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Volatile β-Ketoiminato- and β-Diketiminato-Based Zirconium Complexes as Potential MOCVD Precursors

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An amine elimination pathway has been used to produce a number of homo- and heteroleptic zirconium complexes, starting from tetrakis(dialkylamido)zirconium complexes and β-diketimine or, alternatively, Schiff Base compounds. Reaction of 2 equiv of the bidentate β-diketimine (2*Z*,4*E*)-*N*-methyl-4-(methylimino)pent-2-en-2-amine with $Zr(NR_2)_4$ (R = Me, Et) affords the six-coordinate heteroleptic compounds bis(*N*-methyl-4-(methylimino)pent-2-en-2-amido)-bis(dialkylamido)zirconium **1** (alkyl = Me) and **2** (alkyl = Et). The dynamic behavior of these two compounds in solution has been investigated. Reaction with the isopropyl-substituted β-diketimine (2*Z*)-*N*-isopropyl-4-(isopropylimino)-pent-2-en-2-amine gives the five-coordinate mono(diketiminato)-substituted compound (*N*-isopropyl-4-(isoropylimino)-pent-2-en-2-amido)tris(dimethylamido)zirconium, **3**. With employment of the Schiff base (3*Z*)-4-(methylamino)pent-3-en-2-one, it was also possible to prepare the six-coordinate bis(4-(methylamino)pent-3-en-2-onato)bis(diethyl-amido)zirconium compound **4**. When the bidentate ligand bearing hydrogen as substituent on the imino-nitrogen atom was employed, homoleptic tetrakis(β-ketoiminato)- and tetrakis(β-diketiminato)zirconium compounds **5** and **6** can be obtained. Complexes **1** and **5** have been tested for their air stability with reference to $Zr(NMe_2)_4$. The stability order turned out to be **1** > **5** ≫ $Zr(NMe_2)_4$. The thermal properties and volatility of all the compounds are discussed in view of their potential application in metal–organic chemical vapor deposition processes (MOCVD) of zirconium nitride.

Introduction

Metal−organic chemical vapor deposition (MOCVD) is a well-established method for the growth of thin films of transition metal nitrides.[1] Several groups approached the preparation of group 4 transition metal nitrides, in particular with titanium and zirconium. TiN and ZrN are important for several applications: hard protective coatings;[2−6] diffusion barrier in integrated circuit devices;[7,8] gate materials;[9] thin-film thermistors;[10] Josephson junctions;[11] decorative optical coatings.[12]

One of the most important class of metal organic precursors employed are the four-coordinate tetrakis(dialkylamides) ($M(NR_2)_4$, M = Ti, Zr, Hf),[13] which are highly volatile and thermally stable but very sensitive to air. Using these precursors in combination with ammonia, pure Zr_3N_4 films were obtained by thermal CVD.[14] $Zr(NR_2)_4$ complexes (R = Me or Et) were used with several combinations of carrier gases, also in plasma-assisted CVD experiments (PACVD),

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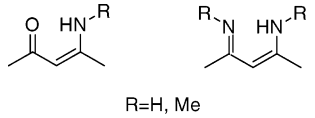
Chart 1. Examples of Ligands Employed in This Work



to obtain mainly carbonitride coatings.[15−17] This class of compounds can be viewed as isoelectronic analogues of the four-coordinated metal alcoxides used for MOCVD of zirconium oxide.[18−20]

In the case of nitrides, only minor efforts have been undertaken to tune the precursors toward improved properties. Some studies have been carried out to tailor precursors for TiN thin films applications.[21,22] In the deposition of ZrO_2 thin films, also six-[23,24] and eight-coordinate[25−29] precursors have been used, affecting coordinative saturation, which is expected to reduce water and oxygen sensitivity. Such an approach has not yet been pursued for the precursors used in the deposition of transition metal nitrides. Existing precursors for this process are by far not taking into account such properties.

In the course of ZrN deposition studies conducted in our laboratories,[30] the studied zirconium tetrakis(dialkylamides) were found to have a practically unacceptable affinity for water and oxygen both during storage and the growth process itself. This prompted us to design new precursors with higher coordination numbers, following the approach already used in the tayloring of zirconium oxide precursors.[24]

Our tuning efforts have been carried out with the ligand systems shown in Chart 1.

These β-ketoimines and β-diketimines are in their deprotonated forms analogues of the β-diketonate fragment and can be combined with dialkylamido ligands to build up compounds of appropriate coordination numbers higher than 4 by analogy with already reported bis(acetylacetonato)bis-(alcoholato)zirconium compounds.[23] The chemistry of β-ketoiminates has been developed earlier.[31,32] These ligands were applied in chemical beam epitaxy (CBE),[33,34] also in group 2[35] and late-transition metal CVD precursors,[36] and as ancillary ligands for the development of ZrO_2 CVD precursors.[26,37] The chemistry of β-diketimines was recently reviewed in detail by Lappert and co-workers.[38] β-Ketoiminates and β-diketiminates have recently been investigated for their use as ancillary ligand in group 4 transition metal complexes.[39] In some papers they were sought to replace cyclopentadienyl moieties in organometallic complexes employed in Ziegler−Natta catalysis.[40−42] They have also been applied in main-group[43−47] and late-transition metal chemistry.[48] Recent literature concerning iron,[49−53] nickel,[54] chromium,[55] and copper complexes[56−58] has been reported They can be prepared in simple ways and in high yield starting from relatively cheap materials.[59] The ligands so far employed in combination with titanium and zirconium were

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mainly all *N*-aryl-substituted compounds, probably due to their specific properties in catalytic applications.[60] Only one example of zirconium-based complex bearing alkyl substituent (for instance, methyl) on the imido nitrogen have been reported so far.[61] These ligands seemed to be of prime choice in terms of increased volatility of the compounds. In this paper we therefore present the synthesis and characterization of zirconium complexes with *N*-alkyl- and N−H-substituted β-ketoiminates and β-diketiminates. Both homoleptic and heteroleptic compounds were studied, in this latter case in combination with dialkylamido ligands. The thermal properties of some of these compounds were also examined in view of their potential application as MOCVD precursors.

Experimental Section

General Procedures. All reactions and manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk techniques or a glovebox. All solvents are dried using conventional methods and freshly distilled before use. NMR spectra were recorded on a Varian Gemini-200 spectrometer, ^{1}H at 199.98 MHz and ^{13}C at 50.29 MHz, and on a Varian Gemini-300 instrument, ^{1}H at 300.08 MHz and ^{13}C at 125.23 MHz. All NMR spectra were recorded at room temperature unless otherwise stated. Elemental analyses: Leco CHN(S)-932 instrument. Thermogravimetry: Perkin-Elmer TGA7 thermobalance, operating under an atmosphere of purified nitrogen at 30 mL/min. Mass spectra: Finnigan-MAT-8400 spectrometer. Differential scanning calorimetry: Perkin-Elmer DSC7 instrument.

All chemicals except for $ZrCl_4$ (99.9%, Aldrich Chemicals) were obtained from Fluka Chemicals Switzerland and dried and distilled before use when necessary.

