FORMATION OF σ AND π COMPLEXES IN THE REACTIONS OF PHENYL DERIVATIVES OF ANTIMONY AND BISMUTH WITH TRIAMMINECHROMIUM TRICARBONYL

> A. A. Alad'in, A. N. Artemov, and G. A. Razuvaev

UDC 542.91:541.49:547.558.3:546.765

Derivatives of metal carbonyls include many aromatic compounds of group V elements. These compounds are mainly two types of complexes. Thus, aniline and other aromatic amines [1] upon heating with chromium hexacarbonyl yield π -arene complexes as single products, in which the chromium tricarbonyl group is directly attached to the aromatic ring of the amine, while virtually all the phenyl derivatives of phosphorus and arsenic form only σ -donor complexes [2-6], in which the bond to chromium is formed by means of the free-electron pairs of the group V heteroatoms. The synthesis of several π -arene complexes of phosphorus by the reaction of π -phenyllithium chromium tricarbonyl with various phosphorus halides [7] and the direct reaction of chromium hexacarbonyl with hindered ortho-substituted tritolylphosphines [8] are an exception to this rule. In the latter case, the reaction leads to a mixture of π -arene complexes of tritolylphosphines containing one, two, and three chromium tricarbonyl groups. However, in the absence of methyl groups which produce steric hindrance or in the case of meta- and para-tritolylphosphines, only σ -donor complexes are formed.

In the present work, we studied the reaction between triphenyl compounds of antimony and bismuth with triamminechromium tricarbonyl $(NH_3)_3Cr(CO)_3$, which is a convenient reagent for obtaining arene π complexes of chromium [9, 10]. The direct reaction of triphenylbismuth with triamminechromium tricarbonyl in dioxane at 120°C leads to a mixture of chromium tricarbonyl π complexes of triphenylbismuth. Extraction and recrystallization permit



separation of $(\pi$ -phenylchromium tricarbonyl)diphenylbismuth (I), $bis(\pi$ -phenylchromium tricarbonyl)phenylbismuth (II), and tris(π -phenylchromium tricarbonyl)bismuth (III) in pure form. The yield of each of these products depended significantly on the ratio of the starting reactants. Thus, an excess of triphenylbismuth leads only to the formation of (I), while an excess of triamminechromium tricarbonyl leads predominantly to (II) and (III).

The reaction of triphenylantimony with triamminechromium tricarbonyl under the same conditions leads to the formation of a mixture of three σ complexes which are readily separated using thin-layer chromatography: In addition to the known triphenylantimony chromium pentacarbonyl (IV) [2-5], we separated and identified bis(triphenylantimony)chromium tetracarbonyl (V) and tris(triphenylantimony)chromium tricarbonyl (VI)

$$Ph_{3}Sb + (NH_{3})_{3}Cr(CO)_{3} \rightarrow Ph_{3}SbCr(CO)_{5} + (Ph_{3}Sb)_{2}Cr(CO)_{4} + (Ph_{3}Sb)_{3}Cr(CO)_{3} + NH_{3}Cr(CO)_{3} + NH_{3}Cr(CO)_{4} + (Ph_{3}Sb)_{3}Cr(CO)_{4} + (Ph_{3}Sb)_{3}Cr(CO)_{3} + NH_{3}Cr(CO)_{4} + (Ph_{3}Sb)_{3}Cr(CO)_{4} + (Ph_{3}Sb)_{3}Cr(CO)_{4} + (Ph_{3}Sb)_{3}Cr(CO)_{3} + NH_{3}Cr(CO)_{4} + (Ph_{3}Sb)_{3}Cr(CO)_{4} + (Ph_{3}Sb)_{3}Cr(CO)_{4} + (Ph_{3}Sb)_{3}Cr(CO)_{4} + (Ph_{3}Sb)_{3}Cr(CO)_{3} + NH_{3}Cr(CO)_{4} + (Ph_{3}Sb)_{3}Cr(CO)_{4} + (Ph_{3}Sb)_{4} + (Ph_{3$$

The absence of ammonia as a ligand in the organoantimony derivatives of chromium indicates that the primary product of this reaction is (VI), which subsequently disproportionates readily by a known mechanism [11], yielding a complex mixture of σ complexes. The products (IV), (V), and (VI) isolated from this mixture were identified using IR and NMR spectroscopy and elemental analysis. Product (VI) was obtained in 77% yield also in the exchange reaction between toluenechromium tricarbonyl and triphenylantimony.

