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Preliminary communication

AROMATIC ANTIMONY COMPOUNDS. TRANSITION METAL COMPLEXES OF 2,5-DIMETHYLSTIBACYCLOPENTADIENYL

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Summary

Hydrostannation of 2,4-hexadiyne with dibutyltin dihydride gave 1,1-dibutyl-2,5-dimethylstannole, which was converted to 2,5-dimethylstibacymantrene and to bis(2,5-dimethylstibacyclopentadienyl)iron.

Since the Group V heterobenzenes Ia—Ic closely resemble benzene [1], it seems reasonable to expect that Group V non-benzenoid aromatics can also be prepared. In particular, Group V heterocyclopentadienides (IIIa—IIIe) should resemble the aromatic cyclopentadienyl anion. The pyrrolyl anion IIIa has been long known while recently Mathey and others have elegantly demonstrated that phosphacyclopentadienyl IIIb [2] and arsacyclopentadienyl (IIIc) [3,4] can serve as 6π-electron aromatic ligands with transition metals. We now report the first synthesis of a stibacyclopentadienyl anion IIId and some studies of its coordination chemistry.

Since organotin compounds have served as versatile precursors for Group V organics [5], we have explored a synthesis via simply-substituted stannoles [6]. Hydrostannation of 2,4-hexadiyne with dibutyltin dihydride gave a 15% yield of 1,1-dibutyl-2,5-dimethylstannole (V)*. ^{1}H NMR ($CDCl_3$): δ 0.9—1.8 (m, 18H, C_4H_9); 2.1 (s, 6H, CH_3); 6.6 (s, 2H, CH) ppm. Mass spectral *m/e*, 314 (M^+, $C_{14}H_{26}{}^{120}Sn$); 257 ($M^+ - C_4H_9$). In spite of this low conversion, the ready availability of 2,4-hexadiyne allows V to be prepared in quantity. The stannole is readily characterized by its acetic acid cleavage [7] to *trans, trans*-2,4-hexadiene. Alternatively, reaction with dimethyl acetylenedicarboxylate gives dimethyl 3,6-dimethylphthalate through the formal loss of dibutylstannylene [8,9].

As anticipated, stannole V undergoes facile exchange with Group V halides

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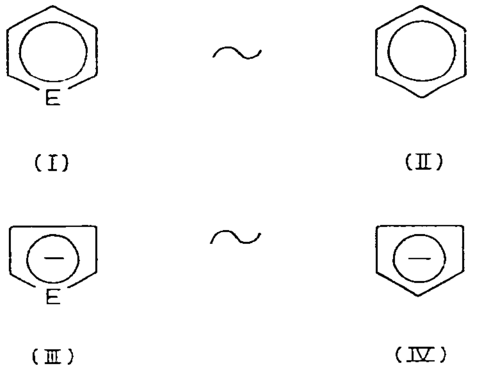
*All new compounds were characterized by elemental, mass spectral and NMR analyses.



(a, E = N ; b, E = P ; c, E = As ; d, E = Sb ; e, E = Bi)

[10]. The reaction of V with phenylarsenic dichloride in tetrahydrofuran for 1 h at 25°C gave a 66% yield of the known 1-phenyl-2,5-dimethylarsole [10], while under the same conditions V and phenylantimony dichloride gave a 65% yield of 1-phenyl-2,5-dimethylstibole (VI), b.p. 74°C (0.05 torr), mass spectral *m/e*, 280 (M^+, $C_{12}H_{13}{}^{123}Sb$). Treating VI with lithium in tetrahydrofuran cleaved the antimony—phenyl bond, affording a solution of phenyllithium and lithium 2,5-dimethylstibacyclopentadienide VII [11]. Reaction of the latter with methyl iodide gave a 27% yield of 1,2,5-trimethylstibole (VIII) as a light yellow oil, mass spectral *m/e*, 218 (M^+, $C_7H_{11}{}^{123}Sb$).

Stibacyclopentadienide (VII) can serve as a six-electron π-ligand towards transition metals. Thus, treating anion VII with bromomanganese pentacarbonyl followed by heating to 140°C gave a 24% yield of 2,5-dimethylstibacymantrene (IX) as a yellow oil, which was purified by chromatography on silica gel. The stibacymantrene was characterized by IR (cyclohexane), 2100 vs, 1948 vs (br) cm^{-1} and mass spectral *m/e*, 342 (M^+, $C_9H_8MnO_3{}^{123}Sb$). The reaction of VII with ferrous chloride afforded a 33% yield of a 2/1 mixture of bis(2,5-dimethylstibacyclopentadienyl)iron (X) and 2,2′,5,5′-tetramethyldistibolyl (XI), which were separated by fractional sublimation. The deep red air-stable X, m.p. 59°C dec, shows mass spectral *m/e* at 462 (M^+ for $C_{12}H_{16}{}^{123}Sb_2Fe$) while the deep blue distibine XI, m.p. 99°C, shows a mass spectral *m/e* at 406 (M^+ for $C_{12}H_{16}{}^{123}Sb_2$). Since the distibaferrocene X is stable under the reaction conditions, it is likely that the distibine XI is produced directly by reduction of $FeCl_2$ to Fe^0.

