Inorganica Chimica Acta, 36 (1979) L389–L390
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Mixed-Ligand Lanthanide Organometallics involving Cyclopentadienyl- and Classical Chelate Ligands

GUDRUN BIELANG and R. DIETER FISCHER*

Institute of Inorganic and Applied Chemistry, University of Hamburg, Martin-Luther-King-Platz 6, D-2000 Hamburg 13, F.R.G.

Received May 4, 1979

The chemistry of purely organometallic complexes of the lanthanide elements such as Cp$_3$Ln^{III} (Cp = η^5-C$_5$H$_5$) [1] as well as of tris(β-diketonato)chelate complexes (diket)$_3$Ln^{III} [2] is fairly well understood while, surprisingly, mixed systems involving both Cp- and typical chelate ligands 'chel' are still unknown [3]. Adopting the very versatile method of liberating cyclopentadiene from a Cp$_n$Ln moiety by the attack of protonic acids stronger than C$_5$H$_6$ [4], we have reacted acetylacetone (H-acac) and 2,2,6,6-tetramethyl-3,5-heptanedione (H-tmd) as well as the unsaturated β-aminoketone, 4-anilino-3-pentene-2-one, (H-apo) [5, 6] with Cp$_3$Yb and Cp$_2$YbCl, respectively (1:1).

While quick colour changes from green and red, to orange, yellow or brown indicate in all cases a prompt reaction of the Yb-organyl with the acid, the two β-diketones give rise to badly tractable, non-sublimable products devoid of distinct melting points. Thus, the orange product *1* of formal composition Cp$_2$Yb(acac) matches poorly with the known monomeric Cp$_2$M(acac) systems of Ti (m.p. with dec.: 71 °C, subl. temp.: 100 °C [7]) and Sc (m.p. 75 °C, subl. temp.: 110 °C [8]), respectively, in that it decomposes without melting above 115 °C and does not sublime *in vacuo*. The product 'Cp$_2$Yb(tmd)' *2* is well soluble in toluene and melts, also with decomposition, above 80 °C. The mass spectra of both *1* and *2* display essentially signals of the fragments Yb(diket)$_n^+$ with n = 1–3 (and of fragments thereof), but of no fragment carrying a Cp-ligand. However, the vibrational spectra of *1* and *2* are fairly indicative of residual η^5-bonded Cp-ligands. The pmr spectrum of *2* (toluene-d$_8$ solution, 300 to 190 K) is more complex than the simple three-line pattern (18:10:1) to be expected for mononuclear Cp$_2$Yb(tmd).

Unlike the β-diketones, the unsaturated β-aminoketone H-apo yields in a clean reaction with Cp$_3$Yb the well-defined complex Cp$_2$Yb(apo) *3*, and with Cp$_2$YbCl the probably oligomeric system CpYb(apo)Cl *4*. The yellow compound *3* which melts at 104 °C and sublimes *in vacuo* above 120 °C (in both cases with simultaneous decomposition) can be purified by extraction with n-pentane and was identified by elemental analysis and mass spectrometry. For *e.g.* the isotope ^{174}Yb, the mass spectrum displays six peaks at M$^+$/e = 478 (*ca.* 30%, M–H), 413 (≡100%, M–Cp–H), 348 (49%, M–2Cp–H), 330 (*ca.* 7%), 304 (*ca.* 4%, Cp$_2$Yb), and 239 (*ca.* 7%, CpYb). The pmr spectrum (toluene-d$_8$) of the paramagnetic complex exhibits between 300 and 190 K six widely spaced resonances of strongly temperature-dependent positions. By virtue of an approximate intensity ratio of 3:3:10, the two different methyl groups and the ten equivalent Cp-ring protons can be assigned to (300 K) signals at δ = 11.9, −11.3 and −33.9 (Cp) ppm, respectively. By reaction with one mol of H-apo, *3* can be converted into the yellow product CpYb(apo)$_2$ *5* (m.p.: 84 °C).

The red-brown compound *4* is non-volatile, somewhat soluble only in THF, and decomposes around 92 °C by simulating a melting process. Its identification is based on the elemental analysis and is further supported by the infrared spectrum which is almost identical with the spectra of *3* and *5*. Characteristic differences between the bis- and monocyclopentadienyl systems are, however, found in the near infrared electronic (f–f ligand field) spectra in that the number of absorptions between 950 and 1.100 nm decreases markedly with the expected Cp:Yb ratio. The reaction of Cp$_2$YbCl with H-acac and H-tmd, respectively, leads to products containing likewise Cp, apo and Cl, but in neither case could a satisfactory means of purification be found.

Although our present results indicate some superiority of the β-ketimino ligand apo over conventional β-diketonato systems as far as the stabilization of a singular complex species** is concerned, all further speculations on the actual structure, *e.g.* of Cp$_2$Yb(apo), might be premature. Further studies, involving also the more voluminous Ln^{3+} systems Sm^{3+}, Nd^{3+} and Pr^{3+}, arepresently in progress.