$ZrCl_4(thf)_2$,[62] $Zr(NMe_2)_4$,[63] and $Zr(NEt_2)_4$[64] were obtained according to published methods. The β-ketoimines[65,66] and β-diketimines[59] were also prepared according to literature procedures.

Synthesis of Bis(*N*-methyl-4-(methylimino)pent-2-en-2-amido)bis(dimethylamido)zirconium *(1)*. $Zr(NMe_2)_4$ (0.636 g, 2.38 mmol) was dissolved in 20 mL of toluene and stirred. The *N*-methyl-4-(methylimino)pent-2-en-2-amine (0.600 g, 4.75 mmol) was dissolved in 10 mL of toluene, and this solution was added to the previous solution. The pale yellow solution was stirred for 19 h at room temperature allowing the gaseous $HNMe_2$ to escape from the reaction vessel. The toluene was removed in vacuo to a volume of 20 mL, and the resulting solution was passed through Celite. The solution was then further concentrated to about 5 mL, and pentane (5 mL) was overlayed: upon standing overnight at −30 °C the crystalline pale yellow precipitate that was formed was filtered out and dried in vacuo for 6 h. Yield of **1**: 0.684 g (67%). As an alternative purification procedure, the solvent was removed in vacuo and the solid obtained was sublimed at 125−130 °C bath temperature and 10^{-1} mbar, recovering the product in 80% yield. ^{1}H NMR (CD_2Cl_2) at −40 °C: δ 4.63 (s, $CH_3NC(CH_3)CHC(CH_3)NCH_3$, 2H), 3.24 (s, $CH_3NC(CH_3)CHC(CH_3)NCH_3$, 6H), 2.93 (s, $N(CH_3)_2$, 12H), 2.47 (s, $CH_3NC(CH_3)CHC(CH_3)NCH_3$, 6H), 1.89 (s, $CH_3NC(CH_3)CHC(CH_3)NCH_3$, 6H), 1.68 (s, $CH_3C(CH_3N)CHC(CH_3N)CH_3$, 6H). ^{13}C{^{1}H} NMR at −40 °C: δ 166.70, 162.56, 99.52, 46.19, 37.65, 36.83, 22.34, 22.14. Anal. Calcd for $C_{18}H_{38}N_6Zr$: C, 50.31; H, 8.77; N, 19.56. Found: C, 50.45; H, 8.88; N, 19.09. MS (EI+, 70 eV): *m*/*z* 428 (M^+, 17), 384 ($M^+ - NMe_2$, 100), 340 ($M^+ - 2 \times NMe_2$, 38).

Synthesis of Bis(*N*-methyl-4-(methylimino)pent-2-en-2-amido)bis(diethylamido)zirconium (2). $Zr(NEt_2)_4$ (0.914, 2.41 mmol) was dissolved in 15 mL of toluene. To this solution the *N*-methyl-4-(methylimino)pent-2-en-2-amine (0.608 g, 4.82 mmol) was added as a solid. The yellow solution was stirred at 90 °C for 25 h. The resulting deep red-brown solution was vacuum-dried, and the remaining solid was dissolved in 25 mL of pentane. This solution was passed through a layer of Celite, and the filtrate was reduced to a volume of 10 mL and cooled to −30 °C. The crystalline solid of **2** was filtered out and washed with 3 mL of cold pentane. Yield: 0.526 g, 45%. ^{1}H NMR (C_6D_6): δ 4.71 (s, $CH_3C(CH_3N)CHC(CH_3N)CH_3$, 2H), 4.01 (m, J = 6.9 Hz, $N(CH_2CH_3)_2$, 8H), 3.66 (m, J = 6.9 Hz, $N(CH_2CH_3)_2$, 8H), 3.38 (s, $CH_3C(CH_3N)CHC(CH_3N)CH_3$, 6H), 2.63 (s, $CH_3C(CH_3N)CHC(CH_3N)CH_3$, 6H), 1.76 (s, $CH_3C(CH_3N)CHC(CH_3N)CH_3$, 6H), 1.67 (s, $CH_3C(CH_3N)CHC(CH_3N)CH_3$, 6H), 1.18 (t, J = 7.0 Hz, $N(CH_2CH_3)_2$). ^{13}C{^{1}H} NMR: δ 166.42, 162.3, 100.3, 42.85, 38.02, 37.37, 21.86, 21.64, 14.02. Anal. Calcd for $C_{22}H_{46}N_6Zr$: C, 54.39; H, 9.54; N, 17.30. Found: C, 54.72; H, 9.90; N, 16.94. MS (EI+, 70 eV): *m*/*z* 412 ($M^+ - NEt_2$, 15), 340 ($M^+ - 2 \times NEt_2$, 25).

Synthesis of (*N*-Isopropyl-4-(isopropylimino)pent-2-en-2-amide)tris(dimethylamido)zirconium *(3)*. $Zr(NMe_2)_4$ (1.428 g, 5.34 mmol) was dissolved in 35 mL of toluene, and to this the liquid ligand *N*-isopropyl-4-(isopropylimino)pent-2-en-2-amine was added. The stirred solution was warmed to 90 °C for 22 h with the reaction vessel connected to an oil bubbler. The solvent was evaporated to leave behind an oily residue that becomes a waxy solid after drying under vacuum for 5 h. The ^{1}H NMR confirmed the quantitative conversion to the desired product. An analytically pure sample was obtained by sublimation at 5×10^{-4} mbar, T = 130 °C, and coldfinger at −20 °C. ^{1}H NMR (C_6D_6): δ 4.58 (s, $CH_3C(^iPrN)CHC(^iPrN)CH_3$, 1H), 3.62 (septet, J = 6.5 Hz, $CH_3C(CH(CH_3)_2N)CHC(CH(CH_3)_2N)CH_3$, 2H), 3.08 (s, $N(CH_3)_2$, 18H), 1.79 (s, $CH_3C(^iPrN)CHC(^iPrN)CH_3$, 6H), 1.13 (d, J = 6.4 Hz $CH_3C(CH(CH_3)_2N)CHC(CH(CH_3)_2N)CH_3$, 12H). ^{13}C{^{1}H} NMR: δ 160.05, 92.53, 51.50, 44.56, 24.01, 21.57. Anal. Calcd for $C_{17}H_{39}N_5Zr$: C, 50.45; H, 9.71; N, 17.30. Found: C, 50.22; H, 10.01; N, 16.96. MS (EI+, 70 eV): *m*/*z* 359 ($M^+ - NMe_2$, 17), 315 ($M^+ - 2 \times NMe_2$, 100), 271 ($M^+ - 3 \times$ NM e$_2$, 40), 228 ($M^+ - 3 \times NMe_2 - {}^iPr$, 16).

