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Preparation and characterization of tris(iso-propyl)stibine complexes of palladium and platinum

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Tris(iso-propyl)stibine complexes of palladium and platinum of the type $[MX_2(Sb^iPr_3)_2]$ [M, X = Pd, Cl (1a), Pd, Br (1b), Pd, I (1c), Pt, Cl (2)] have been prepared and characterized by elemental analysis, IR and ^1H NMR spectral data. The structure of 1a, established by X-ray structural analysis, revealed that the palladium atom is in a square planar environment with mutually *trans* Sb^iPr_3 ligands. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: palladium; platinum; antimony complexes

The increasing role of organopnictogens in deposition of III–V semiconductor materials[1,2] and their versatility as ligands[3] have been the motivation for current interest in the chemistry of Group 15 elements. In contrast to the available wealth of data on metal complexes with lighter pnictogens (*e.g.*, tertiary phosphines and arsines),[4] investigations dealing with heavier pnictogens (*e.g.* stibines) are scarce[5] with only few X-ray structural details. Complexes with such ligands often show markedly different behaviour. Examples include the following: (i) while $[M_2Cl_2(\mu\text{-}Cl)_2(ER_3)_2]$ (M = Pd or Pt; ER_3 = tertiary phosphine or arsine) are stable indefinitely in the solid state and solution[6] the corresponding stibine derivatives decompose readily;[7,8] (ii) bulky phosphines and arsines (*e.g.* E^tBu_3, E = P or As)[9–11] are readily ortho-metallated, but similar reactions with analogous stibines[8] (Sb^tBu_3) are not observed; (iii) unlike phosphines, stibines show little preference for a particular geometry in metal complexes.[12] Recently, Werner and coworkers[13–20] have investigated ruthenium, rhodium and iridium complexes with tri-isopropylstibine and have found that their reactivity is significantly different from the corresponding trialkylphosphine analogues. In view of the above, it was considered worthwhile to prepare and structurally characterize palladium/platinum complexes with a stibine with moderate steric demands, *i.e.* Sb^iPr_3.

RESULTS AND DISCUSSION

Reaction of $[MCl_2(RCN)_2]$ with tris(iso-propyl)stibine in 1:2 molar ratio readily gave $[MCl_2(Sb^iPr_3)_2]$ [M = Pd (**1a**), Pt (**2**)] as a yellow crystalline solid. Treatment of **1a** with excess of KBr or NaI offered substition products $[PdX_2(Sb^iPr_3)_2]$ [X = Br (**1b**), I (**1c**)].

The IR spectrum of **1a** exhibited a strong band at 349 cm^{-1} attributable to $\nu(Pd-Cl)$. This indicates that **1a** has a *trans* configuration[6] and is further confirmed by X-ray structural analysis (see later). However, the corresponding platinum complex **2** displayed two such absorptions at 337 and 308 cm^{-1} indicative of the *cis* configuration.[6,21] The ^1H NMR spectra (Table 1) of Sb^iPr_3 and its complexes displayed a doublet and a septet attributable to methyl and methine protons respectively. In the complexes the methyl and methine proton resonances are deshielded compared with the corresponding signals due to free stibine. Substitution of chloride in **1a** by Br or I (**1b** or **1c**) results in further deshielding of the methine proton resonance. The presence of only one set of SbCH and $SbCHCH_3$ resonances for **1** and **2** suggests that the Sb^iPr_3 complexes exist exclusively in one isomeric form.

The molecular structure of $[PdCl_2(Sb^iPr_3)_2]$ is illusrated in Fig. 1 and the selected bond lengths and angles are given in Table 2. The structure shows that the palladium atom is in a square planar environment. The two Sb^iPr_3 ligands are *trans* disposed. The two Pd–Cl [2.2886(17) Å][22,23] and Pd–Sb [2.5721(7) Å][24–26] distances are the same and are in good agreement with literature values. The Sb–C bond lengths (average 2.167 Å) are in accord with reported values.[12,27,28]

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Table 1. Physical, analytical and NMR data for tri-isopropylstibine complexes of palladium and platinum

Complex	Recrystallization solvent (% yield)	Dec. temp. (°C)	Analysis found (calc.)		^{1}H NMR data (δ, ppm)	ν(M$-$Cl) (cm^{-1})
			C	H		
Sb^iPr_3	–	–	–	–	1.30 (d, 7.3 Hz; $-$CH*Me*$_2$) 1.84 (sep, 7.3 Hz; $-$C*H*)	–
$[PdCl_2(Sb^iPr_3)_2]$	Toluene–hexane	130–132	31.8 (31.8)	6.7 (6.2)	1.54 (d, 7.3 Hz; $-$CH*Me*$_2$) 2.53 (sep, 7.3 Hz; $-$C*H*)	349
$[PtCl_2(Sb^iPr_3)_2]$	Acetone–hexane (71)	143	27.6 (28.1)	5.8 (5.5)	1.54 (d, 7.42 Hz; $-$CH*Me*$_2$) 2.62 (sep, 7.42 Hz; $-$C*H*)	337, 308
$[PdBr_2(Sb^iPr_3)_2]$	Acetone–hexane (70)	148	27.3 (28.1)	5.6 (5.5)	1.54 (d, 7.1 Hz; $-$CH*Me*$_2$) 2.60 (sep, 7.1 Hz; $-$C*H*)	–
$[PdI_2(Sb^iPr_3)_2]$	Acetone–hexane (89)	90–95	24.9 (25.0)	4.8 (4.9)	1.52 (d, 7.4 Hz; $-$CH*Me*$_2$) 2.74 (sep, 7.4 Hz; $-$C*H*)	–

