Journal of Organometallic Chemistry, 125 (1977) 179—183

REACTIONS OF PENTACARBONYLIRON WITH ORGANOTIN DERIVATIVES: FORMATION OF BIS(DIORGANOTIN-TETRACARBONYLIRON) COMPLEXES

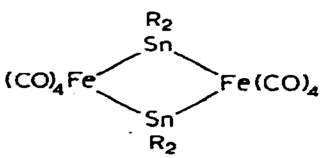
RICHARD A. BURNHAM, MARGARET A. LYLE and STEPHEN R. STOBART *
Department of Chemistry, Queen's University, Belfast BT9 5AG (Great Britain)
(Received July 9th, 1976)

Summary

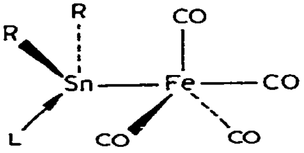
Reactions of diorganotin oxides in refluxing pentacarbonyliron proceed via formation of carbon dioxide to give $[R_2SnFe(CO)_4]_2$ (I) in high yields. Diorganotin sulphides and acetates react similarly under analogous conditions. Carbonyl substitution by triorgano-phosphines and -phosphites in complexes of type I has been investigated.

Introduction

Crystallographic substantiation [1] of the dimeric formulation [2] for iron carbonyl complexes of the type $R_2SnFe(CO)_4$ (I) has been followed by renewed interest in these compounds as precursors to tetracarbonyliron derivatives (II; L = py or THF) in which the main-group metal is formally in the divalent state [3]. During an investigation of reactions of organotin chalcogenides with metal carbonyls we have encountered a facile general synthesis of compounds I which is much more efficient than any described previously [3,4].



(I)



(II)

---

* Author to whom correspondence should be addressed at his present address: Department of Chemistry, University of Victoria, Victoria B.C., V8W 2Y2 (Canada).

Results and discussion

Reaction of dibutyltin oxide in refluxing $Fe(CO)_5$ provides a very effective route to I (R = Bu); after 6 h a yield of 67% was obtained and some Bu_2SnO remained. This reaction was investigated in more detail under sealed-tube conditions, giving 89% of I (R = Bu) together with a corresponding yield of carbon dioxide entirely consistent with the unusual direct elimination of oxygen from tin represented by reaction (1). Further experiments with related organotin derivatives showed this type of reaction

$$2Fe(CO)_5 + 2Bu_2SnO \rightarrow \text{I } (R = Bu) + 2CO_2 \qquad (1)$$

to be general for dialkyltin oxides, bis(trialkyltin) oxides, and for the sulphur analogues (Table 1). All the products, including the liquid di-octyl tin derivative, showed the characteristic [4] pattern of IR bands attributable to $\nu(CO)$ modes. Phenyl-tin compounds appear to be less reactive; with Ph_2SnO no reaction occurred and trimeric [5] $(Ph_2SnS)_3$ gave only 15% of I (R = Ph), while with bis(triphenyltin) species the complex $(Ph_3Sn)_2Fe(CO)_4$ was formed. Involvement of the butyltin analogue of the latter in the formation of I (R = Bu) has been suggested elsewhere [4].

Reactions of $Fe(CO)_5$ with several other organotin derivatives have also been investigated. With dibutyltin diacetate, similarly high yields (Table 1) of I (R = Bu) were obtained, while butyltin trichloride reacted rapidly in refluxing $Fe(CO)_5$ to give the orange complex $(SnBuCl_2)_2Fe(CO)_4$. In the $\nu(CO)$ region, this compound shows IR bands indicative of a *cis*-configuration at ca 30 cm^{-1} to higher energy than those [4] for $(SnBu_2Cl)_2Fe(CO)_4$, consistent with increasingly effective removal of charge from the iron atom with increasing halogen substitution at tin. Longer reaction times gave red oils with IR spectra appropriate for complexes of type I ($R_2 = Cl_2$ or BuCl) but these were not isolated. Addition of tetravinylstannane to refluxing $Fe(CO)_5$ resulted in rapid deposition of an orange solid, from which I ($R = CH{=}CH_2$) was isolated. Essentially the same reaction has recently been described by Garner and Hughes [6]. By con-

TABLE 1

REACTIONS OF ORGANOTIN DERIVATIVES WITH PENTACARBONYLIRON

Reactant (% yield of product)	Product	Found (Calc.)	
		C	H
$SnBu_2(OAc)_2$ (52): $[Bu_2SnO]$ (67): $[Bu_2SnS]_3$ (62): $(SnBu_3)_2O$ (35): $(SnBu_3)_2S$ (45)	$[Bu_2SnFe(CO)_4]_2$	35.96 (35.95)	4.56 (4.54)
$[Me_2SnO]$ (20; 15)	$[Me_2SnFe(CO)_4]_2$ [a] $Sn[Fe(CO)_4]_4$ [a]		
$[Et_2SnO]$ (51)	$[Et_2SnFe(CO)_4]_2$	27.96 (27.87)	2.94 (2.92)
$[Oc_2SnO]$ (60)	$[Oc_2SnFe(CO)_4]_2$	46.14 (46.82)	6.59 (6.68)
$[Ph_2SnO]$	No reaction		
$(Ph_2SnS)_3$ (15)	$[Ph_2SnFe(CO)_4]_2$	45.36 (43.58)	3.45 (2.27)
$(SnPh_3)_2O$ (65): $(SnPh_3)_2S$ (16)	$(SnPh_3)_2Fe(CO)_4$	55.52 (55.32)	3.25 (3.46)

