

Chelate Complexes of Cyclopentadienyl Ligands Bearing Pendant *O*-Donors[†]Ulrich Siemeling[‡]

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Contents

I. Introduction and Background	1495
II. Scope and Limitations	1496
III. Functionalized Ligands	1496
IV. Complexes	1496
A. Main-Group Elements	1496
1. Group 1 Elements	1502
2. Group 2 Elements	1502
B. Transition Metals	1503
1. Group 4 Elements	1503
2. Group 6 Elements	1514
3. Group 7 Elements	1514
4. Group 8 Elements	1515
C. Rare-Earth Elements (Ln)	1515
1. Ln(II) Compounds	1516
2. Ln(III) Compounds	1516
D. Actinoid Elements	1523
V. Applications	1523
VI. Conclusion and Outlook	1523
VII. Acknowledgment	1523
IX. References	1523



Ulrich Siemeling was born in Herford, Germany, in April 1961. He studied chemistry and English at the University of Bielefeld. He received his doctoral degree there under the supervision of Prof. Peter Jutzi in January 1990. After a postdoctoral year at the University of Durham (U.K.) with Dr. Vernon Gibson (now Prof. Gibson of Imperial College, London), he returned to the University of Bielefeld in April 1991, where he started independent research. Immediately after his habilitation there in December 1996, he was appointed Hochschuldozent. He recently moved to the University of Kassel, where he is now Full Professor of Organometallic Chemistry. He has received numerous fellowships and awards, including a doctoral fellowship by the Studienstiftung des deutschen Volkes (1987), a Heisenberg fellowship by the Deutsche Forschungsgemeinschaft (1997), and a Bennisgen-Foerder Award of the State of Northrhine-Westfalia (1999). His current scientific interests are centered around catalysis, supramolecular chemistry, nanostructured materials, and the public understanding of science.

I. Introduction and Background

Cyclopentadienyl ligands (C_5R_5) are ubiquitous in organometallic chemistry. Among the first organometallic compounds containing such a ligand was potassium cyclopentadienide, reported by J. Thiele in 1901.¹ Even earlier came the publication of a species which contained a *functionalized* cyclopentadienyl ligand, namely, sodium nitrocyclopentadienide.² However, it was the serendipitous preparation of ferrocene reported in the early 1950s^{3,4} that triggered the remarkable development of cyclopentadienyl chemistry, which is still going on today at a rapid pace.

In organo-transition-metal chemistry cyclopentadienyl systems show excellent spectator ligand qualities and are reliable workhorses among the ligands available. They normally bind very strongly to transition metal centers (predominantly in an η^5 fashion),⁵ and their steric and electronic properties can easily be modified by variation of the organic sub-

stituents on the C_5 ring.^{6–8} Even chiral systems are very well developed now.^{9,10} It was recently estimated that 80% of all organometallic compounds of the transition metals are cyclopentadienyl complexes, with C_5H_5 (Cp) and C_5Me_5 (Cp*) being the most prominent ligands used.¹¹

In main-group chemistry, on the other hand, both σ -¹² and π -bound¹³ cyclopentadienyl ligands may act as leaving groups.^{14,15} This behavior can be put to good use and in fact gives rise to the arsenal of main-group cyclopentadienyl compounds available as cyclopentadienyl transfer reagents. Nevertheless, bulky cyclopentadienyl ligands have been utilized successfully for the stabilization of low-valent and hypercoordinated main-group element compounds.^{8,11}

Cyclopentadienyl chemistry has clearly attained a state of maturity now. This success is in no small part due to the fact that the steric and electronic properties of cyclopentadienyl ligands can be fine-tuned by the judicious choice of substituents. However, the basic features of these ligands cannot be extended much further this way.

[†] In memoriam for Heinrich Tappe, who lay the earliest foundations of my academic career.

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For the task of “teaching an old dog new tricks” a different and more flexible concept is needed which is based on the interplay of several constituent ligand components. Ligand functionalization is the key here. The introduction of functional groups can give rise to fascinating emergent properties.

The chemistry of phosphanes, which also represent a prominent class of spectator ligands, has led the way with early beginnings in the 1970s. A remarkably successful approach in this area has been the modification of these ligands by fairly weak donor groups, leading to a potentially oligodentate ligand architecture with a hemilabile binding profile¹⁶ (realized, for example, in the phosphane-ether ligands^{16–18}). Such systems have proved to be able to stabilize reactive metal–ligand fragments in a reversible way, which can be very useful for catalytic purposes. Another success story is that of sulfonated arylphosphanes, whose transition-metal complexes are very water-soluble. These functionalized phosphane ligands have made possible a real breakthrough in industrial catalysis, namely, catalytic processes in aqueous biphasic media.¹⁹

Far from mere imitation, the philosophy of ligand functionalization has also been followed in cyclopentadienyl chemistry and again proved to be very successful. The beginnings can be located around about 1980,²⁰ and this now prospering area started to take off in the early 1990s. As a manifestation of this development, a review of this field was imminent, and four such papers appeared between 1994 and 1995 within a period of only 12 months. The earliest of these is by J. Okuda and gives an overview of complexes which contain cyclopentadienyl ligands bearing a whole range of functional groups, namely, alkenyl, amino, amido, ether, alkoxy, phosphanyl, and thioether moieties.²¹ The last three of this quartet concentrate on work from the respective authors' labs (P. Jutzi, U. Siemeling, and C. Qian) and are centered around the coordination chemistry of cyclopentadienyl ligands functionalized with a dimethylaminoethyl side chain,^{22,23} a pendant pyridyl group,²³ and a methoxyethyl group,²⁴ respectively. It is the chemistry of cyclopentadienyl compounds with nitrogen donors in the side chain that has received the most attention over the past few years. This is reflected by fifth and sixth review papers, which appeared only recently. That by P. Jutzi and T. Redeker gives a full account of aminoethyl-functionalized cyclopentadienyl complexes of d-block elements;²⁵ that by J. Okuda and T. Eberle focuses mainly on complexes with linked amido–cyclopentadienyl ligands.²⁶

To date, complexes containing *O*-, *P*- and *S*-functionalized cyclopentadienyl ligands have received considerably less attention by reviewers than *N*-functionalized systems, although their chemistry has equally flourished.

II. Scope and Limitations

This paper is intended to give a comprehensive overview of complexes containing *O*-functionalized cyclopentadienyl ligands (including the closely re-

lated indenyl and fluorenyl systems). The literature is covered up to the fall of 1999.

There are just three limitations: First, only chelate complexes will be considered (in other words, the functional group has to be coordinated to the metal center). Second, the coordinated oxygen atom of the functional group is part of a side chain and therefore not attached directly to the cyclopentadienyl ligand. Cyclopentadienone complexes are thus excluded. Third, work which, in the absence of any supportive data, merely speculates about such chelate complexes will not normally be considered.

In a similar way, *P*- and *S*-functionalized systems are treated in the paper in this issue by H. Butenschön. We hope that these two reviews will prove useful by providing a valuable complement to the existing literature on functionalized cyclopentadienyl compounds.

III. Functionalized Ligands

The ligands encountered in this review are collected in Chart 1. Two principal types can be made out, namely, (i) ligands functionalized with a neutral *O*-donor (mostly an ether group) and (ii) ligands with a formally anionic *O*-donor (mostly an alkoxy or aryloxy group).

A large number of other *O*-functionalized cyclopentadienyl ligands do exist, but they will not be considered here, because they have not been observed to act as chelate ligands.

Generally speaking, the ligands in focus are substituted cyclopentadienyl systems, where at least one substituent bears an *O*-functional group. Since excellent review papers are available which describe the use and formation of substituted (and even of functionalized)^{27,28} cyclopentadienyl ligands in great detail,^{6–11} ligand synthesis need not be covered here.

IV. Complexes

The chelate complexes relevant to this survey are treated according to the central metal. For convenience, the complexes are collected in a Table 1, which contains details of the information available for each compound.

It should be noted that, in the absence of X-ray structural data, it may sometimes be questionable whether a cyclopentadienyl ring functionalized with a neutral *O*-donor is acting as a chelating ligand in a particular complex, and even in cases where this question has been settled for the solid state by a crystal structure analysis it may be unclear for the species in solution. Chelation means metal–oxygen bonding. As a rule, this is accompanied by noticeable shifts of the characteristic $\nu(\text{C–O})$ IR bands to lower wavenumbers and, for diamagnetic compounds, of the NMR signals of the hydrogen and carbon atoms around the coordinated O atom to lower field. In those cases where the chelating coordination is only weak in solution, strongly temperature-dependent NMR signals may be observed.

A. Main-Group Elements

Investigations of chelate complexes of *O*-functionalized cyclopentadienyl ligands are extremely rare for

Chart 1

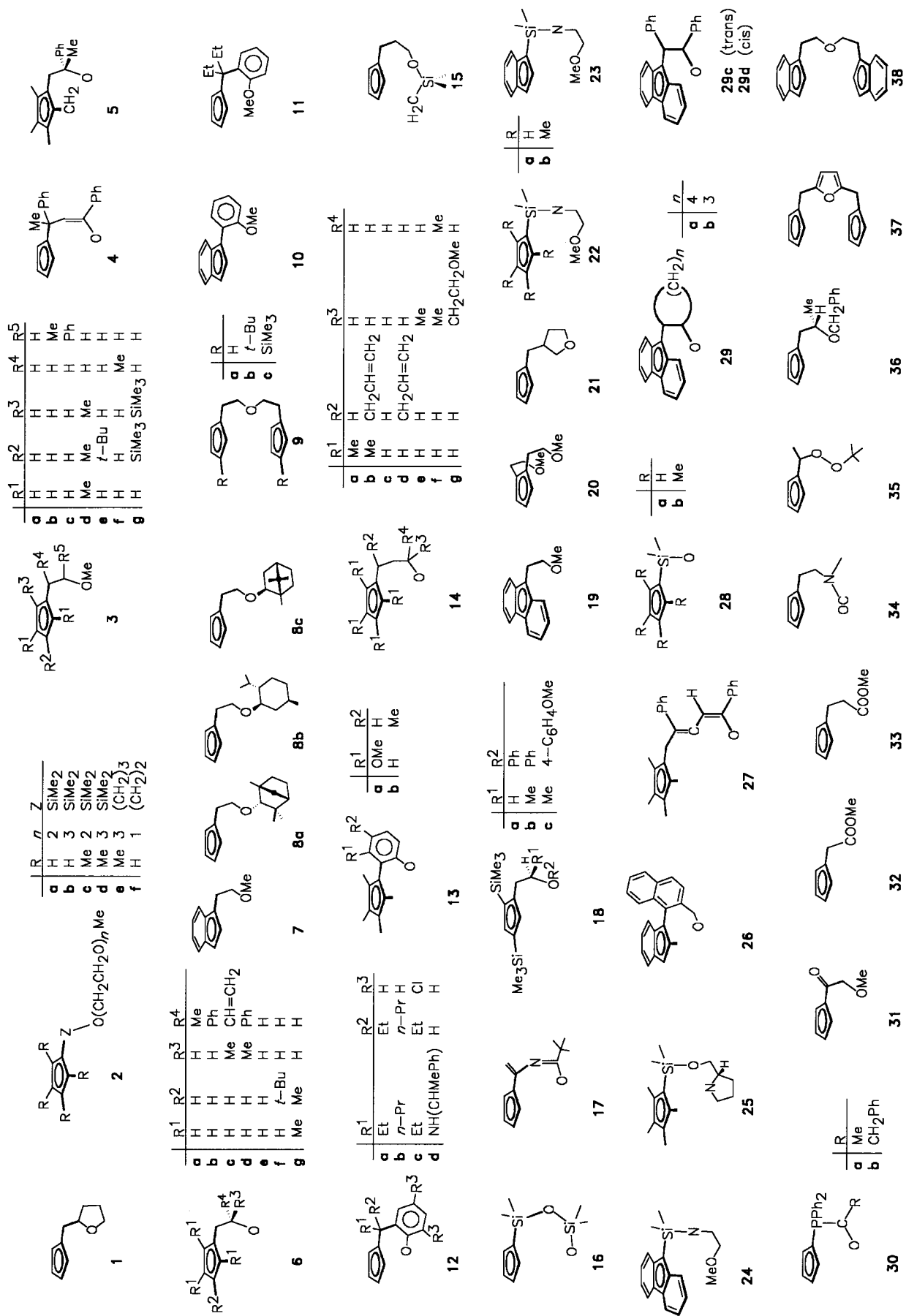


Table 1. Data Available for the Chelate Complexes Discussed in the Text (in the Order of Appearance): Chemical Analysis (CA), IR, MS, NMR, Crystal Structure Determination (CSD), and Further Data (Brackets Denote That Only Selected Values Are Given)

compound	CA	IR	MS	NMR	CSD	further data
1 Na(THF) ²⁹					✓	
2a K ³³						
2b K ³³				¹³ C		MW determ
2c K ³³						
2d K ³³						
2e K ³²						
(3a) ₂ Ca ³⁴	✓	✓		¹ H, ¹³ C	✓	
(3b) ₂ Ca ³⁵	✓		✓	¹ H, ¹³ C		[α] _D ²⁵
(3c) ₂ Ca ³⁵	✓		✓	¹ H, ¹³ C	✓	[α] _D ²⁵
(3a) ₂ Sr ³⁴	✓	✓		¹ H, ¹³ C		
[4 Sr(THF) ₂] ₂ ³⁸	✓	✓	✓	¹ H, ¹³ C	✓	
(3a) ₂ Ba ³⁴	✓	✓		¹ H, ¹³ C		
(2f) ₂ Ba ⁴⁰	✓	✓		¹ H, ¹³ C		
5 TiCp ^{*42}	✓		(✓)	¹ H, ¹³ C	✓	
6a Ti(MeC ₅ H ₄) ⁴³			✓	¹ H, ¹³ C		
6b Ti(MeC ₅ H ₄) ⁴³			✓	¹ H, ¹³ C		
6c Ti(MeC ₅ H ₄) ⁴³			✓	¹ H, ¹³ C		
6d Ti(MeC ₅ H ₄) ⁴³			✓	¹ H, ¹³ C		
3a TiCl ₃ ^{47,50,51}	✓ ^{47,50}	✓ ⁴⁷	✓ ⁴⁷	¹ H, ^{47,50} ¹³ C ⁵⁰	✓ ⁴⁷	
3f TiCl ₃ ⁴⁸		(✓)			✓	
1 TiCl ₃ ⁴⁹	✓	✓	✓	¹ H	✓	
7 TiCl ₃ ⁵¹	✓			¹ H		
8a TiCl ₃ ⁵⁰				¹ H, ¹³ C		
8b TiCl ₃ ⁵⁰				¹ H, ¹³ C		
9a TiCl ₂ ⁵⁵	✓	✓		¹ H		XPS
<i>μ</i> - 9a (CpTiCl ₂) ₂ ⁵⁵	✓	✓		¹ H		XPS
10 TiCl ₃ ⁵¹	✓			¹ H		
(11) ₂ TiCl ₂ ^{56,57}			✓			
[11 TiCl(<i>μ</i> -O)] ₂ ^{56,57}					✓	
12a TiCpCl ₂ ⁵⁶⁻⁶⁰	✓ ^{56,57}	✓ ^{56,57}	✓ ^{56,57}	¹ H, ^{56,57,59} (¹³ C) ⁵⁹	✓ ^{56,57,60}	
12aTi3a Cl ₂ ^{57,60}	✓ ⁵⁷		✓ ⁵⁷	¹ H ⁵⁷		
12aTi1 Cl ₂ ⁶⁰						
12b TiCpCl ₂ ⁵⁷	✓		✓	¹ H		
(12a) ₂ Ti ^{56,57,60}	✓ ⁵⁷		✓ ⁵⁷	¹ H ⁵⁷		
12c TiCl ₂ ⁵⁹	✓	✓	✓	¹ H, (¹³ C)	(✓)	
13a Ti(CH ₂ CMe ₃) ₂ ⁶¹						
13a Ti(CH=CH ₂) ₂ ⁶¹						
13b Ti(CH ₂ Ph) ₂ ⁶²	✓			¹ H, ¹³ C	✓	
[13b Ti(CH ₂ Ph)] ⁺ ⁶²				¹ H, ¹³ C		
[14a Ti(CH ₂ Ph)] ⁺ ⁶³				¹ H, ¹³ C		
14a Ti(CH ₂ Ph) ₂ ⁶³	✓	✓		¹ H, ¹³ C		
14a Ti(CH ₂ CMe ₃) ₂ ⁶³	✓	✓		¹ H, ¹³ C		
14a Ti(CH ₂ SiMe ₃) ₂ ⁶³	✓	✓		¹ H, ¹³ C, ²⁹ Si		
[15 Ti(CH ₂ SiMe ₃)] ⁺ ⁶³				¹ H, ¹³ C, ²⁹ Si		
[14a Ti(CH ₂ SiMe ₂ SiMe ₃)THF] ⁺ ⁶³				¹ H, ¹³ C, ²⁹ Si		
14a TiMe ₂ ⁶³	✓	✓		¹ H, ¹³ C		
14a TiCl ₂ ^{54,63,64}	✓	✓ ^{54,63}	✓ ⁶⁴	¹ H, ¹³ C	✓ ⁵⁴	
14b TiCl ₂ ⁶⁴	✓	✓	✓	¹ H, ¹³ C		
14c TiCl ₂ ^{64,65}	✓	✓	✓	¹ H, ¹³ C	✓ ⁶⁵	
14d TiCl ₂ ⁶⁴	✓	✓	✓	¹ H		
14e TiCl ₂ ⁶⁴	✓	✓	✓	¹ H, ¹³ C		
14f TiCl ₂ ⁶⁴	✓	✓	✓	¹ H, ¹³ C		
14 g TiCl ₂ ⁶⁴	✓	✓	✓	¹ H, ¹³ C	✓	
6e TiCl ₂ ⁶⁵	✓	✓	✓	¹ H, ¹³ C	✓	
16 TiCl ₂ ^{66,67}	✓	✓	✓	¹ H, ¹³ C, ²⁹ Si ⁶⁶		
(17) ₂ Ti ⁶⁸		✓		¹ H, ¹³ C		
3a ZrCl ₃ ^{50,74}	✓ ⁵⁰		✓ ⁵⁰	¹ H, ¹³ C	✓ ⁵⁰	
3g ZrCl ₃ ⁷¹	✓			¹ H, ¹³ C		
18a ZrCl ₃ ⁷¹	✓			¹ H, ¹³ C		
18b ZrCl ₃ ⁷¹	✓			¹ H, ¹³ C		
18c ZrCl ₃ ⁷¹	✓			¹ H, ¹³ C		
3d ZrCl ₃ ⁷²		(✓)		¹ H, ¹³ C	✓	
19 ZrCl ₃ ⁷³	✓			¹ H, ¹³ C	✓	
3a ZrCl ₃ (H ₂ O) ⁷⁴	✓			¹ H	✓	
3a ZrCl ₃ (MeOH) ⁷⁴	✓			¹ H	✓	
20 ZrCl ₃ ⁷⁶			✓	¹ H	✓	
(3a) ₂ Zr(OTf) ₂ ⁷⁷	✓			¹ H, ¹³ C, ¹⁹ F		
(8a) ₂ Zr(OTf) ₂ ⁷⁷				¹ H, ¹³ C		
(8b) ₂ Zr(OTf) ₂ ⁷⁷				¹ H, ¹³ C, ¹⁹ F		
(3a) ₂ ZrCl(OTf) ⁷⁷				¹ H, ¹³ C		
(8a) ₂ ZrCl(OTf) ⁷⁷				¹ H, ¹³ C		

