Insertion of \(^{1}BuNC\) into thorium–phosphorus and thorium–arsenic bonds: phosphaazaallene and arsaazaallene moieties in f element chemistry†

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The reactivity of thorium–phosphido and thorium–arsenido bonds was probed using tert-butyl isocyanide, \(^{1}BuNC\). Reaction of (C\(_{5}\)Me\(_{5}\))\(_{2}\)Th[E(H)R]\(_{2}\), E = P, As; R = 2,4,6-iPr\(_{3}\)C\(_{6}\)H\(_{2}\), 2,4,6-Me\(_{3}\)C\(_{6}\)H\(_{2}\) with \(^{1}BuNC\) affords the first phosphaazaallene and arsaazaallene moieties with an f-element.

Results and discussion

The synthesis of (C\(_{5}\)Me\(_{5}\))\(_{2}\)Th[P(H)Tipp]\(_{2}\), Tipp = 2,4,6-iPr\(_{3}\)C\(_{6}\)H\(_{2}\), 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 (C\(_{5}\)Me\(_{5}\))\(_{2}\)Th[P(H)Mes]\(_{2}\), \(^{1}\)Mes = 2,4,6-Me\(_{3}\)C\(_{6}\)H\(_{2}\), from the stoichiometric salt metathesis reaction between (C\(_{5}\)Me\(_{5}\))\(_{2}\)ThCl\(_{2}\) and KP(H)Mes, eqn (1).

Complex \(^{1}\) was isolated as a vibrant orange crystalline solid in 54% yield. The diagnostic spectroscopic features include the doubly P–H resonance and the \(\nu_{PH}\) stretch centered at 3.80 ppm with \(J_{P-H} = 224\) Hz and 2304 cm\(^{-1}\), respectively. The large \(J_{P-H}\) coupling constant reflects the large amount of s-character in the P–H bond.

The \(^{31}\)P[H] resonance is located at 15.37 ppm and compares well to the \(^{31}\)P[H] resonance of a structurally similar thorium–phosphido compound, (C\(_{5}\)Me\(_{5}\))\(_{2}\)Th[P(H)Tipp]\(_{2}\), located at 1.66 ppm. The molecular structure of \(^{1}\) is shown in Fig. 1 and mimics the bond distances and angles of (C\(_{5}\)Me\(_{5}\))\(_{2}\)Th[P(H)Tipp]\(_{2}\).

While actinide–phosphido complexes are few in number, the number of structurally characterized actinide–arsenido compounds is five: a bimetallic thorium poly-arsenido cluster, \([\text{Cp'}^{\prime}\text{Th}[\mu-\eta^{2:1:2:1}\text{As}_{6}^{2}\text{ThCp'}^{\prime}]\) \(\text{Cp'}^{\prime} = \text{C}_{6}\text{H}_{4}\text{Bu}_{2}\)\(^{29}\) and a series of uranium(v) complexes: \([\text{U(Tren Tip'PS)}][\mu-\eta^{2:1:2:1}\text{As}_{5}^{2}\text{H}_{3}]\)\(^{27}\) \([\text{U(Tren Tip'PS)}][\text{As}_{5}^{2}\text{H}_{3}]\), \([\text{U(Tren Tip'PS)}][\text{As}_{5}^{2}\text{H}_{3}]\) \([\text{K(B15C5)}_{2}]\), and \([\text{U(Tren Tip'PS)}][\text{As}_{5}^{2}\text{H}_{3}]\) \([\text{K(B15C5)}_{2}]\) \([\text{Tren Tip'PS)}][\text{As}_{5}^{2}\text{H}_{3}]\) \([\text{K(B15C5)}_{2}]\) \([\text{Tren Tip'PS)}][\text{As}_{5}^{2}\text{H}_{3}]\) \([\text{K(B15C5)}_{2}]\).\(^{28}\) We hypothesized that the 2,4,6-iPr\(_{3}\)C\(_{6}\)H\(_{2}\) framework would be sterically large enough to stabilize an actinide metal center such as thorium. Using room temperature \(\sigma\)-bond metathesis between (C\(_{5}\)Me\(_{5}\))\(_{2}\)ThMe\(_{2}\) and two equivalents of H\(_{2}\)AsTipp, we successfully isolated the first organothorium primary arsenido complex, (C\(_{5}\)Me\(_{5}\))\(_{2}\)Th[As(H)Tipp]\(_{2}\), eqn (2):

