

New methods for synthesis of platinum(II) dimethyl sulfide complexes

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Abstract

Different methods for the synthesis of anionic dimethyl sulfide platinum complexes of the type $Q[PtCl_3(Me_2S)]$ (Q = triphenylbenzylphosphonium, Ph_3PBzI , or tetrabutylammonium, Bu_4N) and $[Pt(\mu-Cl)Cl(Me_2S)]_2$ are reported. The compounds $Q[PtCl_3(Me_2S)]$ were prepared by interaction of $[PtCl_4]^{2-}$ with an excess of Me_2S in non-aqueous media, reduction of $[PtCl_5(Me_2S)]^-$ with hydrazine sulfate, bridge-splitting reactions of $(Ph_3PBzI)_2[Pt_2(\mu-Cl)_2Cl_4]$ and $[Pt(\mu-Cl)Cl(Me_2S)]_2$ with two equivalents of Me_2S and $(Ph_3PBzI)Cl$, respectively, and substitution of dimethyl sulfide in *trans*- $[PtCl_2(Me_2S)_2]$. The $[Pt(\mu-Cl)Cl(Me_2S)]_2$ dimer was prepared via reaction of *cis*- $[PtCl_2(Me_2S)_2]$ with two equivalents of silver nitrate followed by separation of $AgCl(s)$ and addition of one equivalent of $K_2[PtCl_4]$. The structure of $(Ph_3PBzI)[PtCl_3(Me_2S)]$ was determined by X-ray single crystal analysis. The compound crystallizes in the space group $P2_1/n$ with $a = 9.746(3)$, $b = 19.511(4)$, $c = 14.966(4)$ Å, $\beta = 100.43(2)^\circ$, $V = 2799.0(9)$ Å³ and $Z = 4$.

Key words: Crystal structures; Platinum complexes; Alkyl sulfide complexes

Introduction

Salts containing the complex anion $[PtCl_3L]^-$ are convenient starting materials for the synthesis of a class of compounds with the general formula $[PtCl_2LL^*]$, where L and L^* denote monodentate, neutral ligands. Complexes of the type $[PtCl_3L]^-$ are also suitable models for studies of the ground-state *trans* influence of L on the Pt–Cl bond length under the constant *cis* influence of two chloride ligands [1–3].

Several methods have been reported for the synthesis of complexes of the type $[PtCl_3L]^-$, for instance substitution of one Cl^- by L in $[PtCl_4]^{2-}$ in a suitable solvent [1, 2, 4], substitution of L by Cl^- in $[PtCl_2L_2]$ [3, 5, 6], reduction of Pt(IV) complexes of the type $[PtCl_5L]^-$ [7–9] and bridge-splitting reactions of $[Pt_2(\mu-Cl)_2Cl_4]^{2-}$ by L [10–12] or of $[Pt(\mu-Cl)ClL]_2$ by Cl^- [13]. Compounds with L = dialkyl sulfide, however, have only been little studied. In the present work, we have developed new and simple preparative procedures giving high yields of compounds containing $[PtCl_3(Me_2S)]^-$

and the bulky cations Ph_3PBzI^+ and Bu_4N^+ . The triphenylbenzylphosphonium salt has been characterized with respect to molecular and crystal structure. The synthetic procedures reported in the literature for one of the precursor compounds, $[Pt(\mu-Cl)Cl(Me_2S)]_2$, are fairly complicated [13, 14]. We have worked out a new, much simpler method for its synthesis in high yield.

Experimental

Chemicals and apparatus

The following reagents and solvents were used: dimethyl sulfide (Merck, for synthesis), hydrazine sulfate (Merck, p.a.), silver nitrate (Janssen Chimica, p.a.), potassium tetrachloroplatinate(II) (Janssen Chimica), dichloromethane (Lab-Scan, analytical reagent), dimethylformamide (Mallinckrodt, analytical reagent), nitromethane (Merck, for synthesis), diethyl ether (Riedel-deHaën, p.a.), toluene (Merck, p.a.), CD_2Cl_2 (Sigma, >99.6 at.% D), $CDCl_3$ (Dr Glaser AG, >99.8 at.% D), $(CD_3)_2NCDO$ (Dr Glaser AG, >99.5 at.% D). Elemental analysis for C, H and S was performed by Mikro Kemi AB (Uppsala, Sweden) and for Pt gravimetrically by the authors. Melting or decomposition points were determined in glass capillaries with an

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electrothermal melting point apparatus. IR spectra were recorded using a Nicolet model 20 SXC FT-IR spectrometer with the samples in KBr pellets. Merck Silica gel 60 F₂₅₄ plates (SiO₂) were used for TLC. ¹H NMR spectra were recorded at 299.4 MHz on a Varian model XL-300 spectrometer at ambient temperature. Single crystal intensity data were collected on an Enraf-Nonius CAD-4 diffractometer.

