Ring-Enlargement and Ring-Opening Reactions of Benzoxazole, Thiazoles, and Benzisoxazole by Zirconocene-Alkyne Complexes

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Zirconocene alkyne complexes $Cp_2Zr(L)(Me_3SiC_2R)$ (L = Py, THF; R = $SiMe_3$, *t*Bu) react with heterocyclic compounds like benzoxazole and related thiazoles to yield ring-expanded adducts $Cp_2\overline{Zr-C(SiMe_3)=C(R)-CH=N-o-C_6H_4-X}$ (**1**–**3**) and $Cp_2\overline{Zr-C(SiMe_3)=C(SiMe_3)-CH=N-C(R')=C(R')-X}$ (R' = Me, H) (**4**, **5**) by formal C–X (X = O, S) bond cleavage and coupling with the coordinated alkyne. In the case of benzisoxazole, the alkyne is not coupled but eliminated, and with ring-enlargement of the benzisoxazole a N-bridged dimer $[Cp_2\overline{Zr-N=CH-o-C_6H_4-O}]_2$ (**6**) is formed. The obtained complexes **1**, **3**, and **6** were characterized by NMR spectra and crystal structure analysis.

There is currently considerable interest in the use of organozirconium derivatives as intermediates in organic synthesis. These compounds appear to be useful reagents for a variety of applications. Nevertheless, only a few examples of ring-opening reactions induced by zirconium complexes are known[1].

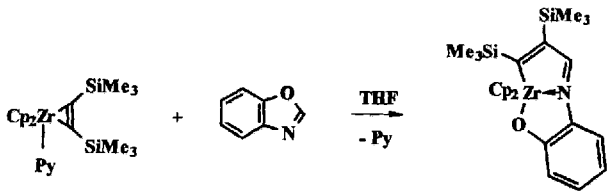
On the other hand studies of the organometallic chemistry and the complexation of oxazoles[2a] and thiazoles are of great interest because of the biological importance of these heterocycles[2b]. The most common coordination mode is η^1-N[3], although oxygen respectively sulfur complexation was observed. Stable structurally characterized gold[4] and lithium carbene complexes[5] with substituted thiazoles are also known.

Ring-opening and the formation of a metallacycle were only reported in the case of the reaction of diphosphaneplatinum(0) complexes with thiazolium salts; a benzothiazolium platinum complex was structurally characterized[6].

It is known that oxazoles, depending on their substituents, exist in a mobile equilibrium with the corresponding isocyano derivatives. The reaction of alkoxyoxazoles with alkyllithium compounds gives rise to a ring-opening and was applied in the synthesis of amino acids[7]. Recently, we described the reactions of the zirconocene generators $Cp_2Zr(L)(Me_3SiC_2SiMe_3)$ (L = THF[8], Py[9]) with C=N bonds of Schiff's bases, which gave, depending on the used substituents, hydrogen migration or coupling products[10]. In this paper we report on novel ring-opening and ring-enlargement reactions of heterocyclic C=N systems, e.g. benzoxazole, benzothiazole, some substituted thiazoles, benzisoxazole, involving treatment with "Cp_2Zr" generating zirconium-substituted heterocyclic systems.

Results and Discussion

The reaction of $Cp_2Zr(L)(Me_3SiC_2SiMe_3)$ (L = Py, THF) with benzoxazole yields already at −10°C spontaneously complex **1** by insertion into the C–O bond and coupling of the alkyne.



1

Complex **1** is a dark red crystalline solid (m.p. 179–180°C dec.), which is air-stable for a short time. The ^{1}H-NMR spectrum shows besides the Cp, Ph, and $SiMe_3$ proton signals in the typical region a unique low-field proton signal at δ = 8.43 of the CH group. In the ^{13}C-NMR spectrum the CH signal also appears in the low range at δ = 162.8. Important is the shift of the signal of the C(1)$SiMe_3$ group, which is directly bound to the zirconium, to δ = 281.4, a range that is typical of σ-alkenyl $ZrCp_2$ groups. This result together with the second signal at δ = 167.4 of C(2)($SiMe_3$) shows a large Δδ value of 114.0 and an extremely high polarization of the two carbon atoms of the former alkyne.

