Tantalum and Titanium Alkylidene Complexes Bearing Phosphinoalkoxide Ligands. Reversible Ortho-Metalation of a Titanium Alkylidene

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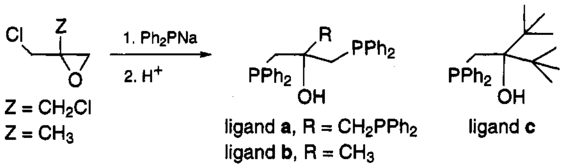
We have prepared dineopentyltantalum and -titanium complexes with phosphinoalkoxide ligands. It appears that the corresponding alkylidene complexes are readily formed by expulsion of neopentane. The molecular structure of one of the tantalum complexes was determined by X-ray crystal structure analysis. Crystal data: [TaCl$_2$(CHMe$_3$){OCMe(CH$_2$PPh$_2$)$_2$}] space group = $P2_1/n$ (No. 14), a = 9.021(3) Å, b = 20.333(6) Å, c = 17.892(5) Å, β = 102.95(2)°, Z = 4, N_o = 4981, R = 0.045. The titanium alkylidene complexes react with the ligand backbone by addition of a phenyl CH fragment across the titanium−carbon double bond leading to a complex with a metalated phenyl moiety and a neopentyl group. Interestingly, the addition reaction is reversible. The structure of metalation product was determined by X-ray crystal structure analysis and NMR spectroscopy. Crystal data: [Ti(η^5-C$_5$H$_5$)(CH$_2$CMe$_3$)(OC^{t}BuCH$_2$PPh-o-C$_6$H$_4$) space group = $C2$ (No. 5), a = 28.759(9) Å, b = 8.767(2) Å, c = 11.722(3) Å, β = 98.67(3)°, Z = 4, R = 0.037.

Introduction

Currently, there is great interest in ligands that may replace cyclopentadienyl ligands in early transition metal chemistry and catalysis. It is expected that this may lead to novel catalytic reactions. Recently many interesting studies have dealt with early transition metal complexes bearing alkoxide ligands.[1] Lappert[2] and Wolczanski[3] have reported on complexes with phosphinoalkoxide ligands. We have considered such ligands for the synthesis of alkylidenes from the corresponding dialkyl complexes. When the alkylidene is formed, it is stabilized by intramolecular coordination of the phosphine moiety. Alkylidene complexes of the early transition metals are important intermediates in the catalytic conversion of olefins (polymerization, dimerization, metathesis, etc.).[4]

Results and Discussion

The di- and triphosphino alcohols **a** and **b** were prepared from the corresponding (chloromethyl)oxiranes and sodium diphenylphosphide by substitution of the chlorine atom(s) and nucleophilic ring-opening of the epoxide. Ligand **c** (see below) was prepared according to Lappert.[2] Reaction of the alcohol **b** with a stoichiometric amount of butyllithium gives an impure alkoxide, probably due to the formation of butyllithium−lithium alkoxide complexes. The corresponding sodium alkoxide was prepared by reaction of the alcohol with sodium hydride in THF in good yield. We have met no problems in the reaction of the more bulky ligands **a** and **c** with butyllithium.



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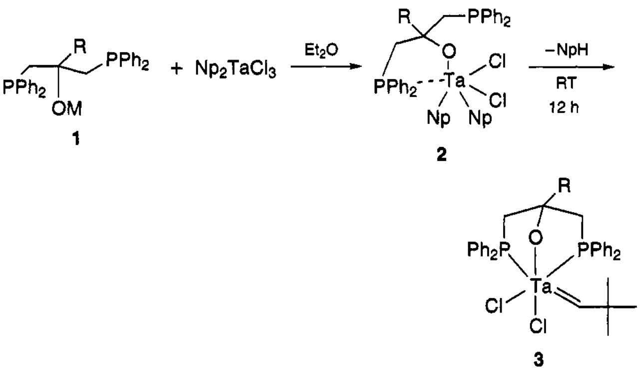
Tantalum Complexes. Reaction of 1 equiv of phosphinoalkoxide **1** with dineopentyltantalum trichloride in diethyl ether leads to replacement of one of the chlorine atoms and to formation of the corresponding tantalum alkoxide complexes **2**. The ^{31}P spectrum shows a broad signal at high field (close to the broad resonance of the alkali metal alkoxide). The broadening is probably caused by an exchange process between uncoordinated phosphorus atoms and a phosphorus atom which has a (weak) interaction with the metal atom. The proton spectra also show broadened signals for the neopentyl resonances. In solution, neopentane is slowly evolved from the complex, and after one night at room temperature all of **2** is converted into the alkylidene species **3**. The presence of the alkylidene moiety is clearly indicated by the typical resonances of the CH fragment in the NMR spectra (^1H 7.7 ppm, ^{13}C 275 ppm) and was confirmed by an X-ray analysis of **3b**. The value of the $^1J(^1H^{13}C)$ coupling constant (ca. 100 Hz) may indicate an agostic interaction between the hydrogen atom and the metal atom (i.e. coordination of the C−H bond). Two phosphorus atoms are coordinated to the metal atom.[5] These atoms are chemically inequivalent, and the large difference in the respective chemical shifts suggests that the coordinated phosphorus atom with the high-field resonance is placed trans to the alkylidene moiety in an octahedral complex as shown below. The orange alkylidene complexes are thermally stable and were isolated in a good yield.



a, R = CH$_2$PPh$_2$, M = Li; **b**, R = CH$_3$, M = Na

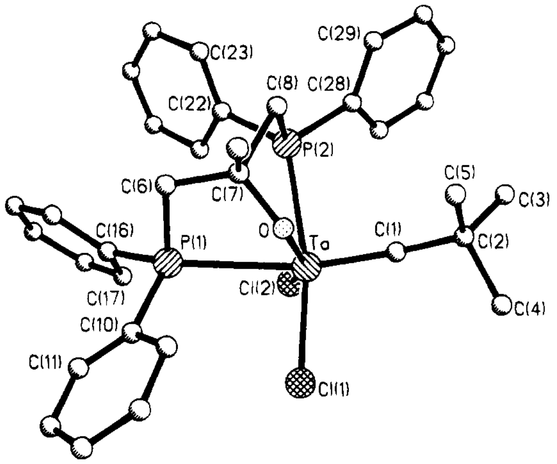


Figure 1. Molecular structure of **3b** showing full atom labeling scheme. Hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3b

Ta−Cl(1)	2.405(2)	Ta−Cl(2)	2.380(2)	Ta−P(1)	2.855(2)
Ta−P(2)	2.651(2)	Ta−O	1.901(4)	Ta−C(1)	1.932(7)
C(1)−C(2)	1.489(10)				

