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

HYDROLYSES OF DIMETHYLCHLOROTIN CARBOXYLATES

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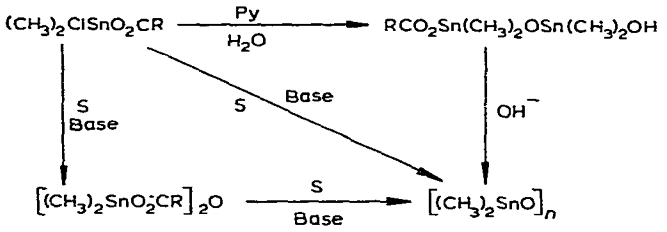
(Received June 2nd, 1972)

SUMMARY

The controlled hydrolyses of dimethylchlorotin carboxylates proceed according to the following scheme:



R=CH_2Cl, $CHCl_2$, CH_2Br, CH_2I, CCl_3, CF_3, C_2F_5, C_3F_7, CF_2Cl; S=$H_2O/(CH_3)_2CO$ as solvent.

INTRODUCTION

Partial hydrolyses of dimethylchlorotin carboxylates $(CH_3)_2Sn(Cl)O_2CR$ (R=H, CH_3) resulted in the respective tetramethyl-1,3-dichlorodistannoxanes[1-3]. In an extension of these early hydrolysis studies, we have found that when R becomes more electron withdrawing (halogen-containing), tetramethyl-1,3-dicarboxydistannoxanes are the intermediate products, *e.g.*, where R=CH_2Cl, $CHCl_2$, CCl_3, CH_2Br, CH_2I, CF_3, C_2F_5, C_3F_7, and CF_2Cl. The yields are high and there is no evidence for the formation of the 1,3-dichloro compounds. The addition of small amounts of water to solutions of $(CH_3)_2Sn(Cl)O_2CR$ in pyridine gives rise to tetramethyl-1-carboxy-3-hydroxydistannoxanes in essentially quantitative yield. Under sufficiently alkaline conditions, the dimethylchlorotin carboxylates, 1,3-dicarboxydistannoxanes or 1-carboxy-3-hydroxydistannoxanes are converted to dimethyltin oxide.

The structures of these new compounds are deduced, primarily through the use of infrared spectra and elemental analyses and based on results in the literature.

EXPERIMENTAL

Starting materials

Dimethylchlorotin carboxylates were prepared by the literature method[4].

(*continued on p.* 274)

TABLE 1

PREPARATION AND ELEMENTAL ANALYSES OF DISTANNOXANES AND HYDROXYDISTANNOXANES

Compound		*Method*	*Yield (%)*	*Analysis*[a] *found (calcd) (%)*		*M.p.*[b] *(°C)*	*$(CH_3)_2SnO$*	
Starting	*Hydrolysis*			*C*	*H*		*Method*	*Yield (%)*
$(CH_3)_2\overset{Cl}{\overset{\mid}{Sn}}O\overset{O}{\overset{\|}{C}}CH_3$	$[(CH_3)_2Sn(Cl)]_2O$	A	~100	[c]		>360°	$D(NH_3)$	100
$(CH_3)_2\overset{Cl}{\overset{\mid}{Sn}}O\overset{O}{\overset{\|}{C}}CH_2Cl$	$[(CH_3)_2SnO\overset{O}{\overset{\|}{C}}CH_2Cl]_2O$	A	~ 90	18.75 (19.20)	3.03 (3.22)	230 ± 0.5[d]	$D(NH_3)$ $D(NH_3)$	100 100
$(CH_3)_2\overset{Cl}{\overset{\mid}{Sn}}O\overset{O}{\overset{\|}{C}}CH_2Br$	$[(CH_3)_2SnO\overset{O}{\overset{\|}{C}}CH_2Br]_2O$	A	75	16.64 (16.30)	2.80 (2.74)	174–176[e]	E $D(NH_3)$	100 100
$(CH_3)_2\overset{Cl}{\overset{\mid}{Sn}}O\overset{O}{\overset{\|}{C}}CH_2I$	$[(CH_3)_2SnO\overset{O}{\overset{\|}{C}}CH_2I]_2O$	A	90	14.39 (14.06)	2.26 (2.36)	171–172	$E(NH_3)$ D	100 80–100
$(CH_3)_2\overset{Cl}{\overset{\mid}{Sn}}O\overset{O}{\overset{\|}{C}}CHCl_2$	$[(CH_3)_2SnO\overset{O}{\overset{\|}{C}}CHCl_2]_2$	B	96	16.90 (16.88)	2.50 (2.48)	244–246[f]	$E(NH_3)$ D	100 100
$(CH_3)_2\overset{Cl}{\overset{\mid}{Sn}}O\overset{O}{\overset{\|}{C}}CCl_3$	$[(CH_3)_2SnO\overset{O}{\overset{\|}{C}}CCl_3]_2O$	B	90–95	15.11 (15.05)	1.91 (1.90)	222–224[g]	$E(NH_3)$ D	100 100
$(CH_3)_2\overset{Cl}{\overset{\mid}{Sn}}O\overset{O}{\overset{\|}{C}}CF_3$	$[(CH_3)_2SnO\overset{O}{\overset{\|}{C}}CF_3]_2O$	B	90	17.95 (17.81)	2.33 (2.24)	232–233	$E(NH_3)$ D	100 63–100
$(CH_3)_2\overset{Cl}{\overset{\mid}{Sn}}O\overset{O}{\overset{\|}{C}}C_2F_5$	$[(CH_3)_2SnO\overset{O}{\overset{\|}{C}}C_2F_5]_2O$	B	80			253–255 (dec.)	$E(NH_3)$ $D(NH_3)$	100 100

