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Lithium and Ytterbium Aminotroponate Complexes

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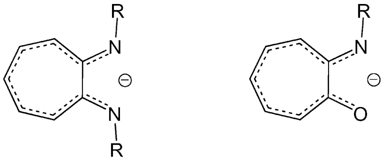
Deprotonation of *i*PrATH [*i*PrAT = 2-(isopropylamino)troponate] with an excess of *n*BuLi resulted in the hexameric lithium 2-(isopropylamino)troponate complex [(*i*PrAT)Li]$_6$. In the solid state the hexameric core can be understood as two six-membered Li_3O_3 rings, which are tied together by the aminotroponate moieties. Further reaction of [(*i*PrAT)Li]$_6$ with $YbCl_3$ in a 1:2 stoichiometric ratio gave the dimeric complex [(*i*PrAT)$_3$Li$_2$Cl$_2$Yb]$_2$, in which the two [(*i*PrAT)$_3$Yb] subunits are bridged by four LiCl units. In the center of this unusual compound an Li–Cl–Li–Cl square is located.

Introduction

In the past decade non-metallocene complexes have attracted considerable attention in *d*-and *f*-metal chemistry.[1,2] In this context, functionalized chelating diamides have been extensively studied as ligands[3] giving highly active precatalysts comparable to the well-established group 4 metallocenes.[4] In lanthanide chemistry anionic nitrogen-based bidentate ligand systems such as diazadienes,[5] benzamidinates,[6,7] guanidinates,[8,9] amido ligands,[10] and other combinations of nitrogen and oxygen atoms[11] were used as cyclopentadienyl replacements to increase the electrophilicity of the metal center and to create a different steric environment at the reactive site. In a recent review article, Piers and Emslie presented a most useful classification of non-cyclopentadienyl ancillaries in organo group 3 metal chemistry covering bi-, tri-, tetra-, and polydentate amido and alkoxido ligands.[12] In this context, we introduced some years ago aminotroponiminato ligands into the chemistry of the lanthanides,[13] whereas a similar approach on group 4 elements was reported by other groups.[14] Aminotroponiminates (**A**, Scheme 1) are bidentate, monoanionic ligands containing a 10π-electron backbone, which can form five-membered metallacycles upon coordination to a metal atom. Due to the presence of the highly delocalised π-electron system, the nearly planar ligand framework shows minimal reactivity towards most nucleophiles and electrophiles. Since the aminotroponiminato ligand was proved to be a formal substitute for cyclopentadienyl, we started to prepare chiral[15] and achiral[16] monobridged aminotroponiminates as alternatives for *ansa*-metallocenes. It was shown that the bridged ligands coordinate in a chelating or a metal-bridging mode to various lanthanides.[16] Motivated by these studies we were interested in aminotroponates (**B**, Scheme 1) as ligands. In these systems the imine group formally is replaced by an oxo group. Thus, both ligand system **A** and **B** are closely related. Whereas, the aminotroponiminato ligand system was introduced into coordination chemistry in the 1960s, and thus a large number of transition metal complexes were prepared,[17–20] only a few aminotroponato complexes of some main group[21] and transition metals[20,22,23] are known. In lanthanide chemistry only the homoleptic tris(aminotroponiminato) complexes of yttrium and samarium, which could structurally not be characterized, were reported.[24]



A **B**

Scheme 1.

Herein we report on the synthesis of a hexameric lithium 2-(isopropylamino)troponate cluster [(*i*PrAT)Li]$_6$ [*i*PrAT = 2-(isopropylamino)troponate] and the further reaction of this compound with anhydrous ytterbium trichloride.