Cl(1)−Ta−Cl(2)	95.6(1)	Cl(1)−Ta−P(1)	86.8(1)
Cl(2)−Ta−P(1)	91.1(1)	Cl(1)−Ta−P(2)	167.9(1)
Cl(2)−Ta−P(2)	86.9(1)	P(1)−Ta−P(2)	81.3(1)
Cl(1)−Ta−O	98.6(1)	Cl(2)−Ta−O	153.0(1)
P(1)−Ta−O	67.0(1)	P(2)−Ta−O	74.7(1)
Cl(1)−Ta−C(1)	101.3(2)	Cl(2)−Ta−C(1)	101.6(2)
P(1)−Ta−C(1)	164.0(2)	P(2)−Ta−C(1)	89.7(2)
O−Ta−C(1)	98.0(2)	Ta−P(1)−C(6)	94.5(2)
Ta−C(1)−C(2)	152.7(5)	C(1)−C(2)−C(3)	111.5(5)
C(1)−C(2)−C(4)	107.7(6)	C(3)−C(2)−C(4)	108.8(6)
C(1)−C(2)−C(5)	110.3(6)	C(3)−C(2)−C(5)	108.9(6)
C(4)−C(2)−C(5)	109.7(6)	P(1)−C(6)−C(7)	111.1(4)

X-ray Structure of 3b. A perspective view of the molecular structure is given in Figure 1. Selected bond lengths and angles are given in Table 1. The crystal structure consists of isolated molecules separated by normal van der Waals contacts. The Ta−C(1) bond is similar to those in other Ta−neopentylidene complexes (1.932(7) Å, cf. median Ta−C for terminal alkylidenes of 1.938 Å quoted in ref 6. The Ta−O−C(7) angle is 130.3(2)°), consistent with approximate sp^2 hybridization of the oxygen atom. The Ta⋯H(1) distance and Ta−C−H(1) angle for the neopentylidene ligand indicate the *possibility* of a weak attractive (α-agostic) interaction between Ta and H(1) (Ta⋯H(1) 2.47(8), C(1)−H(1) 1.14(9) Å, Ta−C(1)−H(1) 104(5)°) but are not sufficiently accurate to permit detailed analysis of the interaction. These features and the Ta−C(1)−C(2) angle of 152.7(5)° are reminiscent of similar distortions observed in tantalum and tungsten neopentyl complexes in the work of Schrock and co-workers. The strong *trans* influence of the neopentylidene ligand may be seen in the wide disparity between the Ta−P distances (Ta−P(1) *trans* to C(1) 2.855(2) Å, Ta−P(2) *trans* to Cl(1) 2.651(2) Å) although both these distances appear longer than typical trialkylphosphine−Ta lengths (average 2.611 Å for Ta−PMe$_3$).[6] Eisenstein and co-workers (see ref 7 and references therein) have pointed out the possibility of α-agostic interactions and distortions from regular octahedral geometry in octahedral or *pseudo*-octahedral

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[5] At −60 °C all three lines of the $^{31}P-\{^1H\}$ spectrum of **3a** are sharp. A broadening of the central signal (in the $-5 > \delta > -10$ area) is observed in the temperature region of −40 to 20 °C. The signal sharpens again at 35 °C. Simultaneously, the position of this signal shifts to higher field with an increase in the temperature (−9.3 ppm at 35 °C, −3.3 ppm at −60 °C). In this entire temperature region, coupling between the two phosphorus atoms which are bound to the tantalum atom is maintained. The value of the $^2J(^{31}P^{31}P)$ coupling constant varies somewhat with the temperature (26 Hz at 35 °C and 29.7 Hz at −60 °C). The line broadening is not dependent on the concentration of the complex. We have observed almost identical spectra in the solvents CD$_2$Cl$_2$ and toluene-d_8. Compound **3b** shows a similar behavior. The value of ^1J(CH) of the alkylidene carbon atom of **3b** does not depend of the temperature (96 Hz at −90 °C and 98 Hz at 25 °C in CD$_2$Cl$_2$). This indicates that there is no major change in either the geometry or the putative agostic bonding of the alkylidene moiety. This broadening may be related to a restricted rotation of the alkylidene. A process where other rotamers "grow in" at higher temperature while the exchange between these rotamers is slow in the region where the signal is broadened may be compatible with the observed spectra.[1b] (a) Guggenberger, L. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6578. (b) Kress, J.; Osborn, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 3953. (c) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

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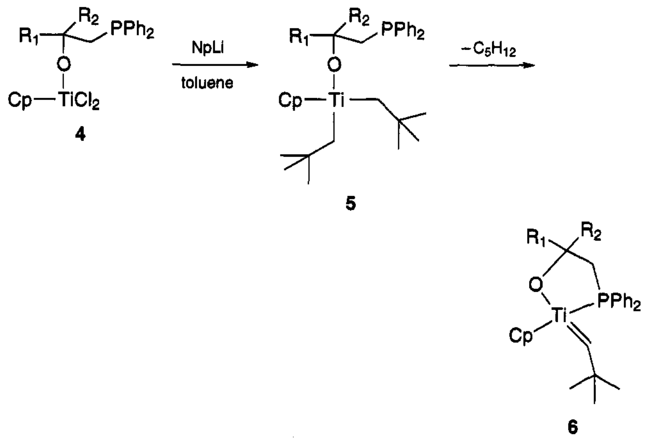
d^0 species such as **3b**. The deviation of the coordination geometry from ideal bond angles at the metal may be clearly observed in **3b**. Thus the largest angular distortions are associated with the oxygen atom of the chelating alkoxydiphosphine ligand, whose restricted bite is presumably responsible in part for these distortions (O–Ta–P(1) 67.0(1)°, O–Ta–P(2) 74.7(1)°, O–Ta–P(1) 98.0(2)°, O–Ta–Cl(2) 153.0(1)°). However, the C–Ta–Cl angles are also highly distorted for reasons which cannot be directly related to chelate ring size (101.3(2)°, 101.6(2)°).

Titanium Complexes. Because the chemistry with tantalum proceeds smoothly, we have turned to a metal where the classical route via α-H abstraction has failed so far. There seems to be consensus that the direct route via a dineopentyl compound cannot be used to prepare dicyclopentadienyltitanium neopentylidenes. This is because the synthesis of the dineopentyl compound from the corresponding dichloride fails. Mononuclear titanium alkylidene complexes with two cyclopentadienyl ligands can exist, however. They have become available by a other routes.[8,9]

Titanium complexes **4a–c** with one Cp, one phosphinoalkoxide ligand, and two chlorine atoms were readily prepared from $CpTiCl_3$. We have used the sodium (**b**) or lithium alkoxide (**a**, **c**), which were prepared from the corresponding alcohols.

