

Communications

Remarkably Stable Titanium Complexes Containing Terminal Alkylidene, Phosphinidene, and Imide Functionalities

Brad C. Bailey,[†] John C. Huffman,[†] Daniel J. Mindiola,^{*,†} Wei Weng,[‡] and Oleg V. Ozerov[‡]

Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405, and Department of Chemistry, Brandeis University, MS015, 415 South Street, Waltham, Massachusetts 02454

Received November 30, 2004

Summary: PNP pincer-type complexes of titanium(III) and -(IV) have been prepared, characterized, and proven to be remarkably stable, despite having terminal alkylidene, phosphinidene, and imide functionalities.

High-oxidation-state early-transition metal–carbon,¹ –phosphorus,² and –nitrogen³ multiple bonds play a crucial role in many transformations that are ubiquitous to chemists. Despite the extensive list of transition-metal alkylidenes, only a handful of group 4 transition-metal alkylidenes^{1,4} and phosphinidenes^{2,5} have been prepared, which is likely due to the highly reactive

nature of these terminal functionalities. Recently, our group has illustrated the use of the sterically demanding Nacnac (Nacnac = [Ar]NC(Me)CHC(Me)N[Ar][–], Ar = 2,6-(CHMe₂)₂C₆H₃) ligand for the preparation of low-coordinate titanium complexes possessing terminal alkylidene,⁶ imide,⁷ and phosphinidene⁸ ligands. Despite the Nacnac ligand being an attractive template in stabilizing low-coordinate titanium systems having terminal metal–ligand multiply bonded scaffolds, this type of ligand is often fraught with undesirable side reactions due to the inherent reactivity of the imine functionality.^{6,7,9} Other drawbacks with the Nacnac ligand include electrophilic attack of the NCCCN γ -C atom and C–H abstraction reactions that occur at both the NCCCN β -C and nitrogen aryl groups.⁹

To avoid such obstacles, we employed the PNP pincer-type ligand (PNP = N[2-P(CHMe₂)₂-4-Me-C₆H₃]₂)[–].¹⁰ The PNP ligand provides a “hybrid-type” coordination environment combining both a hard amide and two soft phosphine donors fixed in a meridional geometry. In addition, this ancillary support is impervious to the intramolecular cross-metathesis (or alternatively referred to as Wittig-type) reactions often encountered with sterically demanding β -diketiminate-based complexes such as (Nacnac)Ti=CH^tBu(OTf)⁶ and (Nacnac)-Ti=PR(CH₂^tBu) (R = C₆H₁₁, 2,4,6-ⁱPr₃C₆H₂).⁸ A true representation of the robust nature of the PNP skeleton was demonstrated recently by Ozerov and co-workers,

* To whom correspondence should be addressed. E-mail: mindiola@indiana.edu.

[†] Indiana University.

[‡] Brandeis University.