$(CH_3)_2\overset{Cl}{Sn}O\overset{O}{C}C_3F_7$	$[(CH_3)_2SnO\overset{O}{C}C_3F_7]_2O$	B	82	20.52 (19.49)	1.74 (1.64)	194–195	$E(NH_3)$	100
$(CH_3)_2\overset{Cl}{Sn}O\overset{O}{C}CF_3$	$CF_3\overset{O}{C}OSn(CH_3)_2OSn(CH_3)_2OH$[h]	C	~100	16.45 (16.24)	2.62 (2.93)	222–223		
$(CH_3)_2\overset{Cl}{Sn}O\overset{O}{C}CCl_3$	$CCl_3\overset{O}{C}OSn(CH_3)_2OSn(CH_3)_2OH$	C	~100	14.67 (14.61)	2.44 (2.63)			
$(CH_3)_2\overset{Cl}{Sn}O\overset{O}{C}C_3F_7$	$C_3F_7\overset{O}{C}OSn(CH_3)_2OSn(CH_3)_2OH$	C	~100	17.73 (17.66)	2.45 (2.39)	241 (dec.)	D	100
$(CH_3)_2\overset{Cl}{Sn}O\overset{O}{C}CF_2Cl$	$CF_2Cl\overset{O}{C}OSn(CH_3)_2OSn(CH_3)_2OH$	C	~100	16.02 (15.65)	2.82 (2.82)	198–199	$E(NH_3)$	100
$(CH_3)_2\overset{Cl}{Sn}O\overset{O}{C}C_2F_5$	$C_2F_5\overset{O}{C}OSn(CH_3)_2OSn(CH_3)_2OH$	C	~100			>300°		
$(CH_3)_2\overset{Cl}{Sn}O\overset{O}{C}CH_2Cl$	$CH_2Cl\overset{O}{C}OSn(CH_3)_2OSn(CH_3)_2OH$	C	~100				$D(NH_3)$ E	100 100

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[a] Analyses by Beller, Mikroanalytisches Laboratorium, Göttingen, Germany or Clare Sieland, University of Idaho. [b] Thomas-Hoover capillary melting point apparatus. [c] IR, see ref. 35, 36. [d] 226–227, see ref. 15. [e] 172–174, see ref. 15. [f] 232–233, see ref. 15. [g] 221–222, see ref. 15. [h] Also prepared from hydrolysis of $(CH_3)_2Sn(Cl)O_2C(CF_3)\cdot(CH_3)_2NH$.

Preparation of tetramethyl-1,3-bis(haloacetoxy)distannoxanes

Method A. All of these compounds were prepared from the dimethylchlorotin carboxylates by essentially the same technique. To a solution of dimethylchlorotin chloroacetate (0.22 mmol) in acetone (5 ml), a few drops (2–3) of distilled water were added. A white precipitate formed with stirring, was washed with acetone which contained a trace of water until the filtrate gave no precipitate with silver nitrate solution and was then air dried.

