Synthesis, Crystal and Molecular Structure of the First Metal Complex $[Pt(PPh_3)_2\{\eta^2\text{-}As{\equiv}C(C_6H_2Bu^t_3)\}]$ derived from an Arsaalkyne

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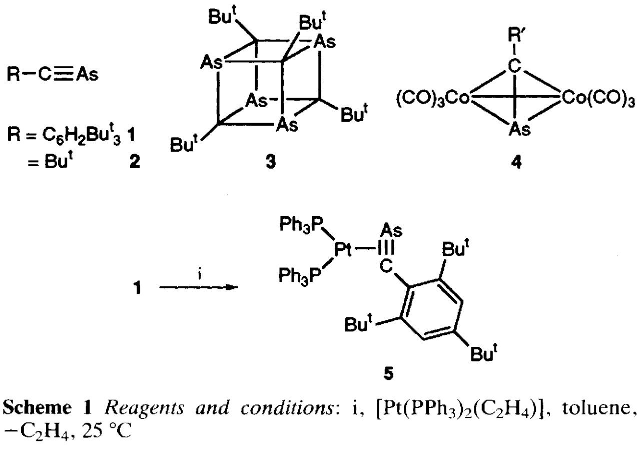
Treatment of $[Pt(PPh_3)_2(C_2H_4)]$ with $As{\equiv}C(C_6H_2Bu^t_3)$ affords the title compound, the X-ray crystal structure of which shows the arsaalkyne ligand to be η^2-ligated; the X-ray crystal structure of the parent arsaalkyne is also reported.

Despite the considerable interest that has been shown in phosphaalkynes and their organometallic chemistry over the past ten years,[1] the chemistry of arsaalkynes has not been similarly investigated. This is presumably a result of the instability inherent in low-coordination arsenic compounds and the fact that arsaalkynes have not been accessible by synthetic routes conventionally used in the preparation of phosphaalkynes. To the best of our knowledge there has been only one report[2] that describes an uncoordinated monomeric arsaalkyne **1**, which is apparently stabilised by the inclusion of the sterically restrictive 2,4,6-tri-*tert*-butylphenyl group. Recent work in our laboratory[3] has shown that when the less bulky *tert*-butyl group is employed, the resulting arsaalkyne **2** has only a transient existence and will tetramerise in the presence of $CoCl_2$ to give the novel tetraarsacubane **3**. Considering the instability of arsaalkynes, it is not surprising that their organometallic chemistry is restricted to one structurally uncharacterised complex type **4**, which was formed indirectly by a dechlorination reaction involving the treatment of $Cl_2R'CAsCl_2$ (R' = H, Me, Ph, $SiMe_3$) with $[Co_2(CO)_8]$.[4] We now report (i) the first X-ray crystal structure of an arsaalkyne **1** (ii) the first direct synthesis of an arsaalkyne–transition metal complex $[Pt(PPh_3)_2\{\eta^2\text{-}As{\equiv}C(C_6H_2Bu^t_3)\}]$ **5**, and (iii) the firxt X-ray crystal structure of an arsaalkyne–transition metal complex **5**.

Treatment of $[Pt(PPh_3)_2(C_2H_4)]$ with **1** resulted in ethylene displacement and the formation of the pale green complex **5** (Scheme 1)† which was purified in high yield (95%) by recrystallisation from toluene. Compound **5** was characterised by elemental analysis, mass spectrometry, ^1H and $^{31}P\{^1H\}$ NMR, and a single crystal X-ray structure determination has been carried out on its toluene solvate.

The molecular structure (Fig. 1)‡ of the almost linear [As–C(1)–C(2) 175.9(5)°] arsaalkyne **1** displays an As≡C bond length of 1.657(7) Å which is good agreement with a high level (VE-CEPA/A) theoretical study[5] on the related compound As≡C–Ph (1.661 Å). It should be noted that an experimental As≡C bond length of 1.651(5) Å for **1** was quoted as a footnote in the same paper but no further crystallographic details were given. The As≡C bond length in the present work also compares well with the sum of the covalent bonding radii for sp-hybridised C and As (1.652 Å) derived from experimental values for HC≡CH[6] and As≡As,[7] and is considerably shorter than is typically seen for As=C double bonds {*e.g.* 1.821(2) Å in $[(C_5H_5)Fe(CO)_2As{=}CBu^t(OSiMe_3)]$[8]}.



