



Cite this: *Dalton Trans.*, 2016, **45**, 10042

Received 26th February 2016,

Accepted 13th April 2016

DOI: 10.1039/c6dt00776g

www.rsc.org/dalton

# Insertion of <sup>t</sup>BuNC into thorium–phosphorus and thorium–arsenic bonds: phosphazaallene 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, <sup>t</sup>BuNC. Reaction of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Th[E(H)R]<sub>2</sub>, E = P, As; R = 2,4,6-<sup>i</sup>Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> with <sup>t</sup>BuNC affords the first phosphazaallene and arsaazaallene moieties with an f-element.

## Introduction

Hydroelementation reactions such as hydrophosphination<sup>1,2</sup> are atom efficient processes which are important in developing building blocks containing phosphorus. For example, tertiary phosphines are of interest as ligands<sup>3–5</sup> and for various applications.<sup>6–8</sup> However, the development of these reactions in organoactinide chemistry<sup>9</sup> has been attenuated by a lack of starting materials.

Despite the intensity with which complexes with actinide–nitrogen bonds have been studied,<sup>10–13</sup> there exists a tremendous knowledge gap with respect to the heavier pnictogen elements. To date, twenty actinide–phosphido or phosphinidene bonds<sup>14–26</sup> and five actinide–arsenido bonds<sup>27–29</sup> 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,<sup>30–37</sup> but Waterman's group has investigated the reactivity of zirconium–phosphorus bonds with <sup>t</sup>BuNC.<sup>38</sup> Interestingly, a proton migration from the phosphorus to the carbon of the isocyanide occurs. Here we describe the synthesis of new thorium phosphido and arsenido complexes and their reactivity with <sup>t</sup>BuNC, which differs from their transition metal analogs.

Department of Chemistry, University of Missouri, Columbia, MO 65211, USA.

E-mail: walenskyj@missouri.edu

† Electronic supplementary information (ESI) available. CCDC 1455163–1455166, 1455345. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt00776g

## Results and discussion

The synthesis of (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Th[P(H)Tipp]<sub>2</sub>, Tipp = 2,4,6-<sup>i</sup>Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, the first primary phosphido complex of thorium, was recently described.<sup>26</sup> 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<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Th[P(H)Mes]<sub>2</sub>, **1**, Mes = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, from the stoichiometric salt metathesis reaction between (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ThCl<sub>2</sub> 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 doublet P–H resonance and the ν<sub>PH</sub> stretch centered at 3.80 ppm with <sup>1</sup>J<sub>P–H</sub> = 224 Hz and 2304 cm<sup>–1</sup>, respectively. The large <sup>1</sup>J<sub>P–H</sub> coupling constant reflects the large amount of s-character in the P–H bond.

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

While actinide–phosphido complexes are few in number, the number of structurally characterized actinide–arsenido compounds is five: a bimetallic thorium poly-arsenide cluster, [Cp'<sub>2</sub>Th(μ-η<sup>2:1:2:1</sup>-As<sub>6</sub>)ThCp'<sub>2</sub>] (Cp' = C<sub>5</sub>H<sub>3</sub><sup>t</sup>Bu<sub>2</sub>),<sup>29</sup> and a series of uranium(IV) complexes: [U(Tren<sup>TIPS</sup>)<sub>2</sub>(μ-η<sup>2:1:2:1</sup>-As<sub>2</sub>H<sub>2</sub>)],<sup>27</sup> [U(Tren<sup>TIPS</sup>)(AsH<sub>2</sub>)], [U(Tren<sup>TIPS</sup>)(AsH)][K(B15C5)<sub>2</sub>], and [U(Tren<sup>TIPS</sup>)(AsK<sub>2</sub>)<sub>4</sub>] Tren<sup>TIPS</sup> = N(CH<sub>2</sub>CH<sub>2</sub>NSiPr<sub>3</sub>)<sub>3</sub>.<sup>28</sup> We hypothesized that the 2,4,6-<sup>i</sup>Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub> framework would be sterically large enough to stabilize an actinide metal center such as thorium. Using room temperature σ-bond metathesis between (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ThMe<sub>2</sub> and two equivalents of H<sub>2</sub>AsTipp, we successfully isolated the first organothorium primary arsenido complex, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Th[As(H)Tipp]<sub>2</sub>, **2**, eqn (2):





Compound **2** was isolated as a ruby red crystalline solid in 70% yield. The diagnostic spectroscopic handles include the As–H resonance at  $\delta$  2.61 in the <sup>1</sup>H NMR spectrum and the  $\nu_{\text{AsH}}$  stretch at 2089 cm<sup>−1</sup> in the IR spectrum. The IR stretching frequencies compare well to the  $\nu_{\text{AsH}}$  stretches at 2061 cm<sup>−1</sup> and 2052 cm<sup>−1</sup> for zirconium(IV) and uranium(IV) primary arsenido complexes, [(N<sub>3</sub>N)ZrAsHR] (R = Mes and Ph; N<sub>3</sub>N =

N(CH<sub>2</sub>CH<sub>2</sub>NSiMe<sub>3</sub>)<sub>3</sub><sup>3−</sup>),<sup>39</sup> [U(Tren<sup>TIPS</sup>)(AsH<sub>2</sub>)<sub>2</sub>]<sup>28</sup> 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(3); P1–Th–P1\*, 102.68(2); Th1–P1–C11, 128.45(9).

