Formation of Metal Carbonyl Derivatives of Monothiocarbamates, Dithiocarbamates, Ureas, and Thioureas from Organotin Intermediates

By **E. W. Abel** * and **M. O. Dunster**, Department of Chemistry, The University, Exeter EX4 4QD

The easily accessible trimethyltin dithiocarbamato-, monothiocarbamato-, ureido-, and thioureido-compounds have been shown to be useful reagents for the preparation of metal carbonyl complexes of these ligands. New dimeric manganese carbonyl-monothiocarbamato-, -ureido- and -thioureido-compounds are recorded and structures are proposed based upon the spectra of these new types of complex.

TRANSITION metal dithiocarbamate complexes[1-6] have been extensively investigated and are of interest in many fields.[7,8] In recent years the dithiocarbamato-metal carbonyls[9,10] have been reported. These usually involve the ligand as an effectively three electron donor with the two sulphur atoms co-ordinated to the metal in the chelate. There are, however, reports of monodentate behaviour for the dithiocarbamate ligand in certain circumstances,[10] where it is, in effect, a one electron donor. Complexes are normally synthesised from the strongly nucleophilic dithiocarbamate ion, or by the homolytic fission of a thiuram disulphide. We have investigated an alternative approach to the synthesis of the metal carbonyl dithiocarbamates under very mild conditions. This has enabled us to obtain complexes which appear to be inaccessible by the above mentioned methods.

Previously we have reported the reactions of the precursors $LSnR_3$ and $LSiR_3$, where L has been alkylthio,[11,12] alkylseleno,[13] diarylphosphido,[14] alkenyl,[15] *etc.* By their reactions with metal halides and metal carbonyl halides it has been possible to synthesise a range of novel metal complexes, and in some cases otherwise inaccessible[15,16] metal carbonyl derivatives.

N,*N*-Dimethyldithiocarbamato-(trimethyl)tin can be obtained quantitatively[17] by the action of carbon disulphide upon dimethylamido(trimethyl)tin, and is thus readily available as a reagent. It undergoes reaction with a variety of metal carbonyl halides according to equation (1).

$$M(CO)_nX + Me_3SnS(S)CNMe_2 \longrightarrow M(CO)_{n-1}S_2CNMe_2 + Me_3SnX + CO \quad (1)$$

The trimethyltin halide formed may be easily removed by water washing, or alternatively if the product

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is water sensitive, the by-product halide is rapidly removed by reduced pressure. A range of dithiocarbamate metal carbonyls synthesised by this method are summarized in Table 1.

The very mild conditions of the reactions appear to be advantageous; and in general yields are high, and an improvement on earlier methods. Thus, for example, the synthesis of $Me_2NCS_2Mn(CO)_4$ using the sodium dithiocarbamate is reported[9] to yield only 16% of product, in contrast to our 90%. A further consequence of the mild conditions is the ability to stop reactions at products which are apparently not otherwise isolable. Thus for example the action of the dialkylcarbamate ion upon iron tetracarbonyl di-iodide produces[9] the bis- and tris-(*N,N*-dimethyldithiocarbamato) complexes $(Me_2NCS_2)_2Fe(CO)_2$ and $(Me_2NCS_2)_3Fe$. On the other hand, the action of *N,N*-dimethyldithiocarbamato(trimethyl)tin upon iron tetracarbonyl di-iodide yielded the interesting mono-dithiocarbamate $Me_2NCS_2Fe(CO)_3I$.

TABLE 1

Dithiocarbamato-, monothiocarbamato-, ureido-, and thioureido-metal carbonyl complexes obtained *via* organotin intermediates

