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CYCLOPENTADIENYLS OF THE GROUP VB ELEMENTS. DIMETHYLARSENIC-σ-CYCLOPENTADIENYL, Me_2AsCp

PETER KROMMES and JÖRG LORBERTH

Fachbereich Chemie der Philipps Universität Marburg, D 3550 Marburg/Lahn, Lahnberge (B.R.D.)

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Summary

The reaction of Me_2AsNMe_2 with monomeric C_5H_6 at low temperature in the presence of Me_3SnCl gives the thermally labile Me_2AsCp in 50% yield. The IR spectrum confirms that the product contains a σ-bonded *monohapto*-C_5H_5 ligand; ^1H NMR spectrum shows a marked temperature dependence. The mass spectrum is reported. Unsuccessful attempts were made to prepare $MeAsCp_2$ and $MeSbCp_2$ in a similar reaction from $MeAs(NMe_2)_2$ or $MeSb(NMe_2)_2$, respectively.

Introduction

Recently we described the preparation and spectroscopic investigation of the hitherto unknown, thermally unstable cyclopentadienyls Me_2SbCp, Me_2BiCp and polymeric Me_2InCp [1]. These compounds were made by the amine-elimination process:

$$Me_2M{-}NR_1R_2 + H{-}Cp \rightarrow Me_2M{-}Cp + HNR_1R_2$$

$(M = In, Sb, R_1 = R_2 = CH_3; M = Bi, R_1 = CH_3, R_2 = SiMe_3)$

When we extended this reaction to aminoarsines, the preparation of pure $Me_2As{-}σ{-}Cp$ was complicated by the long time needed for complete reaction of monomeric cyclopentadiene with Me_2AsNMe_2*. The dimeric cyclopentadiene formed as a byproduct could not be removed by fractional distillation. Carrying out the reaction under reflux, in order to speed up the reaction, led to decomposition of the extremely sensitive product.

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* Me_2AsCp was also reported [3].

Results and discussion

Pure Me_2AsCp was prepared at low temperature in high yield from the spontaneous reaction which occurred when Me_3SnCl and Me_2AsNMe_2 in a 1/1 molar ratio were added to the reaction mixture. A precipitate of $Me_3SnCl \cdot HNMe_2$ was formed:

$$Me_2AsNMe_2 + Me_3SnCl + H{-}Cp \xrightarrow[\text{low temp.}]{Et_2O} Me_2AsCp + Me_3SnCl \cdot HNMe_2$$

This method also proved to be very useful when we prepared organoarsenic compounds from aminoarsines with substrates of low hydrogen acidity, e.g. with diazoalkanes to give arsenicdiazoalkanes [2] of the type $(R_2As)_2CN_2$, $R_2AsC(N_2)R'$, $RAs[C(N_2)R']_2$, $RAs(NMe_2)C(N_2)R'$, $(Me_2N)_2AsC(N_2)R'$ or $(Me_2N)As[C(N_2)R']_2$.

TABLE 1

MASS SPECTRUM OF $(CH_3)_2AsC_5H_5$, at 70 eV

I/base	*m*/*e*	Ion
15.9	65	$C_5H_5^+$
18.9	66	$C_5H_6^+$
79.9	79	$C_5H_4CH_3^+$
4.1	90	CH_3As^+
7.0	105	$(CH_3)_2As^+$
27.6	140	$AsC_5H_5^+$
100.0	155	$CH_3AsC_5H_5^+$
96.4	170	$(CH_3)_2AsC_5H_5^+$

$Me_2AsC_5H_5$ was identified by its elemental analysis (see Experimental), ^1H NMR, mass and IR spectra; data are listed below or in Tables 1 and 2. The mass spectrum of $Me_2AsC_5H_5$ is shown in Fig. 1.

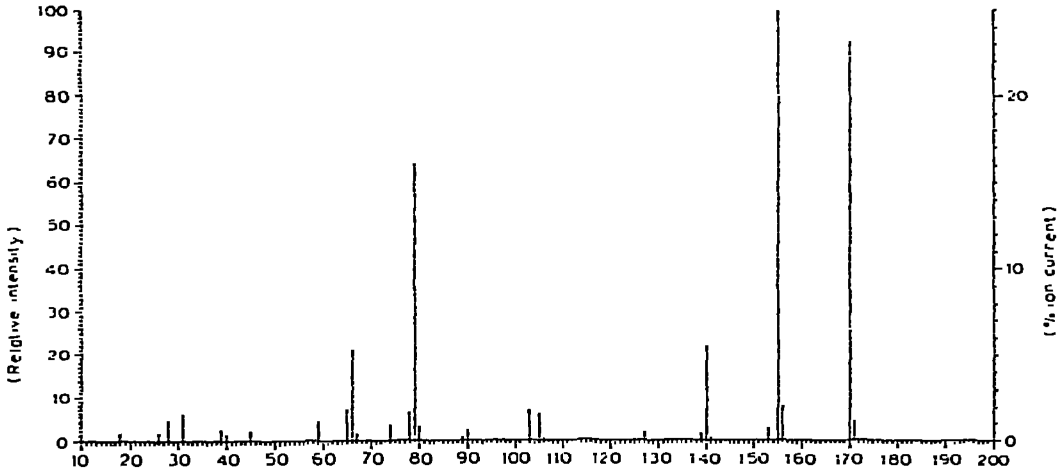

Fig. 1. Mass spectral peaks of $Me_2AsC_5H_5$ (mol. wt. 170) at 70 eV.

