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Titanium Carbene Complexes Stabilized by Alkali Metal Amides

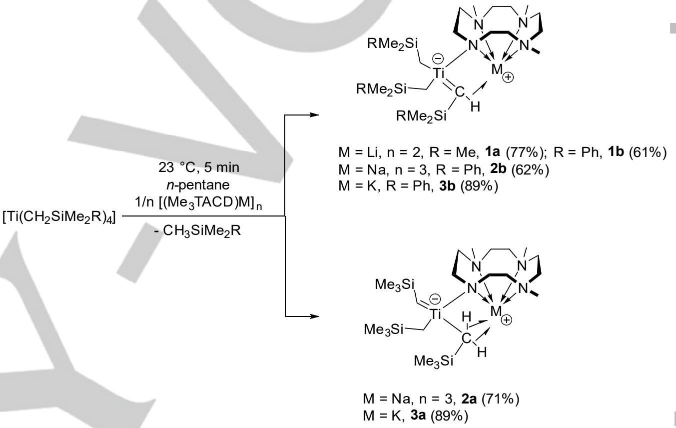
Hassan Osseili,[a] Khai-Nghi Truong,[a] Thomas P. Spaniol,[a] Laurent Maron,*[b] Ulli Englert,*[a] and Jun Okuda*[a]

Abstract: Facile *α-H elimination in tetrakis(trimethylsilylmethyl)-titanium precursors to give adducts of (alkylidene)bis(alkyl)-titanium complexes is induced by light alkali metal amides of the NNNN-type macrocyclic anionic ligand Me$_3$TACD [(Me$_3$TACD)H: 1,4,7-trimethyl-1,4,7,10-tetraazacyclo-dodecane]. In the crystal, the alkali metal interacts with the carbene carbon or with the CH$_2$ group of trimethylsilymethyl ligand. Nucleophilic character of the carbene carbon was shown by the reaction with benzophenone and terminal acetylene.*

Transition metal alkylidene complexes are used in olefin metathesis[1], Wittig-type reactions,[2] and in the transformation of small molecules.[3] Schrock-type metal alkylidenes are commonly formed by α-hydrogen abstraction,[4] promoted by steric repulsion of bulky (alkyl) ligands.[5] A number of group 4 metal alkylidene complexes were reported in the last decades, although a simple trimethylsilylmethylidene bis(trimethylsilylmethyl) complex remained unknown.[6] Here, we present a remarkably facile access to titanium trimethylsilylmethylidene complexes which are stabilized by an alkali metal that carries an *NNNN*-type monoanionic polyamine ligand.

The easily accessible alkali metal amides [(Me$_3$TACD)M] (M = Li, Na, K, (Me$_3$TACD)H = 1,4,7-trimethyl-1,4,7,10-tetraazacyclo-dodecane) contain an amido group that can serve as a π-donor or as a bridging ligand.[7] When this compound was added to a solution of [Ti(CH$_2$SiMe$_2$R)$_4$] (R = Me, Ph) in *n*-pentane at ambient temperature, intramolecular α-hydrogen abstraction instantaneously occurred. The titanium alkylidene complexes [{(Me$_3$TACD)M}Ti(=CHSiMe$_2$R)(CH$_2$SiMe$_2$R)$_2$] with the trimethylsilylmethylidene ligand [R = Me, M = Li (**1a**), Na (**2a**), K (**3a**)] and with the phenyldimethylsilylmethylidene ligand [R = Ph, M = Li (**1b**), Na (**2b**), K (**3b**)] were obtained under elimination of SiMe$_3$R (R = Me, Ph) as the only by-product (Scheme 1).

The titanium carbenes **1-3** were isolated as deep red crystals. ^{1}H NMR spectra in C$_6$D$_6$ show a characteristic signal for the α-proton of the alkylidene moiety at low field (δ 8-9 ppm). The diastereotopic C*H*$_2$SiMe$_3$ methylene groups in **1a** appear as a singlet at δ 1.13 (**1a**) ppm. This may indicate fast dissociation of the [(Me$_3$TACD)M] unit, fast α-hydrogen migration on the NMR time scale down to −80 °C, or isochrony (coincidental overlap). In the ^{13}C NMR spectra, the carbene signal of the Ti=*C*HSiMe$_3$ unit (δ 240-310 ppm) falls within the expected range for a trimethylsilylmethylidene carbon.[6i] AB spin patterns for the diastereotopic protons of the C*H*$_2$SiMe$_2$Ph methylene groups of **1b**, **2b** and **3b** suggest coordination of the [M(Me$_3$TACD)] unit. Such a feature was also observed for [(PNP)Ti(=CH*t*Bu)(CH$_2$SiMe$_3$)] as well as for [(PNP)Ti(=CH*t*Bu)(CH$_2$Ph)].[6s,8]



Scheme 1. Formation of the titanium alkylidene complexes **1-3**.

