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Publisher *Taylor & Francis*

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Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

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To cite this Article Goel, Ram G. and Montemayor, Reynaldo G. (1978) 'PREPARATION AND CHARACTERIZATION OF TRANS-DICHLOROBIS[TRIS(t-BUTYL)STIBINE]- μ -DICHLOROPLATINUM(II) AND -PALLADIUM(II)', *Journal of Coordination Chemistry*, 8: 1, 1 – 3

To link to this Article: DOI: 10.1080/00958977808073063

URL: <http://dx.doi.org/10.1080/00958977808073063>

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PREPARATION AND CHARACTERIZATION OF TRANS-DICHLOROBIS[TRIS(t-BUTYL)STIBINE]- μ -DICHLOROPLATINUM(II) AND -PALLADIUM(II)

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(Received June 13, 1977)

Reaction of tris(t-butyl)stibine with platinum(II) chloride or with sodium tetrachloropalladate(II), in 2:1 mole ratio, yields dinuclear chlorobridged complexes $M_2Cl_4(SbBu_3^t)_2$. These complexes are also formed when tris(t-butyl)stibine is treated with $PtCl_2(C_6H_5CN)_2$ or $PdCl_2(C_6H_5CN)_2$, or with $PdCl_2$ (cycloocta-1,5-diene). The products have been characterized by elemental analysis, molecular weight and conductance measurements and by infrared and proton nmr spectral studies. Infrared spectra of the complexes are in accord with a dinuclear trans-chloro-bridged structure.

In contrast to several studies on complexes of bulky phosphines,¹⁻⁸ little is known about complexes of bulky arsines and stibines. Shaw and co-workers⁹ prepared platinum(II) complexes of t-butylbis(o-tolyl)arsine and o-tolylbis(t-butyl)arsine. Very recently, Schumann and Breunig¹⁰ studied the reactions of tris(t-butyl)stibine with hexacarbonyls of chromium, molybdenum and tungsten and prepared the penta-carbonyltris(t-butyl)stibinechromium(O), -molybdenum(O), and tungsten(O) complexes. Herein, we report on the reactions of tris(t-butyl)stibine with platinum(II) and palladium(II).

Reaction of tris(t-butyl)stibine with platinum(II) chloride or with dichlorodibenzonitrileplatinum(II), in 2:1 mole ratio, afforded the diplatinum trans-chloro-bridged complex, $Pt_2Cl_4(SbBu_3^t)_2$, instead of the expected $PtCl_2(SbBu_3^t)_2$. Similar reactions with sodium tetrachloropalladate(II), with dichlorodibenzonitrilepalladium(II), or with dichlorocycloocta-1,5-dienepalladium(II) gave the dipalladium complex, $Pd_2Cl_4(SbBu_3^t)_2$. The identities of the complexes were established by elemental analyses, conductance and molecular weight measurements and by infrared and proton nmr spectral measurements. The analytical as well as the molecular weight data for both the compounds are in good agreement with the proposed formulation. The molar conductances of 10^{-3} M solutions of the diplatinum and the dipalladium complexes, in nitromethane, were found to be 2 and

5 ohm⁻¹ cm² mole⁻¹, respectively, indicating that both compounds are non-electrolytes. Infrared spectra for both the platinum and the palladium complexes in the region 4000 to 350 cm⁻¹ showed bands which are very similar to those reported¹⁰ for $SbBu_3^t$. In the 350 to 250 cm⁻¹ region, the spectrum of the platinum complex showed bands at 340(s), 315(m), 290(m) and 270(m) cm⁻¹. Similar bands were observed for the palladium complex at 345(s), 320(s), 295(m) and 270(m) cm⁻¹. The 270 cm⁻¹ band is due to $SbBu_3^t$ but the bands at ca. 340, 315 and 290 cm⁻¹ are very similar to those reported for the $Pt_2Cl_4L_2$ and $Pd_2Cl_4L_2$ complexes, where L = a tertiary phosphine or arsine. Following the assignments¹¹ for the $Pt_2Cl_4(PR_3)_2$ and $Pd_2Cl_4(PR_3)_2$ complexes, the bands at 340 and 345 cm⁻¹ can be assigned to the terminal Pt-Cl and Pd-Cl stretching frequencies, respectively. Similarly, the bands in the 315-320 cm⁻¹ and 290-295 cm⁻¹ regions can be assigned to the bridging Pt-Cl or Pd-Cl stretching frequencies. Thus the infrared data indicate that the complexes $Pt_2Cl_4(SbBu_3^t)_2$ and $Pd_2Cl_4(SbBu_3^t)_2$ are structurally similar to the complexes $Pt_2Cl_4(AsMe_3)_2$ and $Pd_2Br_4(AsMe_3)_2$ for which a trans-halogen-bridged structure has been established by crystallographic studies.^{12,13}