Table 1. (Continued)

compound	CA	IR	MS	NMR	CSD	further data
(8b) ₂ ZrCl(OTf) ⁷⁷				¹ H, ¹³ C		
(8c) ₂ ZrCl(OTf) ⁷⁷				(¹³ C)		
[(1) ₂ ZrMe] ⁺ ⁷⁸						calcd energy/geom
[(21) ₂ ZrMe] ⁺ ⁷⁸						calcd energy/geom
22aZrCl ₂ ⁸¹			(✓)	¹ H, ¹³ C, ²⁹ Si		
23ZrCl ₂ ⁸¹			(✓)	¹ H, ¹³ C, ²⁹ Si		
24ZrCl ₂ ⁸¹			(✓)	¹ H, ¹³ C		
22bZrCl ₂ ^{82,83}	✓ ⁸³		✓ ⁸³	¹ H, ⁸³ ¹³ C ⁸³		
22bHfCl ₂ ⁸³	✓		✓	¹ H, ¹³ C	✓	
22bHfI ₂ ^{84,85}	✓ ⁸⁵		✓ ⁸⁵	¹ H, ⁸⁵ ¹³ C ⁸⁵		
22bZrClMe ⁸³			✓	¹ H, ¹³ C		
22bZrCl(CH ₂ Ph) ⁸³	✓		✓	¹ H, ¹³ C		
22bHfCl(CH ₂ Ph) ⁸³	✓		✓	¹ H, ¹³ C		
22bZrCl[<i>o</i> -C ₆ H ₄ (CH ₂ NMe ₂)] ⁸³	✓		✓	¹ H, ¹³ C		
22bHfCl[<i>o</i> -C ₆ H ₄ (CH ₂ NMe ₂)] ⁸³	✓		✓	¹ H, ¹³ C		
22bZrCl(EtC=N- <i>t</i> -Bu) ⁸⁵	✓		✓	¹ H, ¹³ C		
22bHfCl(EtC=N- <i>t</i> -Bu) ⁸⁵	✓		✓	¹ H, ¹³ C		
22bZrMe ₂ ^{82,85}	✓ ⁸⁵		✓ ⁸⁵	¹ H, ⁸⁵ ¹³ C ⁸⁵	✓ ⁸⁵	
22bHfMe ₂ ⁸⁵	✓		✓	¹ H, ¹³ C		
22bZrEt ₂ ⁸⁴				¹ H		
22bHfEt ₂ ^{84,85}	✓		✓	¹ H, ¹³ C		
22bZr- <i>n</i> -Pr ₂ ^{84,85}			✓ ⁸⁵	¹ H, ¹³ C		
22bHf- <i>n</i> -Pr ₂ ^{84,85}			✓	¹ H, ¹³ C		
22bZr- <i>n</i> -Bu ₂ ^{84,85}	✓		✓	¹ H, ¹³ C		
22bHf- <i>n</i> -Bu ₂ ^{84,85}	✓		✓	¹ H, ¹³ C	✓ ⁸⁴	
22bZr(CH ₂ Ph) ₂ ⁸⁵	✓		✓	¹ H, ¹³ C		
22bHf(CH ₂ Ph) ₂ ⁸⁵	✓		✓	¹ H, ¹³ C		
22bZr(CH ₂ SiMe ₃) ₂ ⁸⁵	✓		✓	¹ H, ¹³ C		
22bHf(CH ₂ SiMe ₃) ₂ ⁸⁵	✓		✓	¹ H, ¹³ C		
22bZrPh ₂ ⁸⁵	✓		✓	¹ H, ¹³ C	✓	
22bHfPh ₂ ⁸⁵	✓		✓	¹ H, ¹³ C		
[22bZrMe][MeB(C ₆ F ₅) ₄] ⁸⁵				¹ H, ¹³ C, ¹⁹ F		
22bHfMe(MeC=O) ⁸⁴			✓	¹ H, ¹³ C		
22bHf- <i>n</i> -Bu(<i>n</i> -BuC=O) ^{84,85}				¹ H, ¹³ C		
25Zr(NMe ₂) ₂ ⁸⁶				¹ H, ¹³ C		
(H25)ZrCl ₃ ⁸⁶	✓			¹ H, ¹³ C	✓	
25ZrCl ₂ ⁸⁶	✓			¹ H, ¹³ C		
14aHfCp*(<i>O</i> - <i>t</i> -Bu) ⁸⁷				¹ H		
(12a) ₂ Zr ^{56,60}						
(13b) ₂ Zr ⁶²	✓			¹ H, ¹³ C		
(6f) ₂ Zr ⁸⁸				¹ H	✓	
6fZr3e(OTf) ⁸⁸		(✓)	(✓)	¹ H	✓	
(17) ₂ Zr ⁶⁸	✓	✓		¹ H, ¹³ C	✓	
17Zr(NEt ₂) ₂ ⁶⁸	✓	✓		¹ H, ¹³ C		
6eZr(NMe ₂) ₂ ⁹⁰		✓		¹ H, ¹³ C		
26Zr(NEt ₂) ₂ ⁹¹				¹ H, ¹³ C		
6gZr3dMe ⁹²				¹ H, ¹³ C		
6gZrCp*Me ⁹²			✓	¹ H, ¹³ C		
27ZrCp* ^{93,94}	✓	✓	✓	¹ H, ¹³ C	✓	
[6eZrCl ₃] ₂ [C ₁₄ H ₂₅ S] ₂ ⁵⁰	✓			¹ H, ¹³ C		
[28aZrCl ₂ (PhCHMeNH ₂) ₂] ₂ ⁹⁵	✓			¹ H	✓	
[28bZr(O ₂ CMe) ₂] ₂ ⁹⁶	✓			¹ H, ¹³ C	✓	
29aZrCl ₂ (THF) ₂ ⁹⁷	✓		✓	¹ H		
29bZrCl ₂ (THF) ₂ ⁹⁷			✓	¹ H		
29cZrCl ₂ (THF) ₂ ⁹⁷			✓	¹ H		
29dZrCl ₂ (THF) ₂ ⁹⁷			✓	¹ H		
30aZr(C ₅ H ₄ PPh ₂)Cl ⁹⁸	✓			¹ H, ¹³ C, ³¹ P	✓	
30aZrCpCl ⁹⁹				¹ H, ³¹ P		
30aZrCpMe ⁹⁹				¹ H, ³¹ P		
30bZrCp(CH ₂ Ph) ¹⁰⁰	✓			¹ H, ³¹ P		
30bZr(C ₅ H ₄ PPh ₂)(CH ₂ Ph) ¹⁰⁰	✓			¹ H, ¹³ C, ³¹ P		
[1Mo(CO) ₃] ⁺ ¹⁰¹						E _p (+/0)
[1Mo(CO) ₃] ¹⁰¹						
1Mn(CO) ₂ ¹⁰²		✓				
31Mn(CO) ₂ ¹⁰³		✓				
32Mn(CO) ₂ ¹⁰³		✓				
33Mn(CO) ₂ ¹⁰³		✓				
34Re(CO)Br ¹⁰⁴	✓	✓		¹ H		
34Re(CO)I ¹⁰⁴	✓	✓	✓	¹ H		
34Re(CO)(SPh) ¹⁰⁴	✓	✓	✓	¹ H, ¹³ C		
34Re(CO)(SePh) ¹⁰⁴	✓	✓	✓	¹ H, ¹³ C	✓	
2eFeCl ¹⁰⁵						
35RuCp* ¹¹⁰	✓	✓		¹ H		

Table 1. (Continued)

compound	CA	IR	MS	NMR	CSD	further data
(3a) ₂ Sm ¹¹⁴	✓		(✓)			XPS, χ_M , μ_{eff}
(3a) ₂ Yb ¹¹⁴	✓		(✓)			
(3a) ₂ Yb(THF) ¹¹⁴	✓			¹ H	✓	
(3a) ₂ Sm(THF) ¹¹⁵	✓					
(3b) ₂ Sm ³⁵	✓		✓			
(3b) ₂ Yb ³⁵	✓		✓	¹ H, ¹³ C		
(3c) ₂ Sm ³⁵	✓		✓			
(3c) ₂ Yb ³⁵	✓		✓	¹ H, ¹³ C		
9aSm(THF) ₂ ¹¹⁶	✓	✓	✓			
9aYb(THF) ₂ ¹¹⁶	✓	✓	✓	¹ H		
9aYb(DME) ¹¹⁶	✓				✓	
3aSmI ₂ (THF) ₂ ¹¹⁷	✓		✓		✓	
36LaI ₂ (THF) ₂ ¹¹⁸	✓	✓		¹ H, ¹³ C, ¹³⁹ La		
6aLaI(THF) ₂ ¹¹⁹	✓	✓		¹ H		
6aSmI(THF) ¹¹⁹	✓	✓		¹ H		
3aY[N(SiMe ₃) ₂] ₂ ¹²⁰	✓	✓	✓	¹ H		
3aYb[N(SiMe ₃) ₂] ₂ ¹²⁰	✓	✓	✓			
[3aSm(μ -C ₂₀ H ₂₀ N ₂ O ₂) ₂] ₂ ¹²¹	✓		✓		✓	
[3aDy(μ -C ₂₀ H ₂₀ N ₂ O ₂) ₂] ₂ ¹²¹	✓		✓			
(3a) ₂ YCl ^{122,123,127}	✓	✓	✓ ¹²³	¹ H, ^{123,127} ¹³ C ^{123,127}		XPS ¹²²
(3a) ₂ LaCl ¹²²⁻¹²⁴	✓ ^{122,123}	✓	✓ ¹²³	¹ H, ^{123,124} ¹³ C ^{123,124}	✓ ^{123,124}	XPS ¹²²
(3a) ₂ CeCl ¹²⁵				¹ H		χ_M
(3a) ₂ PrCl ¹²³⁻¹²⁵	✓ ¹²³	✓ ^{123,124}	✓ ¹²³	¹ H ¹²⁵		χ_M ¹²⁵
(3a) ₂ NdCl ^{124,122-125}	✓ ^{122,123}	✓ ¹²²⁻¹²⁴	✓ ¹²³	¹ H ¹²⁵	(✓) ²⁴	XPS ¹²²
(3a) ₂ SmCl ^{123,125}	✓ ¹²³	✓ ¹²³	✓ ¹²³	¹ H ¹²⁵		χ_M ¹²⁵
(3a) ₂ GdCl ^{122,123,125}	✓ ^{122,123}	✓ ^{122,123}	✓ ¹²³	¹ H ¹²⁵		XPS, ¹²² χ_M ¹²⁵
(3a) ₂ DyCl ¹²³	✓	✓	✓		✓	
(3a) ₂ HoCl ^{122,123}	✓	✓	✓ ¹²³			XPS ¹²²
(3a) ₂ ErCl ^{122,123,125,126}	✓ ^{122,123}	✓ ^{122,123}	✓ ¹²³	¹ H ¹²⁵	✓ ¹²⁶	XPS ¹²²
(3a) ₂ TmCl ¹²³	✓	✓	✓			
(3a) ₂ YbCl ^{122,123,125}	✓ ^{122,123}	✓ ^{122,123}	✓ ¹²³	¹ H ¹²⁵	✓ ¹²³	XPS ¹²²
(3a) ₂ LuCl ^{123,125}	✓ ¹²³	✓ ¹²³	✓ ¹²³	¹ H		
(1) ₂ NdCl ^{128,129}	✓	✓	✓			XPS ¹²⁸
(1) ₂ ErCl ¹²⁸	✓	✓	✓			
(1) ₂ DyCl ^{128,129}	✓	✓	✓ ¹²⁹		✓	
(1) ₂ GdCl ^{128,129}	✓	✓	✓ ¹²⁹			XPS ¹²⁸
(1) ₂ YbCl ^{129,130}	✓	✓	✓ ¹²⁹		✓ ¹³⁰	
9aYCl ^{112,131-133}	✓ ¹¹²	✓ ¹¹²	✓ ^{112,132}	¹ H, ^{112,131} ¹³ C ^{112,131}		XPS ¹¹²
9aNdCl ^{112,132}	✓ ¹¹²	✓ ¹¹²	✓			XPS ¹¹²
9aSmCl ¹¹⁶						
9aGdCl ^{112,132}	✓ ¹¹²	✓ ¹¹²	✓			XPS ¹¹²
9aHoCl ^{112,132}	✓ ¹¹²	✓ ¹¹²	✓			XPS ¹¹²
9aErCl ^{112,132}	✓ ¹¹²	✓ ¹¹²	✓			XPS ¹¹²
9aYbCl ^{112,132}	✓ ¹¹²	✓ ¹¹²	✓			XPS ¹¹²
9aLuCl ^{112,131,132}	✓ ¹¹²	✓ ¹¹²	✓ ^{112,132}	¹ H, ^{112,131} ¹³ C ^{112,131}		XPS ¹¹²
9bYCl ¹³⁴	✓	✓	✓	¹ H		
9bNdCl ¹³⁴	✓	✓	✓			
9bSmCl ¹³⁴	✓	✓	✓			
9bYbCl ¹³⁴	✓	✓	✓			
9cYCl ¹³⁴	✓	✓	✓	¹ H		
9cLaCl ¹³⁴	✓	✓	✓	¹ H		
9cNdCl ¹³⁴	✓	✓	✓			
9cYbCl ¹³⁴	✓	✓	✓			
37YCl ¹³⁵	✓	✓	✓	¹ H		
37NdCl ¹³⁵	✓	✓	✓			
37SmCl ¹³⁵	✓	✓	✓			
37YbCl ¹³⁵	✓	✓	✓			
(7) ₂ YCl ¹³⁸	✓	✓	✓	¹ H, ¹³ C	✓	
(7) ₂ LaCl ¹³⁸	✓	✓	✓	¹ H, ¹³ C		
(7) ₂ NdCl ¹³⁸	✓	✓	✓		✓	
(7) ₂ GdCl ¹³⁸	✓	✓	✓		✓	
(7) ₂ HoCl ¹³⁸	✓	✓	✓			
(7) ₂ LuCl ¹³⁸	✓	✓	✓	¹ H, ¹³ C		
38YCl(THF) ¹³⁹	✓	✓	✓	¹ H		
38PrCl(THF) ¹³⁹	✓	✓	✓			
38NdCl(THF) ¹³⁹	✓	✓	✓		✓	
38GdCl(THF) ¹³⁹	✓	✓	✓		✓	
38DyCl(THF) ¹³⁹	✓	✓	✓			
38HoCl(THF) ¹³⁹	✓	✓	✓		✓	
38LuCl(THF) ¹³⁹	✓	✓	✓	¹ H		
38Y(CH ₂ SiMe ₃) ¹⁴⁰	✓	✓	✓	¹ H	✓	
38Lu(CH ₂ SiMe ₃) ¹⁴⁰	✓	✓	✓	¹ H		
(3a) ₂ LaI ^{141,142}	✓ ¹⁴²	✓ ¹⁴²	✓ ¹⁴²	¹ H ¹⁴²	✓	

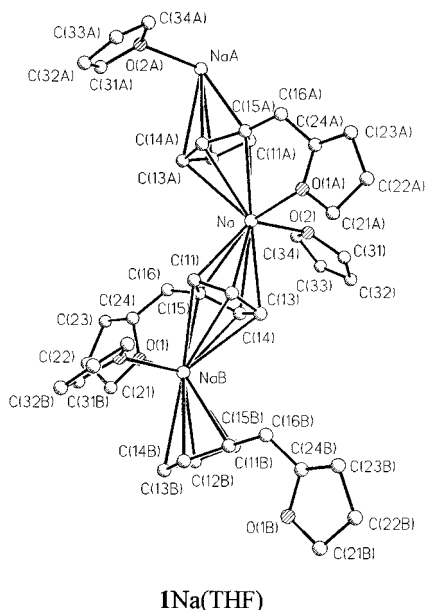
Table 1. (Continued)

compound	CA	IR	MS	NMR	CSD	further data
(3a) ₂ YI ¹⁴²	✓	✓	✓	¹ H	✓	
(3a) ₂ NdI ¹⁴¹						
(3a) ₂ SmI ¹¹⁷	✓		✓		✓	
(3a) ₂ YbI ^{115,144}	✓ ¹⁴⁴		✓ ¹⁴⁴	¹ H ¹¹⁵	✓ ¹⁴⁴	
[(3a) ₂ Nd(THF)][Co(CO) ₄] ¹⁴⁵		(✓)				
[(3a) ₂ Sm(THF)][Co(CO) ₄] ^{115,145}	✓ ¹¹⁵	✓		¹ H ¹¹⁵	✓ ¹⁴⁵	
[(3a) ₂ Yb(THF)][Co(CO) ₄] ¹¹⁵		✓		¹ H	✓	
(36) ₂ LaI ¹¹⁸	✓	✓		¹ H, ¹³ C, ¹³⁹ La		[α] _D
(36) ₂ SmI ¹¹⁸	✓	✓	✓	¹ H, ¹³ C	✓	
(3b) ₂ YCl ¹⁴⁷	✓		✓	¹ H, ¹³ C		[α] _D ²⁵
(3b) ₂ SmCl ¹⁴⁷	✓		✓	¹ H, ¹³ C	✓	[α] _D ²⁵
(3a) ₂ La(C≡CPh) ¹²⁰	✓	✓	✓	¹ H		
(3a) ₂ Yb(C≡CPh) ¹²⁰	✓	✓	✓			
(3a) ₂ Nd(CH ₂ SiMe ₃) ^{148,149}				¹ H ¹⁴⁹		
(3a) ₂ Nd[CH(SiMe ₃) ₂] ^{148,149}				¹ H ¹⁴⁹		
(3a) ₂ Nd(OCHMe ₂) ₂ ^{148,149}				¹ H ¹⁴⁹		
(3a) ₂ Nd(OCHt-Bu) ₂ ^{148,149}	✓ ¹⁴⁹			¹ H ¹⁴⁹		
(3a) ₂ Y(BH ₄) ^{127,150}	✓	✓	✓ ¹⁵⁰	¹ H, ¹³ C ¹²⁷	✓	
(3a) ₂ La(BH ₄) ¹⁵¹	✓	✓	✓			
(3a) ₂ Pr(BH ₄) ¹⁵¹	✓	✓	✓			
(3a) ₂ Nd(BH ₄) ^{149,151}	✓	✓	✓		✓ ¹⁵¹	
(3a) ₂ Sm(BH ₄) ¹⁵¹	✓	✓	✓			
(3a) ₂ Gd(BH ₄) ¹⁵¹	✓	✓	✓			
(3a) ₂ Yb(BH ₄) ¹⁵⁰	✓	✓	✓		✓	
(3a) ₂ Nd(BHEt ₃) ^{148,149}				¹ H, ¹¹ B		
(3a) ₂ Y(AlH ₄) ¹²⁷	✓	✓		¹ H, ¹³ C		
(3a) ₂ Ho(OH) ¹⁵³					✓	
(3a) ₂ Er(OH) ¹⁵⁴					✓	
9aY(OH) ¹⁵⁶	✓	✓		¹ H	✓	
(9aY) ₂ (μ-OH)(μ-C ₅ H ₇ N ₂) ¹⁵⁷	✓	✓		¹ H	✓	
(9aLu) ₂ (μ-OH)(μ-C ₅ H ₇ N ₂) ¹⁵⁷	✓	✓			✓	
(3a) ₂ YH ^{127,153,159}	✓ ^{127,153}	✓	✓ ^{153,159}	¹ H, ¹³ C ¹²⁷	✓ ¹⁵³	XPS ^{153,159}
(3a) ₂ LaH ^{153,159}	✓ ¹⁵³	✓	✓	¹ H		XPS
(3a) ₂ PrH ¹⁵³	✓	✓	✓			
(3a) ₂ HoH ¹⁵³						
9aYH ¹⁶⁰	✓	✓	✓	¹ H		
9aGdH ¹⁶⁰	✓	✓	✓			
9aErH ¹⁶⁰	✓	✓	✓			
9aYbH ¹⁶⁰	✓	✓	✓	¹ H		
9aLuH ¹⁶⁰	✓	✓	✓	¹ H		
9aYD ¹⁶⁰	✓	✓	✓	¹ H		
9aLuD ¹⁶⁰	✓	✓	✓	¹ H		
12dNdCp(THF) ¹⁶¹	✓	✓	✓		(✓)	[α] _D ²⁰
12dSmCp(THF) ¹⁶²	(✓)	✓	✓		✓	[α] _D ²⁰
(3a) ₃ Y ¹⁶³	✓	✓	✓			
(3a) ₃ La ^{163,164}	✓ ¹⁶³	✓ ¹⁶³	✓	¹ H	✓ ¹⁶³	
(3a) ₃ Pr ¹⁶³⁻¹⁶⁵	✓ ¹⁶³	✓ ¹⁶³	✓		✓ ^{163,164}	CF param, ¹⁶⁵ μ _{eff} ¹⁶⁵
(3a) ₃ Nd ^{163,167}	✓	✓	✓		✓ ¹⁶³	
(3a) ₃ Sm ^{144,166}	✓ ¹⁴⁴	✓	✓ ¹⁴⁴	¹³ C ¹⁴⁴	✓ ¹⁴⁴	CF param, ¹⁶⁶ μ _{eff} ¹⁶⁶
(3a) ₃ Gd ¹⁶³	✓	✓	✓		✓	
(3a) ₃ Yb ¹⁴⁴	✓	✓	✓			
(3a) ₂ LaCp ¹⁶⁸	✓	✓	✓	¹ H, ¹³ C		XPS
(3a) ₂ PrCp ¹⁶⁸	✓	✓	✓			XPS
(3a) ₂ NdCp ¹⁶⁸	✓	✓	✓			XPS
3aYCp ₂ ¹⁶⁹	✓	✓	✓	¹ H	✓	
3aLaCp ₂ ¹⁶⁹	✓	✓	✓	¹ H		
3aSmCp ₂ ¹⁶⁹	✓	✓	✓			
3aGdCp ₂ ¹⁶⁹	✓	✓	✓			
3aErCp ₂ ¹⁶⁹	✓	✓	✓			
3aYbCp ₂ ¹⁶⁹	✓	✓	✓			
9aYCp ^{156,170}	✓	✓ ¹⁷⁰	✓ ¹⁷⁰	¹ H, ¹³ C ¹⁷⁰		
9aNdCp ¹⁷⁰	✓	✓	✓			
9aGdCp ¹⁷⁰	✓	✓	✓			
9aHoCp ¹⁵⁶	✓	✓	✓			
9aErCp ¹⁷⁰	✓	✓	✓			
9aYbCp ¹⁷⁰	✓	✓	✓			
9aLuCp ¹⁷⁰	✓	✓	✓	¹ H, ¹³ C		
9aY(C ₅ H ₄ Me) ¹⁷⁰	✓	✓	✓			
9aHo(C ₅ H ₄ Me) ¹⁵⁶	✓	✓	✓			
9aYb(C ₅ H ₄ Me) ¹⁷⁰	✓	✓	✓			
(9bLa) ₂ (μ-9b) ¹³⁴	✓	✓	✓	¹ H		
(3a) ₂ UCl ₂ ^{171,172}	(✓) ¹⁷¹	✓ ¹⁷¹	✓ ¹⁷¹	¹ H ¹⁷¹	✓ ¹⁷²	

main-group elements. To date they have only been reported for some s-block elements, viz., Na, K, Ca, Sr, and Ba. Investigations concerning p-block elements are still lacking.