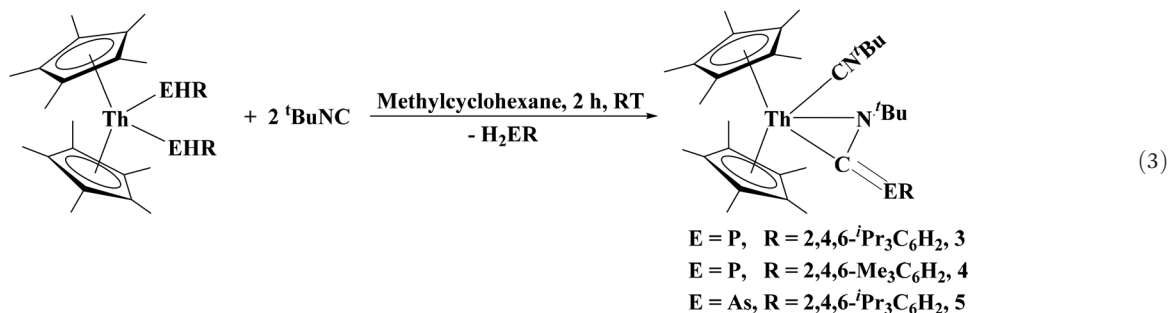


**Fig. 2** Thermal ellipsoid plot of **2** at the 50% probability level. Hydrogens have been omitted for clarity. Selected bond distances (Å) and angles (°): Th1–As1, 3.0028(6); As1–C11, 1.959(5); As1–Th1–As1\*, 88.02(2); Th1–As1–C11, 116.53(15).



bond covalent radii for thorium and arsenic (2.96 Å).<sup>40</sup> 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 phosphalkenes and arsaalkenes from the reaction between a primary phosphido/arsenido organometallic complex and an alkyl isocyanide.<sup>38,39</sup> We anticipated a similar reactivity with our thorium complexes. When *tert*-butyl isocyanide was added to (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Th[P(H)Tipp]<sub>2</sub> 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 η<sup>2</sup>-(N,C)-phosphaazaallene thorium complexes [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Th(CN<sup>t</sup>Bu)(η<sup>2</sup>-N,C)-(<sup>t</sup>BuNC=PTipp)], **3**, and [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Th(CN<sup>t</sup>Bu)(η<sup>2</sup>-N,C)-(<sup>t</sup>BuNC=PMes)], **4**, were isolated as yellow solids.



The diagnostic spectroscopic features associated with **3** and **4** include the stretches at 2181 and 2186 cm<sup>-1</sup>, and 1600 and 1602 cm<sup>-1</sup>, which can be assigned to the ν<sub>CN</sub> and ν<sub>CP</sub> stretches, respectively. The <sup>31</sup>P NMR resonances shifted slightly upfield from the starting material to -21.28 and -10.70 ppm for **3** and **4**, respectively. Additionally, the <sup>13</sup>C NMR resonance of the central carbon of the phosphazaallene was found at 150.85 and 151.05 ppm with <sup>1</sup>J<sub>P-C</sub> = 152.3 Hz and 103.0 Hz, for **3** and **4**, respectively. Compound **2** exhibited a similar reactivity to yield a η<sup>2</sup>-(N,C)-arsaazaallene thorium complex [(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Th(CN<sup>t</sup>Bu)(η<sup>2</sup>-N,C)-(<sup>t</sup>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 arsaazaallene complexes. As with transition metals, such complexes are very rare as only two phosphazaallene compounds have been isolated: (η<sup>1</sup>-Nacnac)Ti(CN<sup>t</sup>Bu)(η<sup>2</sup>-N,C)-<sup>t</sup>BuNC=PMes\*)<sup>41</sup> (Nacnac = [2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]NC(CH<sub>3</sub>)CHC(CH<sub>3</sub>)N[2,6-*i*-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>], Mes\* = 2,4,6-*i*-Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>) and Cp'<sub>2</sub>Nb(Cl)(η<sup>2</sup>-N,C)-PhNC=PMes\*)<sup>42</sup>

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.<sup>43</sup> 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 (C<sub>5</sub>Me<sub>5</sub>)(C<sub>8</sub>H<sub>8</sub>)U[η<sup>2</sup>-(N,C)-C(Ph)=N<sup>t</sup>Bu].<sup>44</sup> 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=P bond distance in **4** of 1.691(6) Å is only slightly longer than the C=P of 1.651(1) Å in

PhN=C=PMes\* and matches the C=P bond length of 1.688(19) Å in (C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>Nb(Cl)[η<sup>2</sup>-(N,C)-PhNC=P(2,4,6-*i*-Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)]. 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, [η<sup>5</sup>-1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]<sub>2</sub>Th(Cl)[N(*p*-tolyl)SiH<sub>2</sub>Ph];<sup>45</sup> 2.322(5) Å, [η<sup>5</sup>-1,2,4-(Me<sub>3</sub>C)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>]<sub>2</sub>Th[N(*p*-tolyl)(Se–Se)];<sup>45</sup> and 2.256(8) Å, (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Th[NC(Ph)(CH<sub>2</sub>Ph)]<sub>2</sub>.<sup>46</sup>

