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THE PREPARATION AND X-RAY STRUCTURE OF [dbuH][$PtBr_5(PPh_3)$]

MAJID MOTEVALLI and MICHAEL B. HURSTHOUSE*
Department of Chemistry, Queen Mary College, Mile End Road, London E1 4NS, U.K.

and

PAUL F. KELLY and J. DEREK WOOLLINS*
Department of Chemistry, Imperial College of Science and Technology, South Kensington, London SW7 2AY, U.K.

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Abstract—In contrast to analogous complexes of smaller phosphines, which react with bromine to give platinum(IV) dibromo species, $[Pt(S_2N_2H)(PPh_3)_2]BF_4$ (**1**) reacts to give a mixture of $PtBr_2(PPh_3)_2$, $PtBr_4(PPh_3)_2$ and, if performed in the presence of [dbuH]Cl, the pentabromo complex $[dbuH][PtBr_5(PPh_3)]$ (**2**). The X-ray crystal structure determination of the latter represents the first such analysis of a complex of this class.

We have recently reported on the reactions of $[Pt(S_2N_2H)(PR_3)_2]BF_4$ ($PR_3 = PMe_2Ph$ and PMe_3) with stoichiometric quantities of bromine which lead to platinum(IV) dibromo complexes of the type $[Pt(S_2N_2H)(Br)_2(PR_3)_2]BF_4$, which in turn spontaneously decompose to the platinum(II) complexes $Pt(S_2N_2H)(Br)(PR_3)$.[1]

This type of reaction is sensitive to the nature of the phosphine present; here we report upon the reaction of the triphenylphosphine complex, $[Pt(S_2N_2H)(PPh_3)_2]BF_4$ (**1**), with bromine which leads, via loss of the sulphur–nitrogen fragment, to simple platinum–triphenylphosphine–bromo complexes. If the reaction is performed in the presence of [dbuH]Cl (a by-product of the preparation of the starting materials) a salt of the pentabromo anion $[PtBr_5(PPh_3)]^-$ is formed. Although complexes of this type have been made previously, the X-ray crystal structure of the latter is the first to be reported.

RESULTS AND DISCUSSION

Complexes of the type $[Pt(S_2N_2H)(PR_3)_2]BF_4$ are readily formed by reaction of BF_3 with the analogous $S_2N_2^{2-}$ complexes, which in turn are prepared in high yield by treatment of a mixture of *cis*-$PtCl_2(PR_3)_2$ and $S_4N_4H_4$ with the base dbu.[2] One by-product of the latter reaction is [dbuH]Cl which can only be completely removed by thoroughly washing the products with water. During our early investigations into the reaction of $[Pt(S_2N_2H)(PMe_2Ph)_2]BF_4$ with bromine, which yields the platinum(IV) dibromo complex $[Pt(S_2N_2H)(Br)_2(PMe_2Ph)_2]BF_4$,[1] the undoubted presence of small amounts of [dbuH]Cl as contaminants did not appear to affect the course of the reaction. However, upon extending the range of reactions to include the PPh_3 complex, it soon became clear that in this case the purity of the starting materials is more important.

The reaction of **1** with bromine proceeds much more slowly than that of the PMe_2Ph analogue; thus the ^{31}P NMR spectrum of the product after 30 min shows $\approx 50\%$ of the platinum species unreacted. Also present in this solution is $PtBr_2(PPh_3)_2$, indicating that the reaction proceeds via a different route to that observed in the other cases, one which involves loss of the $S_2N_2H^-$ ligand. In addition, if the reaction is performed upon starting material which is contaminated with [dbuH]Cl, then another species is seen in the ^{31}P NMR spectrum. This new complex appears as a singlet at $\delta = -7.0$ ppm, together with ^{195}Pt sat-

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* Authors to whom correspondence should be addressed.

