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Effect of Different Bases and Phosphorus Ylide on the Selective Deprotonation of Phosphorus Ylide Adduct $Cp^*TaCl_4(CH_2{=}PPh_3)$

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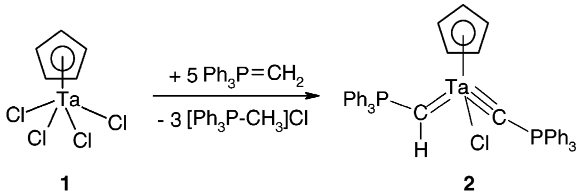
The effect of different bases and phosphorus ylide on the selective deprotonation of phosphorus ylide adduct $Cp^*TaCl_4(CH_2{=}PPh_3)$ (**4**) was studied. The acidity of the methylene hydrogen atoms in ylide adduct complex **4**, $[Cp^*TaCl_4(CH_2{=}PPh_3)]$, is weaker than those in the derivative complex $[CpTaCl_4(CH_2{=}PPh_3)]$. Under the same conditions complex **4** cannot transylidate. With the strong, but weakly coordinating base bis(trimethylsilyl)amide a double deprotonation of two methyl groups on the pentamethylcyclopentadienyl ring occurs, and the novel ylide adduct complex **6**, with an η^3-ally-η^4-butadiene ligand, is obtained. Only when elimination of three chloride ligands is compensated by at least three coordinating ylide molecules can the strong base bis(trimethylsilyl)amide selectively deprotonate in a Ta−CH position, affording the expected carbyne complex **5**.

Introduction

The synthesis of transition metal compounds containing metal−carbon multiple bonds and their applications in olefin/alkyne metathesis is a very important research field in organometallic chemistry. Olefin metathesis reaction is a not only simple but also efficient chemical method to recombine the carbon−carbon bonds and has been widely applied in organic synthesis, fine chemical industry, pharmaceutical chemistry, material chemistry, green chemistry, etc. The development of the chemistry of alkylidene complexes of tantalum was well reviewed by Schrock, Schmidbaur, Johnson and Kolodiazhnyi.[1] In 1986 the first bridged dinuclear four-valent titanium phosphonio carbyne compound was obained from titanium tetrachloride through transylidation reaction.[2]

With the transylidation method we successfully prepared the phosphonio methylidyne complex of tungsten,[3] rhenium[4] and niobium[5] with d^0 electron configuration. The rhenium phosphonio methylidyne complex when reacted with diphenylketene through a Wittig reaction gave rise to an allenylidene complex.[6]

The transylidation reaction of $CpTaCl_4$ **1** with 5 equiv of triphenylmethylenephosphorane gave the complex $[CpTa(\equiv C-PPh_3)(=CH-PPh_3)Cl]$ (**2**) (eq 1) as the first example of a stable tantalum complex with a terminal $[M\equiv C-PR_3]$ function.[7] Instead of the cyclopendienyl ligand (Cp), the pentamethylcyclopentadienyl ligand (Cp*) was introduced to increase the yield and the stability of the phosphonio methylidyne complex.



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In this paper we report the effect of the different bases $CH_2{=}PPh_3$, $(Me_3Si)_2N^-$, and pyridine on the different and regioselective deprotonation in phosphorus ylide adduct $Cp^*TaCl_4(CH_2{=}PPh_3)$ (**4**).

Results and Discussion

Reaction of $Cp^*TaCl_4$with $CH_2{=}PPh_3$. When Cp* is used instead of Cp, the ylide adduct could be obtained (eq 2).[8] With 5 molar equiv of phosphorus ylide the transylidation reaction fails to occur and the corresponding carbyne complex is not obtained (eq 3). Compared with the cyclopentadienyl ligand, the pentamethylcyclopentadienyl ligand has a stronger donor strength with five methyl groups as electron-donating groups, and the positive charge at the metal center in pentamethylcyclopentadienyl tantalum tetrachloride decreases. This leads to a decrease of the acidity of the proton in the ylide adduct **4**, and finally the basicity of the ylide is not able to eliminate a hydrogen chloride molecule.

