Synthesis and structural characterisation of a novel 2,3-distibene-1,4-dione complex, $[Pt(PEt_3)_2\{\eta^2\text{-}Bu^tC(O)Sb{=}SbC(O)Bu^t\}]$

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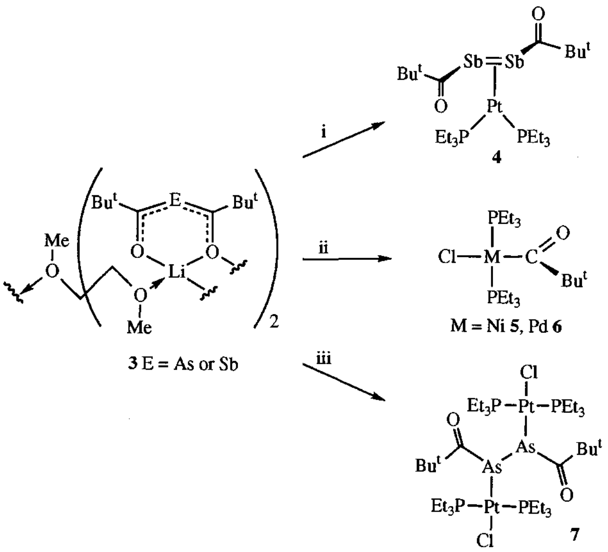
The reaction of *cis*-$[PtCl_2(PEt_3)_2]$ with 2 equiv. of $[\{[Li\{\eta^2\text{-}OC(Bu^t)EC(Bu^t)O\}(DME)_{0.5}]_2\}_\infty]$, E = Sb or As, affords either the first distibene-dione complex, *cis*-$[Pt(PEt_3)_2\{\eta^2\text{-}Bu^tC(O)Sb{=}SbC(O)Bu^t\}]$, or the related diarsenide-dione bridged complex, *trans*-$[\{Pt(PEt_3)Cl\}_2\{\mu\text{-}\eta^1,\eta^1\text{-}Bu^tC(O)AsAsC(O)Bu^t\}]$, the X-ray crystal structures of which are described.

Since the preparation of the first diphosphene, Mes*P=PMes*, Mes* = $C_6H_2Bu^t_3$-2,4,6; by Yoshifuji in 1981[1] the chemistry of these species has developed into a well explored field.[2] By contrast, the heavier Group 15 analogues of diphosphenes have remained scarce and in the case of distibenes can be confined to one very sterically protected example, (Tbt)Sb=Sb(Tbt) **1** {Tbt = $C_6H_2[CH(SiMe_3)_2]_3$-2,4,6}.[3] In addition, three structurally characterised distibene complexes have been reported, *viz.* $[Fe(CO)_4\{\eta^2\text{-}[(SiMe_3)_2CHSb]_2\}]$ **2**[4] and $[\{W(CO)_5\}_3(\eta^2\text{-},\eta^1\text{-},\eta^1\text{-}RSb{=}SbR)]$ R = Ph,[5] Bu^t;[6] none of which contain functionalised distibene substituents. Our interest in low coordination antimony chemistry has recently led to us reporting the first example of a 2-stiba-1,3-dionatolithium complex **3** (E = Sb),[7] which we have begun to investigate as a possible transfer reagent in the formation of transition metal–stibadionate complexes (*cf.* β-diketonate chemistry). This work has led to some unexpected results which include the metal mediated synthesis of the first distibene-dione complex which is reported herein. Several related complexes are also described.

Treatment of *cis*-$[PtCl_2(PEt_3)_2]$ with 2 equiv. of **3** (E = Sb) in DME led to a moderate yield (39%) of **4** after recrystallisation from hexane (Scheme 1). Following this reaction by ^{31}P NMR revealed that the formation of **4** occurs over 5 h without any observable intermediate in the process. The orange crystalline material is air stable, thermally robust in the solid state (mp 112–114 °C decomp.) and stable in solution for days at 25 °C. If the reaction is carried out in a 1 : 1 stoichiometry, compound **4** is the only observable product, and *ca.* 50% of the platinum starting material remains unreacted. Interestingly, when the analogous 2 : 1 reactions of **3** (E = Sb) with *cis*-$[MCl_2(PEt_3)_2]$ (M = Ni, Pd) were carried out antimony mirrors were deposited from the reaction mixtures and the mono-acyl nickel or palladium complexes were isolated in moderate yields, **5** (39%) and **6** (56%), respectively.[8] It is noteworthy that none of the platinum analogue of **5** and **6** was found in the preparation of **4**, and similarly no distibene-dione complexes were identified in the preparations of **5** and **6**. Finally, in an attempt to form the arsenic counterpart of **4** the 2 : 1 reaction of **3** (E = As) with *cis*-$[PtCl_2(PEt_3)_2]$ was carried out but in this case the only tractable product was the diarsenide-dione bridged complex, **7**, which was formed in a low yield (5%, mp 124–126 °C decomp.).

