“Self-Assembly” in Organolanthanide Chemistry: Formation of Rings and Clusters

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The cyclopentadienyl ligand is ubiquitous in organolanthanide chemistry, and due to its steric bulk, rigidity, and thermal and chemical stability it is often referred to as a stabilizing backbone.[1] Variation of the substitution pattern of the cyclopentadienyl anion directs the solubility, reactivity, and molecular structure of the resulting complexes, and promising precursor compounds for the catalysis[2] and material sciences evolve.[3] The bonding in organometallic compounds of the large and hard rare earth cations is commonly described as predominantly ionic.[4] Consequently, in the absence of bulky ligands the metal centers extend their coordination number by intermolecular ligand bridges. However, such oligomerization reactions are as a rule undesired and afford products which are hard to characterize. Therefore, a steady challenge in preparative organolanthanide chemistry is the synthesis of mononuclear, soluble complexes, as in the case of well-defined precatalyst systems. In this hunt for discrete molecules the “less soluble products” were often not given the necessary attention. Recently, an increasing number of more highly associated rare earth cyclopentadienyl compounds with intriguing structural features have been reported. Their structural motifs range from infinite chains and band structures to isolated rings and clusters.[5] A decisive criterion for the formation of ring and cluster structures is the relative number of cyclopentadienyl ligands per metal center, the “Cp/Ln” ratio (Table 1).

Cp/Ln ≥ 2

The ionic character of cyclopentadienyl derivatives becomes obvious in the structural chemistry of homoleptic complexes $Ln^{II}Cp_2$ and $Ln^{III}Cp_3$. Depending on cation size and substitution pattern of the cyclopentadienyl ligand discrete molecules and oligomeric rings or polymeric chains can be observed.[1] However, biscyclopentadienyl or “lanthanidocene” complexes of type Cp_2LnCl have always attracted increased attention, and derivatives of the latter are meanwhile established in homogeneous catalysis.[2] Heteroligands X (e.g., H^-, Cl^-, NR_2^-, OR^-) and the presence of neutral donor ligands (e.g., THF, OEt_2) markedly influence the structure of the usually formed mononuclear or X-bridged dinuclear complexes “Cp_2LnXL”. Cleavage of the donor ligands from thermally stable rare earth cyclopentadienyl derivatives is best achieved by the “toluene method”[6] and often leads to the formation of more highly associated complexes. In the presence of sterically demanding Cp ligands like, for example, pentamethylcyclopentadienyl (Cp*), dinuclear X-bridged complexes are routinely formed.[7] On the other hand, unsubstituted Cp ligands also favor polymeric X-bridged chain and band structures and sometimes even finite ladder motifs.[1]

Thermal cleavage of L or “steric degradation” of the heteroligand X can also result in self-assembly, producing ring systems. In 1985 Bottomley et al. first described the formation

Table 1. Organolanthanide rings and clusters involving cyclopentadienyl ligands.