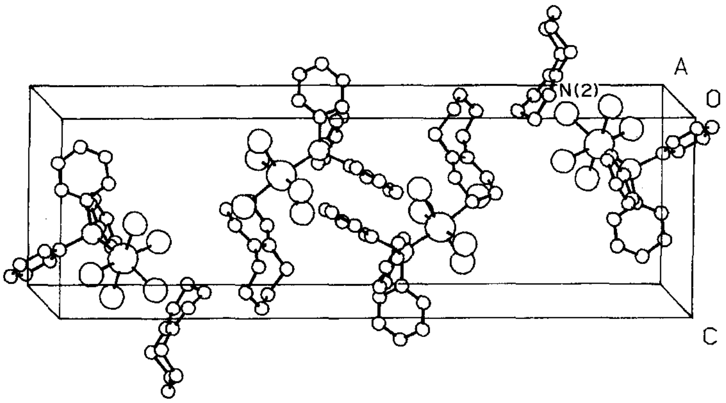


Fig. 1. X-ray structure of [dbuH][PtBr$_5$(PPh$_3$)] showing the unit cell contents.

ellites (${}^1J({}^{195}\mathrm{Pt}$—${}^{31}\mathrm{P})$ 2140 Hz). The low value of the ${}^1J$ coupling suggests the presence of platinum(IV). By slow diffusion into CHCl$_3$ solutions the platinum(IV) complex can be obtained as well-formed red crystals.

On first obtaining crystals of this complex we hoped that it would prove to be a platinum–sulphur–nitrogen species; however their IR spectrum showed none of the expected S—N stretches, and showed a peak at ≈ 1650 cm^{-1}, typical of dbu. Micro-analysis and X-ray crystallography confirmed the complex to be [dbuH][PtBr$_5$(PPh$_3$)].

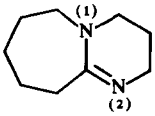
A diagram of the unit cell contents is given in Fig. 1. Selected bond lengths and angles are listed in Table 1. The anion has the expected octahedral geometry with the unique Pt—Br distance being

Table 1. Selected bond lengths and angles for [dbuH][PtBr$_5$(PPh$_3$)]

Bond lengths (Å)			
Br(1)—Pt(1)	2.465(4)	Br(2)—Pt(1)	2.466(4)
Br(3)—Pt(1)	2.470(4)	Br(4)—Pt(1)	2.470(4)
Br(5)—Pt(1)	2.533(5)	P(1)—Pt(1)	2.364(6)
C(11)—P(1)	1.819(13)	C(21)—P(1)	1.817(13)
C(31)—P(1)	1.811(15)	C(1)—N(1)	1.442(26)
C(4)—N(1)	1.351(23)	C(9)—N(1)	1.496(23)
C(2)—N(2)	1.467(27)	C(4)—N(2)	1.324(25)
C(3)—C(1)	1.522(29)	C(3)—C(2)	1.493(28)
C(5)—C(4)	1.530(32)	C(6)—C(5)	1.581(34)
C(7)—C(6)	1.525(32)	C(8)—C(7)	1.540(34)
C(9)—C(8)	1.535(30)		

Bond angles (°)			
Br(2)—Pt(1)—Br(1)	172.8(1)	Br(3)—Pt(1)—Br(1)	90.1(2)
Br(3)—Pt(1)—Br(2)	95.5(2)	Br(4)—Pt(1)—Br(1)	86.6(2)
Br(4)—Pt(1)—Br(2)	87.4(2)	Br(4)—Pt(1)—Br(3)	174.5(1)
Br(5)—Pt(1)—Br(1)	86.2(2)	Br(5)—Pt(1)—Br(2)	89.6(2)
Br(5)—Pt(1)—Br(3)	86.3(2)	Br(5)—Pt(1)—Br(4)	89.1(2)
P(1)—Pt(1)—Br(1)	94.7(2)	P(1)—Pt(1)—Br(2)	90.1(2)
P(1)—Pt(1)—Br(3)	87.4(2)	P(1)—Pt(1)—Br(4)	97.3(2)
P(1)—Pt(1)—Br(5)	173.6(1)	C(11)—P(1)—Pt(1)	114.4(5)
C(21)—P(1)—Pt(1)	116.9(4)	C(21)—P(1)—C(11)	102.3(6)
C(31)—P(1)—Pt(1)	112.2(5)	C(31)—P(1)—C(11)	106.4(6)
C(31)—P(1)—C(21)	103.3(6)	C(4)—N(1)—C(1)	123.4(18)
C(9)—N(1)—C(1)	116.6(16)	C(9)—N(1)—C(4)	119.9(20)
C(4)—N(2)—C(2)	125.4(17)	C(3)—C(1)—N(1)	111.4(17)
C(3)—C(1)—N(2)	107.3(18)	C(2)—C(3)—C(1)	109.9(17)
N(2)—C(4)—N(1)	117.8(21)	C(5)—C(4)—N(1)	122.0(20)
C(5)—C(4)—N(2)	120.2(18)	C(6)—C(5)—C(4)	108.6(20)
C(7)—C(6)—C(5)	113.0(21)	C(8)—C(7)—C(6)	114.7(20)
C(9)—C(8)—C(7)	113.2(19)	C(8)—C(9)—N(1)	110.7(17)

