

Articles

Slip–Inversion–Slip Mechanism of Phosphametallocene Isomerization. Spectroscopic Characterization of an (η^1 -Phosphohyl)titanium Complex. Synthesis and Structures of Chiral Mono(phosphohyl)titanium Complexes

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The first reported synthesis and spectroscopic characterization of a group 4 η^1 -phosphohyl complex, (η^1 -dibenzophosphohyl)tris(dimethylamido)titanium, are documented, which has an η^1 -phosphohyl ligand analogous to those proposed in the slip–inversion–slip mechanism of phosphametallocene isomerization.

Introduction

Heterocyclic π -complexes have been demonstrated to be excellent ligands for asymmetric catalysis.¹ Late-transition-metal phosphametallocenes, including phosphaferrrocene² and phospharuthenocene-based³ diphosphines and mixed P, N phosphaferrrocene ligands have numerous applications.^{4,5} Boratabenzenes bound to transition metals as heterocyclic π -ligands have been found to be excellent polymerization catalysts.^{6,7} More recently, examples with multiple heteroatoms have been reported.⁸

We began developing chiral, bent early-transition-metal phosphametallocenes as ligands for asymmetric catalysis and in the process discovered their facile isomerization.^{9–11} A

detailed understanding of the mechanism of heterocyclic π -ligand isomerization is important for the application of complexes containing these ligands. Recently, we reported the activation parameters for the isomerization of a phosphatitanocene and proposed an intramolecular mechanism for the isomerization.^{12,13} The mechanism involves ring slippage to the $\eta^1(\sigma)$ -bound phosphohyl **1** followed by inversion at P (**2**, Scheme 1). It is termed the slip–inversion–slip mechanism.^{14,15} Such an η^1 structure is consistent with much literature precedent for phosphohyl and pyrrolyl complexes.¹⁶ The η^1 structure has been established by X-ray crystal structure determinations for Ti and Zr pyrrolyl complexes.^{16b} Recent reports have also demonstrated a facile isomerization of certain phosphinoferrrocenes.¹⁷ Herein we report the first spectroscopic evidence for an η^1 -bound phosphohyl ligand of group 4.

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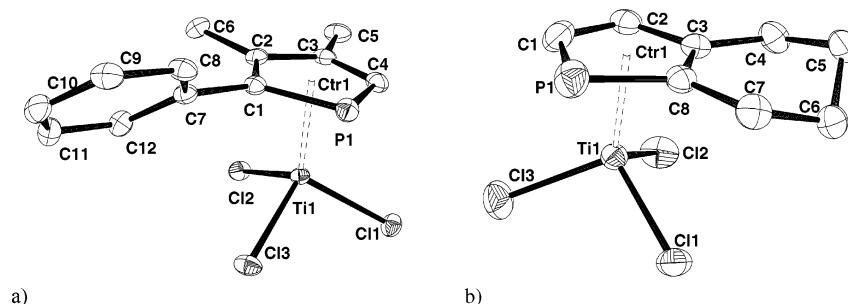
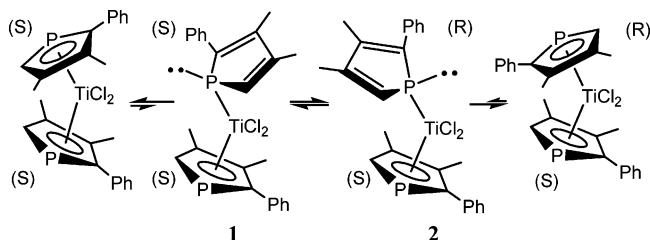


Figure 1. ORTEP representations (50% thermal ellipsoids) of the X-ray crystal structures of (a) **3** and (b) **4**.

