ELSEVIER

Journal of Organometallic Chemistry 559 (1998) 191–196

Journal of Organometallic Chemistry

Organoplatinum compounds VII[1]
Trimethylplatinum fluoride $[(CH_3)_3PtF]_4$, the missing link in organoplatinum cluster chemistry: its synthesis, crystal structure and a comparison to the crystal structure of $[(CH_3)_3PtOH]_4$

Dedicated to: Professor M.F. Lappert on the occasion of his 70th birthday.

H. Donath [a], E.V. Avtomonov [a], I. Sarraje [a], K.-H. von Dahlen [a], M. El-Essawi [a],
J. Lorberth [a,*], B.-S. Seo [b]

[a] *Fachbereich Chemie der Philipps-Universität Marburg, Hans-Meerwein-Strasse, D-35032 Marburg, Germany*
[b] *The Catholic University of Korea, College of Medicine, Chemistry Section, Department of Natural Sciences, 137-701 Seoul, South Korea*

Received 12 December 1997

Abstract

The structural chemistry of organoplatinum clusters $[Me_3PtX]_4$ (X = halide) has been completed with the synthesis and X-ray investigation of $[Me_3PtF]_4$ (**1**) and its structural comparison to the well-known hydroxide $[Me_3PtOH]_4$ (**2**), all members of the 'organoplatinum cubane' family. Compound **1**, long withstanding its attempted synthesis, has been obtained by the reaction of $[Me_3PtI]_4$ with XeF_2 as a mild fluorinating agent in form of colourless crystals: space group $I\bar{4}3m$, $Z = 2$, $a = 10.0878(7)$ Å, $R_1 = 0.0242$, $wR_2 = 0.0563$. In order to discriminate **1** from its possible hydrolysis product, viz. $[Me_3PtOH]_4$ (**2**), the latter was also synthesised according to literature procedures and re-investigated by X-ray crystallography: colourless crystals, space group $I\bar{4}3m$, $Z = 2$, $a = 10.1400(10)$ Å, $R_1 = 0.0238$, $wR_2 = 0.0586$. NMR spectroscopic, mass spectrometric and, in part, IR data are reported for **1** and **2**. A crystalline solid obtained from equimolar chloroform solutions of both **1** and **2** did not reveal any new structural features, e.g. lattice parameters. From this mixture one might have expected a possible formation of strong hydrogen bonds of the type $Me_3Pt{-}F\cdots H{-}O{-}PtMe_3$. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Platinum; Organoplatinum compounds; Platinum fluoride; Platinum hydroxide; Crystal structure; Platinum metal group

---

1. Introduction

For almost 20 years our enduring efforts to complete the series of '*cubane clusters*' in organoplatinum chemistry $[Me_3PtX]_4$, where X denotes the halogens F [1], Cl [2], Br [3], I [4] and pseudohalogens, e.g. N_3 [5] or SCN [6], SMe [7] and OH [8], finally have been rewarded with the successful synthesis and structural characterisation of the fluorine derivative as $[Me_3PtF]_4$, thus concluding our research with the aim to obtain this key compound. Among other reaction sequences, we tried those mentioned in the Scheme 1 without success. It could possibly be noteworthy to comment in detail on our failures in obtaining 'Me_3PtF', but we rather wish to concentrate on the unequivocal characterisation of the trimethylplatinum fluoride tetramer **1** by analytical methods available in our laboratory.

---

* Corresponding author. Fax: +49 6421 285642.

[1] For part VI see Ref. ([4]b).

PII S0022-328X(98)00481-1

Attempted syntheses of "Me$_3$PtF"

$$\mathrm{Me_3PtI} + \mathrm{AgF/AgF_2} \not\longrightarrow \mathrm{AgI}\downarrow + \text{"}\mathrm{Me_3PtF}\text{"}$$

$$2\,\mathrm{Me_3PtI} + \mathrm{HgF_2} \not\longrightarrow \mathrm{HgI_2}\downarrow + 2\,\text{"}\mathrm{Me_3PtF}\text{"}$$

$$\mathrm{Me_3PtCl} + \mathrm{KF/KHF_2} \not\longrightarrow \mathrm{KCl}\downarrow + \text{"}\mathrm{Me_3PtF}\text{"}$$

