Journal of Organometallic Chemistry, 65 (1974) 267—273

ORGANOPLATINUM(IV) COMPOUNDS

I. TRIMETHYLPLATINUM(IV) AZIDE, Me_3PtN_3

KARL-HEINZ VON DAHLEN and JÖRG LORBERTH

Fachbereich Chemie der Philipps-Universität Marburg, D-3550 Marburg/Lahn, Lahnberge (West Germany)

(Received March 23rd, 1973; in revised form May 31st, 1973)

Summary

The preparation of trimethylplatinum azide via trimethylplatinum sulphate is reported; the compound is characterized by ^1H NMR, mass and vibrational spectroscopy and a suggestion is made as to its structure.

Introduction

Although trimethylplatinum iodide was prepared by Pope and Peachey [1] in 1909 organoplatinum(IV) chemistry has developed very slowly despite the interesting structural features of these compounds. Trimethylplatinum derivatives may be monomeric, e.g. $Me_3PtC_5H_5$ [2] or $Me_3PtOSiMe_3$ [3], dimeric, $[Me_3PtCH(COMe_2)]_2$ [4,5] or even tetrameric, e.g. $[Me_3Pt{-}X]_4$ where X = Cl, Br, I, OH, SCN. In these structures the platinum atom has a formal coordination number of 6, which is usual for platinum in the (+4) oxidation state.

The only pseudohalides known are trimethylplatinum cyanide [1] and -thiocyanate [6], and the only platinum azide complex reported hitherto is tetraphenylarsonium hexazidoplatinate [7].

We have now succeeded in preparing trimethylplatinum azide, the first trimethylplatinum compound containing a covalent platinum—nitrogen bond.

Results and discussion

1. Preparation and properties of trimethylplatinum azide

Trimethylplatinum chloride was prepared by the method of eqn. (1), however this equation is not exact since when stoichiometric amounts of reactants are used the mixture becomes black after about 20 min, platinum metal separates, and yields decrease drastically.

$$K_2PtCl_6 + 3\,MeLi \xrightarrow{\text{Dry ether}} Me_3PtCl + 3\,LiCl + 2\,KCl \quad (1)$$

At least a sixfold excess of methyllithium is necessary to achieve good yields of Me_3PtCl; similar results have been reported by Clegg and Hall [8] in the synthesis of Me_3PtI, although their procedure differs somewhat from ours. Inevitably, elementary platinum is formed during treatment of the reaction product with water in the working-up procedure.

Without purification, the chloride was converted in a one-step reaction to the sulphate using the method of Pope and Peachey [1] [eqn. (2)], and the azide was precipitated from aqueous solution by treatment with sodium azide [eqn. (3)]:

$$2\,Me_2PtCl + Ag_2SO_4 \xrightarrow[\text{Benzene}]{\text{Acetone/}H_2O} (Me_3Pt)_2SO_4 + 2\,AgCl \quad (2)$$

$$(Me_3Pt)_2SO_4 + 2\,NaN_3 \xrightarrow{\text{Water}} 2\,Me_3PtN_3 + Na_2SO_4 \quad (3)$$

Trimethylplatinum azide is not shock-sensitive, but on rapid heating or upon exposure to a flame it detonates violently, forming a black residue. In benzene solution it is monomeric (mol.wt., 280; calcd., 282), however, the solid phase structure may be completely different.

2. ^1H NMR spectroscopy

The ^1H NMR spectrum of Me_3PtN_3 in benzene solution shows the typical pattern of a trimethylplatinum group: a sharp methyl resonance which is split in part by the ^{195}Pt nucleus (natural abundance 33.8%) into two symmetrically positioned satellite signals. Chemical shifts δ (in ppm) and coupling constants J (in Hz) for a variety of Me_3PtX derivatives are given in Table 1.

