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COMMUNICATION

Oxidative Addition of Arsenic Halides to Platinum(0)

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Dedicated to Prof. Geoff Cloke on the occasion of his 65th birthday

with Pt(0) complexes $Pt(PCy_3)_2$, Reaction of AsCl₃ Pt(PCy₃)(IMes) and Pt(IMes)₂ (IMes = 1,3-bis(2,4,6trimethylphenyl)imidazol-2-ylidene) resulted in oxidative addition of As-Cl bonds at the Pt centres to form complexes of the form trans-[PtCl(AsCl₂)L₂]. Two of these compounds were characterised by X-ray diffraction, making them the first structurally characterised examples of AsX₂ ligands (X = halogen). AsBr₃ also underwent oxidative addition to Pt(PCy₃)₂, forming trans-[PtBr(AsBr₂)(PCy₃)₂] in situ, as judged by ³¹P NMR spectroscopy. This reaction was unselective, yielding several products, of which a Pt₃As₂ cluster could be identified by single-crystal X-ray diffraction.

The coordination chemistry of arsenic, similarly to that of its neighbour phosphorus, is dominated by neutral, two-electron donor ligands.¹ Negatively charged arsenido ligands are nonetheless relatively well explored, with synthetic routes including σ -bond metathesis,²⁻⁹ electrophilic addition to arsaalkene ligands¹⁰ and the deprotonation of secondary arsine ligands.^{11, 12} Oxidative addition of an arsenic-halide bond has only been reported in a single recent case - albeit to a maingroup element - in the addition of one of the As-Cl bonds of Cp^*AsCl_2 to a highly reducing Ga(I) β -diketiminate complex (Scheme 1a). $^{\rm 13}$ Scapacci and co-workers claimed the oxidative addition of Ph₂AsCl to Pt(0) and Pd(0), but the halide complexes were not characterised.14 Although several reports of metal complexes of AsX_2 ligands exist,¹⁵⁻²⁰ none have thus far been structurally characterised. In fact, group 15 dihalide ligands (EX₂⁻) are in general surprisingly rare, with only 13 structures in total in the Cambridge Structural Database (CSD).

Over the course of the last decade, we have extensively explored the reactivity of simple element halides towards platinum(0) complexes.²¹⁻²⁹ In many cases this resulted in adduct formation between the Lewis-basic platinum centre and more electropositive elements, providing access to Metal-Only

Lewis Pairs (MOLPs, Scheme 1b).³⁰ Moving to group 15, the increased electronegativity of the central atom disfavours MOLP formation, instead resulting in oxidative addition of one of the E-X bonds to the platinum centre.^{26, 31, 32} Thus, the reactions of SbCl₃ and BiCl₃ with [Pt(PCy₃)₂] (1) yielded the Pt(II) complexes *trans*-[PtCl(ECl₂)(PCy₃)₂] (E = Sb (A), Bi (B); Scheme 1c). The nature of the halide also influences reactivity; the reaction of 1 with SbF₃ led to formation of [{(Cy₃P)₂Pt}₂(μ -SbF₂)][SbF₄]. Herein we describe the reactivity of 1 and its related complexes [Pt(IMes)(PCy₃)] (2) and [Pt(IMes)₂] (3) (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) towards the arsenic halides AsCl₃ and AsBr₃.



Fig. 1 a) The only previous example of oxidative addition of an arsenic halide; b) MOLP formation between platinum and element halides; c) Oxidative addition of group 15 halides to Pt(0); d) This work: Oxidative addition of arsenic halides to Pt(0).

Addition of $AsCl_3$ to a solution of **1** in Et_2O at 0 °C resulted in the rapid formation of a pale yellow precipitate. The solid displayed a ³¹P NMR signal at 22.0 ppm (¹J_{P-Pt} = 2595 Hz), which strongly

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resembles that of A and B, suggesting oxidative addition of an As-Cl bond to platinum. Slow evaporation of a benzene solution of the compound produced single crystals suitable for X-ray diffraction, which confirmed the structure as that of trans-[Pt(AsCl₂)Cl(PCy₃)₂] (4, Figures 2 and 3). The isolated yield of 69% indicated selective formation. Analogous procedures using carbene derivatives 2 and 3 as the platinum precursors led to oxidative addition products trans-[Pt(AsCl₂)Cl(IMes)(PCy₃)] (5) and trans-[Pt(AsCl₂)Cl(IMes)₂] (6) in moderate to good yield (5: 74%; 6: 46%). The molecular structures of 4 and 5 are shown in Figure 3. These are the first examples of crystallographically characterised molecules with AsX₂ ligands. The sum of angles around the arsenic atoms of 314.5° (4) and 309.6° (5) indicate a slight opening of the distorted pyramidal geometry at the As atom compared to AsCl₃ itself (293.4°).³³ This suggests only a small degree of π -bonding between arsenic and platinum, in line with other reported arsenide complexes.⁶ In spite of this fact, a CSD search reveals the Pt-As distance of 5 (2.3483(7) Å) to be the shortest yet observed for a Pt arsenide complex (2.403-2.515 Å), while that of **4** is marginally longer (2.3598(3) Å). It has been noted for related Pt boryl complexes³⁴ that electronegative substituents at boron result in greater scharacter of the Pt-B hybrid bonding orbitals, leading to shorter Pt-B and Pt-halide distances; this phenomenon could explain the short bonds between Pt and the AsCl₂ ligand.



