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FORMATION OF ORGANOSTIBONIUM ION $[RR'Sb\{FeCp(CO)_2\}_2]^+$: THE REACTION OF $FeCp(CO)_2Cl$ WITH TERTIARY ALLYLSTIBINES*

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Summary

Some new organostibonium salts, $[RR'Sb\{FeCp(CO)_2\}_2]B(C_6H_5)_4$ ($R = R' = CH_3$, C_6H_5 or $CH_2{=}CHCH_2$; $R = CH_2{=}CHCH_2$, $R' = CH_3$ or C_6H_5) which contain Fe—Sb σ-bonds were prepared by the reaction of $FeCp(CO)_2Cl$ with tertiary allylstibines, $(CH_2{=}CHCH_2)RR'Sb$, in THF, followed by the treatment with $NaB(C_6H_5)_4$ in water.

Halostibonium cations, $[XSb\{FeCp(CO)_2\}_3]^+$ or $[X_2Sb\{FeCp(CO)_2\}_2]^+$, containing Fe—Sb σ-bonds have recently been prepared by the reaction of $NaFeCp(CO)_2$ [1] or $[FeCp(CO)_2]_2$ [2] with SbX_3 (X = halogen). However, very few** such derivatives containing an organoantimony moiety have been reported. We wish to report on an interesting route for the preparation of new organostibonium compounds, $[RR'Sb\{FeCp(CO)_2\}_2]B(C_6H_5)_4$.

In the room temperature reaction of diphenylallylstibine, $(CH_2{=}CHCH_2)(C_6H_5)_2Sb$, with $FeCp(CO)_2Cl$ in THF cleavage of the Sb—allyl bond took place and a yellow unstable compound (I), together with allyl chloride and *trans*-1-chloro-1-propene, was obtained as shown in eqn. 1. The yellow compound was converted in water to the tetraphenylborate salt, the structure of which is thought to be (II) containing two Fe—Sb σ-bonds.

$$(CH_2{=}CHCH_2)(C_6H_5)_2Sb + FeCp(CO)_2Cl \rightarrow \underset{(I)}{[(C_6H_5)_2Sb\{FeCp(CO)_2\}_2]Cl} + CH_2{=}CHCH_2Cl + trans\text{-}CH_3CH{=}CHCl \quad (1)$$

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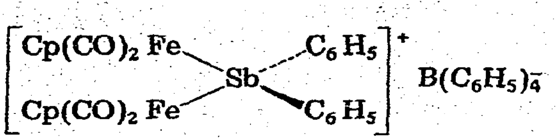
[**] $[(CF_3)_2Sb\{FeCp(CO)_2\}_2][(CF_3)_2SbI_2]$ has been prepared from the reaction of $[FeCp(CO)_2]_2$ with $(CF_3)_2SbI$ [2].



(II)

The cleavage of only one Sb—allyl bond also was observed in the reaction of di- or tri-allylstibines with $FeCp(CO)_2Cl$, and similar compounds were obtained as shown in Table 1.

This type of reaction is different from that of the phosphine or arsine analogues. The reaction of $(CH_2{=}CHCH_2)(C_6H_5)_2E$ (E = P or As) with $FeCp(CO)_2Cl$, followed by the treatment with Y^- [$Y = BF_4$ or $B(C_6H_5)_4$], gave products of type $[(CH_2{=}CHCH_2)(C_6H_5)_2EFeCp(CO)_2]Y$, and even in the presence of excess $FeCp(CO)_2Cl$ the cleavage of E—allyl bond was not observed. The difference in behavior of these allyl substituted Group V elements toward $FeCp(CO)_2Cl$ may be related to the energies of the bonds of these elements with the allyl carbon atom.

Experimental

General

All the reactions were carried out under a nitrogen atmosphere, and nitrogen was bubbled into the solvent just before use. The PMR spectra were measured on Japan Electron Optics JNM-3H-60 or JNM-PS-100 spectrometers, and the data (δ) are given in ppm downfield from internal TMS. The IR spectra were measured on Hitachi 225 spectrophotometer equipped with gratings.

Preparation of $(CH_2{=}CHCH_2)RR'Sb$ ($R = R' = CH_3$, C_6H_5 or $CH_2{=}CHCH_2$; $R = CH_2{=}CHCH_2$, $R' = CH_3$ or C_6H_5)

To an ether solution of allylmagnesium bromide (from Mg, 0.08 mole) dimethylchlorostibine [3] (7.5 g, 0.04 mole) in dry ether (15 ml) was added dropwise at 0°, and then the reaction mixture was heated under reflux for half an hour. After a saturated solution (50 ml) of ammonium chloride was added the organic layer was separated and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the residual liquid was distilled to give 3.9 g (51%) of colorless $(CH_2{=}CHCH_2)(CH_3)_2Sb$: b.p. 54—57°/ 42 mm. PMR (neat), 0.68 (s, $SbCH_3$); 2.17 [d, $SbCH_2$; $J(CH_2{-}CH{=})$ 8.25 Hz]. Since this compound is easily oxidized in air, analysis was performed on the dichloride derivative, which was obtained by adding sulfuryl chloride to the stibine at —70° and followed by the recrystallization from dichloromethane/n-hexane.