Synthesis of Bis(4-(methylamino)pent-3-en-2-onato)bis(diethylamido)zirconium (4). $Zr(NEt_2)_4$ (0.684 g, 1.80 mmol) was dissolved in 20 mL of toluene. To this solution the ligand 4-(methylamino)pent-3-en-2-one (0.408 g, 3.60 mmol) was added as a solid, and the so obtained yellow solution was stirred for 6 h at room temperature. The solvent was removed under vacuum to obtain an oily residue; this was dissolved in 20 mL of pentane and filtered through Celite. The filtrate was reduced to a volume of about 10 mL and was kept overnight at −30 °C; the yellow crystalline product was filtered out and dried under vacuum for 3 h (weight 0.467 g, yield 57%). ^{1}H NMR (C_6D_6): δ 5.00 (s, $CH_3C(CH_3N)CHC(CO)CH_3$, 2H), 3.58 (broad, $N(CH_2CH_3)_2$, 8H), 2.86 (s, $CH_3C(CH_3N)CHC(CO)CH_3$, 6H), 1.92 (s, $CH_3C(CH_3N)CHC(CO)CH_3$, 6H), 1.42 (s, $CH_3C(CH_3N)CHC(CO)CH_3$, 6H), 1.31 (t, J = 6.7 Hz), $CH_3C(CH_3N)CHC(CO)CH_3$, 12H). ^{13}C{^{1}H} NMR:

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Table 1. Crystallographic Data for **1**, **2**, **4**, and **5**

	1	**2**	**4**	**5**
formula	$C_{18}H_{38}N_6Zr$	$C_{22}H_{46}N_6Zr$	$C_{20}H_{40}N_4O_2Zr$	$C_{20}H_{36}N_8Zr$
color	colorless	colorless	pale-yellow	light-yellow
cryst dimens (mm)	0.46 × 0.36 × 0.24	0.27 × 0.23 × 0.16	0.33 × 0.29 × 0.19	0.22 × 0.20 × 0.07
cryst system	monoclinic	monoclinic	monoclinic	monoclinic
space group (No.)	$P2_1/n$ (14)	$P2_1/n$ (14)	$C2/c$ (15)	$P2_1/n$ (14)
a (Å)	9.9555(6)	9.3361(5)	9.5357(6)	20.8142(17)
b (Å)	13.3024(8)	14.3615(7)	15.7375(9)	8.2760(5)
c (Å)	16.7272(11)	19.6856(13)	16.7795(11)	29.569(2)
α, β, γ (deg)	90.0, 100.539(7), 90.0	90, 99.084(7), 90	90, 91.661(7), 90	90, 108.790(8), 90
V (Å^3)	2177.8(2)	2606.3(3)	2517.0(3)	4822.1(6)
Z	4	4	4	8
fw	429.76	485.87	459.78	479.79
d(calcd) (g cm^{-3})	1.311	1.238	1.213	1.322
abs coeff (mm^{-1})	0.518	0.440	0.456	0.478
R1, wR2 (%) all data	3.22, 7.43	7.47, 19.78	4.26, 6.82	17.88, 8.43
goodness-of-fit	1.098	1.142	1.008	0.818

[a] $R1 = (F_o - F_c)/F_o$, $I > 2\sigma(I)$; $wR2 = \{w(F_o^2 - F_c^2)^2/w(F_o^2)^2\}^{1/2}$.

δ 170.65, 169.85, 103.53, 44.61, 37.41, 24.64, 21.12, 15.44. Anal. Calcd for $C_{20}H_{36}O_2N_4Zr$: C, 52.71; H, 7.96; N, 12.29. Found: C, 52.64; H, 7.91; N, 11.92. MS (EI+, 70 eV): m/z 429 ($M^+ -$ Et, 65), 329 ($M^+ -$ Et $-$ MeC(MeN)CHC(O)Me), 25).

Synthesis of Tetrakis(4-iminopent-2-en-2-amido)zirconium (5). Method a. The 4-iminopent-2-en-2-amine ligand (0.243 g, 2.55 mmol) was dissolved in 5 mL of toluene; $Zr(NMe_2)_4$ (0.163 g, 0.612 mmol) was dissolved in 20 mL of toluene and was added slowly to the above solution. The mixture was stirred at room temperature for 4 h while the gaseous products were allowed to escape from the reaction flask. The solvent was subsequently removed in vacuo leaving behind an oily residue that was treated with 5 mL of pentane; upon drying a bright yellow fluffy solid was left behind. The solid was redissolved in 10 mL of pentane and passed through Celite. The yellow solution was concentrated to a volume of about 5 mL and kept at -25 °C overnight. The yellow crystalline precipitate was collected and dried in vacuo. Yield: 0.139 g (47%). ^{1}H NMR (C_6D_6): δ 6.79 (s, $CH_3C(NH)CHC(NH)CH_3$, 8H), 4.60 (s, $CH_3C(NH)CHC(NH)CH_3$, 4H), 1.80 (s, $CH_3C(NH)CHC(NH)CH_3$, 24H). ^{13}C{^{1}H} NMR: δ 163.78, 92.52, 27.73. Anal. Calcd for $C_{20}H_{36}N_8Zr$: C, 50.07; H, 7.56; N, 23.36. Found: C, 50.01; H, 7.82; N, 22.99. MS (EI+, 70 eV): m/z 478 (M^+, 20), 381 ($M^+ -$ MeC(NH)CHC(NH)Me, 100), 284 ($M^+ - 2 \times$ MeC(NH)CHC(NH)Me, 28).

Method b. The ligand 4-iminopent-2-en-2-amine (0.858 g, 8.76 mmol) was dissolved in 10 mL of diethyl ether, and to this stirred solution was added 5.4 mL of 1.6 M butyllithium in Et_2O (8.64 mmol). The solution was stirred for 1 h, and the $ZrCl_4(thf)_2$ (0.819 g, 2.19 mmol) was added as a solid. The yellow solution was allowed to stir for 4 h. The solvent was removed in vacuo and the solid thus obtained extracted with 3 × 10 mL of pentane, filtered, and reduced to a volume of about 10 mL. After the sample was standing in the fridge for 1 night, bright yellow crystals were recovered. Yield: 0.694 g (66%). The compound was identified by NMR spectroscopy.

Synthesis of Tetrakis(4-aminopent-3-en-2-onato)zirconium (6). The 4-aminopent-3-en-2-one ligand (0.391 g, 3.94 mmol) was dissolved in 5 mL of toluene, and to this solution was added slowly a solution of $Zr(NEt_2)_4$ (0.374 g, 0.984 mmol) dissolved in 10 mL of toluene. The pale yellow solution was stirred for 7 h and was then reduced to about 5 mL. After overnight standing at -25 °C, the precipitate was filtered out and the white solid washed with 5 mL of pentane and dried in vacuo for 4 h. Yield: 0.450 g (94%). Anal. Calcd for $C_{20}H_{32}O_4N_4Zr$: C, 49.66; H, 6.67; N, 11.58. Found: C, 49.58; H, 6.73; N, 11.45. ^{1}H NMR (C_6D_6): δ 7.78 (s, $CH_3C(NH)CHC(O)CH_3$, 4H), 4.91 (s, $CH_3C(NH)CHC(O)CH_3$, 4H), 2.06 (s, $CH_3C(NH)CHC(O)CH_3$, 12H), 1.53 (s, $CH_3C(NH)CHC(O)CH_3$, 12H). ^{13}C{^{1}H} NMR: δ 178.16, 168.09, 97.49, 26.93, 26.72. MS (EI+, 70 eV): m/z 384 ($M^+ -$ MeC(NH)CHC(O)Me, 100), 98 ((MeC(NH)CHC(O)Me)$^+$, 55).

