Journal of Organometallic Chemistry, 471 (1994) 87–95

Lanthanocene (Ln = Pr^{III}, Yb^{III}) chlorides involving tetramethyldisiloxane-interlinked cyclopentadienyl ligands

Jens Gräper [a], R. Dieter Fischer [a] and Gino Paolucci [b]

[a] *Institut für Anorganische und Angewandte Chemie der Universität Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg (Germany)*
[b] *Dipartimento di Chimica, Universitá di Venezia, Calle Larga S. Marta 2137, I-30123 Venezia (Italy)*

(Received March 18, 1993; in revised form September 30, 1993)

Abstract

Two new lanthanocenophanes $[\{O(Me_2SiC_5H_4)_2\}Pr^{III}Cl \cdot THF]_x$ (**2**; $x = 1$ or 2) and $[\{O(Me_2SiC_5H_4)_2\}Yb^{III}Cl]_2$ (**3**), were made from $LnCl_3$ (Ln = Pr or Yb) and $K_2[O(Me_2SiC_5H_4)_2]$ in THF. The ^1H NMR spectra of THF-d_8 solutions of paramagnetic **2** (at +35 to −25°C) and **3** (at < 10°C) reflect an asymmetrical disposition of the siloxy linkage, while solutions of **2** in CD_2Cl_2 (at 20°C) and **3** in THF-d_8 (at > 10°C), respectively, display somewhat less complex ^1H NMR spectra consistent with a virtually symmetrical position of the $Me_2SiOSiMe_2$ unit with respect to the cent-Ln-cent′ plane (cent = C_5H_4Si centroid). A low-temperature (−100°C) single-crystal X-ray study of **3** has confirmed the presence of centrosymmetric, Cl-bridged dimers in which the molecular configuration of the mononuclear $\{O(Me_2SiC_5H_4)_2\}Yb^{III}Cl_2$ units correspond to that of the previously described complex $[\{O(Me_2SiC_5H_4)_2Ti^{IV}Cl_2]$ (**1**). The high-resolution mass spectrum of **3** displays several signals from dinuclear fragments, the B/E-linked scans of which suggest, *inter alia*, intramolecular reorientation of at least one $O(Me_2SiC_5H_4)_2$ ligand from the chelating into a metal-bridging position.

Key words: Ytterbium; Praseodymium; Metallocenes; Lanthanides; Chiral metallocenophanes; Crystal structure

1. Introduction

"Lanthanocene" halides, $[(C_5H_5)_2Ln^{III}X]_n$ (n = 1–2), involving "earlier" lanthanoids (Ln = La–Nd), as well as "lanthanocene" adducts, $[(C_5H_5)_2Ln^{II} \cdot L_x]$ (Ln = Sm, Eu, Yb; L = *e.g.* tetrahydrofuran, pyridine *etc.*), are difficult to isolate owing mainly to facile ligand redistribution and/or severe solubility problems. Ways of overcoming such obstacles have been (a) peralkylation of both ring ligands [1], (b) substitution of one or two ring hydrogen atom(s) by sufficiently bulky groups [2–4], and (c) application of suitably tethered pairs of cyclopentadienyl anions, $[\mu\text{-}X(C_5H_4)_2]^{2-}$ [5]. While so far the trimethylene linkage, X = $-(CH_2)_3-$, has appeared to be optimal [6*,7], even five-membered chains of slightly reduced flexibility have been shown to stabilize "early lanthanocene" halides [8–10].

In contrast to the rather flexible $-(CH_2)_3-$ bridge, the similarly triatomic 1,1,3,3-tetramethyldisiloxane bridge, $-Me_2SiOSiMe_2-$, used first by Curtis *et al.* [11], is likely to adopt one clearly favoured conformation in view of the larger space requirement of its four methyl groups, and, possibly, also of some p_π–d_π bonding between the oxygen and the two silicon atoms. We report below the preparation and some characteristic properties of the first lanthanoid(III) congeners (Ln = Pr and Yb) of the structurally well-investigated titanium complex $[\{O(Me_2SiC_5H_4)_2\}Ti^{IV}Cl_2]$ (**1**) [11].

2. General procedures and results

1,1,3,3-Tetramethyl-1,3-dichlorodisiloxane was made by partial hydrolysis of dimethyldichlorosilane and subsequent fractional distillation. Reaction of pure 1,1,3,3,-tetramethyl-1,3-dichloro-disiloxane with cyclopentadienyl potassium (1:2) in THF then afforded 1,1,3,3-tetramethyl-1,3-dicyclopentadienyldisiloxane. The latter was reduced with elemental potassium to $K_2[C_5H_4SiMe_2OSiMe_2C_5H_4]$. This potassium salt was

---

Correspondence to: Prof. R. Dieter Fischer.

* Reference number with an asterisk indicates a note in the list of references.

0022-328X/94/$7.00
SSDI 0022-328X(93)24232-T

then treated in THF with anhydrous $PrCl_3$ or $YbCl_3$ to give the new organolanthanoid complexes $[\{O(Me_2SiC_5H_4)_2\}PrCl(THF)]_x$ (**2**) and $[\{O(Me_2SiC_5H_4)_2\}YbCl]_2$ (**3**). Complex **2** is as a bright yellow, polycrystalline material which is sparingly soluble in solvents other than THF, non-sublimable *in vacuo*, and thermally stable up to 90–100°C. The presence of coordinated THF is confirmed by elemental analysis and the appearance of two relevant ^1H NMR signals in CD_2Cl_2 solution (*vide infra*). While mononuclear **2** would, in view of the recent identification of the complex $[(^tBuC_5H_4)_2Pr^{III}Cl(THF)_2]$ (**4**) [2], be likely to contain two THF ligands per metal ion, a coordinatively saturated dinuclear, chloride-bridged complex is expected to prefer a Pr/THF ratio of 1:1. Complex **2** gives not only informative ^1H NMR spectra but also high quality NIR/VIS and MCD absorption spectra.

Solid **3** is orange-red in colour, sparingly soluble (except in THF) and not sublimable *in vacuo*. Thermal decomposition starts at *ca.* 120°C in that the sample first becomes colourless and then brown. While the ytterbium analogue of **4**, $[(^tBuC_5H_4)_2Yb^{III}Cl(THF)]$, is likewise mononuclear [2], the structural analysis of a single crystal of **3** grown from THF in the presence of little toluene has proved this complex to be dinuclear and free of THF. Crystal data and details of data collection and refinement are given in Table 1.