Reaction of Ylide Adduct 4 with $NaN(SiMe_3)_2$. In trying to deprotonate the relatively weaker ylide methylene protons in complex **4** with a stronger base, the novel complex **6** was

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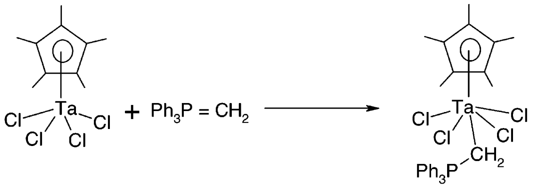
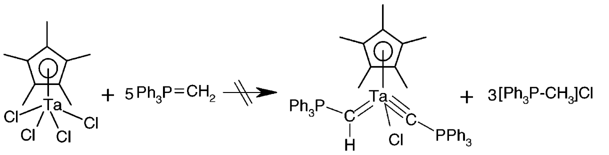


(2)

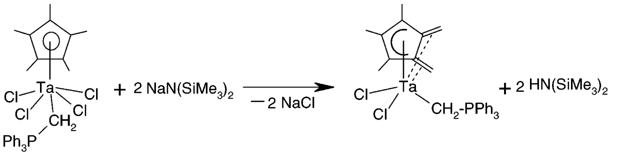
3 **4**



(3)

3 **5**

formed through the reaction of complex **4** with 2 equiv of sodium bis(trimethylsilyl)amide (eq 4). This result shows that the larger pentamethylcyclopentadienyl ligand likely hinders this deprotonation of the ylide adduct in addition to the above-mentioned electronic effect.



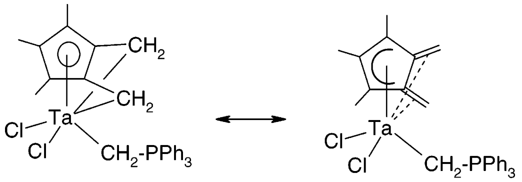
(4)

4 **6**

Complex **6** as red crystals is stable in the air for several hours. It was fully characterized by NMR (C_6D_6) and elemental analysis. The ^{1}H NMR spectrum reveals two methylene groups as doublets with couplings constant $^2J(HH) = 5.5$ Hz at 0.74 and 0.86 ppm, respectively, which implies that they are geminal hydrogen atoms attached to an sp^2-hybridized carbon atom.[9] A singlet at 1.85 ppm is found for the methyl group in the middle of the allyl part, and a signal as a singlet was obtained at 2.16 ppm for the two methyl groups on the two sides of the allyl part. The two methylene protons in ylide ligand are registered at 3.16 ppm as a doublet with a coupling constant $^2J(PH) = 16.5$ Hz. This is typical for a phosphorus ylide ligand. The ^{31}P NMR spectrum of **6** shows one singlet at 34.8 ppm, a characteristic value for phosphorus ylide adducts. In the ^{13}C NMR spectrum, two sp^2-methylene groups on the C_5 ring appear at 64.6 and 64.7 ppm as singlets, respectively, which are comparable with the complex [Cp*(η^3:η^4-$C_5Me_3(CH_2)_2$)Ti].[10]

The bonding mode in complex **6** can be explained with two possible resonance forms (Scheme 1):

Scheme 1. Two Resonance Forms of Complex 6



6A **6B**

(η^5-C_5Me_5)-substituted tantalum complex **6A** with two σ-bonded sp^3-methylene groups, which are formed through the deprotonation of methyl groups of C_5Me_5, or in form **6B** with trimethyl dimethylene groups, which can be considered a η^3-allyl-η^4-butadien coordination. For this reason this mode is referred to as a form of an η^7-ligand containing a doubly "tucked-in" cyclometalated Cp* ligand.[11] In light of the ^{1}H NMR data of complex **6** the form **6B** is a more appropriate representation, because the coupling constant $^2J(HH) = 5.2$ Hz is typical for the geminal hydrogen atoms at an sp^2-hybridized carbon atom. Similar results were reported for the tantalum dihydride [(η^7-$C_5Me_3(CH_2)_2$)Ta(H)$_2$(PMe$_3$)$_2$][9] and [Cp*(η^3:η^4-$C_5Me_3(CH_2)_2$)-Ti] complex.[10]

