Inorganica Chimica Acta, 13 (1975) 11–16

Mass Spectroscopic Studies on Metal Organosilylamides. Part I. Mass Spectra of Tris{bis(trimethylsilyl)amido}lanthanides

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Received May 8, 1974

Mass spectra of $[M\{N(SiMe_3)_2\}_3]$, *where M = Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Ho, Yb and Lu, have been obtained. Parent molecular ions and several metal-containing fragment ions were observed together with metastable peaks and doubly-charged ions implying considerable stability of the metal–nitrogen bonds. The results are discussed in terms of fragmentation patterns and compared with those of the transition metals, M = Sc, Ti, V, Cr and Fe. The derivatives of Ce, Sm, Eu and Yb showed significantly different behaviour from that of the other lanthanides and this appears to be a reflection of their known divergence from the characteristic tervalency.*

Introduction

The preparation of the tris-{bis(trimethylsilyl)amido}-derivatives of a number of the lanthanides and of yttrium, $M(btsa)_3$ has been reported.[1] They are monomeric three-co-ordinate metal compounds[2] which can be sublimed *in vacuo.* In characterizing these compounds we sought the parent molecular ions $[M\{N(SiMe_3)_2\}_3]^+$, (P^+) in their mass spectra, and found some interesting results which we now report.

Results and Discussion

The results may be compared with those given by the transition metal derivatives (M = Sc, Ti, V, Cr and Fe) obtained under similar conditions.[3] The more abundant ions are listed in Table I (the data for the scandium compound are included for comparison). Except for europium all of the compounds gave parent molecular ions P^+ and the base peak was due to the ligand fragment ion $(HL-Me)^+ = HN(SiMe_3)(SiMe_2)^+$. Another common feature was the appearance of the species $(P-HL)^+ = [(Me_3Si)_2NMN(SiMe_3)(SiMe_2CH_2)]^+$ as the strongest metal-containing ion. The spectra of the samarium, europium, and ytterbium compounds showed some significant differences in behaviour from those of the other compounds and will therefore be discussed separately. Another general feature was the presence of several dipositive fragment ions, the more intense of which are listed in Table I. Most of the compounds gave several strong metastable peaks and the common ones are listed in Table II. Clearly elimination of methane is a prevalent feature but loss of the methyl radical, the free ligand HL, the radical $CH_2Si(Me)_3$ or the fragment $Si(CH_2)_2$ also occur. Since the radicals CH_2SiMe_3 and $NSiMe_3$ have the same mass number, accurate masses were determined to distinguish between these alternative modes of breakdown. Measurements on $(P-CH_2SiMe_3)^+$ (M = La), $(P-CH_2SiMe_3-CH_4)^+$ (M = Ce) and $P-CH_2SiMe_3-2CH_4)^+$ (M = Pr), were carried out and confirmed (Table III) the proposed loss of the radical CH_2SiMe_3. Using the above data we have constructed a partial fragmentation pattern (for M = Sc, Y, La, Ce, Pr, Nd, Gd, Ho, Lu) as shown in Scheme A. The full arrows represent processes that have been established by the presence of metastable peaks whilst the dotted arrows connect fragment ions which are present in the spectrum but not accompanied by metastable peaks. In discussing the fragmentation pattern it is helpful to consider possible structures for the metal-containing ions and for the main fragment ions of the ligand.

It seems probable that the free ligand ion HL^+, which is an odd-electron species, will have structure (I) resulting from the loss of an electron from a delocalized $NSi_2p_\pi-d_\pi$ molecular orbital. The more stable even-electron fragment ion $(HL-Me)^+$ could be formulated as (IIa) but it might rearrange to the symmetrical four-membered ring (IIb) containing the quaternary nitrogen and quadrivalent silicons. The "odd-electron"* parent molecular ion P^+ is formulated as (III) with the suggestion that the electron is removed from a delocalized π-molecular orbital of mainly nitrogen lone-pair character. It is hoped that photoelectron spectra will reveal more information on this point. Loss of a methyl group from P^+ gives an "even-electron" species

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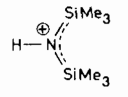
* Strictly speaking some of the P^+ species are even-electron if the metal electrons are also considered. Except where stated otherwise we refer the terms odd-electron and even-electron to ligand $N(SiMe_3)_2^-$ and fragments thereof.

TABLE I. More Abundant Ions.

