

BIS(DIMETHYLARSINO)SULPHIDE (dmas) COMPLEXES OF THE TRIMETHYLPLATINUM HALIDES: THE SYNTHESIS AND CHARACTERIZATION OF *fac*-[(PtXMe₃)(dmas)₂] AND THE BINUCLEAR [(PtXMe₃)₂(dmas)] (X = Cl, Br, I) COMPLEXES, THE CRYSTAL AND MOLECULAR STRUCTURE OF [(PtBrMe₃)₂(dmas)] *

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Summary

The ligand bis(dimethylarsino)sulphide (dmas) undergoes reaction with the tetrameric trimethylplatinum halides to produce the mononuclear type of complex *fac*-[(PtXMe₃)(dmas)₂] in which each ligand is bonded to the platinum centre by only one arsenic atom, and the binuclear type of complex [(PtXMe₃)₂(dmas)] in which the two PtXMe₃ moieties are bridged both by halogen and the dmas molecule. There is no perceivable fluxionality in the mononuclear molecules; but rapid reversal of the Pt–X–Pt–As–S–As six-membered ring is observed in the binuclear species.

An X-ray diffraction study of the structure of [(PtBrMe₃)₂(dmas)] is reported.

Introduction

Bis(dimethylarsino)sulphide, Me₂AsSAsMe₂ (dmas), has lone-pair electrons on the sulphur and arsenic atoms and therefore the possibility exists that it may coordinate to metal centres in a variety of ways; and if such structures are of comparable energies fluxional processes may occur. There are two isolated reports [1,2] on the coordination chemistry of dmas in the literature. It has been shown to behave as a bidentate bridging ligand in (CO)₅M(dmas)M(CO)₅ (M = Cr [1], W [1,2]) and in a monodentate fashion in the related (CO)₅M(dmas) complexes [1] (M = Cr, Mo, W). In all of these metal carbonyl derivatives arsenic is the donor

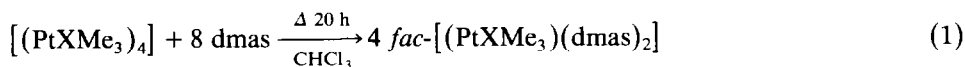
* Dedicated to Professor Geoffrey Coates upon the occasion of his seventieth birthday.

atom in the ligand. The tetrameric trimethylplatinum(IV) halides react readily with both arsenic and sulphur containing ligands to form either the mononuclear products *fac*-[(PtXMe₃)L₂], where L₂ may be two monodentate ligands [3,4] or a bidentate ligand [5,6], or the binuclear halogen and ligand bridged species [5] [(PtXMe₃)₂L₂]. As part of a continuing research program on the arsenic-sulphur electron-rich ligands, we have examined the reactions of dmas with the tetrameric trimethylplatinum(IV) halides.

Results and discussion

Preparation and properties of complexes

Bis(dimethylarsino)sulphur reacted readily in chloroform solution under reflux with the tetrameric trimethylplatinum(IV) halides. Dependent upon reactant ratios and reaction times, different types of product may be isolated. The reaction of excess dmas (greater than two equivalents per platinum centre) produced after 20 h reaction good yields of the mononuclear complexes *fac*-[(PtXMe₃)(dmas)₂] (eq. 1).



(X = Cl, Br, I)

These mononuclear complexes were white/pale yellow crystalline solids readily soluble in all common organic solvents, perfectly air stable in the solid state, but undergoing slow decomposition in solution. They have been characterized by elemental analyses (Table 1) and NMR spectroscopy (vide infra). ¹H NMR studies show that the dmas ligands are monodentate, coordinating to the metal atom by the arsenic lone-pair of electrons with a *fac*-orientation about the platinum(IV) centre (Fig. 1A). Heating solutions of the complexes in toluene-*d*₈ to decomposition

