# Synthesis and Formal Ring-Opening Reactions of ($\eta^5$-$C_5Me_5$)Zr[$\eta^2$-$CH_2CH(C_6H_5)$][N($^i$Pr)C(Me)N($^i$Pr)], a Base-Free $\eta^2$-Styrene Complex of Zirconium

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Synthesis of a base-free $\eta^2$-styrene complex of zirconium has been achieved and its molecular structure analyzed by X-ray crystallography. This compound undergoes protonolysis and $\sigma$-bond metathesis of a formal zirconacyclopropane ring with a variety of reagents. With phenylacetylene, ring opening occurs on the more substituted side, while $Me_3MCl$ (M = Si, Sn) effect ring opening on the least substituted side. Hydrogenolysis further proceeds rapidly to provide a zirconanorbornadiene derivative in high yield under conditions where a structurally related dimethyl complex remains inert.

## Introduction

Since the mid-1980s, systematic investigations of the chemical reactivities of $\eta^2$-alkene and $\eta^2$-alkyne complexes of bis(cyclopentadienyl)zirconium, i.e., "$Cp_2Zr$" (Cp = $\eta^5$-$C_5H_5$) (also known as zirconocene), by Negishi, Takahashi, and Buchwald, to name just a few, have led to the development of a rich collection of useful transformations for organic synthesis.[1] In practice, two limiting structures within the Dewar−Chatt−Duncanson model of bonding,[2] i.e., either a Zr(II) metal−alkene complex or a Zr(IV) metallacyclopropane, are often interchangeably invoked to fit different mechanistic schemes, with the result that a certain degree of ambiguity still exists regarding the nature of the primary steps involved in many key transformations. For instance, the zirconocene-catalyzed hydrosilylation and hydrogenation of alkenes have alternatively been proposed as proceeding either through oxidative addition/reductive elimination reactions involving $Cp_2Zr$(II) metal centers or through $\sigma$-bond metathesis reactions involving Zr(IV) metallacyclopropanes.[3] Complicating this picture further is that electron-deficient zirconocene $\eta^2$-alkene complexes do not appear to be stable toward isolation, and accordingly, to date, the only solid-state structural parameters that are available are for a few examples (i.e., $\eta^2$-ethene, $\eta^2$-diphenylethene, and $\eta^2$-styrene) that have been stabilized as 18-electron species with the addition of strong $\sigma$-donors (i.e., $PR_3$, THF, and pyridine, also known as "bases").[4] In the case of non-zirconocenes, only $\eta^2$-ethene complexes have so far been isolated and, once again, only as adducts with strong $\sigma$-donors, albeit in a few cases with electron counts of $<18$.[5,6]

We have recently documented that, in contrast to zirconocenes, the mono(cyclopentadienyl), mono(amidinate) ligand set appears to be well suited for the stabilization of neutral and cationic zirconium(IV) complexes bearing alkyl substituents with $\beta$-hydrogens, even though these non-metallocene compounds formally possess electron counts lower than those of their zirconocene counterparts.[7,8] These results encouraged us to investigate the stability and reactivity of formal Zr(II) $\eta^2$-alkene complexes that are supported by the same ligand combination. Herein, we now present the synthesis and structural characterization of a formal 14-electron, base-free $\eta^2$-styrene complex of zirconium. We further present a preliminary investigation of the reactivity of this complex that involves formal ring opening of a zirconacyclopropane ring via protonolysis and $\sigma$-bond metathesis.

## Results and Discussion

As shown in Scheme 1, the successful synthesis of a $\eta^2$-styrene complex was achieved through reaction of the known dichloride starting material **1**[7] with 2 equiv of ($\beta$-lithioethyl)benzene[9] to provide dark green **2** in 76% isolated yield. A single-crystal X-ray analysis of **2** was conducted, and Table 1 provides a summary of the X-ray data obtained, while Figure 1 and Table 2 present the molecular structure and a listing of selected structural parameters, respectively.[10] From an analysis of these latter data, it would appear that this compound possesses substantial metallacyclopropane character (cf. bond distances (Å): Zr(1)−C(1) = 2.280(3), Zr(1)−C(2) = 2.300(3), and C(1)−C(2) = 1.449(5) in **2** vs the corresponding values of 2.36(2), 2.43(2), and 1.38(2) in $Cp_2Zr(\eta^2\text{-PhCHCHPh})(PMe_3)$[4b] and 2.35(1), 2.35(2), and 1.46(2) in $Cp_2Zr(\eta^2\text{-CH}_2\text{CHPh})(PMe_3)$[4c]).

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[2] (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C79. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939−2947.

[3] See for instance: (a) Negishi, E.; Huo, S. In ref 1c, p 43. (b) Ura, Y.; Hara, R.; Takahashi, T. *Chem. Lett.* **1998**, 195−196. (c) Takahashi, T.; Bao, F.; Gao, G.; Ogasawara, M. *Org. Lett.* **2003**, *5*, 3479−3481.