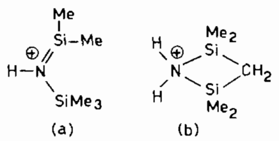
Possible Species	Sc^{45}		Y^{89}		La^{139}		Ce^{140}		Pr^{141}		Nd^{144}		Sm^{152}		Eu^{153}		Gd^{158}		Ho^{165}		Yb^{174}		Lu^{175}	
	m/e	I	m/e	I	m/e	I	m/e	I	m/e	I	m/e	I	m/e	I	m/e	I	m/e	I	m/e	I	m/e	I	m/e	I
P^+ (III)	525	4	569	10	619	15	620	20	621	10	624	2	632	2	-	-	638	5	645	5	654	2	655	20
$(P-Me)^+$ (IV)	510	5	554	10	604	15	605	2	606	10	609	2	617	1	618	2	623	3	630	5	639	5	640	15
$(P-CH_2SiMe_3)^+$ (V)	438	t	482	1	532	1	533	1	534	1	537	1	545	t	-	-	551	t	558	t	567	t	568	1
$(P-HL)^+$ (VI)	364	60	408	100	458	100	459	30	460	100	463	60	471	30	472	50	477	40	484	60	493	40	494	80
$(P-L-Me)^+$ (XV)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	458	8	-	-	-	-	479	2	-	-
$(P-HL-Me)^+$ (VII)	349	4	393	10	443	15	444	1	445	8	448	2	456	1	-	-	462	4	469	6	-	-	479	10
$(P-L-Me-CH_4)^+$ (XVI)	-	-	-	-	-	-	-	-	-	-	-	-	441	3	442	t	-	-	-	-	463	6	-	-
$(P-HL-Me-CH_4)^+$ (VIII)	333	12	377	20	427	15	428	2	429	6	432	2	-	-	-	-	446	5	453	15	-	-	463	20
$(P-HL-Me-2CH_4)^+$ (IX)	317	3	361	5	411	3	412	t	413	1	416	t	-	-	-	-	430	1	437	4	-	-	447	3
$(P-HL-Me-3CH_4)^+$ (X)	301	7	345	8	395	4	396	1	397	5	400	1	-	-	-	-	414	2	421	7	-	-	431	8
$(P-HL-Me-4CH_4)^+$ (XI)	285	3	329	3	379	2	380	t	381	2	384	t	-	-	-	-	398	1	405	5	-	-	415	4
$(P-L-CH_2SiMe_3)^+$ (XVII)	-	-	-	-	-	-	-	-	-	-	-	-	385	1	386	5	-	-	-	-	407	2	-	-
$(P-HL-CH_2SiMe_3)^+$ (XII)	-	-	321	2	371	3	372	3	373	5	376	1	-	-	-	-	390	1	397	3	-	-	407	1
$(P-L-CH_2SiMe_3-CH_4)^+$ (XVIII)	-	-	-	-	-	-	-	-	-	-	-	-	369	1	370	1	-	-	-	-	391	2	-	-
$(P-HL-CH_2SiMe_3-CH_4)^+$	-	-	305	2	355	5	356	2	357	2	360	1	-	-	-	-	374	1	381	3	-	-	391	2
$(P-HL-CH_2SiMe_3-2CH_4)^+$	-	-	289	2	339	4	340	t	341	1	344	t	-	-	-	-	-	-	365	2	-	-	375	1
$(P-HL-CH_2SiMe_3-3CH_4)^+$	-	-	273	1	323	4	324	1	325	2	328	t	-	-	-	-	342	1	349	2	-	-	359	1
$(P-HL-L)^+$ (XVI)	-	-	248	3	298	60	299	15	300	50	303	20	-	-	-	-	317	3	324	5	-	-	334	3
$(P-2L)^+$ (XIX)	-	-	-	-	-	-	-	-	-	-	-	-	312	5	313	40	-	-	-	-	334	12	335	3
$(P-2L-CH_4)^+$ (XX)	-	-	-	-	-	-	-	-	-	-	-	-	296	4	297	10	-	-	-	-	318	10	-	-
$(P-HL-L-CH_4)^+$ (XIV)	-	-	232	5	282	15	283	5	284	40	287	8	-	-	-	-	-	-	-	-	-	-	318	5
$(P-HL-L-2CH_4)^+$	-	-	216	3	266	2	267	1	268	3	271	1	-	-	-	-	-	-	-	-	-	-	302	1
$(HL)^+$ (I)	161	12	161	20	161	20	161	8	161	100	161	40	161	8	161	90	161	100	161	100	161	40	161	5
$(HL-Me)^+$ (II)	146	100	146	100	146	100	146	100	146	100	146	100	146	100	146	100	146	100	146	100	146	100	146	100
$(P-2Me)^{2+}$ (XXII)	247.5	3	269.5	10	294.5	15	295	5	295.5	8	297	4	301	2	302	t	304	5	307.5	10	312	2	-	-
$(P-HL)^{2+}$	-	-	204	1	229	5	229.5	2	230	2	231.5	1	235.5	1	235	t	238.5	t	242	1	-	-	247	t
$(P-HL-2Me)^{2+}$	-	-	189	5	214	15	214.5	5	215	15	216.5	6	220.5	t	-	-	223.5	8	227	5	-	-	232	t
Probe temp. (°C)	75		120		110		80		80		80		100		100		75		80		93		80	