Formula[a]	Cp/Ln (ring atoms)	Ref.
rings		
$[\{(C_5H_5)_2Sc(\mu\text{-}F)\}_3]$ **1**	2(6)	[8]
$[\{(C_5H_4tBu)_2Sm(\mu\text{-}F)\}_3]$ **2**	2(6)	[9]
$[\{(C_5Me_5)_2Sm(\mu\text{-}Cl)\}_3]$ **3**	2(6)	[10]
$[\{(C_5Me_5)_2Sm(CNC_6H_{11})(\mu\text{-}CN)\}_3]$ **4**	2(9)	[11]
$[\{(C_5H_4Me_2\text{-}1,3)_2Y(\mu\text{-}H)\}_3]$ **5**	2(6)	[12a]
$[(C_5Me_5)_6Sm_3(\mu\text{-}SiH_3)(\mu_3\text{-}\eta^1,\eta^1,\eta^2\text{-}SiH_2\text{-}SiH_2)]$ **6**	2(6)	[13]
$[\{(C_5Me_5)_2Sm(\mu\text{-}SiH_3)\}_3]$ **7**	2(6)	[13]
$[(C_5Me_5)_6Yb(\mu\text{-}F)_4]$ **8**	1.5(8)	[14]
$[\{(C_5Me_5)_2Sm(\mu\text{-}CN)\}_6]$ **9**	2(18)	[16]
rings with a central atom		
$[\{(C_5H_5)_2Er\}_3(\mu_3\text{-}H)(\mu\text{-}H)_2(\mu\text{-}Cl)][Li(thf)_4]$ **10**	2(6)	[12b]
$[\{(C_5H_5)_2Y(\mu\text{-}OCH_3)\}_3(\mu_3\text{-}H)]_2[Li(thf)_3]_2$ **11**	2(6)	[12c]
$[\{(C_5H_4)_2Lu\}_3(\mu\text{-}H)_2(\mu_3\text{-}H)]$ **12**	2	[15a]
clusters		
$[(C_5H_3tBu_2\text{-}1,3)LuH]_4[AlH_4(OEt_2)]_2[AlH_4]_2$ **13**	1	[15b]
$[(C_5Me_5)_6Yb_5(\mu_4\text{-}F)(\mu_3\text{-}F)_2(\mu\text{-}F)_6]$ **14**	1.2	[17]
$[Nd_6(2,4\text{-}C_7H_{11})_6Cl_{12}(thf)_2]$ **15**[b]	1	[18]
$[(C_5Me_4SiMe_2tBu)_6Yb_6(\mu_3\text{-}I)_8][Li(thf)_4]_2$ **16**	1	[19]
clusters with a central atom		
$[(C_5H_5)_5Yb_5(\mu_5\text{-}O)(\mu_3\text{-}OCH_3)_4(\mu\text{-}OCH_3)_4]$ **17** (Ln = Yb, **17a**; Gd, **17b**)	1	[20]
$[(C_5Me_5)_6Sm_6Se_{11}]$ **18**	1	[21]
$[(C_5H_5)_3Yb_3(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_3(thf)_3][(C_5H_5)_6Yb_6(\mu_6\text{-}Cl)(\mu\text{-}Cl)_{12}]$ **19**	1	[22]
$[(C_5H_5)_{12}Sm_{12}(\mu_3\text{-}Cl)_{24}]$ **20**	1	[22]

[a] Except for **8** $[Yb^{II}/Yb^{III}]$ and **16** $[Yb^{II}]$ all derivatives contain Ln^{III}.
[b] $(2,4\text{-}C_7H_{11})$ = 2,4-dimethylpentadienyl.

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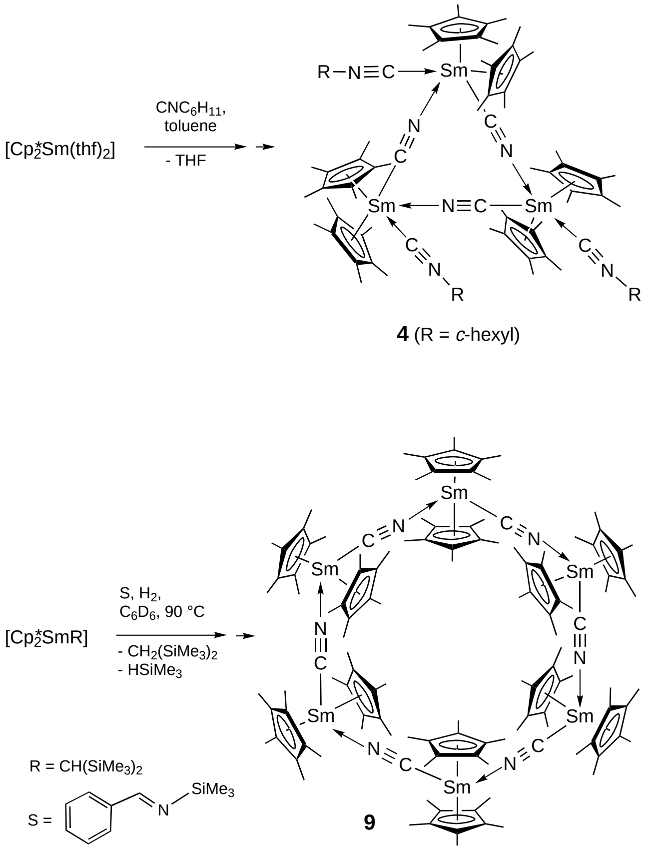
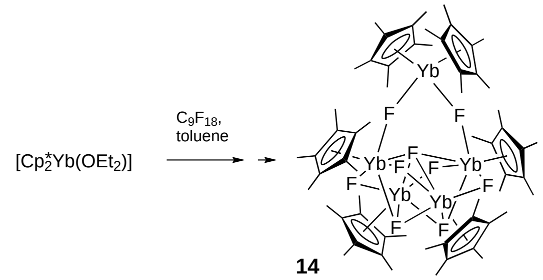
of a ring structure with more than two rare earth atoms and without a central atom for $[Cp_2Sc(\mu\text{-}F)]_3$ (**1**).[8] Later on similar ring arrangements were found for Cp/Ln = 2 (e.g., **2**–**7**, Table 1).[9–13] The 8-ring structure of **8** is a rare exception, displaying a Cp/Ln ratio of 1.5.[14] The presence of small and hard ligands like H^- and F^- seems to encourage ring formation. Additionally, a ring-stabilizing effect is observed by centrally positioned atoms like the (μ_3-H) atoms in complexes **10** and **11**, even accomplishing the exchange of bridging ligands.[12,15] The largest ring system so far was recently isolated in the group of Marks. The 18-membered $[Sm(CN)]_6$ ring in **9** exhibits a S_6-symmetric chair conformation and is formed by a thermal heteroligand degradation according to Scheme 1.[16] In the presence of coordinating isonitrile ligands Evans et al. could isolate a nine-membered $[Sm(CN)]_3$ ring even earlier (**4**, Scheme 1).[11]



