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Reactions of [$Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$] with 1,4-Bis(diphenylphosphanyl)but-2-yne: Coupling and Isomerization versus Phosphorylation

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Dedicated to Dr. Sc. Vladimir V. Burlakov on the occasion of his 60th birthday

Keywords: Metallacycles / Allenes / Phosphorylation / Isomerization / Titanium

The reactions of [$Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$] (**1**; Cp = η^5-cyclopentadienyl) with 1,4-bis(diphenylphosphanyl)but-2-yne (**2**) have been investigated and found to yield a mixture of products. From these, through the coupling of **2**, the tetrasubstituted titanacyclopentadiene [$Cp_2Ti(CCH_2PPh_2)_4$] (**3**) was isolated. In addition, small amounts of very unusual complexes were obtained and characterized. In one case, the substrate **2** isomerized to the allene $Ph_2PC(H)=C=C(H)CH_2PPh_2$, which formed the complex [$Cp_2Ti\{\eta^3\text{-}Ph_2PC(H)=C=C(H)CH_2PPh_2\}$] (**4**) through the coordination of a double bond and one of the phosphorus atoms. Another complex, [$Cp_2Ti\{\text{-}C(CH_2PPh_2)=C(CH_2PPh_2)P(Ph_2)H\text{-}\}$] (**5**), was identified to be the result of a formal hydrophosphorylation of the substrate **2** by $HPPh_2$, and features a Ti–H–P bridge. It is not clear how $HPPh_2$ was formed. One possible explanation is the dehydrophosphorylation of the substrate with the formation of $HPPh_2$ and the butatriene $H_2C=C=C=C(H)PPh_2$ [tautomer of the but-2-en-3-yne $HC\equiv C\text{-}CH=C(H)PPh_2$]. The molecular structures of complexes **4** and **5** were determined by X-ray analysis.

Introduction

Recently, we investigated the reactions of symmetrically dihetero-substituted alkynes $YC\equiv CY$ (Y = BR_2,[1] NR_2,[2] OR, PR_2,[3] SR[4]) with group 4 metallocenes. It became evident that heteroatoms have a significant influence on the structural parameters and reactivities of the obtained complexes as the heteroatoms of α-hetero-substituted alkynes interact directly with the alkyne triple bond and increase its electron density for donor heteroatoms (NR_2, OR, PR_2, SR) or decrease its electron density for acceptor heteroatoms (BR_2). More recently, we extended these investigations to unsymmetrically dihetero-substituted alkynes $YC\equiv CSiMe_3$, for example, the α-donor-substituted trimethylsilylalkynes $R_2NC\equiv CSiMe_3$, $EtOC\equiv CSiMe_3$, and $Me_2PC\equiv CSiMe_3$.[5]

In these investigations we aimed to use donor heteroatoms to supply an additional coordination site directly attached to the alkyne moiety, which could promote the formation of highly strained, four-membered metallacycles with the metals binding to the alkyne moiety as well as to one of the heteroatoms.[6] For the bis-phosphorus-substituted alkyne $Ph_2PC\equiv CPPh_2$,[3] such an interaction was proposed to be dynamic in nature with a rapid exchange in the coordination of both phosphorus atoms in a flip-flop mechanism.[3] It seemed particularly interesting to investigate how the chemistry would change if the P atoms were located not in the α, but in the β positions with respect to the triple bond, for example, in $Ph_2PCH_2C\equiv CCH_2PPh_2$ (**2**). This ligand is typically coordinated through its phosphorus atoms in singly bridged molybdenum, iron, and cobalt complexes,[7] as well as in doubly bridged molybdenum,[8] nickel,[7] and platinum complexes.[7] In one case, the molecule contains three molybdenum tetracarbonyl units coordinated by **2** as a bidentate ligand, these ligands linked side-on through the triple bond to a further molybdenum carbonyl fragment.[8]

Results and Discussion

In the reaction of [$Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$] (**1**, Cp = η^5-cyclopentadienyl)[9] with 1,4-bis(diphenylphosphanyl)but-2-yne (**2**),[7] the metallacyclopentadiene **3** was obtained at room temperature as a result of an oxidative alkyne coupling reaction (Scheme 1).

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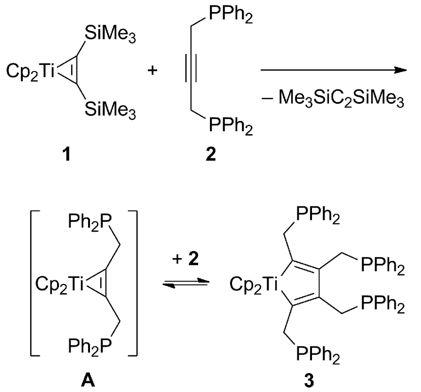


Scheme 1. Reaction of $[Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)]$ (**1**) with $Ph_2PCH_2C{\equiv}CCH_2PPh_2$ (**2**) to yield complex **3**.

