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COORDINATION COMPOUNDS OF INDIUM

XIII*. TRICYCLOPENTADIENYLINDIUM(III) AND SOME RELATED COMPOUNDS

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SUMMARY

Tricyclopentadienylindium(III) ($InCp_3$) has been prepared in high yield by the reaction of indium trichloride and cyclopentadienyllithium; adducts with monodentate and bidentate ligands are readily obtained. The mechanisms of the decomposition of $InCp_3$ to InCp, and of the reaction of InCp with air, are discussed. The related methylcyclopentadienyl species have been studied, as have indium(III)–indenyl compounds. Spectroscopic evidence shows that the indium(III) complexes all involve σ-bonded diene ligands. Fluxional behaviour is observed with the tricyclopentadienyl compounds, but not with the indenyl species.

INTRODUCTION

The preparative and structural chemistry of the organometallic compounds of indium has received relatively little attention, a situation which is in sharp contrast to the many publications dealing with compounds of the other elements of Group III. The literature on organoindium compounds up to 1967 has been reviewed by Coates and Wade[1], and more briefly by Clark and Pickard[2]. As part of a continuing programme of study on the modes of coordination of indium, we have now prepared a number of indium(I) and indium(III) compounds with cyclopentadiene and related molecules, and have established that adduct formation may occur between such indium(III) species and neutral mono- and bidentate organic ligands.

Cyclopentadienylindium(I) was first prepared by Fischer and Hofmann[3], and the electronic structure of this unusual "half-sandwich"[4,5] has been the subject of considerable discussion[3,5–7]. We may note here that InCp is the only organoindium(I) compound reported in the literature, and as such represents a possible starting point for the preparation of other indium(I) species.

One of the interesting features of the original preparative method of Fischer and Hofmann[3] is that although the starting compound is indium(III) chloride, the main product is In^ICp, with tricyclopentadienylindium(III) being obtained in only

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* For part XII see ref. 28.

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trace quantities. This is unusual, since indium(I) is generally readily oxidised to indium(III) and few stable indium(I) compounds are known[8]. We have therefore investigated this reaction, and find that $InCp_3$ can be prepared in good yield by a slight modification of the earlier method. The coordination chemistry of this compound, and of some related species, is in keeping with previous experience of both organic and inorganic complexes of indium(III).

EXPERIMENTAL

All reactions and operations were performed under dry nitrogen using conventional techniques. Infrared spectra were recorded on Perkin–Elmer 457 or Beckman IR-12 spectrophotometers, in the range 4000–250 cm^{-1}, with nujol or hexachlorobutadiene mulls between caesium iodide plates. Raman spectra were measured on a Cary 81 spectrometer, with He/Ne laser excitation, using finely ground samples in sealed tubes. ^1H NMR spectra were recorded on Varian 56/60 or XL-100 instruments. Mass spectra were obtained with a Hitachi Perkin–Elmer RMU-6E operating in the single-focussing mode at an excitation potential of 80 kV. Melting points were measured in sealed tubes under nitrogen, and are uncorrected; most of the compounds investigated underwent some decomposition at the m.p.

Carbon, hydrogen and nitrogen analyses were performed by Mr. M. K. Yang of this Department. Indium was determined either by EDTA titration, using 4-(2-pyridylazo)resorcinol as indicator, or with a Perkin–Elmer Atomic Absorption Spectrophotometer.

Preparative methods

Tricyclopentadienylindium(III). Methyllithium (1.15 g, 52.2 mmoles) in ether (25 ml) was added to freshly distilled cyclopentadiene (4.2 g, 63.7 mmoles) in ether (30 ml) at 0°, and the mixture was refluxed for 1 h. Indium trichloride (3.60 g, 16.3 mmoles) was added to the resultant heavy white precipitate of cyclopentadienyllithium, and the mixture again refluxed (4 h), after which ether was removed under vacuum and the resultant solid dried (0.01 mmHg, 2 h.). Benzene (90 ml) was added to this solid and the mixture heated to reflux. The hot solution was decanted from undissolved solid, and on cooling bright yellow crystals of tricyclopentadienylindium(III) (1.72 g) deposited. Further crystallisation raised the final total yield to 65% (3.28 g). (Found: C, 57.6; H, 4.85; In, 37.4. $C_{15}H_{15}In$ calcd.: C, 58.1; H, 4.87; In, 37.0%.)