TABLE 1. Summary of crystal data and details of data collection and refinement for **3**

Formula	$C_{28}H_{40}Cl_2O_2Si_4Yb_2$
M (g/mol)	937.96
Crystal size (mm)	< 0.1 in diameter
Crystal system	Monoclinic
Space group	$P2_1/c$
a (pm)	1495.3(3)
b (pm)	750.1(2)
c (pm)	1619.0(3)
β (°)	112.35(3)
V (10^{-6} pm^{-3})	1679.3(6)
Z (dimers)	2
D_c (g cm^{-3})	1.855
$F(000)$	908
Temperature (K)	173
Diffractometer	Enraf-Nonius CAD-4
Radiation λ (pm)	154.051 (Cu Kα)
μ(Cu Kα) (mm^{-1})	1.855
Scan technique	$2\theta-\theta$ scan
2θ range (°)	$2.3 < 2\theta < 40.0$
No. reflections	3839
No. unique reflections	3351
No. reflections in refinement	2491
No. refined parameters	173
Goodness-of-fit	1.99
Weighting scheme	$[\sigma^2(F)+0.0004F^2]^{-1}$
Limit of significance	$[\lvert F_o\rvert > 4\sigma(F_o)]$
R	0.0624
R_w	0.0573

3. Molecular and crystal structure of 3

Like three other crystalline $[Cp'_2YbCl]_2$ systems ($Cp' = C_5H_5$ [12], $CH_3C_5H_4$ [13] and $(Me_3Si)_2C_5H_3$ [3]), complex **3** is free of THF and has a planar Yb_2Cl_2 skeleton. The latter deviates only insignificantly from an ideal square in that all Yb–Cl distances are almost equal, while the Yb–Cl–Yb′ and Cl–Yb–Cl′ angles scatter somewhat around 90° (Tables 2 and 3). While the individual Yb–C (ring) distances vary appreciably (as *e.g.* in **1** [11]), the average Yb–C distance compares well with those previously reported for $(C_5H_4R)_2Yb^{III}$ derivatives [12,13]. The Si–C bond lengths, and the angles at the silicon atoms of the siloxy bridge are similar to those reported for complex **1** [11].

TABLE 2. Selected interatomic distances (bonding and non-bonding; in pm) in **3**

Yb1–Cl1	265.7(3)	Yb1–Cl1′	264.2(3)
Yb1–C1	262.2(15)	Yb1–C11	261.5(14)
Yb1–C2	260.5(13)	Yb1–C12	259.3(13)
Yb1–C3	256.8(11)	Yb1–C13	255.1(14)
Yb1–C4	257.1(10)	Yb1–C14	252.8(16)
Yb1–C5	256.8(12)	Yb1–C15	260.0(14)
Si1–C4	185.5(12)	Si1–C21	186.7(11)
Si2–C14	188.3(11)	Si1–C22	185.9(15)
Si1–O1	163.7(11)	Si2–C31	185.0(16)
Si2–O2	162.1(10)	Si2–C32	185.9(16)
Cent1–Yb1 [a]	229.0(7)	Cent2–Yb1 [a]	228.1(7)
Yb1 ··· O1	309.4(10)	Yb1 ··· Yb1′	392.2(2)
C1 ··· C11	509.2(18)	C4 ··· C14	367.4(18)
C2 ··· C12	402.7(18)	C5 ··· C15	489.9(17)
C3 ··· C13	319.7(17)	Cl1 ··· Cl1′	356.5(4)

[a] Cent 1 and Cent 2 denote centroids of the Cp range.

TABLE 3. Selected bond angles [°] in **3**

Cent1–Yb1–Cent2	132.0(3)	C4–Si1–O1	111.1(5)
Yb1–Cl1–Yb1′	95.5(1)	C21–Si1–C22	111.3(6)
Cl1–Yb1–Cl1′	84.5(1)	C14–Si2–C31	109.6(6)
Si1–O1–Si2	151.1(6)	C14–Si2–C32	109.1(5)
C4–Si1–C21	111.9(6)	C14–Si2–O1	109.4(6)
C4–Si1–C22	105.9(6)	C31–Si2–C32	110.1(8)

The most remarkable structural feature of **3** is that its ring-bridging $-Me_2SiOSiMe_2-$ group is positioned in the same manner as in **1**, *i.e.* asymmetrically with respect to the Cl–Yb–Cl′ plane (Fig. 1). The conformation of each mononuclear $\{O(Me_2SiC_5H_4)_2\}YbCl_2$ unit of **3**, which resembles that of **1**, differs notably from the conformations of *e.g.* $[(CH_2)_3(C_5H_4)_2Ti^{IV}Cl_2]$ [14] and $[(CH_2)_3(C_5H_4)_2Yb^{II}(THF)_2]$ [7] in which only one pair of ring carbon atoms displays the widest inter-ring C ··· C distance. In contrast, two pairs of ring carbon atoms show the widest inter-ring separa-

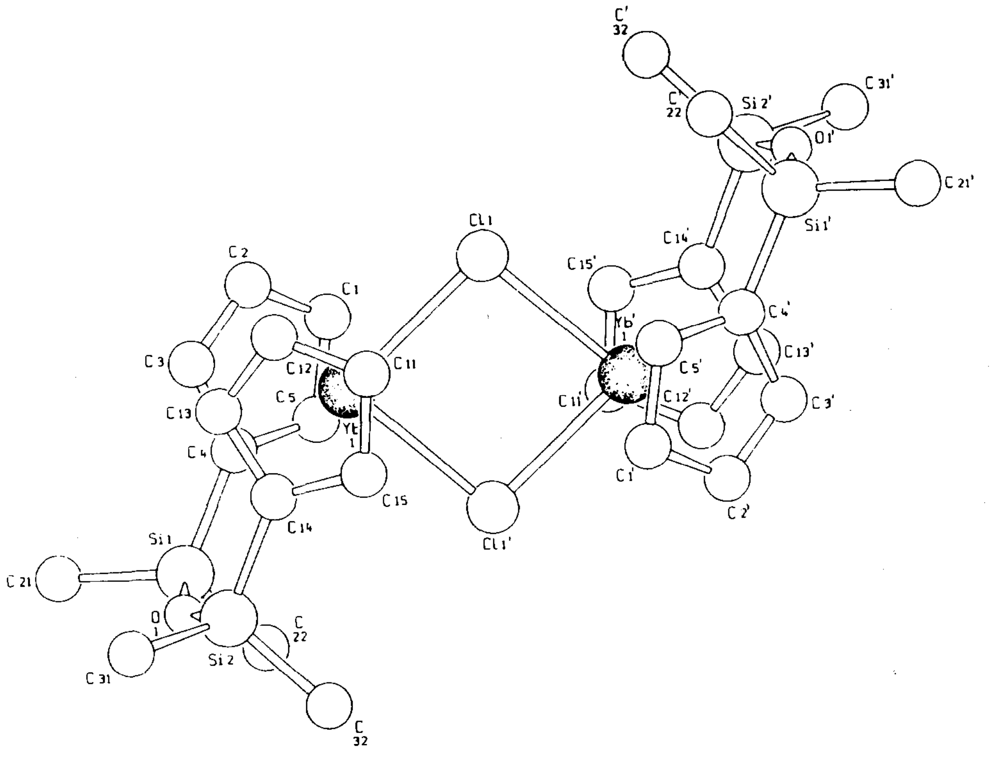

Fig. 1. SCHAKAL plot of the molecular structure of 3 with atomic numbering scheme.