The proton nmr spectra for both complexes showed a single peak which is downfield from the peak due to the free stibine [δ $SbBu_3^t$ = 1.22 ppm,

$\delta \text{Pt}_2\text{Cl}_4(\text{SbBu}_3)_2 = 1.50 \text{ ppm}$ and $\delta \text{Pd}_2\text{Cl}_4(\text{SbBu}_3)_2 = 1.52 \text{ ppm}$].

Both the platinum and the palladium complex decompose gradually at room temperature. Decomposition of these complexes is much faster in solution. Comparatively, the platinum complex appears to be more stable than the palladium complex. Flasks containing solutions of the palladium complex, in benzene or in dichloromethane, were coated with a shiny black deposit after 24 hours. Similar decomposition was observed for the platinum complex after several days.

Formation of the dinuclear chlorobridged complexes instead of the $\text{MCl}_2(\text{SbBu}_3)_2$ complexes, in the present work, is in marked contrast with the behaviour of tri(n-alkyl)stibines which are known to form stable platinum(II) or palladium(II) complexes of the type $\text{MX}_2(\text{SbR}_3)_2$.¹⁴⁻¹⁷ To date only a few dinuclear complexes of stibines have been prepared. Chatt and Venanzi¹⁸ prepared an unstable dipalladium complex, $\text{Pd}_2\text{Cl}_4(\text{SbEt}_3)_2$ by treating Na_2PdCl_4 with SbEt_3 , in 1:1 mole ratio, at -70° . These workers also prepared relatively more stable diplatinum complexes, $\text{Pt}_2\text{Cl}_4(\text{SbR}_3)_2$,¹⁹ where $\text{R} = \text{Me}, \text{Et}$ or Pr^n , by the reaction of the stibine and a dinuclear olefin complex, $(\text{olefin})_2\text{Pt}_2\text{Cl}_4$, at -75° . Recently Cherwinski and Clark,²⁰ prepared cationic diplatinum complexes $[\text{Pt}_2\text{Cl}_2(\text{SbR}_3)_4](\text{BF}_4)_2$, where $\text{R} = \text{Et}$ or Ph , by treating the complexes $\text{PtCl}_2(\text{SbR}_3)_2$ with AgBR_4 . In the present work, the formation of the dinuclear trans-chlorobridged complexes rather than the mononuclear *cis*- or *trans*-complexes is most likely due to the steric effects caused by bulky t-butyl groups.

EXPERIMENTAL SECTION

General Procedures

Tris(t-butyl)stibine and its complexes were handled either in a dry box under an atmosphere of oxygen-free dry nitrogen or in a conventional vacuum system. Tris(t-butyl)stibine was prepared by the method of Schumann and Breunig.¹⁰ Platinum and palladium salts were obtained from Johnson Matthey and Mallory Ltd. Cycloocta-1,5-diene and benzonitrile complexes of platinum(II) or palladium(II) were prepared by literature methods.^{21,22} Solvents were purified and dried following standard procedures. Elemental analyses were performed by H. S. McKinnon of this Department. Molecular weights were determined in benzene with a Hitachi-Perkin Elmer 115 osmometer. Conductance measurements

were made in nitromethane (10^{-3} M solutions). Infrared spectra were recorded on a Beckman IR-12 spectrophotometer. Samples were prepared either as mulls in Nujol or halocarbon oil or as KBr or CsI discs. The infrared spectrum of tris(t-butyl)stibine was measured on a thin film pressed between KBr and CsI plates. Nmr spectra were recorded at ambient temperatures on a Varian A-60 spectrometer. The reported chemical shifts are for solutions, in benzene, containing 1% TMS. Melting points were measured in glass capillary tubes with a Gallenkamp melting point apparatus and are uncorrected.

