Transformation of a Trialkynylarsine Oxide to an Arsacyclobutenyl Ligand Containing a Spirocyclic Arsenic Center

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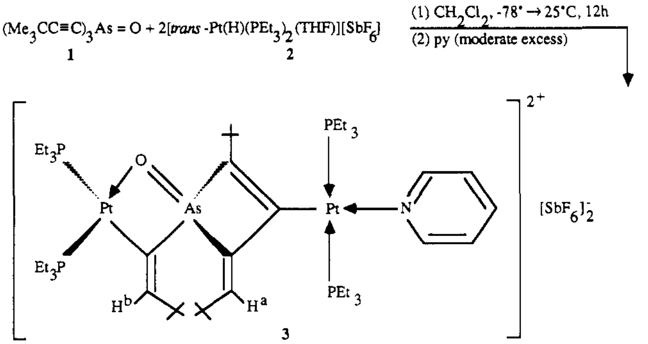
Summary: The trialkynylarsine oxide $(Me_3CC{\equiv}C)_3AsO$ reacts with 2 equiv of [*trans*-Pt(H)$(PEt_3)_2$(THF)][SbF_6], and subsequently with pyridine, to give a spirocyclic arsenic compound in which the arsenic atom participates in two four-membered rings. One ring is an arsacyclobutene that bears an alkylidene substituent at the 2-position.

Small-ring, heterocyclic compounds are of interest because the high strain energy within the ring system may impart exceptional reactivity to these molecules. Organoarsenic compounds of this type are of special interest, since not only are few examples known but also these compounds could possibly serve as precursors to new materials. Only five compounds containing an AsC_3 four-membered ring system have been reported to our knowledge. Mickiewicz and Wild prepared two arsetanes by reductive cyclization and the two corresponding methylarsonium derivatives by subsequent direct alkylation.[1] In very recent work, Tumas and co-workers at Du Pont synthesized the first example of a 1,2-dihydroarsete (arsacyclobutene) by a transmetalation reaction between a titanacyclobutene and $PhAsCl_2$.[2] This latter route has also been used to generate 1,2-dihydrophosphetes by the Du Pont group and by independent work reported earlier by Doxsee and co-workers.[3]

We now report that a cationic Pt–H complex reacts with a trialkynylarsine oxide to form a platinum complex containing an arsacyclobutenyl *As*-oxide ligand. When the trialkynylarsine oxide **1**[4] is treated sequentially with the cationic platinum–hydride complex **2**[5] and pyridine under anhydrous conditions (see eq 1), the product, **3**, is isolated as colorless needles by crystallization from an acetone/hexane solution at −15 °C.[6] Complex **3** is formed even when the reaction is performed with a 1:1 stoichiometry of **1** and **2**. The ^{1}H and ^{31}P NMR data for **3** are consistent with the molecular structure shown in eq 1.[6] For example, the proton resonances of the three *tert*-butyl substituents are nonequivalent, and the resonances of the alkylidene protons H^a and H^b show the multiplicities and coupling expected for their different relative connectivities to platinum centers. The ^{31}P NMR resonances of the phosphorus nuclei of the *cis*-PtL_2 moiety show a small $^2J_{PP}$ coupling of 17.5 Hz and very different $^1J_{PtP}$ coupling constants of 2099 and 3710 Hz, as expected. Because of the dissymmetry of complex **3**, the resonances of the phosphorus nuclei of the *trans*-PtL_2 moiety appear as an AB quartet with an anticipated large $^2J_{PP}$ coupling of 350 Hz and essentially equivalent $^1J_{PtP}$ coupling of 2567 Hz.



(1)

In addition, the molecular structure of **3** has been determined by X-ray crystallography.[7] An ORTEP diagram of the cation **3** showing the atomic numbering scheme is presented in Figure 1. The *trans*-PtL_2(py) and *cis*-PtL_2 fragments both have nearly planar coordination geometries, as expected for Pt(II) centers. Pt(2) is bonded to the arsacyclobutenyl ligand via a Pt(2)–C(3) alkenyl single bond of length 1.97 (1) Å. The (2-alkylidene)arsacyclobutenyl ring system is characterized by endocyclic and exocyclic C–C double-bond distances of 1.32 (3) Å and by a strained, endocyclic C(2)–As(1)–C(4) angle of 68.4 (8)°. The corresponding endocyclic C–C double-bond distance and C–As–C angle reported recently for 1,2,3-triphenyl-1,2-dihydroarsete are respectively 1.358 (6) Å and 69.9