- (1) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145–179.
- (2) (a) Lammertsma, K.; Vlaar, M. J. M. *Eur. J. Org. Chem.* **2002**, 1127–1138 and references therein. (b) Cowley, A. H. *Acc. Chem. Res.* **1997**, *30*, 445–451 and references therein. (c) Cowley, A. H.; Barron, A. R. *Acc. Chem. Res.* **1988**, *21*, 81–87. (d) Mathey, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1578–1604 and references therein.
- (3) (a) Wigley, D. E. *Prog. Inorg. Chem.* **1994**, *42*, 239–482. (b) Nugent, W. A.; Mayer, J. M. In *Metal–Ligand Multiple Bonds*; Wiley: New York, 1988.
- (4) (a) Fryzuk, M. D.; Mao, S. S. H.; Zaworotko, M. J.; MacGillivray, L. R. *J. Am. Chem. Soc.* **1993**, *115*, 5336–5337. (b) Fryzuk, M. D.; Duval, P. B.; Mao, S. S. H.; Zaworotko, M. J.; MacGillivray, L. R. *J. Am. Chem. Soc.* **1999**, *121*, 2478–2487. (c) Fryzuk, M. D.; Duval, P. B.; Patrick, B. O.; Rettig, S. J. *Organometallics* **2001**, *20*, 1608–1613. (d) Barger, P. T.; Santarsiero, B. D.; Armantrout, J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 5178–5186. (e) Cheon, J.; Rogers, D. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1997**, *119*, 6804–6813. (f) Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Chem. Commun.* **1978**, 604–606. (g) Rice, G. W.; Ansell, G. B.; Modrick, M. A.; Zentz, S. *Organometallics* **1983**, *2*, 154–157. (h) van der Heijden, H.; Hessen, B. *J. Chem. Soc., Chem. Commun.* **1995**, 145–146. (i) Meinhardt, J. D.; Anslyn, E. V.; Grubbs, R. H. *Organometallics* **1989**, *8*, 583–589. (j) Gilliom, L. R.; Grubbs, R. H. *Organometallics* **1986**, *5*, 721–724. (k) Hartner, F. W., Jr.; Schwartz, J.; Clift, S. M. *J. Am. Chem. Soc.* **1983**, *105*, 640–641. (l) Weng, W.; Yang, L.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2004**, *23*, 4700–4705. Attempts to prepare group 4 alkylidene species have been reported: (m) Wengrovius, J. H.; Schrock, R. R. *J. Organomet. Chem.* **1981**, *205*, 319–327.
- (5) (a) Hou, Z. M.; Stephan, D. W. *J. Am. Chem. Soc.* **1992**, *114*, 10088–10089. (b) Hou, Z. M.; Breen, T. L.; Stephan, D. W. *Organometallics* **1993**, *12*, 3158–3167. (c) Breen, T. L.; Stephan, D. W. *J. Am. Chem. Soc.* **1995**, *117*, 11914–11921. (d) Graham, T.; Stephan, D. W. Private communication. (e) Urnezis, E.; Lam, K.-C.; Rheingold, A. L.; Protasiewicz, J. D. *J. Organomet. Chem.* **2001**, *630*, 193–197. Other Zr phosphinidene complexes have been isolated by trapping experiments: (f) Mahieu, A.; Igau, A.; Majoral, J.-P. *Phosphorus Sulfur* **1995**, *104*, 235–239.

- (6) (a) Basuli, F.; Bailey, B. C.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *J. Am. Chem. Soc.* **2003**, *125*, 6052–6053. (b) Basuli, F.; Bailey, B. C.; Watson, L. A.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *Organometallics*, in press.

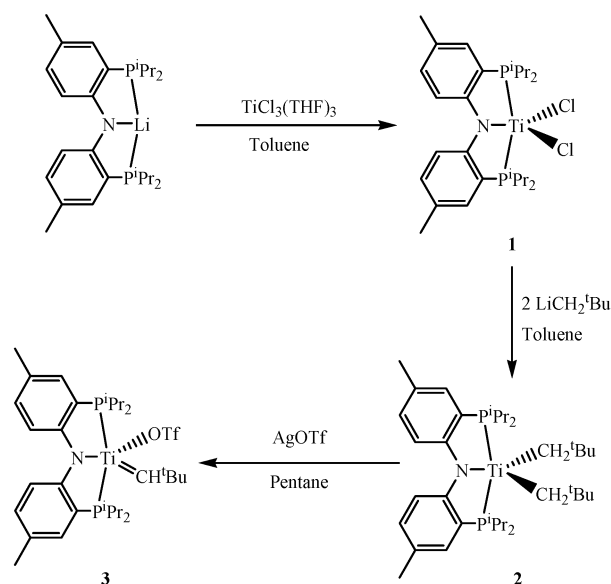
- (7) Basuli, F.; Bailey, B. C.; Huffman, J. C.; Mindiola, D. J. *Chem. Commun.* **2003**, 1554–1555.