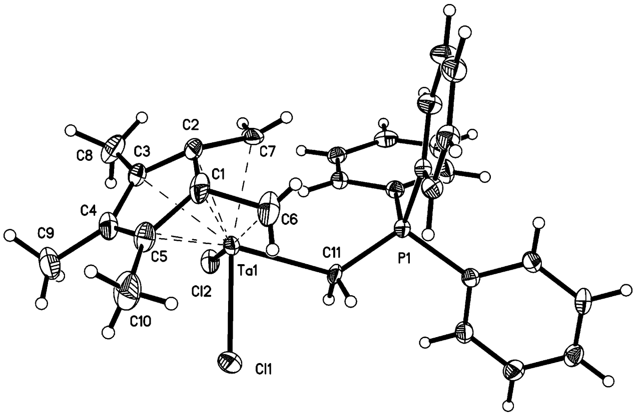


Figure 1. Molecular structure of **6**. The ellipsoids are drawn at 30% probability. Selected bond distances (Å) and angles (deg): C1−C6 1.440(8), C2−C7 1.466(8), C1−C2 1.453(9), C2−C3 1.455(8), C3−C4 1.391(8), C4−C5 1.410(8), C1−C5 1.434(8), C3−C8 1.512(8), C4−C9 1.498(8), C5−C10 1.507(9), C1−Ta1 2.154(5), C2−Ta1 2.173(5), C3−Ta1 2.436(5), C4−Ta1 2.572(5), C5−Ta1 2.410(5), C6−Ta1 2.289(7), C7−Ta1 2.320(6), C11−Ta1 2.313(5), Cl1−Ta1 2.4319(14), Cl2−Ta1 2.4312(13), C11−P1 1.764(5); Cl1−Ta1−Cl2 94.99(6), Cl1−Ta1−C11 79.40(13), Cl2−Ta1−C11 84.85(14), Ta1−C11−P1 131.5(3), C5−C1−C6 120.5(7), C3−C2−C7 118.8(6).

The solution data were substantiated by an X-ray diffraction analysis. In the structure of complex **6** (Figure 1) the tantalum bears one phosphorus ylide ligand, two chloride ligands, and a 1,2,3-trimethyl-4,5-dimethylenecyclopentenyl ligand in an η^3-allyl-η^4-diene coordination mode. The shorter C=CH$_2$ bonds, C2−C7 = 1.466(8) and C1−C6 = 1.440(8) Å, in comparison with the other three carbon−carbon bonds, C3−C8 = 1.512(8), C4−C9 = 1.498(8), and C5−C10 = 1.507(9) Å, the angles H6A−C6−H6B = 116° and H7A−C7−H7B = 119°, and the near-planarity of bonds C7−H7A, C7−H7B, and C2−C7, as well as C6−H6A, C6−H6B, and C1−C6, indicate that C6 and C7 are sp^2-hybridized methylene carbon atoms. However, the elongation of the C=CH$_2$ unit in comparison with the normal C=C bond in olefins[12] also confirms the activation of both C=CH$_2$ units through π-coordination (η^2-bonding) of these two groups to the metal, while the other three carbon−carbon bonds, C3−C8 = 1.512(8), C4−C9 1.498(8), and C5−C10 = 1.507(9) Å, are in the range of lengths for normal carbon−carbon single bonds. Comparing with the other three bonds, C3−Ta1 = 2.436(5), C4−Ta1 = 2.572(5), and C5−Ta1 2.410(5) Å, the especially short distances C1−Ta1 = 2.154(5), C2−Ta1 = 2.173(5), C6−Ta1 = 2.289(7), and C7−Ta1 = 2.320(6) Å also prove this interaction between tantalum and the C=CH$_2$ units. The relatively long C11−Ta1 = 2.313(5) Å implies a weaker