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 [(N<sub>3</sub>N)ZrEHR] (E = P, As; R = Cy, Ph) complexes which can undergo 1,2 rearrangement to phospho/arsa-azaalkenes, **4** and **5** do not undergo rearrangement, rather a double reduction of the alkyl isocyanide with the concomitant release of H<sub>2</sub>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, (η<sup>1</sup>-Nacnac)Ti(CH<sub>2</sub><sup>t</sup>Bu)(PMes\*), with a *tert*-butyl isocyanide to yield the titanium phosphazaallene complex, (η<sup>1</sup>-Nacnac)Ti(CN<sup>t</sup>Bu)(η<sup>2</sup>-N,C)-<sup>t</sup>BuN=C=PMes\*).<sup>41</sup> The other route is 1,1 insertion of the isocyanide to form an η<sup>2</sup>-iminoacyl, followed by an intramolecular deprotonation. To investigate the possible reaction pathway, we attempted the addition of *tert*-butyl isocyanide to (C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Th[P(H)Tipp]<sub>2</sub> at -200 °C and

**Table 1** Spectroscopic features of compounds **3**, **4**, and **5**

	<sup>31</sup> P{ <sup>1</sup> H} (δ)	<sup>13</sup> C{ <sup>1</sup> H} central allene carbon (δ)	ν <sub>CN</sub> (cm <sup>-1</sup> )	ν <sub>CE</sub> (E = P, As) (cm <sup>-1</sup> )
<b>3</b>	-21.28	150.85, <sup>1</sup> J <sub>P-C</sub> = 152.3 Hz	2181	1600
<b>4</b>	-10.70	151.05, <sup>1</sup> J <sub>P-C</sub> = 103.0 Hz	2186	1602
<b>5</b>		154.25	2182	1513



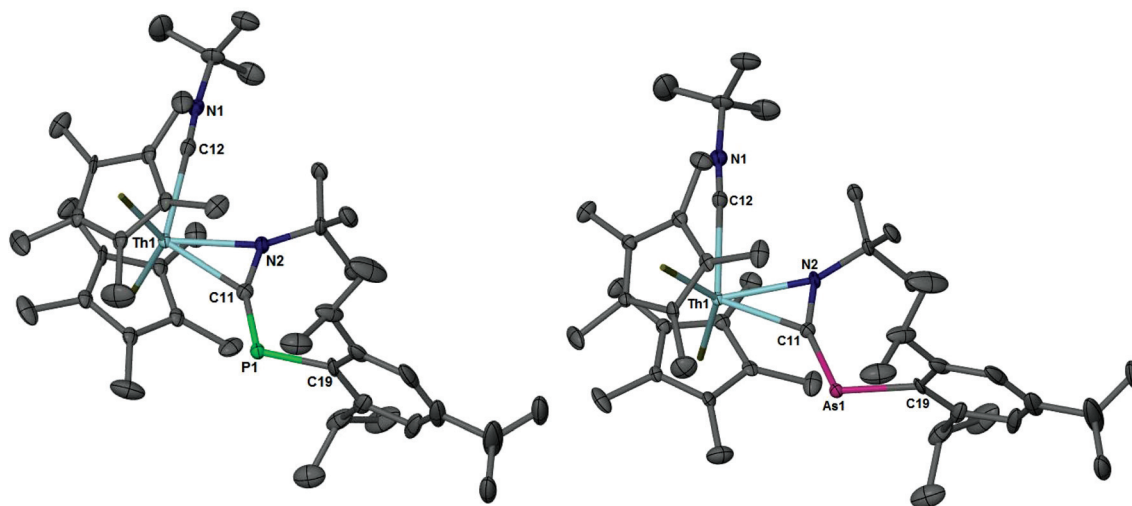


Fig. 3 Thermal ellipsoid plots of 4 and 5 at the 50% probability level. Hydrogens have been omitted for clarity.

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)



E = P, R = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, 3

E = P, R = 2,4,6-*i*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, 4

E = As, R = 2,4,6-*i*-Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, 5

Fig. 4 Possible reaction pathways for the generation of 3, 4 and 5.



slowly warmed the reaction while monitoring the reaction progress using  $^{31}\text{P}$  NMR. At  $-80\text{ }^\circ\text{C}$  we observed the formation of **4**,  $\text{H}_2\text{PTipp}$ ,  $(\text{C}_5\text{Me}_5)_2\text{Th}[\text{P}(\text{H})\text{Tipp}]_2$ , and a singlet at  $-26.5\text{ ppm}$ . Upon heating to  $-70\text{ }^\circ\text{C}$  the reaction was complete with disappearance of the resonance at  $-26.5\text{ ppm}$ . This resonance at  $-26.5\text{ ppm}$  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  $>100\text{ ppm}$  was observed (see ESI†).

