Synthesis, Structure, and Reactivity of Organometallic Lanthanide – Dizirconium Nonaisopropoxide Complexes

William J. Evans,* Michael A. Greci, Matthew A. Johnston, and Joseph W. Ziller[a]

Abstract: The feasibility of using $[\mathrm{Zr_2(O}i\mathrm{Pr)_9}]^-$ as a stabilizing, ancillary ligand in organometallic lanthanide complexes has been examined. The *di*zirconium *n*ona*i*sopropoxide (dzni) ligand has been found to be compatible with cyclopentadienyl and cyclooctatetraenyl reagents and enhances the solubility of divalent lanthanide organometallic species in comparison with $(\mathrm{C_5H_5})^-$ analogues. $[\{[\mathrm{Zr_2(O}i\mathrm{Pr)_9}]\mathrm{LnI}\}_2]$ reacts with $\mathrm{NaC_5H_5}$ to form the hexane-soluble divalent lanthanide complexes $[\{\mathrm{Zr_2(O}i\mathrm{Pr)_9}\}\mathrm{Ln(C_5H_5)}]$ (**1**: Ln = Sm; **2**: Ln = Yb). Complex **1** is the first reported soluble $(\mathrm{C_5H_5})^-$ complex of $\mathrm{Sm^{II}}$. $[\{[\mathrm{Zr_2(O}i\mathrm{Pr)_9}]\mathrm{LnI}\}_2]$ reacts with $\mathrm{K_2C_8H_8}$ to form the bimetallic $\mathrm{Ln^{II}}$ complexes $[\{[\mathrm{Zr_2(O}i\mathrm{Pr)_9}]\mathrm{Ln}\}_2(\mathrm{C_8H_8})]$ (**3**: Ln = Sm; **4**: Ln = Yb), which are also hexane-soluble. Complex **3** reacts with 1,3,5,7-$\mathrm{C_8H_8}$ to form hexane-soluble $[\{\mathrm{Zr_2(O}i\mathrm{Pr)_9}\}\mathrm{Sm(C_8H_8)}]$, **5**, in a manner analogous to the reduction of $\mathrm{C_8H_8}$ by $[\{(\mathrm{C_5Me_5})\mathrm{Sm}\}_2(\mathrm{C_8H_8})]$. In all these complexes, the monoanionic $[\mathrm{Zr_2(O}i\mathrm{Pr)_9}]^-$ unit is attached to the lanthanide metal in a tetradentate fashion.

Keywords: lanthanides · ligand effects · solubility · structure elucidation · zirconium

Introduction

The $[\mathrm{Zr_2(O}i\mathrm{Pr)_9}]^-$ unit in heterometallic zirconium isopropoxide complexes is capable of complexing a wide range of metal ions.[1] Comparison of the structures of $[\{[\mathrm{Zr_2(O}i\mathrm{Pr)_9}]\mathrm{Ln}(\mu\text{-I})\}_2]$ (Ln = Eu, Sm)[2] with that of $[\{(\mathrm{C_5Me_5})(\mathrm{thf})_2\mathrm{Sm}(\mu\text{-I})\}_2]$[3] suggested that the *di*zirconium *n*ona*i*sopropoxide (dzni) ligand could act as an ancillary ligand similar to the cyclopentadienyl ligands commonly occurring in lanthanide halide complexes. This could have important consequences, since the dzni ligand provides a polydentate monoanionic coordination environment like that of cyclopentadienide but it has substantially different electronic properties.

Although the dzni ligand could replace cyclopentadienyl groups in simple inorganic lanthanide halides, its compatibility with organometallic reagents was unknown. Hence, the structural integrity and stability of the dzni unit in the presence of organometallic ligands needed to be examined. We report here on reactions involving $(\mathrm{C_5H_5})^-$ and $(\mathrm{C_8H_8})^{2-}$ reagents, the dzni complexes which result, and their favorable solubility. Preliminary reactivity studies are also described.

Experimental Section

General: The experiments described below were performed under nitrogen with rigorous exclusion of air and water by Schlenk, vacuum line, and glovebox techniques. Solvents were purified as described previously.[4] NMR spectra were acquired and magnetic moments were measured by the method of Evans[5] using a Bruker DRX400 or a General Electric QE500 spectrometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ 85719 (USA) or by Analytische Laboratorien, Lindlar (Germany).