Results and Discussion

The neutral ligand 2-(isopropylamino)tropone [(*i*PrAT)-H] was prepared according to literature procedures from tropolone.[29] Treatment of (*i*PrAT)H with an excess of *n*BuLi in toluene followed by crystallization from hot toluene resulted in the hexameric species [(*i*PrAT)Li]$_6$ (**1**) (Scheme 2). The new complex has been characterized by standard analytical/spectroscopic techniques, and the solid-state structure was established by single-crystal X-ray diffraction. Selected bond lengths are given in the caption of

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Figure 1. Compound **1**, which crystallizes in the triclinic space group $P\bar{1}$, forms a hexameric framework in the solid state (Figure 1). The asymmetric unit consists of lithium 2-(isopropylamino)troponate trimers. The hexamer shown in Figure 1 results when the crystallographically imposed symmetry is applied. Thus, in the center of the hexamer a crystallographic inversion center is observed. The hexameric core can be understood as two six-membered Li_3O_3 rings, which are tied together by the aminotroponate moieties. Each of the Li_3O_3 rings shows a chair-type conformation. Therefore, the Li–O–Li and O–Li–O bond angles of the hexameric Li–O core deviate slightly from the ideal 120° and thus range from 115.0(2)° to 122.5(2)°. The Li–O bond lengths are in the range of 1.929(4) Å to 1.975(4) Å. The aminotroponate moieties, which bridge both six-membered rings, are almost perpendicularly located to the Li_3O_3 ring plane. Since no solvent molecules are bound to the lithium atoms, they are – as a result of the hexamerization – tetracoordinated. Similar hexameric structures were observed before in some lithium alkoxides such as lithium phenolate,[25] $[LiC{\equiv}CSiMe_2C_6H_4OMe]_6$,[26] and the thiophene derivative $[LiOSiMe_2(2\text{-}C_4H_3S)]_6$.[27] The ^1H and $^{13}C\{^1H\}$ NMR spectra of compound **1** show the expected set of signals for the $(i\mathrm{PrAT})^-$ ligand. The signals of the isopropyl C*H* atom of **1** appears as a well-resolved septet at δ = 3.68 ppm, which is in the range of the corresponding potassium compound [(*i*PrAT) K] (δ = 3.61).[24]

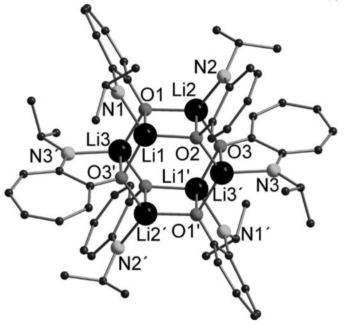
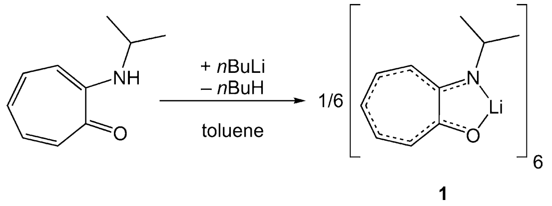
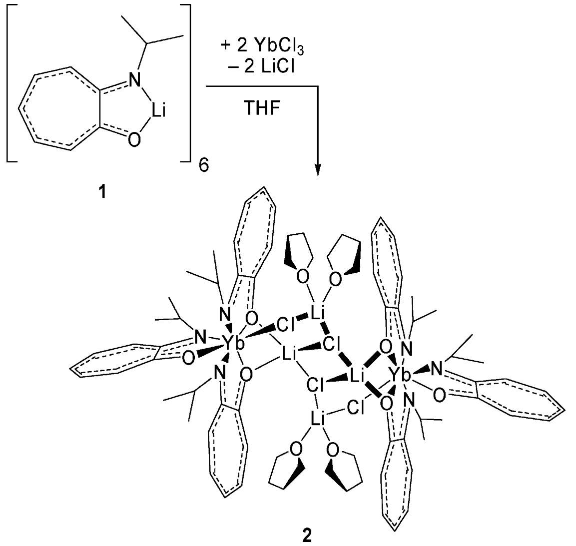


