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STUDIES IN GROUP IV ORGANOMETALLIC CHEMISTRY XXX*. SYNTHESIS OF COMPOUNDS CONTAINING TIN–TITANIUM AND TIN–ZIRCONIUM BONDS**

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SUMMARY

Starting from the tetrakis(diethylamino) derivatives of titanium and zirconium and phenyltin hydrides six intermetallic compounds containing up to nine tin and titanium (or zirconium) atoms have been obtained by hydrostannolysis type reactions.

INTRODUCTION

Numerous compounds have been prepared in recent years which contain a main group metal covalently bound to a transition metal[2]. A frequently employed preparative method involves the reaction of an organometal halide with an organometallic anion, *e.g.*:

$$L_nMX + R_3M^{IV-} \rightarrow R_3M^{IV}-ML_n + X^-$$

or $$L_nM^- + R_3M^{IV}X \rightarrow R_3M^{IV}-ML_n + X^-$$

L (ligand) = CO, π-C_5H_5; M^{IV} = Si, Ge, Sn, Pb; M = transition metal and X = halogen.

Limiting factors in this type of reaction are the occurrence of nucleophilic attack of organometallic anions on metal–metal bonds[3,4] or the occurrence of metal–halogen exchange.

The interaction of reactive organometal hydrides with metal–element bonds (*e.g.* metal–oxygen and –nitrogen[5–9] and metal–carbon[10,11] bonds), offers another general synthesis of compounds having metal–metal bonds. The hydrostannolysis reaction has been particularly useful for the synthesis of compounds with tin–metal bonds[11,12].

Very recently, compounds containing a metal–metal bond between IVth main group and IVth group transition metals have been reported[12–16]. These compounds were prepared via IVth main group alkali metal derivatives. The high reactivity of the metal–nitrogen bond in compounds of the type $M(NR_2)_4$ (where M is a IVth group transition metal) towards proton-active species (*e.g.* hydrolysis, aminolysis and alcoholysis[17]) has led us to study the synthesis of compounds with tin–titanium and tin–zirconium bonds by means of hydrostannolysis reactions[12].

* For Part XXIX see ref. 1.
** Taken from the Ph.D.thesis of one of us (H.M.J.C.C.).

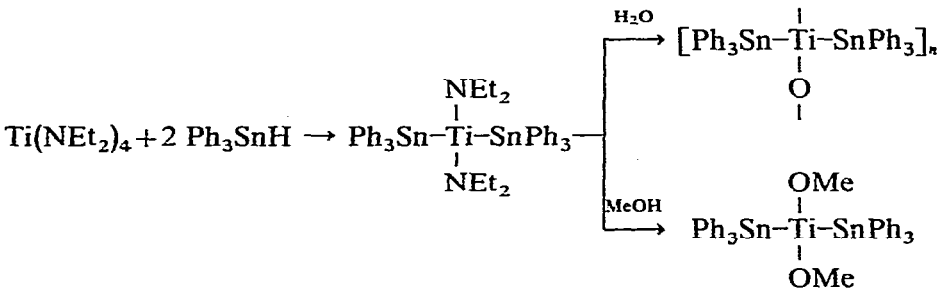
PROCEDURE AND RESULTS

Following the gradual addition, at about 50° in the absence of a solvent, of tetrakis(dimethylamino)titanium to triphenyltin hydride in a ratio 1:4 a resinous product was obtained, from which after purification by column chromatography tetrakis(triphenylstannyl)titanium was isolated as an ochre-yellow solid:

$$Ti(NMe_2)_4 + 4\ Ph_3SnH \rightarrow (Ph_3Sn)_4Ti + 4\ Me_2NH$$

The corresponding tributyltin derivative could not be obtained in this way. The greater reactivity of triphenyltin hydride as compared with trialkyltin hydrides in hydrostannolysis reactions has been noted before[18].

The reaction of Ph_3SnH with $(Et_2N)_4Ti$ *in vacuo* at 80° in a ratio 2 : 1, followed by exposure to humid air or treatment with methanol afforded infusible reaction products which analyzed for the products shown in the equation below. The intermediately formed bis(diethylamino)bis(triphenylstannyl)titanium was not isolated.



Excess cyclopentadiene monomer reacted exothermally with tetrakis(dimethylamino)titanium, only one $-NMe_2$ group being replaced[19]. Upon reaction of the resulting π-cyclopentadienyltris(dimethylamino)titanium with triphenyltin hydride in a 1 : 3 molar ratio, almost the theoretical amount of dimethylamine was liberated, but no well-defined tin–titanium derivative could be isolated. The NMR spectrum revealed that the cyclopentadienyl group had been removed from the titanium.