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Compound 2 was isolated as a ruby red crystalline solid in 70% yield. The diagnostic spectroscopic handles include the \( \text{As}–\text{H} \) resonance at \( \delta 2.61 \) in the \( ^1\text{H} \) NMR spectrum and the \( \nu \text{AsH} \) stretch at 2089 cm\(^{-1}\) in the IR spectrum. The IR stretching frequencies compare well to the \( \nu \text{AsH} \) stretches at 2061 cm\(^{-1}\) and 2052 cm\(^{-1}\) for zirconium(IV) and uranium(IV) primary arsenido complexes, \([(\text{N}_3\text{N})\text{ZrAsHR}] \) \(^{39}\), \([\text{U}(\text{TrenTIPS})(\text{AsH}_2)] \) \(^{28}\) 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

\[
\text{Th1–P1, 2.872(5); P1–C11, 1.829(3); P1–Th–P1*, 102.68(2); Th1–P1–C11, 128.45(9).}
\]

\[
\text{Th1–As1, 3.0028(6); As1–C11, 1.959(5); As1–Th1–As1*, 88.02 (2); Th1–As1–C11, 116.53(15).}
\]
bond covalent radii for thorium and arsenic (2.96 Å). The Th1–As1–C11 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 arsaalkenes from the reaction between a primary phosphido/arsenido organo-metallic complex and an alkyl isocyanide.38,39 We anticipated a similar reactivity with our thorium complexes. When tert-butyl isocyanide was added to [(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. After recrystallization from a concentrated methylcyclohexane solution, the [(C5Me5)2Th(CN

\[\text{H}_2\text{Bu})\] complex was isolated 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 \(\nu_{\text{CN}}\) and \(\nu_{\text{CP}}\) stretches, respectively. The \(^{31}\text{P}\) NMR resonances shifted slightly upfield from the starting material to \(-21.28\) and \(-10.70\) ppm for 3 and 4, respectively. Additionally, the \(^{13}\text{C}\) NMR resonance of the central carbon of the phosphaazalene was found at 150.85 and 151.05 ppm with \(J_{\text{P-C}} = 152.3\) Hz and 103.0 Hz, for 3 and 4, respectively. Compound 2 exhibited a similar reactivity to yield a \(\eta^2-(N,C)\)-arsaazalene thorium complex \([(\text{C}_5\text{Me}_5)_2\text{Th}(\text{CNBu})[\eta^2-N,C]-(\text{BuNC}=\text{AsTipp})]\), 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 isostrophic with one another and represent the first examples of actinide phospha- and arsaazalene complexes. As with transition metals, such complexes are very rare as only two phosphaazalene compounds have been isolated: \([\eta^1-\text{Nacnac}]\text{Ti}(\text{CNBu})[\eta^2-N,C]-(\text{BuNC}=\text{PMes})^*\) (Nacnac = [2,6-Pr₂C₆H₄]NC(2,6-Pr₂C₆H₄)), \([\eta^1-\text{Nacnac}]\text{Ti}(\text{CNBu})[\eta^2-N,C]-(\text{BuNC}=\text{PMes})^*\) (Nacnac = [2,6-Pr₂C₆H₄]NC(2,6-Pr₂C₆H₄)), \(\text{Mes}^* = 2,4,6-\text{Bu}_3\text{C}_6\text{H}_2\) and \(\text{Cp}^*\text{N}β(\text{Cl})\) \([\eta^2-N,C]-(\text{PhNC}=\text{PMes})^*\).

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=C=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 acetylide–alkyl bonds. For example, 1.276(7) Å was observed in [(C5Me5)(C8H8)U][\(\eta^2-(N,C)-(\text{Ph})\text{Bu}]=\text{N}=\text{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=C=PMes*. The C=π bond distance in 4 of 1.691(6) Å is only slightly longer than the C=π of 1.651(1) Å in PhN=C=PMes* and matches the C=π bond length of 1.688(19) Å in [(\text{C}_6\text{H}_4\text{SiMe}_3)_2\text{Nb}(\text{Cl})[\eta^2-(N,C)-(\text{Ph})\text{Bu}=\text{Bu}]=\text{N}]=\text{Bu}].

