NOTIZEN

Synthesis of Trialkylstannanedithiocarboxylato Rhenium(I) Complexes [1]

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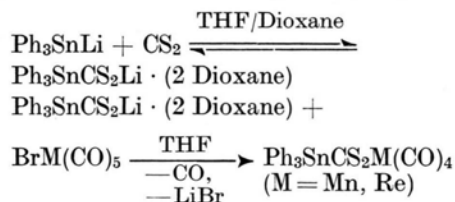Auf der Morgenstelle 18, D-7400 Tübingen

Trialkylstannanedithiocarboxylato Rhenium Complexes

Novel trialkylstannanedithiocarboxylato complexes are formed in a one-pot reaction of R_3SnCS_2Li (R = benzyl, methyl, cyclohexyl) with $BrM(CO)_5$ (M = Mn, Re) in a THF/dioxane solution. Tetracarbonylmetal species could be detected by IR spectroscopy in all cases. The more stable rhenium chelate complexes, $R_3SnCS_2Re(CO)_4$, were isolated by chromatographic separation as yellow, low-melting solids with 10–20% yield.

Introduction

Earlier attempts to obtain tin-substituted dithiocarboxylato ligands by nucleophilic addition of organotin anions to carbon disulfide have failed [2]. We were able to stabilize the CS_2 adduct of triphenylstannyl lithium by solvation with dioxane and to synthesize the corresponding carbonylmanganese and rhenium complexes [3, 4].
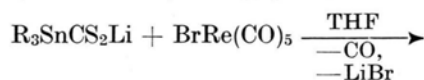
$$Ph_3SnLi + CS_2 \underset{}{\overset{THF/Dioxane}{\rightleftharpoons}}$$

$$Ph_3SnCS_2Li \cdot (2\ Dioxane)$$

$$Ph_3SnCS_2Li \cdot (2\ Dioxane) +$$

$$BrM(CO)_5 \xrightarrow[-LiBr]{\substack{THF \\ -CO,}} Ph_3SnCS_2M(CO)_4 \quad (M = Mn, Re)$$

Apparently, the CS_2 addition is an equilibrium reaction which may be reversed under certain conditions. The "dioxane method" is restricted to triaryltin ligands. We now tried to carry out the reaction in a one-pot procedure, which led to the successful isolation of the first trialkylstannanedithiocarboxylato complexes.

Results

As trialkyltin lithium-carbon disulfide adducts, R_3SnCS_2Li (R = benzyl, methyl, cyclohexyl), do

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not form isolable dioxane solvates, the carbonylmetal halides, $BrM(CO)_5$ (M = Mn, Re), were added to a solution of the lithium stannanedithiocarboxylates in THF/dioxane. Tetracarbonylmanganese moieties were detected by IR spectroscopy but could not be isolated. We were able, however, to separate the corresponding rhenium complexes 1–3 by column chromatography followed by sublimation or recrystallisation (10–20% yield).

$$R_3SnCS_2Li + BrRe(CO)_5 \xrightarrow[\substack{-CO, \\ -LiBr}]{THF}$$

$R_3SnCS_2Re(CO)_4$
1: R = benzyl (m. p. 54 °C)
2: R = methyl (m. p. 38 °C)
3: R = cyclohexyl (wax)

The trialkyltin complexes **1**, **2** are obtained as yellow solids with low melting points and good solubility in organic solvents. The cyclohexyl compound **3** was not isolated in a pure form but sufficiently characterized by its IR spectrum.

Mass spectra

The mass spectra of the complexes **1**, **2** show a regular fragmentation pattern like that of the triphenyltin compound $Ph_3SnCS_2Re(CO)_4$ [4]. A stepwise elimination of the CO groups followed by degradation of the dithiocarboxylate moiety is observed. For R = phenyl, cleavage of metal-CO bonds is clearly preferred whereas for R = benzyl, a tin-alkyl bond is cleaved first. With R = methyl,

Table. IR and UV data of the complexes 1–3.

	1	2	3
IR [cm^{-1}], CCl_4 sol.			
ν(CO)	2105 m	2101 w–m	2108 w–m
	2012 vs	2007 vs	2010 vs
	2000 s	1996 s	1999 s
	1964 s	1958 s	1960 s
KBr disc			
ν(CO)	2106 m	2098 m	2103 m
	2022 s	2005 sh	2004 vs
	2008 vs	2002 vs	1991 s
	1971 s–m	1965 s	1953 s
ν(CS)	946 m	937 m	–
ν(ReS$_2$)^a	381 w–m	392 w^b	
	362 m	359 m	
UV, λ [nm] (lg ε), $CHCl_3$ sol.			
n–V	330 (3.85)	315 (3.72)	
c.t.	351 (3.78)	347 (3.46)	
π–π*	394 (3.42)	395 (3.52)	

^{a} Polyethylene pellet; ^{b} $\nu_a(SnC_3) = 533$ m, $\nu_s(SnC_3) = 511$ w cm^{-1}.

loss of the trimethyltin group followed by CO elimination seems to prevail.

IR spectra

The solution spectra of **1–3** show four absorptions (C_{2v}, $2 A_1 + B_1 + B_2$) in the carbonyl region as expected for a *cis*-M(CO)$_4$ unit. In the ν(CS) range, a characteristic band is observed between 930 and 960 cm^{-1} which may be assigned to ν_a(CS$_2$). The rather low frequency is consistent with the chelate coordination of dithiocarboxylates [4]. Besides the metal-carbonyl deformation vibrations, the rhenium complexes **1–3** show an absorption at 360 cm^{-1} which corresponds to ν(ReS$_2$) [5]. Position and intensity of ν_a and ν_s(SnC$_3$) confirm the tetrahedral configuration of tin in the methyl complex **2**.

