Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

UNSYMMETRICALLY DISUBSTITUTED FERROCENES XII*. 2-SUBSTITUTED FERROCENYLTIN COMPOUNDS, AND FERROCENES RELATED TO POLY(VINYL CHLORIDE) STABILIZERS

D. R. MORRIS AND B. W. ROCKETT
Department of Physical Sciences, The Polytechnic, Wolverhampton. WV1 1LY (Great Britain)

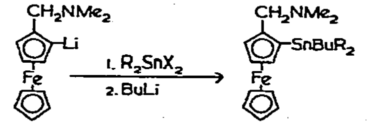
(Received July 27th, 1971)

SUMMARY

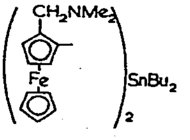
Some dialkyltin halides have been condensed with lithiated [(dimethylamino)methyl]ferrocene to give the corresponding 2-substituted ferrocenyltinalkyls. The ^{57}Fe and ^{119}Sn Mössbauer spectra of one derivative are reported. The dibutyltin derivatives of a ferrocenethiol and a ferrocenecarboxylic acid are reported, these compounds are analogous to organotin stabilizers for vinyl polymers. A related titanium carboxylate is also described. The IR and PMR spectra of the compounds are discussed.

Although organosilicon- and organogermaniumferrocenes were described in 1962[2], the corresponding tin compounds were not reported until 1970[3]. We have applied our well established synthetic procedure[4] to the preparation of the first homoannularly substituted ferrocenyltin compounds. We have examined also some organotin–sulphur derivatives of ferrocene that are structurally analogous to well known poly(vinyl chloride) "stabilizers", or additives that retard the degradation of the polymer at elevated temperatures and under irradiation[5].

Dibutyltin dibromide was stirred with the lithioamine (I)[4a] when one or two bromine atoms in the dibutyl compound were displaced by a ferrocene residue. The product contained both a dialkylferrocenyltin bromide and a dialkyldiferrocenyltin and suffered partial hydrolysis during normal work-up. It was convenient to displace the remaining bromine atom by the addition of an excess of butyllithium to the product mixture when the tributyl-ferrocenyltin (II) was isolated together with the dibutyldiferrocenyltin (IV).



(I) (II) R=Bu (III) R=Me



(IV)

---

* For Part XI see ref. 1.

Treatment of the lithioamine (I)[4a] with dimethyltin dichloride and then an excess of n-butyllithium gave the butyldimethylferrocenyltin (III).

Esters of thioglycollic acid, such as the dithio-dibutyltin compounds have been used as heat degradation inhibitors in vinyl polymers[6]. Substituents that may release electrons by conjugation often improve the stabilizing power of the organotin additive[7] and we have introduced the ferrocenyl group into the appropriate thioglycollate. Thioglycollic acid was esterified with ferrocenemethanol and the resulting thiol (V) was condensed with dibutyltin oxide to give the bis(ferrocene-thio)tin (VI). The dibutyltin dicarboxylate (VII) was also prepared from ferrocenecarboxylic acid and dibutyltin oxide.

$HSCH_2CO_2CH_2Fc$	$Bu_2Sn(SCH_2CO_2CH_2Fc)_2$	$Bu_2Sn(OCOFc)_2$	$(\pi\text{-}C_5H_5)_2Ti(OCOPh)_2$
(V)	(VI)	(VII)	(VIII)

The Mossbauer spectrum of the ferrocene–tin compound (II) was of some interest since it contains two Mossbauer active nuclei (Sn and Fe). The isomer shifts and quadrupole splittings are recorded in the experimental section. The tin spectrum showed a broad singlet, that indicated a small unresolved quadrupole splitting of ca. 0.25 $mm \cdot sec^{-1}$ thus the tin atom was four coordinate as expected. The compound also showed an iron isomer shift near the previously observed value for ferrocene[8]. The iron quadrupole splitting was in accordance with the structure proposed.