TABLE 1
PREPARATION AND CHARACTERISATION OF dmas COMPLEXES OF THE TRIMETHYL-
PLATINUM(IV) HALIDES

Product	Reaction time (h) (Reflux CHCl ₃)	Reactant ratio dmas/Pt	Yield (%)	M.p. (°C)	Elemental analysis (Found (calc) (%))	
					C	H
[(PtClMe ₃)(dmas) ₂]	20	> 2/1	31	78–80 ^b	17.1 (17.4)	4.4 (4.4)
[(PtBrMe ₃)(dmas) ₂]	20	> 2/1	40	81–82 ^b	16.6 (16.4)	4.0 (4.1)
[(PtI Me ₃)(dmas) ₂]	20	> 2/1	61	98–100 ^b	15.8 (15.5)	3.9 (3.9)
[(PtClMe ₃) ₂ (dmas)]	2	1/2	44	156–158 ^b	15.3 (15.2)	3.9 (3.8)
[(PtBrMe ₃) ₂ (dmas)]	2	1/2	55	170 (dec.) ^b	13.7 (13.6)	3.4 (3.4)
[(PtI Me ₃) ₂ (dmas)]	2	1/2	63	155 (dec.) ^a	12.4 (12.3)	3.1 (3.1)

^a Pale yellow does not melt. ^b White crystalline solids.

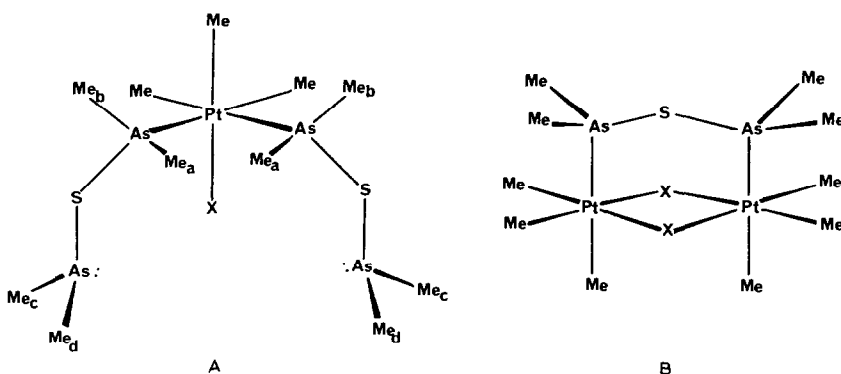
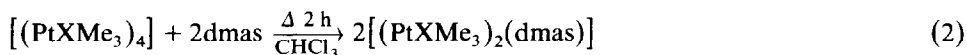


Fig. 1. Schematic structures of: (A) *fac*-[(PtXMe₃)(dmas)₂] showing diastereotopic methyl groups Me_a, Me_b and Me_c, Me_d; and (B) [(PtXMe₃)₂(dmas)].

temperature ($\sim 60^\circ\text{C}$) gave no spectral evidence to suggest fluxionality (such as intramolecular exchange of non-coordinated ligand arsenic atoms with metal bonded arsenic atoms).

The complexes *fac*-[(PtXMe₃)(dmas)₂] have un-utilized lone-pair electrons on arsenic and sulphur atoms, and it was of interest to see if these could be brought into coordination by reaction of the complexes with further trimethylplatinum(IV) halide. Reaction did indeed occur in chloroform under reflux to produce a mixture of trimethylplatinum containing products (observed from ¹H NMR spectra), which was similar to a mixture obtained by direct action of dmas and [(PtXMe₃)₄] in ligand/Pt ratio of 1/1. Efforts to separate the mixture were not pursued, as we quickly found good conditions for high yields of the new type of complex. Under reflux in chloroform for 2 h only, dmas and [(PtXMe₃)₄] in a ligand/Pt ratio of 1/2 produced the binuclear complexes [(PtXMe₃)₂(dmas)] (eq. 2).