$$\mathrm{Me_3PtOH} + \mathrm{HF} \not\longrightarrow \mathrm{H_2O} + \text{"}\mathrm{Me_3PtF}\text{"}\downarrow$$

$$\mathrm{CODPtMe_2} + \mathrm{MeF} \not\longrightarrow \mathrm{COD} + \text{"}\mathrm{Me_3PtF}\text{"}\downarrow$$

$$\mathrm{Me_3PtI} + \text{F-Npyr.trifl.} \not\longrightarrow \tfrac{1}{2}\,\mathrm{I_2} + \text{"}\mathrm{Me_3PtF}\text{"}$$

$$\mathrm{Me_3PtI} + \mathrm{CoCp_2^+F^-} \not\longrightarrow \mathrm{CoCp_2^+I^-}\downarrow + \text{"}\mathrm{Me_3PtF}\text{"}$$

Scheme 1.

2. Results and discussion

Successful synthesis of $[\mathrm{Me_3PtF}]_4$ was finally achieved with the mild fluorinating reagent $\mathrm{XeF_2}$ in $\mathrm{CH_2Cl_2}$ solution of $[\mathrm{Me_3PtI}]_4$ at r.t. for some hours (Scheme 2).

Colourless crystals of **1** behave distinctly different from all other $[\mathrm{Me_3PtX}]_4$ cluster compounds due to hydrolysis on standing at ambient conditions; to our knowledge this is so far the only platinum cluster compound which is sensitive to moisture, forming the cluster hydroxide $[\mathrm{Me_3PtOH}]_4$ (**2**) as the only platinum containing reaction product. There is a report in the literature on the synthesis of 'Me$_3$PtOSiMe$_3$', a compound described with similar properties, but the reaction could never be reproduced [9].

Compound **1** is partially dissociated in solution, consisting of a mixture of clusters in non-polar solvents. This is also reflected by ^{1}H-NMR spectra in chloroform or benzene solutions: a complex set of broad signals is observed in the region between 1.75–0.73 ppm. About a half of the integrated intensity is due to a broadened singlet of protons of the methyl groups of the tetrameric cluster $[\mathrm{Me_3PtF}]_4$ $[^2\mathrm{J}(H_3\mathrm{C}^{195}Pt) = 72.0$ Hz]. When **1** is dissolved in polar solvents, e.g. THF, DMSO, the dissociation equilibrium is shifted towards the monomeric species $\mathrm{Me_3PtF\cdot solv}$, although some amount of polynuclear associates is still present. In the case of the THF solvated complex we observe a doublet at 0.89 ppm with coupling $^3J(H_3\mathrm{CPt}^{19}F)$ in the order of 12.75 Hz, while in DMSO solutions no coupling between ^{1}H and ^{19}F nuclei has been observed. This behaviour can be explained in terms of the dissociation of the Pt–F bond: the 'soft' sulphur atom of DMSO possesses a higher affinity to the platinum centre than the 'hard' oxygen atom of THF, thus being capable of dissociating the weak Pt–F bond. In another platinum(IV) fluoride complex, this type of coupling has also not been observed and we assume that explanation for the lack of this coupling phenomenon can be provided by the formation of solvated cationic species in solution [10].

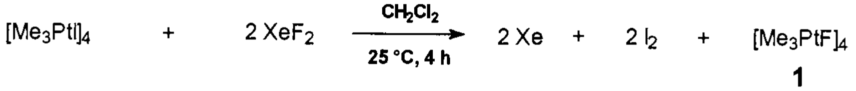
On the contrary, the hydrolysis product of **1**, viz. compound **2**, behaves quite differently in solution: a singlet of the methyl group protons at 0.90 ppm $[^2J(H_3\mathrm{C}^{195}Pt) = 78.3$ Hz] and a 'pseudo quintet' (A-part of $\mathrm{AX_3Y}$ spin-system) of the protons of the hydroxylic groups at -0.53 ppm are indicative for the tetrameric composition of **2** in solution.

