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# Mass Spectra and Thermal Stability of Mixed-Ligand Ytterbium Compounds Involving Cyclopentadienyl and β-Diketonato Chelate Ligands

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The mass spectra and the thermal stability of 12 ytterbium compounds of $Cp_2YbL$ and $CpYbL_2$ types ($Cp = \eta^5\text{-}C_5H_5$; HL = acetylacetone, 2,2,6,6-tetramethyl-3,5-heptanedione, 1,1,1-trifluoroacetylacetone, benzoylacetone, 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone, (trifluoroacetoacetyl)-α-thiophene) have been studied under electron-impact conditions. Disproportionation reactions may take place when these compounds reach a certain evaporation temperature. The disproportionation products $Cp_3Yb^{\bullet+}$ and $YbL_3^{\bullet+}$ have a fragmentation mechanism which differs from that of the molecular ions $Cp_2YbL^{\bullet+}$ and $CpYbL_2^{\bullet+}$.

## Introduction

The mass spectra of lanthanide β-diketonato compounds have recently been reported.[1,2] However, reports concerning the mass spectra of lanthanide organometallics, involving both cyclopentadienyl and β-diketonato chelate ligands, have been few.[3] We have synthesized 12 ytterbium compounds of $Cp_2YbL$ and $CpYbL_2$ types (HL = acetylacetone (H-acac), 2,2,6,6-tetramethyl-3,5-heptanedione (H-tmd), 1,1,1-trifluoroacetylacetone (H-tfacac), benzoylacetone (H-bzac), 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone (H-bmphpz); (trifluoroacetoacetyl)-α-thiophene H-(tfacth)) and reported that all of them tend to disproportionate.

| | | |
|---|---|---|
| $Cp_2Yb(acac)$ | $CpYb(acac)_2$ | $Cp_2Yb(tmd)$ |
| 1 | 2 | 3 |
| $CpYb(tmd)_2$ | $Cp_2Yb(bzac)$ | $CpYb(bzac)_2$ |
| 4 | 5 | 6 |
| $Cp_2Yb(bmphpz)$ | $CpYb(bmphpz)_2$ | $Cp_2Yb(tfacth)$ |
| 7 | 8 | 9 |
| $CpYb(tfacth)_2$ | $Cp_2Yb(tfacac)$ | $CpYb(tfacac)_2$ |
| 10 | 11 | 12 |

Now a systematic study has been carried out on the cleavage reactions and thermal stability of these compounds by using electron-impact and metastable transition analysis. The significant results obtained have provided important information which illuminates the relationship between the structure and properties of these compounds and the understanding of the bonding between the lanthanide metal ions and their ligands.

## Experimental Section

General procedure: $Cp_2YbL$ and $CpYbL_2$ were prepared by the literature methods.[4]

All the mass spectrometric measurements were performed on a MAT 312 mass spectrometer operating in EI mode at a resolving power of 1000 (electron energy, 70 eV; emission current, 1 mA; ion acceleration, 3 kV). The samples were protected under argon and were introduced by direct inlet techniques with a source temperature of 130–180 °C and a samples evaporation temperature in the range of 20–300 °C. The metastable transitions were detected by UA/B and UA/$B^2$ linked scans in the first field-free region.

## Results and Discussion

**1. Spectral Features of $Cp_2YbL$- and $CpYbL_2$-Type Compounds.** The main fragment ions of 1–12 compounds and their abundances are shown in Table Ia,b. The molecular ions of the $Cp_2YbL$ and $CpYbL_2$ compounds 1–12 are clearly observed in the mass spectra. All the molecular ions are characterized by ready loss of the Cp ligand with the $(M - Cp)^+$ ion as the base peak in the mass spectra of most compounds, but no $(M - L)^+$ ion formed by direct

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(1) Xu, G.; Wang, C.; Sun, J.; Tang, Y. *Acta Chim. Sin.* **1984**, *42*, 239–245.

(2) Majer, J. B. In *Mass Spectrometry of Metal Compounds: Coordination Compounds*; Charalambous, J., Ed.; Butterworths: London, Boston, 1975; pp 189–247.

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(4) Ma, H.; Ye, Z. *J. Organomet. Chem.* **1987**, *326*, 369–374.

