Journal of Organometallic Chemistry, 66 (1974) 405—412

COORDINATION COMPOUNDS OF INDIUM

XXIV*. SOME NEUTRAL AND ANIONIC CYCLOPENTADIENYLINDIUM(III) IODIDE COMPOUNDS

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(Received July 12th, 1973)

Summary

Cyclopentadienylindium(I) (CpIn) in chloroform reacts with iodine to yield the solid $CpInI_2$; 2,2′-bipyridine and 1,10-phenanthroline adducts of this compound have been prepared. $CpInI_2$ reacts with tricyclopentadienylindium(III), and with tetra-n-propylammonium iodide, to give the unstable Cp_2InI and the anionic species $[CpInI_3]^-$ respectively. The cyclopentadienyl ligand is in the *monohapto* form in all these compounds. CpIn reacts with methyl iodide, trifluoroiodomethane, and with iodine in the presence of ethanol to yield InI. Possible mechanisms for these reactions are discussed.

Introduction

Cyclopentadienylindium(I), first prepared by Fischer and Hofmann [1], is the only organoindium(I) compound which is readily accessible at the present time. The structure [2,3], described as a "half-sandwich" (i.e. *pentahapto*-cyclopentadienyl), and the bonding, have been the subject of some discussion, to which we return below.

Recent studies have shown that CpIn can act as an electron pair donor, forming $CpIn \cdot BX_3$ compounds ($X = F, Cl, Br, CH_3$) [4]. An apparently related type of reaction involves oxidative insertion into the S—S bond of 1,2-bis(trifluoromethyl)dithiete, to give an indium(III) species [5], a reaction which is also observed with the indium(I) halides [6]. We have now found that the reaction of CpIn with iodine in pure chloroform gives cyclopentadienylindium-

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(III) diiodide, which can be regarded both formally and mechanistically as resulting from the insertion of In^I into the I—I bond. The compound $CpInI_2$ is related to the alkyldiiodoindium(III) species previously prepared by Clark and Pickard [7], and by Poland and Tuck [8]. A number of structurally related organoindium(III) compounds are readily obtained from $CpInI_2$.

By way of investigating the mechanism of the initial CpIn + I_2 reaction, the reactions of CpIn with CH_3I and CF_3I have also been investigated. In both cases, the product is InI and unidentified organic materials. The presence of trace amounts of ethanol in the chloroform also results in the production of indium iodide from CpIn + I_2.

Experimental

Spectroscopic and conductimetric techniques were as described previously [8]. Indium analysis was performed on a Perkin—Elmer Atomic Absorption Spectrophotometer. All preparative and related work was carried out under dry nitrogen in a glove box. Solvents were Reagent grade, and were used without further purification, except for chloroform (see below).

Preparative methods

Cyclopentadienylindium(III) diiodide. When iodine (0.31 g, 1.22 mmole) in freshly distilled chloroform was added dropwise to a solution of CpIn (0.22 g, 1.22 mmole), the colour of the iodine was completely discharged, and a yellow precipitate of $CpInI_2$ quickly formed. This was collected, washed with chloroform and dried in vacuo. The solid is insoluble in chloroform, acetone, and dimethylsulphoxide, and slightly soluble in ether. (Found: C, 13.2; H, 1.1; In, 26.4; I, 58.4. $C_5H_5InI_2$ calcd.: C, 13.8; H, 1.2; In, 26.5; I, 58.5%.) The compound shows signs of decomposition after 3 - 4 days, becoming increasingly dark brown in colour, although the 2,2′-bipyridine adduct (see below) can still be obtained in reasonable yield from this brown material, so that decomposition is clearly far from complete at this stage.

When chloroform was used without prior purification, the reaction of CpIn and I_2 gave an immediate precipitate of indium(I) iodide.

