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INTERACTION OF THIOSILANES AND DISILTHIANES WITH SOME TRANSITIONAL AND POST-TRANSITIONAL METAL HALIDES

E. W. ABEL AND C. R. JENKINS
Department of Inorganic Chemistry, The University, Bristol, 8 (Great Britain)

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SUMMARY

Thiosilanes and disilthianes do not form stable co-ordination complexes with transitional and post-transitional metal halides, but invariably undergo fission of the silicon–sulphur bonds to give alkyl/arylmercaptides, sulphides or sulphonium derivatives of the metals.

Extensive studies of the fission reactions of Group IVB organometallic–sulphur compounds have indicated their effectiveness as synthetic intermediates in the preparation of sulphur-containing inorganic complexes[1]. We report further studies on the halide fissions of silicon–sulphur bonds.

(Alkyl/arylthio)silanes and hexamethyldisilthiane were treated with mercury and cadmium halides in an effort to obtain metal co-ordination complexes of these organosilicon–sulphur compounds. However, in all cases metal mercaptides or metal sulphides were produced (Table 1). From the colour changes which occurred during some of the reactions it is possible that such complexes were formed as intermediates, but underwent rapid elimination of organosilicon halide yielding the mercaptide or sulphide. Efforts to produce phosphine-substituted mercaptides by the use of phosphine mercury halides, again led only to mercaptides (Table 1). It is interesting to note that these reactions closely parallel[2] those of the corresponding organotin–sulphur derivatives, even to the formation of (alkyl/arylthio)metal halides in specific

TABLE 1

INTERACTION OF MERCURY AND CADMIUM HALIDES WITH SILICON–SULPHUR COMPOUNDS

Reagents	Product
$HgCl_2 + Me_3SiSMe$	$Hg(SMe)_2$
$HgBr_2 + Me_3SiSMe$	$BrHgSMe$
$(Ph_3P)_2HgCl_2 + Me_3SiSMe$	$Hg(SMe)_2$
$HgCl_2 + Me_3SiSPh$	$ClHgSPh$
$(Ph_3P)_2HgCl_2 + Me_3SiSPh$	$ClHgSPh$
$HgCl_2 + Me_3SiSSiMe_3$	HgS
$(Ph_3P)_2HgCl_2 + Me_3SiSSiMe_3$	HgS
$CdCl_2 + Me_3SiSPh$	$Cd(SPh)_2$
$CdBr_2 + Me_3SiSMe$	$BrCdSMe$
$CdCl_2 + Me_3SiSSiMe_3$	CdS

cases, despite the presence of an excess of the (alkyl/arylthio)silane.

Nickel chloride and (methylthio)trimethylsilane reacted to give nickel bis(methylmercaptide) (eqn. 1). This was found to be mainly of the polymeric, insoluble variety, but it was also possible to isolate about 10% of the very soluble, cyclic, hexameric variety[3].

$$Me_3SiSMe + NiCl_2 \rightarrow [Ni(SMe)_2]_6 + [Ni(SMe)_2]_n + Me_3SiCl \qquad (1)$$

In a similar reaction with (phenylthio)trimethylsilane, an insoluble, polymeric product $[Ni(SPh)_2]_n$ was again the predominant yield, together with some soluble, oligomeric product $[Ni(SPh)_2]_m$, but the degree of polymerization of this soluble fraction appeared variable.

The ability of the (alkyl/arylthio)trimethylsilanes to effect the replacement of halide by alkyl/arylthio groups on transitional metals was further demonstrated by the formation of the dicyclopentadienyltitanium mercaptides[4] (eqn. 2) in good yields.

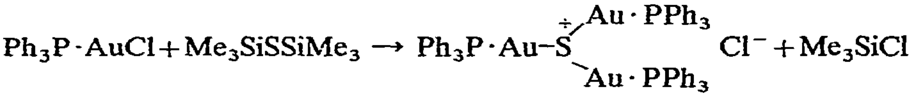
$$(C_5H_5)_2TiCl_2 + 2\ Me_3SiSR \rightarrow (C_5H_5)_2Ti(SR)_2 + 2\ Me_3SiCl \qquad (2)$$
$$(R = Me, Ph)$$

In contrast to the behaviour of the phosphine mercury halides (see Table 1), (triphenylphosphine)gold chloride reacted with (alkyl/arylthio)trimethylsilanes with retention of the co-ordinated phosphine, producing the phosphine gold(I) mercaptides[5,6] (eqn. 3); though the corresponding reaction with an arsine gold chloride does cause removal of the ligand and formation of gold mercaptide (eqn. 4).

$$Ph_3P{\cdot}AuCl + Me_3SiSR \rightarrow Ph_3P{\cdot}AuSR + Me_3SiCl \qquad (3)$$
$$(R = Me, Ph)$$

$$Ph_3AsAuCl + Me_3SiSMe \rightarrow AuSMe + Ph_3As + Me_3SiCl \qquad (4)$$

In an attempt to prepare the phosphine substituted gold(I) sulphide, hexamethyldisilthiane was treated with (triphenylphosphine)gold chloride. The isolated product from this reaction, however, was tris(triphenylphosphinegold)sulphonium chloride[6] (I) (eqn. 5). Efforts to prepare the corresponding triphenylarsine compound resulted only in the formation of gold sulphide.