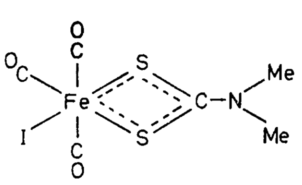
	Calc. (%)				Found (%)						
	C	H	N	M	C	H	N	M	M.p./°C	CO Stretching frequencies cm^{-1} (relative peak height)	N.m.r. τ values
$Mn(CO)_4S_2CNMe_2$	29·2	2·1	4·9		28·8	2·25	4·8		71	2117(2·5), 2020(10), 2005(7·2) 1966(8·4)	6·90(NMe_2)
$Fe(CO)_3IS_2CNMe_2$ [a]	18·6	1·55	3·6	14·4	18·2	1·7	3·55	14·6	135 decomp.	2126(10), 2027(8·3), 2069(7·0)	6·90(NMe_2)
$(\pi\text{-}C_5H_5)Fe(CO)S_2CNMe_2$	40·1	4·1	5·2		40·0	4·25	5·35		153 decomp.	1955	6·90(NMe_2); 5·22(C_5H_5)
$(\pi\text{-}C_5H_5)W(CO)_2S_2CNMe_2$	28·2	2·6	3·3		27·9	2·3	3·1		170 decomp.	1952(10), 1867(7·3)	7·15(NMe_2); 4·58(C_5H_5)
$(\pi\text{-}C_3H_5)Fe(CO)_2S_2CNMe_2$	35·2	4·05	5·15	20·5	34·5	4·15	4·8	20·2	102—104	2021(8·1) 1964(7·4) 2018(10) 1961(8·3)	
$Rh(CO)_2S_2CNMe_2$	21·5	2·2	5·0		21·8	2·1	5·0		128—130	2066(10), 2005(10)	7·00(NMe_2)
$[Mn(CO)_3OSCNMe_2]_2$ [b]	29·6	2·45	5·75	22·6	29·4	2·5	5·55	22·1	138—140 decomp.	2045(4·6), 2028(8·8), 1946(8·1), 1941(10), 1929(6·6), 1922(2·6)	
$[Mn(CO)_3PhNCONMe_2]_2$	47·7	3·65	9·25	18·2	47·7	3·55	9·25	17·7	120 decomp.	2024(10), 1929(8·6), 1917(8·1), ($CHCl_3$ sol.)	
$[Mn(CO)_3PhNCSNMe_2]_2$ [c]	45·3	3·45	8·8	17·3	44·8	3·5	8·9	16·8	128—130 decomp.	2013(10), 1934(8·7), 1921(8·7)	

[a] Iodine analysis: calc. 33·8; found 33·2%. [b] *M*, 481 (calc. 486). [c] *M*, 605 (calc. 632).

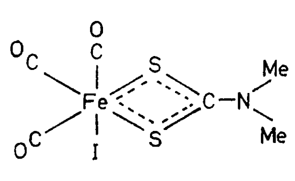
The two likely alternative structures for this complex are illustrated as (I) and (II) below. Both structures have a C_s point group and would be expected to have three active i.r. stretching carbonyl modes. Three i.r. bands of very similar intensity are indeed found for the complex. However, although the numbers of bands does not enable us to decide between the two structures, the band intensities do allow us with reasonable certainty to make such an assignment. From the outlines of the i.r.-active modes below each structure it can be seen that in the case of (I) two strong and one weak band are expected, whereas in (II) all three modes are predicted to be strong. The actual spectrum observed is precisely in accordance with the *cis*-structure (II).

Although with rapid work-up it was possible to obtain $(\pi\text{-}C_3H_5)Fe(CO)_2S_2CNMe_2$ in 65% yield; the complex was not stable in solution, undergoing decomposition to $(Me_2NCS_2)_2Fe(CO)_2$ and a brown precipitate. This unfortunately prevented access to good n.m.r. spectra for this compound, which may have shown fluxional behaviour, or isomers as illustrated by (III) and (IV). Evidence for the presence of the two structures, either as static or fluxional isomers, was obtained from the i.r. spectrum, where both the carbonyl bands were just split, giving a total of four peaks. As the compound decomposed in solution all four absorptions decreased at approximately the same rate.

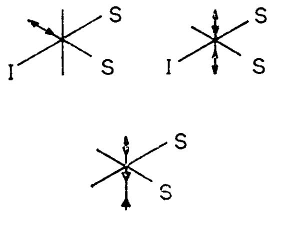
Two main alternatives offer themselves for the mechanism of the reaction of metal carbonyl halides with *N,N*-dimethyldithiocarbamato(trimethyl)tin; in one elimination of organotin halide is followed by displacement of carbon monoxide, and in the other co-ordination of the ligand to the transition metal by displacement of carbon monoxide is followed by elimination of organotin halide. These are outlined respectively as equations (2) and (3) below, and in the case of (3) initial co-ordination by the other sulphur is also a possible first step.