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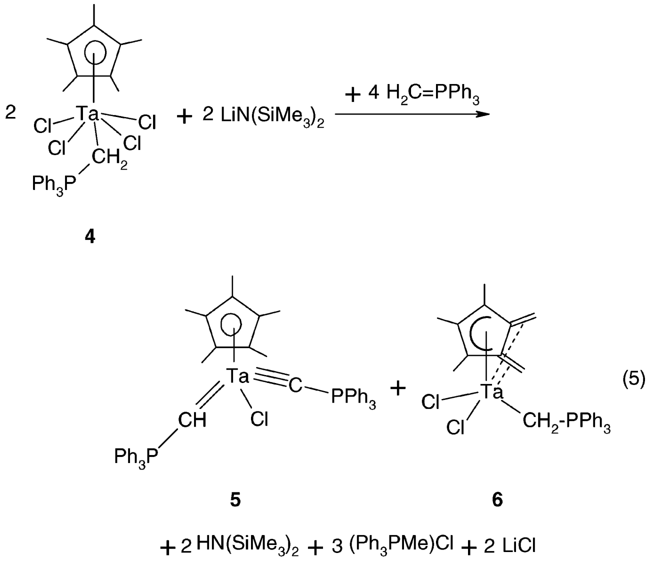
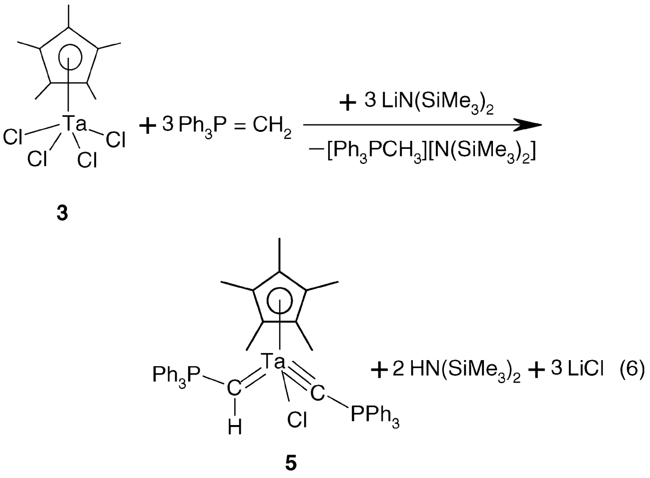
interaction between the tantalum center and the ylide ligand, but corresponds to a single bond and is comparable with the other tantalum phosphorus ylide adduct: Ta−C(ylide) = 2.35 Å in [η^5-C_5Me_5]$Cl_4Ta(CH_2{=}PMePh_2)$].[8]

Reaction of Cp*TaCl$_4$ with CH$_2$=PPh$_3$ and LiN(SiMe$_3$)$_2$. In this case it is considered that sodium bis(trimethylsilyl)amide is a too strong base for this purpose. In order to investigate the effect of different bases upon the deprotonation reaction, lithium bis(trimethylsilyl)amide was selected because it has a basicity between sodium bis(trimethylsilyl)amide and triphenylphosphorus ylide. The larger sodium cation can more strongly activate the chloride ligand at the tantalum center than the smaller lithium cation. This size-dependent counterion effect could be understood from the difference of solubility in organic solvents between sodium chloride and lithium chloride. It was found that under the same reaction conditions apart from the same product complex **6** as in eq 4, the *in situ* ^{31}P NMR spectrum of the mother solution indicates the existence of the less (<5%) expected phosphino carbyne complex **5** (eq 5).