(X = Cl, Br, I)

These binuclear complexes have the trimethylplatinum groups joined by two bridging halides and the dmas ligand (Fig. 1B). They have been characterized by elemental analyses (Table 1), ¹H and ¹³C NMR spectra, and for X = Br by X-ray diffraction measurements. The binuclear compounds are white, air-stable crystalline solids which are readily soluble in all common organic solvents.

Molecular structure of [(PtBrMe₃)₂(dmas)]

A drawing of the molecular structure of [(PtBrMe₃)₂(dmas)] is shown in Fig. 2; interatomic distances and angles are recorded in Table 2. The structure is not dissimilar to those reported [7,8] for [(PtXMe₃)₂(MeSeSeMe)] (X = Br, I). The two platinum atoms of the molecule are octahedrally coordinated by three *fac*-methyl groups, two (bridging) bromines and an arsenic atom.

The Pt---Pt distance is 3.790 Å which compares [7,8] with 3.740(3) and 3.901(2) Å respectively in [(PtBrMe₃)₂(MeSeSeMe)] and [(PtI Me₃)₂(MeSeSeMe)] confirming the dependence of this distance upon the nature of the bridging ligands. The

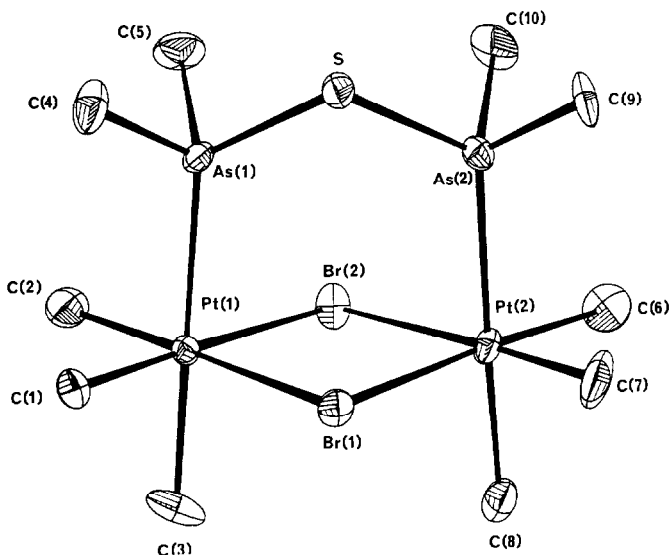


Fig. 2. Drawing of molecular structure of $[(\text{PtBrMe}_3)_2(\text{dmas})]$ with atomic numbering scheme. Pt---Pt distance 3.790 Å; As---As distance 3.516(6) Å. Thermal ellipsoids drawn at 30% probability level.

TABLE 2. INTERNUCLEAR DISTANCES (Å) AND ANGLES ($^\circ$) FOR $[(\text{PtBrMe}_3)_2(\text{dmas})]$ (with e.s.d.'s in parentheses)