Chemical shift data for Me_3PtX compounds recorded in the same solvent system show a marked high field shift for all derivatives with X other than halide, e.g. X = C, O or N (as in the case of the azide). Virtually no difference is to be observed and values range from −0.93 ppm to −0.98 ppm for $PtCH_3$, with a possible slight concentration dependance. This observation is typical for most series of organometallic compounds of the typical elements L_mMX_n where X

TABLE 1

^1H NMR DATA OF Me_3PtX DERIVATIVES

Compound	Solvent	δ(ppm)	J (Hz)	Ref.
Me_3PtCl	Benzene	−1.42	81.7	[6]
Me_3PtBr	Benzene	−1.54	80.1	[6]
Me_3PtI	Benzene	−1.73	77.9	[6]
Me_3PtOH	Benzene	−0.95	80.1	[6]
$Me_3PtOSiMe_3$	CCl_4	−1.15	78.5	[3]
Me_3PtN_3	Acetone-d_6	−1.13	74.6	
	Benzene	−0.98	74.1	
$Me_3PtC_5H_5$	$CDCl_3$	−0.93	80.9	[2]
	$CDCl_3$	−0.88	82.5	[10]

represents a non-metallic element of the first period; explanations for this phenomenon are given in the literature [9]. With some reservations, since no Me_3PtF complex is known so far, the value of $\delta(PtCH_3)$ in Me_3PtN_3 seems to be among the lowest reported, indicating high shielding of the methyl groups.

Coupling constants in the same group of Me_3PtX-derivatives are in the range 74 to 81 Hz, measured in benzene. Decreasing coupling constants may be discussed in terms of less *s*-character in the platinum—carbon bond or, conversely, more *s*-character in the nitrogen to platinum bond. On the basis of these arguments, the smallest coupling constants are to be expected for the elusive Me_4Pt (or perhaps Me_6Pt) and $Me_3Pt—PtMe_3$, compounds, which are still unknown.

3. *Mass spectra*

The base peak in the mass spectrum corresponds to the molecular ion $(Me_3PtN_3)_4^+$ of mass 1128, indicating the unusual stability of a cluster compound containing four platinum atoms. However, this does not exclude the possibility that tetrameric trimethylplatinum azide is part of a highly associated oligomer (possibly the crystallographic cell unit) as indicated by doubly and triply charged species around *m/e* 800 and above. Mass scans up to *m/e* 3,700 yielded no further information, although it would be of interest to find crystallographic features reflected in the mass spectrum of such a compound.

The second most intense peak in the spectrum, at *m/e* 240, arises from Me_3Pt^+, an ion which exhibits great stability even in aqueous solution. There is no evidence for $(Me_3PtN_3)^+$; only a $(M - 1)^+$ peak of low abundance is present. Monomeric Me_3PtX species are known ($Me_3PtC_5H_5$ [10] forms a molecular ion); fragmentation occurs with loss of methyl groups and by dehydrogenation to eliminate neutral H—X fragments. Analogous conclusions may be drawn for the azide, although HN_3 and other reduced nitrogen species seem to be less favoured as neutral leaving groups.

Further fragmentation leads to $(Me_2CH_2PtN_3)^+$ and eventually to $(Me_3Pt)^+$ or $(PtN_2)^+$ as the predominant decomposition pathway; surprisingly no ions $(Me_2Pt)^+$ or $(MePt)^+$ have been detected. This result is identical to the mass spectral behavior of $Me_3PtC_5H_5$ [10].

4. *Vibrational spectroscopy*

In order to establish the structure of trimethylplatinum azide IR and Raman spectra of the solid have been obtained. Both spectra and vibrational modes are given in Table 2.

Assignments. The IR and Raman spectra show a large number of absorptions due to the methyl groups in the region 3000 to 700 cm^{-1}. In addition, vibrations due to the azide groups appear characteristically as a very strong unresolved band $\nu_{as}(N_3)$ at 2071 cm^{-1} (IR). This is split into two bands of lower intensity at 2089/2076 cm^{-1} in the Raman spectrum. Organometallic azide frequencies vary as much as from 2150 to 2000 cm^{-1}, lower frequencies sometimes indicating bridging modes for the azide groups.

