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ORGANOSCANDIUM COMPOUNDS CONTAINING THE η^8 -C₈H₈ LIGAND

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Summary

The compound C₈H₈ScCl · THF has been prepared by reaction of ScCl₃ · 3THF with K₂C₈H₈. Reaction of C₈H₈ScCl · THF with C₅H₅Na and K₂C₈H₈ yields C₈H₈ScC₅H₅ and KSc(C₈H₈)₂, respectively. Spectral evidence is given for the sandwich structure of the latter compounds.

Introduction

Since the preparation of (C₅H₅)₃Sc in 1956 by Wilkinson and Birmingham [1] few papers on organoscandium chemistry have appeared. Hart et al. [2] reported the synthesis of R₃Sc (R = phenyl, phenylethynyl), while Coutts and Wailles [3] prepared (C₅H₅)₂ScCl, which was used for the preparation of (C₅H₅)₂-ScR (R = π -allyl, acetate). In this paper the syntheses of the first organoscandium compounds containing the η^8 -C₈H₈ ligand viz. C₈H₈ScCl · THF, C₈H₈ScC₅H₅, and KSc(C₈H₈)₂ are described.

Experimental

General

All reactions were carried out under dry nitrogen. Tetrahydrofuran (THF) was distilled over LiAlH₄ before use. Other solvents were dried over sodium wire. Elemental analyses were carried out at the Analytical Department of this University; scandium analyses were performed by the method of Yamada et al. [4].

Starting materials

K₂C₈H₈ and C₅H₅Na were prepared in the usual way from C₈H₈ and K, and C₅H₆ and Na.

$\text{ScCl}_3 \cdot 3\text{THF}$ was prepared from $\text{ScCl}_3 \cdot 6\text{H}_2\text{O}$ and predistilled thionyl chloride. $\text{ScCl}_3 \cdot 6\text{H}_2\text{O}$ was added in portions to a mixture of THF and SOCl_2 at room temperature. A violent exothermic reaction occurred and HCl and SO_2 were evolved. After the addition was complete, the mixture was kept at reflux temperature for about 6 h. The excess of THF and SOCl_2 was pumped off and the residue washed with diethyl ether. After drying, pure $\text{ScCl}_3 \cdot 3\text{THF}$ was obtained in 96% yield. (Found: Sc, 12.23. $\text{C}_{12}\text{H}_{24}\text{Cl}_3\text{O}_3\text{Sc}$ calcd.: Sc, 12.20%.)

$\text{C}_8\text{H}_8\text{ScCl} \cdot \text{THF}$

To a stirred suspension of $\text{ScCl}_3 \cdot 3\text{THF}$ (3.67 g, 10 mmol) in THF (100 ml) a solution of $\text{K}_2\text{C}_8\text{H}_8$ (10 mmol) in THF (100 ml) was added at room temperature. The colour gradually changed from dark brown to bright yellow. Stirring was continued for about 30 min. Yellow $\text{C}_8\text{H}_8\text{ScCl} \cdot \text{THF}$ was obtained in almost quantitative yield by THF extraction. Recrystallization from hot chlorobenzene gave the pure compound (yield 50%). (Found: C, 56.12; H, 6.31; Cl, 13.36; Sc, 16.94. $\text{C}_{12}\text{H}_{16}\text{ClOSc}$ calcd.: C, 56.14; H, 6.30; Cl, 13.81; Sc, 17.51%.) The compound is air sensitive and insoluble in non-polar solvents.

$\text{C}_8\text{H}_8\text{ScC}_5\text{H}_5$

$\text{C}_8\text{H}_8\text{ScCl} \cdot \text{THF}$ (2.56 g, 10 mmol) in THF (100 ml) was allowed to react with $\text{C}_5\text{H}_5\text{Na}$ (10 mmol) in THF (100 ml) at room temperature. After 30 min stirring the solvent was pumped off and the residue washed with pentane. Analytically pure $\text{C}_8\text{H}_8\text{ScC}_5\text{H}_5$ was obtained either by crystallization from diethyl ether (yield 55%) or by sublimation at $120^\circ\text{C}/0.1$ mmHg (yield 36%). (Found: C, 72.46; H, 6.23; Sc, 20.94. $\text{C}_{13}\text{H}_{13}\text{Sc}$ calcd.: C, 72.88; H, 6.13; Sc, 20.99%.) The compound is yellowish white, rather air sensitive, and moderately soluble in common organic solvents.