Br(1)–Pt(1)	2.611(5)	Br(2)–Pt(1)	2.638(5)
As(1)–Pt(1)	2.493(4)	C(1)–Pt(1)	2.009(21)
C(2)–Pt(1)	2.047(22)	C(3)–Pt(1)	2.084(21)
Br(1)–Pt(2)	2.613(5)	Br(2)–Pt(2)	2.653(5)
As(2)–Pt(2)	2.493(4)	C(6)–Pt(2)	1.985(21)
C(7)–Pt(2)	1.990(23)	C(8)–Pt(2)	2.037(21)
S–As(2)	2.223(7)	C(9)–As(2)	1.945(19)
C(10)–As(2)	1.943(20)	S–As(1)	2.232(7)
C(4)–As(1)	1.952(20)	C(5)–As(1)	1.995(21)
Br(2)–Pt(1)–Br(1)	87.6(2)	As(1)–Pt(1)–Br(1)	92.6(2)
As(1)–Pt(1)–Br(1)	88.1(2)	C(1)–Pt(1)–Br(1)	90.9(7)
C(1)–Pt(1)–Br(2)	117.9(6)	C(1)–Pt(1)–As(1)	93.5(7)
C(2)–Pt(1)–Br(1)	178.3(6)	C(2)–Pt(1)–Br(2)	91.4(8)
C(2)–Pt(1)–As(1)	88.7(6)	C(2)–Pt(1)–C(1)	90.0(10)
C(3)–Pt(1)–Br(1)	88.6(7)	C(3)–Pt(1)–Br(2)	89.9(7)
C(3)–Pt(1)–As(1)	177.6(6)	C(3)–Pt(1)–C(1)	88.5(9)
C(3)–Pt(1)–C(2)	90.0(9)	Br(2)–Pt(2)–Br(1)	87.3(2)
As(2)–Pt(2)–Br(1)	93.0(2)	As(2)–Pt(2)–Br(2)	88.4(2)
C(6)–Pt(2)–Br(1)	176.1(7)	C(6)–Pt(2)–Br(2)	95.2(8)
C(6)–Pt(2)–As(2)	90.1(7)	C(7)–Pt(2)–Br(1)	89.8(8)
C(7)–Pt(2)–Br(2)	177.0(7)	C(7)–Pt(2)–As(2)	92.4(8)
C(7)–Pt(2)–C(6)	87.7(11)	C(8)–Pt(2)–Br(1)	89.3(7)
C(8)–Pt(2)–Br(2)	91.7(7)	C(8)–Pt(2)–As(2)	177.8(6)
C(8)–Pt(2)–C(6)	87.6(9)	C(8)–Pt(2)–C(7)	87.6(10)
Pt(2)–Br(1)–Pt(1)	93.0(2)	Pt(2)–Br(2)–Pt(1)	91.5(2)
S–As(2)–Pt(2)	121.8(2)	C(9)–As(2)–Pt(2)	117.8(8)
C(9)–As(2)–S	95.7(7)	C(10)–As(2)–Pt(2)	114.4(8)
C(10)–As(2)–S	102.8(8)	C(10)–As(2)–C(9)	100.9(10)
S–As(1)–Pt(1)	122.1(3)	C(4)–As(1)–Pt(1)	117.0(8)
C(4)–As(1)–S	96.5(7)	C(5)–As(1)–Pt(1)	112.8(7)
C(5)–As(1)–S	104.0(7)	C(5)–As(1)–C(4)	101.4(10)
As(1)–S–As(2)	104.2(3)		

Pt–Br–Pt angles have a mean value of 92.3° and the Pt–Br bond lengths are in the range 2.611(5)–2.653(5) Å. These are larger than those in $[\text{Pt}_2\text{Br}_6]^{2-}$ (2.413(7)–2.451(7) Å [9]), but are comparable with those in $[(\text{PtBrMe}_3)_2(\text{MeSeSeMe})]$.

The configuration about each platinum atom is approximately octahedral with interbond angles in the ranges $87.3(2)$ (Br–Pt–Br) – $93.5(7)^\circ$ (C–Pt–As) and $176.1(7)$ – $178.3(6)^\circ$ (both C–Pt–Br). The non-bonding As---As distance is 3.516(6) Å, only 0.12 Å smaller than the Pt---Pt contact, thus enabling the Pt_2Br_2 unit to be close to planar. This is in marked contrast to the Pt_2Br_2 unit in $[(\text{PtBrMe}_3)_2(\text{MeSeSeMe})]$, where the Se–Se bond length is 1.19 Å shorter than the Pt–Pt distance with a resulting fold about the Br–Br vector, with an angle of 29° between the planes of the two Br–Pt–Br moieties in that molecule [7].