[4] (a) Alt, H. G.; Denner, C. E.; Thewalt, U.; Rausch, M. D. *J. Organomet. Chem.* **1988**, *356*, C83−C85. (b) Takahashi, T.; Murakami, M.; Kunishige, M.; Saburi, M.; Uchida, Y.; Kozawa, K.; Uchida, T.; Swanson, D. R.; Negishi, E. *Chem. Lett.* **1989**, 761−764. (c) Binger, P.; Müller, P.; Benn, R.; Rufinska, A.; Gabor, B.; Krüger, C.; Betz, P. *Chem. Ber.* **1989**, *122*, 1035−1042. (d) Fisher, R. A.; Buchwald, S. L. *Organometallics* **1990**, *9*, 871−873. (e) Fischer, R.; Walther, D.; Gebhardt, P.; Görls, H. *Organometallics* **2000**, *19*, 2532−2540. (f) Lee, H.; Hascall, T.; Desrosiers, P. J.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 5830−5831.

[5] (a) Schrock, R. R.; Baumann, R.; Reid, S. M.; Goodman, J. T.; Stumpf, R.; Davis, W. M. *Organometallics* **1999**, *18*, 3649−3670. (b) Fryzuk, M. D.; Duval, P. B.; Rettig, S. J. *Can. J. Chem.* **2001**, *79*, 536−545.

[6] For $Cp^*_2Ti(\eta^2\text{-ethylene})$ ($Cp^*$ = $\eta^5$-$C_5Me_5$), see: Cohen, S. A.; Bercaw, J. E. *Organometallics* **1985**, *4*, 1006−1014.

[7] Keaton, R. J.; Koterwas, L. A.; Fettinger, J. C.; Sita, L. R. *J. Am. Chem. Soc.* **2002**, *124*, 5932−5933.

[8] Harney, M. B.; Keaton, R. J.; Sita, L. R. *J. Am. Chem. Soc.* **2004**, *126*, 4536−4537.

[9] Negishi, E.; Swanson, D. R.; Rousset, C. J. *J. Org. Chem.* **1990**, *55*, 5406−5409.

[10] Details are provided in the Supporting Information.

10.1021/om0508785 CCC: $33.50

**Scheme 1**

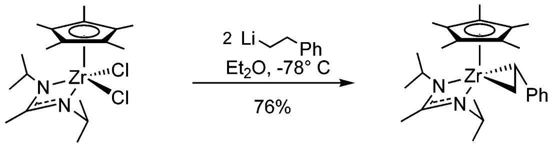


**Table 1. Crystallographic Data for Compounds 2 and 7**

| | 2 | 7 |
|---|---|---|
| formula | $C_{26}H_{40}N_2Zr$ | $C_{26}H_{42}N_2Zr$ |
| $M_r$ | 471.82 | 473.84 |
| $T$, K | 173(2) | 293(2) |
| cryst syst | monoclinic | triclinic |
| space group | $P2_1/n$ | $P\bar{1}$ |
| $a$, Å | 8.9534(3) | 8.7602(3) |
| $b$, Å | 19.0468(7) | 9.7735(4) |
| $c$, Å | 14.3058(5) | 15.5841(6) |
| α, deg | 90 | 79.2240(10) |
| $\beta$, deg | 91.9270(10) | 82.0160(10) |
| $\gamma$, deg | 90 | 69.5270(10) |
| $V$, Å$^3$ | 2438.24 | 1224.03(8) |
| $Z$ | 4 | 2 |
| $F$(000) | 1000 | 504 |
| $D_{calcd}$, g/cm$^3$ | 1.285 | 1.286 |
| $\lambda$, Å | 0.710 73 | 0.710 73 |
| $\mu$, mm$^{-1}$ | 0.465 | 0.463 |
| $\theta_{max}$, deg | 27.50 | 27.50 |
| index ranges | | |
| $h$ | $-11$ to $+11$ | $-11$ to $+11$ |
| $k$ | $-24$ to $+24$ | $-12$ to $+12$ |
| $l$ | $-18$ to $+18$ | $-20$ to $+20$ |
| RC[a] | 21 850 | 19 750 |
| IRC[b] | 5604 ($R$(int) = 0.0471) | 5616 |
| IRCGT[c] | 4100 | 4850 |
| no. of data | 5604 | 5616 |
| no. of restraints | 3 | 15 |
| no. of params | 425 | 433 |
| $R$ for IRCGT | R1 = 0.0344<br>wR2 = 0.0791 | R1 = 0.0304<br>wR2 = 0.0772 |
| $R$ for IRC | R1 = 0.0659<br>wR2 = 0.0905 | R1 = 0.0404<br>wR2 = 0.0816 |
| goodness of fit | 1.078 | 1.073 |
| largest diff peak and hole, e Å$^{-3}$ | 1.090 and $-0.501$ | 0.938 and $-0.452$ |

[a] RC = number of reflections collected. [b] IRC = number of independent RC. [c] IRCGT = number of IRC with $I > 2\sigma(I)$.

On closer inspection, there is also a relatively close approach between Zr(1) and C(3) of the phenyl ring at 2.644(2) Å which might be taken as evidence of a secondary bonding interaction between the electron-deficient metal center and the styrene fragment that contributes to further stabilization of the complex. In contrast, no close metal−phenyl ring interactions appear in the corresponding 18-electron, base-stabilized $\eta^2$-styrene zirconocene, $Cp_2Zr(\eta^2\text{-}CH_2CHPh)(PMe_3)$.[4c]

