$CpCo(PPh_3)_2$, 32993-07-0; $SnPh_3Cl$, 639-58-7; (K-crown)[$CpCo(CN)_3$], 93473-86-0; $CpCo(CN)_2PPh_3$, 38531-03-2; $Hg(CN)_2$, 592-04-1; $CpCo(CO)PPh_3$, 12203-85-9; $CpCo(CN)(CN{\cdot}BF_3)PPh_3$, 114928-62-0; $K_2[CpCo(CN)_2]$, 114928-65-3; $P(\mu\text{-}OCH_2)_3CCH_3$, 1449-91-8; $CpCo(CO)(P(\mu\text{-}OCH_2)_3CCH_3)$, 93473-82-6; K-crown)CN, 42860-64-0; $CpCo(\eta^4\text{-}C_4Ph_4CO)$, 12119-11-8; pivaloyl chloride, 3282-30-2; 1-adamantanecarbonyl chloride, 2094-72-6; diphenylacetylene, 501-65-5.

Mass Spectrometry of Organo-f-Element Systems. 1. Electron-Impact-Induced (C_5-to-C_6) Ring Enlargement in Various Tris(methylcyclopentadienyl)lanthanoid(III) Systems[†]

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The complete mass spectrometric (MS) fragmentation pattern common to base-free organolanthanoid(III) complexes of the type $(CH_3C_5H_4)_3Ln$ (Ln = La, Pr, Nd, Tm, and Yb) has been determined by using B/E- and B^2/E-linked scans as well as CAD MIKE techniques. Apparently six different fragments lose, inter alia, one benzene molecule, the occurrence of any other C_6H_6 isomer (e.g. of fulvene) being ruled out by detailed collisional activation MS including the partially deuteriated complex $(CD_3C_5H_4)_3Pr$. Unlike for other metal-assisted $C_5H_4R \rightarrow C_6H_5R'$ ring enlargement processes, the generation of C_6H_6 is not necessarily preceded by the complete separation of at least one H atom (or another fragment) from the cationic complex. Instead, facile intramolecular migration of one ring methyl H atom either to the central metal atom or to a likewise metal-bonded C_5H_4 fragment (as created by preceding CH_3 radical abstraction from another $CH_3C_5H_4$ ligand) appears to be essential to initiate the final release of C_6H_6.

Introduction

While the mass spectrometric behavior of isoleptic cyclopentadienyl complexes of the trivalent rare-earth elements $(RC_5H_4)_3Ln$ with R = H^{1-4} or C_nH_{2n+1} with $n \geqslant 2^{5-7}$ has been studied in some detail, the corresponding tris(methylcyclopentadienyl) complexes have so far received less attention. According to several more detailed studies of methylmetallocenes of d-transition metals where inter alia fragments of the type $[C_6H_6M]^+$ were observed,[8-10] metal complexes with more than two $CH_3C_5H_4$ ligands might be particularly attractive for further investigations of metal-assisted $CH_3C_5H_4$ ligand rearrangements induced by electron impact. Some earlier MS studies of organouranium(IV) complexes of the type $(CH_3C_5H_4)_3UX$[11] suggest that the number of molecular fragments capable of corresponding rearrangements would in such cases be more numerous. For the present study, isoleptic $(CH_3C_5H_4)_3Ln$ systems with Ln = La (**1**), Pr (**2**), Nd (**3**), Tm (**4**), and Yb (**5**) were selected in order to account for appropriate variation of electron configuration, ionic radii, and redox potentials, respectively, within the Ln^{3+} series.

Results and Discussion

The fragmentation pattern principally common to all five homologues, **1**–**5**,[12a] is shown in Scheme I, the relative abundance[12b] of each individual fragment being listed in Table I.

In analogy to the unmethylated compounds Cp_3Ln,[1-4] the base peak of all metal-containing fragments of **1**–**4** is $[Cp'_2Ln]^+$ (Cp′ = $CH_3C_5H_4$); only in **5** is the base peak $[Cp'Yb]^{\bullet+}$. While one possible sequence of fragmentation:

[†] Also part 6 of the series "Coordination Behaviour in Base-Free Tris(cyclopentadienyl) Complexes of Rare Earth Elements". For part 5 see ref 31.

(1) Müller, J. *Chem. Ber.* **1969**, *102*, 152.

(2) Thomas, J. L.; Hayes, R. G. *J. Organomet. Chem.* **1970**, *23*, 487.

(3) Devyatykh, G. G.; Krasnova, S. G.; Borisov, G. K.; Larin, N. V.; Gaivoronskii, P. E. *Dokl. Akad. Nauk SSSR* **1970**, *193*, 1069.

(4) Devyatykh, G. G.; Gaivoronskii, P. E.; Larin, N. V.; Borisov, G. K.; Krasnova, S. G.; Zyuzina, L. F. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1974**, *19*, 496.

(5) Druzhkov, O. N.; Andrianov, Yu. A.; Dyagileva, L. N. *Zh. Obshch. Khim.* **1977**, *47*, 1836.

(6) Andrianov, Yu. A.; Druzhkov, O. N.; Smirnov, A. S.; Perevozchikova, N. V.; Zhil'tsova, E. E.; Dodonov, V. A. *Zh. Obshch. Khim.* **1978**, *48*, 2097.

(7) Gaivoronskii, P. E.; Gavrishchuk, E. M.; Chernyaev, N. P.; Zverev, Yu. B. *Russ. J. Inorg. Chem.* (Engl. *Transl.*) **1978**, *23*, 1742.