$\text{KSc}(\text{C}_8\text{H}_8)_2$

$\text{C}_8\text{H}_8\text{ScCl} \cdot \text{THF}$ (2.03 g, 8 mmol) in THF (100 ml) was allowed to react with $\text{K}_2\text{C}_8\text{H}_8$ (8 mmol) in THF (100 ml) at room temperature. After 1 hour's stirring $\text{KSc}(\text{C}_8\text{H}_8)_2$ was isolated in almost quantitative yield as a yellow-brown solid by THF extraction. (Found: K, 11.71; Sc, 13.12. $\text{C}_{16}\text{H}_{16}\text{KSc}$ calcd.: K, 13.37; Sc, 15.37%.) Purification was achieved by extraction with hot toluene, which, like other non-polar solvents (except THF), is a very poor solvent for $\text{KSc}(\text{C}_8\text{H}_8)_2$. (Found: Sc, 14.74%.) The compound is extremely air sensitive.

Spectra

Infrared spectra were recorded on a Hitachi EPI-G spectrophotometer using Nujol mulls between KBr windows. The IR spectra are shown in Fig. 1.

^1H NMR spectra were recorded on a Varian A-60 high resolution instrument with TMS as an internal standard. The spectrum of $\text{C}_8\text{H}_8\text{ScC}_5\text{H}_5$ in CS_2 , showed two singlets at δ 6.37 and δ 5.13 ppm with relative intensities of 8 to 5. The spectrum of $\text{KSc}(\text{C}_8\text{H}_8)_2$, in $\text{THF}-d_8$, showed one singlet at δ 5.73 ppm.

The mass spectrum of $\text{C}_8\text{H}_8\text{ScC}_5\text{H}_5$ was recorded on an AEI-MS9 instrument by Mr. A. Kiewiet, and the peaks are listed in Table 1. A reliable mass spectrum of $\text{KSc}(\text{C}_8\text{H}_8)_2$ could not be obtained because of its extreme air sensitivity.