Several points of interest are notable for the bondings about arsenic. The As–Pt bond distances are equivalent at 2.493(4) Å and the As–S distances average at 2.22 Å (2.223(7) and 2.232(7) Å), each of these values corresponds closely with values predicted from single bond covalent radii data for As, Pt and S [10]. The $\text{Pt}_2\text{As}_2\text{S}$ fragment is not planar, and the sulphur atom is displaced from the Pt_2As_2 plane towards Br(1). The As–S–As bond angle at $104.2(3)^\circ$ is close to tetrahedral, but the S–As–Pt bond angles are somewhat larger at $121.8(2)$ and $122.1(3)^\circ$. This distortion from tetrahedral geometry about arsenic is also apparent in the arsenic methyl positions, where the methyl groups are pulled away from the platinum centres (C–As–Pt angles range from $112.8(7)$ to $117.8(8)^\circ$), towards each other (C–As–C angles $101.4(10)$ and $100.9(10)^\circ$) and towards the sulphur atom (C–As–S angles range from $95.7(7)$ to $104.0(7)^\circ$). As a consequence of the open envelope conformation of the $\text{Pt}_2\text{As}_2\text{S}$ ring the arsenic methyls C(4) and C(9) are equivalent, but are different from the two other equivalent arsenic methyl pair C(5) and C(10).

NMR studies

^1H and ^{13}C data for the bimetallic compounds $[(\text{PtXMe}_3)_2(\text{dmas})]$ are reported in Table 3. The solid state structure for these compounds, as reported for X = Br shows symmetry close to C_s , but room temperature ^1H and ^{13}C NMR spectra are consistent with C_{2v} symmetry. The likely explanation for these spectra indicating higher symmetry, is that on the NMR time scale the six-membered Pt–X–Pt–As–S–As ring(s) is undergoing rapid reversal by the sulphur atom flipping from one side to the other. This renders the $\text{Pt}_2\text{As}_2\text{S}$ moiety effectively planar, and the molecule overall C_{2v} . The three ^1H signals (all coupled to ^{195}Pt) of relative intensities 4/4/2 are due to arsenic-methyls, platinum-methyls *trans* to halogen, and platinum-methyls *trans* to arsenic respectively. The $^2J(^{195}\text{Pt}-\text{C}-^1\text{H})$, $^3J(^{195}\text{Pt}-\text{As}-\text{C}-^1\text{H})$, $^1J(^{195}\text{Pt}-^{13}\text{C})$ and $^2J(^{195}\text{Pt}-\text{As}-^{13}\text{C})$ coupling constants that we observe are all in line with those reported for related trimethylplatinum(IV) complexes of Me_2AsPh and Me_2AsSMe behaving as arsenic donor ligands [4,11,12].

We have performed low temperature ^1H NMR experiments on these complexes with the aim of slowing down or stopping the sulphur ring-flip and obtaining accurate data for the activation energy of this process. However, in toluene- d_8 solution at -90°C there were no spectral changes, indicating the process to be still very rapid, with an activation energy too low for us to measure.

The ^1H NMR data for the mononuclear complexes *fac*- $[(\text{PtXMe}_3)(\text{dmas})_2]$ are noted in Table 3, and the ^1H spectrum for X = Cl is illustrated in Fig. 3. This shows five individual resonances with relative intensities of 1/2/4/2/2, from high to low

TABLE 3

¹H NMR DATA FOR THE dmas COMPLEXES OF THE TRIMETHYLPLATINUM(IV) HALIDES ^a

Complex	Platinum-CH ₃				Arsenic-CH ₃		
	<i>trans</i> -halide		<i>trans</i> -arsenic		Coordinated AsMe ₂ Free AsMe ₂		
	δ	² J(PtH)	δ	² J(PtH)	δ	³ J(PtH)	
[(PtClMe ₃)(dmas) ₂]	0.89	73.6	1.19	64.6	1.93	5.0	1.46 ^e
					1.77	5.6	
[(PtBrMe ₃)(dmas) ₂]	1.00	72.9	1.27	64.7	1.98	5.3	1.46 ^e
					1.80	5.8	
[(PtI Me ₃)(dmas) ₂]	1.17	70.6	1.40	65.4	2.08	5.5	1.46 ^e
					1.86	6.0	
[(PtClMe ₃) ₂ (dmas)] ^b	0.90	76.8	1.63	64.9	1.72	5.3	–
[(PtBrMe ₃) ₂ (dmas)] ^c	0.98	76.2	1.79	65.4	1.75	5.5	–
[(PtI Me ₃) ₂ (dmas)] ^d	1.12	74.3	2.11	66.9	1.83	5.6	–

