ORGANOMETALLICS

Diphosphazide-Supported Trialkyl Thorium(IV) Complex

Tara K. K. Dickie, Ashraf A. Aborawi, and Paul G. Hayes*

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ABSTRACT: The potassium salt of a new ligand, $KL_{P=N3}$ (**2**, $L_{P=N3} = \kappa^5$-2,5-$[(4\text{-}^iPrC_6H_4)N_3=P^iPr_2]_2N(C_4H_2)^-$), that features two units of the rare phosphazide ($RN_3=PR_3$) functionality was synthesized via an incomplete Staudinger reaction between $K[2,5\text{-}(^iPr_2P)_2N(C_4H_2)]$ (**1**) and $4\text{-}^iPrC_6H_4N_3$. The diphosphazide ligand was transferred to a thorium(IV) metal center using salt metathesis strategies, yielding $L_{P=N3}ThCl_3$ (**3**), which contains two intact and coordinated phosphazides. Reaction of complex **3** with 3 equiv of $LiCH_2SiMe_3$ resulted in formation of the trialkyl thorium species $L_{P=N3}Th(CH_2SiMe_3)_3$ (**4**). In contrast, attempts to synthesize an organothorium complex supported by the previously reported bisphosphinimine ligand $L_{P=N}$ ($L_{P=N} = \kappa^3$-2,5-$[(4\text{-}^iPrC_6H_4)N=P^iPr_2]_2N(C_4H_2)^-$) afforded the cyclometalated dialkyl complex $L^*_{P=N}Th(CH_2SiMe_3)_2$ (**6**, $L^*_{P=N} = \kappa^4$-2-$[(4\text{-}^iPrC_6H_3)N=P^iPr_2]$-5-$[(4\text{-}^iPrC_6H_4)N=P^iPr_2]N(C_4H_2)^{2-}$) and 1 equiv of free tetramethylsilane.

- Undergoes cyclometallative decomposition
- Phosphazide
- PN_3 chelate prevents cyclometalation
- Phosphinimine
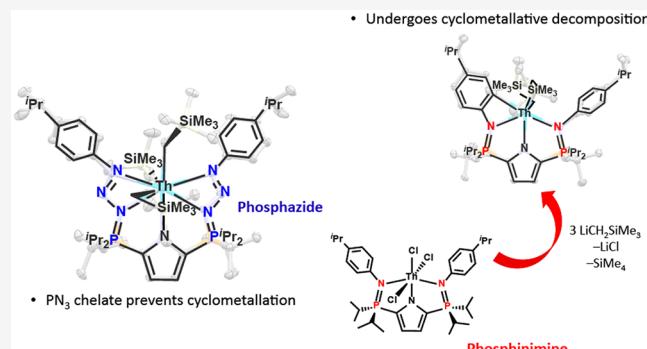
The Staudinger reaction, discovered in 1919,[1] introduced the formation of a phosphinimine group ($R_3P=NR'$) via the reaction of a tertiary phosphine (R_3P) with an organic azide (N_3R'), resulting in concomitant loss of N_2. Since its discovery, the phosphinimine functionality has been extensively utilized in coordination chemistry, largely due to the ease by which the steric and electronic properties can be fine-tuned by varying the phosphine[2] and/or azide[3] reactants. Notably, phosphinimines have been useful for supporting early transition metal olefin polymerization[4] and rare earth metal ring-opening polymerization catalysts.[5]

The Staudinger reaction proceeds via an intermediate phosphazide (R_3PNNNR') (Scheme 1).[6] Until recently, such phosphazides were largely considered transient species, due to

the facile loss of N_2, and, accordingly, were overlooked as viable functional groups in ligand design. Since Staudinger's original work, multiple methods have been developed to stabilize phosphazides and inhibit N_2 loss, including the use of tertiary phosphines and azides with bulky R groups,[7] H-bonding,[8] and the coordination of phosphazides to rare-earth[9a] and transition metals.[6,9b,c,10]

It was recently demonstrated that phosphazide coordination to an alkali metal permits isolation of a "phosphazidosalen" ligand system.[11] Such alkali-metal-stabilized phosphazides proved sufficiently stable for transfer to uranium via a simple salt metathesis protocol. More specifically, the dipotassium salt of the phosphazidosalen ligand K_2L'' [$L'' = \kappa^6$-1,2-$\{(N_3)\text{-}PPh_2(2\text{-}O-C_6H_4)\}_2C_6H_4$] reacted with UCl_4 to afford the first example of an actinide-stabilized phosphazide, $L''UCl_2$. In the solid-state structure of $L''UCl_2$, both phosphazide functionalities were coordinated to uranium; consecutive N_2 loss from the ligand phosphazides was documented.