Figure 1. Solid-state structure of **1** showing the atom labeling scheme. Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°]: Li1–N1 1.990(5), Li1–O1 1.972(4), Li1–O2 1.942(4), Li1–O3′ 1.952(4), Li2–N2 1.985(5), Li2–O1 1.929(4), Li2–O2 1.972(4), Li2–O2′ 1.939(4), Li2–O3 1.954(5), Li3–N3′ 1.988(4), Li3–O1 1.944(4), Li3–O2′ 1.939(4), Li3–O3′ 1.975(4); Li1–O1–Li2 84.5(2), Li1–O1–Li3 83.0(2), Li1–O2–Li2 84.1(2), Li1–O2–Li3′ 118.8(2), Li1–O3′–Li3 82.7(2), Li1′–O3–Li2 122.5(2), Li2–O3–Li3′ 83.0(2), Li2–O2–Li3′ 83.5(2), N1–Li1–O1 82.00(2), N1–Li1–O2 122.3(2), N1–Li1–O3′ 121.7(2), O1–Li1–O2 95.5(2), O1–Li1–O3′ 97.0(2), O2–Li1–O3′ 115.7(2), N2–Li2–O1 124.6(2), N2–Li2–O2 82.1(2), N2–Li2–O3 120.3(2), O1–Li2 O2 95.9(2), O1–Li2 O3 115.0(2), O2–Li2–O3 96.5(2), N3′–Li3–O1 117.5(2), N3′–Li3–O2′ 123.1(2), N3′–Li3–O3′ 82.01(15), O1–Li3–O2′ 119.1(2), O1–Li3 O3′ 97.2(2), O2′–Li3–O3′ 96.9(2).



Scheme 2.

Next, we were interested to learn about the coordination behavior of the $(i\mathrm{PrAT})^-$ ligand in lanthanide chemistry. In an earlier work, we had already reported on the homoleptic tris(aminotroponiminato) complexes of yttrium and samarium $[(i\mathrm{PrAT})_3\mathrm{Ln}]$, which were obtained by treatment of [(*i*PrAT)K] with $LnCl_3$. Unfortunately, these compounds could structurally not be characterized and therefore not much is known about the coordination chemistry of the $(i\mathrm{PrAT})^-$ ligand in lanthanide chemistry. Now, we decided to change the reaction conditions and the aminotroponate starting material to obtain crystalline material. Reaction of **1** and $YbCl_3$ in a 1:2 stoichiometric ratio resulted in the dimeric lithium chloride bridged compound $[(i\mathrm{PrAT})_3\mathrm{Li_2Cl_2Yb}]_2$ (**2**), which is an "ate" complex (Scheme 3). The solid-state structure of compound **2** was investigated by single-crystal X-ray diffraction. Selected bond lengths and angles are given in the caption of Figure 2. Compound **2** crystallizes in the triclinic space group $P\bar{1}$ and has two independent molecules in the asymmetric unit. In the solid state, compound **2** consists of two $[(i\mathrm{PrAT})_3\mathrm{Yb}]$ subunits which are bridged by four LiCl units. In this unique structure, the Yb atoms are heptacoordinated by three $(i\mathrm{PrAT})^-$ ligands and one chlorine atom (Cl2). The center of compound **2** contains an Li–Cl–Li–Cl square with a crystallographic inversion center. Each of the lithium atoms of the central square plane (Li1 and Li1′) is tetracoordinated by two chlorine atoms (Cl1 and Cl1′) and two oxygen atoms of the $(i\mathrm{PrAT})^-$ ligands. The other lithium atom (Li2) bridges the central Li–Cl–Li–Cl square and the $[(i\mathrm{PrAT})_3\mathrm{LnCl}]^-$ subunit by being coordinated by Cl1 and Cl2. The fourfold coordination is completed by two THF molecules. Within this complicated structure, the bond lengths and angles are in the expected range. The bond angles of Cl1–Li1–Cl1′



Scheme 3.

[98.7(4)°] and Li1–Cl1–Li1′ [81.3(4)°] within the central Li–Cl–Li–Cl square indicate a deviation from the ideal square-planar geometry.

