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Binuclear Organo-Rare-Earth-Metal Complexes Containing Silicon-Linked Cyclopentadienyl Ligands in either a Chelating or Metal-Bridging Fashion: A Mass Spectrometric Study[†]

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Four chloride-bridged, binuclear bis(cyclopentadienyl) rare-earth-metal complexes have been subjected to detailed mass spectrometric studies adopting exhaustively the B/E-linked scan technique: $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{Yb}(\mu\text{-Cl})]_2$ (1), $[(\text{Me}_3\text{SiC}_5\text{H}_4)_2\text{Yb}(\mu\text{-Cl})]_2$ (2), $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{Y}(\mu\text{-Cl})]_2$ (3), and $\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{Yb}(\mu\text{-Cl})_2\text{Y}(\text{C}_5\text{H}_4)_2\text{SiMe}_2$ (5). The strict dominance of binuclear fragments in the spectrum of pure 1 indicates, in excellent accordance with a previous crystallographic X-ray study, the presence of metal-bridging $\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2$ ligands in the vapor state. On the other hand, the notably different fragmentation patterns of 3 and 5 suggest chelating $\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2$ ligands and, as in 2, bridging chloride ligands only. A gradual increase of the radius of the metal ion, and hence of the metal-to-ring center distance, should in fact lead rapidly to unfavorable conditions for the isomer with metal-bridging organic ligands. The existence of the new complex 5, which could not be separated chemically from admixtures of 1 and 3 (i.e., from sample 4), has been confirmed unambiguously by deducing its individual fragmentation pattern from a systematic B/E-linked scan analysis. Several fragments of 1, 3, and 5 are likely to contain the novel either metal-bridging or chelating silaallylcyclopentadienyl ligand, $\{(\text{CH}_2)_2\text{Si}(\text{C}_5\text{H}_4)_2\}^{2-}$, while some fragments of 2 seem to again contain the ligand $\{\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\}^{2-}$.

Introduction

Binuclear transition-metal complexes of the general type $[\text{R}_2\text{Si}(\text{C}_5\text{R}'_4)_2\text{M}(\mu\text{-X})]_2$ may principally exist in the two isomeric forms I and II (Figure 1). In type I, the two SiR_2 -linked cyclopentadienyl rings coordinate to one metal ion in a chelating fashion,² while in isomer II both $\text{R}_2\text{Si}(\text{C}_5\text{R}'_4)_2$ units serve as additional bridges between the two metal ions.

As the first example of type II, the complex 1, with $\text{M} = \text{Yb}$, $\text{R} = \text{Me}$, $\text{R}' = \text{H}$, and $\text{X} = \text{Cl}$, was identified in 1986

by a crystallographic X-ray analysis.³ In the meantime, one further example with $\text{M} = \text{Lu}$, $\text{R} = \text{Et}$, $\text{X} = \text{H}$, and the slightly modified organic ligand skeleton $\text{Et}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{C}_5\text{H}_4)$ has been reported.⁴ Mass spectrometry is likely to be a powerful tool for the identification of the specific type of isomer present in the vapor state. Thus,

(1) Paolucci, G.; Fischer, R. D.; Breitbach, H.; Pelli, B.; Traldi, P. *Organometallics* 1988, 7, 1918.

(2) See: (a) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* 1985, 107, 8103. (b) Fendrick, C. M.; Schertz, L. D.; Day, V. W.; Marks, T. J. *Organometallics* 1988, 7, 1828.

(3) Höck, N.; Oroschin, W.; Paolucci, G.; Fischer, R. D. *Angew. Chem.* 1986, 98, 748; *Angew. Chem., Int. Ed. Engl.* 1986, 25, 738.

(4) Stern, D.; Sabat, M.; Marks, T. J. Proceedings of the 196th ACS National Meeting, Los Angeles, CA, Sept 25-30, 1988; Abstr INOR 412.

[†] (a) Presented in part at the XXV International Conference on Coordination Chemistry in Nanjing, China, July 26-31, 1987; Abstr, p 626, C3. (b) Part 2 of the series "Mass Spectrometry of Organof-Element Systems; for Part 1 see ref 1.

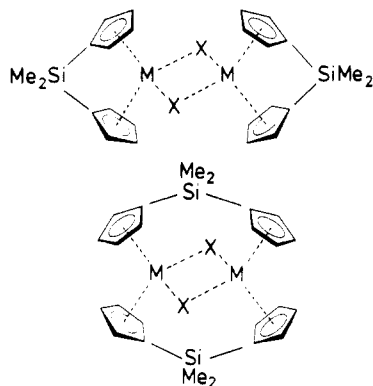


Figure 1. Schematic view of the structures of isomer I (top) and isomer II (bottom) of $[\text{Me}_2\text{Si}(\text{C}_5\text{R}_4)_2\text{M}(\mu\text{-X})]_2$.

Table I. Composition, m/z (Referring to the isotopes ^{35}Cl , ^{28}Si , and ^{174}Yb Only), and Relative Abundance of the Fragments of Compound 1 (Cf. Also Scheme I)