tion in 1 and 3. Interestingly, the conformational similarity of 3 and 1 is maintained despite the markedly different M–cent distances for M = Ti (2.07 Å [11]) and M = Yb (2.29 Å, *cf.* Table 2). The distance between the two bridgehead carbon atoms, C4 and C14, in 3 (3.674 Å) exceeds the corresponding distance in 1 (3.38 Å [11]) by *ca.* 0.3 Å. Somewhat surprisingly, in 3 the ring carbon atoms, C3 and C13, with the shortest inter-ring C · · · C distances do not function as bridgehead atoms. This is accounted for by a substantial widening of the Si–O–Si' angle from 141° in 1 to 151° in 3. A corresponding narrowing of this angle below the usual value common for unstrained siloxanes (*ca.* 140° [15]) to make the carbon atoms C3 and C13 more appropriate bridgehead atoms is obviously less attractive. Since the separation Pr–cent (*ca.* 2.54 Å [16*] is larger than Yb–cent (*vide supra*), the configurations of the $\{O(Me_2SiC_5H_4)_2\}Ln$ units of 2 and 3 may, nevertheless, not be equivalent.

Although several dinuclear $[Cp'_2Ln(\mu\text{-}X)]_2$ systems are known to be not fully coordinatively saturated, and tend to go to oligomers or polymers [17*], the lattice of 3 does not display any relevant intermolecular Yb · · · Cl · · · Yb' or Si_2O · · · Yb' contacts. The in-

TABLE 4. ^1H NMR data of 2 at three selected temperatures

Temperature (°C)	C_5H_4-protons (signal-no.) [a]				CH_3-protons (signal-no.) [a]	
	1	2	3	4	5	6
20 [b]	52.4(4)		35.8(4)		−13.8(12)	
	245		210		75	
34 [c]	52.4(2)	30.0(2)	23.2(2)	14.9(2)	−7.5(6)	−10.6(6)
	64	45	15	7	33	10
−38 [c]	70.1(2)	49.2(2)	33.2(2)	22.2(2)	−15.0(6)	−17.6(6)
	290	180	62	33	240	48
−53 [c]	d	53.9(2)	35.5(2)	24.1(2)	d	−19.3(6)
		210	116	45		90

[a] Upper line: chemical shift (reference TMS); in parentheses: relative intensity (from integral), lower line: half width of signal (in Hz). [b] Solvent CD_2Cl_2. [c] Solvent THF-d_8. [d] Signal probably too broad to be detectable.

tramolecular Yb···O distance (3.094 Å) still exceeds the very long Pr–O contact of 2.836 Å in [(MeOCH$_2$-CH$_2$C$_5$H$_4$)$_3$Pr] [18].

3.1. ^{1}H NMR spectroscopy of 2 and 3

The low solubility of **2** and **3** in solvents other than THF has restricted solution NMR studies almost exclusively to THF-d_8. Only the room temperature spectrum of **2** could be observed in CD$_2$Cl$_2$ solution, and even at slightly lower temperatures the complex rapidly separated out. The appearance of two multiplets of THF protons of the relative intensities four (δ 2.88 and 3.60 ppm) confirms (in accordance with the elemental analysis) the presence of one THF ligand per metal ion in **2**. The chemical shifts assigned to THF resemble, however, those of the uncoordinated ether, suggesting that in CD$_2$Cl$_2$ solution there is a rapid equilibrium of the type

$$n[\mathrm{LPrCl(THF)}] \xrightleftharpoons{\mathrm{CH_2Cl_2}} [\mathrm{LPrCl}]_n + n\mathrm{THF}$$

$$(\mathrm{L} = \{\mathrm{O(Me_2SiC_5H_4)_2}\}) \tag{1}$$

As the C$_5$H$_4$ ring protons give rise to two, widely separated low-field resonances, and the methyl protons to only one high-field singlet (Table 4), molecular configurations involving a (virtually) quite symmetrically disposed siloxy bridge are likely. In contrast to the molecular species present in THF-d_8 solution (*vide infra*), the predominant complex in CD$_2$Cl$_2$ seems to be sterically less congested and, hence, able to undergo rapid (on the NMR time scale) interconversion of one unsymmetrical molecule into its mirror image. Corresponding fluxionality was previously assumed for the diamagnetic **1** in view of its strikingly simple ^{1}H NMR spectrum [11].

In THF-d_8 solution, the two THF resonances of **2** are again unaffected by the paramagnetism of the Pr^{3+} ion(s), indicating rapid THF/THF-d_8 exchange. Yet, even at 34°C, four C$_5$H$_4$ (I_{rel} 2 each) and two CH$_3$ proton resonances (I_{rel} 6 each) of surprisingly different line widths are observed. The corresponding half widths (see Table 4) increase notably as the temperature is lowered, and below −45°C one of the C$_5$H$_4$ signals and one CH$_3$ proton signal have apparently become too broad to be detected. Unexpectedly, the methyl resonance with the weaker high-field displacement shows the stronger line broadening.

The number and relative intensities of the resonances appearing above *ca.* −40°C leave no doubt that in the presence of THF complex **2** has a sterically more congested ligand sphere that inhibits rapid intramolecular interconversion of the {O(Me$_2$SiC$_5$H$_4$)$_2$}Pr fragment. In view of the comparatively large radius of the Pr^{3+} ion, the formation of either mononuclear {O(Me$_2$SiC$_5$H$_4$)$_2$}PrCl(THF)$_2$ (*i.e.* of an analogue of **4** [2]), or of dinuclear [{O(Me$_2$SiC$_5$H$_4$)$_2$}Pr(THF)(μ-Cl)]$_2$ species may be envisaged. Again, the siloxy bridge must be assumed to be unsymmetrically positioned, and the exchange of THF ligands is expected to be notably faster than the intramolecular reorientation of each O(Me$_2$SiC$_5$H$_4$)$_2$ ligand. The UV/VIS spectrum of a solution of **2** in 2-Me-THF, even at 90 K, shows several unusually broad (^{3}H$_4 \rightarrow {}^3$P$_{0-2}$) absorption bands (Fig. 2), suggesting that under these conditions at least two quite similar species are present.