$P = [M\{N(SiMe_3)_2\}_3]$; $L = N(SiMe_3)_2$; m/e values correspond to the metal isotope specified and C^{12}, H^1, N^{14}, Si^{28} isotopes; I values for each compound are relative to $I(HL-Me)^+ = 100$, and correspond to a single mass number only and without correction for C^{13}, Si^{29} etc.; t = trace, i.e. < 1.0 relative to $I(HL-Me)^+ = 100$.

$(P–Me)^+$ which is formulated as (IVa) or (IVb) by analogy with (IIa) and (IIb).

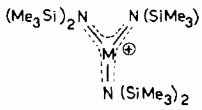


(I) $(HL)^+$

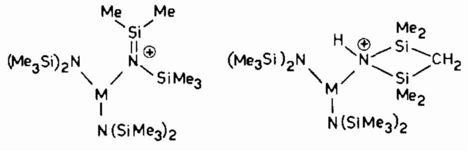


(a) (b)

(II) $(HL–Me)^+$



(III) $(P)^+$



(a) (b)

(IV) $(P–Me)^+$

It is noteworthy that in most cases (Table I) the intensities of P^+ and $(P–Me)^+$ are comparable; the exception being for cerium which strongly favours the parent ion. This is understandable in terms of the known stability of quadrivalent cerium if we assume

TABLE II. Fragmentation Process.

Process	m*[a, c]	Sc[b]	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Ho	Yb	Lu
$P^+ \rightarrow (P{-}CH_2SiMe_3)^+$	obs.	365	408	458	458.5	459.5	462	470	–	476	483	492	493
	calc.	365.4	408.2	458.0	458.1	459.1	462.2	470.0	–	476.0	482.7	491.6	492.6
$P^+ \rightarrow (P{-}HL)^+$	obs.	–	292.5	339	340	341	344	351	352	355.5	363	371.5	373
	calc.	–	292.6	339.0	339.8	340.8	343.6	351.0	352.0	355.6	363.1	371.5	372.6
$(P{-}Me)^+ \rightarrow (P{-}HL{-}Me)^+$	obs.	239	279	325	326	327	329.5	333.5	–	342.5	–	–	358.5
	calc.	238.8	278.8	325.0	325.8	326.8	329.6	333.2	–	342.6	–	–	358.4
$(P{-}HL)^+ \rightarrow (P{-}HL{-}Me)^+$	obs.	335	378.5	428.5	429.5	430.5	433.5	442	–	447	454.5	–	464.5
	calc.	334.6	378.5	428.5	429.5	430.5	433.5	441.6	–	447.4	454.5	–	464.5
$(P{-}HL{-}Me)^+ \rightarrow (P{-}HL{-}Me{-}CH_4)^+$	obs.	318	362	412	412.5	414	417	–	–	430	437.5	–	448
	calc.	317.7	361.8	411.6	412.3	413.6	416.6	–	–	430.4	437.5	–	447.6
$(P{-}HL{-}Me{-}CH_4)^+ \rightarrow (P{-}HL{-}Me{-}2CH_4)^+$	obs.	302	346	396	397	398	400	–	–	414.5	422	–	432
	calc.	301.8	345.8	395.6	396.6	397.8	400.2	–	–	414.7	421.6	–	431.6
$(P{-}HL{-}Me{-}CH_4)^+ \rightarrow (P{-}HL{-}CH_2SiMe_3)^+$	obs.	–	–	322	323.5	–	327	–	–	341	348	–	358
	calc.	–	–	322.3	323.3	–	327.2	–	–	341.0	347.9	–	357.7
$(P{-}HL{-}Me{-}2CH_4)^+ \rightarrow (P{-}HL{-}Me{-}3CH_4)^+$	obs.	286	330	–	381	–	385	–	–	–	406	–	416
	calc.	285.8	329.8	–	380.6	–	384.6	–	–	–	405.7	–	415.7
$(P{-}HL{-}CH_2SiMe_3)^+ \rightarrow (P{-}HL{-}CH_2SiMe_3{-}CH_4)^+$	obs.	–	290	340	340.5	341.5	344.5	–	–	358.5	365.5	–	375.5
	calc.	–	289.8	339.6	340.6	341.7	344.6	–	–	358.6	365.6	–	375.7
$(P{-}HL{-}CH_2SiMe_3{-}CH_4)^+ \rightarrow (P{-}HL{-}CH_2SiMe_3{-}2CH_4)^+$	obs.	–	–	324	325	–	329.5	–	–	342.5	350	–	359.5
	calc.	–	–	323.7	324.8	–	329.7	–	–	342.7	349.7	–	359.6
$(P{-}HL{-}L)^+ \rightarrow (P{-}HL{-}L{-}CH_4)^+$	obs.	–	217	267	268	269	272	–	–	–	293	–	–
	calc.	–	217.0	266.8	267.9	268.9	271.9	–	–	–	292.8	–	–

