Terminal Arsenido Palladium(II) and Platinum(II) Complexes. X-Ray Crystal Structure of [{$N(CH_2CH_2PPh_2)_3$}$PtAsPh_2$]BPh_4

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The Pd^0 three-coordinate $(np_3)Pd$, [$np_3 = N(CH_2CH_2PPh_2)_3$], and the Pt^0 pseudotetrahedral $(np_3)Pt(PPh_3)$ complexes react with R_2AsX (R = Me, X = I; R = Ph, X = Cl) and $NaBPh_4$ to give $[(np_3)MAsR_2]BPh_4$, the first examples of terminal arsenides of platinum metals; the molecular structure of {$[N(CH_2CH_2PPh_2)_3]PtAsPh_2$}$BPh_4$ has been established by single-crystal diffraction methods.

The growing interest in transition metal complexes containing ER_2 groups (E = P, As, Sb) linked in the terminal position mainly stems from the potentially high reactivity both at the E and metal centres.[1] The few so far reported examples of terminal arsenido complexes are limited to molybdenum or tungsten[2] and titanium or zirconium[3] organometallic species. These have been prepared either by metal carbonylate anion nucleophilic attack on haloarsines or by transmetallation of metal halides with metallated arsines.

We report here the synthesis and the structural characterization of $[(np_3)MAsR_2]BPh_4$ (M = Pd, R = Me, **1**, R = Ph, **2**; M = Pt, R = Me, **3**, R = Ph, **4**), $np_3 = N(CH_2CH_2PPh_2)_3$, the first examples of terminal arsenides of platinum metals.

The compounds have been obtained by oxidative addition of the opportune halo-organoarsine to the metal(0) complexes $(np_3)Pd$[4] or $(np_3)Pt(PPh_3)$,[5] in the presence of $NaBPh_4$ (Scheme 1).

Such a method has been previously used only in the case of addition of PX_3 (X = halogen or hydrogen) to Ir^I or Rh^I organometallic species.[6]

The room temperature reactions of $(np_3)Pt(PPh_3)$ [or $(np_3)Pd$] with equimolar quantities of R_2AsX (R = Me, X = I; R = Ph, X = Cl) and $NaBPh_4$ in benzene–ethanol solution, under a nitrogen atmosphere afforded crystalline $[(np_3)MAsR_2]BPh_4$ (yield = 80%). The complexes appear to be light sensitive and slowly decompose both in solution and in the solid state, also under an inert atmosphere.[†] These products behave as 1:1 electrolytes in nitroethane solution. The $^{31}P\{^1H\}$ and ^1H NMR spectra[‡] are consistent with a five-coordinate formulation, the equivalence of the three

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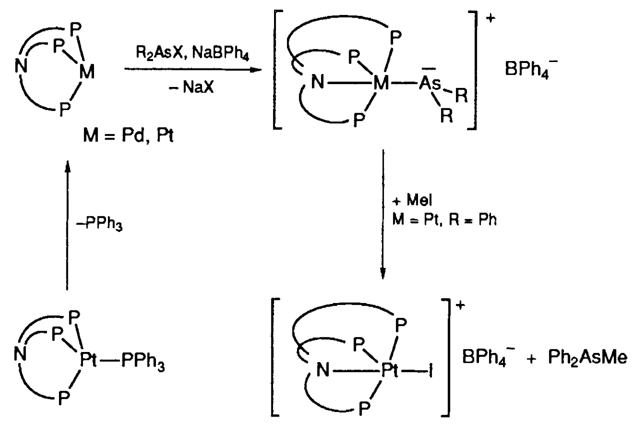
[†] The decomposition is quite rapid in the case of the palladium derivatives (*ca.* 3 days for the solid).

[‡] Selected NMR (δ, ppm, CD_2Cl_2, room temperature) data: **1**: $^{31}P\{^1H\}$, 9.8(s); ^1H, 0.95 (q, $^4J_{P\text{-}H}$ 2.8 Hz, Me_2As). **2**: $^{31}P\{^1H\}$, 9.3(s). **3**: $^{31}P\{^1H\}$, 11.3 (s, $^1J_{Pt\text{-}P}$ 3267 Hz); ^1H, 0.86 (q, with satellites, $^3J_{Pt\text{-}H}$ 31 Hz, $^4J_{Pt\text{-}H}$ 1 Hz, Me_2As). **4**: $^{31}P\{^1H\}$, 9.10 (s, $^1J_{Pt\text{-}P}$ 3136 Hz). The spectra were recorded at 121.421 (^{31}P) and 300 (^1H) MHz by a Varian VXR 300 spectrometer.