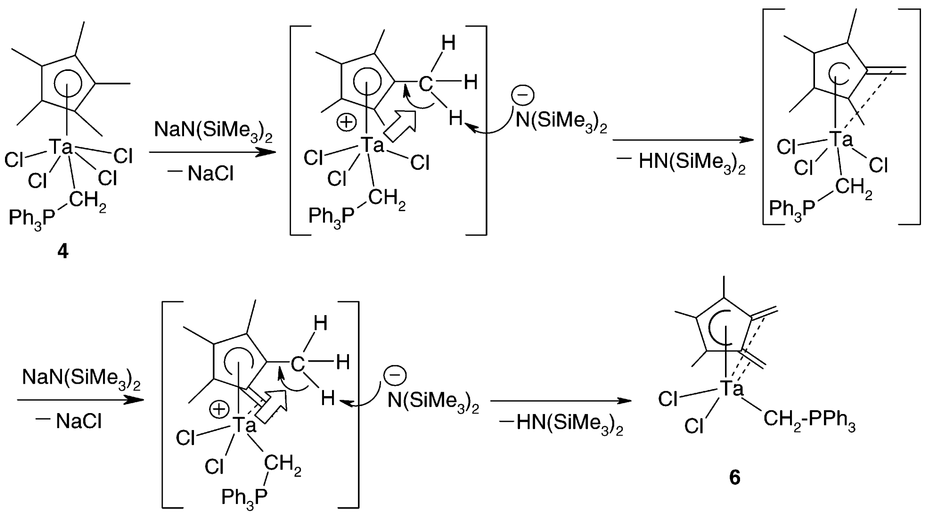
After changing the experimental conditions, it was found that reacting Cp*TaCl$_4$ **4** with 3 equiv of phosphorus ylide affords a carbyne compound not only with lithium salt but also with sodium salt. In order to improve the yield of complex **5** and to avoid the appearance of complex **6**, $CH_2{=}PPh_3$ and $LiN(SiMe_3)_2$ were employed in different ratios. When the reaction was carried out in a ratio of Cp*TaCl$_4$:$CH_2{=}PPh_3$:$LiN(SiMe_3)_2$ of 1:3:1, the *in situ* ^{31}P NMR spectrum of the mother solution indicates the existence of complex **5** and complex **6** with a ratio of 1:1. We could also selectively obtain only complex **5** using a ratio of Cp*TaCl$_4$:$CH_2{=}PPh_3$:$LiN(SiMe_3)_2$ of 1:3:3 (eq 6).



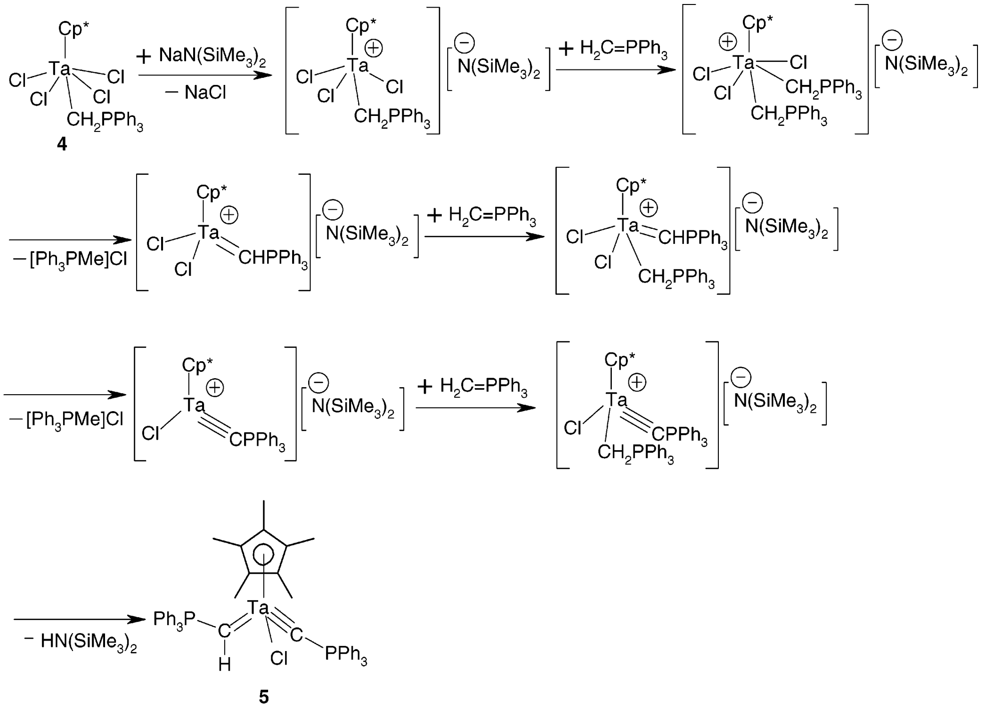
Complex **5** was fully characterized by NMR and elemental analysis. The ^{1}H NMR spectrum of **5** shows one singlet at 2.31 ppm for the five methyl groups on the cyclopentadienyl ring. The carbene hydrogen atom is recorded at 4.72 ppm. In comparison with the corresponding value (5.28 ppm) in complex **2**, this shift to high field is attributed to the five electron-donating methyl groups on the cyclopentadienyl ring, resulting in the weaker acidity of the carbene proton in complex **4**. The ^{31}P NMR spectrum of **5** consists of two doublets for the [Ta=CH−PPh$_3$] and [Ta≡C−PPh$_3$] moieties at 22.2 and −30.0 ppm, respectively, with a coupling constant ^4J(PP) = 5.2 Hz. In comparison with complex **2** these signals are shifted to high field, indicating stronger shielding and a reduced electronegativity of the tantalum center. This difference is also reflected in the ^{13}C NMR spectrum of **5** and **2** for [Ta≡C−PPh$_3$], showing resonances at 198.6 ppm for **5** and 208.0 ppm for **2**.