$(CH_2{=}CHCH_2)(CH_3)_2SbCl_2$: m.p. 53-54°. (Found, C, 22.51; H, 4.50. $C_5H_{11}Cl_2Sb$ calcd.: C, 22.71; H, 4.20%.) PMR (in CCl_4), 2.21 (s, $SbCH_3$); 3.49 [d, $SbCH_2$; $J(CH_2{-}CH{=})$ 7.2 Hz].

Other compounds $(CH_2{=}CHCH_2)_2(CH_3)Sb$, $(CH_2{=}CHCH_2)_2(C_6H_5)Sb$ and $(CH_2{=}CHCH_2)_3Sb$ were prepared in a similar manner from CH_3SbCl_2 [3], $C_6H_5SbCl_2$ [4] and $SbCl_3$, respectively.

$(CH_2{=}CHCH_2)_2(CH_3)Sb$: b.p. 43-44°/3 mm. PMR (neat), 0.66 (s, $SbCH_3$); 2.21 [d, $SbCH_2$; $J(CH_2{-}CH{=})$ 8.25 Hz].

$(CH_2=CHCH_2)_2(C_6H_5)Sb$: b.p. 95-97°/1 mm. PMR (neat), 2.36 [d, $SbCH_2$; $J(CH_2-CH=)$ 8.25 Hz].

$(CH_2=CHCH_2)_2(C_6H_5)SbCl_2$: m.p. 105-106°. (Found: C, 40.81; H, 4.50. $C_{12}H_{15}Cl_2Sb$ calcd.: C, 40.96; H, 4.30%.) PMR (in $CDCl_3$), 3.68 [d, $SbCH_2$; $J(CH_2-CH=)$ 8.25 Hz].

$(CH_2=CHCH_2)_3Sb$: b.p. 66-67°/1 mm (lit. [5] 71/1 mm).

$(CH_2=CHCH_2)(C_6H_5)_2Sb$ was prepared by the reaction of $(C_6H_5)_3Sb$ with Na and subsequent reaction of $CH_2=CHCH_2Cl$ in liquid ammonia. Details of this method have been described in our recent reports [6, 7].

$(CH_2=CHCH_2)(C_6H_5)_2Sb$: b.p. 124-126°/0.5 mm. PMR (in CCl_4), 2.61 [d, $SbCH_2$; $J(CH_2-CH=)$ 8.25 Hz].

$(CH_2=CHCH_2)(C_6H_5)_2SbCl_2$: m.p. 100-101°. (Found: C, 46.29; H, 4.09. $C_{15}H_{15}Cl_2Sb$ calcd.: C, 46.44; H, 3.90%.) PMR (in CCl_4), 3.85 [d, $SbCH_2$; $J(CH_2-CH=)$ 8.25 Hz].

Preparation of $(CH_2=CHCH_2)(C_6H_5)_2E$ (E = P or As)

These compounds were prepared in a manner similar to that for $(CH_2=CHCH_2)(C_6H_5)_2Sb$. Analysis was performed on the onium salts prepared by the reaction with CH_3I and subsequent treatment with $NaB(C_6H_5)_4$.

$(CH_2=CHCH_2)(C_6H_5)_2P$: b.p. 128-130°/1 mm.

$(CH_3)(CH_2=CHCH_2)(C_6H_5)_2PB(C_6H_5)_4$: m.p. 144°. (Found: C, 85.90; H, 6.80. $C_{40}H_{38}BP$ calcd.: C, 85.76; H, 6.83%.)

$(CH_2=CHCH_2)(C_6H_5)_2As$: b.p. 125-126°/2 mm.

$(CH_3)(CH_2=CHCH_2)(C_6H_5)_2AsB(C_6H_5)_4$: m.p. 130°. (Found: C, 79.39; H, 6.38. $C_{40}H_{38}AsB$ calcd.: C, 79.48; H, 6.34%.)