To probe the existence and strength of a possible $\eta^3$ mode of bonding of the styrene fragment that is suggested by the solid-state structure of **2**, the structure of this compound in solution was probed by variable-temperature $^1$H NMR (400 MHz, toluene-$d_8$) spectroscopy. To begin, it was determined that compound **2** is quite robust in solution at elevated temperatures of up to 100 °C. Furthermore, the spectra recorded at 25 °C and above provide no evidence for rotation of the $\eta^2$-styrene fragment about a zirconium−alkene axis that might be possible within a classical Zr(II) metal $\eta^2$-alkene complex, thus lending additional support to the conclusion that **2** possesses substantial Zr(IV) metallacyclopropane character. With respect to the possible existence of any additional secondary bonding interactions involving the styrene fragment and the metal center in solution, the collection of variable-temperature $^1$H NMR spectra provided a calculated barrier to rotation of the phenyl ring about the C(2)−C(3) bond, $\Delta G_c^{\ddagger}(T_c = 292$ K$)$, of 12.5 kcal mol$^{-1}$. However, the magnitude of this barrier can just as easily be accounted for on the basis of nonbonded steric interactions involved with rotation of the phenyl group within the ligand environment as it can be rationalized in terms of a weak secondary bonding interaction. Accordingly, for the purposes of this work, we choose to think of **2** in terms of having a $\eta^2$-styrene interaction with the metal center.

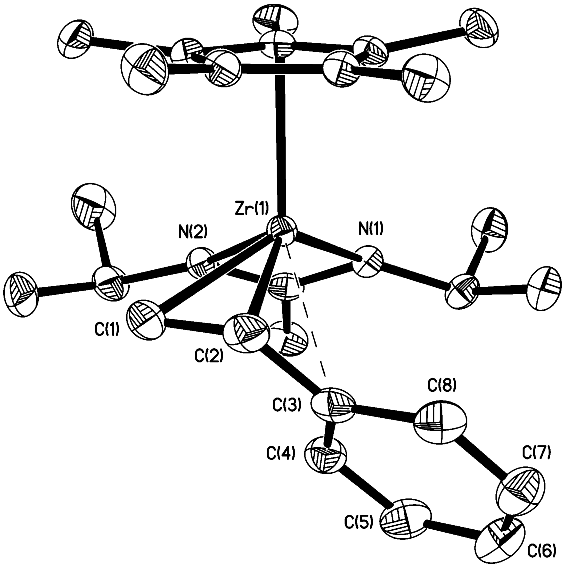


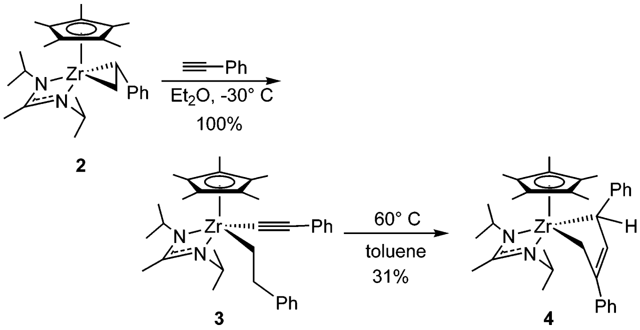
**Figure 1.** Molecular structure (30% thermal ellipsoids) of compound **2**. All hydrogen atoms have been removed for the sake of clarity.

**Table 2. Selected Structural Parameters for Compound 2**

| | | | |
|---|---|---|---|
| Bond Lengths (Å) | | | |
| Zr(1)−CNT1[a] | 2.2210(11) | Zr(1)−C(3) | 2.644(2) |
| Zr(1)−N(1) | 2.2413(19) | N(1)−C(9) | 1.342(3) |
| Zr(1)−N(2) | 2.260(2) | N(2)−C(9) | 1.332(3) |
| Zr(1)−C(1) | 2.280(3) | C(1)−C(2) | 1.449(5) |
| Zr(1)−C(2) | 2.300(3) | C(2)−C(3) | 1.425(4) |
| Bond Angles (deg) | | | |
| N(1)−Zr(1)−N(2) | 59.80(7) | C(1)−C(2)−Zr(1) | 70.82(16) |
| C(1)−Zr(1)−C(2) | 36.89(12) | C(3)−C(2)−Zr(1) | 87.13(16) |
| C(2)−C(1)−Zr(1) | 72.29(16) | C(3)−C(2)−C(1) | 120.8(3) |

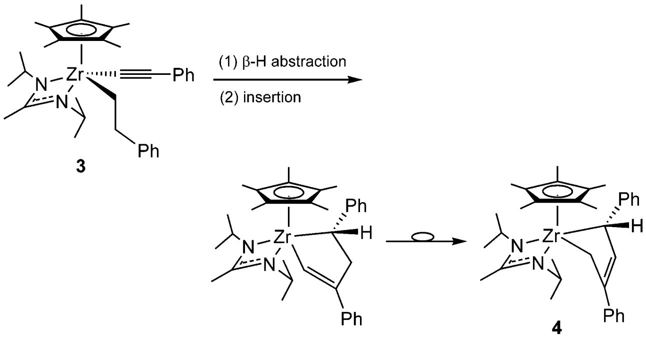
[a] CNT1 is the calculated centroid of the Cp* fragment.