The spectroscopic data† for **4** and **7** support their proposed structures. Of note are the ^{31}P NMR spectra of each complex which display one signal with $^1J_{PtP}$ satellites in the normal coupling range, thus suggesting the equivalence of all phosphine ligands in both complexes in solution. No molecular ions were seen in the mass spectra of **4** and **7**, but in the case of **4** a cluster of signals corresponding to the free distibene-dione ligand was observed. In contrast, the base peak in the mass spectrum of **7** coincides with the loss of a chloride ligand, while a signal relating to the cleavage of the As–As bond (monomer formation) was also detected.

The molecular structures‡ of **4** and **7** are depicted in Figs 1 and 2, respectively. The Pt centres in each have a distorted square planar coordination environment with the PEt_3 ligands *cis*- in **4** and *trans*- in **7**. Not surprisingly, the acyl substituents are *trans*- to each other in both compounds. The Sb–Sb distance in **4** lies almost midway between those for uncoordinated Sb–Sb double and single bonds [*e.g.* 2.642(1) Å in **1**[3] and 2.837 Å in Ph_4Sb_2,[9] respectively] and is slightly shorter than in the only other η^2-distibene complex **2**, 2.774(1) Å.[4] As has been described for **2** and closely related diphosphene complexes, *e.g.* *cis*-$[Pt(dppe)(\eta^2\text{-}PhP{=}PPh)]$,[10] the bonding in **4** can be thought of as lying somewhere between two canonical forms, one an η^2-distibene-Pt(0) complex and the other a three membered σ-bonded metallacycle containing a Pt(II) centre. Consistent with this description is the CSbSbC torsion angle of 173° (*cf.* 153° in **2**) which shows the ligand to be slightly distorted from planarity. In contrast to the distibene-dione ligand in **4**, the ligand in **7** can be thought of as a diarsenide-dione, the As centres of which have distorted trigonal pyramidal geometries (Σ angles = 311.8°). The As–As distance is in the expected region for single bonds and compares well with that in the only other structurally characterised example of a dinuclear complex containing a bridging diarsenide ligand, 2.456(2) Å in *trans*-



Scheme 1 *Reagents and conditions*: i, E = Sb, 1/2 *cis*-$[PtCl_2(PEt_3)_2]$, − LiCl, − $\{Bu^tC(O)\}_2$; ii, E = Sb, 1/2 *cis*-$[MCl_2(PEt_3)_2]$ (M = Ni or Pd); iii E = As, 1/2 *cis*-$[PtCl_2(PEt_3)_2]$