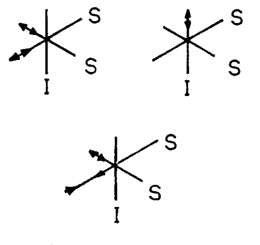


(I)



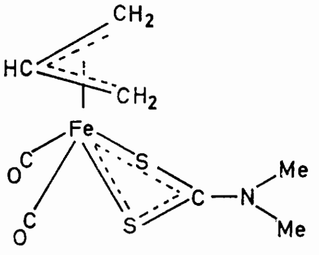
(II)



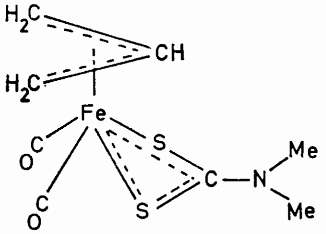


In many reactions reported previously,[11,13,15] the stoicheiometry of the product strongly indicates which of the two mechanisms is operative, but here the evidence is inconclusive. If mechanism (2) were operative we might expect, in certain cases, that products of a monodentate nature might be isolated before the elimination of carbon monoxide took place as such monodentate dialkyldithiocarbamato-carbonyls are known. We tend therefore to favour reaction (3), in the absence of possible evidence for (2).

The mass spectra of some of the dialkyldithiocarbamato-metal carbonyls are reported in Table 2. Not all compounds could be analysed in this way due to decomposition during vaporisation. One interesting feature is the $[MSC]^+$ ion, which is likely to have a metal isothiocarbonyl structure.



(III)



(IV)

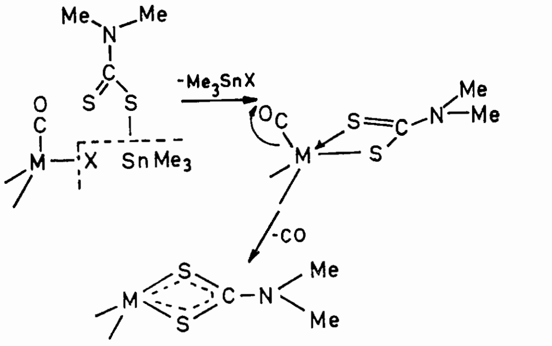
N,*N*-Dimethylmonothiocarbamato(trimethyl)tin is prepared[18] by the treatment of dimethylamido(trimethyl)tin with carbonyl sulphide. By comparison with the above reactions of the *N*,*N*-dimethyldithiocarbamato(trimethyl)tin, the monothio-analogue should be a useful precursor to the previously unknown monothiocarbamato-transition-metal carbonyls. Indeed the first example of a monothiocarbamato-transition-metal complex of any type has only recently been reported.[19]