## Conclusion

In summary we have broadened the scope of actinide–pnictogenide 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 pnictogenide bond resulted in the formation of phospho/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 ( $\text{N}_2$ ) glovebox or a double-manifold Schlenk line. Toluene, 1,2-dimethoxyethane, diethyl ether and hexane were purchased anhydrous, stored over activated  $4\text{ \AA}$  molecular sieves, and sparged with nitrogen prior to use. Methylcyclohexane was dried over activated  $4\text{ \AA}$  molecular sieves and sparged with nitrogen for thirty minutes prior to use. *tert*-Butyl isocyanide was dried over  $4\text{ \AA}$  molecular sieves, freeze–evacuate–thawed three times, distilled, and stored under nitrogen. All available reactants were purchased from suppliers and used without further purification.  $\text{ThCl}_4(\text{DME})_2$ ,<sup>47</sup>  $(\text{C}_5\text{Me}_5)_2\text{ThCl}_2$ ,<sup>48</sup>  $(\text{C}_5\text{Me}_5)_2\text{ThMe}_2$ ,<sup>48</sup>  $\text{TippPCL}_2$ ,<sup>49</sup>  $\text{H}_2\text{PTipp}$ ,<sup>50</sup>  $\text{MesPCL}_2$ ,<sup>51</sup>  $\text{MesPH}_2$ ,<sup>52</sup> and  $(\text{C}_5\text{Me}_5)_2\text{Th}[\text{P}(\text{H})\text{Tipp}]_2$ <sup>26</sup> ( $\text{Tipp} = 2,4,6\text{-}^1\text{Pr}_3\text{C}_6\text{H}_2$ ,  $\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ ) were synthesized as previously described.  $\text{KPH}(\text{Mes})$  was prepared from  $\text{H}_2\text{PMes}$  and  $\text{KN}(\text{SiMe}_3)_2$  in THF. Benzene- $d_6$  and toluene- $d_8$  (Cambridge Isotope Laboratories) were dried over molecular sieves and degassed with three freeze–evacuate–thaw cycles. All  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained on a 500 or 600 MHz DRX Bruker spectrometer. All  $^{31}\text{P}$  NMR spectra were obtained on a 300 MHz ARX spectrometer at 121 MHz.  $^1\text{H}$  NMR shifts given were referenced internally to the residual solvent peak at  $\delta 7.16\text{ ppm}$  ( $\text{C}_6\text{D}_5\text{H}$ ).  $^{13}\text{C}$  NMR shifts given were referenced

internally to the residual peak at  $\delta 128.0\text{ ppm}$  ( $\text{C}_6\text{D}_6$ ).  $^{31}\text{P}$  NMR spectra were externally referenced to 0.00 ppm with 5%  $\text{H}_3\text{PO}_4$  in  $\text{D}_2\text{O}$ . Infrared spectra were recorded as KBr pellets on a Perkin-Elmer Spectrum One FT-IR spectrometer. Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility using a Perkin-Elmer Series II 2400 CHNS analyzer.

**[TippAsCl<sub>2</sub>]**. A two-neck 500 mL Schlenk flask was charged with 1-bromo-2,4,6- $^1\text{Pr}_3\text{C}_6\text{H}_2\text{Br}$  (4.00 g, 14.1 mmol), Mg ribbon (polished and cut into small pieces, 377 mg, 15.5 mmol), and THF (75 mL). A reflux 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  $\text{AsCl}_3$  (2.56 g, 14.1 mmol) and THF (30 mL) and cooled to  $-40\text{ }^\circ\text{C}$  via a  $\text{CO}_2(\text{s})/\text{CH}_3\text{CN}$  bath. The Grignard was added via a cannula to the  $\text{AsCl}_3$  followed by  $\text{ZnCl}_2$  (3.84 g, 28.2 mmol). The reaction mixture was allowed to stir at  $-40\text{ }^\circ\text{C}$  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 ( $2 \times 30\text{ mL}$ ) and added to the filtrate. The solution was concentrated and placed in a  $-20\text{ }^\circ\text{C}$  freezer. Long colorless crystals grew over a period of 36 h. The crystals were isolated and dried (two crops 3.35 g, 68%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $23\text{ }^\circ\text{C}$ ):  $\delta$  7.04 (s, 2H, ArH), 3.92 (sept,  $^3J_{\text{H-H}} = 6.5\text{ Hz}$ , 2H,  $\text{CH}_{ortho}(\text{CH}_3)_2$ ), 2.62 (sept,  $^3J_{\text{H-H}} = 6.5\text{ Hz}$ , 1H,  $\text{CH}_{para}(\text{CH}_3)_2$ ), 1.20 (d,  $^3J_{\text{H-H}} = 6.5\text{ Hz}$ , 12H,  $\text{CH}(\text{CH}_3)_2$ -ortho), 1.10 (d,  $^3J_{\text{H-H}} = 6.5\text{ Hz}$ , 6H,  $\text{CH}(\text{CH}_3)_2$ -para).

**[TippAsH<sub>2</sub>]**. A 3-neck 1000 mL round bottom flask was charged with  $\text{LiAlH}_4$  (1.80 g, 47.3 mmol) and THF (50 mL). A 100 mL Schlenk flask was charged with  $\text{TippAsCl}_2$  (6 g, 17.2 mmol) and THF (50 mL). The  $\text{LiAlH}_4$  was cooled to  $-5\text{ }^\circ\text{C}$  via a  $\text{NaCl}(\text{s})/\text{ice}$  bath and  $\text{TippAsCl}_2$  was added to the mixture via a cannula and allowed to stir for 10 minutes. The salt bath was removed and the reaction mixture was stirred at room temperature for 12 h. The reaction mixture was placed in an ice bath and the excess  $\text{LiAlH}_4$  was quenched dropwise with a degassed  $\text{HCl}/\text{H}_2\text{O}$  mixture (20%  $\text{HCl}$ , extreme care should be taken when first beginning to quench the mixture because the reaction is exothermic and  $\text{H}_2(\text{g})$  is evolved). The organic phase was separated and the aqueous phase was extracted twice with diethyl ether ( $2 \times 40\text{ mL}$ ) and the organic phases were combined. The organic phase was dried over  $\text{MgSO}_4$  and the solvent was removed under vacuum to yield the crude product as a colorless viscous solid. The product can be purified via distillation to yield a colorless liquid (4.10 g, 85%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $23\text{ }^\circ\text{C}$ ):  $\delta$  7.10 (s, 2H, ArH), 3.38 (s, 2H, AsH), 3.36 (sept,  $^3J_{\text{H-H}} = 7.0\text{ Hz}$ , 2H,  $\text{CH}_{ortho}(\text{CH}_3)_2$ ), 2.76 (sept,  $^3J_{\text{H-H}} = 7.0\text{ Hz}$ , 1H,  $\text{CH}_{para}(\text{CH}_3)_2$ ), 1.22 (d,  $^3J_{\text{H-H}} = 7.0\text{ Hz}$ , 12H,  $\text{CH}(\text{CH}_3)_2$ -ortho), 1.21 (d,  $^3J_{\text{H-H}} = 7.0\text{ Hz}$ , 6H,  $\text{CH}(\text{CH}_3)_2$ -para).