Organothorium chemistry has been largely dominated by complexes stabilized by carbocyclic ligands.[12] The development of noncarbocyclic scaffolds has contributed to the diversification of thorium chemistry,[13−16] though, most ancillary ligands employed with actinide metals are either di-

Scheme 1. Phosphinimine Formation and Methods of Phosphazide Stabilization

hydrogen bonding

R = bulky group

steric bulk

trans phosphazide ⇌ cis phosphazide

ML_x

metal coordination

$-N_2$

phosphinimine
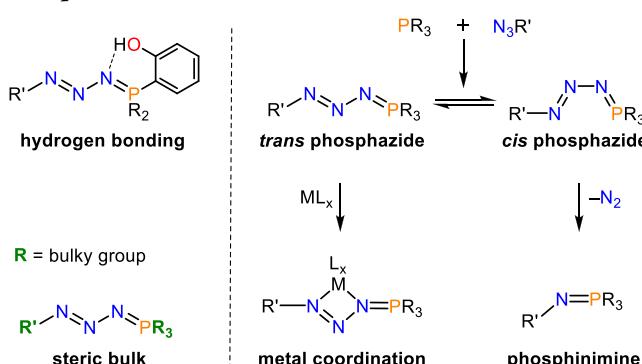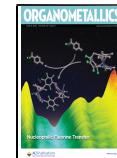
or trianionic. As a consequence, thorium(IV) trialkyl species, which necessarily require a single monoanionic supporting ligand, are rare. To the best of our knowledge, aside from tribenzyl variants of cyclopentadienyl Cp^RThBn_3,[17,18] the only trialkyl thorium complexes have been reported by Cheng and colleagues.[19] Cheng's complexes, $[PhC(NDipp)_2]Th-(CH_2SiMe_3)_3$ (Dipp = 2,6-$^iPr_2C_6H_3$)), $[Ph_2P(NDipp)_2]Th-(CH_2SiMe_3)_3$, $[Ph_2P(NDipp)]Th(p\text{-}CH_2C_6H_4Me)_3$, and $^{Me2}TpTh(CH_2SiMe_3)_3$ (^{Me2}Tp = B(($CH_3)_2C_3N_2H)_3^-$), when combined with 2 equiv of $[CPh_3][B(C_6F_5)_4]$, catalyze the polymerization of isoprene. In general, thorium species bearing noncarbocyclic monoanionic ancillary ligands are uncommon, and they typically contain more than one such ligand.[20−24]

It was hypothesized that the previously reported *NNN* scaffold, $L_{P=N}$ ($L_{P=N}$ = κ^3-2,5-$[(4\text{-}^iPrC_6H_4)N=P^iPr_2]_2N\text{-}(C_4H_2)^-$), which features two phosphinimine groups, could be modified to generate a monoanionic diphosphazide ligand. This ligand framework was targeted because it was anticipated to provide access to a wide array of metal phosphazide complexes, thereby shedding light on the viability of phosphazides to serve as useful donors in coordination and organometallic chemistry.

Alkali salts of $HL_{P=N}$ have been previously prepared by reaction of the requisite group I metal hydride with the product of 2 equiv of *para*-isopropylphenyl azide (PippN$_3$) and 2,5-$(^iPr_2P)_2NH(C_4H_2)$ (Scheme 2, left).[25] In this work,