The Th1–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, \([\eta^5-\text{C},2,4,5-(\text{Me}_3\text{C})_3\text{C}_6\text{H}_2]\text{Th}[\text{Cl}][\text{N}(\text{p-tolyl})\text{SiH}_2\text{Ph}]\), 2.322(5) Å, \([\eta^5-\text{C},2,4,5-(\text{Me}_3\text{C})_3\text{C}_6\text{H}_2]\text{Th}[\text{N}(\text{p-tolyl}){\text{Se}}\text{Se})]\), 2.256(8) Å, \([(\text{C}_5\text{Me}_5)_2\text{Th}[\text{N}(\text{Ph})[(\text{CH}_3)\text{Ph})]]\).

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 \([\text{N}_2\text{N}][\text{ZrEHR}]\) \([E = \text{P}, \text{As}; R = \text{Cy}, \text{Ph})\) complexes which can undergo 1,2 rearrangement to phospha-arsa-azaalkenes, 4 and 5 do not undergo rearrangement, rather a double reduction of the alkyl isocyanide with the concomitant release of \(\text{H}_2\)ER (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, \([\eta^1-\text{Nacnac}]\text{Ti}(\text{CH}_2\text{Bu})[\text{PMes}^*]\), with a tert-butyl isocyanide to yield the titanium phosphaazalene complex, \([\eta^1-\text{Nacnac}]\text{Ti}(\text{CNBu})[\eta^2-N,C]-(\text{BuNC}=\text{PMes})^*\).\(^{44}\) The other route is 1,1 insertion of the isocyanide to form an \(\eta^2\)-iminooxacyl, followed by an intramolecular deprotonation. To investigate the possible reaction pathway, we attempted the addition of tert-butyl isocyanide to \([(\text{C}_5\text{Me}_5)_2\text{Th}[\text{P(H)Tipp}]\] at \(-200 \degree\) C and

| Table 1 Spectroscopic features of compounds 3, 4, and 5 |
|-----------------------------------------------|
| \(\text{\(^{31}\text{P}\)}[\text{\(^1\text{H}\)] (\(\delta\))\text{ \(\text{\(^{13}\text{C}\)}[\text{\(^1\text{H}\)] \text{central \text{allene carbon} (\(\delta\))}\text{ \(\nu_{\text{CN}}\) (cm}\(^{-1}\))\text{ \(\nu_{\text{CE}}\) (E = P, As) (cm}\(^{-1}\))}| |
| 3\text{ } | -21.28 | 150.85, \(J_{\text{P-C}} = 152.3\) Hz | 2181 | 1600 |
| 4\text{ } | -10.70 | 151.05, \(J_{\text{P-C}} = 103.0\) Hz | 2182 | 1513 |
| 5\text{ } | 154.25 | 2181 | 1602 | 2186 |
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

|       | Th1–C11 | Th1–N2 | Th1–C12 | N1–C12 | N2–C11 | C11–E1 | N2–C11–E1 | C11–E1–C19 |
|-------|---------|--------|---------|--------|--------|--------|------------|-------------|
| 4     | 2.430(6) | 2.346(5) | 2.643(6) | 1.131(8) | 1.348(8) | 1.691(6) | 152.1(5) | 115.8(3) |
| 5     | 2.419(5) | 2.364(4) | 2.638(6) | 1.128(7) | 1.347(7) | 1.822(5) | 150.3(4) | 114.5(2) |

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$_3$]$_2$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–pnicto-

genide 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 allyl isocyanide into the thorium–primary pnicto-
genide 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 con-
ducted 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. Methylcyclo-

hexane was dried over activated 4 Å molecular sieves, and sparged with nitrogen prior to use. tert-Butyl iso-
cyanide was dried over 4 Å molecular sieves and stored under nitrogen. All available reactants were purchased from suppliers and used without further purification. ThCl$_4$(DME)$_2$, [C$_5$Me$_3$]$_2$ThCl$_2$, [C$_5$Me$_3$]$_2$ThMe$_2$, TippPCI$_2$, [C$_5$Me$_3$]$_2$Th[P(H)Tipp]$_2$, MesPCI$_2$, MesPH$_2$, and [C$_5$Me$_3$]$_2$Th[P(H)Tipp]$_2$ were synthesized as previously described. KPH(Mes) was prepared from H$_2$PMes and