**$(\text{C}_5\text{Me}_5)_2\text{Th}[\text{P}(\text{H})\text{Mes}]_2$ , **1****. The same procedure was employed as for  $(\text{C}_5\text{Me}_5)_2\text{Th}[\text{P}(\text{H})\text{Tipp}]_2$  using  $(\text{C}_5\text{Me}_5)_2\text{ThCl}_2$  (287 mg, 0.500 mmol) and  $\text{KP}(\text{H})\text{Mes}$  (200 mg, 1.05 mmol) to yield **1** as a bright orange solid (217 mg, 54%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $23\text{ }^\circ\text{C}$ ):  $\delta$  6.99 (s, 4H, ArH), 3.80 (d,  $^1J_{\text{P-H}} = 224\text{ Hz}$ , 2H, PH),



2.67 (s, 12H,  $CH_3$ -ortho), 2.33 (s, 6H,  $CH_3$ -para), 1.89 (s, 30H,  $C_5Me_5$ ).  $^{13}C\{^1H\}$  NMR ( $C_6D_6$ , 23 °C):  $\delta$  140.00 (d,  $^1J_{P-C}$  = 18.0 Hz), 139.16, 133.90 (the  $C(sp^2)$ -H resonance was buried under the solvent resonance), 126.77, 25.42, 20.95, 11.47.  $^{31}P\{^1H\}$  NMR ( $C_6D_6$ , 23 °C):  $\delta$  15.37. IR ( $cm^{-1}$ ): 2910 (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. calcd for  $C_{38}H_{54}P_2Th$ : C, 56.72%; H, 6.76%. Found: C, 56.61%; H, 6.75%.

**( $C_5Me_5$ )<sub>2</sub>Th[As(H)Tipp]<sub>2</sub>, 2.** A 20 mL scintillation vial was charged with ( $C_5Me_5$ )<sub>2</sub>ThMe<sub>2</sub> (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 H<sub>2</sub>AsTipp (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 ( $C_6D_6$ , 23 °C):  $\delta$  7.26 (s, 4H, ArH), 3.66 (sept,  $^3J_{H-H}$  = 6.6 Hz, 4H,  $CH_{ortho}(CH_3)_2$ ), 2.95 (sept,  $^3J_{H-H}$  = 7.2 Hz, 2H,  $CH_{para}(CH_3)_2$ ), 2.61 (s, 2H, AsH), 1.98 (s, 30H,  $C_5Me_5$ ), 1.54 (d,  $^3J_{H-H}$  = 6.6 Hz, 24H,  $CH(CH_3)_2$ -ortho), 1.34 (d,  $^3J_{H-H}$  = 7.2 Hz, 12H,  $CH(CH_3)_2$ -para).  $^{13}C\{^1H\}$  NMR ( $C_6D_6$ , 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 (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. calcd for  $C_{50}H_{78}As_2Th$ : C, 56.60%; H, 7.41%. Found: C, 56.21%; H, 7.38%.

**( $C_5Me_5$ )<sub>2</sub>Th(CN<sup>t</sup>Bu)( $\eta^2$ -N,C)-(<sup>t</sup>BuNCPTipp), 3.** A 20 mL scintillation vial was charged with ( $C_5Me_5$ )<sub>2</sub>Th[P(H)Tipp]<sub>2</sub> (91 mg, 0.0935 mmol), methylcyclohexane (5 mL) and placed in a -23 °C freezer for 30 minutes. The vial was removed from the freezer and *tert*-butyl isocyanide (16 mg, 0.192 mmol) was added dropwise to the ( $C_5Me_5$ )<sub>2</sub>Th[P(H)Tipp]<sub>2</sub> and allowed to

stir for 2 h to yield a yellow reaction mixture. The mixture was filtered over Celite, concentrated to 1–2 mL and placed in a -23 °C freezer. Yellow needle crystals grew after a 48 h period, and were isolated and dried to yield the product (66 mg, 78%).  $^1H$  NMR ( $C_6D_6$ , 23 °C):  $\delta$  7.27 (s, 2H, ArH), 4.87 (s, br, 2H,  $CH_{ortho}(CH_3)_2$ ), 2.95 (sept,  $^3J_{H-H}$  = 7.2 Hz, 1H,  $CH_{para}(CH_3)_2$ ), 2.16 (s, 30H,  $C_5Me_5$ ), 1.65 (d,  $^3J_{H-H}$  = 7.2 Hz, 12H,  $CH(CH_3)_2$ -ortho), 1.36 (d,  $^3J_{H-H}$  = 7.2 Hz, 6H,  $CH(CH_3)_2$ -para), 1.22 (s, 9H, CNCMe<sub>3</sub>), 1.08 (s, br, 9H, CNCMe<sub>3</sub>).  $^{13}C\{^1H\}$  NMR ( $C_6D_6$ , 23 °C):  $\delta$  164.11 (CNCMe<sub>3</sub>), ( $C_{ipso}$ -P could not be located), 152.95, 150.85 (d,  $^1J_{P-C}$  = 152.3 Hz, Me<sub>3</sub>CNCPTipp), 146.56, 122.37, 120.22, 59.80 (d,  $^3J_{P-C}$  = 12.0 Hz, Me<sub>3</sub>CNCPTipp), 56.81 (CNCMe<sub>3</sub>), 34.90, 33.52 (d,  $^3J_{P-C}$  = 6.0 Hz), 32.41 (Me<sub>3</sub>CNCPTipp), 29.14 (CNCMe<sub>3</sub>), 24.62, 23.79, 11.77.  $^{31}P\{^1H\}$  NMR ( $C_6D_6$ , 23 °C):  $\delta$  -21.28. IR ( $cm^{-1}$ ): 2957 (s), 2913 (s), 2864 (s), 2304 (m), 2181(s), 1600 (m), 1450 (s), 1361 (s), 1193 (m), 1092 (m), 1021 (m), 943 (m), 875 (m), 805 (m), 723 (m), 650 (m). Anal. calcd for  $C_{45}H_{71}N_2PTh$ : C, 59.85%; H, 7.92%; N, 3.10%. Found: C, 60.05%; H 7.64%; N, 2.71%.