The ^{1}H NMR spectra of **3** in THF-d_8 solution (Table 5) resemble those of **2** in view of the appearance of signals of unexpectedly different line widths.

TABLE 5. ^{1}H NMR data of **3** at six selected temperatures (solvent THF-d_8)

Temperature (°C)	C$_5$H$_4$-protons (signal-no.) [a]				CH$_3$-protons (signal-no.) [a]	
	1	2	3	4	5	6
45	−55.0(4)		−34.2(4)		14.1(12)	
	ca. 2100		*ca.* 2100		120	
20	−60.3(4)		−38.2(4)		15.5(12)	
	ca. 1800		*ca.* 2000		320	
5	−84.5(2)	−67.9(2)	−44.1(2)	*ca.* −30	15.0(6)	24.9(6)
	520	400	280	[b]	112	180
−25	−99.6(2)	−82.9(2)	−56.0(2)	[c]	18.0(6)	31.0(6)
	560	260	280		44	125
−40	−108.3(2)	−88.0(2)	−59.6(2)	*ca.* −40	19.1(6)	32.8(6)
		320	260	[b]	40	160
−55	−114.0(2)	−94.3(2)	−65.0(2)	[c]	20.3(6)	35.9(6)
		320	240		32	160

[a] Upper line: chemical shift (reference TMS); in parentheses relative intensity (from integral); lower line: half width of signal (in Hz). [b] Extremely broad and flat signal. [c] Signal undetectable.

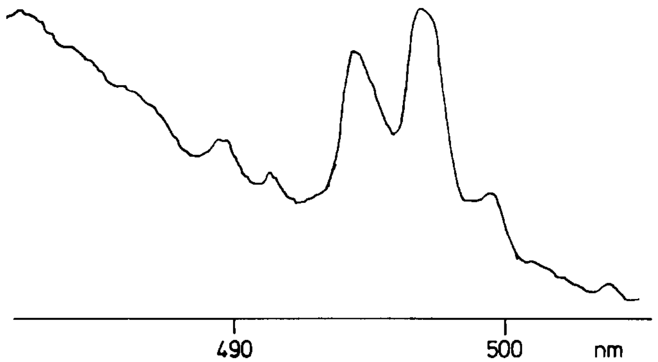

Fig. 2. Low-temperature absorption spectrum of **2** (solvent 2-Me-THF, temperature 90 K) in the $^3H_4 \rightarrow {^3P_{0-2}}$ excitation range. Wavelengths at vertical marks: 489.5, 494.5, 497.0 and 499.5 nm.

However, the ring proton resonances of **3** are displaced to higher fields, and the methyl resonances to lower fields, than expected for a diamagnetic analogue. Moreover, above *ca.* +5°C in THF-d_8 **3** seems to have a fluxional $\{O(Me_2SiC_5H_4)_2\}Yb$ skeleton, and, like **2**, a sufficiently rigid configuration with asymmetrically oriented siloxy bridges below room temperature. While the low-temperature ^1H NMR spectra show throughout two methyl singlets of the expected I_{rel}-value (for non-fluxionality) of six, only three, instead of four, equally intense (I_{rel} 2) C_5H_4 ring proton resonances can be detected. The missing fourth resonance may possibly appear at even higher fields ($\delta < -120$ ppm), or be buried under the solvent resonances (+6 ppm > $\delta > -3$ ppm). Recent ^1H NMR studies of CD_2Cl_2 solutions of the novel complex $[\{2,6\text{-}C_5H_3N(CH_2\text{-}C_5H_4)_2\}Yb^{III}Cl]_2$, involving two cyclopentadienyl ligands interlinked by a 2,6-bis(methylene)pyridine unit [10], revealed two very broad C_5H_4 proton resonances at -24.3 and -158 ppm (room temperature); while *e.g.* the previously described alkynide complex $[(C_5H_5)_2Yb^{III}C_2\text{-}n\text{-}C_4H_9]_n$, with freely rotating C_5H_5 ligands, at -80°C showed one broad signal at -106 ppm [19].

The appearance of time-averaged ^1H NMR spectra of **3** at temperatures above +5°C suggests that there is again rapid intramolecular interconversion of the $\{O(Me_2SiC_5H_4)_2\}Yb$ skeleton. Actually, a $Cp'_2Yb^{III}Cl$ unit is expected to add just one THF molecule [2], giving in spite of the smaller ionic radius of Yb^{3+} (as compared with Pr^{3+}), a sterically less congested species than would arise from the presence two THF molecules in **2** (*vide supra*). Thus, a lower coalescence temperature for **3** than for **2** (in THF-d_8) appears reasonable. It is noteworthy that the mononuclear THF-adduct of **3** (1 : 1) should in principle give rise to one isomer with a cisoid orientation of the chloride ligand with respect to the $O(Me_2Si)_2$ bridge, and to a second with a transoid orientation of these two components. Yet, down to -55°C, THF-exchange at the metal site is apparently too rapid to allow such differences to be detected by ^1H NMR.

3.2. *Mass spectrometric (MS) investigation of 3*

Unexpectedly, **3** is notably less volatile than, *e.g.* $[(Me_3SiC_5H_4)_2YbCl]_2$ (**5**) and $[\{Me_2Si(C_5H_4)_2\}YbCl]_2$ (**6**) so that for MS-studies of **3**, probe temperatures must be higher than those for **5** and **6** [20]. However, only evidence of thermal cleavage into the monomer, $[\{O(Me_2SiC_5H_4)_2\}YbCl]$, is apparent from the MS of **3** (*vide infra*).

The most intense ($I_{rel} > 1$) fragments (containing at least one Yb atom) of the normal MS are listed in Table 6. Eleven dinuclear fragments (including the molecular ion, $M^{+\bullet}$) are seen. Although the base peak ($I_{rel} = 100$) belongs as usual [20–22] to the mononuclear fragment, $Cp'_2Ln^+ = M^{+\bullet}/2\text{-}Cl^\bullet$, the high abundance of the dinuclear fragment $B = A - 2Me^\bullet = M^{+\bullet} - L$ ($L = O(Me_2SiC_5H_4)_2$) is remarkable. In view of the fact that the dinuclear species **3** is held together by Cl-bridges only (*vide supra*), the occurrence of three dinuclear fragments with only one Cl atom, and even of one fragment without any Cl-atom, is also surprising.

