



Organophosphorus compounds. Part 163: Reactivity of phosphalkynes towards in situ-generated titanium imido complexes[†]

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Abstract—Treatment of kinetically stabilized phosphalkynes **5** in toluene with primary amines **4** in the presence of equimolar amounts of cyclopentadienyltitaniumtrichloride (**2**) leads to azaphosphatitanacyclobutane species **6**. The formation of compounds **6** enables a first insight into the mechanism of the reaction of titanium imides with phosphalkynes, presented in several recent papers. © 2001 Elsevier Science Ltd. All rights reserved.

Synthesis and synthetic use of imido complexes of group 4 and 5 elements experienced a tremendous development over the last few years, reflected in a number of articles and reviews.^{2–9} For example, Bergmann et al. presented the formation of azametallacyclobutenes via [2+2] cycloadditions of acetylenes using as well isolable, non base-stabilized titanocene imides⁸ as zirconocene imides,⁹ which were generated in situ from the corresponding zirconocene amides.

Titanium imides were discovered to be valuable tools for cyclization of aminoalkyl functionalized alkynes. Livinghouse et al.^{3–5} realized intramolecular cyclization reactions using various types of in situ generated titanium imides, e.g. starting from cyclopentadienyltitaniumtrichloride (CpTiCl₃, **2**).

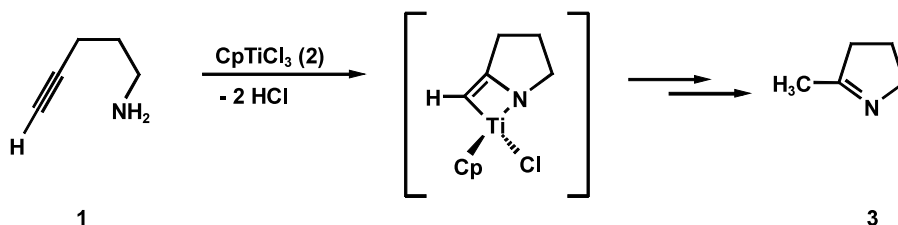
In a first step, the titanium chloride reacted with the primary amine to the corresponding imido complex via elimination of hydrochloride. The titanium imide could not be isolated, however, it is supposed to undergo a [2+2] cycloaddition with the acetylene moiety to form a

bicyclic compound (Scheme 1). After cleavage of the metal, the heterocyclic product **3** was isolated.

Reactions with imidocomplexes of 4th group elements are also in the focus of current interest in phosphalkyne chemistry. Recently Nixon et al. described a titaniumtetrachloride catalyzed hydroamination of phosphalkynes,¹⁰ leading to dialkyldiaminophosphines, presumably via imido titanium intermediates (Scheme 2).

In the present paper we report on the application of a related titanium imido complex with phosphalkynes, which provides an insight into the mechanism of this type of reaction.

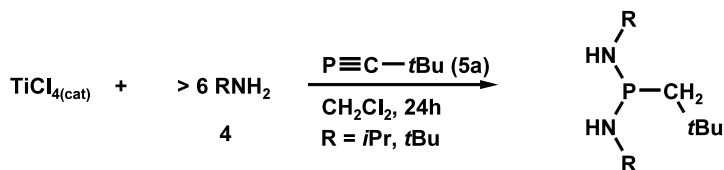
After addition of 2 equiv. of a primary amine RNH₂ **4** to a suspension of CpTiCl₃ (**2**) and phosphalkyne in toluene at room temperature, the color of the mixture turns dark red within a few hours. Complete conversion is achieved by adding a further 2 equiv. of **4**, according to ³¹P NMR monitoring. The yield of pure **6** after



Scheme 1.