Method B. Same as Method A with 2 or 3 drops of 6 *N* NaOH to ensure complete hydrolysis.

Preparation of tetramethyl-1-carboxy-3-hydroxydistannoxanes

Method C. 1 mmol of a dimethylchlorotin carboxylate was dissolved in approximately 1 ml of pyridine. A few drops of distilled water were added; a white solid formed, was filtered, washed with water and dried. Yields ranged between 95–100%.

Preparation of $(CH_3)_2SnO$

Method D. Hydrolysis of $(CH_3)_2Sn(Cl)O_2CR$. This is Method A but concentrated (12 *N*) NaOH was used in addition to distilled water.

Method E. Hydrolysis of $RCO_2Sn(CH_3)_2OSn(CH_3)_2O_2CR$ *(or* $RCO_2Sn(CH_3)_2OSn(CH_3)_2OH$*)*. This is Method D applied to the distannoxane or hydroxydistannoxane.

Infrared spectra

Infrared spectra were recorded with a Perkin–Elmer Model 621 spectrometer. Spectra were calibrated from known peaks of a polystyrene film. Spectra of solids were obtained with pressed KBr discs or Nujol mulls. Spectra of approximately 0.2 *M* solutions in $CHCl_3$ or CH_2Cl_2 were recorded using compensated KBr cells.

All new compounds, method used, % yield, elemental analyses and melting point data are recorded in Table 1.

RESULTS AND DISCUSSION

Preparation

The initial hydrolysis products of the compounds $R_2Sn(Cl)O_2CR'$ might be expected to be $R_2SnX(OH)$ ($X = Cl$ or O_2CR'). Existence of $R_2SnCl(OH)$ in solution has been confirmed[5] but a compound has never been isolated. However, the only known examples of this type of compound are dialkyltin hydroxide nitrates[6] which were isolated from the reactions of dialkyltin oxides with nitric acid. These are stable, high-melting crystalline substances which are resistant to condensations to give distannoxanes. The dimeric $Ph_4Sn_2(NCO)_2(OH)_2$[7] was also claimed to have been isolated but it is a highly reactive intermediate.

Just as the hydrolyses of dialkyltin dihalides and of dialkyltin dicarboxylates led to distannoxanes so the first isolated hydrolysis products from dimethylchlorotin carboxylates are $[(CH_3)_2SnX]_2O$ ($X = Cl$ or O_2CR') formed via intermolecular dehydration of the probably unisolable intermediate, $(CH_3)_2SnX(OH)$. However, all previous reports[1-3,8-10] of the partial hydrolysis of $R_2Sn(X)O_2CR'$ invariably identify $(R_2SnX)_2O$ (X = halogen) as the product with no $(R_2SnO_2CR')_2O$ isolated.

Hydrolyses of a series of compounds, R_2SnXY ($X, Y =$ halogen or carboxylate), in the presence of amines, show that the ease of removal decreases from $X = OAc, I > Br > Cl > F$[8,9], *e.g.*,

$$2\,(C_4H_9)_2SnClF + H_2O \rightarrow [(C_4H_9)_2SnF]_2O + 2\,HCl$$

In our series of compounds, $(CH_3)_2Sn(Cl)O_2CR$, only in the case where $R = CH_3$ is the dichlorodistannoxane, $[(CH_3)_2SnCl]_2O$, obtained[1,2]. With all others, where $R =$ CH_2Cl, $CHCl_2$, CCl_3, CH_2Br, CH_2I, CF_3, C_2F_5, C_3F_7, CF_2Cl, the dicarboxydistannoxanes $[(CH_3)_2SnO_2CR]_2O$ are invariably isolated. This synthetic route has not been reported previously.

Tetraalkyl-1,3-dicarboxydistannoxanes have resulted from partial hydrolyses of diorganotin dicarboxylates, reactions of diorganotin oxides with carboxylic acids or anhydrides, and organotin dihalides with organic acid salts[1,2,9–27].