$[\{\mathrm{Zr_2(O}i\mathrm{Pr)_9}\}\mathrm{Sm(C_5H_5)}]$ (1): In a glovebox, a mixture of $[\{[\mathrm{Zr_2(O}i\mathrm{Pr)_9}]\mathrm{Sm}(\mu\text{-I})\}_2]$[2] (843 mg, 0.850 mmol), $\mathrm{NaC_5H_5}$ (80 mg, 0.911 mmol), and hexanes (20 mL) in an Erlenmeyer flask was gently heated and stirred for 10 min, after which the color began to change from dark blue to green/black. After two days of stirring at room temperature, the solution was centrifuged to remove insoluble material and the supernatant was isolated and evaporated to a final volume of approximately 2 mL. 1,2-Dimethoxyethane (2 mL) was added to the solution, it was cooled to $-30\,^{\circ}\mathrm{C}$, and X-ray quality crystals of **1** (580 mg, 73 %) were grown during three days. $^1\mathrm{H}$ NMR ($\mathrm{C_6D_6}$): $\delta = 32.61$ (s, 12 H, $\mathrm{OCH(C}\mathit{H}_3)_2$), 26.75 (s, 1 H, $\mathrm{OC}\mathit{H}\mathrm{(CH_3)_2}$), 8.29 (s, 5 H, $\mathrm{C_5}\mathit{H}_5$), 1.67 (m, 4 H, $\mathrm{OC}\mathit{H}\mathrm{(CH_3)_2}$), 0.07 (m, 1 H, $\mathrm{OC}\mathit{H}\mathrm{(CH_3)_2}$), -0.47 (d, 12 H, $\mathrm{OCH(C}\mathit{H}_3)_2$), -1.08 (d, 12 H, $\mathrm{OCH(C}\mathit{H}_3)_2$), -3.67 (m, 1 H, $\mathrm{OC}\mathit{H}\mathrm{(CH_3)_2}$), -4.08 (d, 12 H, $\mathrm{OCH(C}\mathit{H}_3)_2$), -4.18 (d, 6 H, $\mathrm{OCH(C}\mathit{H}_3)_2$), -25.71 (m, 2 H, $\mathrm{OC}\mathit{H}\mathrm{(CH_3)_2}$); $^1\mathrm{H}$ NMR ($\mathrm{C_4D_8O}$): $\delta = 25.23$ (s, 12 H, $\mathrm{OCH(C}\mathit{H}_3)_2$), 20.10 (s, 1 H, $\mathrm{OC}\mathit{H}\mathrm{(CH_3)_2}$), 9.21 (s, 5 H, $\mathrm{C_5}\mathit{H}_5$), 3.58 (t, THF), 1.72 (t, THF), 0.91 (m, 4 H, $\mathrm{OC}\mathit{H}\mathrm{(CH_3)_2}$), 0.08 (m, 1 H, $\mathrm{OC}\mathit{H}\mathrm{(CH_3)_2}$), -0.19 (d, 12 H, $\mathrm{OCH(C}\mathit{H}_3)_2$), -0.69 (d, 12 H, $\mathrm{OCH(C}\mathit{H}_3)_2$), -1.54 (d, 12 H, $\mathrm{OCH(C}\mathit{H}_3)_2$), -2.62 (m, 1 H, $\mathrm{OC}\mathit{H}\mathrm{(CH_3)_2}$), -3.46 (d, 6 H, $\mathrm{OCH(C}\mathit{H}_3)_2$), -20.01 (m, 2 H, $\mathrm{OC}\mathit{H}\mathrm{(CH_3)_2}$); $^{13}\mathrm{C}$ NMR ($\mathrm{C_6D_6}$): $\delta = 67.6$ ($\mathrm{O}\mathit{C}\mathrm{H(CH_3)_2}$), 62.9 ($\mathrm{O}\mathit{C}\mathrm{H(CH_3)_2}$), 54.0 ($\mathrm{O}\mathit{C}\mathrm{H(CH_3)_2}$), 27.1 ($\mathrm{OCH(}\mathit{C}\mathrm{H_3)_2}$), 25.0 ($\mathrm{OCH(}\mathit{C}\mathrm{H_3)_2}$), 24.8 ($\mathrm{OCH(}\mathit{C}\mathrm{H_3)_2}$), 23.1 ($\mathrm{OCH(}\mathit{C}\mathrm{H_3)_2}$), 20.0 ($\mathrm{OCH(}\mathit{C}\mathrm{H_3)_2}$), -49.70 ($\mathit{C}_5\mathrm{H_5}$); UV/Vis (THF): $\lambda_{\max} = 695$, 463, 366, 298 nm; $\chi_G^{298\,\mathrm{K}} = 4.5 \times 10^{-6}$; $\mu_{\mathrm{eff}}^{298\,\mathrm{K}} = 3.2\,\mu_B$; IR(KBr): $\tilde{\nu} = 2964$ s, 2924 m, 2854 m, 2624 w, 2361 w, 2334 w, 1461 m, 1373 m, 1358 s, 1336 m, 1262 w, 1164 s,

---

[a] Prof. Dr. W. J. Evans, M. A. Greci, M. A. Johnston, Dr. J. W. Ziller
Department of Chemistry, University of California, Irvine
Irvine, CA 92697 (USA)
E-mail: wevans@uci.edu

1127 s, 1018 s, 1004 s, 950 s, 945 s, 847 m, 827 m, 814 m, 763 m, 740 m cm^{-1}; $\mathrm{Zr_2SmO_9C_{32}H_{68}}$: calcd Sm 16.18, Zr 19.63, C 41.35, H 7.31; found Sm 16.10, Zr 19.85, C 41.20, H 7.44.

X-ray data collection, solution and refinement: A dark green crystal, approximate dimensions 0.44 mm × 0.40 mm × 0.22 mm, was mounted in a glass capillary and transferred to the Siemens P4 diffractometer. The symmetry, crystal class, unit cell parameters, and orientation matrix of the crystal were determined by standard procedures.[6] Attempts to index crystals of the same sample at 163 K were unsuccessful, because they cracked at low temperatures. Intensity data were collected at 293 K using the $2\theta/\omega$ scan technique with $\mathrm{Mo}_{\mathrm{K}\alpha}$ radiation. Decay of approximately 30 % in the intensity of the check reflections during data collection was corrected with FIXDAT[7] using a linear decay model. The raw data were processed with a local version of CARESS[8] which employs a modified Lehman–Larsen algorithm to obtain intensities and standard deviations from the measured 96-step peak profiles. All 3538 data were corrected for absorption and Lorentz and polarization effects, and were placed on an approximately absolute scale. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the centrosymetric monoclinic space group $P2_1/m$.

All calculations were carried out using the SHELXL program.[9] The analytical scattering factors for neutral atoms were used throughout the analysis.[10] The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. Minor disorder in the isopropyl groups was modeled by assigning partial occupancy to components of the disordered groups. Hydrogen atoms were included using a riding model. At convergence, $wR2 = 0.1085$ and GOF = 0.998 for 203 variables refined against all 3366 unique data (for refinement on F, $R1 = 0.0439$ for those 2143 data with $F > 4.0\sigma(F)$).