Structure determination

The intensity data were collected at room temperature. The ω - 2θ scan technique was used and the scan interval, $\Delta\omega$, was extended 25% at both ends for the background measurements. Two standard reflections were measured at regular intervals. A random variation within <3% in the intensities was observed in data collections. Information on the collection and reduction of the data is given in Table 1. The values of I and $\sigma(I)$ were corrected for Lorentz, polarization and absorption effects. The latter was made according to the method by Walker and Stuart [15]. The corrections were in the ranges 0.92–1.20 for $A_{p,s}$ and 0.97–1.04 for A_θ [16]. Cell dimensions were determined by least-squares calculations from the θ angles of 50 reflections for (Ph₃PBzl)[PtCl₃(Me₂S)]. The θ values were obtained as $\theta_{hkl} = (\omega_{hkl} - \omega_{\bar{h}\bar{k}\bar{l}})/2$ with $\omega_{\bar{h}\bar{k}\bar{l}}$ measured at negative θ angle. The compound belongs to Laue class 2/m.

TABLE 1. Crystal data, collection and reduction of intensity data and least-squares refinement

Molecular weight	717.968
Space group	$P2_1/n$
a (Å)	9.746(3)
b (Å)	19.511(4)
c (Å)	14.966(4)
β (°)	100.43(2)
V (Å ³)	2799.0(9)
Z	4
D_x (g cm ⁻³)	1.703
Crystal size (mm)	0.25 × 0.15 × 0.12
λ (Å)	0.71069
μ (mm ⁻¹)	5.50
θ Interval	3.00–23.00
ω - 2θ Scan width, $\Delta\omega$ (°)	1.0 + 0.5 tan θ
$\sigma(I)/I$ Requested in a scan	0.028
Maximum recording time (s)	120
No. measured reflections	4485
No. reflections used in the refinements ($I > 2\sigma(I)$), m	4065
No. parameters refined, n	298
hkl Range	$0 \leq h \leq 10$, $0 \leq k \leq 21$, $-16 \leq l \leq 16$
$R = \Sigma(F_o - F_c)/\Sigma F_o $	0.029
$R_w = [\Sigma w(F_o - F_c)^2/\Sigma F_o ^2]^{1/2}$	0.035
$S = [\Sigma w(F_o - F_c)^2/(m - n)]^{1/2}$	0.981
R_{max}/R_{min}	0.67/0.75
δR slope	1.10
δR intercept	0.01

TABLE 2. Atomic coordinates and isotropic temperature factor coefficients with e.s.d.s for (Ph₃PBzl)[PtCl₃(Me₂S)]

Atom	x/a	y/b	z/c	U_{iso} (Å ²)
Pt	0.50607(4)	0.17988(2)	0.52154(2)	0.0397(1)
Cl(1)	0.36803(24)	0.08353(11)	0.49614(14)	0.0551(8)
Cl(2)	0.39699(25)	0.22451(12)	0.38346(15)	0.0598(9)
Cl(3)	0.63945(29)	0.27679(13)	0.54999(18)	0.0716(10)
S	0.61301(27)	0.13034(12)	0.65102(15)	0.0578(9)
C(1)	0.7910(14)	0.1165(11)	0.6367(11)	0.167(10)
C(2)	0.6270(18)	0.1937(6)	0.7410(8)	0.120(7)
P	0.5562(2)	0.0371(1)	0.2213(1)	0.034(1)
C(10)	0.3724(8)	0.0208(4)	0.1906(5)	0.036(3)
C(11)	0.3230(9)	-0.0299(5)	0.1300(6)	0.053(3)
C(12)	0.1795(11)	-0.0403(5)	0.1033(6)	0.067(4)
C(13)	0.0881(10)	0.0022(6)	0.1360(8)	0.075(5)
C(14)	0.1361(10)	0.0512(6)	0.1958(7)	0.075(5)
C(15)	0.2779(9)	0.0618(4)	0.2257(6)	0.055(4)
C(20)	0.6526(8)	-0.0367(4)	0.1972(5)	0.035(3)
C(21)	0.6840(9)	-0.0455(4)	0.1102(6)	0.050(3)
C(22)	0.7613(10)	-0.1015(4)	0.0930(6)	0.056(4)
C(23)	0.8096(11)	-0.1470(5)	0.1585(8)	0.069(4)
C(24)	0.7786(11)	-0.1405(5)	0.2430(8)	0.068(4)
C(25)	0.6995(9)	-0.0850(4)	0.2641(6)	0.048(3)
C(30)	0.6003(8)	0.1064(4)	0.1530(5)	0.035(3)
C(31)	0.7365(9)	0.1162(4)	0.1430(6)	0.050(3)
C(32)	0.7711(10)	0.1707(5)	0.0943(7)	0.058(4)
C(33)	0.6718(12)	0.2173(5)	0.0567(7)	0.076(5)
C(34)	0.5362(11)	0.2076(5)	0.0655(8)	0.076(4)
C(35)	0.4995(9)	0.1534(4)	0.1133(6)	0.051(3)
C(40)	0.5988(8)	0.0620(4)	0.3399(5)	0.041(3)
C(41)	0.7467(8)	0.0895(4)	0.3647(5)	0.037(3)
C(42)	0.8609(9)	0.0479(4)	0.3915(6)	0.052(3)
C(43)	0.9940(10)	0.0748(5)	0.4091(7)	0.063(4)
C(44)	1.0144(10)	0.1432(5)	0.3977(7)	0.066(4)
C(45)	0.9003(11)	0.1850(5)	0.3722(6)	0.067(4)
C(46)	0.7677(10)	0.1590(4)	0.3550(6)	0.049(3)