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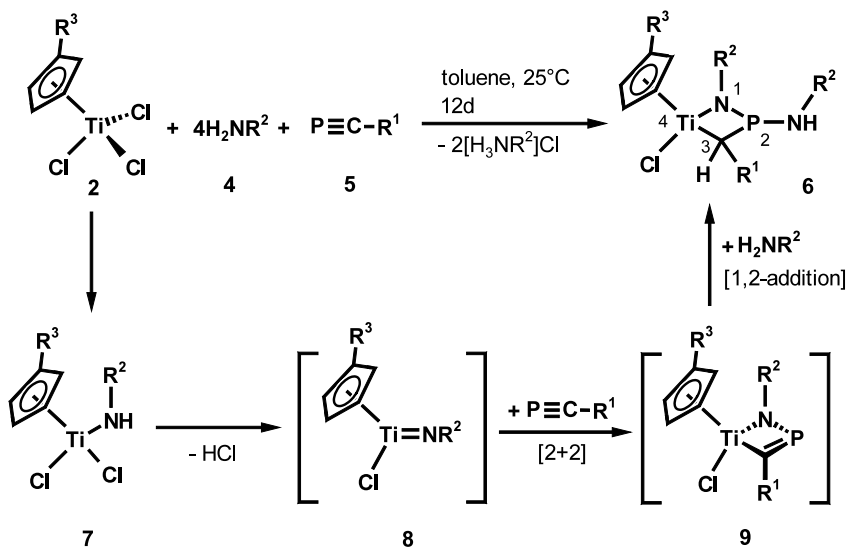
[†] For part 162, see: Ref. 1.








Scheme 2.

filtration and crystallization depends on the sterical demand of the substituent of the amine, rising to a maximum 91% in case of *tert*-octylamin **6b** (Scheme 3).[†] Despite a number of alkyl substituted amines were applied successfully in the reaction sequence, especially anilin derivatives failed.

MS and HR-MS data as well as the specific isotope pattern of the molecular peak confirm the elemental composition and constitution of **6a**.[‡] The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6a** shows a singlet at $\delta -110$, definitely excluding a direct connection of titanium and phosphorus, which would result in a signal shifted to the very low field region.¹¹



	a	b	c	d	e	f	g	h	i	j	k
R ¹	<i>t</i> Bu	<i>t</i> Bu	<i>t</i> Bu	<i>t</i> Bu	<i>t</i> Bu	<i>t</i> Bu	<i>t</i> Bu	<i>t</i> Pen	1-Ad		<i>t</i> Bu
R ²	<i>t</i> Bu	<i>t</i> Oct				1-Ad		<i>t</i> Bu	<i>t</i> Bu	<i>t</i> Bu	<i>t</i> Bu
R ³	H	H	H	H	H	H	H	H	H	H	<i>t</i> Bu
%	81	91	40	45	53	20	51	76	75	45	45
$^{31}\text{P}\{^1\text{H}\}$	-110	-110	-100	-102	-94	-112	-102	-111	-114	-112	-110

Scheme 3.

[†] Analytical data of **6b**: Mp: 118°C. $^1\text{H}(\text{C}_6\text{D}_6)$: 0.98 (s, 18H, $\text{CH}_2(t\text{Bu})_2$); 1.02 (s, 9H, $\text{CH}(t\text{Bu})$); 1.43 (s, 12H, $4\times\text{CH}_3$); 1.54 (s, 4H, $2\times\text{CH}_2$); 3.99 (d, broad, $^2J_{\text{H,P}}=5.86$ Hz, NH); 4.11 (d, $^2J_{\text{H,P}}=4.89$ Hz, CH); 6.33 (s, 5H, C_5H_5). $^{13}\text{C}\{^1\text{H}\}(\text{C}_6\text{D}_6)$: 31.8 (s, $\text{CH}_2\text{C}(\text{CH}_3)_3$); 31.9 (s, $\text{CH}_2\text{C}(\text{CH}_3)_3$); 32.1 (d, $^3J_{\text{C,P}}=9.40$ Hz, CH_3); 33.3 (d, $^3J_{\text{C,P}}=12.20$ Hz, CH_3); 33.9 (d, $^3J_{\text{C,P}}=10.68$ Hz, CH_3); 41.7 (d, $J_{\text{C,P}}=25.94$ Hz, $\text{C}(\text{CH}_3)_3$); 53.9 (s, broad, $\text{CH}_2\text{C}(\text{CH}_3)_3$); 55.4 (s, $\text{CH}_2\text{C}(\text{CH}_3)_3$); 56.0 (d, $^3J_{\text{C,P}}=12.97$ Hz, $\text{NC}(\text{CH}_3)_2$); 58.7 (d, $^3J_{\text{C,P}}=6.10$ Hz, CH_2); 58.9 (d, $^3J_{\text{C,P}}=3.05$ Hz, CH_2); 69.5 (d, $^3J_{\text{C,P}}=14.50$ Hz, $\text{NC}(\text{CH}_3)_2$); 112.6 (s, C_5H_5); 140.9 (d, $^1J_{\text{C,P}}=54.18$ Hz, TiCHP). $^{31}\text{P}\{^1\text{H}\}(\text{C}_6\text{D}_6)$: -110.3 (s). EI-MS (70 eV): 504 (10, M^+); 391 (5, M^+-tOct); 376 (3, $\text{M}^+-\text{HN}t\text{Oct}$); 321 (15); 303 (39); 287 (34); 209 (42); 158 (89); 84 (58); 58 (100); 57 (96). HRMS calcd: 504.2880; found: 504.2877.

