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POLYMERIC METALCARBONYL COMPLEXES WITH BRIDGING DISTIBANE LIGANDS

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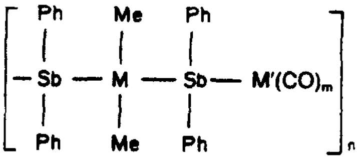
Abstract—The bidentate ligands $(Ph_2Sb)_2MMe_2$ react with $Ni(CO)_4$ to yield the polymeric complexes $[Ph_2SbMMe_2SbPh_2Ni(CO)_2]_n$; **1**: M = C, **2**: M = Ge, **3**: M = Sn. From $(THF)Cr(CO)_5$ and $(Ph_2Sb)_2SnMe_2$ the dinuclear complex $Me_2Sn[SbPh_2Cr(CO)_5]_2$ **4** has been synthesized. Tetramethyldistibane reacts with bicyclo-2,2,1-heptadienetetracarbonylchromium to yield polymeric $[(Me_2SbSbMe_2)Cr(CO)_4]_n$ **5**.

INTRODUCTION

In the course of our investigations of the coordinating properties of organometalstibines[1] and tetraalkyl- and -phenyldistibanes[2] we became interested in reactions between organometaldistibane ligands $(Ph_2Sb)_2MMe_2$; M = Si, Ge, Sn and metalcarbonyls which easily coordinate two ligands, like bicyclo - 2,2,1 - heptadienetetracarbonylchromium and tetracarbonylnickel. We expected the formation of polymers (A) because similar reactions of $(tBu_2P)_2SnMe_2$ and tetracarbonylnickel[3] as well as of tetramethyldiarsane with hexacarbonyl chromium[4] yielded polymeric products. Polymeric distibane complexes (A) consist of chains of metalatoms with saturated covalent bonds. It has been proposed, that polymers with back bones formed of covalently bonded metal atoms might have unusual electric properties[5], due to electron transport along the metal chain.



A

M = Si, Ge, Sn; M′ = Cr, m = 4; M′ = Ni, m = 2

EXPERIMENTAL

All experiments were carried out in a Ar-atmosphere. Metal carbonyls were obtained from commercial sources. Bicyclo - 2,2,1 - heptadienetetracarbonylchromium[6], 2,2 - bis - (diphenylstibido)propane, bid(diphenylstibido)dimethylsilicon, -germanium and -tin[7] as well as tetramethyldistibane[8] were prepared according to published methods. IR spectra were recorded on a Perkin–Elmer spectrometer PE 577 in Nujol mulls. For the mass spectra a Varian MAT CH 7 A spectrometer was used.

Dark conductivities of the pressed powders were measured by a published method[9] at 900 kp/cm², 298°K (1–3), and 303°K, 353°K (**5**).

Preparation of the nickel complexes. Catena - dicarbonyl - μ - [propane - 2 - ylidenbis(diphenylstibine)]nickel **1**, catena - dicarbonyl - μ - [dimethylgermanium- and -tinbis(diphenylstibine)]nickel **2**, **3** were prepared by reaction of stoichiometric amounts of tetracarbonylnickel and the bidentate ligands in 50 ml pentane at room temperature.

When the evolution of CO had finished, the solvent was pumped off and yellow oils **1a**, **2a**, **3a** remained, which solidified, when stored under pentane for some hours to give insoluble yellow compounds (**1**, **2**, **3**).

Preparation of μ - dimethyltinbis(diphenylstibine) - bis - (pentacarbonylchromium) **4**. To an irridiated solution of hexacarbonylchromium in 200 ml tetrahydrofurane the ligand was added dropwise. After stirring for one hour the solvent was removed and the residue recrystallized from pentane as a pale yellow solid.

Preparation of catena - tetracarbonyl - μ - (tetramethyldistibane) - chromium **5**. Bicyclo - 2,2,1 - heptadienetetracarbonylchromium and tetramethyldistibane were stirred for 4 hr in 40 ml pentane. **5** precipitated as an insoluble solid and was purified by extraction with pentane in a Soxhlet apparatus. Quantitative preparative and analytical details of **1–5** are given in Table 1.