The mass spectrum of $[\mathrm{Me_3PtF}]_4$ (**1**) is also definitely different from that of its hydrolysis product. We find Pt$_1$-fragments at 225 *m/z* for Me$_2$Pt and 240 *m/z* for Me$_3$Pt with the typical isotopic pattern for the numerous Pt isotopes. Similarly, in the range of 497–501 *m/z* fragments of medium ion intensity are found for Pt$_2$-fragments, with a broad variability in this range for the possible loss of either CH$_3$/F/HF/ or even CH$_3$F groups during ionisation of the molecular ion. No Pt$_3$-fragments appear in the spectrum, but again a mass region from 995–1002 *m/z* is indicative for a number of Pt$_4$-fragments, resulting from the non-observed mother peak which was expected at 1036 *m/z* with the consecutive loss of small molecules and ions. We have earlier described the complexity of another platinum cluster fragmentation, viz. $[\mathrm{Me_3PtN_3}]_4$ during its mass spectrometric analysis [5].

In order to complete our structural studies of heterocubane platinum clusters we undertook the crystal structure investigation of **1**. Although the crystal structure of $[\mathrm{Me_3PtOH}]_4$ has been reported earlier [8], more accurate data for our comparative study were desirable and therefore we reinvestigated the crystal structure of **2**.

Table 1 shows the experimental details of the crystal structure determination of both **1** and **2**.

The discussion strongly resembles that of already described clusters $[\mathrm{Me_3PtX}]_4$, where a '*pseudo cubane*' is



$$[Me_3PtI]_4 + 2\,XeF_2 \xrightarrow[25\,°C,\,4\,h]{CH_2Cl_2} 2\,Xe + 2\,I_2 + [Me_3PtF]_4$$

1

Scheme 2. Scheme 2

the building block of various three-dimensional networks, e.g. layer structures in combination with solvent molecules. In **1** the Pt_4F_4 core (Fig. 1) forms two interpenetrating distorted tetrahedra, leading to the well-known '*pseudo cubane*' morphology of the isolated clusters with bond angles at platinum ∠(FPtF) of 78.7(4)° and conversely with ∠(PtFPt) of 100.2(3)°, so far only achieved in the structure of the pseudohalogen cluster $[Me_3PtN_3]_4$ with ∠100°, where both bridging anions, fluoride and azide, express their tendency to form the widest possible bond angle in a series of complexes. Table 2 displays the information about bond distances and bond angles in *cubane* skeletons $[Me_3PtX]_4$, with virtually no significant variation in Pt–C bond distances, an expected increase in Pt–X bond lengths from fluorine passing through chlorine and bromine to iodine and according to increasing atomic volume of the halogen with an increase in atomic distances Pt–Pt or X–X in the cluster framework. Factually, the '*hard bases*' fluoride, azide, hydroxide fit very well in these characteristic parameters, whereas the '*soft bases*' like chloride, thiomethylate or thiocyanide form another comparable set of data, according to Table 2.

Table 1
Crystal data and structure refinement for 1 and 2.

Identification code	plaf	ptoh
Empirical formula	$(C_3H_9FPt)_4$	$(C_3H_{10}OPt)_4$
Formula weight	1036.77	1028.80
Temperature (K)	190(2)	190(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Cubic	Cubic
Space group	$I\bar{4}3m$	$I\bar{4}3m$
Z	2	2
Unit cell dimensions		
a (Å)	10.0876(7)	10.1400(10)
b (Å)	10.0876(7)	10.1400(10)
c (Å)	10.0876(7)	10.1400(10)
Volume (Å^3)	1022.97(18)	1042.59(18)
D_{calc} (g cm^{-3})	3.366	3.277
Absorption coefficient (mm^{-1})	27.286	26.759
F(000)	912	912
Crystal size (mm^3)	0.11 × 0.09 × 0.06	0.21 × 0.11 × 0.03
θ-range for data collection	2.86–30.41°	2.84–30.20°
Index ranges	$-14<h, k, l<14$	$-14<h, k, l<14$
Reflections collected/unique	6027/326 [$R_{int}=0.0680$]	5592/326 [$R_{int}=0.0572$]
Absorption correction	Analytical	Analytical
Max. and min. transmission	0.29 and 0.15	0.50 and 0.07
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/parameters	326/15	326/16
Goodness-of-fit on F^2	1.356	1.110
Final R indices [$I>2\sigma(I)$]	$R_1=0.0242$, $wR_2=0.0548$	$R_1=0.0238$, $wR_2=0.0586$
R indices (all data)	$R_1=0.0254$, $wR_2=0.0563$	$R_1=0.0239$, $wR_2=0.0586$
Absolute structure parameter	0.45(15)	0.09(12)
Largest difference peak and hole (e Å^{-3})	0.835 and −1.480	1.073 and −0.983