Scheme 1

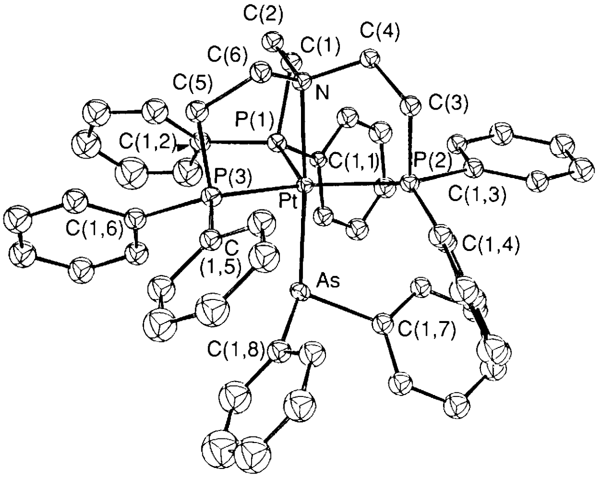


Fig. 1 Perspective view of the complex cation $[(np_3)Pt(AsPh_2)]^+$. ORTEP drawing with 30% probability ellipsoids. Selected bond distances and angles: Pt–As 2.457(1), Pt–P range 2.312(3)–2.388(3), Pt–N 2.276(7), As–C(1,7) 1.973(8), As–C(1,8) 1.951(10) Å, As–Pt–P range 93.24(7)–100.62(8), As–Pt–N 175.2(2), P–Pt–P range 109.8(1)–124.6(1), P–Pt–N range 83.3(2)–84.6(2), Pt–As–C(1,7) 111.6(2), Pt–As–C(1,8) 108.3(3), C(1,7)–As–C(1,8) 97.1(3)°

phosphorus atoms of np_3 is probably due to the rapid rotation about the metal–arsenic bond.

A complete X-ray§ structural determination revealed that the structure of **4** consists of complex cations $[(np_3)Pt(AsPh)_2]^+$ and tetraphenylborate anions. In the complex cation (see Fig. 1) the platinum centre displays a trigonal bipyramidal geometry, the three phosphorus atoms of the np_3 ligand being at the equatorial sites with the axial positions occupied by the np_3 nitrogen atom and the diphenylarsenido group. The arsenic atom shows a distinctly trigonal pyramidal coordination, as evidenced by the angles about arsenic, ranging from 97.1(3) to 111.6(2)°, with a sum of 317°. The value of the Pt–As bond length of 2.457(1) Å, only slightly shorter than the sum of covalent radii (2.50 Å),[7] is significantly shorter compared with the sole measured distances reported for transition metal compounds with a terminal arsenido ligand [Mo–As, 2.616(2) and W–As, 2.595(1) Å].[2] Nevertheless, the pyramidality of the arsenic atom is indicative of a single bond, thus arguing against any significant Pt–As π bonding.

A comparison with the free diphenylarsenido anion[8] $AsPh_2^-$ shows that, upon coordination of the $AsPh_2$ group to the $(np_3)M$ moiety, some reduction in the C–As–C angle occurs, 108.6(2)° *vs.* 97.1(3)°. This fact is probably due to the steric requirements of the phenyl groups of the np_3 ligand, that form a cage below the platinum atom, into which the arsenido unit has to fit. As a matter of fact the $AsPh_2$ group is bent with respect to the np_3Pt fragment [N–Pt–As = 175.2(2)°], in order to avoid crowding between the arsenido and the np_3 phenyl groups: the largest As···P distance involves the phosphorus atom (P2) that shows the shortest contacts with the arsenido carbon atoms. With respect to the As–C bond lengths, the average value of 1.96(1) Å fully matches the values reported in the diphenylarsenido anion.

The reaction of **4** with MeI to form $[(np_3)PtI]BPh_4$[4] and Ph_2AsMe_3 is consistent with the expected nucleophilicity of the arsenic of AsR_2 and with the known lability of the metal–arsenic bond.

These results provide further evidence for: (*a*) the high nucleophilicity of the metals(0) in the trigonal $(np_3)M$ complexes (*e.g.* activation of CH_2Cl_2)[9] and (*b*) the uncommon capability of the tripodal np_3 to stabilize very reactive groups (*e.g.* formation of stable Pt–Hg–alkyl bond).[10]

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§ *Crystal data* for $[(np_3)Pt(AsPh_2)]BPh_4$: M = 1397.19, monoclinic, space group $I2/a$, a = 18.597(6), b = 35.097(16), c = 20.297(8) Å, β = 102.94(5)°, U = 12911.4 Å^3, Z = 8, D_c = 1.44 g cm^{-3}, monochromatic Mo-Kα radiation, λ = 0.7107 Å, μ(Mo-Kα) = 28.2 cm^{-1}. The intensity data were collected within 2θ = 46° on an Enraf Nonius CAD4 diffractometer, using the ω scan technique at 294 K. The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedures. The phenyl rings were treated as rigid bodies and the hydrogen atoms were introduced in calculated positions and not refined. At convergence R and R_w factors are both 0.049 for 5345 observed reflections with $I > 3\sigma(I)$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors Issue No. 1.

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