lustrated. The formation of a three-membered ring via a reductive-elimination reaction of this type is unusual,[14] compared with the reverse reaction, i.e. the oxidative insertion of metal fragments into strained three-membered rings.[15]

In summary, a new and potentially versatile route to η^3-butadienyl complexes has been described, which provides surprising[16] access to the relatively unexplored *exo*-vinylidenemetallacyclobutanes.

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[14] Athough there are examples of reductive-elimination reactions affording cyclopropanes (see: DiCosimo, R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 3601), the formation of methylenecyclopropanes has not been reported.

[15] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 460.

[16] It is hoped that a MO study of these cationic η^3-butadienyl complexes will provide an insight into the regioselectivity observed in this reaction.

Intramolecular C-X Activation as a Synthetic Route to Bidentate Cyclopentadienyl-Alkoxide Ligands: Preparation and Molecular Structure of (3-(2,3,4,5-Tetramethylcyclopentadienyl)propoxy)titanium Dichloride

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Summary: $Cp'TiCl_3$ (**1**; $Cp' = \eta^5\text{-}C_5Me_4(CH_2)_3OMe$) reacts with 2 equiv of the phosphorous ylide $PPh_3{=}CH_2$ (**2**) to yield $Cp'TiCl_2(CHPPh_3)$ (**3**) plus the phosphonium salt $(MePPh_3)Cl$. Complex **3** decomposes thermally to give $[\eta^5{:}\eta^1\text{-}C_5Me_4(CH_2)_3O]TiCl_2$ (**4**), containing a Cp*-alkoxide-functionalized ligand. The molecular structure of **4** shows it as a pseudo three-legged piano-stool complex.

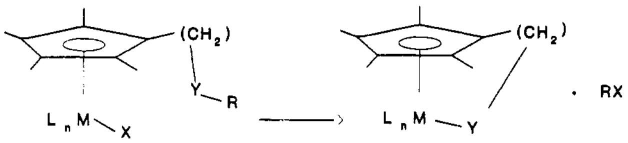
There is a rapidly growing interest in early-transition-metal and lanthanide compounds with bidentate ligands that combine two anionic functions, such as cyclopentadienyl ligands with built-in alkoxide, amide, or similar groups, in order to control their reactivity, e.g. as catalysts in the oligo- or polymerization of olefins. Several approaches have already been attempted,[1] but so far a systematic and convenient synthetic method has not been developed.

We decided to try a route based on the intramolecular thermally induced C-X activation of complexes containing a cyclopentadienyl ligand with a neutral basic function.

Here, we report the successful application of this approach to titanium, using a (tetramethyl(methoxypropyl)cyclopentadienyl)titanium ylide, $[\eta^5\text{-}C_5Me_4(CH_2)_3OMe]TiCl_2(CHPPh_3)$, as starting material. In metal ylides, $L_nMCHPPh_3$, the electronic charge on the ylidic carbon is intermediate between that of free ylides and coordinated ylides[2] so that they can act both as nucleophiles and as electrophiles. This versatility makes them very attractive for our synthetic purposes.

$Cp'TiCl_3$[3] (**1**; $Cp' = \eta^5\text{-}C_5Me_4(CH_2)_3OMe$) reacts instantaneously at room temperature with 2 equiv of CH_2PPh_3 (**2**) to give, through a transylidation process,[4] the titanium ylide $Cp'TiCl_2(CHPPh_3)$ (**3**) and the corresponding phosphonium salt in an essentially quantitative yield (eq 1).

Scheme I



$$\underset{\mathbf{1}}{Cp'TiCl_3} + \underset{\mathbf{2}}{CH_2{=}PPh_3} \rightarrow [Cp'TiCl_3(CH_2PPh_3)] \xrightarrow[-PPh_3MeCl]{+2} \underset{\mathbf{3}}{Cp'TiCl_2(CHPPh_3)} \qquad (1)$$

Ylide **3** is the only titanium product formed. When the reaction is carried out with lower ylide:titanium ratios, the ylide is consumed to produce **3** according to eq 2 and the excess **1** is found unchanged. The mechanism of this reaction has not been studied, but intermediate formation of an ylide adduct, which transfers a proton to the free ylide, followed by extrusion of a chloride ligand seems quite plausible.[5]

Compound **3** is extremely air-sensitive but thermally rather stable. It is very soluble in toluene and ethers but only poorly soluble in alkane solvents.

