

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-dimethylstibacyclopentadiene 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 IIIId 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)*. $^1\text{H NMR}$ (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^+ , $\text{C}_{14}\text{H}_{26}^{120}\text{Sn}$); 257 ($M^+ - \text{C}_4\text{H}_9$). 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

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

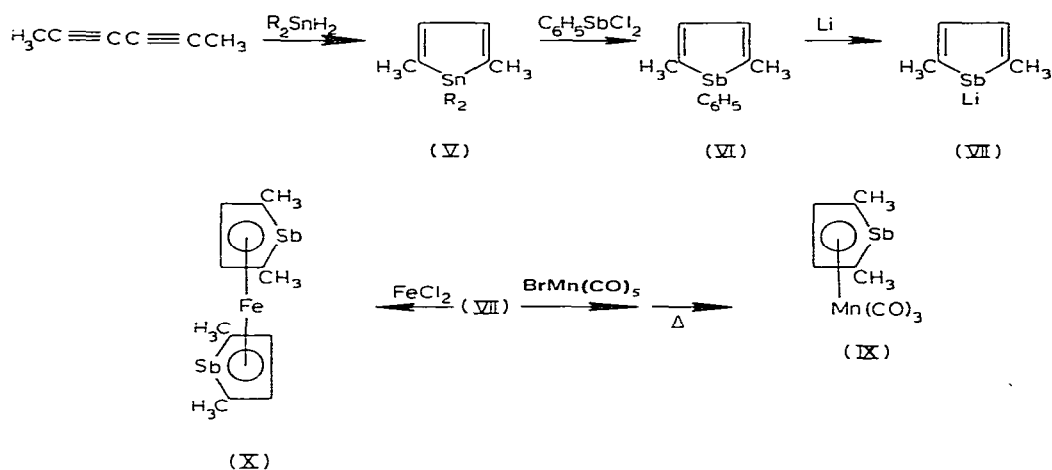


TABLE 1

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

Compound	H ₃ (H ₂)	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 CDCl₃. ^b In C₆D₆. ^c ¹H NMR δ 7.1–7.6 (C₆H₅); ¹³C NMR: δ 135.5, 128.7, 128.3 (C₆H₅). ^d ¹H NMR: δ 0.9 (SbCH₃); ¹³C NMR: δ 29.7 (SbCH₃).

rings [16]. Phosphaferrocenes [2] and arsaferrocenes* undergo electrophilic substitution reactions in the same manner as arsabenzene [17]. We find that distibaferrocene X like stibaferrocene 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-d₁ acid, while it can be acylated using acetyl chloride/aluminum chloride in CH₂Cl₂.

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