**( $C_5Me_5$ )<sub>2</sub>Th(CN<sup>t</sup>Bu)( $\eta^2$ -N,C)-(<sup>t</sup>BuNCPTipp), 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 ( $C_6D_6$ , 23 °C):  $\delta$  7.05 (s, 2H, ArH), 3.10 (s, 6H,  $CH_3$ -ortho), 2.27 (s, 6H,  $CH_3$ -para), 2.16 (s, 30H,  $C_5Me_5$ ), 1.25 (s, 9H, CNCMe<sub>3</sub>), 1.02 (s, br, 9H, CNCMe<sub>3</sub>).  $^{13}C\{^1H\}$  NMR ( $C_6D_6$ , 23 °C):  $\delta$  183.56 (d,  $^1J_{P-C}$  = 56.0 Hz,  $C_{ipso}$ -P), 163.29 (CNCMe<sub>3</sub>), 151.05 (d,  $^1J_{P-C}$  = 103.0 Hz, Me<sub>3</sub>CNCPTipp), 142.65 (d,  $^4J_{P-C}$  = 4.5 Hz), 134.41 (the  $C(sp^2)$ -H resonance was buried under the solvent resonance), 122.42, 59.47 (d,  $^3J_{P-C}$  = 12.0 Hz, Me<sub>3</sub>CNCPTipp), 56.66 (CNCMe<sub>3</sub>), 31.69 (Me<sub>3</sub>CNCPTipp) 29.19 (CNCMe<sub>3</sub>), 24.58, 21.33, 11.87.  $^{31}P\{^1H\}$  NMR ( $C_6D_6$ , 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).  $C_{39}H_{59}N_2PTh$ : 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	TippAsCl <sub>2</sub>
CCDC deposit number	1455163	1455164	1455165	1455166	1455345
Empirical formula	$C_{38}H_{54}P_2Th$	$C_{50}H_{78}As_2Th$	$C_{45}H_{71}N_2PTh$	$C_{45}H_{71}N_2AsTh$	$C_{15}H_{23}AsBr_{0.55}Cl_{1.45}$
Formula weight (g mol <sup>-1</sup> )	804.79	1061.00	903.04	946.99	349.15
Crystal habit, color	Prism, orange	Prism, red	Needle, yellow	Needle, orange	Prism, colorless
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)
Space group	<i>Pbcn</i>	<i>C2/c</i>	<i>Pnma</i>	<i>Pnma</i>	<i>P1</i>
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic	Triclinic
Volume (Å <sup>3</sup> )	3598.3(5)	4809.0(7)	5659.3(6)	5712.6(6)	813.6(2)
<i>a</i> (Å)	11.0230(9)	23.195(2)	28.9553(18)	29.0966(19)	8.3739(12)
<i>b</i> (Å)	15.3941(13)	12.1067(10)	14.5673(9)	14.5564(9)	9.1197(13)
<i>c</i> (Å)	21.2051(18)	17.8732(15)	13.4169(9)	13.4878(9)	11.6208(16)
$\alpha$ (°)	90.00	90.00	90.00	90.00	75.718(2)
$\beta$ (°)	90.00	106.6350(10)	90.00	90.00	71.5280(10)
$\gamma$ (°)	90.00	90.00	90.00	90.00	81.712(2)
<i>Z</i>	4	4	4	4	2
Calculated density (Mg m <sup>-3</sup> )	1.486	1.465	1.060	1.101	1.425
Absorption coefficient (mm <sup>-1</sup> )	4.257	4.497	2.687	3.208	2.400
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> = 0.0211	<i>R</i> = 0.0195	<i>R</i> = 0.0317	<i>R</i> = 0.0330	<i>R</i> = 0.0627
	<i>R</i> <sub>w</sub> = 0.0431	<i>R</i> <sub>w</sub> = 0.0437	<i>R</i> <sub>w</sub> = 0.0823	<i>R</i> <sub>w</sub> = 0.0741	<i>R</i> <sub>w</sub> = 0.1803