The method described here is simple and fast. Addition of distilled water to an acetone solution of the dimethylchlorotin carboxylate followed by stirring for a few minutes at 25° (a small amount of aqueous NaOH is required for the fluorocarboxylates) resulted in the precipitation of distannoxanes in high yields. Several new as well as previously known tetramethyl-1,3-dicarboxydistannoxanes were synthesized via this route (Table 1). These compounds are very stable in water and in moderately basic solutions, *e.g.*, aqueous NaOH (pH ~8–9) or pyridine. Evaporation of a water/acetone solution of the distannoxanes leaves the white solid unscathed. The fluoroacetate compounds are readily soluble in acetone but the others are not.

It has been shown that stable products in the hydrolyses of R_2SnX_2 ($X =$ halogen or carboxylate) are obtained in the following sequence [10,29].

$$R_2SnX_2 \xrightarrow{OH^-} (R_2Sn_2X_2)O \xrightarrow{OH^-} \underset{(I)}{[R_4Sn_2X(OH)]O} \qquad \underset{(II)}{(R_2SnO)_n}.$$

We have been able to isolate the compound (I) of our system $(CH_3)_2Sn(O_2CR)OSn(OH)(CH_3)_2$ by dissolving $(CH_3)_2SnCl(O_2CR)$ in pyridine and then adding water. It was possible to isolate the hydroxy distannoxanes only when $R = CF_3$, C_2F_5, C_3F_7, CF_2Cl, CH_2Cl or CCl_3 (Table 1). However, all attempts to obtain the hydroxy distannoxanes from the dicarboxydistannoxanes resulted either in recovery of starting material or complete hydrolysis to dimethyltin oxide. Other workers have been able to prepare $(AcO)R_2SnOSnR_2OH$ from $[R_2Sn(OAc)]_2O$ when $R = C_2H_5$, C_3H_7, C_4H_9, etc.[22] and $XR_2SnOSnR_2OH$ from $(R_2XSn)_2O$ ($X =$ halogen)[9,10,30].

The final product (II) from exhaustive hydrolysis of the dimethylchlorotin carboxylates or from $[(CH_3)_2SnO_2CR]_2O$ or $RCO_2(CH_3)_2SnOSn(CH_3)_2OH$ is the very insoluble $(CH_3)_2SnO$ when concentrated solutions of NaOH or NH_3 are used.

Infrared

Many compounds of the type $XR_2SnOSnR_2Y$ are known, with X and Y as halogen, pseudohalogen, carboxylate, nitrate, isothiocyanate, alkoxide or phenoxide[12]. Interest in these compounds lies in their dimeric structures, based on a 4-membered $(Sn{-}O)_2$ ring in which the tin atoms are pentacoordinate[12,28,30,32]. The structure has been proposed as shown in the following in which both penta- and tetracoordinate tin atoms are present (III). If the substituent X is a coordinating group, such as OH^-,

TABLE 2

RELEVANT INFRARED VIBRATIONAL FREQUENCIES (cm^{-1}) OF SOLID $[(CH_3)_2SnO_2CR]_2O$

R	*CH_3*[a]		*CH_2Cl*	*$CHCl_2$*	*CCl_3*	*CH_2Br*	*CH_2I*	*CF_3*	*C_2F_5*	*C_3F_7*	*CF_2Cl*
	Solid	*$CHCl_3$*									
CO_2 asym. stretch	1560 s	1630 s	1676 s	1665 s	1683 s	1676 s		1700 s	1693 s	1700 s	1695 s
		1605 m									
		1562 s	1667 s	1620 s	1640 s	1602 s	1580 s	1658 s	1655 s	1663 s	1650 s
CO_2 sym. stretch and	1418 s	1426 s	1419 s	1415 (sh)	1405 m	1419 s	1420 s	1464 m	1438 w	1438 w	1430 s
CH_3 deformation	1398 (sh)	1378 s		1490 s	1375 (sh)	1400 (sh)	1380 s	1420 m	1388 w	1388 w	1380 s
	1334 m	1319 s	1343 s	1350 s	1363 s	1325 s			1330 s	1338 m	
					1309 s						
CH_3(−Sn) rock			787 s	790 s	788 m	790 s	790 s	793 s	795 s	795 s	790 s
CO_2 scissor	666 s		680 m		680 s	678 m	668 s				
	656 s										
Sn−O−Sn stretch and	623 (sh)	645s	635 s	620 s	625 s	636 s	623 s	629 s	620 m	625 s	628 s
CO_2 out-of-plane	610 s										
SnC_2 asym. stretch	579 m	575 s	583 m	582 (sh)	583 m	587 m	587 s	590 m	590 m	590 m	585 w
SnC_2 sym. stretch	530 s	525 m	525 (sh)	525 (sh)	524 m	530 m	527 m	525 (sh)		530 w	525 w
SnO ring and	505 s	505 s	507 s	497 s	502 s	510 s	501 s	499 s	500 s	499 s	504 s
CO_2 rock	493 (sh)	481 (sh)	480 m	450 w	480 (sh)						
			440 w	473 w	445 w	445 m	440 w	460 w	430 w	430 w	430 w
SnO	300 s	278 s	273 m	285 m	285 m	275 s	280 s	290 m		290 m	285 m

