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THE CLEAVAGE OF TIN—ALLYL BONDS IN $R_2(CH_2{=}CH{-}CH_2)_2Sn$ SUBSTRATES AS A ROUTE TO ORGANOSTANNOXANES

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Summary

Tetrabutyl-1,3-diacyloxydistannoxanes, $(RCOO)Bu_2SnOSnBu_2(OOCR)$ (A) and/or tetrabutyl-1-acyloxy-3-hydroxydistannoxanes, $(RCOO)Bu_2SnOSnBu_2(OH)$ (B), can be prepared from equimolecular amounts of dibutyldiallyltin and carboxylic acid, RCOOH (R = H, CH_3, CH_2Cl, $CHCl_2$, CCl_3, CF_3) in moist methanol or acetone/water (50/50, v/v). Isolation of compounds (A) or (B) depends upon the hydrolyzing power of the medium and the nature of R.

Introduction

We previously succeeded in preparing allylstannoxanes [1], $(R_2SnOOCR')_2O$ (R = allyl, R′ = CH_2Cl, $CHCl_2$ and CCl_3) by treating equimolecular amounts of tetraallyltin and carboxylic acid in moist methanol at room temperature. Since this reaction seemed promising as route to organostannoxanes, we have now examined the reactions involving mixed substrates of the type $R_2(CH_2{=}CH{-}CH_2)_2Sn$.

We describe below the preparation of tetrabutyl-1,3-diacyloxydistannoxanes (A) and/or tetrabutyl-1-acyloxydistannoxanes (B) by use of the reaction between dibutyldiallyltin and RCOOH acids in moist methanol or in aqueous acetone.

Experimental

Commercially available dibutyldiallyltin was used without further purification. Carboxylic acids and all solvents were of reagent grade. IR spectra were recorded on a Perkin—Elmer Model 457 spectrophotometer with KBr optics, using Nujol mulls or chloroform solutions. Molecular weights were determined in chloroform with a Mechrolab Model 302B vapour phase osmometer. Melting points (uncorrected) were taken with a Büchi apparatus (Switzerland).

TABLE 1

INTERACTION OF $Bu_2(CH_2{=}CH{-}CH_2)_2Sn$ AND RCOOH IN METHANOL ISOLATED COMPOUNDS, WITH ANALYTICAL AND PHYSICAL DATA

No.	R (RCOOH)	Prepared compound	Yield (%)	M.P. (°C)	Analysis found (Calcd.) (%) C	H	Cl	F	Mol.wt.($CHCl_3$) found (conc.→0) (calcd.)
(I)	H	$Bu_2(CH_2{=}CH{-}CH_2)SnOOCH$	79	[a]	44.51 (45.16)	7.51 (7.58)			316[c] (318.8)
(II)	CH_3	$Bu_2(CH_2{=}CH{-}CH_2)SnOOCCH_3$	59	[b]	46.54 (46.86)	7.58 (7.87)			408 (332.9)
(III)	CH_2Cl	$[Bu_2SnOOCCH_2Cl]_2O$	99	38	35.70 (35.89)	6.11 (6.03)	10.23 (10.60)		829 (668.6)
(IV)	$CHCl_2$	$[Bu_2SnOOCCHCl_2]_2O$	85	210	32.39 (32.54)	5.21 (5.19)	18.67 (19.23)		1138 (737.4)
(V)	CCl_3	$[Bu_2SnOOCCCl_3]_2O$	98	175	29.52 (29.76)	4.45 (4.50)	26.16 (26.37)		988 (806.3)
(VI)	CF_3	$(CF_3COO)Bu_2SnOSnBu_2(OH)$	83	180	35.05 (35.31)	6.25 (6.09)		9.28 (9.32)	607 (611.6)

[a] Liquid. [b] Liquid, b.p. 127°/10 mm. [c] Determined in CCl_4.