**Scheme 2**



As Scheme 2 reveals, reaction of **2** with 1 equiv of phenylacetylene led to a quantitative yield of the yellow crystalline acetylide complex **3** through formal protonolysis of the zirconacyclopropane ring at the carbon atom bearing the phenyl substituent. Cohen and Bercaw[6] reported similar protonolysis of a titanocene $\eta^2$-ethene complex with terminal alkynes, and Negishi and co-workers[11] demonstrated that a high yield of 1,2-

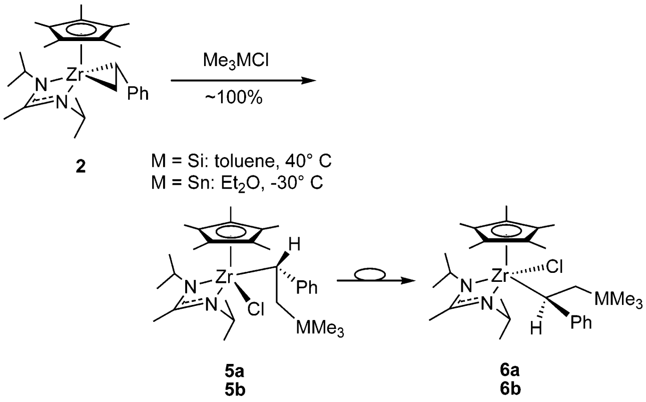
**Scheme 3**



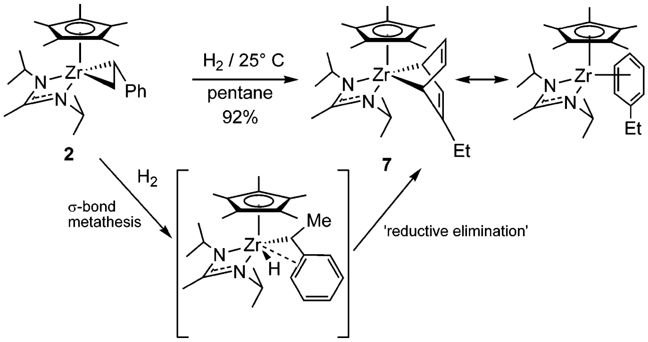
diphenylethane is produced when in situ generated $Cp_2Zr$-($\eta^2$-PhCHCHPh) is treated in solution with HCl. A crystal structure of **3** confirms the structural assignment that is shown in Scheme 2, and the molecular structure of this compound displays no unusual geometric features.[10] Surprisingly, however, although compound **3** was found to be stable in solution for short periods of time (<24 h), benzene solutions of this complex become noticeably purple-tinged after 1 day, and heating a toluene solution for 48 h at 60 °C subsequently provided the purple crystalline zirconacyclopent-3-ene complex **4**, which was also structurally characterized by single-crystal X-ray analysis.[10] Although no specific mechanistic details are yet known regarding this transformation, it can be noted that **4** is formally an isomeric product expected from alkyne insertion of phenylacetylene into **2**. Given this, we tentatively propose that **3** can undergo intramolecular $\beta$-hydrogen abstraction by the acetylide $\alpha$-carbon to regenerate **2** and phenylacetylene. Reinsertion of the latter back into the least hindered Zr−C bond of **2** could then form the zirconacyclopent-1-ene product shown in Scheme 3, which subsequently undergoes isomerization to the potentially more thermodynamically stable zirconacyclopent-3-ene isomer **4**. In this regard, the solid-state structure of **4** is strongly suggestive of a $\sigma^2,\pi$ interaction of the formal butadiene fragment with the metal center.[7,12] It can be mentioned that Cohen and Bercaw[6] also observed the room-temperature isomerization of the initial titanocene alkyl acetylide complex $Cp^*_2Ti(Et)$-(CHCHMe) ($Cp^* = \eta^5$-$C_5Me_5$), arising from protonolysis of $Cp^*_2Ti(\eta^2$-$CH_2CH_2)$ with propene, to an analogous titanacyclopent-1-ene, which serves to support a more general nature for the first two steps in Scheme 3.

As shown in Scheme 4, reaction of **2** with $Me_3MCl$ (M = Si, Sn) effected formal metallacyclopropane ring opening through $\sigma$-bond metathesis on the least hindered side. More specifically, with $Me_3SiCl$ in toluene at 40 °C, $^1H$ NMR analysis revealed initial formation of a 5:1 mixture of two diastereomeric products, which over the course of 18 h converted entirely to the initial minor species. Recrystallization of the crude product then afforded a 93% yield of **6a**, which was structurally characterized by X-ray analysis.[10] In the case of $Me_3SnCl$, the reaction with **2** was carried out in $Et_2O$ at −30 °C to quantitatively provide diastereomer **5b**, which crystallographic analysis confirmed to have the stereochemistry depicted in Scheme 4.[10] As with **5a**, this kinetic product was then observed by $^1H$ NMR to quantitatively isomerize in solution through metal-centered epimerization to the more thermodynamically stable product **6b** at room temperature. Analysis of space-filling representations of structural models suggest that the **5** → **6** isomerization is most likely driven by relief of steric interactions.

**Scheme 4**



**Scheme 5**



Hydrogenolysis of **2** with dihydrogen in pentane proceeded rapidly at room temperature to provide the $\eta^2$-arene complex **7** in near-quantitative yield according to Scheme 5.[10,13] Once again, compound **7** was subjected to crystallographic analysis and Table 1 provides a summary of the X-ray data obtained, while Figure 2 and Table 3 provide the molecular structure and a listing of selected structural parameters, respectively. These crystallographic data confirm that the structure of **7** is best represented as a Zr(IV) zirconanorbornadiene rather than as a Zr(II) $\eta^4$- or $\eta^6$-arene complex, which is somewhat surprising, given the formal 14-electron count that this high-oxidation-state

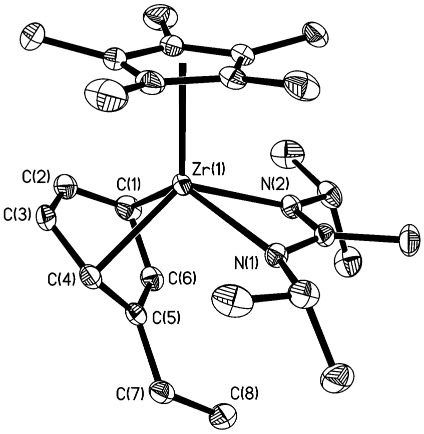


**Figure 2.** Molecular structure (30% thermal ellipsoids) of compound **7**. All hydrogen atoms have been removed for the sake of clarity.