A strong symmetric stretching mode $\nu_s(N_3)$ is observed at 1199 (IR) and

TABLE 2

IR AND RAMAN SPECTRUM[a] OF $[Me_3PtN_3]_4$

IR (cm^{-1})	Raman (cm^{-1})	Vibration modes
3239 m		$\nu_{as} + \nu_s(N_3)$
2976 m (sh)	2990 m	$\nu_{as}(CH_3)$
2958 m	2968 m	$\nu_{as}(CH_3)$
2899 m	2908 s	$\nu_s(CH_3)$
2451 w		Combination
2378 w		Combination
2071 vs	2089 m—s	$\nu_{as}(N_3)$
	2976 m—s	
1445 w (sh)	1437 w	
1418 w	1413 w	
1403 w		$\delta_{as}(CH_3)$
1385 w (sh)		
1270 m	1289 m	
1246 m	1248 s	$\delta_s(CH_3)$
1199 s	1210 m	$\nu_s(N_3)$
1050 w		$\delta_s(CH_3)$
876 w	885 w	$\rho(CH_3)$
	857 w	
790 w		
768 w (sh)		
632 m		$\delta(N_3)$
590 vw	590 vs	ν_{as}(Pt—C)
560 w	581 vs	ν_s(Pt—C)
432 vw (br)		$\delta(PtC_3)$?
323 m—s	318 m	ν_s(Pt—N)
246 w	257 vs	$\delta(PtC_3)$

[a] vw = Very weak; w = weak; m = medium; m—s = medium to strong; s = strong; vs = very strong; br = broad; sh = shoulder.

at 1210 cm^{-1} (medium intensity) (Raman). Both asymmetric and symmetric modes give rise to a weak, but distinct combination band at 3239 cm^{-1} (IR), which is somewhat lower than the calculated frequency 3270 cm^{-1}, due to anharmonic vibration. Azide deformations δ (N_3) of azides with lower symmetry are often split into two bands at *ca.* 550 - 520 cm^{-1} and 670 - 650 cm^{-1}. Trimethylplatinum azide shows a single absorption at 632 cm^{-1} $\delta(N_3)$, which is again consistent with data for other organometallic azides [13].

Metal—carbon stretching modes are relatively weak in the IR spectrum, but are amongst the strongest absorptions in the Raman spectrum. Bands at 590/560 cm^{-1} (IR) and at 590/581 cm^{-1} (Raman) are readily assigned to Pt—C stretching frequencies.

A PtC_3-deformation mode has been identified in the literature [14] at 259 cm^{-1} for $Me_3Pt(OH_2)_3{}^+$ which compares well with 246 cm^{-1} (IR)/257 cm^{-1} (Raman) for the azide.

Pt—X stretching frequencies have consistently been found below 500

TABLE 3

CLUSTER FREQUENCIES OF $[Me_3PtX]_4$ DERIVATIVES

Compound	ν(Pt—Pt) (cm^{-1})			f(M—M) (mdyn/Å)	$n/2$	r(M—M) (Å)
	A_1	T_2	E			
$(Me_3PtI)_4$ [a]	88	65	48	0.49	0	4.0
$(Me_3PtCl)_4$ [a]	99	79	57	0.50	0.064	3.73
$(Me_3PtOH)_4$ [a]	137	97	75	0.79	0.118	3.42
$(Me_3PtN_3)_4$	147	95	65			

[a] Data taken from [12].

cm^{-1}, covering a wide range: ν(Pt—O) 430 -340 cm^{-1}, ν(Pt—Cl) 300—140 cm^{-1} and ν(Pt—I) 130 - 90 cm^{-1}. We assign a band at 323 cm^{-1} (IR)/318 cm^{-1} (Raman) with medium to strong intensity to a platinum—nitrogen stretching mode.

The low frequency part of the Raman spectrum is characteristic for metal—metal interactions such as have been described by Spiro et al. [12]: spectra of various platinum compounds $[Me_3PtX]_4$ are very similar with regard to band intensities and regularities in frequency increments. Comparing the Pt—Pt cluster frequencies of the compounds listed in Table 3 we can assume that increasing A_1 frequencies are paralleled by greater force constants and higher bond orders with a maximum for $[Me_3PtN_3]_4$. Conversely, this is accompanied by shorter metal—metal distances. This would explain the unusual stability and high abundance of the parent ion in the mass spectrum.