In this reaction, 1 equivalent of the metallocene precursor **1** always reacted with 2 equivalents of the alkyne, regardless of whether a 1:2 or a 1:1 stoichiometry was applied. Metallacyclopentadienes usually form via the corresponding metallacyclopropene **A** (Scheme 1) by insertion of a second alkyne. This reaction is sometimes reversible and causes an equilibrium to form between the metallacyclopropene and -pentadiene. In the formation of **3**, no metallacyclopropene **A** could be detected, which reveals that the equilibrium lies far to the side of the five-membered ring in **3**. Its structure was established by 2D NMR spectroscopy. These investigations revealed that the CH_2 groups at the α positions of the ring show a much broader signal than those at the β positions (Figure 1, bottom).

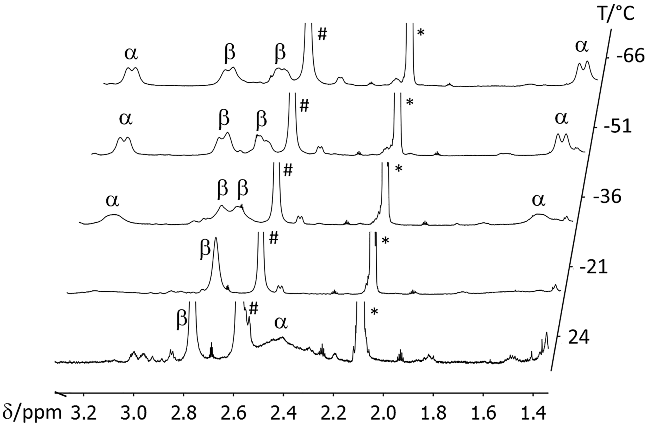
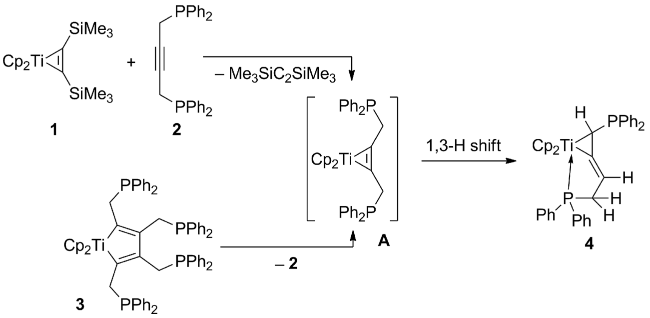


Figure 1. ^1H NMR spectra of **3** in $[D_8]$toluene showing the CH_2 resonances at selected temperatures (#: **2**, *: toluene).

When the solution was cooled stepwise to –66 °C, both signals split into two. Although the signals of the β-CH_2 groups are only about 0.2 ppm apart, those of the α-CH_2 groups differ by about 1.8 ppm. The splitting of the β-CH_2 signals could be caused by hindered rotation of the CH_2PPh_2 substituents on the sterically crowded five-membered ring. The far greater splitting of the α-CH_2 signals may not only be a consequence of hindered rotation, because the neighboring metal atom may interact with one of the hydrogen atoms and thus alter its electronic environment. This would explain the greater difference in the chemical shifts of the α-CH_2 protons at –66 °C and the broader signal at 24 °C in comparison with the β-CH_2 protons. This observation is supported by the larger signal splitting of the *ortho*-phenyl protons at the α positions ($\Delta\delta$ = 0.64 ppm) compared with those at the β positions of the titanacyclopentadiene ($\Delta\delta$ = 0.2 ppm; see Figure S3 in the Supporting Information).

The metallacyclopentadiene **3** is not very stable and decomposes slowly (about 8 d) at room temperature and quickly at 60 °C in a toluene solution, in which the reaction is completed after 3 h.

The decomposition product **4** was identified to be the result of an isomerization of **2** to the allene $Ph_2PC(H){=}C{=}C(H)CH_2PPh_2$ followed by the coordination of a double bond and one of the phosphorus atoms. It is formed most likely via the intermediary metallacyclopropene **A** by a 1,3-hydrogen atom shift from one of the CH_2 groups to the remote alkynic carbon atom. This fast hydrogen shift might explain why no metallacyclopropene **A** could be detected during the ^1H and ^{13}C NMR analyses of **3**. The same product **4** was obtained from the reaction of the metallocene precursor **1** and the alkyne **2** in a 1:1 ratio at elevated temperatures (Scheme 2). The isomerization by 1,3-H shift seems to be irreversible because solutions of pure samples of the allene complex **4** did not show any traces of the metallacyclopentadiene **3**, even with a slight excess of the free alkyne **2**. It should be noted that we were able to isolate a small amount of *trans*-1,4-bis(diphenylphosphanyl)-1,3-butadiene during the thermal treatment of a toluene solution of **4**. The butadiene was identified by X-ray crystallography and NMR spectroscopy (for re-determined structural data see the Supporting Information).[10] The formation of this butadiene fits well with the isomerization theory and can be explained by an additional 1,3-H shift from the remaining CH_2 group to the quaternary carbon of the allene unit. Although the isomerization of alkynes to allenes in the presence of strong bases is well known,[11a] the transition-metal-mediated isomerization is very rare.[11b]



Scheme 2. Formation of **4** directly or from **3** by a 1,3-H shift in the intermediary metallacyclopropene **A**.