We have found that the chlorine atoms of **4a** and **4c** can be replaced with neopentyl groups in a stepwise process. Reaction with a substoichiometric amount of neopentyllithium leads to the mononeopentyl complex. The dineopentyltitanium compounds **5a** and **5c** can be prepared by reaction of the chloride with 2 equiv of neopentyllithium. With the less bulky phosphinoalkoxide (**b**), we obtained a complex mixture and not the dineopentyl complex. A transmetalation reaction occurs in which the alkoxide ligand is removed from the titanium atom. With (trimethylsilyl)methyllithium we obtain the lithium alkoxide and the stable compound $CpTi[CH_2Si(CH_3)_3]_3$. The alkylating reagent seems to bind to the alkoxide moiety by coordination of the metal atom to the oxygen atom. This coordination makes the alkoxide a better leaving group and the lithium or sodium alkoxide of **b** is formed slowly, together with a dialkylchlorotitanium complex which reacts further. We conclude that the alkoxide moiety has to be bulky in order to allow for the synthesis of the dineopentyltitanium complex.

Warming of **5a** to 60 °C leads to formation of the alkylidene complex **6a** and neopentane. No phosphorus resonance is observed, due to strong broadening of the signal. This is probably caused by an exchange process between bonded and free phosphine moieties. When an excess of trimethylphosphine (ca. 5 equiv) is added to the solution, the diphenylphosphine moiety is displaced from the metal by the more powerful donor trimethylphosphine. A sharp signal is observed at −18.4 ppm for all three uncoordinated diphenylphosphine moieties. A very broad resonance is observed for trimethylphosphine at −55 ppm due to an exchange between free and uncoordinated trimethylphosphine. The alkylidene **6a** is stable enough to allow characterization by NMR spectroscopy ($\delta(^1H)$ =CH 10.92). Unfortunately, the alkylidene was not isolated in a pure state due to a sequential reaction (see below). Addition of trimethylphosphine leads to a suppression of this reaction. Thus, we were not able to isolate the alkylidene **6a** in a pure state but the result clearly shows that synthesis of an alkylidene at a titanium center by the classical route via the dineopentyl complex is possible.



(**a**) $R_1 = R_2 = CH_2PPh_2$; (**b**) $R_1 = CH_3$, $R_2 = CH_2PPh_2$; (**c**) $R_1 = R_2 = t\text{-}Bu$

Alkylidene complex **6c** ($\delta(^1H)$ =CH 12.4; $\delta(^{13}C)$ =CH 287.3 ppm, $^1J(^1H^{13}C)$ 92 Hz) is formed at mild conditions (ca. 5 °C) from dineopentyl compound **5c**. In addition, a product (**7**) with a metalated phenyl group (see below) is obtained (ratio ca. 1:1). Eventually, both compounds disappear simultaneously at 50 °C and rearrange to a single product (**8**) which was characterized by X-ray diffraction. The structure is discussed in the next paragraph.

We were able to determine some essential NMR data of compound **7** by analysis of the mixture. It appears that the ^{13}C chemical shifts are very similar to those of **8**. Both compounds clearly show a resonance for a metalated phenyl carbon atom, a Cp moiety, a neopentyl group, etc. Because of the great similarity in the chemical shifts of the two compounds, we conclude that **7** and **8** are (diastereo)isomers. The structure of **7** could be assigned on the basis of phosphorus couplings. According to the X-ray analysis of compound **8**, the lone pair of the phosphorus atom is directed toward the Cp group. Those carbons couple with phosphorus whereas they do not in compound **7**. In compound **8** we observe no coupling of the CH_2 hydrogens of the neopentyl group with phosphorus. Its CH_2 carbon atom couples weakly (2.9 Hz). In compound **7**, however, one of the CH_2 hydrogens couples with phosphorus and also the carbon atom shows appreciable coupling (22 Hz). These coupling patterns point to a structure for the metalation product (**7**) in which the lone pair of the phosphorus atom is directed toward the CH_2 of the neopentyl group. The signals due to the two *tert*-butyl groups attached to the ligand in **8** are very broad when measured in benzene-d_6. In CD_2Cl_2 only one of these groups leads to a broad resonance at room temperature. We have found that rotation of the *tert*-butyl group is very slow on the NMR time scale at −60 °C; three separate resonances for the methyl groups are obtained. Meanwhile the resonance of the second *tert*-butyl group of the ligand moiety starts to broaden. Apparently, rotation

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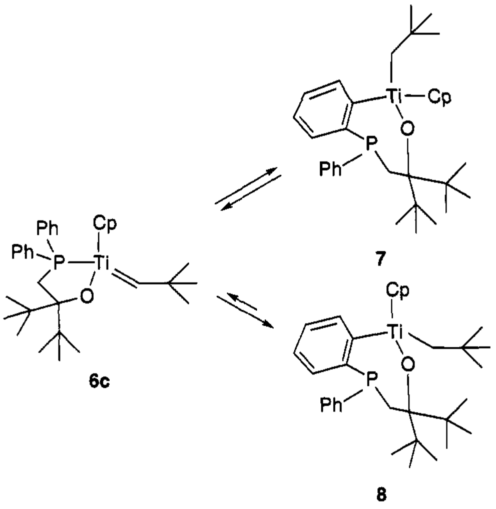

of the *tert*-butyl groups is restricted in **8** due to steric congestion. The methyl signal of the neopentyl group is sharp down to −80 °C. By contrast, the ^1H signals of **7** are sharp; thus in this molecule the *tert*-butyl groups of the alkoxide ligand rotate freely on the NMR time scale. We cannot explain why the uncongested compound **7**, which is formed as a kinetic product, rearranges to the congested compound **8**, which is the apparent thermodynamic product.

We would like to draw attention to the $^2J(^{13}C^{31}P)$ coupling constants of the metalated phenyl groups in **7** and **8**. This value is much larger than the value of ca. 20 Hz which is usually observed in phenylphosphines. Recently, Harder[10] has reported a very large value (ca. 100 Hz) for this constant in triphenylphosphine which is lithiated at the ortho position. There appears to be a relation between the electronegativity of the metal atom and the value of this coupling constant. Strongly electropositive elements will lead to a large value and strongly electronegative elements will lead to a relatively small value. Our finding of a moderately large value for this constant for a titanated phenylphosphine nicely fits into the theory presented by Harder.