[a] Metastable peaks were determined only to *ca.* ±0.5 m/e units due to the broadness caused by isotopic complexity and overlap with fragment ions. [b] Data taken from reference 2. [c] In addition to the above data the following metastable peaks were also observed:

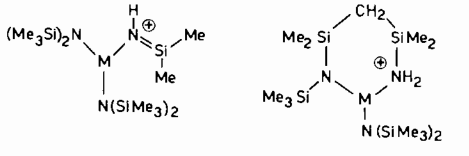
$(P{-}L{-}Me)^+ \rightarrow (P{-}L{-}Me{-}CH_4)^+$, Eu 426.5, Yb 448.5; $(P{-}HL{-}Me)^+ = (P{-}HL{-}2Me)^+$, Sm 426.5; $(P{-}L{-}Me{-}CH_4)^+ \rightarrow (P{-}L{-}Me{-}2CH_4)^+$, Sm 410, Eu 410.5, Yb 431.5; $(P{-}L{-}Me{-}2CH_4)^+ \rightarrow (P{-}L{-}Me{-}3CH_4)^+$, Sm 393, Yb 416; $(P{-}L{-}Me{-}CH_4)^+ \rightarrow (P{-}L{-}CH_2SiMe_3)^+$, Sm 337, Eu 337, Yb 358; $(P{-}L{-}CH_2SiMe_3)^+ \rightarrow (P{-}L{-}CH_2SiMe_3{-}CH_4)^+$, Sm 354, Eu 354.5, Yb 376; $(P{-}L{-}CH_2SiMe_3{-}CH_4)^+ \rightarrow (P{-}L{-}CH_2SiMe_3{-}2CH_4)^+$, Sm 337, Eu 339, Yb 359.5; $(P{-}2L)^+ \rightarrow (P{-}2L{-}CH_4)^+$, Sm 281, Eu 282, Yb 303; $(P{-}2L{-}CH_4)^+ \rightarrow (P{-}2L{-}2CH_4)^+$, Eu 266, Yb 287; $(P{-}HL{-}L{-}CH_4)^+ \rightarrow (P{-}HL{-}L{-}2CH_4)^+$, Y 201, Ce 252, Pr 253.5; $(P{-}Me)^+ \rightarrow (P{-}L{-}Me)^+$, Eu 339, Yb 359.

TABLE III. Mass Spectral Data.