Bis(cyclopentadienyl)indium(III) iodide. $CpInI_2$ (1.2 mmole) was suspended in a solution of an equimolar quantity of tris(cyclopentadienyl)indium(III) in hot benzene. This supension was refluxed for 10 h, after which the resulting brown solid was filtered off, washed with benzene and dried. The solid is insoluble in all the common solvents. Carbon and hydrogen microanalysis yielded persistently low values, as the compound is quite unstable, but it was possible to analyse for In and I under nitrogen. (Found: In, 30.8; I, 34.3. $C_{10}H_{10}InI$ calcd.: In, 30.9; I, 34.1%.) The decomposition was immediately obvious, as the compound became greenish-brown on standing, and we were not able to obtain stable derivatives of Cp_2InI.

Tetra-n-propylammoniumcyclopentadienyl-triiodoindate(III). 1.13 Mmole of tetra-n-propylammonium iodide dissolved in anhydrous methanol was added to a suspension of cyclopentadienylindium(III) diiodide (1.13 mmole) in ether. The resulting solution was stirred for 24 h at room temperature; removal of the solvent gave a solid, insoluble in most of the common solvents except nitrobenzene, in which it is slightly soluble. The yield was quantitative. (Found: C, 26.3; H, 4.7; N, 1.6; In, 15.3; I, 50.9. $C_{17}H_{33}NInI_3$ calcd.: C, 27.3; H, 4.4; N, 1.8; In, 15.4; I, 51.0%.) This compound shows no signs of decomposition over a period of some weeks.

Adducts of cyclopentadienylindium(III) diiodide

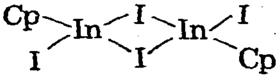
2,2'-Bipyridine. 1.3 Mmole of 2,2'-bipyridine dissolved in dry ether was added to a suspension of 1.3 mmole of cyclopentadienylindium(III) diiodide. The yellow precipitate which immediately formed in quantitative yield was collected, washed with ether, and dried. This material, cyclopentadienyl(2,2'-bipyridine)indium(III) diiodide, m.p. 198° (dec.), is soluble in acetone, acetonitrile and nitromethane, and appears to be stable over some weeks. (Found: C, 29.1; H, 2.1; N, 4.9; In, 19.5; I, 43.1. $C_{15}H_{13}N_2InI_2$ calcd.: C, 30.5; H, 2.2; N, 4.7; In, 19.3; I, 43.0%.)

1,10-Phenanthroline. Similar reactions with 1,10-phenanthroline, using dichloromethane as solvent, gave the expected $CpInI_2 \cdot Phen$, m.p. 200° (dec.). (Found: C, 33.1; H, 2.7; N, 4.1; In, 18.7; I, 41.2. $C_{17}H_{13}N_2InI_2$ calcd.: C, 33.2; H, 2.2; N, 4.6; In, 18.7; I, 41.4%.) The properties of this compound are very similar to those of the bipyridine adduct.

Results and discussion

Preparative studies

As described above, the reaction of cyclopentadienylindium(I) with iodine in freshly distilled chloroform yields the indium(III) compound $CpInI_2$. The insolubility of this substance in most common organic solvents, and its low volatility, are surprising since the simplest structure, by analogy with $RInI_2$ ($R = C_2H_5$, n-C_4H_9), would be the dimer:



The mass spectra (see below) suggest that such molecules may indeed exist, but there may be additional interactions involving bridging cyclopentadienyl groups as in Cp_3In [9]. In any case, adducts are easily formed with 2,2'-bipyridine and 1,10-phenanthroline. We were not able to carry out molecular weight measurements on these adducts in the complete absence of air, but the molar conductivities in acetonitrile (mM concn.) are low, with values of 5.7 and 8.7 $ohm^{-1} \cdot cm^2$ for the Bipy and Phen derivatives respectively (c.f. values of 90 - 130 for 1/1 electrolytes in this solvent [10]). These compounds are therefore formulated as neutral five-coordinate indium(III) monomers, an increasing number of which are now known [5 - 8]. The reaction of $CpInI_2$ and Cp_3In produces Cp_2InI, but this compound is too unstable for any derivatives to be obtained. Some difficulties were encountered in obtaining meaningful spectra of this compound.