Metal π-coordination of the stibacyclopentadienyl rings of IX and X is clearly indicated by the upfield shifts of the NMR proton and carbon signals relative to the uncomplexed stibacyclopentadiene rings of VI, VIII, and XI (see Table 1). The observed shifts of X are rather typical of those found for η^5-cyclopentadienylmetal complexes [12]. We have also found that the one-bond ^{13}CH coupling constant for the ring protons of X is 164 Hz, only slightly smaller than that of ferrocene (175 Hz) [13] and that of the corresponding bis(2,5-dimethylarsacyclopentadienyl)iron (168 Hz) [14]. This difference is an expected consequence [15] of the larger CCC bond angles of aromatic antimony-carbon

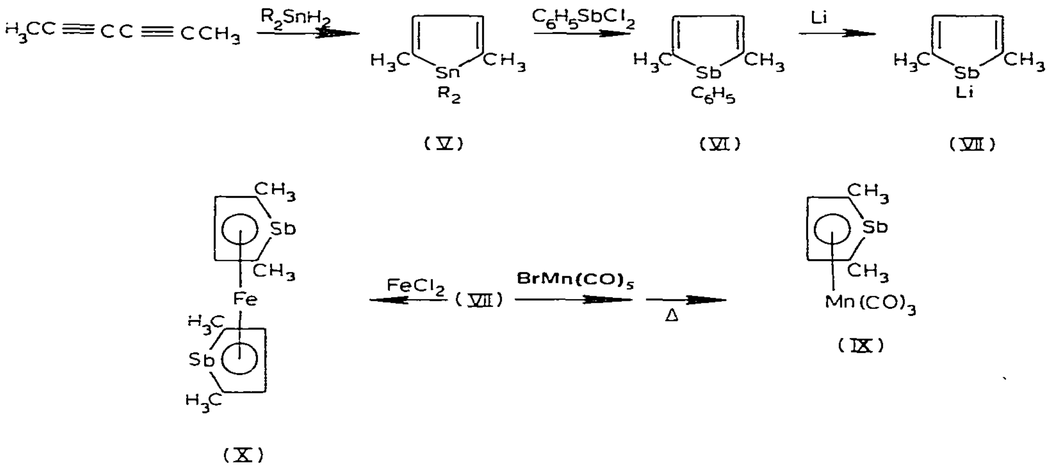


TABLE 1

PROTON AND CARBON-13 CHEMICAL SHIFT VALUES (δ, ppm) OF 2,5-DIMETHYLSTIBACYCLOPENTADIENYL DERIVATIVES

Compound	H_3 (H_4)	C-methyl protons	C_2 (C_5)	C_3 (C_4)	C-methyl carbon
VI [a,c]	6.8	2.1	154.5	141.6	21.9
VIII [a,d]	6.6	2.1	154.7	140.7	22.1
IX [a]	6.0	1.9	134.3	98.5	22.0
X [b]	5.5	1.8	113.6	93.5	23.0
XI [b]	6.7	2.1	151.7	140.6	22.5

[a] In $CDCl_3$. [b] In C_6D_6. [c] ^1H NMR δ 7.1—7.6 (C_6H_5); ^{13}C NMR: δ 135.5, 128.7, 128.3 (C_6H_5). [d] ^1H NMR: δ 0.9 ($SbCH_3$); ^{13}C NMR: δ 29.7 ($SbCH_3$).

rings [16]. Phosphaferrocenes [2] and arsaferrocenes* undergo electrophilic substitution reactions in the same manner as arsabenzene [17]. We find that distibaferrocene X like stibabenzene Id is destroyed by the strong Lewis acidic conditions needed for the Friedel—Crafts acylation or acid deuterium exchange.

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*Bis(2,5-dimethylarsacyclopentadienyl)iron undergoes deuterium exchange at 25°C in trifluoroacetic-d_1 acid, while it can be acylated using acetyl chloride/aluminum chloride in CH_2Cl_2

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