Scheme 1. Slip–Inversion–Slip Mechanism of Phosphametalloocene Isomerization



Results and Discussion

Previous work by Basolo to identify ring slippage in phospholyl complexes led to the conclusion that no ring slippage occurred for the complexes evaluated.¹⁸ The electron-deficient ring-slipped intermediate **1** appears ready to accept additional ligands to produce a more stable molecule. Undoubtedly, such coordination is responsible for the isomerization rate enhancements seen in THF or when PMe_3 is added.^{9,10} Despite this rate enhancement, all efforts to isolate complexes such as **1** by adding pyridine, bipy, or phen as trapping agents led, at best, to broadened signals in the ^{31}P NMR spectra and to recovery of the η^5 -phosphametalloocene. These results indicate a strong preference for the π -complex as the thermodynamically most favored state. Additionally, the η^1 : η^5 -bis(phospholyl) intermediates are relatively sterically congested, which would disfavor strong coordination of the additional ligand. Therefore, we decided to evaluate monophospholyl complexes for coordination of exogenous ligand to induce ring slippage.¹⁹ The two chiral monophospholyl Ti complexes **3** (^{31}P NMR, δ 185, 82% from Sn) and **4** (^{31}P NMR, δ 198, 28% from Sn) were prepared as illustrated in Scheme 2. Established synthetic methods were employed.¹¹ The molecular structures of **3** and **4** are depicted in Figure 1. The crystal data and structural refinement details may be found in Table 1, and selected bond distances and angles are reported in Table 2. The data for (DMP) $\text{Ti}^{\text{IV}}\text{Cl}_3$ (DMP = η^5 -3,4-dimethylphospholyl) are included in Table 2 for comparison.^{11a} The metric data on these compounds are similar to those of previously reported achiral monophospholyl complexes of Ti.

Addition of phosphine ligands to early-transition-metal piano-stool complexes to generate higher coordinate complexes is well established.²⁰ Addition of 1,2-bis(dimethylphosphino)ethane

Scheme 2. Synthesis of Chiral Monophospholyl Titanium Trichloride Complexes

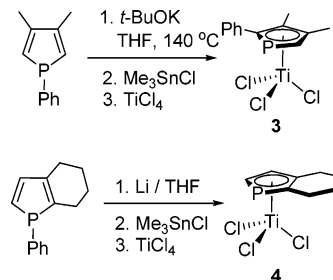


Table 1. Crystal Data and Structure Refinement Details

	3	4
formula	$\text{C}_{12}\text{H}_{12}\text{Cl}_3\text{PTi}$	$\text{C}_8\text{H}_{10}\text{Cl}_3\text{PTi}$
formula wt	341.44	291.38
cryst dims, mm	$0.31 \times 0.22 \times 0.09$	$0.47 \times 0.41 \times 0.31$
temp, K	100(2)	218(2)
wavelength (Å)	0.71073	0.71073
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
<i>a</i> , Å	16.7957(13)	6.7877(9)
<i>b</i> , Å	7.1120(5)	6.9647(9)
<i>c</i> , Å	12.4481(9)	12.9311(17)
α , deg	90	102.390(2)
β , deg	109.797(2)	92.824(2)
γ , deg	90	109.062(2)
<i>V</i> , Å ³	1399.06(18)	559.60(13)
<i>Z</i>	4	2
<i>D_c</i> , Mg/m ³	1.621	1.729
abs coeff, mm ^{−1}	1.272	1.573
<i>F</i> (000)	688	292
θ range, deg	1.29–30.51	1.63–28.28
index ranges	$-21 \leq h \leq 23$ $-8 \leq k \leq 10$ $-17 \leq l \leq 15$	$-9 \leq h \leq 9$ $-9 \leq k \leq 9$ $-17 \leq l \leq 17$
no. of rflns	19445	9563
no. of indep rflns	4230 (<i>R</i> (int) = 0.0276)	2754 (<i>R</i> (int) = 0.0225)
no. of data/restraints/params	4230/0/156	2754/0/128
goodness of fit on <i>F</i> ²	1.032	1.019
final <i>R</i> indices (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> 1 = 0.0270 <i>wR</i> 2 = 0.0729	<i>R</i> 1 = 0.0281 <i>wR</i> 2 = 0.0768
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0307 <i>wR</i> 2 = 0.0750	<i>R</i> 1 = 0.0296 <i>wR</i> 2 = 0.0783
largest diff peak and hole, e Å ^{−3}	0.988 and −0.406	0.559 and −0.348