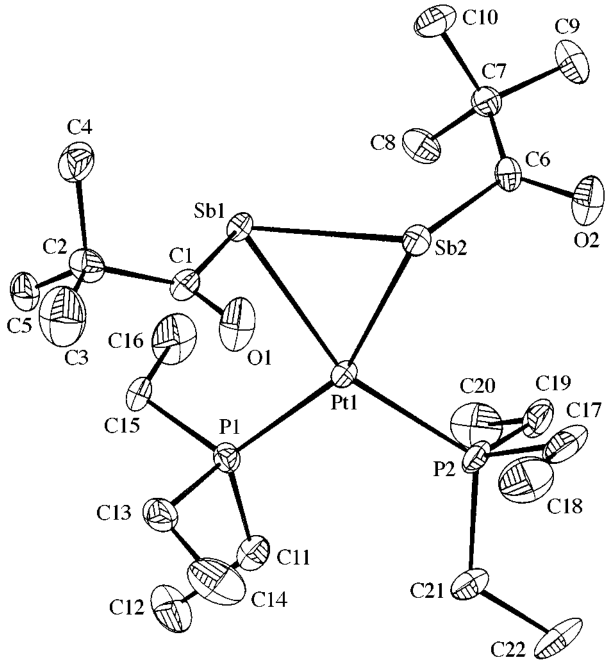


Fig. 1 Molecular structure of *cis*-[Pt(PEt$_3$)$_2${η^2-Bu^{t}C(O)Sb=SbC(O)Bu^t}] **4**. Selected bond lengths (Å) and angles (°): Sb(1)–Sb(2) 2.7551(12), Sb(1)–Pt(1) 2.6667(9), Sb(2)–Pt(1) 2.6501(10), Sb(1)–C(1) 2.279(12), Sb(2)–C(6) 2.224(12), Pt(1)–P(1) 2.281(3), Pt(1)–P(2) 2.286(3), C(1)–O(1) 1.205(13), O(2)–C(6) 1.235(13); C(1)–Sb(1)–Sb(2) 90.8(3), C(6)–Sb(2)–Sb(1) 108.0(3), Pt(1)–Sb(1)–Sb(2) 58.50(3), Pt(1)–Sb(2)–Sb(1) 59.08(2), O(1)–C(1)–Sb(1) 119.0(9), O(2)–C(6)–Sb(2) 112.6(9).

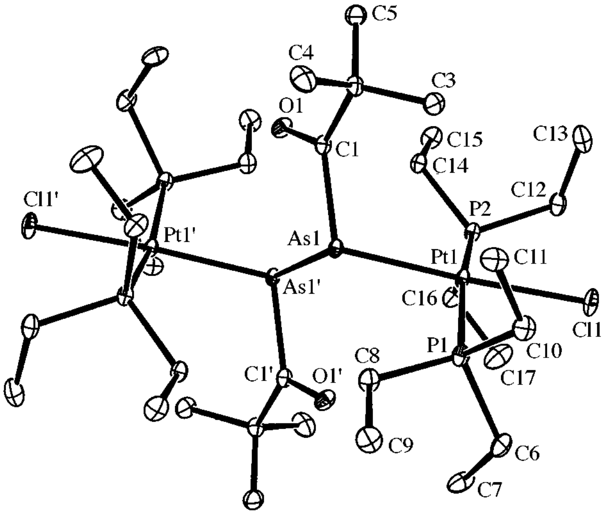


Fig. 2 Molecular structure of *trans*-[{Pt(PEt$_3$)Cl}$_2${μ-η^1,η^1-Bu^{t}C(O)As-AsC(O)Bu^t}] **7**. Selected bond lengths (Å) and angles (°): As(1)–As(1′) 2.4595(9), Pt(1)–As(1) 2.4425(5), As(1)–C(1) 2.010(5), Pt(1)–P(1) 2.3320(13), Pt(1)–P(2) 2.3078(13), Pt(1)–Cl(1) 2.4003(13); C(1)–As(1)–As(1′) 91.86(14), O(1)–C(1)–As(1) 119.3(4), Pt(1)–As(1)–As(1′) 110.63(3), C(1)–As(1)–Pt(1) 109.23(14), Cl(1)–Pt(1)–As(1) 170.95(4), P(1)–Pt(1)–P(2) 166.49(5).

[{CpFe(CO)$_2$}$_2$(μ-η^1,η^1-Ph$_2$As$_2$)].[11] All other bond lengths and angles in **4** and **7** lie in the expected regions.

At present the mechanism of formation of **4** can only be speculated upon but it seems that the likely intermediate is *cis*-[Pt(PEt$_3$)$_2${η^1-Sb[C(O)Bu^t]$_2$}$_2$] **8**, from which each η^1-Sb coordinated stibadionate ligand eliminates an acyl fragment, ·C(O)Bu^t, in a homolytic process. This would leave two coordinated [·SbC(O)Bu^t]$^-$ fragments which could couple, with an accompanying electron transfer to the Pt(II) centre, to give **4**. Although there is no spectroscopic evidence for the Sb-coordinated intermediate, **8**, its existence seems feasible considering that related 2-arsa-1,3-dionato ligands generally prefer η^1-As coordination over η^2-O,O-chelation in late transition metal complexes.[12] The fate of the acyl fragment is also a coupling reaction to give the known diketone, Bu^{t}C(O)C(O)-Bu^t, which was detected as the major product in the GC–MS analysis of the reaction volatiles.

We are currently investigating the mechanisms of formation of **4**–**7** which, when elucidated, should shed light on why such a variety of products result from supposedly similar reactions. These studies will form the basis of a forthcoming publication.