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2.67 (s, 12H, CH₃-ortho), 2.33 (s, 6H, CH₃-para), 1.89 (s, 30H, C₆Mes). ¹³C[¹H] NMR (CD₂Cl₂, 23 °C): δ 140.00 (d, 3J_C-Br = 18.0 Hz), 139.16, 133.90 (the C(sp³)-H resonance was buried under the solvent resonance), 126.77, 52.45, 20.97, 11.47. ³¹P{¹H} NMR (CD₂Cl₂, 23 °C): δ 15.37. IR (cm⁻¹): 2970 (s), 2855 (s), 2341 (m), 1446 (s), 1433 (s), 1378 (m), 1257 (m), 1100 (m), 1067 (m) 1024 (m), 952 (w), 940 (w), 894 (w), 847 (m), 703 (w). Anal. calc. for C₃₈H₅₄P₂Th: C, 56.72%; H, 6.76%. Found: C, 56.61%; H, 6.75%.

(C₆Me₅)₂Th[As(H)Tipp], 2. A 20 mL scintillation vial was charged with [C₆Me₅]₂ThMe₅ (100 mg, 0.188 mmol), toluene (8 mL), and placed in a −23 °C freezer for 30 minutes. The vial was removed from the freezer and H₂AsTipp (106 mg, 0.378 mmol) was added dropwise and allowed to stir at room temperature for 12–14 h to yield a cherry red solution. The solvent was removed under vacuum, extracted with hexane, filtered over Celite, concentrated to 1–2 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%). ¹H NMR (CD₂Cl₂, 23 °C): δ 7.26 (s, 4H, ArH), 3.66 (sept, 3J_H-H = 6.6 Hz, 4H, CH₂-or (CH₂)₃), 2.95 (sept, 3J_H-H = 7.2 Hz, 2H, CH₂-or (CH₂)₃), 2.61 (s, 2H, ArSH), 1.98 (s, 30H, C₆Mes), 1.54 (d, 3J_H-H = 6.6 Hz, 24H, CH₂(or)-CH₂), 1.34 (d, 3J_H-H = 7.2 Hz, 12H, CH₂(or)-CH₂). ¹³C[¹H] NMR (CD₂Cl₂, 23 °C): δ 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 (m), 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 C₃₉H₅₉N₂PTh: C, 56.60%; H, 7.41%. Found: C, 56.21%; H, 7.38%.

(C₆Me₅)₂Th(CN'Bu)[n²-N,C]-BuNCNPMes, 4. The same procedure was employed as for 3 using 1 (100 mg, 0.124 mmol) and tert-butyl isocyanide (21 mg, 0.253 mmol) to yield 4 as a yellow solid (81 mg, 80%). ¹H NMR (CD₂Cl₂, 23 °C): δ 7.05 (s, 2H, ArH), 3.10 (s, 6H, CH₂(or), 2.27 (s, 6H, CH₂-par), 2.16 (s, 30H, C₆Mes), 1.25 (s, 9H, C₅Me₅), 1.02 (s, 9H, C₅Me₅). ¹³C[¹H] NMR (CD₂Cl₂, 23 °C): δ 183.56 (d, 3J_C-Br = 5.60 Hz, C₂ipso-P), 163.29 (CNCMe₃), 151.05 (d, 3J_C-Br = 103.0 Hz, Me₅CNCMe₃), 142.65 (d, 3J_C-Br = 4.5 Hz, 134.41 (the C(sp³)-H resonance was buried under the solvent resonance), 122.42, 59.47 (d, 3J_C-Br = 12.0 Hz, Me₅CNCMe₃), 56.66 (CNCMe₃), 31.69 (Me₅CNCMe₃), 24.58, 21.33, 11.87. ³¹P{¹H} NMR (CD₂Cl₂, 23 °C): δ −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). C₉H₂₈N₂PTh: C, 57.20%; H, 7.26%; N, 3.42%. Found: C, 57.40%; H, 6.99%; N, 3.30%.

