Journal of Organometallic Chemistry, 361 (1989) 17–19
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

New preparation of tetraindenylthorium

J. Goffart * and **S. Bettonville** **

Laboratory of Analytical and Radiochemistry, University of Liège, Sart Tilman, B-4000 Liège (Belgium)

(Received June 2nd, 1988)

Abstract

Treatment of triindenylthorium chloride with metallic potassium in boiling benzene has given tetraindenylthorium. No thorium(III) species was detected.

Introduction

Attempts to prepare triindenylthorium(III) by reduction of triindenylthorium chloride with metallic potassium failed, and tetraindenylthorium (**a**) was obtained. The first preparation of **a** was by Rebizant et al., who also determined the crystal structure (1). The coordination polyhedron about the central metal has the indenyl five-membered rings at the apices of a distorted polyhedron, with the indenyl rings deviating slightly from the planarity.

Experimental

Special precautions were taken to exclude oxygen and moisture during reactions. Benzene was purified by distillation over sodium-potassium alloy under argon. Triindenylthorium chloride was prepared by a published method [2]. The infrared, NIR/VIS, NMR, and mass spectra were recorded on Perkin–Elmer 580B, Perkin–Elmer Lambda 9, Bruker AM400 and Varian MAT-112 instruments, respectively. The magnetic susceptibility was measured with a Faraday balance between 4 and 300 K.

Preparation

Clean metallic potassium (3 mmol) was added to a clear yellow solution of triindenylthorium chloride (3 mmol) in benzene. The mixture was stirred under

---

* Research Associate, Inter-University Institute for Nuclear Sciences (Brussels, Belgium).
** Research Assistant, National Fund for Scientific Research (Brussels, Belgium).

0022-328X/89/$03.50

reflux for 2 days and then filtered in a glove box under pure nitrogen. The filtrate was evaporated under reduced pressure (1 torr) at room temperature to give yellow crystals of **a** (yield 20–25%). (Found C, 62.17; H, 4.11; Th, 33.49, Cl, 0.0. $C_{20}H_{20}Th$ calcd.: C, 62.43; H, 4.07; Th, 33.50%.)

Results and discussion

The infrared spectrum of compound **a** is characteristic of an indenyl organometallic [3]. The bands between 3100 and 3000, at 1340, at 1040 cm^{-1}, and between 800 and 700 cm^{-1} are attributable to C–H vibrations, and those at 1608 and 1405 cm^{-1} to C–C vibrations. The band at 220 cm^{-1} in $(C_9H_7)_3ThCl$, which has been assigned to C_9H_7Th vibration is shifted to 203 cm^{-1} in **a**.

The NIR/VIS spectrum shows no band between 2500 and 400 nm. The magnetic susceptibility data recorded between 4 and 300 K correspond to a diamagnetic compound ($\chi_m = -(350 \pm 7) \cdot 10^{-6}$ emu/mol).

The main peaks in mass spectrum are observed at $m/e = 579$ ($[C_{27}H_{21}Th]^+$), 462 ($[C_{10}H_{14}Th]^+$) and 347 ($[C_9H_7Th]^+$). There was no peak corresponding to $[C_{36}H_{28}Th]^+$. The relative lability of one indenyl ligand is demonstrated by the immediate reaction of a solution of **a** with a stoechiometric amount of dry hydrogen chloride to give triindenylthorium chloride.

An X-ray diffraction study on crystals of **a** showed that the compound was identical with the tetraindenylthorium prepared by Rebizant et al. [1].

For various indenyl compounds, the metal–carbon distances of bridging [8,9] and non-bridging carbons [1,2,3] and of their averages, differ significantly; some relevant data are presented in Table 1. The magnitude of the difference by *DL* (see Table 1) can be regarded as a measure of the contribution of η^3-bonding in the complexes. *DL* increases normally from triindenyluranium to tetraindenylthorium, in which there are dihedral angles of 6 to 9° between the five- and the six-membered ring sections of the four indenyl ligands. The non-planarity of the indenide ligand, an