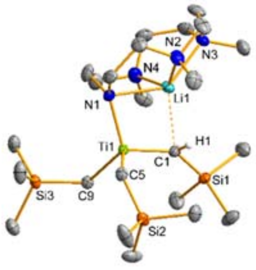


Figure 1. Molecular structure of **1a**. Displacement parameters are displayed at 50% probability. Only the hydrogen atoms of the carbene unit Ti=C*H* is shown. Selected interatomic distances (Å) and angles (°): Ti1−C1: 1.929(4), Ti1−C5: 2.130(4), Ti1−C9: 2.105(4), Ti1−N1: 1.996(3), Li1···C1: 2.299(7), Li1−N1: 2.306(6); ∠(Ti1−C1···Li1): 83.92(19), ∠(Ti1−C1−H1): 104(3), ∠(Ti1−C1−Si1): 139.8(2).

Both lithium complexes **1a** and **1b** have been characterized by single crystal X-ray diffraction (Fig. 1 and Fig. S24) and show a closely related molecular framework. The titanium center is tetrahedrally coordinated, the lithium ion interacts with the four nitrogen atoms of the Me$_3$TACD ligand and the carbene carbon in distorted square-pyramidal geometry. Compared to the Ti−C$_{\mathrm{Alkyl}}$ distances [2.105(4)−2.130(4) Å], the short distances between titanium and the carbene carbon Ti1−C1 of 1.929(4) Å (**1a**) and 1.923(4) Å (**1b**) indicate double bond character. The distance between the lithium center and the carbene carbon Li1−C1 of 2.299(7) Å (**1a**) and 2.368(8) Å (**1b**) suggests a strong interaction as in the structurally related compound [(Me$_3$SiCH$_2$)(ArN=)Ta(*μ*-CHSiMe$_3$)(*μ*-*η*^{1}:*η*^{3}-*i*Pr$_2$-TACN)Li].[4b, 4c, 9]

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This is associated with distortions [∠(Ti1−C1···Li1) of 83.92(19)° (**1a**) and 83.2(2)° (**1b**), ∠(Ti1−C1···H1) of 104(3)° (**1a**) and 108(3)° (**1b**), ∠(Ti1−C1−Si1) of 139.8(2)° (**1a**) and 137.8(2)° (**1b**)]. The phenyl ring of the $CHSiMe_2Ph$ unit in **1b** is directed towards the lithium center. This additional interaction is not very pronounced [Ti1−C4: 3.844(6) Å], but explains the slightly smaller Li1-C1 distance in **1b** than in **1a**. Geometry optimizations were carried out on complexes **1a** and **1b** at the DFT level (B3PW91). In both cases, the HOMO displays a Ti-carbene π-interaction (Fig. 2) that is stabilized by hyperconjugation with either the Si-C bond (**1a**) or the phenyl ring (**1b**) and to a lesser extent by the interaction with the lithium center (Fig. 2).

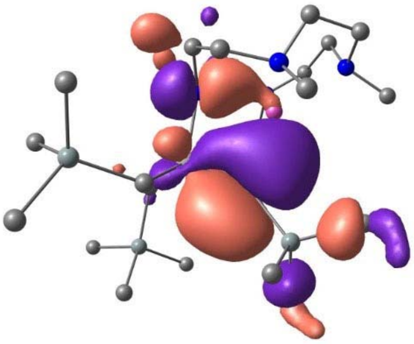
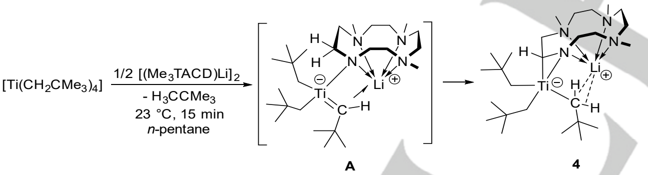


Figure 2. Representation of the HOMO in the lithium compound **1a**.

The reaction of the lithium amide $[(Me_3TACD)Li]_2$ with the neopentyl compound $[Ti(CH_2CMe_3)_4]$ did not give alkylidene complex **A** as would be expected from the analogous reaction with $[Ti(CH_2SiMe_3)_4]$, but the alkyl derivative **4**. This compound could be isolated by crystallization from *n*-pentane at −30 °C after 24 h.



Scheme 2. Formation of CH-bond activated complex **4**.

