(Allyl)zirconium(IV) Complexes with the *N,N'*-Bis(trimethylsilyl)benzamidinato ("siam") Ligand – Molecular Structures and η^1-η^3 Interconversions of the Allyl Groups☆

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Received June 21, 1996

Key Words: Benzamidinate / Zirconium complexes / Allyl ligands

Complexes of the type $(siam)_2Zr(allyl)_2$ (**1a**) and $(siam)Zr(allyl)_nCl_m$ are described (**2a**: $n = 1$, $m = 2$; **2b**: $n = 2$, $m = 1$; **2c**: $n = 3$, $m = 0$; siam: *N,N'*-bis(trimethylsilyl)benzamidinato group). The molecular structure of **1a** shows that both allyl groups are differently bonded. One allyl ligand is η^3-, the other η^1-coordinated. The X-ray crystal structure of the tris(allyl) complex **2c** shows a chiral molecule with two η^3-allyl ligands. The third allyl ligand is coordinated in a mode intermediate between η^3 and η^1, thus serving as a model for an intermediate in the η^3-η^1 intramolecular rearrangement of the allyl ligands observed in solution. Temperature-dependent ^1H- and ^{13}C-NMR spectra of **1a**, **2b** and **2c** indicate a rapid η^1-η^3 rearrangement of the allyl groups at 60°C. At −50°C two different coordination modes of the allyl groups can be observed in the case of **2b** and **2c**.

In contrast to the rich organometallic chemistry of group-4 metallocene-type compounds, complexes structures and reactions of its cp-free organometallics have rarely been reported so far. A variety of $cp_nZr(allyl)_m$ complexes were investigated in more detail due to their theoretical importance to stoichiometric and catalytic C–C linkage reactions[1,2]. On the other hand cp-free bis- or tris(allyl) complexes have previously not been known. To our knowledge only the structures of two mono-allyl cp-free complexes of zirconium were investigated[3,4].

In this paper we describe structures and some reactions of cp-free bis- and tris(allyl)-zirconium(IV) compounds, which contain the bis(trimethylsilyl)benzamidinato ligand ("siam"). This ligand is a formal four-electron donating group coordinated via two sp^2 N donor atoms. The inorganic chemistry of this ligand was developed by Roesky[5] and Dehnicke[6]. Edelmann discussed the relationship of this ligand to cp[7]. Teuben investigated some organometallic and catalytic reactions[8]. Syntheses and structures of alkylzirconium and -titanium complexes were also described[9–12]. Very recently, we published structures of $(siam)_2Zr(alkyl)_2$ compounds and their reactions including their properties in Ziegler-Natta catalysts[13].

$(siam)_2Zr(allyl)_2$ (1a): Molecular Structure and NMR Spectra

1a was prepared by treatment of a suspension of $(siam)_2ZrCl_2$ with two equivalents of (allyl)MgCl in THF in good yields as a red-orange crystalline compound. It is thermally stable in the solid state but light-sensitive. The ^1H-NMR spectrum at room temperature exhibits only one sharp signal for the Me_3Si protons. At −27.5°C coalescence is observed and at lower temperatures two signals for the Me_3Si groups indicate that the rotation of the ligand is frozen. Even at −80°C the allyl groups still undergo rapid interconversion. The ^1H-NMR spectrum shows only one quintet for the CH_2 protons of the allyl groups and one doublet for their CH protons.

Single crystals of **1a** could be isolated from hexane solutions at −20°C. The X-ray crystal structure of the compound is shown in Figure 1.

The identical C–N distances in the siam ligands indicate full electron delocalization in the amidinate groups. The torsion angles between the NCN fragments and the phenyl rings exclude conjugation between the aromatic rings and the amidinate groups, which correspond to the $C(sp^2)$–$C(sp^2)$ single bonds. The siam ligands act as bidendate ligands to form four-membered chelate rings with typical Zr–N bond distances. The central atom has the coordination number seven with a "capped octahedral" structure. Of special interest is the different mode of the allyl-Zr coordination. One allyl group (C-30, C-31, C-32) is η^3-coordinated with two equal C–C bond distances in the ligand. The distances between zirconium and the three carbon atoms of the allyl group are similar.