1. Group 1 Elements

a. Sodium. The only species known in this category is the sodium cyclopentadienide **1Na(THF)**, which was reported by W. Chen et al.²⁹ The compound was



obtained in 50% yield from the reaction of sodium metal with the tetrahydrofuryl-functionalized cyclopentadiene **1H** in THF. A single-crystal X-ray structure determination revealed a zigzag arrangement typical of solvated polymeric alkali-metal cyclopentadienides.³⁰ Each sodium atom is sandwiched between two nonparallel μ - π -cyclopentadienyl ligands and is further coordinated by two oxygen atoms. The distance to the THF O atom [242.4(3) pm] is significantly longer than that to the chelating tetrahydrofuryl O atom [237.5(4) pm].

b. Potassium. In the early 1990s U. Siemeling reported on the cyclopentadienes $R_4HC_5-Z-(OCH_2CH_2)_nOMe$ (**2aH**: R = H, $n = 2$, Z = SiMe₂; **2bH**: R = H, $n = 3$, Z = SiMe₂; **2cH**: R = Me, $n = 2$, Z = SiMe₂; **2dH**: R = Me, $n = 3$, Z = SiMe₂; **2eH**: R = Me, $n = 3$, Z = CH₂CH₂CH₂) functionalized with an oligoethylene glycol ether "tentacle".^{31,32} They were found to react cleanly with potassium metal in benzene or toluene, affording the corresponding potassium cyclopentadienides **2K**,^{32,33} which were shown to be essentially monomeric in benzene solution. This is in contrast to unfunctionalized systems such as CpK or Cp*K, which are insoluble coordination polymers that only dissolve in Lewis basic solvents.

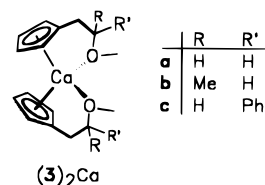
The monomeric nature of the functionalized species has been ascribed to an intramolecular coordination of the Lewis basic tentacle, whose coordination behavior was investigated for compound **2bK** by a variable-temperature ¹³C NMR study (C₆D₆ sol-

vent).³³ Temperature dependence was observed only for the signals of the two tentacle C atoms of the SiMe₂OCH₂CH₂O unit, which is in accord with the expectation that an intramolecular coordination will reduce the flexibility of just this unit mostly.

It stands to reason that, although not explicitly investigated so far, a large number of related ether-functionalized alkali-metal cyclopentadienides are chelates, too.

2. Group 2 Elements

a. Calcium. The three calcium compounds belonging in this category were all published in 1996. The calcocene (**3a**)₂Ca, which was reported by T. P. Hanusa et al., was isolated in 64% yield from the reaction of calcium bis(trimethylsilylamide) with the ether-functionalized cyclopentadiene **3aH** in toluene.³⁴ ¹H NMR spectroscopic data are in accord with a coordination of the ether groups to the metal in THF solution. However, it was found that the compound partially binds THF when recrystallized from the solvent. This is not the case for the optically active methyl- and phenyl-substituted derivatives (**3b**)₂Ca and (**3c**)₂Ca, which were obtained by H.



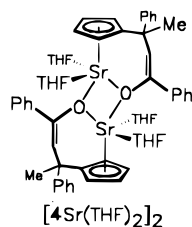
Schumann, G. A. Molander, and co-workers in 79% yield each from the respective potassium cyclopentadienide and calcium iodide in THF.³⁵ The inability to bind THF is quite remarkable when the tenacity of coordinated THF in other calcocenes is considered.³⁶

The crystal structure of (**3a**)₂Ca reveals that both ether groups are coordinated to the metal. The Ca–O bond lengths are identical within experimental error [241.2(3) and 240.1(3) pm] and compare well with corresponding values in unchelated analogues such as, for example, (*t*-BuC₅H₄)₂Ca(THF)₂,³⁷ where Ca–O bond lengths of 240.5(4) and 239.8(4) pm have been reported. Hence, the fact that the oxygen atoms are part of a chelate ring has no significant effect on their distance to the metal. The ring centroid–Ca–ring centroid and O–Ca–O angles are 136.6° and 88.4-(1)°, respectively. Both angles are slightly larger than the corresponding values observed for unchelated analogues. The crystal structure of (**3c**)₂Ca shows that the molecular parameters of this compound are fairly similar to those of (**3a**)₂Ca with the exception of the much larger O–Ca–O angle [102.54(16)°].³⁵

b. Strontium. The strontocene (**3a**)₂Sr was prepared in analogy to the corresponding calcium compound (63% yield) and showed similar behavior, including coordination of the pendant ether groups in THF solution.³⁴

The only other species known in this category is the dinuclear complex [4Sr(THF)₂]₂, which was ob-

tained by M. Westerhausen et al. in 40% yield from

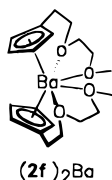


the one-pot reaction of strontium bis(trimethylsilylamide) with acetophenone and 6-methyl-6-phenylfulvene in THF.³⁸ An X-ray diffraction study shows that the molecule adopts C_i symmetry in the crystal. Each strontium atom is bound to four oxygen atoms. Owing to the formally anionic charge of the bridging enolate oxygen atoms their distances to the strontium atoms [242.1(2) and 247.6(2) pm] are much shorter than the bonds between the strontium atoms and their respective THF ligands [256.5(2) pm].

c. Barium. As for strontium, only two well-characterized barium chelates have been described to date, namely, the barocenes (**3a**)₂Ba and (**2f**)₂Ba. The former was obtained in 81% yield from barium bis(trimethylsilylamide) and **3aH** in analogy to its lighter congeners.³⁴ As for these, NMR spectroscopic data (THF-*d*₈ solvent) are in accord with coordinated ether groups.

In two earlier papers by W. S. Rees, Jr., and co-workers the synthesis of (**3a**)₂Ba and some closely related barocenes from finely divided barium metal and the ether-functionalized cyclopentadiene in THF is mentioned.^{39,40} However, the authors report that all of these compounds are particularly insoluble in common organic solvents so that relevant data could not be obtained for them.

(**2f**)₂Ba was prepared by W. S. Rees, Jr., et al. in 67% yield from barium iodide and the tentacle-bearing potassium cyclopentadienide **2fK** in THF.⁴⁰



The compound was obtained as a viscous oil, which showed moderate solubility in toluene (≥ 23 g/L). This behavior is typical of metal compounds functionalized with oligoethylene glycol ether groups and is due to the high flexibility of the amphiphilic tentacles. As a rule, such compounds crystallize only when the flexibility of the tentacle is severely restricted by coordination.⁴¹

A comparison of the ¹³C NMR spectra of (**2f**)₂Ba and the ferrocene (**2f**)₂Fe, for which ether coordination can be excluded, indicates coordination of all four oxygen atoms for (**2f**)₂Ba in C₆D₆. This appears reasonable in view of the large ionic radius of Ba²⁺. However, according to the authors an intermolecular coordination cannot be excluded, since a molecular mass determination to probe the nuclearity of the

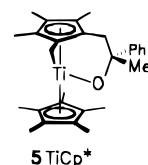
compound in solution has not been possible due to poor solubility in benzene.

B. Transition Metals

With the exception of a few rare examples from the chemistry of molybdenum, manganese, rhenium, iron, and ruthenium, chelate complexes of *O*-functionalized cyclopentadienyl ligands have only been reported in this category for the very oxophilic group 4 metals, preferentially in their highest and most Lewis acidic oxidation state. Linked alkoxy- or aryloxy-cyclopentadienyl and ether-cyclopentadienyl systems are almost equally abundant for these metals.

1. Group 4 Elements

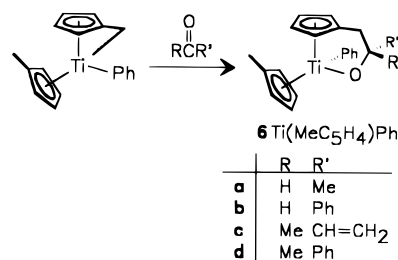
a. Titanium. The first contribution in this area was made by J. H. Teuben and co-workers in 1985.⁴² Reaction of acetophenone with [η^7 -C₅Me₃(CH₂)₂]-TiCp* in pentane afforded the alkoxy-functionalized complex **5**TiCp* in 60% yield. The reaction involves



insertion of the carbonyl function into a titanium-methylene bond. Only one diastereomer was formed due to efficient stereochemical control by the neighboring CH₂-containing metallacycle. The Ti–O bond length is 187.3 pm and the Ti–O–C angle has a value of 130.9°, which are in accord with partial double bond character. This complex turns out to be a borderline case for this review, since NMR data as well as the results of the X-ray diffraction study are more in accord with a description of this species as a fulvene complex with an sp²-hybridized methylene carbon atom.

In an analogous reaction reported by G. Erker and U. Korek in 1989, the alkoxy-linked cyclopentadienyl complexes **6a**Ti(MeC₅H₄)Ph to **6d**Ti(MeC₅H₄)Ph were formed from the precursor fulvene complex by insertion of acetaldehyde, benzaldehyde, methyl vinyl ketone, and acetophenone, respectively, into the Ti–CH₂ bond (Scheme 1).⁴³ **6a**Ti(MeC₅H₄)Ph to **6c**Ti(MeC₅H₄)Ph were obtained as red, viscous oils in almost quantitative yield, whereas **6d**Ti(MeC₅H₄)Ph was isolated as a light brown solid in 63% yield. The reactions proved to be stereoselective, yielding in each case $\geq 95\%$ of the diastereomer, whose sterically

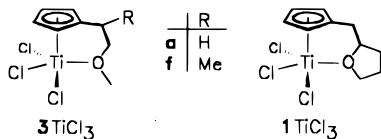
Scheme 1



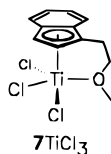
more demanding side-chain substituent is positioned *cis* with respect to the metal-bound phenyl group according to NOE experiments.

In 1985 Y. Qian and co-workers published the preparation and structural characterization of the titanocene dichloride $(\mathbf{3a})_2\text{TiCl}_2$.⁴⁴ Although this compound is not a chelate,⁴⁵ it is mentioned here due to its historic relevance. It is among the very first examples of complexes containing a cyclopentadienyl ligand with an *O*-functionalized side chain,⁴⁶ namely, $\text{C}_5\text{H}_4(\text{CH}_2\text{CH}_2\text{OMe})$ ($\mathbf{3a}$), which has meanwhile become one of the most prominent ligands employed in the subject area of this review. Furthermore, $(\mathbf{3a})_2\text{TiCl}_2$ has served as a valuable starting material for the preparation of chelate complexes.

The first well-characterized chelate complex of $\mathbf{3a}$ to be reported is the half-sandwich titanium trichloride $\mathbf{3aTiCl}_3$. This compound was first prepared in 1990 by Y. Qian and co-workers by refluxing $(\mathbf{3a})_2\text{TiCl}_2$ in a mixture of SO_2Cl_2 and SOCl_2 (95% yield).⁴⁷ The closely related $\mathbf{3fTiCl}_3$ ⁴⁸ and $\mathbf{1TiCl}_3$ ⁴⁹ were obtained analogously in 41% and 88% yield, respectively.



An alternative synthesis published in 1997 by A. A. H. van der Zeijden et al. and independently by M. D. Rausch et al. afforded $\mathbf{3aTiCl}_3$ by reaction of titanium tetrachloride with the silylated cyclopentadiene $\mathbf{3aSiMe}_3$ in either dichloromethane⁵⁰ or toluene⁵¹ in 65% and 80% yield, respectively. The latter authors also succeeded in the preparation of the indenyl analogue $\mathbf{7TiCl}_3$, which was obtained in 75%

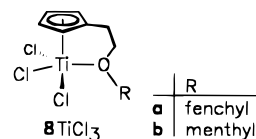


yield from the silylated indene and TiCl_4 in dichloromethane.⁵¹ Although very likely, no direct evidence is presented for its chelate structure. Very recently, Y. Qian's group applied the same method to the synthesis of $\mathbf{3fTiCl}_3$ (83% yield).⁴⁸

$\mathbf{3aTiCl}_3$ is thermally less stable than CpTiCl_3 and is also much more sensitive toward moisture. The crystal structure analysis reveals Ti–O bond lengths of 221.7(10) and 221.1(10) pm, respectively, for the two independent molecules.⁴⁷ The closely related chiral $\mathbf{3fTiCl}_3$ has a very similar structure with titanium–oxygen bond lengths of 222(3) and 226(2) pm for the two independent molecules.⁴⁸ These Ti–O distances are longer than the value of 216.5(4) pm found for $\mathbf{1TiCl}_3$,⁴⁹ which may reflect a higher Lewis basicity of the ether oxygen in the latter. The intramolecular coordination found in the crystal is fluxional in solution for such species. A variable-temperature ^1H NMR study (CD_2Cl_2 solvent) performed for $\mathbf{3aTiCl}_3$ shows that at -80°C only the chelate is present, while at room temperature the

unchelated form prevails with a proportion of ca. 70%.⁵⁰ Treatment of $\mathbf{1TiCl}_3$, $\mathbf{3aTiCl}_3$, and $\mathbf{7TiCl}_3$ with an excess of methylaluminoxane (MAO) most likely produces a cationic monoalkyl complex⁵² in each case, whose comparatively low activity in the polymerization of styrene and ethene may be due to a number of factors,⁵¹ possibly including strong intramolecular coordination of the ether function to the metal center even at higher temperatures.⁵³

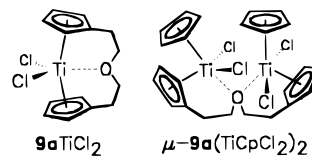
In comparison to $\mathbf{3aTiCl}_3$ and related species just described, the coordination is very much weaker for the sterically crowded analogues $\mathbf{8aTiCl}_3$ and $\mathbf{8bTiCl}_3$,



which bear large terpene-derived chiral substituents at the ether oxygen.⁵⁰ These complexes, which were prepared by A. A. H. van der Zeijden et al. from the respective silylated cyclopentadiene and titanium tetrachloride in dichloromethane, could not be obtained in analytically pure form due to their extremely high solubility.

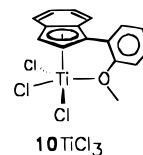
It is instructive to compare $\mathbf{3aTiCl}_3$ with the closely related, but unchelated, $[(\text{MeOCH}_2\text{CH}_2\text{CH}_2)\text{C}_5\text{H}_4]\text{-TiCl}_3$ ⁴⁸ and $[(\text{MeOCH}_2\text{CH}_2\text{CH}_2)\text{C}_5\text{Me}_4]\text{TiCl}_3$,⁵⁴ whose different structures may be attributed to the longer and more flexible spacer between the oxygen atom and the cyclopentadienyl ring (three instead of two CH_2 groups). A similar effect of the spacer length has been noted in the chemistry of complexes containing alkenyl-functionalized cyclopentadienyl ligands.²¹

S. Chen et al. have reported two titanocene derivatives, $\mathbf{9aTiCl}_2$ and $\mu\text{-9a}(\text{CpTiCl}_2)_2$, where there is evidence from XPS data for an intramolecular coordi-

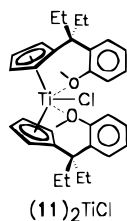


dination of an ether oxygen which is part of an *ansa*-bridge.⁵⁵ These compounds were obtained from the reaction of the sodium cyclopentadienide $\mathbf{9aNa}$ with TiCl_4 (41% yield) and CpTiCl_3 (94% yield), respectively.

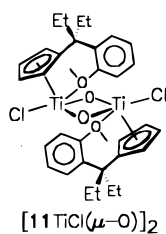
A number of compounds have been described which contain an aromatic ether group as donor. M. D. Rausch and co-workers have reported the titanium(IV) indenyl complex $\mathbf{10TiCl}_3$, which they prepared in 63% yield from TiCl_4 and $\mathbf{10SiMe}_3$ in toluene. As for the methoxyethyl analogue $\mathbf{7TiCl}_3$ (vide supra), no direct evidence is presented for its chelate structure in the paper.⁵¹



For the Ti(III) compound $(\mathbf{11})_2\text{TiCl}$, prepared in 60% yield from $\text{TiCl}_3(\text{THF})_3$ and $\mathbf{11Li}$ by Y. Qian et al., an intramolecular Ti–O coordination was confirmed by IR spectroscopic data [$\nu(\text{C}=\text{O})$ shift to lower wavenumbers with respect to unchelated analogues], although no spectral details are available.^{56,57}



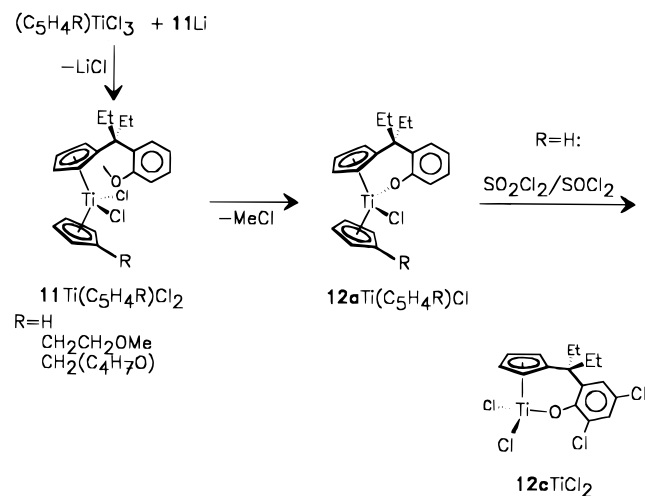
Treatment of this compound with concentrated hydrochloric acid produced a small amount of the dinuclear oxidation product $[\mathbf{11TiCl}(\mu\text{-O})]_2$, whose



formation seems to be affected by aerial conditions. It was characterized by X-ray diffraction and proved to be a chelate with molecular C_2 symmetry.^{56,57} The coordinative Ti–O bond [246.2(3) pm] is considerably longer than the bonds in the Ti_2O_2 ring [181.0(3) and 187.4(3) pm].

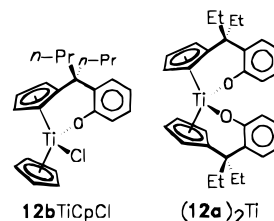
Reaction of $\mathbf{11Li}$ with CpTiCl_3 has afforded the titanocene derivative $\mathbf{11TiCpCl}_2$ in 55% yield.^{56–58} Although spectroscopic data do not indicate ether coordination in this species, it has turned out to tend to form the alkoxo-linked cyclopentadienyl chelate $\mathbf{12aTiCpCl}$ [Ti–O 187.9(6) pm]^{56,57} by elimination of methyl chloride (Scheme 2).^{57,59} A four-membered cyclic transition state has been proposed for this process. The reaction has not been observed below 10 °C, but has been reported to be fast and quantitative at higher temperatures (30%, 50%, and 88%

Scheme 2



conversion after 1 h at 30, 60, and 80 °C).⁵⁷ It is greatly accelerated by alkali-metal bromides and iodides and also by Br_2 and I_2 . These reagents, of which LiI has been found to be the most effective, lead to halogen exchange and subsequent elimination of MeBr or MeI , which is more facile than MeCl elimination.

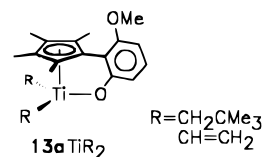
When $\mathbf{11Li}$ which contained LiBr was used in the synthesis of $\mathbf{11TiCpCl}_2$, MeBr elimination readily occurred in situ, leading directly to $\mathbf{12aTiCpCl}$ (63% yield).^{56,57,60} The closely related species $\mathbf{12aTi3aCl}$ ^{57,60} (62% yield) and $\mathbf{12aTi1Cl}$ ⁶⁰ as well as the dipropyl analogue $\mathbf{12bTiCpCl}$ ⁵⁷ (45% yield) were obtained similarly. The in situ elimination can even occur twice as is evidenced by the preparation of the spiro titanocene derivative $(\mathbf{12a})_2\text{Ti}$ from TiCl_4 and $\mathbf{11Li}/\text{LiBr}$ (30% yield).^{56,57,60}



The elimination reaction apparently fails in sterically less crowded cases. It has been reported that a single methyl substituent at the benzylic carbon atom suffices to prevent this process, even when the second substituent is an *i*-Bu group.⁵⁷ A possible explanation for this behavior is that steric interactions between the substituents at the benzylic carbon atom bend the methoxyphenyl group toward the metal center, thus lowering the activation energy barrier of the methyl halide elimination.

Treatment of $\mathbf{12aTiCpCl}$ with a mixture of SO_2Cl_2 and SOCl_2 at room temperature afforded the mono-(cyclopentadienyl) complex $\mathbf{12cTiCl}_2$ [Ti–O 180.3(3) pm, Ti–O–C 143.6°] in 52% yield (Scheme 2).⁵⁹ This reaction is similar to the preparation of $\mathbf{3aTiCl}_3$ from $(\mathbf{3a})_2\text{TiCl}_2$ (vide supra), except that in the present case the electron-rich phenoxy group is chlorinated, too.

