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NEW ORGANOSCANDIUM COMPOUNDS

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SUMMARY

The compound $(C_5H_5)_2ScCl$ has been prepared from scandium trichloride and magnesium cyclopentadienide as a yellow-green moisture-sensitive solid. The chloride group has been replaced by treatment with sodium salts or Grignard reagents to give four new classes of mixed ligand derivatives represented by $(C_5H_5)_2ScOCOCH_3$, $(C_5H_5)_2ScAcac$, $(C_5H_5)_2ScC{\equiv}CPh$ and $(C_5H_5)_2Sc(CH_2CH{=}CH_2)$.

INTRODUCTION

Although tricyclopentadienylscandium has been known since 1954[1], organoscandium derivatives had received little mention in the literature until 1968 when the triphenyl and triphenylethynyl compounds were reported[2] by Hart and co-workers*. $Sc(C_6H_5)_3$ and $Sc(C{\equiv}CC_6H_5)_3$ were found to be pyrophoric in air and could not be analyzed satisfactorily for carbon and hydrogen[2]. By analogy with the higher lanthanides and also with titanium, it should be possible to increase the stability of organoscandium compounds by introducing cyclopentadienyl groups. In particular the preparation of $(C_5H_5)_2ScCl$ and subsequent replacement of the chloride with other ligands could lead to many new organoscandium derivatives stabilized by the presence of the cyclopentadienyl ligands. An added benefit would be a decrease in the degree of association compared with $Sc(C_6H_5)_3$ and $Sc(C{\equiv}CPh)_3$, giving increased solubility and an opportunity for solution studies.

Although previous workers have failed to isolate derivatives of the type $(C_5H_5)_2MCl$ for any lanthanide below samarium[4], scandium differs sufficiently from the lanthanides to warrant an attempt at the preparation of $(C_5H_5)_2ScCl$.

RESULTS AND DISCUSSION

The reagent $Mg(C_5H_5)_2$ was chosen for the introduction of cyclopentadienyl groups since it can be obtained pure and neutral by sublimation[5]. On mixing equimolar amounts of $ScCl_3$ and $Mg(C_5H_5)_2$ in tetrahydrofuran, a yellow solution was obtained from which large yellow-green crystals of $(C_5H_5)_2ScCl$ were isolated in 75% yield by evaporation and sublimation. The compound is moderately soluble in ben-

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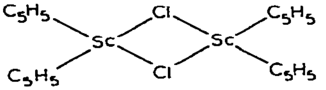
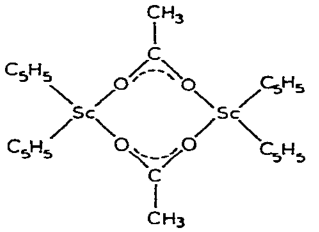
* A 1938 report[3] of the preparation of $ScEt_3(Et_2O)$ appears to have been discounted[2].

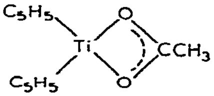
zene, in which ebulliometric molecular weight measurements show it to be dimeric, probably with structure (I). Similar chloride-bridged dimeric structures are common to the higher lanthanides[4] and titanium[6], and dissociate in polar solvents such as THF.



(I)

$(C_5H_5)_2ScCl$ is extremely sensitive to moisture; it hydrolyzes rapidly in air liberating cyclopentadiene; in this respect it behaves like an ionic cyclopentadienide. With anhydrous sodium acetate in THF the chloro compound (I) was converted to the corresponding acetate $(C_5H_5)_2ScOCOCH_3$ (II), a yellow sublimable solid. Molecular weight measurements in benzene showed it to be dimeric, the separation of symmetric and asymmetric OCO stretching frequencies in the infrared (135 cm^{-1}), suggesting bidentate, and therefore bridging, acetate groups. Similar dimeric species occur with the lanthanides[4] but not with titanium(III). $(C_5H_5)_2TiOCOCH_3$ is monomeric with a symmetrical bidentate acetate ligand[7] as in (III):

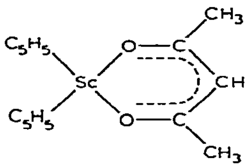




(III)

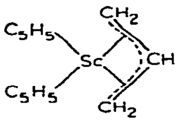
(II)

The pale yellow acetylacetonate, $(C_5H_5)_2ScAcac$, is monomeric in boiling benzene and sublimes at 110°/10^{-3} mm. Its infrared spectrum is almost identical with that of the corresponding titanium compound[8] with bands at 1575, 1515 and 1370 cm^{-1} characteristic of bidentate acetylacetonate (see Experimental) and indicative of structure (IV).