The formation of the anion $[CpInI_3]^-$ from $CpInI_2$ is in keeping with other preparative studies of $[RInX_3]^-$ anions ($X = Cl, Br, I$; $R = CH_3, C_2H_5$, etc.) in this laboratory [11]. The molar conductivity of n-$Pr_4N[CpInI_3]$ in

TABLE 1

MASS SPECTRA OF CYCLOPENTADIENYLINDIUM(III) IODIDE COMPOUNDS

Compound	Source temp. (°C)	Predominant[a] peaks		Other peaks		Unassigned[b] (m/e)	
$CpInI_2$	100	C_5H_3	(100)				
		Cp	(29)	Cp_2	(10)	77	(17)
		In	(36)	InI_3	(7)	78	(11)
		I	(13)				
		InI	(18)				
		InI_2	(15)				
$CpInI_2 \cdot Bipy$	220	Cp	(22)			78	(24)
		In	(10)				
		I	(18)				
		Bipy	(100)				
$CpInI_2 \cdot Phen$	220	Cp	(40)	In	(5)	90	(13)
		Phen	(100)	I	(8)	154	(19)
Cp_2InI	280	Cp	(100)	In	(7)		
				I	(7)		
				Cp_2	(6)		
				InI	(6)		

[a] Relative intensities in parentheses. [b] Unassigned peaks with relative intensity greater than 10%.

nitrobenzene (mM concn.) is 26 $ohm^{-1} \cdot cm^2$, showing that the compound is a 1/1 electrolyte in this solvent (cf. values of 20 - 40 $ohm^{-1} \cdot cm^2$ reported [12] for such compounds).

Mass spectroscopy

The mass spectra of the compounds other than the involatile $(n\text{-}Pr)_4N[CpInI_3]$, are shown in Table 1. The spectra of $CpInI_2 \cdot Bipy$ and Phen are, predictably, quite similar, with the main features being the absence of a peak for InI^+, and the low intensity of the In^+ ion relative to the most abundant bidentate ligand peak. Molecular ion peaks were absent in both cases, as were $InBipy^+$ (or Phen) peaks.

A comparison of the mass spectra of $CpInI_2$ and Cp_2InI reveals some important differences. In the former, a peak of low intensity located at $m/e = 496$, due to the InI_3^+ ion, was detected, as well as InI_2^+ ions at 369. Neither peak was observed in the spectrum of Cp_2InI, although in view of the instability of this compound it would be unwise to draw structural conclusions from this. The InI_2^+ and InI_3^+ ions are also a feature of the mass spectrum [13] of In_2I_6, and we believe that their appearance in the spectrum of $CpInI_2$ is a result of the existence of iodine-bridged dimers of this compound.

Vibrational spectra

Table 2 lists the important bands in the infrared and Raman spectra of the compounds prepared in this study, together with the probable assignments. No results are given for Cp_2InI because of the instability of this substance.

The use of vibrational spectroscopy in identifying the mode of bonding of the cyclopentadienyl ligand is now well-established [14 - 16]. In *monohapto*-cyclopentadienyl derivatives, three bands between 850 - 650 cm^{-1} due to the ring (C—H) out-of-plane vibrations are generally observed; in the high frequency

TABLE 2

IR AND RAMAN BANDS OF THE CYCLOPENTADIENYLINDIUM(III) DERIVATIVES[a]