TABLE 2

PREPARATION OF DIBUTYLTIN CARBOXYLATES: EXPERIMENTAL CONDITIONS, AND ANALYTICAL AND PHYSICAL DATA

No.	Prepared compound	[A] or [B] / [RCOOH]	Yield (%)	M.p. (°C)	Analysis found (calcd) (%) C	H	Cl	F
(VII)	$Bu_2Sn(OOCCH_2Cl)_2$	0.50	41	87—88 (87—89)[a]	34.23 (34.32)	5.48 (5.28)	16.72 (16.89)	
(VIII)	$Bu_2Sn(OOCCHCl_2)_2$	0.50	64	112—113 (112—114)[a]	29.23 (29.48)	3.98 (4.12)	28.92 (29.01)	
(IX)	$Bu_2Sn(OOCCCl_3)_2$	0.50	39	113	25.20 (25.83)	3.12 (3.25)	38.05 (38.15)	
(X)	$Bu_2Sn(OOCCF_3)_2$	0.33	47	57	31.16 (31.40)	3.91 (3.95)		24.24 (24.86)

[a] See ref. [4].

Reaction of dibutyldiallyltin and RCOOH in methanol

Equimolecular amounts of dibutyldiallyltin (2 g, 6.35 mmole) and RCOOH acid were stirred together in moist methanol (60 - 70 ml) for about 24 h at room temperature. Evaporation of the solvent left an oil or solid, depending upon the acid used. Solid residues were crystallized from chloroform/n-hexane mixture. The compounds obtained are listed in Table 1, which also gives analytical data and physical constants.

Preparation of $(RCOO)Bu_2SnOSnBu_2(OH)$, $(R = H, CH_3)$ *by hydrolysis of* $Bu_2(CH_2{=}CH{-}CH_2)SnOOCR$ *in methanol/water*

A solution (50 ml) of dibutylallyltin formate [cf. Table 1, compound (I)] (0.5 g) in methanol/water (98/2, v/v) was stirred for one week at room temperature. Solvent was removed under reduced pressure to leave a solid residue, which was crystallized from chloroform/n-hexane to give tetrabutyl-1-formoxy-3-hydroxydistannoxane (80% yield), m.p. 110°. (Found: C, 37.10; H, 7.19. $C_{17}H_{38}O_4Sn_2$ calcd.: C, 37.52; H, 7.04%.)

The same procedure was used for the dibutylallyltin acetate [cf. Table 1, compound (II)]. Tetrabutyl-1-acetoxy-3-hydroxydistannoxane was recovered (50% yield) m.p. 128° (Lit. [2,3], 129°). (Found: C, 38.05; H, 7.23. $C_{18}H_{40}O_4Sn_2$ calcd.: C, 38.73; H, 7.23%.)

Preparation of $Bu_2Sn(OOCR)_2$ *compounds by treating compounds (A) or (B) with RCOOH in benzene*

Compounds of the type (A), $(Bu_2SnOOCR)_2O$ ($R = CH_2Cl, CHCl_2, CCl_3$) and the compound $(CF_3COO)Bu_2SnOSnBu_2(OH)$ reacted with the appropriate carboxylic acid in benzene to give the corresponding dibutyltin dicarboxylates. Benzene (50 ml) containing 0.5 g of (A) or (B) and the appropriate acid RCOOH were refluxed for 1 h. Distillation of the solvent left a solid residue which was crystallized from chloroform. Table 2 shows the experimental conditions, the products obtained, and their analytical and physical data.

Hydrolysis of $Bu_2Sn(OOCR)_2$ *in water*

Compounds (A) or (B) were prepared by treating $Bu_2Sn(OOCR)_2$ (0.5 mmole) with a large amount of water (100 ml) under nonhomogeneous conditions.

Hydrolysis of $Bu_2Sn(OOCCH_2Cl)_2$ gave tetrabutyl-1-monochloroacetoxy-3-hydroxydistannoxane, m.p. 139°. From $Bu_2Sn(OOCCHCl_2)_2$, compound (IV) (cf. Table 1) was obtained, m.p. 209°. Compounds of the type (B) $(CCl_3COO)Bu_2SnOSnBu_2(OH)$ and $(CF_3COO)Bu_2SnOSnBu_2(OH)$ were isolated from the carboxylates having $R = CCl_3$ and CF_3, m.p. 164° and 180° respectively.

Reaction of dibutyldiallyltin and RCOOH in acetone/water (50/50, v/v)

Dibutyldiallyltin (2 g, 6.35 mmole) and RCOOH acids (R = CH_2Cl, $CHCl_2$, CCl_3 and CF_3) in the ratio 1/1, were allowed to react in acetone/water medium (50/50, v/v) at room temperature. Compounds of type (A) or (B) were obtained: some comments on this reaction are given below.