^a Recorded at room temperature in CDCl₃ solution with tms as reference material. δ in ppm; J in Hz.^b δ(¹³C): -2.73, ¹J(PtC) 697.2 Hz, Pt-methyl *trans* Cl; +16.42, ¹J(PtC) 600.8 Hz, Pt-methyl *trans* As; +12.11, ²J(PtC) 10.3 Hz, Me₂As; (CDCl₃). ^c δ(¹³C): +1.61, ¹J(PtC) 682.9 Hz, Pt-methyl *trans* Br; +14.51, ¹J(PtC) 590.1 Hz, Pt-methyl *trans* As; +12.06, ²J(PtC) 10.2 Hz, Me₂As; (CDCl₃). ^d δ(¹³C): +7.10, ¹J(PtC) 651.8 Hz, Pt-methyl *trans* I; +10.00, ¹J(PtC) 576.5 Hz, Pt-methyl *trans* As; +12.12, ²J(PtC) 9.3 Hz, Me₂As; (CDCl₃). ^e Two partially resolved singlets centred at δ 1.46 ppm.

field respectively. The signal of highest intensity appears as two barely resolved singlets (separation < 0.01 ppm), and the other four signals all show ¹⁹⁵Pt coupling. The number of signals and their relative intensities is consistent only with a *fac* orientation of ligands around the Pt^{IV} centre, and with the two dmas ligands behaving in a monodentate manner via arsenic (Fig. 1A). The two signals at highest field in the spectrum illustrated in Fig. 3 are assigned to the methyl-platinum resonances with the one at highest field (relative intensity 1) assigned to the methyl-platinum *trans* to chloride, and the one at lower field (relative intensity 2)

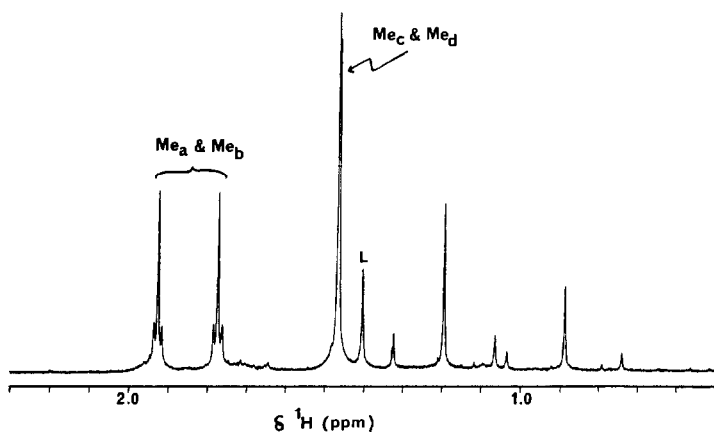


Fig. 3. 250 MHz ¹H spectrum of *fac*-[(PtClMe₃)(dmas)₂] showing anisochronous methyl groups as illustrated in Fig. 1(A). The resonance L arises from free ligand (dmas) impurity in sample.