Tris(methylcyclopentadienyl)indium(III). The above procedure was employed, using methyllithium (0.46 g, 20.9 mmoles) in ether (10 ml), freshly distilled methylcyclopentadiene (1.5 g, 22.8 mmoles) in ether (30 ml), and indium trichloride (1.38 g, 6.3 mmoles). After removal of ether from the reaction product, extraction with benzene (75 ml), followed by concentration of the extract, gave bright yellow crystals of tris(methylcyclopentadienyl)indium(III) (0.124 g, 56% yield). M.p. 124–126° (dec.). (Found: C, 58.9; H, 6.68; In, 32.4. $C_{18}H_{21}In$ calcd.: C, 60.8; H, 6.81; In, 32.3%.)

(Methylcyclopentadienyl)indium(I). With the same reagents and conditions as in the preceding paragraph, removal of ether *in vacuo* was followed by sublimation of pale yellow crystals of (methylcyclopentadienyl)indium(I) at 60–80° (0.1 mmHg). This compound proved to be extremely air-sensitive, like many other methylcyclopentadiene compounds[9] and as a result, carbon and hydrogen analyses were not possible. (Found: In, 59.9. C_6H_7In calcd.: In, 59.2%.)

Triindenylindium(III) etherate. Methyllithium (0.46 g, 20.9 mmoles) in ether (10 ml) was added to indene (2.6 g, 22.4 mmoles) in ether (30 ml) at room temperature, and the mixture refluxed (1 h). Indium trichloride (1.54 g, 7.0 mmoles) was then added and the mixture heated in refluxing ether (12 h). Ether was removed under vacuum, dichloromethane (75 ml) added, the resulting solution filtered, and dichloromethane removed from the filtrate under vacuum to give triindenylindium etherate (2.76 g, 74%) as a bright yellow glue. Attempted crystallisations from several solvent systems always produced a thick oil. (Found: C, 69.2; H, 5.62; In, 21.8. $C_{31}H_{31}InO$ calcd.: C, 69.7; H, 5.85; In, 21.5%.)

Lithium tetraindenylindate(III) etherate. The method described above, using methyllithium (0.46 g, 20.9 mmoles) in ether (10 ml), indene (2.6 g, 22.4 mmoles) in ether (30 ml) and indium trichloride (1.11 g, 5.0 mmoles), yielded, after removal of ether from the reaction mixture, a yellow intractible mass. This was washed with a mixture of petroleum ether (10 ml) and benzene (5 ml) to give a solid; refluxing in benzene and crystallisation produced pale yellow crystals of lithium tetraindenylindate(III) etherate (1.91 g, 58%), m.p. 120–125°. (Found: C, 73.9; H, 5.92; In, 17.4. $C_{40}H_{38}LiInO$ calcd.: C, 73.2; H, 5.83, In, 17.5%.)

Lithium tetraindenylindate(III). Reaction conditions and reagents described above, except for the use of benzene as solvent throughout yielded, after reduction *in vacuo* of the final volume to 20 ml at 50°, crystals of lithium tetraindenylindate(III) (1.22 g, 42%), m.p. 120–125°. (Found: C, 73.8; H, 4.80; In, 20.1. $C_{36}H_{28}LiIn$ calcd.: C, 74.2; H, 4.85; In, 19.7%.)

Adducts of tricyclopentadienylindium(III)

2,2′-Bipyridine. Tricyclopentadienylindium(III) was suspended in a solution of 2,2′-bipyridine in ether. After 3 h vigorous stirring, the resultant yellow solid was collected, washed with ether and petroleum ether, and dried. Analysis showed that this material was the 1/1 adduct of 2,2′-bipyridine and $InCp_3$, m.p. 132–140° (dec). (Found: C, 62.9; H, 4.93; N, 6.10; In, 25.3. $C_{25}H_{23}InN_2$ calcd.: C, 64.6; H, 4.97; H, 6.00; In, 24.6%.)