Scheme 2. Synthesis of Compound 2
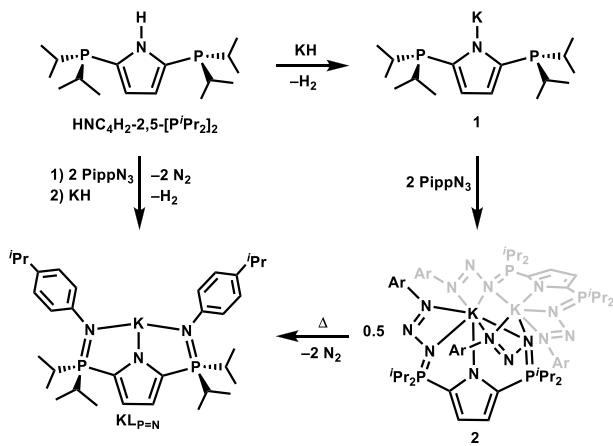
however, the pyrrole nitrogen was deprotonated to give $K[2,5\text{-}(^iPr_2P)_2N(C_4H_2)]$ (**1**) prior to introduction of the azide, as the presence of potassium was deemed necessary to stabilize the resultant phosphazides in $KL_{P=N3}$ (**2**, $L_{P=N3}$ = κ^5-2,5-$[(4\text{-}^iPrC_6H_4)N_3=P^iPr_2]_2N(C_4H_2)^-$, Scheme 2).

Diphosphazide **2** exhibits a diagnostic downfield singlet at δ 44.7 in the $^{31}P\{^1H\}$ NMR spectrum (cf. δ −4.9 for compound **1**). A low-quality solid-state structure obtained via X-ray diffraction studies served to establish the atom connectivity within compound **2**, confirming two intact phosphazide units (see Supporting Information for additional details). Upon heating a sample of **2** at 55 °C for 24 h in benzene-d_6, the $^{31}P\{^1H\}$ NMR spectrum revealed the signal at δ 44.7 had been completely supplanted by an upfield-shifted resonance at δ 22.7, which closely matches that observed for $NaL_{P=N}$.[25] This information suggests the loss of 2 equiv of N$_2$ from diphosphazide **2** to afford $KL_{P=N}$ (Scheme 2, bottom).

Due to the success of stabilizing two phosphazides in a phosphazidosalen complex of uranium,[11] thorium was selected as an appropriate candidate for this system considering their similar ionic radii (1.05 Å for Th(IV) vs 1.00 Å for U(IV), C.N. 8).[26] Additionally, the pentadentate, monoanionic ligand L_{PN3} was anticipated to sufficiently sterically saturate the thorium center to provide access to an unusual trialkyl species.

Reaction of $ThCl_4(dme)_2$ (dme = dimethoxyethane) with 1 equiv of compound **2** in THF at −35 °C yielded an off-white solid which gave rise to a $^{31}P\{^1H\}$ NMR signal at δ 63.0 (Scheme 3, left). The atom connectivity of thorium

Scheme 3. Synthesis of Compounds 3−6
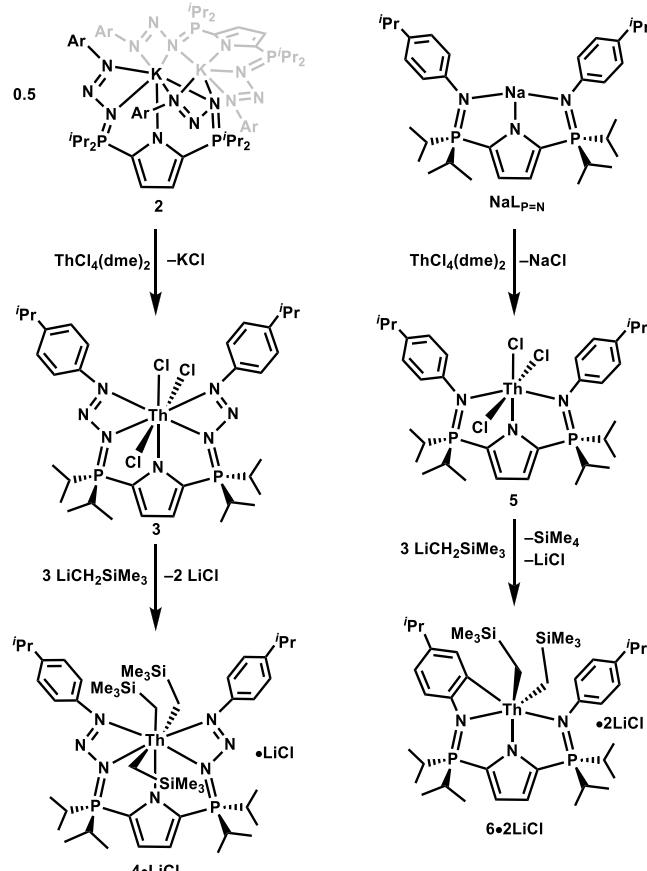
diphosphazide $L_{P=N3}ThCl_3$ (**3**) was revealed by a low-quality solid-state structure. Complex **3** contains three chloride ligands, as well as two phosphazide groups that are bound to the thorium centers in a κ^2 fashion via the α- and γ-nitrogen atoms. Notably, ^1H and $^{31}P\{^1H\}$ NMR studies indicate that complex **3** is remarkably robust in solution, with no appreciable decomposition or loss of N$_2$ after 24 h at 55 °C in benzene-d_6. Such thermal stability lies in stark contrast to $L''UCl_2$, which readily loses 1 equiv of N$_2$ at ambient temperature and a second equivalent upon heating.[11]