TABLE 2

IR DATA (cm^{-1}) FOR $Me_2AsC_5H_5$. CAPILLARY FILM, CsI DISCS

Absorption	Vibrational mode	Absorption	Vibrational mode
3120 w(sh)		1020 vs	
3085 m	ν(C—H), (Cp)	1010 vs	δ(C—H), (ring)
3062 m		998 vs	
3000 w(sh)	ν_{as}(C—H), (Me)	940 vs	δ ring + δ(C—H)
2975 s		912 m	ρ(Me)
		890 m	
2900 vs	ν_s(C—H), (Me)		
2805 w-m	2 × 1415 = 2830	850 840 m(br)	ρ(Me) δ ring
1818 m	2 × 912 = 1824		
1660 w	2 × 840 = 1680		
1625 m	ν(C=C)	820 810 vw(br)	
1555 w			
1478 vs	δ_{as} (Me)	755 vs(br)	π(C—H)
1415 s(br)	δ(C—H) + δ_{as}(Me)	715 vw	
1375 vs	δ(C—H)	690 vw(sh)	
		680 w	
1342 m			
1292 m	δ(C—H) + δ ring	655 645 vs(br)	δ(C—H) δ(Me)
1255 vs			
1240 w(sh)	δ_s(Me)		
1220 m		580 vs	ν_{as}(As—C_2)
		572 vs	ν_s(As—C_2)
1118 w	δ(C—H)		
1090 s	δ(Me)	378 m(br)	ν(As—Cp)
		350 vs	
		322 vw	
		250 m	δ_s(CAsC)

^{1}H NMR spectrum

The ^{1}H NMR spectrum of Me_2AsCp (10% in toluene-d_8, external TMS as a standard) shows a marked temperature dependence; from −77° to −1° cyclopentadienyl resonances where observed at δ 5.94 m, 5.80 m and 2.9 s ppm, while δ(As—CH_3) appears at 0.2 ppm. The expected integration pattern, 2/2/1/6, was observed. The ^{1}H NMR pattern is typical of σ-bonded cyclopentadienyl ligands, warming from −1° to +30° caused disappearance of the resonance at δ 2.9 and a broad signal appeared at 5.8-5.9 ppm. This process is completely reversible and shows the wellknown averaging of signals in sigmatropic rearrangements.

We tried to complete the series Me_nMCp_{3-n} by treating bis(dimethylamino)-arsines and -stibines with monomeric cyclopentadiene:

$$\mathrm{MeM(NMe_2)_2} \xrightarrow[\text{low temp.}]{\text{excess Cp—H, Et}_2\text{O}} \mathrm{MeMCp_2} + 2\ \mathrm{HNMe_2}$$

(M = As, Sb)

In the case of arsenic compound we obtained a polymer, containing a few percent of nitrogen, which could not be identified. With $MeSb(NMe_2)_2$, amine elimination took place at −80°, a brown precipitate was formed which gradually decomposed on warming to room temperature. In view of these experiments it seems unlikely that $MeAsCp_2$ and $MeSbCp_2$ will be obtained by other methods requiring more vigorous conditions.

Experimental

The spectrometers used in this work have been specified previously [1]. Elemental analysis was performed by A. Bernhardt, Analytical Laboratory, Elbach über Engelskirchen, (B.R.D.). Me_2AsNMe_2, $MeAs(NMe_2)_2$ [4] and $MeSb(NMe_2)_2$ [5] were prepared by standard procedures and purified by fractional distillation; monomeric cyclopentadiene was obtained by crack-distillation of the dimer.

Me_2AsCp

A solution of Me_2AsNMe_2 (3.76 g, 2.5 mmol) in 5 ml of dry Et_2O was cooled to —30° and an excess of monomeric cyclopentadiene was added. Me_3SnCl (5.03 g, 2.5 mmol) dissolved in 20 ml dry Et_2O, was added dropwise and $Me_3SnCl \cdot HNMe$ precipitated immediately. After completion of the reaction $HNMe_2$ was condensed into the mixture to precipitate all the Me_3SnCl. The $Me_3SnCl \cdot HNMe_2$ was removed by filtration, and evaporation of volatiles yielded a pale yellow liquid which was purified by fractional distillation. Me_2AsCp(2.12 g, yield 50%), pale yellow liquid, b.p. 39°/4 Torr with a characteristic odour; mol. wt. (mass) 170. (Found: C, 49.23; H, 6.44; As, 43.81. $C_7H_{11}As$ calcd.: C, 49.44; H, 6.47; As, 44.09%.)

$MeAsCp_2$

A solution of $MeAs(NMe_2)_2$ (11.05 g, 62 mmol) in 25 ml of Et_2O was treated at —78° with an excess (10 ml) of monomeric cyclopentadiene. $HNMe_2$ was removed by a stream of dry nitrogen. The yellow precipitate formed was filtered off and washed with dry ether. Drying in vacuo yielded a yellow-to-cream-coloured product, which decomposed without melting at 190-200°. The elemental analysis was quite different from that expected for $MeAsCp_2$. No useful spectroscopic information was obtained from the mass, IR or ^1H NMR spectra, the compound decomposing rapidly during the recording of the spectra.

$MeSbCp_2$

A solution of $MeSb(NMe_2)_2$ (5.2 g, 23.2 mmol) in 20 ml dry ether was heated with 10 ml of monomeric cyclopentadiene at —78°. A yellow precipitate was immediately formed, and on warming to —50°, this turned orange. At —30° it decomposed to a black mass, and no $MeSbCp_2$ could be isolated.

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