1,10-Phenanthroline. An analogous procedure gave in this case a red powder, 125–135° dec., identified as tricyclopentadienyl(1,10-phenanthroline)indium(III). (Found: C, 65.1; H, 4.65; In, 23.1. $C_{27}H_{34}N_2In$ calcd.: C, 66.1; H, 4.72; In 23.4%.)

Triphenylphosphine. Reaction of $InCp_3$ with an ether suspension of excess triphenylphosphine for 4 h yielded a cream coloured product, tricyclopentadienyl(triphenylphosphine)indium(III), m.p. 150–154° (dec.). (Found: C, 68.2; H, 5.25; In, 20.3. $C_{33}H_{30}InP$ calcd.: C, 69.2; H, 5.28; In, 20.0%.)

No attempts were made to prepare adducts of tris(methylcyclopentadienyl)indium or trisindenylindium(III).

DISCUSSION

Preparative studies

In addition to showing that tricyclopentadienylindium(III) can be prepared in high yield by a modification of the method of Fischer and Hofmann[3], the present work serves to clarify the reactions involved. Fischer and Hofmann suggested that the adduct $InCp_3 \cdot Et_2O$ decomposes on heating to cyclopentadienylindium(I). We have observed however that although addition of ether to $InCp_3$ does indeed lead to the formation of an etherate, this adduct is rather unstable, losing ether readily *in vacuo* at room temperature, and it therefore seems unlikely that $InCp_3 \cdot Et_2O$ can be an important reaction intermediate in the formation of the indium(I) species. Furthermore, while $InCp_3$ does decompose on heating *in vacuo* to give InCp, the yield is only significant above approx. 150°. In contrast, heating the $NaCp/InCl_3/Et_2O$ reaction mixture to ~100° readily produces cyclopentadienylindium(I), and this latter substance can be continuously obtained from the mixture by sublimation for at least 6 h. Under these reaction conditions, the yields are highest with an initial $InCl_3$/NaCp mole ratio of 1/4. Finally, we note that the yield of the indium(I) compound from the $LiCp/InCl_3/Et_2O$ reaction is much lower than from the analogous NaCp system, while the yield of $InCp_3$ is correspondingly higher.

We therefore conclude that the important reactions are:

$$InCl_3 + 3\,MCp \rightarrow In^{III}Cp_3 + 3\,MCl \qquad (1)$$

$$In^{III}Cp_3 + Cp^- \rightarrow In^{I}Cp + 3/2\,Cp_2 \qquad (2)$$

in which the formation of $In^{I}Cp$ involves reduction by the cyclopentadienyl anion. This latter reaction (2) apparently proceeds at significant rates only at temperatures well above ambient. On this basis, the difference in the $In^{I}Cp/In^{III}Cp_3$ product ratios with lithium and sodium cyclopentadienyl is seen as being due to the greater ionic character of the sodium salt, as in other Group I alkyl compounds[10].

The formation of the methylcyclopentadienyl compounds of both indium(I) and indium(III) apparently involves similar reactions, although (methylcyclopentadienyl)indium(I) can be obtained from the original reaction mixture at lower temperatures than are required in the cyclopentadienyl system. With indene, the stabilities of the indium(III) compounds appear to be enhanced. The etherate of $In^{III}(Indene)_3$ is a sufficiently strong adduct such that we were not able to obtain the uncomplexed parent compound. The four-coordinate anion, the first aromatic ligand anionic complex of indium(III) isolated, has similar stability; we suggest that the etherate of $Li[In(Indenyl)_4]$ may involve coordination of ether to the cation. Attempts to obtain fluorene analogues of the cyclopentadienyl compounds were unsuccessful, and it is possible that steric factors prevent the formation of such compounds.

The reasons underlying these different stabilities are not clear, although on the basis of earlier work on the coordination chemistry of indium(III), the relative electronegativities of the ligand anions may be an important factor[11].