Thus, in contrast to triphenylbismuth, the direct reaction between triphenylantimony and triamminechromium tricarbonyl does not lead to the formation of π complexes of chromium

Institute of Chemistry, Academy of Sciences of the USSR, Gorki. Chemistry Research Institute, N. I. Lobachevskii Gorki State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1874-1879, August, 1981. Original article submitted December 23, 1980.

	Yield, %		Found, %			Calculated, %		
Compound		mp, c	С	н	Cr	G	H	Cr
$\begin{array}{l} Ph_{2}BiPhCr\left(CO\right)_{3}\left(I\right)\\ PhBi[PhCr\left(CO\right)_{3}]_{2}\left(II\right)\\ Bi[PhCr\left(CO\right)_{3}]_{3}\left(III\right)\\ Ph_{3}Sbcr\left(CO\right)_{3}\left(IV\right)\\ [Ph_{3}Sb]_{2}Cr\left(CO\right)_{4}\left(V\right)\\ [Ph_{3}Sb]_{3}Cr\left(CO\right)_{3}\left(VI\right)\\ Ph_{3}SbPhCr\left(CO\right)_{3}\left(VII\right)\\ PhSb[PhCr\left(CO\right)_{3}\left(VII\right)\\ PhSb[PhCr\left(CO\right)_{3}]_{2}\left(VIII\right)\\ \end{array}$	13 43 31 65 23 5 19 33	110 196 240 * 149 174 207 131 173	43,61 37,98 38,45 50,78 55,03 57,18 51,94 46,25	2,45 2,22 1,96 2,56 2,95 3,57 2,97 2,31	8,83 15,17 18,46 9,63 6,08 4,59 10,73 16,85	43,85 38,03 38,20 50,64 55,17 57,23 51,53 46,08	2,73 2,49 2,04 2,76 3,04 3,76 3.06 2,40	8,37 14,96 18,15 9,54 5,97 4,43 10,63 16,64

TABLE 1. Physical Data for the Products of the Reaction of Triamminechromium Tricarbonyl with Triphenylbismuth and Triphenylantimony

*dec.

TABLE 2. IR and PMR Spectra of σ and π Complexes of Triphenylantimony and Triphenylbismuth

Com-		IR spectru	PMR spectrum, δ, ppm			
pound	ρCrCO	oCH (free)	ρCH (coord.)	vCO	(free)	ہ (coord.)
	1		1			
(I)	545	705	812	1875	7.90 - 7.42	5.75-5.40
(1)	665	740	880	1980	.,	
(III)	540	705	810	1880	7,78 - 7,34	5,94-5,48
1(11)	665	740	890	1980	• •	
(III)	535	—	820	1910		6,00-5,62
()	660	· ·	880	1995		
(IV)	575	695		1943	7,51	-
	650	735		1988		
	677			2065		
(V)	563	695	-	1810	7,31	-
	643	735		1900		
	675			1995		
(VI)	560	695		1820		-1
	633	730		1910		
	677					F 00 F 0 F
(VII)	535	700	820	1885	7,82-7,39	5,99-5,31
	655	740	890	1990		0.0 7 - 0 0
(VIII)	535	700	815	1890	7,94-7,44	6,07-5,38
	660	740	885	1980		
(IX)	538		820	1880		5,945,45
	655		1 885	1980		

but yields only σ derivatives of antimony $(Ph_3Sb)_nCr(CO)_{6}-n$ (n = 1-3). The reason for this discrepancy lies in the greater donor properties of the aromatic derivatives of antimony relative to triphenylbismuth, permitting more facile exchange involving the free-electron pairs. Apparently, the replacement may be avoided and the reaction entirely directed towards the formation of π complexes if a free-electron pair of the antimony atom is bound by complexation with suitable acceptors.