The molecular structure of complex **4** is depicted in Figure 2. The titanium center is surrounded by two Cp ligands and the allene, which forms a titanacyclopropane by coordination of two of the allenic carbon atoms (C1, C2) as well as a five-membered metallacycle with three carbon atoms (C2, C3, C4) and one of the phosphorus atoms (P2). To the best of our knowledge, there is only one structurally examined example of a phosphorus-stabilized η^2-bound allene–titanium complex, which was described by Binger et al. in 1994.[12] In contrast to the complex **4**, the Binger complex (1,2-η^2-3,3-diphenylallene)(trimethylphosphane)titanocene ([$Cp_2Ti(PMe_3)\{\eta^2\text{-}CH_2{=}C{=}CPh_2\}$], **B**) is stabilized by the PMe_3 ligand, which is located next to the less sterically demanding side of the allenic unit in the solid state (Scheme 3). The major structural differences between **4** and **B** can be attributed to the intramolecular coordination of phosphorus in **4** (Table 1).

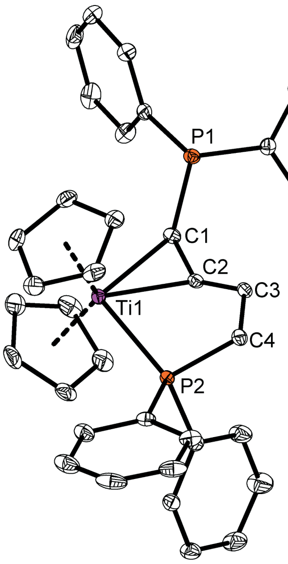
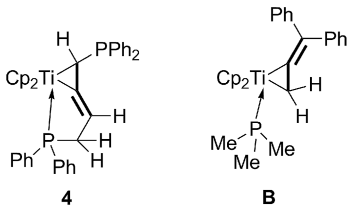


Figure 2. Molecular structure of complex **4**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–P1 1.801(1), C1–C2 1.410(2), C2–C3 1.326(2), C3–C4 1.503(2), C4–P2 1.843(1), Ti1–C1 2.364(1), Ti1–C2 2.149(1), Ti1–P2 2.5808(4), P1–C1–C2 116.8(1), C1–C2–C3 139.3(1), C2–C3–C4 118.0(1), C3–C4–P2 102.39(8).



Scheme 3. Allene complexes **4** and **B**. The allene units are highlighted in bold.

Table 1. Comparison of selected structural features of **4** and **B**.

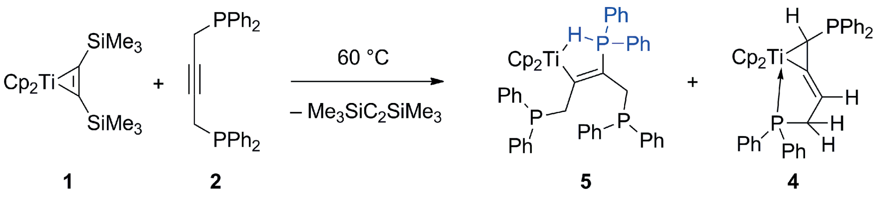
	C1–C2[a] [Å]	C2–C3[b] [Å]	Ti–C1 [Å]	Ti–C2 [Å]	C1–C2–C3[c] [°]
4	1.410(2)	1.326(2)	2.364(1)	2.149(1)	139.31(12)
B[d]	1.423(5)	1.344(4)	2.241(3)	2.188(3)	132.8(2)

[a] C1 and C2 form the titanacyclopropane ring. [b] C2 quaternary carbon atom. [c] Angle of the allene unit. [d] Data taken from ref.[12]

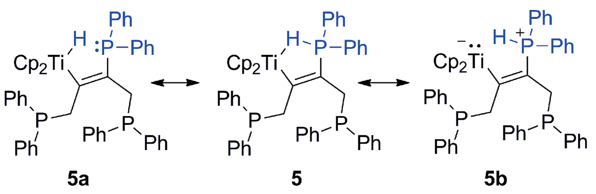
The C1–C2 bond lengths of the titanacyclopropane rings in **4** and **B** are nearly equal and lie between a C_{sp^2}–C_{sp^2} double and a single bond due to coordination to the titanium center. The C2–C3 bond length in **4** is in the same range as the corresponding bond in **B** and can be described as a double bond [cf. Σr_{cov}(C=C) = 1.34 Å].[13] The bond length C3–C4 in **4** is in the range of typical C_{sp^2}–C_{sp^3} single bonds [1.503(2) Å]. Comparison of the Ti–C bonds in **4** and **B** reveals that the bonds to the quaternary carbon atom C2 are shorter than those to the secondary (**B**) and tertiary (**4**) carbon atoms (C1). The C1–C2–C3 bond angle in **4** is about 6.5° greater than in **B**. This might be a consequence of the P2 atom connecting both the titanium center and the allene unit. Interestingly, the structures of **4** and **B** show smaller deviations than expected, and even the ^{1}H and ^{13}C NMR analyses of **4** indicate the similarity of the two complexes. For example, the ^{13}C resonances of the quaternary carbon atoms (C2) can be found, as expected, in the low-field region at δ = 197.0 ppm for **4** and δ = 194.9 ppm for **B**.[12]