symbol	formula	m/z	$I_{\text{rel}}/\%$
M^{++}	$\text{C}_{24}\text{H}_{28}\text{Cl}_2\text{Si}_2\text{Yb}_2$	790	11
a	$\text{C}_{24}\text{H}_{27}\text{Cl}_2\text{Si}_2\text{Yb}_2$	789	10
b	$\text{C}_{19}\text{H}_{22}\text{Cl}_2\text{Si}_2\text{Yb}_2$	724	7
c	$\text{C}_{23}\text{H}_{25}\text{Cl}_2\text{Si}_2\text{Yb}_2$	775	<1
d	$\text{C}_{24}\text{H}_{28}\text{ClSi}_2\text{Yb}_2$	755	5
e	$\text{C}_{24}\text{H}_{28}\text{Si}_2\text{Yb}_2$	720	≈ 100
f	$\text{C}_{14}\text{H}_{16}\text{Cl}_2\text{Si}_2\text{Yb}_2$	658	15
g	$\text{C}_{19}\text{H}_{22}\text{ClSi}_2\text{Yb}_2$	689	2
h	$\text{C}_{19}\text{H}_{22}\text{Si}_2\text{Yb}_2$	654	6
i	$\text{C}_{18}\text{H}_{19}\text{Cl}_2\text{Si}_2\text{Yb}_2$	709	25
k	$\text{C}_{22}\text{H}_{22}\text{Cl}_2\text{Si}_2\text{Yb}_2$	760	2
l	$\text{C}_{23}\text{H}_{25}\text{Si}_2\text{Yb}_2$	705	1
m	$\text{C}_{14}\text{H}_{16}\text{ClSi}_2\text{Yb}_2$	623	1
n	$\text{C}_{14}\text{H}_{16}\text{Si}_2\text{Yb}_2$	588	8
o	$\text{C}_{18}\text{H}_{19}\text{Si}_2\text{Yb}_2$	639	1
p	$\text{C}_{22}\text{H}_{22}\text{Si}_2\text{Yb}_2$	690	1

the almost exclusive appearance of binuclear fragments in the original mass spectrum of 1³ corresponds well with the reported solid-state structure II, while the predominance of mononuclear fragments, e.g., in case of the dimers $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2\text{LnH}]_2$ (Ln = Nd, Sm, Lu)⁵ might suggest the presence of hydride bridges only.⁶

The present contribution consists in part of an extension of the initial mass spectrometric study of complex 1,³ followed by a comparative study of the mass spectrum of the exclusively chlorine-bridged dimer $[(\text{Me}_3\text{SiC}_5\text{H}_4)_2\text{Yb}(\mu\text{-Cl})]_2$ (2), which is expected to dissociate into mononuclear units under notably milder conditions than 1.⁸ Furthermore, the mass spectra of two new homologues of 1 involving the slightly larger (as compared with ytterbium) yttrium ion were carefully analyzed: While the new homobinuclear complex $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{Y}(\mu\text{-Cl})]_2$ (3) was obtained analytically pure, the first heterobimetallic system $\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{Yb}(\mu\text{-Cl})_2\text{Y}(\text{C}_5\text{H}_4)_2\text{SiMe}_2$ (5) became available only together with admixtures of the complexes 1 and 3 (i.e., in sample 4).

Results

Mass Spectrometric Behavior of the Complexes 1 and 2.

A comparison of the actual m/z and I_{rel} values of

(5) Schumann, H., personal communication; see also ref 2a.

(6) Simple molecular model considerations predict for isomer II an unfavorable proximity of β -methyl groups of noninterlinked pairs of C_5Me_4 rings.

(7) Lappert, M. F.; Yarrow, P. I. W.; Atwood, J. L.; Shakir, R.; Holton, J. J. *Chem. Soc., Chem. Commun.* 1980, 987.

(8) See: (a) Müller, J. *Chem. Ber.* 1969, 102, 152. (b) Ni, C.-Z.; Zhang, Z.; Deng, D.; Qian, C.-T. *J. Organomet. Chem.* 1986, 306, 209.

Table II. Composition, m/z (Referring to the isotopes ^{35}Cl , ^{28}Si , and ^{174}Yb Only), and Relative Abundance of the Fragments of Compound 2 (Cf. Also Scheme II)^a

symbol	formula	m/z	$I_{\text{rel}}/\%$
M^{++}	$\text{C}_{32}\text{H}_{52}\text{Cl}_2\text{Si}_4\text{Yb}_2$	966	4
a	$\text{C}_{32}\text{H}_{51}\text{Cl}_2\text{Si}_4\text{Yb}_2$	965	3
b	$\text{C}_{31}\text{H}_{49}\text{Cl}_2\text{Si}_4\text{Yb}_2$	951	<1
c	$\text{C}_{32}\text{H}_{52}\text{Si}_4\text{Yb}_2$	896	<1
d	$\text{C}_{24}\text{H}_{38}\text{Cl}_2\text{Si}_3\text{Yb}_2$	828	16
d'	$\text{C}_{24}\text{H}_{39}\text{Cl}_2\text{Si}_3\text{Yb}_2$	829	a
$[\text{M}/2]^{++}$	$\text{C}_{16}\text{H}_{26}\text{ClSi}_2\text{Yb}$	483	45
e	$\text{C}_{15}\text{H}_{23}\text{ClSi}_2\text{Yb}$	468	≈ 100
f	$\text{C}_{16}\text{H}_{24}\text{ClSiYb}$	395	7
g	$\text{C}_{16}\text{H}_{26}\text{Si}_2\text{Yb}$	448	20
h	$\text{C}_{13}\text{H}_{17}\text{SiYb}$	375	45
i	$\text{C}_{15}\text{H}_{23}\text{Si}_2\text{Yb}$	433	4
k	$\text{C}_{12}\text{H}_{14}\text{SiYb}$	360	30
l	Yb	174	10
m	$\text{C}_{11}\text{H}_{11}\text{SiYb}$	345	5
n	$\text{C}_7\text{H}_9\text{SiYb}$	294	<1

^a I_{rel} weak, but difficult to estimate more quantitatively.