$$Ph_3P{\cdot}AuCl + Me_3SiSSiMe_3 \rightarrow Ph_3P{\cdot}Au{-}\overset{+}{S}\begin{matrix}\nearrow Au{\cdot}PPh_3\\ \searrow Au{\cdot}PPh_3\end{matrix}\ Cl^- + Me_3SiCl \qquad (5)$$

(I)

EXPERIMENTAL

All compounds containing silicon–sulphur bonds are sensitive to moisture, and all reactions were carried out under anhydrous conditions. Elemental analyses were performed at the Microanalytical Laboratories of the University of Bristol and Imperial College, London. Proton magnetic resonance data were obtained on a Varian A 60 instrument with TMS as internal standard.

(Methylthio)trimethylsilane[7], (phenylthio)trimethylsilane[8], hexamethyldisilthiane[9], bis(triphenylphosphine)mercury(II) chloride[10], (triphenylphosphine)gold(I) chloride[11], (triphenylarsine)gold(I) chloride[11] were prepared by literature methods, and other reagents were the commercial products.

In all reactions the appropriate halotrimethylsilane was evolved and satisfactorily characterised. Molecular weight measurements were made in a vapour pressure osmometer in benzene.

Interaction of mercuric and cadmium halides with (methylthio)trimethylsilane, (phenylthio)trimethylsilane and hexamethyldisilthiane

The metal halide (1 mol.) was extracted with dry solvent (15 cc) into an excess (>2 mols.) of the organosilicon sulphur compound. The precipitated product was removed by filtration, washed with solvent (3 × 10 cc) and dried.

TABLE 2

RESULTS OF THE REACTIONS CARRIED OUT

Reagents	Solvent	Product	Yield (%)	Found (%)		Calcd. (%)	
				C	H	C	H
$HgCl_2 + Me_3SiSMe$	Et_2O	$Hg(SMe)_2$	95	8.5	2.3	8.2	2.1
$HgBr_2 + Me_3SiSMe$	Et_2O	BrHgSMe	77	3.5	0.9	3.7	0.9
$(Ph_3P)_2HgCl_2 + Me_3SiSMe$	$CHCl_3$	$Hg(SMe)_2$	91	8.1	2.0	8.2	2.1
$HgCl_2 + Me_3SiSPh$	Et	ClHgSPh[a]	85	20.7	1.5	20.8	1.5
$(Ph_3P)_2HgCl_2 + Me_3SiSPh$	$CHCl_3$	ClHgSPh	52	20.6	1.2	20.8	1.5
$HgCl_2 + Me_3SiSSiMe_3$	Et_2O	HgS[b]	91				
$(Ph_3P)_2HgCl_2 + Me_3SiSSiMe_3$	$CHCl_3$	HgS	58				
$CdCl_2 + Me_3SiSPh$	$(CH_2OMe)_2$	$Cd(SPh)_2$	57	43.5	2.9	43.6	3.0
$CdBr_2 + Me_3SiSMe$	$(CH_2OMe)_2$	BrCdSMe	65	5.0	1.3	5.0	1.3
$CdCl_2 + Me_3SiSSiMe_3$	$(CH_2OMe)_2$	CdS	85				

[a] S found 9.0%, calcd. 9.3%. [b] S found 13.6%, calcd. 13.8%.

Interaction of nickel chloride and (methylthio)trimethylsilane

The thiosilane (5 cc, excess) and anhydrous nickel chloride (1.10 g) were heated under reflux with stirring for 3 h. After filtration and washing with acetone/dichloromethane, the brown residue was dried to yield the polymeric form of nickel bis(methylmercaptide) (0.34 g). (Found: C, 16.4; H, 3.7. $C_2H_6NiS_2$ calcd.: C, 15.7; H, 4.0%.) Removal of solvent from the combined filtrate and washings yielded the cyclic form of nickel bis(methylmercaptide) (0.13 g, 10%). (Found: C, 16.0; H, 3.8; mol.wt., 950. $[C_2H_6NiS_2]_6$ calcd.: C, 15.7; H, 4.0%; mol.wt., 918.)

Interaction of nickel chloride and (phenylthio)trimethylsilane

Anhydrous nickel chloride (1.29 g) was heated (100°) with (phenylthio)trimethylsilane (6 cc excess) for 6 h with stirring. After filtration, the residue was washed with diethyl ether and benzene and the residue dried (80°/0.2 mm) to yield the polymeric form of nickel bis(phenylmercaptide) (0.54 g). (Found: C, 49.8; H, 4.0. $C_{12}H_{10}NiS_2$ calcd.: C, 52.0; H, 3.6%.) Solvent removal from the filtrate gave a brown residue, dried at 70°/0.1 mm to give a soluble form of nickel bis(phenylmercaptide)

(0.14 g, 5%). (Found: C, 51.6; H, 3.6%.) Solutions of this oligomer were unstable and slowly deposited the polymer on standing. Inconsistent molecular weight values were obtained, and it is possible that this soluble form consists of short linear chains of the Ni(SPh)$_2$ units.