[{Zr$_2$(O*i*Pr)$_9$}Yb(C$_5$H$_5$)] (2): In a glovebox, [{[Zr$_2$(O*i*Pr)$_9$]Yb(μ-I)}$_2$][2] (1.087 g, 1.071 mmol), $\mathrm{NaC_5H_5}$ (103 mg, 1.17 mmol), and hexanes (20 mL) were combined and handled as described for **1** above. X-ray quality crystals of **2** (605 mg, 59 %) were grown over two days. ^{1}H NMR ($\mathrm{C_6D_6}$): $\delta = 6.54$ (s, 5 H, $\mathrm{C_5}H_5$), 4.66 (m, 2 H, $\mathrm{OC}H(\mathrm{CH_3})_2$), 4.33 (m, 7 H, $\mathrm{OC}H(\mathrm{CH_3})_2$), 1.44 (d, 12 H, $\mathrm{OCH(C}H_3)_2$), 1.40 (d, 12 H, $\mathrm{OCH(C}H_3)_2$), 1.27 (d, 6 H, $\mathrm{OCH(C}H_3)_2$), 1.24 (d, 12 H, $\mathrm{OCH(C}H_3)_2$), 1.24 (d, 12 H, $\mathrm{OCH(C}H_3)_2$); ^{1}H NMR ($\mathrm{C_4D_8O}$): $\delta = 6.03$ (s, 5 H, $\mathrm{C_5}H_5$), 4.63 (m, 2 H, $\mathrm{OC}H(\mathrm{CH_3})_2$), 4.38 (m, 7 H, $\mathrm{OC}H(\mathrm{CH_3})_2$), 3.62 (t, THF), 1.78 (t, THF), 1.42 (d, 12 H, $\mathrm{OCH(C}H_3)_2$), 1.40 (d, 12 H, $\mathrm{OCH(C}H_3)_2$), 1.27 (d, 6 H, $\mathrm{OCH(C}H_3)_2$), 1.25 (d, 12 H, $\mathrm{OCH(C}H_3)_2$), 1.24 (d, 12 H, $\mathrm{OCH(C}H_3)_2$); ^{13}C NMR ($\mathrm{C_6D_6}$): $\delta = 108.9$ ($C_5\mathrm{H_5}$), 71.8 ($\mathrm{O}C\mathrm{H(CH_3)_2}$), 70.4 ($\mathrm{O}C\mathrm{H(CH_3)_2}$), 69.1 ($\mathrm{O}C\mathrm{H(CH_3)_2}$), 68.7 ($\mathrm{O}C\mathrm{H(CH_3)_2}$), 27.0 ($\mathrm{OCH(}C\mathrm{H_3)_2}$), 26.9 ($\mathrm{OCH(}C\mathrm{H_3)_2}$), 26.8 ($\mathrm{OCH(}C\mathrm{H_3)_2}$), 26.6 ($\mathrm{OCH(}C\mathrm{H_3)_2}$), 26.4 ($\mathrm{OCH(}C\mathrm{H_3)_2}$); UV/Vis (THF): $\lambda_{\max} = 514$, 435, 303 nm; IR(KBr): $\tilde{\nu} = 2964$ s, 2923 m, 2857 m, 2623 w, 1462 m, 1376 m, 1362 s, 1337 m, 1258 w, 1232 w, 1167 s, 1130 s, 1020 s, 1009 s, 958 s, 848 m, 830 m, 806 m, 744 m, 665 w, 552 m cm^{-1}; $\mathrm{Zr_2YbO_9C_{32}H_{68}}$: calcd C 40.34, H 7.20; found C 40.33, H 7.05.

X-ray data collection, solution and refinement: A red crystal, dimensions 0.44 mm × 0.12 mm × 0.08 mm, was handled as described above for **1**. All 3089 data were corrected for absorption and Lorentz and polarization effects, and were placed on an approximately absolute scale. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the centrosymetric monoclinic space group $P2_1/m$. All calculations were carried out as for **1**, above. At convergence, $wR2 = 0.0810$ and GOF = 1.143 for 202 variables refined against all 2931 unique data (for refinement on F, $R1 = 0.0404$ for those 2002 data with $F > 4.0\sigma(F)$).

[{[Zr$_2$(O*i*Pr)$_9$]Sm}$_2$(C$_8$H$_8$)] (3): [{[Zr$_2$(O*i*Pr)$_9$]Sm(μ-I)}$_2$] (160 mg, 0.08 mmol) and $\mathrm{K_2C_8H_8}$ (15 mg, 0.08 mmol) were combined in THF (8 mL). The reaction mixture was initially deep purple but changed slowly to red-brown during 4 h. It was centrifuged after 4 h to remove gray insoluble material and the solvent was removed by rotary evaporation to yield **3** as a brown powder (118 mg, 80 %). ^{1}H NMR ($\mathrm{C_6D_6}$, 20 °C): $\delta = 7.76$ (s, 8 H, $\mathrm{C_8}H_8$), 4.59 (m, 12 H, $\mathrm{OC}H(\mathrm{CH_3})_2$), 4.47 (m, 6 H, $\mathrm{OC}H(\mathrm{CH_3})_2$), 1.54 (d, 12 H, $\mathrm{OCH(C}H_3)_2$), 1.46 (d, 48 H, $\mathrm{OCH(C}H_3)_2$), 1.39 (d, 24 H, $\mathrm{OCH(C}H_3)_2$), 1.19 (d, 24 H, $\mathrm{OCH(C}H_3)_2$); ^{1}H NMR ($\mathrm{C_4D_8O}$): $\delta = 7.22$ (s, 8 H, $\mathrm{C_8}H_8$), 4.54 (m, 12 H, $\mathrm{OC}H(\mathrm{CH_3})_2$), 4.45 (m, 6 H, $\mathrm{OC}H(\mathrm{CH_3})_2$), 3.65 (t, THF), 1.78 (t, THF), 1.52 (d, 12 H, $\mathrm{OCH(C}H_3)_2$), 1.47 (d, 48 H, $\mathrm{OCH(C}H_3)_2$), 1.36 (d, 24 H, $\mathrm{OCH(C}H_3)_2$), 1.22 (d, 24 H, $\mathrm{OCH(C}H_3)_2$); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta = 70.6$, 67.8 ($\mathrm{O}C\mathrm{H(CH_3)_2}$), 28.4, 27.6, 27.0, 25.4 ($\mathrm{OCH(}C\mathrm{H_3)_2}$); UV/Vis (hexanes): $\lambda_{\max} = 710$, 510, 300 nm; IR (KBr): $\tilde{\nu} = 3163$ m, 2794 s, 1914 w, 1554 s, 1387 s, 1173 w, 1012 m, 897 m, 735 w cm^{-1}; $\mathrm{Sm_2Zr_4O_{18}C_{62}H_{134}}$: calcd C 40.65, H 7.38, Zr 19.65, Sm 16.43; found C 40.59, H 7.45, Zr 19.60, Sm 16.55. Recrystallization from a concentrated THF solution yielded red-brown crystals suitable for X-ray analysis.

X-ray data collection, solution, and refinement: A red-brown crystal, dimensions 0.13 mm × 0.15 mm × 0.23 mm, was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[11] program package was used to determine the unit-cell parameters and for data collection (scan time 20 s/frame for a sphere of diffraction data). The raw frame data were processed using SAINT[12] and SADABS[13] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[14] program. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/n$, which was later confirmed.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[10] for neutral atoms were used throughout the analysis. The molecule was located about an inversion center at the centroid of the cyclooctatetraenide ligand. Six of the nine isopropyl groups were disordered. The carbon atoms of the disordered groups were included with two components and assigned partial site-occupancy factors (listed in the CIF file). Hydrogen atoms were included using a riding model. There was residual electron density associated with the cyclooctatetraenide ligand, but unsuccessful attempts to refine a disordered model resulted in a poorly defined geometry of the cyclooctatetraenide ring and higher-than-expected residuals. At convergence, $wR2 = 0.1328$ and GOF = 1.054 for 351 variables refined against 9903 unique data (in comparison: for refinement on F, $R1 = 0.0500$ for those 7626 data with $I > 2.0\sigma(I)$).