Reaction of $(CH_2=CHCH_2)RR'Sb$ with $FeCp(CO)_2Cl$

A mixture of $FeCp(CO)_2Cl$ (1.06 g, 5 mmol) and $(CH_2=CHCH_2)(C_6H_5)_2Sb$ (1.59 g, 5 mmol) in THF (30 ml) was stirred at room temperature. A yellow precipitate appeared gradually, and after the stirring for 2 days, the precipitate was filtered and dried. From the filtrate, allylchloride (59%)* and *trans*-1-chloro-1-propene (24%)* were detected by GLC using a 2 m column packed with 25 wt. % dinonyl phthalate on 40-60 mesh Celite 545. The yellow precipitate was dissolved in water and treated with excess $NaB(C_6H_5)_4$. The yellow-white precipitate which appeared was filtered off, dried and recrystallized from acetone/ether to give yellow crystals of $[(C_6H_5)_2Sb\{FeCp(CO)_2\}_2]B(C_6H_5)_4$ (1.70 g, 72%*).

The reactions of other tertiary allylstibines were carried out similarly and the yields of the tetraphenylborate salts were ca. 70%. The tetraphenylborate salts thus obtained are stable in the solid state and decompose gradually in solution. The properties of these compounds are listed in Table 1.

Reaction of $(CH_2=CHCH_2)(C_6H_5)_2E$ (E = P or As) with $FeCp(CO)_2Cl$

The reaction was carried out in a manner similar to the above procedure. Pale yellow crystals were obtained in a yield of ca. 40%.

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* Yield is based upon $FeCp(CO)_2Cl$.

TABLE 1

PROPERTIES OF $[RR'Sb\{FeCp(CO)_2\}_2]B(C_6H_5)_4$

Compounds		M.p. [a] (°C)	Analysis found (calcd.)(%)		IR (cm^{-1}) [b]	PMR (ppm) [c]
R	R'		C	H	ν(CO)	FeC_5H_5
CH_3	CH_3	176-177	58.14 (58.24)	4.54 (4.40)	2039 (s), 2022 (vs), 1986 (vs)	5.40 [d]
C_6H_5	C_6H_5	199-200	63.22 (63.27)	4.17 (4.25)	2041 (s), 2023 (vs), 1996 (s), 1985 (sh)	5.34
CH_2=$CHCH_2$	CH_3	172-173	59.37 (59.26)	4.77 (4.54)	2038 (s), 2023 (vs) [e], 1989 (vs)	5.35 [f]
CH_2=$CHCH_2$	C_6H_5	147-149	61.61 (61.88)	4.64 (4.42)	2043 (s), 2026 (vs) [g], 1996 (vs)	5.30 [h]
CH_2=$CHCH_2$	CH_2=$CHCH_2$	146-147	60.03 (60.26)	4.75 (4.60)	2039 (s), 2025 (vs) [i], 1988 (vs)	5.41 [j]

[a] With decomposition. [b] In CH_2Cl_2 solution. [c] In acetone-d_6 at 23°; downfield from internal TMS. [d] $SbCH_3$, 1.70 ppm. [e] ν(C=C), 1624 cm^{-1} (w). [f] $SbCH_3$, 1.61; $SbCH_2$, 3.16 ppm doublet [$J(CH_2—CH=)$ 8.25 Hz]. [g] ν(C=C), 1628 (w). [h] $SbCH_2$, 3.19 ppm doublet [$J(CH_2—CH=)$ 8.25 Hz]. [i] ν(C=C), 1628 cm^{-1} (w). [j] $SbCH_2$, 3.20 ppm doublet [$J(CH_2—CH=)$ 8.25 Hz].

$[(CH_2=CHCH_2)(C_6H_5)_2PFeCp(CO)_2]BF_4$: m.p. 164-165°, (Found: C, 54.00; H, 4.38. $C_{22}H_{20}BF_4FeO_2P$ calcd.: C, 53.92; H, 4.11%.) IR (in CH_2Cl_2), 2013, 2058 [ν(CO)]; 1633 cm^{-1} [ν(C=C)]. PMR (in acetone-d_6), 3.76 [quart, PCH_2; J(P—H) 11.25; $J(CH_2—CH=)$ 6.75 Hz]; 5.57 [d, FeC_5H_5; J(P—H) 1.7 Hz]

$[(CH_2=CHCH_2)(C_6H_5)_2AsFeCp(CO)_2]B(C_6H_5)_4$: m.p. 163-164°. (Found: C, 71.73; H, 5.26. $C_{46}H_{40}AsBFeO_2$ calcd.: C, 72.09; H, 5.26%.) IR (in CH_2Cl_2), 2015, 2055 [ν(CO)]; 1633 cm^{-1} [ν(C=C)]. PMR (in acetone-d_6), 3.67 [d, $AsCH_2$; $J(CH_2—CH=)$ 7.5 Hz]; 5.43 (s, FeC_5H_5).

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