[[C<sub>5</sub>Me<sub>5</sub>]<sub>2</sub>Th(CN<sup>t</sup>Bu)(η<sup>2</sup>-N,C)-(<sup>t</sup>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. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 23 °C): δ 7.32 (s, 2H, ArH), 4.84 (s, br, 2H, CH<sub>ortho</sub>(CH<sub>3</sub>)<sub>2</sub>), 2.98 (sept, <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz, 1H, CH<sub>para</sub>(CH<sub>3</sub>)<sub>2</sub>), 2.16 (s, 30H, C<sub>5</sub>Me<sub>5</sub>), 1.67 (d, <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz, 6H, CH(CH<sub>3</sub>)<sub>2-ortho</sub>), 1.38 (d, <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz, 3H, CH(CH<sub>3</sub>)<sub>2-para</sub>), 1.24 (s, 9H, CNCMe<sub>3</sub>), 0.97 (s, br, 9H, CNCMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 23 °C): δ 164.41 (CNCMe<sub>3</sub>), (C<sub>ipso</sub>-As could not be located), 154.25 (Me<sub>3</sub>CNCAsTipp), 154.05, 146.65, 122.65, 120.24, 60.30 (Me<sub>3</sub>CNCAsTipp), 57.01 (CNCMe<sub>3</sub>), 35.63, 34.90, 32.03 (Me<sub>3</sub>CNCAsTipp), 29.01 (CNCMe<sub>3</sub>), 26.91, 24.67, 11.79. IR (cm<sup>-1</sup>): 2958 (s), 2917 (s), 2865 (s), 2182 (m), 1513 (m), 1452 (s), 1367 (m), 1312 (m), 1214 (m), 1109 (m), 1027 (m), 877 (w), 805 (m), 624 (m). Anal. calcd for C<sub>45</sub>H<sub>71</sub>N<sub>2</sub>AsTh: 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 diffractometer with monochromated Mo-Kα radiation (λ = 0.71073 Å). The data collection and processing were performed using a Bruker Apex2 suite of programs.<sup>53</sup> The structures were solved by direct methods and refined by full-matrix least-squares methods on F<sup>2</sup> using the Bruker SHELX-2014/7 program.<sup>54</sup> 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<sup>55</sup> 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

- V. Koshti, S. Gaikwad and S. H. Chikkali, *Coord. Chem. Rev.*, 2014, **265**, 52.
- L. Rosenberg, *ACS Catal.*, 2013, **3**, 2845.
- K. B. Dillon, F. Mathey and J. F. Nixon, in *Phosphorus: The Carbon Copy*, Wiley, Chichester, 1998.
- L. Ackermann, *Synthesis*, 2006, 1557.
- P. Garcia, P. R. Payne, E. Chong, R. L. Webster, B. J. Barron, A. C. Behrle, J. A. R. Schmidt and L. L. Schafer, *Tetrahedron*, 2013, **69**, 5737.
- N. R. Price and J. Chambers, in *The Chemistry of Organophosphorus Compounds*, ed. F. R. Hartley, Chichester, 1990, vol. 1.
- D. E. C. Corbridge, in *Phosphorus: Chemistry, Biochemistry, and Technology*, CRC Press, Boca Raton, FL, 2013, 6th edn, p. 1473.
- E. Rafter, T. Gutmann, F. Low, G. Buntkowsky, K. Philippot, B. Chaudret and P. W. N. M. van Leeuwen, *Catal. Sci. Technol.*, 2013, **3**, 595.
- I. S. R. Karmel, M. Tamm and M. S. Eisen, *Angew. Chem., Int. Ed.*, 2015, **54**, 12422.
- T. W. Hayton, J. M. Boncella, B. L. Scott, P. D. Palmer, E. R. Batista and P. J. Hay, *Science*, 2005, **310**, 1941.
- D. M. King, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Science*, 2012, **337**, 717.
- N. H. Anderson, S. O. Odoh, Y. Yao, U. J. Williams, B. A. Schaefer, J. J. Kiernicki, A. J. Lewis, M. D. Goshert, P. E. Fanwick, E. J. Schelter, J. R. Walensky, L. Gagliardi and S. C. Bart, *Nat. Chem.*, 2014, **6**, 919.
- N. H. Anderson, H. Yin, J. J. Kiernicki, P. E. Fanwick, E. J. Schelter and S. C. Bart, *Angew. Chem., Int. Ed.*, 2015, **54**, 9386.
- B. M. Gardner, G. Balázs, M. Scheer, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Angew. Chem., Int. Ed.*, 2014, **53**, 4484.
- D. S. J. Arney, R. C. Schnabel, B. C. Scott and C. J. Burns, *J. Am. Chem. Soc.*, 1996, **118**, 6780.
- M. R. Duttera, V. W. Day and T. J. Marks, *J. Am. Chem. Soc.*, 1984, **106**, 2907.
- D. Patel, F. Tuna, E. J. L. McInnes, W. Lewis, A. J. Blake and S. T. Liddle, *Angew. Chem., Int. Ed.*, 2013, **52**, 13334.
- N. Tsoureas, A. F. R. Kilpatrick, O. T. Summerscales, J. F. Nixon, F. G. N. Cloke and P. B. Hitchcock, *Eur. J. Inorg. Chem.*, 2013, **2013**, 4085.
- A. S. P. Frey, F. G. N. Cloke, P. B. Hitchcock and J. C. Green, *New J. Chem.*, 2011, **35**, 2022.
- O. J. Scherer, B. Werner, G. Heckmann and G. Wolmershäuser, *Angew. Chem., Int. Ed.*, 1991, **30**, 553.
- S. W. Hall, J. C. Huffman, M. M. Miller, L. R. Avens, C. J. Burns, A. P. Sattelberger, D. S. J. Arney and A. F. England, *Organometallics*, 1993, **12**, 752.
- P. J. Hay, R. R. Ryan, K. V. Salazar, D. A. Wroblewski and A. P. Sattelberger, *J. Am. Chem. Soc.*, 1986, **108**, 313.
- D. A. Wroblewski, R. R. Ryan, H. J. Wasserman, K. V. Salazar, R. T. Paine and D. C. Moody, *Organometallics*, 1986, **5**, 90.
- J. M. Ritchey, A. J. Zozulin, D. A. Wroblewski, R. R. Ryan, H. J. Wasserman, D. C. Moody and R. T. Paine, *J. Am. Chem. Soc.*, 1985, **107**, 501.
- A. Formanuk, F. Ortu, R. Beekmeyer, A. Kerridge, R. W. Adams and D. P. Mills, *Dalton Trans.*, 2016, **45**, 2390.
- A. C. Behrle, L. Castro, L. Maron and J. R. Walensky, *J. Am. Chem. Soc.*, 2015, **137**, 14846.
- B. M. Gardner, G. Balázs, M. Scheer, A. J. Wooles, F. Tuna, E. J. L. McInnes, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Angew. Chem., Int. Ed.*, 2015, **54**, 15250.