Ion[a]		m/e Obs.	m/e Calc.
$La^{139}C^{12}{}_{14}H^{1}{}_{43}N^{14}{}_{3}Si^{28}{}_{5}$	$[P–CH_2SiMe_3]^+$	532.135624	532.136389
$Ce^{140}C^{12}{}_{13}H^{1}{}_{39}N^{14}{}_{3}Si^{28}{}_{5}$	$[P–CH_2SiMe_3–CH_4]^+$	517.106105	517.104309
$Ce^{140}C^{12}{}_{12}H^{1}{}_{35}N^{14}{}_{2}Si^{28}{}_{4}$	$[P–HL]^+$	459.091344	459.093009
$Pr^{141}C^{12}{}_{18}H^{1}{}_{54}N^{14}{}_{3}Si^{28}{}_{6}$	$[P^+]$	621.201596	621.200721
$Pr^{141}C^{12}{}_{12}H^{1}{}_{35}N^{14}{}_{3}Si^{28}{}_{5}$	$[P–CH_2SiMe_3–2CH_4]^+$	502.076084	502.075119
$Eu^{153}C^{12}{}_{18}H^{1}{}_{54}N^{14}{}_{3}Si^{28}{}_{6}$	$[P]^+$	633.215659	633.214311
$Eu^{153}C^{12}{}_{6}H^{1}{}_{18}N^{14}Si^{28}{}_{2}$	$[P–2L]^+$	313.017979	313.018757
$Yb^{174}C^{12}{}_{18}H^{1}{}_{54}N^{14}{}_{3}Si^{28}{}_{6}$	$[P]^+$	654.231059	654.232161
$Lu^{175}C^{12}{}_{6}H^{1}{}_{18}N^{14}Si^{28}{}_{2}$	$[P–2L]^+$	335.037409	335.038537
$Lu^{175}C^{12}{}_{6}H^{1}{}_{17}N^{14}Si^{28}{}_{2}$	$[P–HL–L]^+$	334.029770	334.030712

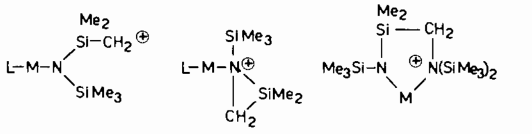
[a] L = $N(SiMe_3)_2$; P = ML_3.

that the cerium parent ion corresponds to the loss of the 4f electron giving a stable cation $Ce[N(SiMe_3)_2]_3^+$. Loss of the radical CH_2SiMe_3 from the parent ion giving $(P–CH_2SiMe_3)^+$ (Va) or (Vb) was clearly established by metastable peak and accurate mass measurement but this fragment ion constitutes only a minor component of the Scheme. The major process is clearly



(a) (b)

(V) $(P–CH_2SiMe_3)^+$



(a) (b) (c)