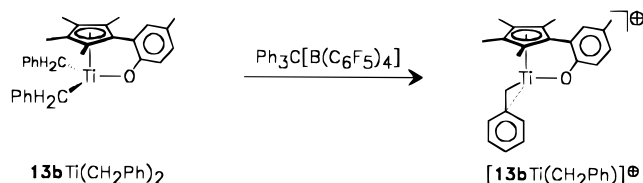
Several compounds which are akin to species of type $\mathbf{12TiCl}_2$, but bear a permethylated donor-linked cyclopentadienyl ligand, have been reported by the groups of J. H. Teuben and T. J. Marks. $\mathbf{13aTi}(\text{CH}_2\text{CMe}_3)_2$ and $\mathbf{13aTi}(\text{CH}=\text{CH}_2)_2$ are briefly mentioned



in a paper by the Dutch group.⁶¹ These species have proved to be active and remarkably robust catalysts for the hydroboration of 1-hexene with catecholborane. However, details concerning the synthesis and characterization of these two compounds are not available.

T. J. Marks and co-workers have synthesized $\mathbf{13bTi}(\text{CH}_2\text{Ph})_2$ from $\text{Ti}(\text{CH}_2\text{Ph})_4$ and 2-(tetrameth-

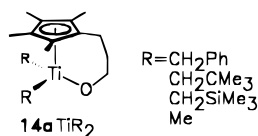
Scheme 3



ylcyclopentadienyl)-4-methylphenol (**13bH₂**) in toluene at 60 °C (yield 50%).⁶² The crystal structure shows that the Ti–O bond length is 185.1(7) pm and the Ti–O–C angle has a value of 126.6(6)°, which are in accord with partial double bond character. The two benzyl groups are inequivalent in the solid state, with one engaging in normal η^1 -bonding and the other in partial η^2 -bonding.

In an NMR tube experiment (CD_2Cl_2 solvent, –60 °C) this compound reacted cleanly with the tritylium salt $\text{Ph}_3\text{C}[\text{B}(\text{C}_6\text{F}_5)_4]$, affording the cationic titanium benzyl species $[\text{13bTi}(\text{CH}_2\text{Ph})]^+$ (Scheme 3), which proved to be an active, albeit temperature-sensitive, catalyst for the polymerization of α -olefins, producing high-molecular-weight polyethylenes as well as atactic polypropylene and polystyrene. The catalyst showed almost equal activities for the polymerization of ethene and propene. However, polypropylene was produced with a much narrower polydispersity than polyethylene.

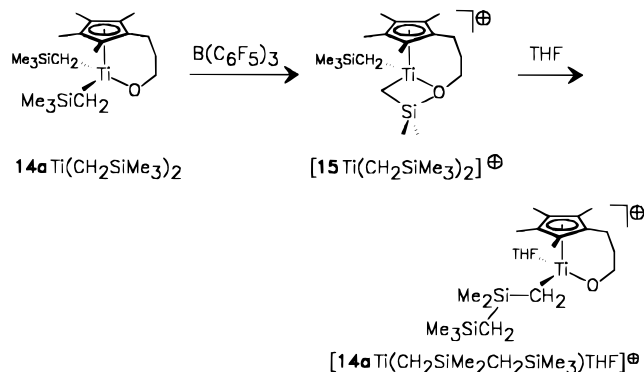
A similarly high activity for the polymerization of propene was found for $[\text{14aTi}(\text{CH}_2\text{Ph})]^+$, which contains an alkoxo-linked tetramethylcyclopentadienyl ligand. This species was reported by B. Hessen and co-workers to be formed cleanly in the reaction of **14aTi(CH₂Ph)₂** with $\text{B}(\text{C}_6\text{F}_5)_3$ in bromobenzene.⁶³ It is stable in PhBr solution at room temperature for several days, which is in contrast to the thermal instability of the phenoxy analogue $[\text{13bTi}(\text{CH}_2\text{Ph})]^+$.



The di(neopentyl) complex **14aTi(CH₂CMe₃)₂** turned out to be unreactive toward $\text{B}(\text{C}_6\text{F}_5)_3$ under such conditions, a possible explanation being that the steric bulk of the neopentyl groups prevents attack of the borane on the nucleophilic neopentyl methylene carbon atoms. The (trimethylsilyl)methyl analogue **14aTi(CH₂SiMe₃)₂**, on the other hand, reacted cleanly and swiftly with this reagent in PhBr, affording $[\text{15Ti}(\text{CH}_2\text{SiMe}_3)]^+$, which contains a coordinated silyl ether oxygen atom (Scheme 4).

The facile generation of this species involves transfer of a methyl group from silicon to boron and O–Si bond formation in the coordination sphere of the titanium atom and is due to the fact that the Si–CH₃ bond is comparatively reactive and easily accessible. Attack of the Lewis base THF at the most Lewis acidic center of this compound (the Ti atom) induces an intramolecular nucleophilic attack of the CH_2SiMe_3 group on the oxygen-bound Si atom, which

Scheme 4



entails cleavage of the Si–O bond and leads to the restoration of the alkoxo unit in the product $[\text{14aTi}(\text{CH}_2\text{SiMe}_2\text{CH}_2\text{SiMe}_3)\text{THF}]^+$ (Scheme 4). Details concerning the chemistry of the simplest di(hydrocarbyl) derivative in this series, **14aTiMe₂**, have not been reported.

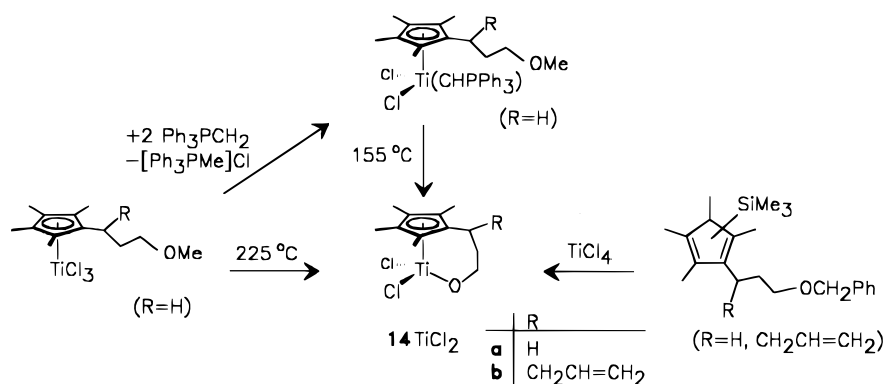
The dialkyl derivatives **14aTiR₂** just mentioned were prepared from the dichloride **14aTiCl₂** and the appropriate alkylolithium (RLi, R/yield = Me/62%, CH_2CMe_3 /81%, CH_2SiMe_3 /73%) or Grignard reagent (PhCH_2MgCl , 79% yield).⁶³ Owing to the key importance of **14aTiCl₂**, several syntheses have been developed for this compound (Scheme 5). The first preparation, reported by J. H. Teuben and co-workers, started from the unchelated $[(\text{MeOCH}_2\text{CH}_2\text{CH}_2)\text{C}_5\text{Me}_4]\text{TiCl}_3$, which afforded the titanium ylide $[(\text{MeOCH}_2\text{CH}_2\text{CH}_2)\text{C}_5\text{Me}_4]\text{TiCl}_2(\text{CHPPH}_3)$ upon reaction with 2 equiv of Ph_3PCH_2 . Thermolysis of the titanium ylide at 155 °C in benzene yielded **14aTiCl₂** as the main product together with unidentified phosphorus compounds.⁵⁴ A more direct and much cleaner synthesis is the thermolysis of the trichloride $[(\text{MeOCH}_2\text{CH}_2\text{CH}_2)\text{C}_5\text{Me}_4]\text{TiCl}_3$ (225 °C, toluene solvent), giving the product in 86% yield by elimination of methyl chloride.⁶³ This method is reminiscent of the preparation of **12aTiCpCl** from **11TiCpCl₂** (vide supra). An even more direct method is provided by the reaction of titanium tetrachloride with the silylated cyclopentadiene $(\text{Me}_3\text{Si})\text{C}_5\text{Me}_4(\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{Ph})$, which contains a reactive benzyl ether moiety.⁶⁴ **14aTiCl₂** (45% yield) was formed together with Me_3SiCl and PhCH_2Cl in dichloromethane solution already at room temperature.

Analogously, the related **14bTiCl₂** was obtained in 62% yield. This compound contains a second donor unit, namely, a dangling propenyl group attached to the first carbon atom of the side chain.

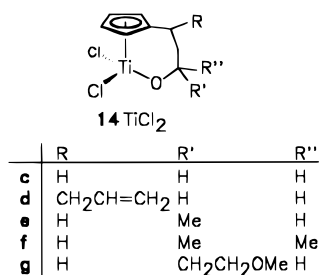
The structure of **14aTiCl₂** was determined by X-ray diffraction.⁵⁴ The Ti–O bond length [176.7(1) pm] and the Ti–O–C bond angle [146.1(1)°] are in accord with a titanium–oxygen bond order close to 2.

The unmethylated analogue of this compound is **14cTiCl₂**. It was prepared in 21% yield from TiCl_4 and the silylated cyclopentadiene $(\text{Me}_3\text{Si})\text{C}_5\text{H}_4(\text{CH}_2\text{CH}_2\text{OSiMe}_3)$ in pentane by J. H. Teuben and co-workers,⁶⁵ and in 32% yield from the same starting materials in dichloromethane by R. J. Whitby et al.⁶⁴ Alternatively, the *tert*-butyl and benzyl ethers of the

Scheme 5



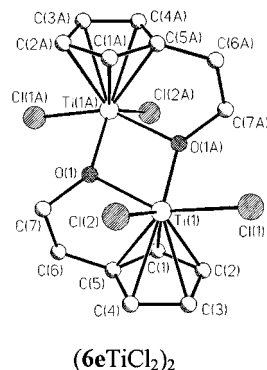
silylated cyclopentadiene or the *tert*-butyl ether of the lithiated cyclopentadiene could also be used (yields 15%, 49%, and 22%, respectively).⁶⁴ Compounds **14d**TiCl₂ to **14g**TiCl₂, which contain substituents in



the side chain, were obtained analogously in ca. 20% yield.⁶⁴ Similarly, **6e**TiCl₂, which contains a shorter side chain, was obtained in 21% yield from the reaction of (Me₃Si)C₅H₄(CH₂CH₂OSiMe₃) with TiCl₄ in pentane.⁶⁵

The structure of **14c**TiCl₂ is very similar to that of **14a**TiCl₂ [two independent molecules: Ti–O 175.5(2) and 176.2(2) pm, Ti–O–C 146.7(2) and 145.8(2)°].⁶⁵ The structure of **14g**TiCl₂ demonstrates that the ether substituent in this compound has no significant influence on the titanium coordination sphere [Ti–O 173(1) pm, Ti–O–C 149.6(9)°].⁶⁴

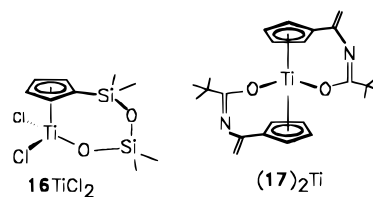
In contrast, shortening of the side chain by one methylene group has a dramatic structural effect. **6e**TiCl₂ is dimeric in the solid state with unsym-



metrically bridging O atoms (molecular point group *C*₂). Each Ti atom is chelated by one alkoxy-linked cyclopentadienyl ligand, forming a comparatively

weak dative Ti–O bond [207.26(17) pm, Ti–O–C 115.71(14)°]. The alkoxy function interacts strongly with the other titanium atom, forming a Ti–O σ-bond [194.72(17) pm, Ti–O–C 134.0(2)°].⁶⁵ Apparently, the coordination sphere of the titanium atom is opened up by tying back the intramolecularly coordinated oxygen atom with a short CH₂CH₂ bridge, thus providing space for an additional Ti–O bond to form. Since only the monomer is observed under mass spectrometric conditions, it appears that **6e**TiCl₂ dissociates easily in the gas phase. Unfortunately, no data are available for the nuclearity of this compound in solution.

Two more titanium compounds are known which contain a chelating *O*-functionalized cyclopentadienyl ligand. One of them is the siloxo complex **16**TiCl₂, which was obtained by P. Royo et al. from [(C₅H₄)-SiMe₂Cl]TiCl₃ either in very low yield by treatment with water in toluene⁶⁶ or more rationally and in 45% yield with SiPh₂(OH)₂ and NEt₃ in hexane.⁶⁷ The second one is the spiro titanocene derivative (**17**)₂Ti

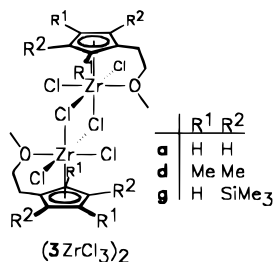


reported by G. Erker and co-workers. It contains a carboxamido-linked cyclopentadienyl ligand and was synthesized in 58% yield from TiCl₄(THF)₂ and **17**Li₂ in THF.⁶⁸ The structure of its zirconium analogue was determined by X-ray diffraction and showed no interaction of the nitrogen atoms with the metal center (*vide infra*).

b. Zirconium and Hafnium. Owing to their very similar chemical behavior, zirconium and hafnium can be treated together here. Their effective ionic radii are almost identical and considerably larger than for Ti.⁶⁹ Consequently, in comparison to related titanium compounds, a dominant feature of their chemistry is the tendency to form complexes with higher coordination numbers by binding additional neutral or anionic ligands.

As a manifestation of this fact **3a**ZrCl₃ is a *C*_{2v}-symmetric chloro-bridged dimer in the solid state,⁵⁰

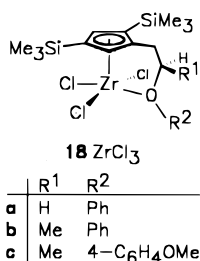
whereas the titanium analogue is monomeric (vide supra). However, the association is not very strong,



since the zirconium complex is monomeric in dichloromethane solution even at $-50\text{ }^{\circ}\text{C}$. If the cyclopentadienyl ligand is viewed as occupying a single coordination site, the coordination of each Zr atom in the dimer can be described as distorted pseudooctahedral. The oxygen atom is positioned trans to a terminal chloro ligand [Zr–O 226.4(4) pm]. The bridging Zr–Cl bonds are significantly longer than the terminal ones [245.5(2) and 247.2(2) pm], with a noticeable difference between the bond trans to the cyclopentadienyl ligand [264.2(2) pm] and that trans to the terminal chloro ligand [256.2(2) pm]. **3aZrCl₃** has been prepared by A. A. H. van der Zeijden et al. in analogy to CpZrCl₃(DME)⁷⁰ by the reaction of the silylated cyclopentadiene **3aSiMe₃** with ZrCl₄(SME₂)₂ in dichloromethane (yield 80%).

The same group has also synthesized the planar chiral bis(trimethylsilyl) derivative **3gZrCl₃**, which was isolated in 88% yield from the reaction of **3gLi** with ZrCl₄ in diethyl ether.⁷¹ Its solid-state structure is assumed to be similar to that of **3aZrCl₃**. According to an NMR spectroscopic investigation, the monomeric chelate structure present in most solvents (vide infra) gives rise to two conformers, which differ in the steric interaction between the tether and its neighboring SiMe₃ group and are hence observed in unequal proportion.

The aryl ether-functionalized analogues **18aZrCl₃** to **18cZrCl₃** have been prepared by the same synthetic method (yields 51%, 48%, and 37%, respectively).⁷¹ As for **3gZrCl₃**, two conformers are present

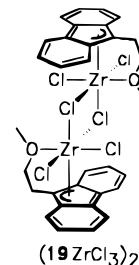


in solution in the case of the planar chiral **18aZrCl₃**. The other two of this trio contain a chiral cyclopentadienyl ligand and were each isolated as two diastereomers in a ratio of 73:27. No dynamic equilibrium is observed between the diastereomers in solution.

3dZrCl₃, which is the tetramethyl analogue of **3aZrCl₃**, was obtained by D. P. Krut'ko and co-workers in 54% yield from the reaction of **3dLi** with

ZrCl₄ in diethyl ether.⁷² Its structure is very similar to that of **3aZrCl₃**. The lengths of the respective bonds between the metal atom and the coordinated heteroatoms are identical within experimental error for both compounds with the exception of the Zr–Cl bond trans to the cyclopentadienyl ring, which is considerably longer for **3dZrCl₃** [271.8(1) vs 264.2(2) pm]. This probably reflects the larger trans influence of the permethylated cyclopentadienyl ligand **3d** vis-à-vis its unmethylated analogue **3a**.

A. A. H. van der Zeijden et al. have also synthesized the fluorenyl complex **19ZrCl₃** from ZrCl₄ and **19Li** in diethyl ether.⁷³ This compound is the first mono-



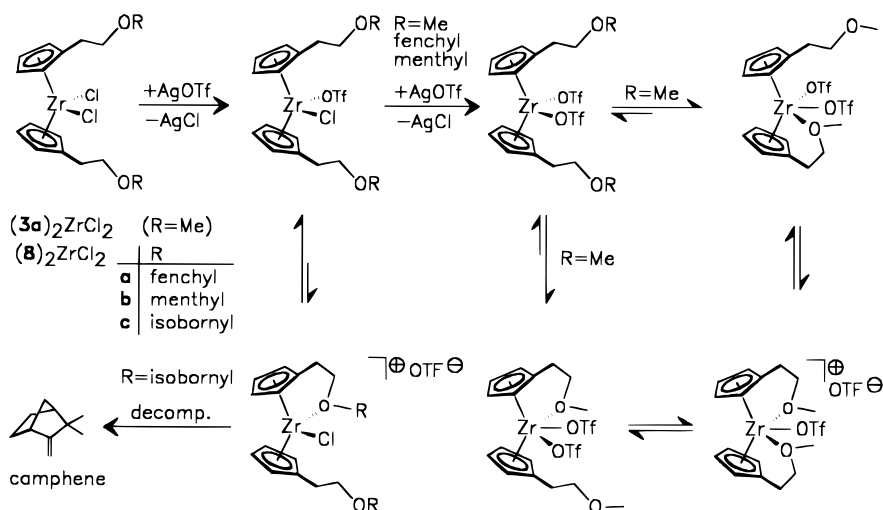
fluorenyl zirconium trichloride, and it owes much of its stability to the presence of the chelate ligand **19**, whose coordination mode is best described as $\eta^3\text{:}\kappa\text{-O}$, since one short (ca. 237 pm), two medium (ca. 257 pm), and two very long (ca. 274 pm) Zr–C distances are observed [Zr–O 229.2(2) pm].

In comparison to its relative **3aZrCl₃**, which contains an $\eta^5\text{:}\kappa\text{-O}$ -cyclopentadienyl ligand, the bonding of the organic ligand is fairly weak, and this causes a much higher reactivity for **19ZrCl₃**. The coordination parameters of the other ligands are similar to those of **3aZrCl₃**, the major difference being that now the bridging Cl atoms are almost equidistant from each metal center [262.70(7) and 266.57(7) pm]. It appears that intramolecular repulsion of the fluorenyl moieties prevents the shortening of one pair of bridging bonds, which is observed for **3aZrCl₃**.

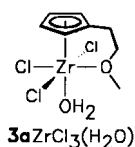
According to NMR spectroscopic investigations, the ether oxygen essentially remains coordinated to the metal center for the OMe-functionalized compounds in dichloromethane solution and, with the exception of the fluorenyl species **19ZrCl₃**, even in donor solvents such as THF.^{50,71–74} This indicates the exceptional strength (noticeable double bond character) of the Zr–O interaction in these complexes and has been explained by a particularly favorable π -overlap, which is geometrically induced.⁷⁴ This intramolecular coordination is noticeably weaker in the case of the aryl ether-functionalized species **18aZrCl₃** to **18cZrCl₃**, where even weak donors such as benzaldehyde can easily disrupt the chelate structure.⁷¹ Not surprisingly, therefore, the use of **18bZrCl₃** and **18cZrCl₃** as chiral Lewis acids in the enantioselective hydrocyanation of benzaldehyde has not been successful.

In the case of the strong chelate **3aZrCl₃** the intramolecular ether coordination has been shown to be easily broken by an excess of water or methanol in solution. Nevertheless, when such solutions were

Scheme 6

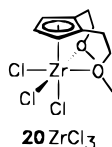


reduced to dryness, the monomeric chelate complexes $\mathbf{3aZrCl}_3(\text{H}_2\text{O})$ and $\mathbf{3aZrCl}_3(\text{MeOH})$ were isolated.⁷⁴



The water ligand is coordinated trans to the cyclopentadienyl ring [Zr–OH₂ 222.1(4) pm] and is hydrogen-bonded to a THF molecule of crystallization. The Zr–O(ether) distance of 234.5(4) pm is significantly longer than that in dimeric $\mathbf{3aZrCl}_3$, while the Zr–Cl bonds are only slightly elongated. The structure is similar to that of CpZrCl₃(THF)₂,⁷⁵ with the notable exception that the water ligand trans to the cyclopentadienyl ring is much smaller than a THF ligand and consequently experiences the sterically induced trans influence of the cyclopentadienyl ligand to a lesser extent. Therefore, a very short Zr–O bond can be realized. The methanol compound probably has a similar structure.