[a] Identified by IR spectroscopy.

trast, no complexes could be crystallized from the viscous oils formed by reaction between tributyl(vinyl)stannane and $Fe(CO)_5$.

Reactions of the complexes I with tri-organophosphines have been only cursorily investigated. Kahn and Bigorgne have reported [7] that at ambient temperature with PEt_3 monosubstitution of I (R = Bu) occurs giving $\{(CO)_4Fe\text{-}\mu\text{-}(SnBu_2)_2Fe(CO)_3(PEt_3)\}$ while heating gives $[Bu_2SnFe(CO)_3(PEt_3)]_2$; IR spectra of these products were discussed but no yields were recorded. Marks and Newman have described [3] an 8% conversion of I (R = Me) to the disubstituted product $[Me_2SnFe(CO)_3(PBu_3)]_2$. Much higher yields (35—75%) of complexes III and IV of the latter type result when I (R = Bu) is treated in solution with PPh_3 or 1,2-bis(diphenylphosphino)ethane; likewise, with a range of other tri-organophosphines and with tri-organo-arsines although difficulty was encountered in isolating analytically pure derivatives IR spectroscopy confirmed (by lowering in energy of CO stretching bands) that substitution had taken place. With triphenylphosphite under very mild conditions, monosubstitution occurs giving $\{Bu_4Sn_2Fe_2(CO)_7P(OPh)_3\}$, (V), while heating in undiluted $P(OMe)_3$ affords a complex (VI) tentatively formulated on the basis of IR and analytical measurements to be the totally substituted compound in which the fourmembered Sn_2Fe_2 ring has been retained. These observations confirm that compounds I undergo carbonyl substitution reactions with phosphorus donor molecules, in contrast to the homolysis of the polymetallic ring brought about [3] by treatment with nitrogen- or oxygen-containing bases.

Experimental

Reactions were carried out in an atmosphere of dry dinitrogen gas. Products were isolated by removal of excess pentacarbonyliron, followed by extraction of the solid residue first with pentane and then with dichloromethane whence concentration and cooling of the extracts to —78°C induced crystallization. The complexes were characterized by elemental microanalysis, IR (Perkin—Elmer 457, cyclohexane or chloroform solution) and mass (AEI MS902) spectroscopy.

Reactions of pentacarbonyliron

(i) With dibutyltin diacetate Gentle refluxing of a mixture of $Bu_2Sn(OAc)_2$ (13 g, 37 mmol) and $Fe(CO)_5$ (37 g, 187 mmol) for 60 h was accompanied by evolution of CO and led to the formation of a metallic mirror and a dark, red-green solution from which was obtained after recrystallization from pentane pale yellow $[Bu_2SnFe(CO)_4]_2$, (7.8 g, 9.7 mmol) m.p. 110—111°C (lit. [4] 112°C). Found: C, 35.96; H, 4.56. $C_{24}H_{36}Fe_2O_8Sn_2$: calc. C, 35.95; H, 4.54%. Shorter reflux times afforded lower yields of the complex. Pentane insoluble material in this reaction was identified as iron(II) acetate.

(ii) With diorganotin oxides, diorganotin sulphides, bis(triorganotin)-oxides, and bis(triorganotin)sulphides A series of reactions with $Fe(CO)_5$ were carried out as detailed in (i) by refluxing the organotin compound either in liquid iron pentacarbonyl or in a mixture of the latter in 100—120°C petroleum ether, di-n-butyl ether or diglyme. Representative yields and analytical data for the products are collected in Table 1.

TABLE 2

REACTIONS OF BIS(DI-N-BUTYLSTANNYLTETRACARBONYLIRON)

Reactant	Product	Colour, yield (%)	Found (calc.)			ν(CO) (cm^{-1})
			C	H	P	
PPh_3 [a]	$[Bu_2SnFe(CO)_3PPh_3]_2$ (III)	Golden-yellow, 34	55.57 (54.84)	5.24 (5.25)		1970s, 1940vs, 1920s, 1890m(sh), 1876m [e]
$Ph_2P(CH_2)_2PPh_2$ [b]	$\{Bu_2SnFe(CO)_2[PPh_2(CH_2)_2PPh_2]\}_2$ (IV)	Yellow, 74	58.54 (58.18)	5.86 (5.70)	8.12 (8.34)	2033s, 1992m(sh), 1984s, 1974s, 1967vs, 1940w(sh), 1910w, 1884m, 1850w [f]
$P(OPh)_3$ [c]	$\{Bu_4Sn_2Fe_2(CO)_7[P(OPh)_3]\}$ (V)	Pale yellow, 40	45.65 (45.41)	4.71 (4.71)		2038s, 2000m, [e] 1978s(sh), 1976vs [e]
$P(OMe)_3$ [d]	$\{Bu_2SnFe[P(OMe)_3]_4\}_2$ (VI)	Yellow, 65	28.60 (30.58)	6.09 (6.88)		