Very fortunately, we were once able to isolate one crystal of pure **7**. This was dissolved in C_6D_6, and NMR spectra were recorded at 7 °C immediately after dissolution of the crystal and after allowing the solution to stand overnight at 7 °C. It appears that overnight the alkylidene **6c** was formed (ratio **6c**:**7** = ca. 1:1). This suggests that the metalation reaction leading to **7** is reversible and that **6c** and **7** are in a true dynamic equilibrium (K = ca. 1).

We have done some preliminary reactions with ethene. Interestingly, both metalated compounds react with ethene, forming a product which is also obtained by reaction of the alkylidene **6c** at a low temperature (where the metalated products are not converted). The reaction compound contains two phenyl groups and does not contain a C_6H_4 fragment that could be the result of an insertion of ethene in the titanium−aryl bond. This would indicate that the addition reaction that leads to **8** is also reversible.

At this stage in our investigation we have again inspected the spectra of the "decomposition" product of the alkylidene **6a**. The data strongly suggest that this product also is the result of a rearrangement and contains a metalated phenyl group. We propose a structure similar to **7** or **8**.

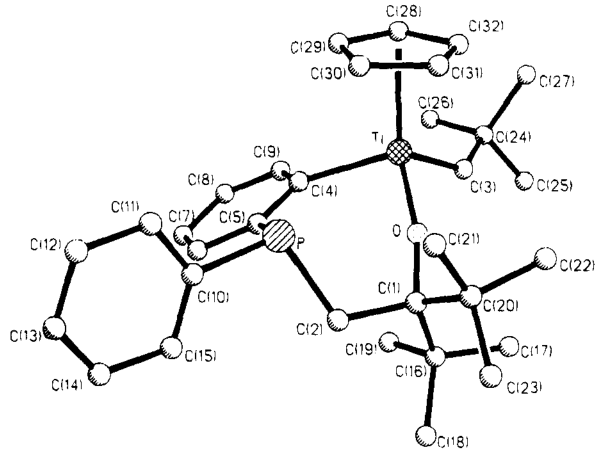

Figure 2. Molecular structure of **8** showing full labeling scheme. Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 8

Ti−O	1.787(2)	Ti−C(3)	2.120(4)	Ti−C(4)	2.149(4)
Ti−C(28)	2.425(4)	Ti−C(29)	2.399(3)	Ti−C(30)	2.363(4)
Ti−C(31)	2.355(4)	Ti−C(32)	2.398(4)	P−C(2)	1.861(3)
C(1)−C(2)	1.563(4)	C(3)−C(24)	1.543(6)	O−C(1)	1.435(4)

O−Ti−C(3)	96.0(1)	O−Ti−C(4)	93.8(1)
C(3)−Ti−C(4)	109.4(2)	O−Ti−C(28)	158.4(1)
C(3)−Ti−C(28)	90.9(1)	C(4)−Ti−C(28)	103.2(1)
O−Ti−C(29)	141.1(1)	C(3)−Ti−C(29)	122.3(1)
C(4)−Ti−C(29)	80.9(1)	C(28)−Ti−C(29)	33.7(1)
O−Ti−C(30)	109.1(1)	C(3)−Ti−C(30)	143.8(2)
C(4)−Ti−C(30)	94.9(1)	C(28)−Ti−C(30)	56.8(2)
C(29)−Ti−C(30)	34.5(1)	O−Ti−C(30)	102.4(1)
C(3)−Ti−C(31)	115.6(2)	C(4)−Ti−C(31)	129.8(1)
C(28)−Ti−C(31)	56.3(2)	C(29)−Ti−C(31)	56.9(1)
C(30)−Ti−C(31)	34.9(1)	O−Ti−C(32)	125.8(1)
C(3)−Ti−C(32)	87.1(1)	C(4)−Ti−C(32)	135.9(1)
C(28)−Ti−C(32)	33.9(1)	C(29)−Ti−C(32)	56.5(1)
C(30)−Ti−C(32)	57.2(1)	C(31)−Ti−C(32)	33.8(2)
Ti−O−C(1)	167.7(2)	Ti−C(3)−C(24)	140.7(3)

X-ray Structure of 8. Perspective views of the molecular structure are given in Figure 2. Selected bond lengths and angles are given in Table 2. The crystal structure consists of isolated molecules separated by normal van der Waals contacts. The molecule consists of a titanium atom which is ligated by an η^5-cyclopentadienyl ligand and further bonded to a neopentyl ligand; finally the ortho-metalated ligand ($OC^tBu_2CH_2PPh$-*o*-C_6H_4) chelates the titanium binding through alkoxy oxygen and a C−Ti σ-bond. The latter ligand is formally the product of addition of the ortho-CH of the alkoxyphosphine ligand across the Ti=$CHCMe_3$ bond accompanied by uncoupling of the Ti−P bond leading to the observed ($OO^tBu_2CH_2PPh$-*o*-C_6H_4)CH_2CMe_3 stoichiometry. The Ti−O bond is rather short (1.787(2) Å, cf. average Ti−O for terminal alkoxides of 1.847 Å quoted in ref 6, and the Ti−O−C angle rather large (167.7(2)°), consistent with considerable Ti−O π-bonding and approximately sp hybridization of the oxygen atom. The two Ti−C σ-bond distances are 2.120(4) (for the neopentyl carbon C(3)) and 2.149(4) Å (for the aryl carbon C(4)). It is notable that the bond length for the sp^3 carbon is less than that for the sp^2 carbon, the opposite of what would be expected for simple σ-bonds. This may be due to a degree of multiple

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bonding arising as part of an α-agostic interaction involving the neopentyl group. The Ti⋯H distance and Ti–C–H angles for the neopentyl ligand indicate the *possibility* of a weak attractive (α-agostic) interaction between Ti and H(3A) and H(3B) (Ti⋯H(3A) 2.40(7) Å, Ti–H(3B) 2.43(7) Å, Ti–C(3)–H 93(4)°, and 100(4)°) but are not sufficiently accurate to permit detailed analysis of the interaction. These features and the Ti–C(3)–C(24) angle of 140.7(3)° are reminiscent of similar distortions observed in tantalum and tungsten neopentyl complexes in the work of Schrock and co-workers. Eisenstein and co-workers (see ref 7 and references therein) have pointed out the possibility of α-agostic interactions and distortions between Ti and alkyl ligands in octahedral or *pseudo*-octahedral d^0 species such as **8**.