Scheme 1. Formation of $[Sm(CN)]_n$ ring structures through ligand degradation.

Cp/Ln < 2

A lower Cp/Ln ratio inevitably creates further coordination sites at the metal center. This favors the formation of oligonuclear metal–ligand cluster compounds, mostly with total absence or at least a clearly substoichiometric amount of denucleating donor ligands (**13**–**20**, Table 1).[15,17–22] A byproduct (**14**) isolated by Watson et al. in 1989 according to Scheme 2 turned out to be a "ring–cluster hybrid" with Cp/Ln = 1.2, which nicely underlines this trend.[17] While the "Cp^*_2Yb" unit participates in a six-membered ring, the "Cp*Yb" units form a "butterfly cluster".[23]



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Scheme 2. Formation of Yb^{III} ring-cluster hybrids through fluorination of a Yb^{II} complex (C_9F_8 = perfluoro-2,4-dimethyl-3-ethylpent-2-ene).

The class of monocyclopentadienyl systems (Cp/Ln = 1) was neglected for a long time due to its apparent "steric unsaturation".[24] In the meantime however, even for these rare earth derivatives some catalytic activity was detected.[25]

The formation of cluster compounds with Cp/Ln = 1 was first established for oxo-centered, heteroleptic alkoxide clusters (**17**, Ln = Yb, Gd).[20] The recently isolated "Sm_6Se_{11}" cluster **18** confirms the stabilizing effect of centrally positioned heteroatoms in Ln^{III} clusters.[20] These so-called interstitial atoms can often be observed in metal-rich rare earth halides.[26] On the other hand, the outer ligand sphere of the dianionic, highly symmetrical "Yb_6I_8" cluster **16** seems to compensate the lower charge density at the softer Yb^{II} fairly well.[19] A recent publication of Kretschmer, Teuben, and Troyanov finally pushed organolanthanide cluster compounds into the center of interest,[22] abandoning former terms such as "random product" or "result of insufficient handling techniques". Starting with an improved synthesis of complexes $[CpLnCl_2(thf)_x]$[27] where ate complex formation is prevented under mild reaction conditions (Scheme 3), desolvation/recrystallization procedures lead to less soluble products, which could be identified by X-ray analysis as highly symmetrical cyclopentadienyl clusters (Figure 1).

$$[LnCl_3(thf)_3] + Me_3SiCp \xrightarrow[\text{2) THF}]{\text{1) toluene, - }Me_3SiCl} [CpLnCl_2(thf)_3] \xrightarrow{\Delta,\text{ - THF}} \mathbf{19}\text{ (Ln = Yb)}, \mathbf{20}\text{ (Ln = Sm)}$$

Scheme 3. Improved synthesis of monocyclopentadienyl rare earth complexes.

