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Preliminary communication

SYNTHESIS OF MIXED SANDWICH COMPLEXES OF THE LANTHANIDES, $(h^8\text{-}C_8H_8)Ln(h^5\text{-}C_5H_5)$

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Summary

The synthesis of $(h^8\text{-}C_8H_8)Ln(h^5\text{-}C_5H_5)$ is reported for Ln = Y, Nd, Sm, Ho, Er; IR evidence indicates electrostatic interaction between the lanthanide metal and the organic ligands; the Lewis acidity of the above complexes was ascertained by the isolation of $(C_8H_8)Ho(C_5H_5)L$, where L = NH_3, pyridine, THF, CNC_6H_{11}.

The organometallic chemistry of the lanthanides and actinides is receiving a renewed and active interest [1]. However, to date, there are no reports of mixed sandwich complexes for these metals. Here we wish to communicate our successful synthesis of lanthanide complexes containing both cyclopentadienyl and cyclooctatetraenyl groups, i.e. compounds of the type $(h^8\text{-}C_8H_8)Ln(h^5\text{-}C_5H_5)$ [$(h^5\text{-}C_5H_5)Ti(h^8\text{-}C_8H_8)$ [2] is the only other complex where both the C_5H_5 and C_8H_8 rings coexist]. The complexes were synthesized from known starting materials [3, 4], with the exception of yttrium*, as shown by equation (1) which also indicates that the choice of starting material is dictated by the particular lanthanide metals.

$$\left.\begin{array}{l}(C_5H_5)LnCl_2\cdot 3THF \xrightarrow[THF]{K_2C_8H_8}\\ \quad Ln = Y, Sm, Ho, Er\\ [(C_8H_8)LnCl\cdot 2THF]_2 \xrightarrow[THF]{NaC_5H_5}\\ \quad Ln = Y, Nd\end{array}\right] \longrightarrow (C_8H_8)Ln(C_5H_5)\cdot THF \qquad (1)$$

The complexes are exceedingly air sensitive, inflamming in contact with air, and, although isolated as a THF adduct, can be liberated from the coordinated THF molecule rather easily by vacuum drying, 10^{-3} mmHg at 50° C. We have

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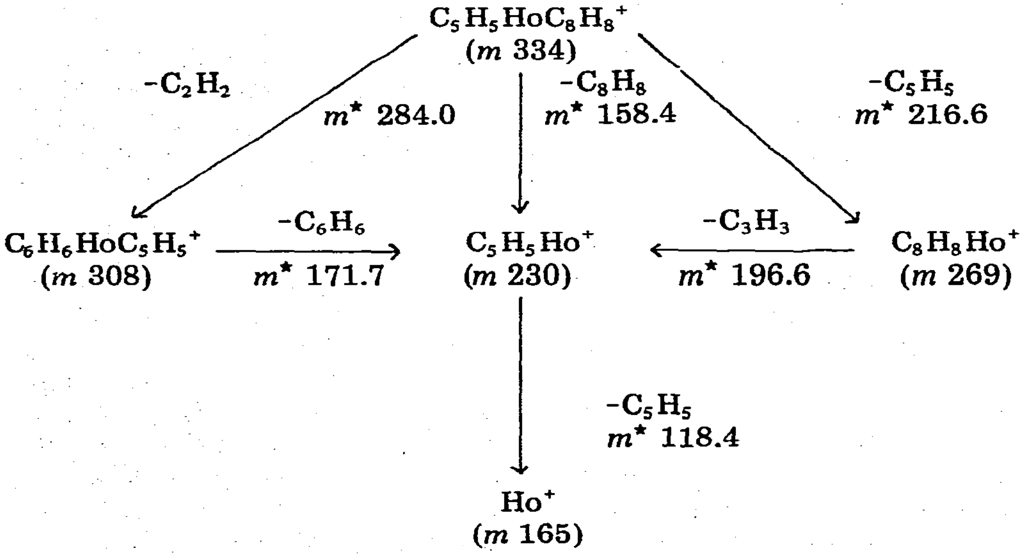
*This is the first reported preparation of $(h^5\text{-}C_5H_5)YCl_2$ and $(h^8\text{-}C_8H_8)YCl$. The Y complex can be conveniently purified by vacuum sublimation (10^{-3} mmHg and 100° C).

ascertained the constitution of the complexes by classical spectroscopic methods and by mass spectrometry.

The mass spectra of the complexes proved to be invaluable. The observation of a parent ion peak, $C_{13}H_{13}Ln^+$, for all the complexes provided unequivocal evidence for their formation and gave exact numbers for their molecular weights. In addition, however, it allowed an easy identification of $(C_5H_5)_3Ln$, a sometimes troublesome by-product, and hence served as a very useful indirect measure of purity. The extreme air sensitivity of these complexes makes the carrying out of elemental analysis time consuming and difficult, therefore an independent assessment of the purity of the complexes is indeed very important. Finally the fragmentation pattern, Scheme 1, by virtue of the presence of almost equal amounts of the ions, $C_5H_5Ln^+$ and $C_8H_8Ln^+$ *, indicates similar stability for them and presumably similar bonding between the central lanthanide metal and the organic ligands (see IR evidence below). The ^{1}H NMR spectrum of the yttrium complex showed the expected two sharp resonances in the ratio 8/5**. Unfortunately, we have not been able to record reliable spectra for the other complexes presumably due to a combination of low solubility and paramagnetism of the compounds. The infrared spectra for the complexes are very close to what would be expected for symmetrically bonded h^8-C_8H_8 and h^5-C_5H_5 ligands [5]. The presence of extra bands is likely the result of a solid state structure more complicated than well separated monomeric units. The

Scheme 1



Scheme 1. Partial Fragmentation Scheme of $C_5H_5HoC_8H_8$. The mass spectra were recorded on an AEI MS-12 at 70 eV. m^* = Metastable peaks as calculated and observed.