assigned to the two methyl-platinum groups *trans* to arsenic. The three remaining signals are assigned to ligand methyl resonances. With the absence of symmetry planes through either of the Pt–As bonds, both ligand arsenic atoms are prochiral centres with consequent diastereotopic methyl groups [13]. Thus the two resonances at lowest field (of relative intensity 2/2) show small coupling to ^{195}Pt and these are assigned to the anisochronous arsenic-methyls of the coordinating arsenic(s) of the dmas ligands (Me_a and Me_b in Fig. 1A), whilst the resonance composed of two barely resolved singlets (relative intensity 4) is assigned to the arsenic-methyls of the uncoordinated arsenic atoms. $^5J(^{195}\text{Pt}\text{--As}\text{--S}\text{--As}\text{--C}\text{--}^1\text{H})$ was not detectable for this resonance, but the observed doublet results from the fact that albeit distanced from the asymmetric centre, the un-coordinated arsenic atom is also a prochiral centre. Magnitudes of the various $^nJ(^{195}\text{Pt}\text{--}^1\text{H})$ couplings are comparable to the corresponding values reported [4,6,11] for related *fac*- $[(\text{PtXMe}_3)(\text{Me}_2\text{AsR})_2]$ complexes.

The chemical shifts of the arsenic-methyl protons for the coordinating arsenic centre in both the mononuclear and binuclear complexes is ca. 0.5 ppm (in CDCl_3) downfield of the free ligand (δ 1.39), but in the bis(monodentate) dmas complexes the ‘free’ arsenic-methyl protons are shifted downfield by only ca. 0.1 ppm. Such shifts are closely analogous to those reported [1] in $[\text{Cr}(\text{CO})_5 \text{dmas}]$.

Experimental

General

Reactions were carried out using standard Schlenk conditions under nitrogen, and solvents were dried and distilled under nitrogen from the appropriate drying agent (CHCl_3 , CaH_2 ; 60–80 °C light petroleum, Na benzophenoneketyl) before use. Bis(dimethylarsino)sulphide (dmas) was prepared by a literature [14] method and the tetrameric trimethylplatinum halides were prepared by established routines [15–17]. Preparations of the complexes *fac*- $[(\text{PtXMe}_3)(\text{dmas})_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and $[(\text{PtXMe}_3)_2(\text{dmas})]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) are exemplified below for $\text{X} = \text{Br}$.

Preparation of *fac*- $[\text{PtBrMe}_3(\text{dmas})_2]$

The tetrameric trimethylplatinum(IV) bromide (240 mg, 0.187 mmol) and an excess (390 mg, 1.61 mmol) of dmas were heated together under reflux in dry chloroform (5 cm^3) for 20 h. The reaction mixture was pumped to dryness and the residue extracted with warm (40 °C) 60–80 °C light petroleum (10 cm^3). The filtered extract was cooled to –20 °C overnight and the product was obtained as white crystals (240 mg, 40%). Analytical data for all *fac*- $[(\text{PtXMe}_3)(\text{dmas})_2]$ complexes are in Table 1.

Preparation of $[(\text{PtBrMe}_3)_2(\text{dmas})]$

dmas (200 mg, 0.83 mmol) and $[(\text{PtBrMe}_3)_4]$ (530 mg, 0.41 mmol) were heated together in chloroform (5 cm^3) for 2 h under reflux. The resulting solution was reduced in volume to ca. 0.5 cm^3 and 5 cm^3 of 60–80 °C light petroleum was added to precipitate the crude product. Excellent crystals of a quality suitable for X-ray diffraction measurements were obtained by recrystallization of the crude product from 60–80 °C light petroleum by cooling to –20 °C. Yield was 390 mg (55%), and analytical data for the $[(\text{PtXMe}_3)_2(\text{dmas})]$ complexes are recorded in Table 1.