The second allyl group (C-27, C-28, C-29) is η^1-coordinated, the Zr–C-27 bond length is significantly shorter than the distances of Zr to the other carbon atoms of the allyl group. A usual C–C bond length and a C=C bond in the allyl group confirm the η^1 coordination. Thus, the solid-

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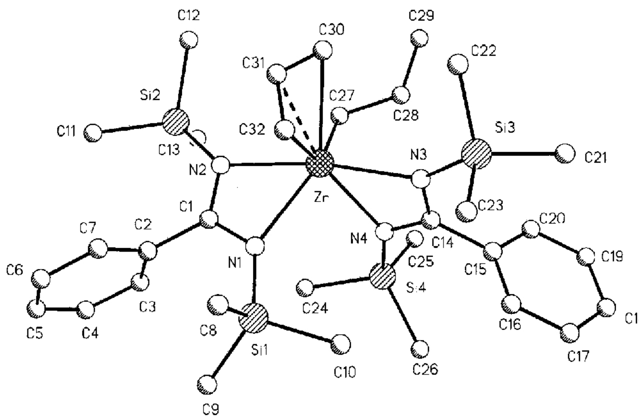
Figure 1. Crystal structure of **1a**[a]



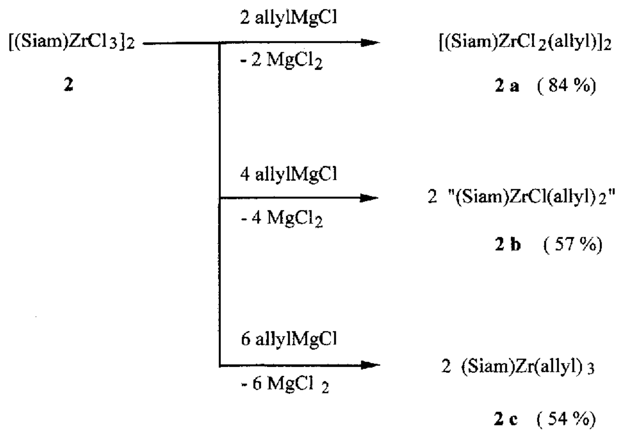
[a] Selected bond lengths [Å] and angles [°]: Zr−N-1 2.294(2), Zr−N-2 2.284(2), Zr−N-3 2.318(2), Zr−N-4 2.264(2), Zr−C-27 2.334(2), Zr−C-30 2.451(3), Zr−C-31 2.525(2), Zr−C-32 2.466(2), C-1−N-1 1.332(3), C-1−N-2 1.330(3), C-1−C-2 1.502(3), C-14−N-3 1.334(3), C-14−N-4 1.334(3), C-14−C-15 1.497(3), C-27−C-28 (1.474(4), C-28−C-29 1.334(5), C-30−C-31 1.384(4), C-31−C-32 1.398(4); N-1−Zr−N-2 59.6(1), N-3−Zr−N-4 59.6(1), N-2−Zr−N-3 169.3(1), N-1−Zr−N-2 87.1(1), C-27−Zr−C-30 76.7(1), C-27−Zr−C-31 104.0(1), C-27−Zr−C-32 136.1(1), C-27−C-28−C-29 126.5(3), C-30−C-31−C-32 125.0(3); torsion angles [°]: N-1−C-1−C-2−C-3 −96.6(1), N-3−C-14−C-15−C-20 −102.2(1).

state structure of **1a** can be regarded as a model for an intermediate in the η^3-η^1 intramolecular rearrangement of the allyl ligands observed in solution.

The binuclear cp-type complex [η^5:η^5-fulvalene][CpZr(allyl)$_2$]$_2$ shows a comparable η^1-η^3 coordination of the allyl groups[2] according to its X-ray crystal structure.