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[*] It is to be noted that for the titanium complex [2] no fragment corresponding to $C_8H_8Ti^+$ was observed.

[**] $(h^8$-$C_8H_8)Y(h^5$-$C_5H_5)$, in pyridine-d_5, chemical shifts in ppm upfield from internal benzene: 1.09 (singlet, 8), 1.76 (singlet, 5).

reasonableness of this assumption comes from the structure of $(h^5\text{-}C_5H_5)_3Sm$ [6]. X-ray crystallography established a crystal structure consisting of closed-packed infinite chains [6], with bridging cyclopentadienyl groups. Even with the above reservation, the main bands in the IR can be confidently assigned [5] as indicated in Table 1. These IR spectral data, based on previous observations [5], can be advantageously utilized to obtain hints about the nature of the bond between the cyclic ligands and the central lanthanide. The absence of a bond around ~1100 cm^{-1} [$(A_1(C_{5v})\gamma(\text{CH})$], the high position of the asymmetric ring breathing modes [$(E(C_{5v}), E_1\ (C_{8v})\ \omega(\text{C-C})$] and the low frequency of the out-of-plane C—H deformations [$(E(C_{5v}), E_1\ (C_{8v})\ \gamma(\text{CH})$] all indicate largely ionic interactions between the lanthanide metal and both $h^8\text{-}C_8H_8$ and $h^5\text{-}C_5H_5$ ligands.

Since the complexes were originally isolated as their THF adducts we were anxious to extend such adduct formation to other Lewis bases. Preliminary results, based mainly on holmium, indicate that ammonia, pyridine and, interestingly, cyclohexylisocyanide will coordinate to these mixed sandwich complexes. These adducts are somewhat less air sensitive, darker colored and the bonds between the metal and the cyclic ligands even more ionic than in the parent complexes; as indicated by the shift of the γ(CH) to lower frequency in the adducts, see Table 1. The bond between the lanthanide and the donor atom seems to be weaker than in the corresponding $(h^5\text{-}C_5H_5)_3\text{Ln}\cdot\text{L}$. Evidence of this, albeit not iron clad, comes from: (1) the position of the CN stretching frequencies of the coordinated isocyanide in the two classes of compounds: $(h^8\text{-}C_8H_8)\text{Ho}(h^5\text{-}C_5H_5)$ 2192 cm^{-1}, $(h^5\text{-}C_5H_5)_3\text{Ho}$, 2205 cm^{-1} [7]. Since in these complexes the isocyanide functions solely as a σ donor ligand, no back donation from the lanthanide metals, the rise in ν(CN) from that of the free ligand reflects the amount of charge transferred from the ligand to the metal and hence gives a measure of the strength of the bond [8]. (2) The observation that the coordinated THF is lost more readily than in the corresponding $(h^5\text{-}C_5H_5)_3\text{Ln}$.

TABLE 1

INFRARED SPECTRA OF $(h^8\text{-}C_8H_8)\text{Ln}(h^5\text{-}C_5H_5)$ AND $(h^8\text{-}C_8H_8)\text{Ln}(h^5\text{-}C_5H_5)\cdot\text{L}^a$

Ln	L	C_8H_8 (cm^{-1})			C_5H_5 (cm^{-1})			
		ω(C—C)	δ(C—H)	γ(C—H)	ω(C—C)	δ(C—H)	γ(C—H)	ν(CN)
Y		1432	883	728/720	1432	1013	792/779	
Ho		1434	886	730/722	1434	1015	798/780	
Nd		1437	882	727/719	1437	1010	789/772	
Ho	THF	1438	897	714/697	1438	1012	798/781	
Ho	NH_3	1438	897	712/698	1438	1009	780	
Ho	$C_6H_{11}NC$	1438	897	708/700	1438	1011	788/774	2192
Y	Py	1438	897	708	1438	1008	782/770	

^{a}The spectra were recorded on a Perkin—Elmer 467 as Nujol mulls.

We are currently extending our studies to the synthesis of other mixed sandwich complexes of the lanthanides and actinides. The chemistry of these complexes, especially their Lewis acidic behavior, is also under continuing investigation.

References

1 (a) H. Gysling and M. Tsutsui, Advan. Organometal. Chem., 9 (1970) 361;
(b) R.G. Hayes and J.L. Thomas, Organometal. Chem. Rev., A, 7 (1971) 1;
(c) B. Kanellakopulos and K.W. Bagnall in H.J. Emeleus and K.W. Bagnall (Eds.), MTP International Review of Science, Inorganic Chemistry Series One, Vol. 7, University Park Press, Baltimore, Md., 1971, 229.
2 H.O. van Oven and H.J. De Liefde Meijer, J. Organometal. Chem., 19 (1969) 373.
3 S. Manastyrskyj, R.E. Maginn and M. Dubeck, Inorg. Chem., 2 (1963) 904.
4 F. Mares, K.O. Hodgson and A. Streitwieser, Jr., J. Organometal. Chem., 28 (1971) C24.
5 H.P. Fritz, Advan. Organometal. Chem., 1 (1964) 239.
6 C.-H. Wong, T.-Y. Lee and Y.-T. Lee, Acta Cryst., B, 25 (1969) 2580.
7 E.O. Fischer and H. Fischer, J. Organometal. Chem., 6 (1966) 141.
8 F.A. Cotton and F. Zingales, J. Amer. Chem. Soc., 83 (1961) 351.