

Phosphaazaallene and phosphinylimide complexes stemming from a terminal and four-coordinate titanium phosphinidene†

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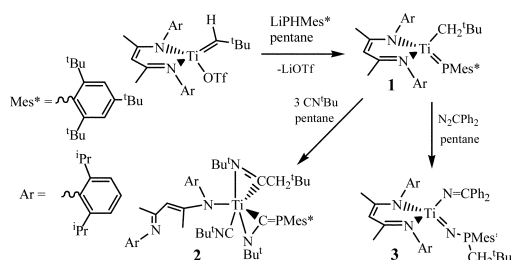
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Treatment of the terminal titanium–phosphinidene (Nacnac)Ti=PMes*(CH₂^tBu) (Nacnac⁻ = [2,6-ⁱPr₂C₆H₃]-NC(CH₃)CHC(CH₃)N[2,6-ⁱPr₂C₆H₃], Mes*⁻ = 2,4,6-^tBu₃-C₆H₂) with CN^tBu and N₂CPh₂, in pentane at -35 °C, affords η²-(N,C)-phosphaazaallene and phosphinylimide complexes, respectively.

Titanium phosphinidene complexes are rare, presumably due to the mismatch between the hard titanium atom and the soft P-containing ligand.^{1,2} To date, only a handful of group 4³ and 5⁴ terminal phosphinidene complexes have been described in the literature. The pursuit of systems having such a reactive functionality stems from their ability to engage in “phospha-Staudinger or Wittig”-type transformations.^{3,4} We recently reported the synthesis of a four-coordinate titanium phosphinidene complex (Nacnac)Ti=PMes*(CH₂^tBu) **1** (Scheme 1) by α-hydrogen migration.⁵ The preparation of **1** was remarkable since organotransition-metal complexes with low-coordination numbers are inherently reactive and consequently provide useful templates to study fundamental processes such as small-molecule activation and group transfer.^{3,4a,5,6} The present study establishes that a coordinatively unsaturated and terminal titanium–phosphinidene complex⁴ supported by a sterically demanding β-diketiminato ligand, denoted “Nacnac” (Nacnac⁻ = ArNC(Me)CHC(Me)NAr, Ar = 2,6-ⁱPr₂C₆H₃), can react with CN^tBu and N₂CPh₂ to afford novel complexes having bound η²-(N,C)-phosphaazaallene and phosphinylimide ligands, respectively.



Scheme 1 Synthesis of titanium phosphinidene **1** and subsequent reactions to prepare complexes **2** and **3**.

Isolation of complex **1** was achieved by kinetic stabilization using a sterically bulky substituent on P (Mes*). Otherwise, complex **1** transforms by a “phospha-Staudinger” reaction.⁵ However, the low-coordination environment coupled with the kinetic stability of the Ti=P bond, the unusually short Ti–P bond (2.1831(4) Å)⁵ and the obtuse Ti–P–C_{ipso} angle (164.44(5)°)⁵ raised fundamental questions regarding the nature of bonding and structure in complex **1**. Theoretical calculations were thus performed on the titanium phosphinidene model complex (Nacnac*)Ti=PMes(Me) (Nacnac*⁻ =

ArNCHCHCHNAr, Ar = 2,6-Me₂C₆H₃, Mes = 2,4,6-Me₃C₆H₂) using density functional theory (DFT).† The optimized geometry of the model complex is in close agreement with the experimentally observed X-ray structural parameters of **1**.† When inspecting the frontier orbitals in (Nacnac*)Ti=PMes(Me), it is observed that the HOMO is the π-bond of the Ti–P double linkage (Fig. 1), while the LUMO† is composed predominantly of π* character localized about the N–C bonds of the Nacnac* backbone and a node at the γ-C. More important, the stability of the Ti–P bond and the linear Ti–P–C_{ipso} angle is attributed to the HOMO-1 orbital. The HOMO-1, which is orthogonal to the HOMO, indicates that there is significant π-donation of the lone pair on P to an empty d-orbital on titanium (Fig. 1). Theoretical results suggest tantalizingly that complex **1** has a reactive phosphinidene functionality and that the bonding in Ti–P should be better portrayed as a pseudo-triple bond (Ti≡P).