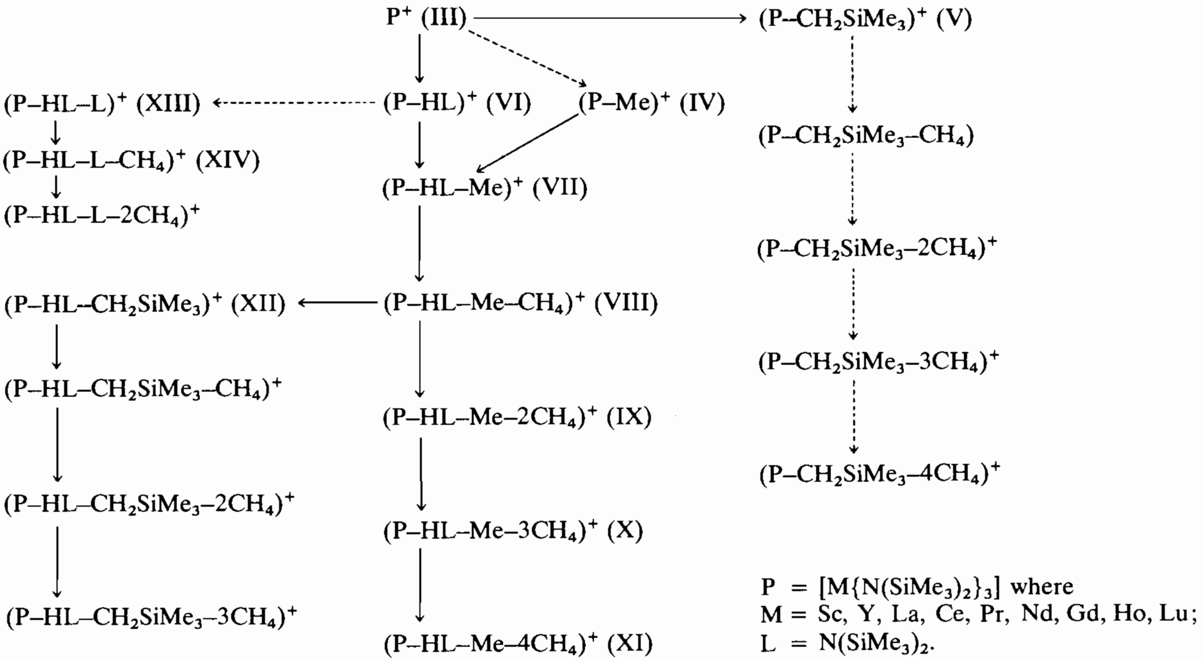
(VI) $(P–HL)^+$

the loss of free ligand base (HL) giving $(P–HL)^+$ which may be represented by (VIa), (VIb) or (VIc) which involve various modes of stabilisation of this important fragment ion. The process: $P^+ \rightarrow (P–HL)^+ + HL$ probably accounts for a major proportion of the ligand fragment ions $(HL)^+$ and $(HL–Me)^+$ observed in most of the spectra. Loss of a methyl radical from $(P–HL)^+$ to form $(P–HL–Me)^+$ seems to be a significant process which is established by the metastable peak but the $(P–HL–Me)^+$ species is also produced by elimination of HL from (P–Me). A succession of methane elimination steps follows from (P–HL–Me) and each step has an appropriate metastable peak up to the formation of $(P–HL–Me–3CH_4)^+$ and the spectra also contain small concentrations of the fragment ion $(P–HL–Me–4CH_4)^+$. It is difficult to imagine the elimination of methane from these ions without the formation of $\geqq$Si–CH$_2$–Si$\leqq$ bridges. The limit of methane elimination in this sequence seems to be reached with the formation of $(P–HL–Me–4CH_4)^+$. It is noteworthy that $(P–HL–CH_2SiMe_3)^+$ undergoes consecutive loss of two molecules of methane. With each step characterized by a metastable peak. Plausible structures for these fragments and $(P–HL–CH_2SiMe_3–3CH_4)^+$ involve the formation of $\geqq$Si–CH$_2$–Si$\leqq$ bridges. It seems significant that the integrity of the MN_2 unit is maintained througout the range of fragment ions (VI)–(XII) implying considerable stability for the metal–nitrogen bonds.

A few fragment ions containing only one metal–nitrogen bond were also detected, the main one being $(P–HL–L)^+$ and in several cases (M = La, Ce, Pr, Nd, Gd and Ho) this species was one of the major metal-containing fragment ions. The exceptions were given by M = Sm, Eu and Yb, which favoured the species (P–2L)+ instead and Lu which gave roughly equal intensities of $(P–HL–L)^+$ and $(P–2L)^+$. Since these species differ by only one mass unit some accurate mass measurements were carried out on $(P–HL–L)^+$ (M = Lu) and $(P–2L)^+$ (M = Eu and Lu) to confirm these assignments (Table III). No metastable peaks corresponding to the formation of $(P–HL–L)^+$, either by loss of the L radical from $(P–HL)^+$ or, by loss of HL and L from the parent ion P^+ were detected and we presume that this fragment is produced either very rapidly from these precursors or directly in the initial ionization process. Further examples of the characteristic elimination of methane were given by the presence of $(P–HL–L–CH_4)^+$ and $(P–HL–L–2CH_4)^+$ with each step being substantiated by the appropriate metastable peak.