(8) Spilners, I. J.; Larson, J. G. *Org. Mass Spectrom.* **1970**, *3*, 915.

(9) Zhuk, B. V.; Domrachev, G. A.; Semenov, N. M.; Mysov, E. I.; Materikova, R. B.; Kochetkova, N. S. *J. Organomet. Chem.* **1980**, *184*, 231.

(10) Müller, J.; Lüdemann, F. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 74 and further references therein.

(11) Sienel, G. R. Doctoral Dissertation, Universität Erlangen, Erlangen, FRG 1976, pp 33, 112, 124.

(12) (a) Occasionally observed ions whose m/z exceeds that of **a**, as well as ions with probably CH_2-interlinked ring ligands, have been omitted in Table I and will be discussed in a different context elsewhere. (b) In some instances, the most intense peak appears at m/z 79 ($[CH_3C_5H_4]^+$). This may be due to thermal decomposition as the source temperature (200 °C) approaches that of the melting (or decomposition) points of the samples. The intensity ratio $m/z(C_6H_6^{\bullet+})/m/z$(**a**) remains almost unchanged when the ion source temperature is varied between 80 and 200 °C.

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Table I. Relative Intensities and Assignment of the 18 Best-Detectable Metal-Containing Fragments of the Compounds 1–5

fragment	m/z (rel int)				
	1 (^{139}La)	**2** (^{141}Pr)	**3** (^{142}Nd)	**4** (^{169}Tm)	**5** (^{174}Yb)
a (= M^+), $(CH_3C_5H_4)_3Ln^{\bullet+}$	376 (20)	378 (16)	379 (4)	406 (4)	411 (37)
b, $[(CH_3C_5H_4)_2Ln]^+$	297 (100)	299 (100)	300 (100)	327 (100)	332 (96)
c, $[(CH_3C_5H_4)Ln]^{\bullet+}$	218 (0.6)	220 (60)	221 (58)	248 (23)	253 (100)
d, $[(CH_3C_5H_4)_2(C_5H_4)Ln]^+$	361 (8)	363 (6)	364 (2)	391 (2)	396 (4)
e, $[(CH_3C_5H_4)_2HLn]^{\bullet+}$	298 (4.5)	300 (13)	301 (58)	328 (14)	333 (17)
f, $[(CH_3C_5H_4)HLn]^+$	219 (0.2)	221 (19)	222 (78)	249 (2)	254 (7)
g, $[(CH_3C_5H_4)(C_5H_5)Ln]^+$	283 (10)	285 (11)	286 (6)	313 (6)	318 (1)
h, $[(C_5H_5)Ln]^{\bullet+}$	204 (0.2)	206 (2)	207 (6)	234 (5)	239 (4)
j, $[(C_5H_5)HLn]^+$	205 (0.1)	207 (2)	208 (4)	235 (0.5)	240 (3)
k, $[(C_6H_6)Ln]^+$	217 (7)	219 (1.5)	220 (60)	247 (4)	252 (55)
l, $[(CH_3C_5H_4)(C_6H_6)Ln]^{\bullet+}$	296 (1)	298 (4)	299 (5)	326 (0.5)	331 (63)
m, $[(CH_3C_5H_4)(C_5H_4)Ln]^{\bullet+}$	282 (0.1)	284 (0.1)	285 (2)	312 (1)	317 (1)
n, $[(C_6H_6)(C_5H_4)Ln]^+$	281 (0.2)	283 (0.2)	284 (1.5)	311 (0.5)	316 (1)
o, $[(C_6H_5)Ln]^{\bullet+}$	216 (0.1)	218 (0.1)	219 (4)	246 (0.1)	251 (70)
p, $[(C_6H_4)Ln]^+$	215 (0.2)	217 (0.2)	218 (2)	245 (0.1)	250 (46)
q, $[(C_4H_4)Ln]^+$	191 (0.1)	193 (3)	194 (1.5)	221 (0.1)	226 (1)
r, $[(C_2H_2)Ln]^+$	165 (0.1)	167 (19)	168 (1.5)	195 (0.1)	200 (0.1)
Ln^+	139 (0.1)	141 (39)	142 (20)	169 (10)	174 (55)

[a] Data uncorrected for eventual isotopic contributions of neighboring ions.

$M^{\bullet+}$ (≡ **a**) → **b** → **c** → Ln^+ of Scheme I also corresponds to the main fragmentation pattern of $M^{\bullet+} = [Cp_3Ln]^{\bullet+}$ (i.e. $M^{\bullet+} \rightarrow [M-Cp]^+ \rightarrow [M-2Cp]^{\bullet+} \rightarrow Ln^+$),[1-4] **a** of **1**–**5** may alternatively undergo three additional modes of fragmentation (i.e. the loss of $H^\bullet$, $CH_3^\bullet$, and C_6H_6, respectively). Likewise, ion **b** may lose either $Cp'^\bullet$, $H^\bullet$, $CH_3^\bullet$ or Cp′H while, in contrast to $[Cp_2Ln]^+$,[1] neither C_2H_2 nor C_2H_4 is extruded at this stage. The facile separation of radicals from **b** does not follow the well-established "even-electron rule"[13] and might be due to the relatively high stabilities of the resulting ions **c**, **l**, and **m**, respectively.