Syntheses of 2a−2c, NMR-Spectroscopic Investigations of the Allyl Interconversion Reactions and Crystal Structure of (siam)Zr(allyl)$_3$ (2c)

In ether the dimeric compound [(siam)ZrCl$_3$]$_2$[6] was treated with (allyl)MgCl in different molar ratios to form the complexes **2a**−**2c** (Scheme 1).



The light yellow mixed complex **2a** and the yellow **2b** slowly undergo ligand exchange reactions according to eq. 1 and eq. 2:

$$\underset{\mathbf{2a}}{[(\text{siam})\text{Zr(allyl)Cl}_2]_2} + 2\ \text{THF} \xrightarrow[\text{hexane}]{\text{THF}} \underset{\mathbf{1a}}{(\text{siam})_2\text{Zr(allyl)}_2} + \text{ZrCl}_4(\text{THF})_2 \quad (1)$$

$$6\ \underset{\mathbf{2b}}{(\text{siam})\text{Zr(allyl)}_2\text{Cl}} \longrightarrow [(\text{siam})\text{ZrCl}_3]_2 + 4\ \underset{\mathbf{2c}}{(\text{siam})\text{Zr(allyl)}_3} \quad (2)$$

These reactions might be the reason that all attempts to isolate single crystals of **2a** and **2b** failed. It is of interest that the tris(allyl) complex **2c** is quite stable both in solution and in the solid state. This is in contrast to the behavior of the cp complex CpZr(allyl)$_3$[1] which decomposes in solution at −10°C.

The mixed allylchloro complex **2b** is excellently soluble in toluene and does not undergo intermolecular ligand exchange reactions even at higher temperatures. Therefore, it is possible to record the temperature-dependent NMR spectra.

At +90°C the compound is characterized by a very simple ^{1}H- and ^{13}C-NMR spectrum in [D$_8$]toluene. Both the proton signals for the trimethylsilyl group (at $\delta = -0.3$) and the signals for the allyl groups [$\delta(\text{CH}_2) = 3.85$ and $\delta(\text{CH}) = 6.28$] are equivalent, indicating rapid interconversion of the allyl groups (Figure 2a). At room temperature a broadening of the signals of the CH$_2$ is observed and at 0°C coalescence of the Me$_3$Si signals occurs. At lower temperatures the signals of both the η^1- and the η^3-bonded allyl groups can be observed (Figure 2a), indicating that the exchange of the allyl groups is frozen. The temperature-dependent ^{13}C-NMR spectra (Figure 2b) are also in agreement with these observations.

The complex (siam)Zr(allyl)$_3$ (**2c**) exhibits in [D$_8$]toluene a similar dynamic behaviour of the allyl groups. The doublet of the CH$_2$ groups at room temperature appears at $\delta = 3.07$ (12H). At −60°C two broad signals at $\delta = 3.6$ (8H) and 2.6 (4H) indicate that both the η^1 and the η^3-coordination form is frozen.

To gain a deeper insight into the geometry of **2c**, a low-temperature X-ray structure determination was carried out. Figure 3 shows that **2c** is a chiral molecule.

The identical C−N bond lengths in the siam ligand indicate full electron delocalization within the amidinate groups. The torsion angle between the NCN fragment and the phenyl ring excludes conjugation between the aromatic ring and the amidinate groups, which correspond to the C(sp^2)−C(sp^2) single bonds. The (siam)Zr fragment again forms a four-membered chelate ring. The coordination of the three allyl groups is unsymmetrical. Two of the allyl ligands are η^3-coordinated groups with typical bond lengths between Zr and C-1, C-2, and C-3, respectively, as well as between Zr and C-4, C-5, and C-6, respectively. The third allyl group exhibits an unusual ligand bonding intermediate between the η^1 and the η^3 coordination. This is indicated by the short Zr−C-9 bond length [2.465(7) Å] and the longer Zr−C-7 [2.613(7) Å] and Zr−C-8 [2.563(7) Å] distances. As expected, different bond distances within the carbon atoms of the allyl system were found [C-7−C-8