(IV)

Allylmagnesium chloride with dicyclopentadienylscandium chloride gave the orange-coloured, monomeric allyl derivative (V). This is directly analogous to the several allyltitanium derivatives prepared by Jellinek and collaborators[9], although the



(V)

scandium compound appears to be more stable thermally since it is readily sublimed at 70–80° under high vacuum. Confirmation of the symmetrical nature of the allyl group came from the spin decoupled PMR spectrum, which consisted of a quintet and a doublet in the integrated intensity ratio 1/4 (see Table 1).

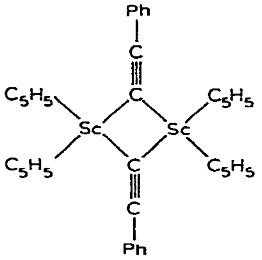
TABLE 1

PROPERTIES OF ORGANOSCANDIUM COMPOUNDS

Compound	Colour	M.p. (°C)	Sublim. temp. at 10^{-3} mm (°C)	PMR	
				τ	J(Hz)
$(C_5H_5)_2ScCl$	yellow-green	313–315	220	3.84[a]	
$(C_5H_5)_2ScOCOCH_3$	yellow	282 (decomp.)	160	4.07 (C_5H_5)	
				8.49 (CH_3)	
$(C_5H_5)_2ScAcac$	pale yellow	75	110	4.06 (C_5H_5)	
				4.94 (CH)	
				8.49 (CH_3)	
$(C_5H_5)_2Sc(CH_2CH=CH_2)$	orange	151 (decomp.)	75	2.71 (CH) quintet	12
				4.10 (C_5H_5)	
				6.95 (CH_2) doublet	12
$(C_5H_5)_2ScC{\equiv}CPh$	yellow	254 (decomp.)		2.69 (C_6H_5) multiplet[a]	
				3.75 (C_5H_5)	

[a] THF as solvent, all others in C_6D_6.

The only derivative which did not sublime was $(C_5H_5)_2ScC{\equiv}CPh$ (VI); it is insoluble in benzene but moderately soluble in THF in which it shows a molecular weight somewhat higher than that of the monomer, so that it is still associated to some extent. Since the triple bond stretching frequency in the IR has been reduced to 2045 cm^{-1}, it is probable that the PhC≡C groups are bridging[10] as in (VI) and that the compound is a dimer at least.



(VI)

In contrast to the triphenyl and triphenylethynyl derivatives[2], all the compounds described above, with the exception of (VI), could be analyzed satisfactorily for carbon and hydrogen by the encapsulation technique described in the Experimental Section. All were soluble enough for the determination of molecular weights, the values of which indicate that scandium prefers to have four ligands around it in complexes of this type. The ready hydrolysis of the cyclopentadienyl groups attached to scandium is typical of the ionic lanthanide cyclopentadienides rather than of π-bonded titanium derivatives[4].

EXPERIMENTAL

General

All solid compounds were handled in a nitrogen-filled glovebox and all reactions were carried out under purified argon in a Schlenk tube system[11]. Molecular weights were determined ebulliometrically in a Gallenkamp ebulliometer modified to take a 3 ml cell with N_2 inlet. PMR spectra were measured on a Varian A-60 or HA-100 instrument. Infrared spectra were run on a Perkin–Elmer 521 or 137 spectrophotometer calibrated with polystyrene.

Materials

Anhydrous $ScCl_3$ was prepared from Sc_2O_3 and NH_4Cl by the method of Reed *et al.*[12] All solvents were purified by distillation under N_2 from $LiAlH_4$. Magnesium cyclopentadienide was prepared by dropping cyclopentadiene monomer on to a column of magnesium heated to 550° in a slow stream of argon[5].

Analyses

Scandium was determined by ignition to the oxide after treatment of pellets of the sample with water and nitric acid. Carbon and hydrogen were determined by the Australian Microanalytical Service, on pelleted samples sealed in aluminium capsules of the type used in calorimetry (Perkin–Elmer liquid sample capsules).