In the reaction of **1** with **2**, alongside **3** and **4**, a few crystals of the complex **5** were isolated as an additional product (Scheme 4). In this complex, the coordination of a phosphorylated ligand was identified, which is the result of a formal insertion of H–PPh_2 into the Ti–C bond of the metallacyclopropene **A** to yield [$Cp_2Ti\{\text{-}C(CH_2PPh_2){=}C(CH_2PPh_2)P(Ph_2)H\text{-}\}$] (**5**). The alkenyl complex **5** shows an interaction of the hydrogen atom with titanium and the phosphorus atom of the inserted PPh_2 group (Scheme 5).

The molecular structure of complex **5** is depicted in Figure 3. The titanium center is surrounded by two Cp ligands and the phosphorylated substrate, which forms a five-membered metallacycle containing the titanium atom, the former acetylenic carbon atoms (C1, C2), and the inserted P–H unit (P1, H1). To the best of our knowledge, compound



Scheme 4. Synthesis of **5** as well as **4**.



Scheme 5. Possible resonance structures of **5**.

5 is the first example of this unusual structural motif. The C1–C2 bond is a typical C_{sp^2}–C_{sp^2} double bond [1.352(2) Å]. All the other bonds in the central unit (C1–C3, C2–C4, C1–P1, C4–P3, C3–P2) are single bonds. The distance between C1 and Ti1 is larger than the sum of the covalent radii [2.9 Å, cf. Σr_{cov}(Ti–C) = 2.11 Å],[13] which confirms the absence of a direct C1–Ti1 interaction. This C1 atom is planar and the sum of the angles is 360.0(1)°. The huge deviation of the C2–C1–P1 angle [105.1(1)°] from 120° indicates the ring strain of the metallacycle. The P1–C1–C2–Ti1 torsion angle of 11.4(1)° shows the five-membered ring to have a disturbed planarity. Unfortunately, the very low yield of complex **5** did not allow further investigations of the bonding in this intriguing molecule. Nevertheless, the results of the elemental analysis (calcd. C 76.34, H 5.77; found C 76.50, H 5.77) and the mass spectra (*m*/*z* = 785 $[\mathbf{5}]^+$, 607 $[\mathbf{5} - Cp_2Ti]^+$) correspond very well to the description of complex **5**. On the basis of this data, **5** can be described either as a hydrido alkenyl species **5a** or an inner phosphonium ate complex **5b** (Scheme 5).

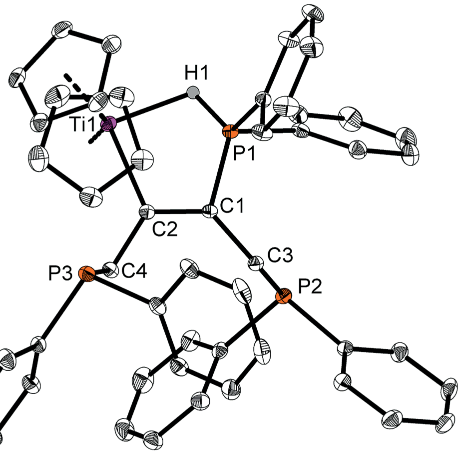
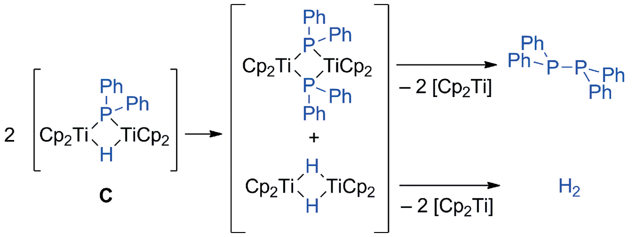
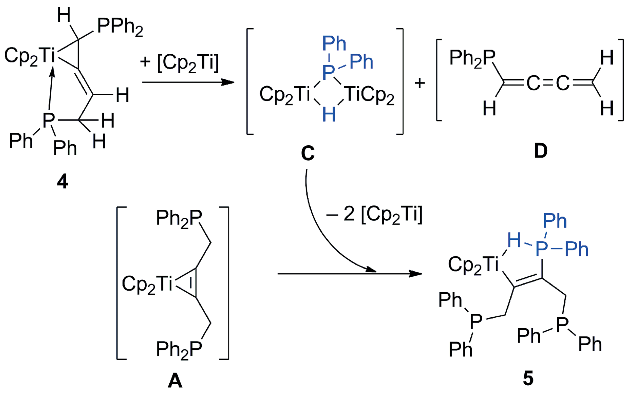