The "self-organization" of 12 "$CpSmCl_2$" fragments in **20**, producing a highly symmetrical icosahedral cluster unit with a molecular formula of $Cp_{12}Sm_{12}Cl_{24}$, is so far unique in transition metal chemistry. The electrostatic stabilization of the Sm_{12} icosahedron through a centered Cl_4 tetrahedron inspires a discussion whether even larger anion clusters could be enclosed in even larger metal cation clusters. Surprisingly, under similar crystallization conditions the smaller and more Lewis acidic Yb^{III} forms a cation–anion pair with a reduced degree of aggregation. This behavior is certainly directed by the cation size. However, because of increased affinity of the

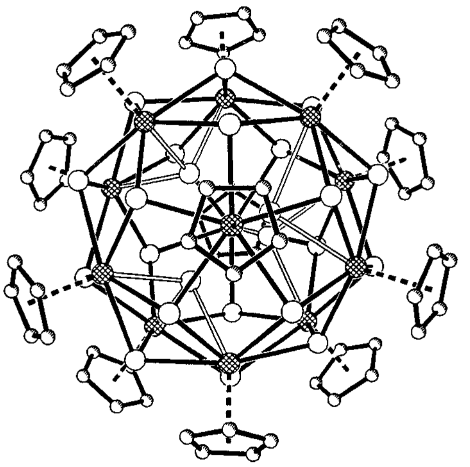


Figure 1. Molecular structure of $[Cp_{12}Sm_{12}Cl_{24}]$ (**20**).

Yb^{III} cation for THF, the desolvation is uncomplete. Therefore, comparison based on size effects remains rather vague. Again, a central μ_6-Cl atom stabilizes the anionic $[Cp_6Yb_6Cl_{13}]^-$ cluster.

"Self-assembly" along with other metalorganic rare earth compounds

While relatively few ring and cluster structures with Cp ligands could be isolated so far, cluster formation has long been an integral part of rare earth alkoxide chemistry.[28] In contrast to the purely academic interest for cyclopentadienyl cluster compounds, studies of alkoxide clusters are of considerable importance for the sol–gel technology (as model for precursor and intermediate compounds).[29] Due to their electronic and steric equivalence to the cyclopentadienyl ligand, alkoxide ligands are often discussed as alternative auxiliary ligands.[30] In homoleptic as well as in heteroleptic alkoxide complexes the presence of "central spherical charge density" like chloride, oxo and hydroxo functionalities often account for the driving force of cluster formation. But also desolvation may play a decisive role.[30] The self-organization to certain cluster sizes like in **21**–**26** seems to be partly influenced by the intra- and intermolecular coordination of additional neutral ligands.[29–33] From a thermodynamic and structural viewpoint a most interesting feature of alkoxide chemistry is the formation of rings. This is demonstrated with the intriguing 20-membered ring structure of decameric **27**[33] and the 8-ring structure of **28**[34] which is stabilized through agostic interactions (Scheme 4).

$[Nd_6(\mu_6\text{-}Cl)(\mu_3\text{-}O\mathit{i}Pr)_2(\mu\text{-}O\mathit{i}Pr)_9(O\mathit{i}Pr)_6]$ **21**

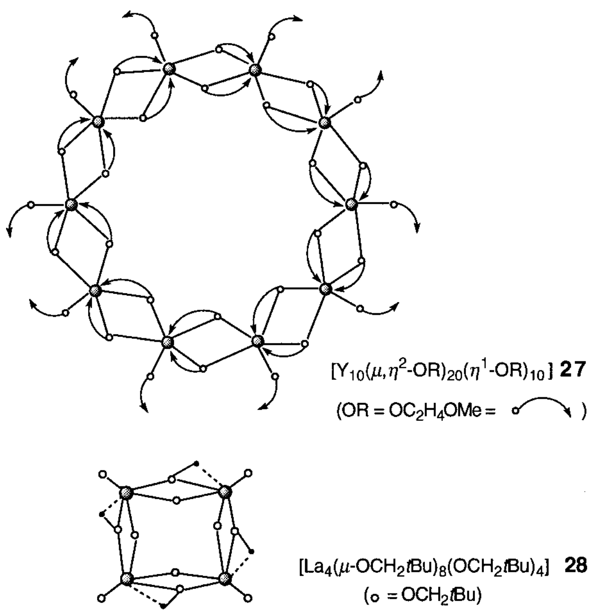
$[Y_5(\mu_5\text{-}O)(\mu_3\text{-}O\mathit{i}Pr)_4(\mu\text{-}O\mathit{i}Pr)_4(O\mathit{i}Pr)_5]$ **22**