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(6) Complex **3** is isolated by crystallization as indicated above in 36% yield. Examination by NMR spectroscopy of the crude reaction product obtained from a 1:2 reaction of **1** and **2** indicates a nearly quantitative formation of **3** and no byproducts. Similarly, analysis of the crude reaction product obtained from a 1:1 reaction of **1** and **2** indicates nearly quantitative formation of **3** with the appropriate amount of unreacted **1** and no byproduct formation. Complex **3**: mp 222–226 °C; ^{1}H NMR ($CD_2Cl_2/CDCl_3$) δ 0.85–1.20 (m, 36, PCH_2CH_3), 1.12 (s, 9, CMe_3), 1.22 (s, 9, CMe_3), 1.52 (s, 9, CMe_3), 1.55–1.75 (m, 12, PCH_2CH_3), 1.75–2.00 (m, 12, PCH_2CH_3), 6.25 (d, 1, C=CH^{b}CMe$_3$, $^4J_{PH}$ = 7.2 Hz, $^3J_{PtH}$ = 62 Hz), 6.59 (s, 1, C=CH^{a}CMe$_3$, $^4J_{PtH} < 15$ Hz), 7.75 (t, 1, C_5H_5N, $^3J_{HH}$ = 6.6 Hz), 7.82 (t, 1, C_5H_5N, $^3J_{HH}$ = 6.6 Hz), 8.01 (t, 1, C_5H_5N, $^3J_{HH}$ = 7.8 Hz), 8.7 (d of d, 2, C_5H_5N, $^3J_{HH}$ = 5.3, 14.6 Hz); $^{31}P\{^1H\}$ NMR ($CD_2Cl_2/CDCl_3$) δ 7.10 (d, $PEt_{3(cis)}$, $^2J_{PP}$ = 17.5 Hz, $^1J_{PtP}$ = 3710 Hz), 6.16, 9.90 (AB q, PEt_3(trans), $^2J_{PP}$ = 350 Hz, $^1J_{PtP(A)} = {}^1J_{PtP(B)}$ = 2567 Hz), 17.0 (d, PEt_3(cis), $^2J_{PP}$ = 17.5 Hz, $^1J_{PtP}$ = 2099 Hz). Anal. Calcd for $C_{47}H_{94}AsF_{12}NOP_4Pt_2Sb_2$: C, 32.26; H, 5.42. Found: C, 31.73; H, 5.44.

(7) Crystal data: $C_{50}H_{100}AsF_{12}NO_2P_4Pt_2Sb_2$ (**3**·$(CH_3)_2CO$), M_r = 1807.84, triclinic, space group $P\bar{1}$ (C_i^1) (No. 2), a = 16.646 (3) Å, b = 22.281 (3) Å, c = 10.389 (2) Å, α = 92.86 (2)°, β = 107.88 (2)°, γ = 103.79 (2)° (from 25 orientation reflections, $40° < \theta < 45°$), V = 3530 (3) Å^3, Z = 2, d_{calcd} = 1.701 g cm^{-3}, μ(Cu Kα) = 154.5 cm^{-1}. Crystal dimensions: 0.08 × 0.10 × 0.30 mm (sealed inside a thin-walled glass capillary). Intensity data ($+h,\pm k,\pm l$, 11 077 nonequivalent, absorption-corrected reflections; θ_{max} = 62°) were recorded on an Enraf-Nonius CAD-4 diffractometer (Cu Kα radiation, λ = 1.5418 Å; graphite monochromator; ω–2θ scans). The crystal structure was solved by direct methods (MULTAN-11/82). Full-matrix least-squares refinement of atomic parameters (anisotropic non-hydrogen atoms; fixed H contributions) converged (maximum shift 0.06σ) at R = 0.079 (R_2 = 0.099; GOF = 1.97) over 6057 reflections with $I > 2.0\sigma(I)$. Further details are provided as supplementary material.

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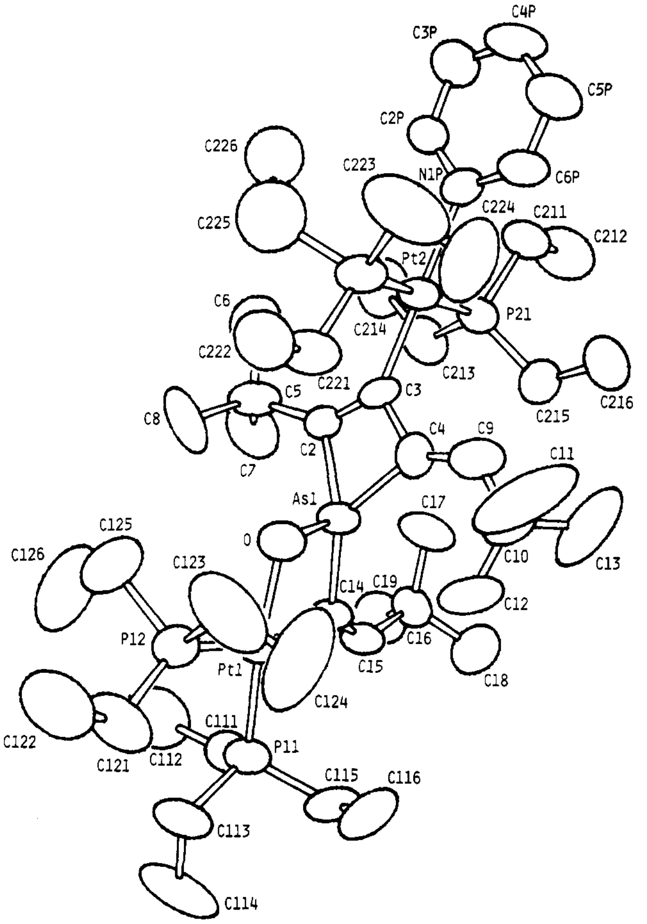