[‡] Analytical data of **6a**: Mp: 135°C. NMR: $^1\text{H}(\text{C}_6\text{D}_6)$: 1.04 (d, $^4J_{\text{H,P}}=0.73$ Hz, 9H, $\text{C}(\text{CH}_3)_3$); 1.34 (d, $^4J_{\text{H,P}}=1.22$ Hz, 9H, $\text{C}(\text{CH}_3)_3$); 1.44 (s, 9H, $\text{C}(\text{CH}_3)_3$); 3.94 (d, broad, $^2J_{\text{H,P}}=5.48$ Hz, 1H, NH); 4.26 (d, $^2J_{\text{H,P}}=5.12$ Hz, 1H, CH); 6.40 (s, 5H, C_5H_5). $^{13}\text{C}\{^1\text{H}\}(\text{C}_6\text{D}_6)$: 32.3 (d, $^3J_{\text{C,P}}=8.0$ Hz, $\text{C}(\text{CH}_3)_3$); 33.1 (d, $^3J_{\text{C,P}}=12.9$ Hz, $\text{C}(\text{CH}_3)_3$); 33.8 (d, $^3J_{\text{C,P}}=8.8$ Hz, $\text{C}(\text{CH}_3)_3$); 41.3 (d, $^2J_{\text{C,P}}=24.9$ Hz, $\text{C}(\text{CH}_3)_3$); 51.5 (s, $\text{NC}(\text{CH}_3)_3$); 65.1 (d, $^2J_{\text{C,P}}=15.3$ Hz, $\text{NC}(\text{CH}_3)_3$); 112.5 (s, C_5H_5); 140.9 (d, $^1J_{\text{C,P}}=54.6$ Hz, TiCHP). $^{31}\text{P}\{^1\text{H}\}(\text{C}_6\text{D}_6)$: -110.2 (s). EI-MS (70 eV): 392 (47, M^+); 335 (8, M^+-tBu); 321 (11, $\text{M}^+-\text{N}t\text{Bu}$); 279 (5); 265 (100, $[\text{M}-\text{HC}t\text{Bu}-t\text{Bu}]^+$); 209; 173; 148; 113; 57. HRMS calcd 392.1628; found: 392.1629.

A strong contribution for resolving the structures of compounds **6** is obtained from the ^{13}C and $^{13}\text{C}\{^1\text{H}\}$ NMR analysis. In case of **6a**, signals for three *tert*-butyl groups are detected, two of them shifted to a low-field region in case of the quarternary carbon atoms (δ 65.1, 51.5), indicating amino substitution. The presence of the cyclopentadiene ring is proved by the singlet at δ 112.5. A doublet ($^1J_{\text{C,P}}=54.6$ Hz) in an unexpected low field region at δ 140.9 reveals unambiguously that an sp^3 carbon atom must be located between titanium and phosphorus (C3).

The ^1H NMR spectrum confirms three different *tert*-butyl protons. Additionally, two doublets are detected at δ 3.94 and 4.26, with coupling constants of $^2J_{\text{H,P}}=5.48$ and 5.12 Hz, respectively. Due to the nitrogen quadrupolar moment the NH-signal at δ 3.94 is broadened, while the signal at lower field of the CH must be explained by the deshielding effect of the titanium.