Fragment **c**, $[C_6H_7Ln]^{\bullet+}$, the formal homologue of $[C_5H_5Ln]^{\bullet+}$ in the unmethylated series,[1-4] loses $H^\bullet$ as well, which dominates always over the expected abstraction of $Cp'^\bullet$. While the latter is even nonobservable for Ln = La, the two alternative pathways leading either to $[C_6H_6Ln]^+$ or to $[Ln]^+$ are almost equally favored for Ln = Yb.

The most unexpected fragment **e** might, in view of its B/E-linked scans which indicate the loss of either $H^\bullet$, $CH_3^\bullet$, $CH_3C_5H_4^\bullet$, or $CH_3C_5H_5$, be best formulated as $[(\eta^5\text{-}CH_3C_5H_4)_2LnH]^+$. The question on the origin of **e** appears to be of intrinsical importance. First of all, the B/E-linked scans performed on $M^{\bullet+}$ (**a**) unequivocally prove that **e** is a direct fragment of **a**.[14] Studies of the relative abundances of the "primary ions" **e** and **b** in three different "time windows" (i.e. inside the ion source, 10^{-7} s, in the first field-free region; 5×10^{-7} s, and in the second field-free region; 10^{-6} s, respectively) have revealed that in fact comparatively slow EI-induced decomposition pathways are leading to ion **e** (cf. Figure 1). These findings suggest that some skeletal and/or hydrogen rearrangements might precede the formation of **e**, but not that of **b**.

As, at lower m/z values, signals corresponding to m/z 78 are always very intense, uncharged C_6H_6 that could subsequently experience electron impact is likely to be extruded after the skeletal and/or hydrogen rearrangement. The CAD MIKE spectra of these $C_6H_6^{\bullet+}$ ions strongly resemble those of authentic benzene (Figure 2) which is in favor of the extrusion of benzene (and not, e.g., of fulvene) molecules. Corresponding EI-initiated reactions have been proposed for several alkylferrocenes[8,9] but could never be confirmed conclusively.

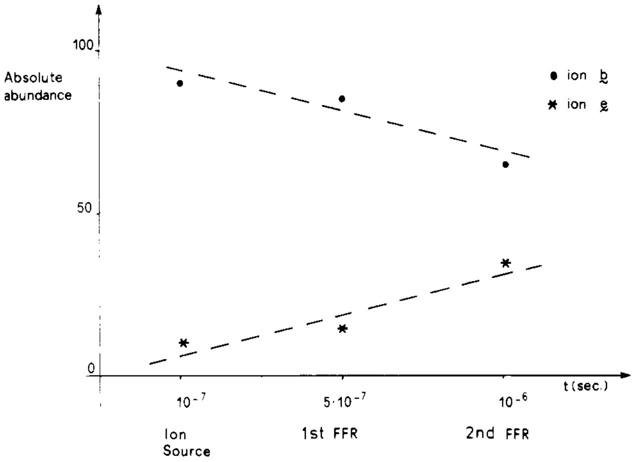

Figure 1. Variation of the absolute abundance of the primary fragments **b** and **e** (of sample **2**) in three different regions of the spectrometer.

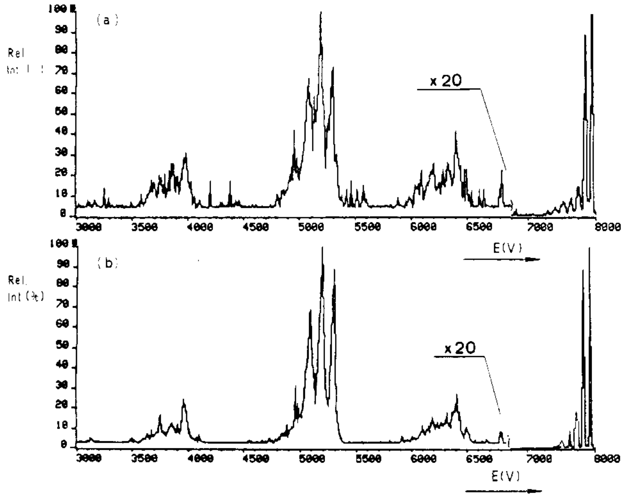

Figure 2. CAD MIKE spectra of the fragment with m/z 78 of (a) authentic benzene and (b) sample **1**.

Appropriate B^2/E-linked scan studies demonstrate that in addition to fragment **a**, at least five other fragments, namely, **c**, **d**, **g**, **k**, and **m**, may be a source of C_6H_6 and