Figure 3. Molecular structure of complex **5**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity, exept for H1. Selected bond lengths [Å] and angles [°]: C1–P1 1.798(1), C1–C2 1.352(2), C1–C3 1.511(2), C2–C4 1.511(2), C3–P2 1.862(1), C4–P3 1.858(2), Ti1–C2 2.214(1), Ti1–P1 2.6598(5), Ti1–H1 1.93(2), H1–P1 1.28(2), C2–C1–P1 105.1(1), C1–C2–Ti1 111.0(1), P1–C1–C2–Ti1 11.4(1), C2–C1–C3–P2 97.8(2), C1–C2–C4–P3 94.9(1).

To rationalize the formation of **5**, we investigated the reactions of **1** as well as of **3** in the presence of $HPPh_2$. Although the reaction of **1** with $HPPh_2$ led to hydrogen and the diphosphine Ph_2PPPh_2, the reaction of **3** with $HPPh_2$ gave a more complex mixture of compounds, including NMR silent species such as **5** in addition to Ph_2PPPh_2 and other unknown products. The formation of the diphosphine can potentially be explained via a species **C** (Scheme 6 and Scheme 7), as expected on the basis of the report of Harrod, Samuel and co-workers.[14]



Scheme 6. Possible generation of H_2 and Ph_2PPPh_2 from **C**.



Scheme 7. Possible mechanism for the formation of complex **5**.

Additional experiments underlined the observation that the PP coupling reaction proceeded irrespective of the presence of alkynes (see Figure S8 in the Supporting Information). Furthermore, the thermal treatment of **4** dissolved in toluene without the addition of $HPPh_2$ also resulted in the formation of a complex reaction mixture containing Ph_2PPPh_2, $Ph_2PC(H)=C(H)–C(H)=C(H)PPh_2$, and compound **5** as identified products. Although we were not able to isolate compound **5** during these reactions, we unambiguously determined its presence by mass spectroscopy (see the Supporting Information). These experiments supported the idea of a stepwise dehydrophosphorylation of **4** to the presumed compounds **C** and **D**, followed by a formal phosphorylation of **2** or **A** to yield **5** (Scheme 7). It should be noted that we observed a ^{31}P NMR resonance at δ = 178 ppm during these experiments, which could be evidence for the formation of compound **C** (see the Supporting Information).

Nevertheless, no further information can be presented on how $HPPh_2$ and the resulting complex **5** were formed and what byproducts were generated. Complex **5** formally contains a molecule of **2** as ligand together with an additional $HPPh_2$ group. Because no other phosphine was added, a second molecule of **2** must be the source of $HPPh_2$. One possible explanation for its formation could be the dehydrophosphorylation of the substrate with the formation of

$HPPh_2$ [and eventually the butatriene $H_2C{=}C{=}C{=}C(H)PPh_2$ (**D**) or the but-2-en-3-yne $HC{\equiv}C{-}CH{=}C(H)PPh_2$ as its tautomer]. Both compounds should be very reactive byproducts that reduce the yield of **4** and disturb the synthesis of **5**. It is worth mentioning that such butatrienes and but-2-en-3-ynes are coordinated by group 4 metallocenes to give strained metallacycles such as 1-metallacyclopenta-3-ynes and metallacycloallenes.[15] Like compound **2** used herein, the very similar 1,4-disubstituted but-2-yne substrate 1,4-dichlorobut-2-yne also forms 1-metallacyclopentynes.[16] Also, $ClMe_2SiC{\equiv}CSiMe_2Cl$ yields 1-metalla-2,5-disilacyclopentynes after Cl abstraction.[17] All the postulated unsaturated byproducts, the butatriene $H_2C{=}C{=}C{=}C(H)PPh_2$ and the but-2-en-3-yne $HC{\equiv}C{-}CH{=}C(H)PPh_2$ (or the diacetylene $HC{\equiv}C{-}C{\equiv}CH$ as a product from its subsequent dehydrophosphorylation with the formation of $HPPh_2$) should be very reactive without any chance of their isolation as products. In addition, by alkyne exchange of $[Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)]$ (**1**) with **2**, an intermediary titanacyclopropene $[Cp_2Ti(\eta^2\text{-}Ph_2PCH_2C{\equiv}CCH_2PPh_2)]$ (**A**) is proposed, into which is inserted $HPPh_2$, leading to complex **5**. In principle, this reaction is very similar to the reactions of group 4 metallocene alkyne complexes $[Cp_2M(L)(\eta^2\text{-}Me_3SiC_2R)]$ with diisobutylaluminium hydride $HAl(iBu)_2$. The resulting complexes of the type $[(Cp_2M)(\mu\text{-}\eta^1{:}\eta^2\text{-}RCCSiMe_3)(\mu\text{-}H)\{Al(iBu)_2\}]$ (Cp_2Ti: R = Ph, $SiMe_3$; Cp_2Zr: R = $SiMe_3$)[18] show a similar structural motif as found in **5**. In contrast to complex **5**, an additional interaction between the metal center and the planar β-C atom was observed in these complexes. Similar compounds have been described previously for zirconium by Erker and co-workers[19] and for titanium by Binger and co-workers.[20] Compounds like these as well as **5** provide the basics for understanding hydroheterofunctionalization reactions such as hydroalumination,[21] hydroamination,[22] and hydrophosphorylation. Westerhausen and co-workers reported such a calcium-catalyzed hydrophosphorylation of a 1,3-butadiyne.[23]