(dmpe) to solutions of **3**, **4**, and the known (η^5 -3,4-dimethylphospholyl) TiCl_3 ^{11a} resulted in quantitative generation of new signals in the ^{31}P NMR spectrum. The structures of the new complexes were assigned on the basis of the chemical shift

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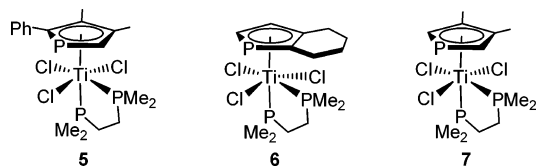
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Table 2. Selected Bond Distances (Å) and Angles (deg) for **3**, **4**, and (DMP)TiCl₃ (DMP = η^5 -3,4-Dimethylphospholyl)

	3	4	(DMP)TiCl ₃ ^a
Ti–Ctr	2.068	2.065	2.058
Ti–P	2.5836(4)	2.5796(6)	2.549
Ti–C(1)	2.4571(13)	2.3594(17)	2.386
Ti–C(2)	2.4593(13)	2.4053(16)	2.442
Ti–C(3)	2.3987(13)	2.4457(16)	2.432
Ti–C(4),C(8)	2.3741(13)	2.4696(16)	2.379
Ti–Cl(1)	2.2230(4)	2.2269(5)	2.233
Ti–Cl(2)	2.497(4)	2.412(6)	2.232
Ti–Cl(3)	2.2244(4)	2.2312(5)	2.216
Ctr–Ti–Cl(1)	117.78	114.47	118.18
Ctr–Ti–Cl(2)	112.74	113.29	112.16
Ctr–Ti–Cl(3)	117.97	118.56	116.92
Cl(1)–Ti–Cl(2)	100.312(15)	102.82(2)	101.43
Cl(1)–Ti–Cl(3)	102.756(16)	102.29(2)	103.83
Cl(2)–Ti–Cl(3)	102.821(16)	102.34(2)	102.07

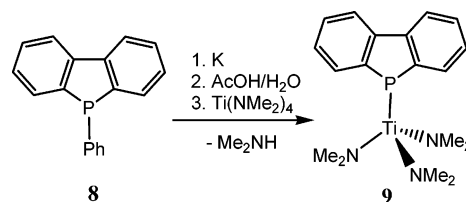
^a See ref 11a.

position and P–P coupling to the coordinated dmpe and are shown by **5** (³¹P NMR, δ 83.9), **6** (³¹P NMR, δ 82.7), and **7** (³¹P NMR, δ 64.7). The ³¹P NMR chemical shifts were in the



region typical of η^5 -phospholyl complexes of Ti.^{11a,12} The unique chemical shifts for the coordinated dmpe ligand are consistent with the pseudoequatorial and pseudoaxial shifts reported for the crystallographically characterized example CpTiCl₃(dmpe).²⁰ Complexes **5**–**7** proved to be unstable over long periods in solution and, hence, were not characterized further. This instability may be due to increased access to the ring-slipped complex, generating a more reactive metal center that leads to decomposition. With no conclusive data to support the formation of η^1 coordination in the monophospholyl complexes, an additional element to favor η^1 coordination was needed.

This feature was found in a dibenzophospholyl (DBP) ligand derived from phenyldibenzophosphole (**8**; Scheme 3).^{21,22} DBP has two fused benzene rings that will rearomatize upon ring slippage to an η^1 -phospholyl ligand, providing a double-indenyl effect,²³ which counterbalances the driving force for $\eta^5(\pi)$ -complexation. The dibenzophospholyl anion was prepared according to literature procedures and reacted with Me₃SnCl followed by TiCl₄. Despite repeated attempts, no stable isolable products were obtained. With an η^1 -dibenzophospholyl ligand, (DBP)TiCl₃ would be, formally, an eight-electron complex. Such a complex would be extremely reactive, which would make isolation difficult. Having successfully synthesized η^5 -monophospholyl titanium trichlorides (Scheme 2), the decomposition of the DBP complexes was attributed to their inherent instability. Therefore, auxiliary ligands that were better π -donors were sought. If each Cl is replaced with a 4-electron-donating amido ligand the formal electron count for the complex would be 14, which is still unsaturated but was anticipated to be less reactive