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[11] Negishi, E.; Cederbaum, F. E.; Takahashi, T. *Tetrahedron Lett.* **1986**, *27*, 2829−2832.

[12] Erker, G.; Kruger, C.; Muller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1−39.

[13] Ortiz, C. G.; Abboud, K. A.; Cameron, T. M.; Boncella, J. M. *Chem. Commun.* **2001**, 247−248.

**Table 3. Selected Structural Parameters for Compound 7**

| Bond Lengths (Å) | | | |
|---|---|---|---|
| Zr(1)−CNT1[a] | 2.2658(9) | Zr(1)−C(6) | 2.5190(19) |
| Zr(1)−N(1) | 2.2989(15) | C(1)−C(2) | 1.444(4) |
| Zr(1)−N(2) | 2.2886(15) | C(2)−C(3) | 1.357(4) |
| Zr(1)−C(1) | 2.313(2) | C(3)−C(4) | 1.438(3) |
| Zr(1)−C(2) | 2.510(2) | C(4)−C(5) | 1.469(3) |
| Zr(1)−C(3) | 2.514(2) | C(5)−C(6) | 1.358(3) |
| Zr(1)−C(4) | 2.3501(19) | C(6)−C(1) | 1.457(3) |
| Zr(1)−C(5) | 2.5597(18) | | |
| **Bond Angles (deg)** | | | |
| N(2)−Zr(1)−N(1) | 57.86(6) | C(2)−C(1)−C(6) | 112.9(2) |
| C(1)−Zr(1)−C(4) | 75.74(8) | C(3)−C(4)−C(5) | 113.5(2) |
| C(2)−C(1)−Zr(1) | 80.22(13) | C(1)−C(2)−C(3) | 120.9(2) |
| C(6)−C(1)−Zr(1) | 80.36(12) | C(1)−C(6)−C(5) | 122.4(2) |
| C(3)−C(4)−Zr(1) | 79.17(12) | C(4)−C(3)−C(2) | 122.1(2) |
| C(5)−C(4)−Zr(1) | 80.59(11) | C(6)−C(5)−C(4) | 119.44(18) |

[a] CNT1 is the calculated centroid of the Cp* fragment.

designation requires vs either a 16- or 18-electron count that the alternative reduced metal structural formalizations provide.[13,14] Further support for a zirconanorbornadiene structure is provided by the observed thermal robustness of **7**, which fails to undergo arene substitution in toluene at 100 °C, and by the $^1$H chemical shifts of the resonances for the metallanorbornadiene fragment (i.e., $C_6H_5Et$), which occur between 3.64 and 3.86 ppm.[13] Mechanistically, since no styrene production is observed and **7** cannot function as a catalyst for the hydrogenation of styrene, we propose that the **2** → **7** transformation proceeds through initial $\sigma$-bond metathesis of the metallacyclopropane to provide a zirconium alkyl hydride that then undergoes $\pi$-assisted reductive elimination, followed by formal arene reduction, to generate **7** (see Scheme 5). Of final note, this facile hydrogenolysis of **2** stands in sharp contrast to the inertness of the structurally related dimethyl complex Cp*Zr(Me)$_2$[N($^i$Pr)C(Me)N($^i$Pr)], which remains unchanged under identical conditions.

## Conclusion

In summary, a new, base-free $\eta^2$-styrene complex of zirconium bearing the mono(cyclopentadienyl), mono(amidinate) ligand set has been prepared. A preliminary survey of reactivity has revealed that this compound can formally undergo ring opening of a zirconacyclopropane ring via either protonolysis, in the case of phenylacetylene, or $\sigma$-bond metathesis, in the case of group 14 metal chlorides and hydrogenolysis. Additional studies of this compound, and in particular, insertion chemistry of alkenes to form zirconacyclopentanes, will be published in due course.

## Experimental Details

**General Considerations.** All manipulations were carried out in a glovebox or using standard Schlenk-line techniques under an atmosphere of dinitrogen. All solvents were dried (Na/benzophenone for diethylether and pentane, Na for toluene, $CaH_2$ for chlorobenzene) and distilled under dinitrogen prior to use. Benzene-$d_6$ and toluene-$d_8$ were vacuum-transferred from NaK alloy, and chlorobenzene-$d_5$ was vacuum-transferred from $CaH_2$ prior to use as NMR solvents. Cp*ZrCl$_2$[$^i$PrNC(Me)NPr$^i$] (**1**) was prepared according to previously published procedures.[7] $^1$H and $^{13}$C{$^1$H} NMR spectra were recorded at 400 and 100 MHz, respectively. Elemental analyses were performed by Midwest Microlab.