Dicyclopentadienylscandium chloride

A solution of magnesium cyclopentadienide (30.8 g) in tetrahydrofuran (500 ml) was added slowly with ice cooling to $ScCl_3$ (30.3 g) in THF (500 ml). After addition was complete the solution was warmed to 50° for 1 h, at which stage it was pale yellow in colour. Solvent was removed under reduced pressure and the residue was sublimed in batches at 220°/10^{-3} mm giving large yellow-green crystals of $(C_5H_5)_2ScCl$ (26.5 g, 75%), m.p. 313–315°. (Found: C, 57.2; H, 4.8; Sc, 21.8; mol.wt. in benzene, 404; in THF, 231. $C_{10}H_{10}ClSc$ calcd.: C, 57.00; H, 4.75; Sc, 21.40%; mol. wt., 210.6.)

Dicyclopentadienylscandium acetate

Anhydrous sodium acetate (2 g) was stirred with a solution of $(C_5H_5)ScCl$ (1 g) in THF (20 ml) for 2 days giving a pink-coloured solution. The solvent was removed under reduced pressure and the residue was sublimed at 160°/10^{-3} mm, the colour changing to yellow on heating. The straw-coloured sublimate of $(C_5H_5)_2ScOCOCH_3$ (0.72 g, 65%) had m.p. 283° (with decomposition). (Found: C, 61.7; H, 5.5; Sc, 19.4; mol.wt. in benzene, 440. $C_{12}H_{13}O_2Sc$ calcd.: C, 61.50; H, 5.60; Sc, 19.20%; mol.wt., 234.) In the IR spectrum (KBr disc) the symmetric and asymmetric OCO stretching bands occurred at 1445 and 1580 cm^{-1} respectively.

Dicyclopentadienylscandium acetylacetonate

Sodium acetylacetonate was prepared by stirring acetylacetone (0.5 g) with sodium in benzene (25 ml). To this suspension was added a solution of $(C_5H_5)_2ScCl$ (1 g) in benzene (30 ml). After stirring overnight the yellow suspension was reduced to dryness and the residue sublimed at 110°/10^{-3} mm. Pale yellow $(C_5H_5)_2ScAcac$ was collected as a solid (0.82 g, 60%), m.p. 75° (decomp.) (Found: C, 65.1; H, 6.2; Sc, 16.1; mol. wt. in benzene, 278. $C_{15}H_{17}O_2Sc$ calcd.: C, 65.70; H, 6.25; Sc, 16.40%; mol.wt., 274.) The IR spectrum showed bands at 1575 (C=C str.), 1515 (C=O str.) and 1370 cm^{-1} (C=O str.) indicative of a bidentate acetylacetonate.

(Allyl)dicyclopentadienylscandium

A benzene solution of $(C_5H_5)_2ScCl$ (1 g) was added to allylmagnesium chloride (from 0.3 g Mg+allyl chloride) in THF (15 ml). An orange colour developed with slight heat evolution. After 1 h the solvent was removed under vacuum and the residue was extracted with light petroleum (100 ml) giving an orange-coloured solution which was filtered under argon to remove insoluble magnesium salts, then evaporated. Sublimation at 75°/10^{-3} mm gave orange $(C_5H_5)_2Sc(CH_2CH{=}CH_2)$, (0.6 g, 60%), m.p. 151° (decomp.). (Found: C, 71,5; H, 6.8; Sc, 21.2; mol. wt. in benzene, 243. $C_{13}H_{15}Sc$ calcd.: C, 72.25; H, 6.99; Sc, 20.80%; mol. wt., 216.) In the IR spectrum (KBr disc) the C=C stretching frequency of the allylic ligand occurred at 1475 cm^{-1}.

(Dicyclopentadienyl)phenylethynylscandium

Sodium (0.12 g) and naphthalene (0.65 g) were stirred in THF (15 ml) until the metal had dissolved. Phenylacetylene was now added dropwise until the green colour of sodium naphthalenide was discharged (0.8 ml required). To the resultant white suspension of sodium phenylacetylide was added $(C_5H_5)_2ScCl$ (1 g) in benzene (30 ml). After stirring for 2 h the solvent was removed under reduced pressure and naphthalene and other hydrocarbons were removed by extraction with petroleum (3 × 20 ml) followed by benzene (1 × 20 ml). Extraction of the residue with THF followed by filtration through Celite under argon and evaporation gave yellow $(C_5H_5)_2ScC{\equiv}CPh$ (0.93 g, 67 %), m.p. 254° (decomp.) which decomposed on attempted sublimation. (Found: C, 75.0; H, 5.5; Sc, 16.5; mol. wt. in THF, 350. $C_{18}H_{15}Sc$ calcd.: C, 78.30; H, 5.47; Sc, 16.28%; mol. wt., 276.) In the IR spectrum the C≡C stretching frequency occurred at 2045 cm^{-1}.

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