Mass spectrometry

Solid source mass spectra were obtained for a number of the compounds prepared, with the results summarised in Table 1. In general, the modes of decomposition are those to be expected on the basis of the preparative work. The indium(I) compounds both give stable molecular ions, whereas the InL_3 species yield InL plus L_2 and other decomposition products. It is relevant here to note that triphenylindium(III), although it yielded no $InPh^+$ ions, does give biphenyl and related products in analogous experiments, suggesting some structural relationship between these three $In(Aryl)_3$ compounds. The phenanthroline adduct of $InCp_3$ obviously undergoes thermal decomposition on heating.

We have also briefly investigated the products formed when InCp and In-

TABLE 1

MASS SPECTRA OF CYCLOPENTADIENYLINDIUM AND RELATED COMPOUNDS

Compound	*Sample temp. (°C)*	*Principal mass peak*	*Other important mass peaks*
InCp[a]	100	*M*[c]	In^+, Cp_2^+, Cp^+
$InCp_3$	190	InCp	$InCp_2^+$, In^+, Cp_2^+, Cp^+
In(CpMe)[b]	75	*M*[c]	In^+, $CpMe^+$, Cp^+
$In(CpMe)_3$[b]	90	In(CpMe)	$In(CpMe)_2^+$, $(CpMe)_2^+$, In^+, $CpMe^+$
$LiIn(Indenyl)_4 \cdot EtO_2$	80	$Indenyl^+$	In^+, Et_2O^+, $In(Indenyl)^+$
$InCp_3 \cdot Phen$[d]	230	$InCp^+$	In^+, Cp_2^+, Cp^+, Phen decomposition products

[a] Prepared by the method of Fischer and Hofmann (ref. 3). [b] CpMe = methylcyclopentadienyl anion. [c] *M* = Molecular peak. [d] Phen = 1,10-phenanthroline.

(CpMe) were exposed to the atmosphere for approximately 1 min. In the case of cyclopentadienylindium(I), the principal mass peaks (sample temperature 250°) in the spectrum of an oxidised sample are at *m/e* 278 (In_2O_3), 164 ($(C_5H_5OH)_2$), 130 (Cp_2), 115 (In) and 82 (C_5H_5OH). This suggests that the reactions are:

$$InCp + O_2 \rightarrow [O(InCp)_2] \rightarrow In_2O_3 + (C_5H_5OH)_2$$

For a sample of the methylcyclopentadienyl compound similarly treated, the mass spectrum was of low intensity (sample temperature 310°), but a peak at *m/e* 96 corresponds to $CH_3C_5H_4OH$, in keeping with the above scheme.

Adducts of tricyclopentadienylindium(III)

Trimethylindium(III) and the alkyl–indium halides are known to form adducts with both monodentate and bidentate donors[1,2,12,13]. Cyclopentadienylindium(I) has no detectable acceptor property, but the tris-compound readily forms $InCp_3 \cdot Bipy$, $InCp_3 \cdot Phen$ and $InCp_3 \cdot Ph_3P$ (Bipy = 2,2′-bipyridine, Phen = 1,10-phenanthroline): we were unable to obtain a stable adduct with pyridine. The stereochemistry of these compounds presumably involves 5-coordinate indium(III) with the bidentate donors, and 4-coordination in the case of triphenylphosphine. Solutions of these adducts in nitromethane or nitrobenzene were always cloudy, and conductivity measurements were therefore not attempted. As noted above, the compound $In(Indenyl)_3 \cdot Et_2O$ has high thermal stability. In these respects, the behaviour of the tridienyl compounds of indium appears to fit nicely with the well-established acceptor behaviour of indium(III) compounds.

Vibrational spectroscopy

The vibrational spectra of the cyclopentadienide anion, and of a large number of its complexes with metals, have been reviewed in some detail by Fritz[14]. We follow his analysis in general.

For cyclopentadienylindium(I), we find bands at 3070 vw, 1430 w(br), 998 m, 765 s, 737 m, and 720 ms cm^{-1} in the infrared, very similar to the results quoted by Fritz for TlCp, for which a "centrally σ-bonded" structure is favoured. This agreement is in keeping with the known solid state structure[4] of InCp. The spectra of samples deliberately exposed to the atmosphere showed a strong broad band at 720–780 cm^{-1}, and absorptions at ~400 and 300 cm^{-1} which increased in intensity with exposure time. These latter two low frequency bands can be readily assigned to ν(In–C) and ν(In–O) modes of the proposed decomposition products (see above). The instability of the methyl analogue was such that no infrared spectra could be obtained.