The isostructural complexes $[Me_3PtX]_4$ for X = N_3, F and OH show as symmetry label a C_3 axis through the corners of the cubane; the crystal packing of the cubanes occurs with highest possible density, thus not allowing for co-crystallisation of solvent molecules (Fig. 3). Our observation, that some of these structures are only formed in the presence of solvent molecules is limited by the space demand of the cubanes packed in trimethylplatinum azide, fluoride and hydroxide, as can be principally demonstrated by $[Me_3PtF]_4$. Interesting to note that in $[Me_3PtOH]_4$ (Fig. 2) we have a compound potentially active for hydrogen bonding via hydroxylic groups; one straightforward test for the feasible existence of strong Pt–***F–H–O***–Pt bonds through mixing of the two components **1** and **2** in chloroform solution with the assumed formation of

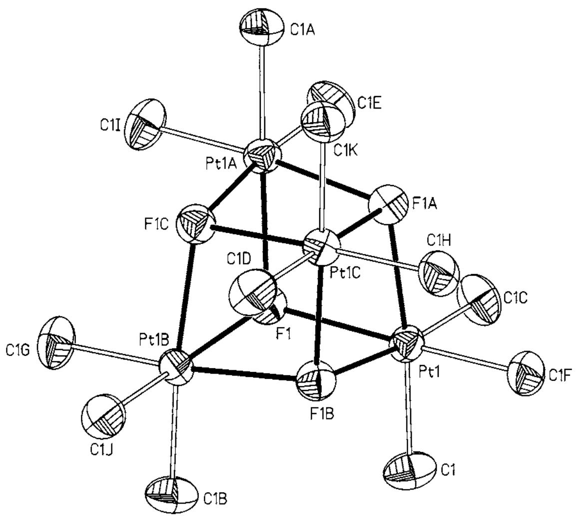


Fig. 1. ORTEP plot of $[Me_3PtF]_4$ (**1**) with atomic-numbering scheme. The thermal displacement ellipsoids are scaled to the 50% probability level.

Table 2
Comparison of trimethylplatinum structures exhibiting a '*cubane skeleton*' $[Me_3PtX]_4$

X	Pt–X	Pt···Pt	X···X	X–Pt–X	Pt–X–Pt	Pt–C	Literature
F	225.1(6)	345.4	285.5	78.7(4)	100.2(3)	200.9(10)	[1]
Cl	248(11)	373	328	81	99	205.7	[2]
Br	267.7	393.0	363.2	85.4	94.3	201	[3]
I	282.4(1)	410.5	387.8	86.6	93.1	205	[4]
I	281.9(6)	411.2	385.2	86.2	93.7	202	[4]
N_3	225(5)	344.9(4)	289	80	100	205(6)	[5]
OH	221.7(5)	343.53(5)	276.5(9)	77.1(4)	101.6(3)	202.6(8)	[1]
OH	222(1)	343.0	278	77.6	101.2	204	[8]
S–Me	247.1(4)	378.0	315.2	79.3	99.1	207	[7]
S–Me	248(2)	380(2)	310.7	79.1(7)	102.3	200(4)	[7]
S–CN[a]	255(2)	383	337.6	82.4(6)	97.3(6)	203	[6]

[a] This is not a true 'cubane' structure, but the rectangular skeleton shows Pt-S and Pt–N co-ordination.

new structures was carried out accordingly to Scheme 3. However, crystals of **3** obtained from the 1:1 molar solution and investigated by X-ray diffractometry did not exhibit any new structural features, viz. cell parameters were found to be almost identical to those obtained for both starting materials.