0.06 Å longer than the four equivalent "equatorial" Pt—Br distances, as a result of the *trans* influence of the phosphine. The hydrogen atoms on the dbu cation were not located and we cannot identify the point of protonation in this way. However, the bridgehead nitrogen, N(1), is nearly planar (sum of angles = 359.9°) so it is likely that N(2) carries the proton.



Complexes of this class have been reported previously; treatment of halogen-bridged complexes of the type [PtX$_2$(PR$_3$)]$_2$ with [^{n}Pr$_4$N]X yields salts of [PtX$_3$(PR$_3$)]$^-$ which can be oxidized with the appropriate halogen to give the corresponding platinum(IV) species.[3] This technique has been used to produce complexes of PMe$_3$, although to our knowledge none of the products has been analysed by X-ray crystallography.

The precise mechanism for the production of **2** in this case is unclear, as is the reason for the contrast between the reactions of the PMe$_2$Ph and PPh$_3$ complexes. However, the role of the [dbuH]Cl is crucial; if the reaction is performed upon a compound known to be completely free of the latter then no [PtBr$_5$(PPh$_3$)]$^-$ is formed. In this case, addition of excess bromine, followed by slow hexane diffusion yields a mass of micro-crystals which analyse as a mixture of PtBr$_2$(PPh$_3$)$_2$ and PtBr$_4$(PPh$_3$)$_2$. Possibly [dbuH]Cl can react with the latter platinum(IV) species to yield a salt of [PtBr$_4$Cl(PPh$_3$)]$^-$, via loss of triphenylphosphine, and this in turn reacts with the bromine in the system to give the final product. It is worth noting that although the precise mechanism for the reaction is unclear, and obviously our first preparation of **2** was totally fortuitous, the reaction is reproducible so long as care is taken to leave [dbuH]Cl in the system.

We have yet to fully characterize the products of the reaction of [Pt(S$_2$N$_2$H)(PPh$_2$Me)$_2$]BF$_4$ with bromine; ^{31}P NMR reveals the presence of a platinum(IV) complex, consistent with [Pt(S$_2$N$_2$H)(Br)$_2$(PPh$_2$Me)$_2$]BF$_4$, but this rapidly decomposes in a matter of minutes to give a mixture with a similar ^{31}P NMR spectrum to that of the decomposition products from the PMe$_2$Ph analogue. Thus, there appears to be two distinct effects brought about by the introduction of more phenyl groups into the phosphines present. The first of these is the destabilizing effect upon the resulting platinum(IV) dibromo species, as witnessed by the greater instability of the PPh$_2$Me complex, which is stable only for minutes, compared to the PMe$_3$ and PMe$_2$Ph analogues which are stable for days.

Another effect appears to be at work in the PPh$_3$ case, since ^{31}P NMR shows no evidence for the presence of [Pt(S$_2$N$_2$H)(Br)$_2$(PPh$_3$)$_2$]BF$_4$, even as a short lived species. Rather, it would seem that in this case the reaction proceeds via an entirely different mechanism, since it is slower and eventually results in the loss of the sulphur–nitrogen ligand. It may well be that the crucial factor is the steric influence of the bulky triphenylphosphine groups, although it is unclear why this should have the effect of labilizing the S$_2$N$_2$H$^-$ ligand.

