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SYNTHESIS AND DISPROPORTIONATION OF MIXED LIGAND YTTERBIUM ORGANOMETALLICS INVOLVING CYCLOPENTADIENYL AND β-DIKETONATO CHELATE LIGANDS *

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Summary

Twelve compounds either of type $Cp_2Yb(diket)$ or $CpYb(diket)_2$ ($Cp = \eta^5$-C_5H_5, diket = β-diketonato) have been synthesized. Compounds of the former type are much more thermally stable than those of the latter. But, all twelve compounds tend to disproportionate into Cp_3Yb and $Yb(diket)_3$ at moderately high temperatures.

Introduction

Up to now only two lanthanoid organometallics involving both Cp (η^5-C_5H_5) and diket (β-diketonato) chelate ligands have been prepared (by Bielang and Fischer) [1], namely, $Cp_2Yb(acac)$ and $Cp_2Yb(tmd)$ (where Hacac = acetylacetone, Htmd = 2,2,6,6-tetramethyl-3,5-heptanedione). They reported that both compounds did not sublime in vacuo and that the mass spectra of both compounds displayed essentially the signals of the $Yb(diket)_n^+$ (with $n = 1$–3) fragments (and signals of fragments thereof), but not of fragments carrying a Cp-ligand. However, the vibrational spectra of both compounds are fairly indicative of residual π-bonded Cp-ligands. We presume that these two compounds are not stable to heat, and disproportionation owing to rearrangement of ligands would probably take place at a moderately high temperature.

Results and discussion

For the purpose of studying the thermal stability of lanthanoid organometallics of this class, and adopting the very versatile method of liberating cyclopentadiene

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from a Cp_nYb moiety by the action of protonic acids stronger than C_5H_6, we have synthesized twelve compounds by the reaction of Cp_3Yb with acetylacetone (H-acac), 2,2,6,6-tetramethyl-3,5-heptanedione (H-tmd), 1,1,1-trifluoroacetylacetone (H-tfacac), benzoylacetone (H-bzac), trifluoroacetoacetyl-α-thiophene (H-tfacth) and 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone (H-bmphpz).

They are:

1 : 1 ratio of reactants		1 : 2 ratio of reactants	
$Cp_2Yb(acac)$	(I)	$CpYb(acac)_2$	(II)
$Cp_2Yb(tmd)$	(III)	$CpYb(tmd)_2$	(IV)
$Cp_2Yb(tfacac)$	(V)	$CpYb(tfacac)_2$	(VI)
$Cp_2Yb(bzac)$	(VII)	$CpYb(bzac)_2$	(VIII)
$Cp_2Yb(tfacth)$	(IX)	$CpYb(tfacth)_2$	(X)
$Cp_2Yb(bmphpz)$	(XI)	$CpYb(bmphpz)_2$	(XII)

(I) and (III) are known compounds, but the others are new.

All compounds were identified by elemental analysis, IR (Table 1) and MS (Table 2) spectroscopy.

All twelve compounds exhibit four characteristic Cp absorption at about 780, 1010, 1440, 3100 cm^{-1} and an absorption peak at about 250 cm^{-1} for Ln–C of the π-bonded Cp group [2]. All of them exhibit the characteristic $C\overset{\dots}{=}O$ and $C\overset{\dots}{=}C$ multiple absorption bands of O-chelate complexes [3].