TABLE 3. Bond lengths (Å) and bond angles (°) in the [PtCl₃(Me₂S)]⁻ ion

Pt-S	2.246(2)	Pt-Cl(1)	2.303(2)
S-C(1)	1.806(14)	Pt-Cl(2)	2.316(2)
S-C(2)	1.815(12)	Pt-Cl(3)	2.291(3)
Cl(1)-Pt-Cl(2)	89.98(8)	Cl(1)-Pt-Cl(3)	178.26(9)
Cl(1)-Pt-S	87.54(8)	Cl(2)-Pt-Cl(3)	90.51(9)
Cl(2)-Pt-S	176.42(8)	Cl(3)-Pt-S	92.05(9)
Pt-S-C(1)	105.55(55)	Pt-S-C(2)	107.91(42)
C(1)-S-C(2)	104.20(80)		

Systematic extinctions are consistent with the space group $P2_1/n$. The structure was solved by Patterson and difference Fourier methods and refined by full-matrix least-squares calculations employing programs compiled and amended by Lundgren [17]. The hydrogen atoms of the cation at calculated positions (C-H = 0.95 Å) with U_{iso} fixed at 0.08 Å² were included in the final refinement and anisotropic temperature factors were applied to all non-hydrogen atoms. Scattering factors with corrections for anomalous dispersion were taken

from ref. 18. In the final difference Fourier map $\Delta\rho_{\max}=0.67$ and $\Delta\rho_{\min}=-0.75$ e $\text{\AA}^{-3}$. Both peaks are close to the position of Pt. Atomic parameters are given in Table 2 and distances and angles in Table 3.

Synthetic work

$(\text{Ph}_3\text{PBzI})[\text{PtCl}_3(\text{Me}_2\text{S})]$

(i) Reaction of $\text{trans}[\text{PtCl}_2(\text{Me}_2\text{S})_2]$ with $(\text{Ph}_3\text{PBzI})\text{Cl}$

A solution of $\text{trans}[\text{PtCl}_2(\text{Me}_2\text{S})_2]$ (0.374 g, 0.96 mmol) and $(\text{Ph}_3\text{PBzI})\text{Cl}$ (0.374 g, 0.96 mmol) in nitromethane (15 ml) was kept at 100 °C for 1.5 h. It was cooled to room temperature, ether (100 ml) was added and the mixture was placed in a refrigerator (5 °C). After 2 h the solvent was decanted and the orange–yellow precipitate was suspended in ethanol (7 ml) and filtered off. The precipitate was washed on the filter with ethanol (2×3 ml) and ether (3×3 ml) and dried in air at 20–25 °C. Yield of $(\text{Ph}_3\text{PBzI})[\text{PtCl}_3(\text{Me}_2\text{S})]$ was 0.355 g, 52% based on Pt.