X-ray Crystal Structure Analyses on 1, 2, 4, and 5. Crystallographic data are summarized in Table 1 The X-ray diffraction data were collected at 183(1) K for compounds **2**, **4**, and **5** and at 153(1) K for **1** using an imaging plate detector system (Stoe IPDS) with graphite-monochromated Mo Kα radiation.

The intensities were integrated after using a dynamic peak profile analysis, and an estimated mosaic spread (EMS) check was performed to prevent overlapping intensities.

In general the structures were solved with an incomplete data set while the measurement was still performed, just to confirm the proposed chemical formula or otherwise to find potential additional solvent molecules that cocrystallized with the compound under investigation. The corrected formula was then used for the final numerical absorption correction. All these procedures were calculated by using the Stoe IPDS software, Version No. 2.92 (1999).

The Patterson method was used to solve the crystal structures by applying the software options of the program SHELXS-97. All structure refinements were performed with the program SHELXL-97. Further programs used: PLATON, PLUTON (Spek, 1990, 1997).

Results and Discussion

Synthesis of Bis(*N*-methyl-β-diketiminato)bis(dialkylamido)zirconium Complexes. As mentioned above, some five- and six-coordinated complexes with β-diketiminato and dialkylamido ligands in a 2:2 ratio have been already described recently by Collins and co-workers[40] and by Smith and co-workers.[41,42] Amide substitution is a suitable synthetic route to introduce weakly acidic ligands into the coordination sphere of homoleptic compound such as $M(NR_2)_4$.[63,67] Reaction of 2 equiv of *N*-methyl-4-(methylimino)pent-2-en-2-amine with $Zr(NMe_2)_4$ (Scheme 1) proceeds smoothly at room temperature with elimination of $HNMe_2$ and provides the desired compound **1** in good yields. Reaction with $Zr(NEt_2)_4$ requires higher temperatures (90 °C), which results

(67) Bowen, D. E.; Jordan, R. F.; Rogers, R. D. *Organometallics* **1995**, *14*, 3630.

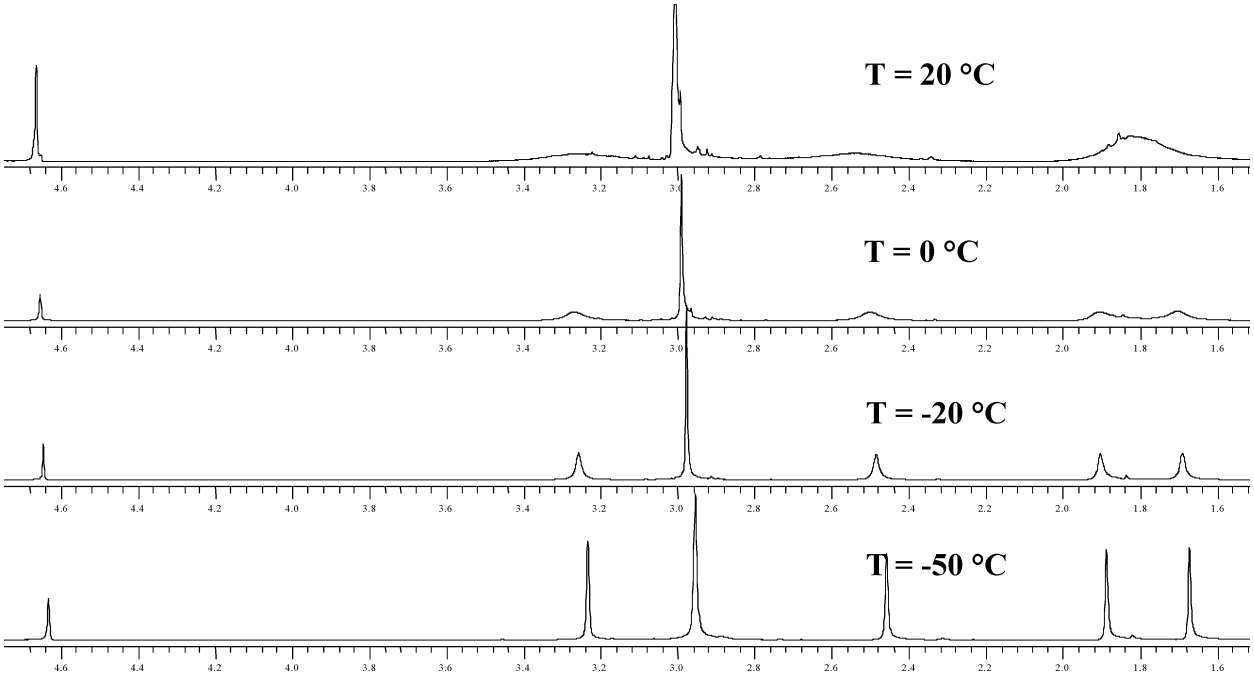
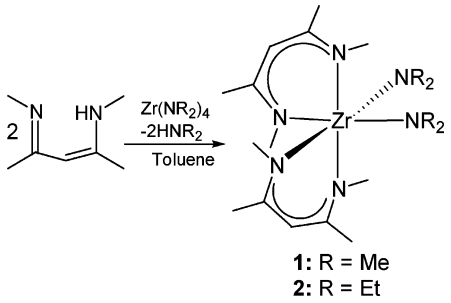


Figure 1. Variable-temperature NMR for compound **1**.

Scheme 1. Synthesis of Six-Coordinate Compounds **1** and **2**



in lower yields, presumably due to partial thermal degradation. Attempts to obtain compounds **2** under milder conditions (for instance 70 °C) and longer reaction time (48 h) were unsuccessful. Under these conditions zirconium tetrakis(dialkyl)amides bearing alkyl substituents other than CH_3, are reluctant to undergo amine elimination. This has already been reported by Jordan and co-workers[64,68] and is likely due to the higher steric congestion around the metal center.

Despite their similarities, compounds **1** and **2** display different dynamic behavior in solution. The ^{1}H NMR spectra of compound **1** between −40 and 20 °C are shown in Figure 1. At 20 °C it is possible to detect the singlet of the methyne ring proton at 4.66 ppm, the singlet of the methylamido group at 3.00 ppm, and only very broadened signals for the other resonances. At 0 °C two resonances for the methyl of the imido group and two resonances for the methyl group of the ring start to appear as broad signals. As shown in Figure 1, these resonances become sharp singlets at −40 °C, centered at 3.33 and 2.46 ppm and at 1.89 and 1.67 ppm for the imido and the ring methyls, respectively. No splitting of the signals of the dimethylamido group is observed as a function of temperature. This is typically seen in the presence of an enantiotopic center, in which two diastereotopic sites are rapidly exchanging at high temperature, but can be distinguished at lower temperature. This phenomenon has been observed recently for six-coordinate zirconium compounds containing *N*-aryl-substituted β-diketiminato ligands and has been interpreted as a process evolving along a Bailar-twist mechanism.[40,41,69] The ^{13}C NMR spectra also reveal this kind of dynamic feature. For example, in the region around 160 ppm, the imido carbon resonances were expected to appear, but this chemical shift region was completely free of signals, whereas at lower temperature of −40 °C two sharp singlets at 166.7 and 162.6 ppm evolved.