The twelve compounds can be classified into two types: $CpYb(diket)_2$ and $Cp_2Yb(diket)$. The mass spectra of all the compounds were recorded at different temperatures of vaporization. Contrary to earlier observations [4], that no peak which can be assigned to diytterbium species is displayed in the mass spectra of $Cp_2Yb(acac)$(I) (or any other compounds), our mass spectra of $Cp_2Yb(diket)$ displayed signals of $Cp_2Yb(diket)^+$ and of fragments thereof even when the temperature was raised to 180 °C. However, at much higher temperatures of 200–350 °C, signals of both Cp_3Yb^+ and $Yb(diket)_3^+$ appeared. In contrast, the mass spectra of $CpYb(diket)_2$ at 50–180 °C displayed signals of $Yb(diket)_3{}^+$ and $Cp_2Yb(diket)^+$ in addition to $CpYb(diket)_2{}^+$. As the temperature was raised to between 200–300 °C, the mass spectra showed signals of Cp_3Yb^+ in addition to $CpYb(diket)_2{}^+$, $Cp_2Yb(diket)^+$ and $Yb(diket)_3{}^+$. Heat can bring about the disproportionation of these two types of compounds, however, $CpYb(diket)_2$ is thermally less stable than $Cp_2Yb(diket)$. In view of the MS data, the disproportionation presumably involves the following equilibria:

$$2CpYb(diket)_2 \rightleftharpoons Cp_2Yb(diket) + Yb(diket)_3$$

$$3Cp_2Yb(diket) \rightleftharpoons 2Cp_3Yb + Yb(diket)_3$$

We attempted to verify the above disproportionation reactions spectrophotometrically. Only one product, of composition Cp_3Yb, was confirmed, but the mixtures of disproportionation products could not be fully characterized. Each of the twelve compounds was heated at 250–300 °C in a capillary tube filled with argon for 4 hours, then cooled down, and dissolved in THF. Several peaks of the absorption spectrum of this THF solution appeared at the same wavelengths as those of the THF solution of pure Cp_3Yb [5]. But, no characteristic peaks of $Cp_2Yb(diket)$, $CpYb(diket)_2$ or $Yb(diket)_3$ in THF solution were found in the UV/VIS spectrum.

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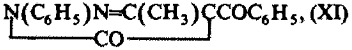
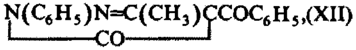
TABLE 1

ANALYTICAL AND PART OF IR DATA [a] FOR THE COMPOUNDS I–XII

Compounds $(C_5H_5)_nYb(diket)_{3-n}$	Yield (%)	M.P. (°C) [b] (d = decomp.)	Colour	Analysis [c] (Found (calcd.)(%))				IR (cm^{-1}) 1500–1600 cm^{-1}
				Yb	C	H	N	
diket = $CH_3COCHCOCH_3$, (I)	40	60–62	orange	43.36	44.15	4.01		
$n = 2$				(43.03)	(44.78)	(4.23)		
diket = $CH_3COCHCOCH_3$, (II)	57	134	orange	39.95	40.79	4.03		
$n = 1$				(39.68)	(41.28)	(4.36)		
diket = $(CH_3)_3CCOCHCOC(CH_3)_3$, (III)	68	87	yellow	35.82	51.15	6.00		1547, 1581, 1595
$n = 2$				(35.60)	(51.85)	(5.97)		
diket = $(CH_3)_3CCOCHCOC(CH_3)_3$, (IV)	66	109.5	pale yellow	28.91	53.35	6.66		1551, 1581, 1594
$n = 1$				(28.64)	(53.64)	(7.12)		
diket = $CH_3COCHCOCF_3$, (V)	35	88–90	orange	38.30	39.01	2.88		
$n = 2$				(37.94)	(39.47)	(3.07)		
diket = $CH_3COCHCOCF_3$ (VI)	68	185(d)	orange	31.78	32.48	2.37		
$n = 1$				(31.80)	(33.09)	(2.39)		
diket = $C_6H_5COCHCOCH_3$, (VII)	58	101.5	yellow	37.65	50.94	4.29		1513, 1566, 1598
$n = 2$				(37.28)	(51.72)	(4.09)		
diket = $C_6H_5COCHCOCH_3$, (VIII)	60	129–130	yellow	31.04	53.54	4.16		1511, 1567, 1597
$n = 1$				(30.89)	(53.57)	(4.11)		
diket =  $\underbrace{\mathrm{CH{=}CHCH{=}C}}_{\mathrm{S}}\mathrm{COCHCOCF_3}$, (IX)	60	160(d)	yellow	33.52	40.84	2.60		1510, 1537, 1595
$n = 2$				(33.01)	(41.23)	(2.69)		
diket =  $\underbrace{\mathrm{CH{=}CHCH{=}C}}_{\mathrm{S}}\mathrm{COCHCOCF_3}$, (X)	50	163.5(d)	yellow	26.04	36.65	1.74		1518, 1538, 1592
$n = 1$				(25.52)	(37.08)	(1.92)		
diket =  $\underbrace{\mathrm{N(C_6H_5)N{=}C(CH_3)C}}_{\mathrm{CO}}\mathrm{COC_6H_5}$, (XI)	52	190(d)	yellow	29.94	56.62	3.93	4.67	1529, 1573, 1585
$n = 2$				(29.82)	(55.86)	(3.99)	(4.82)	
diket =  $\underbrace{\mathrm{N(C_6H_5)N{=}C(CH_3)C}}_{\mathrm{CO}}\mathrm{COC_6H_5}$,(XII)	60	215(d)	gray yellow	22.09	58.37	3.71	6.64	1512, 1571, 1593
$n = 1$				(21.84)	(59.09)	(3.94)	(6.76)	