Conclusions

The reaction of $[Cp_2Ti(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$ (**1**) and $Ph_2PCH_2C{\equiv}CCH_2PPh_2$ (**2**) has been investigated. Initially, the coupling of two alkynes **2** led to metallacyclopentadiene **3**, the structure of which was determined by 2D NMR spectroscopy. This compound was found to undergo elimination of one alkyne and a 1,3-H shift in the remaining alkyne unit to form the allene complex **4**. In addition, the compound $[Cp_2Ti\{\text{-}C(CH_2PPh_2){=}C(CH_2PPh_2)P(Ph_2)H\text{-}\}]$ (**5**) was isolated alongside **4**, showing an unusual Ti–H–P bridge. Its formation most likely proceeds by phosphorylation of an intermediary titanacyclopropene. Because no source of phosphorus other than alkyne **2** is present in the reaction mixture, a dehydrophosphorylation of this alkyne is assumed. Prolonged heating of the reaction mixture resulted in the formation of molecular hydrogen and the diphosphine Ph_2PPPh_2, thus validating the dehydrophosphorylation step. Therefore we must conclude that the alkyne complex **1** acts as a titanocene source that is stabilized by alkyne coordination (**A** and its follow-up products) and simultaneously as an agent that cleaves phosphorus–element bonds.

Experimental Section

General: All manipulations were carried out in oxygen- and moisture-free argon using standard Schlenk and drybox techniques. The solvents were purified by using the Grubbs-type column system “Pure Solv MD-5” and dispensed into thick-walled glass Schlenk bombs equipped with Young-type Teflon valve stopcocks. Diphenylphosphine (99%, Strem Chemicals) was used as received. $[Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)]$ (**1**, Cp = η^5-cyclopentadienyl) and $Ph_2PCH_2C{\equiv}CCH_2PPh_2$ (**2**) were prepared according to literature procedures.[7,9a] NMR spectra: Bruker AV300 and AV400 spectrometers. ^1H and ^{13}C chemical shifts were referenced to the solvent signal: [D$_6$]benzene: δ_H = 7.16 ppm, δ_C = 128.0 ppm; [D$_8$]toluene: δ_H = 2.09 ppm, δ_C = 20.4 ppm. IR: Bruker Alpha FT-IR spectrometer. MS: Finnigan MAT 95-XP (Thermo-Electron). Elemental analysis: Leco Tru Spec elemental analyzer. Melting points: Mettler-Toledo MP 70. The melting points were measured in sealed capillaries.

Diffraction data for **4** and **5** were collected with Bruker APEX-II CCD and STOE-IPDS II diffractometers, respectively, using graphite-monochromated Mo-K_α radiation. The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 with the SHELXTL software package.[24] Diamond was used for the graphical representation.[25]

Crystal Data for 4: $C_{38}H_{34}P_2Ti$, M = 600.49 g mol^{-1}, triclinic, space group $P\bar{1}$, a = 9.7272(2), b = 12.7932(3), c = 13.8751(3) Å, α = 65.6182(7), β = 80.8831(7), γ = 76.9664(7)°, V = 1527.98(6) Å^3, T = 150(2) K, Z = 2, 31461 reflections measured, 7380 independent reflections (R_{int} = 0.0228), final R values [$I > 2\sigma(I)$]: R_1 = 0.0294, wR_2 = 0.0716, final R values (all data): R_1 = 0.0356, wR_2 = 0.0756, 378 parameters.

Crystal Data for 5: $C_{50}H_{45}P_3Ti$, M = 786.67 g mol^{-1}, monoclinic, space group $P2_1/n$, a = 10.1847(5), b = 36.955(2), c = 11.0612(6) Å, β = 101.967(1)°, V = 4072.7(4) Å^3, T = 150(2) K, Z = 4, 61953 reflections measured, 9845 independent reflections (R_{int} = 0.0303), final R values [$I > 2\sigma(I)$]: R_1 = 0.0352, wR_2 = 0.0832, final R values (all data): R_1 = 0.0430, wR_2 = 0.0876, 491 parameters.