The formation of complex **6** can be explained as in Scheme 2. The sodium salt and lithium salt are stronger bases than the ylide, but the bis(trimethylsilyl)amide anion is a weaker coordination ligand. After the addition of the sodium salt or

Scheme 2. Formation of Complex 6



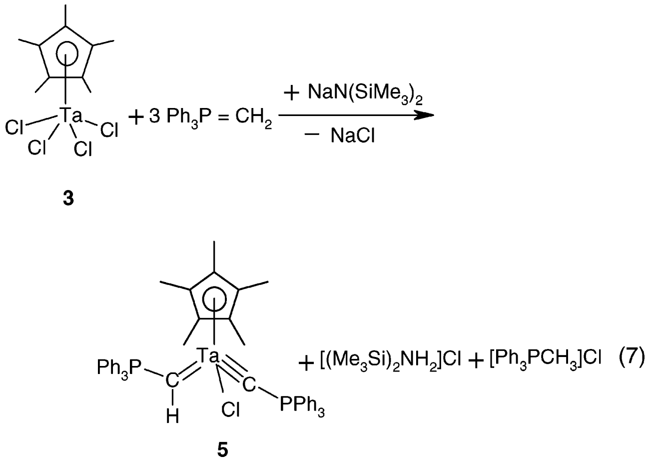
Scheme 3. Formation Mechanism of Complex 5



lithium salt, sodium chloride or lithium chloride precipitates; at the same time, one coordination cation forms, in which the tantalum center is unsaturated because of no coordination of the bis(trimethylsilyl)amide anion. This anion stays in the outer sphere. The C−H bond of the methyl group on the C5 ring will be activated by this active "naked" tantalum center with high positive charge. Complex **6** is finally formed with the formation of $HN(SiMe_3)_2$.

With the existence of the other phosphorus ylide molecules, the coordination of the ylide shields the naked metal center. This makes it impossible for the positive tantalum to attack the C−H bonds of the methyl group on the C5 ring. Then the whole transformation is a transylidation reaction with the formation of final carbyne compound **5** (Scheme 3).

The overall reaction can be expressed as in eq 7.



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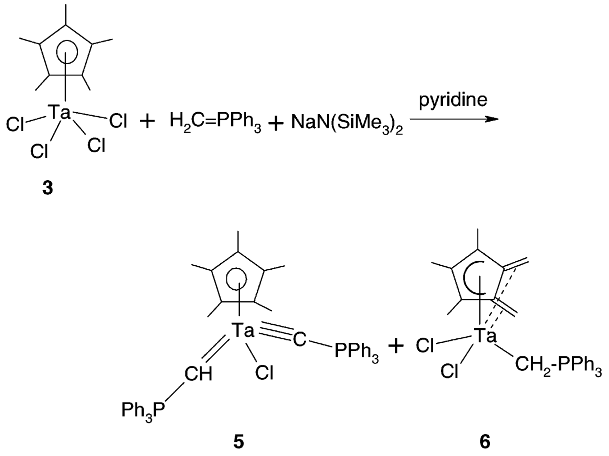
Influence of the Coordinative Base Pyridine on the Selectivity. In order to confirm the reaction mechanism (Scheme 3), a strong base, pyridine, with coordinative activity, was added to the reaction system (eq 8). As expected, the coordination of pyridine blocked the attack of the tantalum center on the methyl group on the pentamethylcyclopentadienyl ring. In this case under the same reaction conditions, the *in situ* ^{31}P spectrum indicates the existence of **5** and **6** with a ratio of 1:1.