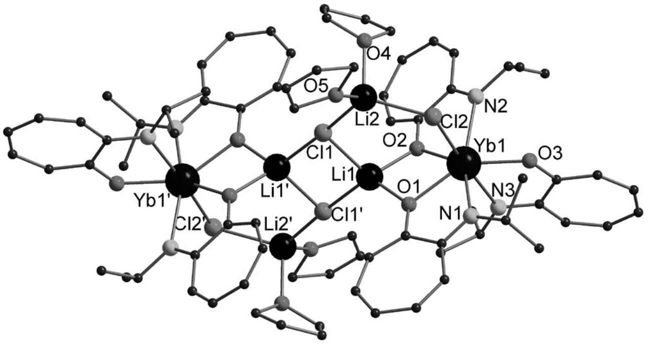


Figure 2. Solid-state structure of one of the two independent molecules of **2** showing the atom labeling scheme. Hydrogen atoms are omitted for clarity. Selected distances [Å] and angles [°] of one of the two independent molecules in the unit cell: Li1–O1 1.921(13), Li1–O2 1.920(12), Li1–Cl1 2.334(11), Li1–Cl1′ 2.355(13), Li2–O4 1.939(14), Li2–O5 1.922(13), Li2–Cl1 2.323(13), Li2–Cl2 2.366(13), Yb1–O1 2.251(4), Yb1–O2 2.225(5), Yb1–O3 2.152(5), Yb1–N1 2.506(6), Yb1–N2 2.517(6), Yb1–N3 2.468(6), Yb1–Cl2 2.663(2); O1–Li1–O2 83.9(5), O1–Li1–Cl1 117.2(6), O2–Li1–Cl1 113.2(6), O2–Li1–Cl1′ 121.9(6), O1–Li1–Cl1′ 123.2(6), Cl1–Li1–Cl1′ 98.7(4), O4–Li2–O5 103.3(6), O4–Li2–Cl1 106.1(6), O4–Li2–Cl2 105.0(6), O5–Li2–Cl1 109.9(6), O5–Li2–Cl2 112.8(7), Cl1–Li2–Cl2 118.2(5), Li1–Cl1–Li1′ 81.3(4), O1–Yb1–O2 70.0(2), O1–Yb1–O3 144.3(2), O1–Yb1–N1 65.6(2), O1–Yb1–N2 133.5(2), O1–Yb1–N3 95.7(2), O2–Yb1–O3 136.6(2), O2–Yb1–N1 135.6(2), O2–Yb1–N2 65.5(2), O2–Yb1–N3 88.3(2), O3–Yb1–N1 83.6(2), O3–Yb1–N2 81.1(2), O3–Yb1–N3 67.3(2), N1–Yb1–N2 157.4(2), N1–Yb1–N3 93.4(2), N3–Yb1–N2 95.9(2), O1–Yb1–Cl2 87.40(13), O2–Yb1–Cl2 97.11(13), O3–Yb1–Cl2 107.63(14), N1–Yb1–Cl2 83.64(14), N2–Yb1–Cl2 85.27(14), N3–Yb1–Cl2 174.5(2).

Whereas the incorporation of one LiCl unit into the coordination sphere is quite common {e.g. in $[(\eta^5\text{-}C_5Me_5)_2Sm(\mu\text{-}Cl)_2Li(THF)_2]$[28]}, the inclusion of four units of an alkali metal salt is, to the best of our knowledge, unique in lanthanide chemistry.

Conclusion

We have prepared the hexameric lithium 2-(isopropylamino)troponate complex $[(i\text{PrAT})Li]_6$ by reaction of (iPrAT)H with nBuLi. Further reaction of $[(i\text{PrAT})Li]_6$ with $YbCl_3$ in a 1:2 stoichiometric ratio resulted in the unusual dimeric complex $[(i\text{PrAT})_3Li_2Cl_2Yb]_2$, in which the two $[(i\text{PrAT})_3Yb]$ subunits are bridged by four LiCl units. Even though the incorporation of one LiCl unit is well known in lanthanide chemistry, the insertion of four LiCl units is, to the best of our knowledge, unknown.