Fig. 2 Synthesis of dichloroarsenido complexes 4-6 and attempted synthesis of dibromoarsenido complex 7.

As previously noted,^{22, 26, 31} the Pt-Cl distance of trans-[PtCl(ECl₂)(PCy₃)₂] complexes can be related to the transinfluence of the ECl_2 ligand. The Pt1-Cl1 bond length in 4 is 2.3927(5) Å, slightly shorter than that in antimony derivative A (2.413(2) Å)²⁶ and bismuth derivative **B** (2.4155(9) Å),³¹ and considerably shorter than that in boryl complex trans-

Fig. 3 Molecular structures of compounds 4 (top left), 5 (top right) and 8 (bottom) with displacement ellipsoids at the 50% probability level. Hydrogen atoms and co-crystallised solvent molecules (where present) are omitted for clarity. Selected bond lengths (Å) and angles (°): 4: Pt1-P1 2.3581(6), Pt1-P2 2.3623(6), Pt1-Cl1 2.3927(5), Pt1-As1 2.3598(3), P1-Pt1-P2 167.52(2), Cl1-Pt1-As1 167.60(2); 5: Pt1-P1 2.3425(9), Pt1-C1 2.055(3), Pt1-Cl1 2.391(1), Pt1-As1 2.3483(7), P1-Pt1-C1 174.23(7), Cl1-Pt1-As1 175.49(2); 8: As1-As2 2.685(1), Pt1-As1 2.5184(9), Pt1-As2 2.4804(9), Pt2-As1 2.4164(9), Pt2-As2 2.443(1), Pt3-As1 2.464(1), Pt3-As2 2.3672(9).

Treatment of 1 with AsBr₃ also led to an immediate reaction, with a new signal at 18.6 ppm (J_{P-Pt} = 2613 Hz) in the ³¹P NMR spectrum strongly indicative of formation of trans-[Pt(AsBr₂)Br(PCy₃)₂] (7, Figure 2). In this case, however, the desired compound was accompanied by the formation of trans- $[PtBr_2(PCy_3)_2]$. Leaving the mixture to stand for 30 min led to further decomposition of 7 to several species. Repeated attempts to crystallise compound 7 at low temperature resulted in formation of deep red crystals of the cluster compound, $[(Cy_3P)_2Pt(\mu_3-As)_2{PtBr(PCy_3)}_2]$ (8, Figure 3). Although arseniccontaining cluster compounds are relatively well known, only two have been previously structurally confirmed that contain platinum.^{36, 37} In compound **8**, the two arsenic atoms bridge between all three platinum atoms. Atoms Pt1 and Pt3 are square planar, as expected for Pt(II), whereas Pt2 adopts a distorted tetrahedral geometry with respect to one PCy₃ ligand, one bromide and both arsenic atoms. The Pt1-Pt2 distance of 2.862(1) Å is also indicative of a Pt-Pt bonding interaction. The As1-As2 distance of 2.685(1) Å is roughly 0.2 Å longer than a typical As-As single bond,³⁸ suggesting a weak interaction.



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Unfortunately, compound **8** could not be isolated in pure form despite repeated crystallisations, and the large number of signals in the ³¹P NMR prevented assignment of the four expected signals for **8**. Although the precise route of formation of **8** is unclear, evidently the weaker As-Br bond as compared to the As-Cl bond results in a less selective reaction and multiple oxidative addition steps involving a single arsenic centre. We note in this regard that while GaBr₃ undergoes oxidative addition to **1**, GaCl₃ prefers to form a MOLP between the platinum and gallium atoms.²³

In conclusion, we have reported the first confirmed oxidative addition reactions of arsenic halides to a transition metal element (Pt). The Pt(II) arsenide complexes represent the first structurally characterised metal complexes bearing AsX_2^- ligands. The nature of the halide is crucial in determining the outcome of the reaction; whereas $AsCl_3$ underwent a single oxidative addition, use of $AsBr_3$ led to the formation of a Pt_3As_2 cluster alongside the oxidative addition compound and other products. We are now focussed on exploring the reactivity of the halides of the remaining group 15 elements towards electron-rich transition metal compounds in order to gain a full understanding of this chemistry.

Conflicts of interest

There are no conflicts to declare.

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 $AsCl_3$ and $AsBr_3$ are shown to undergo oxidative addition to Pt(0) complexes. With $AsCl_3$, a single As-Cl oxidative addition step selectively yields (chloro)(arsenido)-Pt(II) complexes, whereas with $AsBr_3$ both monomeric and cluster compounds are produced.