TABLE 6. Mass spectrometric data for **3** (normal MS; m/z values considering the isotopes ^{28}Si, ^{35}Cl and ^{174}Yb only; EI, 70 eV, probe temperature *ca.* 300°C

Fragment	Formula	m/z	I_{rel} (%)
$M^{+\bullet}$	$C_{28}H_{40}Si_4O_2Yb_2Cl_2$	938	19
$M^{+\bullet} - Me^\bullet]^+$	$C_{27}H_{37}Si_4O_2Yb_2Cl_2$	923	6
$M^{+\bullet} - Cl^\bullet]^+$	$C_{28}H_{40}Si_4O_2Yb_2Cl$	903	3
$M^{+\bullet} - C_5H_6]^+$	$C_{23}H_{34}Si_4O_2Yb_2Cl_2$	872	2
$M^{+\bullet} - 2Cl^\bullet$	$C_{28}H_{40}Si_4O_2Yb_2$	868	2
$M^{+\bullet} - C_5H_4Si_2Me_3O$	$C_{19}H_{24}Si_2OYb_2Cl_2$	742	2
$M^{+\bullet} - (C_5H_4)_2Si_2Me_2O$ (A)	$C_{16}H_{26}Si_2OYb_2Cl_2$	708	5
(A) − $2Me^\bullet$ (B)	$C_{14}H_{20}Si_2OYb_2Cl_2$	678	83
(A) − $Cl^\bullet$	$C_{16}H_{26}Si_2OYb_2Cl$	673	18
(B) − $Me^\bullet$	$C_{13}H_{17}Si_2OYb_2Cl_2$	663	4
(B) − $Cl^\bullet$	$C_{14}H_{20}Si_2OYb_2Cl$	643	2
$M^{+\bullet}/2$	$C_{14}H_{20}Si_2OYbCl$	469	19
$M^{+\bullet}/2 - Me^\bullet$	$C_{13}H_{17}Si_2OYbCl$	454	7
$M^{+\bullet}/2 - Cl^\bullet$	$C_{14}H_{20}Si_2OYb$	434	100
$M^{+\bullet}/2 - Me^\bullet - Cl^\bullet$ (C)	$C_{13}H_{17}Si_2OYb$	419	24
(C) − $Me^\bullet$	$C_{12}H_{14}Si_2OYb$	404	17
(C) − $2Me^\bullet$	$C_{11}H_{11}Si_2OYb$	389	11
$M^{+\bullet}/2 - Cl^\bullet - C_5H_6$	$C_9H_{14}Si_2OYb$	368	5
(C) − C_5H_6	$C_8H_{11}Si_2OYb$	353	7
(C) − $Me^\bullet - C_5H_4Me^\bullet$	$C_7H_{10}Si_2OYb$	340	3
(C) − $(C_5H_5)(C_5H_4)Si_2Me_4O$	$C_{14}H_{21}Si_2O$	261	24
(C) − $(C_5H_4)_2Si_2Me_4O$	$C_{14}H_{20}Si_2O$	260	38
(C) − C_5H_5Yb	C_5H_5Yb	239	17

To provide further insight into the electron-impact-induced fragmentation, and potential intramolecular rearrangements of **3**, the B/E-linked scans of four dinuclear fragments (including $\mathrm{M}^{+\bullet}$), and of four mononuclear fragments, were investigated. The results of these eight separate studies are summarized in Tables 7 and 8, respectively. From these data, the "complete" fragmentation pattern of **3** can be straightforwardly deduced. Interestingly, $\mathrm{M}^{+\bullet}$ not only loses one or two Cl atoms, but most frequently ($I_{\mathrm{rel}} = 100$) even a complete $\mathrm{O(Me_2SiC_5H_4)_2}$ ligand, affording fragment B, which is also the second most abundant in the normal MS (Table 6).

Other unexpected findings are that $\mathrm{M}^{+\bullet}$ does not undergo electron-impact-induced symmetrical cleavage into $\mathrm{M}^{+\bullet}/2$, and that the generation of at least ten dinuclear daughter ions (of $\mathrm{M}^{+\bullet}$) contrasts with that of only one mononuclear fragment. Further inspection of Table 7 reveals that none of the dinuclear fragments of **3** subjected to a B/E-linked scan study generates the mononuclear ion $\mathrm{M}^{+\bullet}/2$ (*m/z* 469). Thus, its appearance in the survey MS (Table 6) is most probably exclusively the result of purely thermal cleavage. The rather facile loss of one complete $\mathrm{O(Me_2SiC_5H_4)_2}$ ligand (from $\mathrm{M}^{+\bullet}$) is reminiscent of the MS results reported for mononuclear complexes of the type $[\{\mathrm{O(CH_2CH_2C_5H_4)_2}\}\mathrm{LnC_5H_4R}]$ [23] for which the molecular ion may lose either $\mathrm{C_5H_4R}$ or $\mathrm{O(CH_2CH_2C_5H_4)_2}$ units. Since on simple geometric grounds a $\mathrm{O(Me_2SiC_5H_4)_2}$ ligand could in principle also occupy a metal-bridging (*i.e.* a non-chelating) position, intramolecular ligand rearrangement from chelating to metal-bridging cannot be ruled out. It is even possible that, *e.g.*, the halide-deficient, dinuclear fragments owe their relative stability to the presence of at least one metal-bridging $\mathrm{O(Me_2SiC_5H_4)_2}$ ligand. While the loss of one complete $\mathrm{O(Me_2SiC_5H_4)_2}$ unit is mainly induced by electron impact, its intramolecular rearrangement (isomerization) could in principle also be induced thermally. Very recently, the mononuclear ferrocenophane, $\mathrm{Me_2Si(C_5H_4)_2Fe}$, has been shown to polymerize at elevated temperatures, in that the functionality of the $\mathrm{Me_2Si(C_5H_4)_2}$ ligand changes from chelating to metal-bridging [24].