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Notes and References

† *Spectroscopic data* **4**: ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K) δ 0.89 [dt, 18H, $^3J_{\mathrm{PH}}$ 17.2 Hz, $^3J_{\mathrm{HH}}$ 7.1 Hz, P(CH$_2$C*H*$_3$)$_3$], 1.22 (s, 18H, Bu^t), 1.95 [dq, 12H, $^2J_{\mathrm{PH}}$ 22.4, $^3J_{\mathrm{HH}}$ 7.1 Hz, P(C*H*$_2$CH$_3$)$_3$]; ^{13}C NMR (100.6 MHz, C$_6$D$_6$, 298 K) δ 9.3 [d, $^2J_{\mathrm{PC}}$ 2.0, $^3J_{\mathrm{PtC}}$ 25.0 Hz, P(CH$_2$*C*H$_3$)$_3$], 24.6 [d, $^1J_{\mathrm{PC}}$ 27.6 Hz, $^2J_{\mathrm{PtC}}$ 43.1 Hz, P(*C*H$_2$CH$_3$)$_3$], 27.25 [s, C(*C*H$_3$)$_3$], 53.26 [s, *C*(CH$_3$)$_3$], 242.0 (s, Sb*C*OBu^t); ^{31}P NMR (101.4 MHz, C$_6$D$_6$, 298 K) δ 12.75 (s, $^1J_{\mathrm{PtP}}$ 3251.5 Hz, PEt$_3$); IR (Nujol) ν/cm^{-1} 1689m), 1641m; FABMS (NBA matrix) *m/z* 431 [M$^+$ − (SbCOBu^t)$_2$, 100%], 414 [M$^+$ − Pt(PEt$_3$)$_2$, 5%]; Found C 31.42; H 5.47; Calc. for C$_{22}$H$_{48}$P$_2$O$_2$Sb$_2$Pt: C, 31.44; H, 5.76. **7**: ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K) δ 1.12 [dt, 36H, $^3J_{\mathrm{PH}}$ 16.1, $^3J_{\mathrm{HH}}$ 7.4 Hz, P(CH$_2$C*H*$_3$)$_3$], 1.26 [dq, 24H, $^2J_{\mathrm{PH}}$ 25.2 Hz, $^3J_{\mathrm{HH}}$ 7.4 Hz, P(C*H*$_2$CH$_3$)$_3$], 1.55 (s, 18H, Bu^t); ^{31}P NMR (101.4 MHz, C$_6$D$_6$, 298 K) δ 10.15 (s, $^1J_{\mathrm{PtP}}$ 2401.1 Hz, *P*Et$_3$; IR (Nujol) ν/cm^{-1} 1675m FABMS (NBA matrix) *m/z* 1217 (M$^+$ − Cl, 100%), 626 [M$^+$ − PtCl(PEt$_3$)$_2$AsCOBu^t, 20%].

‡ *Crystal data:* **4**, C$_{22}$H$_{48}$O$_2$P$_2$PtSb$_2$, M = 845.13, monoclinic, space group $P2_1/n$, a = 19.919(2), b = 16.062(4), c = 20.132(2) Å, β = 108.48(1), V = 6109(2) Å^3, Z = 8, D_{c} = 1.838 g cm^{-3}, F(000) = 3248, μ = 64.44 cm^{-1}, crystal 0.30 × 0.25 × 0.15 mm, radiation Mo-Kα (λ = 0.71069 Å), 150(2) K, 8946 data, 547 parameters, $R_1[F^2 > 2\sigma(F^2)] = 0.0377$, wR_2 = 0.0826 (all data). **7**: C$_{34}$H$_{78}$As$_2$Cl$_2$O$_2$P$_4$Pt$_2$, M = 1253.76, monoclinic, space group $P2_1/n$, a = 11.2307(4), b = 18.2118(7), c = 11.6766(5) Å, V = 2353.3(2) Å^3, Z = 2, D_{c} = 1.769 g cm^{-3}, F(000) = 1228, μ = 76.10 cm^{-1}, crystal 0.10 × 0.10 × 0.10 mm, radiation Mo-Kα (λ = 0.71070 Å), 100(2) K, 4621 data, 209 parameters, $R_1[F^2 > 2\sigma(F^2)] = 0.0374$, wR_2 = 0.0928 (all data). Full details of data collections and solution and refinement of both structures are included as supplementary material, CCDC 182/1008.

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