Concluding Remarks

We have shown that tantalum alkylidenes bearing a phosphinoalkoxide ligand are readily formed. We have also shown that titanium dineopentyl complexes can be obtained by reaction between neopentyllithium and a tetravalent cyclopentadienyltitanium dichloride which bears a phosphinoalkoxide ligand. The ligand should bear bulky groups adjacent to the oxygen atom in order to allow for the synthesis of the dineopentyl complex. The dineopentyltitanium compounds readily form an alkylidene complex by expulsion of neopentane; simultaneously the phosphine atom of the ligand becomes coordinated to the metal, thus forming a bidentate system. The alkylidenes react with the phenyl groups of the phosphine moiety. Similar addition reactions have been described for tungsten alkylidene[1b] and alkylidyne[1c] complexes which bear alkoxy ligands. This process may very well involve an agostic interaction of the ortho hydrogen atom with the metal center before the addition process takes place. At this time, however, we do not have a detailed insight into the mechanism of this reaction. Interestingly, the metalation process is reversible. It does, however, complicate a study of the reactions of the alkylidene with olefins. Therefore, we will further adapt the ligand structure by replacing all the phenyl groups with alkyl groups. In this way we hope to avoid the metalation reaction.

Experimental Section

General Information. All operations with air-sensitive materials were performed either in an argon atmosphere using Schlenk techniques or under nitrogen in a glovebox. THF, hexane, and ether were freshly distilled from sodium/benzophenone. Ammonia was distilled from a cylinder. All materials that are not mentioned in the Experimental were prepared by well-established literature methods or were obtained commercially. Ligand **c** was prepared according to Lappert.[2] The NMR data were obtained with Varian 200 and 300 MHz instruments. The data are given in the tables and with the experimental procedures. Coupling constants with phosphorus are given in parentheses; $^1H^{13}C$ couplings are given in square brackets.

X-ray Structure Analysis. Single crystals of **3b** and **8** were mounted in a thin-walled glass capillary under N_2 and held in place with silicone grease. All diffraction measurements were made at low temperature (200 K) on a Nicolet P3m diffractometer fitted with an LT-1 crystal cooling device, using graphite-monochromated Mo Kα X-radiation. The structures were solved by Patterson and Fourier methods. All non-hydrogen atoms were assigned anisotropic displacement parameters and all hydrogen atoms fixed isotropic displacement parameters. All non-hydrogen atoms and the hydrogen atoms H(1) of **3b** and H(3A) and H(3B) of **8** (which were located in a difference Fourier synthesis) were refined without positional constraints. All other hydrogen atoms were constrained to idealized geometries (C–H 0.96 Å, H–C–H 109.5°). All calculations were carried out on a Nicolet R3m/V structure determination system using programs of the SHELXTL-PLUS package.[11] Complex neutral-atom scattering factors were taken from ref 12. Details of crystallographic data are given in Table 3.

Table 3. Crystallographic Data for 3b and 8

	3b	8
chem formula	$C_{33}H_{37}Cl_2OP_2Ta$	$C_{32}H_{45}OPTi$
M_r	763.46	524.59
space group	$P2_1/n$ (No. 14)	$C2$ (No. 5)
a, Å	9.021(3)	28.759(9)
b, Å	20.333(6)	8.757(2)
c, Å	17.892(5)	11.722(3)
β, deg	102.95(2)	98.67(3)
U, Å^3	3197.5(15)	2918.3(14)
D_x, g cm^{-1}	1.59	1.19
Z	4	4
λ, Å	0.71069	0.71069
μ(M0 Kα), cm^{-1}	36.9	3.6
spec size, mm	0.45 × 0.55 × 0.7	0.65 × 0.55 × 0.6
$2\theta_{max}$, deg	50	50
N_v	355	321
N_o	4981	2584
R	0.045	0.037
wR	0.055	0.047
S^a	1.86	1.66

[a] $R = \Sigma|\Delta|/\Sigma|F_o|$; $wR = [\Sigma w\Delta^2/\Sigma wF_o^2]^{1/2}$; $S = [\Sigma w\Delta^2/(N_o - N_v)]^{1/2}$; $\Delta = |F_o| - |F_c|$.

3b. Unit cell dimensions were determined from 29 centerd reflections in the range $16.0 < 2\theta < 29.0°$. A total of 6441 diffracted intensities, including check reflections, were measured in a unique quadrant of reciprocal space for $4.0 < 2\theta < 50.0°$ by Wyckoff ω scans. Three check reflections (2,1,−11, 292, 5,3,−9) remeasured after every 100 ordinary data showed a decay of ca. 7% and variation of ±2% over the period of data collection; an appropriate correction was therefore applied. Of the 6225 intensity data (other than checks) collected, 5670 unique observations remained after averaging of duplicate and equivalent measurements ($R_{merg} = 0.047$) and deletion of systematic absences, of these, 4981 with $I > 2\sigma(I)$ were retained for use in structure solution and refinement. An absorption correction was applied on the basis of 392 azimuthal scan data; maximum and minimum transmission coefficients were 0.140 and 0.063, respectively. Lorentz and polarization corrections were applied. Full-matrix least-squares refinement of this model converged to final residual indices given in Table 3. Weights, w, were set equal to $[\sigma_c^2(F_o) + gF_o^2]^{-1}$, where $\sigma_c^2(F_o)$ is the variance in F_o due to counting statistics and $g = 0.0005$ was chosen to minimize the variation in S as a function of $|F_o|$. Final difference electron density maps showed no features outside the range +2.5 to −2.2 e Å^{-3}, the largest of these being close to (<1.2 Å) the tantalum atom. Atomic coordinates are listed in the supplementary material.

8. Unit cell dimensions were determined from 49 centered reflections in the range $17.0 < 2\theta < 32.0°$. A total of 3218 diffracted intensities, including check reflections, were measured in a unique quadrant of reciprocal space by Wyckoff ω scans. Three check reflections (10,6,1, $\overline{20}$,$\overline{2}$,1, 2,2,$\overline{7}$) remeasured after every 100 ordinary data showed no decay and

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(11) Sheldrick, G. M. SHELXTL-PLUS Rev. 4.2, Göttingen, FRG, 1990.

(12) *International Tables for X-ray crystallography*, Vol. IV; Birmingham: Kynoch Press, 1974.