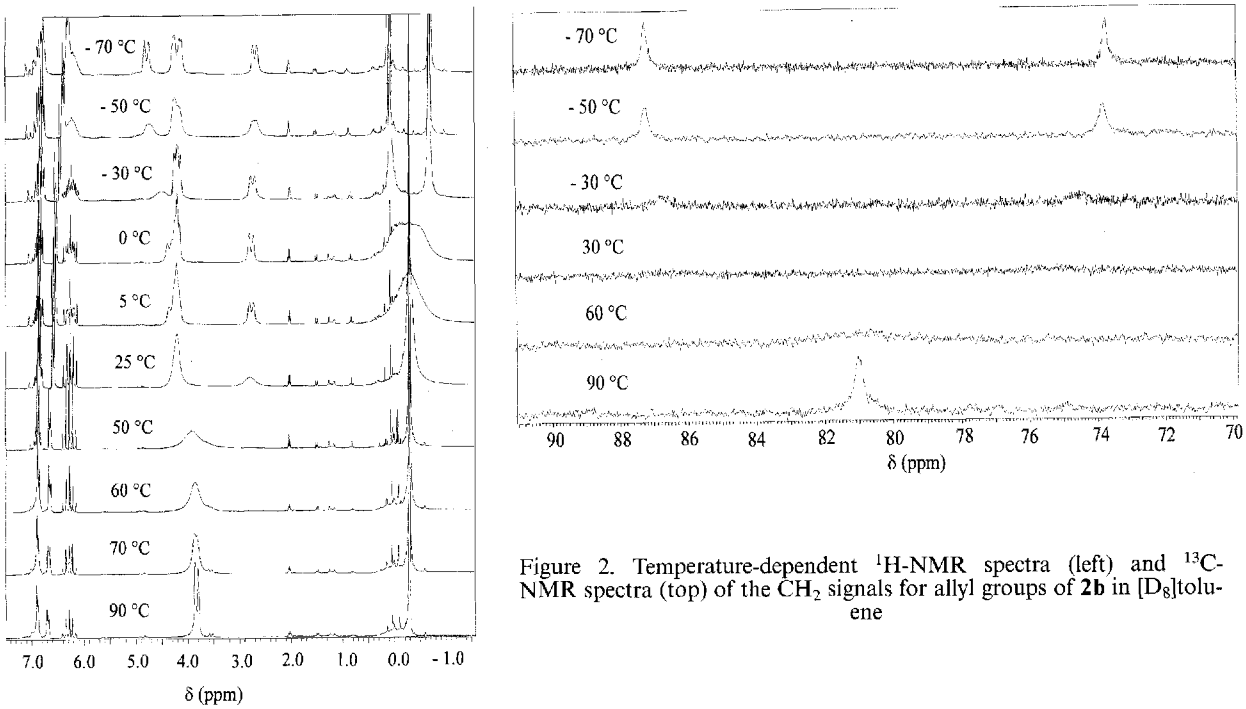
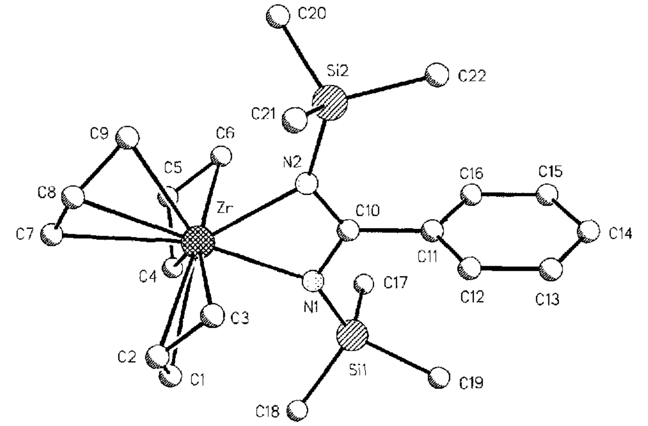


