Divinyltin Bistrifluoroacetate and its Reactions with Sodium Salts of Metal-carbonyl Anions

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The compound $[(CH_2{=}CH)_2Sn(O_2CCF_3)_2]$, (I), has been prepared and characterised by elemental analysis, and ^1H, ^{19}F, i.r., and mass spectra. Salt-elimination reactions of compound (I) with $Na[Mn(CO)_5]$, $Na_2[Fe(CO)_4]$, and $Na[Co(CO)_4]$ afford $[(CH_2{=}CH)_2Sn(O_2CCF_3)_2\{Mn(CO)_5\}]$, (II), $[(CH_2{=}CH)_2Sn\{Mn(CO)_5\}_2]$, (III), $[\{(CH_2{=}CH)_2Sn[Fe(CO)_4]\}_2]$, (IV), and $[(CH_2{=}CH)_2Sn\{Co(CO)_4\}_2]$, (V).

REPLACEMENT of the vinyl groups of tetravinyltin by trifluoroacetate ions has been studied by Peruzzo *et al.*[1] who obtained the compound $[(CH_2{=}CH)_3Sn(O_2CCF_3)]$ by the reaction between $Sn(CH{=}CH_2)_4$ and $Na(O_2CCF_3)$ in methanol, and by Kaesz and Stone[2] who reported that a maximum of three vinyl groups were replaced when a mixture of $Sn(CH{=}CH_2)_4$ and CF_3CO_2H was heated at 100 °C for several hours. Prompted by this work and the general observation[3] that some carboxylic acids do not effect complete removal of the vinyl groups of $Sn(CH{=}CH_2)_4$, we have investigated the reaction between this compound and CF_3CO_2H under mild conditions. The product of this reaction, $[(CH_2{=}CH)_2Sn(O_2CCF_3)_2]$, (I), has unusually stable tin–vinyl group bonds and is a useful synthetic intermediate for preparation of divinyltin(IV) compounds. Here we report the products of reactions between compound (I) and $Na[Mn(CO)_5]$, $Na_2[Fe(CO)_4]$, and $Na[Co(CO)_4]$, which have afforded divinyltin(IV)–metal carbonyl derivatives.

EXPERIMENTAL

The compounds $Sn(CH{=}CH_2)_4$ (Pfalz and Bauer), CF_3CO_2H (Koch–Light), and $Fe(CO)_5$ (Fluka A.G.) were used without purification; $Mn_2(CO)_{10}$ was prepared from $[(\eta\text{-mcp})Mn(CO)_3]$ (η-mcp = η-methylcyclopentadienyl) (Strem Chemicals) according to the method of King *et al.*[4] and $Co_2(CO)_8$ was kindly supplied by Mr. J. Hickson of this Department. Solvents were dried over calcium hydride or sodium and distilled immediately prior to use. Manipulations were either carried out using standard vacuum-line techniques or under an atmosphere of deoxygenated dry nitrogen.

^{19}F and ^1H N.m.r. spectra were determined on a Varian HA-100 instrument at 100 MHz using benzotrifluoride and tetramethylsilane, respectively, as internal standards. The values of proton–proton coupling constants of the former were calculated using the Laocoon (1968) program[5] based on assignments of Moore and Happe.[6] Mass spectra were recorded on an A.E.I. MS 12 spectrometer using a 70 eV beam and i.r. spectra obtained using Perkin-Elmer 225 and 457 spectrometers calibrated with polystyrene film. Molecular-weight data were obtained by vapour-phase osmometry with a Mechrolab 301A osmometer and these determinations, together with elemental analyses, were carried out by the Microanalytical Department of Manchester University.