Interaction of dicyclopentadienyltitanium dichloride with (methylthio)trimethylsilane and (phenylthio)trimethylsilane

The halide (2.49 g) in tetrahydrofuran (20 cc) was heated (100°) with the thiosilane (6 cc excess) for 24 h with stirring. Solvent was removed from the resulting purple solution, and the residue was extracted with the minimum of benzene. Chromatography of the resulting solution on an alumina column (washed with ethyl acetate and dried overnight at 120°) produced a violet band, eluted with benzene/60–80 petrol ether (1/1 mixture). Removal of solvent from the eluate afforded purple crystals of dicyclopentadienyltitanium bis(methylmercaptide) (0.91 g, 33%), m.p. 185–186° (lit.[4] 184°). (Found: C, 53.2; H, 5.6. $C_{12}H_{16}S_2Ti$ calcd.: C, 52.9; H, 5.9%.)

Similarly was prepared dicyclopentadienyltitanium bis(phenylmercaptide) (2.80 g, 71%), m.p. 205–206° [lit.[4] 202° (dec.)]. (Found: C, 66.6; H, 4.8; S, 16.2. $C_{22}H_{20}S_2Ti$ calcd.: C, 66.7; H, 5.1; S, 16.2%.)

τ values for the proton magnetic resonance spectra of the above two products are:

$(C_5H_5)_2Ti(SCH_3)_2$: 3.90 (C_5H_5 ring), 7.38 (methyl); intensity ratio 5/3
$(C_5H_5)_2Ti(SC_6H_5)_2$: 4.01 (C_5H_5 ring), 2.77 (phenyl multiplet); intensity ratio 1/1

Interaction of (triphenylphosphine)gold(I) chloride with (methylthio)trimethylsilane and (phenylthio)trimethylsilane

The gold complex (0.50 g) was extracted with carbon disulphide (15 cc) into the thiosilane (5 cc excess) and heated under reflux (3 h). Filtration and removal of solvent from the filtrate yielded pale-yellow crystals of (triphenylphosphine)gold(I) methylmercaptide (0.51 g, ~100%), m.p. 157° (lit.[6] 155–157°). (Found: C, 45.6; H, 3.4. $C_{19}H_{18}AuPS$ calcd.: C, 45.1; H, 3.5%.) τ values of proton magnetic resonances at 2.61 (phenyl multiplet) and 8.77 (methylthio) were in the relative intensities of 5/1.

Similarly was obtained (triphenylphosphine)gold phenylmercaptide (0.48 g, 83%), m.p. 161° (lit.[6] 161–163°). (Found: C, 51.0; H, 3.4; S, 5.8. $C_{24}H_{20}AuPS$ calcd.: C, 50.7; H, 3.5; S, 5.6%.)

Interaction of (triphenylarsine)gold(I) chloride with (methylthio)trimethylsilane and (phenylthio)trimethylsilane

The gold complex (0.50 g) in carbon disulphide (10 cc) was treated with the thiosilane (5 cc, excess) at 18°. A yellow colouration rapidly developed and precipitation occurred. After standing for 1 h the mixture was heated under reflux for 2 h and then filtered. The yellow precipitate was washed with carbon disulphide (2×10 cc) and dried (70°/0.1 mm) to produce gold methylmercaptide (0.18 g, 73%) as an insoluble, presumably polymeric, yellow solid. (Found: C, 5.6; H, 1,1; S, 13.5. CH_3AuS calcd.: C, 4.9; H, 1.2; S, 13.2%.)

Similarly was prepared gold phenylmercaptide (0.26 g, 84%). (Found: C, 23.8; H, 1.7; S, 10.3. C_6H_5AuS calcd.: C, 23.5; H, 1.6; S, 10.5%.)

Interaction of (triphenylphosphine)gold(I) chloride and hexamethyldisilthiane

The gold complex (0.50 g) was extracted with carbon disulphide (10 cc) into the disilthiane (2 cc, excess) and heated under reflux for 3 h. Removal of solvent and rapid recrystallisation from ethanol yielded tris[(triphenylphosphine)gold] sulphonium chloride, m.p. 192° (lit.[6] 191°). (Found: C, 45.2; H, 3.3. $C_{54}H_{45}Au_3ClP_3S$ calcd.: C, 44.9; H, 3.1%.) A conductivity measurement in nitrobenzene gave Λ 19.8 $\text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mole}^{-1}$.

An effort to produce the corresponding compound of triphenylarsine from (triphenylarsine)gold chloride and hexamethyldisilthiane resulted only in the formation of gold sulphide (0.15 g, 70%).

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