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CYCLOPENTADIENYLS $(CH_3)_2M—\sigma\text{-}C_5H_5$ OF INDIUM, ANTIMONY AND BISMUTH

PETER KROMMES and JÖRG LORBERTH
Fachbereich Chemie der Philipps-Universität, D-3550 Marburg/Lahn, Lahnberge (B.R.D.)
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Summary

The reaction of Me_3In with monomeric cyclopentadiene yields the stable Me_2InCp (I): the same product may be obtained by the reaction of $(Me_2InNMe_2)_2$ with C_5H_6 via a soluble adduct $Me_2InCp \cdot HNMe_2$ (II) which is easily converted into Me_2InCp, for which a polymeric structure is suggested.

Reactions of Me_2SbNMe_2 and $Me_2BiN(Me)SiMe_3$ with C_5H_6 afford thermally labile cyclopentadienyls Me_2SbCp (III) and Me_2BiCp (IV). Compounds I-IV have been studied through IR, ^1H NMR and mass spectroscopy; the cyclopentadienyl ligand is σ-bonded to the metals in Me_2SbCp and Me_2BiCp.

Introduction

Interest in cyclopentadienyl-Group IIIB compounds, $R_2M—Cp$ (Cp = cyclopentadienyl), has so far focussed on derivatives of boron [1], aluminium [2-4] and thallium [5]. The structure and bonding in these compounds vary considerably among members of this series, and our work was intended to fill the gap for gallium and indium.

Results and discussion

The simple method of preparation available for Me_3In [6] allows extensive use of this reagent, as in reactions 1-3:

$$\underset{}{Me_3In + C_5H_6 \rightarrow \underset{(I)}{Me_2InCp} + CH_4} \qquad (1)$$

$$\begin{aligned} &2\,Me_3In + 2\,HNMe_2 \rightarrow 2\,Me_3In \cdot HNMe_2 \\ &2\,Me_3In \cdot HNMe_2 \xrightarrow{T} (Me_2InNMe_2)_2 + 2\,CH_4 \end{aligned} \qquad (2)$$

$$(Me_2InNMe_2)_2 + 2\,C_5H_6 \rightarrow \underset{(II)}{2\,Me_2InCp \cdot HNMe_2} \qquad (3)$$

In reaction 1 $\mathrm{Me_3In}$ was treated with freshly distilled $\mathrm{C_5H_6}$ in toluene for a prolonged period . Methane was gradually evolved and a colourless precipitate was formed which analyzed correctly for $\mathrm{Me_2InCp}$ (I).

The ^{1}H NMR spectrum of I in DMF (slow dec.) shows only two resonances in an intensity ratio of 6/5 for methyl and cyclopentadienyl protons: $\delta(\mathrm{In{-}CH_3})$ -1.25 ppm; $\delta(\mathrm{In{-}C_5H_5})$ $+5.63$ ppm; TMS was used as an external standard. The presence of a singlet for the cyclopentadienyl ring protons indicates rapid rotation of the ring, providing another example of a fluxional molecule in solution.

The inertness of I towards air, and its insolubility in non-polar solvent suggested a polymeric structure such as that in $(\mathrm{Me_2AlCp})_n$ [3]; the IR-spectrum shows comparatively few absorptions as one would expect for a model compound with C_{5v}-symmetry for the $\mathrm{C_5H_5}$-anion. The main absorptions (cm^{-1}) in the low-frequency region are: 700 s, $\delta(\mathrm{CH_3{-}In})$; 530 s, $\nu_{as}(\mathrm{InC_2})$; 410-470 s-m(br), $\nu_s(\mathrm{InC_2})$; 330 m $\nu(\mathrm{In{-}C_5H_5})$.

Unfortunately we failed to obtain a reasonable Raman spectrum of I.

The mass spectrum of I at 25°C/70 eV shows no masses higher than the molecular ion at *m/e* 210; fragmentation occurs with the appearance of peaks at *m/e* 195 (MeInCp), 180 (InCp), 145 ($\mathrm{Me_2In}$), 130 (MeIn) and 115 (In). The spectrum is rather similar to those of other σ-bonded cyclopentadienyls of the typical elements [7,8].

Compound I was also obtained in reactions 2 and 3; evidence for the four-coordinate adduct II of medium stability is provided by spectroscopic studies: an H—N absorption in the IR and signals for $\mathrm{HNMe_2}$ groups in the ^{1}H NMR spectra strongly support a formula $\mathrm{Me_2InCp \cdot HNMe_2}$, although analytical data vary considerably with different ways of isolating II, which is completely soluble in toluene. Evaporation of the solvent, prolonged drying in vacuo, redissolving in toluene and filtration yielded, identical to I, colourless, insoluble $\mathrm{Me_2InCp}$ in a 90% yield.