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**Table I**[a]

(a) The Relative Abundances of Main Fragment Ions of Compounds 1–8

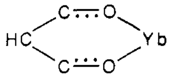
| | *m/z* (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| ions | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** |
| $M^+$ | 403 (46.7) | 437 (16.3) | 487 (27.7) | 605 (11.0) | 465 (90.0) | 561 (11.5) | 582 (32.0) | 793 (0.5) |
| $(M - Cp)^+$ | 338 (100) | 372 (100) | 422 (100) | 540 (100) | 400 (100) | 496 (100) | 517 (100) | 728 (1.5) |
| $(M - 2Cp)^+$ | 273 (78.3) | | 357 (83.6) | | 335 (98.0) | | 452 (70.8) | |
| $(M - (Cp + R))^+$ | | 357 (14.3) | 365 (3.0) | 483 (15.0) | | 419 (8.1) | | |
| $(M - (Cp + L))^+$ | 239 (7.8) | 273 (50.0) | 239 (28.3) | 357 (58.0) | | 335 (96.5) | | 452 (100) |
| $(M - L)^+$ | 304 (2.8) | | | | | 400 (85.0) | | 517 (97.5) |
| $Yb(L - R)^+$ | 258 (19.6) | 258 (20.4) | 300 (14.1) | 300 (8.0) | 320 (47.6) | 320 (97.0) | | |

(b) The Relative Abundances of Main Fragment Ions of Compounds 9–12

| | *m/z* (%) | | | |
|---|---|---|---|---|
| ions | **9** | **10** | **11** | **12** |
| $M^+$ | 525 (78.6) | 681 (5.6) | 457 (20.3) | 545 (1.4) |
| $(M - Cp)^+$ | 460 (100) | 616 (100) | 392 (12.2) | 480 (100) |
| $(M - (Cp + CF_2))^+$ | 410 (45.7) | 566 (56.3) | 342 (18.9) | 430 (84.3) |
| $(M - 2Cp)^+$ | 395 (32.8) | | 327 (14.9) | |
| $(M - L)^+$ | 304 (14.8) | | 304 (4.8) | |
| $Yb(L - CF_3)^+$ | 326 (9.8) | | 258 (24.3) | 258 (71.5) |
| $YbF(L - CF_3)^+$ | 345 (27.1) | | 277 (27.0) | 277 (13.9) |
| $YbF_2(L - CF_3)^+$ | | 364 (80.2) | | 296 (70.8) |
| $YbF^+$ | 193 (28.6) | | 193 (100) | 193 (98.2) |
| $YbF_2^+$ | | 212 (92.3) | | 212 (57.6) |
| $YbF_2(L - CF_3)_2^+$ | | 516 (10.3) | | 380 (29.5) |

[a] All MS data are based on the isotopes $^{174}Yb$, $^{32}S$, and $^{14}N$.

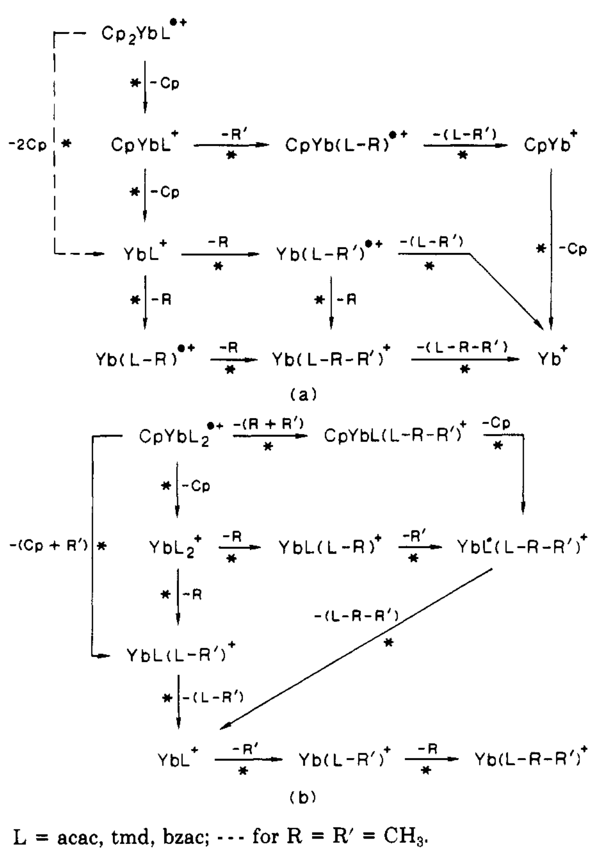
loss of the β-diketonato ligand (L) of the molecular ion is observed. This is consistent with the result reported in the literature[4] that cyclopentadienyl (Cp) forms $\eta^5$ bonds with ytterbium, whereas two carbonyl groups of β-diketonato ligand chelate with the ytterbium atom to form a chelate ring of the type