The bond in the titanium ylide can be represented as being composed of forms A and B.

$$\underset{\mathbf{A}}{Ti{-}C^{-}H{-}P^{+}Ph_3} \qquad \underset{\mathbf{B}}{Ti^{-}{=}CH{-}P^{+}Ph_3}$$

^1H and ^{13}C NMR spectroscopy[6] points to a large con-

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[1] (a) Pattiasina, J. W.; Hissink, C. E.; de Boer, J. L.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 7758. (b) Pattiasina, J. W. Doctoral Thesis, Groningen, The Netherlands, 1988. (c) Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867.

[2] Gell, K. I.; Schwartz, J. *Inorg. Chem.* **1980**, *19*, 3207.

[3] Full experimental details on compounds 1, 3, and 4 are given in the supplementary material of this communication.

[4] Bestmann, H. J. *Chem. Ber.* **1962**, *95*, 58.

[5] (a) Kaska, W. C. *Coord. Chem. Rev.* **1983**, *48*, 1. (b) Schmidbaur, H. *Angew. Chem.* **1983**, *95*, 980.

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tribution of the form B, as shown by the shift observed for the ylidic proton and carbon [^{1}H NMR 9.25 ppm (d, $^2J_{\mathrm{H\text{-}P}}$ = 7.69 Hz); ^{13}C NMR 194.90 ppm (dd, $^1J_{\mathrm{C\text{-}H}}$ = 133.52 Hz and $^2J_{\mathrm{C\text{-}P}}$ = 11.51 Hz)]. The signals are at lower field than those observed in titanocene analogues,[7] as may be expected for more unsaturated complexes.

When a solution of **3** in benzene is heated at 155 °C, a reaction is observed, yielding **4** as the main titanium product together with unidentified phosphorus compounds (eq 2).

$$\underset{\mathbf{3}}{[\mathrm{C_5Me_4(CH_2)_3OMe]TiCl_2(CHPPh_3)}} \xrightarrow{\Delta} \underset{\mathbf{4}}{[\mathrm{C_5Me_4(CH_2)_3O]TiCl_2}} + \ldots \quad (2)$$

4 has been characterized by ^{1}H and ^{13}C NMR[8] and IR spectroscopy, IR, elemental analysis, and a single-crystal X-ray structure determination. Complex **4** has a pseudo three-legged piano-stool structure,[9] as expected for complexes of the type CpTi(X)Cl$_2$ (Figure 1). The C–C distances in the ring vary in a narrow range (1.430 (3)–1.421 (3) Å), and the metal to ring plane distance is 2.015 (6) Å. Both features are quite normal for pentamethylcyclopentadienyl complexes,[10,11] and this reflects that functionalization of a Cp* ligand in the way that has been achieved here leaves sufficient flexibility in the system to warrant normal η^5 bonding of the cyclopentadienyl ring. The chain C(10)–C(11)–C(12) has angles and distances (C–C and C–H) characteristic of sp^3 carbon atoms. Apparently this new bidentate cyclopentadienyl–alkoxide ligand is very flexible and exerts little steric constraint.