Figure 2. Temperature-dependent ^{1}H-NMR spectra (left) and ^{13}C-NMR spectra (top) of the CH_2 signals for allyl groups of **2b** in [D_8]toluene

Figure 3. Crystal structure of **2c**[a]



[a] Selected bond lengths [Å] and angles [°]: Zr–N-1 2.304(4), Zr–N-2 2.339(5), Zr–C-1 2.448(7), Zr–C-2 2.538(7), Zr–C-3 2.519(7), Zr–C-4 2.440(6), Zr–C-5 2.535(6), Zr–C-6 2.549(6), Zr–C-7 2.613(7), Zr–C-8 2.563(7), Zr–C-9 2.465(7), C-10–N-1 1.351(7), C-10–N-2 1.286(8), C-10–C-11 1.505(7), C-1–C-2 1.37(1), C-2–C-3 1.38(1), C-4–C-5 1.40(1), C-5–C-6 1.37(1), C-7–C-8 1.34(1), C-8–C-9 1.40(1); N-1–Zr–N-2 57.9(2), C-1–Zr–C-3 58.6(3), C-4–Zr–C-6 58.4(3), C-7–Zr–C-9 56.6(3), C-1–C-2–C-3 124.2(7), C-4–C-5–C-6 123.0(6), C-7–C-8–C-9 123.2(7); torsion angle [°]: N-1–C-10–C-11–C-12 –91.6(4).

1.339(11) Å, C-8–C-9 1.398(13) Å]. This type of allyl coordination might be regarded as a model of an intermediate stage along the reaction coordinate of the η^1-η^3 interconversion observed in solution.

A comparison of **2c** with Erker's $CpZr(allyl)_3$ complex[1] clearly demonstrates the difference between cp and siam. In the cp complex the 16 valence electron count of Zr is achieved by η^3-coordination of two allyl groups, whereas the third allyl ligand is η^1-bonded. In $(siam)Zr(allyl)_3$ **2c** the 4-electron donor ligand siam causes that the third allyl group is transformed into a coordination mode intermediate between that of η^3 and η^1.

To find out if weak acids are able to cleave the allyl–zirconium bonds and which consequences this substitution reaction would have for the structure of the product we checked the reaction of **2c** with phenylacetylene, piperidine, diphenylamine, and *tert*-butyl alcohol. Surprisingly, at room temperature we observed a reaction only in the case of *tert*-butyl alcohol. The other substrates were unreactive. In the case of *tert*-butyl alcohol (molar ratio 1:1) the expected mixed ligand complex $(siam)(allyl)_2Zr(OtBu)$ could not be obtained. Only the insoluble final product of alcoholysis "$(siam)Zr(OtBu)_3$" and **2c** was isolated.

Conclusions

The X-ray crystal structures of compound **1a** and **2c** indicate that siam-stabilized zirconium prefers the coordination number 7 in this complexes. At room temperature we observed in solution a rapid exchange of the allyl groups and a fast rotation of the siam ligands. Compound **1a** containing two siam ligands does not change this behavior up to −90 °C. In contrast, the molecular motions of the complexes **2b** and **2c**, which bear only one siam ligand are much slower. Because of the higher activation energies we were able to freeze the ligand movement in these complexes step by step.

On the other hand, the thermal stability of the allyl complexes is increased if cp in $cpZr(allyl)_3$ is replaced by siam (compound **2c**).

Financial support by the *Bundesministerium für Forschung und Technologie*, the *Max-Planck-Gesellschaft* and the *Fonds der Chemischen Industrie* is gratefully acknowledged.