$CpInI_2$	$CpInI_2$·Bipy[b]	$CpInI_2$·Phen[b]	$[CpInI_3]^-$[c]	Assignment
	3072ms	3070ms	3045	ν(C—H) (ring)
	2965mw	2990mw	2965s	$\nu(C_1$—H)
2923w	2925mw	2925mw	2940s	
1388ms	1408s			δ(C—H)
1342s	1385s	1385m	*d*	
1155w	1105m	1105s	1095ms	ν(C—C)
1070	1072w	1078w		
1058m	1042mw		*d*	
1002w	1015ms		*d*	
983s	*d*	*d*	982s	ν(C—C)
905w	892w			ring deform
863s	871w	869m	*d*	
835w	836m		*d*	
805s	803	813m	800s	γ(C—H)
762s	746s	748ms	751s	
665mw	622m	627w	660mw	
598				
315w	325m	329m	321w	ν(In—C)
	305m	292m		ν(In—N)
		192m	190mw	
155w	176mw	186m		
139w	143m	139mw	140vs	
	138m	130mw		
	115mw	113mw	114m	
	111m	96mw		
	77w	79w		
		62w	43m	

[a] All the bands below 211 cm^{-1} are Raman bands. [b] Bands due to Bipy or Phen not shown. [c] The bands due to the cation have been subtracted. [d] Region obscured by bands of Bipy, Phen, or cation, as appropriate. Abbreviations: vs, very strong; s, strong; ms, medium strong; m, medium; w, weak.

region a ν(C—H) band at about 2950 cm^{-1} is assigned to the vibrations at the carbon bonded to the metal (C_1), in addition to ν(C—H) bands of the other ring protons. The infrared spectra (Table 2) in this region (mulls in hexachlorobutadiene) show good agreement with these criteria in each case, showing that the cyclopentadienyl ring is in the σ-bonded (*monohapto*) form. This is supported by the presence of three bands in the 800 - 600 cm^{-1} region. The presence of *monohapto*-cyclopentadienyl in these indium(III) species is in keeping with previous work on the reaction of CpIn with 1,2-bis(trifluoromethyl)dithiete (L) which yielded CpInL and adducts such as CpInL·Bipy, etc. [5]. A similar conclusion applies to the adducts CpIn·BX_3 (X = F, Cl, Br or CH_3) [4]. From this collection of results, it seems clear that the *pentahapto* stereochemistry [2,3] is peculiar to the ground state of CpIn, and that any increase in the electropositive character of the metal, either by oxidation or by electron pair donation, favours the *monohapto* form, which also occurs in Cp_3In [9].

Each compound shows a band at approx. 320 cm^{-1}, which is assigned to ν(In—C). This mode occurs at similar frequencies in Cp_3In (339, 316) [8], in Cp_3In·Bipy and Phen (290) [8], and in CpInL and its derivatives (325—340 cm^{-1} [5] L = 1,2-bis(trifluoromethyl)dithiete).

The vibrations below 200 cm^{-1} must be In—I modes in the main. For $[CpInI_3]^-$, the intense Raman band at 140 cm^{-1} must be $\nu_s(InI_3)$, which has been observed in other $[RInI_3]^-$ species; the 190 cm^{-1} vibration may be the corresponding $\nu_{as}(InI_3)$, although the frequency is higher than in analogous systems [11]. Bands at lower frequencies are presumably bending modes. In $CpInI_2$, the Raman spectrum shows two weak bands at 139 and 155 cm^{-1}, assigned to the bridging and terminal In—I stretching modes. The ratio ν(In—I)bridging/ν(In—I) terminal is 0.89, in reasonable agreement with that found in other iodide-bridged compounds of indium, (i.e., In_2I_6 0.81 [17], $MeInI_2$ 078, and Me_2InI 0.75 [8]). The spectra of the Bipy and Phen adducts are surprisingly unalike, and contain more bands in the ν(In—I) region than would be expected for an InI_2 unit. This may be the result of extensive mixing of the vibrational modes in these molecules.