(ii) Reduction of $[\text{PtCl}_5(\text{Me}_2\text{S})]^-$ with hydrazine sulfate

Hydrazine sulfate (0.09 g, 0.7 mmol) was added to a suspension of $(\text{Et}_4\text{N})[\text{PtCl}_5(\text{Me}_2\text{S})]$ (0.74 g, 1.3 mmol) in water (15 ml). The mixture was stirred under heating up to 55–60 °C. The reaction mixture was kept at this temperature until no more N_2 bubbles were evolved (c. 5–8 min). The suspension was cooled to room temperature and filtered. A concentrated aqueous solution of $(\text{n-Bu}_4\text{N})\text{Cl}$ or $(\text{Ph}_3\text{PBzI})\text{Cl}$ was added dropwise to the filtrate until precipitation was complete. The solid compound was collected on a filter, washed with water and dried in air at 20–25 °C.

$(\text{n-Bu}_4\text{N})[\text{PtCl}_3(\text{Me}_2\text{S})]$ (yield 28% based on Pt) was isolated as an oily residue from a preparation *in situ* in an aqueous solution of $(\text{Et}_4\text{N})[\text{PtCl}_3(\text{Me}_2\text{S})]$. It crystallizes within 12 h under a layer of ether at 5 °C. The compound has a pale orange colour. It can be recrystallized and obtained in form of orange rod-like crystals from acetone by slow addition of ether at room temperature. $(\text{n-Bu}_4\text{N})[\text{PtCl}_3(\text{Me}_2\text{S})]$ has no characteristic melting point. On heating, the solid phase melts in the interval 57–62 °C. *Anal.* Calc. for $\text{C}_{18}\text{H}_{42}\text{Cl}_3\text{NPtS}$: Pt, 32.2. Found: Pt, 32.1%. ^1H NMR (CD_2Cl_2): 2.37 ppm ($^3J(\text{PtH})$ 47.5 Hz) (lit.: 2.34 ppm ($^3J(\text{PtH})$ 47.3 Hz) in the same solvent [13]). IR spectrum (selected bands, cm^{-1}): 993m and 1037m $\rho(\text{CH}_3)$, 320s and 306m $\nu(\text{PtCl})$. TLC: $R_f=0.65$ ($\text{CHCl}_3\text{:Me}_2\text{CO}=1\text{:}1$ by volume).

$(\text{Ph}_3\text{PBzI})[\text{PtCl}_3(\text{Me}_2\text{S})]$ (yield 34% based on Pt) forms needle-like orange–yellow crystals on evaporation from a chloroform–toluene mixture (1:1). It can be

recrystallized as orange–yellow plates by slow addition of ether to a nitromethane solution. The melting point is 182–183 °C (from $\text{MeNO}_2\text{--Et}_2\text{O}$). *Anal.* Calc. for $\text{C}_{27}\text{H}_{28}\text{Cl}_3\text{PPtS}$: C, 45.2; H, 3.9; S, 4.5. Found: C, 45.6; H, 4.1; S, 4.5%. ^1H NMR (CD_2Cl_2): 2.28 ppm ($^3J(\text{PtH})$ 47.4 Hz). IR spectrum (all bands in the $\nu(\text{PtCl})$ region, cm^{-1}): 347vw, 334m-s, 324m-s, 310m-s, 303m-w. TLC: $R_f=0.63$ ($\text{CHCl}_3\text{:Me}_2\text{CO}=2\text{:}1$, in volume).

(iii) Bridge-splitting of $(\text{Ph}_3\text{PBzI})_2[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_4]$ by Me_2S

$(\text{Ph}_3\text{PBzI})_2[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_4]$ was prepared as described in ref. 19 but dichloromethane was used instead of nitromethane. Dimethyl sulfide (0.035 ml, 0.49 mmol) was added to a solution of $(\text{Ph}_3\text{PBzI})_2[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_4]$ (0.32 g, 0.24 mmol) in dimethylformamide (1.5 ml) at room temperature. The colour of the solution changed from dark red to orange in a few seconds. The reaction mixture was kept at 20–25 °C for 15 min whereafter ether (30 ml) was added. After decanting of the solvent, an oily residue remained. It was kept under a layer of ethanol at 5 °C overnight. Orange–yellow crystals of $(\text{Ph}_3\text{PBzI})[\text{PtCl}_3(\text{Me}_2\text{S})]$ were formed. They were filtered off, washed with ether (2×3 ml) and dried in air at 20–25 °C. Yield of $(\text{Ph}_3\text{PBzI})[\text{PtCl}_3(\text{Me}_2\text{S})]$ was 0.27 g, 77% based on Pt.