Crystal structure determination by X-ray diffraction revealed the molecular structure (Fig. 3). In spite of significant disorder, the refinement could be carried out with split positions and confirms the connectivity. The five-coordinate lithium center is found in distorted square pyramidal geometry coordinated by the four nitrogen atoms of the macrocyclic ligand and by a carbon atom of an alkyl group [Li1-C17A: 2.481(13) Å; Li1-C17B: 2.435(18) Å]. Striking feature is the Ti1-C1A distance of 2.176(7) Å indicating bonding between titanium and a carbon atom of the deprotonated carbon atom within the ligand Me_3TACD. Similar CH-bond activation was reported for complex $[(L)Ti(benzyl)]_2$ (L = 3,3-dimethyl-1,5-diaza-8-oxacyclodecane).[10] The coordination of the macrocyclic ligand after CH-activation leads to a C_1-symmetric molecular structure which is also suggested by the signal pattern in the ^1H NMR spectrum. The ^1H and the ^{13}C NMR spectra do not show a signal that would correspond to a carbene unit. We explain the formation of **4** by intermediate formation of a carbene complex, that activates a CH-bond of the macrocyclic ligand whereby the titanium-carbon double bond is re-protonated. This reaction can only occur if the basicity of the carbene unit in the intermediate is sufficiently strong. DFT calculations confirm a carbene as a potential intermediate (Fig. S59), that reacts further to the more stable CH-bond activation product **4** (Fig. S60). The titanium carbene complexes **1-3** also decomposed after 20 min to give products of intramolecular CH-bond activation along with unidentified byproducts (see SI).

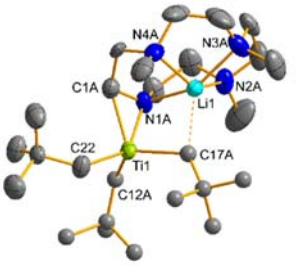


Figure 3. Molecular structure of **4**. Displacement parameters are shown at 50% probability. Atom sites with minor occupancies are omitted for clarity. Selected interatomic distances (Å): Ti1−C1A: 2.176(7), Ti1−C12A: 2.178(9), Ti1−C17A: 2.328(12), Ti1−C22: 2.114(5), Ti1−N1A: 1.989(5), Li1···C17A: 2.44(2).

The sodium congener **2b** shows a similar molecular structure as the lithium compound **1b** in the solid state (Fig. 4), with the Me_3TACD ligand κ^4-coordinated to the sodium center and the titanium in tetrahedral geometry.

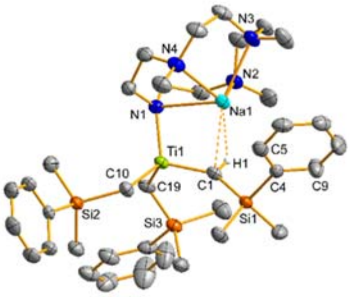


Figure 4. Molecular structure of **2b**. Displacement parameters are displayed at 50% probability. Only the hydrogen atom of the T=C*H* is shown. Selected interatomic distances (Å) and angles (°): Ti1−C19: 2.135(3), Ti1−C10: 2.118(3), Ti1−C1: 1.921(3), Ti1−N1: 1.963(2), Na1···C1: 2.624(3), Na1−N1: 2.655(2), Na1···C4: 3.385(4), Na1···C5: 3.227(4), Na1···C9: 4.212(4); ∠(Ti1−C1···Na1): 87.55(10); ∠(Ti1−C1−H1): 106.6(18), ∠(Ti1−C1−Si1): 142.41(14).

As in **1b**, the phenyl substituent in **2b** is directed towards the alkaline metal ion, caused by the π-interaction to the slightly tilted phenyl ring with short $Na1-C_{Phenyl}$ distances [Na1···C4: 3.385(4) Å, Na1···C5: 3.227(4) Å] rather than due to a strong interaction between sodium and the carbene unit [Na1···C1: 2.624(3) Å] (*vide infra*). Non-covalent $M^{+}\cdots C_{Phenyl}$ interactions for group 1 metals are common, especially for the heavier congeners resulting in coordinative saturation.[11]

In the closely related structures of the sodium and the potassium compounds **2a** and **3a**, the trimethylsilylmethylidene ligand [Ti1−C1: 1.879(3) Å (**2a**), 1.867(9) Å (**3a**)] is pointing away from the alkali metal. The latter shows a weak interaction to one of the CH_2SiMe_3 methylene groups [Na1···C5: 2.893(4) Å (**2a**); K1···C5: 3.163(8) Å (**3a**)] (Fig. 5). Neither the sodium nor the potassium center seems Lewis acidic enough to interact with the carbene moiety. Fig. 5 shows the free open site at the alkali metal which easily coordinates thf as a donor ligand. Whereas the potassium compound **3a** is insoluble in pentane, a trace of thf transforms **3a** into the soluble derivative **3a*thf**. Apart from the additional donor ligand, the main structural framework within **3a** and **3a*thf** is closely comparable (see Fig. 4 and Fig. S17).