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for 3b

atom	x	y	z	U_{eq}[a]
Ta	731(1)	763(1)	2816(1)	25(1)
Cl(1)	3372(2)	693(1)	3456(1)	43(1)
Cl(2)	1175(2)	929(1)	1568(1)	34(1)
P(1)	821(2)	−630(1)	2637(1)	28(1)
P(2)	−2162(2)	566(1)	2137(1)	24(1)
O	−110(4)	298(2)	3544(2)	28(1)
C(1)	233(7)	1643(3)	3087(4)	35(2)
C(2)	−216(7)	2132(3)	3616(4)	35(2)
C(3)	−1278(9)	2659(4)	3174(4)	50(3)
C(4)	1238(8)	2465(4)	4062(5)	51(3)
C(5)	−1016(10)	1789(4)	4173(5)	57(3)
C(6)	−913(7)	−782(3)	3006(4)	35(2)
C(7)	−1331(6)	−171(3)	3433(3)	29(2)
C(8)	−2736(6)	200(3)	2966(3)	30(2)
C(9)	−1639(8)	−362(4)	4217(4)	41(2)
C(10)	2350(7)	−1030(3)	3341(4)	33(2)
C(11)	3311(8)	−1485(4)	3132(4)	49(3)
C(12)	4538(10)	−1743(5)	3684(5)	66(3)
C(13)	4778(8)	−1531(4)	4431(4)	53(3)
C(14)	3829(8)	−1079(4)	4642(4)	50(3)
C(15)	2601(8)	−841(4)	4095(4)	45(2)
C(16)	639(7)	−1132(3)	1775(3)	30(2)
C(17)	1238(7)	−887(3)	1188(4)	34(2)
C(18)	1049(7)	−1220(3)	496(4)	36(2)
C(19)	259(8)	−1806(4)	400(4)	42(2)
C(20)	−304(8)	−2064(4)	995(4)	47(2)
C(21)	−118(8)	−1731(3)	1674(4)	42(2)
C(22)	−2866(7)	2(3)	1347(3)	26(2)
C(23)	−4295(7)	−313(3)	1272(4)	38(2)
C(24)	−4814(8)	−735(3)	672(4)	43(2)
C(25)	−3972(9)	−854(3)	130(4)	44(2)
C(26)	−2598(8)	−537(3)	193(4)	40(2)
C(27)	−2050(7)	−118(3)	797(3)	33(2)
C(28)	−3337(6)	1288(3)	1847(3)	25(2)
C(29)	−4728(7)	1392(3)	2039(4)	36(2)
C(30)	−5583(7)	1956(3)	1780(4)	41(2)
C(31)	−5060(8)	2400(3)	1330(4)	42(2)
C(32)	−3684(8)	2308(3)	1126(4)	41(2)
C(33)	−2817(7)	1757(3)	1386(3)	34(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

variation of $\pm 2\%$ over the period of data collection; an appropriate correction was therefore applied. Of the 3092 intensity data (other than checks) collected, 2748 unique observations remained after averaging of duplicate and equivalent measurements and deletion of systematic absences; of these, 2584 with $I > 2\sigma(I)$ were retained for use in structure solution and refinement. An absorption correction was applied on the basis of 159 azimuthal scan data; maximum and minimum transmission coefficients were 0.734 and 0.617, respectively. Lorentz and polarization corrections were applied.

The chirality of the crystal used was confirmed by an η refinement (η = 1.00(15)).[13] Full-matrix least-squares refinement of this model converged to final residual indices given in Table 1. Weights, w, were set equal to $[\sigma_c^2(F_o) + gF_o^2]^{-1}$, where $\sigma_c^2(F_o)$ is the variance in F_o due to counting statistics and g = 0.0005 was chosen to minimize the variation in S as a function of $|F_o|$. Final difference electron density maps showed no features outside the range +0.35 to −0.25 e Å^{-3}, the largest of these being close to the center of the P−C bonds. Atomic coordinates are given in the supplementary material.

1,3-Bis(diphenylphosphino)-2-hydroxy-2-((diphenylphosphino)methyl)propane (a). An epoxide was prepared from 2-chloro-3-(chloromethyl)-1-propene and 3-chloroperbenzoic acid in chloroform at 0 °C by the standard procedure. The crude product was purified by flash chromatography (silica 60, Merck, eluent hexane:CH_2Cl_2 1:1). In this way we obtained a number of fractions with fairly pure material which were used as such for the synthesis of the phosphino alcohol. Yield ca. 40% after chromatography.

Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for 8

atom	x	y	z	U_{eq}[a]
Ti	921(1)	0	2251(1)	22(1)
P	1162(1)	−1273(1)	−301(1)	24(1)
O	1483(1)	−751(3)	2069(2)	23(1)
C(1)	1897(1)	−1317(5)	1664(3)	23(1)
C(2)	1797(1)	−1325(5)	316(3)	26(1)
C(3)	1171(1)	1397(5)	3691(3)	31(1)
C(4)	856(1)	1347(5)	702(3)	26(1)
C(5)	1022(1)	778(5)	−287(3)	27(1)
C(6)	1033(2)	1733(5)	−1251(3)	35(1)
C(7)	880(2)	3232(5)	−1231(3)	42(1)
C(8)	709(2)	3794(6)	−271(3)	44(1)
C(9)	700(2)	2862(5)	681(3)	37(1)
C(10)	1199(1)	−1693(4)	−1824(3)	26(1)
C(11)	825(1)	−2510(5)	−2419(3)	33(1)
C(12)	829(2)	−2953(6)	−3569(3)	43(1)
C(13)	1207(2)	−2572(5)	−4105(3)	42(1)
C(14)	1576(2)	−1761(6)	−3534(3)	40(1)
C(15)	1573(1)	−1313(6)	−2389(3)	35(1)
C(16)	2301(1)	−108(5)	2050(3)	29(1)
C(17)	2437(1)	5(7)	3373(3)	40(1)
C(18)	2755(1)	−410(5)	1525(4)	40(1)
C(19)	2130(1)	1502(5)	1639(4)	37(1)
C(20)	1961(1)	−3019(5)	2146(3)	30(1)
C(21)	1571(1)	−4043(5)	1509(4)	39(1)
C(22)	1911(2)	−3121(6)	3432(3)	45(1)
C(23)	2431(1)	−3732(6)	1978(4)	41(1)
C(24)	989(1)	2505(5)	4547(3)	31(1)
C(25)	1421(2)	3200(6)	5304(4)	45(1)
C(26)	711(2)	3786(6)	3898(4)	52(2)
C(27)	697(2)	1709(6)	5349(3)	41(1)
C(28)	133(1)	43(6)	2748(3)	33(1)
C(29)	98(1)	−363(5)	1585(3)	34(1)
C(30)	331(1)	−1770(5)	1515(3)	38(1)
C(31)	508(1)	−2207(5)	2660(4)	37(1)
C(32)	389(1)	−1104(5)	3410(3)	34(1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

NMR ($CDCl_3$): ^{1}H, CH_AH_BCl 3.77 and 3.69, $J(H_AH_B)$ 20 Hz, CH_2O 2.95; ^{13}C, CH_2O 53.3, CO 58.2, CCl 44.6.