On the other hand, the spectrum of compound **2** (Figure 2) displays at room temperature two sets of multiplets for the two chemically inequivalent methylene signals (4.01 and 3.66 ppm) and two signals for the methyl-imido protons (3.38 and 2.63 ppm) and for the ring methyls (1.77 and 1.67 ppm). No exchange has been observed for the methyl protons of the ethyl groups, which appear as a unique triplet centered at 1.18 ppm. In this case, the higher steric demand of the ethyl groups further hinders the equilibration of the two enantiomers. By an increase of the temperature, coalescence in a single broad peak of the two ring methyls resonances can be observed at 70 °C. A full line-shape analysis of the exchanging signals of compounds **1** and **2** has been performed to determine the rate constant for the site exchange process. By means of an Eyring plot the values of the activation parameters were determined. The values of $\Delta H^{\ddagger}$ for compounds **1** and **2** are 10.9 ± 0.6 and 19.5 ± 0.5 kcal mol^{-1}, respectively. For compound **2** the higher activation barrier could be attributed to the higher steric demand of the ethyl groups, although in this case a mechanism being more dissociative in character or even fully dissociative cannot be ruled out. These values are in the same range of

(68) Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4045.

(69) Bailar, J. C. *J. Inorg. Nucl. Chem.* **1958**, *8*, 165.

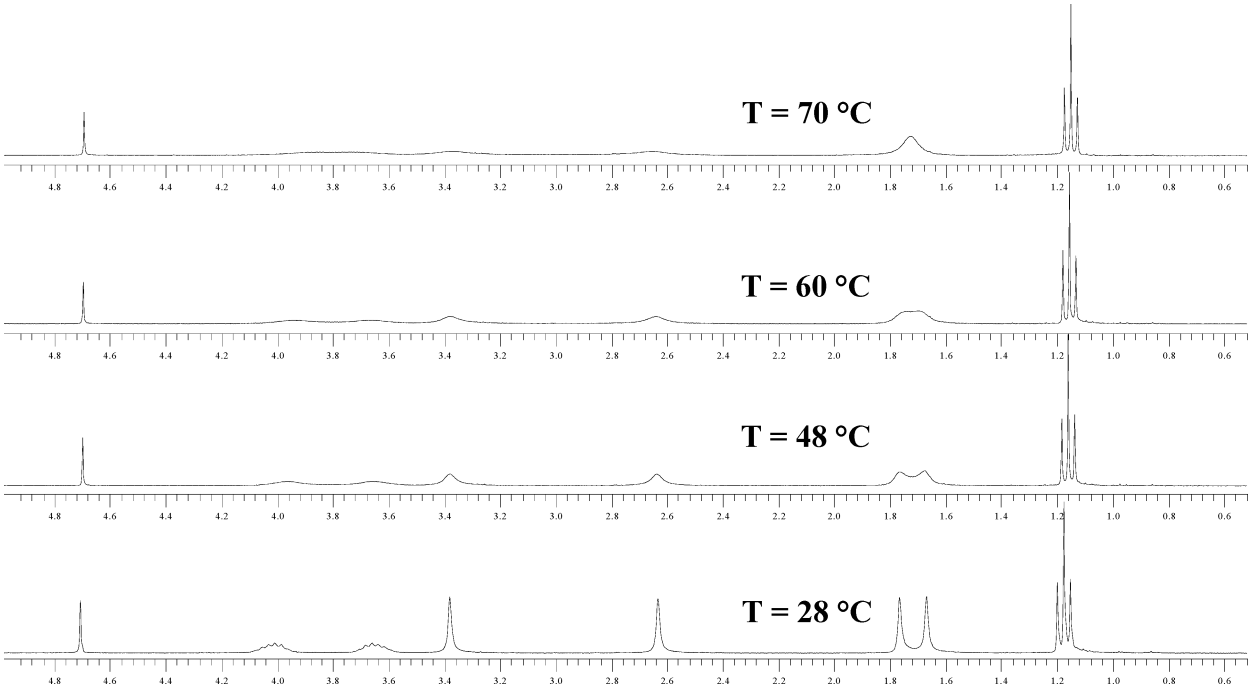


Figure 2. Variable-temperature NMR for compound **2**.

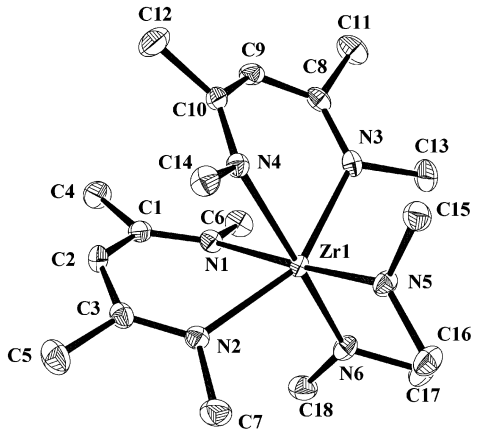


Figure 3. Structure of compound **1.** Displacement ellipsoids are shown with the 50% probability level. H atoms are omitted for clarity.

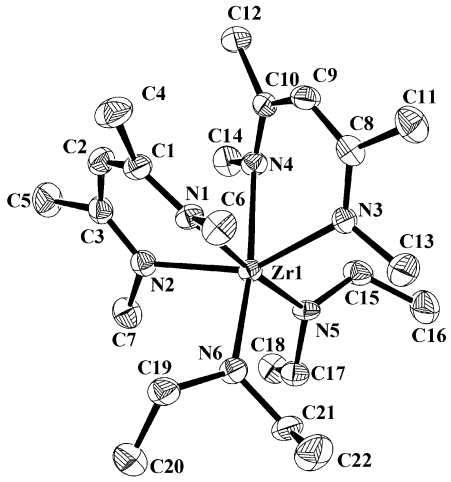


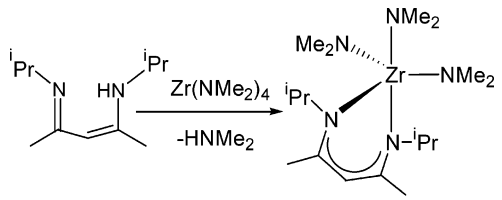
Figure 4. Structure of compound **2.** Displacement ellipsoids are shown with the 50% probability level. H atoms are omitted for clarity.

those obtained by Collins and co-workers and by Smith and co-workers.[40,41] The $\Delta S^{\ddagger}$ values are -10 ± 2 and 8 ± 1 cal $mol^{-1}K^{-1}$ for compounds **1** and **2,** respectively: the first negative value is in agreement with a transition state of higher symmetry that is assumed in the Bailar twist mechanism. The positive value obtained for compound **2** could be explained by an increased steric hindrance affecting the transition state by a quite strong bond loosening or even full dissociation of one of the Zr−N bonds. The structures of both compounds **1** and **2** have been determined by single-crystal X-ray diffraction: the two ORTEP drawings are displayed in Figures 3 and 4, and selected bond lengths and angles, in Table 2. The dialkylamido ligands are cis to each other and both compounds are arranged in a distorted octahedral geometry. The C−N−C atoms of the dialkylamido groups and the Zr atom are in the same plane. Due to the trans influence of the dialkylamido groups, the Zr−N bonds of the β-diketiminato ligand trans to these groups are longer: for example Zr−N(4) and Zr−N(1) are 2.3071(13) and 2.3119(13) Å, respectively, compared to Zr−N(2) and Zr−N(3), which are 2.2284(13) and 2.2295(14) Å, respectively, of compound **1**. For compound **2** one finds Zr−N(1) = 2.309(3) Å and Zr−N(4) = 2.306(3) Å, in comparison