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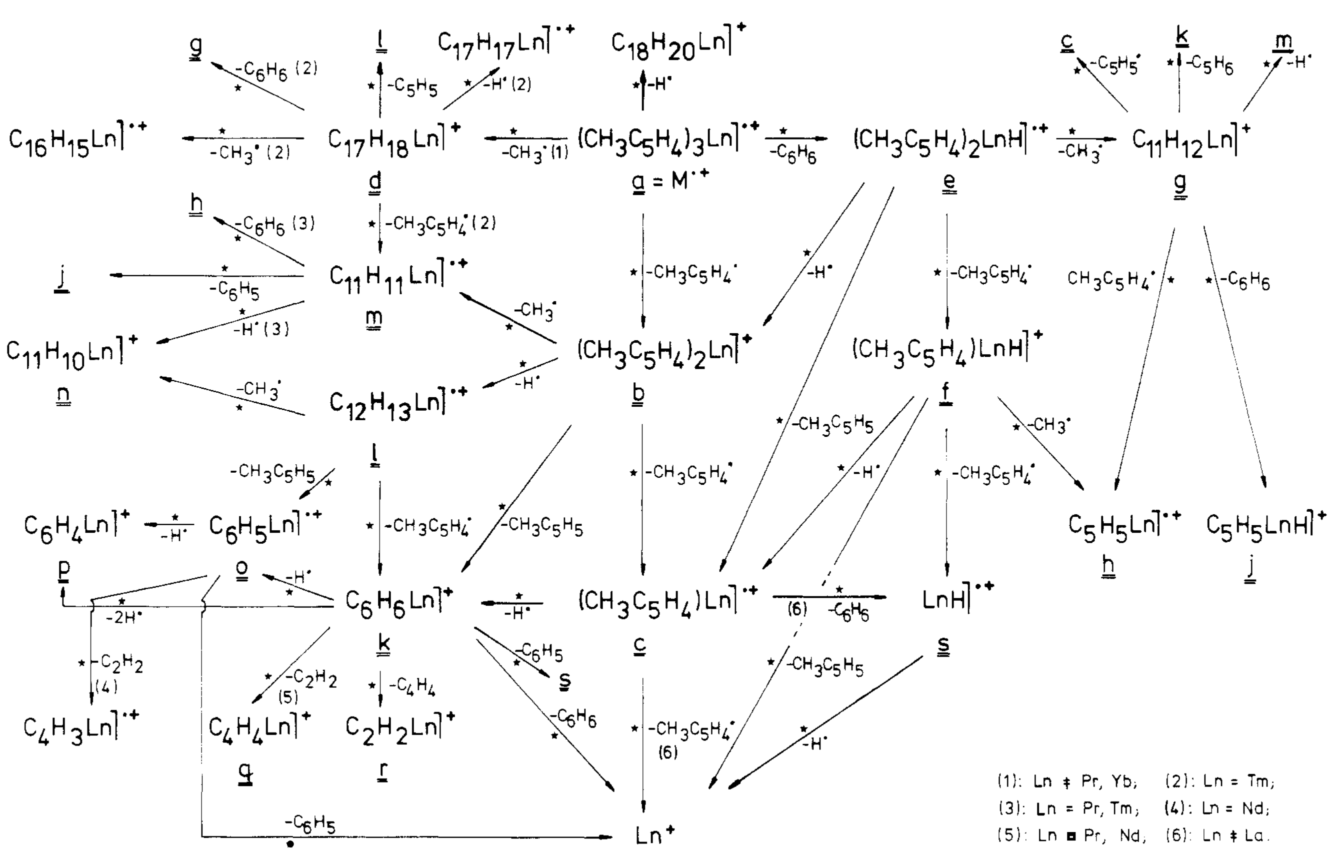
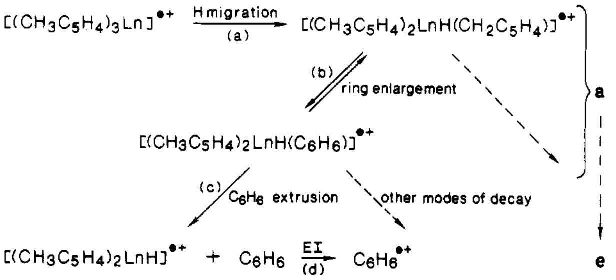
(13) Stevenson, D. P. *Discuss. Faraday Soc.* **1951**, *10*, 35. Audier, H. E. *Org. Mass Spectrom.* **1969**, *2*, 283.

(14) Owing to the high reactivity of **b** and the availability of H atoms in the environment of the ion source, ion **e** could in principle also originate from ion–molecule reactions. However, the independence of the intensity ratio $m/z(\mathbf{e})/m/z(\mathbf{a})$ of the vapor pressure of the sample makes this view less probable.

Scheme I. Total Fragmentation Pattern of Compounds 1–5

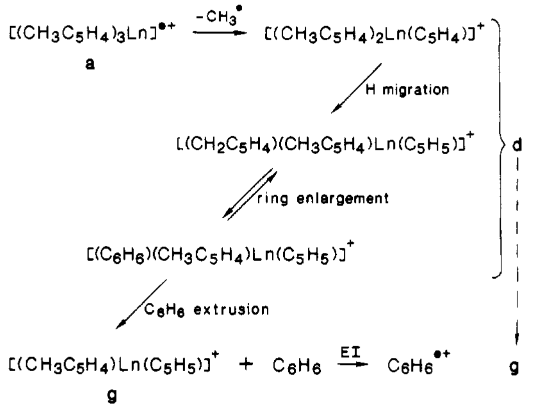


Scheme II. Loss of C_6H_6 Initiated by Intramolecular H Migration[a]



[a] Exemplified for the fragmentation a → e.

Scheme III. Loss of C_6H_6 Initiated by Loss of a CH_3 Radical



$C_6H_6^{•+}$, respectively. While each of these six C_6H_6-releasing ions located at different stages of Scheme I may alternatively lose several other metal-free fragments (including H•), it is interesting that unlike in many classical cases [e.g., toluene(1+) $\xrightarrow{-H^•}$ tropylium(1+)] C_6H_6 extrusion is not invariably preceded by the complete loss of one H atom.