- (8) Basuli, F.; Tomaszewski, J.; Huffman, J. C.; Mindiola, D. J. *J. Am. Chem. Soc.* **2003**, *125*, 10170–10171.

- (9) Bourget-Merle, L.; Lappert, M. F.; Severn, J. R. *Chem. Rev.* **2002**, *102*, 3031–3066.

- (10) The PNP ligand has been used in the chemistry of group 9 and 10 metals, and J_{P-P} values have been reported. (a) Fan, L.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2004**, *23*, 326–328. (b) Ozerov, O. V.; Guo, C.; Fan, L.; Foxman, B. M. *Organometallics* **2004**, *23*, 5573–5580. (c) Ozerov, O. V.; Guo, C.; Papkov, V. A.; Foxman, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 4792–4793. (d) Fan, L.; Yang, L.; Guo, C.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2004**, *23*, 4778–4787. The PNP relative bis(2-diphenylphosphino)amide has also been reported: (e) Liang, L.-C.; Lin, J.-M.; Hung, C.-H. *Organometallics* **2003**, *22*, 3007–3009.

Scheme 1. Synthesis of Complexes 1–3



in which they reported the isolation of a terminal zirconium alkylidene-alkyl complex $(\text{PNP})\text{Zr}=\text{CHPh}(\text{CH}_2\text{Ph})$.⁴¹ Herein, the following paper demonstrates that the PNP ligand can be incorporated readily onto Ti and that such a template can stabilize terminal alkylidene, phosphinidene, and imide functionalities.

In contrast to the Zr chemistry,⁴¹ attempts to integrate the alkylidene functionality directly on $\text{Ti}(\text{IV})$ proved difficult, inasmuch as treatment of $(\text{PNP})\text{TiCl}_3$, prepared directly from TiCl_4 and $\text{Li}(\text{PNP})$, with alkyl Grignard reagents (2–3 equiv) led to undesired reduction instead of alkylation.¹¹ This difference between the reactivities of $(\text{PNP})\text{ZrCl}_3$ and $(\text{PNP})\text{TiCl}_3$ is not surprising, since reduction of M^{IV} to M^{III} should be more facile for $\text{M} = \text{Ti}$ than for the heavier congener $\text{M} = \text{Zr}$.

To avoid redox pathways during the transmetalation process, we resorted to an approach that worked well previously for the preparation of titanium alkylidenes with the Nacnac system: alkylation of a Ti^{III} precursor followed by one-electron oxidation. To prepare the $\text{Ti}(\text{III})$ precursor $(\text{PNP})\text{TiCl}_2$ (**1**), a toluene solution of $\text{Li}(\text{PNP})$ was cooled to -35°C and added dropwise to a cold toluene suspension of $\text{TiCl}_3(\text{THF})_3$. After 12 h and upon removal of salts, a violet powder of $(\text{PNP})\text{TiCl}_2$ (**1**) was isolated in 58% yield (Scheme 1). Satisfactorily elemental analysis and isolation of X-ray-quality single crystals has so far eluded us; however, the room-temperature X-band EPR measurements of **1** in THF displayed a g_{iso} value of 1.949 and well-resolved hyperfine and superfine coupling to titanium ($A_{\text{iso}} = 17.4$ G) and both phosphorus atoms ($A_{\text{iso}} = 8.8$ G), respectively. When purple solids of **1** are dissolved in THF, the solutions turn red, suggesting that coordination of the solvent might be occurring to form a putative $(\text{PNP})\text{TiCl}_2(\text{THF})$ complex, but coordination appears to be weak and reversible, since red solids turn back to purple under reduced pressure. It is also possible that complex **1** could exist as a dimer in the absence of coordinating solvents. However, we have found that complex **1** (possibly $(\text{PNP})\text{TiCl}_2(\text{THF})$ or the dimer) readily abstracts Cl from CCl_4 to afford $(\text{PNP})\text{TiCl}_3$.¹¹

(11) See the Supporting Information for complete experimental, crystallographic, and DFT calculation details.