(iv) Bridge-splitting of $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\text{Me}_2\text{S})]_2$ by $(\text{Ph}_3\text{PBzI})\text{Cl}$

Triphenylbenzylphosphonium chloride (0.27 g, 0.70 mmol) was added in small portions over 3–5 min to a stirred suspension of $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\text{Me}_2\text{S})]_2$ (0.42 g, 0.64 mmol) in dimethylformamide (15 ml). After the addition of $(\text{Ph}_3\text{PBzI})\text{Cl}$, the reaction mixture turned homogeneous and orange in colour. The solution was kept at 20–25 °C for 15 min whereafter ether (40 ml) was added. After decanting the solvent, the oily residue was covered with a layer of ethanol, and left at room temperature for 10–15 min. The orange–yellow precipitate formed was filtered off, washed on a filter with ether (2×3 ml), and dried in air at 20–25 °C. Yield of $(\text{Ph}_3\text{PBzI})[\text{PtCl}_3(\text{Me}_2\text{S})]$ was 0.77 g, 84% based on Pt.

(v) Reaction of $(\text{Ph}_3\text{PBzI})_2[\text{PtCl}_4]$ with a stoichiometric amount of Me_2S

$(\text{Ph}_3\text{PBzI})_2[\text{PtCl}_4]$ was prepared as described in ref. 20. Dimethyl sulfide (0.11 ml, 1.36 mmol) was added to a solution of $(\text{Ph}_3\text{PBzI})_2[\text{PtCl}_4]$ (1.42 g, 1.36 mmol) in dichloromethane (20 ml). After equilibration (24 h), four new compounds were identified in the reaction mixture by TLC: $(\text{Ph}_3\text{PBzI})[\text{PtCl}_3(\text{Me}_2\text{S})]$, *trans*- and *cis*- $[\text{PtCl}_2(\text{Me}_2\text{S})_2]$, $(\text{Ph}_3\text{PBzI})\text{Cl}$ and the starting material, $(\text{Ph}_3\text{PBzI})_2[\text{PtCl}_4]$.

Single crystals of $(\text{Ph}_3\text{PBzI})[\text{PtCl}_3(\text{Me}_2\text{S})]$ were prepared from this mixture as follows. The mixture was dissolved in a chloroform–toluene mixture (1:1 by volume). After 12 h of evaporation at ambient conditions, two types of crystals were formed: yellow plates of $\text{trans-}[\text{PtCl}_2(\text{Me}_2\text{S})_2]$ and orange–yellow needles of $(\text{Ph}_3\text{PBzI})[\text{PtCl}_3(\text{Me}_2\text{S})]$. A single crystal of the latter was used for the crystallographic study. Attempts to obtain single crystals suitable for X-ray analysis directly by evaporation of a clean $(\text{Ph}_3\text{PBzI})[\text{PtCl}_3(\text{Me}_2\text{S})]$ solution failed.

(vi) Reaction of $(\text{Ph}_3\text{PBzI})_2[\text{PtCl}_4]$ with a large excess of Me_2S

$(\text{Ph}_3\text{PBzI})_2[\text{PtCl}_4]$ (1.27 g, 1.22 mmol) and dimethyl sulfide (1.78 ml, 24.3 mmol) were refluxed for 10 min in 7 ml of dichloromethane (chloroform can be used instead of dichloromethane). The solvent was removed *in vacuo*, and ethanol (10 ml) was added to the residue. The yellow precipitate was filtered off, washed on the filter with ethanol (2×2 ml) and ether (3×2 ml) and dried in air at room temperature. $\text{trans-}[\text{PtCl}_2(\text{Me}_2\text{S})_2]$ (0.44 g) obtained in this way contains less than 5% of $(\text{Ph}_3\text{PBzI})[\text{PtCl}_3(\text{Me}_2\text{S})]$ (as estimated from integration of the peaks in the ^1H NMR spectrum of the mixture in CDCl_3).

$[\text{Pt}(\mu\text{-Cl})\text{Cl}(\text{Me}_2\text{S})]_2$

(vii) Halide abstraction from $\text{cis-}[\text{PtCl}_2(\text{Me}_2\text{S})_2]$ followed by addition of $\text{K}_2[\text{PtCl}_4]$

$\text{cis-}[\text{PtCl}_2(\text{Me}_2\text{S})_2]$ (2.16 g, 5.53 mmol) and AgNO_3 (1.88 g, 11.07 mmol) were suspended in water (60 ml) and the mixture was stirred for about 24 h at 20–25 °C. After filtration of precipitated AgCl , a solution of $\text{K}_2[\text{PtCl}_4]$ (2.30 g, 5.53 mmol) in water (10 ml) was added to the greenish-yellow mother liquor. The suspension obtained was kept under stirring for 2 h. The precipitate formed was filtered off, washed on a filter with water (2×3 ml) and acetone (3×3 ml) and dried in air at 20–25 °C. Yield of $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\text{Me}_2\text{S})]_2$ was 2.79 g (77%, based on the starting $\text{cis-}[\text{PtCl}_2(\text{Me}_2\text{S})_2]$).