Scheme 3. Preparation of the Dibenzophospholyl (DBP) Derivative **9**

and thus isolable. Reductive cleavage of the Ph–P bond of **8** with K and protonation with AcOH yielded 9H-dibenzophosphole (Scheme 3).²⁴ Subsequent reaction with Ti(NMe₂)₄, as illustrated in Scheme 3, produced complex **9**, which was first indicated by the new ³¹P NMR signal at δ 16.8 and the ¹H NMR integral ratios. The ¹³C NMR data for **9** reveal significantly smaller and fewer *J*(PC) couplings than were reported for 1-phenyldibenzophosphole.²⁵ This observation is attributed to an increased rate of inversion at P in **9**. When the synthesis was carried out in an NMR tube, 1 equiv of free Me₂NH was observed by ¹H NMR spectroscopy. Mass spectral analysis (LDIMS) of the product revealed a peak at *m/z* 773 and an isotopic distribution that was consistent with the dimeric molecular formula [C₃₈H₅₂N₆P₂Ti₂ + Me₂NH + 2H]⁺ in the spectrometer. We propose a dimeric Ti structure with bridging amido groups and a coordinated amine plus two protons. The coordination of amines to such complexes has been documented by X-ray structural determination.^{16b} The available solution data do not distinguish between a monomeric or dimeric structure. It is known that Zr(NMe₂)₄ exists as a dimer in the solid state.²⁶ Compound **9** is exceedingly air sensitive, and with proper precautions satisfactory elemental analyses were obtained for C and H.

The dibenzophospholyl complex **9** has a chemical shift significantly different from those of other phospholyl Ti(IV) complexes (δ 16.8 vs δ 65–190; vide supra). This unique property was the first indication that an η^1 complex had in fact been achieved. Such an upfield shift is consistent with a pyramidal P.²⁷ This observation is attributed to an increased rate of inversion at P in **9**. Numerous attempts have been made to obtain X-ray-quality crystals, but only thin plates that did not diffract well were obtained. Attempts to obtain a satisfactory elemental analysis were unsuccessful, due to the extreme air sensitivity of the sample, which resulted in decomposition (see Experimental Section). There are several precedents that support the assignment of compound **9** as the $\eta^1(\sigma)$ -bound complex. First, previous structural characterization of DBP anion complexes revealed η^1 coordination.²² Second, we have performed a computational study using Gaussian 03 to evaluate the potential bonding modes of the DBP complex **9** and (C₄H₄P)–Ti(NMe₂)₃ (**10**) that support the structural assignment.²⁸ The structural minimizations for **9** and **10** were approached from

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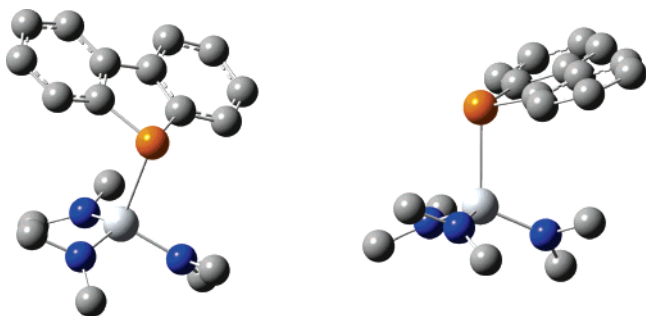


Figure 2. Two views of the molecular structure of **9** calculated with Gaussian 03 at the B3LYP/6-311+G(d,p) level. Carbon atoms are shown in grey, phosphorus atoms in orange, and nitrogen atoms in blue. Ti–P = 2.56 Å, Ti–N = 1.90 Å, and P–C = 1.83 Å.

both η^5 and η^1 structures. The simple mono(phospholyl) complex (C₄H₄P)Ti(NMe₂)₃ (**10**) minimized to an η^5 structure, regardless of the starting geometry. In contrast, the DBP complex **9** minimized to an η^1 complex in both cases. Final optimizations were performed at the B3LYP/6-311+G(d,p) level. The optimized structure for **9** is depicted in Figure 2. The pyramidalization of P can be noted in the sum of the angles, 296°. Additional geometric data are included in Figure 2.