Tetrabutyl-1-monochloroacetoxy-3-hydroxydistannoxane

After about 24 h an heavy oil was formed, and this was converted after a week into a white solid. The solid residue (85% yield) was filtered off and recrystallized from chloroform; it had m.p. 138 - 140°. (Found: C, 36.18; H, 6.09; Cl, 5.67. $C_{18}H_{39}O_4ClSn_2$ calcd.: C, 36.47; H, 6.64; Cl, 5.98%.)

Tetrabutyl-1,3-dichloroacetoxydistannoxane

The oil formed after one hour gave a solid residue after 5 - 6 h (84% yield). M.p. 210° [cf. Table 1, compound (IV)].

Tetrabutyl-1-trichloroacetoxy-3-hydroxydistannoxane

After 2 - 3 h a solid was precipitated (88% yield). The pure product melts at 164 - 165°. (Found: C, 32.39; H, 5.65; Cl, 16.18. $C_{18}H_{37}O_4Cl_3Sn$ calcd.: C, 32.67; H, 5.64; Cl, 16.09%.)

Tetrabutyl-1-trifluoroacetoxy-3-hydroxydistannoxane

Similarly after 2 - 3 h, a solid precipitate was formed (87% yield), and after purification the product had m.p. 180°. [cf. Table 1, compound (VI)].

TABLE 3

MOLECULAR WEIGHTS OF TETRABUTYL-1,3-DIACYLOXYDISTANNOXANES IN $CHCl_3$ (37°)

No.	Compound. (Mol.wt. calcd)	Concn. (mg/ml)	Mol.wt. found	i^a
(III)	$[Bu_2SnOOCCH_2Cl]_2O$	15.12	1052	1.57
	(668.60)	7.56	1090	1.63
		3.78	950	1.42
		1.89	983	1.36
			890^b	1.33
(IV)	$[Bu_2SnOOCCHCl_2]_2O$	14.16	1111	1.50
	(737.48)	7.08	1146	1.55
		3.59	1070	1.45
		1.79	1032	1.40
			1138^b	1.54
(V)	$[Bu_2SnOOCCCl_3]_2O$	12.71	1148	1.42
	(806.37)	6.35	1105	1.37
		3.18	1052	1.30
		1.59	1005	1.24
			988^b	1.12

[a] i = Mol.wt. found/mol.wt. calcd. [b] Extrapolated value, concn.→0.

TABLE 4

MOLECULAR WEIGHTS OF TETRABUTYL-1-ACYLOXY-3-HYDROXYDISTANNOXANES IN $CHCl_3$ (37°)

No.	Compound (Mol.wt. calcd.)	Concn. (mg/ml)	Mol.wt. found	i^a
(XI)	$(HCOO)Bu_2SnOSnBu_2(OH)$	13.72	1085	1.99
	(543.66)	6.86	1133	2.08
		3.43	1089	2.00
		1.71	1062	1.95
			1060^b	1.95
(XII)	$(CH_3COO)Bu_2SnOSnBu_2(OH)$	7.42	2074	1.92
	(557.70)	3.71	1059	1.90
		1.85	996	1.78
		0.93	982	1.74
			982^b	1.74
(XIII)	$(CH_2ClCOO)Bu_2SnOSnBu_2(OH)$	15.91	1182	1.99
	(592.14)	7.95	1134	1.91
		3.98	731	1.23
		1.99	670	1.13
			595^b	1.00
(XIV)	$(CCl_3COO)Bu_2SnOSnBu_2(OH)$	14.85	1392	2.10
	(661.02)	7.43	1275	1.93
		3.71	919	1.39
		1.85	826	1.25
			705^b	1.06
(VI)	$(CF_3COO)Bu_2SnOSnBu_2(OH)$	15.44	1108	1.81
	(611.67)	7.72	1073	1.75
		3.86	650	1.06
		1.93	618	1.01
			607^b	0.99

[a] i = Mol.wt. found/mol.wt. calcd. [b] Extrapolated value, concn.→0.