A number of compounds containing zirconium–tin bonds were obtained starting from tetrakis(diethylamino)zirconium and triphenyltin hydride in different molar ratios. *E.g.* reaction in a 1 : 4 ratio (60°, *in vacuo*; no solvent) yielded tetrakis(triphenylstannyl)zirconium.

$$Zr(NEt_2)_4 + Ph_3SnH \rightarrow (Ph_3Sn)_4Zr + 4\ Et_2NH$$

The IR spectra in the 2–25 mμ region of $(Ph_3Sn)_4Ti$ and $(Ph_3Sn)_4Zr$ were nearly identical with those of the corresponding main group IV metal–metal derivatives $(Ph_3Sn)_4Ge$ and $(Ph_3Sn)_4Sn$[20].

The following reaction sequence led to a tin–zirconium compound with nine interjoined metal atoms. Tetrakis(diethylamino)zirconium and triphenyltin hydride were reacted in a ratio of 1 : 3 and the reaction product was subjected to transamination with *N*-phenylformamide. This transamination is necessary in order to prevent diethylamine-catalyzed decomposition of diphenyltin dihydride in the next reaction step (*cf.* ref. 8). The resulting tris(triphenylstannyl)(*N*-phenylformamido)zirconium upon reaction, without prior isolation, with diphenyltin dihydride in a 2 : 1 molar

ratio afforded the desired compound in reasonable purity:

$$Zr(NEt_2)_4 + 3\ Ph_3SnH \rightarrow (Ph_3Sn)_3ZrNEt_2 + 3\ Et_2NH$$
$$(Ph_3Sn)_3ZrNEt_2 + HN(Ph)C(O)H \rightarrow (Ph_3Sn)_3ZrN(Ph)C(O)H + Et_2NH$$
$$2\ (Ph_3Sn)_3ZrN(Ph)C(O)H + Ph_2SnH_2 \rightarrow (Ph_3Sn)_3ZrSnPh_2Zr(SnPh_3)_3 + 2\ HN(Ph)C(O)H$$

Following the same reaction sequence but now starting from the zirconium compound and triphenyltin hydride in a molar ratio of 1 : 2, a polymeric compound with alternating zirconium and tin atoms in the polymer chain has been synthesized:

$$Zr(NEt_2)_4 + 2\ Ph_3SnH \rightarrow (Ph_3Sn)_2Zr(NEt_2)_2 + 2\ Et_2NH$$
$$(Ph_3Sn)_2Zr(NEt_2)_2 + 2\ HN(Ph)C(O)H \rightarrow (Ph_3Sn)_2Zr[N(Ph)C(O)H]_2 + 2\ Et_2NH$$
(A)

$$n\,(A) + n\ Ph_2SnH_2 \rightarrow \left[\begin{array}{c} Ph_3 \\ Sn\ Ph \\ | \quad | \\ -Zr-Sn- \\ | \quad | \\ Sn\ Ph \\ Ph_3 \end{array}\right]_n + 2n\ HN(Ph)C(O)H$$

No definite products could be isolated when using trialkyltin hydrides in these reactions instead of triphenyltin hydride. Analytical data and melting points of the various compounds prepared are given in Table 1.

EXPERIMENTAL

Since the organometallic compounds mentioned in this study are air-sensitive all manipulations were carried out in an atmosphere of dry nitrogen. Benzene was treated with lithium aluminium hydride and distilled before use in an atmosphere of nitrogen. Butyronitrile was distilled three times from phosphorus pentoxide and once under nitrogen from potassium carbonate.

N-Phenylformamide was removed from the final reaction mixtures by treatment with anhydrous methanol; the Sn–Ti and –Zr derivatives were further purified by column chromatography under an inert atmosphere. Residual traces of hexaphenylditin were removed by treatment with benzene in which hexaphenylditin is virtually insoluble.

The Ti–N and Zr–N derivatives were prepared according to published procedures[17]. The metal content was determined by wet combustion with a mixture of conc. sulphuric acid and fuming nitric acid. The infrared spectra were run using a Grubb–Parson Spectromaster.