In conclusion, we obtained a novel bridged organoplatinum pseudohalide complex $[Me_3PtN_3]_4$ with structural features similar to the halides and the hydroxide; therefore we suggest the distorted cubane structure for trimethylplatinum azide shown in Fig. 1; the bond platinum to nitrogen is predominantly covalent and vibrational modes for this bond have been assigned; there is evidence for considerable metal—metal interaction.

Experimental

1. *Spectra and analysis*

IR spectra were recorded on Perkin - Elmer PE 457 and PE 225 instruments using KBr and CsI plates. Trimethylplatinum azide was suspended in Hostaflon (4000 to 1350 cm^{-1}) or in Nujol (1350 to 200 cm^{-1}).

Raman spectra were recorded on a Coderg PH 1 spectrometer with laser excitation by Spectra Physics types 135 and 141.

NMR spectra were recorded on HA-100 and T 60 Varian spectrometers. Chemical shifts are quoted in ppm with reference to TMS as internal standard.

Mass spectra were recorded using a direct inlet system attached to a Master 711 Varian Mat, with an ion energy of 70 eV and an ion source temperature of 135°.

Elemental analysis was performed by A. Bernhardt, Analytical Laboratory, Elbach über Engelskirchen, West Germany.

Molecular weight was determined cryoscopically in benzene solution.

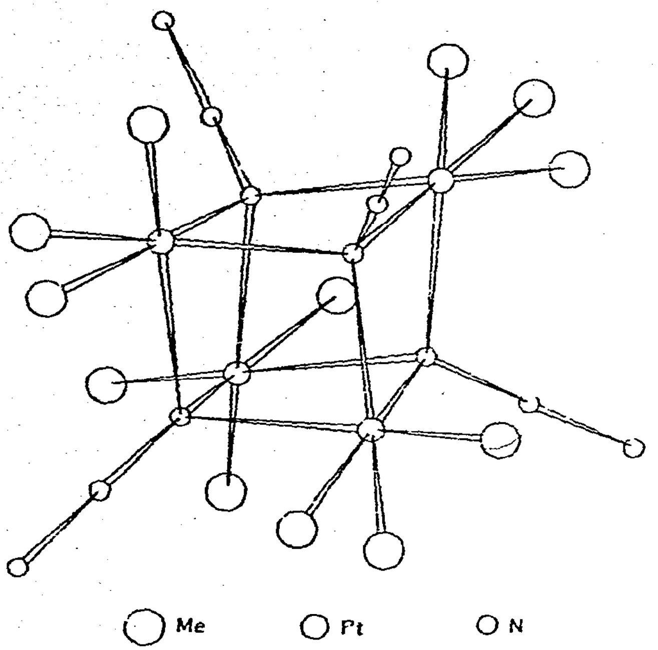

Fig. 1. Structure of trimethylplatinum azide.

2. *Starting materials*

Potassium hexachloroplatinate (Degussa, Hanau) was dried at 100°/10^{-4} mm. Silver sulphate (Riedel de Haen, Hannover) was used without further purification. Solvents were distilled and dried over molecular sieves.

Methyllithium was prepared from methyl iodide and lithium metal in dry ether; the solution was decanted under nitrogen and evaporated to dryness. The residue was dried at 80°/10^{-4} mm to remove unreacted methyl iodide.

3. *Preparation of trimethylplatinum azide*

K_2PtCl_6 (10 g; 20 mmol) was suspended in 30 ml of dry ether in a 250 ml two-necked flask, the flask was placed in an ice bath and 3 g MeLi (136 mmol) dissolved in 150 ml dry ether was added. The reaction mixture was stirred until the yellow of K_2PtCl_6 had completely disappeared (about 4 h). A colourless solution and a white solid were obtained. With continued cooling 100 ml of 10% hydrochloric acid was slowly added. The solution became yellow first, but changed later to black. The etheral layer was decanted and the aqueous solution was extracted three times with 100 ml portions of boiling benzene during 20 min. The combined orange extracts contained some black material, but this sometimes changed to a violet upon standing.