The complex $Cp_2\overline{Zr-C(SiMe_3)=C(tBu)-CH=N-o-C_6H_4-O}$ (**2**) was prepared as described for **1** by using $Cp_2Zr(L)(Me_3SiC_2tBu)$ (L = THF)[11] as starting material. In the ^{1}H-NMR spectrum, the CH signal at δ = 5.73 gives, if saturated, a positive NOE of the *t*Bu protons. The strong NOE on the Cp groups shows that the $SiMe_3$ group is a substituent of C(1). So the ^{1}H-NMR spectrum indicates a regioselective coupling and the sequence Zr–C(1)($SiMe_3$)=C(2)(*t*Bu)–C(3) in the expanded oxazole ring of **2**. These results together with the found coupling pattern in the ^{13}C-NMR spectrum allowed the following assignment: δ = 205.6 for C(1)($SiMe_3$) and δ = 179.9 for C(2)(*t*Bu).

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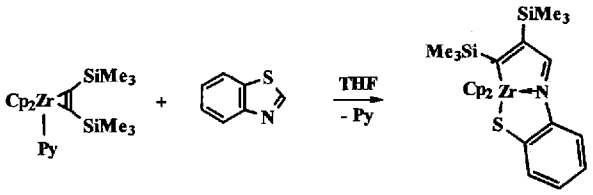
An analogous benzothiazole complex **3** was prepared in 71% yield by the reaction of $Cp_2Zr(L)(Me_3SiC_2SiMe_3)$ (L = THF, Py) with benzothiazole.

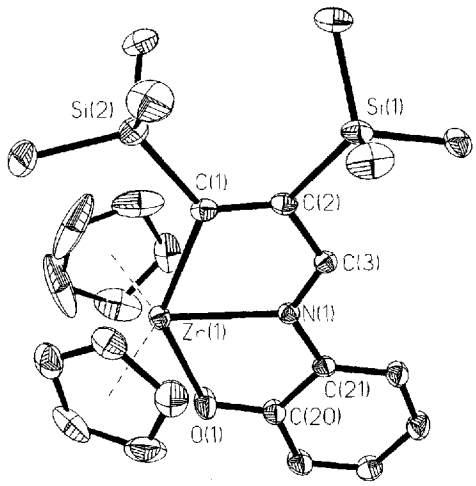


3

Complex **3** is a black-red crystalline substance [m.p. 138–140 °C (dec.)]. The spectral data are similar to those of complex **1**. The above-discussed low-field shifted signals of CH appear in the ^{1}H-NMR as a singlet at δ = 8.02, in the ^{13}C-NMR spectrum a signal of C(1) is observed at δ = 276.4.

An X-ray diffraction study of **1** (Figure 1) and **3** (Figure 2) was performed to give an accurate description of these unusual molecules. Selected bond lengths and angles are summarized in Table 1.

Figure 1. Molecular structure of complex **1**, shown by an ORTEP plot. The thermal ellipsoids correspond to 20% probability. The Cp ring of **1** [C(5), C(6), C(7), and C(8)] seems to be disordered due to large aniostropic displacement factors. Refinement as ideal disordered Cp ring did not give more accurate results



Compounds **1** and **3** have similar structural features. The products are bicyclic eight-membered metallacycles consisting of two five-membered ring systems. One ring is connected with an *o*-phenylene and contains the coordinating O (or S) and N atoms, originating from the starting benzazole. The N atom is also a part of the second ring system, formed by an additional CH group and two C atoms from the starting alkyne. The Zr–C(1) bond lengths are with 2.426(3) Å (**1**) and 2.405(11) Å (**3**) in the typical range of a Zr–C single bond. On the other hand, the N–C(3) bond lengths of 1.287(4) Å (**1**) and 1.293(13) Å (**3**) are significantly shorter compared with those of oxa- or thiazoles[12], indicating a high double-bond character, despite the out-of-plane distortion (Table 1).