TABLE 2

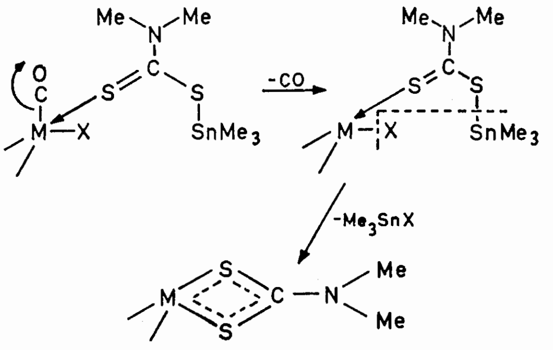
Mass spectra and proposed assignments

$Rh(CO)_2S_2CNMe_2$			$(\pi\text{-}C_3H_5)Fe(CO)_2S_2CNMe_2$			$[Mn(CO)_3OSCNMe_2]_2$		
m/e	Rel. Int.	Assignment	*m/e*	Rel. Int.	Assignment	*m/e*	Rel. Int.	Assignment
42	100	$[N(CH_2)_2]^+$	39	67	$[C_3H_3]^+$	42	61	$[NCO]^+$
76	12	$[CS_2]^+$	41	47	$[C_3H_5]^+$	55	51	$[Mn]^+$
103	46	$[Rh]^+$	56	11	$[Fe]^+$	72	100	$[Me_2NCO]^+$
135	19	$[RhS]^+$	76	12	$[CS_2]^+$	99	47	$[MnSC]^+$
147	15	$[RhS]^+$	88	25	FeS_2^+	144	13	
167	17	$[RhS_2]^+$	89	21		159	46	$[MnOSCNMe_2]^+$
189	19	$[Rh(SCN)CO]^+$	100	15	$[FeSC]^+$	174	20	$[Mn_2S_2]^+$
208	31	$[RhS_2CNMe]^+$	132	13	$[FeS_2C]^+$	186	13	$[Mn_2(SC)S]^+$
223	40	$[P - 2CO]^+$	176	100	$[Fe(CO)_2S_2CNMe_2]^+$	219	7	$[Mn_2(OSC)(OSCNMe_2)]^+$
251	34	$[P - CO]^+$	217	83	$[P - 2CO]^+$	246	42	$[Mn_2S_2OCNMe_2]^+$
279	25	$[P]^+$	245	4	$[P - CO]^+$	262	5	$[MnSNMe_2]_2^+$
			273	6	$[P]^+$	290	32	$[Mn_2(OSCNMe_2)(SNMe_2)]^+$
						318	96	$[P - 6CO]^+$
						346	7	$[P - 5CO]^+$
						374	19	$[P - 4CO]^+$
						402	26	$[P - 3CO]^+$
						486	1	$[Mn(CO)_3OSCNMe_2]_2^+[P]^+$

Bromopentacarbonylmanganese and *N*,*N*-dimethylmonothiocarbamato(trimethyl)tin undergo reaction to displace carbon monoxide and trimethyltin bromide according to equation (4). No evidence was obtained for a monomeric manganese containing product.



(2)



(3)

$$2Mn(CO)_5Br + 2Me_3SnSC(O)NMe_2 \longrightarrow [Mn(CO)_3OSCNMe_2]_2 + 2Me_3SnBr + 4CO \quad (4)$$

Evidence for the formulation of the product is based upon elemental analysis, molecular weight measurement, and mass spectrometry. This formation of a dimer by the monothiocarbamato-ligand in contrast to the monomer formed by the dithiocarbamate is of particular

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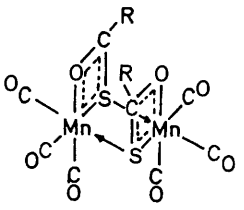
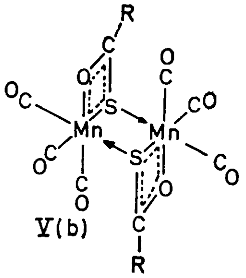
interest. We propose the structure (V) for this dimer, especially from the presence of the $Mn_2S_2^+$ moiety in the mass spectrum of the compound. The six observed bands in the metal carbonyl region of the i.r. spectrum are more than the predicted three A_μ bands for V(b), but in agreement with the six active ($3A + 3B$) modes predicted for the V(a) structures in which both chelates are on one side of the Mn_2S_2 plane.

Recrystallization of the dimer does not alter the relative intensities of the i.r. bands, which strongly commends structure (Va) for this particular complex. Further, a typical feature [9] of dithiocarbamate transition metal complexes is a C–N band of medium intensity in the 1480—1550 cm^{-1} region, which is intermediate between the C–N (1250—1350 cm^{-1}) frequency of amines, and the C=N (1640—1690 cm^{-1}) frequency. The C–N stretch of bis(thiocarbamatomanganese tricarbonyl) appears at 1585 cm^{-1} lending further support to structure V.



V(a)

(R = NMe_2)



V(b)

Models indicate that structure (Va) is not sterically crowded in any way.

Dimethylamido(trimethyl)tin undergoes insertion type reactions [17] with phenyl isothiocyanate and phenyl isocyanate to yield respectively *N*,*N*-dimethyl-*N*′-phenyl-*N*′-trimethylstannylthiourea and *N*,*N*-dimethyl-*N*′-phenyl-*N*′-trimethylstannylurea. Both of these organotin compounds react with bromopentacarbonylmanganese according to equations (5) and (6) below. The formulations of the products are based upon analyses and molecular weight determinations.

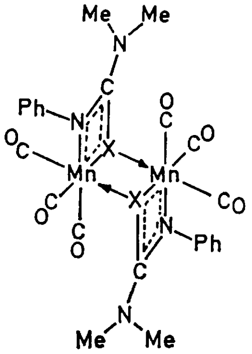
$$2Me_3Sn(Ph)NC(O)NMe_2 + 2Mn(CO)_5Br \longrightarrow [Mn(CO)_3PhNCONMe_2]_2 + 2Me_3SnBr + 4CO \quad (5)$$

$$2Me_3Sn(Ph)NC(S)NMe_2 + 2Mn(CO)_5Br \longrightarrow [Mn(CO)_3PhNCSNMe_2]_2 + 2Me_3SnBr + 4CO \quad (6)$$

The structures proposed for these two complexes are illustrated as (VI), and are obviously analogous to that proposed for the monothiocarbamate dimer (V).