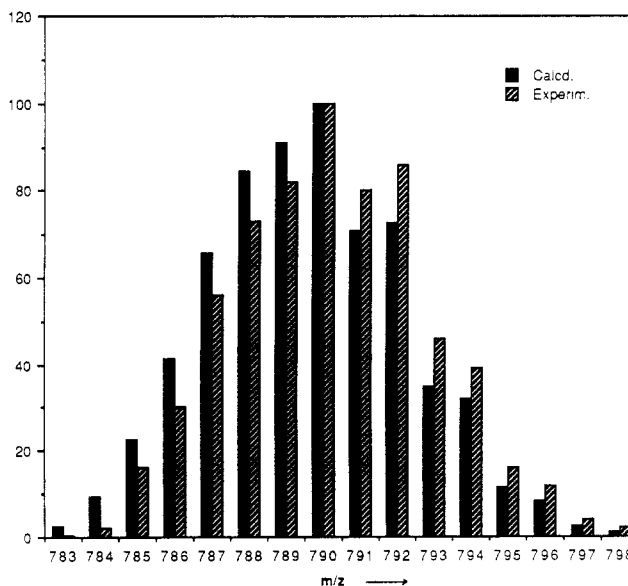


Figure 2. Calculated and experimental abundance of isotopomers of M^{++} of sample 1.

repeatedly studied 1 and 2 (Tables I and II) leaves no doubt that the mass spectrum of pure 1 consists almost exclusively of binuclear fragments ($m/z > 400$), the I_{rel} values of potential mononuclear fragments being at least too weak to be detected simultaneously. On the other hand, the spectrum of 2 displays, besides the molecular ion $[\text{M}(2)]^{++}$, no more than one or two notably intense line groups of binuclear fragments ($m/z = 828$ and 829), while at least eight well-discernible and intense groups typical of mononuclear fragments appear (cf. Table II). Thus the mass spectrometric behavior of 2 clearly resembles that reported earlier for the dimers $[(\text{C}_5\text{H}_5)_2\text{M}(\mu\text{-Cl})]_2$ ⁸ by indicating that probably a concerted, symmetric cleavage of two Yb-($\mu\text{-Cl}$) bonds in the dimeric cation $[\text{M}(2)]^{++}$ dominates over all other fragmentation processes.

As natural Yb involves seven, Si three, and Cl two different isotopes, respectively, mononuclear fragments of 1 and 2 may give rise to "clusters" of up to 10 easily detectable lines, and binuclear fragments to groups of up to 16 lines. The optimally resolved line clusters of three selected ions of 1 and 2 are depicted in Figures 2-4. As no suitable system of known isotopic abundances that would be optimal for a calibration of the relative peak heights is presently available, the peak height adjustment is simply based on setting $I_{\text{max}}(\text{calc}) \equiv I_{\text{max}}(\text{obs})$, where I_{max}

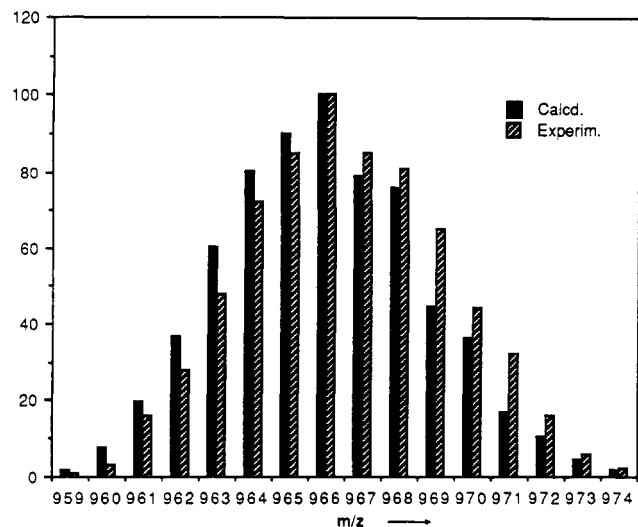


Figure 3. Calculated and experimental abundance of isotopomers of M^{2+} of sample 2.

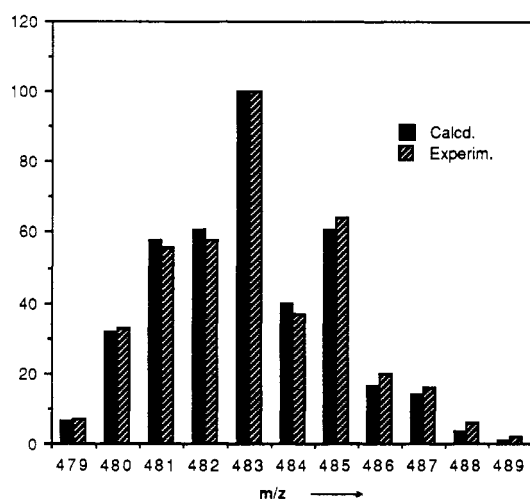


Figure 4. Calculated and experimental abundance of isotopomers of $[M/2]^{2+}$ of sample 3.

refers to the intensity of the most intense line of each cluster.

In Figure 5, the B/E-linked scans of the molecular ions of 1 and 2 are compared: While $[M(1)]^{2+}$ loses, without any evidence of cleavage into mononuclear fragments, in a decreasing order (with respect to I_{rel}) C_5H_6 , CH_3^* , Cl_2 , and Cl^* , respectively, $[M(2)]^{2+}$ undergoes primarily dissociation and loses less frequently $C_5H_4SiMe_3$, $2Cl^*$, CH_3^* , and H^* , respectively, under conservation of the binuclear character.

The "complete" fragmentation scheme of compound 1 as deduced from the individual B/E-linked scans of all fragments that give likewise rise to observable daughter fragments is shown in Scheme I. C_5H_6 extrusion, which appears to be the most frequent fragmentation mode of $[M(1)]^{2+}$, is seen to take place at four subsequent stages of Scheme I. As all fragments remain binuclear, the C_5H_6 -deficient ligands left in the respective daughter fragments are likely to be still metal-bridging. Any reasonable mechanism of this C_5H_6 extrusion should involve a transfer of two H atoms from adjacent methyl groups to the leaving five-membered ring (cf. Figure 6). In view of the rather low coordination number to be ascribed to one of the Yb ions if only a new Yb-C σ -bond would result (possibility a), the formulation of a novel $\mu-\eta^3-\eta^5$ -(3-silallyl)cyclopentadienyl ligand (possibility b) might offer a somewhat more satisfactory alternative. Interestingly,