Experimental

All preparations and manipulations were carried out under dry and oxygen-free nitrogen. Solvents were dried with sodium and triethylaluminium. The compound H-apo was prepared as formerly described [5, 6]. All reactions were conducted at room temperature by the slow addition of a solution of the acid to a suspension of an equimolar quantity

---

*Author to whom correspondence should be addressed.

**According to some preliminary results, variable temperature studies suggest a decrease of configurational stability if the N-phenyl group is replaced by the n-butyl group.

of the Yb-organyl in either toluene or pentane. With the exception of the acid H-tmd, the green colour of Cp_3Yb disappeared after less than five minutes. Stirring of the reaction mixtures was continued for *ca.* 12 h. After removal of the solution, the solid residue was washed with cold pentane and finally dried *in vacuo.* Monomeric cyclopentadiene was found by g.c. in the reaction media.

$Cp_2Yb(acac)$, 1

Reaction in n-pentane, yield: 58.0%. Found: C, 44.91; H, 5.21; O, 8.50; Yb, 38.31%; $C_{15}H_{17}O_2Yb$ requires C, 44.78; H, 4.26; O, 7.95; Yb, 43.01%. Electronic f–f transitions (n-pentane solution) at 10.018, 10.126, 10.199, 10.224, 10.381, 10.582, 10.669, 10.751, 10.896, 11.185 and 11.481 cm^{-1}.

$Cp_2Yb(tmd)$, 2

Reaction in n-pentane with complete colour change after *ca.* 0.5 h, yield: 86.7%. Found: C, 51.66; H, 7.67%; $C_{21}H_{29}O_2Yb$ requires C, 51.84; H, 6.01%. Principal pmr signal at $\delta = -1.08$ (half width: 8.8 Hz, 300 K) and $\delta = -9.28$ (200 Hz, 190 K), respectively.

$Cp_2Yb(apo)$, 3

Reaction in toluene, yield: 74.4%. Found: C, 50.94; H, 4.93; N, 2.67; Yb, 34.60%; $C_{21}H_{22}ONYb$ requires C, 52.72; H, 4.84; N, 2.93; Yb, 36.17%. Electronic f–f transitions (in toluene) at 10.030, 10.138, 10.230, 10.569, 10.757, 10.889, 11.017 and 11.504 cm^{-1}.

$CpYb(apo)Cl$, 4

Reaction in toluene, yield: 65.9%. Found: C, 40.43; H, 4.23; N, 2.92; Cl, 10.37; Yb, 37.03%; $C_{16}H_{18}ONClYb$ requires C, 42.91; H, 3.83; N, 3.13; Cl, 7.92; Yb, 38.64%. Electronic f–f transitions (in THF) at 10.132 and 10.242 cm^{-1}. Very similar f–f spectra result for other CpYb(chel)Cl-systems.

$CpYb(apo)_2$, 5

Reaction in toluene, yield: 68.0%. Found: C, 56.67; H, 5.68; N, 4.41%; $C_{27}H_{29}N_2O_2Yb$ requires C, 55.29; H, 4.98; N, 4.78%.

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft (Bad Godesberg) and the Fonds der Chemischen Industrie (Frankfurt/M.) for financial support.

References

1 T. J. Marks, *Progr. Inorg. Chem., 23,* 51 (1978), and further literature cited therein.

2 (a) Th. Moeller, MTP International Review of Science, Inorganic Chemistry, Series One, Vol. 7, H. J. Emeléus and K. W. Bagnall, Eds., University Park Press, Baltimore, 1971, p. 275;
(b) R. C. Mehrotra, R. Bohra and D. P. Gaur, 'Metal β-Diketonates and Allied Derivatives', Academic Press, London, New York and San Francisco, 1978.

3 Carboxylate anions as typical 'small-bite' chelate ligands give rise to μ-carboxylato dimers, *cf.* R. E. Maginn, S. Manastyrskyj and M. Dubeck, *J. Am. Chem. Soc. 82,* 672 (1963).

4 B. Kanellakopulos, E. Dornberger and H. Billich, *J. Organomet. Chem., 76,* C42 (1974); E. Dornberger, R. Klenze and B. Kanellakopulos, *Inorg. Nucl. Chem. Letters, 14,* 319 (1978).

5 M. A. Combes, *Bull. Soc. Chim. France* [2], *49,* 89 (1888).

6 H. F. Holtzclaw, Jr., J. P. Collman and R. M. Alire, *J. Am. Chem. Soc. 80,* 1100 (1958).

7 R. S. P. Coutts and P. C. Wailes, *J. Organomet. Chem., 25,* 117 (1970).

8 R. S. P. Coutts and P. C. Wailes, *Austr. J. Chem., 22,* 1547 (1969).