CCDC-1043501 (for **4**) and -1043502 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of $[Cp_2Ti(CCH_2PPh_2)_4]$ (3): 1,4-Bis(diphenylphosphanyl)but-2-yne (**2**; 0.211 g, 1.0 mmol) in toluene (5 mL) was added dropwise to a stirred solution of $[Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)]$ (**1**; 0.175 g, 0.5 mmol) in toluene (10 mL) at ambient temperature. The resulting brownish solution was stirred at this temperature for 12 h. The solvent was then removed in vacuo and the resulting residue was dried for 1 h. The reaction mixture was treated with *n*-hexane (15 mL) and filtered. The resulting brownish solution was stored at –78 °C over a period of 12 h, which resulted in the deposition of a yellow solid. Removal of supernatant by syringe and drying in vacuo at ambient temperature for 1 h yielded **3** as a yellow solid. It should be mentioned that **3** was always contaminated with **4**, yield 110 mg, 0.11 mmol, 21%; M(**3**) = 1023.0 g mol^{-1}; m.p. 61 °C.

^{1}H NMR (25 °C, [D$_6$]benzene, 400.13 MHz): δ = 2.30–2.70 (m, 4 H, α-CH$_2$), 2.89 (s, 4 H, β-CH$_2$), 5.94 (s, 10 H, Cp), 7.02–7.13 (m, 8 H, α/β-*p*-C$_6$H$_5$), 7.15–7.23 (m, 16 H, α/β-*m*-C$_6$H$_5$), 7.45–7.54 (m, 8 H, α-*o*-C$_6$H$_5$), 7.55–7.61 (m, 8 H, β-*o*-C$_6$H$_5$) ppm. ^{1}H NMR (25 °C, [D$_8$]toluene, 400.13 MHz): δ = 2.3–2.5 (m, 4 H, α-CH$_2$), 2.76 (s, 4 H, β-CH$_2$), 7.43 (m, 8 H, α-*o*-C$_6$H$_5$), 7.51 (m, 8 H, β-*o*-C$_6$H$_5$) ppm. ^{1}H NMR (–66 °C, [D$_8$]toluene, 400.13 MHz): δ = 1.40 (m, 2 H, α-CH$_2$), 2.60 (s, 2 H, β-CH$_2$), 2.81 (s, 2 H, β-CH$_2$), 3.20 (m, 2 H, α-CH$_2$), 7.17 (m, 4 H, α-*o*-C$_6$H$_5$), 7.53 (m, 4 H, β-*o*-C$_6$H$_5$), 7.73 (m, 4 H, β-*o*-C$_6$H$_5$), 7.81 (m, 4 H, α-*o*-C$_6$H$_5$). ^{13}C NMR (25 °C, [D$_6$]benzene, 100.62 MHz): δ = 30.9 (m, β-CH$_2$), 37.4 (m, α-CH$_2$), 113.7 (m, Cp), 128.6 (m, *m*-C$_6$H$_5$), 128.6 (s, *p*-C$_6$H$_5$), 128.8 (m, *m*-C$_6$H$_5$), 133.0–134.3 (m, α-*o*-C$_6$H$_5$), 133.8 (d, β-*o*-C$_6$H$_5$), 141.0 (d, J = 18.4 Hz, *ipso*-C$_6$H$_5$), 141.2 (d, J = 17.3 Hz, β-C$_q$), 195.1 (m, α-C$_q$) ppm. ^{31}P{^{1}H} NMR (25 °C, [D$_6$]benzene, 161.98 MHz): δ = –15.9 (AA′BB’ pattern) ppm. IR (ATR, 32 scans): ṽ = 3066 (w), 3048 (w), 3012 (w), 2997 (w), 1583 (w), 1570 (w), 1560 (w), 1478 (w), 1430 (m), 1370 (w), 1359 (w), 1304 (w), 1271 (w), 1181 (w), 1155 (w), 1092 (w), 1067 (w), 1013 (m), 933 (w), 910 (w), 879 (w), 843 (w), 807 (m), 732 (s), 692 (s), 590 (w), 500 (m), 474 (m), 440 (w) cm^{-1}. MS (CI): *m/z* = 835 [M – HPPh$_2$]$^+$; M$^+$ could not be detected. C$_{66}$H$_{58}$P$_4$Ti (1023.0): calcd. C 77.45, H 5.72, P 12.11; found C 77.46, H 5.81, P 12.07.

Synthesis of [Cp$_2$Ti(η^3-Ph$_2$PCH=C=CHCH$_2$PPh$_2$)] (4): 1,4-Bis(diphenylphosphanyl)but-2-yne (**2**; 0.138 g, 0.33 mmol) in toluene (5 mL) was added dropwise to a stirred solution of [Cp$_2$Ti(η^2-Me$_3$SiC$_2$SiMe$_3$)] (**1**; 0.114 g, 0.33 mmol) in toluene (10 mL) at ambient temperature. The resulting brownish solution was heated at 60 °C for 4 h. All the volatiles were removed in vacuo and the residue dissolved in diethyl ether (10 mL) and filtered through a cannula. The filtrate was stored at –40 °C over a period of 12 h, which resulted in the deposition of a brownish solid. The supernatant was decanted and the residue dissolved in diethyl ether (8 mL). This solution was then concentrated to a volume of 5 mL in vacuo and stored for 3 d at ambient temperature, which resulted in the deposition of a red microcrystalline solid. Removal of the supernatant by syringe and drying in vacuo at ambient temperature for 1 h yielded **4** as a red solid. In addition, a few crystals of **5** suitable for X-ray crystallography were isolated.