**Preparation of Compound 2.** To a solution of 0.75 mL (5.17 mmol) of (2-iodoethyl)benzene in 50 mL of $Et_2O$ cooled to −78 °C was added 7.3 mL of 1.5 M $^t$BuLi (11.0 mmol) in pentane. The reaction mixture was then warmed to ambient temperature over 1 h, whereupon it was cooled to −30 °C and 1.08 g (2.46 mmol) of **1** was added. The reaction mixture was stirred overnight at ambient temperature, and then all the volatiles were removed under vacuum, the green residue was extracted with pentane, and the extract filtered through Celite and re-evaporated. The green solid material was taken up into a small (ca. 10 mL) amount of pentane, passed through a small pad of Celite, and crystallized at −30 °C to give 0.89 g (76% yield) of **2** as a deep green crystalline material. $^1$H NMR (benzene-$d_6$, 25 °C): $\delta$ 0.11, 0.88, 1.06, 1.28 (d, 3 H, $J$ = 6.8 Hz, CH*Me$_2$*); 1.35, 2.16 (br s, 1 H, *CH$_A$H$_B$*CHPh); 1.43 (s, 3 H, C*Me*); 1.84 (s, 15 H, C$_5$*Me$_5$*); 3.53 (br s, 1 H, CH$_A$H$_B$*CH*Ph); 2.99, 3.75 (sept, 1 H, $J$ = 6.8 Hz, *CH*Me$_2$); 6.24 (br s, 2 H, *o*-Ph); 6.41 (t, 1 H, $J$ = 7.2 Hz, *p*-Ph); 6.97 (t, 2 H, $J$ = 7.2 Hz, *m*-Ph). $^{13}$C{$^1$H} NMR (benzene-$d_6$, 25 °C): $\delta$ 11.7 (C$_5$*Me$_5$*); 12.3 (C*Me*); 23.0, 24.6, 25.7, 25.8 (CH*Me$_2$*); 47.2, 50.4 (*CH*Me$_2$); 60.1 (*CH$_A$H$_B$*CHPh); 81.2 (CH$_A$H$_B$*CH*Ph); 118.4 (*C$_5$*Me$_5$); 116.2, 130.9, 139.1, 146.4 (*Ph*); 164.1 (*C*Me). Anal. Calcd for $C_{26}H_{40}N_2Zr$: C, 66.18; H, 8.54; N, 5.94. Found: C, 65.80; H, 8.57; N, 6.01.

**Preparation of Compound 3.** To a solution of 0.13 g (0.28 mmol) of **2** in 5 mL of $Et_2O$ cooled to −30 °C was added 3.0 $\mu$L (0.28 mmol) of phenylacetylene. The reaction mixture was then warmed to ambient temperature over 1 h, whereupon it was evaporated to dryness. The residue was taken up into a small (ca. 5 mL) amount of pentane, passed through a small pad of Celite, and crystallized at −30 °C to give 0.10 g (62% isolated yield) of **3a** as a yellow crystalline material. On a smaller scale, $^1$H NMR revealed the reaction to have proceeded quantitatively. $^1$H NMR (benzene-$d_6$, 25 °C): $\delta$ 0.65, 0.99 (t of d, 1 H, $^1J$ = 12.8 Hz, $^2J$ = 5.2 Hz, *CH$_2$*CH$_2$Ph); 1.14 (br s, 12 H, CH*Me$_2$*); 1.55 (s, 3 H, C*Me*); 2.09 (s, 15 H, C$_5$*Me$_5$*); 3.29 (sept, 2 H, $J$ = 6.8 Hz, *CH*Me$_2$); 3.69 and 3.74 (t of d, 1 H, $^1J$ = 11.0 Hz, $^2J$ = 5.2 Hz, CH$_2$*CH$_2$*Ph); 6.97−7.53 (m, 10 H, CH$_2$CH$_2$*Ph*, CC*Ph*). $^{13}$C{$^1$H} NMR (benzene-$d_6$, 25 °C): $\delta$ 12.2 (C$_5$*Me$_5$*); 12.3 (C*Me*); 23.9 (CH*Me$_2$*); 24.4 (*CH$_2$*-CH$_2$Ph); 32.2 (CH$_2$*CH$_2$*Ph); 48.1 (*CH*Me$_2$); 72.7 (*C*CPh); 108.8 (C*C*Ph); 121.7 (*C$_5$*Me$_5$); 124.7, 126.2, 125.5, 127.4, 127.6, 131.1, 148.2, 150.4 (CH$_2$CH$_2$*Ph*, CC*Ph*); 175.9 (*C*Me). Anal. Calcd for $C_{34}H_{46}N_2Zr$: C, 71.15; H, 8.08; N, 4.88. Found: C, 70.44; H, 8.12; N, 5.07.