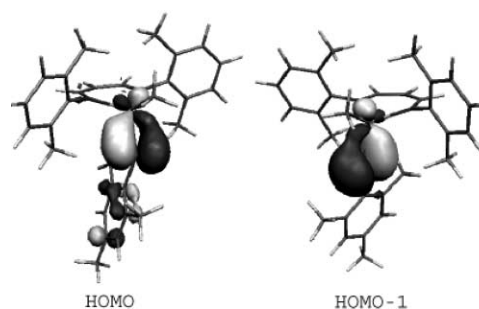


Fig. 1 A perspective view showing the Ti≡P π-orbitals (HOMO and HOMO-1) for the model complex of **1**, namely (Nacnac*)Ti=PMes(Me).

In order to demonstrate the reactivity of the Ti≡P functionality we carried out reactions of complex **1** with CN^tBu and N₂CPh₂. When a pentane solution of **1** is treated with 3 equiv of CN^tBu, the color rapidly changes from green to dark brown. After recrystallization from pentane, the η²-(N,C)-phosphaazaallene titanium complex (η¹-Nacnac)Ti(CN^tBu)(η²-(N,C)-^tBuN=CCH₂^tBu)(η²-(N,C)-^tBuN=C=PMes*) (**2**) is isolated in 60% yield as dark plates. Diagnostic features associated with **2** include the observation of stretches at 2210 and 2187 cm⁻¹, and 1551 and 1528 cm⁻¹, which may be assigned to ν_{CN} and ν_{CP} stretches, respectively. There are two ³¹P NMR resonances centered at -8.53 and -17.58 ppm, which we attribute to the presence of two isomers in solution. In addition, the ¹³C NMR resonance of the central allene carbon of the coordinated phosphaazaallene is consistent with η²-(N,C) binding (δ 217.6 and 213.8 ppm, J_{CP} = 166 and 172 Hz, respectively)† for the two isomers.⁷ Phosphaazaallenes are reactive molecules, and examples of early-transition metal complexes having this type of ligand are scarce.^{7,8}

To further support the connectivity in **2**, single crystals were grown from a saturated pentane solution cooled to -35 °C, and the molecular structure was determined by X-ray diffraction studies (Fig. 2).‡ The structure of **2** displays one of the two possible isomers and reveals a coordinatively saturated titanium

† Electronic supplementary information (ESI) available: Complete experimental, spectroscopic, analytical, and crystallographic details for **2** and **3**, as well as DFT computational details for the model complex of **1**, namely (Nacnac*)Ti=PMes(Me). See <http://www.rsc.org/suppdata/dt/b311748k/>

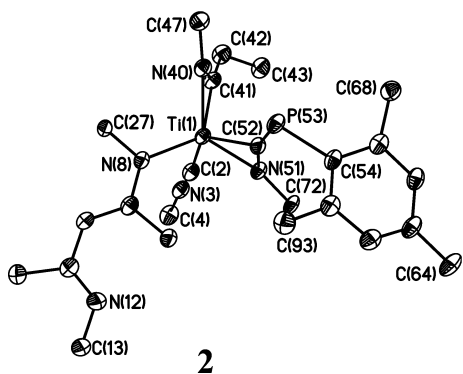


Fig. 2 Molecular structure of **2** with thermal ellipsoids at the 50% probability level. All H-atoms and aryl groups on the nitrogens with the exception of the *ipso*-carbon atoms C(27) and C(13) have been omitted for clarity. Methyl groups on the 'Bu fragments (C(4), C(47), C(43), C(68), C(64), C(72), and C(93)) have been also removed for clarity.

center with an η^1 -bound Nacnac⁻ ligand, one isonitrile occupying the axial position, as well as two additional isonitriles inserting into the Ti–C and Ti=P bonds. Both the iminato and phosphazaaallene ligands are η^2 -(N,C) bound to the titanium center. † There is substantial reduction of the N=C bond (N(51)–C(52), 1.307(5) Å) of the phosphazaaallene ligand relative to that for the metal-free form.^{7–9}

When diphenyldiazomethane is added slowly to **1** in pentane, complex (Nacnac)Ti=N[P(CH₂^tBu)(Mes*)](N=CPh₂) (**3**) is formed cleanly in 68% yield subsequent to recrystallization from pentane at –35 °C. † Phosphinylimide complex **3** displays one ³¹P NMR resonance at 99.7 ppm and represents the first example of an sp²-phosphorus attached to a titanium–imide motif. Single and dark-brown crystals of **3** also support the proposed connectivity revealing a four-coordinate titanium complex containing a short Ti=N_{imide} bond length of 1.727(3) Å (Ti(1)–N(47)) and Ti–N–P angle of 157.4(7)° with a substantially pyramidalized phosphino-P (Fig. 3). Other salient features in the structure of **3** include a linear ketiminate ligand (Ti(1)–N(33)–C(34), 174.5(3)°) having a short Ti(1)–N(33) bond of 1.918(3) Å, both of which indicate considerable π -bonding character in the titanium–N_{ketiminate} linkage. Complex **3** forms likely from insertion of N₂CPh₂ into the Ti=P bond, and subsequent alkyl insertion as well as unusual N–N bond cleavage of the putative phosphazaine intermediate. Phosphinylimide **3** could be best described as a η^1 -phosphahydrazido complex of titanium. Analogous Ti and Zr η^1 -hydrazido complexes display rich chemistry differing significantly from monomeric alkyl and aryl imido complexes.¹⁰ Compounds **2** and **3** are exceedingly reactive and decompose over several hours in solution or in the solid state.