3. Experimental section

All manipulations were performed (unless stated otherwise) in an atmosphere of dried, oxygen-free argon using standard Schlenk techniques; solvents were appropriately dried and saturated with argon. -NMR: Bruker ARX-200, AC-300 and AMX-500 spectrometers (200, 300, 500 and 50, 75.4, and 125 MHz, for ^1H and ^{13}C, respectively). -FT-IR: Nicolet 501. -EI-MS: Varian CH-7a MAT spectrometer, electron impact ionisation with 70 eV excitation energy. -Elemental analyses were performed by the analytical division of the Fachbereich Chemie der Philipps-Universität Marburg. $[Me_3PtOH]_4$ (**2**) was prepared by a modified literature procedure [11]: ^1H-NMR (200 MHz, $CDCl_3$, 25°C) δ (ppm): 0.90 (s + d, 36 H, $^2J(H_3C^{195}Pt) = 78.3$ Hz), -0.53 (s + *pseudo*-qi, 4 H, A-part of AX_3Y spin-system). ^{13}C-NMR (50 MHz, $CDCl_3$, 25°C) δ (ppm): -11.5 ($^1J(H_3^{13}C^{195}Pt) = 720$ Hz). IR (KBr): 3595 cm^{-1} (s, –OH).

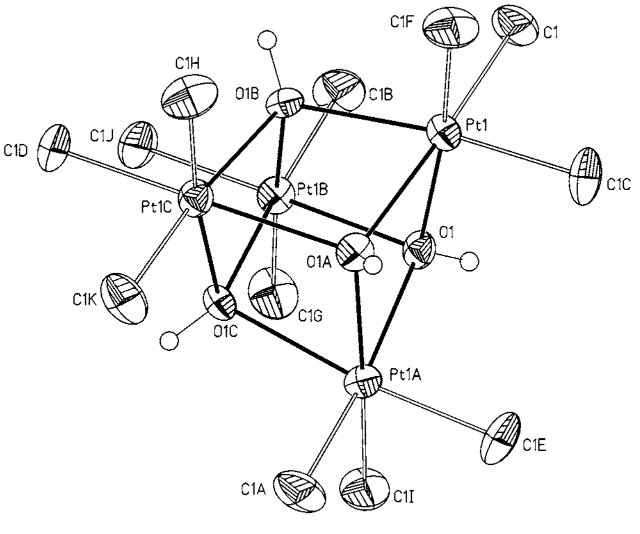


Fig. 2. ORTEP plot of $[Me_3PtOH]_4$ (**2**) with atomic-numbering scheme. The thermal displacement ellipsoids are scaled to the 50% probability level.

3.1. *$[Me_3PtF]_4$* (**1**)

A 0.36 g mass (2.10 mmol) of XeF_2 was dissolved in ca. 50 ml of dry CH_2Cl_2 in a 100 ml flask under an argon atmosphere. A mass of 1.525 g (4.14 mmol) of crystalline Me_3PtI was added under argon; immediate colouring due to iodine formation took place together with gas evolution (Xe)[2]. The mixture was stirred with exclusion of light for 12 h and the solvent was removed in vacuum; iodine was sublimed from the residue in vacuum. Yield: 0.8 g (74.7%) of colourless crystals (after cryst. from $CHCl_3$), based on Me_3PtI; the crude yield is quantitative (1.07 g). Anal. Found: C 13.64; H 3.43; F 5.27%. $[C_3H_9PtF]_4$ (1036.77 g mol^{-1}) Calc.: for C_3H_9PtF C 13.90; H 3.50; F 7.33%. The analytical data for the fluorine analysis are neither particularly reliable, nor reproducible. ^1H-NMR (200 MHz, $CDCl_3$, 25°C) δ (ppm): 1.60 (br. q), 1.41 (br. q), 1.25 (br. s + d, $^2J(H_3C^{195}Pt) = 72.0$ Hz), 1.18 (br. q), 1.04 (br. q), 0.85 (br. q); (300 MHz, DMSO-d_6, 25°C) δ (ppm): 0.81 (s + d, $^2J(H_3C^{195}Pt) = 78.8$ Hz); (500 MHz, THF-d_8, 25°C) δ (ppm): 0.89 (d + dd, $^3J(H_3CPt^{19}F) = 12.75$ Hz, $^2J(H_3C^{195}Pt) = 78.7$ Hz). EI-MS, m/z (rel. int. %, assign.): 995–1002 (to 6%, Pt_4-clusters), 497–501 (to 4%, Pt_2-clusters), 240 (26.2, Me_3Pt), 225 (8, Me_2Pt).