TABLE 4. CRYSTAL DATA, DETAILS OF INTENSITY MEASUREMENTS AND STRUCTURE REFINEMENT FOR [(PtBrMe₃)₂(dmas)]

Formula	C ₁₀ H ₃₀ As ₂ Br ₂ Pt ₂ S
<i>M</i>	882.24
Crystal system	Orthorhombic
Space group	<i>Pbca</i> (No. 61)
<i>a</i> (Å)	14.045(2)
<i>b</i> (Å)	12.409(2)
<i>c</i> (Å)	24.078(3)
<i>U</i> (Å ³)	4196
<i>Z</i>	8
<i>D_c</i> (g cm ⁻³)	2.793
<i>F</i> (000)	3184
Crystal size (mm)	0.50 × 0.33 × 0.28
<i>μ</i> (cm ⁻¹)	204.4
Absorption correction	
(a) AZIMUTHAL-SCAN (min., max.)	0.79, 1.00
(b) DIFABS (min., max.)	0.83, 1.49
<i>θ</i> -range	1.5, 25.0
<i>h, k, l</i> range	0 → 15, 0 → 14, 0 → 28
Intensity variation	< 2%
Total no. of reflections	4156
No. of unique reflections	3695
Significance test	<i>F_o</i> > 6σ(<i>F_o</i>)
No. of reflections used in the refinement	2212
No. of refinement parameters	184
Max. least-squares shift-to-error ratio	0.6
Min. and max. height in final difference Fourier map,	-0.61, 0.43
<i>Δρ</i> (e Å ⁻³)	
Function minimized	Σ _w (<i>F_o</i> - <i>F_c</i>) ²
Weighting scheme parameter	0.00001
<i>g</i> in <i>w</i> = 1/[σ ² (<i>F_o</i>) + <i>gF_o</i> ²]	
Final <i>R</i>	0.0367
Final <i>R_w</i>	0.0338

Crystallography

Unit-cell parameters and intensity data were obtained by following previously detailed procedures [18], using a CAD4 diffractometer operating in the ω - 2θ scan mode, with monochromated Mo-*K*_α radiation (λ 0.71069 Å). The reflection intensities were corrected for absorption by using both the AZIMUTHAL-SCAN [19] and DIFABS [20] methods. The relevant experimental data are summarized in Table 4.

The structure was solved by the application of routine heavy-atom methods (SHELX84 [21]), and refined by full-matrix least-squares (SHELX76 [22]). The final cycle of refinement included all hydrogen atoms in their calculated positions (C-H 0.96 Å, *U* 0.10 Å²). All non-hydrogen atoms were refined with anisotropic thermal coefficients. The source of atomic scattering factors and anomalous scattering parameters are as given in ref. 18. All computations were made on a DEC VAX-11/750 computer. Final atomic positional parameters are given in Table 5. Tables of isotropic hydrogen atom coordinates and *F_o*/*F_c* values are available from the authors.

TABLE 5
FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) FOR $[(\text{PtBrMe}_3)_2(\text{dmas})]$

Atom	x	y	z
Pt(1)	123(1)	2135(1)	798.8(3)
Pt(2)	-1002(1)	4075(1)	1822.6(3)
Br(1)	-1298(1)	3492(2)	794(1)
Br(2)	322(2)	2553(2)	1867(1)
As(1)	1309(1)	3583(2)	608(1)
As(2)	267(1)	5382(2)	1558(1)
S	973(4)	5324(4)	732(2)
C(1)	-82(16)	1810(15)	-10(8)
C(2)	1217(15)	1047(15)	821(10)
C(3)	-839(16)	910(15)	988(9)
C(4)	1765(17)	3717(16)	-155(8)
C(5)	2527(14)	3372(17)	1020(8)
C(6)	-873(18)	4510(17)	2612(7)
C(7)	-2019(17)	5183(17)	1752(9)
C(8)	-2031(15)	3023(15)	2070(8)
C(9)	-72(17)	6899(13)	1521(8)
C(10)	1338(14)	5431(18)	2068(9)

NMR studies

^1H and ^{13}C experiments were performed on a Bruker AM250 instrument at 250 and 62.8 MHz respectively. Samples were dissolved in CDCl_3 for room temperature spectra, and variable temperature ^1H spectra (-90 to $+80^\circ\text{C}$) were recorded in toluene- d_8 .

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