$[Y_{14}(\mu_4\text{-}O)_2(\mu_3\text{-}Cl)_2(\mu_3\text{-}O\mathit{t}Bu)_4(\mu\text{-}O\mathit{t}Bu)_{14}(\mu\text{-}Cl)_8(O\mathit{t}Bu)_{10}(thf)_4]$ **23**

$[Lu_4(\mu_4\text{-}O)(\mu_3\text{-}OH)(\mu_3,\eta^2\text{-}OR)(\mu,\eta^2\text{-}OR)_3(\mu,\eta^1\text{-}OR)(\eta^1\text{-}OR)_4]$ **24**
$R = CMe_2CH_2OMe$

$[Gd_6(\mu_4\text{-}O)(\mu_3,\eta^2\text{-}OR)_4(\mu,\eta^2\text{-}OR)_6(\mu,\eta^1\text{-}OR)_2(\eta^1\text{-}OR)_4]$ **25**
$R = C_2H_4OMe$

$[Pr_8(\mu_4\text{-}O)_4(\mu_3,\eta^2\text{-}OR)_4(\mu,\eta^2\text{-}OR)_8(\mu,\eta^1\text{-}OR)_2(\eta^1\text{-}OR)_2(OPMe_3)_2]$ **26**
$R = C_2H_4OMe$



$[Y_{10}(\mu,\eta^2\text{-}OR)_{20}(\eta^1\text{-}OR)_{10}]$ **27**
(OR = OC_2H_4OMe =)

$[La_4(\mu\text{-}OCH_2\mathit{t}Bu)_8(OCH_2\mathit{t}Bu)_4]$ **28**
(o = $OCH_2\mathit{t}Bu$)

Scheme 4. Ring formation in rare earth alkoxide chemistry.

The most recent developments in classic rare earth coordination chemistry concerning "self-organization" also require mention. Large, oligonuclear heterobimetallic clusters of type **29**[35a] and **30** (with a central μ_{12}-ClO_4 anion)[35b] may be useful not only for the synthesis of magnetic nanomaterials. The study of intermetallic, magnetic interactions could also help to unravel the nature of high-temperature superconductivity in the related metal oxides. The self-assembly of heterobimetallic complexes **31** is based on polyfunctionalized podate ligands, whose single ligand segments code for different metal cations.[36] This concept creates fascinating possibilities for the development of programmable, molecular luminescent probes, as well as biological and analytical sensors.

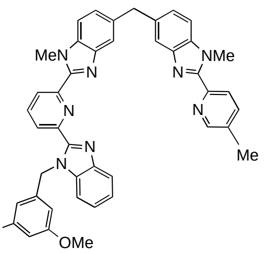
Finally it can be concluded that organolanthanide cluster syntheses (still) cannot yet be planned and are inevitably characterized by random self-organization. Recently, Schnöckel

$[La_8Cu_{12}(\mu\text{-}OH)_{24}(NO_3)_{21.2}(Hmhp)_{13}(H_2O)_{5.5}][NO_3]_{2.8}\cdot 2\,Hmhp$ **29**
Hmhp = 6-methyl-2-hydroxypyridine

$[Gd_6Cu_{12}(\mu_{12}\text{-}ClO_4)(\mu_3\text{-}OH)_{24}(\mu\text{-}pyb)_{12}(H_2O)_{18}][ClO_4]_{17}\cdot n\,H_2O$ **30**
pyb = pyridineacetate