The reaction of triphenylantimony with triamminechromium tricarbonyl in the presence of boric acid in 1:3:1 molar ratio leads to the formation of a mixture of (π -phenylchromium tricarbonyl)diphenylantimony (VII), bis(π -phenylchromium tricarbonyl)phenylantimony (VIII), and tris(π -phenylchromium tricarbonyl)antimony (IX), each of which was isolated. Thus of BF₃ etherate instead of H₃BO₃ leads to some decrease in the yields of (VII), (VIII), and (IX). For triphenylphosphine, the reaction in all cases proceeds to the formation only of σ complexes. The yields, melting points, and elemental analytical data for (I)-(IX) are given in Table 1.

 $\begin{array}{c} Ph_{3}Sb + (NH_{3})_{3}Cr(CO)_{3} \xrightarrow{H_{3}BO_{3}} & & \\ C_{r} & & \\ (CO)_{3} & (CO)_{3} & \\ (VII) & (VIII) & \\ \end{array} \\ \begin{array}{c} SbPh \\ + & \\ C_{r} \\ (CO)_{3} \\ (VII) & \\ (IX) \end{array} \\ \end{array}$



Fig. 1. DTA diagrams of chromium carbonyl complexes of antimony and bismuth: 1) tris(π phenylchromium tricarbonyl)bismuth (III); 2) tris(triphenylantimony)chromium tricarbonyl (VI); 3) tris(π -phenylchromium tricarbonyl)antimony (IX); a) DTA curves; b) gas liberation curves.

All the σ and π derivatives of antimony and bismuth are yellow crystalline compounds which are relatively stable in the air at ~ 20 °C. Upon prolonged storage in the air, the π complexes slowly oxidize, while they decompose rather rapidly in solution. Furthermore, the bismuth compounds are extremely sensitive to light. The solubility of these compounds in organic solvents markedly drops in going from mono- to tricoordinated products. The tricoordinated products have low solubility even in such polar solvents as acetone and dimethoxyethane. The mono- and dicoordinated compounds dissolve also in benzene and other aromatic hydrocarbons. Compounds (I) and (VII) are soluble in cyclohexane.

The IR and PMR spectral data in Table 2 are in accord with the proposed structure for the compounds obtained. Compounds (I)-(IX) all have carbonyl group absorption. The vCO band is gradually shifted towards lower frequencies for antimony σ complexes in going from (IV) to (VI). This shift was observed previously [12, 13] in carbonyl complexes of molybdenum with the progressive replacement of CO groups by σ -donor ligands. The IR spectra of (IV), (V), and (VI) also have two relatively strong bands at 695 and 735 cm⁻¹ assigned to deformation vibrations (ρ CH) of the free arene ring.

The IR spectra of the π -complexes of antimony and bismuth have two strong bands between 1875 and 1995 cm⁻¹ in the carbonyl group region and strong CO deformation bands between 530 and 670 cm⁻¹. The shift in the ν_{CO} band relative to benzenechromium tricarbonyl towards shorter wavelengths indicates the electron-donor nature of the antimony and bismuth atoms in these compounds. In addition, the IR spectra of (I), (II), (VII), and (VIII) have two medium-intensity bands at 700 and 740 cm⁻¹ assigned to the out-of-plane vibrations of the C-H group of the free arene, while there are no bands in the spectra of (III) and (IX) which may be assigned to vibrations of the uncoordinated ring. In accord with the expected structure, the PMR spectra of the σ derivatives of triphenylantimony have signals only in the region characteristic for protons of a free arene ring (δ 7.51-7.31 ppm), while the PMR spectra of the π -arene complexes (III) and (IX) show only protons of coordinated rings (δ 6.00-5.45 ppm). The spectra of (I), (II), (VII), and (VIII) have both these groups of signals, thus indicating the presence of both free and π -bonded aromatic rings. The relative integral intensity of these signals exactly correspond to the number of protons of free and coordinated phenyl groups of the proposed chemical formulas. Thus, the IR and PMR spectral data and the elemental analytical data unequivocally indicate that (IV), (V), and (VI) are σ -donor complexes of antimony $[Ph_3Sb]_nCr(CO)_{\delta-n}$ (n = 1-3) while (I)-(III) and (VII)-(IX) are the corresponding π complexes of antimony and bismuth $[Ph]_{9-n}E[PhCr(CO)_3]_n$ (E = Sb and Bi, n = 1-3).

