Chen, J.; Li, G.; Liu, Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 5500−5504. (d) Fu, X.; Yu, S.; Fan, G.; Liu, Y.; Li, Y. *Organometallics* **2012**, *31*, 531−534. (e) Yu, S.; You, X.; Liu, Y. *Chem. Eur. J.* **2012**, *18*, 13936−13940.

(6) (a) Yu, T.; Deng, L.; Zhao, C.; Li, Z.; Xi, Z. *Tetrahedron Lett.* **2003**, *44*, 677−679. (b) Sun, X.; Wang, C.; Li, Z.; Zhang, S.; Xi, Z. *J. Am. Chem. Soc.* **2004**, *126*, 7172−7173. (c) Yu, T.; Sun, X.; Wang, C.; Deng, L.; Xi, Z. *Chem. Eur. J.* **2005**, *11*, 1895−1902. (d) Zhang, W.-X.; Zhang, S.; Sun, X.; Nishiura, M.; Hou, Z.; Xi, Z. *Angew. Chem., Int. Ed.* **2009**, *48*, 7227−7231. (e) Zhang, S.; Sun, X.; Zhang, W.-X.; Xi, Z. *Chem. Eur. J.* **2009**, *15*, 12608−12617. (f) Zhang, S.; Zhang, W.-X.; Xi, Z. *Chem. Eur. J.* **2010**, *16*, 8419−8426.

(7) (a) Zhao, J.; Zhang, S.; Zhang, W.-X.; Xi, Z. *Organometallics* **2011**, *30*, 3464−3467. For other well-defined keteniminate complexes, see: (b) Zarges, W.; Marsch, M.; Harms, K.; Boche, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1392−1394. (c) Langlotz, I.; Marsch, M.; Harms, K.; Boche, G. *Z. Kristallogr.* **1999**, *214*, 509−510. (d) Fulton, J. R.; Sklenak, S.; Bouwkamp, M. W.; Bergman, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 4722−4737. (e) Culkin, D. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 9330−9331. (f) Farwell, J. D.; Hitchcock, P. B.; Lappert, M. F.; Protchenko, A. V. *Chem. Commun.* **2005**, 2271−2273. (g) Min'ko, Y. A.; Belina, N. V.; Sushev, V. V.; Fukin, G. K.; Bubnov, M. P.; Kornev, A. N. *J. Organomet. Chem.* **2007**, *692*, 4157−4160. (h) Honzíček, J.; Vinklárek, J.; Erben, M.; Střižík, L.; Císařová, I.; Padělková, Z. *J. Organomet. Chem.* **2009**, *694*, 4250−4255. For a review of ketenimines, see: (i) Lu, P.; Wang, Y. *Chem. Soc. Rev.* **2012**, *41*, 5687−5705.

(8) For selected examples of allenylzirconocene complexes, see: (a) Binger, P.; Langhauser, F.; Gabor, B.; Mynott, R.; Herrmann, A. T.; Krüger, C. *J. Chem. Soc. Chem. Commun.* **1992**, 505−506. (b) Pellny, P.-M.; Kirchbauer, F. G.; Burlakov, V. V.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Chem. Eur. J.* **2000**, *6*, 81−90. (c) Burlakov, V. V.; Arndt, P.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Organometallics* **2006**, *25*, 1317−1320. (d) Ugolotti, J.; Dierker, G.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G. *Angew. Chem., Int. Ed.* **2008**, *47*, 2622−2625. (e) Suzuki, N.; Hashizume, D.; Koshino, H.; Chihara, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 5198−5202. (f) Ugolotti, J.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G. *J. Am. Chem. Soc.* **2009**, *131*, 1996−2007. (g) Ugolotti, J.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G. *Chem. Commun.* **2009**, 6572−6573. (h) Zhang, H.; Fu, X.; Chen, J.; Wang, E.; Liu, Y.; Li, Y. *J. Org. Chem.* **2009**, *74*, 9351−9358. (i) Xi, C.; Yan, X.; You, W.; Takahashi, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 8120−8123. (j) Suzuki, N.; Shimura, T.; Sakaguchi, Y.; Masuyama, Y. *Pure Appl. Chem.* **2011**, *83*, 1781−1788. (k) Kaleta, K.; Ruhmann, M.; Theilmann, O.; Beweries, T.; Roy, S.; Arndt, P.; Villinger, A.; Jemmis, E. D.; Schulz, A.; Rosenthal, U. *J. Am. Chem. Soc.* **2011**, *133*, 5463−5473. (l) Bender, G.; Kehr, G.; Fröhlich, R.; Petersen, J. L.; Erker, G. *Chem. Sci.* **2012**, *3*, 3534−3540.

(9) (a) Zhang, S.; Zhang, W.-X.; Zhao, J.; Xi, Z. *J. Am. Chem. Soc.* **2010**, *132*, 14042−14045. (b) Zhang, S.; Zhang, W.-X.; Zhao, J.; Xi, Z. *Chem. Eur. J.* **2011**, *17*, 2442−2449.

(10) For examples of an N atom attacking the C(sp) atom in the allenyl moiety, see: (a) Farnham, W. B.; Middleton, W. J.; Fultz, W. C.; Smart, B. E. *J. Am. Chem. Soc.* **1986**, *108*, 3125−3127. (b) Man, S.; Buchlovič, M.; Potáček, M. *Tetrahedron Lett.* **2006**, *47*, 6961−6963. (c) Hamaguchi, H.; Kosaka, S.; Ohno, H.; Fujii, N.; Tanaka, T. *Chem. Eur. J.* **2007**, *13*, 1692−1708. (d) Benedetti, E.; Lemière, G.; Chapellet, L.-L.; Penoni, A.; Palmisano, G.; Malacria, M.; Goddard, J.-P.; Fensterbank, L. *Org. Lett.* **2010**, *12*, 4396−4399. (e) Wang, X.; Liu, J.; Guo, H.; Ma, C.; Gao, X.; Zhou, K.; Huang, G. *Synthesis* **2012**, *44*, 1037−1042.

(11) (a) Xi, Z.; Fischer, R.; Hara, R.; Sun, W.; Obora, Y.; Suzuki, N.; Nakajima, K.; Takahashi, T. *J. Am. Chem. Soc.* **1997**, *119*, 12842−12848. (b) Takahashi, T.; Xi, Z.; Obora, Y.; Suzuki, N. *J. Am. Chem. Soc.* **1995**, *117*, 2665−2666.