Addition of 3 equiv of $LiCH_2SiMe_3$ to thorium trichloride **3** gave rise to a new resonance (δ 59.4) in the $^{31}P\{^1H\}$ NMR spectrum, along with concomitant disappearance of the resonance attributed to **3** (δ 63.0). The ^1H NMR spectrum exhibited a sharp singlet (δ 0.34, 27H) and a broad resonance (δ 0.15, 6H), consistent with chemical shifts for known organothorium complexes (δ −0.58 to 0.51, Si*Me$_3$*; δ −0.43 to 0.50, Th−C*H$_2$*)[19,27] and, hence, indicative of three Th−
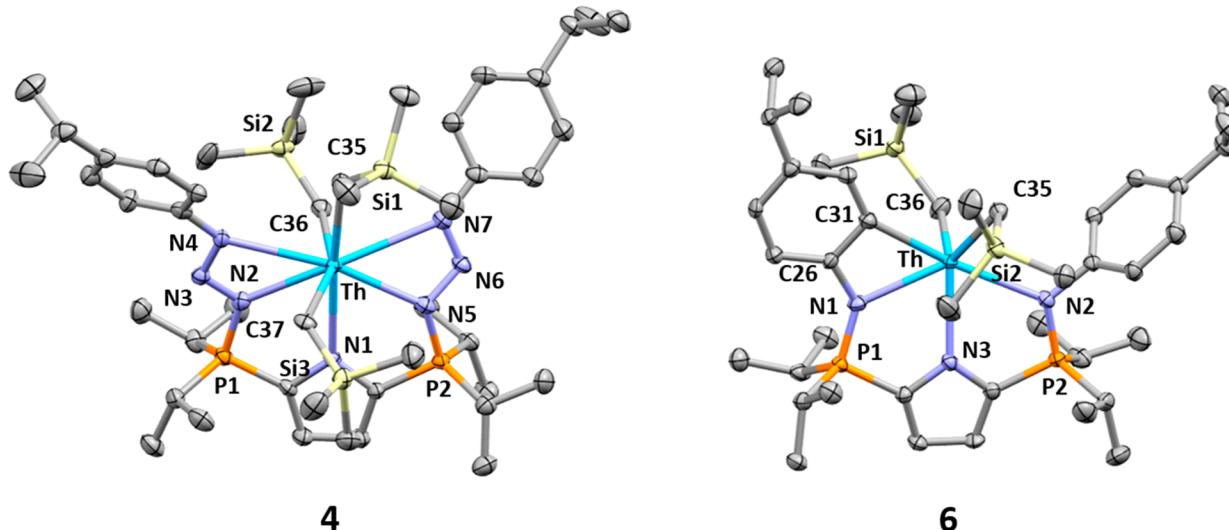
Figure 1. Left: X-ray crystal structure of complex **4**. Thermal ellipsoids are represented at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Th1−N1 = 2.709(3), Th1−N2 = 2.570(3), Th1−N4 = 2.888(3), Th1−N5 = 2.551(3), Th1−N7 = 2.910(3), Th−C35 = 2.519(4), Th1−C36 = 2.513(4), Th1−C37 = 2.581(4), N2−N3 = 1.350(5), N3−N4 = 1.277(4), N5−N6 = 1.363(4), N6−N7 = 1.268(4), P1−N2 = 1.648(3), P2−N5 = 1.658(3), N2−N3−N4 = 108.9(3), N5−N6−N7 = 109.4(3). Right: X-ray crystal structure of **6**. Thermal ellipsoids are represented at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg): Th1−N1 = 2.483(4), Th1−N2 = 2.577(3), Th1−N3 = 2.508(3), Th1−C31 = 2.531(4), Th−C35 = 2.509(4), Th1−C36 = 2.477(5), P1−N1 = 1.601(3), P2−N2 = 1.619(3).