Preparations.—Divinyltin Bistrifluoroacetate, (I).—Tetravinyltin (2·3 g, 10 mmol) was added dropwise onto anhydrous trifluoroacetic acid (4·56 g, 40 mmol) at room temperature. An exothermic reaction occurred immediately to afford a colourless solution which, on evaporation at room temperature under reduced pressure, yielded a white solid. This *product* sublimed at 65 °C *in vacuo* (10^{-2} mmHg) as colourless needles, m.p. 126—127 °C, yield 90% (Found: C, 24·0; H, 1·6; Sn, 29·5. Calc. for $C_8H_6F_6O_4Sn$: C, 24·0; H, 1·5; Sn, 29·8%). The molecular weight was determined in acetone solutions (0·1, 0·05, and 0·01M) as 390 ± 15 (calc. for monomer: 399). The compound is a non-electrolyte in this solvent, a molar conductance of 8·5 Ω^{-1} cm^{-1} being obtained for a 0·1M-solution. Mass spectrum *m/e* (relative intensities): 373 (35), $[(CH_2{=}CH)Sn(O_2CCF_3)_2]^+$; 287 (100), $[(CH_2{=}CH)_2Sn(O_2CCF_3)]^+$; 279 (20), $[(CH_2{=}CH)Sn(O_2CCF_3)F]^+$; 260 (15), $[(CH_2{=}CH)Sn(O_2CCF_3)]^+$; 233 (45), $Sn(O_2CCF_3)^+$; 193 (95), $[(CH_2{=}CH)_2SnF]^+$; 171 (40), $(CH_2{=}CH)_2Sn^+$; 147 (35), $(CH_2{=}CH)Sn^+$; 139 (30), SnF^+; 120 (25), Sn^+; 69 (90), CF_3^+; and 44 (100), CO_2^+, based on ^{120}Sn for tin-containing fragments. Compound (I) is stable in air over prolonged periods without decomposition. It may be recovered unchanged from a solution of CF_3CO_2H after heating under reflux at atmospheric pressure for several days.

(Pentacarbonylmanganio)(trifluoroacetato)divinyltin, (II).—The salt $Na[Mn(CO)_5]$ (1·08 g, 5 mmol), prepared[7] from $Mn_2(CO)_{10}$ and dissolved in tetrahydrofuran (thf) (10 cm³), was added to a stirred solution of compound (I) (1·99 g, 5 mmol) in thf (10 cm³). The resultant mixture was stirred at room temperature for 15 min whence an i.r. spectrum indicated that reaction was complete. Evaporation of the solvent under reduced pressure afforded a yellow solid which was extracted with dichloromethane (15 cm³). The solution was then filtered, prior to evaporation of some solvent and cooling to −10 °C. A bright yellow microcrystalline *product* was thus obtained, m.p. 121—122 °C (decomp.), in 77% yield (Found: C, 27·1; H, 1·3; Mn, 11·9. Calc. for $C_{11}H_6F_3MnO_7Sn$: C, 27·4; H, 1·2; Mn, 11·4%). The mass spectrum of the compound also supports this composition: 482 (10), $[(CH_2{=}CH)_2Sn(O_2CCF_3)\{Mn(CO)_5\}]^+$; 455 (45), $[(CH_2{=}CH)Sn(O_2CCF_3)\{Mn(CO)_5\}]^+$; 428 (20), $[Sn(O_2CCF_3)\{Mn(CO)_5\}]^+$; 390 (50), $Mn_2(CO)_{10}^+$; 369 (35), $[(CH_2{=}CH)_2Sn\{Mn(CO)_5\}]^+$; 342 (25), $[(CH_2{=}CH)Sn\{Mn(CO)_5\}]^+$; 315 (30), $[Sn\{Mn(CO)_5\}]^+$; 287 (100), $[(CH_2{=}CH)_2Sn(O_2CCF_3)]^+$; 260 (10), $[(CH_2{=}CH)Sn(O_2CCF_3)]^+$; and 250 (45), $Mn_2(CO)_5^+$, based on ^{120}Sn for tin-containing fragments. Other peaks corresponding to further subdivision of these units were observed below

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m/e 250. ν(CO) (hexane) at 2 125w, 2 042w, 2 018vs, and 1 985vs cm^{-1}.