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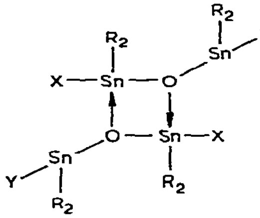
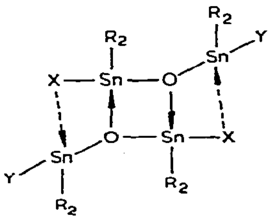
[a] See ref. 22.

NCS$^-$, OCH$_3^-$, there are additional weak intramolecular coordinations as in (IV) which give rise to a ladder type structure.



(III)



(IV)

The dimeric ladder type structure of $R'CO_2SnR_2OSnR_2O_2CR'$ as (IV) in the solid state or in moderately concentrated solutions has been supported by infrared[22], ^{119}Sn Mössbauer[33,34], ^{119}Sn NMR[34], molecular weight[9], and X-ray[31,39,40] studies. The structure of the series of distannoxanes investigated here has no reason to be an exception.

In the infrared spectra, the positions of relevant absorption bands and their assignments, made by referring to the spectrum of $[(CH_3CO_2)(CH_3)_2Sn)_2O]$[22,35] are listed in Table 2. The compounds $[(AcO)R_2Sn]_2O$ (R=CH_3, C_2H_5, n-C_3F_7, n-C_4H_9) have been considered to be dimeric at moderate concentrations and to dissociate to monomers in dilute benzene and chloroform solutions[22]. The infrared spectra of these compounds change in the CO_2 asymmetric stretching region with change in state. However, the compounds $RCO_2Sn(CH_3)_2OSn(CH_3)_2O_2CR$ (R= CH_2Cl, $CHCl_2$, CCl_3, CH_2Br, CF_3, C_2F_5, C_3F_7, CF_2Cl) show two CO_2 asymmetric bands in the solid state and in CH_2Cl_2 or $CHCl_3$ solution (~0.2 *M*) (Table 3). The very broad single CO_2 band in $[(CH_2ICO_2Sn(CH_3)_2]_2O$ in solid state splits into two bands in CH_2Cl_2 solution. No additional CO_2 asymmetric stretching bands appeared in solutions of the compounds and the CO_2 asymmetric stretching frequencies of the tetramethyldistannoxanes are essentially constant in both solid state and in solution which may be explained by the presence of the same configuration in both states. From the values of C–O stretching frequencies, the RCO_2 groups are not of the ester type and must act as chelate or bridging groups. For comparison, the $\nu_a(CO_2)$ values for $RCO_2Sn(Cl)(CH_3)_2$ are also listed in Table 3. These are in the range expected for $\nu_a(CO_2)$ in a bridging RCO_2 group in the solid state. The intensities of two $\nu_a(CO_2)$ frequencies differ with the one at lower energy being more intense. It is noted in the fluorocarboxy distannoxanes that the band at higher energy is close to the $\nu_a(CO_2)$ frequencies in $(CH_3)_2Sn(Cl)O_2CR$ with the exception of the C_3F_7 compound. In the other halo-substituted acetoxy distannoxanes, the band at higher energy occurs higher than in the chlorotin carboxylates. However, the high frequency one is closer to the $\nu(CO_2)$ frequency of $RCO_2Sn(Cl)(CH_3)_2$ in solution. Davies *et al.*[34] explained the infrared spectra of $[CH_3C(O)\text{–}O\text{–}Sn(C_4H_9)_2\text{–}]_2O$ by assigning the two carbonyl absorptions at 1560 and 1418 cm^{-1} to a symmetrical (bridging) carboxylate group, and the two bands at 1630 and 1362 cm^{-1} to a non-bridging group. Therefore, the lower frequency RCO_2 stretch of the tetramethyldistannoxanes must be due to the absorption of bridging carboxylate groups.