Our efforts to prepare $\mathrm{Me_2GaCp}$ by use of reactions analogous to 1-3 were unsuccessful*; a small scale reaction according to eqn. 4 yielded decomposition products:

$$\mathrm{Me_2GaCl \cdot OEt_2 + LiC_5H_5 \xrightarrow[T]{THF} dec.\ products} \qquad (4)$$

Only a few cyclopentadienyls of the Group VB elements are known [9], e.g. $\mathrm{MCp_3}$ (M = As [10], Sb [11], Bi [11]); $\mathrm{M(C_5H_4{-}CH_3)_3}$ (M = Bi [10]); $\mathrm{Sb_2Cp_4}$ [10] and $\mathrm{Cp_2BiCl}$ [10]. The thermal stability of $\mathrm{MCp_3}$ derivatives decreases with variation of the metal from arsenic to bismuth, and different types of bonding, σ and π bonded ligands, have been suggested [11]. Attempts to prepare mixed phenylcyclopentadienyls of bismuth failed due to symmetrisation reactions similar to those occurring with mixed alkylarylstibines [10,11]:

$$\mathrm{Ph_2BiCl + NaCp \xrightarrow[-NaCl]{THF} (Ph_2BiCp) \xrightarrow{3\times} 2\ Ph_3Bi + BiCp_3} \qquad (5)$$

We have synthesized dialkylcyclopentadienyl metal compounds of antimony

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* The preparation of $\mathrm{Me_2GaCp}$ was recently reported [26].

and bismuth by reactions 6 and 7:

$$\mathrm{Me_2SbNMe_2 + C_5H_6 \xrightarrow[-T]{Et_2O} \underset{(III)}{Me_2SbCp} + HNMe_2} \tag{6}$$

$$\mathrm{Me_2BiN(Me)SiMe_3 + C_5H_6 \xrightarrow[-T]{Et_2O} \underset{(IV)}{Me_2BiCp} + HN(Me)SiMe_3} \tag{7}$$

Compounds III and IV are readily soluble in degassed, dry, aprotic solvents, such as benzene, ether and toluene, in which they decompose after a short period at room temperature; the initial yellow colour turns to brown-black. Both compounds are prone to hydrolysis and are air-sensitive; they may be sublimed in high vacuum onto a cold surface (−80°C) in moderate yield, but storage at room temperature leads to quick decomposition. The ^{1}H NMR spectra in benzene with TMS as internal standard show resonances in the correct integration ratio of 6/5 for Me_2SbCp at +0.6 ppm ($\delta(CH_3Sb)$), +5.95 ppm ($\delta(Sb{-}C_5H_5)$), and for Me_2BiCp at +0.85 ppm ($\delta(CH_3Bi)$), +5.98 ppm ($\delta(Bi{-}C_5H_5)$). Both spectra indicate a low activation enthalpy of the order of a few cal/mol for the rotation of the cyclopentadienyl ring along the metal—carbon axis. This phenomenon has been widely observed, e.g. for $MeHg{-}\sigma\text{-}C_5H_5$ [8].

The mass spectra of Me_2SbCp (III) and Me_2BiCp (IV) are listed in Tables 1 and 2. The spectrum of IV obtained with a direct inlet system (at 25°C/20 eV or 70 eV, respectively) consists in the high mass region only of a few peaks: Bi^+ at *m/e* 209, BiH^+ 210, $MeBi^+$ 224, Me_2Bi^+ 239 and Me_3Bi^+ 254; no molecular ion was found*. The spectrum of Me_2SbCp could be similarly interpreted.

TABLE 1

MASS SPECTRUM OF Me_2BiCp, 70 eV/25°C

I/base (%)	Mass	Ion
15	65	$C_5H_5^+$
23	66	$C_5H_6^+$
2	127	$C_{10}H_7^+$
1	128	$C_{10}H_8^+$
1	129	$C_{10}H_9^+$
1	130	$C_{10}H_{10}^+$
0.2	142	$C_{10}H_7{-}CH_3^+$
100	209	Bi^+
1	221	BiC^+
2	222	$BiCH^+$
6	223	$BiCH_2^+$
38	224	$BiCH_3^+$
41	239	$Bi(CH_3)_2^+$
18	254	$Bi(CH_3)_3^+$
38	274	$BiC_5H_5^+$
42	289	$CH_3BiC_5H_5^+$
10	304	$(CH_3)_2BiC_5H_5^+$
29	336	$BiC_{10}H_7^+$
50	351	$CH_3BiC_{10}H_7^+$
44	366	$(CH_3)_2BiC_{10}H_7^+$

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* *Note added in proof:* Under strictly low-temperature conditions and nitrogen atmosphere a freshly sublimed sample of Me_2BiCp, investigated by the direct insertion probe, yielded exactly the same spectrum as listed in Table 1.