The structure of complex $\mathbf{20ZrCl}_3$, obtained in 2% yield as a side product of the synthesis of $\mathbf{3aZrCl}_3$, proves that even ethers may disrupt the chloro-bridged dimeric structure in the case of an intramolecular coordination [Zr–O 229.8(3) and 234.2(3) pm].⁷⁶



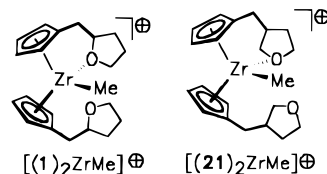
Reaction of the unchelated zirconocene dichloride $(\mathbf{3a})_2\text{ZrCl}_2$ with 2 equiv of silver triflate (AgOTf) in toluene afforded $(\mathbf{3a})_2\text{Zr}(\text{OTf})_2$ (70% yield) (Scheme 6).⁷⁷ A temperature-dependent NMR spectroscopic study revealed that in solution this species shows dynamic intramolecular coordination of the pendant ether groups, facilitating partial dissociation into the ionic $[(\mathbf{3a})_2\text{Zr}(\text{OTf})\text{OTf}]^+$. In the case of the unstable analogues containing cyclopentadienyl ligands $\mathbf{8a}$ and $\mathbf{8b}$, which bear the much bulkier chiral terpene-

derived ether groups, the resultant bis(triflate) complexes seem to dissociate to a lesser degree, since the ether coordination is comparatively weak. These complexes catalyze Diels–Alder reactions. However, no asymmetric induction could be achieved with the chiral systems.

Reaction of $(\mathbf{3a})_2\text{ZrCl}_2$ with 1 equiv of silver triflate in CDCl₃ afforded a mixture of the $(\mathbf{3a})_2\text{ZrCl}(\text{OTf})$, the bis(triflate) $(\mathbf{3a})_2\text{Zr}(\text{OTf})_2$, and starting material.⁷⁷ This behavior is in contrast to that observed for $(\mathbf{8a})_2\text{ZrCl}_2$ and $(\mathbf{8b})_2\text{ZrCl}_2$, where essentially clean formation of the mono(triflate) species occurred (Scheme 6). These two compounds are stable for days in chloroform solution. The isonorbonyl analogue $(\mathbf{8c})_2\text{ZrCl}(\text{OTf})$, on the other hand, is much more reactive and decomposes within several hours at room temperature.

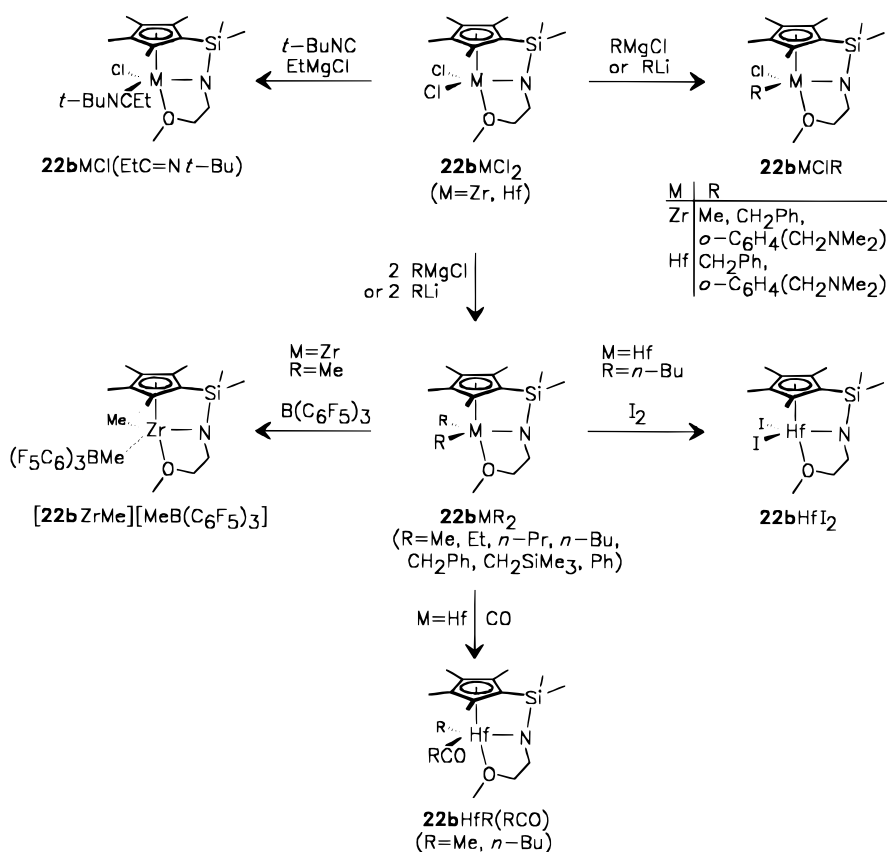
The decomposition pathway clearly involves intramolecular coordination of a pendant ether group, since Lewis-acid-induced ether cleavage was observed, leading to the isonorbonyl carbocation and finally to camphene (Scheme 6). From this finding at least a weak dynamic intramolecular coordination of the ether moiety with concomitant dissociation of the triflate, resulting in the formation of the monochelates $[(\mathbf{3a})_2\text{ZrCl}]^+$ and $[(\mathbf{8})_2\text{ZrCl}]^+$, respectively, can be deduced for these compounds.

The closely related cationic zirconocene alkyl derivatives $[(\mathbf{1})_2\text{ZrMe}]^+$ and $[(\mathbf{21})_2\text{ZrMe}]^+$ were investigated by quantum-chemical methods.⁷⁸



Such compounds are relevant to the Ziegler–Natta-type polymerization of α -olefins.⁵² According to a calculation using DFT methods, the former turned out to be more stable as a monochelate (calculated Zr–O 218 pm) by 21.6 kcal/mol due to steric strain in the longer side chain of $[(\mathbf{21})_2\text{ZrMe}]^+$ (calculated Zr–O 219 pm). This is in line with the chain-length

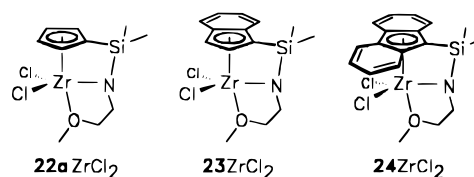
Scheme 7



effect observed for the titanium complexes **3a**TiCl₃ and **1**TiCl₃ on one hand (chelates, vide supra) and [(MeOCH₂CH₂CH₂)C₅H₄]₂TiCl₃ and [(MeOCH₂CH₂-CH₂)C₅Me₄]₂TiCl₃ on the other hand (no chelates, vide supra) and is also in accord with the finding that (**21**)₂ZrCl₂ polymerizes ethene in the presence of methylaluminoxane (MAO), whereas (**1**)₂ZrCl₂ is inactive under similar experimental conditions, indicating that the catalytic site is effectively blocked by a chelating ether group.⁷⁹

An interesting extension of the ether-linked cyclopentadienyl ligands so far described is realized in the amido-linked systems **22**, containing an ether group tethered to the cyclopentadienyl ring via the amido nitrogen atom. In general, group 4 metal complexes of linked amido-cyclopentadienyl ligands have been widely investigated as constrained-geometry⁸⁰ metallocene analogues for α -olefin polymerization.²⁶ The oligodentate architecture of **22** comprises two formally anionic components, which are usually found to bind strongly to a transition-metal center, as well as the neutral ether moiety, which may act as a third ligating unit if required by the metal center. **22a**ZrCl₂, recently described by H. G. Alt et al., is the only example reported so far where the unmethylated ligand uses all three ligating units.⁸¹ The complex was obtained in 73% yield by the reaction ZrCl₄ with **22a**Li₂ in a mixture of diethyl ether and toluene. The indenyl and fluorenyl analogues **23**ZrCl₂ and **24**ZrCl₂ were prepared analogously in 65% and 57% yield, respectively.⁸¹ All three compounds show a dynamic

coordination behavior of the ether moiety in chloro-carbon solution.



A large number of group 4 metal compounds containing the ether-functionalized amido-linked tetramethylcyclopentadienyl ligand **22b** have been published by J. Okuda and co-workers (Scheme 7). Coordination of the ether oxygen atom is well documented only for Zr and Hf complexes, although it has been tentatively invoked also for some titanium compounds. In most cases both the zirconium and the analogous hafnium compounds have been prepared. For the sake of brevity this will be denoted in the following by using M instead of Zr and Hf for the metal center in such pairs of compounds.

The dichloro derivatives **22b**MCl₂ are versatile starting materials for the preparation of a large variety of mono- and dialkyl compounds **22b**MCIR and **22b**MR₂. The dichlorides were obtained in 78% (Zr)^{82,83} and 58% (Hf)⁸³ yield from the reaction of MCl₄(THF)₂ with the dilithiated cyclopentadiene **22b**Li₂ in toluene. The hafnium complex was characterized by X-ray diffraction. Its core geometry is best described as distorted trigonal bipyramidal, if the cyclopentadienyl ligand is viewed as occupying a single coordination site. The ether oxygen occupies

the axial position trans to the cyclopentadienyl ring [Hf–O 232.4(5) pm]. The nitrogen atom is trigonal planar and the Hf–N bond length is 203.8(6) pm, implying strong π donation of the amido ligand to the metal. The iodo analogue **22bHfI₂** has been prepared from **22bHf-*n*-Bu₂** (vide infra) and iodine in an essentially quantitative reaction.^{84,85}

Selective monoalkylation of **22bMCl₂** could not easily be achieved (Scheme 7).⁸³ Reaction with MeMgCl afforded unseparable mixtures of **22bZrClMe** and the starting material **22bZrCl₂** (no mention is made of the hafnium analogue). With PhCH₂MgCl the desired **22bMCl(CH₂Ph)** could be prepared in 80% (Zr) and 66% (Hf) yield. However, microanalytical data revealed that the products obtained were not pure. This is also the case for **22bZrCl[*o*-C₆H₄(CH₂NMe₂)]** (63% yield), and only the hafnium analogue could be isolated in analytically pure form (69% yield). No indication was found for a coordination of the amino group in the last two compounds.

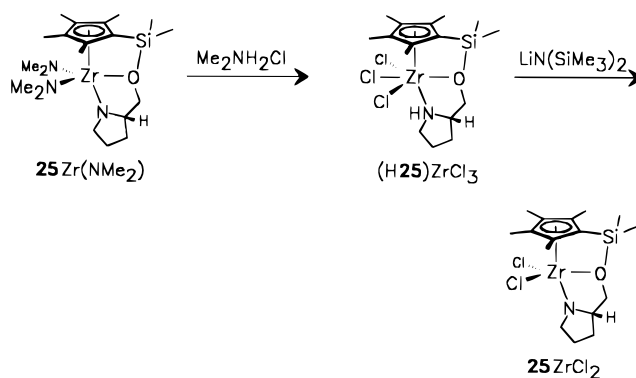
Addition of EtMgCl to a mixture of **22bMCl₂** and *tert*-butyl isocyanide in hexane afforded **22bMCl(EtC=N-*t*-Bu)** in 64% (Zr) and 51% (Hf) yield (Scheme 7). Their formation can be rationalized in several ways. It may involve insertion of the isocyanide into the M–Et bond of an intermediate monoethyl complex, but it can also be explained by substitution of one of the chloro ligands in the starting material by the metalated aldimine, which results from the reaction of *t*-BuNC with EtMgCl. NMR data suggest a dynamic coordination behavior for the tethered ether ligand and also for the (imino)propionyl group, whose coordination mode may be either η^1 or η^2 .⁸⁵

Dialkylation of **22bMCl₂** using alkylolithium or Grignard reagents in hexane turned out to be straightforward, affording **22bMR₂** (R = Me, Et, *n*-Pr, *n*-Bu, CH₂Ph, CH₂SiMe₃, Ph) in yields between 55% and 87% (Scheme 7).^{82,84,85} The structures of **22bZrMe₂**,⁸⁵ **22bZrPh₂**,⁸⁵ and **22bHf-*n*-Bu₂**⁸⁴ have been determined and were found to be similar to that of **22bHfCl₂** (vide supra), although these three compounds exhibit M–O and M–N bonds which are each elongated slightly by ca. 5 pm with respect to **22bHfCl₂**. NOE measurements performed for **22bZrMe₂** in C₆D₆ showed that intramolecular coordination of the ether group prevails in this solvent, leading to the conclusion that the $\eta^{5:\kappa\text{-N}:\kappa\text{-O}}$ coordination mode is the dominant one in solution for all of these compounds.⁸⁵ This has important consequences for the reactivity of these species.

The thermal stability of the dialkyl derivatives **22bMR₂** depends on the substituent and follows the order Et < *n*-Pr < *n*-Bu < CH₂SiMe₃ < Me < Ph < CH₂Ph. It also depends on the metal, with hafnium compounds being more stable than their zirconium analogues. It is remarkable that these complexes are isolable even when they contain two alkyl groups with β -hydrogen atoms, since analogous derivatives lacking the ether unit are thermally much more unstable. This observation is in accord with, but does not prove, the assumption that ether coordination effectively blocks β -H elimination pathways.⁸⁴

Intramolecular ether coordination has also been made responsible for the finding that, relative to

Scheme 8



ether-free analogues, MAO-activated **22bMMe₂** and related species polymerize ethene with lower activity.⁸⁵ To obtain a well-defined single-component polymerization catalyst, **22bZrMe₂** was allowed to react with B(C₆F₅)₃ in C₆D₅Br at ca. –30 °C, giving a solution of [**22bZrMe**][MeB(C₆F₅)₃], in which, according to NMR spectroscopic data, the borate anion is coordinated to the metal center (Scheme 7). Ethene polymerization experiments with this species gave erratic results.

The insertion of carbon monoxide into the M–R bond of **22bMR₂** was studied for the dimethyl- and di-*n*-butylhafnium compounds and was found to proceed smoothly under an atmospheric pressure of CO, affording the monoacyl complexes **22bHfR(RC=O)** in high yield (Scheme 7).^{84,85} The acyl ligands in these species rotate freely about the metal–carbon bond via an η^1 -coordinated form.

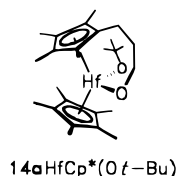
W. E. Piers et al. have developed the chiral ligand **25**, which is related to **22b**, but owing to its architecture forces the amido nitrogen, instead of the ether oxygen, in the position trans to the cyclopentadienyl ring upon complexation.⁸⁶ Metathesis of **25H₂** (*S*-enantiomer) with Zr(NMe₂)₄ in toluene gave crude **25Zr(NMe₂)₂** in almost quantitative yield. Reaction of **25Zr(NMe₂)₂** with dimethylammonium chloride afforded the trichloro derivative (H**25**)ZrCl₃ as two diastereomers (*S,S* and *S,R*) in 59% yield (Scheme 8).

The more abundant *S,S*-isomer (ca. 88%) was analyzed by X-ray diffraction. To a first approximation, the Zr–O [224.4(6) pm] and Zr–N [242.1(9) pm] distances are both in accord with single bonds. However, the former is the shortest Zr–O bond so far observed between a zirconium center and its chelating ether-linked cyclopentadienyl ligand, which may indicate weak π donation and a bond order slightly larger than 1. The oxygen atom is trigonal planar (sum of angles 357°). Its close proximity to the zirconium atom is made possible, inter alia, by the exceptionally low value of the cyclopentadienyl C–Si–O bond angle [91.4(4)°] and the comparatively long Si–O bond [170.1(6) pm]. The length of the Zr–N bond is similar to that observed for the Zr–O single bond trans to the cyclopentadienyl ring in the structurally characterized amido complexes **22bZrR₂** (R = Me, Ph; vide supra), when the differing covalent radii of O vs N (Δ ca. 5 pm) are taken into account.

Deprotonation of (H**25**)ZrCl₃ was complicated by the nucleophilic properties of the bases employed,

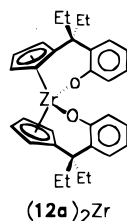
leading to side reactions. It was best achieved with $\text{LiN}(\text{SiMe}_3)_2$ in toluene, affording $(\mathbf{25ZrCl}_2)$ of ca. 80% purity in 71% yield (Scheme 8).

A good number of zirconium and hafnium chelate complexes are known which contain an alkoxo- or aryloxo-linked cyclopentadienyl ligand. The first example was published in 1986 by J. E. Bercaw and co-workers and was produced by thermolysis of the alkyl peroxy compound $\text{Cp}^*\text{Hf}[(\text{Me}_4\text{C}_5)\text{CH}_2\text{CH}_2\text{CH}_2](\text{OO}-t\text{-Bu})$, which is a chelate itself (the propylene side chain of the cyclopentadienyl ligand is connected to the metal center).⁸⁷ Warming of this species in benzene solution was found to lead to a rearrangement to $\mathbf{14aHfCp}^*(\text{O}-t\text{-Bu})$, containing one tethered and one untethered alkoxo ligand.



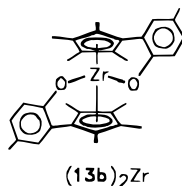
$\mathbf{14aHfCp}^*(\text{O}-t\text{-Bu})$

The spiro zirconocene derivative $(\mathbf{12a})_2\text{Zr}$, which was obtained from ZrCl_4 and $\mathbf{11Li/LiBr}$ (16% yield) similar to its Ti analogue (vide supra), represents another example of a chelate, where the alkoxo oxygen atom is connected to the cyclopentadienyl ring with a C_3 linker.^{56,60}



$(\mathbf{12a})_2\text{Zr}$

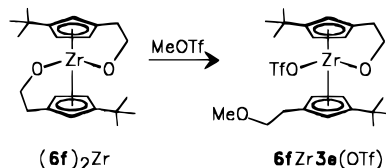
Further spiro zirconocene species were prepared in the groups of T. J. Marks, R. G. Bergman, and G. Erker. Reaction of $\mathbf{13bH}_2$ with $\text{Zr}(\text{CH}_2\text{Ph})_4$ in toluene at 110 °C afforded $(\mathbf{13b})_2\text{Zr}$ (35% yield), while attempts to synthesize $\mathbf{13bZr}(\text{CH}_2\text{Ph})_2$ by using more moderate reaction conditions (cf. the preparation of the Ti analogue, vide supra) only led to mixtures of products.⁶²



$(\mathbf{13b})_2\text{Zr}$

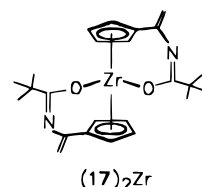
The related OH-functionalized cyclopentadiene $\mathbf{6fH}_2$ was used for the preparation of $(\mathbf{6f})_2\text{Zr}$, which was obtained stereospecifically in 92% yield from ZrCl_4 and $\mathbf{6fLi}_2$ in THF.⁸⁸ The molecule is C_2 -symmetric in the solid state. The Zr–O distance of 200.6(6) pm and

Scheme 9



the Zr–O–C angle of 126.1(6)° are compatible with π donation, leading to a bond order significantly larger than 1. Methylation of one of the two homotopic oxygen atoms in $(\mathbf{6f})_2\text{Zr}$ with methyl triflate afforded $\mathbf{6fZr3e}(\text{OTf})$ as a single diastereomer in quantitative yield (Scheme 9).

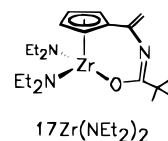
The last example in this category is $(\mathbf{17})_2\text{Zr}$, which contains a carboxamido-linked cyclopentadienyl ligand



$(\mathbf{17})_2\text{Zr}$

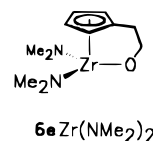
and was synthesized in 74% yield from $\text{ZrCl}_4(\text{THF})_2$ and $\mathbf{17Li}_2$ in THF in analogy to the corresponding titanium complex (vide supra).⁶⁸ The molecule has approximate C_2 symmetry in the solid state. The carbon–nitrogen distances of the NCO units are indistinguishable and clearly correspond to a double bond (ca. 128 pm). The nitrogen atoms are not involved in metal coordination. The Zr–O distances (ca. 203 pm) and Zr–O–C angles (ca. 136°) are each identical within experimental error and are in agreement with a Zr–O π interaction.

As an example of a half-sandwich complex, $\mathbf{17Zr}(\text{NEt}_2)_2$ was isolated in 70% yield from the reaction of $(\text{Et}_2\text{N})_2\text{ZrCl}_2$ with $\mathbf{17Li}_2$ in THF.⁶⁸ Spectroscopic data indicate that again the nitrogen atom of $\mathbf{17}$ does not participate in metal coordination.