All of the tetramethyldistannoxanes show a strong band near 600 cm^{-1}

TABLE 3

$\nu_a(CO_2)$ (cm^{-1}) FOR TIN CARBOXYLATES, DISTANNOXANES AND HYDROXYDISTANNOXANES

R	$(CH_3)_2Sn(Cl)O_2CR$	$[(CH_3)_2SnO_2CR]_2O$	$(CH_3)_2Sn(O_2CR)OSn(CH_3)_2(OH)$
CF_3	1691^a	1700, 1658	1678
	1692^b	1712, 1657^b	
C_2F_5	1696^a	1693, 1658	1678
	1690^b	1700, 1655^b	
C_3F_7	1655^a	1700, 1663	1681
	1685^b	1700, 1650^b	
CF_2Cl	1688^a	1690, 1650	1676
	1680^b	1713, 1665^b	
CH_2Cl	1598^a	1676, 1607	1617
	1635^b	1650, 1600^b	
$CHCl_2$	1624^a	1665, 1623	
	1643^b	1660, 1620^b	
CCl_3	1635^a	1683, 1640	1665
	1650^b	1687, 1642^b	
CH_2Br	1590^a	1676, 1602	
	1620^b		
CH_2I	1550^a	1580 v(br)	
	1610^b	1610, 1580^b	
CH_3^{c}	1550^a	1580	

^{a} Solid. ^{b} In CH_2Cl_2 or $CHCl_3$ solution. ^{c} Ref. 3.

TABLE 4

RELEVANT INFRARED VIBRATIONAL FREQUENCIES (cm^{-1}) OF $(RCO_2)(CH_3)_2SnOSn(CH_3)_2(OH)$

	CH_2Cl	CCl_3	CF_3	C_2F_5	C_3F_7	$CClF_2$
OH stretch	3400 s (br)	3400 s (br)	3400 s (br)	3440 s (br)	3440 s (br)	3400 s (br)
CO_2 asym. stretch	1615 s	1665 s	1678 s	1678 s	1681 s	1665 s
CO_2 sym. stretch and CH_3 deformation	1405 (sh)	1383 (sh)	1434 ms	1405 m	1401 m	1405 (sh)
	1390 m					1390 m
	1360 m	1335 s		1325 m	1335 m	
$CH_3(-Sn)$ rock	780 s	780 m	790 s	775 m (br)	770 m	775 m
SnOSn stretch and SnC_2 asym. stretch	590–570 s (br)	570 s (br)	570 s (br)	560–540 s (br)	570 s (br)	580–540 s (br)
SnC_2 sym. stretch		520 w (sh)	525 m	530 (sh)	530 (sh)	528 (sh)
CO_2 rock		478 w	462 m	490 m	495 m	
			440 m			
SnO ring	418 w	418 w				
		380 w	380 w		383 w	382 m
SnO			280 m	285 w	285 w	

(Table 2) which is the characteristic Sn–O–Sn stretching vibration in the dimeric structure[9,22,30,36–38]. Therefore, all of the carboxydistannoxanes very likely do have the central ladder structure of (IV) although it would be interesting to learn about the type of coordination exhibited by the non-bridging RCO_2 groups. X-ray structure determinations would be very helpful in solving this question.

The relevant absorptions for $RCO_2Sn(CH_3)_2OSn(CH_3)_2OH$ are listed in Table 4. The OH stretching vibrations appear around 3400 cm^{-1} and Sn–O–Sn stretching bands around 600 cm^{-1}. The compounds show one kind of $\nu_a(CO_2)$ absorption in the infrared spectra. The position of $\nu_a(CO_2)$ absorption is intermediate to those found for the 1,3-dicarboxydistannoxanes which suggests either bridging or chelating RCO_2 groups.

ACKNOWLEDGEMENTS

Fluorine research at the University of Idaho is suppoerted by the Office of Naval Research and the National Science Foundation, J. M. S. is an Alfred P. Sloan Foundation Fellow.

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