(8)

Conclusions

Different bases and phosphorus ylide have a synergistic effect on the regioselective deprotonation of the phosphorus ylide adduct $Cp^*TaCl_4(CH_2{=}PPh_3)$ **4**. The acidity of the methylene hydrogen atoms in complex $[Cp^*TaCl_4(CH_2{=}PPh_3)]$, **4**, is weaker than those in complex $[CpTaCl_4(CH_2{=}PPh_3)]$. Under the same conditions complex **4** cannot transylidate. With the strong, but weakly coordinating base bis(trimethylsilyl)amide, a double deprotonation, i.e., a metal-induced C−H activation, of two methyl groups on the pentamethylcyclopentadienyl ring occurs, and the η^5-pentamethylcyclopantadienyl group is converted to an η^3-ally-η^4-butadiene ligand. Only when elimination of three chloride ligands is compensated by at least three coordinating ylide molecules can the strong base bis(trimethylsilyl)amide selectively deprotonate in a Ta−CH position in the phosphrous ylide adduct.

Experimental Section

General Procedures and Materials. Standard vacuum techniques were used in manipulations of volatile and air-sensitive materials. Cp*$TaCl_4$ **3**[13] and $H_2C{=}PPh_3$[14] were synthesized according to literature procedures. NMR spectra were recorded using a Bruker Avance 300 MHz spectrometer. ^{13}C and ^{31}P NMR resonances were obtained with broad-band proton decoupling.

Synthesis of 5. Method a. To a suspension of 1.23 g (2.68 mmol) of Cp*$TaCl_4$ **3** and 1.48 g (5.36 mmol) of $H_2C{=}PPh_3$ in 60 mL of toluene was added dropwise 1.34 g (8.04 mmol) of $LiN(SiMe_3)_2$ dissolved in 20 mL of toluene with stirring at 0 °C. The reaction mixture immediately changed from yellow to brown. After 3 h at room temperature the reaction solution was filtered. The solid residue was dried and extracted with pentane and diethyl ether, respectively. Complex **5** as an orange powder and complex **6** as red crystals were obtained in yields of 28% (0.68 g) and 26% (0.49 g), respectively.

Method b. Cp*$TaCl_4$ **3** (1.23 g, 2.68 mmol) and 2.22 g (8.04 mmol) of $H_2C{=}PPh_3$, as well as 1.34 g (8.04 mmol) of $LiN(SiMe_3)_2$, were used under the same reaction conditions and with the same workup as in method a. Only complex **5** was obtained in 52% yield (1.26 g).

Method c. Cp*$TaCl_4$ **3** (1.23 g, 2.68 mmol) and 2.22 g (8.04 mmol) of $H_2C{=}PPh_3$, as well as 1.47 g (8.04 mmol) of $NaN(SiMe_3)_2$, were used under the same reaction conditions and with the same workup as in method a. Complex **5** was obtained in 45% yield (1.10 g). Anal. Calcd for $C_{48}H_{46}ClP_2Ta$ (901.7 g/mol)%) **5**: C 63.94, H 5.14. Found: C 63.69, H 5.32. ^1H NMR (300.1 MHz, C_6D_6, 300 K): δ 2.31(s, 15H, CCH_3, 4.72 (t′, $|^2J(PH) + {}^4J(PH)| = 3.0$ Hz, Ta$C\mathit{H}$P), 7.07−8.09 (m, 30H, PC_6H_5). ^{13}C NMR (75.5 MHz, C6D6, 300 K): δ 11.1 (s,$\mathit{C}H_3$), 113.1 (s,$C_5(C\mathit{H}_3)_5$), 117.6 (d,$^1J(PC) = 46.1$ Hz), 128.5 (d,$^4J(PC) = 2.3$ Hz), 128.8 (d,$^4J(PC) = 2.3$ Hz), 131.9 (d, $^3J(PC) = 9.8$ Hz), 132.7 (d, $^3J(PC) = 9.1$ Hz), 134.9 (d, $^1J(PC) = 83.8$ Hz), 134.1 (d, $^1J(PC) = 83.1$ Hz), 198.6 (t, $|^1J(PC) + {}^4J(PC)| = 7.5$ Hz,Ta*C*P). ^{31}P NMR (121.5 MHz, C_6D_6, 300 K): δ 22.2 (d, $^4J(PP) = 5.2$ Hz, 1P, TaCH*P*), −30.0(d, $^4J(PP) = 5.2$ Hz, 1P, TaC*P*).