The mechanism of the formation of azaphosphatitanacyclobutanes has to explain the observed regio- and stereoselectivity of the sequence. In a first step, amido complex **7** eliminates hydrochloride leading to the imido species **8**. Though this process is possibly reversible, no equilibrium is established, since the imido species is quenched by the phosphalkyne, producing azaphosphatitanacyclobutene **9**. The final 1,2-addition of the corresponding primary amine to the activated, highly reactive P/C-double bond proceeds fast and leads to the kinetically and thermodynamically favoured regioisomer **6a**, where all *tert*-butyl groups occupy positions of minimum hindrance.

Concerning the stereoselectivity of **6a** at the C4 atom, we assume a cisoid position of the cyclopentadiene ligand and the *tert*-butyl groups connected to the four-membered ring. This is supported by crystallographic methods¹² and MM2-calculations.¹³

Several kinetically stabilized phosphalkynes **5** lead to the corresponding phosphaheterocycles. Surprisingly, the increase of sterical demand of the cyclopentadienyl ligand does not result in an increased stability of the system, instead, **6k** reveals thermal lability. Utilization of pentamethylcyclopentadienyl or bis(*tert*-butyl)-cyclopentadienyl ligands lead to an unselective decomposition of the phosphalkyne.

In a further experiment starting from bis(cyclopentadienyl)titaniumdichloride and *tert*-butylamine, an hydroamination of the phosphalkyne takes place, corresponding to the results with titanium tetrachloride described by Nixon et al.¹⁰ With a reaction temperature

of 120°C for five days and a catalytic amount of the bis(cyclopentadienyl)titaniumdichloride, phosphalkyne **5** is converted completely (^{31}P NMR: δ 42). Apparently, the second cyclopentadienyl ligand lowers the reactivity of the titanium species compared to **2**. On the other hand the steric demand of the bis(cyclopentadienyl)titanium moiety is too high to form a stable four-membered ring (which is consistent with the lowered stability of **6** in case of substituted Cp-ligands). However, a selective cleavage of the titanium from the heterocyclic system **6** is not achievable, neither by applying heat nor by common chemical methods.

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References

1. Hofmann, M.; Bergsträßer, U.; Szieberth, D.; Nyulászi, L.; Heydt, H.; Regitz, M. *Chem. Eur. J.* **2001**, in preparation.
2. Mountford, P. *Chem. Commun.* **1997**, 2127–2134.
3. Fairfax, D.; Stein, M.; Livinghouse, T. *Organometallics* **1997**, *16*, 1523–1525.
4. McGrane, P. L.; Jensen, M.; Livinghouse, T. *J. Am. Chem. Soc.* **1992**, *114*, 5459–5460.
5. McGrane, P. L.; Livinghouse, T. *J. Am. Chem. Soc.* **1993**, *114*, 11485–11489.
6. Tabellion, F.; Nachbauer, A.; Leininger, S.; Peters, C.; Regitz, M.; Preuss, F. *Angew. Chem.* **1998**, *110*, 1318–1321; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1241–1243.
7. Cloke, F. G. N.; Hitchcock, P. B.; Nixon, J. F.; Wilson, D. J.; Mountford, P. *Chem. Commun.* **1999**, 661–662.
8. Polse, J. L.; Andersen, R. A.; Bergmann, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 13405–13414.
9. Walsh, P. J.; Baranger, A. M.; Bergmann, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1708–1719.
10. Cloke, F. G. N.; Hitchcock, P. B.; Nixon, J. F.; Wilson, D. J. *Chem. Commun.* **2000**, 2387–2388.
11. Beckhaus, R.; Strauß, I.; Wagner, T. *Angew. Chem.* **1995**, *107*, 738–740; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 688–690.
12. Main structural features of **6a** were proved by X-ray structure analysis. A discussion of structural details is not possible due to the poor quality of the data set.
13. According to MM2 calculations, the *cisoid* position of **6a** is at least 3.3 kcal/mol favored compared to other consti-tutions.