Our work in the synthesis of a titanium phosphazaaallene complex contrasts with previous experiments by Cowley and co-workers where it was shown that WL₄Cl₂ (L=PMePh₂) can

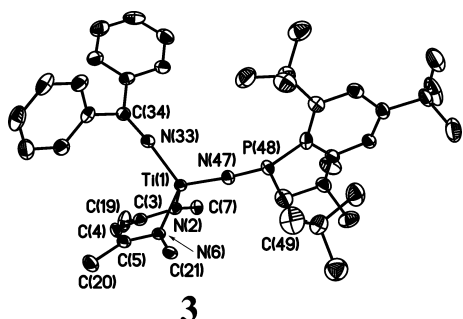


Fig. 3 Molecular structure of **3** with thermal ellipsoids at the 50% probability level. All H-atoms and aryl groups on the nitrogens with the exception of the *ipso*-carbon atoms (C(7) and C(21)) have been omitted for clarity.

cleave the P=C bond of Mes*P=C=NPh to afford the phosphinidene–isocyanide complex *trans*-WCl₂(CNPh)(PMes*).¹¹ The microscopic reverse of the bond breaking reaction of phosphazaaallenes support the notion that Ti=P bonds are inherently reactive scaffolds and powerful phosphinidene group-transfer reagents.

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Notes and references

‡ *Crystal data for 2*, C₇₇H₁₃₂N₅PTi; triclinic, $P\bar{1}$, $a = 12.297(2)$, $b = 13.182(3)$, $c = 24.843(5)$ Å, $\alpha = 103.400(5)$, $\beta = 92.806(6)$, $\gamma = 91.863(6)^\circ$, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 0.171 \text{ mm}^{-1}$, $V = 3908.8(13) \text{ \AA}^3$, $D_c = 1.025 \text{ mg mm}^{-3}$, GoF on $F^2 = 1.022$. Out of a total of 47023 reflections collected, 13721 were independent and 9219 were observed ($R_{\text{int}} = 0.116$) with $I > 2\sigma(I)$ (dark plate, $0.35 \times 0.30 \times 0.30 \text{ mm}$, $25.01^\circ \geq \theta \geq 1.97^\circ$). All non-hydrogen atoms were refined with anisotropic displacement parameters. The final full matrix least squares refinement converged to $R_1 = 0.0869$ (F) and $wR_2 = 0.2567$ (F^2). Two disordered pentane molecules were confined in the asymmetric unit.

§ *Crystal data for 3*, C₆₅H₉₁N₄PTi; triclinic, $P\bar{1}$, $a = 11.696(2)$, $b = 13.078(4)$, $c = 20.218(4)$ Å, $\alpha = 81.562(6)$, $\beta = 78.932(5)$, $\gamma = 80.736(5)^\circ$, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 0.212 \text{ mm}^{-1}$, $V = 2974.1(11) \text{ \AA}^3$, $D_c = 1.125 \text{ mg mm}^{-3}$, GoF on $F^2 = 0.915$. Out of a total of 12447 reflections collected, 11628 were unique and 6497 were observed ($R_{\text{int}} = 0.053$) with $I > 2\sigma(I)$ (dark brown block, $0.25 \times 0.25 \times 0.25 \text{ mm}$, $27.54^\circ \geq \theta \geq 2.22^\circ$). There is an occupational disorder of the phosphorus atom with an approximate ratio of 84 : 16. In addition, there is a rotational disorder about two methyl groups of the ¹Pr ligand having alternate positions. The final full matrix least squares refinement converged to $R_1 = 0.0624$ (F) and $wR_2 = 0.1530$ (F^2). CCDC reference numbers 218483 and 218484. See <http://www.rsc.org/suppdata/dt/b3/b311748k/> for crystallographic data in CIF or other electronic format.

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