Experimental Section

General Considerations: All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high-vacuum (10^{-3} Torr) line, or in an argon-filled MBraun glove box. THF was predried with Na wire and distilled under nitrogen from Na/K alloy benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and n-pentane) were distilled under nitrogen from $LiAlH_4$. All solvents for vacuum-line manipulations were stored in vacuo over $LiAlH_4$ in resealable flasks. Deuterated solvents were obtained from Chemotrade or Euriso-Top GmbH (99 atom-% D). NMR spectra were recorded with a Jeol JNM-LA 400 FT-NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. IR spectra were obtained with a Shimadzu FTIR-8400s spectrometer. Raman spectra were recorded with a Bruker RFS 100 instrument. The melting point was measured with a hot-stage microscope under vacuum in a sealed capillary and is uncorrected. Elemental analyses were carried out with an Elementar vario EL III apparatus. 2-(Isopropylamino)tropone[29] and $YbCl_3$[30] were prepared according to literature procedures.

$[(i\text{PrAT})Li]_6$ (1): A 2.5 M solution of nBuLi in hexane (6.0 mL, 15.0 mmol) was slowly added to a cooled (0 °C) solution of (iPrAT)H (2.0 g, 12.0 mmol) in toluene (20 mL). The solution was slowly warmed to room temperature, and subsequently stirred for another 2 h. The solution was concentrated in vacuo, and the product was obtained analytically pure as a yellow powder. X-ray quality crystals were obtained from an oversaturated toluene solution at 60 °C. Yield: 1.0 g (50%). M.p. 114 °C. ^1H NMR ([D$_8$]THF, 400 MHz, room temp.): δ = 1.15 [d, $^3J_{H,H}$ = 6.2 Hz, 6 H, $CH(CH_3)_2$], 3.68 [sept, $^3J_{H,H}$ = 6.2 Hz, 1 H, $CH(CH_3)_2$], 5.92 (d, $^3J_{H,H}$ = 9.3 Hz, 1 H, CH_{ring}), 6.35 (d, $^3J_{H,H}$ = 10.4 Hz, 1 H, CH_{ring}), 6.59 (m, 3 H, CH_{ring}) ppm. $^{13}C\{^1H\}$ NMR ([D$_8$]THF, 110.4 MHz, room temp.): δ = 23.9 [$CH(CH_3)_2$], 48.6 [$CH(CH_3)_2$], 108.5 (C_{ring}), 115.8 (C_{ring}), 116.1 (C_{ring}), 133.6 (C_{ring}), 134.9 (C_{ring}), 165.2 (C_{ring}), 179.7 (C_{ring}). Raman (solid): $\tilde{\nu}$ = 3048 (w), 3024 (w), 2966 (w), 2929 (w), 2914 (w), 2866 (w), 1610 (m), 1574 (m), 1518 (vs), 1484 (s), 1410 (vs), 1278 (s), 1233 (m), 951 (m), 756 (s), 486 (s) cm^{-1}.

$[(i\text{PrAT})_3Li_2Cl_2Yb]_2$ (2): THF (30 mL) was condensed into a mixture of $[(i\text{PrAT})Li]_6$ (1.1 g, 1.1 mmol) and $YbCl_3$ (0.61 g, 2.2 mmol) at –78 °C, and the mixture was stirred at room temp. for 30 h. The solvent was removed in vacuo, and the remaining residue was extracted with a mixture of toluene and THF. The product was obtained after several crystallization steps as yellow X-ray quality crystals from hot THF. Yield: 0.56 g (29%). IR (KBr): $\tilde{\nu}$ = 2966 (m), 2928 (m), 2876 (m), 1599 (m), 1576 (m), 1508 (vs), 1470 (m), 1443 (s), 1408 (s), 1337 (s), 1273 (m), 1219 (m), 1165 (w), 1132 (w), 1045 (w), 885 (w), 752 (w), 719 (m) cm^{-1}. $C_{76}H_{104}Cl_4Li_4N_6O_{10}Yb_2$ (1777.35): calcd. C 51.36, H 5.90, N 4.73; found C 51.28, H 5.58, N 4.64.