Table 1

Influence of the molecular structure on the mean metal–carbon distances

Compounds	$ML \cdot 10^2$ (nm) [a]	$DL \cdot 10^2$ (nm) [a]	Ref.
Ind_3U	27.95	0.19	4
$IndUBr_3 \cdot THF \cdot TPhPO$	27.59	0.62	5
$IndUBr_3 \cdot 2THF$	27.28	0.70	6
$IndUCl_3 \cdot 2THF$	27.43	0.80	7
$Ind_2U(BH_4)_2$	28.88	0.77	8
$[(IndUBr(CH_3CN)_4)_2]O^{2+}$	28.55	1.15	9
$[IndUBr_2(CH_3CN)_4]$	28.15	1.52	9
Ind_3UCl	27.77	1.38	10
Ind_3UBr	27.78	1.39	11
Ind_3UI	27.82	2.02	12
TMI_3ThCl	28.63	1.67	13
TMI_3UCl	27.94	1.05	14
Ind_4Th	29.28	2.77	1
η^3-$IndIr[PR_3]_3$	25.14	8.52	15

[a] $ML = \overline{\mathrm{Me{-}C}_{1.2.3.4.5}}$ (mean distance), $DL = (\overline{\mathrm{Me{-}C}_{8.9}}) - (\overline{\mathrm{Me{-}C}_{1.2.3}})$ (mean difference), Ind = C_9H_7, TMI = $1.4.7(CH_3)_3C_9H_4^-$, $PR_3 = P(C_6H_5)(CH_3)_2$.

Table 2

NMR spectra (C_6D_6) (δ, ppm)

	Ind_3ThCl	Ind_4Th
H(1)–H(3)	5.68	5.69
H(2)	6.16	5.27

angle of 28° between the C(5) and C(6) rings, is also observed in a pure η^3-compound such as $C_9H_7Ir(PR_3)_3$ [15].

NMR spectroscopy can be used to estimate the trihapto contribution in the bonding mode, the changes in NMR spectra of the indenyl ligand on going from η^5 to η^3 coordination being quite striking, especially for C(2)–H(2) [15]. The values of the chemical shifts of H(1) and H(3) in triindenylthorium chloride and **a** are respectively δ 5.68 and 5.69 ppm, whereas the signal from H(2) shows a substantial upfield shift on going to **a**, reflecting formation of a partial trihapto bond in the complex, in accord with the X-ray diffraction data (Table 2) and published NMR results [15].

Acknowledgment

We thank Dr J. Rebizant (Euratom, Karlsruhe, F.R.G.) for confirmation of the structure of tetraindenylthorium. Financial support by Inter-University Institute for Nuclear Science (Brussels) is gratefully acknowledged.

References

1 J. Rebizant, M.R. Spirlet, B. Kanellakopulos and E. Dornberger, Acta Cryst. C, 42 (1986) 1497.

2 J.H. Burns and P.G. Laubereau, Inorg. Chem., 10 (1971) 2789.

3 J. Goffart in T.J. Marks and R.D. Fischer (Eds.), Organometallics of *f*-Elements, Reidel Publ. Company, Dordrecht, 1979.

4 J. Goffart, unpublished results, J. Meunier-Piret, J. P. Declercq, G. Germain and M. Van Meerssche, Bull. Soc. Chim. Belg., 89 (1980) 121.

5 J. Meunier-Piret, G. Germain, J.P. Declercq and M. Van Meerssche, Bull. Soc. Chim. Belg., 89 (1980) 241.

6 J. Rebizant, M.R. Spirlet and J. Goffart, Acta Cryst. C, 41 (1985) 334.

7 J. Rebizant, M.R. Spirlet and J. Goffart, Acta Cryst. C, 39 (1983) 1049.

8 M.R. Spirlet, J. Rebizant, S. Bettonville and J. Goffart, to be published.

9 W. Beeckman, J. Goffart, J. Rebizant and M.R. Spirlet, J. Organomet. Chem., 23 (1986) 307.

10 J.H. Burns and P.G. Laubereau, Inorg. Chem., 10 (1971) 2789.

11 M.R. Spirlet, J. Rebizant and J. Goffart, Acta Cryst. C, 43 (1987) 354.

12 M.R. Spirlet, J. Rebizant and J. Goffart, to be published.

13 M.R. Spirlet, J. Rebizant and J. Goffart, Acta Cryst. B, 38 (1982) 2400.

14 J. Meunier-Piret and M. Van Meerssche, Bull. Soc. Chim. Belg., 93 (1984) 299.

15 J.S. Merola, R.T. Kacmarcik and D. Van Engen, J. Am. Chem. Soc., 108 (1986) 329.