TABLE 2

MASS SPECTRUM OF Me_2SbCp, 70 eV/25°C

I/base (%)	Mass	Ion
84	65	$C_5H_5^+$
100	66	$C_5C_6^+$
1	136	$CH_3{}^{121}Sb^+$
≈1	138	$CH_3{}^{123}Sb^+$
5	151	$(CH_3)_2{}^{121}Sb^+$
2	153	$(CH_3)_2{}^{123}Sb^+$
2	186	$^{121}SbC_5H_5^+$
1	188	$^{123}SbC_5H_5^+$
3	201	$CH_3{}^{121}SbC_5H_5^+$
2	203	$CH_3{}^{123}SbC_5H_5^+$
≈0.5	216	$(CH_3)_2{}^{121}SbC_5H_5^+$
≈0.5	218	$(CH_3)_2{}^{123}SbC_5H_5^+$

Problems arise with spectra of Me_2BiCp scanned with a gas-inlet system HTE Varian (at 250°C/20 eV or 70 eV, respectively) connected to a Varian Master 711. Though no metastable transitions were observed in these spectra, detailed investigations of the mass spectroscopic behaviour of metal cyclopentadienyls MCp_3 and MCp_4 [12] are helpful in the discussion of fragmentation patterns. In addition to the known fragmentation:

$MCp_3^+ \rightarrow MCp_2^+ + Cp^\bullet$

dialkylcyclopentadienyl metals follow two different decomposition paths on electron bombardment:

$Me_2MCp^+ \rightarrow Me_2M^- + Cp^\bullet$

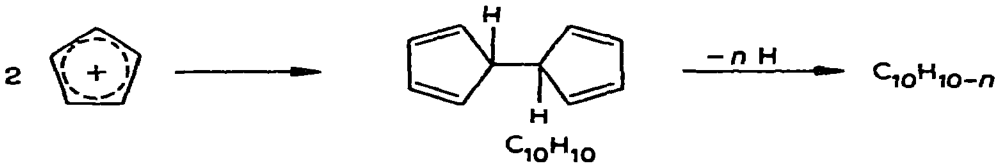
$Me_2MCp^+ \rightarrow MeMCp^+ + Me^\bullet$ etc.

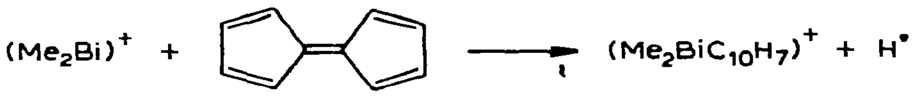
In compound IV both radicals, $CH_3^\bullet$ and $C_5H_5^\bullet$, may be formed, and give peaks in the spectra arising from recombination products formed in the 250°C gas-storage of the HTE-system.

Thus, the recombination products from the methyl radicals are, in addition to the low-mass hydrocarbons, fragments such as $C_5H_4{-}CH_3^+$ and $C_{10}H_7{-}CH_3^+$; moreover, reactions of the cyclopentadienyl radical, which have been studied in detail [13], lead to fulvalenes, which in turn combine with Me_2Bi-, MeBi- and Bi-moieties to give the corresponding organometallic fulvalenes $Me_2BiC_{10}H_7^+$, $MeBiC_{10}H_7^+$ and $BiC_{10}H_7^+$.

It is known that pyrolysis of nickelocene yields mainly cyclopentadiene, naphthalene and 9,10-dihydrofulvalene; a comparison of the mass spectrum of naphthalene with that of Me_2BiCp rules out the possible existence of bismuth naphthalide ions.

It is suggested, that in a first step the cyclopentadienyl radical forms its dimer, viz. 9.10-dihydrofulvalene, which by a series of dehydrogenation reactions and/or migration of hydrogen atoms yields $C_{10}H_{10-n}$, thus leading to the formation of organometallic fulvalenes:





The formation of similar hydrocarbons was reported by Müller [12], and metastable transitions have been observed for the process:

$AsCp_2^+ \rightarrow C_{10}H_9^+ + AsH$

The metal-bonded C_5H_5 group is attacked in a different way by a cyclopentadienyl radical, with consecutive abstraction of hydrogen atoms:

$Me_2BiCp^+ + Cp^\bullet \rightarrow Me_2BiC_5H_4{-}C_5H_5^+ + H^\bullet$

Both mechanisms are open to objections; the mass spectrum of 9,10-dihydrofulvalene, as reported by Hedaya [13], does not show fulvalene ions formed by the abstraction of hydrogen atoms, a surprising fact, which argues strongly against such abstraction. More generally, the possibility of the existence of C_5H_5 radicals must be examined by comparing the mass spectrum of Me_2BiCp with that of Me_3PbCp, which was obtained in reaction 8 in high yield:

$$Me_3PbN(SiMe_3)_2 + Cp{-}H \rightarrow Me_3PbCp + HN(SiMe_3)_2 \qquad (8)$$

The Me_3PbCp, which is a known compound [14,15], should serve as a model compound for the formation of methyl and cyclopentadienyl radicals; however, no ions for $C_{10}H_{10-n}$ groups are observed (see Table 3). We prefer a mechanism wherein a four-coordinate bismuth ion, e.g. $(Me_2BiCp_2)^+$, undergoes fragmentation as listed in Table 1. It is of interest to note that the 70 eV spectrum of Me_2BiCp shows Bi^+ as the base peak, whereas $Me_2BiC_{10}H_7^+$ is the base peak in the spectrum of the same compound at 20 eV.

We have confirmed our suggestion by repeated sublimation of Me_2BiCp at 10^{-3} mm Hg/40°C and examination of the sublimed materials by ^1H NMR; under these mild conditions no organobismuth-fulvalenes are formed, and therefore the reaction seems to be restricted to pyrolytic and catalytic effects occurring in the inlet system of the mass spectrometer.

IR spectra of Me_2SbCp (III) and Me_2BiCp (IV) were recorded with capillary films on KBr discs; the data and vibrational assignments are listed in Table 4.

TABLE 3

MASS SPECTRUM OF Me_3PbCp, 70 eV/25°C

I/base (%)	Mass	Ion
11	65	$C_5H_5^+$
100	66	$C_5H_6^+$
5	132	$(C_5H_6)_2^+$
99	208	$^{208}Pb^+$
37	223	$CH_3{}^{208}Pb^+$
8	238	$(CH_3)_2{}^{208}Pb^+$
99	253	$(CH_3)_3{}^{208}Pb^+$
96	273	$^{208}PbC_5H_5^+$
1	288	$CH_3{}^{208}PbC_5H_5^+$
2	303	$(CH_3)_2{}^{208}PbC_5H_5^+$
4	318	$(CH_3)_3{}^{208}PbC_5H_5^+$

TABLE 4

IR DATA FOR Me_2SbCp AND Me_2BiCp

Me_2SbCp [a]	Me_2BiCp [a]	Mode
3090 (sh)	3090 (sh)	ν (C—H) (ring)
3078 w	3075 m	
3050 w	3060 (sh)	
2970 w	2985 m	ν_{as} (C—H)
2895 m	2900 m	ν_s (C—H)
1615 w (br)	1610 w (br)	ν (C=C) (ring)
1448 m	1435 m-s	δ (C—H) (ring)
1398 vw	1415 m-s	
1376 w	1378 m	δ_{as} (CH_3)
1290 vw	1295 vw	δ (C—H) (ring) δ_s(CH_3) + ring def.
1220 vw	1234 vw	
1196 w	1145 (sh)	
	1135 w	
1080 w	1074 w	δ $(\overset{\mathrm{H}}{\mathrm{C}}\text{—})$ (ring)
1015 w	1024 m	
990 w	988 w	δ (CH) (ring)
954 w	960 m	
915 s		
891 s	865 s	δ (ring)
814 w	810 vw	ρ (CH_3)
755 (sh)	765 (sh)	π (C—H) (ring)
733 vs	735 vs	ρ (CH_3)
710 (sh)	720 (sh)	π (C—H) (ring)
625 m	614 s	γ (C—H)
507 s	450 s	(ν_s/ν_{as}) (MC_2)

[a] vw = very weak; w = weak; (sh) = shoulder; m = medium; s = strong; vs = very strong; (br) = broad.

Raman spectra of III and IV were not available due to their thermal instability, but the many IR absorptions show that both compounds are of low symmetry and thus a C_{5v}-model for the cyclopentadienyl ring, which would give only a few absorptions for the ligand, is not applicable [16]. The spectra, in fact, resemble a large part of the cyclopentadiene spectrum [17] with additional absorptions arising from Me_2M vibration modes; the published spectra of Me_2TlCp [18] and MeHgCp [8] were valuable for the analyses. Unfortunately, the use of KBr discs precludes identification of metal—ring stretching frequencies, which are located around 330 cm^{-1} [8,18].