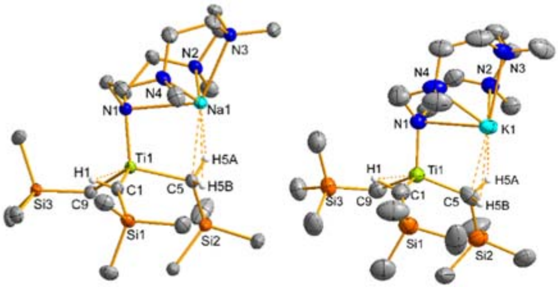


Figure 5. Molecular structures of **2a** and **3a**. Displacement parameters are shown at 50% probability. Hydrogen atoms except Ti=C*H* and TiC*H*$_2$SiMe$_3$ are omitted for clarity. Selected interatomic distances (Å) and angles (°): for **2a** = Ti1−C1: 1.879(3), Ti1−C5: 2.150(3), Ti1−C9: 2.160(3), Ti1−N1: 1.964(3), Na1···C5: 2.893(4), Na1···H5A: 2.408(4), Na1···H5B: 2.802(4), Na1−N1: 2.613(3); ∠(Ti1−C5···Li1): 80.1(1), ∠(Ti1−C1−H1): 87.0(2), ∠(Ti1−C1−Si1): 151.9(2). For **3a** = Ti1−C9: 2.164(8), Ti1−C5: 2.128(9), Ti1−C1: 1.867(9), Ti1−N1: 1.958(6), K1···C5: 3.163(8), K1···H5A: 2.832(2), K1···H5B: 2.944(2), K1−N1: 2.928(6); ∠(Ti1−C5···K1): 79.2(3), ∠(Ti1−C1−H1): 96.9(6), ∠(Ti1−C1−Si1): 145.3(5).

DFT calculations were carried out to determine the role of the alkali metal center. The coordination geometries in **2b**, **2a** and **3a** were reproduced. As in **1a** and **1b**, the HOMO shows strong π interactions between titanium and the carbene ligand as well as hyperconjugation to the SiR$_3$ units (Fig. 2 and Fig. 6). **2a** and **3a** (Fig. 6) were found as conformers where the carbene unit does not show an interaction with the alkali metal, unlike for **1a** (Fig. 2).

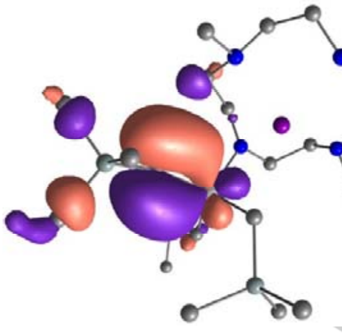
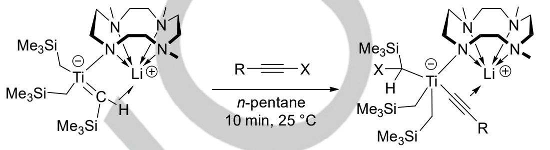


Figure 6. Representation of the HOMO in the sodium compound **2a**.

An isomer of lithium compound **1a** with a larger distance between the carbene and the alkali metal (like in **2a**) would also be stable, but 3.3 kcal·mol^{-1} higher in energy. This situation is even more pronounced in the SiMe$_2$Ph substituted sodium complex **2b**, because no other stable conformer with the carbene ligand pointing away from the alkali metal was located on the potential energy surface (PES). The experimentally observed complex **2a** is actually 3.0 kcal·mol^{-1} less stable than the calculated conformer where the carbene ligand interacts closer with the alkali metal (like in **1a** and **2b**). The geometry in **2a** with the carbene ligand poining away from the alkali metal is therefore due to steric effects that block the structure in a secondary minimum.