Scheme 1 *Reagents and conditions*: i, $[Pt(PPh_3)_2(C_2H_4)]$, toluene, $-C_2H_4$, 25 °C

The molecular structure of **5** (Fig. 2)§ shows the arsaalkyne bonds in a side-on fashion to the platinum centre, and it appears that the arsenic lone pair does not interact significantly with the metal. The coordination environment around the metal is approximately square planar, the dihedral angle between the planes Pt–P(1)–P(2) and Pt–As–C(1) being only 7.1°. There is considerable lengthening (*ca.* 8%) of the coordinated arsaalkyne As≡C bond [1.786(10) Å] in **5** compared with that of the free ligand **1**, which probably reflects the effect of back-bonding from the zero-valent platinum, lowering its effective bond order. Concomitant with this lengthening is a deviation from linearity for the coordinated arsaalkyne in which the $C_6H_2Bu^t_3$ group attached to the As≡C unit is bent away from the platinum by 39.5(7)°. In the related phosphaalkyne complex $[Pt(PPh_3)_2(\eta^2\text{-}P{\equiv}CBu^t)]$[9] **6**, this bend back angle is significantly larger (48.0°) which suggests that back bonding from the metal is more significant in this case. Conceivably, this could arise from a closer side-on approach of the phosphaalkyne to the metal centre, allowed by the smaller covalent radius of P over As, and the variation in bulk between the two alkyl groups involved. In fact the alkyne carbon [C(1)] is further from the platinum in **5** [2.075(8) Å] than in **6** [1.973(21) Å]. The Pt–P bond lengths in **5** are unexceptional.

The $^{31}P\{^1H\}$ NMR spectrum of **5** (Fig. 3) is in accord with the solid state structure and consists of two distinct resonances for the non-equivalent phosphine ligands, each possessing ^{195}Pt satellites which coincidentally overlap on the high field side of the parent signals. This pattern indicates that there is no rotation of the arsaalkyne about the metal–ligand axis at room temperature. It is noteworthy that the ^1J[Pt–P(2)] coupling (3930 Hz) in **5** is significantly larger than that in the

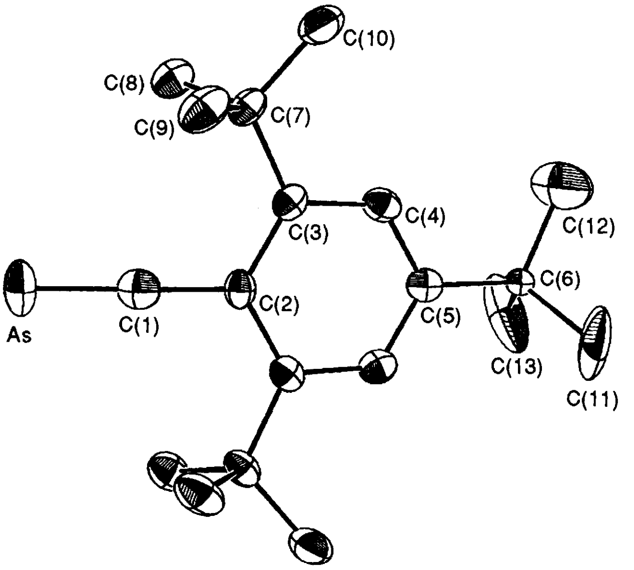


Fig. 1 Molecular structure (ORTEP, 50% thermal ellipsoids) of **1**. Selected bond lengths (Å) and angles (°): As–C(1) 1.657(7), C(1)–C(2) 1.441(9), C(2)–C(3) 1.430(5), C(3)–C(4) 1.393(6), C(4)–C(5) 1.378(5), As–C(1)–C(2) 175.9(5), C(1)–C(2)–C(3) 119.8(3).

related **6** (3587 Hz) while the ^1J[Pt–P(1)] couplings remain similar (**5** 3219, **6** 3206 Hz). The experimental $^{31}P\{^1H\}$ NMR spectrum of **5** has been satisfactorily simulated as an ABX spin system.

All the above data show a tendency for the arsaalkyne **1**, like phosphaalkynes, to exhibit alkyne-like behaviour by preferring side-on coordination over heteroatom lone pair donation. In phosphaalkynes, photoelectron spectroscopic studies[10] imply that this arises because the HOMO is of the π-type and the π–n separation is greater than in corresponding nitriles. We are currently carrying out comparable photoelectron spectroscopic and theoretical studies on **1**.