Synthesis of 6. Cp*$TaCl_4$ (1.31 g, 2.84 mmol) was dissolved in 50 mL of toluene, and 0.79 g (2.84 mmol) of $Ph_3P{=}CH_2$ in 20 mL of toluene was added dropwise with stirring at 0 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 4 h. During this period, the reaction mixture turned orange in color. $NaN(SiMe_3)_2$ (1.14 g, 5.72 mmol) in 10 mL of toluene was added dropwise at −80 °C to the above mixture with the color rapidly turning to red. The reaction mixture was allowed to warm to ambient temperature and stirred for 2 h. Evaporation of the filtrate under vacuum followed by washing with pentane resulted in a red powder, which was crystallized from diethyl ether at −30 °C. Complex **6** was obtained as red cubic crystals suitable for X-ray diffraction. Yield: 1.20 g (60.0%). Anal. Calcd for $C_{29}H_{30}TaPCl_2$ (661.38 g/mol)%) **6**: C 52.67, H 4.57. Found: C 52.48, H 4.73. ^1H NMR (300.1 MHz, C_6D_6, 300 K): δ 0.74 (d, $^2J(HH) = 5.5$ Hz, 2H, $C{=}CH_2$), 0.86 (d, $^2J(HH) = 5.5$ Hz, 2H, $C{=}CH_2$), 1.85 (s, 3H, $\mathit{C}H_3$), 2.16 (s, 6H, $\mathit{C}H_3$), 3.16 (d, $^2J(PH) = 16.5$ Hz, 2H, $TaC\mathit{H}_2$-PPh_3), 6.85−7.62 (m, 15 H, $PC_6\mathit{H}_5$). ^{13}C NMR (75.5 MHz, C_6D_6, 300 K): δ 10.2 (s, $\mathit{C}H_3$), 10.4 (s, $\mathit{C}H_3$), 18.7 (d, $^1J(PC) = 25.0$ Hz, $Ta\mathit{C}H_2P$), 64.6 (s, $C{=}\mathit{C}H_2$), 64.7 (s, $C{=}\mathit{C}H_2$), 127.0 (s, C-CH_3), 128.7 (d, $^3J(PC) = 11.6$ Hz, Ph-C_{meta}), 131.0 (s, C-CH_3), 132.1 (d, $^4J(PC) = 2.6$ Hz, Ph-C_{para}), 133.8 (d, $^4J(PC) = 9.7$ Hz, Ph-C_{ortho}). ^{31}P NMR (121.5 MHz, C_6D_6, 300 K): δ 35.2 (s, $TaCH_2\mathit{P}Ph_3$).

Crystallographic data for (6 + Et_2O): $C_{33}H_{40}Cl_2OPTa$, M_r = 735.47, crystal dimensions 0.48 × 0.27 × 0.27 mm, monoclinic, space group $P2_1/n$, $a = 11.6458(5)$ Å, $b = 13.1279(5)$ Å, $c = 20.9329(10)$ Å, $\beta = 96.311(6)°$, $V = 3180.9(2)$ Å^3, $T = 193(2)$ K, $Z = 4$, $D_c = 1.536$ g cm^{-3}, $\mu = 3.697$ mm^{-1}. A total of 24 697 reflections were collected, 6195 unique ($R_{int} = 0.0635$), $\theta_{max} = 25.95°$, semiempirical absorption correction. R1 = 0.0397 (for 4741 reflections with $I > 2\sigma(I)$), wR2 = 0.0874 (all data). The structure was solved by direct methods and refined with full-matrix least-squares on all F^2 (SHELXL-97) with non-hydrogen atoms anisotropic.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-616486 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Tables containing full X-ray crystallographic data for **4**. This materials is available free of charge via the Internet at http://pubs.acs.org.

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