Bis(pentacarbonylmanganio)divinyltin, (III).—The salt Na[Mn(CO)$_5$] (2·01 g, 9·2 mmol), prepared as above and dissolved in thf (15 cm^3), was added to a stirred solution of compound (I) (1·83 g, 4·6 mmol) in thf (10 cm^3) and the resultant mixture stirred for 15 min before treatment in the manner described above, which afforded yellow crystalline *platelets* in 83% yield (Found: C, 29·5; H, 1·0; Mn, 19·4. Calc. for $C_{14}H_6MnO_{10}Sn$: C, 29·8; H, 1·1; Mn, 19·5%). The mass spectrum of the compound is consistent with this composition, and contained medium-to-low intensity sets of peaks corresponding to the ions $[(CH_2{=}CH)_2Sn\{Mn_2(CO)_n\}]^+$ (where n = 10—0 inclusively) and a relatively intense set of peaks corresponding to $SnMn_2^+$ in addition to peaks due to further fragmentation of these moieties. The compound does not melt but decomposes over the range 150—180 °C accompanied by sublimation of $Mn_2(CO)_{10}$. ν(CO) (hexane) at 2 104w, 2 079s, 2 047vw, 2 010vs, 2 006(sh), 1 989s, and 1 961vw cm^{-1}.

Bis[(tetracarbonylferrio)divinyltin], (IV). Compound (I) (1·4 g, 3·5 mmol) was dissolved in thf (10 cm^3) and to this was added a solution of the salt Na$_2$[Fe(CO)$_4$] (0·79 g, 3·5 mmol) in diglyme (15 cm^3), prepared by reduction of Fe(CO)$_5$ with NaBH$_4$.[8] The resultant mixture was magnetically stirred for 30 min and then methanol (10 cm^3) added, followed by sufficient water (*ca.* 20 cm^3) to initiate crystallisation, and the solution was then set aside at −10 °C overnight. Very pale-yellow crystals which formed were filtered off, washed with methanol, and further purified by sublimation at 90 °C under reduced pressure (10^{-2} mmHg) to yield bright-yellow *crystals* in 34% yield (Found: C, 28·1; H, 1·7; Fe, 16·3. Calc. for $C_8H_6FeO_4Sn$: C, 28·2; H, 1·8; Fe, 16·4%). The molecular weight was determined in CHCl$_3$ solutions (0·1, 0·05, and 0·02M) as 665 ± 30 (calc. for dimer: 684). The mass spectrum of the compound also supports a dimeric structure and contained sets of peaks corresponding to the ions $[(CH_2{=}CH)_4Sn_2\{Fe_2(CO)_n\}]^+$ (n = 8—0 inclusively), in addition to a relatively strong set of peaks corresponding to $Sn_2Fe_2^+$ and other peaks due to further subdivision of these units. The compound does not melt but decomposes over the range 125—150 °C. It is photosensitive and produces a brown compound on exposure to light for several days. ν(CO) (hexane) at 2 052vs, 2 005s, and 1 995vs cm^{-1}. Compound (IV) may also be prepared by reaction of stoicheiometric amounts of (I) and Fe(CO)$_5$ in refluxing nonane, or at room temperature in this solvent with a trace of CF$_3$CO$_2$H.