$\mathbf{17Zr}(\text{NEt}_2)_2$

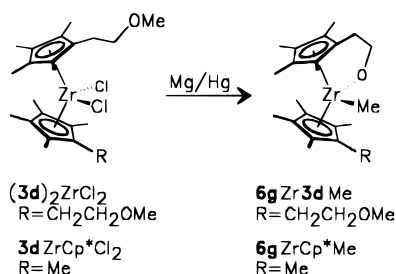
The closely related $\mathbf{6eZr}(\text{NMe}_2)_2$, reported by W. A. Hermann et al., was prepared in quantitative yield by aminolysis⁸⁹ of $\text{Zr}(\text{NMe}_2)_4$ with the OH-functionalized cyclopentadiene $\mathbf{6eH}_2$.⁹⁰



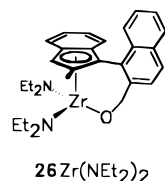
$\mathbf{6eZr}(\text{NMe}_2)_2$

In an analogous way, R. W. Baker and B. J. Wallace have isolated the planar chiral $\mathbf{26Zr}(\text{NEt}_2)_2$ in quantitative yield from the reaction of $\text{Zr}(\text{NEt}_2)_4$

Scheme 10

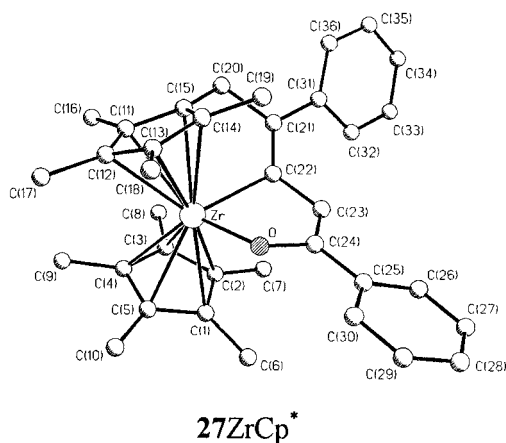


with the enantiomerically pure OH-functionalized indene **26H₂**.⁹¹



The zirconocene derivative **6gZr3dMe**, reported by D. A. Lemenovskii and co-workers, was generated from the unchelated **(3d)₂ZrCl₂** upon treatment with amalgamated magnesium in THF under nitrogen (Scheme 10).⁹² Analogously, **6gZrCp*Me** was obtained from **3dZrCp*Cl₂** (40% yield), while performing the reaction under an atmospheric pressure of carbon monoxide afforded the unchelated zirconium(II) carbonyl complex **(3d)ZrCp*(CO)₂**. The reaction mechanism is far from simple. It seems to involve reduction of the metal center, coordination of a pendant ether group, cleavage of the methyl–oxygen bond, and formation of MeMgCl, which substitutes the remaining chloro ligand.

A complex reaction sequence was also followed in the preparation of **27ZrCp*** reported by R. G. Bergman and co-workers.^{93,94} The compound was obtained

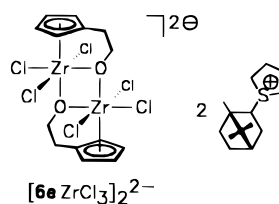


by thermolysis of Cp*₂Zr(OH)Ph in benzene at 160 °C in the presence of (PhC≡C)₂ (84% yield). Its formation involves α-elimination of benzene from the starting material, reaction of the resultant unstable oxo complex Cp*₂ZrO with 1,4-diphenyl-1,3-butadiene to give a zirconaoxetene, and isomerization to the

final zirconaoxole by a CH activation process, leading to the integration of one Cp* ligand into the coordinated enolate moiety. The short Zr–O distance [205.9(1) pm] is indicative of partial double bond character.

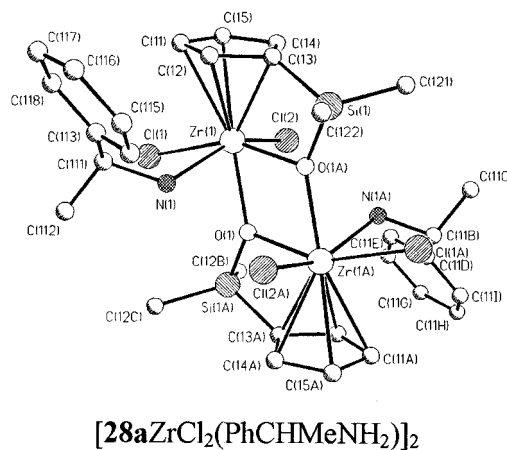
In the compounds so far described in this subsection the metal center is tetracoordinate, if cyclopentadienyl ligands are counted as occupying one coordination site. In the preceding part dealing with ether-functionalized zirconium and hafnium complexes, we have already seen that these metals can extend their coordination sphere and are easily able to accommodate more than four ligands. Not surprisingly, therefore, a number of alkoxy-linked cyclopentadienyl species which contain hexa- or even heptacoordinate zirconium(IV) have been reported.

The dinuclear alkoxy-bridged zirconate [**6e**ZrCl₃]₂²⁻, reported by A. A. H. van der Zeijden et al., was obtained in 95% yield from the reaction of ZrCl₄(THT)₂ (THT = tetrahydrothiophene) with the sily-



lated cyclopentadiene **8cSiMe₃**.⁵⁰ The authors explain the formation of the unusual isobornyltetrahydrothiophenium counterion by metal-induced ether cleavage and concomitant alkylation of THT by the isobornyl cation in the zirconium coordination sphere, which most likely occurs prior to the formation of the zirconium–cyclopentadienyl bond.

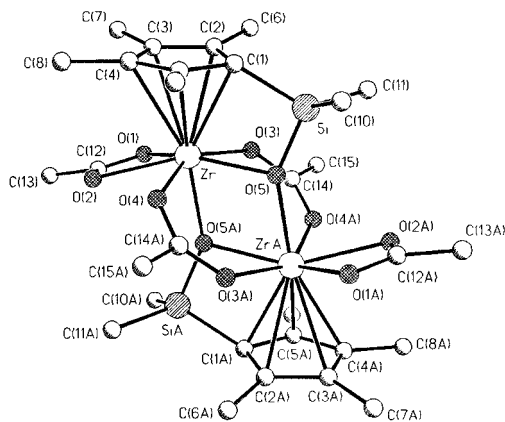
The closely related neutral alkoxy-bridged dimer [**28a**ZrCl₂(PhCHMeNH₂)₂]₂ was prepared by P. Royo and co-workers.⁹⁵ The compound was obtained in low



yield from {(H₄C₅)SiMe₂[NH(CHMePh)]}ZrCl₃(NEt₃) in wet toluene. The reaction involves hydrolytic cleavage of the Si–N bond in the starting material, leading to the formation of the amine PhCHMeNH₂ and a tethered silanol group. The two independent molecules found in the crystal both adopt C_i symmetry. Their bond parameters are essentially indis-

tinguishable. The lengths of the four bonds in the diamond-shaped Zr_2O_2 unit are identical within experimental error (ca. 219 pm). Owing to the formally anionic charge of the alkoxo oxygen atoms, these bonds are shorter than that observed for the silyl ether-coordinated species (H25)ZrCl₃ (vide supra). In both cases, the cyclopentadienyl C–Si–O angles are close to 90°.

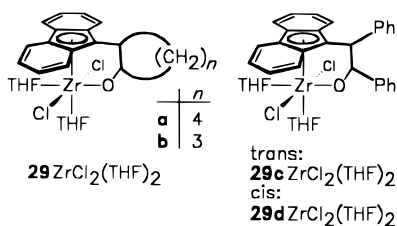
A more complex structure was reported for [28bZr(O₂CMe)₂]₂, obtained in 70% yield from the constrained-geometry metallocene analogue [(Me₄C₅–



[28bZr(O₂CMe)₂]₂

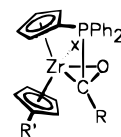
SiMe₂(N-*t*-Bu)]ZrMe₂ with carbon dioxide by J. L. Petersen.⁹⁶ The Zr atoms of the *C_r*-symmetric dimer are part of a central Zr₂O₂ unit, which exhibits two distinctly different bond lengths [212.60(13) and 225.70(13) pm]. They are further connected by two bridging acetate ligands, which are positioned above and below the Zr₂O₂ ring. The chelating zirconium–oxygen interaction is weaker than the bridging one, the interatomic distance being in the range usually observed for ether-coordinated species. Consequently, the ligand framework is less distorted (cyclopentadienyl C–Si–O 95.8°) than in the related (H25)ZrCl₃ and [28aZrCl₂(PhCHMeNH₂)₂]₂ (vide supra).

The chiral OH-functionalized fluorenes **29a**H₂ to **29d**H₂ were utilized by B. Rieger for the preparation of the alkoxo-linked fluorenyl complexes **29ZrCl₂**·(THF)₂, which were obtained from the reaction of ZrCl₄ with **29**Li₂ in THF.⁹⁷



The substituents at the asymmetric carbon atoms of the C₂ linker between the oxygen atom and the fluorenyl group are either in a trans (**29a–c**) or in a cis (**29d**) arrangement. For all compounds NMR spectroscopic data indicate dynamic coordination behavior of the THF ligands in solution similar to that of CpZrCl₃(THF)₂.⁷⁵

Chart 2



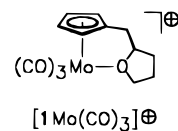
	R	R'	X
30a Zr(C ₅ H ₄ PPh ₂)Cl	Me	PPh ₂	Cl
30a ZrCpCl	Me	H	Cl
30a ZrCpMe	Me	H	Me
30b ZrCp(CH ₂ Ph)	CH ₂ Ph	H	CH ₂ Ph
30b Zr(C ₅ H ₄ PPh ₂)(CH ₂ Ph)	CH ₂ Ph	PPh ₂	CH ₂ Ph

The last compounds to be discussed in this section are **30a**Zr(C₅H₄PPh₂)Cl,⁹⁸ **30a**ZrCpCl,⁹⁹ **30a**ZrCpMe,⁹⁹ **30b**ZrCp(CH₂Ph),¹⁰⁰ and **30b**Zr(C₅H₄PPh₂)(CH₂Ph),¹⁰⁰ which were reported by W. Tikkanen et al. to be formed quantitatively by insertion of CO into a zirconium–alkyl bond of the respective precursor complex and subsequent nucleophilic attack of the newly formed acyl C atom by a phosphanyl P atom (Chart 2). The chelate ligand in these compounds is best described as a cyclopentadienyl ring functionalized with a phosphonium–alkoxo moiety, as is evidenced by the result of an X-ray structure analysis of **30a**Zr(C₅H₄PPh₂)Cl.⁹⁸

The Zr–O distance of 206.5(2) pm is similar to the corresponding values of the alkoxo-linked species (**17**)₂Zr, (**6f**)₂Zr, and **27**ZrCp* (vide supra), which fall in the range between ca. 201 and 206 pm. The distances of the O-bound carbon atom to its four bonding partners (Zr, P, O, and C) are each in agreement with a single bond. The bond parameters of the four-coordinate P atom are typical of a phosphonium center. Specifically, the distance of 178.2(3) pm between this P atom and the O-bound C atom is too long to be that of an ylide. This P–C bond can be broken in solution, where all compounds show a dynamic behavior on the NMR time scale owing to the participation of the acyl structure.

2. Group 6 Elements

a. Molybdenum. W. E. Jones, Jr., and co-workers very recently provided direct experimental evidence for the single species known in this category, namely, [1Mo(CO)₃]⁺, which was formed from [1Mo(CO)₃]₂

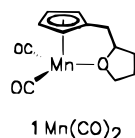


after electrochemical oxidation.¹⁰¹ Only indirect evidence (based on transient absorption spectroscopy) has been reported for the existence of the neutral 19-valence-electron chelate **1**Mo(CO)₃, which appears to be formed in equilibrium with the unchelated 17-valence-electron isomer produced by photolysis of [1Mo(CO)₃]₂.

3. Group 7 Elements

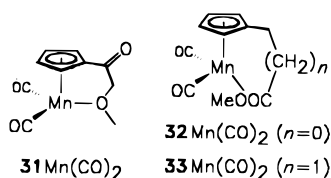
a. Manganese. The earliest example from this category is the carbonyl complex **1**Mn(CO)₂ reported

by T. E. Bitterwolf et al. in 1991.¹⁰² IR spectroscopic



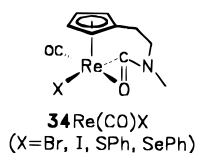
data revealed that the chelate was generated together with an unchelated isomer by photolysis of **1Mn(CO)₃** in Nujol solution at liquid nitrogen temperature (77 K). Enhancement of molecular motion by modest warming of the matrix to 100 K resulted in the conversion of the unchelated isomer to the chelate. Upon further warming, reversion to **1Mn(CO)₃** by reaction with CO occurred.

R. F. Johnston and co-workers have described an analogous reaction for the ether-functionalized complex **31Mn(CO)₃** as well as the ester-functionalized species **32Mn(CO)₃** and **33Mn(CO)₃**, producing **31Mn(CO)₂**, **32Mn(CO)₂**, and **33Mn(CO)₂**, respectively,



which were identified as chelates by IR spectroscopy.¹⁰³ No further data are available for these compounds, and consequently the coordination mode of the ester group in **32Mn(CO)₂** and **33Mn(CO)₂** is unclear. The thioether analogue of **31Mn(CO)₂** was sufficiently stable for isolation and structural characterization (the reader is referred to the paper by H. Butenschön in this issue, which treats, inter alia, chelate complexes of *S*-functionalized cyclopentadienyl ligands).

b. Rhenium. T. Wang et al. have reported that deprotonation of the coordinated amino group in the chelates $[\{C_5H_4(CH_2CH_2NHMe)\}Re(CO)_2X]^-$ ($X = Br, I, SPh, SePh$) with triethylamine in dichloromethane induced a migratory insertion of the carbonyl ligand into the Re–N bond, and thus afforded the η^2 -carbamoyl complexes **34Re(CO)X** in ca. 60% yield.¹⁰⁴



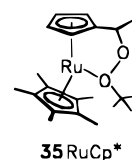
The structure of **34Re(CO)(SePh)** was determined by X-ray diffraction and shows a remarkably short carbamoyl C–Re distance of 201.5(11) pm and a much longer Re–O bond length of 237.1(8) pm. The bond lengths of the carbamoyl unit are unexceptional [C–O 125.6(15) pm, C–N 130.8(16) pm] and compatible with partial double bond character of the carbon–nitrogen interaction.

4. Group 8 Elements

a. Iron. An intramolecular coordination of the pendant oligoethylene glycol ether moiety has been

put forward by U. Siemeling as an explanation for the unusual stability of the half-sandwich iron(II) chloride $[Me_4C_5(CH_2)_3(OCH_2CH_2)_3OMe]FeCl$ (**2eFeCl**), which was chemically characterized by derivatization reactions.¹⁰⁵ The compound was prepared from **2eLi** and $FeCl_2$ at low temperature in THF. Although stable in THF solution at room temperature, it has not proved possible to isolate the compound. This is reminiscent of the behavior of the chelate complexes $Cp^*Fe(acac)(piperidine)$ ¹⁰⁶ and $Cp^*Fe(acac)$.¹⁰⁷ In contrast, donor-free half-sandwich iron(II) halides such as Cp^*FeBr ¹⁰⁸ or $[(Me_3Si)_2C_5H_3]FeBr$ ¹⁰⁹ have been described to decompose in THF solution well below 0 °C.

b. Ruthenium. The unusual (*tert*-butylperoxyethyl)-ruthenocene **35RuCp***, reported by H. Suzuki et al., was prepared in 74% yield from the cationic fulvene complex $[\{H_4C_5(CHMe)\}RuCp^*]^+$ and lithium *tert*-



butylperoxide in dichloromethane at –35 °C.¹¹⁰ The *O*-functionalized cyclopentadienyl ligand is formed by nucleophilic attack of *t*-BuOO[–] on the α -carbon atom of the coordinated 6-methylfulvene ligand. **35RuCp*** was found to be thermally quite stable, showing only slow decomposition to *tert*-butyl alcohol and the acetyl ruthenocene $[H_4C_5(COMe)]RuCp^*$ at 80 °C in benzene.

C. Rare-Earth Elements (Ln)

Yttrium and the 15 elements from lanthanum to lutetium are commonly known as the rare-earth elements. The symbol Ln will generically be used for any such element in this review.

They are base metals, and their most common oxidation state is +III. The corresponding metal ions Ln^{3+} are hard and oxophilic Lewis acids. It is therefore not surprising that chelate complexes of *O*-functionalized cyclopentadienyl ligands with these elements in the +III oxidation state are abundant. In fact, such complexes form the largest group of compounds in this review.

The effective ionic radii for hexacoordinate Ln^{3+} vary from ca. 117 pm for La^{3+} to ca. 100 pm for Lu^{3+} ,⁶⁹ resulting in noticeable differences between the complex chemistry of the larger ions, which favor higher coordination numbers, and that of the smaller ones, where coordination numbers will generally be lower and bond lengths smaller. This is in principle very similar to the differences observed between titanium on one hand and zirconium and hafnium on the other hand (*vide supra*).

However, for the sake of brevity the rare-earth elements will be treated together here, since a huge number of analogous compounds have been published in this area. During the following discussion, pertinent differences between the larger and the smaller metal centers will be highlighted at the appropriate place. It is noteworthy that for three rare-earth

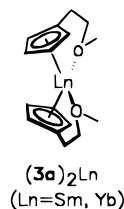
elements, namely, promethium, europium, and terbium, no compounds relevant to this review have been described.

The most popular ligand in this area is **3a**. It was introduced in 1985 by Y. Qian and co-workers, who have used this ligand extensively in transition-metal chemistry (vide supra). In rare-earth-element chemistry it has been employed mainly by the group of C. Qian,¹¹¹ who in 1987 introduced the second most popular ligand, namely, **9a**.¹¹² Their investigations were in part stimulated by the relevance of organometallic compounds of these elements to important catalytic reactions such as olefin polymerization and hydrogenation.¹¹³

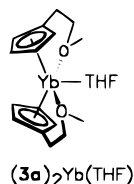
1. Ln(II) Compounds

Samarium, europium, and ytterbium are the only rare-earth elements which exhibit an extensive chemistry in the oxidation state +II. Indeed, a few chelate complexes of ether-functionalized cyclopentadienyl ligands are known for samarium(II) and ytterbium(II).

C. Qian and co-workers have reported the synthesis of $(\mathbf{3a})_2\text{Sm}$ and $(\mathbf{3a})_2\text{Yb}$ from the respective metal diiodide and **3aK** in THF in 75% and 80% yield,

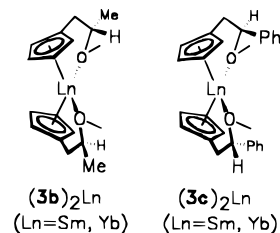


respectively.¹¹⁴ The ¹H NMR spectrum of the diamagnetic ytterbium complex is in accord with an intramolecular coordination of both ether groups in THF-*d*₈ solution. This is corroborated by the result of an X-ray structure analysis performed for $(\mathbf{3a})_2\text{Yb}(\text{THF})$, which was obtained by recrystallizing $(\mathbf{3a})_2\text{Yb}$

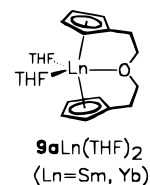


from THF at room temperature.¹¹⁴ The Sm analogue has also been obtained, although details are not available for this compound.¹¹⁵ The THF ligand is only loosely bound and can be removed in vacuo at 50 °C. $(\mathbf{3a})_2\text{Yb}(\text{THF})$ adopts *C*₂ symmetry in the crystal. The THF ligand is coordinated [Yb–O 249.6(4) pm] in the wedge formed by the Yb atom and the two pendant ether O atoms [both Yb–O 256.4(3) pm, O–Yb–O 143.5(2)°]. The ytterbium–oxygen distances are much longer than those found in the cationic ytterbium(III) species $[(\mathbf{3a})_2\text{Yb}(\text{THF})]^+$ (vide infra). G. A. Molander, H. Schumann, and co-workers have prepared the closely related chiral $(\mathbf{3b})_2\text{Ln}$ (Ln/yield = Sm/66%, Yb/54%) and $(\mathbf{3c})_2\text{Ln}$ (Ln/yield = Sm/33%, Yb/71%) in an analogous way.³⁵ The NMR spectra of the diamagnetic ytterbium complexes are

in accord with the presence of a single diastereomer in each case.



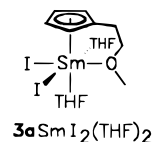
The last compounds to be mentioned in this subsection are $\mathbf{9aLn}(\text{THF})_2$ (Ln = Sm, Yb) and $\mathbf{9aYb}(\text{DME})$ reported by C. Qian et al.¹¹⁶ The THF com-



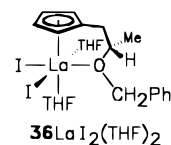
plexes were prepared by the reduction of $\mathbf{9aLnCl}$ with sodium metal in THF in 74% (Sm) and 67% (Yb) yield. Alternatively, $\mathbf{9aSm}(\text{THF})_2$ was prepared in 62% yield from SmI_2 and $\mathbf{9aK}_2$. Recrystallization of the ytterbium complex from DME afforded $\mathbf{9aYb}(\text{DME})$, which was characterized crystallographically. The three Yb–O distances are very similar (ca. 248 pm) and on average slightly shorter than those in the less rigid $(\mathbf{3a})_2\text{Yb}(\text{THF})$.