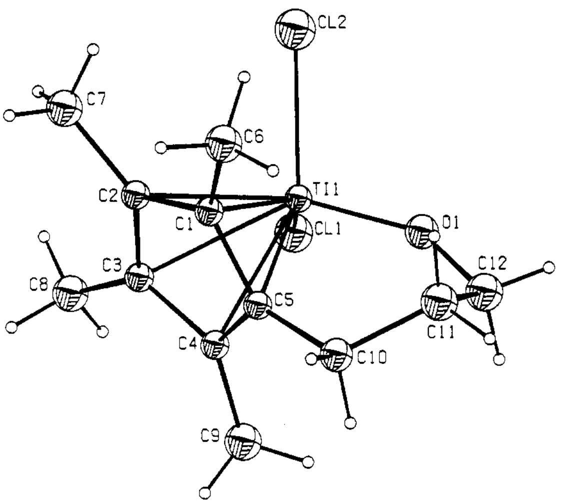

Figure 1. Crystal structure of [C$_5$Me$_4$(CH$_2$)$_3$O]TiCl$_2$ (**4**). Selected structural parameters: Ti(1)–O(1) = 1.767 (1) Å, Ti(1)–Cl(1) = 2.2886 (8) Å, Ti(1)–Cl(2) = 2.2809 (8) Å, Ti(1)–O(1)–C(12) = 146.1 (1)°, Cl(1)–Ti(1)–Cl(2) = 103.70 (3)°, Cl(1)–Ti(1)–O(1) = 102.68 (5)°, Cl(2)–Ti(1)–O(1) = 104.75 (5)°.

The Ti–O bond length (1.767 (1) Å) is very short and the Ti–O–C(12) angle, 146.1 (1)°, rather obtuse. Both data indicate a partially double Ti–O bond. The Ti–Cl(1) and Ti–Cl(2) distances are 2.2886 (8) and 2.2809 (8) Å, as expected for an electronically unsaturated Ti(IV) complex.[12]

Although it was not possible to establish the mechanism through which the reaction takes place, a probable route is intramolecular nucleophilic attack of the partially negatively charged ylidic carbon, at the methyl group of the ether function, with formation of a new ylide, CH$_3$CHPPh$_3$, which decomposes under the reaction conditions applied.[13] This nucleophilic attack could have been facilitated by intramolecular coordination of the ether function in **3**. IR spectra indicate that the methoxy group is free, in both **1** and **3**. The expected shift of ν(COC) to lower energy is not observed (free ligand and **1**, 1120 cm^{-1}; **3**, 1115 cm^{-1}).

We have seen in the first reaction (eq 1) that coordinated ylides are able to act as proton sources, yielding the titanium complex **3** having an anionic ylide. We have shown that an ylide function as in **3** may act as a nucleophile on the ether function connected to the cyclopentadienyl ring, taking off the methyl substituent of an ether function and leaving an alkoxide to form a Ti–O bond.

Investigations to explore the scope of the method in the preparation of related bifunctional dianionic ligands, e.g. with thiolate, phosphide, or amide functionalities, are in progress.

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Supplementary Material Available: Experimental procedures and details of the structure determination, including tables of refined parameters, bond distances and angles, and torsion angles for **4** (15 pages); a listing of structure factors for **4** (12 pages). Ordering information is given on any current masthead page.

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(6) ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 °C): δ 1.84 (m, 2 H, CH$_2$), 2.24 (s, 6 H, Cp′), 2.33 (s, 6 H, Cp′), 2.99 (m, 2 H, CH$_2$), 3.15 (s, 3 H, CH$_3$), 3.25 (m, 2 H, CH$_2$), 7.15 (m, 9 H, Ph), 7.75 (m, 6 H, Ph), 9.25 (d, $^2J_{\mathrm{P\text{-}H}}$ = 7.69 Hz, 1 H, CH). ^{13}C NMR (75.4 MHz, C$_6$D$_6$, 20 °C): δ 13.63 (q, $^1J_{\mathrm{C\text{-}H}}$ = 127.76 Hz, Cp′), 13.68 (q, $^1J_{\mathrm{C\text{-}H}}$ = 127.76 Hz, Cp′), 25.64 (t, $^1J_{\mathrm{C\text{-}H}}$ = 127.76 Hz, CH$_2$), 31.00 (t, $^1J_{\mathrm{C\text{-}H}}$ = 126.62 Hz, CH$_2$), 58.27 (q, $^1J_{\mathrm{C\text{-}H}}$ = 139.27 Hz, CH$_3$), 72.11 (t, $^1J_{\mathrm{C\text{-}H}}$ = 139.28 Hz, CH$_2$), 124.98 (s, Cp′), 125.72 (s, Cp′), 128.72 (dd, $^3J_{\mathrm{P\text{-}H}}$ = 11.71, $^1J_{\mathrm{C\text{-}H}}$ = 155.39 Hz, Ph), 129.92 (d, $^1J_{\mathrm{C\text{-}P}}$ = 84.02 Hz, *o* Ph), 130.48 (s, Cp′), 131.79 (dd, $^4J_{\mathrm{C\text{-}P}}$ = 2.39 Hz, $^1J_{\mathrm{C\text{-}H}}$ = 158.84 Hz, Ph), 133.81 (dd, $^2J_{\mathrm{C\text{-}P}}$ = 10.36 8 Hz, $^1J_{\mathrm{C\text{-}H}}$ = 158.84 Hz, Ph), 194.90 (dd, $^1J_{\mathrm{C\text{-}P}}$ = 11.51 Hz, $^1J_{\mathrm{C\text{-}H}}$ = 133.52 Hz, CHP).

