Insertion of $^1$BuNC into thorium–phosphorus and thorium–arsenic bonds: phosphaazaallene and arsaazaallene moieties in f element chemistry†

Andrew C. Behrle and Justin R. Walensky*

The reactivity of thorium–phosphido and thorium–arsenido bonds was probed using tert-butyl isocyanide, $^1$BuNC. Reaction of (C₅Me₅)₂Th[E(H)R]₂, E = P, As; R = 2,4,6-iPr₃C₆H₂, 2,4,6-Me₃C₆H₂ with $^1$BuNC affords the first phosphazaallene and arsaazaallene moieties with an f-element.

**Results and discussion**

The synthesis of (C₅Me₅)₂Th[P(H)Tipp]₂, Tipp = 2,4,6-iPr₃C₆H₂, the first primary phosphido complex of thorium, was recently described.²⁶ In the same vein, we have begun investigating the reactivity of primary phosphido and arsenido complexes. In an effort to expand the scope of thorium–pnictogen complexes, we synthesized (C₅Me₅)₂Th[P(H)Mes]₂, Mes = 2,4,6-Me₃C₆H₂, from the stoichiometric salt metathesis reaction between (C₅Me₅)₂ThCl₂ and KP(H)Mes, eqn (1).

**Introduction**

Hydroelementation reactions such as hydrophosphination¹,² are atom efficient processes which are important in developing building blocks containing phosphorus. For example, tertiary phosphines are of interest as ligands³–⁵ and for various applications.⁶–⁸ However, the development of these reactions in organoactinide chemistry⁹ has been attenuated by a lack of starting materials.

Despite the intensity with which complexes with actinide–nitrogen bonds have been studied,¹⁰–¹³ there exists a tremendous knowledge gap with respect to the heavier pnictogen elements. To date, twenty actinide–phosphido or phosphindene bonds¹⁴–²⁶ and five actinide–arsenido bonds²⁷–²⁹ have been reported. Of these, only nine thorium–phosphorus and one thorium–arsenic bond are known.

Due to the dearth of actinide–phosphorus and actinide–arsenic bonds, the reactivity of these bonds is unknown. Migratory insertion, the initial step in many catalytic cycles, has been used historically to probe reactivity. In transition metals, primary phosphido complexes are also sparse,³⁰–³⁷ but Waterman’s group has investigated the reactivity of zirconium–phosphorus bonds with $^1$BuNC.³⁸ Interestingly, a proton migration from the phosphorus to the carbon of the isocyandic occurs. Here we describe the synthesis of new thorium phosphido and arsenido complexes and their reactivity with $^1$BuNC, which differs from their transition metal analogs.

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Compound 2 was isolated as a ruby red crystalline solid in 70% yield. The diagnostic spectroscopic handles include the As–H resonance at δ 2.61 in the 1H NMR spectrum and the ν_{AsH} stretch at 2089 cm$^{-1}$ in the IR spectrum. The IR stretching frequencies compare well to the ν_{AsH} stretches at 2061 cm$^{-1}$ and 2052 cm$^{-1}$ for zirconium(iv) and uranium(iv) primary arsenido complexes, [(N₃N)ZrAsHR] (R = Mes and Ph; N₃N = N(CH₂CH₂NSiMe₃)$_₃$) [39] [U(TrenTIPS)(AsH₂)]$_₂$ [28] reported by Waterman and Liddle’s groups, respectively. The molecular structure of 2 is shown in Fig. 2. The Th1–As1 bond length is 3.0028(6) Å and is slightly longer than the sum of the single

Fig. 1 Thermal ellipsoid plot of 1 at the 50% probability level. Hydrogens have been omitted for clarity. Selected bond distances (Å) and angles (°): Th1–P1, 2.872(5); P1–C11, 1.829(5); P1–Th–P1*, 102.68(2); Th1–P1–C11, 128.45(9).

Fig. 2 Thermal ellipsoid plot of 2 at the 50% probability level. Hydrogens have been omitted for clarity. Selected bond distances (Å) and angles (°): Th1–As1, 3.0028(6); As1–C11, 1.959(5); As1–Th1–As1*, 88.02(2); Th1–As1–C11, 116.53(15).
bond covalent radii for thorium and arsenic (2.96 Å). The Th−As bond angle is 116.53(15)°. We sought to investigate the reactivity of 1 and 2 through insertion reaction with CO surrogates. Waterman’s group has reported on the generation of phosphaalkenes and arsaaalkenes from the reaction between a primary phosphido/arsenido organometallic complex and an alkyl isocyanide.38,39 We anticipated from the reaction between a primary phosphine had been formed in the reaction. After recrystallization from a concentrated methylcyclohexane solution, the η²-(N,C)-phosphaazaallene thorium complexes [(C5Me5)2Th[P(H)Tipp]]2, or 1 the solution underwent a color change to yellow, eqn (3). Initial spectroscopic experiments showed that one equivalent of the primary phosphine had been formed in the reaction. The 31P NMR resonances shifted slightly upfield as yellow solids.