Molecular weights

Molecular weights were determined in chloroform for all tetrabutylstannoxanes. The results, shown in Table 3 and 4, indicate that the compounds exist in chloroform as dimers and monomers. From examination of the *i*-values, the following points emerge: (*i*) compounds of type (A) are more associated than compounds of type (B), (*ii*) depolymerization is greater for compounds having carboxylate groups with a pronounced electron-withdrawing power which are involved in holding together monomeric entities to form dimeric species: carboxylate ligands which are less coordinating, owing to the presence of R electron-withdrawing groups, are less effective in bringing about the dimerization, as usually observed for organotin carboxylates [5 - 8]. The results also confirm that a Dimer ⇌ Monomer equilibrium exists in solution: the degree of association depends on the concentration, as shown by the IR pattern of two of the compounds (cf. Fig. 1 and 2).

Infrared spectra

The infrared pattern (cf. Table 5 and 6) of the tetrabutylstannoxanes shows two COO asymmetric and symmetric vibration bands which are normally observed with this kind of compounds [5,9,10]. In the COO asymmetric vibra-

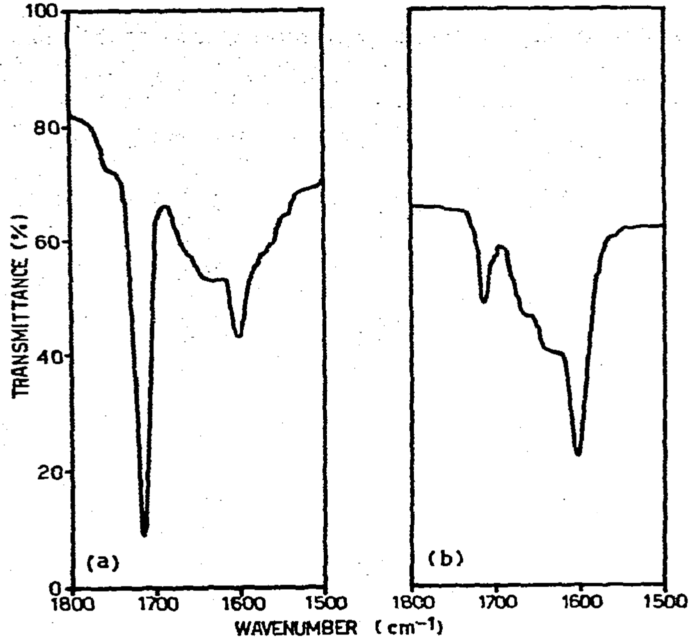


Fig. 1. IR spectra in chloroform of tetrabutyl-1-formoxy-3-hydroxydistannoxane, optics KBr, 0.2 mm. (a) 9 mg/ml; (b) 18 mg/ml.

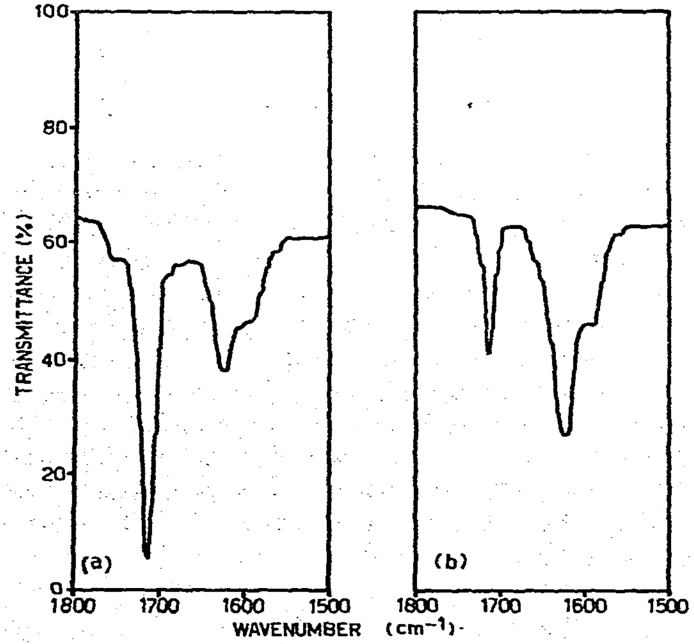


Fig. 2. IR spectra in chloroform of tetrabutyl-1,3-monochloroacetoxydistannoxane. (a) 15.5 mg/ml, optics KBr, 0.1 mm. (b) 20 mg/ml, optics KBr, 0.2 mm.