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compounds **1** and **2**

	1	**2**
Zr1−N6	2.0966(14)	2.109(3)
Zr1−N5	2.1078(13)	2.124(3)
Zr1−N3	2.2295(14)	2.236(3)
Zr1−N2	2.2284(13)	2.225(3)
Zr1−N4	2.3071(13)	2.306(3)
Zr1−N1	2.3119(13)	2.309(3)
N6−Zr1−N5	93.97(5)	94.77(11)
N2−Zr1−N1	77.55(5)	77.68(10)
N3−Zr1−N4	77.90(5)	77.39(10)
N3−Zr1−N2	153.82(5)	149.81(10)
N5−Zr1−N1	175.20(5)	175.92(10)
N2−Zr1−N1	77.55(5)	77.68(10)

Scheme 2. Synthesis of a Five-Coordinate Compound



3

with Zr−N(2) = 2.225(3) Å and Zr−N(3) = 2.236(3) Å. The zirconium atom lies in both cases slightly above the plane formed by the β-diketiminato ligands (on the average 0.8 Å for both **1** and **2**).

Reactions with (2*Z*)-*N*-Isopropyl-4-(isopropylimino)-pent-2-en-2-amine. Attempts to obtain six-coordinate compounds containing two *N*-isopropyl-substituted β-diketiminato ligands and two dialkylamido groups were unsuccessful. The reaction of 2 equiv of (2*Z*)-*N*-isopropyl-4-(isopropylimino)pent-2-en-2-amine with 1 equiv of $Zr(NMe_2)_4$ gave, after a reaction time of 24 h at 90 °C, a clean mixture of 1 equiv of the unreacted ligand, plus a product that is consistent with a 1:3 stoichiometric ratio between the bidentate ligand and the dimethylamido ligand (Scheme 2). Therefore this compound was then prepared by mixing 1 equiv of $Zr(NMe_2)_4$ plus 1 equiv of (2*Z*)-*N*-isopropyl-4-(isopropylimino)pent-2-en-2-amine, affording the five-coordinate compound **3** in a quantitative yield. Reaction of the same β-diketimine ligand with $Zr(NEt_2)_4$ in a 1:1 stoichiometric ratio gave no reaction products even after repeated stirring at 110 °C for 48 h.

The ^{1}H NMR of **3** shows a single sharp resonance at 3.08 ppm for the three chemically equivalent dialkylamido groups: on cooling to −80 °C in CD_2Cl_2 the NMR spectrum shows no splitting in any of the resonances. Due to fluxional processes in solution, the molecule appears to be of a higher symmetry on the NMR time scale. It was not possible to grow single crystals suitable for X-ray analysis of this compound.

Reaction of 4-(Methylamino)pent-3-en-2-one. 4-(Methylamino)pent-3-en-2-one is an intermediate in the synthesis of the previously prepared β-diketimine derivatives. We thought it would have been interesting to prepare complexes with a mixed coordination sphere around the zirconium metal center, not only bearing nitrogen donor atoms. In view of an application as a zirconium nitride CVD precursor, however, these ligands appear not to be the best choice. However, the presence of oxygen atoms directly bound to zirconium could be exploited to produce Zr(O, N) layers. Furthermore it was planned to investigate how the type of coordinative environment could influence the thermal stability and the volatility of the precursor compound. As a first starting point we aimed at the generation of six-coordinate compounds isostructural with complex **1** and **2**. Reaction of 2 equiv of 4-(methylamino)pent-3-en-2-one with $Zr(NEt_2)_4$ at room temperature (Scheme 3) produces the desired species in 57% yield after crystallization.

The complex bears two ethylamido and two β-ketoiminato moieties (**4**). The same reaction with $Zr(NMe_2)_4$ gave a

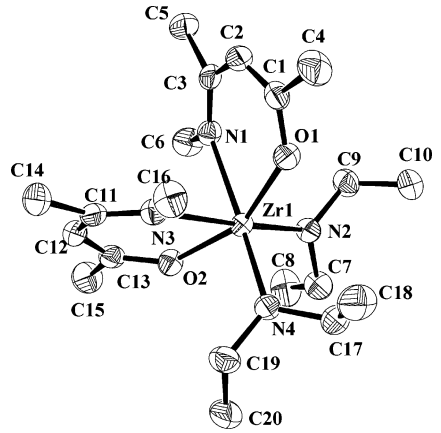
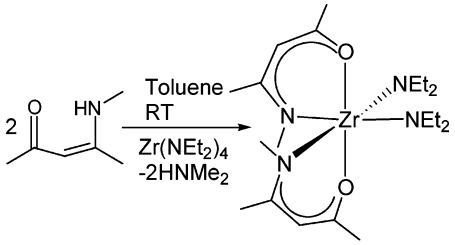


Figure 5. Structure of compound **4.** Displacement ellipsoids are shown with the 50% probability level. H atoms are omitted for clarity.

Scheme 3. Synthesis of a Six-Coordinate β-Ketoiminato-Substituted Compound



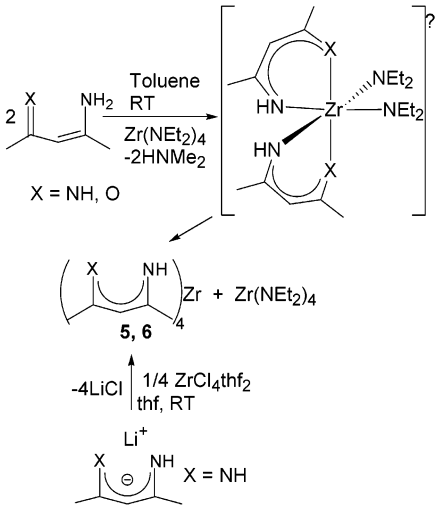
4

complex mixture, which could not be fully characterized. On the basis of the ^{1}H NMR spectra the desired product seemed to be present, but it was not possible to isolate it from the reaction mixture. This is explained on the basis of the assumption that amine elimination proceeds well when slow exchange allows to control the stoichiometry. β-Diketimines are less acidic and more sterically encumbered than the corresponding β-ketoimines; therefore, the reactions proceeded smoothly. In the case of the reaction with $Zr(NEt_2)_4$, the presence of an ethyl group slows down the substitution, thereby allowing the desired stoichiometry to be obtained. The reason for the unsuccessful reaction of the β-ketoimine with $Zr(NMe_2)_4$ may be an intrinsic thermal instability of the β-ketoiminato complexes. Compound **4**, if allowed to stand for 72 h at room temperature, starts to decompose even under nitrogen, as indicated by a change in color from yellow to deep red. In contrast, it can be stored for an indefinite time at −20 °C and, if care is taken, it is possible to obtain a satisfactory elemental analysis and also to grow good quality single crystals for an X-ray diffraction study. The proton NMR reveals the presence of only one of the possible isomers for this compound; these data only did not allow us to establish the exact structure of **4**. This was achieved by the single-crystal X-ray diffraction study (see Figure 5 and Table 3 for relevant distances and angles). The coordination geometry is a significantly distorted octahedron. The two β-ketoiminato ligands are arranged in a way such that the two oxygens are trans to each other and the two nitrogen atoms are located cis to each other. This finding is in agreement with the observation that as the steric demand of the imido nitrogen substituent increase, this kind of