$[LaZnL_3][ClO_4]_5$ **31**

L =



et al. reported an alternative route to metalorganic cluster synthesis: Reaction of Al^I iodide and $Li[N(SiMe_3)_2]$ resulted in the extraordinary cluster **32**.[37] The chemical relationship of

$$[Al_{77}\{N(SiMe_3)_2\}_{20}]^{2-}\,2\,[Li(OEt_2)_3(\mu\text{-}I)Li(OEt)_2]^{+}\cdot 2\,C_7H_8 \qquad \mathbf{32}$$

rare earth elements and aluminum certainly has to be discussed, and reduced halides are well investigated, especially in rare earth chemistry.[26] Apart from chain, layer, and network structures isolated clusters are also formed, often containing interstitial main group atoms or electron-rich transition metals. Could these cluster associations possibly be transformed to soluble, molecular compounds by allowing them to react with, for example, $Li[N(SiMe_3)_2]$?

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[1] a) H. Schumann, J. A. Meese-Marktscheffel, L. Esser, *Chem. Rev.* **1995**, *95*, 865–986; b) F. T. Edelmann in *Comprehensive Organometallic Chemistry II, Vol. 4* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**, Chap. 2.

[2] F. T. Edelmann, *Top. Curr. Chem.* **1996**, *179*, 247–276.

[3] Y. K. Gun'ko, F. T. Edelmann, *Comm. Inorg. Chem.* **1997**, *19*, 153–184.

[4] K. N. Raymond, C. W. Eigenbrot, Jr., *Acc. Chem. Res.* **1980**, *13*, 276–283.

[5] Organolanthanide clusters have already been isolated as catalytically active species in diene oligomerization reactions, like $[\{Al_3Nd_6(\mu_3\text{-}Cl)_6(\mu\text{-}Cl)_6(\mu\text{-}Et)_9Et_5(OiPr)\}_2]$: C. Shan, Y. Lin, J. Ouyang, Y. Fan, G. Yang, *Makromol. Chem.* **1987**, *188*, 629–635.

[6] C. J. Burns, R. A. Andersen, *J. Organomet. Chem.* **1987**, *325*, 31–37.

[7] W. J. Evans, S. E. Foster, *J. Organomet. Chem.* **1992**, *433*, 79–94.

[8] F. Bottomley, D. E. Paez, P. S. White, *J. Organomet. Chem.* **1985**, *291*, 35–41.

[9] H. Schumann, M. R. Keitsch, J. Winterfeld, J. Demtschuk, *J. Organomet. Chem.* **1996**, *525*, 279–281.

[10] W. J. Evans, D. K. Drummond, J. W. Grate, H. Zhang, J. L. Atwood, *J. Am. Chem. Soc.* **1987**, *109*, 3928–3936.

[11] W. J. Evans, D. K. Drummond, *Organometallics* **1988**, *7*, 797–802.

[12] a) W. J. Evans, D. K. Drummond, T. P. Hanusa, R. J. Doedens, *Organometallics* **1987**, *6*, 2279–2285; b) W. J. Evans, J. H. Meadows, A. L. Wayda, W. E. Hunter, J. L. Atwood, *J. Am. Chem. Soc.* **1982**, *104*, 2015–2017; c) W. J. Evans, M. S. Sollberger, S. I. Khan, R. Bau, *J. Am. Chem. Soc.* **1988**, *110*, 439–446.

[13] a) S. Ya. Knjazhanskij, B. M. Bulychev, O. K. Kireeva, V. K. Belsky, G. L. Soloveichik, *J. Organomet. Chem.* **1991**, *414*, 11–22; b) S. Ya. Knjazhanskij, E. B. Lobkovsky, B. M. Bulychev, V. K. Belsky, G. L. Soloveichik, *ibid.* **1991**, *419*, 311–324.

[14] N. S. Radu, F. J. Hollander, T. D. Tilley, A. L. Rheingold, *Chem. Commun.* **1996**, 2459–2460.

[15] C. J. Burns, D. J. Berg, R. A. Andersen, *J. Chem. Soc. Chem. Commun.* **1987**, 272–273.

[16] Y. Obora, T. Ohta, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1997**, *119*, 3745–3755.

[17] P. L. Watson, T. H. Tulip, I. Williams, *Organometallics* **1990**, *9*, 1999–2009.

[18] J. Sieler, A. Simon, K. Peters, R. Taube, M. Geitner, *J. Organomet. Chem.* **1989**, *362*, 297–303.