[a] IR were recorded on a Perkin–Elmer 983(G) (CsI crystal plate, Nujol and Fluorolube mulls) instrument. [b] Melting points were determined in sealed argon-filled capillaries and were uncorrected. [c] Elemental analysis results were obtained on a Yanaco MT-2 analyzer. The elemental analysis data for Yb were obtained by a published method [2].

TABLE 2

MS DATA[a] FOR COMPOUNDS I–XII AT DIFFERENT TEMPERATURES OF VAPORIZATION

Compounds $Cp_nYb(diket)_{3-n}$ ($Cp = C_5H_5$) and mol. species	Temp. of vaporization (°C)	Main peaks, m/e [b]
(I) $n = 2$, diket = $CH_3COCHCOCH_3$.	50, 100, 170	403(M); 338($M-$Cp); 273($M-$2Cp); 239($M-$Cp$-$diket); 174(Yb).
M = Cp_2Yb(diket), M' = Yb(diket)$_3$, M'' = Cp_3Yb.	200, 250, 280	471(M'); 403(M); 369(M''); 338($M-$Cp); 273($M-$2Cp); 239($M-$Cp$-$diket); 174(Yb).
(II) $n = 1$, diket = $CH_3COCHCOCH_3$.	50, 100, 170	471(M'); 437(M); 403(M'''); 174(Yb).
M = CpYb(diket)$_2$, M' = Yb(diket)$_3$, M'' = Cp_3Yb, M''' = Cp_2Yb(diket).	200, 280, 320	471(M'); 437(M); 403(M'''); 369(M''); 174(Yb).
(III) $n = 2$, diket = $(CH_3)_3CCOCHCOC(CH_3)_3$.	50, 90, 180	487(M); 422 ($M-$Cp); 357($M-$2Cp); 239($M-$Cp$-$diket).
M = Cp_2Yb(diket), M' = Yb(diket)$_3$, M'' = Cp_3Yb.	200, 250, 320	723(M'); 487(M); 422($M-$Cp); 369(M''); 357($M-$2Cp); 239($M-$Cp-diket); 174(Yb).
(IV) $n = 1$, diket = $(CH_3)_3CCOCHCOC(CH_3)_3$,	50, 100, 170	723(M'); 605(M); 540($M-$Cp); 487(M'''); 422($M-$diket); 357($M-$Cp$-$diket).
M = CpYb(diket)$_2$, M' = Yb(diket)$_3$, M'' = Cp_3Yb, M''' = Cp_2Yb(diket).	200, 240, 310	723(M'); 605(M); 540($M-$Cp); 487(M'''); 422($M-$diket); 369(M''); 357($M-$Cp$-$diket); 174(Yb).
(V) $n = 2$, diket = $CH_3COCHCOCF_3$.	100, 130, 180	457(M); 392($M-$Cp); 327($M-$2Cp); 239($M-$Cp$-$diket); 174(Yb).
M = Cp_2Yb(diket), M' = Yb(diket)$_3$, M'' = Cp_3Yb.	210, 270, 320	633(M'); 457(M); 392($M-$Cp); 369(M''); 327($M-$2Cp); 239($M-$Cp$-$diket); 174(Yb).
(VI) $n = 1$, diket = $CH_3COCHCOCF_3$. M = CpYb(diket)$_2$,	80, 140, 170	633(M'); 545(M); 457(M'''); 480($M-$Cp); 392($M-$diket); 327($M-$Cp$-$diket); 174(Yb).
M' = Yb(diket)$_3$, M'' = Cp_3Yb, M''' = Cp_2Yb(diket).	210, 260, 320	633(M'); 545(M); 457(M'''); 480($M-$Cp); 392($M-$diket); 369(M''); 327($M-$Cp$-$diket); 174(Yb).