The diagnostic spectroscopic features associated with 3 and 4 include the stretches at 2181 and 2186 cm−1, and 1600 and 1602 cm−1, which can be assigned to the νCN and νCP stretches, respectively. The 31P NMR resonances shifted slightly upfield from the starting material to −21.28 and −10.70 ppm for 3 and 4, respectively. Additionally, the 13C NMR resonance of the central carbon of the phosphaazaallene was found at 150.85 and 151.05 ppm with Jp−c = 152.3 Hz and 103.0 Hz, for 3 and 4, respectively. Compound 2 exhibited a similar reactivity to yield a η²-(N,C)-arsaaallene thorium complex [(C5Me5)2Th(CN-Bu)[η²-N,C]2(BuNC=AsTipp)], 5, as an orange solid. The spectroscopic features of 5 can be found in Table 1. The solid-state structures of 4 and 5 were determined using X-ray diffraction studies, Fig. 3. Table 2 lists selected bond distances (Å) and angles (°). Compounds 4 and 5 are isostructural with one another and represent the first examples of actinide phospha- and arsaaazaallene complexes. As with transition metals, such complexes are very rare as only two phosphaaazaallene compounds have been isolated: [η1-Nacnac]Ti(CN′Bu)[η1-N,C]2BuNC=PMes* (Nacnac = [2,6-Pr2C6H4]NC(CH3)CHC(CH3)2N)[2,6-Pr2C6H4] and Cp′,Nb(φ)(η1-N,C)-PhNC=PMes*.42

There is a substantial elongation of the N−C bond (N2−C11) to 1.348(8) and 1.347(7) Å in 4 and 5, respectively, compared to a metal free heterocumulene such as PhN=CC=PMes*, with a N−C bond distance of 1.210 Å.33 The N−C bonds in 4 and 5 are also longer than those found in products of isocyanide insertion into actinide–alkyl bonds. For example, 1.276(7) Å was observed in (C5Me5)2(C8H8)U[η2-(N,C)-C(Ph)=N′Bu].44 Additionally the N−C−E bond angle is decreased to 152.1(5) and 150.3(4)°, respectively, relative to the N−C−E bond angle of 171.0° of PhN=CC=PMes*. The C=E bond distance in 4 of 1.691(6) Å is only slightly longer than the C=E of 1.651(1) Å in PhN=CC=PMes* and matches the C=E bond length of 1.688(19) Å in [(C6H5SiMe3)2Nb(C)[η2-(N,C)-PhNC=PM(2,4,6′-Bu2C6H2)]]. The Th−N2 bond distances of 2.346(5) and 2.364(4) Å in 4 and 5, respectively, compare well to other thorium–amido bond lengths of 2.389(2) Å, [η5-1,2,4-(Me3C)3C5H2]2Th[Cl][N(p-tolyl)SiH2Ph]45 2.322(5) Å, [η5-1,2,4-(Me3C)3C5H2]2Th[N(p-tolyl)(Se-Se)]46 and 2.256(8) Å, [(C5Me5)2Th[N(Ph)(CH3)Ph]]46.

The formation of 4 and 5 is expected to occur through a 1,1 insertion of the alkyl isocyanide in the Th−P bond. Unlike the ([N3N]ZrEHR) E = P, As; R = Cy, Ph) complexes which can undergo 1,2 rearrangement to phospha-arsaaalkenes, 4 and 5 do not undergo rearrangement, rather a double reduction of the alkyl isocyanide with the concomitant release of H2ER (E = P, As; R = Tipp, Mes). There are two conceivable reaction pathways for the generation of 4 and 5, Fig. 4. The first involves a transient terminal thorium−phosphinidene intermediate. There is a literature precedent for this route as Mindiola’s group have reported the reaction of a terminal titanium phosphinidene, (η1-Nacnac)Ti(CH2Bu)[PMes*], with a tert-butyl isocyanide to yield the titanium phosphaazaallene complex, (η1-Nacnac)Ti(CH2Bu)[η1-N,C]2BuNC=PMes*.44 The other route is 1,1 insertion of the isocyanide to form an η2-iminoacyl, followed by an intramolecular deprotonation. To investigate the possible reaction pathway, we attempted the addition of tert-butyl isocyanide to (C5Me5)2Th[PH(Tipp)]2 at −200 °C and

<table>
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<th>Table 1 Spectroscopic features of compounds 3, 4, and 5</th>
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<tr>
<td>P[H] (δ)</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
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<td>5</td>
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Fig. 3 Thermal ellipsoid plots of 4 and 5 at the 50% probability level. Hydrogens have been omitted for clarity.