[{[Zr$_2$(O*i*Pr)$_9$]Yb}$_2$(C$_8$H$_8$)] (4): [{[Zr$_2$(O*i*Pr)$_9$]Yb(μ-I)}$_2$] (0.200 g, 0.1 mmol) and $\mathrm{K_2C_8H_8}$ (0.018 g, 0.1 mmol) were combined in toluene (6 mL). The mixture was initially yellow, but after 3 h an orange-yellow color was observed. Gray-white solids and solvent were removed by centrifugation after 8 h to yield **4** as an orange powder (0.145 g, 79 %). ^{1}H NMR ($\mathrm{C_6D_6}$, 20 °C): $\delta = 6.70$ (s, 8 H, $\mathrm{C_8}H_8$), 4.58 (m, 18 H, $\mathrm{OC}H(\mathrm{CH_3})_2$), 1.59 (d, 24 H, $\mathrm{OCH(C}H_3)_2$), 1.35 (overlapping d, 60 H, $\mathrm{OCH(C}H_3)_2$), 1.25 (d, 24 H, $\mathrm{OCH(C}H_3)_2$); ^{1}H NMR ($\mathrm{C_4D_8O}$): $\delta = 6.41$ (s, 8 H, $\mathrm{C_8}H_8$), 4.51 (m, 18 H, $\mathrm{OC}H(\mathrm{CH_3})_2$), 3.63 (t, THF), 1.76 (t, THF), 1.48 (d, 24 H, $\mathrm{OCH(C}H_3)_2$), 1.35 (overlapping d, 60 H, $\mathrm{OCH(C}H_3)_2$), 1.23 (d, 24 H, $\mathrm{OCH(C}H_3)_2$); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta = 90.4$ ($C_8\mathrm{H_8}$), 69.3 ($\mathrm{O}C\mathrm{H(CH_3)_2}$), 27.4, 27.1, 26.8, 26.6 ($\mathrm{OCH(}C\mathrm{H_3)_2}$); UV/Vis (hexanes): $\lambda_{\max} = 750$, 460 nm; IR (KBr): $\tilde{\nu} = 2984$ s, 2873 s, 1591 w, 1459 m, 1363 s, 1166 s, 1125 w, 1019 m, 958 m, 827 m, 715 w, 660 w, 574 m cm^{-1}; $\mathrm{Yb_2Zr_4O_{18}C_{62}H_{134}}$: calcd C 39.69, H 7.20, Zr 19.19, Yb 18.46; found C 39.37, H 7.04, Zr 19.40, Yb 18.55.

[{Zr$_2$(O*i*Pr)$_9$}Sm(C$_8$H$_8$)] (5): A red-brown solution of **3** (119 mg, 0.06 mmol) in toluene (4 mL) was added to a solution of $\mathrm{C_8H_8}$ (6 mg, 0.06 mmol) in toluene (4 mL). After 1 h, the reaction mixture began to change to purplish-red; after 6 h, it was deep purple. Removal of solvent by rotary evaporation yielded **5** as a purple powder (93 mg, 74 %). ^{1}H NMR ($\mathrm{C_6D_6}$, 20 °C): $\delta = 10.09$ (s, 8 H, $\mathrm{C_8}H_8$), 4.63, 4.51 (overlapping m, 9 H, $\mathrm{OC}H(\mathrm{CH_3})_2$), 1.64 (d, 6 H, $\mathrm{OCH(C}H_3)_2$), 1.48 (d, 12 H, $\mathrm{OCH(C}H_3)_2$), 1.35 (d, 24 H, $\mathrm{OCH(C}H_3)_2$), 1.29 (d, 12 H, $\mathrm{OCH(C}H_3)_2$); ^{1}H NMR ($\mathrm{C_4D_8O}$): $\delta = 9.76$ (s, 8 H, $\mathrm{C_8}H_8$), 4.58, 4.52 (overlapping m, 9 H, $\mathrm{OC}H(\mathrm{CH_3})_2$), 3.63 (t, THF), 1.73 (t, THF), 1.48 (d, 6 H, $\mathrm{OCH(C}H_3)_2$), 1.41 (d, 12 H, $\mathrm{OCH(C}H_3)_2$), 1.39 (d, 24 H, $\mathrm{OCH(C}H_3)_2$), 1.22 (d, 12 H, $\mathrm{OCH(C}H_3)_2$); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$): $\delta = 84.0$ ($C_8\mathrm{H_8}$), 72.7, 72.0 ($\mathrm{O}C\mathrm{H(CH_3)_2}$), 28.5, 27.2, 26.9, 25.5 ($\mathrm{OCH(}C\mathrm{H_3)_2}$); $\chi_{\mathrm{G}}^{298\,\mathrm{K}} = 6.64 \times 10^{-7}$, $\mu_{\mathrm{eff}}^{298\,\mathrm{K}} = 1.3\,\mu_{\mathrm{B}}$; IR (KBr): $\tilde{\nu} = 3002$ m, 2852 s, 1733 m, 1595 w, 1456 w, 1375 s, 1277 m, 1139 s, 1023 s, 827 m, 556 w cm^{-1}; UV/Vis (hexanes): $\lambda_{\max} = 560$, 380 nm; $\mathrm{SmZr_2O_9C_{35}H_{71}}$: calcd C 43.42, H 7.40; found C 43.19, H 7.50. Recrystallization from a concentrated solution in toluene at −30 °C yielded large purple crystals suitable for X-ray analysis.

X-ray data collection, solution, and refinement: A purple crystal, approximate dimensions 0.06 mm × 0.22 mm × 0.23 mm, was mounted on a glass fiber, transferred to a Bruker CCD platform, and handled as described above for **3** (scan time 20 s/frame for a sphere of diffraction data). There were no systematic absences or diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later confirmed. At convergence, $wR2 = 0.1679$ and GOF = 1.229 for 421 variables refined against 9967 unique data (in comparison: for refinement on F, $R1 = 0.0690$ for those 8603 data with $I > 2.0\sigma(I)$).