It appears, however, justifiable to assume that some of the C_6H_6-releasing fragments of 1–5 may display facile, albeit experimentally undetectable, fluxionality of a H atom between various active molecular sites. Thus, the liberation of C_6H_6 from fragment **a** might involve the three individual steps (a)–(c) of Scheme II. Step (a) appears reasonable in view of various well-documented cases of preparative metal-induced (alkyl) C–H bond cleavage[15] as well as the existence of numerous organolanthanoid complexes with stable Ln–H bonds.[16] Most interesting in this context is the facile formation of structurally well-documented complexes of the type $[(Cp'_3Ln)_2H]^-$.[16c,d]

Since in our CAD MIKE experiments the spectrum of free fulvene could never be detected and because of the apparent unability of authentic fulvene to rearrange to benzene under experimental conditions comparable to those adopted for the metal complexes, the three (or two) steps of Scheme II might alternatively merge to a concerted process during which coordinated fulvene would only be passed as a very short-lived intermediate. In accordance with earlier findings,[10] the mass spectrum of neat methylcyclopentadiene showed likewise no $C_6H_6^{•+}$ CAD

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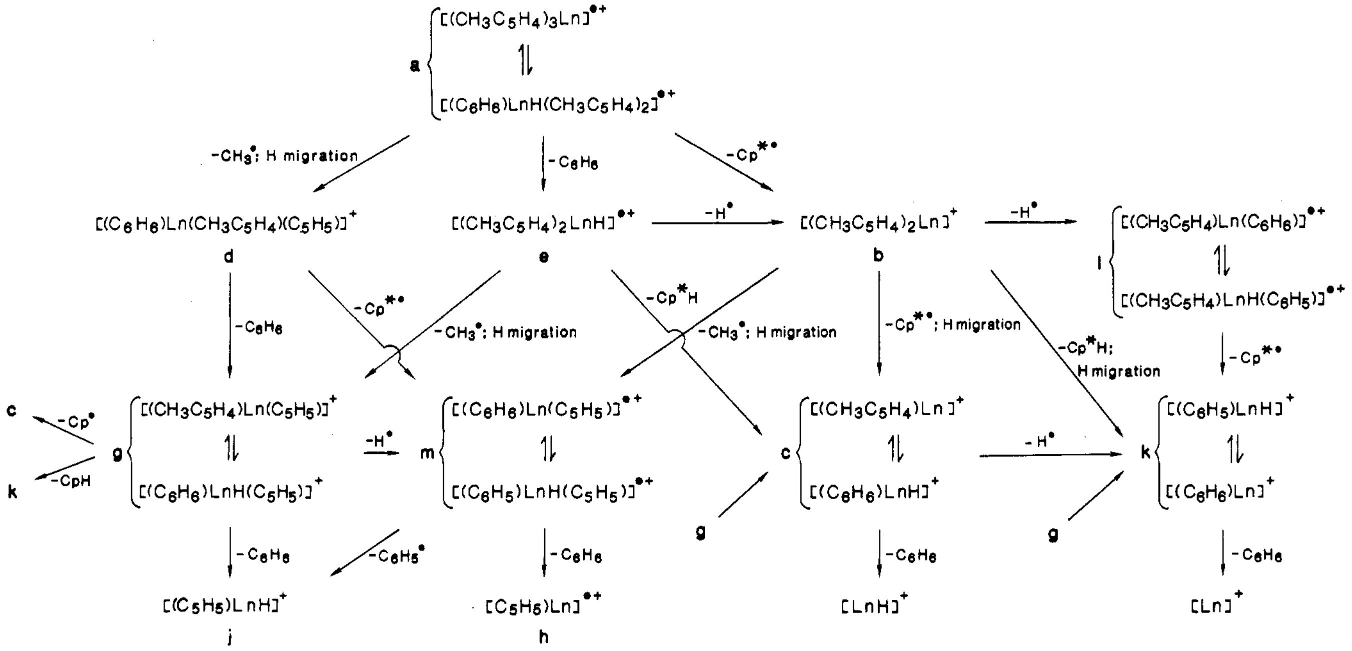
[15] See: Teuben, J. H. In *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragalà, I. L., Eds.; D. Reidel: Dordrecht, The Netherlands, 1985; p 195 and further literature therein.

[16] (a) Evans, W. J.; Meadows, J. H.; Hanusa, T. P. *J. Amer. Chem. Soc.* **1984**, *106*, 4454 and further references therein. (b) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51. (c) $[(Cp_3Ln)_2H]^-$ (Ln = Lu): Schumann, H.; Genthe, W.; Hahn, E.; Hossain, M. B.; van der Helm, D. *J. Organomet. Chem.* **1986**, *299*, 67. (d) Ln = Nd: Sun, Y.-M.; Jin, S. C.; Shen, Q.; Lin, Y.-H. *Proc. Int. Conf. Coord. Chem. 25th* **1987**, *No. C1*, 355.

Scheme IV. Modified Fragmentation Pattern of 1–5[a]



[a] Most of the fragmentation steps without any relevance for C_6H_6 extrusion have been omitted for clarity (see Scheme I). Abbreviations: $Cp^{*\bullet}$, $CH_3C_5H_4^{\bullet}$; Cp*H, $CH_3C_5H_5$; $Cp^{\bullet}$, $C_5H_5^{\bullet}$; CpH, C_6H_6; Ln, lanthanoid atom.