The literature on metal—carbon vibration modes $\nu(MC_2)$ and $\nu(M_2C)$ covers a wide range of compounds [19-21]: SbC_2stretching frequencies are consistently observed around 500 cm^{-1}, BiC_2-stretching frequencies at 450 cm^{-1}. In the IR spectrum of Me_2SbCp and Me_2BiCp, as in many cases, $\nu_{as}(MC_2)$ and $\nu_s(MC_2)$ are degenerate modes and only one absorption band is observed; this "heavy atom" effect for antimony and bismuth is emphasized by Maslowsky [22] and has important structural implications for the organometallic chemistry of these metals.

Experimental

The spectroscopic equipment used is described elsewhere [8]. Elemental analyses were performed by A. Bernhardt, Analytical Laboratory, 5251 Elbach über Engelskirchen (W. Germany). Me_3In [6], $(Me_2InNMe_2)_2$ [23], Me_2SbNMe_2 [24] and $Me_2BiN(Me)SiMe_3$ [25] were prepared following standard literature procedures; monomeric cyclopentadiene was obtained by crack-distillation of the cyclopentadiene dimer.

Preparation of Me_2InCp (I)

(a) 2.03 g (12.7 mmol) Me_3In, sublimed in vacuo into a Schlenk tube, were dissolved in 15 ml dry toluene and 0.88 g (13.0 mmol) C_5H_6 were added. Stirring for 48 h at room temperature yielded methane and a white precipitate which was filtered off, washed with toluene and dried in vacuo. M.p. (uncorr.) 195°C (dec.). Yield: 73%. (Found: C, 39.62; H, 5.14. $C_7H_{11}In$ calcd.: 40.0; H, 5.24%.

(b) A solution of 1.5 g (4 mmol) $(Me_2InNMe_2)_2$ and 0.55 g (8.3 mmol) C_5H_6 in toluene was stirred for 3 days at room temperature; the solution was pink coloured, no precipitate was formed. Gentle removal of solvent afforded a pink solid which decomposed with KOH to give Me_2NH. Redissolving in toluene yielded a pink-coloured solution and an insoluble, white compound, identical to Me_2InCp prepared according to (a).

Preparation of Me_2SbCp (III)

A mixture of 2.5 g (12.8 mmol) Me_2SbNMe_2 in 5 ml dry ether with 0.85 g (12.8 mmol) C_5H_6 was made up at −196°C and slowly warmed to −80°C. A pale-yellow precipitate was formed. The mixture was stirred for an additional 30 min. Removal of all volatile products at −80°C in vacuo yielded a pale-yellow solid, which becomes a liquid at ca. −40°C. Me_2SbCp (III) is extremely air and moisture sensitive, and decomposes rapidly at room temperature and on exposure to light. Yield: 2.11 g (76.3%). (Found: C, 38.57; H, 4.96; Sb, 55.93. $C_7H_{11}Sb$ calcd.: C, 38.75; H, 5.08; Sb, 56.17%.) The mass spectroscopic molecular weight was 216 (for ^{121}Sb).

Preparation of Me_2BiCp (IV)

0.354 g (5.35 mmol) C_5H_6 and 5 ml dry ether were condensed onto 1.83 g (5;35 mmol) $Me_2BiN(Me)SiMe_3$ at −190°C. Stirring of the components was continued for 1 h at −80°C, and a yellow precipitate was formed. This was filtered off at low temperature. Purification was achieved by high-vacuum sublimation of Me_2BiCp onto a cold surface (−78°C). Yield: 0.81 g (49.6%). (Found: C, 27.62; H, 3.78; Bi, 68.31. $C_7H_{11}Bi$ calcd.: C, 27.63; H, 3.62; Bi, 68.75%.) Mol. wt. (mass): 304.

Preparation of Me_3PbCp

A mixture of 12.4 g (30 mmol) $Me_3PbN(SiMe_3)_2$ with a large excess (ca. 15 ml) of freshly distilled monomeric C_5H_6 was kept for 12 h at −10°C; volatiles were removed at reduced pressure yielding a yellow-brown, crystalline solid of m.p. −5°C in quantitative yield. The IR and ^1H NMR data agreed with published values [14,15].

Sublimation at 10^{-3} mm Hg and 40-50°C decreases the yield drastically to about 50%, yielding bright-yellow crystals with the same chemical and spectroscopic characteristics as the "crude" product.

(Found: C, 30.53; H, 4.48; Pb, 64.92. $C_8H_{14}Pb$ calcd.: C, 30.28; H, 4.42; Pb, 65.30%.)

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