Results

Synthesis: The $[\{[Zr_2(OiPr)_9]LnI\}_2]$ complexes[2] readily react with NaC_5H_5 to form alkane-soluble $[\{Zr_2(OiPr)_9\}Ln(C_5H_5)]$ products (Ln = Sm, **1**; Yb, **2**) [Eq. (1)].

$$[\{[Zr_2(OiPr)_9]LnI\}_2] + 2\,NaC_5H_5 \longrightarrow 2\,[[Zr_2(OiPr)_9]Ln(C_5H_5)] + 2\,NaI \quad (1)$$

Complexes **1** and **2** were characterized by NMR and IR spectroscopy and elemental analysis and their structures were determined by X-ray crystallography (Figure 1). In contrast to the only other known $Sm^{II}-(C_5H_5)^-$ complex, $[\{(C_5H_5)_2Sm(thf)\}_n]$, which is insoluble in solvents with which it does not react,[15] **1** is soluble in hexanes. Hence the replacement of $(C_5H_5)^-$ by $[Zr_2(OiPr)_9]^-$ enhances alkane solubility. In this sense, the dzni ligand is similar to $(C_5Me_5)^-$.[16] The $[\{Zr_2(OiPr)_9\}Ln(C_5H_5)]$ complexes are more soluble than the $[(C_5Me_5)_2Ln]$ complexes in alkanes;[16] **2** is also more soluble than $[(C_5H_5)_2Yb]$,[17] which only dissolves in coordinating solvents that form adducts.

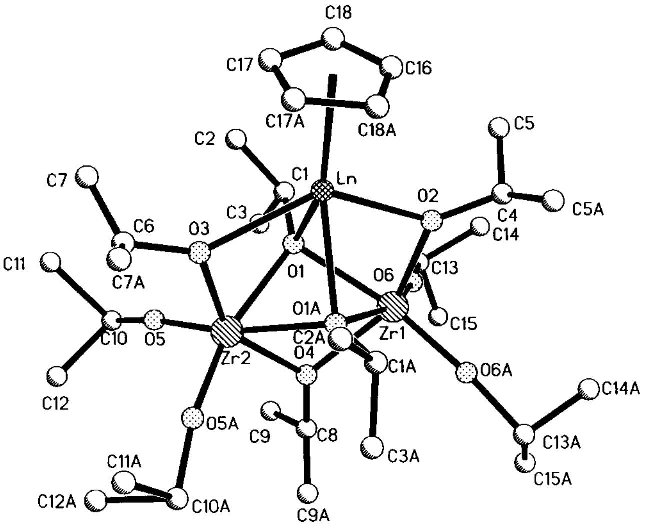

Figure 1. Ball-and-stick representation of the isostructural complexes **1** and **2**.

The $[\{[Zr_2(OiPr)_9]LnI\}_2]$ complexes react with $K_2C_8H_8$ to form the alkane-soluble $[\{[Zr_2(OiPr)_9]Ln\}_2(C_8H_8)]$ products (Ln = Sm, **3**; Ln = Yb, **4**) [Eq. (2)]. Complexes **3** and **4** were

$$[\{[Zr_2(OiPr)_9]LnI\}_2] + K_2C_8H_8 \longrightarrow 2\,[\{[Zr_2(OiPr)_9]Ln\}_2(C_8H_8)] + 2\,KI \quad (2)$$

also characterized by NMR and IR spectroscopy and elemental analysis and the structure of **3** was determined by X-ray crystallography (Figure 2). There are no known $(C_5H_5)^-$ analogues of **3** and **4** but the $(C_5Me_5)^-$ analogues, $[\{(C_5Me_5)Ln\}_2(C_8H_8)]$ (Ln = Sm, **6**; Ln = Yb, **7**),[18, 19] have similar solubility.

Reactivity: It was of interest to compare the chemistry of **1**–**4** with that of their $(C_5R_5)^-$ (R = H, Me) analogues. The $[(dzni)Ln(C_5H_5)]$ complexes are quite different from $[(C_5H_5)_2Ln]$ and $[(C_5Me_5)_2Ln]$ in that they do not form isolable adducts with THF, Et_2O, or DME. They are crystallized solvate-free from hexanes/DME (**1** and **2**) and THF (**3** and **4**). The NMR spectra of **1** and **2** in $[D_8]$THF show two distinct THF environments, suggesting coordination of THF in solution, but removal of solvent leads to the isolation of solvent-free species. Similar behavior is observed for **3** and **4** in $[D_8]$THF. In contrast, the analogous complexes with cyclopentadienyl ligands in place of dzni form solvates. The cyclopentadienyl complexes $[(C_5H_5)_2LnL_x]$,[15, 17] $[(C_5Me_5)_2LnL_2]$[19] and $[\{(C_5Me_5)LnL_x\}_2(C_8H_8)]$[18, 19] (L = ethers) are typically isolated as solvates. They desolvate only upon heating under vacuum and in some cases the desolvation is tedious. Hence, these dzni complexes provide a much easier route to unsolvated organometallic complexes of Sm^{II} and Yb^{II}.

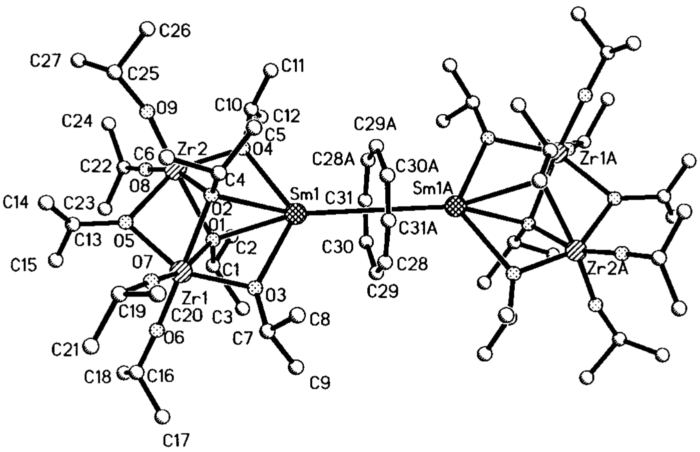

Figure 2. Ball-and-stick representation of **3**.