The complex obtained has an orange–yellow colour. The melting point is 177–180 °C with decomposition (m.p. lit. is 200 °C with decomposition [14]). *Anal.* Calc. for $\text{C}_4\text{H}_{12}\text{Cl}_4\text{Pt}_2\text{S}_2$: C, 7.3; H, 1.8; S, 9.8. Found: C, 7.6; H, 1.9; S, 10.2%. The ^1H NMR spectrum is described below. IR spectrum (selected bands, cm^{-1}): 339s and 322sh $\nu(\text{PtCl})$ (lit. 338s and 325sh in *nujol* [14]).

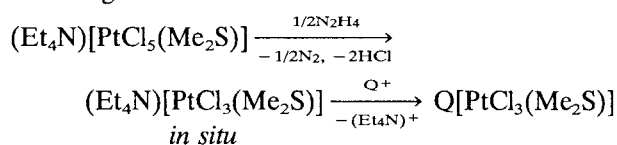
Discussion

Anionic-type compounds $Q[\text{PtCl}_3(\text{Me}_2\text{S})]$, where Q denotes $n\text{-Bu}_4\text{N}$ and Ph_3PBzI

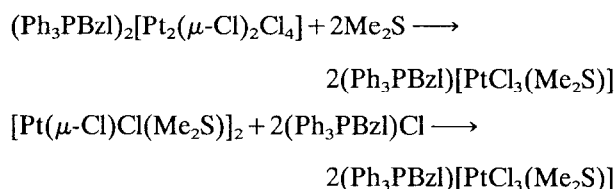
It is well known that the reaction of $\text{K}_2[\text{PtCl}_4]$ with dimethyl sulfide in water leads to a rapid precipitation

of a mixture of $\text{cis-}[\text{PtCl}_2(\text{Me}_2\text{S})_2]$, $\text{trans-}[\text{PtCl}_2(\text{Me}_2\text{S})_2]$ and $[\text{Pt}(\text{Me}_2\text{S})_4][\text{PtCl}_4]$ [21, 22]. However, the present experiments show that the reaction of $[\text{PtCl}_4]^{2-}$ with one equivalent of dimethyl sulfide in organic solvents results in a mixture of $(\text{Ph}_3\text{PBzI})[\text{PtCl}_3(\text{Me}_2\text{S})]$ as the main product, and trans- and $\text{cis-}[\text{PtCl}_2(\text{Me}_2\text{S})_2]$ together with unreacted starting Pt material. A large excess of dimethyl sulfide in this reaction leads mainly to $\text{trans-}[\text{PtCl}_2(\text{Me}_2\text{S})_2]$, and only very small amounts of $(\text{Ph}_3\text{PBzI})[\text{PtCl}_3(\text{Me}_2\text{S})]$ are formed. It was also observed that in nitromethane solution, one dimethyl sulfide in $\text{trans-}[\text{PtCl}_2(\text{Me}_2\text{S})_2]$ is substituted by chloride with formation of $(\text{Ph}_3\text{PBzI})[\text{PtCl}_3(\text{Me}_2\text{S})]$. This reaction is useful for the synthesis of compounds of the type $Q[\text{PtCl}_3(\text{R}_2\text{S})]$, due to its simplicity, accessibility of starting materials, and good yield.

Another method used to synthesize $Q[\text{PtCl}_3(\text{Me}_2\text{S})]$ is the reduction of $Q[\text{Pt}^{\text{IV}}\text{Cl}_5(\text{Me}_2\text{S})]$ according to the following scheme:



This method is more complicated and time-consuming but might be useful as an alternative. Probably, the most general method for synthesis of $Q[\text{PtCl}_3(\text{Me}_2\text{S})]$ is reaction between the bridged compounds $Q_2[\text{Pt}_2(\mu\text{-Cl})_2\text{Cl}_4]$ or $[\text{PtL}(\mu\text{-Cl})\text{Cl}]_2$ with two equivalents of L or Q^+Cl^- , according to methods (iii) and (iv) described above. These reactions have been successfully used for the synthesis of $(n\text{-Pr}_4\text{N})[\text{PtCl}_3(\text{Me}_2\text{S})]$ [14] and $(n\text{-Bu}_4\text{N})[\text{PtCl}_3(\text{Me}_2\text{S})]$ [13]. The present study shows that $(\text{Ph}_3\text{PBzI})[\text{PtCl}_3(\text{Me}_2\text{S})]$ can be easily and quickly obtained with good yield in accordance with the following reactions:



The final product of the second reaction is very clean with no by-products detectable by TLC. Apparently, it may be attributed to a more accurate addition of the solid triphenylbenzylphosphonium chloride in this method. However, previous methods for the preparation of the precursor $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\text{Me}_2\text{S})]_2$ [13, 14, 23] are complicated. The simple procedure for synthesis of this bridged complex described here makes the bridge-splitting reaction useful for synthesis.