Treatment of complex **1a** with one equivalent of benzophenone in C$_6$D$_6$ led to a color change from deep red to light yellow within 15 min. The ^{1}H NMR spectrum confirms the formation of (2,2-diphenylethenyl)trimethylsilane as characterized by ^{1}H NMR spectroscopy in comparison with literature values after work-up.[13] The formation of this silane is expected if a Wittig−type reaction occurs and confirms a Schrock−type alkylidene ligand in **1a**. The reactivity resembles that of Tebbe's reagent or that of the comparable complex [(Me$_3$SiCH$_2$)(ArN=)Ta(μ-CHSiMe$_3$)(μ-*η*^{1}:*η*^{3}-*i*Pr$_2$-tacn)Li] reported by Arnold and coworkers.[4b, 4c, 6f, 6j,12] Notably, the complex **1a** did not react with olefins such as styrene or 1-hexene even at 60 °C.

When **1a** was treated with one equivalent of phenyl- or trimethylsilylacetylene in *n*-pentane at ambient temperature, the solution turned orange. Cooling to −30 °C gave the acetylide complexes **5a** or **5b** as orange crystals (Scheme 3).



R = SiMe$_3$, X = H, **5a** (66%)
R = Ph, X = H, **5b** (72%)
R = Ph, X = D, ***5-d$_1$*** (63%)

Scheme 3. Reaction of **1a** with phenyl- and trimethylsilylacetylene.

The ^{1}H NMR spectra show the CH$_2$SiMe$_3$ fragments with singlets for the methylene groups [*δ* 2.20 ppm (**5a**) and 2.10 ppm (**5b**)], and for the methyl groups [*δ* 0.55 ppm (**5a**) and 0.52 ppm (**5b**)]. The signal of the *α*-hydrogen atom of the carbene C*H* unit disappeared. In a deuterium labelling study, the reaction of **1a** with phenylacetylene-*d*$_1$ provided the deuterated complex ***5b-d$_1$*** which was also characterized by ^{2}H NMR spectroscopy. The deuterium signal appeared as a singlet at *δ* 2.21 ppm.

The crystal structures of **5a** and **5b** show a titanium center in distorted trigonal bipyramidal geometry (Fig. 7 and Fig. S50).

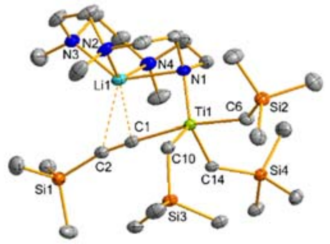


Figure 7. Molecular structure of **5a**. Displacement parameters are shown at 50% probability. Selected interatomic distances (Å): Ti1−C1: 2.258(2), Ti1−C6: 2.171(2), Ti1−C10: 2.135(2), Ti1−C14: 1.149(2), Ti1−N1: 1.939(2), Li1···C1: 2.218(4), Li1···C2: 2.568(5), Li1−N1: 2.394(4), C1−C2: 1.226(3).

All titanium-carbon distances are in the range of Ti–C single bonds [**5a**: Ti1−C1: 2.258(2) Å, Ti1−C10: 2.171(2) Å, Ti1−C10: 2.135(2) Å, Ti1−C14: 2.149(2) Å; **5b**: Ti1−C1: 2.225(3) Å, Ti1−C9: 2.166(3) Å, Ti1−C13: 1.162(3) Å; Ti1−C17: 2.125(3) Å] (Fig. 7). The C1−C2 distance of 2.226(3) Å (**5a**) and 1.221(4) Å (**5b**) corresponds to the expected triple bond and in both complexes the alkyne moiety exhibits an intramolecular interaction with the lithium center [**5a**: Li1···C1: 2.218(4) Å, Li1···C2: 2.568(5) Å; **5b**: Li1···C1: 2.201(5) Å, Li1···C2: 2.569(5) Å]. Similar interactions between alkali metals and triple bonds in titanium complexes have been reported.[13] The lithium amide Li{N(SiHMe$_2$)$_2$} without a Me$_3$TACD ligand did not react with [Ti(CH$_2$SiMe$_3$)$_4$].

In conclusion, we have reported the facile formation of a series of titanium alkylidene complexes with the trimethylsilylmethylidene (**1a**, **2a**, **3a**) and phenyldimethylsilylmethylidene (**1b**, **2b**, **3b**) ligand. The neopentyl derivative [Ti(CH$_2$CMe$_3$)$_4$] reacted with [M(Me$_3$TACD)] to give the product of the CH-bond activation at the *NNNN*-type macrocyclic ligand. Computational studies agree with the alkylidene carbon in **1a** to be stabilized by interaction with the Lewis acidic lithium center. Wittig-type reaction of **1a** with benzophenone as well as protonation by terminal acetylene to give alkyl acetylide complexes **5a** and **5b** confirmed the presence of nucleophilic carbene ligands.

Acknowledgments

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Keywords: titanium • carbene • alkylidene • alkali metal • Wittig reaction

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