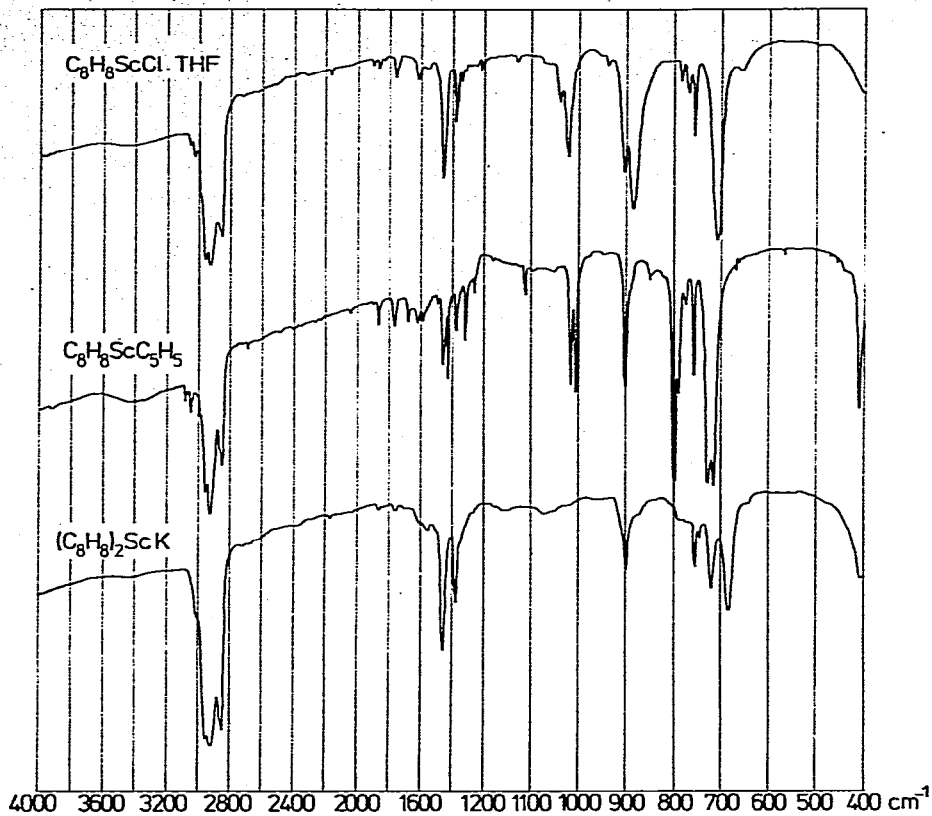


Fig. 1. IR spectra of $C_8H_8ScCl \cdot THF$, $C_8H_8ScC_5H_5$ and $KSc(C_8H_8)_2$ in Nujol.

TABLE 1

MASS SPECTRUM OF $C_8H_8ScC_5H_5$

m/e	Relative abundance	Ion	Metastable peaks
214	100	$C_{13}H_{13}Sc^+$	
188	17	$C_{11}H_{11}Sc^+$	$m^* = 165 \xrightarrow{-C_2H_2} C_{11}H_{11}Sc^+$
149	28	$C_8H_8Sc^+$	$C_{13}H_{13}Sc^+ \xrightarrow{-C_2H_2} C_{11}H_{11}Sc^+$
147	34	$C_8H_6Sc^+$	
110	95	$C_5H_5Sc^+$	$m^* = 64.5$
104	10	$C_8H_8^+$	$C_{11}H_{11}Sc^+ \xrightarrow{-C_6H_6} C_5H_5Sc^+$
94	13	$C_{11}H_{11}Sc^{2+}$	
84	20	$C_3H_3Sc^+$	
83	13	$C_3H_2Sc^+$	
78	20	$C_6H_6^+$	
70	18	C_2HSc^+	
66	12	$C_5H_6^+$	
45	20	Sc^+	
39	14	$C_3H_3^+$	

Discussion

The IR and ^1H NMR spectra indicate that $\text{C}_8\text{H}_8\text{ScC}_5\text{H}_5$ is a sandwich-type complex, in which the planar five- and eight-membered rings are π -bonded to the metal. The characteristic absorptions of $\pi\text{-C}_5\text{H}_5$ in the IR spectrum [5] are found at 3040, 1018 and 800 cm^{-1} , while the absorptions at 900, 790, 729, 714 cm^{-1} can be ascribed to $\pi\text{-C}_8\text{H}_8$. The spectrum is almost identical with that of the titanium analogue [6], the sandwich structure of which has been proven by X-ray analysis [7]. The mass spectra of $\text{C}_8\text{H}_8\text{ScC}_5\text{H}_5$ and $\text{C}_8\text{H}_8\text{TiC}_5\text{H}_5$ also are closely similar. The mass spectra of analogous compounds of yttrium and a number of lanthanides show $\text{C}_5\text{H}_5\text{Ln}^+$ and $\text{C}_8\text{H}_8\text{Ln}^+$ in almost equal abundances [8] in contrast with the mass spectra of $\text{C}_8\text{H}_8\text{ScC}_5\text{H}_5$ and $\text{C}_8\text{H}_8\text{TiC}_5\text{H}_5$ [6], where the $\text{C}_5\text{H}_5\text{M}^+$ ion is much more abundant than $\text{C}_8\text{H}_8\text{M}^+$. This difference is in keeping with the larger size of Y and Ln, which is expected to favour the bonding to the larger ring system.

The IR and ^1H NMR spectra of $\text{KSc}(\text{C}_8\text{H}_8)_2$ strongly suggest that it contains the sandwich anion $[\text{Sc}(\text{C}_8\text{H}_8)_2]^-$, by analogy with similar compounds of yttrium and a number of lanthanides [9].

Preparation of other organoscandium compounds and the nature of metal-carbon bonding in such compounds will be the subject of further research.

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