X-ray Crystallographic Studies of 1 and 2: Crystals of **1** were obtained from toluene. Crystals of **2** were grown from hot THF. A suitable crystal was covered with mineral oil (Aldrich) and mounted onto a glass fiber. The crystal was transferred directly to the cold (–73 °C) N_2 stream of a STOE IPDS 2T diffractometer. Subsequent computations were carried out with an Intel Pentium IV PC. Data collection and refinement: SHELXS-97,[31] SHELXL-97.[32] $C_{60}H_{72}Li_6N_6O_6$ (**1**): triclinic, space group $P\bar{1}$ (No. 2); lattice constants a = 10.4506(13), b = 12.9331(15), c = 13.149(2) Å, α = 63.654(9), β = 66.625(9), γ = 75.714(9)°, V = 1456.4(3) Å^3, Z = 1; μ(Mo-K_α) = 0.073 mm^{-1}; $2\theta_{max.}$ = 50.2°; 4846 [R_{int} = 0.0485] independent reflections measured, of which 4846 were considered observed with $I > 2\sigma(I)$; max. residual electron density 0.034 and –0.170 e/A^{-3}; 352 parameters (all non-hydrogen atoms were calculated anisotropically; the positions of the hydrogen atoms were calculated for idealised positions); $R1$ = 0.0545; wR_2 = 0.1208. $C_{76}H_{104}Cl_4Li_4N_6O_{10}Yb_2$ (**2**): triclinic, space group $P\bar{1}$ (No. 2); lattice constants a = 12.7077(8), b = 16.6165(9), c =

20.1610(11) Å, α = 99.400(4), β = 94.849(5), γ = 103.038(5)°, V = 4058.9(4) Å^3, Z = 2; μ(Mo-K_α) = 2.479 mm^{-1}; $2\theta_{\text{max.}}$ = 50.2°; 14276 [R_{int} = 0.0741] independent reflections measured, of which 10562 were considered observed with $I > 2\sigma(I)$; max. residual electron density 1.085 and –1.350 e/A^{-3}; 859 parameters (all non hydrogen atoms except the disordered THF molecules were calculated anisotropically; the positions of the hydrogen atoms were calculated for idealised positions); $R1$ = 0.0523; wR_2 = 0.1384. CCDC-669222 and -669223 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] Review: a) G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem.* **1999**, *111*, 448–468; *Angew. Chem. Int. Ed.* **1999**, *38*, 428–447; b) R. Kempe, *Angew. Chem.* **2000**, *112*, 478–504; *Angew. Chem. Int. Ed.* **2000**, *39*, 468–493.

[2] Review: a) F. T. Edelmann, *Angew. Chem.* **1995**, *107*, 2647–2669; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2466–2488; b) F. T. Edelmann, D. M. M. Freckmann, H. Schumann, *Chem. Rev.* **2002**, *102*, 1851–1896; c) F. T. Edelmann, in: R. H. Crabtree, D. M. P. Mingos, *Comprehensive Organometallic Chemisty III*, Pergamon Press, Oxford, **2007**, p. 1–190.

[3] a) R. R. Schrock, *Acc. Chem. Res.* **1997**, *30*, 9–16; b) L. H. Gade, *Acc. Chem. Res.* **2002**, *35*, 575–582.

[4] a) F. Guérin, D. H. McConville, J. J. Vittal, *Organometallics* **1996**, *15*, 5586–5590; b) V. C. Gibson, B. S. Kimberley, A. J. P. White, D. J. Williams, P. Howard, *Chem. Commun.* **1998**, 313–314.

[5] a) H. Görls, B. Neumüller, A. Scholz, J. Scholz, *Angew. Chem.* **1995**, *107*, 732–735; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 673–676; b) J. Scholz, H. Görls, H. Schumann, R. Weimann, *Organometallics* **2001**, *20*, 4394–4402.