NMR spectra

The low solubility of most of the compounds hindered the recording of ^1H NMR spectra. The spectrum of $CpInI_2$·Bipy in acetone showed the typical resonances of the Bipy protons, and a similar NMR spectrum was found with a dichloromethane solution of the phenanthroline adduct, for which the Cp proton resonance was at 5.83 ppm from TMS. In both cases, the resonance was a sharp singlet at room temperature; solubility restrictions prevented us from exploring the effect of temperature. The resonances of the cyclopentadienyl protons in a variety of indium(III)—*monohapto*-cyclopentadienyl compounds have been found in the 5.5 - 6.4 ppm region, depending on solvent, and in all cases the appearance of a single resonance has been ascribed to the fluxional behaviour of the ligand [5,8].

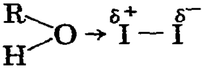
Reaction mechanism

The reaction of cyclopentadienylindium(I) with iodine in chloroform to yield $CpInI_2$ involves oxidative insertion into the I—I bond, and the present work serves to clarify the mechanism of this process. As noted above, when the reaction was carried out in the presence of a small amount of ethanol the resulting product was not $CpInI_2$ but InI, which was obtained in quantitative yield (> 99%). Similarly, when CpIn reacted with methyl iodide or trifluoromethyl iodide, indium(I) iodide was obtained in 100% yield in either the presence or absence of ethanol.

The important bonding orbitals in CpIn, following the work of Bartell et al. [3], are those involving indium p_z (or sp hybrid) with the ring carbon orbitals (a_1), and the indium p_x and p_y (e_1), with the appropriate Cp π-orbitals. We suggest that the formation of the cyclopentadienylindium(III) diiodide occurs via the interaction of the e_1 orbital of the InCp (the HOMO orbital in the Woodward—Hofmann approach) and the LUMO π^*-orbital of I_2, which have the same u-symmetry in the presumed transition state:

This state, in which electrons can flow from the InCp to the iodine, allows the formation of In—I bonds, and a concomitant weakening of the I—I bond, since the electrons are going into an I_2 antibonding molecular orbital. The symmetry requirement that the e_1 orbital of CpIn be involved in the reaction is interesting, since this orbital involves the diene form of the cyclopentadienyl group, which is the structure identified in $CpInI_2$.

The effect of ethanol on the reaction is explicable in terms of solvation of I_2. The formation of a charge transfer complex between the iodine and ethanol, of the type



$$\begin{matrix}R\\H\end{matrix}\!\!>O \rightarrow \overset{\delta+}{I} - \overset{\delta-}{I}$$

in which the iodine molecule is already polarized, would alter the orbital levels of the iodine. More importantly, the presence of a dipole in I_2 would encourage the formation of a linear transition state Cp—In—I—I, from which InI could be eliminated. With CH_3I and CF_3I, polarisation of the C—I bond is a permanent feature of the molecule, and a linear transition state is again favoured. As noted above, InI is the only product in the reaction of these substances with CpIn, in keeping with the above argument.

Reaction by-products

In certain reactions of cyclopentadienylindium(I) with iodine in the presence of added ethanol, the InI formed was filtered off and the filtrate evaporated to dryness. In all cases, the residue was a brown pasty solid, which we were unable to characterise. Dissolution of the solid in chloroform, followed by evaporation of the solvent, apparently left the material unchanged. The proton NMR spectra, recorded in $CDCl_3$, showed no resonance due to the diene protons, but rather a number of peaks due to the CH_3—CH_2—O group, and to C—CH_2—C cyclic protons. No infrared absorption due to the C=C stretching modes was detected, but a strong broad band at about 3380 cm^{-1} was observed, which may be evidence of association via intermolecular hydrogen bonding. It seems that the reactions give as primary products Cp and R (= CH_3, I, etc.) radicals, whose reactions with each other, and with the solvent, are complex. We did not pursue the identification of these organic reaction products further.

The reaction of CpIn with bromine in chloroform gave an unstable product too unstable for isolation. The reaction of stoichiometric amounts of CpIn + Br_2 + Bipy in dilute solution in chloroform yielded a solid with the ratio Br/In $\approx$ 5, suggesting bromination of either the Cp ring, or the Bipy, or both.

Acknowledgement

This research was supported by an operating grant from the National Research Council of Canada.

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