TABLE 7. Daughter fragments ($I_{\mathrm{rel}} > 1\%$) of selected dinuclear parent ions, as determined from B/E-linked scan studies

Parent fragment	Eliminated group	Daughter fragment	
		m/z	I_{rel} (%)
$\mathrm{M}^{+\bullet}$	$\mathrm{Me}^{\bullet}$	923	2
$\mathrm{M}^{+\bullet}$	$\mathrm{Cl}^{\bullet}$	903	17
$\mathrm{M}^{+\bullet}$	$\mathrm{C_5H_6}$	872	6
$\mathrm{M}^{+\bullet}$	$\mathrm{2Cl}^{\bullet}$	868	6
$\mathrm{M}^{+\bullet}$	$\mathrm{C_5H_4Si_2Me_3O}$	742	5
$\mathrm{M}^{+\bullet}$	$\mathrm{(C_5H_4)_2Si_2Me_2O}$	708	26
$\mathrm{M}^{+\bullet}$	$\mathrm{(C_5H_4)_2Si_2Me_4O}$	678	100
$\mathrm{M}^{+\bullet}$	$\mathrm{(C_5H_4)_2Si_2Me_2O;\ Cl}^{\bullet}$	673	2
$\mathrm{M}^{+\bullet}$	$\mathrm{(C_5H_4)_2Si_2Me_4O;\ Me}^{\bullet}$	663	2
$\mathrm{M}^{+\bullet}$	$\mathrm{(C_5H_4)_2Si_2Me_4O;\ Cl}^{\bullet}$	643	2
$\mathrm{M}^{+\bullet}$	$\mathrm{Yb(C_5H_4)_2Si_2Me_4O;\ 2Cl^{\bullet};\ C_5H_6}$	368	11
$\mathrm{M}^{+\bullet}-\mathrm{Me}^{\bullet}$	$\mathrm{Me}^{\bullet}$	908	2
$\mathrm{M}^{+\bullet}-\mathrm{Me}^{\bullet}$	$\mathrm{Cl}^{\bullet}$	888	8
$\mathrm{M}^{+\bullet}-\mathrm{Me}^{\bullet}$	$\mathrm{C_5H_6}$	857	6
$\mathrm{M}^{+\bullet}-\mathrm{Me}^{\bullet}$	$\mathrm{Yb(C_5H_4)_2Si_2Me_3O;\ 2Cl}^{\bullet}$	434	100
$\mathrm{M}^{+\bullet}-\mathrm{Cl}^{\bullet}$	$\mathrm{Me}^{\bullet}$	888	12
$\mathrm{M}^{+\bullet}-\mathrm{Cl}^{\bullet}$	$\mathrm{Cl}^{\bullet}$	868	17
$\mathrm{M}^{+\bullet}-\mathrm{Cl}^{\bullet}$	$\mathrm{C_5H_6}$	837	39
$\mathrm{M}^{+\bullet}-\mathrm{Cl}^{\bullet}$	$\mathrm{C_5H_4Si_2Me_4O}$	707	100
B	$\mathrm{Me}^{\bullet}$	663	12
B	$\mathrm{Cl}^{\bullet}$	643	7
B	$\mathrm{C_5H_5,\ 2Cl}^{\bullet}$	543	7
B	$\mathrm{YbCl_2}$	434	100

TABLE 8. Daughter fragments ($I_{\mathrm{rel}} > 1\%$) of selected mononuclear parent ions, as determined from B/E-linked scan studies

Parent fragment	Eliminated group	Daughter fragment	
		m/z	I_{rel} (%)
$\mathrm{M}^{+\bullet}/2$	$\mathrm{H}^{\bullet}$	468	100
$\mathrm{M}^{+\bullet}/2$	$\mathrm{2H}^{\bullet}$	467	80
$\mathrm{M}^{+\bullet}/2$	$\mathrm{Me}^{\bullet}$	454	34
$\mathrm{M}^{+\bullet}/2$	$\mathrm{Cl}^{\bullet}$	434	31
$\mathrm{M}^{+\bullet}/2$	$\mathrm{C_5H_6}$	403	3
$\mathrm{M}^{+\bullet}/2-\mathrm{2Cl}^{\bullet}$	$\mathrm{H}^{\bullet}$	433	100
$\mathrm{M}^{+\bullet}/2-\mathrm{2Cl}^{\bullet}$	$\mathrm{2H}^{\bullet}$	432	89
$\mathrm{M}^{+\bullet}/2-\mathrm{2Cl}^{\bullet}$	$\mathrm{Me}^{\bullet}$	419	46
$\mathrm{M}^{+\bullet}/2-\mathrm{2Cl}^{\bullet}$	$\mathrm{C_5H_6}$	368	2
C	$\mathrm{H}^{\bullet}$	418	100
C	$\mathrm{2H}^{\bullet}$	417	35
C	$\mathrm{Me}^{\bullet}$	404	20
C	$\mathrm{C_5H_6}$	353	5
C	$\mathrm{C_5H_4Si_2Me_2CH_2O}$	239	9
$\mathrm{C}-\mathrm{Me}^{\bullet}$	$\mathrm{H}^{\bullet}$	403	100
$\mathrm{C}-\mathrm{Me}^{\bullet}$	$\mathrm{2H}^{\bullet}$	402	15
$\mathrm{C}-\mathrm{Me}^{\bullet}$	$\mathrm{Me}^{\bullet}$	389	7
$\mathrm{C}-\mathrm{Me}^{\bullet}$	SiO	360	11

The dinuclear fragments, $\mathrm{M}^{+\bullet}-\mathrm{Me}^{\bullet}$, $\mathrm{M}^{+\bullet}-\mathrm{Cl}^{\bullet}$ and $\mathrm{M}^{+\bullet}-\mathrm{L}$ (= B; $\mathrm{L} = \mathrm{O(Me_2SiC_5H_4)_2}$) also give rise to predominantly dinuclear daughter fragments. Throughout, the most frequently occurring mononuclear ion is the apparently most stable fragment $\mathrm{M}^{+\bullet}/2 - \mathrm{Cl}^{\bullet}$ (*m/z* 434).

4. Experimental details

4.1. General

All operations were carried out under pure nitrogen. Infrared spectra were recorded on the Perkin Elmer model 1720 (FT-technique, KBr pellets), NIR/VIS absorption spectra on a Cary 17 spectrometer, and ^1H NMR spectra on a Bruker WP 80 instrument (80 MHz). Mass spectrometric studies were carried out as described in [20,22].

4.2. Preparation of $(SiMe_2Cl)_2O$

A slightly modified version of the procedure described by Gerber *et al.* [25] was used. In this a solution of 553.41 g (4.29 mol) of $SiMe_2Cl_2$ in 500 ml of anhydrous Et_2O under nitrogen in a three-necked 2 l flask fitted with a dropping funnel and reflux condenser was treated with a water/dioxane mixture (42.5 g (2.36 mol) of H_2O/40 ml of $C_4H_8O_2$). After overnight stirring at room temperature, the ether was removed and the residue fractionated through a 20 cm Vigreux column (see Table 9). The products 1,1,3,3-tetramethyl 1,3-dichlorodisiloxane and 1,1,5,5-hexamethyl dichlorotrisiloxane were identified by ^1H NMR spectroscopy: δ (ppm) 0.790 or 0.490 (I_{rel} 2) and 0.537 (I_{rel} 1).