[6] Review: a) F. T. Edelmann, *Coord. Chem. Rev.* **1994**, *137*, 403–481; b) F. T. Edelmann, *Top. Curr. Chem.* **1996**, *179*, 113–148.

[7] a) S. Bambirra, D. van Leusen, A. Meetsma, B. Hessen, J. H. Teuben, *Chem. Commun.* **2003**, 522–523; b) S. Bambirra, M. W. Bouwkamp, A. Meetsma, B. Hessen, *J. Am. Chem. Soc.* **2004**, *126*, 9182–9183.

[8] P. J. Bailey, S. Pace, *Coord. Chem. Rev.* **2001**, *214*, 91–141.

[9] a) Y. Zhou, G. P. A. Yap, D. S. Richeson, *Organometallics* **1998**, *17*, 4387–4391; b) J. Zhang, R. Cai, L. Weng, X. Zhou, *Organometallics* **2004**, *23*, 3303–3308; c) A. A. Trifonov, G. G. Skvortsov, D. M. Lyubov, N. A. Skorodumova, G. K. Fukin, E. V. Baranov, V. N. Glushakova, *Chem. Eur. J.* **2006**, *12*, 5320–5327; d) D. Heitmann, C. Jones, P. C. Junk, K.-A. Lippert, A. Stasch, *Dalton Trans.* **2007**, 187–189; e) C. Pi, R. Liu, P. Zheng, Z. Chen, X. Zhou, *Inorg. Chem.* **2007**, *46*, 5252–5259.

[10] a) T. I. Gountchev, T. D. Tilley, *Organometallics* **1999**, *18*, 2896–2905; b) D. D. Graf, W. M. Davis, R. R. Schrock, *Organometallics* **1998**, *17*, 5820–5824; c) A. Spannenberg, M. Oberthür, H. Noss, A. Tillack, P. Arndt, R. Kempe, *Angew. Chem.* **1998**, *110*, 2190–2192; *Angew. Chem. Int. Ed.* **1998**, *37*, 2079–2082; d) W. P. Kretschmer, A. Meetsma, B. Hessen, T. Schmalz, S. Qayyum, R. Kempe, *Chem. Eur. J.* **2006**, *12*, 8969–8978; e) M. Zimmermann, K. W. Törnroos, R. Anwander, *Angew. Chem.* **2007**, *119*, 3187–3191; *Angew. Chem. Int. Ed.* **2007**, *46*, 3126–3130.

[11] R. Duchateau, T. Tuinstra, E. A. C. Brussee, A. Meetsma, P. T. van Duijnen, J. H. Teuben, *Organometallics* **1997**, *16*, 3511–3522.

[12] W. E. Piers, D. J. H. Emslie, *Coord. Chem. Rev.* **2002**, *233–234*, 131–155.

[13] a) P. W. Roesky, *Chem. Ber./Recueil* **1997**, *130*, 859–862; b) P. W. Roesky, *Eur. J. Inorg. Chem.* **1998**, 593–596; c) M. R. Bürgstein, H. Berberich, P. W. Roesky, *Organometallics* **1998**, *17*, 1452–1454.

[14] a) H. V. R. Dias, W. Jin, Z. Wang, *Inorg. Chem.* **1996**, *35*, 6074–6079; b) D. P. Steinhuebel, S. J. Lippard, *Organometallics* **1999**, *18*, 109–111; c) D. P. Steinhuebel, S. J. Lippard, *Inorg. Chem.* **1999**, *38*, 6225–6233.

[15] a) M. R. Bürgstein, P. W. Roesky, *Organometallics* **2003**, *22*, 1372–1375; b) N. Meyer, A. Zulys, P. W. Roesky, *Organometallics* **2006**, *25*, 4179–4182; c) N. Meyer, P. W. Roesky, *Dalton Trans.* **2007**, 2652–2657.