Preliminary studies of the reactivity of **3** and **4** with 1,3,5,7-C_8H_8 were conducted for comparison with the reactions of $[\{(C_5Me_5)Ln\}_2C_8H_8]$ with 1,3,5,7-C_8H_8, which yield trivalent mixed-ligand products, $[(C_5Me_5)Ln(C_8H_8)]$ (Ln = Sm, **6**; Ln = Yb, **7**) [Eq. (3)].

$$[\{(C_5Me_5)Ln\}_2(C_8H_8)] + C_8H_8 \longrightarrow 2\,[(C_5Me_5)Ln(C_8H_8)] \quad (3)$$

Like its $(C_5Me_5)^-$ analogue, the Sm^{II} complex **3** reduces C_8H_8 to form $[\{Zr_2(OiPr)_9\}Sm(C_8H_8)]$, **5** [Eq. (4)].[19]

$$\underset{\mathbf{3}}{[\{[Zr_2(OiPr)_9]Sm\}_2(C_8H_8)]} + C_8H_8 \longrightarrow 2\,\underset{\mathbf{5}}{[[Zr_2(OiPr)_9]Sm(C_8H_8)]} \quad (4)$$

Complex **5** was characterized by IR, NMR, elemental analysis and its structure was determined by single-crystal X-ray diffraction (Figure 3). In contrast, $[\{[Zr_2(OiPr)_9]Yb\}_2(C_8H_8)]$ does not appear to react with C_8H_8, even after several days, whereas $[\{(C_5Me_5)Yb\}_2(C_8H_8)]$ readily reduces C_8H_8 to form **7**.[18] The NMR spectrum of **5** in $[D_8]$THF also shows two THF environments, as found for **1**–**4**.

Structure: Both **1** and **2** crystallize from hexanes/DME at low temperature as the monomers $[\{Zr_2(OiPr)_9\}Ln(C_5H_5)]$ (Figure 1). In both cases, the dzni ligand binds to the metal with four isopropoxide oxygen donor atoms. In each dzni ligand in

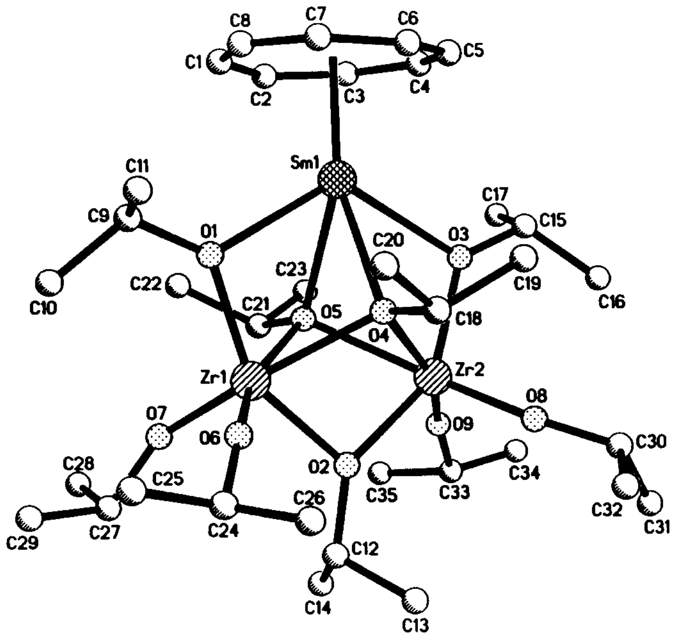

Figure 3. Ball-and-stick representation of **5**.

1 and **2** there is a face-sharing bioctahedral arrangement of nine isopropoxide ligands surrounding the two zirconium centers and each zirconium is six-coordinate, as has been observed in other structurally characterized lanthanide dzni complexes.[2] The Zr–O(O*i*Pr) distances are consistent with other dzni complexes in the literature.[1, 2] The Ln–O(O*i*Pr) distances in **1** (2.549(6)–2.595(4) Å) and **2** (2.444(6)–2.469(4) Å) are within the range of Eu–O(O*i*Pr) distances in $[\{[Zr_2(O\mathit{i}Pr)_9]Eu(\mu\text{-}I)\}_2]$,[2] when differences in the ionic radii of the metals are taken into account.[21]

The lanthanide metals in **1** and **2** are formally seven-coordinate. Since only two polydentate ligands generate the seven coordination positions, the complex does not have a regular seven-coordinate geometry. Even the $(C_5H_5)^-$ ring centroid and the four oxygen donor atoms fail to describe a regular five-coordinate geometry since the O-Ln-O angles in **1** (58.23(17)–125.2(2)°) and **2** (61.6(2)–130.4(2)°) are far from linear, which excludes a trigonal bipyramidal geometry, and the four oxygen donor atoms are not coplanar (with deviations of 0.54 Å from the best plane of the four), which excludes a square pyramidal geometry. By considering these $[(dzni)Ln(C_5H_5)]$ complexes as two-ligand ML_2 entities, one can examine the orientation of the C_5H_5 ring centroid relative to the "center" of the dzni ligand[22] to see if a bent or linear structure is present.[16, 23] In both **1** and **2**, the ring centroid-Ln-(Zr–Zr centroid) angles are 180°, so the complexes are linear.

The Ln–C(C_5H_5) distances in **1** and **2** are difficult to evaluate. Since **1** is the first soluble and structurally characterized Sm^{II}–$(C_5H_5)^-$ complex to be reported, there are no other Sm^{II} $(C_5H_5)^-$ complexes with which to compare it. The closest analogue to **2**, namely $[(C_5H_5)_2Yb]$,[17a] is a polymeric compound with bridging cyclopentadienyl rings. Since bridging ligands generally have longer bond distances, the 2.67(2)–2.728(12) Å Yb–C(C_5H_5) distances in **2** appear normal compared with the 2.769 Å average Yb–C(η^5:η^1-C_5H_5) distance in $[Yb(C_5H_5)_2]$. The Yb–C distances in $[Yb[C_5H_3(SiMe_3)_2\text{-}1,3]_2]$[17a] (2.654(5) Å), $[(C_5H_5)_2Yb(dme)]$[17b] (2.72(8) Å), and $(C_5H_4SiMe_3)_2Yb(thf)_2$[17c] (2.75 Å), are in the range of those in **2**, within the limits of error. The 2.803(10)–2.825(11) Å Sm–C(C_5H_5) distances in **1** are consistent with those in **2** when the 0.14 Å difference in the seven-coordinate Shannon radii of the metals is taken into account.[21]

Complex **3** crystallizes from THF as a centrosymmetric dimer with a $[\{[Zr_2(O\mathit{i}Pr)_9]Sm\}_2(\mu\text{-}\eta^8\text{:}\eta^8\text{-}C_8H_8)]$ structure analogous to that in $[[(C_5Me_5)Sm]_2(C_8H_8)]$.[18] The dzni ligand in **3** is again tetradentate, which gives a formally nine-coordinate samarium center. Although the structure of complex **3** has been established by X-ray data, disorder in the structure precludes a detailed discussion of bond lengths and angles.