Finally, we calculated the chemical shift for the η^1 complex **9** and (η^5 -C₄H₄P)Ti(NMe₂)₃ (**10**) using the GIAO method at the HF/6-311+G(d,p) level and using the minimized structures as the input geometry and compared the results to those for PH₃.²⁹ The ³¹P NMR chemical shift for **9** in C₆H₆ is δ 16.8, and that for PH₃ is δ 238,³⁰ which gives $\Delta\delta$ = 255 ppm. The calculated magnetic shielding was σ = 350 for **9** and σ = 587 for PH₃, which gives $\Delta\delta$ = 237 ppm. The predicted chemical shift for **9** is –1 ppm, which is very close to the observed value. Considering solvent effects and the standard error in the computations, the observed $\Delta\delta$ values are in close agreement (237 vs 255, a difference of 18 ppm). Additional confidence in the structural and spectroscopic assignment was gained when a comparison was made to the calculated absolute magnetic shielding of σ = 240 for the η^5 -phospholyl tris(amido) Ti complex **10**, which is 110 ppm further downfield. The predicted ³¹P chemical shift for **10** is 109 ppm, which is typical of η^5 -Ti(IV) complexes (vide supra).

In conclusion, despite much effort, the η^1 intermediates in phosphametalocene isomerization have resisted trapping for bis-(phospholyl)MCl₂ and (phospholyl)MCl₃ complexes. Strong spectroscopic and computational evidence have been amassed in support of an (η^1 -DBP)Ti(NMe₂)₃ structure, which is the first reported confirmation of an η^1 -phospholyl ligand bonded to group 4 metals, an important step in establishing viability for the *slip*–*inversion*–*slip* mechanism. A detailed understanding of phosphametalocene isomerization is critical for applications of phosphametalocenes as catalysts and as ligands in asymmetric catalysis. It also provides insight into the behavior of other heterocyclic π -ligands. The first chiral monophospholyl complexes of group 4 have been prepared and spectroscopically characterized. Work to structurally characterize an η^1 complex and to further establish the *slip*–*inversion*–*slip* mechanism is ongoing.

Experimental Section

All reactions were carried out under an inert atmosphere of Ar using standard Schlenk and glovebox techniques.³¹ [(η^5 -3,4-dimethylphospholyl)TiCl₃] was prepared according to the literature procedure.^{11a}

(η^5 -3,4-Dimethyl-2-phenylphospholyl)titanium Trichloride (3). 1-(Trimethylstannyl)-3,4-dimethyl-2-phenylphosphole¹² (0.36 g, 1.0 mmol) in pentane (5 mL) was rapidly added to a solution of TiCl₄·2THF (0.33 g, 1.0 mmol) in toluene (5 mL) at 0 °C. The solution was warmed to room temperature and stirred overnight. All volatiles were evaporated under high vacuum, and the resulting red residue was extracted with toluene (30 mL) followed by removal of the solvent to obtain a red crystalline solid (0.28 g, 82%). X-ray-quality crystals were grown from a saturated toluene solution at –35 °C. ¹H NMR (C₆D₆, 300.052 MHz): δ 7.38–6.94 (m, 6H, *Ph* and *PCH*), 2.11 (s, 3H, *CH*₃), 1.88 (s, 3H, *CH*₃). ³¹P{¹H} NMR (C₆D₆, 121.469 MHz): δ 185.0 (s).