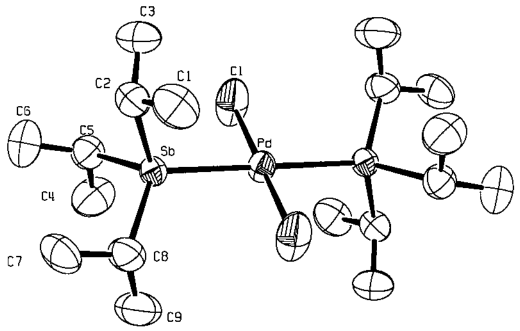

Figure 1. ORTEP diagram for *trans*-[$PdCl_2(Sb^iPr_3)_2$].

The coordination around stibine is typically pyramidal with C—Sb—C angles lying in the range 100.8(2)–110.2(3) °.

EXPERIMENTAL

Tris(iso-propyl)stibine was prepared by the reaction of $SbCl_3$ with ^iPrMgBr in diethyl ether[29] and distilled *in vacuo* (b.p. 48 °C/3 mm) prior to use. [$PdCl_2(MeCN)_2$] and [$PtCl_2(PhCN)_2$] were prepared as described in the literature.[6] All reactions were carried out under a nitrogen atmosphere in dry and distilled analytical-grade solvents. The ^1H NMR spectra were recorded on a Bruker DPX-300 spectrometer operating at 300 MHz. Chemical shifts are relative to internal chloroform peak (δ 7.26 ppm). IR spectra were recorded as Nujol mulls using CsI plates on a Bomen MB-102 FT IR spectrometer in the range 4000–200 cm^{-1}. Microanalysis of the complexes was carried out in the Analytical Chemistry Division of this research centre.

Yellow crystals of [$PdCl_2(Sb^iPr_3)_2$] were selected for single crystal X-ray data collection. All measurements were performed at room temperature on an Enraf Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) employing the $\omega = 2\theta$ scan technique. The unit cell parameters were determined from 25 reflections measured by random search routine and indexed by the method of short vectors followed by least-squares refinement. The intensity data were corrected for Lorentz, polarization and absorption effects. The structure was solved using the SHELXS-86[30] computer program and refined using the SHELXL-93[31] program. Figure 1 shows the ORTEP[32] diagram with atomic numbering scheme. The crystallographic data and data collection details are given in Table 3.

Table 2. Selected bond lengths (Å) and angles (deg) of [$PdCl_2(Sb^iPr_3)_2$]

Pd—Cl	2.2886(17)
Pd—Sb	2.5721(7)
Sb—C(2)	2.159(5)
Sb—C(5)	2.181(6)
Sb—C(8)	2.161(6)
Cl—Pd—Cl	180.0
Cl—Pd—Sb	90.75(5)
Cl—Pd—Sb	89.25(5)
Sb—Pd—Sb	180.0
C(2)—Sb—C(8)	100.8(2)
C (2)—Sb—C(5)	101.9(2)
C (8)—Sb—C (5)	110.2(3)

Table 3. Crystal data and refinement details for *trans*-[$PdCl_2(Sb^iPr_3)_2$]

Chemical formula	$C_{18}H_{42}Cl_2Sb_2Pd$
Formula weight	679.32
Crystal size (mm^3)	0.15 × 0.1 × 0.1
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	
a/Å	8.0425(18)
b/Å	16.127(3)
C/Å	10.054(5)
β/°	94.29(3)
V/Å^3	1300.3(7)
Z	2
D_c/Mg m^{-3}	1.735
Absorption coefficient μ/mm^{-1}	2.951
F(000)	664
Range of data collection	2.39 to 24.96
Refinement method	Full matrix least squares on $F^2 > 0$
Reflections collected/unique	3414/2276
Data/restraints/parameters	2276/0/106
Final R indices	$R_1 = 0.0388$, $wR_2 = 0.0361$
R indices (all data)	$R_1 = 0.1050$, $wR_2 = 0.1005$

Preparation of [$PdCl_2(Sb^iPr_3)_2$] (1a)

To a stirred benzene solution (10 ml) of [$PdCl_2(MeCN)_2$] (302 mg, 1.16 mmol) $^iPr_3Sb$ (585 mg, 2.33 mmol) was added under a nitrogen atmosphere and stirred for 45 min. The solvent was evaporated *in vacuo* and the residue was recrystallized from a toluene–hexane mixture as a yellow crystalline solid in 71% (130 mg) yield. Similarly, [$PtCl_2(Sb^iPr_3)_2$] was prepared from [$PtCl_2(PhCN)_2$] and $^iPr_3Sb$.