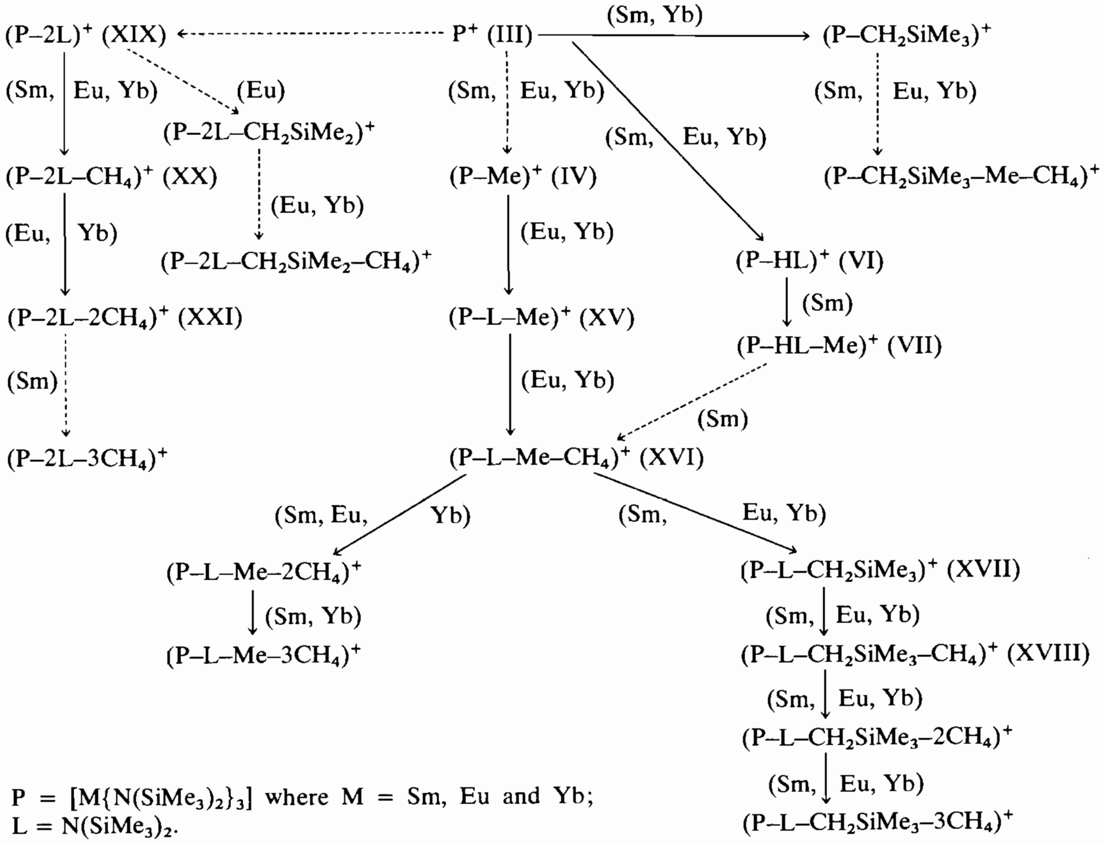
Concerning the doubly charged ions, there is no obvious reason why the species $(P–2Me)^{2+}$, $(P–HL)^{2+}$ and $(P–HL–2Me)^{2+}$, should have such high stability (Table I) but it is presumably influenced by the ability

Scheme A



P = $[M\{N(SiMe_3)_2\}_3]$ where
M = Sc, Y, La, Ce, Pr, Nd, Gd, Ho, Lu;
L = $N(SiMe_3)_2$.

Scheme B



P = $[M\{N(SiMe_3)_2\}_3]$ where M = Sm, Eu and Yb;
L = $N(SiMe_3)_2$.

of the metal–nitrogen–silicon framework to stabilize two units of positive charge by delocalization.

Samarium, Europium and Ytterbium Compounds

Reference to Table I shows that the europium compound gave no detectable parent ion P^+ although in one spectrum a parent ion (m/e, 633) was observed but impurities were also present as shown by an unidentified europium-containing fragment ions (m/e, 679.143295). The parent ion was also obtained when some lithium bis-trimethylsilylamide was added to the europium compound and an accurate mass determination (Table III) confirmed its constitution as $(EuL_3)^+$ although it might be a fragment ion of some higher derivative such as $LiEuL_4$. However, repeated experiments with the pure europium compound gave reproducible spectra which did not contain the parent ion [the highest mass peak corresponds to $(P–Me)^+$] which therefore must be unstable relative to the main fragment ions $(P–HL)^+$ and $(P–2L)^+$. Since the parent ion may be formally considered as a quadrivalent unipositive cation (*cf.* high stability of P^+ for M = Ce) it is not surprising that this species is rare for europium which prefers a valency of two as an alternative to the normal tervalent state. Moreover, the high stability of $(P–2L)^+$ for europium is understandable if it is considered as a bivalent unipositive cation (XIX), and it seems highly significant that the only other metals which gave strong $(P–2L)^+$ ions and no $(P–HL–L)^+$ ions were samarium and ytterbium which also have accessible bivalent states. Lutetium was interesting in giving approximately equal concentrations of $(P–2L)^+$ and $(P–HL–L)^+$ both of which were checked by accurate mass measurements (Table III). The derivatives of Sm, Eu and Yb, were also noteworthy in forming $(P–L–Me)^+$ (XV), $(P–L–Me–CH_4)^+$ XVI), $(P–L–CH_2SiMe_3)^+$ (XVII), $(P–L–CH_2SiMe_3–CH_4)^+$ (XVIII), $(P–2L–CH_4{}^+$ (XX), and $(P–2L–2CH_4)^+$ (XXI), instead of respectively $(P–HL–Me)^+$ (VII), $(P–HL–Me–CH_4)^+$ (VIII), $(P–HL–CH_2SiMe_3)^+$ (XII), $(P–HL–CH_2SiMe_3–CH_4)^+$, $(P–HL–L–CH_4)^+$ (XIV), and $(P–HL–L–2CH_4)^+$. Reference to Table II shows that Sm, Eu, and Yb compounds also differed significantly from the other lanthanides in the matter of metastable peaks and confirmed that there are differences in the fragmentation patterns. Scheme B summarizes the fragmentation pattern given by the compounds of Sm, Eu, and Yb.