Table 2 Selected bond distances (Å) and angles (°) for 4 and 5

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<tr>
<th></th>
<th>Th1–C11</th>
<th>Th1–N2</th>
<th>Th1–C12</th>
<th>N1–C12</th>
<th>N2–C11</th>
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<td>4</td>
<td>2.430(6)</td>
<td>2.346(5)</td>
<td>2.643(6)</td>
<td>1.131(8)</td>
<td>1.348(8)</td>
<td>1.691(6)</td>
<td>152.1(5)</td>
<td>115.8(3)</td>
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<tr>
<td>5</td>
<td>2.419(5)</td>
<td>2.364(4)</td>
<td>2.638(6)</td>
<td>1.128(7)</td>
<td>1.347(7)</td>
<td>1.822(5)</td>
<td>150.3(4)</td>
<td>114.5(2)</td>
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</table>

Fig. 4 Possible reaction pathways for the generation of 3, 4 and 5.
slowly warmed the reaction while monitoring the reaction progress using $^{31}$P NMR. At $-80$ °C we observed the formation of 4, H$_3$PTipp, [C$_5$Me$_5$)$_2$Th[P(H)Tipp]$_2$, and a singlet at $-26.5$ ppm. Upon heating to $-70$ °C the reaction was complete with disappearance of the resonance at $-26.5$ ppm. This resonance at $-26.5$ ppm has not been identified but it is possible that it is 4 without a coordinated isocyanide. We saw no evidence of a transient terminal phosphinidene as no resonance $>100$ ppm was observed (see ESI).

**Conclusion**

In summary we have broadened the scope of actinide–nitrogen–arsenic complexes by the isolation and characterization of new thorium primary phosphido and arsenido compounds. Both compounds exhibited spectroscopic diagnostic features in the infrared and heteronuclear NMR experiments. Insertion reactions of an alkyl isocyanide into the thorium–primary phosphanide bond resulted in the formation of phospha-/arsaazaallene complexes that do not exhibit any type of rearrangement. Further investigation is required to elucidate whether this reactivity is unique to the actinides or Lewis acids coordinated to two primary phosphido or arsenido ligands. Therefore group IV and alternative actinide metals are under investigation.

**Experimental**

**General considerations**

The syntheses and manipulations described below were conducted using standard Schlenk and glovebox techniques. All the reactions were conducted in a Vacuum Atmospheres inert atmosphere (N$_2$) glovebox or a double-manifold Schlenk line. Toluene, 1,2-dimethoxyethane, diethyl ether and hexane were purchased anhydrous, stored over activated 4 Å molecular sieves, and sparged with nitrogen prior to use. Methylcyclohexane was dried over activated 4 Å molecular sieves and sparged with nitrogen for thirty minutes prior to use. tert-Butyl isocyanide was dried over 4 Å molecular sieves, freeze–evacuate–thawed three times, distilled, and stored under nitrogen. All available reactants were purchased from suppliers and used without further purification. ThCl$_4$(DME)$_2$, THF (75 mL). A reflex condenser was attached under nitrogen and 1–2 mL of 1,2-dibromoethane were added to the reaction. The reaction was heated to reflux and allowed to react for 8 h. The Grignard reaction was allowed to cool to room temperature. A 250 mL Schlenk flask was charged with AsCl$_3$ (2.56 g, 14.1 mmol) and THF (30 mL) and cooled to $-40$ °C via a CO$_2$ bath. The Grignard was added via a cannula to the AsCl$_3$ followed by ZnCl$_2$ (3.84 g, 28.2 mmol). The reaction mixture was allowed to stir at $-40$ °C for 6 h, slowly warmed to room temperature and allowed to stir for an additional 24 h at room temperature. The filtrate was isolated via cannula filtration and the white solid was extracted twice with diethyl ether (2 × 30 mL) and added to the filtrate. The solution was concentrated and placed in a $-20$ °C freezer. Long colorless crystals grew over a period of 36 h. The crystals were isolated and dried (two crops 3.35 g, 68%).