**Preparation of Compound 4.** A solution of 0.13 g (0.28 mmol) of **3** in 5 mL of toluene was heated at 60 °C for 48 h, whereupon it was evaporated to dryness. The residue was taken up into a small (ca. 10 mL) amount of pentane, passed through a small pad of Celite, concentrated to a volume of ca. 5 mL, and crystallized at −30 °C. The mother liquor was decanted, concentrated to 0.5 mL volume, and crystallized at −30 °C to give 0.04 g (31% yield) of **4** as a purple crystalline material. $^1$H NMR (benzene-$d_6$, 25 °C): $\delta$ −0.08, 0.75, 0.77, 0.95 (d, 3 H, CH*Me$_2$*); 0.50, 0.81 (dd, 1 H, $^1J$ = 8.0 Hz, $^2J$ = 0.2 Hz, *CH$_2$*Ph); 1.29 (s, 3 H, C*Me*); 1.69 (d, 1 H, $J$ = 8.0 Hz, *CH*Ph); 1.87 (s, 15 H, C$_5$*Me$_5$*); 2.22 (d, 1 H, $J$ = 8 Hz, ═*CH*); 3.0, 3.24 (sept, 1 H, $J$ = 6.8 Hz, *CH*Me$_2$); 6.97−7.53 (m, 10 H, CH$_2$CH$_2$*Ph*, CC*Ph*). $^{13}$C{$^1$H} NMR (benzene-$d_6$, 25 °C): $\delta$ 11.6 (C$_5$*Me$_5$*); 12.2 (C*Me*); 25.7, 24.8, 23.8, 23.0 (CH*Me$_2$*); 13.8 (*CH$_2$*Ph); 22.3 (*CH*Ph); 46.1, 47.0 (*CH*Me$_2$); 58.4 (═*CH*); 74.6 (═*C*Ph); 119.4 (*C$_5$*Me$_5$); 119.9, 121.1, 123.7, 124.4, 125.5, 127.9, 144.9, 145.8 (*Ph*); 157.4 (*C*Me). Anal. Calcd for $C_{34}H_{46}N_2Zr$: C, 71.15; H, 8.08; N, 4.88. Found: C, 71.27; H, 7.99; N, 5.07.

**Preparation of Compound 5b.** To a solution of 0.20 g (0.46 mmol) of **2** in 20 mL of $Et_2O$ cooled to −30 °C was added 0.09 g (0.23 mmol) of trimethyltin chloride. Immediately after that the reaction mixture was evaporated to dryness while the solution was kept at 0 °C, the residue was extracted with a 5:1 pentane/toluene mixture, the extracts were filtered through a small pad of Celite, and then the solvents were removed in vacuo to provide a crude

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[14] For titananorbornadiene complexes, see: (a) Hagadorn, J. R.; Arnold, J. *Angew. Chem., Int. Engl.* **1998**, *37*, 1729−1731. (b) Ozerov, V.; Patrick, B. O.; Ladipo, F. T. *J. Am. Chem. Soc.* **2000**, *122*, 6423−6431.

material that was recrystallized at −30 °C from a 5:1 pentane/toluene mixture (ca. 4 mL) to give 0.13 g (41% yield) of **5b** as an orange crystalline material. $^1$H NMR (toluene-$d_8$, −10 °C): $\delta$ 0.18 (s, 9 H, SnMe$_3$); 1.07, 1.11, 1.25, 1.39 (d, 3 H, $J$ = 6.8 Hz, CH*Me*$_2$); 1.42 (s, 3 H, C*Me*); 1.23 and 1.74 (dd, 1 H, $^1J$ = 16.0 Hz, $^2J$ = 8.0 Hz, C$H_AH_B$SnMe$_3$); 1.95 (s, 15 H, C$_5$*Me*$_5$); 2.52 (d, 1 H, $^1J$ = 8.6 Hz, C*H*Ph); 3.45 (sept, 2 H, $J$ = 6.8 Hz, *CH*Me$_2$); 6.83−7.21 (m, 5 H, Ph). $^{13}$C{$^1$H} NMR (benzene-$d_6$, 25 °C): $\delta$ −8.7 (SnMe$_3$); 9.5 ($CH_AH_B$SnMe$_3$); 12.5 (C$_5$*Me*$_5$); 15.1 (CMe); 23.7, 234.0, 24.9, 25.9 (CH*Me*$_2$); 47.0, 49.2 (*CH*Me$_2$); 78.7 (*CH*Ph); 122.2 ($C_5$Me$_5$), 122.9, 127.4, 128.2, 149.5 (*Ph*); 174.5 (*C*Me).

**Preparation of Compound 6a.** A solution of 0.11 g (0.23 mmol) of **2** and 29 $\mu$L (0.23 mmol) of trimethylchlorosilane in 5 mL of toluene was kept overnight at 40 °C. After that the reaction mixture was evaporated to dryness, the residue was extracted with a 5:1 pentane/toluene mixture, the extracts were filtered through a small pad of Celite, and then solvents were removed in vacuo to provide a crude material that was recrystallized at −30 °C from a 5:1 pentane/toluene mixture (ca. 4 mL) to give 0.12 g (93% yield) of **6a** as an orange crystalline material. Note: single-crystal X-ray analysis provided a 0.09% Br occupancy at the Cl (0.91%) site in the refined solid-state structure of **6a**.[10] At the present time, we do not know the source of this contaminant, but we note that the chemical analysis of **6a** (vide infra) did not reflect this level of bromide contamination within the bulk material. $^1$H NMR (benzene-$d_6$, 25 °C): $\delta$ −0.08 (s, 9 H, SiMe$_3$); 1.00, 1.03, 1.27, 1.36 (d, 3 H, $J$ = 6.8 Hz, CH*Me*$_2$); 1.21 (dd, 1 H, $^1J$ = 14.6 Hz, $^2J$ = 2.4 Hz, C$H_AH_B$SiMe$_3$); 1.40 (dd, 1 H, $^1J$ = 14.6 Hz, $^2J$ = 2.4 Hz, C$H_AH_B$SiMe$_3$); 1.51 (s, 3 H, C*Me*); 1.81 (s, 15 H, C$_5$*Me*$_5$); 2.56 (dd, 1 H, $^1J$ = 14.6 Hz, $^2J$ = 12.4 Hz, C*H*Ph); 3.31, 3.49 (sept, 1 H, $J$ = 6.8 Hz, *CH*Me$_2$); 6.82−7.16 (m, 5 H, Ph). $^{13}$C{$^1$H} NMR (benzene-$d_6$, 25 °C): $\delta$ 0.0 (SiMe$_3$); 11.9 (C$_5$*Me*$_5$); 13.5 (CMe); 13.9 ($CH_AH_B$SiMe$_3$); 23.3, 23.7, 24.5, 25.0 (CH*Me*$_2$); 47.2, 48.5 (*CH*Me$_2$); 78.6 (*CH*Ph); 121.8 ($C_5$Me$_5$), 122.6, 127.4, 127.9, 149.1 (*Ph*); 174.0 (*C*Me). Anal. Calcd for $C_{29}H_{49}ClN_2SiZr$: C, 60.0; H, 8.51; N, 4.82. Found: C, 59.90; H, 8.59; N, 4.88.