Table 3. Selected Distances (Å) and Angles (deg) for Compound **4**

	Bond Lengths (Å)		
Zr1−O1	2.0658(11)	C1−C2	1.357(3)
Zr1−N2	2.0698(13)	C2−C3	1.440(2)
Zr1−N1	2.3896(13)		
	Bond Angles (deg)		
O1−Zr1−N2	95.90(5)	N2−Zr1−N1	88.71(5)
O1−Zr1−N1	77.52(5)		

Scheme 4. Synthesis of Homoleptic Eight-Coordinate Compounds



arrangement becomes favored for the bidentate β-ketoiminato moiety.[41] Also in this case the metal atom lies slightly above the plane formed by the bidentate ligand, with values of dihedral angles being for example Zr−O1−C1−C2 = −20.7(3)° and Zr−N1−C3−C2 = 7.0(2)°.

Reactions with 4-Iminopent-2-en-2-amine and 4-Aminopenten-2-one. We have also investigated the reactivity of the less sterically demanding *N*-hydrogen-substituted β-diketiminato ligands with respect to an amido exchange reaction of the $Zr(NR_2)_4$ complexes; however, in this case a completely different reactivity was found (Scheme 4). As one might expect the reaction of 2 equiv of the above ligand proceeds faster than in the case of the *N*-methyl-substituted compound. A sudden change in color is observed (from yellow to deep red), and the NMR analysis of the crude reaction product revealed the presence of a mixture of $Zr(NR_2)_4$ (R = Me, Et), plus signals typical of β-diketiminate ligands. This was attributed to the formation of an homoleptic, eight-coordinate compound tetrakis(β-diketiminato)-zirconium (see Scheme 4). This molecule (**5**) has been prepared by the reaction of 4 equiv of the ligand with $Zr(NMe_2)_4$, recovering the desired product in 47% yield. The same behavior was observed also for the parent β-aminoketone (Scheme 4). Reaction between 4 equiv of 4-amino-3-penten-2-one affords the eight-coordinate molecule **6** as a white solid. The reason the heteroleptic six-coordinate compound cannot be isolated is presumably that as soon as it forms, it undergoes a ligand disproportionation in solution, to rearrange and give the thermodynamically more stable eight-coordinate compound. Compound **5** can also be synthesized in higher yield by salt metathesis in the reaction of 4 equiv of the lithium salt of 2-amino-4-imino-2-pentene

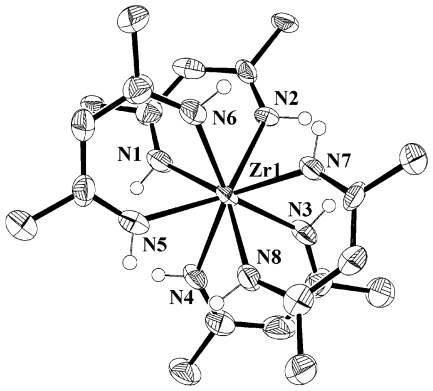


Figure 6. Structure of compound **5.** Displacement ellipsoids are shown with the 50% probability level. H atoms are omitted for clarity. Only N atoms are labeled for clarity.

Table 4. Selected Bond (Å) Lengths and Angles (deg) for Compound **5**

	Bond Lengths (Å)		
Zr1−N1	2.276(5)	Zr1−N2	2.301(4)
Zr1−N8	2.277(5)	Zr1−N7	2.304(5)
Zr1−N6	2.281(5)	Zr1−N5	2.318(5)
Zr1−N3	2.285(5)	Zr1−N4	2.332(5)
	Bond Angles (deg)		
N6−Zr1−N5	72.22(19)	N3−Zr1−N7	76.43(18)
N1−Zr1−N2	72.34(18)	N1−Zr1−N5	76.21(18)
N8−Zr1−N7	72.17(17)	N6−Zr1−N2	75.75(18)
N3−Zr1−N4	71.84(18)	N1−Zr1−N3	110.05(19)
N8−Zr1−N4	75.12(18)	N2−Zr1−N4	121.78(18)

(generated in situ with BuLi) and 1 equiv of $ZrCl_4(thf)_2$ in tetrahydrofuran.

Compound **5** has been obtained in crystals suitable for X-ray diffraction. It turns out to be isostructural with $(acac)_4Zr$ (acac = acetyacetonato), which has been studied by X-ray diffraction earlier.[70,71] Another related molecule is the eight-coordinate sandwichlike zirconium tetraazamacrocyclic compound prepared by Jordan and co-workers[72] for which no single-crystal structural analysis was reported. The ORTEP drawing of compound **5** is presented in Figure 6 along with selected bond lengths and angles given in Table 4. The coordination geometry is square antiprismatic, with each of the Zr−N−C−C−C−N rings displaying two different sets of Zr−N distances: a short one falling into the range between 2.276 and 2.285 Å and a longer one spanning the range of 2.301 and 2.331 Å. Once again the zirconium atom is slightly displaced from the plane formed by the N−C−C−C−N ring.

Air Stability. All compounds synthesized are not indefinitely air-stable. The reaction of a solid, air-sensitive compound with moisture or oxygen upon exposure to air depends, besides on chemical factors, on several other factors such as the particle size, relative humidity, temperature, and turnover of the air, just to cite a few of them. These reactions are normally carried out in a less defined manner, and many of the important parameters are not exactly known. In our

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case experiments were performed to estimate qualitatively whether an increased coordination sphere implies decreased moisture sensitivity. The six-coordinate compound **1** and the eight-coordinate compound **5** were considered for this purpose. Equimolar amounts of **1**, **5,** and the four-coordinate $Zr(NMe_2)_4$ as a reference compound were placed in a vial and exposed to the air in a fume hood for 5 min. During exposure, it was possible to see that the four-coordinate compound visually underwent a reaction with moisture: the color changed quickly from pale yellow/white to bright white. Compound **1** did not display any color change, whereas the eight-coordinate **5** started to change from bright yellow to pale yellow. The vials were subsequently closed, transferred into a nitrogen-filled glovebox, and immediately dried in vacuo, to remove residues of moisture adsorbed on the surface of the powders. All samples where then dissolved in 20 mL of pentane, and the insoluble part was filtered off. After solvent removal from the filtrates, the weight losses were about 11% in the case of compound **1**, 24% in the case of $Zr(NMe_2)_4$, and 13% in the case of **5**. We did not fully characterize the insoluble portions, but the reaction that is more likely to occur when complexes **1** and $Zr(NMe_2)_4$ react with water is the replacement of the NMe_2 groups with an OH with elimination of $HNMe_2$ (which could explain the strong amine smell produced by these compounds when they are exposed to the air). In the case of compound **1**, the insoluble residue left behind after air exposure was analyzed by NMR; the spectrum was that of compound **1**, plus some weak resonances presumably due to partial hydrolysis products. This insoluble portion was, therefore, mainly due to the partial solubility of complex **1** in pentane. The filtrate, after solvent evaporation, revealed the unaffected spectrum of compound **1.** In the case of **5** and of $Zr(NMe_2)_4$, the solid residue remaining on the filter was insoluble in most common organic solvents, and the solubilized portion revealed still the signals of **5** and $Zr(NMe_2)_4$ plus some impurities probably due to hydrolysis.