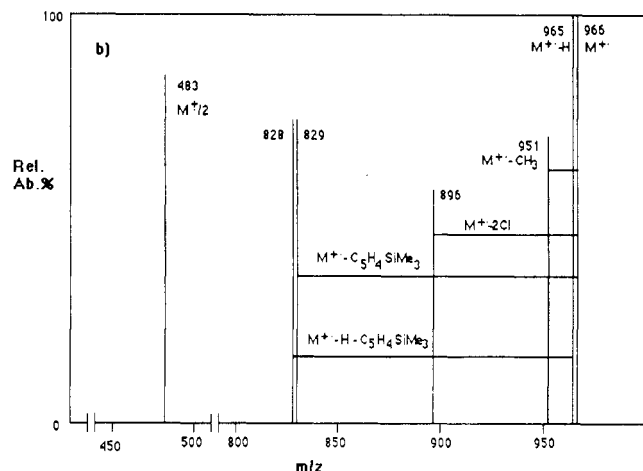
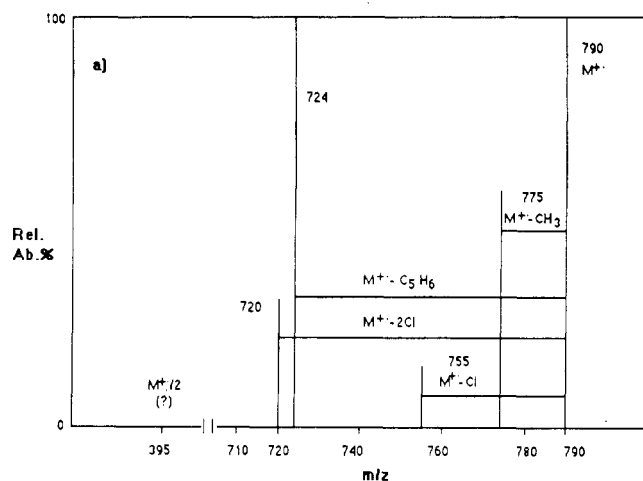


Figure 5. B/E-linked scans of M^{2+} of samples 1 (a) and 2 (b).

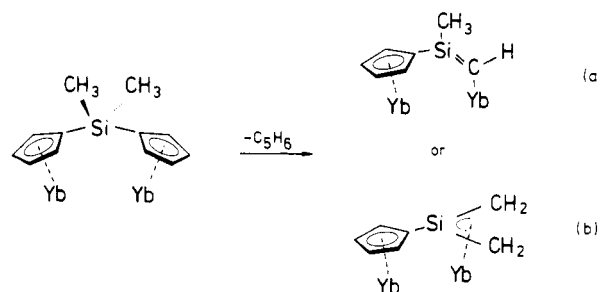
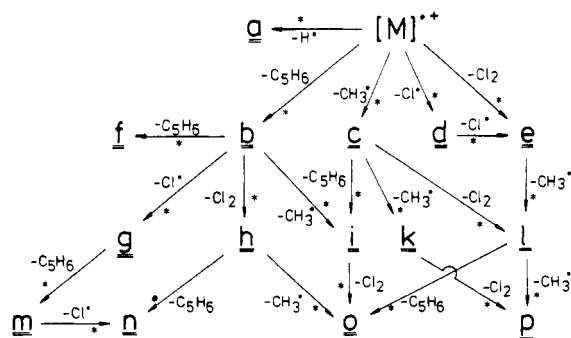


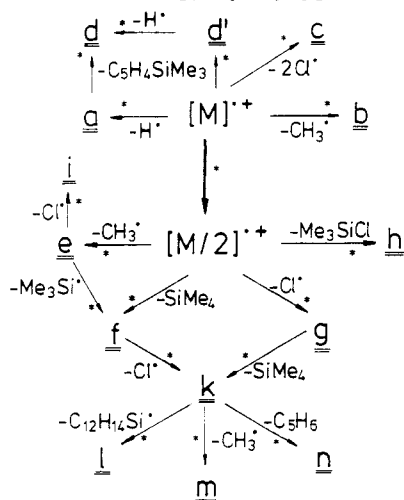
Figure 6. Attempted description of C_5H_6 elimination from a metal-bridging $Me_2Si(C_5H_4)_2$ ligand.

Scheme I. Complete Fragmentation Pattern (According to B/E-Linked Scans) of $[Me_2Si(C_5H_4)_2Yb(\mu-Cl)]_2$ (1^a)



^a For a list of the individual fragments see Table I.

complex 3 (and likewise complex 5) also loses C_5H_6 (vide infra). In the mononuclear fragments g and k of 3 the

Scheme II. Complete Fragmentation Pattern (According to B/E-Linked Scans) of $[(\text{Me}_3\text{SiC}_5\text{H}_4)_2\text{Yb}(\mu\text{-Cl})_2]_2$ (2)^a

^a For a list of the individual fragments see Table II.

$(\text{CH}_2)_2\text{SiC}_5\text{H}_4$ ligand probably coordinates in a chelating fashion.

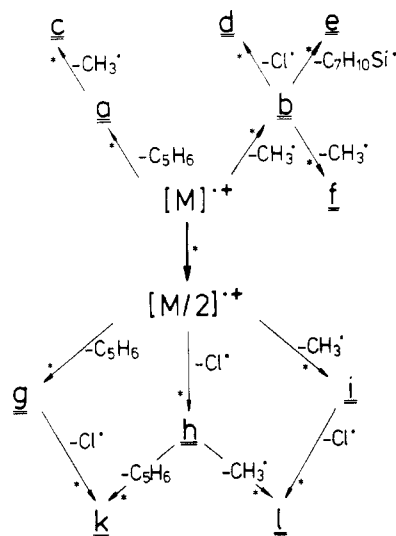
Another remarkable feature is the frequently (cf. Scheme I) occurring *simultaneous* loss of two Cl atoms (or, alternatively, the extrusion of one Cl_2 molecule) from $[\text{M}(1)]^{2+}$ and the fragments b, c, i, and k, respectively. As ionization of complex 2 (and likewise of 3, vide infra) leads most frequently to the cleavage of two $\mu\text{-Yb}\cdots\text{Cl}$ bonds, along with the formation of two mononuclear fragments, it might be reasonable to assume for 1 a concerted electron redistribution within the four-center Yb_2Cl_2 skeleton involving the rupture of all $\text{Yb}\cdots\text{Cl}$ linkages and the loss of a Cl_2 molecule.