---

[2] Note: $CHCl_3$ is not suitable for this reaction, immediate decomposition of XeF_2 occurs!

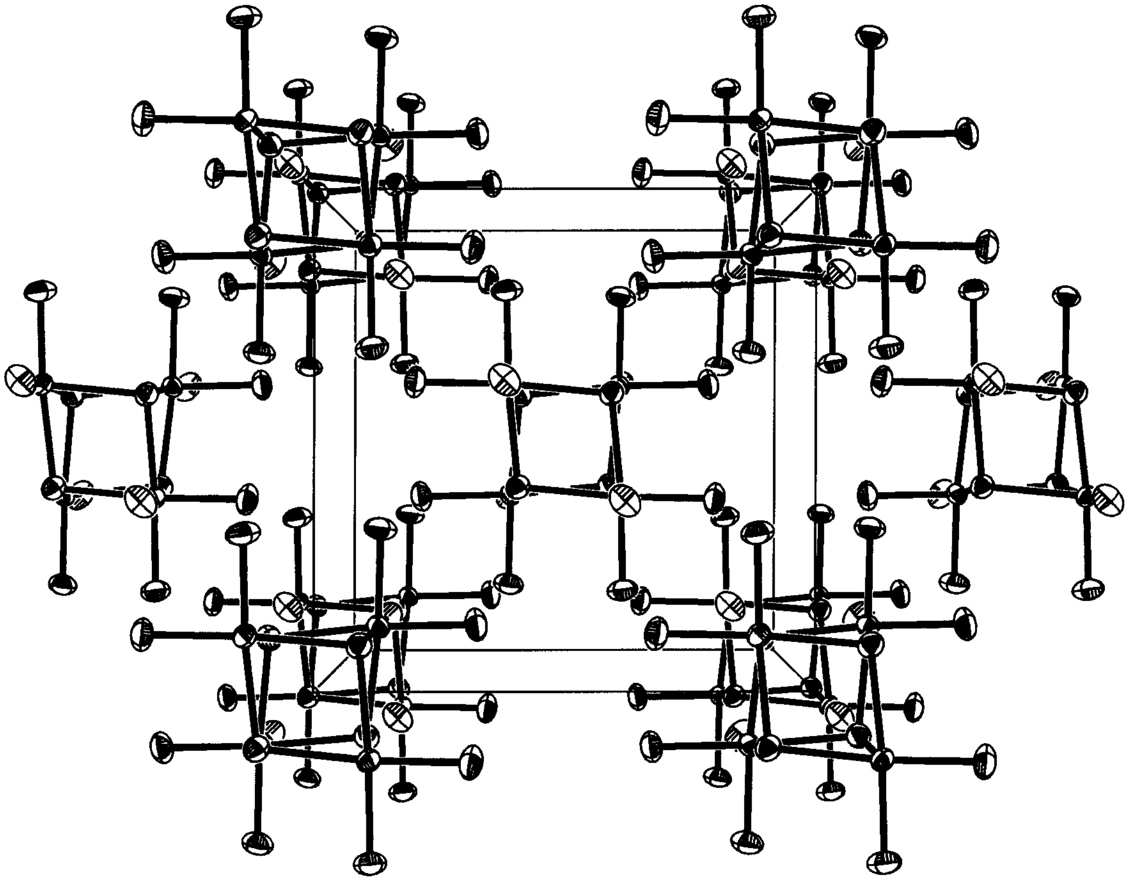


Fig. 3. Plot of the crystal packing of $[Me_3PtF]_4$ (**1**).

3.2. Crystal structure determination of **1** and **2**

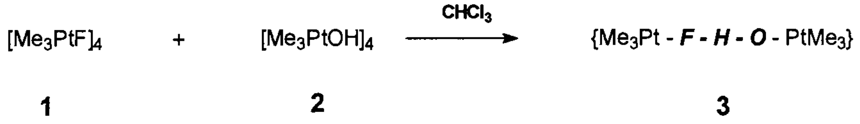
Crystals of both compounds were grown under similar conditions by cooling $CHCl_3$ solutions at −30°C. Small specimens were mounted onto glass capillaries and investigated using a Stoe IPDS area detector system (Mo–K_α, graphite monochromator) at −83°C.