It is tempting to explain this behaviour in terms of the more stable bivalencies of Sm, Eu and Yb.

In summary we note that the mass spectra of the Sc, Y, and lanthanide tris-bistrimethylsilylamides contain numerous positive ions containing MN_3, MN_2 or Mn units attached to ligand fragments, emphasizing the thermodynamic stability of the metal–nitrogen bonds in these compounds which we take to imply substantial covalent character. Finally, we note that the transition metal derivatives (M = Ti, V, Cr, Fe) gave rather fewer fragment ions (notably (III), (IV) and (VIII), in common) and only one metastable peak $\{(III) \rightarrow (IV)$, M = V$\}$.[3]

Experimental

The compounds were prepared as previously described.[1] The mass spectra were obtained with an AEI MS902 instrument operating at 70 eV and *ca.* 10^{-7} mm Hg pressure using a special technique devised by P. Cook for dealing with highly reactive compounds. The optimum probe temperature for each compound is given in Table I. For several of the lanthanides the metal-containing ions were easily identified by the appearance of the characteristic isotopic pattern of the metal modified by the ^{13}C, ^{29}Si and ^{30}Si abundances. Similarly the doubly-charged ions were also easily recognized but metastable peaks were broad and more difficult to locate accurately.

In addition to the common data listed in Tables I and II the following were also observed (intensities as in Table I in parentheses):

YL_3: $(P–CH_2SiMe_3–2CH_4)^+$ *1*, $(P–CH_2SiMe_3–5CH_4)^+$ *1*, $(P–CH_2SiMe_3–6CH_4)^+$ *1*.

LaL_3: $(P–CH_2SiMe_3–2CH_4)^+$ *1*, $(P–HL–SiMe_3)^+$ *1*, $(226)^+$ *4*, $(P–2HL–CH_2SiMe_3)^+$ *1*.

CeL_3: $(P–2L–SiMe_3)^+$ *2*.

PrL_3: $(P–CH_2SiMe_3–2CH_4)^+$ *1*, $(P–CH_2SiMe_3–Me–2CH_4)^+$ *1*, $(438)^+$ *1*, $(P–HL–SiMe_3)^+$ *1*, $(P–2L–SiMe_3)^+$ *1*, $(P–2L–5CH_4)^+$ *15*, $(218)^+$ *30*, $(P–2HL–CH_2SiMe_3)^+$ *2*.

SmL_3: (P–2L–2Me) *1*.

EuL_3: $(P–2L–2CH_4)^+$ *1*, $(P–2HL–SiMe_3–Me–CH_4)^+$ *1*.

HoL_3: $(462)^+$ *1*, $(P–2HL–2CH_4)^+$ *5*, $(P–2HL–3CH_4)^+$ *2*, $(P–2HL–2Me–2CH_4)^+$ *1*, $(P–2HL–SiMe_3–CH_4)^+$ *2*, $(P–2HL–CH_2SiMe_3–CH_4)^+$ *7*.

YbL_3: $(P–CH_2SiMe_3–Me–CH_4)^+$ *1*, $(YbNH)^+$ *3*.

LuL_3: $(P–CH_2SiMe_3–2CH_4)^+$ *1*, $(P–2HL–SiMe_3)^+$ *1*.

Acknowledgments

We thank P. Cook for his great perseverance and skill in obtaining the mass spectra. One of us (J.S.G.) thanks the Commonwealth Universities Association for a postdoctoral Commonwealth Scholarship during the early part of this work and we thank S.R.C. for supporting the final part of the research.

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