Bis(tetracarbonylcobaltio)divinyltin, (V).—The salt Na[Co(CO)$_4$] (1·93 g, 10 mmol), prepared[9] from Co$_2$(CO)$_8$, dissolved in thf (10 cm^3) was added to a stirred solution of compound (I) (2·00 g, 5 mmol) in thf (10 cm^3). This mixture was treated as described for the preparation of compound (II) and an orange-brown microcrystalline *solid* was obtained in 81% yield (Found: C, 27·6; H, 1·0; Sn, 22·9. Calc. for $C_{14}H_6CoO_8Sn$: C, 28·0; H, 1·1; Sn, 23·2%). The mass spectrum of the compound is consistent with this composition and contained sets of peaks corresponding to the ions $[(CH_2{=}CH)_2Sn\{Co_2(CO)_n\}]^+$ (where n = 7—0 inclusively), as well as an intense set of peaks due to $SnCo_2^+$ and other peaks due to further breakdown of these species. The product is pyrophoric and it does not melt but decomposes over the range 140—170 °C. ν(CO) (hexane) at 2 098w, 2 083s, 2 028(sh), 2 020s, 2 011vs, and 1 999s cm^{-1}.

RESULTS AND DISCUSSION

The mass-spectral data, together with the molecular-weight and conductance data in acetone solution, confirm that $[(CH_2{=}CH)_2Sn(O_2CCF_3)_2]$, (I), exists as discrete monomeric molecules. The low melting point and volatility of the compound suggest that these monomers persist into the solid phase. There are several structures that these molecules could possess depending on the relative positions of the ligands about the metal atom and the mode of co-ordination of the trifluoroacetato-groups, which may be unidentate, unsymmetrically bidentate, or symmetrically bidentate. *trans*-Octahedral structures have been confirmed by *X*-ray crystallography for the compounds $[Me_2Sn(NO_3)_2]$[10] and $[Me_2Sn(acac)_2]$,[11] the former containing two unsymmetrically bidentate nitrato-groups and the latter two symmetrically bidentate acetylacetonato-groups. The i.r. spectra of compound (I) (Table 1), which have been assigned following the studies of Redington and Lin[12] and Miller *et al.*,[13] do not offer a clear distinction between the various modes of bonding of the trifluoroacetato-groups. However, the positions of the asymmetric carboxylato-stretching frequencies at *ca.* 1 700 cm^{-1} are perhaps more consistent with unidentate or unsymmetrically bidentate co-ordination than symmetrically bidentate co-ordination of these groups.[14]

TABLE 1

I.r. spectra of the compound $[(CH_2{=}CH)_2Sn(O_2CCF_3)_2]$, (I)

	Wavenumber/cm^{-1}	
Assignment	Nujol mull	CHCl$_3$ solution
C–H Stretch	3 119vw	†
	3 062vw	
	3 000vw *	
	2 950vw *	
CO$_2$ Asym. stretch	1 715s	1 715s
	1 660vs	1 665vs
C=C Stretch	1 593w	1 589w
CO$_2$ Sym. stretch	1 462m *	1 435m,b
	1 417m *	
	1 393m *	1 389m
CF$_3$ Stretch	1 205vs	†
	1 180vs	†
	1 153vs	1 145vs
C–H and CH$_2$ Out-of-plane def.	984s	989s
	953s	960m
C–C Stretch	851s	†
OCO Def.	790s	†
CF$_3$ Bend	727s	†
	634s	†

* Recorded in hexachlorobutadiene mull. † Obscured by solvent absorption.

vs = Very strong, s = strong, m = medium, w = weak, vw = very weak, b = broad; asym. = asymmetric, sym. = symmetric, and def. = deformation.

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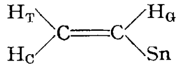
The ^{19}F n.m.r. spectrum of compound (I), recorded in acetone solution, consists of a single resonance 77·5 p.p.m. upfield of $CFCl_3$ in the range (69·1—78·5 p.p.m. upfield of $CFCl_3$) observed for trifluoroacetates.[14] The ^1H n.m.r. spectrum of this compound (Table 2) is a typical collapsed ABC system[15] and resembles that reported for tetravinyltin.[6,16,17]

The facts that compound (I) may be recovered unchanged from CF_3CO_2H after heating under reflux at atmospheric pressure for several days and that, even at 100 °C, this reagent only replaces one further vinyl group,[2] are in marked contrast to ready replacement of all the vinyl groups of $(CH_2{=}CH)_4Sn$ by alkanoic acids.[3]