- 28 B. M. Gardner, G. Balázs, M. Scheer, F. Tuna, J. L. McInnes, Eric, J. McMaster, W. Lewis, A. J. Blake and S. T. Liddle, *Nat. Chem.*, 2015, **7**, 582.
- 29 O. J. Scherer, J. Schulze and G. Wolmershäuser, *J. Organomet. Chem.*, 1994, **484**, c5.
- 30 B. A. Vaughan, E. M. Arsenault, S. M. Chan and R. Waterman, *J. Organomet. Chem.*, 2012, **696**, 4327.
- 31 A. J. Roering, S. N. MacMillan, J. M. Tanski and R. Waterman, *Inorg. Chem.*, 2007, **46**, 6855.
- 32 M. R. Douglass, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 2001, **123**, 10221.
- 33 A. V. Firth and D. W. Stephan, *Inorg. Chem.*, 1998, **37**, 4732.
- 34 N. C. Zanetti, R. R. Schrock and W. M. Davis, *Angew. Chem., Int. Ed.*, 1995, **34**, 2044.
- 35 J. Ho, Z. Hou, R. J. Drake and D. W. Stephan, *Organometallics*, 1993, **12**, 3145.
- 36 J. Ho and D. W. Stephan, *Organometallics*, 1992, **11**, 1014.
- 37 G. A. Vaughan, G. L. Hillhouse and A. L. Rheingold, *Organometallics*, 1989, **8**, 1760.
- 38 A. J. Roering, L. T. Elrod, J. K. Pagano, S. L. Guillot, S. M. Chan, J. M. Tanski and R. Waterman, *Dalton Trans.*, 2013, **42**, 1159.
- 39 A. F. Maddox, J. J. Davidson, T. Shalumova, J. M. Tanski and R. Waterman, *Inorg. Chem.*, 2013, **52**, 7811.
- 40 P. Pyykkö and M. Atsumi, *Chem. – Eur. J.*, 2009, **15**, 186.
- 41 F. Basuli, L. A. Watson, J. C. Huffman and D. J. Mindiola, *Dalton Trans.*, 2003, 4228.
- 42 J. B. Alexander, D. S. Glueck, G. P. A. Yap and A. L. Rheingold, *Organometallics*, 1995, **14**, 3603.
- 43 M. Yoshifuji, T. Niitsu, K. Toyota, N. Inamoto, K. Hirotsu, Y. Odagaki, T. Higuchi and S. Nagase, *Polyhedron*, 1988, **7**, 2213.
- 44 W. J. Evans, M. K. Takase, J. W. Ziller and A. L. Rheingold, *Organometallics*, 2009, **28**, 5802.
- 45 E. Zhou, W. Ren, G. Hou, G. Zi, D.-C. Fang and M. D. Walter, *Organometallics*, 2015, **34**, 3637.
- 46 K. C. Jantunen, C. J. Burns, I. Castro-Rodriguez, R. E. Da Re, J. T. Golden, D. E. Morris, B. L. Scott, F. L. Taw and J. L. Kiplinger, *Organometallics*, 2004, **23**, 4682.
- 47 T. Cantat, B. L. Scott and J. L. Kiplinger, *Chem. Commun.*, 2010, **46**, 919.
- 48 P. J. Fagan, J. M. Manriquez, E. A. Maatta, A. M. Seyam and T. J. Marks, *J. Am. Chem. Soc.*, 1981, **103**, 6650.
- 49 V. Chandrasekhar, P. Sasikumar, R. Boomishankar and G. Anantharaman, *Inorg. Chem.*, 2006, **45**, 3344.
- 50 Y. van den Winkel, H. M. M. Bastiaans and F. Bickelhaupt, *J. Organomet. Chem.*, 1991, **405**, 183.
- 51 S. T. Liddle and K. Izod, *Organometallics*, 2004, **23**, 5550.
- 52 J. D. Masuda, K. C. Jantunen, O. V. Ozerov, K. J. T. Noonan, D. P. Gates, B. L. Scott and J. L. Kiplinger, *J. Am. Chem. Soc.*, 2008, **130**, 2408.
- 53 *APEX2 Suite*, Bruker AXS Inc., Madison, Wisconsin, USA, 2007.
- 54 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112.
- 55 L. J. Barbour, *J. Supramol. Chem.*, 2001, **1**, 189.