The solution was filtered and concentrated to ca. 50 ml; 200 ml of acetone, 30 ml of water and 3.28 g Ag_2SO_4 (10.5 mmol) were added and the mixture refluxed and stirred for 6 h. The yellow (or sometimes slightly greenish coloured) precipitate was filtered off and washed with 50 ml of acetone, leaving an almost colourless solution which was evaporated to dryness. The residue was redissolved in ca. 200 ml of water and refiltered to remove unreacted trimethylplatinum chloride. With magnetic stirring an excess of sodium azide, dissolved in water, was added.

The initially-formed fine white precipitate of trimethylplatinum azide was difficult to filter, but after standing for some time separation by this method was possible. Recrystallization from aqueous alcohol yielded colourless, glittering leaf-shaped hexagonal crystals. These were filtered off and the mother liquor was evaporated to dryness and the residue again recrystallized. After repeating this operation 4 to 5 times and drying at 40°/10^{-4} mm the total yield was 4.22 g (74.8% based on K_2PtCl_6 as starting material). (Found: C, 12.95; H, 3.22; N, 14.65; Pt, 68.77. CH_3PtN_3 calcd.: C, 12.77; H, 3.19; N, 14.89; Pt, 69.15%.)

It is of interest to note that the bromide and iodide can also be prepared from the sulphate solution, using KBr or KI instead of NaN_3. Yields are higher than 70% (based on K_2PtCl_6) and derivatives are of high purity, the iodide being formed in its colourless modification.

The compound does not melt but turns yellow at 183°, then darkens and finally decomposes at 188° leaving a black mass.

Trimethylplatinum azide is soluble in methanol, ethanol, acetone and dioxane, sparingly soluble in diethylether and benzene and practically insoluble in water. Halogenated hydrocarbons, e.g. CH_2Cl_2, $CHCl_3$ or CCl_4, react with trimethylplatinum azide as is indicated by ^1H NMR spectra of solutions in these solvents; the products of these reactions have not been investigated.

Acknowledgement

Experiments were financed by the Fachbereich Chemie, Philipps-Universität Marburg/Lahn, West Germany. Additional support was given by Schering AG, Werk Bergkamen, Fonds der Chemischen Industrie e.V. (VCI) and the Deutsche Forschungsgemeinschaft (DFG) whose generosity is gratefully acknowledged.

Raman spectra were kindly supplied by Dr. R. Schmitt, Marburg, and Dozent Dr. J. Weidlein, Stuttgart. We thank Dozent Dr. I. Wilson for reading the manuscript.

References

1 W.J. Pope and S.J. Peachey, J. Chem. Soc., 95 (1909) 571.
2 S.D. Robinson and B.L. Shaw, Z. Naturforsch. B, 18 (1963) 507.
3 S.D. Robinson and B.L. Shaw, J. Chem. Soc., (1965) 1529.
3 M. Bergfeld, Ph.D. Thesis Würzburg, 1967; F. Schindler and H. Schmidbaur, Angew. Chem., 79 (1967) 697.
4 R.C. Menzies, J. Chem. Soc., (1928) 565.
5 A.G. Swallow and M.R. Truter, Proc. Roy. Soc. A, 252 (1960) 205.
6 J.S. Thayer, Organometal. Chem. Rev. A, 5 (1970) 53.
7 W. Beck, E. Schuierer and K. Feldl, Angew. Chem., 78 (1966) 267.
8 D.E. Clegg and J.R. Hall, Inorg. Syn., 10 (1967) 71.
9 J. Lorberth and H. Vahrenkamp, J. Organometal. Chem., 11 (1968) 111.
10 K.W. Egger, J. Organometal. Chem., 24 (1970) 501.
11 R.B. King, Appl. Spectrosc., 23 (1969) 148.
12 P.A. Bulliner, V.A. Maroni and T.G. Spiro, Inorg. Chem., 9 (1970) 1887.
13 J.S. Thayer, Organometal. Chem. Rev. A, 1 (1966) 157.
14 D.E. Clegg and J.R. Hall, Spectrochim. Acta, 21 (1965) 357.