Triphenylphosphine (9.8 g, 37.4 mmol) was added to a solution of 1.72 g (74.8 mmol) of sodium in ca. 300 mL of liquid ammonia at −78 °C. The mixture was stirred at this temperature for ca. 1 h and subsequently 1.76 g (32.7 mmol) of ammonium chloride was added. After ca. 30 min a solution of 1.52 g (ca. 10.8 mmol) of fairly pure (90−95%) 1-chloro-2,3-epoxy-2-methylpropane in 30 mL of THF was added. No more dry ice was added to the cooling bath, and the ammonia was allowed to evaporate overnight. Volatiles were removed in vacuo, and to the residue were added water and dichloromethane. The organic layer was separated and filtered. Subsequently the solvent was removed, and to the residual oil was added ca. 20 mL of ethanol to induce crystallization. The white crystals, which contain a trace of diphenylphosphine oxide, were collected by filtration and dried in vacuo. Yield 3.35 g (ca. 50%). The mother liquor contains triphenylphosphine, diphenylphosphine, a monophosphine, a diphosphine, and some of the desired product.

NMR ($CDCl_3$): ^{1}H, CH_2 2.91 (d 2.6), OH 2.10 (q 1), ArH 7.0−7.55; ^{13}C, CH_2P 43.2 (16, −8) [128], CO 75.5 (q 13.8), i 139.0 (11), o 133.0 (20) [161], m 128.3 (6.9), p 128.4 [161], ^4J(PP) = 2.57; ^{31}P −25.7.

1,3-Bis(diphenylphosphino)-2-hydroxy-2-methylpropane (b). Triphenylphosphine (22.8 g, 86.95 mmol) was added to a solution of 4.0 g (174 mmol) of sodium in ca. 400 mL of liquid ammonia at −78 °C. The mixture was stirred at this temperature for ca. 45 min, and subsequently 4.2 g (78.5 mmol) of ammonium chloride was added. After ca. 30 min, a solution of 4.63 g (43.5 mmol) of 1-chloro-2,3-epoxy-2-methylpropane in 150 mL of THF was added. No more dry ice was added to

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(13) Rogers, D. *Acta Crystallogr. A* **1981**, *37*, 734.

the cooling bath, and the ammonia was allowed to evaporate overnight. Volatiles were removed in vacuo, and to the residue were added water and dichloromethane. The organic layer was separated and filtered. Subsequently the solvent was removed. The solid residue was washed with hexane. Yield 14 g (31.6 mmol, 72.7%).

NMR ($CDCl_3$): ^{1}H, CH_AH_BP 2.58 (2.8) and 2.67 (3), $J(H_AH_B)$ = 14.3, CH_3 1.37 (t 1), OH 2.23 (br), ArH 7.3−7.6; ^{13}C, CH_2P 44.85 (15.7, −7.8) [127], CO 73.2 (t 14.7), CH_3 30.8 (t 8.5) [129], i 140.3, o 128.6, m 128.6, p 128.50 and 128.53, $^4J(PP)$ = 3.7; ^{31}P −25.8.

Lithium 1-(Diphenylphosphino)-2-*tert*-butyl-3,3-dimethyl-2-butoxide (c·Li). A solution of butyllithium in hexane (1.6 M, 25.4 mmol) was added to a slurry of 8.65 g (25.3 mmol) of 1-(diphenylphosphino)-2-*tert*-butyl-3,3-dimethyl-2-butanol in hexane. After 2 h of stirring, the solid material was filtered, washed with hexane, and dried in vacuo. Yield 8.37 g (95%).

Tantalum Alkylidene 3b. To a solution of dineopentyltantalum trichloride (250 mg, 0.58 mmol) in ca. 10 mL of diethyl ether was added solid sodium alkoxide {$(Ph_2PCH_2)_2(CH_3)CONa$, 270 mg, 0.58 mmol}. After overnight stirring, 20 mL of pentane was added. The resulting precipitate was washed with pentane and dried in vacuo. The resulting material was extracted with dichloromethane, the solvent was removed, and the solid material was washed with pentane. Yield 350 mg (79%) of an orange powder. The orange crystals for the X-ray analysis were grown from a CH_2Cl_2/ether solution.

Anal. Calcd: C, 51.92; H, 4.88; Cl, 9.29; P, 8.11; Ta, 23.70. Found: C, 51.60; H, 4.78; Cl, 9.16; P, 7.95; Ta, 23.80.

NMR (CD_2Cl_2): ^{1}H, alkylidene, =CH 7.76 (2, 4), CH_3 0.89, alkoxide, CH_3, 1.81 (2.2 t), CH_AH_BP, 2.56 (8, 1) and 2.70 (4.5), $J(H_AH_B)$ = 15, CH_CH_DP, 3.21 (8.5, 1) and 3.44 (10), $J(H_CH_D)$ = 14.5; ^{13}C, alkylidene, =CH 274.8(9.5, 37), *C*(CH_3) 44.3 (1.5, 4.5), CH_3 33.7 (1.5), alkoxide, CH_2P, 41.9 (12.5), 47.9 (25.5), CH_3 33.2 (8.5), CO 90.3 (10, 12); ^{31}P, 35 °C, 17.5 and −11.4, $J(PP)$ = 25.6, −40 °C, 16.3 and −5.8, $J(PP)$ = 28.3.

Alkylidene 3a was prepared from Np_2TaCl_3 and **a·Li** in a similar manner. Yield ca. 60%.

Anal. Calcd: C, 57.04; H, 4.89; Cl, 7.48; P, 9.81; Ta, 19.09. Found: C, 56.76; H, 5.02; Cl, 7.75; P, 9.95; Ta, 19.20.

NMR (CD_2Cl_2): ^{13}C, alkylidene, =CH 274.5 (10.5, 38.7) [100], *C*(CH_3) 44.3 (1.6, 5.2), CH_3 33.7 (2.2) [125], alkoxide, CH_2P, 41.0 (2.1, 7.1, 12.1) [130], 47.5 (7.7, 25.8) [130], and 47.6 (2.4, 7.5, 17.8) [130], CO 92.3 (10.4, 13.1, 19.4); ^{31}P, 35 °C, P_1 17.5, P_2 −9.3, P_3 − 21.0, $J(P_1P_2)$ = 26, −40 °C, P_1 16.1, P_2 −4.27, P_3 −22.4, $J(P_1P_2)$ = 29.7.

Cyclopentadienyldichlorotitanium 1-(Diphenylphosphino)-2-*tert*-butyl-3,3-dimethyl-2-butoxide (4c). **c·Li** (3.5 g, 0.01 mol) was added with stirring to a mixture of $CpTiCl_3$ (2.2 g, 0.01 mol) in 150 mL of toluene at room temperature. After continued stirring for 2 h, the solvent was removed in vacuo, 50 mL of dichloromethane was added, and the organic layer was filtered. The solvent was removed in vacuo, and the resulting precipitate was washed with ether. Yield 4.7 g (84.9%).