The order of stability according to the described experiments is thus **1** > **5** ≫ $Zr(NMe_2)_4$; i.e., the six-coordinate compound is the most stable species closely followed by **5**. This could be interpreted in term of a better shielding of the metal center in the case of the compound with higher coordination numbers. The somewhat lower stability of **5** with respect to **1** may be due to the lower protecting efficiency of the polar NH functionality than that of the NCH_3 moiety. Furthermore the higher coordination numbers affect somewhat longer bonds to the metal centers, which counteracts and may therefore overcompensate the shielding advantage of the ligands in the eight-coordinate compound.

Volatility and Thermal Properties. Both compounds **1** and **2** can be sublimed at a temperature of 125−130 °C (oil bath temperature) at 0.1 mbar, which makes them interesting candidates for the use as CVD precursors. They are both less volatile than the corresponding isostructural bis(acetylacetonato)−bis(alcoholato) compounds.[24] The five-coordinate compound **3** is less volatile than the six-coordinate compounds **1** and **2**. It was possible to sublime it at 135 °C at a pressure of about 10^{-4} mbar (coldfinger temperature of −10 °C). A freshly crystallized batch of **4** was attempted to sublime, but once a temperature of about 100 °C was reached an evident color change occurred apparently due to thermal decomposition. The eight-coordinate compound **5** results to be less volatile than the six-coordinate **1** and **2**. **5** sublimes at 140−145 °C and 0.1 mbar with a reasonable evaporation rate.

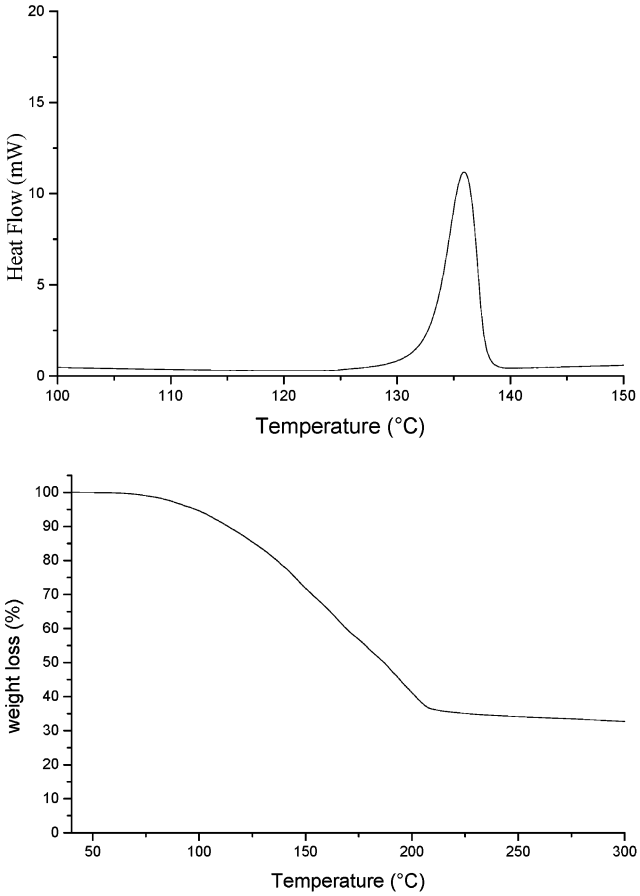

Figure 7. DSC and TG traces for compound **2**.

The thermal behavior of compounds **1**−**3**, **5**, and **6** has been also investigated by DSC and TG. Compound **4** has not been taken into consideration due to its thermal instability. The DSC and TG traces of **1** and **2** are quite similar, and therefore only those of compound **2** are displayed in Figure 7. The DSC shows a single sharp endothermal peak at about 137 °C corresponding to the melting point of the compound; after melting has occurred the compound undergoes partial decomposition with a slight change in color to brown.

The thermogravimetric curve shows that already around 100 °C the weight loss becomes relevant and the curve reaches a plateau when the percent amount of remaining solid is about 35%. Compound **3** is also thermally much more robust than the above-discussed six-coordinate compounds but evidently less volatile. The TG trace of compound **3** (not shown) reveals a slow weight loss as a function of temperature between 50 and 350 °C with a residue of about 40% of the initial weight when the plateau is reached. This example demonstrates that there is no simple correlation between the coordination number and the volatility, other

factors being involved as the molecular weight (i.e. higher electronic polarizability), dipole moment, and packing effects in the solid state. From DSC data for compound **5**, it is possible to observe a sharp, endothermic melting peak at around 190 °C. Over this temperature the substance partially decompose. The TG trace displays a slow weight loss, and the curve reaches a plateau at 300 °C when about 30% of the initial weight is left. Complex **6** can be sublimed at 0.1 mbar and 135 °C. It seems to have an increased thermal stability with respect to all the compounds so far analyzed: it melts at 212 °C and loses weight more rapidly than the parent eight-coordinate compound **5**. So in this last case we have observed that the β-ketoiminato-substituted compound is much more thermally robust than the β-diketiminato, in contrast to what was seen for the six-coordinate compounds.

Conclusions. Amide substitution reactions are convenient routes to obtain heteroleptic five- and six-coordinate complexes with β-ketoiminate and β-diketiminate ligands bearing alkyl substituents on the imino nitrogen. The fluxional properties of the two β-diketiminato-substituted molecules **1** and **2** have been studied, and in the case of compound **2**, it is suggested that at room temperature the Bailar twist interconversion is not allowed, as a consequence of the higher steric hindrance of the ethyl group. Molecules **1** and **2** display sufficient volatility and thermal stability to be considered as precursors for chemical vapor deposition of ZrN. Further testing of such complexes is currently ongoing work in our laboratories. Homoleptic eight-coordinate compounds can be synthesized if bidentate ligands bearing a hydrogen substituent on the imino nitrogen are employed. These compounds display a higher thermal stability with respect to the six-coordinate ones, but among the homoleptic compounds, the eight-coordinate β-ketoiminato substituted ones are more stable. These findings make clear that there is no simple structure−volatility and structure−thermal stability correlation and that there is a need of a deeper insight into the understanding of intermolecular forces. This work provides interesting hints as to which direction a ligand tuning should take place, for example using trifluoromethyl-substituted β-diketimines.

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Supporting Information Available: CIF files for structures **1**, **2**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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