CH_2SiMe_3 alkyl groups that are chemically equivalent on the NMR time scale. In addition, the observed CH_2SiMe_3 $^{13}C\{^1H\}$ NMR resonance (δ 85.4) falls within the range reported (δ 70.7−102.7) for published thorium complexes that bear at least one CH_2SiMe_3 substituent.[19,27]

The X-ray crystal structure of $L_{P=N3}Th(CH_2SiMe_3)_3$ (**4**) (Figure 1, left) confirms that both phosphazide groups remain intact with slightly strained N−N−N angles of 108.9(3) and 109.4(3)° when compared to the average N−N−N angle of metal-free and uncoordinated phosphazides (112.2°). The geometry at thorium is best described as distorted hexagonal bipyramidal with the five coordinated nitrogen atoms and C35 comprising the meridional plane (N7 lies 1.031(4) Å out of the N4−N2−N1−N5−C35 plane) and C36 and C37 occupying the axial sites (C36−Th−C37: 157.5(1)°). Notably, one of the Th−C bonds (Th1−C37: 2.581(4) Å) is substantially longer than the other two (Th1−C35: 2.519(4) Å, Th1−C36: 2.513(4) Å). Although these distances are among the more elongated of reported Th−CH_2SiMe_3 lengths, they still fall within the range of thorium−alkyl contacts in the chemical literature (2.433(4)−2.598(3) Å).[19,27] The anionic pyrrole nitrogen−thorium distance (Th−N1 = 2.708(3) Å) is long, which we attribute to the propensity for thorium to sit in the center of the pentadentate ligand binding pocket. The N3−N4 (1.277(4) Å), N6−N7 (1.268(4) Å), P1−N2 (1.648(3) Å), and P2−N5 (1.658(3) Å) distances are consistent with localized double bonds, thus supporting the motif of alternating double (P=N), single (N−N), and double (N=N) bonds in the phosphazide unit. Surprisingly, complex **4** displays significant stability at ambient temperature in solution, with no change observed after 24 h in benzene-d_6. At 55 °C, however, decomposition into an intractable mixture occurs in 2 h.

Given the relative dearth of chemistry featuring metal-coordinated phosphazides, we aimed to compare the chemistry of related phosphazide and phosphinimine complexes. As pincer ligands have been previously employed to support

actinide complexes[28] and the pyrrole-based bisphosphinimine analogue ($L_{P=N}$) of $L_{P=N3}$ has been used in conjunction with metals across the periodic table (e.g., Sc, Lu, and Rh),[25,29] we thereby endeavored to prepare thorium complexes thereof.

Reaction of $NaL_{P=N}$ with $ThCl_4(dme)_2$ in dme afforded $L_{P=N}ThCl_3$ (**5**) as an off-white solid in 89.4% yield (Scheme 3, right). The formation of complex **5** was supported by the emergence of a new resonance (δ 56.1), along with simultaneous disappearance of the signal attributed to $NaL_{P=N}$ (δ 28.0) in the $^{31}P\{^1H\}$ NMR spectrum.[25] Notably, the ^{31}P NMR chemical shift for bisphosphinimine **5** appears 7.1 ppm upfield of complex **3** (δ 63.0), which matches the empirical trend that phosphazides generally resonate between 7 and 20 ppm downfield of their phosphinimine congeners.[11] An X-ray crystal structure of complex $5\cdot C_7H_8$ (see Supporting Information for details) revealed the geometry at thorium to be pseudo-octahedral, with a Cl−Th−Cl angle of 174.34(3)°. However, thorium sits slightly outside the typical bonding pocket of the ligand, causing the small $N_{phosphinimine}$−Th−$N_{phosphinimine}$ angle (135.2(1)°) and long Th−$N_{pyrrole}$ distance (2.474(4) Å; cf. 2.394(4) and 2.378(3) Å for Th−$N_{phosphinimine}$). The P=N lengths (1.634(4) Å) are on the long end for coordinated phosphinimines in this ligand system. For example, the P=N bonds in the rhodium complexes $L_{P=N}Rh(CO)$ and $L_{P=N}Rh(CO)_2$ are 1.629(3) and 1.612(2) Å, respectively.[25]