TABLE 5

INFRARED VIBRATIONAL FREQUENCIES (cm^{-1}) OF $[Bu_2SnOOCR]_2O$ COMPOUNDS IN THE CARBOXYLIC AND Sn—O STRETCHING REGIONS

No.	Compound	Medium	ν_a(COO)	ν_s(COO)	ν(Sn—O—Sn)
(III)	$[Bu_2SnOOCCH_2Cl]_2O$	Nujol	1655m(br)	1415m	620m
			1605s	1340m	
		$CHCl_3$[a]	1715m	1410m	615m
			1660(sh)	1375m	
			1630(sh)		
			1600s		
(IV)	$[Bu_2SnOOCCHCl_2]_2O$	Nujol	1625s(br)	1410m	600m
				1350(sh)	
		$CHCl_3$[b]	1715m	1390m	610w
			1660(sh)	1335m	
			1630s		
(V)	$[Bu_2SnOOCCCl_3]_2O$	Nujol	1690s	1410m	615s
			1655s	1300s	
		$CHCl_3$[c]	1715m	1360m	610w
			1685(sh)	1310m	
			1660(sh)		
			1655s		

[a] 20 mg/ml. [b] 15 mg/ml. [c] 16 mg/ml; (optics KBr, 0.2 mm).

tion region, the lower band is attributed to bridging carboxylate groups, and the higher to non-bridging groups. It can be seen (cf. Table 5) that the lower ν_a(COO) bands, which lie at 1605, 1625, 1655 cm^{-1} for the three considered compounds, do not significantly change their positions on passing from the solid to solution, for which the values are found at 1600, 1630 and 1655 cm^{-1} respectively.

With most of the compounds of type (A) and (B), there appears in solution (mainly in the more dilute solutions) a band at 1715 cm^{-1}, which arises from a stretching vibration of an ester-like carboxylic group, which is probably present in the monomeric form of the stannoxanes. It is noteworthy that the intensity of this band relative to that at lower wavenumber (bridging carboxylate group) is concentration dependent as can be seen from Fig. 1 and 2, which represent the IR spectra in chloroform solution for the asymmetric stretching vibration region of tetrabutyl-1-formoxy-3-hydroxydistannoxane and tetrabutyl-1,3-dichloroacetoxydistannoxane, respectively.

Conclusion

Organostannoxanes of type (A), $(XR_2Sn)_2O$ or (B), $(XR_2SnOSnR_2OH)$, having X = acyloxy group, have previously been synthesized by hydrolysis of dialkyltin diacetates, reactions of diorganotin oxides with carboxylic acids or anhydrides, and reactions of organotin dihalides with organic acid salts [2,3,5]. More recently, tetramethyl-1,3-diacyloxy- and tetramethyl-1-acyloxy-3-hydroxydistannoxanes have been prepared by controlled hydrolysis of dimethylchlorotin carboxylates [10].

Our method, which has been previously used to prepare some tetraallyltin-1,3-diacyloxydistannoxanes by treatment of tetraallyltin with carboxylic acids in methanol [1], seems to be simple and of wide application in view of the results reported above for tetrabutylstannoxanes, and for some work now in progress in our laboratory involving vinyltin derivatives.