Toluene solutions of complex **1** react smoothly with 2 equiv of neopentyl lithium at -35°C over 1 h to afford a red solution. Upon removal of the salts and recrystallization from cold (-35°C) saturated pentane solutions, red-brown crystalline $(\text{PNP})\text{Ti}(\text{CH}_2\text{tBu})_2$ (**2**) is obtained in 52% yield (Scheme 1). A single-crystal X-ray diffraction study of **2** agrees with the proposed connectivity and displays no significant $\alpha\text{-H}$ interactions in the solid state,¹¹ while Evans magnetic susceptibility measurements are in accord with a titanium(III) species ($\mu_{\text{eff}} = 2.11 \mu_{\text{B}}$). The room-temperature X-band solution EPR spectrum of **2** reveals not only hyperfine coupling of the unpaired electron to the titanium center ($A_{\text{iso}} = 10.5$ G) but also superhyperfine coupling to the proximal phosphorus atoms ($A_{\text{iso}} = 10.1$ G) and the nitrogen ($A_{\text{iso}} = 34.9$ G) and super-superhyperfine coupling to all four $\alpha\text{-H}$'s on the neopentyl ligands ($A_{\text{iso}} = 1.7$ G).¹¹ Alternatively, it was found that complex **2** can be prepared in a "one pot" synthesis of $\text{Li}(\text{PNP})$ and $\text{TiCl}_3(\text{THF})_3$, followed by the addition of 2 equiv of LiCH_2tBu after 12 h (63% yield based on $\text{TiCl}_3(\text{THF})_3$).¹¹

To promote α -abstraction⁶ and form $(\text{PNP})\text{Ti}=\text{CHtBu}(\text{OTf})$ (**3**), complex **2** was oxidized with AgOTf at -35°C in pentane. Upon filtration of the Ag^0 mirror, complex **3** is generated quantitatively on the basis of the combination of ^1H , ^{31}P , ^{13}C , and $^{13}\text{C}\{^{31}\text{P}\}$ NMR spectra.¹¹ Diagnostic spectroscopic features for **3** include a ^{13}C NMR resonance centered at 301 ppm, which is consistent with a terminal C_α -alkylidene ligand.^{1,4,6} The $\alpha\text{-H}$ is significantly downfield (8.42 ppm) in the ^1H NMR spectrum, and the low $J_{\text{C-H}}$ value of 102.6 Hz for the alkylidene resonance lends support to an α -agostic interaction being present in solution. The ^{31}P NMR spectrum of **3** displays two doublets centered at 33.6 and 24.2 ppm ($J_{\text{P-P}} = 55$ Hz), which would be in agreement with the molecule retaining C_1 symmetry in solution. This $J_{\text{P-P}}$ coupling constant is low in comparison to similar chelate trans-phosphine systems (100–300 Hz)^{41,10,12} and is thus indicative of the phosphines being significantly skewed from a strict trans geometry ($\text{P-Ti-P} = 180^\circ$). Such a geometrical constraint is arguably a result of the aryl motifs in the PNP ligand or is based on an electronic reason involving a compromise between the soft P and hard Ti and N atoms. Rigidity is probably more pronounced in this class of ligand than in the SiPNP ligand system utilized by Fryzuk and co-workers ($\text{SiPNP} = \text{N}[\text{SiMe}_2\text{CH}_2\text{P}(\text{tBu})_2]_2^-$).¹³ Interestingly, compound **3** resembles an electron-deficient and unsaturated version of Schrock and Baumann's complex $(\text{NON})\text{Ti}=\text{CHtBu}(\text{PMe}_3)_2$ ($\text{NON} = [\text{PrN-}o\text{-C}_6\text{H}_4]_2\text{O}^{2-}$).¹⁵

X-ray-quality single crystals of **3** were slowly grown from pentane at room temperature (Figure 1).¹⁶ The molecular structure of **3** reveals a short $\text{Ti}=\text{C}$ bond (1.883(7) Å) and a metal center residing in a pseudo-trigonal-bipyramidal geometry with "trans-like" phos-

(12) (a) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 3rd ed.; Wiley-Interscience: New York, 2001; pp 260–262.