The Yb–Cp bond is weaker than the Yb–L bond, and the former breaks easily under electron impact. It can be seen from Table I that the relative abundances of $CpYbL_2$ molecular ions are lower than those of the corresponding $Cp_2YbL$ molecular ions. It is probably because in the $CpYbL_2$ compound the ytterbium atom chelates two β-diketonato ligands, thereby weakening the Yb–Cp bond strength, and thus the Cp ligand is more easily lost.

By means of the measurements of metastable ions the major fragmentation patterns in Schemes I–III have been deduced. Schemes I–III show that generally the Cp ligands of most $Cp_2YbL^{\bullet+}$ ions are lost stepwise, and only the $Cp_2Yb(acac)^{\bullet+}$ ion can lose two Cp ligands simultaneously. The β-diketonato ligand (L), however, is difficult to fragment as a unit. Because α-cleavage easily takes place at the carbonyl group of β-diketonates, the substituent R or R′ at either end frequently breaks first, and the relevant metastable transition can be observed. This is a common feature. The extent of losing the R or R′ substituent for molecular ions is $R = Ph$, $R' = CH_3 < R = R' = CH_3 < R = R' = C(CH_3)_3 < R = -\overline{C{=}CHCH{=}CHS}$, $R' = CF_3 < R = CH_3$, $R' = CF_3$. It can be seen from Scheme I, parts a and b, that the fragmentation features of $Cp_2YbL$ molecular ion are, first, to lose the Cp ligand and then the competitive cleavage process occurs between the Cp and the substituent R or R′ of the β-diketonate ligand. On the other hand, in the fragmentation of the $CpYbL_2$ molecular ion, the competitive cleavage appears at the very beginning between the Cp and the substituent R or R′.

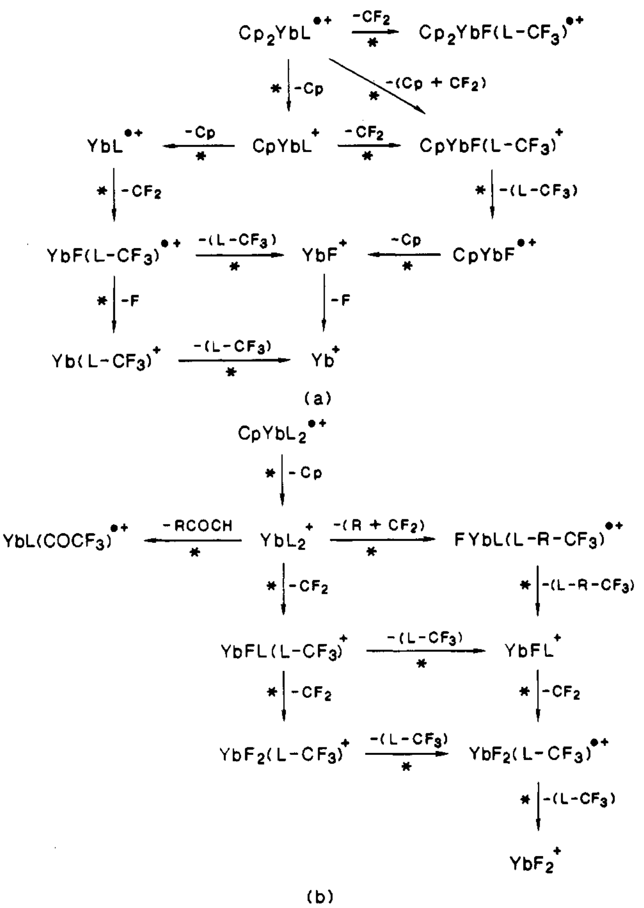
**Scheme I. The Major Fragmentation Pathways of $Cp_2YbL$ (Path a) and $CpYbL_2$ (Path b) Compounds**



L = acac, tmd, bzac; --- for $R = R' = CH_3$.