Tetrakis(triphenylstannyl)titanium

Triphenyltin hydride (4.5 g, 0.0128 mole) was brought into a two-necked round-bottomed flask fitted with a distillation head and connected via a receiver cooled in Dry-Ice with a water-pump. The flask was heated at 50° and 0.72 g (0.003 mole) of tetrakis(dimethylamino)titanium was added by means of a syringe with stirring. Immediately an evolution of gas set in, and after 20 min heating 1 g of dimethylamine had been collected in the receiver. The resinous product left in the flask was taken up

TABLE 1

COMPOUNDS CONTAINING Sn–Ti AND Sn–Zr BONDS[a]

Compound	Formula	Found (%)				Calcd. (%)				Yield	M.p.	Appearance
		C	H	Sn	Ti or Zr	C	H	Sn	Ti or Zr	(%)	(°C)	
$(Ph_3Sn)_4Ti$	$C_{72}H_{60}Sn_4Ti$			34.6	3.5			32.79	3.31	30	130	Ochre solid
$[Ph_3SnTiSnPh_3]_n$ (O bridge)	$C_{36}H_{30}OSn_2Ti$	56.5	4.2			56.60	3.96			40	>260	White solid
$Ph_3SnTi(OMe)_2SnPh_3$	$C_{38}H_{36}O_2Sn_2Ti$	55.6	4.1	30.8	5.9	56.35	4.48	29.31	6.21	40	>260	Yellow solid
$(Ph_3Sn)_4Zr$	$C_{72}H_{60}Sn_4Zr$[b]			32.9	6.3			31.84	6.12		Sinters at 65° 70–73	Yellow solid
$(Ph_3Sn)_3ZrSnPh_2Zr(SnPh_3)_3$	$C_{120}H_{100}Sn_7Zr_2$	55.3	4.1	31.5	6.9	56.40	3.92	32.51	7.14	22	Sinters at 85° 100° (dec.)	Yellow solid
$[(Ph_3Sn)_2Zr{-}SnPh_2]_n$	$(C_{48}H_{40}Sn_3Zr)_n$[c]	54.4	4.1	32.2	8.25	54.18	3.79	33.46	8.57	49	Sinters at 110° 160° (dec.)	Orange-yellow solid

[a] Difficulties were encountered in obtaining satisfactory analytical data for these compounds. Whether this is due to failures in the analytical procedure or to traces of impurities (oxides) cannot be decided. Further purification by the normal procedures was not possible, because of the extreme susceptibility of the compounds towards traces of oxygen. [b] Mol.wt. (ebull.): found 1424; calcd. 1491. [c] Mol.wt. (ebull.): found 1890; calcd. $(1020)_n$.

in 3 ml of benzene. After the addition of 15 ml of light petroleum a brown paste precipitated, which turned into an ochre solid on grinding. This was again taken up in benzene, the insoluble part filtered off and the benzene solution brought on a chromatography column. Elution with benzene yielded 1 g (30%) of an ochre-coloured solid with m.p. 130°.

Reaction of tetrakis(diethylamino)titanium with triphenyltin hydride (1 : 2)

3.1 g (0.0125 mole) of tetrakis(diethylamino)titanium were heated towards 80° when 6.7 g (0.019 mole) of triphenyltin hydride were added. The reaction mixture solidified and 1.2 g (theor. 1.4 g) of diethylamine were collected in the trap. The reaction product was dissolved in benzene, the insoluble part filtered off and absolute methanol (30 ml) added to the brown-coloured filtrate. The ochre-yellow solid which precipitated was further purified by dissolution in benzene and precipitation with light petroleum. The final product analyzed for bis(triphenylstannyl)titanium dimethoxide.

Tetrakis(triphenylstannyl)zirconium

In the course of 40 min 7 g (0.02 mole) of triphenyltin hydride was added gradually to 1.9 g (0.005 mole) of tetrakis(diethylamino)zirconium. The temperature was kept at 60°, vacuum being applied to the apparatus. An amount of 1.3 g (theoretically 1.46 g) of diethylamine was collected in the receiver. The dark brown product left in the reaction flask was taken up in benzene and purified by column chromatography. Evaporation of the eluate gave a yellow solid (m.p. 70–73°; sintering at 65°).

Bis[tris(triphenylstannyl)zirconyl]diphenyltin

Tris(triphenylstannyl)(diethylamino)zirconium was prepared by the procedure in the preceding experiment from 2 g (0.0052 mole) of tetrakis(diethylamino)zirconium and 5.5 g (0.015 mole) of triphenyltin hydride (ratio 1 : 3 instead of 1 : 4). The addition of 0.64 g of *N*-phenylformamide in 5 ml benzene to the residue caused an exothermic reaction. After additional refluxing for 1 h the solvent and diethylamine were distilled off and replaced by 5 ml of butyronitrile. By means of a syringe 0.7 g of diphenyltin dihydride was added and the mixture stirred at 65° for $1\frac{1}{2}$ h. The IR spectrum then failed to show any residual Sn–H absorption. Purification by column chromatography yielded 1.3 g (22%) of a yellow solid which melted at 100° with decomposition (sintering set in at 85°).