DISCUSSION

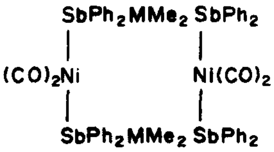
(1) *Derivatives of tetracarbonylnickel*

The reactions of the bidentate ligands $(Ph_2Sb)_2MMe_2$ (M = C, Ge, Sn) with tetracarbonylnickel yield the complexes **1**, **2** and **3** according to eqn (1).

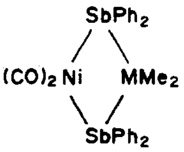
$$Ni(CO)_4 + (Ph_2Sb)_2MMe_2 \longrightarrow 1/n\,[Ph_2SbMMe_2SbPh_2Ni(CO)_2]_n + 2CO \quad \mathbf{1}: M = C,\ \mathbf{2}: M = Ge,\ \mathbf{3}: M = Sn. \qquad (1)$$

The IR-spectra of **1**, **2** and **3** show two strong absorptions in the ν(CO) range (**1**: 1990 cm⁻¹, 1948 cm⁻¹; **2**: 1980 cm⁻¹, 1940 cm⁻¹; **3**: 1995 cm⁻¹, 1940 cm⁻¹). This pattern is typical for $L_2Ni(CO)_2$-complexes (see: $(Et_3Sb)_2Ni(CO)_2$: 2004 cm⁻¹, 1948.5 cm⁻¹[10]).

The structures I, II and III are compatible with the analytical data for **1–3**. Compounds of type I and II



I



II

$[Ph_2SbMMe_2SbPh_2Ni(CO)_2]_n$

III

Table 1. Preparative and analytical data of cpds. 1–5

		starting materials								analysis			
		$Ni(CO)_4$		$(Ph_2Sb)_2MMe_2$			yield		m.p.	% carbon		% hydrogen	
		g	mmol	M	g	mmol	g	%	°C	calcd.	found	calcd.	found
$[CMe_2(Ph_2Sb)_2Ni(CO)_2]_n$	1	0,33	1,93	C	1,15	1,93	0,80	58	65 dec.	49,14	49,95	3,66	3,71
$[GeMe_2(Ph_2Sb)_2Ni(CO)_2]_n$	2	0,26	1,52	Ge	1,00	1,52	0,81	69	67 dec.	43,72	43,02	3,41	3,84
$[SnMe_2(Ph_2Sb)_2Ni(CO)_2]_n$	3	0,49	2,85	Sn	2,00	2,85	1,60	69	70 dec.	41,24	42,08	3,21	3,70
		$Cr(CO)_6$											
		g	mmol										
$[Me_2Sn\ SbPh_2Cr(CO)_5]_2$	4	1,40	6,34	Sn	2,20	3,14	2.42	71	95	39,86	39,20	2,41	2,40
		$norCr(CO)_4$			Me_4Sb_2								
		g	mmol		g	mmol							
$[Me_4Sb_2Cr(CO)_4]_n$	5	1,60	6,25		1,90	6,25	2,40	82	200 dec.	20,55	20,57	2,57	2,57

should be appreciably soluble in organic solvents. We therefore believe that polymers (type III) were formed. We have no information about *n*. It is possible that very long chains have formed. In the first step of reaction (1) we observe the formation of oily soluble products. These show additional IR-absorptions (**1a**: 2060 cm^{-1}, 1980 cm^{-1}; **2a**: 2060 cm^{-1}, 1980 cm^{-1}; **3a**: 2070 cm^{-1}, 2000 cm^{-1}) which are typical for $LNi(CO)_3$ complexes (see: $Et_3SbNi(CO)_3$: 2067 cm^{-1}, 1996 cm^{-1}[10]).