The i.r. spectra of these ureido- and thioureido-complexes, consisting of three distinct bands only in the metal carbonyl region, are quite different, however, from the complex six band spectrum of the monothiocarbamato-dimer.

This we believe is due to the ureido- and thioureido-complexes taking up the configuration illustrated in (VI) where the two chelating groups are on opposite sides of the Mn_2X_2 plane. Models suggest that the alternative of both chelates on the same side of the Mn_2X_2 plane is too crowded to form. The structures (VI) would be predicted to have three i.r.-active A_μ modes, in agreement with the observed simple spectra.



(VI)

(X = O and S)

EXPERIMENTAL

N,*N*-Dimethyldithiocarbamato(trimethyl)tin,[17] *N*,*N*-dimethylthiocarbamato(trimethyl)tin,[18] *N*,*N*-dimethyl-*N*′-phenyl-*N*′-trimethylstannylurea, [17] and *N*,*N*-dimethyl-*N*′-phenyl-*N*′-trimethylstannylthiourea [17] were prepared by literature methods. The various reactions between these organotin precursors and metal carbonyl halides are described below, and the detailed characterizations are contained in the Tables 1 and 2.

All reactions were carried out under an atmosphere of dry nitrogen. All solvents were dried by distillation from lithium aluminium hydride. I.r. spectra were recorded in cyclohexane solution in calcium fluoride 0·1 mm space cells on a Perkin-Elmer 257 spectrophotometer, n.m.r. spectra were recorded in carbon tetrachloride solutions using cyclohexane as internal reference on a Varian T60 spectrometer, mass spectra were recorded on an A.E.I. MS9 instrument. Analyses and molecular weight measurements (vapour pressure in chloroform solution) were determined by Pascher Microanalytical Laboratories, Germany.

N,N-*Dimethyldithiocarbamato*(*tetracarbonyl*)*manganese*.—*N*,*N*-Dimethyldithiocarbamato(trimethyl)tin (0·70 g, 2·5 mmol) was added to bromopentacarbonylmanganese (0·65 g, 2·5 mmol) in dry tetrahydrofuran (30 ml). After stirring at room temperature (15 min) solvent was removed at reduced pressure and the solid residue pumped at 0·01 mmHg for 15 min to remove all trimethyltin bromide which was trapped out and characterised. Sublimation of the crude product (50°, 0·01 mmHg), yielded pure *N*,*N*-dimethyldithiocarbamato(tetracarbonyl)manganese (0·64 g, 90%).

N,N-*Dimethyldithiocarbamato*(π-*cyclopentadienyl*)*carbonyliron*.—A mixture of π-cyclopentadienyldicarbonyliron chloride (0·212 g, 1 mmol) and *N*,*N*-dimethyldithiocarbamato(trimethyl)tin (0·285 g, 1 mmol) were heated under reflux in tetrahydrofuran (30 ml). After 1 h the colour of $(\pi\text{-}C_5H_5)Fe(CO)_2Cl$ had disappeared, but the carbonyl region of the i.r. spectrum continued to change for a further 12 h, when a single band at 1954 cm^{-1} was present. It is possible that other bands observed during the course of the reaction may be due to intermediate steps in the reaction, but none of these could be isolated and characterised. Removal of the solvent left a brown residue which was taken up in hexane and after chromatography gave pure *N*,*N*-dimethyldithiocarbamato(π-cyclopentadienyl)carbonyliron (0·114 g, 43%).

N,N-*Dimethyldithiocarbamato*(π-*cyclopentadienyl*)*dicarbonyltungsten*.—A mixture of *N*,*N*-dimethyldithiocarbamato(trimethyl)tin (0·285 g, 1 mmol) and π-cyclopentadienyl(tricarbonyl)tungsten chloride (0·368 g, 1 mmol) in tetrahydrofuran (30 ml) was heated under reflux for 8 h, after which solvent was removed to yield a purple residue. Recrystallization from benzene–hexane gave deep red crystals of *N*,*N*-dimethyldithiocarbamato(π-cyclopentadienyl)dicarbonyltungsten (0·271 g, 65%).

