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The Preparation of Some Trialkylstannylferrocenes[*1]

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During the last decade, several papers dealing with triorganosilyl-,[1-5] triorganogermyl-[6] and diorganophosphyl[7]-substituted ferrocenes have appeared. However, there has been an entire absence of descriptions of the triorganostannyl-substituted ferrocenes. The present authors wish to report herewith on the preparation of a series of mono- and 1,1′-bis(trialkylstannyl)substituted ferrocenes, as shown in Table 1, by the reaction of lithioferrocenes with the corresponding trialkyltin chlorides. The NMR and IR data of the products well characterized their chemical structure; they are given in Table 2.

Experimental

Trialkylstannylferrocenes. The lithiation of ferrocenes was performed by the use of *n*-butyllithium

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Table 1. Trialkylstannylferrocenes

Compd.	Yield (%)	Bp(°C/mmHg) n_D^{25}	Formula	Analysis (%) Found Calcd C	 H	 $Sn^{a)}$	 $Fe^{b)}$	Mol wt$^{c)}$
$CpFeC_5H_4SnEt_3$	10.7	135—140/1.0 1.5860	$C_{16}H_{24}SnFe$	47.07 46.60	6.04 6.14	30.87 30.40	14.55 14.30	388 391
$Fe(C_5H_4SnEt_3)_2$	19.4	160—164/1.0 1.5761	$C_{22}H_{38}Sn_2Fe$	44.45 44.35	6.39 6.38	40.11 39.88	9.63 9.38	595 597
$CpFeC_5H_4SnPr_3$	11.5	122—125/0.5 1.5689	$C_{19}H_{30}SnFe$	53.36 52.71	7.27 6.93	28.10 27.44	13.13 12.91	440 433
$Fe(C_5H_4SnPr_3)_2$	20.8	187—193/0.5 1.5571	$C_{28}H_{50}Sn_2Fe$	49.96 49.46	7.49 7.36	35.22 34.96	8.45 8.22	670 679
$CpFeC_5H_4SnBu_3$	9.7	140—146/0.5 1.5540	$C_{22}H_{36}SnFe$	55.67 55.63	7.62 7.58	25.78 25.01	12.10 11.67	481 475
$Fe(C_5H_4SnBu_3)_2$	20.4	170—173/0.17 1.5437	$C_{234}H_{62}Sn_2Fe$	53.43 53.45	7.30 7.12	31.55 31.10	7.52 7.31	758 763

a) Determined volumetrically with EDTA and Zz^{2+}. b) Determined colorimetrically with thiocyanate.
c) Determined cryoscoipically in benzene.

Table 2. NMR and IR data of trialkylstannylferrocenes

NMR CCl_4 (τ value)

Compound	$H_{u.r}$	$H_{\alpha,\beta}$		H_b
$CpFeC_5H_4SnEt_3$	5.92^s (5.0)	5.76^t (2.3)	6.08^t (2.2)	7.98—9.52^m (18.5)
$Fe(C_5H_4SnEt_3)_2$		5.82^t (4.0)	6.11^t (4.0)	7.99—9.50^m (29.4)
$CpFeC_5H_4SnPr_3$	6.01^s (5.0)	5.77^t (2.0)	6.09^t (1.9)	7.83—9.54^m (23.0)
$Fe(C_5H_4SnPr_3)_2$		5.86^t (4.0)	6.14^t (4.0)	7.82—9.55^m (42.6)
$CpFeC_5H_4SnBu_3$	6.01^s (5.0)	5.76^t (2.1)	6.09^t (2.1)	7.82—9.60^m (30.0)
$Fe(C_5H_4SnBu_3)_2$		5.84^t (4.0)	6.12^t (4.0)	7.82—9.60^m (53.6)

$H_{u.r}$: unsubstituted ring protons, $H_{\alpha,\beta}$: alpha and beta protons on stannyl substituted rings,
H_b: protons of alkyl groups, s: singlet, t: triplet, m: multiplet

IR data

Compound	Wave number (cm^{-1})								
$CpFeC_5H_4SnEt_3$	3061m	2928vs	2896vs	2851 s	1462m	1417m	1377m	1136 s	1106 s
	1023 s	998 s	957w	943w	814 s				
$Fe(C_5H_4SnEt_3)_2$	3063m	2930vs	2904vs	2859 s	1464 s	1419m	1378m	1297w	1233w
	1178m	1139 s	1052 s	1025 s	958m	943m	823 s		
$CpFeC_5H_4SnPr_3$	3060m	2936vs	2916vs	2844 s	1462m	1412m	1377m	1300m	1274w
	1181w	1136m	1106 s	1060 s	1023 s	998m	814 s	793m	
$Fe(C_5H_4SnPr_3)_2$	3058m	2940vs	2916vs	2846 s	1452m	1414m	1376m	1330m	1296w
	1274w	1180w	1137m	1060 s	1024 s	986m	822 s	793m	
$CpFeC_5H_4SnBu_3$	3063m	2947vs	2913vs	2844 s	1456 s	1413m	1376 s	1355w	1337m
	1289m	1248w	1181m	1136 s	1105 s	1069 s	1047 s	1022m	995m
	959m	873m	863m	805 s					
$Fe(C_5H_4SnBu_3)_2$	3065m	2950vs	2914vs	2844 s	1457 s	1414m	1376 s	1357w	1338m
	1291m	1248w	1180m	1136 s	1070 s	1049m	1023 s	998m	873m
	863m	820 s	808m						

according to a method previously reported;[1] the metalation was confirmed in advance of the reaction with trialkyltinchloride by carbonation to give the mixed mono- and dicarboxyferrocenes. As an example, the preparation of the triethylstannylferrocenes will be described.

Triethylstanylferrocenes. A 20.0 g (0.11 mol) sample of ferrocene in 300 m*l* of anhydrous tetrahydrofuran was lithiated by the use of 300 m*l* of a 0.41 molar solution of *n*-butyllithium in anhydrous ether. A solution of triethyltin chloride (132.7 g 0.6 mol) in 180 m*l* of ether was added to the above orangeyellow lithiated ferrocene suspension over a period of 4 hr at below −60°C. After the addition, the mixture was stirred at −30°C for 15 hr, and then at room temperature for a further 30 hr, during which period the colored precipitate seemed to be dissolved to give a dark red solution. The whole mixture was then concentrated on a steam bath to about 500 m*l*, and the concentrate was repeatedly washed with water to neutrality and dried over calcium chloride. The complete removal of unreacted ferrocene was effected by repeated freezing out in a dry ice-acetone mixture followed by sublimation at 3 mmHg. The remaining liquid was fractionated through a packed column to give triethylstannylferrocene (4.7 g 10.7%) and 1,1′-bis-(triethylstannyl)-ferrocene (12.5 g, 19.4%), both being high-boiling mobile liquids with a distinct brown color.

Procedures analogous to those used for the triethyl-derivatives gave the tributyl- and tripropyl-derivatives, as is shown in Table 1.

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