Complex **5** crystallizes from toluene as a monomer, $[\{Zr_2(O\mathit{i}Pr)_9\}Sm(C_8H_8)]$, which is analogous to $[(C_5Me_5)Sm(C_8H_8)]$, **6**.[18] The 2.665(8)–2.701(8) Å Sm–C(C_8H_8) distances in **5** are longer than those (2.565(4)–2.615(4) Å) in **6**. Since **5** has a higher formal coordination number than **6**, this might be expected. However, Shannon's radius increases by only 0.05–0.06 Å for an increase of 1 in coordination number. The 2.491(4)–2.619(4) Å Sm–O(O*i*Pr) distances in **5** are similar to those in **1**, but the range is greater. The (C_8H_8 ring centroid)-Sm-(Zr–Zr centroid) angle (180°) is linear and differs from the (C_5Me_5 ring centroid)-Sm-(C_8H_8 ring centroid) angle (164.3°) in **6**.[18]

Discussion

The mixed-ligand dzni halide complexes, $[\{[Zr_2(O\mathit{i}Pr)_9]LnI\}_2]$, are good precursors for the formation of organometallic derivatives containing cyclopentadienyl and cyclooctatetraenyl ligands. Neither NaC_5H_5 nor $K_2C_8H_8$ decomposes the $[Zr_2(O\mathit{i}Pr)_9]^-$ components in the starting materials and the mixed ligand dzni organometallic complexes are obtainable in 60–80% yield.

The new products $[\{Zr_2(O\mathit{i}Pr)_9\}Ln(C_5H_5)]$ and $[\{[Zr_2(O\mathit{i}Pr)_9]Ln\}_2(C_8H_8)]$ have the advantage of being soluble in alkanes. This is most important for $[\{Zr_2(O\mathit{i}Pr)_9\}Sm(C_5H_5)]$, since no soluble Sm^{II}–$(C_5H_5)^-$ complexes are known and Sm^{II} has extensive chemistry.[24–27] Given the use of $[SmI_2(thf)_x]$[25] in organic syntheses[26] and the attempts to use $(C_5H_5)_2Sm$ in organic syntheses[27] despite its insolubility, the enhanced solubility of $[\{Zr_2(O\mathit{i}Pr)_9\}Sm(C_5H_5)]$ could have interesting implications. The $[\{Zr_2(O\mathit{i}Pr)_9\}Ln(C_5H_5)]$ and $[\{[Zr_2(O\mathit{i}Pr)_9]Ln\}_2(C_8H_8)]$ complexes are also novel in that they do not form adducts with THF or other coordinating ethers, in contrast to their cyclopentadienyl analogues. This suggests that the dzni unit sterically saturates the lanthanide metal to a greater extent than even a $(C_5Me_5)^-$ ligand. A similar conclusion was drawn from comparison of $[\{(C_5Me_5)(thf)_2Sm(\mu\text{-}I)\}_2]$ and $\{[Zr_2(O\mathit{i}Pr)_9]Sm(\mu\text{-}I)\}_2]$.[2] The greater Sm–C($C_8H_8$) bond lengths in **5** than in **6** are also consistent with this, although the difference also follows the trend expected on the basis of coordination numbers. However, since the NMR data indicate that THF adducts can form in solution, free coordination sites are evidently still available in these complexes.

The analogy between the reduction of 1,3,5,7-C_8H_8 by $[\{[Zr_2(O\textit{i}Pr)_9]Sm\}_2(C_8H_8)]$ to form $[\{Zr_2(O\textit{i}Pr)_9\}Sm(C_8H_8)]$ and the reduction of 1,3,5,7-C_8H_8 by $[\{(C_5Me_5)Sm\}_2(C_8H_8)]$ suggests that the chemistry of $[Zr_2(O\textit{i}Pr)_9]^-$-substituted complexes and of the cyclopentadienyl systems may be similar. That $[\{[Zr_2(O\textit{i}Pr)_9]Yb\}_2(C_8H_8)]$ appears to be less reactive than $[\{(C_5Me_5)Yb\}_2(C_8H_8)]$ is consistent with an assessment of the dzni ligand as less electron-donating than $(C_5Me_5)^-$. Electrochemical studies will be required for confirmation. The utility of the enhanced solubility of the dzni complexes compared with the cyclopentadienyl analogues is being explored.

Conclusion

Dzni lanthanide halides have been proven to be useful precursors to organometallic lanthanide dzni species. The organometallic complexes have enhanced solubility compared with the cyclopentadienyl analogues and a diminished tendency to crystallize as ether adducts. Preliminary reactivity studies show a parallel chemistry.

Acknowledgements

For support of this research, we thank the Division of Chemical Sciences of the Office of Basic Energy Sciences of the Department of Energy.

---

[1] a) B. A. Vaarstra, J. C. Huffman, W. E. Streib, K. G. Caulton, *J. Chem. Soc. Chem. Commun.* **1990**, 1750–1751; b) B. A. Vaarstra, W. E. Streib, K. G. Caulton, *J. Am. Chem. Soc.* **1990**, *112*, 8593–8594; c) B. A. Vaarstra, J. C. Huffman, W. E. Streib, K. G. Caulton, *Inorg. Chem.* **1991**, *30*, 3068–3072; d) B. A. Vaarstra, J. A. Samuels, E. H. Barash, J. D. Martin, W. E. Streib, C. Gasser, K. G. Caulton, *J. Organomet. Chem.* **1993**, *449*, 191–201; e) J. A. Samuels, W.-C. Chiang, J. C. Huffman, K. L. Trojan, W. E. Hatfield, D. V. Baxter, K. G. Caulton, *Inorg. Chem.* **1994**, *33*, 2167–2179; f) T. J. Teff, J. C. Huffman, K. G. Caulton, *Inorg. Chem.* **1995**, *34*, 2491–2492; g) S. Sogani, A. Singh, R. Bohra, R. C. Mehrotra, M. Noltemeyer, *J. Chem. Soc. Chem. Commun.* **1991**, 738–739; h) M. Veith, S. Mathur, V. Huch, *J. Chem. Soc. Dalton Trans.* **1996**, 2485–2496; i) M. Veith, S. Mathur, V. Huch, *J. Am. Chem. Soc.* **1996**, *118*, 903–904; j) G. Garg, A. Singh, R. C. Mehrotra, *Polyhedron* **1993**, *12*, 1399–1402; k) A. Singh, R. C. Mehrotra, *Polyhedron* **1998**, *17*, 689–704.