Figure 2. Molecular structure of complex **3**, shown by an ORTEP plot. The thermal ellipsoids correspond to 40% probability

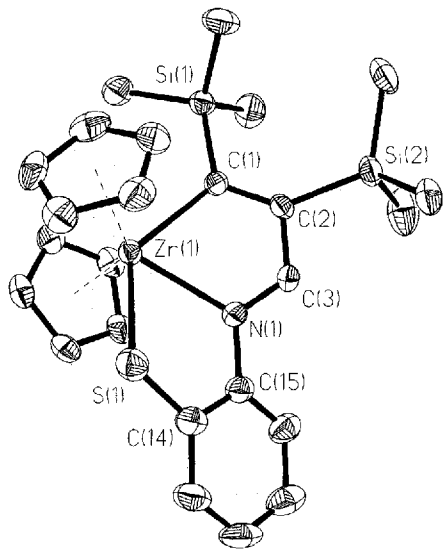


Table 1. Selected bond lengths [Å] and angles [deg.] of **1** (X = O) and **3** (X = S)

	1	**3***
Zr-C(1)	2.426(3)	2.405(11)
Zr-N(1)	2.301(3)	2.330(8)
C(1)-C(2)	1.373(5)	1.380(15)
C(2)-C(3)	1.458(4)	1.477(15)
C(2)-Si(2)	1.920(3)	1.907(11)
C(1)-Si(1)	1.902(3)	1.907(11)
Zr-X	2.144(2)	2.663(4)
C(3)-N(1)	1.287(4)	1.293(13)
C(2)-C(1)-Zr	115.7(2)	114.8(7)
C(1)-C(2)-C(3)	114.3(3)	113.9(4)
C(1)-C(2)-Si(2)	134.2(2)	137.4(9)
C(2)-C(1)-Si(1)	121.2(2)	117.6(8)
C(3)-C(2)-Si(2)	111.5(2)	108.7(7)
N(1)-Zr-C(1)	69.2(10)	69.7(17)

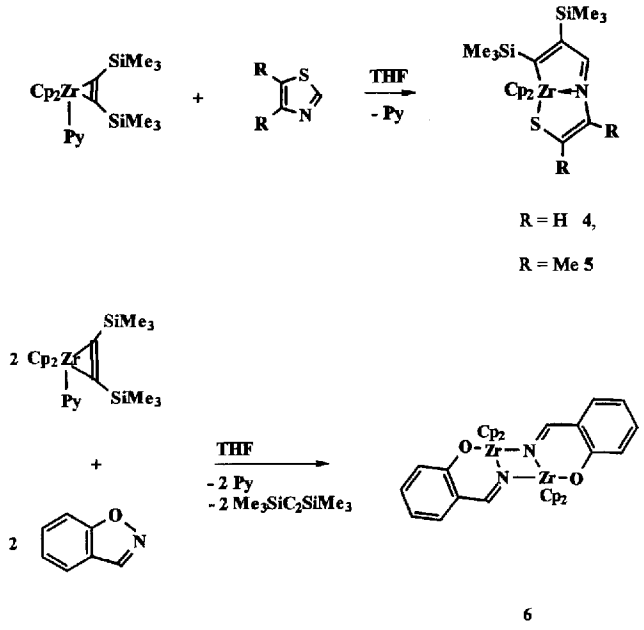
* Compound **3** has two symmetry-independent molecules per asymmetric unit. Selected bond lengths and angles are averaged.

The angles C(2)C(1)Si(1) 121.2(2) in **1** and 117.6(8) in **3** and the angles C(1)C(2)Si(2) 134.2(2) in **1** and 137.4(9) in **3** are in the same range as found for dimeric zirconafuranones and zirconadihydrofurans, which contain also comparable five-membered ring systems[13]. Coordination of O (or S), N, and C gives the zirconocene complex an 18-electron count.

The experiments described above demonstrate the novel and extremely facile insertion of zirconocene alkyne complexes into the C–X bond (X = O, S) of oxa- and thiazoles, and it was of interest to test the generality of this observation.

The reaction of $Cp_2Zr(L)(Me_3SiC_2SiMe_3)$ (L = Py, THF) with 2,3-substituted thiazoles follows a course similar to the metallacyclic systems **4** and **5** like **3** which exhibit similar NMR analytical results.

The reaction of $Cp_2Zr(L)(Me_3SiC_2SiMe_3)$ (L = Py) with benzisoxazole yields the dimeric complex **6** while the alkyne

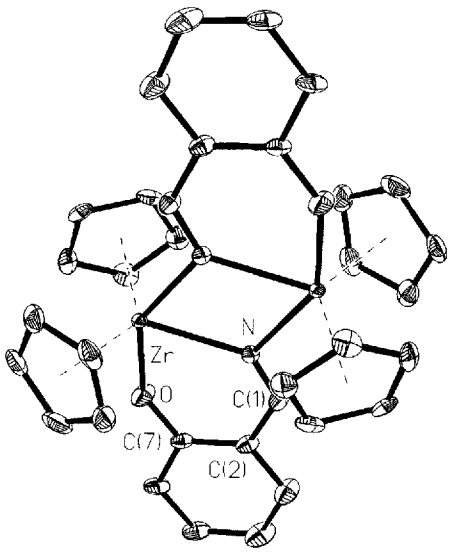


is released and the zirconocene inserted into the N–O bond.