(13) (a) Fryzuk, M. D.; Mao, S. S. H.; Zaworotko, M. J.; MacGillivray, L. R. *J. Am. Chem. Soc.* **1993**, *115*, 5336–5337. (b) Fryzuk, M. D.; Duval, P. B.; Mao, S. S. H.; Zaworotko, M. J.; MacGillivray, L. R. *J. Am. Chem. Soc.* **1999**, *121*, 2478–2487.

(14) Baumann, R.; Stumpf, R.; Davis, W. M.; Liang, L.-C.; Schrock, R. R. *J. Am. Chem. Soc.* **1999**, *121*, 7822–7836.

(15) Basuli, F.; Bailey, B. C.; Huffman, J. C.; Baik, M.; Mindiola, D. J. *J. Am. Chem. Soc.* **2004**, *7*, 1924–1925.

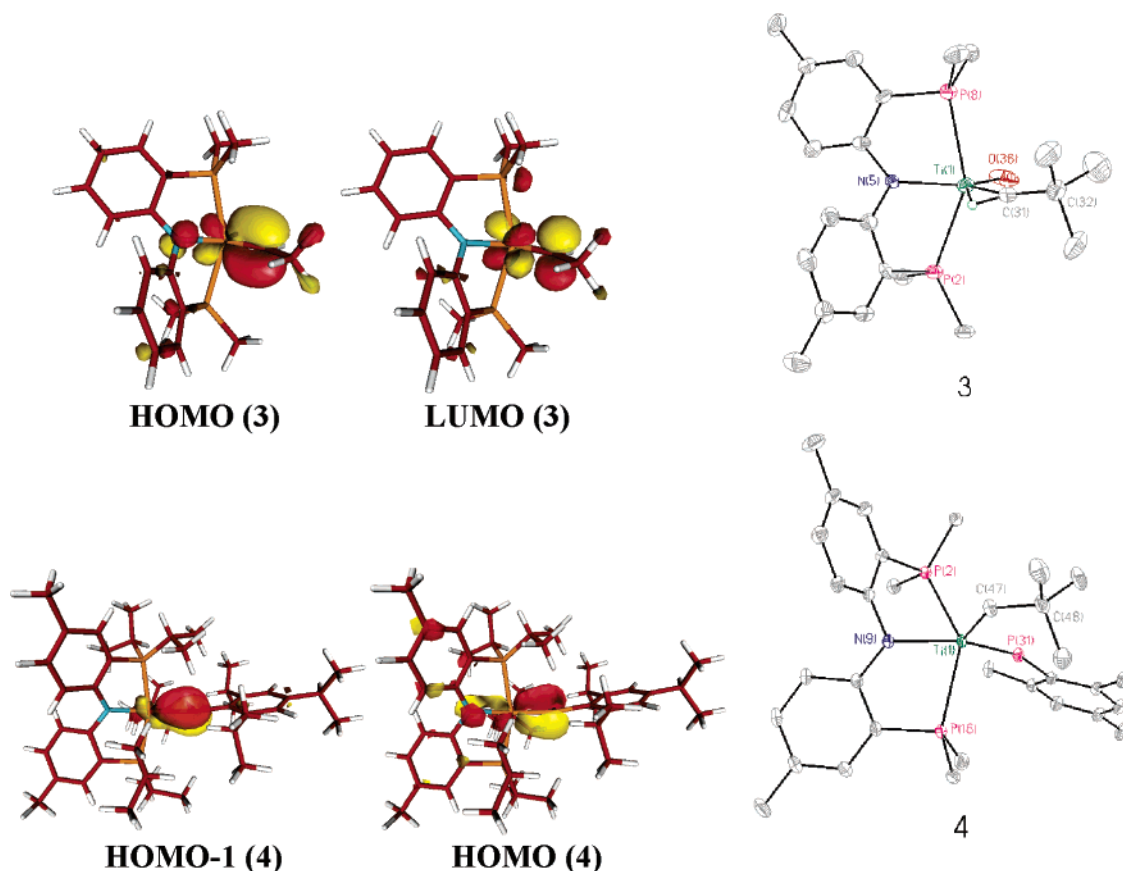
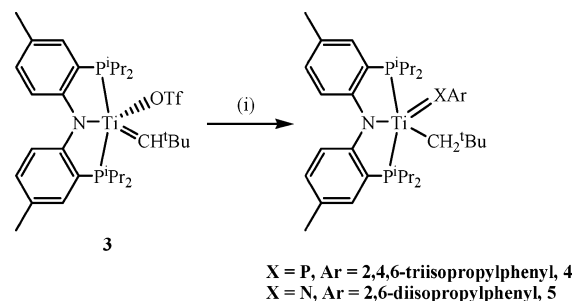