Bis(triphenylstannyl)zirconyl–diphenyltin polymer

Bis(triphenylstannyl)bis(diethylamino)zirconium (9.3 g), prepared from 3.8 g (0.01 mole) of tetrakis(diethylamino)zirconium and 7 g (0.02 mole) triphenyltin hydride was dissolved in 5 ml of benzene. On the addition of 2.4 g of *N*-phenylformamide a highly exothermic reaction set in. The bis-formamido compound formed (10.3 g) after being freed from solvent and diethylamine was dissolved in 5 ml of butyronitrile and 2.7 g of diphenyltin dihydride were added. After stirring the mixture at 50° for 30 min the Sn–H absorption had disappeared from the IR spectrum. Volatiles were evaporated *in vacuo* and the residue treated with absolute methanol to remove *N*-phenylformamide. The methanolic extract was removed by centrifugation. The remaining solid was taken up in 20 ml of benzene, the insoluble part (2 g) filtered off and the orange filtrate evaporated to dryness leaving a sticky mass. This was convert-

ed into a crystalline solid by stirring with light petroleum. Yield 4.9 g (m.p. 160° with decomposition; sintering at about 110°).

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REFERENCES

1 A. J. LEUSINK, H. A. BUDDING AND W. DRENTH, *J. Organometal. Chem.*, 13 (1968) 163.
2 H. R. H. PATIL AND W. A. G. GRAHAM, *Inorg. Chem.*, 5 (1966) 1401 and references cited therein.
3 R. E. DESSY AND P. M. WEISSMAN, *J. Amer. Chem. Soc.*, 88 (1966) 5129.
4 E. J. BULTEN AND J. G. NOLTES, *Tetrahedron Lett.*, (1967) 1443.
5 H. M. J. C. CREEMERS, J. G. NOLTES AND G. J. M. VAN DER KERK, *Rec. Trav. Chim.*, 83 (1964) 1284.
6 H. M. J. C. CREEMERS AND J. G. NOLTES, *Rec. Trav. Chim. Pays-Bas.*, 84 (1965) 382.
7 W. P. NEUMANN, B. SCHNEIDER AND R. SOMMER, *Justus Liebigs Ann. Chem.*, 692 (1966) 1.
8 H. M. J. C. CREEMERS AND J. G. NOLTES, *J. Organometal. Chem.*, 7 (1967) 237.
9 D. J. CARDIN AND M. F. LAPPERT, *Chem. Commun.*, (1966) 506.
10 N. S. VYAZANKIN, G. A. RAZUVAEV, O. A. KRUGLAYA AND G. S. SEMCHIKOVA, *J. Organometal. Chem.*, 6 (1966) 474.
11 F. J. A. DES TOMBE, G. J. M. VAN DER KERK, H. M. J. C. CREEMERS AND J. G. NOLTES, *Chem. Commun.*, (1966) 914.
12 H. M. J. C. CREEMERS, *Hydrostannolysis*, Ph. D. Thesis, State University of Utrecht, 1967.
13 D. J. CARDIN, S. A. KEPPIE, B. M. KINGSTON AND M. F. LAPPERT, *Chem. Commun.*, (1967) 1035.
14 R. S. P. COUTTS AND P. C. WAILES, *Chem. Commun.*, (1968) 260.
15 E. HENGGE AND H. ZIMMERMAN, *Angew. Chem.*, 80 (1968) 153.
16 B. M. KINGSTON AND M. F. LAPPERT, *Inorg. Nucl. Chem. Lett.*, 4 (1968) 371.
17 D. C. BRADLEY AND I. M. THOMAS, *J. Chem. Soc.*, (1960) 3857.
18 H. M. J. C. CREEMERS, F. VERBEEK AND J. G. NOLTES, *J. Organometal. Chem.*, 8 (1967) 469.
19 G. CHANDRA AND M. F. LAPPERT, *Inorg. Nucl. Chem. Lett.*, 1 (1965) 83.
20 L. C. WILLEMSENS AND G. J. M. VAN DER KERK, *J. Organometal. Chem.*, 2 (1964) 260.