[2] W. J. Evans, M. A. Greci, M. A. Ansari, J. W. Ziller, *J. Chem. Soc. Dalton Trans.* **1997**, *23*, 4503–4508.

[3] W. J. Evans, J. W. Grate, H. W. Choi, I. Bloom, W. E. Hunter, J. L. Atwood, *J. Am. Chem. Soc.* **1985**, *107*, 941–946.

[4] W. J. Evans, L. R. Chamberlain, T. A. Ulibarri, J. W. Ziller, *J. Am. Chem. Soc.* **1988**, *110*, 6423–6432.

[5] a) D. F. Evans, *J. Chem. Soc.* 1959, 2003–2005; b) J. K. Becconsall, *Mol. Phys.* **1968**, *15*, 129–139.

[6] XSCANS Software Users Guide, Version 2.1, Siemens Industrial Automation, Inc., Madison (WI), **1994**.

[7] a) UCLA Crystallographic Computing Package, University of California, Los Angeles, **1981**; b) C. Strouse, personal communication.

[8] R. W. Broach, Argonne National Laboratory, Illinois (IL), **1978**.

[9] G. M. Sheldrick, SHELXL, Siemens Analytical X-Ray Instruments, Inc., Madison (WI), **1994**.

[10] *International Tables of X-Ray Crystallography*, *vol. C*, Kluwer Academic Publishers, Dordrecht, **1992**.

[11] SMART Software Users Guide, Version 4.21, Bruker Analytical X-Ray Systems, Inc., Madison (WI), **1997**.

[12] SAINT Software Users Guide, Version 4.05, Bruker Analytical X-Ray Systems, Inc., Madison (WI), **1997**.

[13] G. M. Sheldrick, SADABS, Bruker Analytical X-Ray Systems, Inc., Madison (WI), **1997**.

[14] G. M. Sheldrick, SHELXTL v 5.10, Bruker Analytical X-Ray Systems, Inc., Madison (WI), **1997**.

[15] G. W. Watt, E. W. Gillow, *J. Am. Chem. Soc.* **1969**, *91*, 775–776.

[16] a) W. J. Evans, L. A. Hughes, T. P. Hanusa, *J. Am. Chem. Soc.* **1984**, *106*, 4270–4272. b) W. J. Evans, L. A. Hughes, T. P. Hanusa, *Organometallics* **1986**, *5*, 1285–1289.

[17] a) C. Apostolidis, G. B. Deacon, E. Dornberger, F. T. Edelmann, B. Janellakopulos, P. MacKinnon, D. Stalke, *Chem. Commun.* **1997**, 1047–1048; b) P. B. Hitchcock, J. A. K. Howard, M. F. Lappert, S. Prashar, *J. Organomet. Chem.* **1992**, *437*, 177–189; c) G. B. Deacon, P. I. MacKinnon, T. W. Hambley, J. C. Taylor, *J. Organomet. Chem.* **1983**, *259*, 91–97; d) H. A. Zinnen, J. P. Pluth, W. J. Evans, *J. Chem. Soc. Chem. Commun.* **1980**, 810–812; e) M. F. Lappert, P. I. W. Yarrow, J. L. Atwood, R. Shakir, J. Holton, *J. Chem. Soc. Chem. Commun.* **1980**, 987–988.

[18] W. J. Evans, R. D. Clark, M. A. Ansari, J. W. Ziller, *J. Am. Chem. Soc.* **1998**, *120*, 9555–9563.

[19] W. J. Evans, M. A. Johnston, M. A. Greci, J. W. Ziller, *Organometallics* **1999**, *18*, 1460–1464.

[20] W. J. Evans, J. W. Grate, H. W. Choi, I. Bloom, W. E. Hunter, J. L. Atwood, *J. Am. Chem. Soc.* **1985**, *107*, 941–946.

[21] R. D. Shannon, *Acta. Crystallogr. Sect. A* **1976**, *32*, 751–755.

[22] For which we will use the centroid of the Zr–Zr vector.

[23] a) J. V. Ortiz, R. Hoffman, *Inorg. Chem.* **1985**, *24*, 2095–2204; b) M. Kaupp, P. von R. Schleyer, H. Stoll, H. Preuss, *J. Am. Chem. Soc.* **1991**, *113*, 6012–6020; c) M. Kaupp, P. v. R. Schleyer, M. Dolg, H. Stoll, *J. Am. Chem. Soc.* **1992**, *114*, 8202–8210; d) T. K. Hollis, J. K. Burdett, B. Bosnich, *Organometallics* **1993**, *12*, 3385–3386; e) B. Bosnich, *Chem. Soc. Rev.* **1994**, 387–395; f) E. A. Bordreaux, E. Baxter, *Int. J. Quantum Chem.: Quantum Chem. Symp.* **1994**, *28*, 565–569; g) T. V. Timofeeva, J-H. Lii, N. L. Allinger, *J. Am. Chem. Soc.* **1995**, *117*, 7452–7459.

[24] a) W. J. Evans, *Polyhedron* **1987**, *6*, 803–835; b) C. J. Schaverien, *Adv. Organomet. Chem.* **1994**, *36*, 283–290; c) F. T. Edelmann in *Comprehensive Organometallic Chemistry II*, *Vol. 4* (Ed.: M. F. Lappert), Pergamon, Oxford, **1995**, Ch. 2; d) H. Schumann, J. A. Marktscheffel, L. Esser, *Chem. Rev.* **1995**, *95*, 865–986.

[25] W. J. Evans, T. S. Gummersheimer, J. W. Ziller, *J. Am. Chem. Soc.* **1995**, *117*, 8999–9002.

[26] a) P. Girard, J. L. Namy, H. B. Kagan, *J. Am. Chem. Soc.* **1980**, *102*, 1980–1984; b) H. B. Kagan, J. L. Namy, *Tetrahedron*, **1986**, *42*, 6573–6614; c) G. A. Molander, *Chem. Rev.* **1992**, *92*, 29–68.

[27] J. L. Namy, J. Collin, J. Zhang, H. B. Kagan, *J. Organomet. Chem.* **1987**, *328*, 81–86.

Received: March 22, 1999 [F 1690]