4.3. Preparation of $K_2[\{O(Me_2SiC_5H_4)_2]$

A solution of 6.88 g (0.078 mol) of NaC_5H_5 in *ca.* 20 ml of THF was added dropwise at room temperature during 0.5 h to a solution of 7.72 g (0.038 mol = 7.43 ml) of $(SiMe_2Cl)_2O$ in *ca.* 40 ml of THF. The mixture was stirred for a further 1 h and the solvent was then evaporated off and the residue extracted twice with *ca.* 20 ml of n-hexane. After solvent evaporation, the yellowish, viscous $(Me_2C_5H_5Si)_2O$ was dissolved in 50 ml of THF and allowed to react overnight with 3.13 g (0.08 mol) of finely divided potassium. The colourless solution was filtered and the solvent then evaporated to leave the product. Yield: 11.6 g (90%). ^1H NMR (THF-d_8): δ 5.800 (m, 4H, C_5H_4); δ 5.566 (m, 4H, C_5H_4); δ 0.195 (s, 12H, CH_3).

4.4. Preparation of $[\{O(Me_2SiC_5H_4)_2\}PrCl \cdot THF]_n$ (2)

A greenish-white suspension of 0.366 g (1.48 mmol) of anhydrous $PrCl_3$ in *ca.* 30 ml of THF was vigorously stirred for *ca.* 20 h and then added dropwise to a solution of 0.502 g (1.48 mmol) of $K_2[O(Me_2SiC_5H_4)_2]$ in *ca.* 15 ml of THF. After 3 days stirring, the THF was evaporated off and the residue extracted twice (for 1 h in each case) with *ca.* 30 ml of toluene. After separation of the clear yellow solution from the insoluble KCl, the toluene was evaporated off to leave, after drying *in vacuo* 0.34 g (45.6% yield) of a light yellow product. Decomp.-temperature (colour change to light brown): 90–100°C. Anal. Found: C, 40.02; H, 5.51; Pr 27.80. $C_{18}H_{28}ClO_2Si_2Pr$ calcd.: C, 42.48; H, 5.55; Pr 27.69%.

4.5. Preparation of $[\{O(Me_2SiC_5H_4)_2\}YbCl]_2$ (3)

A grey suspension of 0.436 g (1.56 mmol) of anhydrous $YbCl_3$ in 15 ml of THF was stirred for 1 h, cooled in ice, and treated dropwise with a solution of 0.528 g (1.56 mmol) of $K_2[O(Me_2C_5H_4)_2]$ in 20 ml of THF. After overnight stirring, the red supernatant was removed from a brownish red solid. The latter was extracted with *ca.* 10 ml of THF, and the THF removed (*in vacuo*) from the extract to leave, after drying, 0.70 g (96% yield) of an orange-red solid. Anal. Found: C, 34.38; H, 4.35; Yb, 37.14. $C_{28}H_{40}Cl_2O_2Si_4Yb_2$ calcd.: C, 35.86; H, 4.30; Yb, 36.90%.

4.6. X-Ray crystallography

Single crystals of **3** were grown from concentrated THF solutions to which a few drops of toluene had been added. The solution was kept at −30°C and at intervals over a period of 2 months, the volume of the solution was slightly reduced.

Since the red, rhombic crystal selected for the crystallographic X-ray analysis was too small to fit into a 0.1 mm Lindemann capillary, it was coated with mineral oil, cooled and mounted on a glass fibre. A continuous stream of cold N_2 during the introduction into the diffractometer, and during the period of data collection ensured rigid positioning of the sample. The space group ($P2_1/c$) was determined by means of the program RAUM [23] which makes a statistical analysis of the intensities of all reflections to allow detection of the systematic absences. The position of the Yb atom was found by direct methods. The positions of the C, Cl and Si atoms were subsequently determined by means of difference Fourier and least-squares refinements.

TABLE 9. Data of relevance for the separation of compounds containing one, two and three silicon atoms

	Cl_2SiMe_2	$(ClMe_2Si)_2O$	$(ClMe_2SiO)_2SiMe_2$
Boiling point (°C)	69–71 (70) [a]	41–45	82–86
pressure (Torr)	760	22	22
Yield			
g	51.2	106.7	91.8
%	9.8 (12.8) [a]	24.5 (24.6) [a]	23.1 (14.4) [a]

[a] *cf.* Ref. 25.

TABLE 10. Positional parameters and temperature factors for **2**, with e.s.d.s in parentheses

	x	y	z	U_{eq}
Yb(1)	10653(4)	65681(7)	7073(3)	178(2)
Cl(1)	7218(21)	30909(34)	4756(16)	230(9)
C(1)	1858(95)	71279(165)	18094(71)	306(48)
C(2)	6923(88)	86950(158)	18075(67)	256(44)
C(3)	16852(90)	83422(146)	21737(69)	252(44)
C(4)	18477(85)	64990(153)	24221(68)	238(41)
C(5)	9200(84)	57960(157)	21967(67)	218(42)
C(11)	14246(93)	72830(164)	−7170(73)	276(46)
C(12)	17543(87)	87723(155)	−1348(72)	258(45)
C(13)	25158(89)	82344(153)	6244(70)	264(45)
C(14)	26890(99)	63990(155)	5651(66)	293(47)
C(15)	20418(86)	58310(152)	−2787(67)	225(43)
Si(1)	30176(25)	53504(46)	30075(19)	268(12)
Si(2)	37053(24)	50777(44)	13951(20)	238(12)
O(1)	36434(68)	52182(135)	23713(49)	434(38)
C(21)	37902(81)	65681(204)	40375(71)	375(49)
C(22)	27073(109)	30812(182)	32761(93)	427(59)
C(31)	48786(100)	60245(191)	14783(90)	425(59)
C(32)	36096(115)	27170(203)	10218(102)	496(68)

In view of the considerable absorption coefficient of 1.855 mm^{-1} arising from use of Cu Kα radiation (instead of Mo Kα), an empirical absorption correction was carried out by use of the program DIFABS [27]. Although desirable, a numerical absorption correction was not practicable because the special low-temperature positioning of the crystal did not allow precise determination of the crystal dimensions.