(η^5 -Cyclohexa[b]phospholyl)titanium Trichloride (4). 1-Phenylcyclohexa[b]phosphole³² (1.50 g, 7.0 mmol) and Li (220 mg, 32 mmol) were stirred in THF (10 mL) for 4 h at room temperature. The resulting dark violet solution was filtered, and then t-BuCl (1.8 mL, 17 mmol) was added and this mixture heated for 45 min at 55 °C. The light brown solution was cooled, and trimethyltin chloride (1.37 g, 6.9 mmol) was added. The reaction mixture was stirred for 15 min, and the solvent was removed under vacuum. The residue was extracted with pentane (80 mL) and concentrated, yielding 1-(trimethylstannyl)cyclohexa[b]phosphole as a yellow oil (1.84 g, 84%). ¹H NMR (C₆D₆, 300.052 MHz): δ 6.93 (dd, ³J_{PH} = 10.8, *J* = 6.9 Hz, 1H, *H*-C₂), 6.77 (dd, ²J_{PH} = 41.1, *J* = 6.9 Hz, 1H, *H*-C₃), 2.53 (bd, *J* = 13.2 Hz, 4H), 1.59 (m, 4H), 0.04 (d, ³J_{PH} = 2.1 Hz, 9H, Sn(CH₃)₃). ³¹P{¹H} NMR (C₆D₆, 121.469 MHz): δ –51.96 (s).

A solution of stannylphosphole (0.30 g, 1.0 mmol) in pentane (10 mL) was rapidly added to a solution of TiCl₄·2THF (0.33 g, 1.0 mmol) in toluene (10 mL) at 0 °C. The resulting red solution was stirred for 10 h at room temperature, and the solvent was removed under vacuum. The residue was filtered through Celite with toluene (50 mL) and concentrated, yielding a red powder (0.073 g, 28%). X-ray-quality crystals were grown from a saturated toluene solution at –35 °C. ¹H NMR (CDCl₃, 300.052 MHz): δ 7.93 (dd, ²J_{PH} = 36.0 Hz, ³J_{HH} = 5.6 Hz, 1H, *H*-C₂), 7.52 (m, 1H, *H*-C₃), 3.59–2.83 (m, 4H, *H*-C₄, *H*-C₇), 1.93–1.83 (m, 4H, *H*-C₅, *H*-C₆). ³¹P{¹H} NMR (CDCl₃, 121.469 MHz): δ 197.8 (s). ¹³C-{¹H} NMR (CDCl₃, 75.456 MHz): δ 163.8 (d, ¹J_{PC} = 60.1 Hz), 150.9 (d, ²J_{PC} = 7.8 Hz), 142.9 (d, ¹J_{PC} = 60.7 Hz), 136.2 (d, ²J_{PC} = 6.5 Hz), 29.4 (d, ²J_{PC} = 17.5 Hz), 28.0, 25.6 (d, ³J_{PC} = 5.7 Hz), 21.7.

(3,4-Dimethyl-2-phenylphospholyl)titanium Trichloride Bis(dimethylphosphino)ethane (5). (3,4-Dimethyl-2-phenylphospholyl)titanium trichloride (**3**; 7 mg, 0.02 mmol) and bis(dimethylphosphino)ethane (8.0 μ L, 0.04 mmol) were mixed in THF (1 mL). ³¹P{¹H} NMR (C₆D₆, 121.469 MHz): δ 83.9 (d, ²J_{PP} = 9.9 Hz, *P*_{phospholyl}), 35.1 (dd, ²J_{PP} = 47.1 Hz, ²J_{PP} = 9.9 Hz, *P*_{pseudo-equatorial}), 26.5 (d, ²J_{PP} = 47.1 Hz, *P*_{pseudo-axial}).

(η^5 -Cyclohexa[b]phospholyl)titanium Trichloride Bis(dimethylphosphino)ethane (6). (η^5 -Cyclohexa[b]phospholyl)titanium trichloride (**4**; 5 mg, 0.019 mmol) and bis(dimethylphosphino)ethane (3.0 μ L, 0.019 mmol) were mixed in THF (1 mL). ³¹P{¹H} NMR (121.469 MHz): δ 82.7 (dd, ²J_{PP} = 9.2 Hz, ²J_{PP} = 4.2 Hz, *P*_{phospholyl}), 33.3 (dd, ²J_{PP} = 49.8 Hz, ²J_{PP} = 9.4 Hz, *P*_{pseudo-equatorial}), 25.9 (dd, ²J_{PP} = 49.6 Hz, ²J_{PP} = 4.2 Hz, *P*_{pseudo-axial}).

(3,4-Dimethylphospholyl)titanium Trichloride Bis(dimethylphosphino)ethane (7). Bis(dimethylphosphino)ethane (48 mg,

(29) van Wullen, C. *Phys. Chem. Chem. Phys.* **2000**, *2*, 2137. HF results were closer to experimental results than did B3LYP in our case.