Complex **6** crystallizes as pale yellow prisms (m.p. 218–220°C dec.), which contain uncoordinated THF as solvate molecules. At room temperature the crystals rapidly lose their THF to yield a yellow powder.

The ^{1}H-NMR spectrum exhibits besides the signals of Cp and Ph groups only a singlet at δ = 8.78 for the CH group of the former isoxazole ring, indicating elimination of the alkyne. The ^{13}C-NMR signal of this CH group is also observed in the low range at δ = 172.1.

Figure 3. Molecular structure of complex **6**, shown by an ORTEP plot. The thermal ellipsoids correspond to 40% probability



Selected bond lengths [Å] and angles [deg.]: Zr–O 2.101(4), Zr–N(1) 2.260(5), Zr–N(2) 2.327(5), N–C(1) 1.287(8), C(1)–C(2) 1.452(8), C(2)–C(7) 1.389(9), C(7)–O 1.312(8); O–Zr–N 147.2(2), N–Zr–N 68.7(2), C(7)–O–Zr 140.1 (4).

Crystals suitable for an X-ray structure analysis were obtained by crystallization of **6** from THF at –10°C.

The X-ray structure of **6** (Figure 3) exhibits a dimer, in which two metallacycles, formed by insertion of a metallocene moiety "Cp_2Zr" into the O–N bond of the isoxazole, are bridged by nitrogen-zirconium interactions. The bond lengths in the central Zr–N–Zr–N four-membered ring are Zr–N(1) 2.260(5) and Zr–N(2) 2.327(5) Å. Some comparable bond lengths in the six-membered ring system, resulting from the opened isoxazol system, Zr–N 2.260(5), Zr–O 2.101(4) and N–C(1) 1.287(8) are in the same range as found in the five-membered ring of the oxazole metallacycle **1**.

The fact, that benzoxazole and benzothiazole or benzisoxazole react with zirconocene-alkyne complexes to different products (with coupling or elimination of the alkyne) can be explained by a mechanism, in which the formation of η^2-imine complexes[14] (aza-zircona-cyclopropanes) is assumed in both cases.

These can in principle insert the alkyne to form aza-zircona-cyclopentenes[14]. The so obtained benzoxazole or thiazole products rearrange by β-OR or β-SR elimination directly to products **1** and **3**. Due to steric restrictions (*o*-phenylen group) an analogous coupling product with benzisoxazole seems to be impossible or less stable and the system is stabilized by a ring-opening reaction to yield the dimeric product **6**.

This explanation is in good agreement with recently observed results concerning sterical restriction in coupling reaction of $Me_3SiC{\equiv}CSiMe_3$ with $Ph_2C{=}O$[13] and $Ph(Me)C{=}NPh$[15].

Concepts to extend the ring-opening and ring-enlargement reactions to well-known titanocene complexes failed so far. Only by use of benzimidazole, a dark green binuclear paramagnetic benzimidazolato Ti(III) complex was obtained, for which a dinuclear structure as found in the bibenzimidazolato Ti(III) complex[16] was assumed.

Conclusion

The ring-opening and coupling of heterocycles like benzoxazole, thiazoles and benzisoxazole with $Cp_2Zr(L)(Me_3SiC_2SiMe_3)$ (L = Py, THF) to yield novel metallacyclic compounds, which have not previously observed, demonstrate the great synthetic potential of such zirconocene-alkyne complexes. The reactions suggest a number of further investigations of reactions with other heterocyclic systems and synthetic applications of the obtained products.