[19] S. P. Constantine, G. M. De Lima, P. B. Hitchcock, J. M. Keates, G. A. Lawless, *Chem. Commun.* **1996**, 2421–2422.

[20] a) W. J. Evans, M. S. Sollberger, *J. Am. Chem. Soc.* **1986**, *108*, 6095–6096; b) H. Schumann, G. Kociok-Köhn, J. Loebel, *Z. Anorg. Allg. Chem.* **1990**, *581*, 69–81.

[21] W. J. Evans, G. W. Rabe, M. A. Ansari, J. W. Ziller, *Angew. Chem.* **1994**, *106*, 2200–2201; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2110–2111.

[22] W. P. Kretschmer, J. H. Teuben, S. I. Troyanov, *Angew. Chem.* **1998**, *110*, 92–94; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 88–90.

[23] The structural chemistry of oxo-centered cyclopentadienyl clusters additionally emphasizes this trend: a) A. Zalkin, D. J. Berg, *Acta Crystallogr. Sect. C* **1989**, *45*, 1630–1631; b) X. Zhou, H. Ma, Z. Wu, X. You, Z. Xu, X. Huang, *J. Organomet. Chem.* **1995**, *503*, 11–13.

[24] R. Poli, *Chem. Rev.* **1991**, *91*, 509–551.

[25] R. Taube, H. Windisch, *J. Organomet. Chem.* **1994**, *472*, 71–77.

[26] Reviews: a) J. D. Corbett, *Pure Appl. Chem.* **1984**, *56*, 1527–1543; b) G. Meyer, *Chem. Rev.* **1988**, *88*, 93–107; c) A. Simon, H.-J. Mattausch, G. J. Miller, W. Bauhofer, R. K. Kremer in *Handbook on the Physics and Chemistry of Rare Earths, Vol. 15* (Eds.: K. A. Gschneidner, Jr., L. Eyring), Elsevier, **1991**, pp. 191–285.

[27] a) S. Manastyrskyj, R. E. Maginn, M. Dubeck, *Inorg. Chem.* **1963**, *2*, 904–905; b) C. S. Day, V. W. Day, R. D. Ernst, S. H. Vollmer, *Organometallics* **1982**, *1*, 998–1003; c) M. Adam, X.-F. Li, W. Oroschin, R. D. Fischer, *J. Organomet. Chem.* **1985**, *296*, C19–C22; d) P. N. Hazin, J. C. Huffman, J. W. Bruno, *Organometallics* **1987**, *6*, 23–27.

[28] R. C. Mehrotra, A. Singh, *Chem. Soc. Rev.* **1996**, 1–13.

[29] L. G. Hubert-Pfalzgraf, *New J. Chem.* **1995**, *19*, 727–750.

[30] W. J. Evans, M. S. Sollberger, *Inorg. Chem.* **1988**, *27*, 4417–4423.

[31] R. A. Andersen, D. H. Templeton, *Inorg. Chem.* **1978**, *17*, 1962–1965.

[32] R. Anwander, F. C. Munck, T. Priermeier, W. Scherer, O. Runte, W. A. Herrmann, *Inorg. Chem.* **1997**, *36*, 3545–3552.

[33] O. Poncelet, L. G. Hubert-Pfalzgraf, J.-C. Daran, R. Astier, *J. Chem. Soc. Chem. Commun.* **1989**, 1846–1848.

[34] D. M. Barnhart, D. L. Clark, J. C. Gordon, J. C. Huffman, J. G. Watkin, B. D. Zwick, *J. Am. Chem. Soc.* **1993**, *115*, 8461–8462.

[35] a) A. J. Blake, R. O. Gould, C. M. Grant, P. E. Y. Milne, S. Parsons, R. E. P. Winpenny, *J. Chem. Soc. Dalton Trans.* **1997**, 485–495; b) X.-M. Chen, S. M. J. Aubin, Y.-L. Wu, Y.-S. Yang, T. C. W. Mak, D. N. Hendrickson, *J. Am. Chem. Soc.* **1995**, *117*, 9600–9601.

[36] C. Piguet, *Chimia* **1996**, *50*, 144–153.

[37] A. Ecker, E. Weckert, H. Schnöckel, *Nature* **1997**, *387*, 379–381.