(30) (a) In the gas phase PH₃ has a chemical shift of –266.1 ppm extrapolated to zero pressure. Jameson, C. J.; De Dios, A.; Jameson, A. K. *Chem. Phys. Lett.* **1990**, *167*, 575–582. (b) Solution: Van Wazer, J. R.; Callis, C. F.; Shoolery, J. N.; Jones, R. C. *J. Am. Chem. Soc.* **1956**, *78*, 5715–5726.

(31) Shriver, D. F.; Drezdson, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

(32) Quin, L. D.; Mesch, K. A.; Orton, W. L. *Phosphorus Sulfur Relat. Elem.* **1982**, *12*, 161–177.

0.32 mmol) was added to a solution of (3,4-dimethylphospholyl)-titanium trichloride (**17**; 70 mg, 0.30 mmol) in THF (5 mL) at room temperature. After the mixture was stirred for 10 min, all volatiles were removed under vacuum. ^1H NMR (C_6D_6 , 300.052 MHz): δ 6.60 (d, $^2J_{\text{PP}} = 37.7$ Hz, 2H, $\text{PCHC}(\text{CH}_3)$), 2.38 (s, 6H, $\text{PCHC}(\text{CH}_3)$), 1.52 (d, $^2J_{\text{PP}} = 10.9$ Hz, 6H, $\text{P}(\text{CH}_3)_2$), 1.29 (d, $^2J_{\text{PP}} = 9.4$ Hz, 6H, $\text{P}(\text{CH}_3)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 121.469 MHz): δ 64.7 (dd, $^2J_{\text{PP}} = 9.4$ Hz, $\text{P}_{\text{phospholyl}}$), 34.6 (dd, $^2J_{\text{PP}} = 52.3$ Hz, $^2J_{\text{PP}} = 10.2$ Hz, $\text{P}_{\text{pseudo-equatorial}}$), 27.4 (dd, $^2J_{\text{PP}} = 52.3$ Hz, $^2J_{\text{PP}} = 8.6$ Hz, $\text{P}_{\text{pseudo-axial}}$).

(η^1 -Dibenzophospholyl)tris(dimethylamido)titanium (**9**). 9H-dibenzophosphole²⁴ (0.27 g, 1.5 mmol) in benzene (5 mL) was added dropwise to a solution of $\text{Ti}(\text{NMe}_2)_4$ (340 μL , 1.5 mmol) in benzene (5 mL). After the mixture was stirred for 2 h at room temperature, volatiles were removed under vacuum at 70 $^\circ\text{C}$ for 1 h. After evaporation of the solvent a brown solid was obtained (0.22 g, 41%). The resulting dark brown solid was extracted with toluene and crystallized in benzene. ^1H NMR (C_6H_6): δ 8.12 (d, $J = 7.41$ Hz, 2H), 7.92 (t, $J = 12$ Hz, 2H), 7.32 (m, 4H), 2.80 (s, 18H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz): δ 148.2 (d, $J = 23.6$ Hz), 141.1, 125.5 (d, $J = 9$ Hz), 123.7, 121.6, 121.4, 43.5. $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 121.469 MHz): δ 16.8 (s). MS (LDIMS): m/z 771, 772, 773 (100%), 774, 775 (with the expected isotope distribution for the

dimer $[\text{C}_{36}\text{H}_{52}\text{N}_6\text{P}_2\text{Ti}_2 + \text{NMe}_2\text{H} + 2\text{H}]^+$). Anal. Calcd for $\text{C}_{18}\text{H}_{26}\text{N}_3\text{PTi}$: C, 59.51; H, 7.21. Found: C, 59.28; H, 7.04.

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Supporting Information Available: Text giving further experimental details of the compounds prepared in this paper, figures giving spectroscopic data for compounds **3**–**7** and **9** (^1H , ^{13}C , and ^{31}P NMR and MS spectra), tables giving computational details for **9** and **10**, including Cartesian coordinates for the minimized structures, and CIF files giving crystallographic data for **3** and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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