Preparation of [$PdBr_2(Sb^iPr_3)_2$] (1b)

To an acetone solution (15 ml) of [$PdCl_2(Sb^iPr_3)_2$] (177 mg, 0.26 mmol) a large excess of KBr (348 mg, 2.9 mmol) was added and stirred at room temperature for 8 h. This was filtered and the filtrate was concentrated in vacuum and the residue was recrystallized from acetone–hexane in 70% yield (140 mg). Similarly, [$PdI_2(Sb^iPr_3)_2$] was prepared by the reaction of [$PdCl_2(Sb^iPr_3)_2$] with NaI.

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REFERENCES

1. Bruce DW and Hare DO. *Inorganic Materials*. John Wiley: New York, 1992.
2. Hitchman ML and Jensen KF. *Chemical Vapour Deposition, Principles and Applications*. Academic Press: London, 1993.
3. Abel EW, Stone FGA and Wilkinson G. *Comprehensive Organometallic Chemistry-II*. Pergamon Press: Oxford, UK, 1995.
4. McAuliffe CA and Levason W. *Phosphine, Arsine and Stibine Complexes of the Transition Elements*. Elsevier Scientific, 1979.
5. Champness NR and Levason W. *Coord. Chem. Rev.* 1994; **133**: 115.
6. Hartley FR. *The Chemistry of Platinum and Palladium*. Applied Science: London, 1973.
7. Chatt J and Venanzi LM. *J. Chem. Soc.* 1957; 2351.
8. Goel RG and Montemayor RG. *J. Coord. Chem.* 1978; **8**: 1.
9. Dehand J and Pfeffer M. *Coord. Chem. Rev.* 1976; **18**: 327.
10. Clark HC, Goel AB and Goel S. *Inorg. Chem.* 1980; **19**: 3220.
11. Goel AB, Goel S and Vanderveer D. *Inorg. Chem. Acta* 1981; **54**: L267.
12. Even T, Gange ARJ, Hill AM, Holmes NJ, Levason W and Webster M. *J. Chem. Soc. Dalton Trans.* 2000; 655.
13. Schwab P, Mahr N, Wolf J and Werner H. *Angew Chem. Int. Ed. Engl.* 1994; **33**: 97.
14. Werner H, Schwab P, Mahr N and Wolf J. *Chem. Ber.* 1992; **125**: 2641.
15. Werner H, Schwab P, Heinemann A and Steinert P. *J. Organomet. Chem.* 1995; **496**: 207.
16. Werner H, Ortmann DA and Gevert O. *Chem. Ber.* 1996; **129**: 411.
17. Werner H, Gruenwald C, Laubender M and Gevert O. *Chem. Ber.* 1996; **129**: 1191.
18. Braun T, Laubender M, Gevert O and Werner H. *Chem. Ber.* 1997; **130**: 559.
19. Gruenwald C, Laubender M, Wolf J and Werner H. *J. Chem. Soc. Dalton Trans.* 1998; 833.
20. Werner H, Gruenwald C, Steinert P, Gevert O and Wolf J. *J. Organomet. Chem.* 1998; **565**: 231.
21. Jain VK, Kannan S and Tiekink ERT. *J. Chem. Res. (M)* 1994; 501.
22. Garje SS, Jain VK and Varghese B. *Appl. Organomet. Chem.* 1999; **13**: 47.
23. Jain VK, Patel RP, Muralidharan KV and Bohra R. *Polyhedron* 1989; **8**: 2151.
24. Roberts NK, Skelton BW, White AH and Wild SB. *J. Chem. Soc. Dalton Trans.* 1982; 2093.
25. Mathew M, Palenik GJ and McAuliffe CA. *Acta Crystallogr. Sect. C.* 1987; **43**: 21.
26. Barton DHR, Khamsi J, Ozbalik N and Reibenspies J. *Tetrahedron* 1990; **46**: 3111.
27. Wendt OF and Elding LI. *J. Chem. Soc. Dalton Trans.* 1977; 4725.
28. Wendt OF, Scodinu A and Elding LI. *Inorg. Chim. Acta* 1998; **277**: 237.
29. Dyke WJC, Davies WC and Jones WJ. *J. Chem. Soc.* 1930; 463.
30. Sheldrick GM. SHELXS-86, *Program for Crystal Structure Determination*, University of Göttingen, Germany, 1986.
31. Sheldrick GM. SHELXSL-93, *Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1993.
32. Johnson CK. ORTEP II, A FORTRAN *Thermal Ellipsoid Plot Program for Crystal Structure Illustrations*, ORNL 5138, 1976.