Reaction of Tris(t-butyl)stibine with PtCl_2

Tris(t-butyl)stibine (2 mmol) was dissolved in 25 ml benzene and PtCl_2 (1 mmol) was added to the solution. The mixture was stirred for three days, at room temperature, to give a greenish-yellow solution containing some suspended solid. The solid was filtered off and the filtrate was evaporated under vacuum, at room temperature, to give a greenish-yellow solid which when extracted with hexane or petroleum ether yielded a yellow solution. Upon concentrating the yellow solution under vacuum, at room temperature, a crystalline yellow solid was obtained which was characterized to be dichlorobis[tris(t-butyl)stibine]- μ -dichlorodiplatinum(II), $\text{Pt}_2\text{Cl}_4(\text{SbBu}_3)_2$, mp., 133°C (decomposed). Yield: 70%. Anal. calcd. for $\text{Pt}_2\text{Cl}_4(\text{SbBu}_3)_2$: C, 25.76; H, 4.83. Found: C, 25.40; H, 4.70. Molecular weight: Calcd., 1118, found: 1093.

Reaction of Tris(t-butyl)stibine with Dichlorodibenzonitrileplatinum(II)

A greenish-yellow solution was formed when SbBu_3^t (2 mmol) and $\text{PtCl}_2(\text{C}_6\text{H}_5\text{CN})_2$ (1 mmol) were mixed in 25 ml benzene and the mixture was stirred for three hours, at room temperature. After filtration and evaporation of the filtrate, *in vacuo*, at room temperature, a yellow solid was isolated which was extracted with hexane. Yellow needles of $\text{Pt}_2\text{Cl}_4(\text{SbBu}_3^t)_2$ were obtained upon concentrating the hexane solution under vacuum, at room temperature. Yield: 80%.

Reaction of Tris(t-butyl)stibine with Sodium Tetrachloropalladate(II)

SbBu_3^t (2 mmol) and Na_2PdCl_4 (1 mmol) were mixed in methanol and the mixture was stirred for two hours, at room temperature. Filtration gave a dark

brown solution which yielded a tan-coloured solid upon removal of the solvent under vacuum, at room temperature. The solid was extracted with hexane or petroleum ether giving an orange solution. Upon concentrating the orange solution under vacuum, at room temperature, yellow crystals separated which were filtered off and were characterized as dichlorobis[tris(*t*-butyl)stibine]- μ -dichlorodipalladium(II), Pd₂Cl₄(SbBu₃^t)₂, mp., 110°C (decomposed). Yield: 60%. Anal. calcd. for Pd₂Cl₄(SbBu₃^t)₂: C, 30.64; H, 5.74, found: C, 30.20; H, 5.70. Molecular weight: Calcd., 940, found: 870.

Reaction of Tris(t-butyl)stibine with Dichlorobenzonitripalladium(II)

A greenish-black solution was formed when PdCl₂(C₆H₅CN)₂ (1 mmol) and SbBu₃^t (2 mmol) were allowed to react in benzene for 2 hours, at room temperature. A yellow-orange solid was obtained after filtration and removal of the solvent *in vacuo*, at room temperature. Recrystallization of the solid from hexane gave yellow crystals of Pd₂Cl₄(SbBu₃^t)₂. Yield: 74%.

Reaction of Tris(t-butyl)stibine with Dichlorocycloocta-1,5-dienepalladium(II)

PdCl₂(COD), (1 mmol) and SbBu₃^t (2 mmol) were stirred in 25 ml benzene. After two hours the solution was filtered and the filtrate was evaporated under vacuum, at room temperature, to give an orange solid from which Pd₂Cl₄(SbBu₃^t)₂ was obtained by crystallization from hexane. Yield: 70%.

ACKNOWLEDGEMENTS

This work was supported by the National Research Council of Canada.

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