All non-hydrogen atoms were refined anisotropically. Hydrogen positions were calculated and included with fixed parameters with a common temperature factor. (The fixed C–H distance was 96 pm). A maximal residual electron density of 2.99 $e^- \text{Å}^{-3}$ was found close to the heavy metal atom (Yb), probably arising from unsatisfactory absorption correction. The positions and temperature factors of all non-hydrogen atoms are listed in Table 10. Interatomic distances and bond angles (*cf.* Tables 2 and 3) were obtained by means of the programs SHELXS 86 [28] and PLATON 90 [29]. Further details about the X-ray structure may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information m.b.H., D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD 57132, the names of the authors, and the journal citation.

Acknowledgment

The authors are grateful for financial support by the Deutsche Forschungsgemeinschaft (Bonn). Drs. P. Traldi and R. Seraglia (CNR Padua, Italy) kindly allowed use of their mass spectrometers, and Drs. G. Massarweh and J. Stehr (Hamburg) contributed valuable advice during the X-ray crystallographic study.

References and notes

1 H. Schumann, I. Albrecht, J. Loebel, E. Hahn, M.B. Hossain and D. van der Helm, *Organometallics*, *5* (1986) 1296 and refs. therein.

2 Q. Shen, M.-H. Qi, J.W. Guan and Y.-H. Lin, *J. Organomet. Chem.*, *406* (1991) 353 and refs. therein

3 M.F. Lappert, A. Singh, J.L. Atwood and W.E. Hunter, *J. Chem. Soc., Chem. Commun.*, (1981) 1190, 1191.

4 E.B. Lobkovsky, Yu.K. Gun'ko, B.M. Bulychev, V.K. Belsky, G.L. Solveichik and M.Yu. Antipin, *J. Organomet. Chem.*, *406* (1991) 343 and refs. therein

5 C.-T. Qian, X.-R. Wang, Y.-Q. Li and C.-Q. Ye, *Polyhedron*, *9* (1990) 479 and refs. therein.

6 (a) C.-T. Qian, C.-Q. Ye, H. Lu, Y.-Q. Li and Y.-Z. Huang, *J. Organomet. Chem.*, *263* (1984) 333 and refs. therein; (b) For a structurally investigated lanthanoid complex with a two-atomic bridge, see: P. Yan, N. Hu, Z. Jin and W. Chen, *J. Organomet. Chem.*, *391* (1990) 313.

7 S.J. Swamy, J. Loebel and H. Schumann, *J. Organomet. Chem.*, *379* (1989) 51

8 (a) C.-T. Qian, Z.-W. Xie and Y.-Z. Huang, *Inorg. Chim. Acta*, *139* (1987) 195; (b) C.-T. Qian, Z.-W. Xie and Y.-Z. Huang, *J. Organomet. Chem.*, *323* (1987) 285.

9 (a) H. Schumann, J. Loebel, J. Pickardt, C. Qian and Z. Xie, *Organometallics*, *10* (1991) 215; (b) H. Schumann, F.H. Görlitz, F.E. Hahn, J. Pickardt, C. Qian and Z. Xie, *Z. Anorg. Allg. Chem.*, *609* (1992) 131.

10 (a) C.-Q. Ye, Y.-Q. Li, X. Yang, C.-T. Qian and G. Paolucci, *Chin. Sci. Bull.*, *34* (1989) 1788; (b) G. Paolucci, R.D. Fischer, F. Benetollo, R. Seraglia and G. Bombieri, *J. Organomet. Chem.*, *412* (1991) 327.

11 M.D. Curtis, J.J. D'Errico, D.N. Duffy, P.S. Epstein and L.G. Bell, *Organometallics*, *2* (1983) 1808.

12 (a) H. Lueken, J. Schmitz, W. Lamberts, P. Hannibal and K. Handrick, *Inorg. Chim. Acta*, *156* (1989) 119; (b) T. Akhnoukh, J.

Müller, K. Qiao, X.-F. Li and R.D. Fischer, *J. Organomet. Chem.*, *408* (1991) 47.

13 E.C. Baker, L.D. Brown and K.N. Raymond, *Inorg. Chem.*, *14* (1975) 1376.

14 (a) B.R. Davies and I. Bernal, *J. Organomet. Chem.*, *30* (1971) 75; (b) E.F. Epstein and I. Bernal, *Inorg. Chim. Acta*, *7* (1973) 211.

15 A.F. Wells, *Structural Inorganic Chemistry*, 4th edn, Clarendon, Oxford, 1975, p. 800.

16 Found in the case of the new bis(cyclopentadienyl)praseodymium(III) derivative: $[(C_5H_5)_2PrOCH(Me)COO^iBu]_2$: J. Stehr, *Doctoral Dissertation*, Universität Hamburg, 1993 (see also [30]).

17 Thus, several polymeric $[Cp'_2LnX]_n$ systems with three Ln ··· X contacts per Ln^{3+} ion have been observed; see: (a) W. Lamberts, B. Hessner and H. Lueken, *Inorg. Chim. Acta*, *139* (1987) 215; (b) W. Lamberts and H. Lueken, *Inorg. Chim. Acta*, *132* (1987) 119 and refs. therein.

18 C. Qian, B. Wang and D. Deng, *J. Organomet. Chem.*, *427* (1992) C29.

19 R.D. Fischer and G. Bielang, *J. Organomet. Chem.*, *191* (1980) 61.

20 K. Qiao, R.D. Fischer, G. Paolucci, P. Traldi and E. Celon, *Organometallics*, *9* (1990) 1361

21 D. Deng, C. Qian, G. Wu and P. Zheng, *Chem. Commun.* (1990) 880.

22 K. Qiao, R.D. Fischer and G. Paolucci, *J. Organomet. Chem.*, *456* (1993) 185.

23 C. Qian, Z. Xie and Y. Huang, *J. Organomet. Chem.*, *398* (1990) 251 and refs. therein.

24 D.A. Foucher, B.-Z. Tang and I. Manners, *J. Am. Chem. Soc.*, *114* (1992) 6246

25 G. Gerber and L. Metzinger, *Makromol. Chem.*, *39* (1960) 167.

26 G. Fendesak, unpublished programme, Universität Hamburg, 1989.

27 N. Walker and D. Stuart, *Acta Crystallogr. Sect. A*, *39* (1983) 158.

28 G.M. Sheldrick, *Programs for the Crystal Structure Solution*, Universität Göttingen, 1986.

29 A.L. Spek, *Acta Crystallogr. Sect. A*, *46* (1990) C31.

30 J. Stehr and R.D. Fischer, *J. Organomet. Chem.*, *459* (1993) 79.