Upon addition of 3 equiv of $LiCH_2SiMe_3$ to a toluene solution of complex **5**, two new ^{31}P NMR resonances (δ 47.7, δ 49.5) of equal intensity, as well as two P^{i}Pr methine ^1H NMR signals, were observed, suggesting the formation of a C_s-symmetric product. Furthermore, 1 equiv of $SiMe_4$ (^1H NMR: δ 0.00) was generated, and only two Th−CH_2SiMe_3 groups were present. The Th−CH_2 methylene protons appear as two doublets ($^2J_{HH}$ = 11.5 Hz) due to geminal coupling (confirmed by a 2D $^1H−^1H$ COSY experiment) and both CH_2SiMe_3 groups are chemically equivalent on the NMR time scale, giving rise to one singlet at δ 0.33 which integrates as 18H.

Examples in the literature which also exhibit geminal Th–CH_2SiMe_3 coupling have $^2J_{HH}$ values (10.2 Hz, 12 Hz) that agree well with these findings.[27d,j] In the $^{13}C\{^1H\}$ NMR spectrum, the Th–CH_2SiMe_3 resonance was located at δ 87.3, similar to that of complex **4** (δ 85.4). A diagnostic signal indicative of a cyclometalated Th–C_{aryl} was found at δ 203.5. Altogether, these data strongly imply that the putative organothorium product, $L_{P=N}Th(CH_2SiMe_3)_3$, readily decomposed via cyclometalation of an *N*-aryl substituent.

The solid-state structure of $L^*_{P=N}Th(CH_2SiMe_3)_2$ (**6**, $L^*_{P=N}$ = 2-[(4-^{i}PrC$_6$H$_3$)N=P^{i}Pr$_2$]-5-[(4-^{i}PrC$_6$H$_4$)N=P^{i}Pr$_2$]-N(C_4H_2)$^{2-}$), was confirmed by X-ray diffraction studies (Figure 1, right). The six-coordinate thorium(IV) center exhibits pentagonal pyramidal geometry; the two phosphinimine nitrogen donors, the anionic pyrrole nitrogen, the cyclometalated aryl substituent (C31), and one CH_2SiMe_3 group (C35) comprise the pyramid base, whereas the remaining CH_2SiMe_3 (C36) occupies the apical site. Thorium sits 0.581(2) Å above the N1–N2–N3–C31–C35 plane. Notably, the Th–C distances in complex **6** (Th1–C35: 2.509(4) Å, Th1–C36: 2.477(5) Å, Th1–C31: 2.531(4) Å) are similar to those in eight-coordinate trialkyl **4** (2.513(4)–2.581(4) Å).

Although intramolecular C–H activation of $L_{P=N}$ is not common, it appears to be more prevalent for large metals, such as samarium.[30] The enhanced thermal stability of diphosphazide **4** relative to complex **6** is likely a consequence of the pentadentate bonding mode of $L_{P=N3}$, which more completely coordinatively and electronically saturates the metal center, thereby mitigating the propensity for cyclometalation. In addition, the phosphazide groups necessarily enforce a larger distance between the *N*-aryl *ortho*-CHs and the metal center.

By a straightforward modification to the synthetic protocol for $L_{P=N}$, a versatile and robust diphosphazide ancillary ligand, $L_{P=N3}$, was prepared. Actinide complexes thereof, which can be generated via standard salt metathesis routes, are resistant to N_2 loss at ambient temperature and display different chemistry than their bisphosphinimine analogues. As the chemistry of this often overlooked functionality continues to be developed, its incorporation into new ligand designs will continue to reveal its under-realized value to the fields of coordination and organometallic chemistry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00231.

> Experimental and crystallographic details, molecular structures of **2** and **3**, atomic coordinates, interatomic distances and angles, anisotropic thermal parameters, and hydrogen parameters for **4**, **5**, and **6** (PDF)

Accession Codes

CCDC 1973166−1973168 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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