Figure 1. Molecular structures of **3** and **4** with thermal ellipsoids at the 50% probability level. All H atoms, with the exception of the α -H on C(31), and the O_2SCF_3 and $i\text{Pr}$ methyl groups on the P atoms and aryl positions (complex **4**) have been omitted for clarity. Next to each structure are the DFT calculations (HOMO and LUMO for **3** and HOMO-1 and HOMO for **4**) depicting bonding interactions involving the $\text{Ti}=\text{C}$ and $\text{Ti}=\text{P}$ linkages.

phines ($148.43(8)^\circ$). The distorted $\text{Ti}(1)=\text{C}(31)-\text{C}(32)$ angle ($157.6(6)^\circ$) coupled with the low $\alpha\text{-C } J_{\text{C-H}}$ (vide supra) and short $\text{Ti}-\text{H}(6)$ distance ($2.09(6)$ Å) are all consistent with an $\alpha\text{-H}$ agostic interaction being present in complex **3**.^{1,14}

It was presaged by the nucleophilic character of the α -carbon in early-transition-metal alkylidenes^{1,8,15} that complex **3** would undergo $\alpha\text{-H}$ migration reactions with primary phosphide or amide reagents. Given the low number of terminal titanium phosphinidenes,^{5d,8} we proceeded to treat **3** with 1 equiv of LiPHTrip ($\text{Trip} = 2,4,6\text{-}i\text{Pr}_3\text{C}_6\text{H}_2$). Upon addition, the solution rapidly changed color from red to purple concomitant with generation of LiOTf . Large purple blocks of $(\text{PNP})\text{Ti}=\text{P}(\text{Trip})(\text{CH}_2^t\text{Bu})$ (**4**) were isolated in 70% yield from pentane at -35°C (Scheme 2).¹⁷ Formation of **4** likely proceeds via the hypothetical alkylidene–phosphide complex $(\text{PNP})\text{Ti}=\text{CH}^t\text{Bu}(\text{PHTrip})$, which undergoes $\alpha\text{-H}$ migration to furnish the $\text{Ti}=\text{P}$ linkage in **4**. Solu-

Scheme 2. Formation of Phosphinidene **4** and Imido **5** from **3**^a



^a Legend: (i) LiXAr is added to **3** in Et_2O at -35°C .

tions of **4** exhibit three inequivalent phosphorus resonances resolving into three doublets of doublets centered at 31 ($J_{\text{P-P}} = 40$ and 12 Hz), 37 ($J_{\text{P-P}} = 44$ and 40 Hz), and 237 ppm ($J_{\text{P-P}} = 44$ and 12 Hz). The ^{31}P NMR