Lorentz factors and polarisation effects were taken into account. Structure solutions were carried out by heavy atom methods with the SHELXS-97 programme [12], and refinement was performed by full-matrix least-squares on F^2 on the basis of all reflections with SHELXL-97 [13]. All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were included as idealised contributions and refined using a riding model except for H(1) at O(1) in **2**. The latter was found in a difference Fourier-map and then refined using a riding model. Additionally, analytical absorption corrections based on face-indexing were applied to the data sets of **1** and **2**.

Further details of the crystal structure determinations may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository numbers CSD-408075 (**1**), -408074 (**2**), the names of the authors and the journal citation.

Acknowledgements

B.-S. Seo expresses his sincere gratitude to the DAAD (Bonn) for a research grant and to the Catholic University, Medical College, Seoul (South Korea) for an extended leave of absence. I. Sarraje and M. El-Essawi received adequate support for various parts of this project from DAAD which is gratefully acknowledged. Generous support from the Fonds der Chemischen Industrie, VCI, for J. L. was supplied throughout these years and has been accepted with great gratitude. E. V. Avtomonov received a maintenance grant from the HSP-III programme of the Government of Hessen, Germany. Finally, the authors wish to thank DEGUSSA (Hanau-Wolfgang) for their continuous support of our platinum research projects through generous gifts of platinum starting materials.



$$\underset{\mathbf{1}}{[Me_3PtF]_4} + \underset{\mathbf{2}}{[Me_3PtOH]_4} \xrightarrow{CHCl_3} \underset{\mathbf{3}}{\{Me_3Pt\text{-}F\text{-}H\text{-}O\text{-}PtMe_3\}}$$

Scheme 3.

References

[1] This paper; the assistance of Professor W. Massa is gratefully acknowledged.

[2] R.E. Rundle, J.H. Sturdivant, J. Am. Chem. Soc. 69 (1947) 1561.

[3] W. Massa, G. Baum, B.-S. Seo, J. Lorberth, J. Organomet. Chem. 352 (1988) 415.

[4] (a) R. Allmann, D. Kucharczyk, Z. Kristallographie 165 (1983) 227. (b) K.H. Ebert, W. Massa, H. Donath, J. Lorberth, B.-S. Seo, E. Herdtweck, J. Organomet. Chem. (1997), submitted for publication. (c) see also: G. Donnay, L.B. Coleman, N.G. Krieghoff, D.O. Cowan, Acta Cryst. B 24 (1968) 287.

[5] (a) K.-H. von Dahlen, J. Lorberth, J. Organomet. Chem. 65 (1974) 267. (b) M. Atam, U. Müller, J. Organomet. Chem. 71 (1974) 435.

[6] T.G. Spiro, H.D. Templeton, A. Zalkin, Inorg. Chem. 7 (1968) 2165.

[7] (a) R. Allmann, D. Kucharczyk, Z. Kristallographie 165 (1983) 227. (b) G. Smith, C.H.L. Kennard, T.C.W. Mak, J. Organomet. Chem. 290 (1985) C7.

[8] B. Vance, J. Organomet. Chem. 336 (1987) 441.

[9] (a) M. Bergfeld, Ph.D. Thesis, Würzburg, 1967. (b) F. Schindler, H. Schmidbaur, Angew. Chem. 79 (1967) 697; Angew. Chem. Int. Ed. Engl. 6 (1967) 683.

[10] C.M. Anderson, R.J. Puddephatt, G. Ferguson, A.J. Longh, J. Chem. Soc. Chem. Commun. (1989) 1297.

[11] P.A. Bulliner, V.A. Maroni, T.G. Spiro, Inorg. Chem. 9 (1970) 1887.

[12] G.M. Sheldrick, SHELXS-97, Programme for Solution of Crystal Structures, University of Göttingen, 1997.

[13] G.M. Sheldrick, SHELXL-97, Programme for Crystal Structure Refinement, University of Göttingen, 1997.