Experimental

All operations were carried out under argon with standard Schlenk techniques. Prior to use solvents were freshly distilled from sodium tetraethylaluminate and stored under argon. Deuterated solvents were treated with sodium or sodium tetraethylaluminate, distilled, and stored under argon. – Mass spectra: AMD 402. – NMR spectra: Bruker ARX 400. Chemical shifts referenced to signals of the used solvents: [D_8]THF (β-CH_2: δ_H = 1.73, δ_C = 25.2) or C_6D_6 (δ_H = 7.16, δ_C = 128.0). The spectra were assigned with the help of Dept, NOE, and COSY experiments. – Melting points: scaled capillaries, Büchi 535 apparatus. – Elemental analyses: Leco

CHNS-932 elemental analyzer. – X-ray diffraction data: CAD4 MACH3 diffractometer using graphite-monochromated Mo-K_α radiation. The crystals were sealed inside capillaries (**1**, **3**) or mounted in a cold nitrogen stream (**6**). Absorption correction was carried out by Ψ scan. The structure was solved by direct methods (SHELXS-86[17]) and refined by full-matrix least-squares techniques against F^2 (SHELXL-93[18]). XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations. Further details of the crystal structure investigations are available upon request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ (UK), on quoting the full journal citation.

Preparation of $Cp_2\overline{Zr-C(SiMe_3)=C(SiMe_3)-CH=N-o-C_6H_4-O}$ (**1**): A solution of 140 mg (1.18 mmol) of benzoxazole in 2 ml of THF was added to a solution of 538 mg (1.14 mmol) of $Cp_2ZrMe_3SiC_2SiMe_3$(Py) in 10 ml of THF at −10 °C. After stirring at −10 °C for 30 min and subsequent stirring of the red solution at room temp. for 2 h, the solvent was removed in vacuo. The residue was dissolved in 10 ml of *n*-hexane at 40 °C. Red prisms crystallized at room temperature overnight. Yield of **1** 395 mg, 68%, m.p. 179−180 °C (dec.). – ^{1}H NMR ([D$_8$]THF, 303 K): δ = 0.34 and 0.38 [2 s, 2 × 9H, Si(CH$_3$)$_3$]; 6.02 (s, 10H, Cp); 6.27 (m, 2H, ar), 6.82 (t, 1H, ar), 7.11 (d, 1H, ar); 8.43 (s, 1H, CH). – ^{13}C NMR ([D$_8$]THF, 303 K): δ = 2.9 and 5.4 (SiMe$_3$); 111.8 (Cp); 113.7, 114.6, 118.2, 129.9 (CH ar), 139.3, 160.1 (C ar); 162.8 (CH); 167.4, 281.4 (*C*SiMe$_3$). – $C_{25}H_{33}NOSi_2Zr$ (510.9): calcd. C 58.77, H 6.51, N 2.74, Zr 17.85; found C 58.56, H 6.69, N 2.70, Zr 17.58. – MS (FAB), *m/z*: 509 [M$^+$], 436 [M$^+$ − SiMe$_3$], 338 [M$^+$ − Me$_3$SiC$_2$SiMe$_3$].

Preparation of $Cp_2\overline{Zr-C(SiMe_3)=C(tBu)-CH=N-o-C_6H_4-O}$ (**2**): According to the same procedure as described for **1** with 565 mg (1.22 mmol) of $Cp_2ZrMe_3SiC_2tBu$(THF) in 10 ml of THF and 150 mg (1.26 mmol) of benzoxazole. Orange prisms deposited at −30 °C over night. Yield of **2** 275 mg, 55%, m.p. 118−120 °C (dec.). – ^{1}H NMR (C_6D_6): δ = 0.26 [s, 9H, Si(C*H*$_3$)$_3$]; 1.14 (s, 9H, Me), 5.65 (s, 10H, Cp); 5.73 (s, 1H, CH), 7.15 (m, 2H, ar), 7.57 (d, 1H, ar), 7.92 (d, 1H, ar). – ^{13}C NMR (C_6D_6): δ = 2.9 (SiMe$_3$); 30.0 [(*C*H$_3$)$_3$C], 36.5 [(CH$_3$)$_3$*C*], 108.4 (Cp); 113.3, 119.0, 122.7, 122.9 (CH ar), 144.8, 154.3 (C ar); 109.3 (CH); 179.9, 205.6 (*C*SiMe$_3$). – $C_{26}H_{33}NOSiZr$ (493.1): calcd. C 63.11, H 6.72, N 2.83, Zr 18.43; found C 62.63, H 6.66, N 2.72, Zr 17.96. – MS (FAB), *m/z*: 491 [M$^+$].