Table II. Fragments of the Partially Deuteriated Sample $(CD_3C_5H_4)_3Pr$ (2a) and Some Tentative Assignments

m/z (rel int)	assignmt	*m/z* (rel int)	assignmt	*m/z* (rel int)	assignmt
387 (19)	**a** + 9	225 (4)		168 (1)	**r** + 0
369 (5)	**d** + 6	223 (21)	*c* + 3	167 (3)	
307 (2)	**e** + 7	222 (29)	**k** + 3; **c** + 2	...	
306 (29)	**e** + 6; **b** + 7	221 (64)	**k** + 2; **c** + 1	83 (54)	$[CD_3C_5H_5]^{\bullet+}$
305 (≡ 100)	**b** + 6	220 (6)		82 (74)	$[CD_3C_5H_4]^+$
304 (7)	**b** + 5; **l** + 6	219 (2)		81 (39)	$[CHD_2C_5H_4]^+$
303 (2)	**l** + 5	218 (3)		80 (41)	$[C_6H_4D_2]^{\bullet+}$
289 (6)	**g** + 4; **m** + 5	209 (1)		79 (34)	$[C_6H_5D]^{\bullet+}$
288 (33)	**g** + 3; **m** + 4; **n** + 5	208 (2)	**j** + 1	78 (11)	$[C_6H_6]^{\bullet+}$
287 (1)		207 (5)	**h** + 1	54 (16)	$[C_4H_2D_2]^{\bullet+}$
286 (2)		206 (9)	**h** + 0	53 (23)	$[C_4H_3D]^{\bullet+}$
284 (1)		195 (1)		52 (20)	$[C_4H_4]^{\bullet+}$
		194 (2)			

MIKE spectrum reminiscent of that of benzene.

The loss of a methyl radical from one coordinated $CH_3C_5H_4$ ligand as observed at various stages of the total fragmentation pattern (Scheme I) offers particularly favorable conditions for intramolecular hydrogen transfer from an intact $CH_3C_5H_4$ ligand to the metal-bonded C_5H_4 fragment. Scheme III demonstrates that, e.g., fragment **d** which results after $CH_3^{\bullet}$ abstraction from **a** should be able to rearrange to an isomer that could extrude C_6H_6 equally well as the corresponding tautomer of **a** (cf. Scheme II).

Three of the six C_6H_6 abstractions mentioned above (involving **d**, **g**, and **m**) could in fact be initiated by the loss of $CH_3^{\bullet}$. It is noteworthy that fragment **e** may even lose another $CH_3^{\bullet}$ radical instead of the probably metal-bonded H atom and that this step appears in part to be followed by H migration from the last available CH_3 group to the unsaturated C_5H_4 ligand. Without this kind of rearrangement the subsequent abstraction of $C_5H_5^{\bullet}$ or C_5H_6 from **d** (and of $C_5H_5^{\bullet}$ from **g**) would be hard to rationalize. Scheme IV presents a more systematic view of all sections of Scheme I involved in direct C_6H_6 abstraction or in essential preparatory steps. Interestingly, neither of the two fragments **b** and **l** extrudes C_6H_6: the usually maximal abundance of **b** suggests particular stability (most probably of the untautomerized form). Fragment **l** might, in view of its reluctance to also lose $H^{\bullet}$ or $C_6H_5^{\bullet}$ actually represent one surprisingly stable benzene complex, $[(CH_3C_5H_4)Ln(C_6H_6)]^{\bullet+}$. The very high relative intensity of fragment **l** of sample **5**, the isomer $[(CH_3C_5H_4)Yb(C_6H_6)]^{\bullet+}$ of which would formally require Yb^{2+}, correlates well with the particularly facile reducibility of Yb^{3+} (vide infra).

The mass spectrum of the partially deuteriated complex $(CD_3C_5H_4)_3Pr$ (**2a**) is richer in fragments (Table II) than the spectrum of **2** which suggests that some intramolecular scrambling of methyl D and ring H atoms cannot be ruled out. While the fragments with *m/z* 387 (**a**′ ≅ **a** + 9) and 305 (**b**′ ≅ **b** + 6) are comparable in intensity with the fragments of **a** and **b**, the intensity of **c**′ at *m/z* 223 (≅ **c** + 3) turns out to be notably weaker than that of **c**. The influence of D/H scrambling is expected to increase with the number of alternative fragmentation pathways leading independently to one distinct ion. Thus, the rather intense signal of **2a** at *m/z* 221 might be due to both **k**′ (≅ **k** + 2) and **c**‴ (≅ **c** + 1) while the likewise intense signal of **2a** at *m/z* 222 could be due to both **k**″ (≅ **k** + 3) and **c**″ (≅ **c** + 2). The variety of metal-free ionic fragments of **2a** (*m/z* <100) is likewise indicative of the liberation of partially deuteriated benzene. Thus, the otherwise most intense peak at *m/z* 78 (C_6H_6) is now exceeded by one with *m/z* 80 ($C_6H_4D_2$).

Conclusions

Despite the nonuniform variation of the relative intensities of several fragments[17] (e.g. of **d**, **e**, **f**, **k**, etc. of Table I) with the nature of Ln, the abstraction of a benzene molecule from the molecular ion **a**, and subsequently also from the potential arene complexes **c**, **d**, **g**, **m**, and **k** (cf. Scheme IV), appears to be common to samples **1**–**5** and, most probably, to all other $(CH_3C_5H_4)_3Ln$ homologues too.