4: Yield: 130 mg, 0.1653 mmol, 50 %; M(**4**) = 600.5 g mol^{-1}; m.p. 140 °C. For the NMR assignment scheme, see the Supporting Information. ^{1}H{^{31}P} NMR (25 °C, [D$_6$]benzene, 400.13 MHz): δ = 2.16 (m, 1 H), 3.00 (m, 1 H), 3.41 (m, 1 H), 5.03 (s, 5 H, Cp$_1$) 5.20 (s, 5 H, Cp$_2$), 6.81 (m, 2 H, *m*-Ph), 6.87 (m, 1 H, *p*-Ph), 6.92 (m, 1 H), 7.14 (m, 1 H, *p*-Ph), 7.15 (m, 1 H, *p*-Ph), 7.16 (m, 3 H, *m,p*-Ph), 7.25 (m, 2 H, *m*-Ph), 7.28 (m, 2 H, *m*-Ph), 7.30 (m, 2 H, *o*-Ph), 7.35 (m, 2 H, *o*-Ph), 7.89 (m, 2 H, *o*-Ph), 7.94 (m, 2 H, *o*-Ph) ppm. ^{13}C NMR (25 °C, [D$_6$]benzene, 100.62 MHz): δ = 27.9 (q, J = 40.0, 8.2 Hz, C$_A$), 43.6 (d, J = 37.1 Hz, C$_B$), 100.2 (s, Cp), 101.7 (d, J = 6.6 Hz, Cp), 118.8 (q, J = 18.0, 8.2 Hz, α-C), 127.6 (m, *m*-Ph), 127.7 (m, *m*-Ph), 128.1 (d, J = 7.0 Hz, *m*-Ph), 128.4 (d, J = 5.7 Hz, *m*-Ph), 128.5 (d, J = 5.7 Hz, *p*-Ph), 128.9 (d, J = 6.6 Hz, *p*-Ph), 128.9 (d, J = 1.7 Hz, *p*-Ph), 129.9 (d, J = 1.7 Hz, *p*-Ph), 130.8 (d, J = 6.4 Hz, *o*-Ph), 133.2 (d, J = 16.8 Hz, *o*-Ph), 133.4 (d, J = 18.8 Hz, *o*-Ph), 133.7 (d, J = 8.7 Hz, *o*-Ph), 138.4 (m, J = 4.2, 1.3 Hz, *ipso*-Ph), 141.4 (d, J = 20.4 Hz, *ipso*-Ph), 144.9 (d, J = 13.7 Hz, *ipso*-Ph), 147.0 (d, J = 25.9 Hz, *ipso*-Ph), 197.0 (d, J = 18.1 Hz, C$_V$) ppm. ^{31}P{^{1}H} NMR (25 °C, [D$_6$]benzene, 161.98 MHz): δ = 7.1 [d, ^3J(^{31}P-^{31}P) = 13 Hz, P1], 89.7 [d, ^3J(^{31}P-^{31}P) = 13 Hz, P2] ppm. IR (ATR, 32 scans): ṽ = 3060 (w), 2969 (w), 2893 (w), 2800 (w), 1648 (w), 1583 (w), 1569 (w), 1477 (w), 1433 (m), 1364 (w), 1307 (w), 1235 (m), 1179 (w), 1157 (w), 1119 (w), 1100 (m), 1068 (m), 1008 (w), 983 (w), 939 (w), 923 (w), 866 (w), 841 (w), 804 (s), 789 (m), 775 (m), 749 (m), 736 (s), 715 (m), 692 (s), 622 (m), 606 (m), 515 (s), 505 (s), 474 (m), 443 (m) cm^{-1}. MS (CI): *m/z* = 602 [M]$^+$, 417 [M – PPh$_2$]$^+$. C$_{38}$H$_{34}$P$_2$Ti (600.5): calcd. C 76.01, H 5.71, P 10.32; found C 75.91, H 5.88, P 10.20.

5: MS (CI): *m/z* = 785 [M]$^+$, 607 [C(CH$_2$PPh$_2$)=C(PPh$_2$)(CH$_2$PPh$_2$)]$^+$, 423 [C(CH$_2$PPh$_2$)=CH(CH$_2$PPh$_2$)]$^+$, 239 [C{CH$_2$P(H)Ph$_2$}=CCH$_3$]$^+$. C$_{50}$H$_{45}$P$_3$Ti (786.7): calcd. C 76.34, H 5.77; found C 76.50, H 5.77.

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