The infrared and Raman spectra of tricyclopentadienylindium(III) show a large number of bands:

InCp$_3$: IR; 3060 vw(br), 1610 w(br), 1354 s, 1074 s, 1056 m, 1044 s, 988 s, 972 s, 905 s, 884 s, 855 s, 834 s, 819 m, 799 m, 785 s, 748 s, 739 s, 622 m, 602 s, 339 s, 316 m, 282 m cm^{-1}. Raman; 3090, 3074, 3062, 3038 (all w), 1465 m, 1414 s, 1354 s, 1336 s, 1108 s, 1068 m, 906 w, 850 w, 835 m, 812 vs, 788 m, 624 vs, 593m, 338m, 322 s, 283 s, 115 w cm^{-1}. For the methyl analogue, the Raman spectrum showed an unusually high background, so that the results are certainly incomplete, but within this limitation there is general agreement with the data for InCp$_3$:

In(CpMe)$_3$: IR; 3065 w(br), 1410 m, 1072 mw, 1024 m(br), 998 s, 920 mw, 865 m, 844 m, 804 s(br), 786 vs, 739 m, 608 s, 349 m, 322 m cm^{-1}. Raman; 927 w, 795 m(br), 622 m, 610 m, 347 (sh), 329 m, 248 m cm^{-1}. The present infrared spectrum of InCp$_3$ is similar to, but more complex than, that published by Fritz, who argues that the compound involves σ-bonded diene-type organic ligands in the solid state. This conclusion is in agreement with other evidence in the present paper, and with the spectroscopic similarities between InCp$_3$ and HgCp$_2$, for which a diene-ligand structure is indicated[15]. The results of X-ray crystal structure investigations of InCp$_3$ should eventually allow a detailed analysis of these vibrational spectra.

No attempt has been made to assign the spectra of the indenyl compounds, or of the adducts of InCp$_3$, in detail; the bands observed in the ν(In–C) region, which Fritz gives as 309 cm^{-1} in InCp$_3$, are shown in Table 2. These frequencies are similar to those assigned by Samuel and Bigorgne[16] to the Raman-active ν(Hg–C) modes of HgCp$_2$ and Hg(Indenyl)$_2$ (345 and 370 cm^{-1}). Both these latter species are formulated as σ-bonded complexes. The increase of approximately 30 cm^{-1} in the highest frequency ν(In–C) mode of [In(Indenyl)$_4$]$^-$ over InCp$_3$ is also similar to the comparable $\Delta\nu$ in the mercury complexes. The almost identical vibrational spectra of Li[In(Indenyl)$_4$] and LiIn(Indenyl)$_4$·Et$_2$O in this region support the suggestion made

TABLE 2

ν(In–C) VIBRATIONS IN TRICYCLOPENTADIENYLINDIUM(III) AND RELATED COMPOUNDS

Compound	*Infrared*	*Raman*
InCp$_3$	339 s, 316 m (282 m)[a]	338 m, 322 s (283 s)
In(CpMe)$_3$	349 m, 322 s	347 (sh), 329 m
InCp$_3$·Ph$_3$P	321 s, 303 w	322 m, 308 s
InCp$_3$·Bipy	290 m(br)	325 m, 300 s
InCp$_3$·Phen	293 m(br)	[b]
Li[In(Indenyl)$_4$]	371 s, 352 m, 340 m (270 w)	352 vs
LiIn(Indenyl)$_4$·Et$_2$O	371 s, 351 m, 340 (sh) (280 w)	354 vs (197 m)

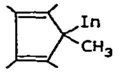
[a] Values in parentheses are probably deformational modes of the In–C kernel. [b] Could not be obtained.

above that the ether molecule is associated with the cation rather than being part of a 5-coordinate anionic complex.