Experimental

General: All reactions were carried out under argon by standard Schlenk techniques by using dry, air-free solvents. The following instruments were used for product characterization. – IR: Perkin-Elmer "System 2000" in Nujol mulls. – NMR: AC 200, Bruker (200 MHz and 50.3 MHz for ^1H and ^{13}C, respectively). For ^1H NMR and ^{13}C NMR, C_6D_6 and $CDCl_3$ as solvent, cyclohexane $\delta_H = 1.40$ and $\delta_C = 27.8$ as internal standard. The temperature-dependent NMR spectra were recorded in [D$_8$]toluene. – Elemental analysis: Friedrich-Schiller-Universität Jena, Institut für Organische und Makromolekulare Chemie. – X-ray diffraction data: CAD4 diffractometer using graphite-monochromatic Mo-K_α radiation. The crystals were mounted in a cold nitrogen stream. Data were corrected for Lorentz and polarization effects, but not for absorption[14]. The structures were solved by direct methods (SHELXS[15]) and refined by full-matrix least-squares techniques against F^2 (SHELXL-93[16]). For **1a** the hydrogen atoms were located by difference Fourier synthesis and refined isotropically, for **2c** hydrogen atoms were included at calculated positions with fixed thermal parameters; all nonhydrogen atoms were refined anisotropically. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for **1a**[17]: $C_{32}H_{56}N_4Si_4Zr$, M_r = 700.4 g mol^{-1}, light yellow brick-shaped crystal, size 0.41 × 0.38 × 0.38 mm, triclinic, space group $P\bar{1}$, a = 10.016(2), b = 14.133(3), c = 14.867(3) Å, α = 85.59(3), β = 75.42(3), γ = 74.80(3)°, V = 1965.4(7) Å^3, Z = 2, $\rho_{calcd.}$ = 1.184 g cm^{-3}, μ (Mo-K_α) = 4.27 cm^{-1}, F(000) = 744, 8954 reflections in $\pm h$, $+k$, $\pm l$, measured in the range 2.30° $\leq \Theta \leq$ 27.41°, 8615 independent reflections, R_{int} = 0.029, 7384 reflections with $F_o > 4\sigma(F_o)$, 594 parameters, R = 0.035, wR^2 = 0.106, $GOOF$ = 1.13, largest difference peak: 0.53 eÅ^{-3}.

Crystal Data **2c**[17]: $C_{22}H_{38}N_2Si_2Zr$, M_r = 477.9 g mol^{-1}, orange brick-shaped crystal, size 0.40 × 0.40 × 0.20 mm, orthorhombic, space group $P2_12_12_1$, a = 7.394(1), b = 18.551(3), c = 18.559(3) Å, V = 2545.7(7) Å^3, Z = 4, $\rho_{calcd.}$ = 1.247 g cm^{-3}, μ (Mo-K_α) = 5.35 cm^{-1}, F(000) = 1008, 3882 reflections in $-h$, $+k$, $-l$, measured in the range 2.30° $\leq \Theta \leq$ 27.41°, 3882 independent reflections, 3154 reflections with $F_o > 4\sigma(F_o)$, 244 parameters, Flack parameter: −0.04(9), R = 0.041, wR^2 = 0.119, $GOOF$ = 0.302, largest difference peak: 0.79 e Å^{-3}.

Zirconium tetrachloride, *n*-butyllithium, hexamethyldisilazane, and benzonitrile were purchased from Aldrich Chemical Co. Allylmagnesium chloride was prepared in ether by reaction of Rieke magnesium with allyl chloride at −78 °C. The starting compounds **1** and **2** were prepared according to literature methods[5,6]. For **2** we used alternatively the ligand exchange reaction of **1** and zirconium tetrachloride in equimolar ratio as following:

[N,N'-Bis(trimethylsilyl)benzamidinato]zirconium Trichloride (**2**): To a solution of 5.3 g (7.6 mmol) of (siam)$_2$ZrCl$_2$ in 50 ml of methylene chloride 1.8 g (7.7 mmol) of zirconium tetrachloride was added and the suspension was stirred for 10 min. When all the zirconium tetrachloride had dissolved the nearly clear solution was refluxed for 1 h. Crystallization of the product already started during refluxing and was completed at 0 °C; yield of **2** 3.7 g (53%). – ^1H NMR ($CDCl_3$): δ = 0.01 (s, 9H, SiMe$_3$), 0.11 (s, 9H, SiMe$_3$), 7.32–7.99 (m, 5H, Ph). – ^{13}C NMR ($CDCl_3$): δ = 1.4 (SiMe$_3$), 2.6 (SiMe$_3$), 127.1, 129.3, 129.9, 130.4, 133.6, 139.6, 175.1 (CN$_2$).