Table 3: X-ray crystallography data for complexes 1, 2, 3, and 5

| 1         | 2         | 3         | 5         | TippAsCl₂ |
|-----------|-----------|-----------|-----------|-----------|
| CCDC deposit number | 1455163 | 1455164 | 1455165 | 1455166 |
| Empirical formula | C₃₈H₅₄P₂Th | C₃₈H₅₄P₂Th | C₃₈H₅₄P₂Th | C₃₈H₅₄P₂Th |
| Formula weight (g mol⁻¹) | 804.79 | 1061.00 | 903.04 | 946.99 |
| Crystal habit, color | Prism, orange | Prism, red | Needle, yellow | Needle, orange |
| Temperature (K) | 100(2) | 100(2) | 100(2) | 100(2) |
| Space group | Pbcn | C2/c | Pnma | Pnma |
| Crystal system | Orthorhombic | Monoclinic | Orthorhombic | Orthorhombic |
| Volume (Å³) | 3598.3(5) | 4809.0(7) | 5693.6(9) | 5712.6(6) |
| a (Å) | 11.0230(9) | 23.195(2) | 28.9553(18) | 29.0966(19) |
| b (Å) | 15.3941(13) | 12.1067(10) | 13.4169(9) | 13.4879(5) |
| c (Å) | 21.2051(18) | 17.8722(15) | 14.00(1) | 14.00(1) |
| V (Å³) | 0.00 | 0.00 | 0.00 | 0.00 |
| β (°) | 90.00 | 90.00 | 90.00 | 90.00 |
| γ (°) | 90.00 | 90.00 | 90.00 | 90.00 |
| Z | 4 | 4 | 4 | 4 |
| Calculated density (Mg m⁻³) | 1.486 | 1.465 | 1.060 | 1.101 |
| Absorption coefficient (mm⁻¹) | 4.257 | 4.497 | 2.687 | 2.308 |
| Final R indices (I > 2σ(I)) | R = 0.0211 | R = 0.0195 | R = 0.0317 | R = 0.0330 |
| Rw = 0.0431 | Rw = 0.0437 | Rw = 0.0823 | Rw = 0.0741 |
| 1455345 | 1455345 | 1455345 | 1455345 |
| C₅H₅AsBr₀.₃₅Cl₁.₄₅ | 349.15 | 813.6(2) | 8.3739(12) | 9.1197(13) |
| Crystallographic data for complexes 1, 2, 3, and 5. | | | | |
[(C₅Me₅)₂Th(C≡N)(η⁵-C₆H₅)][(Me₃CN)₂C(Tipp)], 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 (CDCl₃, 23 °C): δ 7.32 (s, 2H, ArH), 4.84 (s, br, 2H, CH₂(ortho)(CH₃)₂), 2.98 (sept, 3JH-H = 7.2 Hz, 6H, CH₂(ortho)(CH₃)₂), 2.16 (s, 30H, C₅Me₅), 1.67 (d, 3JH-H = 7.2 Hz, 6H, CH₂(ortho)(meta)), 1.38 (d, 3JH-H = 7.2 Hz, 3H, CH(CH₃)₂-para), 1.24 (s, 9H, CNC₆Me₅), 0.97 (s, br, 9H, CNC₆Me₅). ¹³C{¹H} NMR (CDCl₃, 23 °C): δ 164.41 (NC₆Me₅), δ 58.72; H, 7.45%; N, 2.71%. 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 K. X-ray data were collected on a Bruker CCD diffractometer with monochromated Mo-Kα radiation (λ = 0.71073 Å). The data collection and processing were performed using a Bruker Apex2 suite of programs. The structures were solved by direct methods and refined by full-matrix least-squares methods on F² 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 a riding model. Thermal ellipsoid plots were prepared using a Bruker SHELX-2014/7 program. The structures were solved by direct methods and refined by full-matrix least-squares methods on F² 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-seed 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.

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