NMR spectroscopy

The room temperature ^{1}H NMR spectra of all the compounds prepared, with the exception of the unstable (methylcyclopentadienyl)indium(I), are shown in Table 3.

The presence of a single proton resonance in the spectrum of InCp and InCp$_3$, and the adducts of the latter, implies that the cyclopentadienyl ring is fluxional in these molecules in solution. No change was observed on lowering the temperature to $-70°$, and for InCp$_3$, spectra at $-90°$ in methylene dichloride still showed only a single resonance. The "ring-whizzing" process is apparently dominant even at these temperatures. Fluxional behaviour has also been reported[17] for HgCp$_2$ and CpHgX (X = Cl, Br, or I). The instantaneous structure of the σ-bonded diene ligand of HgCp$_2$ in tetrahydrofuran solution was only observed at $-140°$.

With In(CpMe)$_3$ in chloroform, the solution was unstable even at room temperature, with visible precipitation occurring rapidly; the simplest interpretation of the spectra is in terms of 

groups, as postulated by Fritz and Kreiter[18] for Sn(CpMe)$_4$. The instability of the solution prevented an investigation of this in detail; the co-existence of ligand isomers in methylcyclopentadienyl complexes has also been reported[19].

The three indium indenyl species show very similar spectra; the frequency changes observed, especially in the case of Li[In(Indenyl)$_4$] are probably due to changes in bulk susceptibility, since the difference in frequency between the triplet and doublet is constant throughout at approx. 45 Hz. The coupling constants in both doublet and triplet are the same within experimental error for all three compounds, with J 3.0 Hz.

The NMR spectrum of the indenyl ion has been discussed by Schaefer and

TABLE 3

NMR SPECTRA OF CYCLOPENTADIENYL AND INDENYL COMPLEXES OF INDIUM IN CDCl$_3$ AT ~35° (Hz FROM EXTERNAL TMS, AT 60 HMz)

Compound	*5-Membered ring resonances*[a]	*Other resonances*
InCp	368 s	
InCp$_3$	356 s	
In(CpMe)$_3$	362 m(6) 342 m(6)	134 s(9) CH$_3$
InCp$_3$ · Ph$_3$P	358 s(25)	445 m(18) C$_6$H$_5$
InCp$_3$ · Bipy	359 s(15)	440–520 m(8) Bipy[b]
InCp · Phen[d]	333 s(15)	470–560 m(8) Phen[c]
In(Indenyl)$_3$ · OEt$_2$	353 t(3) 306 d(6)	428 m(12) phenyl 189 q(4), 55 t(6) Et$_2$O
Li[In(Indenyl)$_4$]	370 t(4) 327 d(8)	443 m(16) phenyl
LiIn(Indenyl)$_4$ · Et$_2$O	354 t(4) 304 d(8)	429 m(16) phenyl 187 q(4), 50 t(6) Et$_2$O

[a] s = Singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Values in parentheses are relative integrated intensities. [b] *Cf.* ref. (20). [c] *Cf.* ref. (21). [d] Spectrum recorded in tetrahydrofuran solution.

Schneider[22], and by Fritz and Kreiter[23]. Cotton and his co-workers[24] have examined the spectrum of $(\pi\text{-}C_5H_5)Fe(CO)_2$(1-Indenyl), and have shown that the absence of fluxional behaviour in the indenyl five-membered ring confirms a 1,2-shift mechanism in the "ring-whizzing" of σ-bonded cyclopentadienyl compounds[25]. Fluxional behaviour has however been reported for Me_3MCp (M = Si, Ge or Sn)[26] and for $Hg(Indenyl)_2$[27]. In all these compounds, the metal is believed to be bonded at the 1-(or 3-) position, undergoing exchange between these two sites.

Comparison of our spectra with that published by Cotton, Musco and Yagupsky[24] shows clearly that the indium(III) indenyl complexes do not have the metal statically bonded to the 1-position of the indenyl group. The coupling constants are close to those in the indenyl anion. Comparison with studies of other main group indenyl species quoted above[26,27] implies that the complex may be undergoing rapid 1,3 exchange at 35°. Further work on this problem is planned.

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