As for the mass spectra of trifluorinated $Cp_2YbL$ and $CpYbL_2$, it can be seen that the chief difference from the behavior mentioned above lies in the fact that the molecular ion abundances are low (except that of molecular ion of $Cp_2Yb(tfacth)$), and the loss of $CF_2$ fragments with rearrangement of fluorine (migration) to ytterbium occurs during the cleavage. These features can be attributed to the following. First, the existence of the electron-withdrawing group $CF_3$ weakens the C–$CF_3$ bond strength, thus leading to an easy fragmentation of the molecular ions. Second, the relative stability of fragment ions allows rearrangement to form strong Yb–F bonds. It is surprising

**Scheme II. The Major Fragmentation Pathways of $Cp_2Yb(RCOCHCOCF_3)$ (Path a) and $CpYb(RCOCHCOCF_3)_2$ (Path b) Compounds**



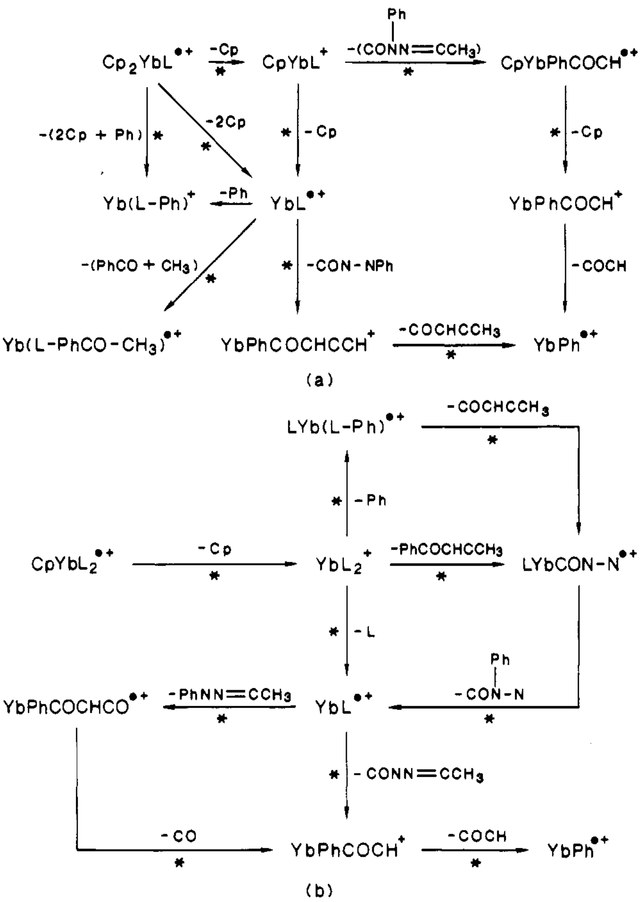
$R = CH_3, -\overline{C{=}CHCH{=}CHS}.$

that no fragment ions formed by losing $CF_3$ are observed. Scheme II shows that the competitive cleavage of the fragmentation of trifluorinated $Cp_2YbL$ molecular ions occurs initially between the Cp and $CF_3$ or the substituent R of the $\beta$-diketonate ligand. However, with the trifluorinated $CpYbL_2$ molecular ions, only the simple Yb–Cp bond breaking takes place initially. When it cleaves further, various competitive cleavage processes can then occur.

Since the $\beta$-diketonate ligand in the compounds $Cp_2Yb(bmphpz)$ and $CpYb(bmphpz)_2$ is heterocyclic, the fragmentation of their molecular ions is complex (shown in Scheme III). The major fragmentation features of $Cp_2Yb(bmphpz)$ and $CpYb(bmphpz)_2$, however, are similar to those of $Cp_2YbL^{\bullet+}$ and $CpYbL_2^{\bullet+}$ containing $CF_3$.