[16] a) P. W. Roesky, *Inorg. Chem.* **1998**, *37*, 4507–4511; b) P. W. Roesky, M. R. Bürgstein, *Inorg. Chem.* **1999**, *38*, 5629–5632; c) P. W. Roesky, *J. Organomet. Chem.* **2000**, *603*, 161–166.

[17] Review: R. H. Holm, *Prog. Inorg. Chem.* **1971**, *14*, 241–401.

[18] a) H. V. R. Dias, W. Jin, Z. Wang, *Inorg. Chem.* **1996**, *35*, 6074–6079; b) H. V. R. Dias, W. Jin, *Inorg. Chem.* **1996**, *35*, 6546–6551; c) H. V. R. Dias, Z. Wang, W. Jin, *Coord. Chem. Rev.* **1998**, *176*, 67–86.

[19] a) A. Zulys, M. Dochnahl, D. Hollmann, K. Löhnwitz, J.-S. Herrmann, P. W. Roesky, S. Blechert, *Angew. Chem.* **2005**, *117*, 7972–7976; *Angew. Chem. Int. Ed.* **2005**, *44*, 7794–7798; b) M. Dochnahl, J.-W. Pissarek, S. Blechert, K. Löhnwitz, P. W. Roesky, *Chem. Commun.* **2006**, 3405–3407.

[20] a) N. Meyer, K. Löhnwitz, A. Zulys, P. W. Roesky, M. Dochnahl, S. Blechert, *Organometallics* **2006**, *25*, 3779–3783; b) J. Meiners, J.-S. Herrmann, P. W. Roesky, *Inorg. Chem.* **2007**, *46*, 4599–4604.

[21] D. Pappalardo, M. Mazzeo, P. Montefusco, C. Tedesco, C. Pellecchia, *Eur. J. Inorg. Chem.* **2004**, 1292–1298.

[22] Ti: M. Mazzeo, M. Lamberti, A. Tuzi, R. Centore, C. Pellecchia, *Dalton Trans.* **2005**, 3025–3031. Ni:; a) F. A. Hicks, M. Brookhart, *Organometallics* **2001**, *20*, 3217–3219; b) F. A. Hicks, J. C. Jenkins, M. Brookhart, *Organometallics* **2003**, *22*, 3533–3545; c) J. C. Jenkins, M. Brookhart, *J. Am. Chem. Soc.* **2004**, *126*, 5827–5842.

[23] V, Mn, Ni, Cu, Zn: A. Mori, R. Mori, M. Takemoto, S. Yamamoto, D. Kuribayashi, K. Uno, K. Kubo, S. Ujiie, *J. Mater. Chem.* **2005**, *15*, 3005–3014.

[24] S. Dehnen, M. R. Bürgstein, P. W. Roesky, *J. Chem. Soc., Dalton Trans.* **1998**, 2425–2430.

[25] L. M. Jackman, D. Cizmeciyan, P. G. Williard, M. A. Nichols, *J. Am. Chem. Soc.* **1993**, *115*, 6262–6267.

[26] B. Goldfuss, P. von Rague Schleyer, F. Hampel, *J. Am. Chem. Soc.* **1997**, *119*, 1072–1080.

[27] B. Goldfuss, P. von Rague Schleyer, F. Hampel, *Organometallics* **1997**, *16*, 5032–5041.

[28] W. J. Evans, J. A. Grate, I. Bloom, T. T. Peterson, R. J. Doedens, H. Zhang, J. L. Atwood, *Inorg. Chem.* **1986**, *25*, 3614–3619.

[29] H. V. R. Dias, W. Jin, R. E. Ratcliff, *Inorg. Chem.* **1995**, *34*, 6100–6105.

[30] M. D. Taylor, C. P. Carter, *J. Inorg. Nucl. Chem.* **1962**, *24*, 387–391.

[31] G. M. Sheldrick, *SHELXS-97, Program of Crystal Structure Solution*, University of Göttingen, Germany, **1997**.

[32] G. M. Sheldrick, *SHELXL-97, Program of Crystal Structure Solution*, University of Göttingen, Germany, **1997**.

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