Preparation of $Cp_2\overline{Zr-C(SiMe_3)=C(SiMe_3)-CH=N-o-C_6H_4-S}$ (**3**): 0.17 ml (1.55 mmol) of benzothiazole was added to a solution of 670 mg (1.42 mmol) of $Cp_2ZrMe_3SiC_2SiMe_3$(Py) in 10 ml of THF at −30 °C. After stirring at −30 °C for 30 min and subsequent stirring of the violet solution at room temp. for 2 h, THF was removed in vacuo. The residue was dissolved in 10 ml of *n*-hexane at 40 °C. Deep red prism crystallized at room temperature over 2 d. Yield of **3** 530 mg, 71%, m.p. 138−140 °C (dec.). – ^{1}H NMR ([D$_8$]THF, 303 K): δ = 0.33 and 0.43 [2 s, 2 × 9H, Si(CH$_3$)$_3$]; 5.91 (s, 10H, Cp); 6.75 (d, 1H, ar), 6.88 (t, 1H, ar), 7.07 (m, 2H, ar); 8.02 (s, 1H, CH). – ^{13}C NMR ([D$_8$]THF, 303 K): δ = 2.6 and 5.3 (SiMe$_3$); 110.1 (Cp); 116.7, 122.5, 127.9, 130.3 (CH ar), 149.1, 150.8 (C ar); 164.0 (CH); 165.0, 276.4 (*C*SiMe$_3$). – $C_{25}H_{33}NSSi_2Zr$ (526.9): calcd. C 56.98, H 6.31, N 2.66, S 6.08, Zr 17.31; found C 56.62, H 6.27, N 2.60, S 6.06, Zr 17.14. – MS (FAB), *m/z*: 525 [M$^+$], 452 [M$^+$ − SiMe$_3$], 356 [M$^+$ − Me$_3$SiC$_2$SiMe$_3$].

Preparation of $Cp_2\overline{Zr-C(SiMe_3)=C(SiMe_3)-CH=N-CH=CH-S}$ (**4**): According to the same procedure as described for **3** with 490 mg (1.04 mmol) of $Cp_2ZrMe_3SiC_2SiMe_3$(Py) in 10 ml of THF and 0.1 ml (1.1 mmol) of thiazole. Red, microcrystalline samples were obtained from *n*-hexane. Yield of **4** 200 mg, 42%, m.p. 136−140 °C (dec.). – ^{1}H NMR (C_6D_6): δ = 0.32 and 0.36 [2 s, 2 × 9H, Si(CH$_3$)$_3$]; 5.91 [s, 2H, CH(thiazole)], 6.01 (s, 10H, Cp); 8.00 (s, 1H, CH). – ^{13}C NMR (C_6D_6): δ = 2.0 and 3.7 (SiMe$_3$); 111.2 (Cp); 148.3 (N=CH); 137.3 and 140.2 (CH=CH), 166.1 and 236.1 (*C*SiMe$_3$). – $C_{21}H_{31}NSSi_2Zr$ (476.9): calcd. C 52.89, H 6.55, N 2.94, S 6.72, Zr 19.13; found C 52.51, H 6.11, Zr 18.33. – MS (FAB), *m/z*: 475 [M$^+$].

Preparation of $Cp_2\overline{Zr-C(SiMe_3)=C(SiMe_3)-CH=N-C(CH_3)=C(CH_3)-S}$ (**5**): A solution of 471 mg (1.00 mmol) of $Cp_2ZrMe_3SiC_2SiMe_3$(Py) in 10 ml of THF was treated with 0.12 ml (1.06 mmol) of 4,5-dimethylthiazole in the same solvent at −30 °C. After stirring for 2 h, the deep violet solution was warmed to room temp. and the solvent removed in vacuo. The black residue was dissolved in 10 ml of *n*-hexane. Deep violet prisms crystallized at −10 °C. Yield of **5** 350 mg, 69%, m.p. 188−190 °C (dec.). – ^{1}H-NMR (C_6D_6): δ = 0.25 and 0.35 [2 s, 2 × 9H, Si(CH$_3$)$_3$]; 1.60 and 2.10 (2 s, 2 × 3H, Me), 5.89 (s, 10H, Cp); 7.58 (s, 1H, CH). – ^{13}C-NMR (C_6D_6): δ = 2.9 and 5.6 (SiMe$_3$); 15.3 and 24.4 (Me), 110.0 (Cp); 162.0 (CH); 161.2 and 275.0 (*C*SiMe$_3$). – $C_{23}H_{35}NSSi_2Zr$ (504.9): calcd. C 54.70, H 6.99, N 2.77, S 6.35, Zr 18.06; found C 54.66, H 6.41, N 2.78, S 6.36, Zr 17.78. – MS (FAB), *m/z*: 503 [M$^+$], 430 [M$^+$ − SiMe$_3$].