**2. Thermal Stability of $Cp_2YbL$ and $CpYbL_2$ Compounds and Spectra of Disproportionation Products.** When the evaporation temperature of samples is manually raised and the samples scanned rapidly, the spectra of 12 compounds of $Cp_2YbL$ and $CpYbL_2$ at different evaporation temperatures are obtained. It is interesting to note that when the evaporation temperature of a sample of these two types of compounds reaches a certain value for each, not only are molecular ion $Cp_2YbL^{\bullet+}$ or $CpYbL_2^{\bullet+}$ peaks observed in the spectra, but also the peaks corresponding to $YbL_3^{\bullet+}$ and its fragments at a greater mass range than the molecular ion are observed as well. At the same time, the peaks coresponding to $Cp_3Yb^{\bullet+}$ ion also appear. Furthermore, with the increase of evaporation temperature, the molecular ion peaks gradually disappear and the peaks of $YbL_3^{\bullet+}$ and $Cp_3Yb^{\bullet+}$ are enhanced (as shown in Figures 1 and 2). Moreover, the measurement

**Scheme III. The Major Fragmentation Pathways of $Cp_2Yb(bmphpz)$ (Path a) and $CpYb(bmphpz)_2$ (Path b) Compounds**



of metastable ions shows that $Cp_3Yb^{\bullet+}$ and $YbL_3^{\bullet+}$ have no relevant precursor ions, do not have any relation with the molecular ion cleavage of the samples, and, thus, must result from the disproportionation of hot neutrals in the ion source rather than from ion–molecular reactions of the molecular ions. The following disproportionation reaction may take place:

$$3CpYbL_2 \rightleftharpoons Cp_3Yb + 2YbL_3 \tag{1}$$

$$3Cp_2YbL \rightleftharpoons 2Cp_3Yb + YbL_3 \tag{2}$$

The experimental results indicate that the disproportionation temperature of most of $Cp_2YbL$-type compounds is higher than that of $CpYbL_2$-type compounds. Furthermore, the disproportionation temperature of the compounds containing N or S heteroatoms is higher than 150 °C, while that of the compounds containing no heteroatom is lower than 100 °C (see Table II). It can be seen that the disproportionation product $YbL_3^{\bullet+}$ of the $CpYbL_2$-type compounds is more intense than that of the relevant $Cp_2YbL$-type compounds. This is in good agreement with the disproportionation reactions (1) and (2): the amount of $YbL_3$ formed by the disproportionation of $Cp_2YbL$ is less than that of $YbL_3$ formed by the disproportionation of equimolar $CpYbL_2$. With another disproportionation product $Cp_3Yb$, the $Cp_3Yb^{\bullet+}$ ion peaks can be observed in the spectra of most compounds but are generally very weak. The $Cp_2Yb^+$ and $CpYb^+$ are also observed in the spectra, which are more intense than $Cp_3Yb^{\bullet+}$. This is consistent with the results reported in literature.[5]

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(5) Thomas, J. L. *J. Organomet. Chem.* **1970**, *23*, 487–489. Müller, J. *Chem. Ber.* **1969**, *102*, 152.