2. Ln(III) Compounds

a. Mono(cyclopentadienyl) Complexes. Only a few compounds have been reported in this category. C. Qian et al. have prepared $\mathbf{3aSmI}_2(\text{THF})_2$ in 68% yield from SmI_3 and **3aK** in THF.¹¹⁷ The core geometry



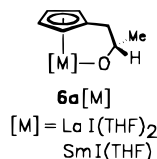
may be described as distorted pseudo-octahedral, if the cyclopentadienyl ligand is viewed as occupying a single coordination site. The two iodo ligands are in a cis arrangement. One short [245.6(5) pm] and two long [251.4(6) and 251.9(7) pm] Sm–O bonds are observed, the short one being that to the THF positioned trans to an iodo ligand. The closely related $\mathbf{36LaI}_2(\text{THF})_2$ has been synthesized analogously in



81% yield from $\text{LaI}_3(\text{DME})_2$ and **36K** by J. Collin and co-workers.¹¹⁸ Although the structure of this compound has not been elucidated, it is most likely similar to that of $\mathbf{3aSmI}_2(\text{THF})$. The species was used as a chiral Lewis acid for catalyzing the Diels–Alder

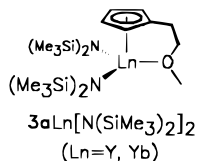
reaction of cyclopentadiene with methacrolein, giving 90% of the *exo* isomer with a modest e. e. of 13%.

The same group has also published two complexes containing a related chiral alkoxy-functionalized cyclopentadienyl ligand.¹¹⁹ **6a**LaI(THF)₂ and **6a**SmI(THF) were prepared by the reaction of **6a**K₂ with

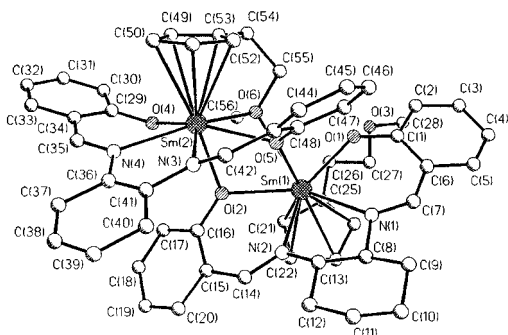


LaI₃(DME)₂ and SmI₃(THF)₃, respectively (yields 79% and 83%). These two compounds are rare examples of Ln complexes containing an alkoxy-linked cyclopentadienyl ligand. No mention is made that, owing to the presence of a chiral metal center, the samarium complex may be a mixture of two diastereomers.

C. Qian et al. have synthesized the half-sandwich amido complexes **3a**Y[N(SiMe₃)₂]₂ and **3a**Yb[N(SiMe₃)₂]₂ in 72% and 56% yield, respectively, by the one-pot reaction of **3a**Na, LiN(SiMe₃)₂, and the respective metal trichloride in THF.¹²⁰ Structural data are not available for these compounds.



A complicated unsymmetrical structure has been found by Y. Qian and co-workers for the dinuclear complex [**3a**Sm(μ-C₂₀H₂₀N₂O₂)₂]₂, which was isolated

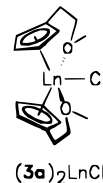


[**3a**Sm(μ-C₂₀H₂₀N₂O₂)₂]₂

in 30% yield from the reaction of (**3a**)₃Sm with a C₂-symmetric Schiff base derived from *trans*-1,2-diaminocyclohexane, namely, *cyclo*-C₆H₁₀[N=CH(*o*-C₆H₄-OH)]₂.¹²¹ Each Sm atom is bound to the four heteroatoms of one Schiff base and additionally to a bridging oxygen atom of the second Schiff base, giving rise to a central Sm₂O₂ unit. Each Sm atom bears one η⁵-cyclopentadienyl ligand **3a**. Interestingly, only one of the two cyclopentadienyl ligands acts as a chelate ligand, forming a coordinative bond with an Sm–O distance of 268.0(4) pm. Owing to the formally anionic charge of the Schiff base oxygen atoms, their distances to the samarium atoms [225.4(4)–252.7-

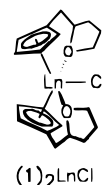
(4) pm] are much shorter than that. The dysprosium analogue [**3a**Dy(μ-C₂₀H₂₀N₂O₂)₂]₂ has been prepared similarly in 26% yield, but has not been structurally characterized.¹²¹

b. Di(cyclopentadienyl) Complexes. Almost the complete set of rare-earth metal compounds of the type (**3a**)₂LnCl has been reported by the group of C. Qian

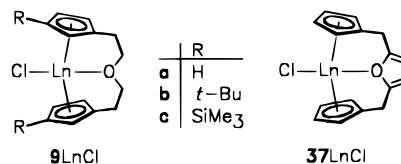


(Ln/yield = Y/49%,¹²² 77%;¹²³ La¹²⁴/64%,¹²² 74%;¹²³ Ce,¹²⁵ Pr^{124,125}/71%;¹²³ Nd^{124,125}/70%;^{122,123} Sm¹²⁵/69%;¹²³ Gd¹²⁵/56%,¹²² 80%;¹²³ Dy/60%;¹²³ Ho/53%;^{122,123} Er¹²⁵/60%;^{122,123} 61%;¹²⁶ Tm/60%;¹²³ Yb¹²⁵/51%,¹²² 60%;¹²³ Lu¹²⁵/65%¹²³).

These species have been prepared from **3a**Na and the appropriate metal trichloride in THF. The yttrium complex has also been obtained in 63% yield from the same starting materials by J. H. Teuben et al. using a mixture of toluene and tmeda as solvent.¹²⁷ Closely related complexes of the type (**1**)₂LnCl (Ln/yield = Nd/38%,^{128,129} Er/47%,¹²⁸ Dy/50%,^{128,129} Gd/42%,^{128,129} Yb/47%^{129,130}) have been synthesized by W. Chen et al. from **1**Na and the respective metal trihalide in THF.

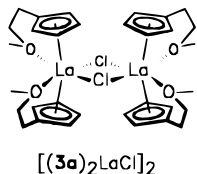


C. Qian et al. have also reported a large number of *ansa*-metallocene derivatives which contain an ether oxygen atom in the bridge between the two cyclopentadienyl ligands, namely, **9a**LnCl (Ln/yield = Y^{131,132,133}/88%,¹¹² Nd¹³²/45%,¹¹² Sm,¹¹⁶ Gd¹³²/59%,¹¹² Ho¹³²/65%,¹¹² Er¹³²/64%,¹¹² Yb¹³²/77%,¹¹² Lu^{131,132}/49%¹¹²), **9b**LnCl (Ln/yield = Y/64%, Nd/59%, Sm/65%, Yb/72%),¹³⁴ **9c**LnCl (Ln/yield = Y/76%, La/61%, Nd/65%, Yb/72%),¹³⁴ and **37**LnCl (Ln/yield = Y/72%, Nd/71%, Sm/61%, Yb/77%).¹³⁵ Again, these compounds have been prepared from the appropriate metal trihalide and **9**Na₂ and **37**Na₂, respectively, in THF.



In general, all these complexes are considerably more stable toward air and moisture than donor-free analogues. According to the data available, the ether groups are coordinated to the metal center in each case. Crystallographic data have been reported only for compounds belonging to the (**1**)₂LnCl and (**3a**)₂LnCl families. The latter were originally formulated as

chloro-bridged dimers. However, X-ray structural investigations performed for $(\mathbf{3a})_2\text{LnCl}$ (Ln = La, ^{123,124} Nd, ²⁴ Dy, ¹²³ Er, ¹²⁶ Yb¹²³) have shown that the majority of these compounds are in fact monomeric in the solid state. Only for the complex containing the largest metal center, lanthanum, has a dimeric structure been proven by an X-ray diffraction study.¹³⁶



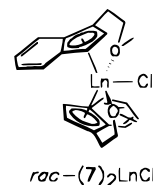
Closer inspection of the bond parameters reveals that the metal centers in this species are coordinatively oversaturated. The La–O distances are quite different, and at least one of them is conspicuously long [266.5(2) and 277.5(2) pm]. The structures of the monomeric chloro complexes $(\mathbf{3a})_2\text{LnCl}$, as far as they are known, are all very similar. Their O–Ln–O angles are ca. 151°. The two Ln–O distances tend to be only slightly different (Δ ca. 6 pm). Their average values (Dy, 249 pm; Er, 246 pm; Yb, 247 pm) are almost identical, when the differences in ionic radii are taken into account. They are slightly larger than Ln–O distances in unchelated monosolvates such as $\text{Cp}^*_2\text{SmCl}(\text{THF})$ (248 pm) and $\text{Cp}^*_2\text{YCl}(\text{THF})$ (241 pm).¹³⁷

The crystallographically characterized $(\mathbf{1})_2\text{DyCl}$ ^{128,129} and $(\mathbf{1})_2\text{YbCl}$ ¹³⁰ are structurally not much different. However, the average values of their metal–oxygen distances (Dy, 245 pm; Yb, 239 pm) are significantly shorter than those found in their $(\mathbf{3a})_2\text{LnCl}$ analogues, which probably reflects the comparatively high Lewis basicity of the tetrahydrofuran oxygen atom in **1**. The shortened bond lengths coincide with slightly larger O–Ln–O angles (ca. 156°) relative to those in $(\mathbf{3a})_2\text{LnCl}$.

For the compounds of type $\mathbf{9aLnCl}$ monomeric structures have been suggested on the basis of mass spectrometric investigations.¹¹² Such monomeric structures are certainly reasonable for the sterically crowded complexes of **9b** and **9c**. In contrast, MS data have been taken as evidence for a dimeric structure of $\mathbf{37LnCl}$.¹³⁵ Such a structural difference seems questionable in view of the similarity of the cyclopentadienyl ligands **9a** and **37**. Unfortunately, molecular mass determinations to probe the nuclearity of these compounds in solution are not available, although the chloro complexes $\mathbf{9aLnCl}$ have been reported to be readily soluble in various solvents¹¹² (including CCl_4 , which was used for NMR studies).¹³¹

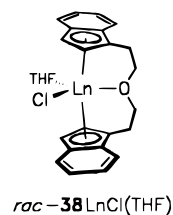
Analogous η^5 -indenyl complexes of the types $(\mathbf{7})_2\text{LnCl}$ (Ln/yield = Y/69%, La/54%, Nd/58%, Gd/62%, Ho/62%, Lu/50%)¹³⁸ and $\mathbf{38LnCl}(\text{THF})$ (Ln/yield = Y/65%, Pr/66%, Nd/59%, Gd/51%, Dy/73%, Ho/67%, Lu/69%)¹³⁹ have also been prepared by C. Qian et al., using again the metathesis of the appropriate metal trihalide with the respective alkali-metal cyclopentadienide. Four members of the $(\mathbf{7})_2\text{LnCl}$ family have

been characterized crystallographically, namely, those with Ln = Y, La, Nd, and Gd.¹³⁸ They turned out to be chiral monomeric rac isomers with a trans ar-



rangement of both the side chains and the indenyl rings. The two metal–oxygen bond lengths are indistinguishable in each case and essentially identical for all four compounds when the differences in ionic radii are taken into account (Y, 247 pm; La, 260 pm; Nd, 256 pm; Gd, 252 pm). The O–Ln–O angles vary from 159.0(1)° for the smallest metal center, Y, to 167.1(3)° for the largest one, La. The rac configuration also predominates in THF solution, although for the larger metal centers minor isomers could be detected, as was shown by a ¹H NMR study of the diamagnetic Y, La, and Lu compounds. For the smallest metal center, Lu, only the rac isomer was observed. For the largest, La, all of the four possible isomers were found to be present in solution, with the rac isomer prevailing only marginally, its proportion being 55%. The behavior of the yttrium complex comes close to that of the lutetium analogue, with 96% of the rac isomer and 4% of a second isomer present.

The *ansa*-metallocene derivatives $\mathbf{38LnCl}(\text{THF})$ have been structurally characterized by X-ray diffraction for Ln = Nd, Gd, and Ho.¹³⁹ All were found to be isostructural chiral rac isomers. As for $(\mathbf{7})_2\text{LnCl}$,

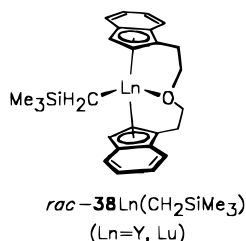


the two metal–oxygen distances are indistinguishable in each case (Nd–O 251 pm, Gd–O 247 pm, Ho–O 244 pm) and are essentially identical for all three compounds after ionic radius corrections. They are, however, slightly, but not significantly, shorter than those found in their $(\mathbf{7})_2\text{LnCl}$ analogues, which may be an effect of the less rigid ligand framework in the latter.

It is remarkable that the compounds have been isolated as THF solvates, while their cyclopentadienyl analogues $\mathbf{9aLnCl}$ were obtained solvent-free. The THF is bound fairly loosely and is partially given off in vacuo. An NMR spectroscopic investigation of the diamagnetic yttrium and lutetium complexes has revealed that the rac isomer equilibrates with the meso isomer in THF-*d*₈ solution, the rac/meso equilibrium ratio being ca. 6:1 for these compounds.

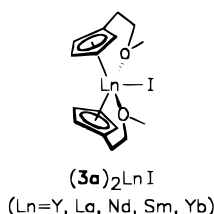
Reaction of $\mathbf{38LnCl}(\text{THF})$ (Ln = Y, Lu) with $\text{LiCH}_2\text{-SiMe}_3$ in toluene furnished $\mathbf{38Ln}(\text{CH}_2\text{SiMe}_3)$ in 53%

(Y) and 48% (Lu) yield, respectively.¹⁴⁰ These unsol-



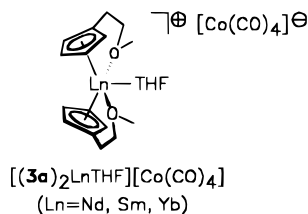
vated species were exclusively formed as *rac* isomers due to steric interactions of the six-membered portion of the indenyl moiety and the bulky alkyl group. The yttrium complex has been structurally characterized by X-ray diffraction. Two independent molecules with very similar bond parameters are present in the crystal. The Y–O distances of 232.3(6) and 233.7(6) pm for molecules 1 and 2, respectively, is the shortest of its kind so far observed and reflects the comparatively low coordination number of Y in this species.

The fact that the indenyl complex (**7**)₂LaCl is monomeric¹³⁸ whereas the cyclopentadienyl analogue (**3a**)₂LaCl is a dimer in the solid state^{123,124} may be attributed to the enhanced steric bulk of the indenyl vis-à-vis the cyclopentadienyl ligand. A similar effect is observed when the chloro ligand in (**3a**)₂LaCl is exchanged for an iodo ligand. This was achieved in 65% yield by the metathetical reaction of the chloro compound with sodium iodide in THF.^{141,142} (**3a**)₂LaI proved to be monomeric in the solid state with two indistinguishable, and comparatively short, La–O bond lengths [258.3(11) and 258.4(11) pm], which compare well with the La–O bond length of 257(1) pm in Cp₃La(THF).¹⁴³ (**3a**)₂YI¹⁴² and (**3a**)₂NdI¹⁴¹ were



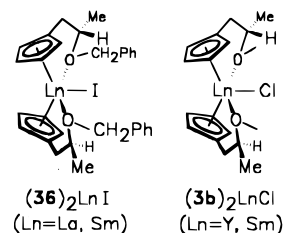
prepared analogously in 60% and 65% yield, respectively, while (**3a**)₂SmI¹¹⁷ and (**3a**)₂YbI¹⁴⁴ were obtained from the reaction of SmI₃ and YbI₃, respectively, with **3aK** in THF (65% yield each). The structures of the yttrium, samarium, and ytterbium complexes have been determined and are very similar to that of (**3a**)₂LaI, when the differences in ionic radii are taken into account.

Reaction of (**3a**)₂LnI with K[Co(CO)₄] in THF afforded the ionic compounds [(**3a**)₂Ln(THF)][Co(CO)₄] (Ln/yield = Nd/60%, Sm/62%, Yb/65%).^{115,145}



The samarium¹⁴⁵ and ytterbium¹¹⁵ species have been characterized crystallographically and were found to contain discrete anions and cations, whereas in the closely related unfunctionalized ytterbium complex Cp*₂Yb(OC)Co(CO)₃(THF) an Yb–OC–Co interaction (i.e., an isocarbonyl bridge) is observed.¹⁴⁶ This reflects nicely the coordinative saturation effected by the intramolecular coordination in the ether-functionalized complexes. Both cations adopt C₂ symmetry (approximate for Sm, crystallographically exact for Yb) and contain two chelating ether groups [Sm–O 249.6(10) and 249.9(10) pm, O–Sm–O 150.5(3)°; Yb–O 241(1) pm, O–Yb–O 147.8(5)°]. The THF ligand is coordinated in the O–metal–O wedge [Sm–O(THF) 242.2(6), Yb–O(THF) 232(1) pm]. As a consequence of the presence of a positively charged Yb(III) center, the metal–oxygen distances in [(**3a**)₂Yb(THF)]⁺ are ca. 16 pm shorter than the respective distances found in the neutral divalent species (**3a**)₂Yb(THF) (vide supra), and the distances between the metal and the pendant ether oxygen atoms are also slightly shorter (ca. 4 pm) than those in the neutral trivalent (**3a**)₂YbI (vide supra).

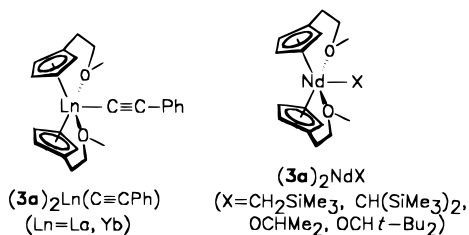
Not unexpectedly, (**36**)₂LaI and (**36**)₂SmI reported by J. Collin et al.¹¹⁸ as well as the chloro complexes (**3b**)₂YCl and (**3b**)₂SmCl prepared by H. Schumann



et al.¹⁴⁷ have also turned out to be monomeric. These compounds are all chiral, containing *S*-configured cyclopentadienyl ligands. They were isolated from the reaction of the respective potassium cyclopentadienide with the appropriate metal trihalide in THF. Their NMR spectra are in accord with, but do not prove, the presence of a single diastereomer in each case. The crystal structures of the two samarium complexes have been determined. In the case of (**3b**)₂SmCl two independent molecules with significantly different bond parameters are present in the crystal [molecule 1, Sm–O 251(1)/253.5(8) pm, O–Sm–O 156.9(3)°; molecule 2, Sm–O 254.7(9)/258(1) pm, O–Sm–O 167.4(3)°], which indicates that these parameters are somewhat soft.¹⁴⁷ A slightly more symmetric structure was found for (**36**)₂SmI [Sm–I 256.3(15) and 257.5(20) pm, O–Sm–O 159.4(4)°].¹¹⁸ This species was used as a chiral Lewis acid for catalyzing the Diels–Alder reaction of cyclopentadiene with methacrolein in dichloromethane, affording 92% of the *exo* isomer with a modest enantiomeric excess of 11% (*R* over *S*). The lanthanum analogue (**36**)₂LaI gave a poor 3% ee under essentially identical conditions. For both compounds a dynamic coordination behavior of the pendant ether groups was observed in solution.

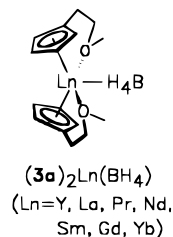
Derivatives of the type (**3a**)₂LnR [Ln = La, R = C≡CPh; Ln = Nd, R = CH₂SiMe₃, CH(SiMe₃)₂, OCHMe₂, OCH*t*-Bu₂; Ln = Yb, R = C≡CPh] are also

monomeric with two chelating ether groups, as are the tetrahydroborato complexes $(\mathbf{3a})_2\text{Ln}(\text{BH}_4)$ ($\text{Ln} = \text{Y}, \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Yb}$) and the related $(\mathbf{3a})_2\text{Nd}(\text{BHEt}_3)$ and $(\mathbf{3a})_2\text{Y}(\text{AlH}_4)$. In contrast, the hydrido and hydroxo species $(\mathbf{3a})_2\text{LnH}$ ($\text{Ln} = \text{Y}, \text{La}, \text{Pr}, \text{Ho}$) and $(\mathbf{3a})_2\text{Ln}(\text{OH})$ ($\text{Ln} = \text{Ho}, \text{Er}$) are dimeric with only one of the two pendant ether groups coordinated by the metal center. Similarly, it was found that the *ansa*-metallocene derivatives $\mathbf{9aLnH}$ ($\text{Ln} = \text{Y}, \text{Gd}, \text{Er}, \text{Yb}, \text{Lu}$) and $\mathbf{9aLnD}$ ($\text{Ln} = \text{Y}, \text{Lu}$) as well as $\mathbf{9aY}(\text{OH})$ are all dimeric.



The phenylacetylides were obtained from the metathesis of $\text{NaC}\equiv\text{CPh}$ with the respective chloro complex $(\mathbf{3a})_2\text{LnCl}$ in THF in 77% (La) and 66% (Yb) yield.¹²⁰ The alkyl complexes $(\mathbf{3a})_2\text{Nd}(\text{CH}_2\text{SiMe}_3)$ and $(\mathbf{3a})_2\text{Nd}[\text{CH}(\text{SiMe}_3)_2]$ were formed almost quantitatively from $(\mathbf{3a})_2\text{NdCl}$ and the respective alkyllithium reagent in toluene or benzene solution; the alkoxo species $(\mathbf{3a})_2\text{Nd}(\text{OCHMe}_2)$ and $(\mathbf{3a})_2\text{Nd}(\text{OCH}(t\text{-Bu})_2)$ have been obtained from the reaction of $(\mathbf{3a})_2\text{Nd}(\text{BHEt}_3)$ with acetone and pivalone, respectively.^{148,149} Of all the neodymium compounds just described only $(\mathbf{3a})_2\text{NdOCH}(t\text{-Bu})_2$ has been isolated in pure form (71% yield) and subjected to the standard methods of characterization.