Some of the characteristic IR absorption frequencies of the compounds are recorded in Table 1. The bands associated with the carboxyl group in the ester (V) are typical of the unidentate group. Conversion of the thiol (V) into the tin salt (VI) caused large shifts in the carboxyl bands in the solid state and similar shifts in solution. These bands indicated that the carboxyl groups were bidentate and chelated[9] and that the tin atom was hexacoordinated as expected. The solid and solution spectra of the organotin carboxylate (VII) also showed that the carbonyl groups were bidentate and chelated[9]. The titanium dicarboxylate (VIII) was prepared from di-π-cyclopentadienyltitanium dichloride and sodium benzoate. The low frequency carbonyl band in the solid state and solution spectra of this compound were consistent with bidentate

TABLE 1

INFRARED ABSORPTION FREQUENCIES OF SOME ORGANOTINFERROCENES AND AN ORGANOTITANIUM COMPOUND (cm^{-1})

Compound	ν_{as}(COO)	ν_s(COO)	Other bands
(V)[a]	1694	1320	SH 2595, 2695
(VI)[a]	1608, 1594 (sh)	1370	
(VI)[b]	1601	1365	
(VII)[a]	1582	1320	
(VII)[b]	1585	1315	
(VIII)[a]	1627	1360	
(VIII)[b]	1630	1370 (br)	

[a] Potassium bromide disc. [b] Solution in chloroform.

carboxyl groups (Table 1). However, the high frequency band fell between the values expected for mono- and bidentate groups. We conclude that the bonding of the carboxyl groups cannot be assigned unambiguously from the spectrum[10].

The PMR spectra of the disubstituted ferrocenes (II, III and IV) (see Experimental) showed AB quartet resonances for the geminal methylene protons in the (dimethylamino)methyl residue[11]. The chemical shift differences between the component doublets of the quartet were large in the presence of the bulky 2-substituents as has been observed previously[11].

The ferrocenetin compounds (VI) and VII) and the titanium carboxylate (VIII) were evaluated as heat stabilizers for poly(vinyl chloride) by milling each compound in turn into the polymer and then following the rate of colour formation in polymer discs at constant temperature[12]. The compounds were poor heat stabilizers and this may be attributed to rapid breakdown of the metallocene group to give organoiron or organotitanium chlorides. These chlorides acted as Lewis acids and catalysed the degradation of the polymer. This effect outweighed any stabilizing effect from the electron-rich metallocene group. Simple organotin stabilizers such as dibutyltin bis (methylthioglycolate) and dibutyltin dibenzoate break down slowly to form organotin chlorides with Lewis acid character[5]. In these cases, the stabilizing power of the compound outweighs the degradative influence of the organotin chlorides.

EXPERIMENTAL

For general directions see Part I[13].

bis(methylthioglycolate) and dibutyltin dibenzoate break down slowly to form orga-

1-*Lithio*-2-[*(dimethylamino)methyl*] *ferrocene* (*I*)

1-Lithio-2-[(dimethylamino)methyl]ferrocene was prepared in ether from [(dimethylamino)methyl]ferrocene (4.9 g, 0.02 mole) and a 22% solution of n-butyllithium (8 ml, 0.02 mole) in hexane[4].

{2-[*(Dimethylamino)methyl*] *ferrocenyl*}*tributyltin* (*II*)

To a stirred solution of the lithioamine (I) prepared as described above, was added a solution of dibutyltin dibromide (3.1 g, 0.008 mole) in dry ether (100 ml). The mixture was heated to reflux for 21 h. A 22% solution of n-butyllithium (8 ml, 0.02 mole) was added and the mixture stirred for 1 h. An excess of aqueous sodium bicarbonate was added to the cooled reaction mixture and it was then extracted with ether. The dried ($MgSO_4$) extracts were evaporated to afford a red oil which was dissolved in light petroleum and chromatographed on alumina.

Light petroleum eluted the product (II) (3.28 g, 88%[*]) as a yellow oil. The methiodide was prepared by the reaction of the tertiary amine with excess methyl iodide in methyl cyanide and was precipitated by the addition of dry ether as a yellow solid which decomposed at 180°. (Found: C, 46.32; H, 6.85; Fe, 7.98. $C_{26}H_{46}FeINSn$ calcd.: C, 46.33; H, 6.88; Fe, 8.29%.) The PMR spectrum showed resonances at δ 0.7–1.6, multiplet (27H, butyl); 3.3, singlet (9H, N–Me); 4.1, multiplet (1H, substituted ring proton); 4.6, multiplet (1H, substituted ring proton); 4.95, multiplet (1H, substituted ring proton); 4.25 singlet (5H, unsubstituted ring proton); doublets centred at

---

[*] Yields were based on unrecovered starting material.

5.45 and 3.77 ppm (J 13.8 Hz) (2H, methylene protons). The ^{57}Fe Mossbauer spectrum showed an isomer shift of 0.79 mm·sec^{-1} {relative to $Na_2[Fe(CN)_5NO]\cdot 2H_2O$} and a quadrupole splitting of ~2.4. The ^{119}Sn spectrum showed an isomer shift of 1.20 mm·sec^{-1} (relative to SnO_2) and a quadrupole splitting of ~0.25.