(7) Erker, G.; Czisch, P.; Mynott, R. *J. Organomet. Chem.* **1987**, *334*, 91.

(8) ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 °C): δ 1.51 (m, 2 H, CH$_2$), 1.60 (s, 6 H, Me), 1.96 (m, 2 H, CH$_2$), 2.09 (s, 6 H, Me), 3.72 (m, 2 H, CH$_2$). ^{13}C NMR (75.4 MHz, C$_6$D$_6$, 20 °C): δ 12.67 (q, $^1J_{\mathrm{C\text{-}H}}$ = 127.76 Hz, Me), 12.96 (q, $^1J_{\mathrm{C\text{-}H}}$ = 128.91 Hz, Me), 21.93 (t, $^1J_{\mathrm{C\text{-}H}}$ = 127.76 Hz, CH$_2$), 34.92 (t, $^1J_{\mathrm{C\text{-}H}}$ = 127.76 Hz, CH$_2$), 74.78 (t, $^1J_{\mathrm{C\text{-}H}}$ = 146.81 Hz, CH$_2$), 125.58 (s, *C*-Me), 131.59 (s, *C*-Me), 131.95 (s, Cp*).

(9) Crystal data for **4**: monoclinic, space group $P2_1/n$, with a = 11.257 (1) Å, b = 8.879 (2) Å, c = 13.788 (1) Å, β = 98.081 (7)°, V = 1364.4 (3) Å^3, Z = 4, D_{exptl} = 1.446 g cm^{-3}, λ(Mo K$\bar{\alpha}$) = 0.71073 Å, μ = 9.9 cm^{-1}, F(000) = 616, T = 130 K. The crystal structure was solved by standard Patterson methods and subsequent partial structure expansion and difference Fourier techniques. The least-squares refinement on F with anisotropic thermal parameters for all non-hydrogen atoms converged at R_F = 0.034 (R_w = 0.045) for 2585 unique observed reflections with $I \geq 2.5\sigma(I)$ and 217 parameters. The unit cell contains four independent molecules of the title compound separated by normal van der Waals distances.

(10) (a) Sikora, D. J.; Rausch, M. D.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 1265. (b) Rogers, R. D.; Benning, M. M.; Kurihara, L. K.; Moriaty, K. J.; Rausch, M. D. *J. Organomet. Chem.* **1985**, *293*, 51.

(11) Mena, M.; Pellinghelli, M. A.; Royo, P.; Serrano, R.; Tiripicchio, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1118.

(12) Reetz, M. T. *Organotitanium Reagents in Organic Synthesis*; Springer: Berlin, 1986; p 43.

(13) NMR experiments show that CH$_3$CHPPh$_3$ decomposes in C$_6$D$_6$ at 155 °C. This also happens in the presence of **4**. No attempts were made to identify the organophosphorus products formed.