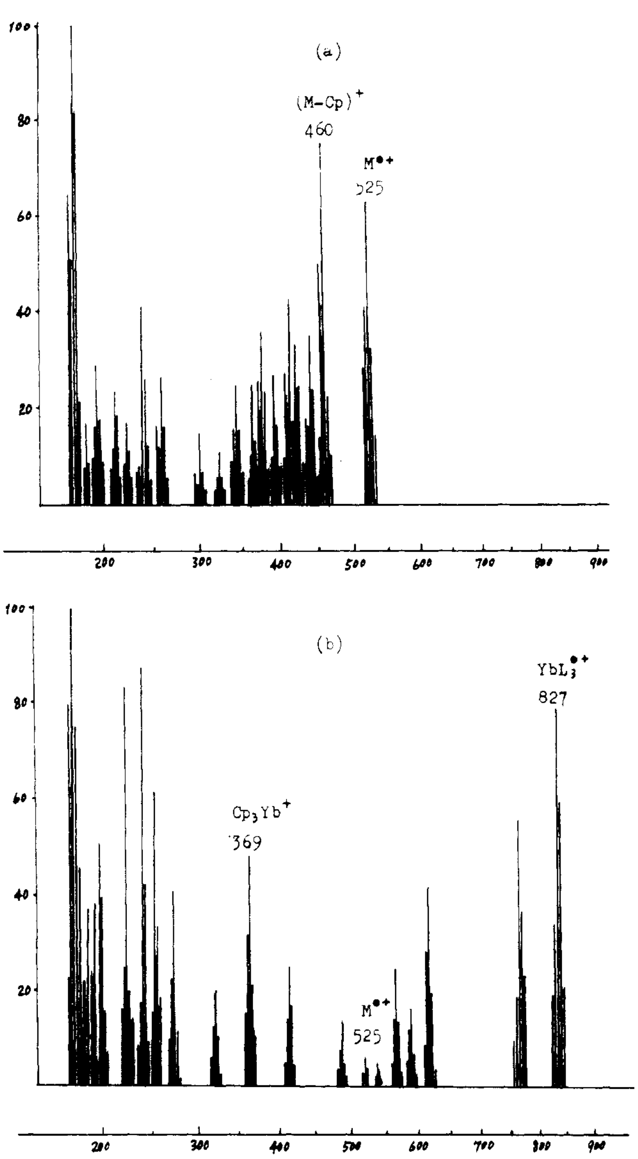


**Figure 1.** Mass spectra of $Cp_2Yb(tfacth)$: (a) evaporation temperature, 120 °C; (b) evaporation temperature, 180 °C.

**Table II. Disproportionation Temperature and Products for $Cp_2YbL$ and $CpYbL_2$[a]**

| compds | dispro-portnatn temp, °C | molecular ion, *m/z* (%) | disproportionatn products: $Cp_3Yb^{\bullet+}$ (369%) | disproportionatn products: $YbL_3^{\bullet+}$ *m/z* (%) |
|---|---|---|---|---|
| $Cp_2Yb(acac)$ | 65 | 403 (46.7) | (48.5) | 471 (39.2) |
| $CpYb(acac)_2$ | 60 | 437 (16.3) | (6.2) | 471 (78.4) |
| $Cp_2Yb(tmd)$ | 50–65 | 487 (27.7) | weak | 723 (44.4) |
| $CpYb(tmd)_2$ | 20–45 | 605 (11.0) | weak | 723 (100) |
| $Cp_2Yb(bzac)$ | 65–95 | 465 (90) | (46.1) | 657 (5) |
| $CpYb(bzac)_2$ | 100–110 | 561 (11.5) | (7.1) | 657 (100) |
| $Cp_2Yb(bmphpz)$ | 155–165 | 582 (32.0) | (8.4) | 1008 (38.2) |
| $CpYb(bmphpz)_2$ | 150–160 | 795 (0.5) | weak | 1008 (76.2) |
| $Cp_2Yb(tfacth)$ | 170 | 525 (78.6) | (8.2) | 837 (17.6) |
| $CpYb(tfacth)_2$ | 160 | 681 (5.6) | weak | 837 (62.7) |
| $Cp_2Yb(tfacac)$ | 200 | 457 (20.3) | weak | 633 (1.2) |
| $CpYb(tfacac)_2$ | 50–100 | 545 (1.4) | (14.2) | 633 (89.6) |

[a] MS data are based on the isotopes $^{174}Yb$, $^{32}S$, and $^{14}N$.

The metastable ion measurements of the disproportionation products $YbL_3^{\bullet+}$ of various compounds have been carried out. It is found that the β-diketonate ligand can directly be lost in $YbL_3^{\bullet+}$, whereas in $CpYbL_2^{\bullet+}$ and $Cp_2YbL^{\bullet+}$, no direct cleavage of β-diketonate ligand can be found. This is probably due to the stearic and induction effects caused by the existence and nature of the substituents R and R′ in the β-diketonate ligands in $YbL_3^{\bullet+}$, which reduces the bond energy of Yb–L, leading to easy cleavage of the Yb–L bond in $YbL_3^{\bullet+}$. The fragmentation pattern of various $YbL_3^{\bullet+}$ species is shown in Scheme IV. The $Cp_3Yb^{\bullet+}$ ion peaks are so weak in the spectra of most compounds that it is impossible to carry out the metastable ion measurement.