UV spectra

Unsubstituted BrMn(CO)$_5$ shows an absorption band at 386 nm which represents a charge transfer from a b_2 molecular orbital (d_{xy}) to an e orbital (π^*) [6]. In monosubstituted complexes, *cis*-(CO)$_4$Mn(L)Br, the position of the c.t. band depends on the π acceptor strength of the ligand L. Similar relations hold for the rhenium complexes **1–3**. The chelate ligand itself causes two characteristic transitions at 320 and 390 nm. The additional band at 350 nm is assigned to a charge transfer.

NMR spectra

The ^{1}H NMR spectra of **1, 2** show, besides the aromatic proton signals, a singlet for the CH$_2$ and CH$_3$ groups. The chemical shifts and ^2J(Sn–C–H) coupling constants correspond to related tribenzyl- and trimethyltin halides [7].

In the ^{13}C$\{^1$H$\}$ NMR spectra of **1, 2**, the CS signal is observed at $\delta = 225$ ppm. This is a high-field shift of -41 ppm relative to the ester Ph$_3$SnCS$_2$Me [8]. Two CO signals appear in the δ 185–190 ppm region for the axial and equatorial carbonyl groups. Chemical shifts and ^1J(Sn–C) coupling constants of the CH$_2$ and CH$_3$ groups are related to the appropriate triorganotin halides [9].

Experimental Section

General comments

All syntheses were carried out in carefully dried solvents under nitrogen atmosphere. The trialkyltin halides were prepared according to standard methods; pentacarbonylrhenium bromide was obtained by bromination of decacarbonyldirhenium [10].

Applied spectrometers

IR: Perkin Elmer 598 with Data Station 3600 and Bruker IFS 114 C Fourier spectrometer. – NMR: Bruker WP 80 multicore spectrometer. – MS: MAT 711 A mass spectrometer from Varian, Bremen (70 eV, 200 °C source temp., direct inlet). UV: Beckman Acta MVII.

Syntheses

10 mmol of Bz$_3$SnCl, Me$_3$SnCl or Cy$_3$SnCl are dissolved in 40–50 ml of freshly distilled tetrahydrofuran and stirred with an excess of activated lithium wire (etching with isopropanol or treating with ultrasound) for 1–3 days. When the reduction is finished, excess lithium is separated by filtration through glass wool. 10 mmol CS$_2$, dissolved in 10 ml dioxane, are added to the R$_3$SnLi solution and stirred until the solution attains a permanent deep red colour (30–45 min). After evaporation of THF, the residue is separated by a D3 frit and washed four times with 10 ml dioxane. 10 mmol of BrRe(CO)$_5$ are added to the collected dioxane extracts and stirred for 20–25 h at 60 °C. The progress of the reaction are followed by IR spectroscopy. After evaporation of the solvent, the product is purified by column chromatography (silica gel Merck, CCl$_4$/*n*-hexane*) and the first yellow fraction is eluated with *n*-hexane. **1** is recrystallized from a small volume of *n*-hexane, **2** is sublimed at 30–40 °C under high vacuum.

Tetracarbonyl(tribenzylstannanedithiocarboxylato-S,S)rhenium(I) (**1**, yield 18%)

C$_{26}$H$_{21}$O$_4$ReS$_2$Sn (766.5)

Calcd	C 40.74	H 2.76	S 8.37,
Found	C 40.81	H 2.81	S 8.59.

Molar mass 768 (MS, ^{187}Re, ^{120}Sn)

NMR: δ [ppm], J [Hz] (CDCl$_3$ sol., int. TMS; coupling constants ^2J(^{119}Sn, ^{117}Sn–C–^{1}H), ^1J(^{119}Sn, ^{117}Sn–^{13}C)). ^{1}H: C$_6$H$_5$, 7.2–6.9; CH$_2$, 2.47 (63.9, 61.8). – ^{13}C$\{^1$H$\}$: CS$_2$, 223.4; CO^{eq}, 188.0; CO^{ax}, 186.2; C$_6$H$_5$–C1, 139.5; C2, 6, 128.9; C3, 5, 127.9; C4, 124.6; CH$_2$, 20.3 (289.5, 277.2).

Tetracarbonyl(trimethylstannanedithiocarboxylato-S,S)rhenium(I) (**2**, yield 12%)

C$_8$H$_9$O$_4$ReS$_2$Sn (538.2)

Calcd	C 17.85	H 1.69	S 11.92,
Found	C 18.20	H 1.60	S 12.37.

Molar mass 540 (MS, ^{187}Re, ^{120}Sn)

NMR: δ [ppm], J [Hz] (CDCl$_3$ sol., int. TMS; coupling constants as for 1). ^{1}H: CH$_3$, 0.35 (58.1, 55.1). – ^{13}C$\{^1$H$\}$: CS$_2$, 226.7; CO^{eq} 187.5; CO^{ax}, 185.4; CH$_3$, –0.6 (^{119}Sn, ^{117}Sn satellites not detected).

[1] Part V of "Nucleophilic Addition of Triorganotin Anions to Carbon Disulfide"; for Part IV see U. Kunze and P. R. Bolz, Z. Anorg. Allg. Chem., in press.

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