TABLE 2

Proton–proton coupling constants (J/Hz) and proton chemical shifts (τ/p.p.m. upfield of Me_4Si) of divinyltin(IV) compounds



Compound	τ_G	τ_T	τ_C	J_{CT}	J_{CG}	J_{GT}	ΣJ_{ij}
$(CH_2{=}CH)_4Sn$ [a]	3·7	3·9	4·3	3·7	13·2	20·3	37·2
$[(CH_2{=}CH)_2Sn(O_2CCF_3)_2]$, (I) [b]	3·9	4·0	4·2	5·4	13·6	17·7	36·7
$[(CH_2{=}CH)_2Sn\{Mn(CO)_5\}_2]$, (III) [b]	3·1	3·7	4·2	2·4	13·0	19·0	34·4
$[\{(CH_2{=}CH)_2Sn[Fe(CO)_4]\}_2]$, (IV) [b]	3·0	3·8	4·1	1·8	12·7	19·6	34·1
$[(CH_2{=}CH)_2Sn\{Co(CO)_4\}_2]$, (V) [b]	3·0	3·8	4·2	1·5	12·7	19·1	33·3

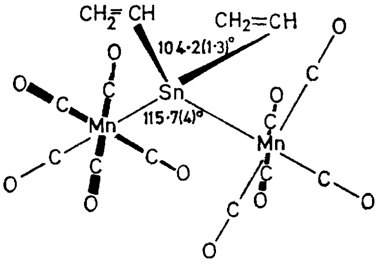
[a] Ref. 6. [b] This work; spectra recorded in perdeuteriochloroform.

* Estimated maximum error in τ values is ±0·1 p.p.m. and in coupling constants ±0·5 Hz.

Thus trifluoroacetato-groups appear to confer kinetic inertness and/or thermodynamic stability to tin–vinyl group bonds such that with compound (I) reactions occur at a $(CH_2{=}CH)_2Sn$ centre to afford a convenient route to $(CH_2{=}CH)_2Sn^{IV}$ compounds. Salt-elimination reactions with metal-carbonyl anions, analogous to those described for halogeno-complexes,[18] afford compounds containing tin–transition metal bonds. Compound (I) and $Na[Mn(CO)_5]$ (1 : 1 or 1 : 2) afford $[(CH_2{=}CH)_2Sn(O_2CCF_3)\{Mn(CO)_5\}]$, (II), or $[(CH_2{=}CH)_2Sn\{Mn(CO)_5\}_2]$, (III), respectively; with $Na_2[Fe(CO)_4]$, $[\{(CH_2{=}CH)_2Sn[Fe(CO)_4]\}_2]$, (IV), is obtained, and with $Na[Co(CO)_4]$ (1 : 2) $[(CH_2{=}CH)_2Sn\{Co(CO)_4\}_2]$ is produced. The latter compound was reported earlier[19] but no detailed characterisation given.

Mass spectra of (II)—(V) conclusively support the chemical characterisation of these compounds. The fragmentation pattern observed for compound (II) is markedly different from that of the other three. Loss of $Mn(CO)_5$ by cleavage of the Sn–Mn bond appears to be the favoured fragmentation path for $[(CH_2{=}CH)_2Sn(O_2CCF_3)\{Mn(CO)_5\}]^+$, although some loss of $CH_2{=}CH$ and O_2CCF_3 groups also occurs. In all these compounds, loss of carbonyl groups from the parent ion is favoured over that of vinyl groups and it is interesting to note that the 'isoelectronic' ions $[(CH_2{=}CH)_2Sn\{Mn_2(CO)_3\}]^+$ and $[(CH_2{=}CH)_2SnCoCO]^+$ are particularly abundant in the appropriate spectra.