[a] 4 mol. equiv., 8 h in refluxing diglyme. [b] 2.5 mol. equiv., 12 h in refluxing 100—120°C pet. ether. [c] 2.5 mol. equiv., 4 h at 35°C. [d] Starting complex dissolved in neat $P(OMe)_3$, 60°C for 8 h. [e] KBr disc. [f] Cyclohexane solution.

(iii) With dibutyltin oxide In a Carius tube at 90°C for 19 h, Bu_2SnO (230 mg, 0.92 mmol) and $Fe(CO)_5$ (3 g, 15 mmol) yielded CO (IR, 1.18 mmol), CO_2 (IR, 0.91 mmol) and pure $[Bu_2Fe(CO)_4]_2$ (353 mg, 0.44 mmol). Similar sealed tube reactions with $(R_2SnS)_3$ (R = Me or Bu) provided no evidence for the formation of either COS or CS_2.

(iv) With triorganotin halides With tri-n-propyltin chloride, $Fe(CO)_5$ yielded an orange yellow solid from pentane with a complex IR spectrum (νCO, 2078s, 2058(sh), 2049vs, 2030m, 2018s as well as several weak bands) tentatively attributable to the presence of a mixture of $(Pr_2ClSn)_2Fe(CO)_4$ and $[Pr_2SnFe(CO)_4]_2$. Refluxing triphenyltin chloride in $Fe(CO)_5$/diglyme for 24 h led only to recovery of unreacted halide.

(v) With butyltin trichloride Short reflux (3 h) of a mixture of $BuSnCl_3$ (3.9 g, 13.8 mmol) and $Fe(CO)_5$ (15 g, 75 mmol) yielded a pale orange solid from dichloromethane. Recrystallization (CH_2Cl_2) gave bis(n-butyl-dichlorostannyl)-tetracarbonyliron (2.5 g, 3.8 mmol). (Found: C, 21.1; H, 2.6. $C_{12}H_{18}Cl_4FeO_4Sn_2$ calc.: C, 21.8; H, 2.7%). IR: νCO ($CHCl_3$ soln.), 2130w, 2105vw, 2060s, 2035vs, 2000w (sh). ν(Sn—Cl) (CsI disc), 325s, 305s cm^{-1}. Longer reaction times (17 h) yielded bright red, viscous oils.

(vi) With vinylstannanes Tributylvinylstannane with $Fe(CO)_5$ afforded only dark oils following extraction with either pentane or CH_2Cl_2. In refluxing $Fe(CO)_5$ tetravinyltin rapidly deposited an orange solid which yielded (pentane) yellow bis(divinylstannyltetracarbonyliron) (ca 40%; Found: C, 28.6; H, 1.9. $C_{16}H_{12}Fe_2O_8Sn_2$ calc.: C, 28.2; H, 1.8%). IR (cyclohexane soln.) 2054s (sh), 1992vs cm^{-1}. This complex rapidly darkened even in vacuo to give a deep orange, pentane insoluble material.

Reactions of bis(di-n-butylstannyltetracarbonyliron) (I, R = Bu) with organophosphines, -arsines, and -phosphites

Reactions of I (R = Bu) with a variety of PR_3, AsR_3 and $P(OR)_3$ ligands were investigated, mainly by refluxing the reactants in 100—120°C petroleum ether or diglyme. While in all cases IR spectroscopy provided evidence for carbonyl displacement, isolation of pure products was generally difficult; some representative analytical data are presented in Table 2.

References

1 C.J. Gilmore and P. Woodward, J. Chem. Soc. Dalton, (1972) 1387.
2 R.B. King and F.G.A. Stone, J. Amer. Chem. Soc., 82 (1960) 3833.
3 T.J. Marks and A.R. Newman, J. Amer. Chem. Soc., 95 (1973) 769; M.D. Brice and F.A. Cotton, ibid., p. 4529.
4 J.D. Cotton, S.A.R. Knox, I. Paul and F.G.A. Stone, J. Chem. Soc. (A), (1967) 264.
5 P.G. Harrison and S.R. Stobart, J. Organometal. Chem., 47 (1973) 89.
6 C.D. Garner and B. Hughes, J. Chem. Soc. Dalton, (1974) 1306.
7 O. Kahn and M. Bigorgne, J. Organometal. Chem., 10 (1967) 137.