The thermal behavior of these compounds was studied using differential thermal analysis (DTA) for (III), (VI), and (IX). Figure 1 shows that the maxima for the thermal decomposition of (III), (VI), and (IX) occur at $\sim 250^{\circ}$ C. In addition, a melting peak is found for (VI) at 207°C. The endothermal signals for (VI) and (IX) in the range from 260 to 320°C correspond to sublimination of triphenylantimony, the major decomposition product. Hence the decomposition of the σ complex of antimony occurs at the Cr-Sb bond

$$(VI) \rightarrow Ph_{3}Sb + Cr + Cr (CO)_{6} + CO$$

while the π complex of antimony reacts with breakage of the bond of chromium to the aromatic ring. On the other hand, decomposition at the C-Bi bond is found for (III) in addition to breakage of the arene-chromium bond with the formation of intermediate phenylchromium tricarbonyl radicals

 $(III) \longrightarrow Ph_{3}Bi + [Cr + Cr(CO)_{6} + CO]$ $(III) \longrightarrow Bi + [PhCr(CO)_{3}] \longrightarrow PhHCr(CO)_{3}$ $(FhCr(CO)_{3}]_{2} \rightarrow Ph_{2}Cr(CO)_{3} \rightarrow Ph_{2} + Cr + Cr(CO)_{6} + CO$

All the products indicated in this scheme were identified using thin-layer and gas chromatography.

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrophotometer in Vaseline oil. The PMR spectra of saturated acetone solutions of the compounds studied were taken on a Tesla BS-487C spectrometer at 80 MHz with the solvent as standard. The TLC qualitative analysis was performed on Silufol plates with 7:3 hexane-dioxane as the mobile phase and development in iodine vapor.

All operations were carried out in vacuum or in an inert-gas atmosphere and solvents purified to eliminate oxygen and moisture.

Reaction of Triphenylbismuth with Triamminechromium Tricarbonyl. A mixture of 4.4 g (0.01 mole) triphenylbismuth, 5.7 g (0.03 mole) triamminechromium tricarbonyl, and 40 ml dioxane was heated with stirring for 7 h. After separation of the calculated amount of NH₃, the cooled mixture was filtered, the clear yellow solution was evaporated in vacuum, and the residue was treated with hot hexane. The solution was decanted and the residue was dried in vacuum. Extraction with hot cyclohexane yielded 0.73 g yellow crystals soluble in benzene and acetone. After recrystallization from ethanol, (I) was obtained. Extraction with hot benzene of a portion of the product after the separation of (I) yielded 3.05 g of a yellow compound which was recrystallized from benzene to give (II). Recrystallization of 2.62 g of the residue from dioxane gave (III).

Reaction of Triphenylantimony with Triamminechromium Tricarbonyl. The reaction of 5.61 g (0.03 mole) triamminechromium tricarbonyl with 3.60 g (0.01 mole) triphenylantimony in 30 ml dioxane was carried out under conditions analogous to those described above. After elimination of the calculated amount of NH₃, the cooled reaction mixture was filtered, the solvent was partially distilled off in vacuum, and the product was crystallized by the addition of hexane. Hot hexane extraction of the residue dried in vacuum yielded 3.9 g (IV). Recrystallization of 1.1 g of the yellow crystalline material remaining after the hexane extraction from benzene yielded (V).