(VII)	$n = 2$, diket = $\mathrm{C_6H_5COCHCOCH_3}$.	145, 180	465(M); 400 ($M - \mathrm{Cp}$); 304($M -$ diket); 239($M - \mathrm{Cp} -$ diket); 174(Yb).
	$M = \mathrm{Cp_2Yb(diket)}$, $M' = \mathrm{Yb(diket)_3}$, $M'' = \mathrm{Cp_3Yb}$.	220, 270, 320	657(M'); 465(M); 400($M - \mathrm{Cp}$); 369(M''); 335($M - 2\mathrm{Cp}$); 239($M - \mathrm{Cp} -$ diket); 174(Yb).
(VIII)	$n = 1$, diket = $\mathrm{C_6H_5COCHCOCH_3}$.	120, 180	657(M'), 561(M); 496($M - \mathrm{Cp}$); 465(M'''); 400($M -$ diket); 335($M - \mathrm{Cp} -$ diket); 174(Yb).
	$M = \mathrm{CpYb(diket)_2}$, $M' = \mathrm{Yb(diket)_3}$, $M'' = \mathrm{Cp_3Yb}$, $M''' = \mathrm{Cp_2Yb(diket)}$.	210, 280, 320	657(M'); 561(M); 465(M'''); 400($M -$ diket); 369(M''); 174(Yb).
(IX)	$n = 2$, diket = $\underbrace{\mathrm{CH{=}CHCH{=}C}}_{\mathrm{S}}\mathrm{COCHCOCF_3}$.	120, 170	525(M); 460($M - \mathrm{Cp}$); 304($M -$ diket); 239($M - \mathrm{Cp} -$ diket); 174(Yb).
	$M = \mathrm{Cp_2Yb(diket)}$, $M' = \mathrm{Yb(diket)_3}$ $M'' = \mathrm{Cp_3Yb}$	200, 285, 320	837(M'); 525(M); 369(M''); 304($M -$ diket); 239($M - \mathrm{Cp} -$ diket); 174(Yb).
(X)	$n = 1$, diket = $\underbrace{\mathrm{CH{=}CHCH{=}C}}_{\mathrm{S}}\mathrm{COCHCOCF_3}$	120, 180	837(M'); 681(M); 616($M - \mathrm{Cp}$); 525(M'''); 460($M -$ diket); 395($M - \mathrm{Cp} -$ diket); 369(M''); 174(Yb).
	$M = \mathrm{CpYb(diket)_2}$, $M' = \mathrm{Yb(diket)_3}$, $M'' = \mathrm{Cp_3Yb}$, $M''' = \mathrm{Cp_2Yb(diket)}$.	210, 280, 330	837(M'); 681(M); 616($M - \mathrm{Cp}$); 525(M'''); 460($M -$ diket); 395($M - \mathrm{Cp} -$ diket); 369(M''); 174(Yb.
(XI)	$n = 2$, diket = $\underbrace{\mathrm{N(C_6H_5)N{:}C(CH_3)C}}_{\mathrm{CO}}\mathrm{COC_6H_5}$	100, 150, 180	581(M); 516($M - \mathrm{Cp}$); 451($M - 2\mathrm{Cp}$); 239($M - \mathrm{Cp} -$ diket); 174(Yb).
	$M = \mathrm{Cp_2Yb(diket)}$, $M' = \mathrm{Yb(diket)_3}$, $M'' = \mathrm{Cp_3Yb}$	200, 280, 350	1005(M'); 581(M); 516($M - \mathrm{Cp}$); 451($M - 2\mathrm{Cp}$); 369(M'''): 239($M - \mathrm{Cp} -$ diket); 174(Yb).
(XII)	$n = 1$, diket = $\underbrace{\mathrm{N(C_6H_5)N{:}C(CH_3)C}}_{\mathrm{CO}}\mathrm{COC_6H_5}$	100, 150, 180	1005(M'); 793(M); 728($M - \mathrm{Cp}$); 663($M - 2\mathrm{Cp}$); 581(M'''); 451($M - \mathrm{Cp} -$ diket); 174(Yb).
	$M = \mathrm{CpYb(diket)}$, $M' = \mathrm{Yb(diket)_3}$, $M'' = \mathrm{Cp_3Yb}$, $M''' = \mathrm{Cp_2Yb(diket)}$.	200, 280, 340	1005(M'); 793(M); 728($M - \mathrm{Cp}$); 663($M - 2\mathrm{Cp}$); 581(M'''); 451($M - \mathrm{Cp} -$ diket); 369(M'').