Allyl[N,N'-bis(trimethylsilyl)benzamidinato]zirconium Dichloride (**2a**): To a suspension of 2.0 g (4.34 mmol) of **2** in 30 ml of ether 15.5 ml (4.34 mmol) of allylmagnesium chloride (0.28 M) in ether was dropped at −50 °C during 1 h. The color of the mixture changed from white to yellow. Then the cooling bath was removed and the reaction mixture was allowed to warm to room temperature. The magnesium chloride was precipitated by dioxane addition and separated by filtration with a frit. The precipitate was washed with 50 ml of ether. The filtrate was evaporated to dryness and the residue recrystallized from a mixture of ether and hexane to afford 0.5 g (84%) of **2a** as pale yellow plates. – $C_{16}H_{28}Cl_2N_2Si_2Zr$ (466.7): calcd. C 41.18, H 6.05, N 6.00; found C 40.34, H 6.19, N 5.98. – IR: $\tilde{\nu}$ = 1500 cm^{-1}, 1533 cm^{-1}. – ^1H NMR (C_6D_6): δ = 0.09 (s, 18H, SiMe$_3$), 4.09 (br, 4H, CH$_2$=), 6.30 (quint, J = 12.8 Hz, 1H, −CH=), 6.60–7.15 (m, 5H, Ph). – ^{13}C NMR (C_6D_6): δ = 2.1 (SiMe$_3$), 91.4 (=CH$_2$), 126.8, 128.3, 129.2, 138.9, 139.1 (CH=), 177.5 (CN$_2$).

Diallyl[N,N'-bis(trimethylsilyl)benzamidinato]zirconium Chloride (**2b**): To a suspension of 1.7 g (3.69 mmol) of **2** in 20 ml of ether 26.3 ml (7.36 mmol) of allylmagnesium chloride (0.28 M) in ether was dropped at −50 °C. The color of the mixture changed from white to yellow-orange. The reaction mixture was slowly (12 h) allowed to warm to room temp. All the magnesium chloride was separated by dioxane addition and filtration of the precipitate by means of a frit. The precipitate was washed with 50 ml of ether, the filtrate was evaporated to dryness and the residue was recrystallized from 15 ml of hexane at −78 °C to yield 1.0 g (57%) of **2b** as yellow light-sensitive crystals. – $C_{19}H_{33}ClN_2Si_2Zr$ (472.3): calcd. C 48.31, H 7.04, N 5.95; found C 47.44, H 7.25, N 5.98. – IR: $\tilde{\nu}$ = 1506 cm^{-1}, 1525 cm^{-1}. – ^1H NMR (C_6D_6): δ = −0.22 (s br, 18H, SiMe$_3$), 2.93 (s br, 2H, CH$_2$=), 4.30 (s br, 6H, CH$_2$=), 6.36 (quint, J = 12.6 Hz, 2H, CH=), 6.60–6.95 (m, 5H, Ph). – ^{13}C-NMR (C_6D_6): δ = 1.7 (SiMe$_3$), 75.2 (br, CH$_2$=), 86.4 (br, CH$_2$=), 126.4, 128.3, 128.7, 139.8, 144.9 (CH=), 174.2 (CN$_2$).