<table>
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<th>Compound</th>
<th>Formula</th>
<th>Molecular Weight</th>
<th>Purity</th>
<th>Yield</th>
<th>References</th>
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<td>263.2</td>
<td>95%</td>
<td>63%</td>
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<td>TippAsH$_2$</td>
<td>(C$_5$H$_5$)$_2$AsH$_2$</td>
<td>245.2</td>
<td>92%</td>
<td>51%</td>
<td>(a)</td>
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In summary we have broadened the scope of actinide chemistry by the isolation and characterization of new actinide primary phosphido and arsenido compounds. This work highlights the potential for using actinide chemistry to access novel nitrogenuous or arsenic–nitrogen–arsenic complexes.
freezer and 0.0935 mmol), methylcyclohexane (5 mL) and placed in a −23 °C freezer. Red prism crystals grew after 36 h, and were isolated and dried to yield the product (two crops, 140 mg, 70%). $^1$H NMR (CD$_2$Cl$_2$, 23 °C): $\delta$ 7.26 (s, 4H, ArH), 3.66 (sept, $^3$J$_{H-H}$ = 6.6 Hz, 4H, CH$_{ortho}$(CH$_3$)$_3$), 2.95 (sept, $^3$J$_{H-H}$ = 7.2 Hz, 2H, CH$_{para}$(CH$_3$)$_3$), 2.61 (s, 2H, AsH), 1.98 (s, 30H, C$_5$(Me)$_5$), 1.54 (d, $^3$J$_{H-H}$ = 6.6 Hz, 24H, CH(CH$_2$)$_{ortho}$), 1.34 (d, $^3$J$_{H-H}$ = 7.2 Hz, 12H, CH(CH$_2$)$_{para}$). $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$, 23 °C): $\delta$ 151.07, 146.69, 141.44, 127.33, 120.45, 35.77, 34.51, 24.75, 24.50, 11.99. IR (cm$^{-1}$): 2959 (s), 2917 (s), 2870 (s), 2089 (m), 1599 (m), 1551 (s), 1455 (s), 1373 (m), 1307 (m), 1245 (w), 1162 (m), 1098 (m), 1061 (m), 1021 (m), 934 (m) 870 (m), 805 (m), 744 (m), 609 (m). Anal. calc. for C$_{42}$H$_{50}$As$_2$Th: C, 56.60%; H, 7.41%. Found: C, 56.21%; H, 7.38%.

(C$_6$Me$_{5}$)$_2$Th(CN'Bu)(N$_2$N$_3$-C) (BuNCNTPt), 4. The same procedure was employed as for 3 using 1 (100 mg, 0.124 mmol) and tert-butyl isocyanide (21 mg, 0.233 mmol) to yield a yellow solid (81 mg, 80%). $^1$H NMR (CD$_2$Cl$_2$, 23 °C): $\delta$ 7.05 (s, 2H, ArH), 3.10 (s, 6H, CH$_{ortho}$(CH$_3$)$_3$), 2.27 (s, 6H, CH$_{para}$(CH$_3$)$_3$), 1.26 (s, 30H, C$_5$(Me)$_5$), 1.25 (s, 9H, CNCMe$_3$), 1.02 (s, br, 9H, CNCMe$_3$). $^{13}$C($^1$H) NMR (CD$_2$Cl$_2$, 23 °C): $\delta$ 183.56 (d, $^3$J$_{P-C}$ = 5.60 Hz, C$_{ipso}$-P), 163.29 (CNCMe$_3$), 151.05 (d, $^3$J$_{P-C}$ = 103.0 Hz, Me$_2$CNCMe$_3$), 142.65 (d, $^3$J$_{P-C}$ = 4.5 Hz, 134.41 (the C(sp$^2$)-H resonance was buried under the solvent resonance), 122.42, 59.47 (d, $^3$J$_{P-C}$ = 12.0 Hz, Me$_2$CNCMe$_3$), 56.66 (CNCMe$_3$), 31.69 (Me$_2$CNCMe$_3$), 25.48, 21.33, 11.87. $^{1}$H NMR (CD$_2$Cl$_2$, 23 °C): $\delta$ −10.70. IR (cm$^{-1}$): 2956 (s), 2913 (s), 2304 (w), 2186 (s), 1602 (m), 1448 (s), 1355 (s), 1191 (s), 1093 (s), 1030 (s), 846 (m), 708 (m), 648 (m). C$_{42}$H$_{50}$NSnPTb: C, 57.20%; H, 7.26%; N, 3.42%. Found: C, 57.40%; H, 6.99%; N, 3.30%.