An interesting question is whether or not a genuine Yb–Yb bond may be formed in the completely Cl free but still binuclear fragments of 1: As Yb is well-known to also adopt the oxidation number +II, fragment e could in principle also be considered as the molecular ion of the still hypothetical binuclear Yb(II) complex $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{Yb}]_2$, and the cations h, l, n, o, and p as fragments thereof. By intramolecular energy transfer, one metal electron might be promoted from a 4f to a 5d orbital, which could favor the formation of a $\text{Yb}\cdots\text{Yb}$ one-electron bond within the cationic fragments. On the other hand, notably asymmetrical distributions of the positive charge without any metal–metal bonding cannot be ruled out. Interestingly, the three detectable fragments in which one Cl atom is left (i.e., d, g and m) show a pronounced tendency to also lose this atom. Conclusive arguments for or against metal–metal bonding as a potential factor supporting the predominance of binuclear species may be obtained from additional experiments including, e.g., the binuclear lutetium homologue of 1.

The complete fragmentation scheme of compound 2 based on exhaustively examined B/E-linked scans is shown in Scheme II. As indicated in Figure 5b, the dominant process is the cleavage of one $\text{Yb}\cdots\text{Cl}$ bond within each $\text{Yb}(\mu\text{-Cl})\text{Yb}$ bridge leading primarily to the mononuclear fragments $[(\text{Me}_3\text{SiC}_5\text{H}_4)_2\text{YbCl}]^{2+} = [\text{M}(2)/2]^{2+}$, and $[(\text{Me}_3\text{SiC}_5\text{H}_4)_2\text{YbCl}]^{\pm 0}$. The former loses most readily one CH_3^\bullet radical and, to a lesser extent, also Me_4Si , Me_3SiCl , and Cl^\bullet . Interestingly, after extrusion of one Me_4Si molecule, the two five-membered rings appear to be tied together as in a chelating $\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2$ ligand. Actually, fragment k of 2 is seen to subsequently lose that ligand in one step. Although in fragment h, which is arrived at after Me_3SiCl extrusion from $[\text{M}(2)/2]^{2+}$, subsequent in-

Table III. Composition, m/z (Referring to the Isotopes ^{35}Cl and ^{28}Si Only), and Relative Abundance of the Fragments of Compound 3 (Cf. Also Scheme III)

symbol	formula	m/z	$I_{\text{rel}}/\%$
M^{2+}	$\text{C}_{24}\text{H}_{28}\text{Cl}_2\text{Si}_2\text{Y}_2$	620	6
a	$\text{C}_{19}\text{H}_{22}\text{Cl}_2\text{Si}_2\text{Y}_2$	554	2
b	$\text{C}_{23}\text{H}_{25}\text{Cl}_2\text{Si}_2\text{Y}_2$	605	22
c	$\text{C}_{18}\text{H}_{19}\text{Cl}_2\text{Si}_2\text{Y}_2$	539	5
d	$\text{C}_{23}\text{H}_{25}\text{ClSi}_2\text{Y}_2$	570	1
e	$\text{C}_{16}\text{H}_{15}\text{Cl}_2\text{SiY}_2$	483	3
f	$\text{C}_{22}\text{H}_{22}\text{Cl}_2\text{SiY}_2$	590	6
$[\text{M}/2]^{2+}$	$\text{C}_{12}\text{H}_{14}\text{ClSiY}$	310	5
g	$\text{C}_7\text{H}_5\text{ClSiY}$	244	3
h	$\text{C}_{12}\text{H}_{14}\text{SiY}$	275	≈ 100
i	$\text{C}_{11}\text{H}_{11}\text{ClSiY}$	295	4
k	$\text{C}_7\text{H}_5\text{SiY}$	209	6
l	$\text{C}_{11}\text{H}_{11}\text{SiY}$	260	3

Scheme III. Complete Fragmentation Pattern (According to B/E-Linked Scans) of $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{Y}(\mu\text{-Cl})]_2$ (3)^a

^a For a list of the individual fragments see Table III.

tramolecular H-atom transfer¹ is likely, no daughter fragment (e.g., via $\text{h}' \cong [\text{C}_5\text{H}_4\text{SiMe}_2\text{CH}_2\text{C}_5\text{H}_4\text{YbH}]^{2+}$) could be detected. In view of the originally noninterlinked $\text{Me}_3\text{SiC}_5\text{H}_4$ ligands, the formation of the low-abundant, still binuclear fragment c from $[\text{M}]^{2+}$ would definitely require some simultaneous rearrangements of other ligand atoms.