Elution with benzene afforded bis{2-[(dimethylamino)methyl]ferrocenyl}-dibutyltin (0.21 g, 8%) which was characterised as its methiodide. The methiodide was prepared as described above, as an orange solid that did not melt and decomposed at 180°. (Found: C, 43.52; H, 5.29; Fe 11.02. $C_{36}H_{56}Fe_2I_2N_2Sn$ calcd.: C, 43.23; H, 5.64; Fe, 11.17%). The PMR spectrum [$(CD_3)_2SO$] showed resonances at δ 0.8–1.8, multiplet (18H, butyl protons); 2.93, singlet (18H, methyl protons); doublet centred at 3.65, (J 13.2 Hz) (2H, methylene protons), the other members of the quartet were obscured by two of the substituted cyclopentadienyl ring protons; 3.95, multiplet (2H, substituted cyclopentadienyl ring protons); 4.82, multiplet (3H, substituted cyclopentadienyl ring protons); 4.12 ppm, singlet (10H, unsubstituted cyclopentadienyl ring protons). Elution with ether/light petroleum mixtures afforded [(dimethylamino)methyl]ferrocene (3.2 g).

{2-[(*Dimethylamino*)*methyl*]*ferrocenyl*}*butyldimethyltin*

To a stirred solution of the lithioamine (I) (0.005 mole) in ether was added a solution of dimethyltin dichloride (1.5 g, 0.0068 mole) in dry ether (200 ml). The mixture was then stirred for 17 h. A solution of butyllithium (4 ml, 0.08 mole) was added and the mixture stirred for a further 1 h. Excess saturated aqueous sodium bicarbonate was added to the cooled reaction mixture which was then extracted with ether. The dried ($MgSO_4$) extracts were evaporated to afford a red oil which was dissolved in light petroleum and chromatographed on alumina. Ether/light petroleum mixtures eluted {2-[(dimethylamino)methyl]ferrocenyl}butyldimethyltin (0.49 g, 85%). The methiodide was prepared by the reaction of the tertiary amine with excess methyl iodide in methyl cyanide and was precipitated by the addition of dry ether as yellow plates which decomposed at 180°. (Found: C, 40.83; H, 5.75; Fe 9.39. $C_{20}H_{34}FeINSn$ calcd.: C, 40.78; H, 5.82; Fe, 9.4%.) The PMR spectrum showed resonances at δ 0.35, singlet (6H, tinmethyl protons); 0.7–1.5, multiplet (9H, butyl protons); 3.275, singlet (9H, *N*-methyl protons); doublets centred at 5.375 and 3.775 (J 13.5 Hz) (2H, methylene protons); 4.075, multiplet (1H, substituted cyclopentadienyl ring proton); 4.18, singlet (5H, unsubstituted cyclopentadienyl ring protons); 4.475, multiplet (1H, substituted cyclopentadienyl ring proton); 4.85 ppm, multiplet (1H, substituted cyclopentadienyl ring proton). Elution with ether/light petroleum mixtures yielded [(dimethylamino)-methyl]ferrocene (0.91 g).

Ferrocenyl thioglycolate (*V*)

Ferrocenylmethanol (2.8 g, 0.012 mole) was heated under reflux with thioglycollic acid (1.84 g, 0.02 mole) for 4 h in benzene (100 ml). The water formed during the reaction was removed by azeotropic distillation. Ether was then added and the reaction mixture was extracted with aqueous sodium bicarbonate and the aqueous layer retained. The aqueous solution was made weakly acid with dilute phosphoric acid and was extracted with ether. The dried ether extracts ($MgSO_4$) were evaporated to afford ferrocenyl thioglycolate (2.12 g, 56%) that crystallised from benzene/light petroleum as orange needles m.p. 123–125°. (Found: C, 53.70; H, 4.76, Fe, 19.16.

$C_{13}H_{14}FeO_2S$ calcd.: C, 53.84; H, 4.87; Fe, 19.26%.) The PMR spectrum showed resonances at δ 3.17, singlet (2H, methylene protons); 3.68, singlet (2H, methylene protons); 4.15 ppm, singlet overlapped by multiplets (9H, ferrocene ring protons).