<table>
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<th>Table 3 X-ray crystallography data for complexes 1, 2, 3, and 5</th>
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<td>2</td>
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<th>CCDC deposit number</th>
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<th>Formula weight (g mol$^{-1}$)</th>
<th>Crystal habit, color</th>
<th>Temperature (K)</th>
<th>Space group</th>
<th>Crystal system</th>
<th>Volume (Å$^3$)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>$\beta$ (°)</th>
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<td>1455163</td>
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<td>Prism, orange</td>
<td>100(2)</td>
<td>Pccn</td>
<td>Orthorhombic</td>
<td>3598.3(5)</td>
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<td>12.1067(10)</td>
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<td>4809.0(7)</td>
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<tr>
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<td>100(2)</td>
<td>$\bar{P}$m</td>
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<td>29.9966(19)</td>
<td>14.5456(9)</td>
<td>13.4870(9)</td>
<td>90.00</td>
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| Calculated density (Mg m$^{-3}$) | 1.486 |
| Absorption coefficient (mm$^{-1}$) | 4.257 |
| Final R indices ($R > 2\sigma$) | 0.0211 |
| $R_w = 0.0431$ | $R_w = 0.0437$ | 0.0193 |

| 1455345 | C$_{42}$H$_{50}$SnBr$_{0.5}$Cl$_{1.45}$ | 349.15 |
| Prism, colorless | 100(2) | $\bar{P}$ | Triclinic |
| 813.6(2) | 8.3739(12) |
| 9.1197(13) | 11.6208(16) |
| 75.718(2) | 71.5280(10) |
| 81.712(2) | 71.5280(10) |

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[(C₉Me₃)₂Th(CN₂Bu)(η²-N,C)(BuNCAsTipp)], 5. The same procedure was employed as for 3 using 2 (200 mg, 0.188 mmol) and tert-butyl isocyanide (32 mg, 0.385 mmol) to yield 5 as an orange solid (146 mg, 82%). X-ray quality crystals were grown from a toluene/hexane mixture at −23 °C. 1H NMR (CD₂Cl₂, 23 °C): δ 7.32 (s, 2H, ArH), 4.84 (s, br, 2H, CH⁻ortho(CH₃)₂), 2.98 (sept, 3JH-H = 7.2 Hz, 1H, CH₃para(CH₃)₂), 2.16 (s, 30H, C₉Me₃), 1.67 (d, 3JH-H = 7.2 Hz, 2H, CH₂(CH₃)₂ortho), 1.38 (d, 3JH-H = 7.2 Hz, 3H, CH(CH₃)₂ortho), 1.24 (s, 9H, CNCMe₃), 0.97 (s, br, 9H, CNCMe₃). 13C{¹H} NMR (CD₂Cl₂, 23 °C): δ 164.41 (CN(C₉Me₃), (C₉Me₃−As could not be located), 154.25 (Me-CNCAsTipp), 154.05, 146.65, 122.65, 120.24, 60.30 (Me₂CNCAsTipp), 57.01 (CN(C₉Me₃)), 35.63, 34.90, 32.03 (Me₂CNCAsTipp), 29.01 (CN(C₉Me₃)), 26.91, 24.67, 11.79. IR (cm⁻¹): 2958 (s), 2917 (s), 2865 (s), 2182 (m), 1513 (m), 1452 (m), 1367 (m), 1312 (m), 1214 (m), 1109 (m), 1027 (m), 877 (w), 805 (m), 624 (m). Anal. calcd for C₄₅H₇₁N₂AsTh: C, 57.08%; H, 7.56%; N, 2.96%. Found: C, 58.72%; H, 7.45%; N, 2.71%.

Crystallographic data collection and structure determination

The selected single crystal was mounted on nylon cryoloops using viscous hydrocarbon oil. X-ray data collection was performed at 100(2) K. X-ray data were collected on a Bruker CCD ractometer with monochromated Mo-Kα radiation (λ = 0.71073 Å). The data collection and processing were performed using the Bruker SHELX-2014/7 program. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed at calculated positions and included in the refinement using a riding model. Thermal ellipsoid plots were prepared using X-seed55 with 50% of probability displacements for non-hydrogen atoms. Crystal data and details of data collection for complexes 1, 2, 3, and 5 are provided in Table 3.

Acknowledgements

We gratefully acknowledge the U.S. Department of Energy, Office of Science, Early Career Research Program under award DE-SC-0014174 for support of this work.

References