Figure 1. ORTEP diagram (33% probability ellipsoids) of the cation **3** showing the atomic numbering scheme; hydrogen atoms have been omitted for clarity. Values of selected interatomic distances (Å) and angles (deg) are as follows: Pt(1)–P(11) = 2.219 (4), Pt(1)–P(12) = 2.313 (7), Pt(1)–O = 2.08 (1), Pt(1)–C(14) = 2.03 (2), Pt(2)–P(21) = 2.318 (6), Pt(2)–P(22) = 2.328 (7), Pt(2)–C(3) = 1.97 (1), Pt(2)–N(1P) = 2.11 (1), As(1)–C(2) = 1.94 (1), As(1)–C(4) = 1.89 (2), As(1)–C(14) = 1.94 (1), As(1)–O = 1.73 (1), C(2)–C(3) = 1.32 (3), C(2)–C(5) = 1.61 (3), C(3)–C(4) = 1.47 (2), C(4)–C(9) = 1.32 (3), C(9)–C(10) = 1.47 (3), C(14)–C(15) = 1.33 (3), C(15)–C(16) = 1.56 (3); P(11)–Pt(1)–P(12) = 103.5 (2), C(14)–Pt(1)–O = 78.4 (5), P(21)–Pt(2)–P(22) = 176.5 (2), C(3)–Pt(2)–N(1P) = 178.3 (7), C(2)–As(1)–C(4) = 68.4 (8), As(1)–C(2)–C(3) = 97 (1), C(2)–C(3)–C(4) = 101 (1), C(3)–C(4)–As(1) = 94 (1), Pt(1)–O–As(1) = 98.2 (5), C(14)–As(1)–O = 90.1 (7), Pt(1)–C(14)–As(1) = 93 (1).

(2)°.[2] The Pt(μ-alkenylidene)(μ-oxo)As fragment is characterized by an exocyclic C(14)–C(15) double-bond length of 1.33 (3) Å and by a strained, endocyclic C(14)–As(1)–O angle of 90.1 (7)°. The As atom, which is located at a spirocyclic center, is represented best as an arsonium atom in a pyramidal, four-coordinate bonding mode with the As–O distance of 1.73 (1) Å being significantly longer than the average As–O distance of 1.673 (8) Å found in the complex cation $[(Ph_3AsO)_2H]^+$.[8]

We suggest that the arsacyclobutenyl portion of complex **3** is formed by a mechanism similar to that proposed earlier for the formation of a related 4-alkylidene-1-silacyclobut-2-enyl ligand.[9] At some point in the reaction sequence, a second molecule of **2** adds regio- and stereoselectively to the C–C triple bond of the remaining alkynyl substituent of **1** to give the Pt, As μ-alkenylidene ligand of **3**. This addition product is stabilized by coordination of the oxygen atom of the arsine oxide group to this Pt(II) center. A similar coordination mode is observed in the complex $[Ph_2P(\mu\text{-}C{=}CPhH)(\mu\text{-}O)PtL_2]^+$, where L is PEt_3, although the structure of this compound has not been confirmed by X-ray crystallography.[10] Presumably, the strong preference for addition of a second equivalent of **2** to the remaining alkynyl substituent of the arsine oxide is driven by the high polarity of the As–O bond, which enhances the polarization of the C–C triple bond. A like preference is not observed with trialkynylphosphine oxide reagents.[10]

The general scope of this synthetic route to arsenic heterocycles and the chemical reactivity of complex **3** are under current investigation.

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Registry No. **1**, 131296-24-7; **2**, 119455-71-9; **3**, 131276-13-6.

Supplementary Material Available: Tables of crystallographic data, atomic positional and thermal parameters, bond lengths and angles, torsion angles, and least-squares planes for complex **3** (17 pages); a table of observed and calculated structure factors for complex **3** (41 pages). Ordering information is given on any current masthead page.

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