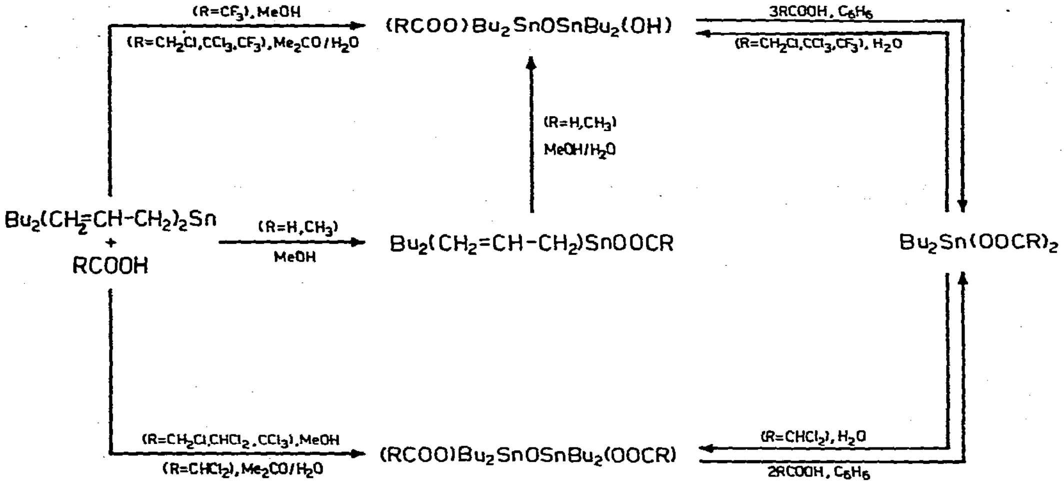
TABLE 6

INFRARED VIBRATIONAL FREQUENCIES (cm^{-1}) OF (RCOO)Bu$_2$SnOSnBu$_2$(OH) COMPOUNDS IN THE (OH), (COO) AND (Sn—O) STRETCHING REGIONS

No	Compound	Medium	ν(OH)	ν_a(COO)	ν_s(COO)	ν(Sn—O—Sn)
(XI)	(HCOO)Bu$_2$SnOSnBu$_2$(OH)	Nujol	3300(br)	1615 s	1315 m	610 (sh)
		CHCl$_3$^{a}	3650 vw	1715 m	1415 vw	600 m(br)
				1625 s	(1360w)	
				1590(sh)		
(XII)	(CH$_3$COO)Bu$_2$SnOSnBu$_2$(OH)^e	Nujol	3280(br)	1605s (br)	1330s	610(sh)
(XIII)	(ClCH$_2$COO)Bu$_2$SnOSnBu$_2$(OH)	Nujol	3380(br)	1645s		610(sh)
				1610s		
		CHCl$_3$^{b}	3650vw	1650(sh)	1350m	590m(br)
				1620(br)		
(XIV)	(CCl$_3$COO)Bu$_2$SnOSnBu$_2$(OH)	Nujol	3520(br)	1650s	1325s	620m
		CHCl$_3$^{c}	3650vw	1715m	1315s	650m(br)
				1680s(br)		
(VI)	(CF$_3$COO)Bu$_2$SnOSnBu$_2$(OH)	Nujol	3420(br)	1680s(br)		625m
		CHCl$_3$^{d}	3650vw	1690s(br)	(1415m)	610(br)

[a] 18 mg/ml. [b] 13 mg/ml. [c] 18 mg/ml. [d] 19 mg/ml; (optics KBr, 0.2 mm). [e] Not new compound, see ref. [2] and [3].

SCHEME 1



The results are summarized in Scheme 1. The following features emerge: (*i*) formation of stannoxanes goes through the hydrolysis of the monocarboxylate, $Bu_2(CH_2{=}CH{-}CH_2)SnOOCR$, which has been isolated in the case of R = H and CH_3; (*ii*) the rate of hydrolysis depends upon the nature of the carboxylate group, and increases in the sequence (R=) $H < CH_3 < CH_2Cl < CHCl_2 < CCl_3 < CF_3$ (a carboxylate centre involving an R group with enhanced electron-withdrawing power makes the tin centre more susceptible to the nucleophilic attack by water); (*iii*) recovery of compounds of type (A) or (B) depends upon the hydrolyzing power of the medium and the nature of the carboxylate group.

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References

1 V. Peruzzo, G. Plazzogna and G. Tagliavini, J. Organometal. Chem., 40 (1972) 121.
2 Y. Maeda and R. Okawara, J. Organometal. Chem., 10 (1967) 247.
3 D.L. Alleston, A.G. Davies and M. Hancock, J. Chem. Soc., (1963) 5469.
4 A.K. Sawyer and H.G. Kuivila, J. Org. Chem., 27 (1962) 610.
5 R. Okawara and M. Wada, Advan. Organometal. Chem., 5 (1967) 137 and references therein.
6 P.B. Simons and W.A.G. Graham, J. Organometal. Chem., 8 (1967) 479.
7 V. Peruzzo, G. Plazzogna and G. Tagliavini, J. Organometal. Chem., 18 (1969) 89.
8 V. Peruzzo, G. Plazzogna and G. Tagliavini, J. Organometal. Chem., 24 (1970) 347.
9 A.G. Davies, L. Smith, P.J. Smith and W.Mc. Farlane, J. Organometal. Chem., 29 (1971) 245.
10 C. Shiow-Chyn Wang and J.M. Shreeve, J. Organometal. Chem., 46 (1972) 271.