The initially unexpected fragmentation **a** → **e** + C_6H_6 suggests remarkable mobility of H atoms over complex **a**. Müller has stated[1] that owing to interligand migration of *ring* H atoms even cyclopentadiene is extruded from dipositive $(C_5H_5)_3Ln^{2+}$ ions (Ln = Pr, Ho, Lu). The same author has confirmed by a systematic inspection of the appearance potentials[1] that the abundance of fragments $[(C_5H_5)_2Ln]^+$ throughout should actually display optimal relative stability; thus, corresponding stability is also expected for the related fragments $(CH_3C_5H_4)_2Ln^+$ (**b**) which show in fact no evidence of C_6H_6 abstraction. The mixed-ligand homologue **g**, $(CH_3C_5H_4)(C_5H_5)Ln^+$, however, loses C_6H_6, suggesting some preponderance of the tautomer $[C_6H_6LnH(C_5H_5)]^+$.

In 1986, the first arene complex of a tripositive lanthanoid ion was prepared and characterized by X-ray crystallography.[19] Most recently, the description of the first genuine bis(arene) sandwich complexes of some zerovalent rare-earth elements has followed.[20] The respective thermal stabilities and metal-to-ring distances leave no doubt that zerovalent lanthanoid atoms may form notably stronger Ln-to-arene bonds than the corresponding tripositive metal ions. From ion-beam studies of the interaction of the gas-phase metal ions La^+[21] and Gd^+[22] with various unsaturated and saturated hydrocarbons (e.g. cyclohexene, cyclohexane, and even *n*-hexane) apparently fragment **k**, i.e., $[(C_6H_6)Ln]^+$, is readily formed. In accordance with the energetically reduced availability of electron configurations like f^qds or f^qd^2 in case of Pr^+ and Eu^+,[23] the latter metal ions turned out to be practically incapable of producing $[C_6H_6Ln]^+$.[22] Corresponding arguments[23] would predict even more stringently the (experimentally confirmed) superiority of Ln^0-to-arene over Ln^{III}-to-arene bonding.

Müller has shown that $[C_6H_6M]^+$ fragments involving d-transition-metal atoms may, depending on the mode of their origin, not always contain a genuine benzene ligand.[10] Thus in some of the fragments of **1**–**5**, the formal oxidation number of the metal ion could likewise fluctuate between two (or more) different values, e.g. in case of **l**, **m**, and **k** between 3+ and 2+ (cf. Scheme IV). The lowest electron configuration of Ln^{2+} involving at least one 5d electron lies approximately 0 (La), 12.8 (Pr), 15.2 (Nd), 16.6 (Tm) and 33.4 (Yb) × 10^3 cm^{-1} above the ground configuration of the respective Ln^{2+} ion.[23]

The rather nonuniform variation in the relative intensities of a number of the fragments listed in Table I may have its origin in the co- and counteroperation, respectively, of several independent influences: (i) the relative ease of an initially tripositive metal ion to reach its dipositive (or even monopositive) state, (ii) the availability of low energetic electron configurations involving at least one 4d valence electron for metal-to-ligand (benzene) backbonding, (iii) the variation in the ionic radius of M^{3+}, M^{2+}, and M^+, respectively, and (iv) the variation in the first ionization potential of **1**–**5** with Ln. The latter does not vary notably owing to the reluctance of organolanthanoid(III) compounds to lose an electron from a partially occupied 4f shell when subjected to EI[1] or to PE spectroscopy.[24] While a change from Ln(III) to Ln(II) will most readily take place for Ln = Yb, the subsequent *stabilization* of genuine arene complexes (by low-valent Ln) should be most effective for Ln = La and Pr. The lanthanide contraction causes (at a constant oxidation state) a decrease of the ionic radius with increasing atomic number: thus fragments displaying relatively low coordination numbers (or integral ligand hapticities) are expected to undergo rearrangement reactions more readily than fragments with well-saturated coordination spheres and usually also a higher oxidation number of the central metal atom. From Table I it appears that all influences mentioned above might interfere in quite a complicated way. To mainly focus here on the phenomenon of C_6H_6 formation and extrusion, further differences between the mass spectra of **1**–**5** (like the occurrence of CH_2-interlinked binuclear cations with Ln = Tm, but not Yb[12a]) have been omitted in this paper.

Organouranium(IV) complexes of the general type $(CH_3C_5H_4)_3U^{IV}X$ with X = alkyl, aryl, (pseudo)halide, amide, oxide, etc. seem to prefer direct metal oxidation via EI-induced 5f-electron removal[24] which is likely to also modify some mechanisms of fragmentation. The reexamination of the mass spectra of some $(CH_3C_5H_4)_3UX$ systems[11] employing improved instrumentation and focusing on specific differences between related lanthanoid and actinoid complexes will be the subject of a forthcoming study.

Experimental Section

All mass spectrometric measurements were carried out on a VG ZAB 2F instrument, interfaced with a VG 11/250 data system operating under electron-impact (EI) conditions (70 eV, 200 μA). Samples were introduced by direct probe inlet without any heating. The ion source temperature was 200 °C.

Metastable transitions were detected by B/E-linked scans.[25] Exact mass measurements were obtained by the peak matching technique at 10 000 resolving power (10% valley definition). Collisional-activated-decomposition (CAD), mass-analyzed ion kinetic energy (MIKE)[26] spectra were obtained for 8-keV ions colliding with air in the second field-free region. The pressure in the collision cell was chosen such that the main beam intensity reached at most 40% of its usual value.