The structure of $(\text{Ph}_3\text{PBzI})[\text{PtCl}_3(\text{Me}_2\text{S})]$ is composed of $(\text{Ph}_3\text{PBzI})^+$ and $[\text{PtCl}_3(\text{Me}_2\text{S})]^-$ ions, Figs. 1, 2. The closest contacts between the phenyl rings of the cation

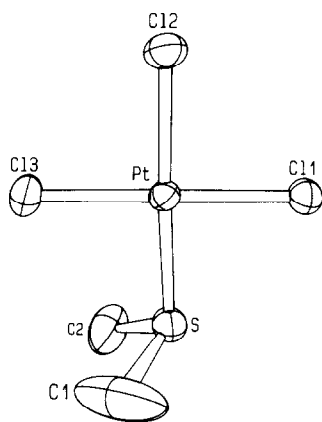


Fig. 1. Perspective view of the $[\text{PtCl}_3(\text{Me}_2\text{S})]^-$ ion with the atomic numbering.

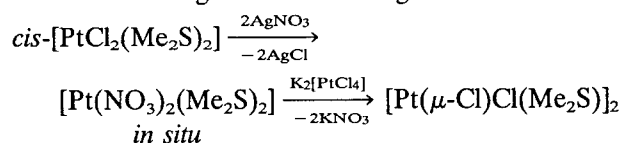
and the Cl atoms are normal van der Waals contacts. One of the benzyl carbon atoms is so close to the Pt atom (3.79 Å), that an agostic $\text{C-H}\cdots\text{Pt}$ interaction cannot be excluded. Three Cl and one S atom form a pseudo-planar coordination polyhedron around the Pt atom. The deviations from a least-squares plane through these atoms are: Pt 0.0067(3), Cl(1) 0.041(2), Cl(2) -0.045(2), Cl(3) 0.040(3), S -0.043(2) Å.

The sulfur atoms bind to Pt through one of the lone pairs, the angle Pt-S-C being between 105 and 109°. Bond distances and angles within the Me_2S molecules are normal (Table 3) and agree with those observed in other compounds [24, 25]. The Pt-S bond is substantially longer in $(\text{Ph}_3\text{PBzI})[\text{PtCl}_3(\text{Me}_2\text{S})]$, 2.246(2) Å, than that in $(\text{Ph}_3\text{PBzI})[\text{PtCl}_3(\text{Me}_2\text{SO})]$, 2.185(5) Å [26].

The same situation is observed in $\text{cis-}[\text{PtCl}_2(\text{Me}_2\text{S})_2]$, 2.27 Å [25], compared to $\text{cis-}[\text{PtCl}_2(\text{Me}_2\text{SO})_2]$, 2.24 Å [27, 28]. It has been noticed previously [29] that comparable Pt-S bond distances in sulfoxide complexes are shorter than in thioether ones. The Pt-Cl(2) bond distance in $[\text{PtCl}_3(\text{Me}_2\text{S})]^-$ is significantly longer (2.316(2) Å) than the two Pt-Cl distances in *cis* position to S (Table 3).

Bridged complexes

Dimers $[\text{Pt}(\mu\text{-X})\text{XL}]_2$, X = halide or pseudohalide, play an important role in the coordination chemistry of Pt(II). Reaction with various ligands L^* in non-aqueous solvents splits the bridge, giving mononuclear complexes $[\text{PtX}_2\text{LL}^*]$, which are not always easily obtained by other methods. The reaction is attributed to the fact that the bridging halide ligands are less strongly bound to the Pt(II) ion than the terminal ones [19]. We have shown that $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\text{Me}_2\text{S})]_2$ can be obtained according to the following scheme:



The proposed method has some advantages over previously described ones. The starting materials are simple and easily accessible compounds compared to the ones used in the method described in refs. 13 and 23, where a three-step procedure with $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\text{C}_2\text{H}_4)]_2$ as starting material was used. Moreover, $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\text{Me}_2\text{S})]_2$ can be isolated with good yield (77%)