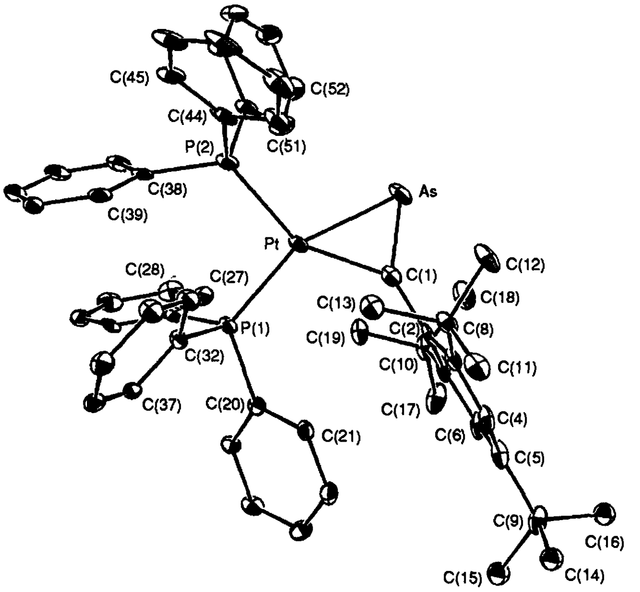


Fig. 2 Molecular structure (ORTEP, 20% thermal ellipsoids) of **5**. Selected bond lengths (Å) and angles (°): As–C(1) 1.786(10), C(1)–C(2) 1.459(13), Pt–As 2.437(1), Pt–C(1) 2.075(8), Pt–P(1) 2.278(2), Pt–P(2) 2.290(3), As–C(1)–C(2) 141.5(7), P(1)–Pt–As 156.45(7), P(2)–Pt–C(1) 149.1(3), As–Pt–C(1) 45.8(3), P(1)–Pt–P(2) 99.59(8), Pt–As–C(1) 56.4(3), Pt–C(1)–As 77.9(4), P(1)–Pt–C(1) 111.3(3), P(2)–Pt–As 103.56(7).

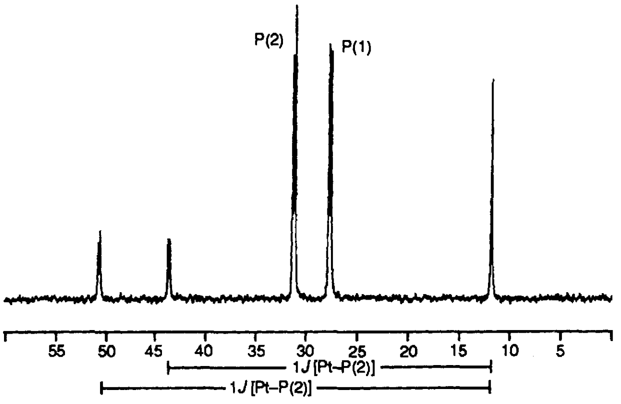


Fig. 3 $^{31}P\{^1H\}$ NMR spectrum of **5**

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Footnotes

† *Preparation of Compound* **5**: A solution of **1** (30 mg, 9 × 10^{-5} mol) in toluene (3 ml) was added over 5 min to a solution of $[Pt(PPh_3)_2(C_2H_4)]$ (67 mg, 9 × 10^{-5} mol) in toluene (5 ml) at 25 °C. The resulting solution was stirred for 5 h, concentrated to *ca.* 2 ml and placed at −30 °C overnight to yield pale green crystals of **5**·$2C_6H_5Me$: 106 mg, 95%, mp 130 °C (decomp.); $^{31}P\{^1H\}$ NMR (101.256 MHz, C_6D_6, 85% H_3PO_4) δ: 27.7 {d, P(1), ^1J[P(1)–P(2)] 20.8, ^1J [P(1)–^{195}Pt] 3219 Hz}, 31.5 {d, P(2), ^1J[P(2)–^{195}Pt] 3930 Hz}; ^1H NMR (250 MHz, C_6D_6) δ: 1.46 (s, 9H, Bu^t), 1.63 (s, 18H, $2Bu^t$), 6.71–7.72 (m, 32H, Ar); mass spectrum (EI): *m/z* 1052 (M^+, 2%), 332 ($AsCC_6H_2Bu^t{}_3{}^+$, 70), 262 ($PPh_3{}^+$, 100); satisfactory microanalytical data were obtained.

‡ *Crystal data* for **1**: $C_{19}H_{29}As$, $M = 332.4$, orthorhombic, space group *Pnma*, $a = 19.122(7)$, $b = 15.651(6)$, $c = 6.015(2)$ Å, $V = 1800$ Å^3, $Z = 4$, $D_c = 1.23$ g cm^{-3}, $F(000) = 704$, $\mu = 18.7$ cm^{-1}, crystal size 0.2 × 0.15 × 0.2 mm, radiation Mo-Kα (λ = 0.7107 Å); 173 K; the structure was solved by heavy atom methods and refined to $R = 0.052$, $R' = 0.051$ for 1052 reflections ($I \geqslant 2\sigma$), number of parameters 112, on an Enraf-Nonius CAD4 diffractometer.

§ *Crystal data* for **5**·$2C_6H_5Me$: $C_{69}H_{75}AsP_2Pt$, $M = 1236.3$, triclinic, space group $P\bar{1}$, $a = 13.057(9)$, $b = 14.229(5)$, $c = 17.274(3)$ Å, $\alpha = 95.04(2)$, $\beta = 92.54(3)$, $\gamma = 113.59(4)°$, $V = 2919(2)$ Å^3, $Z = 2$, $D_c = 1.41$ g cm^{-3}, $F(000) = 1260$, $\mu = 30.8$ cm^{-1}, crystal size 0.4 × 0.3 × 0.2 mm, radiation Mo-Kα (λ = 0.7107 Å); 293 K; the structure was solved by heavy atom methods and refined to $R = 0.052$, $R' = 0.060$ for 5834 reflections ($I \geqslant 2\sigma$), number of parameters 577, on an Enraf-Nonius CAD4 diffractometer. The methyl C atoms on C(9) are disordered over 2 sites and were refined isotropically, as were all the C atoms from both toluene solvate molecules.

Atomic coordinates, bond lengths and angles, and thermal parameters for **1** and **5** have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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