**Preparation of Compound 6b.** A solution of 0.13 g (0.19 mmol) of **5b** was dissolved in benzene-$d_6$ and kept overnight at an ambient temperature, whereupon complete isomerization of **5b** into **6b** was observed. All the volatiles were removed in vacuo to give 0.13 g (∼100% yield) of **6b** as an orange crystalline material. $^1$H NMR (benzene-$d_6$, 25 °C): $\delta$ −0.06 (s, 9 H, SnMe$_3$); 1.04, 1.09, 1.29, 1.36 (d, 3 H, $J$ = 6.8 Hz, CH*Me*$_2$); 1.21 (dd, 1 H, $^1J$ = 16.0 Hz, $^2J$ = 4.0 Hz, C$H_AH_B$SnMe$_3$); 1.54 (s, 3 H, C*Me*); 1.74 (dd, 1 H, $^1J$ = 16.0 Hz, $^2J$ = 8.0 Hz, C$H_AH_B$SnMe$_3$); 1.85 (s, 15 H, C$_5$*Me*$_5$); 2.32 (dd, 1 H, $J_1$ = 8.0 Hz, $J_2$ = 4.0 Hz, C*H*Ph); 3.35, 3.52 (sept, 1 H, $J$ = 6.8 Hz, *CH*Me$_2$); 6.83−7.16 (m, 5 H, Ph). $^{13}$C{$^1$H} NMR (benzene-$d_6$, 25 °C): $\delta$ −8.0 (SnMe$_3$); 12.2 (C$_5$*Me*$_5$); 12.9 ($CH_AH_B$SnMe$_3$); 14.7 (CMe); 23.8, 23.9, 24.4, 25.6 (CH*Me*$_2$); 47.5, 48.7 (*CH*Me$_2$); 79.4 (*CH*Ph); 122.3 ($C_5$Me$_5$), 122.6, 122.7, 127.8, 149.8 (*Ph*); 174.2 (*C*Me). Anal. Calcd for $C_{29}H_{49}ClN_2SnZr$: C, 51.90; H, 7.36; N, 4.17. Found: C, 51.72; H, 7.30; N, 4.20.

**Preparation of Compound 7.** A solution of 0.12 g (0.24 mmol) of **2** in 10 mL of Et$_2$O was pressurized with dihydrogen at 40 psi. The color immediately changed to brown, whereupon the solution was evaporated to dryness. The residue was taken up into a small (ca. 5 mL) amount of pentane, passed through a small pad of Celite, and crystallized at −30 °C to give 0.11 g (92.2% yield) of **7** as a brown crystalline material. $^1$H NMR (benzene-$d_6$, 25 °C): $\delta$ 0.87, 1.20 (d, 6 H, $J$ = 6.8 Hz, CH*Me*$_2$); 0.89 (t, 3 H, $J$ = 7.6 Hz, $CH_3$CH$_2$C$_6$H$_5$); 1.37 (q, 2 H, $J$ = 7.6 Hz, CH$_3$$CH_2$C$_6$H$_5$); 1.52 (s, 3 H, C*Me*); 1.85 (s, 15 H, C$_5$*Me*$_5$); 3.32 (sept, 2 H, $J$ = 6.8 Hz, *CH*Me$_2$); 3.64−3.86 (m, 5 H, CH$_3$CH$_2$$C_6H_5$). $^{13}$C{$^1$H} NMR (benzene-$d_6$, 25 °C): $\delta$ 12.6 (C$_5$*Me*$_5$); 13.7 ($CH_3$CH$_2$C$_6$H$_5$); 13.8 (C*Me*); 25.3, 26.6 (CH*Me*$_2$); 28.6 (CH$_3$$CH_2$C$_6$H$_5$); 47.1 (*CH*Me$_2$); 94.0, 95.2, 111.5, 112.2 (CH$_2$CH$_2$$C_6H_5$); 126.3 ($C_5$Me$_5$); 171.9 (*C*Me). Anal. Calcd for $C_{26}H_{42}N_2Zr$: C, 65.90; H, 8.93; N, 5.91. Found: C, 65.20; H, 8.96; N, 5.29.

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**Supporting Information Available:** Details of the crystallographic analyses of **2**−**4**, **5b**, **6a**, and **7**, including tables of atomic positions, isotropic thermal parameters, and anisotropic thermal displacement coefficients; crystal data are also given as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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