Mass Spectrometric Behavior of Complex 3 and Sample 4 (Including Complex 5). Owing to the monoisotopic nature of yttrium-89 and to the appearance of relatively few binuclear (and even mononuclear) fragments, the complete mass spectrum of 3 (Table III) is notably simpler than the spectra of 1 and 2. One rather weak peak at $m/z = 692$, which can be attributed to the THF adduct (1:1) of binuclear 3, apparently reflects the fact that 3 was prepared from YCl_3 and $\text{Na}_2[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2]$ in THF before going over to toluene as the final solvent (cf. Experimental Section). Interestingly, the low number of readily detectable binuclear fragments of 3 practically equals that in the case of 2, while the number of reasonably intense mononuclear fragments (i.e., six) clearly exceeds that of 1. According to the B/E-linked scan-supported fragmentation scheme of 3 (cf. Scheme III), only a few formal analogues of the daughter fragments of $[\text{M}(1)]^{2+}$ are observed. In particular, with the exception of fragment d, all homologues of the numerous binuclear Cl-deficient, or Cl-free, fragments of 1 are absent in the spectrum of 3. As in the case of complex 2, the predominant fragmentation mode of $[\text{M}(3)]^{2+}$ is the symmetrical cleavage of the dimer, the mononuclear fragment $[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{Y}]^{2+}$ giving rise

Table IV. Composition, m/z (Referring to the Isotopes ^{35}Cl , ^{28}Si , and ^{174}Yb Only), and Relative Abundance of Compound 5 (Cf. Also Scheme IV)

symbol	formula	m/z	$I_{\text{rel}}/\%$
M^{++}	$\text{C}_{24}\text{H}_{28}\text{Si}_2\text{Cl}_2\text{YbY}$	705	21
a	$\text{C}_{23}\text{H}_{26}\text{Si}_2\text{Cl}_2\text{YbY}$	690	20
b	$\text{C}_{19}\text{H}_{23}\text{Si}_2\text{Cl}_2\text{YbY}$	640	2
c	$\text{C}_{24}\text{H}_{26}\text{Si}_2\text{ClYbY}$	670	1
d	$\text{C}_{24}\text{H}_{27}\text{Si}_2\text{Cl}_2\text{YbY}$	704	20
e	$\text{C}_{19}\text{H}_{22}\text{Si}_2\text{Cl}_2\text{YbY}$	639	9
f	$\text{C}_{22}\text{H}_{22}\text{Si}_2\text{Cl}_2\text{YbY}$	675	4
g	$\text{C}_{18}\text{H}_{19}\text{Si}_2\text{Cl}_2\text{YbY}$	624	15
h	$\text{C}_{23}\text{H}_{24}\text{Si}_2\text{Cl}_2\text{YbY}$	689	1
i	$\text{C}_{19}\text{H}_{21}\text{Si}_2\text{Cl}_2\text{YbY}$	638	8
k	$\text{C}_{14}\text{H}_{16}\text{Si}_2\text{Cl}_2\text{YbY}$	573	2
l	$\text{C}_{19}\text{H}_{22}\text{Si}_2\text{ClYbY}$	604	42
$[\text{M}(\text{Y})/2]^{++}$	$\text{C}_{12}\text{H}_{14}\text{SiClY}$	310	58
$[\text{M}(\text{Yb})/2]^{++}$	$\text{C}_{12}\text{H}_{14}\text{SiClYb}$	395	25
$[\text{M}(\text{Y})/2 - \text{Cl}]^+$	$\text{C}_{12}\text{H}_{14}\text{SiY}$	275	78
$[\text{M}(\text{Y})/2 - \text{CH}_3]^+$	$\text{C}_{11}\text{H}_{13}\text{SiClY}$	295	25
$[\text{M}(\text{Yb})/2 + \text{Cl}]^+$	$\text{C}_{13}\text{H}_{14}\text{SiCl}_2\text{Yb}$	430	18
$m \cong [\text{M}(\text{Yb})/2 - \text{Cl}]^+$	$\text{C}_{12}\text{H}_{14}\text{SiYb}$	360	$\cong 100$
n	Yb	174	20
o	$\text{C}_{11}\text{H}_{11}\text{SiYb}$	345	16
p	$\text{C}_7\text{H}_8\text{SiYb}$	264	5

Table V. Comparison of Selected Fragments of 1, 2, 3, and 5 of (within Each Column) Corresponding Elemental Composition

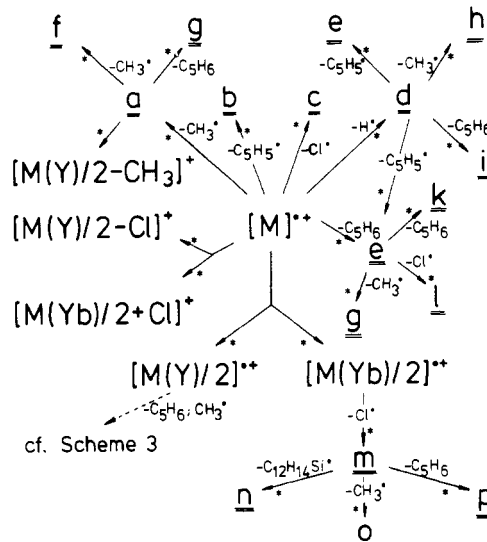
fragment	1	2	3	5
$[\text{M} - \text{C}_5\text{H}_6 - \text{CH}_3]^+$	i		c	g
$[\text{M} - 2\text{C}_5\text{H}_6]^{++}$	f			k
$[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{MCl}]^{++}$		f	$[\text{M}/2]^+$	$[\text{M}/2]^+$
$[\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{M}]^+$		k	h	$[\text{M}/2 - \text{Cl}]^+$
$[(\text{CH}_2)_2\text{Si}(\text{C}_5\text{H}_4)\text{M}]^+$		n	k	p
$[\text{MeSi}(\text{C}_5\text{H}_4)_2\text{M}]^+$		m	l	o

to the most intense line in the spectrum.

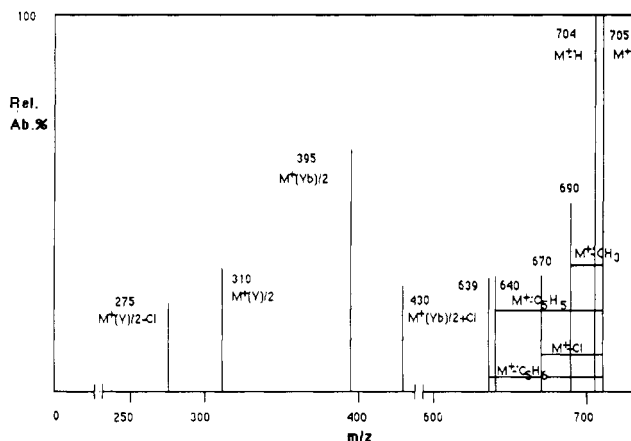
All features discussed above suggest convincingly that, unlike 1, its yttrium homologue 3 prefers the structure of isomer I (Figure 1) at least in the vapor state. This conclusion is in excellent agreement with the larger ionic radius of Y^{3+} (relative to that of Yb^{3+}) and the notably strained molecular skeleton of 1 (vide infra), making different crystal structures of 1 and 3 also very likely.