Reaction of Triphenylantimony with Triamminechromium Tricarbonyl in the Presence of Boric Acid. A mixture of 1.76 g (5 mmoles) triphenylantimony, 2.8 g (15 mmoles) triamminechromium tricarbonyl, 0.3 g (5 mmoles) H_3BO_3 , and 30 ml dioxane was stirred for 7 h at 120°C. The cooled mixture was filtered through a layer of Al₂O₃. The solution was evaporated in vacuum and a yellow crystalline product was precipitated after dissolving the residue in a small amount of ether and subsequent addition of hexane. The precipitate was washed with hexane and dried in vacuum to yield 1.5 g (IX). The ethereal solution remaining after the removal of (IX) was evaporated to dryness; 0.45 g (VII) was extracted with hot hexane. The yellow crystalline residue (1.02 g) was composed of (VIII).

The yields, melting points, elemental analytical data, and IR and PMR spectra data are given in Tables 1 and 2.

Reaction of Triphenylphosphine with Triamminechromium Tricarbonyl. A mixture of 0.78 g (0.03 mole) triphenylphosphine, 1.87 g (0.01 mole) triamminechromium tricarbonyl, and 30 ml dioxane was stirred for 2 h at 120°C. At the termination of gas liberation, the cooled mixture was filtered through a layer of Al_2O_3 . The solvent was evaporated in vacuum and the residue was extracted with hexane. Recrystallization from hexane yielded pale yellow crystalline triphenylphosphine chromium pentacarbonyl in 80% yield with mp 129°C. Found: C 60.94; H 3.19; Cr 11.67%. Calculated for $C_{23}H_{15}CrO_5P$: C 60.79; H 3.30; Cr 11.45%.

The residue after hexane extraction was bis(triphenylphosphine)chromium tetracarbonyl (20% yield, mp 250°C). Found: C 70.90; H 4.15; Cr 7.85%. Calculated for C₄₀H₃₀CrO₄P₂: C 69.76; H 4.36; Cr 7.56%.

Thermal Decomposition of Tris(triphenylantimony)chromium Tricarbonyl (VI). A sample of 0.12 g (0.1 mole) (VI) was heated for 5 h in a 50-ml ampul at 230°C. The ampul contents were washed with benzene, and 0.1 g colorless crystals were isolated. Thin-layer chromatography showed that this product was virtually pure triphenylantimony in 94% yield.

Thermal Decomposition of Tris(π -phenylchromium tricarbonyl)antimony (IX). A sample of 0.253 g (2 mmoles) (IX) was heated for 5 h in an ampul at 240°C to yield 0.11 g (91%) triphenylantimony.

<u>Thermal Decomposition of Tris(π -phenylchromium tricarbonyl)bismuth (III).</u> A sample of 0.212 g (0.25 mmole) (III) was heated for 10 h in vacuum at 235°C with constant evacuation. The volatile products were sublimated onto a "finger" cooled with dry ice. Qualitative analysis of the sublimate by gas and thin-layer chromatography showed the presence of triphenyl-bismuth, benzenechromium tricarbonyl, diphenylchromium tricarbonyl, and diphenylbis(chromium tricarbonyl).

Reaction of Triphenylantimony with Toluenechromium Tricarbonyl. An ampul with 0.353 g (1 mmole) Ph_3Sb and 2.23 g (10 mmoles) toluenechromium tricarbonyl was heated for 3 h on an oil bath at 150°C. The yellow crystalline product was washed with benzene and hexane to remove the starting compounds and then dried in vacuum to yield 0.29 g (77%) (VI) with mp 207°C.

CONCLUSIONS

1. The reaction of phenyl derivatives of antimony and bismuth with $(NH_3)_3Cr(CO)_3$ was studied. In the case of triphenylbismuth, the reaction proceeds to give a mixture of complexes, while triphenylantimony yields only σ -donor complexes.

2. The introduction of a complexing agent binding the free-electron pair of the antimony atom directs the reaction towards the formation of a mixture of chromium tricarbonyl π complexes of triphenylantimony.