Anal. Calcd: C, 61.73; H, 6.72; P, 5.90; Ti, 9.11. Found: C, 61.49; H, 6.55; P, 6.18; Ti, 9.00.

NMR (C_6D_6): ^{1}H, Cp 6.44, CH_2P 3.03, CH_3 1.08, Ar 7.0−7.2 and 7.6−7.7; ^{13}C, Cp 120.9 (2.8) [177], CH_2P 36.5 (21.4) [127], CO 110.4 (2.3), CH_3 30.5 (4.8) [126], *C*CH_3 45.6, Ar, i 141.3 (14.9), o 133.4 (21.1) [160], m 129.1 (7) [162], p 129.2 [162]; ^{31}P, −21.85.

Dichlorides 4a and 4b. These compounds were prepared as described above for **4c**. The yields are ca. 70%.

4a, NMR (C_6D_6): ^{1}H, Cp 6.29, CH_2P 3.21 (2), Ph 6.9−7.1 (18H) and 7.4−7.6 (12H); ^{31}P, −25.5.

4b, NMR (C_6D_6): Cp 6.28, CH_2P 2.92 (2), CH_3 1.50, Ph 7.15−7.55; ^{31}P, −24.5.

Reaction of 4a and Neopentyllithium. To a suspension of 30 mg (0.037 mmol) of the dichloride **4a** in 1 mL of C_6D_6 was added 6 mg (0.076 mmol) of solid neopentyllithium. After 10 min of stirring, a precipitate was removed. In the ^{1}H NMR spectrum of the resulting solution, only the dineopentyl complex **5a** was observed. The solution was heated to 50 °C for 1.5 h. According to the ^{1}H NMR spectrum of the reaction mixture, 40% of **5a** was converted to the alkylidene complex **6a** and 10% to a compound with an ortho-metalated phenyl group. The latter product is the main product after heating for an additional 5 h.

5a, NMR (C_6D_6): ^{1}H, Cp 6.53, CH_2P 2.94 (2.3), neopentyl, H_A 1.90, H_B 2.08, $J(H_AH_B)$ = 10.5, ^{t}Bu 1.10; ^{31}P, −27.16.

6a, NMR: ^{1}H, Cp 6.07, CH_2P 2.4 broad, alkylidene, CH 10.92, CH_3 0.91.

Metalation product, NMR: ^{1}H, Cp 6.47, neopentyl CH_aH_b 2.42 and 2.03, CH_3 1.32; ^{31}P, −25.1, −25.2, and −30.0.

Metalation Product 8. The dichloride **4c** was "titrated" with 2 equiv of neopentyllithium in C_6D_{12}. The reaction was monitored with ^{13}C and ^{31}P NMR. A precipitate was removed by filtration, and the liquid fraction was kept at 10 °C overnight. According to NMR, the solution contains neopentane, the dineopentyl complex **5c**, the alkylidene **6c**, the metalation product **7**, and its isomer **8** (ratio of titanium compounds 1:1:1:ca.0.1). This mixture was converted to complex **8** by warming to 50 °C for 2 h. The final product was crystallized from ether. Yield 60%.

Anal. Calcd: C, 73.27; H, 8.65; P, 5.90; Ti, 9.13. Found: C, 73.05; H, 8.46; P, 6.12; Ti, 9.08.

5c, NMR (C_6D_6): ^{1}H, Cp 6.44, CH_2P 3.12 (5.5), Ar 6.4−7.2, 7.65−7.8, ^{t}Bu 1.34 and 1.09, $TiCH_A$ 2.40 $J(H_AH_B)$ = 11, $TiCH_B$ not observed; ^{13}C, (C_6D_{12}) recorded at 10 °C, Ar, i 143.1 (16.8), o 133.6 (21.3), m 128.8 (7.1), p 128.7, Cp 112.1, alkoxide, CO 99.5 (3.7), CH_2P 38.9 (24), CH_3 31.4 (5.3), *C*$(CH_3)_3$ ligand 44.8, neopentyl, CH_3 38.4, $C(CH_3)_3$ 34.3; ^{31}P −21.43.

6c, NMR (C_6D_6) recorded at 10 °C: ^{1}H, Cp 6.15 (1), Ti=CH 12.4 (2), CH_aH_bP 3.83 (10.8) and 3.62 (11.2), $J(H_AH_B)$ = 16, *^{t}Bu* 1.45, 1.38, and 1.18; ^{13}C, CH 287.3 (8) [92], CH_2P 50.0 (21.6), CO 94.3 (6.1), Cp 107.9; ^{31}P 44.1.

7, NMR: ^{1}H (C_6D_6), Cp 6.46, alkoxide PCH_AH_B 2.59 (5) and 3.20 (6.7), $J(H_AH_B)$ = 14, ^{t}Bu 1.296 and 1.291, Ar 6.7−7.86, neopentyl, ^{t}BuCH_CH_D 1.78 and 3.82 (5.2), $J(H_CH_D)$ = 11, ^{t}Bu 1.06; ^{13}C (C_6D_{12}), TiC 198.7 (46), Cp 114.8, CO 100.3 (4.9), $TiCH_2$ 106.6 (22), CH_2P 30.6 (6.8); ^{31}P −18.36.

8, NMR: ^{1}H, (C_6D_6) ^{1}H, Cp 6.62, alkoxide PCH_AH_B 2.26 (3.6) and 3.07 (7.5), $J(H_AH_B)$ = 13.8, ^{t}Bu 1.3 broad, Ar 6.7−7.7, neopentyl, ^{t}BuCH_CH_D 1.38 and 2.82, $J(H_CH_D)$ = 9.8, ^{t}Bu 1.15; ^{13}C (C_6D_{12}) recorded at 10 °C, alkoxide, PPh, i 137.7 (14), o 134.8 (21.5), m 128.8 (6.9), p 129.0, metalated phenyl, CP 149.6 (9.6), CTi 196.9 (48.6), 133.3 (17.7), 130.3 (2), 126.7, 126.1, CO 100.3 (4.6), Cp 114.8 (4.6), CH_2P 32.9 (13.2), CH_3 (in CD_2Cl_2) 29.7 (3.2), 29.6 (3.3), *C*$(CH_3)_3$ 45.6, 44.2; neopentyl, CH_3 34.6, C 40.4, CH_2Ti 106.5 (2.9) [110]; ^{31}P −20.8.

Supplementary Material Available: Full tables of atomic coordinates, crystal and intensity collection data, anisotropic thermal parameters, and bond lengths and angles for **3b** and **8** (10 pages). Ordering information is given on any current masthead page.

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