Although, owing to the absence of Me_3Si groups in 3, SiMe_4 extrusion does not take place, the fragmentation patterns of $[\text{M}(2)/2]^{++}$ and $[\text{M}(3)/2]^{++}$ show several similarities. Thus, at least with respect to the elemental composition, a clear 1:1 correspondence of several fragments of 2, 3, and 5 is found (Table V), lending support to the aforementioned spontaneous formation of a $\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2$ ligand in f and k of 2. The C_5H_6 -deficient fragments g and k of 3 are likely to also contain the new $(\text{CH}_2)_2\text{Si}(\text{C}_5\text{H}_4)$ ligand (vide supra).

Sample 4 was expected to also contain, together with 1 and 3, the interesting new heterobinuclear complex $\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{Y}(\mu\text{-Cl})_2\text{Yb}(\text{C}_5\text{H}_4)_2\text{SiMe}_2$ (5). Sample 4 was obtained by reacting the two probably mononuclear THF adducts $\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{MCl}(\text{THF})$ ($\text{M} = \text{Y}$ and Yb) first in THF and subsequently in toluene solution. Actually, the mass spectrum of the carefully dried, light-red mixture 4 displays numerous signals of both mono- and binuclear fragments and turns out even more complex than a superposition of the individual spectra of 1, 2, and 3. As the molecular ion $[\text{M}(5)]^{++}$ of the expected new complex 5 was in fact detected, a stepwise evaluation of the appropriate individual fragmentation pattern of 5 was possible via a systematic B/E-linked scan analysis (Scheme IV and Table IV). All individual fragments of 5 found by this procedure were subsequently identified in the mass spectrum of sample 4, too. Interestingly, the spectrum of 5 turns out

Scheme IV. Complete Fragmentation Pattern (According to B/E-Linked Scans) of $\text{Me}_2\text{Si}(\text{C}_5\text{H}_4)_2\text{Y}(\mu\text{-Cl})_2\text{Yb}(\text{C}_5\text{H}_4)_2\text{SiMe}_2$ (5)^a

^a For a list of the individual fragments see Table IV.

**Figure 7.** B/E-linked scans of M^{++} of sample 5.

richer in well-detectable fragments than the corresponding spectra of 1 and 3. Figure 7 shows the B/E-linked scan of $[\text{M}(5)]^{++}$ ($m/z = 705$) based on the mass spectrum of sample 4.

All signals of 5 with m/z values typical of binuclear fragments display the isotope pattern of only one Yb atom, which feature confirms the anticipated heterobinuclear nature of 5. The intensities of binuclear fragments are, however, relatively weak, and the almost exclusive absence of Cl- and Cl_2 -free fragments suggests, along with the dominating dissociation of $[\text{M}(5)]^{++}$, that complex 5 favors like 3 the ligand arrangement of isomer I (Figure 1). The B/E-linked scan of $[\text{M}(5)]^{++}$ indicates (inter alia) not only the expected daughter ions $[\text{M}/2]^{++}$ with both Y and Yb, but, quite surprisingly, also the two asymmetric cleavage products $[\text{M}(\text{Y})/2 - \text{Cl}]^+$ and $[\text{M}(\text{Yb})/2 + \text{Cl}]^+$, while the corresponding pair of fragments with an inverse distribution of Y and Yb is missing. Interestingly, I_{rel} of $[\text{M}/2]^{++}$ with Y exceeds I_{rel} of the Yb homologue, while the reverse is true for the I_{rel} values of $[\text{M}/2 - \text{Cl}]^+$ (Table IV). Actually, the mononuclear fragment $[\text{M}(\text{Yb})/2 - \text{Cl}]^+$ is most abundant in the spectrum of 5 but completely absent in that of 1. Moreover, quite a few mononuclear fragments of 5 are reminiscent of fragments of 2 and 3 (Table V). Like the fragmentation patterns of 1 and 3, that of 5 also shows numerous cases of C_5H_6 extrusion that are likely to

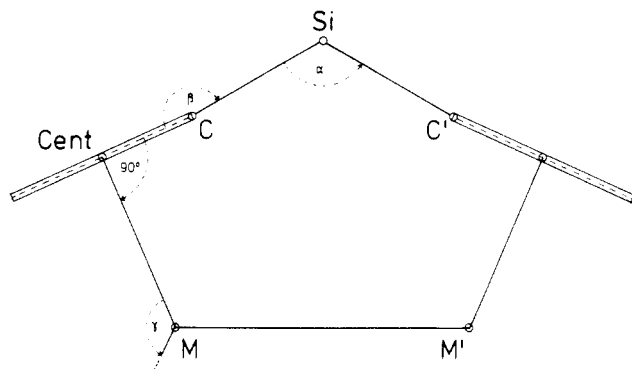


Figure 8. Schematic view of the $M_2(\text{centroid})_2C_2Si$ heptagon of complex 1 (for simplicity, strict planarity has been assumed).

give rise to the $(CH_2)_2Si(C_5H_4)$ ligand (cf. Figure 6 and Table V).