(16) Crystal data for **3**: $\text{C}_{32}\text{H}_{50}\text{F}_3\text{NO}_3\text{P}_2\text{STi}$, $M_w = 695.63$, monoclinic, space group $P2_1/n$, $a = 9.823(2)$ Å, $b = 20.914(6)$ Å, $c = 18.009(5)$ Å, $\beta = 103.524(6)^\circ$, $V = 3597.4(16)$ Å³, $T = 122(2)$ K, $Z = 4$, $D_c = 1.284$ Mg m⁻³, $\mu(\text{Mo K}\alpha) = 0.432$ mm⁻¹, 8035 unique reflections ($F > 4\sigma(F)$), 2160 observed reflections ($R_{\text{int}} = 0.2052$). Final $R1(I > 2\sigma(I)) = 0.0698$ and $wR2(\text{all data}) = 0.1312$. All hydrogen atoms were located in subsequent Fourier maps. Attempts to refine all hydrogen atoms were not successful. Although all were refined to qualitatively correct positions, there were several in which the C–H distance was as large as 1.26 Å and angles were similarly distorted. For this reason all hydrogen atoms with the exception of that on C(31) were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The hydrogen on C(31) was allowed to vary isotropically to verify its correct assignment.

(17) Crystal data for **4**: $\text{C}_{54}\text{H}_{92}\text{NP}_3\text{Ti}$, $M_w = 896.10$, triclinic, space group $P1$, $a = 10.4954(10)$ Å, $b = 14.5554(14)$ Å, $c = 19.3081(18)$ Å, $\alpha = 107.202(2)^\circ$, $\beta = 103.737(2)^\circ$, $\gamma = 95.098(2)^\circ$, $V = 2696.5(4)$ Å³, $T = 125(2)$ K, $Z = 2$, $D_c = 1.104$ Mg m⁻³, $\mu(\text{Mo K}\alpha) = 0.281$ mm⁻¹, 20 639 unique reflections ($F > 4\sigma(F)$), 13 889 observed reflections ($R_{\text{int}} = 0.1657$). Final $R1(I > 2\sigma(I)) = 0.0463$ and $wR2(\text{all data}) = 0.1194$. The structure was found as proposed with $1\frac{1}{2}$ pentane solvent molecules in the asymmetric cell. Two regions of disorder indicated that solvent was present in the cell, and the solvent was modeled using partial-occupancy on carbon atoms. One of the two sites resulted in a reasonable model, while the other (located at a center of inversion at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) was not readily modeled. All non-hydrogen atoms were refined with anisotropic displacement parameters. All nonsolvent hydrogen atoms were located in subsequent Fourier maps and included as isotropic contributors in the final cycles of refinement.

Table 1. Comparison of Experimental Data and Theoretical Results (B3LYP Level of Theory)

	bond length (Å) or angle (deg)	
	exptl from X-ray data	calcd
Compound 3		
Ti1–C31	1.883(7)	1.85
Ti1–N5	2.034(5)	2.06
P2–Ti1–P8	148.43(8)	148.4
Ti1–C31–C32	157.6(6)	147.0
Compound 4		
Ti1–P31	2.2066(4)	2.19
Ti1–N9	2.1023(11)	2.14
Ti1–C47	2.0847(14)	2.08
Ti1–P31–C32	163.44(4)	164.2
P2–Ti1–P16	137.409(15)	137.7

resonance centered at 237 ppm is strong evidence of a linear phosphinidene structure.¹⁸