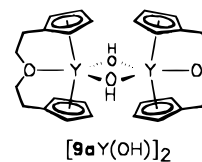
The tetrahydroborato complexes have been obtained by C. Qian et al. from the respective chloro complex $(\mathbf{3a})_2\text{LnCl}$ and sodium borohydride in THF ($\text{Ln}/\text{yield} = \text{Y}/70\%, \text{La}/90\%, \text{Pr}/68\%, \text{Nd}/77\%, \text{Sm}/71\%, \text{Gd}/70\%, \text{Yb}/59\%$).^{150,151} Alternatively, the neodymium complex has been prepared in quantitative yield from $(\mathbf{3a})_2\text{NdCl}$ and thallium(I) borohydride in toluene as well as from $(\mathbf{3a})_2\text{Nd}(\text{BHEt}_3)$ and $\text{H}_3\text{B}(\text{SMe}_2)$ in benzene.¹⁴⁹ Lithium borohydride was used for the preparation of $(\mathbf{3a})_2\text{Y}(\text{BH}_4)$ by J. H. Teuben et al., who also obtained the analogous $(\mathbf{3a})_2\text{Y}(\text{AlH}_4)$ by using LiAlH_4 (71% yield).¹²⁷ The triethylboranato species $(\mathbf{3a})_2\text{Nd}(\text{BHEt}_3)$ was synthesized from the chloro complex and sodium triethylborate in benzene.^{148,149}



According to IR spectroscopic data and the results of X-ray structure analyses, which were performed for the tetrahydroborato complexes of Y,^{127,150} Pr,¹⁵¹ Nd,¹⁵¹ and Yb,¹⁵⁰ the coordination mode of the BH_4 unit most likely is κ^3 in the compounds containing

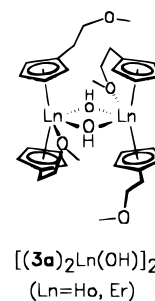
the larger metal centers (La, Pr, Nd) and κ^2 for the smaller ones (Y, Sm, Gd, Yb). In analogy, a κ^2 binding mode also seems reasonable for $(\mathbf{3a})_2\text{Y}(\text{AlH}_4)$. Both ether groups are coordinated in an essentially symmetric way to the metal center in all structurally characterized cases. At first glance, the crystallographically determined metal–oxygen distances are less similar than expected, and two surprising facts may be noted. First, the Y–O distances (ca. 244 pm)¹⁵² are smaller than the Yb–O distances (ca. 245 pm), although the ionic radius of yttrium is larger than that of ytterbium. Second, the Pr–O distances (ca. 261 pm) are considerably larger than the Nd–O distances (ca. 256 pm), although the difference in ionic radii is small. Closer inspection of the crystal structures reported reveals, however, that a detailed comparison of the bond parameters is of limited value. A variable-temperature NMR study performed for $(\mathbf{3a})_2\text{Y}(\text{BH}_4)$ has indicated a fast fluxional behavior of the BH_4 ligand in solution, as expected for this type of compound.¹²⁷

The hydroxo complexes $(\mathbf{3a})_2\text{Ho}(\text{OH})$ ¹⁵³ and $(\mathbf{3a})_2\text{Er}(\text{OH})$,¹⁵⁴ reported by C. Qian et al., were formed from the respective chloro complex and trace amounts of water present in the solvent. The lutetium analogue has been suggested as the final product of the hydrolysis of $(\mathbf{3a})_2\text{LuCl}$, which was investigated by IR spectroscopy.¹⁵⁵ The related yttrium compound $\mathbf{9aY}(\text{OH})$ was obtained by H. Schumann et al. from



the reaction of the tri(cyclopentadienyl) species $\mathbf{9aY}(\text{C}_5\text{H}_4\text{Me})$ with trace amounts of water.¹⁵⁶ The species is an OH-bridged C_2 -symmetric dimer in the crystal. The bond lengths in the Y_2O_2 core are indistinguishable [223.7(3) and 223.8(3) pm] and much shorter than the distance between the metal atom and its coordinated ether oxygen atom [250.0(3) pm].

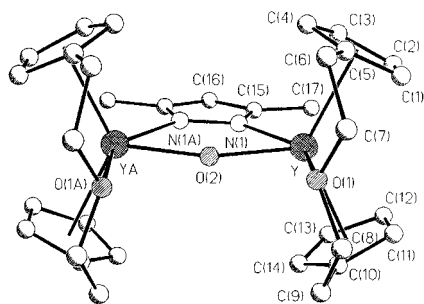
The holmium and erbium complexes of $\mathbf{3a}$ were also found to be OH-bridged dimers in the solid state. Only one of the two functionalized cyclopentadienyl rings coordinated to each metal center acts as a



chelate ligand, so that, similar to $\mathbf{9aY}(\text{OH})$, each metal center forms one bond to an ether O atom [Ho–O 253.8(2) pm, Er–O 254.2(3) pm] and two much shorter bonds to the hydroxo O atoms [both Ho–O 225.0(3) pm, Er–O 221.6 and 225.8(2) pm]. The

Er–O distance of 254.2(3) pm is considerably longer than those found in the monomeric chloro complex $(\mathbf{3a})_2\text{ErCl}$ [243(1) and 247.7(9) pm] (vide supra).

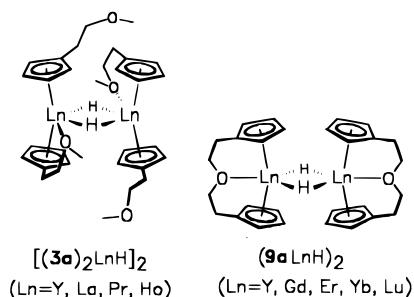
Even longer metal–oxygen distances have been observed in the 3,5-dimethylpyrazolato (DMP, $\text{C}_5\text{H}_7\text{N}_2$) complexes $(\mathbf{9aLn})_2(\mu\text{-OH})(\mu\text{-DMP})$ (Ln = Y, Lu),¹⁵⁷



$(\mathbf{9aY})_2(\mu\text{-OH})(\mu\text{-DMP})$

which were obtained by H. Schumann, C. Qian, and co-workers from the reaction of $\mathbf{9aLn}(\text{DMP})$ ¹⁵⁸ with traces of water in toluene. Both complexes show molecular C_s symmetry in the crystal. Each metal atom forms a short bond to the hydroxo oxygen atom and a very long bond to the ether oxygen atom [Y, 220.2(2) and 266.2(4) pm; Lu, 215.4(3) and 266.7(7) pm], whereas the respective metal–nitrogen bond length has an intermediate value [Y, 244.5(5) pm; Lu, 239.2(8) pm].

The structural motif of doubly bridged dimers has also been reported for the hydrido complexes $(\mathbf{3a})_2\text{LnH}$ (Ln/yield = Y/75%,^{153,159} La/74%,^{153,159} Pr/81%,¹⁵³ Ho/80%¹⁵³) as well as $\mathbf{9aLnH}$ (Ln/yield = Y/71%, Gd/74%,



$[(\mathbf{3a})_2\text{LnH}]_2$

(Ln = Y, La, Pr, Ho)

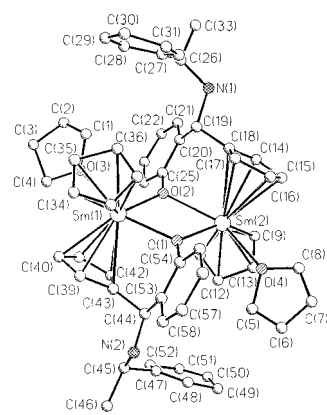
$(\mathbf{9aLnH})_2$

(Ln = Y, Gd, Er, Yb, Lu)

Er/46%, Yb/81%, Lu/75%)¹⁶⁰ and $\mathbf{9aLnD}$ (Ln = Y/68%, Lu/80%)¹⁶⁰ in the solid state. These compounds were synthesized by C. Qian and co-workers from the respective chloro complex and NaH (KH for $\mathbf{9aYH}$) or NaD in THF. Alternatively, J. H. Teuben et al. have prepared $(\mathbf{3a})_2\text{YH}$ in 52% yield from $(\mathbf{3a})_2\text{Y}(\text{AlH}_4)$ by reaction with triethylamine in a mixture of toluene and pentane.¹²⁷ $(\mathbf{3a})_2\text{YH}$ was characterized by X-ray diffraction.¹⁵³ Two crystallographically different C_2 -symmetric molecules are present, whose bond parameters are identical within experimental error [Y–O 246.2(5) pm]. A dimeric hydrogen-bridged structure has also been observed for the compound in benzene¹²⁷ as well as in THF solution,¹⁵³ where the hydrido ligands give rise to a triplet with $^1J_{\text{YH}} = 28$ Hz, similar to related hydrido complexes of yttrium. Owing to the very similar IR spectroscopic features of $(\mathbf{3a})_2\text{LnH}$, C. Qian et al. have argued that the structures are essentially the same for all these species.¹⁵³

The *ansa*-metallocene derivatives $\mathbf{9aLnH}$ have been used for stoichiometric and catalytic reductions of organic substrates.¹⁶⁰ All of them were found to reduce terminal alkenes such as 1-hexene stoichiometrically, with the yttrium and lutetium compounds being the most effective. The best results were obtained with a 1:4 mixture of $\mathbf{9aYH}$ and NaH in boiling THF, where quantitative conversion to hexane was achieved after 48 h. The system is specific for terminal alkenes. $\mathbf{9aYH}$ is also active in the catalytic reduction of alkyl and aryl bromides with sodium hydride in boiling THF. For example, quantitative conversion of *p*-bromoanisole to anisole and of 1-bromohexadecane to hexadecane was effected with a 1:10:20 mixture of $\mathbf{9aYH}$, RBr, and NaH. Not surprisingly, similar reduction reactions were observed when hydrido species were generated in situ from the chloro complexes $\mathbf{9LnCl}$ and $\mathbf{37LnCl}$ with NaH in THF.^{133–135} In general, the ether-functionalized systems investigated by C. Qian and co-workers have proved to be much more effective in these reduction reactions than unfunctionalized analogues. This has been ascribed to the lower solubilities of the latter.¹³³

Only very few rare-earth-element chelate complexes have been reported which contain an alkoxy-linked cyclopentadienyl ligand. Two examples are $\mathbf{12dNdCp}(\text{THF})$ ¹⁶¹ and $\mathbf{12dSmCp}(\text{THF})$,¹⁶² which were



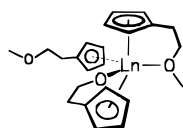
$[\mathbf{12dSmCp}(\text{THF})]_2$

obtained in 61% and 32% yield, respectively, by subsequent addition of SmCl_3 (1 equiv) and the Schiff base (*S*)-*N*-1-phenylethylsalicylideneamine (1 equiv) to CpNa (3 equiv) in THF. Both compounds have been characterized crystallographically by X-ray diffraction and were found to be C_2 -symmetric alkoxy-bridged dimers in the crystal. Each metal atom forms two bonds to three oxygen atoms. The two bonds to the formally anionic alkoxy oxygen atoms are considerably shorter [Nd, 232.7(6)–249.9(6) pm, average 241 pm; Sm, 227.8(12)–248.4(13) pm, average 238 pm] than the bond to the THF oxygen atom [Nd, 255.2(6) and 265.2(6) pm; Sm, 255(2) and 265.0(14) pm]. This structural motif resembles that of the hydroxo-bridged dimers $[(\mathbf{3a})_2\text{Ln}(\text{OH})]_2$ (Ln = Er, Ho) and $[\mathbf{9aY}(\text{OH})]_2$ (vide supra).

The mechanism of the formation of the complexes from the three starting materials has not been elucidated. Interestingly, the configuration at the

asymmetric carbon atom of the CHMePh group, which was *S* in the starting material, changes to *R* during the course of the reaction, while the configuration at the newly formed asymmetric carbon atom, which bridges the cyclopentadienyl and phenoxy rings, was found to be *S* or *R*, leading to the optically active diastereomer with *R,R,R,S*-configuration at the four asymmetric carbon atoms.

c. Tri(cyclopentadienyl) Complexes. The homoleptic complexes (**3a**)₃Ln (Ln/yield = Y/60%,¹⁶³ La/65%,^{163,164} Pr¹⁶⁵/75%,^{163,164} Nd/70%,¹⁶³ Sm¹⁶⁶/89%,¹⁴⁴ Gd/62%,¹⁶³ Yb/91%¹⁴⁴) have been prepared by C. Qian and co-



(**3a**)₃Ln
(Ln=Y, La, Pr, Nd, Sm, Gd, Yb)

workers by metathesis of the appropriate metal trichloride with **3aK** (for Ln = Sm, Yb) or **3aNa** (for the other metals) in THF. The neodymium complex had already been prepared earlier by W. A. Herrmann et al. in 72% yield from NdCl₃ and **3aK**.¹⁶⁷ The two papers do not agree about the color of (**3a**)₃Nd, which is described as deep blue by the German group and as violet-red by the Chinese. X-ray structural analyses have been performed for Ln = La,¹⁶³ Pr,^{163,164} Nd,¹⁶³ Sm,¹⁴⁴ and Gd.¹⁶³ Two of the three oxygen atoms are coordinated to the metal center in each case with an O–Ln–O angle of ca. 175° for all five compounds. However, only one of the two metal–oxygen distances follows the trend expected on the basis of the ionic radii, which decrease from La to Gd, while the other metal–oxygen distance gets considerably longer from La to Gd [La, 275.2(7) and 280.6(6) pm; Pr, 274.0(3) and 283.6(3) pm; Nd, 272.4(3) and 283.9(3) pm; Sm, 274.4(3) and 292.3(4) pm; Gd, 270.1(4) and 298.5(5) pm]. This behavior, which seems counterintuitive at first glance, clearly demonstrates that the complexes become coordinatively oversaturated as the radius of the metal center decreases. The comparatively low volatility of (**3a**)₃Nd has been ascribed to an asymmetric structure of this species, which apparently lacks the spherical shape necessary for high volatility and therefore proved to be unsuitable for CVD purposes.¹⁶⁷

On the basis of these results it is most likely that both ether oxygen atoms are coordinated to the metal center in (**3a**)₂LnCp (Ln = La, Pr, Nd), which were prepared in ca. 30% yield from (**3a**)₂LnCl and CpNa in THF.¹⁶⁸

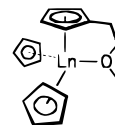


(**3a**)₂LnCp
(Ln=La, Pr, Nd)

The homoleptic lanthanum complex (**3a**)₃La has also been investigated in some detail in solution by

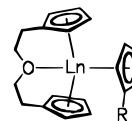
NMR spectroscopy. At –112 °C two signals were observed for the protons of the three methoxy groups in a 2:1 ratio (THF-*d*₈ solvent), compatible with a rigid dichelate structure on the NMR time scale, while at room temperature only one resonance was detected for the OMe protons.^{163,164}

It has been suggested that for the smallest metal centers only one of the three oxygen atoms in (**3a**)₃Ln may be coordinated, and the isolation of the monochelate **3a**YCp₂¹⁶⁹ [Yb–O 241.4(13) pm] in 46% yield from the one-pot reaction of YCl₃ with 1 equiv of **3aNa** and 2 equiv of CpNa in THF has been taken as evidence for this.^{24,163} However, the one-pot method was successfully applied to the synthesis of complexes of type **3a**LnCp₂ with small and large metal centers alike (Ln/yield = La/45%, Sm/58%, Gd/50%, Er/40%, Yb/46%).¹⁶⁹



3aLnCp₂
(Ln=Y, La, Sm, Gd, Er, Yb)

Among the last category of compounds to be mentioned in this subsection are **9a**LnCp (Ln/yield = Y/53%,¹⁵⁶ 60%;¹⁷⁰ Nd/93%,¹⁷⁰ Gd/91%,¹⁷⁰ Ho/30%,¹⁵⁶ Er/91%,¹⁷⁰ Yb/90%,¹⁷⁰ Lu/61%¹⁷⁰) and **9a**Ln(C₅H₄Me)

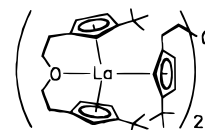


9aLn(C₅H₄R)

R	Ln
H	Y, Nd, Gd, Ho, Er, Yb, Ln
Me	Y, Ho, Yb

(Ln/yield = Y/72%,¹⁷⁰ Ho/30%,¹⁵⁶ Yb/74%¹⁷⁰), which were synthesized by the group of C. Qian from the respective chloro complex **9a**LnCl and CpNa or (C₅H₄Me)Na in THF. None of these complexes has been characterized crystallographically. Their monomeric chelate structure, which has been deduced from IR and MS data, is in line with the structural motif found for the monochelates **3a**LnCp₂.

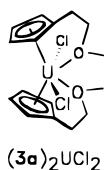
A related, but structurally more complex, species was unexpectedly obtained in an attempt to prepare **9b**LaCl from LaCl₃ and **9b**Na₂ in THF, in analogy to the synthesis of **9c**LaCl (vide supra). The dinuclear (**9b**La)₂(μ-**9b**) was isolated in 85% yield from this reaction.¹³⁴ Its formation is due to the fact that the desired product readily disproportionates, which is in contrast to the behavior of the silylated analogue **9c**LaCl.



(**9b**La)₂(μ-**9b**)

D. Actinoid Elements

A single compound has been reported in this section, namely the uranocene derivative **(3a)₂UCl₂**, which was prepared by C. Qian et al. in 31% yield



from UCl₄ and **3aNa** in THF.^{171,172} The molecule is C₂ symmetric in the crystal. Both ether oxygen atoms are coordinated to the metal center. The core geometry may be described as distorted pseudooctahedral, when the cyclopentadienyl ligand is viewed as occupying a single coordination site. The chloro ligands are in a trans arrangement, whereas the cyclopentadienyl and ether groups are each positioned cis.

V. Applications

Chelate complexes of *O*-functionalized cyclopentadienyl ligands have been utilized mainly as catalysts for Diels–Alder reactions and hydrogenations and for the polymerization of α -olefins. However, if patents are taken as indicators for technological significance, olefin polymerization is the only relevant field of application here. There are no patents for such compounds outside this area, at least not in the literature covered by CAS, whereas a rather large number of patents exist which describe the use of these complexes in olefin polymerization. All of them are very recent, dating from the second half of the 1990s. Some of the patents are quite comprehensive. One of them encompasses all rare-earth-element complexes of any kind of donor-functionalized cyclopentadienyl ligand.¹⁷³ Another one covers all complexes of cyclopentadienyl ligands containing more than one donor group in the side chain with p- and d-block elements as well as the lanthanide metals.¹⁷⁴ A third one is concerned with complexes of any metal-containing cyclopentadienyl ligands which have two or three group 15 or 16 element donor atoms in the side chain (oxygen being the relevant donor atom for this review).¹⁷⁵ The largest number of patents has apparently been filed for group 4 metal complexes which contain alkoxo-^{176,177} or aryloxo-linked cyclopentadienyl ligands.^{178–180} Such systems have attracted a lot of attention as analogues of, and alternatives to, the extensively patented class of group 4 *ansa*-metallocene precatalysts.¹⁸¹ Investigations in this area have been spurred, inter alia, by the great success of constrained-geometry metallocene analogues containing amido-linked cyclopentadienyl ligands in ethene/1-alkene copolymerizations. Ether-functionalized systems have been widely covered, too,¹⁸² and even the elaborate motifs of ligands **17**,¹⁸³ **22**,¹⁸⁴ and **25**¹⁸⁵ have not gone unnoticed by the patentees. However, to the best of my knowledge material advancements based on such species have not been reported so far in the scientific literature.

VI. Conclusion and Outlook

Cyclopentadienyl systems bearing pendant *O*-donors act as chelating ligands mainly for oxophilic metal centers. Surprisingly, only a limited number of such metals have been investigated in this respect. For example, of the so-called early transition metals, only the group 4 elements have been used, although a similarly rich coordination chemistry can be expected for the other early transition metals, especially in higher oxidation states, and also for certain p-block elements such as, for example, aluminum.

To date the area where cyclopentadienyl ligands with pendant *O*-donors have proved most useful is rare-earth-element chemistry. Cyclopentadienyl complexes of these metals are usually strong Lewis acids and, although they can in principle be prepared fairly easily, it is often notoriously difficult to free them from residual amounts of salts (LiCl, MgCl₂, etc.) and solvents which are present in the crude product for synthetic reasons. These problems are conveniently avoided by using an ether-substituted cyclopentadienyl ligand, which can act as internal solvent, as it were. It is quite remarkable that, with the exception of **6a** and **12d**, alkoxo-linked cyclopentadienyl ligands have not been utilized so far in rare-earth-element chemistry, and this leaves fertile ground which still remains to be plowed.¹⁸⁶

In comparison to related *N*-functionalized cyclopentadienyl complexes, where catalytic applications of such species have been remarkably successful (especially in olefin polymerization), the use of *O*-functionalized compounds in catalysis still seems underdeveloped. However, the patent literature is rapidly growing in this area, which reflects the great potential for such applications that has been realized in industry and academia alike.

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