LITERATURE CITED

1.	Β.	Nicholls	and	Μ.	С.	Whiting,	J.	Chem.	Soc.,	551	(1959).	
----	----	----------	-----	----	----	----------	----	-------	-------	-----	---------	--

- 2. T. A. Magee, C. N. Matthews, T. S. Wang, and J. H. Wotiz, J. Am. Chem. Soc., <u>83</u>, 3200 (1961).
- 3. J. Chatt, C. J. Leigh, and N. Thankajan, J. Organomet. Chem., 29, 105 (1971).
- 4. C. N. Matthews, T. A. Magee, and J. H. Wotiz, J. Am. Chem. Soc., <u>81</u>, 2273 (1959).
- 5. J. T. Debbeke and G. P. Van den Kelen, J. Organomet. Chem., <u>64</u>, 239 (1974).
- 6. E. W. Abel, M. A. Bennet, and G. Wilkinson, J. Chem. Soc., 2323 (1959).
- 7. M. D. Rausch and R. G. Gloth, J. Organomet. Chem., 153, 59 (1978).
- 8. J. A. Bowden and R. Colton, Austral. J. Chem., 24, 2471 (1971).
- 9. M. D. Rausch, G. A. Moser, E. J. Zaiko, and A. J. Lipman, J. Organomet. Chem., <u>23</u>, 185 (1970).

- 10. G. A. Razuvaev, A. N. Artemov, A. A. Alad'in (Aladjin), and N. I. Sirotkin, J. Organomet. Chem., 111, 131 (1976).
- 11. J. A. Bowden, R. Colton, and C. J. Commons, Austral. J. Chem., 26, 655 (1973).
- 12. C. Barbeau and J. Turcotte, Can. J. Chem., 48, 3583 (1970).
- V. T. Aleksanyan and B. V. Lokshin, Vibrational Spectra of Complexes of Transition Metals. Molecular Structure and the Chemical Bond [in Russian], Vol. 5, VINITI, Moscow (1976).

THIO DERIVATIVES OF MACROPOROUS SILICAS. 3. SYNTHESIS OF MACROPOROUS SILICA CHEMISORBENTS WITH GRAFTED POLYMER COATINGS

V. I. Lozinskii and S. V. Rogozhin

UDC 542.91:541.183:666.192:541.64

We have previously reported the preparation of 2-pyridyl disulfide and o-nitrophenyl disulfide derivatives of macroporous silicas (silochromes) [1, 2], which are used in the chemispecific chromatography [3] of thiol-containing biopolymers. Unfortunately, at basic pH values, the stability of the silica matrix to the hydrolytic action of the aqueous medium is low. In addition, marked nonspecific adsorption on silochromes of substances such as peptides and proteins is observed [4]. Improvements in matrix stability in aqueous media are achieved by modification of the surface using zirconium or aluminum salts [4, 5] and a reduction in the amount of nonspecific adsorption with a concurrent increase in the support's capacity for functional groups is achieved by the addition of a suitable polymer coating to the inorganic surface [6-8].

In the present work, such improved matrices composed of macroporous silica with a surface modified using Al_2O_3 [9] and with grafted polymer coatings were employed for the preparation of chemisorbents with o-nitrophenyl disulfide (S-NPS) groups. The use of a similar type of composite material for the preparation of supports for biospecific chromatography was described recently [10].

Silochrome with 1130 Å pore diameter containing $\sqrt{5\%}$ Al₂O₃ was the starting inorganic adsorbent. Then, a polyacrylic acid or polymethyl acrylate polymer coating was grafted onto the inorganic surface by our previous method [7]. After thorough washing to remove soluble homopolymers by extraction for several hours using boiling solvent in a Soxhlet extractor and subsequent drying, we obtained products (I) and (VI). The support with the grafted polyacrylic acid surface (I) contained 6.2% C (1.7 mmole CO₂H groups/g), while the support with polymethyl acrylate coating (VI) contained 8.7% C (1.8 mmole CO₂CH₃ groups/g).

Further modification of the functional groups of the grafted polymers was achieved using the previously proposed S-NPS derivatives of 2-mercaptoethylamine (V) or thioglycolic acid (X) [11]. To add these compounds to the supports, we used activated N-hydroxysuccinimide ethers [12]. An S-NPS support (III) was obtained in two steps from (I) with \sim 140 µmoles S-NPS groups/g, i.e., the modification affected about 8% of the CO₂H groups present under the experimental conditions.



A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1879-1884, August, 1981. Original article submitted December 17, 1980.