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[17] Interestingly, the relative abundances of the fragments **b** and **c** (Table I) are inversely related with the appearance potentials of the homologous fragments $[(Cp_2Ln)]^+$ and $[CpLn]^{\cdot+}$:

Ln	$[Cp_3Ln]^{\cdot+}$	$[Cp_2Ln]^+$	$[CpLn]^{\cdot+}$
La	7.9	10.2	17.3
Nd	8.0	9.8	16.8
Pr	8.2	10.0	17.0

Appearance energies (in eV; deduced from EI), see: Ambler, E. In *Ionization Potentials and Appearance Potential Measurements*; Levin, R. D., Lias, S. G., Eds.; National Bureau of Standards: Washington, D.C., 1982.

[18] The mass spectrum of the corresponding thulium complex **4a** has turned out more complicated than that of **2a**, probably due to inter- and/or intramolecular H/D scrambling.

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The preparation of the complexes **1**,[27] **2**,[28] **3**,[29] **4**, and **5**[28] was carried out following the procedure of Reynolds and Wilkinson.[30] Analytically pure products were obtained in yields of 60–70% by high vacuum sublimation (80–130 °C).

For the preparation of **2a** (and **4a**), $Na(CH_3C_5H_4)$ was replaced by $Na(CD_3C_5H_4)$ (**6**): 3.0 mL (47.6 mmol) of CD_3I (Fluka, 99% deuteriation) was added dropwise under stirring at −15 to −20 °C to a solution of 4.4 g (50 mmol) of $Na(C_5H_5)$ in 100 mL of THF. After 1 h the mixture was exposed to room temperature and the resulting $CD_3C_5H_5$ (together with the solvent) condensed into a flask cooled by liquid N_2 (pressure: ca. 1300 Pa). Sodium sand (1.4 g, 61 mmol) was added at room temperature and stirred over 12 h. After filtration (G3 frit), solvent evaporation, and drying of the residue at the high vacuum (3 h, 80 °C), all THF was removed. Yield of pure **6**: 3.6 g (72.5%).

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Registry No. **1**, 99080-23-6; **2**, 78869-44-0; **2a**, 114928-58-4; **3**, 39470-13-8; **4**, 114928-57-3; **5**, 74858-41-6; $Na(CD_3C_5H_4)$, 114862-55-4; CD_3I, 865-50-9; $Na(C_5H_5)$, 4984-82-1.

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Electronic Structure of Metal Dimers. Photoelectron Spectra and Molecular Orbital Calculations of Dicarbonyl- and Dinitrosyl-Bridged Cobalt, Rhodium, and Iridium Cyclopentadienyl Dimers

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Gas-phase, ultraviolet photoelectron spectra, and molecular orbital calculations are reported for $Cp^*_2M_2(\mu\text{-}CO)_2$ ($Cp^* = C_5(CH_3)_5$; M = Co, Rh, Ir) and $Cp_2M_2(\mu\text{-}NO)_2$ ($Cp = C_5H_5$; M = Co, Rh). Comparison between series of calculations and series of spectra enable us to reassign the "frontier" region of the spectra as well as more thoroughly assign the "metal" and "cyclopentadienyl" regions of the spectra. Our results suggest that the two lowest energy ionizations, which occur from frontier orbitals of b_g and b_u symmetry, reverse their order in the dicarbonyl-bridged Co dimer relative to the dicarbonyl-bridged Rh and Ir dimers. Although others have suggested that $Cp_2Co_2(NO)_2$ has a triplet ground state, our spectra rule out this possibility for both $Cp_2Co_2(NO)_2$ and $Cp_2Rh_2(NO)_2$. Also discussed is the correlation of molecular orbital theory and valence bond theory in the description of the interfragment bonding in these dimers. Only by counting 5σ carbonyl to metal donations and metal to 2π carbonyl donations as contributing to metal–metal bonds can we arrive at the formal single and double metal–metal bonds required by the 18-electron rule for these dimers. Overlap populations suggest weak metal–metal bonds and strong metal–bridging ligand bonds for all of these dimers.

Introduction

The electronic structure of dibridged transition-metal dimers of the type $(C_5R_5)_2M_2(\mu\text{-}CO)_x(\mu\text{-}NO)_{2-x}$ (R = H or CH_3, henceforth Cp and Cp*, respectively; M = Fe, Co, Ni) has received a lot of attention in recent years. These dimers provide good models for experimental and theoretical studies of metal–metal and metal-bridging π acid interactions.

In spite of the volume of work existent there remain unanswered questions about the electronic structures of dimers doubly bridged by π acids. Although investigators agree that metal–bridging ligand interactions are more important than metal–metal interactions in stabilizing these types of dimers,[1] there exists no consensus on the extent of metal–metal bonding. Studies employing photoelectron (PE) spectroscopy and extended Hückel calculations of nitrosyl- and carbonyl-bridged cobalt, rhodium, and nickel dimers reported no evidence of metal–metal bonding.[2,3]

Another issue that needs to be more thoroughly addressed is the correlation of valence bond theory with molecular orbital theory in the description of metal–metal and metal–bridging ligand bonding in these dibridged binuclear complexes. The 18-electron rule requires that metal dimers with 34 (d^9–d^9), 33 (d^8–d^9), or 32 (d^8–d^8) electrons should have metal–metal bond orders of 1.0, 1.5, or 2.0, respectively. Crystallographic studies, however, have demonstrated that all dimers of this series, with the exception of $Cp_2Ni_2(CO)_2$, are isostructural, featuring planar $M_2(CO)_x(NO)_{2-x}$ cores and metal–metal bond distances insensitive to changes in formal metal–metal bond order.[4]

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