EXPERIMENTAL

General reaction conditions and techniques were as described previously.[1] Compound **1** was prepared from Pt(S$_2$N$_2$)(PPh$_3$)$_2$, the latter from PtCl$_2$(PPh$_3$)$_2$ and S$_4$N$_4$H$_4$/dbu.[2] The bromine solution used consisted of 0.2 cm^3 of Br$_2$ in 20 cm^3 CH$_2$Cl$_2$ (i.e. 0.195 M w.r.t. Br$_2$).

Reaction of 1 *with* Br$_2$ *in the absence of* [dbuH]Cl

A solution of **1** (0.25 g, 0.28 mmol) in CH$_2$Cl$_2$ (20 cm^3) was treated with Br$_2$ in CH$_2$Cl$_2$ (1.5 cm^3, 0.29 mmol) and stirred for 30 min, during which time the solution gradually darkened from orange to light red and deposited some pale solid. The volume of the solvent was reduced to ≈ 5 cm^3 *in vacuo* and Et$_2$O (40 cm^3) added giving a bright orange precipitate. ^{31}P NMR of a CDCl$_3$ solution of the product showed the presence of the starting material together with PtBr$_2$(PPh$_3$)$_2$ (ratio ≈ 1 : 1.2).

The solution was treated with more bromine solution (0.75 cm^3, 0.15 mmol) and stirred overnight. The resulting red solution was reduced in volume and hexane (30 cm^3) layered on top. Slow diffusion of the hexane resulted in a mass of yellow micro-crystals. Micro-analysis suggested a mixture of PtBr$_2$(PPh$_3$)$_2$ and PtBr$_4$(PPh$_3$)$_2$. Found: C, 47.2; H, 3.2. Calc. for dibromide: C, 49.2; H, 3.4 and for tetrabromide C, 41.6; H, 2.9%.

Reaction in the presence of [dbuH]Cl

A solution of **1** (0.25 g, 0.28 mmol), known to be contaminated with [dbuH]Cl, in CH$_2$Cl$_2$ (10 cm^3) was treated with bromine solution (1.5 cm^3, 0.29 mmol). After stirring for 30 min the solvent was reduced in volume; the ^{31}P NMR spectrum of the product showed the presence of PtBr$_2$(PPh$_3$)$_2$ and a platinum(IV) complex (ratio 2 : 1). The mixture was taken up in CH$_2$Cl$_2$ (10 cm^3) and treated with toluene (20 cm^3). The rest of the CH_2Cl_2 was removed *in vacuo* and the resulting orange solid filtered off and washed with cold toluene followed by Et_2O. The solid obtained was redissolved in CH_2Cl_2 (3 cm^3) and hexane layered on top; slow diffusion yielded **2** as well-formed orange–red crystals. Found: C, 32.0; H, 3.0; N, 2.8. Calc. C, 32.1; H, 3.2; N, 2.8%.

Crystal data. $C_{27}H_{32}N_2Br_5Pt$, $M = 1010.1$, monoclinic, $a = 9.583(6)$, $b = 32.523(6)$, $c = 10.115(3)$ Å, $\beta = 94.74(4)°$, $U = 3141.7$ Å^3, space group $P2_1/n$, $Z = 4$, $D_c = 2.14$ g cm^{-3}, μ(Mo-K_α) 108.8, $\lambda = 0.71069$ Å, $F(000) = 1904$.

Data collection and processing. ($1.5\theta \leqslant 25°$), graphite monochromated Mo-K_α radiation; 5518 independent measured reflections, 3677 observed [$|F_o| > 6\sigma(|F_o|)$], corrected for Lorentz and polarization factors; empirical absorption correction.

Structure analysis and refinement. The structure was solved by the heavy-atom method and all the non-hydrogen atoms refined anisotropically. The hydrogen atoms were idealized (C—H = 0.96 Å), assigned group isotropic thermal parameters $U(H) = 1.2U$eq(C) and allowed to ride on their parent carbons. Refinement was by full-matrix least-squares to $R = 0.045$, ($R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$), $R_w = 0.046$ ($w^{-1} = \sigma^2(F) + 0.00035F^2$). Computations were carried out on a VAX 11/750 computer using the SHELX76 program system.*

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* Atomic coordinates, thermal parameters, full lists of bond lengths and angles and lists of F_o/F_c values have been deposited as supplementary data with the Editor, from whom copies are available on request. Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.