Preparation of $[Cp_2\overline{Zr-N=CH-o-C_6H_4-O}]_2$ (**6**): A solution of 0.140 ml (1.18 mmol) of benzisoxazole in 2 ml of THF was added to a solution of 540 mg (1.14 mmol) of $Cp_2ZrMe_3SiC_2SiMe_3$(Py) in 10 ml of THF at −10 °C. During stirring of the solution at −10 °C for 2 h its color turned from deep brown to light yellow. After warming to room temp., the volatile components were removed in vacuo. Then the yellow residue was washed twice with small portions of cold *n*-hexane and dissolved in 2.5 ml of THF. On standing at −10 °C for 3 d, yellow crystals deposited. Yield of **6** 275 mg, 80%, m.p. 218−220 °C (dec.). – ^{1}H NMR ([D$_8$]THF):

Table 2. Crystallographic data of **1**, **3**, and **6**

compd.	**1**	**3**	**6** × 2 THF
formula	$C_{25}H_{33}NOSi_2Zr$	$C_{50}H_{66}N_2S_2Si_4Zr_2$	$(C_{21}H_{23}O_2Zr)_2$
mol. mass	510.92	1053.97	412.62
cryst. color	red	black	yellow
cryst. descript	prism	prism	prism
cryst. size (mm)	0.3 × 0.3 × 0.2	0.5 × 0.5 × 0.4	0.6 × 0.5 × 0.5
cryst. system	monoclinic	triclinic	triclinic
space group	$P2_1/n$	P-1	P-1
lattice constants			
a (Å)	12.766(1)	10.169(1)	8.503(1)
b (Å)	14.905(1)	10.298(1)	10.766(1)
c (Å)	13.784(1)	26.092(3)	11.516(1)
α (deg)	90	88.23(1)	115.56(1)
β (deg)	106.072(6)	83.84(1)	105.43(1)
γ (deg)	90	72.26(1)	96.45(1)
Z	4	2	1
temp. (K)	293(2)	293(2)	173(2)
μ (mm^{-1})	0.548	0.611	0.635
abs. cor.	Ψ scan	Ψ scan	Ψ scan
transm.(%)			
min./max.	98.1 / 100.0	89.9 / 100.0	86.6 / 99.8
θ range (deg)	2.36 - 24.99	2.33 - 24.97	2.57 - 25.00
largest diff. (e Å^{-3})			
peak / hole	0.4 / -0.5	1.0 / -0.8	1.1 / -1.1
no. of rflns. (measd.)	4618	9633	3285
no. of rflns. (indep.)	4425	9076	3104
R (int)	0.0163	0.0203	0.0295
no. of rflns. (obsd.) (I > 2σ(I))	3329	6893	3037
R1 (I > 2σ(I))	0.036	0.044	0.048
no. of parameters	275	541	286
wR2 (all data)	0.106	0.175	0.142

δ = 1.76 and 3.65 (m, THF), 6.08 (s, 10H, Cp); 6.57 (d, 1H, ar), 6.68 (t, 1H, ar), 7.19 (t, 1H, ar); 7.28 (t, 1H, ar), 8.78 (s, 1H, CH). – ^{13}C NMR ([D$_8$]THF, 303 K): δ = 113.4 (Cp); 116.4, 119.8, 133.1, 133.2 (CH ar), 127.6, 164.2 (C ar); 172.1 (CH). – $C_{34}H_{30}N_2O_2Zr_2$ (678.04): calcd. C 60.17, H 4.46, N 4.13, Zr 26.52; found C 59.92, H 4.46, N 4.15, Zr 25.88. – MS (FAB), *m/z*: 339 [$Cp_2ZrC_7H_5ON$].

X-ray Structure Determination of Compounds **1**, **3** *and* **6**: Crystal data parameters are summarized in Table 2.

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