

Preliminary communication

SYNTHESIS AND ^1H NMR SPECTRA OF FERROCENE AND CYMANTRENE DERIVATIVES OF DIVALENT YTTERBIUM

G.Z. SULEIMANOV*, P.V. PETROVSKII, Yu.S. BOGACHEV, I.L. ZHURAVLEVA,
 E.I. FEDIN and I.P. BELETSKAYA

Karpov' Institute of Physical Chemistry, 10 Ulitza Obukha, 107120 Moscow (U.S.S.R.)

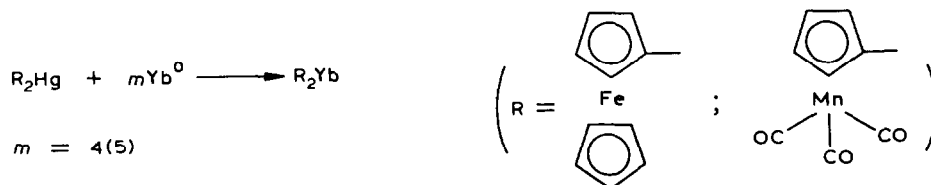
(Received October 25th, 1983)

Summary

The interaction of Yb^0 with $(\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4)_2\text{Hg}$ and $[(\text{OC})_3\text{MnC}_5\text{H}_4]_2\text{Hg}$ in THF resulted in the formation of ferrocenyl and cymantrenyl derivatives of divalent ytterbium. Derivatives of the RLnI type may be obtained in low yields from the basis of ferrocene (cymantrenyl) iodides and Yb^0 in THF. The structures of the resulting compounds were characterized by ^1H NMR spectra.

Ferrocenyl (Fc) and cymantrenyl (Ctm) derivatives of ytterbium (R_2Yb ; $\text{R} = \text{Fc}, \text{Ctm}$) were prepared by the reaction of the corresponding organomercury compounds with Yb .

In the case of $\text{R} = \text{Fc}$, the reaction in THF and at 20°C proceeded very slowly, affording only a 16% yield of Fc_2Yb after 120 h of stirring. The reactions of Yb^0 with Ctm_2Hg was more facile, yielding 78% of the product after 5 h.



In contrast to the ferrocenyl derivative, dicymantrenylytterbium was isolated in the form of a complex with a THF molecule.

Organic ytterbium salts of the RYbI type were prepared by oxidative addition of the corresponding iodides. However, unlike the reaction of ytterbium with iodobenzene [1] and iodo-C-carborane [2], the product yield did not exceed

17%. These compounds were then treated with trimethylchlorosilane and acetyl (benzoyl) chloride without preliminary isolation. (The percentage yield was estimated, as described in ref. 3, by the amount of RSiMe_3 and RCOR' which formed.)

The structures of the symmetrical R_2Yb compounds were confirmed by the data obtained from elemental analysis and IR and ^1H NMR spectra, whereas the data for RLnI were obtained from ^1H NMR spectra only. The ^1H NMR spectral parameters for the diferrocenyl and dicymantrenyl derivatives of ytterbium, as well as those of the isostructural mercury derivatives, are presented in Table 1.

TABLE 1

CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR THE FERROCENYL AND CYMANTRENYL DERIVATIVES OF MERCURY AND YTTERBIUM (SOLVENT $\text{C}_4\text{D}_8\text{O}$ REF. TO TMS)

Compound	C_2H_5 (ppm)	C_2H_4 (ppm)		$J(^{199}\text{Hg}-^1\text{H}_{\alpha,\beta})$		$J(^{171}\text{Yb}-^1\text{H}_{\alpha,\beta})$		(H-H β) (Hz)
		H α	H β	α	β	α	β	
$\text{C}_2\text{H}_5\text{FeC}_2\text{H}_2$	4.255							
$[\text{C}_2\text{H}_5\text{FeC}_2\text{H}_4]_2\text{Hg}$	4.292	4.497	4.176	17	34			1.8
$[\text{C}_2\text{H}_5\text{FeC}_2\text{H}_4]_2\text{Yb}$	4.264	4.458	4.151			20	36	1.9
$\text{C}_2\text{H}_5\text{FeC}_2\text{H}_4\text{I}$	4.270	4.482	4.298					2.2
$\text{C}_2\text{H}_5\text{FeC}_2\text{H}_4\text{YbI}$	4.268	4.391	4.096			14	34	1.8
$\text{C}_2\text{H}_5\text{Mn}(\text{CO})_3$	4.951							
$[(\text{OC})_3\text{MnC}_2\text{H}_4]_2\text{Hg}$		5.226	4.916	19	38			2.1
$[(\text{OC})_3\text{MnC}_2\text{H}_4]_2\text{Yb}$		5.157	4.797			12	34	2.0
$(\text{OC})_3\text{MnC}_2\text{H}_4\text{I}$		5.156	4.787					2.1
$(\text{OC})_3\text{MnC}_2\text{H}_4\text{YbI}$		5.153	4.794			10	32	1.8

As previously noted [4], the changes in the ^1H NMR chemical shifts of the isostructural $\text{C}_2\text{H}_5\text{M}$ fragment are essentially (and sometimes decisively) due to the redistribution of electron density in the fragment under consideration.

The purpose of this work was to study the type of interaction between the lanthanides, as well as mercury, and the cyclopentadienyl ring in the ferrocene and cymantrene derivatives.

It appeared that during the passage from mercurial derivatives to isostructural ytterbium compounds, the ^1H NMR chemical shifts did not undergo substantial changes, whereas such changes occurred in the cymantrene derivatives.

The upfield displacement of the NMR signals due to the proton in the α -position in diferrocenyl- and dicymantrenylytterbium relative to the corresponding signal in diferrocenyl- and dicymantrenyl-mercury is apparently due to the weaker electron-withdrawing effect of the ytterbium atom compared with the mercury atom (see Table 1).

The ^1H NMR spectra were recorded with a Bruker WP-200 SY spectrometer (200.13 MHz) in $\text{C}_4\text{D}_8\text{O}$ at $\sim 35^\circ\text{C}$. The chemical shifts were measured relative to TMS with a precision of ± 0.005 ppm, the accuracy of the measurement and the constant coupling being ± 1 Hz.

References

- 1 D.F. Evans, G.V. Fazakerley and R.F. Phillips, *J. Chem. Soc. A*, (1971) 1931.
- 2 G.Z. Suleimanov, V.I. Bregadze, N.A. Koval'chuk, Kh.S. Khalilov and I.P. Beletskaya, *J. Organomet. Chem.*, 255 (1983) C5.
- 3 T. Fukagawa, Y. Fujiwara and H. Taniguchi, *Chem. Lett.*, (1982) 601.
- 4 E.I. Fedin, P.V. Petrovskii, L.A. Fedorov, Yu.V. Makarov, N.E. Kolobova and K.N. Anisimov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1973) 2142.