Carbonyl stretching frequencies observed for compound (II) are very similar to those observed in other $(CO)_5Mn$–Sn compounds[20] and, assuming that local C_{4v} symmetry is appropriate for the $Mn(CO)_5$ group, these frequencies may be assigned as 2 125w (A_1 equatorial), 2 042w (B_1), 2 018vs (E), and 1 985s (A_1 axial). An X-ray diffraction study of single crystals of compound (III) has been carried out[21] and, although not yet completely refined, the molecular structure has been identified reasonably well and shown to be analogous to that reported[22] for $[Ph_2Sn\{Mn(CO)_5\}_2]$. The tin atom is situated in an approximately tetrahedral environment with the two $Mn(CO)_5$ groups in a pseudo-staggered conformation, thus reducing the interactions between them and resulting in the molecular symmetry being no higher than C_s. Carbonyl stretching frequencies observed for (III) are similar to those reported for analogous dichloro-, dimethyl-, and diphenyl-compounds.[23] The assignment of several of the frequencies follows from data presented for compound (II). However, complete assignment of these data in terms of C_s molecular symmetry [for which 10 i.r. ν(C≡O) bands would be expected] is inappropriate here. The carbonyl stretching frequencies of compound (IV) are very similar to those



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obtained[24] for other $\{R_2M[Fe(CO)_4]\}_2$ species (R = alkyl, phenyl, or halide; M = Ge, Sn, or Pb). These data, together with the other properties of the compound, thus strongly suggest that (IV) has an analogous structure to that determined[25] for $\{Me_2Sn[Fe(CO)_4]\}_2$, and the carbonyl stretching frequencies may be assigned as 2 052vs (B_{2u} axial), 2 005s (B_{3u} equatorial), and 1 995vs (B_{1u} axial), from the normal-co-ordinate analyses of Kahn and Bigorgne.[26] Lewis bases cleave[27] the four-membered metal ring of (IV) in an analogous manner to that described for other compounds of this type.[28] The carbonyl i.r. stretching frequencies obtained for (V) agree well with those reported earlier for this compound and are similar to those of the analogous compounds $[R_2Sn\{Co(CO)_4\}_2]$ (R = Me, Ph, or Cl)[19] and may be similarly assigned.

The major factors which are likely to affect ^1H n.m.r. spectra of vinyltin compounds have been discussed.[16] Factors considered were the diamagnetic anisotropies of the Sn–C and C=C bonds, the electronegativity difference between the α-carbon atom of the vinyl group and the tin atom, and the extent of d_π–p_π bonding between these two atoms, and Blears *et al.* concluded that there was a significant diamagnetic-deshielding contribution due to the latter interaction. The ^1H n.m.r. spectra obtained in this study are also consistent with d_π–p_π bonding being an important effect. Thus appreciable deshielding of the vinyl groups was observed (Table 2) in the metal-carbonyl derivatives, where the $M(CO)_n$ groups are not only strongly electron withdrawing, but are also able to effectively delocalise any π-electron density transferred to the tin atom from the α-carbon atoms. Therefore, carbon–tin p_π–d_π bonding is encouraged in these molecules. This bonding should thus enhance the strength of the vinyl group–tin bonds. In so far as fragmentation patterns of positive ions can be used to provide evidence about relative bond strengths in the corresponding neutral species, the mass-spectral data indicate that cleavage of the tin–vinyl group bonds occurs much less readily for the metal-carbonyl derivatives (III)—(V), than for compound (I). Concerning compound (I), the ^1H n.m.r. spectral data obtained for $Sn(CH=CH_2)_4$ and (I) (Table 2) indicate that substitution of two vinyl groups by trifluoroacetates does not lead to significant deshielding of the remaining vinyl protons. Thus, although the trifluoroacetate groups are strongly electron withdrawing and contain empty π^*-orbitals, the extent to which they encourage the carbon–tin p_π–d_π interaction is minimal compared to that of $M(CO)_n$ groups (M = Mn, $n = 5$; M = Co or Fe, $n = 4$).

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