N,N-*Dimethyldithiocarbamato*(*iodo*)*tricarbonyliron*.—To a solution of iron tetracarbonyl di-iodide (0·442 g, 1 mol) in ether (30 ml) at 0°, was added dropwise *N*,*N*-dimethyldithiocarbamato(trimethyl)tin (0·285 g, 1 mmol) in ether (5 ml), and the solution was stirred at 0° for 1 h. After filtration solvent was removed partially, and on recooling the product appeared as brown crystals. After washing with hexane (2 × 2 ml) to remove traces of trimethyltin iodide, these crystals were dried (20°, 0·01 mmHg). Yield 0·16 g, (41%).

N,N-*Dimethyldithiocarbamato*(π-*allyl*)*dicarbonyliron*.— To a solution of π-allyltricarbonyliron iodide (0·308 g, 1 mmol) in tetrahydrofuran (25 ml) at 0° was added dropwise a solution of *N*,*N*-dimethyldithiocarbamato(trimethyl)tin (0·285 g, 1 mmol) in tetrahydrofuran (5 ml). After standing at 0° for 3 h, the solvent and by-product trimethyltin iodide were removed at 30°, 40 mmHg. The quite volatile crude product was then sublimed as yellow-brown needles (45°, 0·05 mmHg) onto a probe cooled at −78°. Yield 0·17 g, (65%).

N,N-*Dimethyldithiocarbamato*(*dicarbonyl*)*rhodium*.—To a solution of rhodium carbonyl chloride [$Rh_2(CO)_4Cl_2$] (0·389 g, 1 mmol) in ether (25 ml) was added a solution of *N*,*N*-dimethyldithiocarbamato(trimethyl)tin (0·570 g, 2 mmol) in ether (5 ml). An immediate red colouration was followed by the rapid deposition of red crystals of the product. These were filtered off, washed with hexane (2 × 2 ml) and dried (20°, 0·05 mmHg). Yield 0·403 g (72%). (See Tables 1 and 2). It is likely in this reaction that the first step involved bridge breaking of the dimeric rhodium carbonyl chloride by co-ordination of the tin complex, followed by elimination of trimethyltin chloride, thus carbon monoxide is not displaced.

Bis[(N,N-*dimethylthiocarbamato*)*tricarbonylmanganese*].—To a suspension of bromopentacarbonylmanganese (0·55 g, 2 mmol) in ether (5 ml) was added a solution of *N*,*N*-dimethylthiocarbamato(trimethyl)tin (0·538 g, 2 mmol) in ether (5 ml), and the mixture stirred for 10 h at 25°. Solvent and trimethyltin bromide were removed at 25°, 0·1 mmHg, and the residue recrystallized from benzene–hexane 50% to give red-orange crystals (*ca*. 60% yield). The entire product was further recrystallized to obtain a very pure sample (0·10 g, 10%) for mass spectrometry. (See Tables 1 and 2).

Bis[N,N-*dimethyl*-N′-*phenylureido*)*tricarbonylmanganese*].—To a suspension of bromopentacarbonylmanganese (0·275 g, 1 mmol) in ether (20 ml) was added to *N*,*N*-dimethyl-*N*′-phenyl-*N*′-trimethylstannylurea (0·326 g, 1 mmol). The mixture was heated under reflux for 30 min, during which time the bromopentacarbonylmanganese disappeared and was replaced by the precipitation of bright yellow crystals. These were removed by filtration, washed with hexane and dried at 25°, 0·01 mmHg. Yield 0·20 g, (57%).

Bis[(N,N-*dimethyl*-N-*phenylthioureido*)*tricarbonylmanganese*].—To a suspension of bromopentacarbonylmanganese (0·275 g, 1 mmol) in ether (20 ml) was added *N*,*N*-dimethyl-*N*′-phenyl-*N*′-trimethylstannylthiourea (0·342 g, 1 mmol) in ether (10 ml). The mixture was heated under reflux for 2·5 h during which red-orange crystals were deposited. These were removed by filtration, washed with hexane (4 × 2 ml) and dried (25°, 0·01 mmHg). Yield 0·41 g (65%).

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