Conclusions

As in part 1 of this series,¹ the present contribution demonstrates that modern mass spectrometry may serve as a very powerful and versatile tool even in organo-rare-earth-metal chemistry, a field that has often been stated to involve only complexes with pronounced electrostatic metal-to-ligand bonds. While part 1 was mainly focused on the surprising consequences of (mono)methylation of each cyclopentadienyl ligand in a number of homoleptic Cp'_3Ln systems ($Ln = La, Pr, Nd, Tm,$ and Yb), the present study illustrates primarily the usefulness of mass spectrometry for the unambiguous identification not only of different members (with respect to the nature of Ln) but, moreover, of different structural isomers of representatives of one homologous series of complexes.

Thus, it has been possible to prove the expectation that the reaction product of $Me_2Si(C_5H_4)_2LnCl \cdot THF$ with $Ln = Yb$ and Y (sample 4) is a mixture of three different species including the novel heterobinuclear complex $[Me_2Si(C_5H_4)_2]_2YbY(\mu-Cl)_2$ (**5**), which is not accessible as an isolated species. Moreover, detailed analyses of the individual fragmentation patterns of the complexes **1**, **3**, and **5** have led to the conclusion that the three binuclear homologues display different tendencies to adopt the structure of isomer I or of isomer II (see Figure I). While pure (i.e., strictly base-free) **1** seems to be virtually free of form I even in the vapor state, **3** and **5** are most likely to occur as equilibrium mixtures in which isomer I strongly predominates. As binuclear fragments are more numerous in the spectrum of **5**, one might be tempted to deduce a slightly higher amount of isomer II in **5** than in **3**. However, one possible critical feature is that, unlike the spectrum of **1**, those of **3** and **5** do not display any binuclear fragments completely devoid of Cl atoms.

A gradual decrease of the predominance of isomer II in the sense $1 > 5 > 3$ is in fact expected if several structural features were more stringently taken into account: Although in the structure of **1**³ the angles α and β (Figure 8) deviate notably from 109.5° and 180° , respectively, the actual $Yb \cdots Yb'$ distance remains still shorter than in the exclusively Cl-bridged complex $[(C_5H_5)_2Yb(\mu-Cl)]_2$.^{9,12} Assuming the same distortion of the $Me_2Si(C_5H_4)_2$ ligands in complex **3** ($M = Y$), too, its longer Y -centroid distances

(as compared with Yb -centroid) would lead to a further shortening of $d(Y \cdots Y)$ relative to $d(Yb \cdots Yb)$, whereas the likewise longer $Y \cdots Cl$ distances would require an increase of $d(Y \cdots Y)$ within the unperturbed (by metal-bridging $Me_2Si(C_5H_4)_2$ ligands) $Y_2(\mu-Cl)_2$ skeleton. According to a first estimate, the difference $\Delta d(M \cdots M')$ between $[(C_5H_5)_2Ln(\mu-Cl)]_2$ and isomer II should increase from ca. 0.25 \AA for $Ln = Yb$ to ca. 0.40 \AA for $Ln = Y$. One possibility to circumvent this rapidly growing (i.e., from $Ln = Yb$ to La) discrepancy with respect to $d(M \cdots M')$ will be a structural change from II to I.

The "critical" radius of Ln^{3+} at which the transition from isomer II to isomer I occurs is of course expected to vary with the size of the primary bridging ligand X. According to a most recent, combined XRS/MS study of the bromine-bridged homologue **6** of **1**, isomer II is again realized in the lattice owing to an unexpectedly large deformation of the "softer" $Yb_2(\mu-Br)_2$ skeleton.¹² Most gratifyingly, the mass spectrum of **6** differs strongly from those of **2**, **3**, and **5** but appears straightforwardly compatible with the spectrum of **1**, i.e. with the presence of metal-bridging $Me_2Si(C_5H_4)_2$ ligands.¹³ Preliminary results of MS studies, including also $X = H$ and $M =$ both Yb and Lu , suggest the likewise unexpected formation of oligomers rather than of dimers.

Experimental Section

Complex **1** was prepared following the procedure of ref 1, and complex **2** according to ref 7. For the preparation of complex **3**, a mixture of anhydrous YCl_3 (1.0 g, 5.12 mmol) and $Na_2[Me_2Si(C_5H_4)_2]$ (1.2 g, 5.12 mmol) was dissolved/suspended in a mixture of 40 mL of toluene and 20 mL of tetrahydrofuran. After this was stirred at room temperature for 48 h and after complete removal of the solvents, the solid residue was partially redissolved in 80 mL of toluene. After filtration, removal of the solvent and drying under high vacuum (4 h, room temperature), complex **3** was obtained analytically pure¹⁰ as a yellowish powder in a yield of 60% (0.95 g). Sample **4** (i.e., a mixture of **1**, **3**, and **5**) was obtained by stirring a mixture of **1** (200 mg, 0.32 mmol), **3** (250 mg, 0.32 mmol), and 30 mL of tetrahydrofuran (30 min, room temperature). After solvent removal (high vacuum), the residue was stirred under 30 mL of toluene (30 min, room temperature). Solvent removal (high vacuum, room temperature), and drying (4 h, room temperature) yielded a homogeneously looking light red powder.

All mass spectrometric measurements were carried out on a VG ZAB 2F instrument, interfaced with a VG 11/250 data system and operating under electron-impact (EI) conditions (70 eV, 200 μA). Samples were introduced by direct probe inlet at temperatures between 100 and 150 $^\circ C$. The ion source temperature was 200 $^\circ C$. Exact mass measurements were obtained only for ions containing the monoisotopic central metal yttrium by adopting the peak-matching technique at 10000 resolving power (10% valley definition). Metastable transitions were detected by B/E-linked scans.¹¹

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Registry No. **1**, 103439-81-2; **2**, 76547-96-1; **3**, 126061-73-2; **5**, 126035-62-9; YCl_3 , 10361-92-9; $Na_2[Me_2Si(C_5H_4)_2]$, 103457-56-3.

(10) Calculated for $C_{24}H_{28}Si_2Cl$: C, 46.39; H, 4.45; Cl, 11.41. Found: C, 45.96; H, 4.63; Cl, 11.17.

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