As with **3**, the molecular structure of **4** also exhibits a pseudo-trigonal-bipyramidal titanium center, but with the PNP phosphine donors being more acutely oriented (137.49(15)°). The Ti=P distance is exceedingly short (2.2066(4) Å) in comparison to the two dative Ti–PⁱPr₂ distances in the same system (2.60–2.61 Å; Figure 1) but is similar to the only structurally characterized titanium phosphinidene complex, (Nacnac)Ti=PMe^s·(CH₂^tBu) (Me^s = 2,4,6-tri-*tert*-butylphenyl).⁸ Complex **4** also contains an obtuse Ti=P–C_{ipso} angle of 163.44(4)°, which suggests that there might be some significant amount of multiple-bond character between P and Ti. In contrast to (Nacnac)Ti=PMe^s·(CH₂^tBu), complex **4** is kinetically and thermally stable, which is rather remarkable, considering the hard–soft mismatch among these elements. We have also determined that complex **3** reacts cleanly with LiNHAr (Ar = 2,6-(CHMe₂)₂C₆H₃) to afford the titanium nitrogen analogue of **4**, namely (PNP)Ti=NAr(CH₂^tBu) (**5**), as red blocks in 78% yield (Scheme 2).¹¹

To probe why complexes **3** and **4** are much more stable than the Nacnac analogues, DFT calculations were carried out on the actual compound for each system.¹¹ Theoretical values closely match the experimental parameters obtained from the X-ray data (Table 1). For **3**, the HOMO displays strictly Ti=C π bond character, while the LUMO is the Ti=C π^* orbital, which lies high in energy relative to the HOMO (Figure 1; ΔE = 3.441 eV). Upon significant simplification of the model for **3** (the ⁱPr groups were changed to Me, and the ^tBu

substituent was changed to Me), all bond angles and distances remained relatively close to those of the actual compound, suggesting that steric interactions do not appear to be a prerequisite for the stability of **3**. Unlike (Nacnac)Ti=CH^tBu(OTf),⁶ the LUMO of compound **3** has mostly Ti=C π^* character without too much ligand contribution.

Theoretical investigations of **4**, on the other hand, displayed results in contrast with those for **3**. Although the actual compound of **4** closely reproduces the bond angles and distances seen in the crystal structure (Table 1), the geometry of the model appears sensitive to any structural simplifications. More specifically, when the ⁱPr groups on the PNP, the phosphinidene aryl, and the neopentyl group were simplified to methyl groups, the Ti=P bond length was comparable (2.23 Å) but the Ti=P–C_{ipso} angle deviated severely (127.7°).¹¹ Careful examination of the frontier orbitals on the actual compound of **4** suggest that a pseudo Ti=P bond can be in fact conceivable, since the HOMO and HOMO-1 display orthogonal Ti=P π bond sets (Figure 1). On the basis of this argument it is proposed that sterically demanding substituents appear to enforce sp hybridization of P in **4**.

In conclusion, the robust “(PNP)Ti” scaffold has been shown to stabilize terminal ligands such as [CR₂]^{2–}, [PAr]^{2–}, and [NAr]^{2–}. Unlike titanium β -diketimate complexes having alkylidene and phosphinidene ligands, this pincer-based class of compounds does not appear to generate unstable kinetic products and thus offers an attractive opportunity to study the chemical reactivity of the metal–ligand multiple bond.

Acknowledgment. For financial support of this research D.J.M. thanks Indiana University–Bloomington, the Camille and Henry Dreyfus Foundation, and the National Science Foundation (CAREER Award, Grant No. CHE-0348941). B.C.B. acknowledges the Department of Education for a GAANN Fellowship and Prof. M.-H. Baik for insightful comments and discussions. Acknowledgment is made by O.V.O. and W.W. to Brandeis University, to Research Corp., and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank the reviewers for insightful comments.

Supporting Information Available: Text, tables, and figures giving complete experimental details (**1–5**), CIF files giving crystallographic data (**2–5**), and text, tables, and figures giving theoretical data (**3** and **4**). This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM0490583

(18) Group 4–6 transition-metal complexes having a bent geometry at the terminal phosphinidene ligand exhibit ³¹P NMR spectral resonances >330 ppm.^{2,5} In contrast, linear phosphinidene ligands of the early transition metals (e.g. Ti, Ta, and W) have been reported to have ³¹P NMR resonances between 270 and 170 ppm.^{2,8} However, we are not entirely confident about making discriminations between linear and bent phosphinidene geometries from just the ³¹P NMR spectroscopic data.