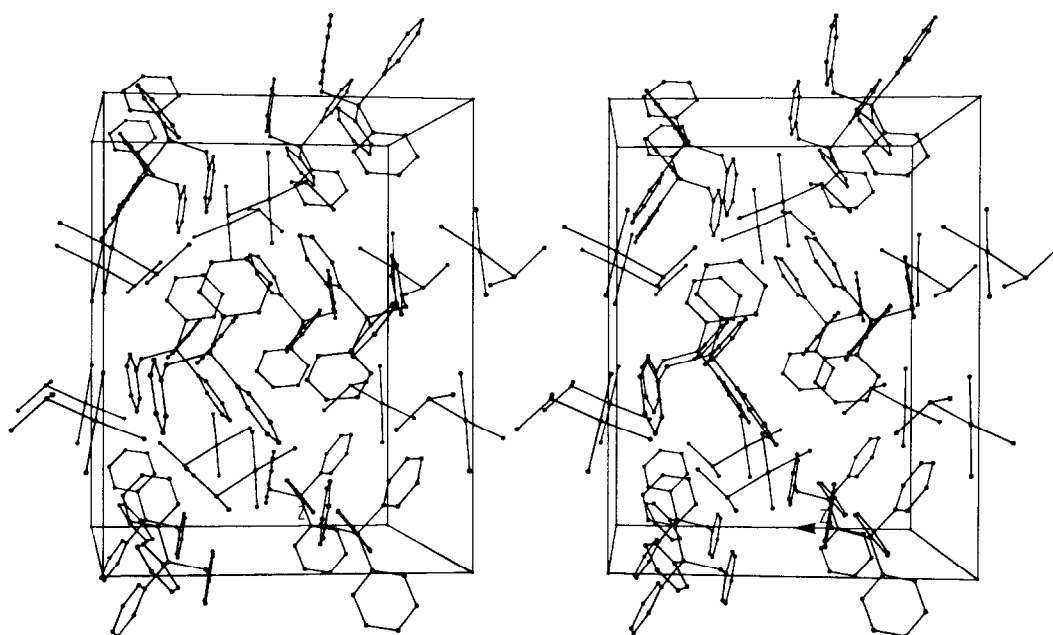
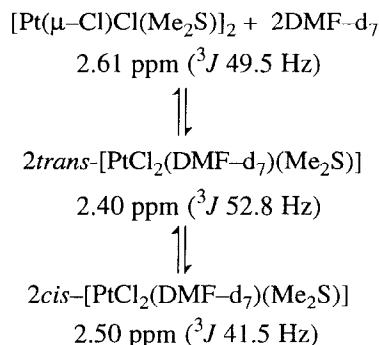


Fig. 2. Stereoscopic pair of drawings of the unit cell of $(\text{Ph}_3\text{PBzI})[\text{PtCl}_3(\text{Me}_2\text{S})]$.

compared to the reaction of $[\text{PtCl}_2(\text{Me}_2\text{S})_2]$ with PtCl_2 in xylene or halide abstraction from $(n\text{-Pr}_4\text{N})[\text{PtCl}_3(\text{Me}_2\text{S})]$ using MeSO_3F , which are reported to give yields of only 16 and 40%, respectively [14].

The complex $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\text{Me}_2\text{S})]_2$ is a yellow–orange compound practically insoluble in water and common organic solvents. The authors of ref. 14 reported that they could not find a solvent in which $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\text{Me}_2\text{S})]_2$ is sufficiently soluble to give ^1H NMR spectra even with spectrum accumulation. Our attempts to measure ^1H NMR spectra in DMF-d_7 gave the following results. In a ^1H NMR spectrum measured 10 min after the dissolution of $[\text{Pt}(\mu\text{-Cl})\text{Cl}(\text{Me}_2\text{S})]_2$ there are signals at 2.61 ppm ($^3J(\text{PtH})$ 49.5 Hz) and 2.40 ppm ($^3J(\text{PtH})$ 52.8 Hz) and a small peak at 2.50 ppm ($^3J(\text{PtH})$ 41.5 Hz). Integration of these resonances gave the relative intensity ratio 0.72:1.00:0.03, respectively. After 7 days this ratio was 0.48:1.00:0.28, and after establishment of equilibrium (1 month) 0.42:1.00:0.29. The reaction can most likely be described as follows:



Dimethylformamide is a very weak donor towards Pt(II) [30]. In most cases, such weakly bound solvent ligands can be easily substituted by ligands with higher donor ability [31, 32]. Therefore, $[\text{PtCl}_2(\text{Me}_2\text{S})(\text{DMF})]$ generated *in situ* may also be a suitable starting material for synthesis of other platinum complexes, by substitution reactions performed directly in the homogeneous liquid phase.

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