Triallyl[N,N'-bis(trimethylsilyl)benzamidinato]zirconium (**2c**): At −50 °C to a suspension of 0.9 g (1.95 mmol) of **2** in 30 ml of ether 22.0 ml (6.15 mmol) of allylmagnesium chloride (0.28 M) in ether was dropped. The color of the mixture changed from white first to yellow, then to orange and finally to red. Then the cooling bath was removed and the reaction mixture was allowed to warm to room temp. MgCl$_2$ was precipitated by dioxane addition and separated by use of a frit. The precipitate was washed with 50 ml of ether. After evaporation of the solvent to dryness the residue was recrystallized from hexane to yield 0.5 g (54%) of **2c** as red-orange light-sensitive crystals. – $C_{22}H_{38}N_2Si_2Zr$ (477.9): calcd. C 55.29, H 8.01, N 5.86; found C 52.81, H 7.98, N 6.05. – IR: $\tilde{\nu}$ = 1663 cm^{-1}, 1530 cm^{-1}, 1498 cm^{-1}. – ^1H-NMR (C_6D_6): δ = −0.11 (s, 18H, SiMe$_3$), 3.13 (d, J = 12.5 Hz, 12H, CH$_2$=), 5.55 (quint, J = 12.5 Hz, 3H, −CH=), 6.70–6.97 (m, 5H, Ph). – ^{13}C-NMR ([D$_8$]toluene): δ = 3.1 (SiMe$_3$), 74.5 (=CH$_2$), 126.4, 128.1, 128.3, 141.5, 140.8 (CH=), 182.0 (CN$_2$). – The ^1H-NMR spectrum of **2c** in [D$_8$]toluene at room temp. exhibits for the allyl groups a doublet at δ = 3.07 (J = 12.8 Hz, 12H) and a quintet at 5.51 (J = 12.8 Hz, 3H). The line broadening of the first signal increases at lower temperatures more and more. At −50 °C the coalescence temperature for the signal at δ = 3.0 is reached. At −60 °C the signal begins to separate into two broad signals at δ = 3.6 (8H) and 2.6 (4H). The singlet for the SiMe$_3$ groups at δ = −0.15 does not change during cooling up to −90 °C.

Diallylbis[N,N'-bis(trimethylsilyl)benzamidinato]zirconium (**1a**): To a stirred suspension of 4.7 g (6.82 mmol) of **1** in 100 ml of ether, 7.0 ml (14.0 mmol) of allylmagnesium chloride (2.0 M) in THF was dropped at 0 °C. The color of the reaction mixture immediately turned yellow. The ice bath was removed and the precipitated magnesium chloride was separated by use of a frit. The precipitate was washed with 50 ml of ether. The filtrate was evaporated to dryness and the residue recrystallized from 70 ml of hexane at −20 °C to yield 1.7 g (35%) to **1a** as yellow-orange light-sensitive crystals. Single crystals of this complex were isolated by careful recrystallization of a pure sample of **1a** from hexane at −20°C. – $C_{22}H_{56}N_4Si_4Zr$ (700.4): calcd. C 54.87, H 8.06; found C 55.80, H 8.22. – ^1H NMR (C_6D_6): δ = 0.01 (s, 36H, $SiMe_3$), 3.71 (d, J = 11.9 Hz, 8H, CH_2=), 6.70 (quint, J = 11.9 Hz, 2H, CH=), 6.97–7.21 (m, 10H, Ph). – ^{13}C-NMR (C_6D_6): δ = 3.5 ($SiMe_3$), 86.7 (=CH_2), 127.1, 128.7, 129.4, 141.3, 143.3 (CH=), 182.0 (CN_2).

Temperature-dependent ^1H-NMR spectra were recorded in [D_8]toluene. The sharp signal of the $SiMe_3$ groups at δ = 0.01 starts broadening at −20°C, and at −27.5°C we found the coalescence temperature. At lower temperatures two singlets of the same intensity are observed. The signals of the allyl ligands do not change in the range from room temp. to −90°C.

[☆] Dedicated to Professor *R. Gleiter* on the occasion of his 60th birthday.

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[17] Further details of the crystal structure investigations are available on requests from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-405459 (**1a**) and -405460 (**2c**), the names of the authors, and the journal citation.

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