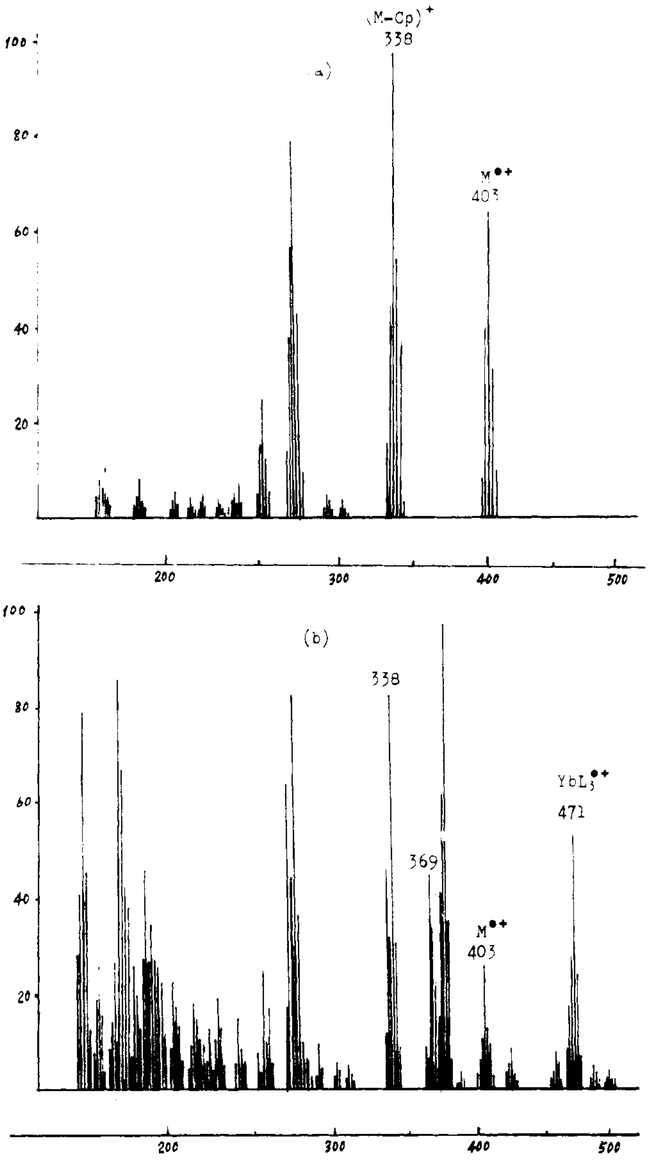
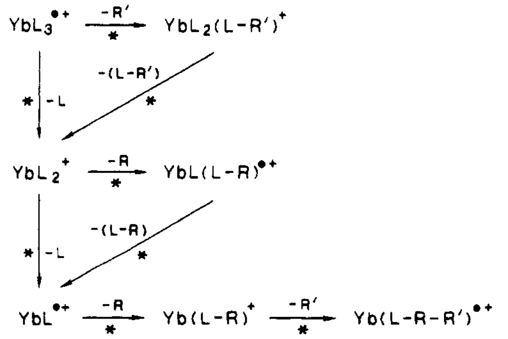


**Figure 2.** Mass spectra of $Cp_2Yb(acac)$: (a) evaporation temperature, 40 °C; (b) evaporation temperature, 200 °C.

**Scheme IV. The Major Fragmentation Pathways of $YbL_3$**



To sum up, molecular ions are clearly observed in the EI mass spectra of two types of compounds, $Cp_2YbL$ and

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$CpYbL_2$, and the former is more intense than the latter. The fragmentation of these molecular ions are characterized by their loss of the Cp ligand. The $\beta$-diketonato ligand, however, is difficult to fragment as a unit, and frequently the substituent R or R′ at either end cleaves first. The extent of cleavage depends on the properties of R or R′. Although the thermal stability of 12 $Cp_2YbL$- and $CpYbL_2$-type compounds are different, disproportionation reaction may take place, resulting in the creation of $Cp_3Yb$ and $YbL_3$, when these compounds reach a certain evaporation temperature. The disproportionation products $Cp_3Yb^{\bullet +}$ and $YbL_3^{\bullet +}$ have a fragmentation mechanism that is different from that of the corresponding molecular ions.

**Registry No.** **1**, 72105-01-2; **2**, 106043-08-7; **3**, 72105-02-3; **4**, 113753-81-4; **5**, 113753-76-7; **6**, 113753-94-9; **7**, 113753-97-2; **8**, 113753-82-5; **9**, 106018-28-4; **10**, 106018-29-5; **11**, 113753-95-0; **12**, 113753-96-1.