Dibutyltin-S,S'-bis(ferrocenyl thioglycolate) (VI)

Ferrocenyl thioglycolate (1 g, 0.0034 mole) and dibutyltin oxide (0.42 g, 0.0017 mole) in benzene were heated under reflux and the water formed during the reaction was azeotropically distilled. On removing the solvent, yellow semi-solid was obtained that crystallised from benzene/light petroleum as old gold plates (0.88 g, 64%) m.p. 72.5–73°. (Found: C, 50.20; H, 5.41; Fe, 13.51. $C_{30}H_{44}Fe_2O_4S_2Sn$ calcd.: C, 50.35; H, 5.47, Fe 13.79%.) The PMR spectrum showed resonances at δ 0.8–1.8, multiplet (18H, butyl protons); 3.2, singlet (4H, methylene protons); 3.62, singlet (4H, methylene protons); 4.1 ppm, singlet overlapped by multiplets (18H, ferrocene ring protons).

Dibutyltin bis(ferrocenylcarboxylate) (VII)

A reaction between ferrocenylcarboxylic acid (1.15 g, 0.0048 mole) and dibutyltin oxide (0.615 g, 0.00247 mole) in benzene was carried out as described in the previous experiment. The product (1.11 g, 67%) crystallised from benzene/light petroleum as orange needles 187–189°. (Found: C, 52.34; H, 5.17; Fe, 16.12. $C_{30}H_{36}Fe_2O_4Sn$ calcd.: C, 52.22; H, 5.11; Fe, 16.19%.) The PMR spectrum showed resonances at δ 0.8–1.75, multiplet (18H, butyl protons); 4.22, singlet (10H, unsubstituted cyclopentadienyl ring protons); 4.40, triplet (4H, substituted cyclopentadienyl ring protons); 5.85 ppm, triplet (4H, substituted cyclopentadienyl ring protons).

Di-π-cyclopentadienyltitanium dibenzoate (VIII)

Di-π-cyclopentadienyltitanium dichloride (4.94 g, 0.019 mole) was stirred with sodium benzoate (9.6 g, 0.08 mole) in benzene for 12 h. The excess sodium benzoate was collected by filtration and the solvent removed from the filtrate on the rotary evaporator to give an orange solid. The product (5.0 g, 52%) crystallised from benzene as large yellow prisms m.p. 190–192° (dec.) (Found: C, 68.72; H, 4.92; Ti, 11.41. $C_{24}H_{20}O_4Ti$ calcd.: C, 68.63, H, 4.80; Ti 11.40%.) The PMR spectrum showed resonances at δ 6.6, singlet (10H, cyclopentadienyl ring protons); 7.32–7.50 ppm, multiplet (10H, phenyl protons).

ACKNOWLEDGEMENTS

We thank The Polytechnic, Wolverhampton for a research assistantship (D.R.M.); Messrs. Robinson Brothers Ltd., West Bromwich for polymer processing facilities and gifts of organotin compounds and Dr. R. C. Poller, Queen Elizabeth College, University of London for the Mossbauer determinations.

REFERENCES

1 D. J. Booth and B. W. Rockett, *J. Chem. Soc. C*, (1971) 3341.
2 D. Seyferth, H. P. Hofmann, R. Burton and J. F. Helling, *Inorg. Chem.*, 1 (1962) 227.
3 T. Dods, H. Suzaki and T. Takiguch, *Bull. Chem. Soc. Jap.*, 43 (1970) 288.
4 (a) D. W. Slocum, B. W. Rockett and C. R. Hauser, *J. Amer. Chem. Soc.*, 87 (1965) 1241;
(b) D. J. Booth, G. Marr, B. W. Rockett and A. Rushworth, *J. Chem. Soc. C*, (1969) 2701.

5 W. C. GEDDES, *Rubber Chem. Technol.*, 40 (1967) 177; M. ONOZUKA AND M. ASAHINA, *J. Macromol. Sci.*, C3 (1969) 235.
6 A. ROSS, *Anal. New York Acad. Sci.*, 125 (1965) 107.
7 B. W. ROCKETT, M. HADLINGTON AND W. R. POYNER, unpublished results.
8 R. L. COLLINS, *J. Chem. Phys.*, 42 (1965) 1072.
9 A. S. MUFTI AND R. C. POLLER, *J. Chem. Soc. C*, (1967) 1362; H. SATO AND R. OKAWARA, *International Symposium on Molecular Structure and Spectroscopy*, Tokyo, 1962; T. TANAKA, *Organometal. Chem. Rev. A*, 5 (1970) 1.
10 I. R. BEATTIE AND T. GILSON, *J. Chem. Soc.*, (1961) 2585.
11 G. MARR, R. E. MOORE AND B. W. ROCKETT, *Tetrahedron Lett.*, (1968) 2521.
12 *Int. Org. Standardisation*, R.305, 1963.
13 M. HADLINGTON, B. W. ROCKETT AND A. G. NELHANS, *J. Chem. Soc. C*, (1967) 1436.