Therefore these species may be considered as monomeric tricarbonylnickelcomplexes which polymerize with elimination of CO to yield **1–3**. In addition **1** shows a weak absorption at 2060 cm^{-1}, due either to monomeric **1a** or to $LNi(CO)_3$ end groups in the polymer.

The conductivity of **1** ($\kappa_{298} = 1.7\ 10^{-10}\ \Omega^{-1}\ cm^{-1}$), **2** ($\kappa_{298} = 3.5\ 10^{-8}\ \Omega^{-1}\ cm^{-1}$) and **3** ($\kappa_{298} = 2.3\ 10^{-8}\ \Omega^{-1}\ cm^{-1}$) is in the order of magnitude of semiconductors. The increase of the conductivity from **1**, where carbonatoms interrupt the polymer metal chain to **2** and **3** where the polymer chain consists only of metal atoms suggests that there might be some participation of the metal chain in the process of electron transport.

In contrast to the linear chain of one dimensional metals[11] the backbones of the polymers **1–3** are certainly folded due to the tetrahedral coordination of each metal.

(2) *Derivatives of hexacarbonylchromium*

The reaction of bis(diphenylstibido)dimethyltin with pentacarbonyl(tetrahydrofurane)chromium in a ratio 1/2 yielded the expected binuclear complex **4** (see eqn 2).

$$2THFCr(CO)_5 + (Ph_2Sb)_2SnMe_2 \longrightarrow Me_2SN[Sb_4Ph_2Cr(CO)_5]_2 + 2THF \quad (2)$$

Spectroscopic data (IR: ν(CO) 2060 cm^{-1}, 1938 cm^{-1}; ^{1}H-NMR: $\delta(C_6H_5) = 7.40$ (10), $\delta(CH_3) = 0.1$ (3)); MS: $M^{\oplus}-CH_3-2CO$, *m/e* = 1014, rel. Int. < 1%) support our formulation of **4** as a binuclear complex.

In contrast to this result the reactions of $(Ph_2Sb)_2GeMe_2$ and $(Ph_2Sb)_2CMe_2$ with $THFCr(CO)_5$ yielded pentacarbonyl(triphenylstibine)chromium which was identified by its MS-data (30 eV, M^+: *m/e* = 544, rel. int. 15%). Apparently these unsymmetric bidentate ligands decomposed to the symmetric monodentate triphenylstibine and therefore they could not be used for the synthesis of polymeric chromium carbonylcomplexes.

A polymeric complex **5** was the product of the reaction of tetramethyldistibane with bicyclo-2,2,1-heptadienetetracarbonylchromium (eqn 3).

$$Me_4Sb_2 + norCr(CO)_4 \longrightarrow 1/n[Me_4Sb_2Cr(CO)_4]_n + nor \quad (3)$$

$$nor = C_7H_8 \qquad \mathbf{5}$$

5 shows one signal at 1860 cm^{-1} in the ν(CO) region of the IR-spectrum.

This is typical for transdisubstituted complexes $L_2Cr(CO)_4$ like *trans*$(Ph_3P)_2Cr(CO)_4$ (νCO = 1889 cm^{-1})[10]. In contrast to the soluble diarsine complex $[Me_4As_2Cr(CO)_4]_n$ which was described by Hayter[4] **5** is completely insoluble in organic solvents. As a consequence of the *trans* substitution at the chromium we have to assume linearity in the Sb–Cr–Sb fragments of the metal chain The tetrahedral coordination of antimony however prevents linearity of the whole chain.

The conductivity of **5** ($\kappa_{303} = 4.8\ 10^{-14}\ \Omega^{-1}\ \mathrm{cm}^{-1}$) is smaller than the values of the polymeric nickel complexes **1–3**. It can be raised either by heating ($\kappa_{353} = 8.4\ 10^{-13}\ \Omega^{-1}\ \mathrm{cm}^{-1}$) or by adding an electron acceptor (**5** + 1% tetracyanoethylene: $\kappa_{303} = 7.2\ 10^{-12}\ \Omega^{-1}\ \mathrm{cm}^{-1}$).

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