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# Carbonylation of ($\eta^5$-Indenyl)(CO)$_2$Fe–$\alpha$-Alkoxyalkyl Complexes Using Bimetallic $\alpha$-Alkoxyacyl Intermediates

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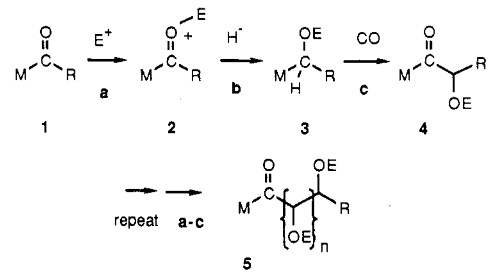
Treatment of alkoxymethyl complexes $In(CO)_2Fe–CH_2OR$ (In = $\eta^5$-indenyl; R = Me, Et) with the metalate $In(CO)_2Fe^-Na^+$ in THF solution affords bimetallic alkoxyacetyl intermediates $In(CO)Fe(\mu\text{-}CO)_2Fe(In)(COCH_2OR)^-Na^+$ (**13a,b**). IR spectra of these intermediates closely resemble the data for the fully characterized $In_2(CO)_3Fe_2(COCH_3)^-$ and $CpIn(CO)_3Fe_2(COCH_3)^-$ salts. Alkoxyacetyl dimers **13a,b** react with MeI and CO (1 atm) to give (3 h) the mononuclear alkoxyacetyl compounds $In(CO)_2Fe–COCH_2OR$ in 50–60% yields. The acetyl complex $In(CO)_2Fe–COCH_3$ upon activating ($Et_3O^+PF_6^-$) and reducing ($NaBH_4$) gives $In(CO)_2Fe–CH(OEt)CH_3$ (**12**). Subjecting **12** to the same two-step carbonylation procedure—treatment with $In(CO)_2Fe^-Na^+$ and then MeI/CO (1 atm)—produces $In(CO)_2Fe–COCH(OEt)CH_3$ (59% yield). This procedure thus is used in carbonylating $\alpha$-alkoxyalkyl complexes that otherwise are inert toward CO (100 atm). A mechanism involving reversible $\eta^5$–$\eta^3$ indenyl ring slippage during both formation and cleavage of bimetallic acyl complexes (e.g., **13**) is advanced.

## Introduction

Poly(alkoxymethylene) acyl ligands (**5**) that retain an oxygen functionality at each carbon center and derive from carbon monoxide are attractive synthetic objectives.[1-3] In one synthetic approach these transition organometallic acyl complexes result from repeating a three-step sequence of ligand reactions (eq 1): (a) electrophilic activation of an acyl ligand, (b) hydride transfer to its oxycarbenoid derivative **2**, and (c) carbonylation of the resulting alkoxyalkyl group on **3**. Selecting the organometallic template for supporting these ligand construction reactions, however, is complicated by their antithetical requirements. The first two ligand reactions a and b, resulting in net reduction of the acyl ligand, require a coordinatively saturated, nonlabile metal center in order to contain the chemistry at the acyl ligand.[4] The carbonylation reaction, in contrast, requires a relatively labile metal center for the alkyl-CO migratory-insertion step.[5] We recently demonstrated that using the (dppe)(CO)$_2$Co system as the organometallic template balances these contradictory requirements.[6,7]



(1)

Cp(CO)$_2$Fe or Fp complexes and their phosphine- or phosphite-substituted derivatives Cp(CO)(L)Fe are desirable systems for supporting the ligand reactions depicted in eq 1.[2,8] The corresponding acyl ligand reduction steps

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(1) Reviews concerned with the stoichiometric reduction of ligated CO: (a) Keim, W. In *Catalysis in $C_1$ Chemistry*; Keim, W., Ed.; D. Reidel Publishing Co.: Boston, 1983; Chapter 1. (b) Herrmann, W. A. *Angew Chem., Int. Ed. Engl.* **1982**, *21*, 117. (c) Sneedon, R. P. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1982; Chapter 502. (d) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1.

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(7) In related studies, Stimson and Shriver obtained $C_1$–$C_4$ alkenes by reacting $(CO)_5Mn–CH_3$ with CO plus diborane. Chain growth apparently entails $BH_3$ reduction of an acyl to its homologus saturated alkyl ligand, which then inserts CO. Stimson, R. E.; Shriver, D. F. *Organometallics* **1982**, *1*, 787. Brown, S. L.; Davies, S. G. *J. Chem. Soc., Chem. Commun.* **1986**, 84.

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