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[a] MS spectra were recorded on a Finnigan MAT-312 mass spectrometer. [b] MS data are given for the isotopes $^{174}\mathrm{Yb}$, $^{32}\mathrm{S}$ and $^{14}\mathrm{N}$, the peak patterns correspond to theoretical values based on the natural abundance of isotopes.

Bagnall [6] pointed out that the β-diketonato ligand in actinoid complexes and that the η^5-Cp ligand in both lanthanoid and actinoid complexes are quite labile. So, it may be assumed that the lability of ligands is the cause of the disproportionation reactions. It is also possible that the disproportionation reaction takes place via an intermediate bimolecular complex in which the Cp groups are bonded in an η^5-fashion to one molecule, and in an η^1 fashion to the second molecule of the complex. The transfer of one Cp ligand from one molecule to another is probably more facile than the transfer of two ligands at the same time. So, this may be the reason why $CpYb(diket)_2$ is thermally less stable than $Cp_2Yb(diket)$.

Experimental

All operations were performed under prepurified argon using Schlenk techniques or in a glovebox. All solvents were refluxed and distilled over $LiAlH_4$ or sodium benzophenone under argon immediately before use. The liquid β-diketones were dried over anhydrous Na_2SO_4 and distilled under argon. The solid β-diketones were dried in vacuo for 4 h.

Cp_3Yb [7] was prepared by a published procedure.

General method of the synthesis of $Cp_2Yb(diket)$ or $CpYb(diket)_2$

To a suspension of Cp_3Yb (1 equiv.) in n-hexane was added the β-diketone (1 or 2 equiv.). The reaction suspension gradually turned from green to yellow under stirring at room temperature. After stirring for 20 h, the n-hexane was removed in vacuo and the resulting solid was recrystallized from THF/n-hexane (twice) to afford $Cp_2Yb(diket)$ or $CpYb(diket)_2$.

Yields, analyses and physical properties of all 12 compounds are listed in Table 1.

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