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Published in:
Journal of Organometallic Chemistry

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
1991

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Luinstra, G. A., & Teuben, J. H. (1991). Oxidative Methylation of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiX}$ (X = Cl, OMe, Me) with Group 12 Dimethyl Complexes to Diamagnetic $(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiX}(\text{Me})$. *Journal of Organometallic Chemistry*, 420(3).

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Preliminary Communication

Recl. Trav. Chim. Pays-Bas **110**, 57-58 (1991)

0165-0513/91/02057-02\$1.00

OXIDATIVE METHYLATION OF $(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiX}$ ($\text{X} = \text{Cl, OMe, Me}$) WITH GROUP 12 DIMETHYL COMPLEXES TO DIAMAGNETIC $(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiX(Me)}$

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(Received January 2nd, 1991)

Abstract. Tervalent titanium compounds $(\text{C}_5\text{Me}_5)_2\text{TiX}$ ($\text{X} = \text{OMe, Cl, Me}$) are selectively oxidized and alkylated at room temperature by ZnMe_2 to diamagnetic monomethyl derivatives $(\text{C}_5\text{Me}_5)_2\text{TiX(Me)}$.

Recently we reported the clean oxidation of tervalent titanium compounds $(\text{C}_5\text{Me}_5)_2\text{TiR}$ ($\text{R} = \text{alkyl, aryl, H, OR}$ etc) to diamagnetic $(\text{C}_5\text{Me}_5)_2\text{TiR(Cl)}$ complexes by PbCl_2 ¹. This reaction is very useful since consecutive halide substitution with alkyl alkali metal reagents gives mixed complexes $(\text{C}_5\text{Me}_5)_2\text{TiR}^1\text{R}^2$. We now have developed a direct route to complexes $(\text{C}_5\text{Me}_5)_2\text{TiX(Me)}$ ($\text{X} = \text{OMe, Cl, Me}$), starting from $(\text{C}_5\text{Me}_5)_2\text{TiX}$ by oxidative alkylation with ZnMe_2 .

Analogous to the clean oxidation of $(\text{C}_5\text{Me}_5)_2\text{TiX}$ derivatives with PbCl_2 , the synthetic strategy is based on simultaneous oxidation of the metal and introduction of an alkyl group, using homoleptic metal alkyls (eq 1).



$\text{X} = \text{OMe}$ (**1**), Cl (**2**), Me (**3**)

The thermodynamic boundary conditions which this reaction has to meet is that the titanium carbon

bond in $(\text{C}_5\text{Me}_5)_2\text{TiX(Me)}$ is stronger than the mean M-C bond strength in MMe_n . Literature data on the titanium methyl bond indicate a bond dissociation energy of approximately 280 kJ/mol², making the readily available homoleptic group 12 complexes with mean bond dissociation energies of 126 kJ/mol (Hg) to 184 kJ/mol (Zn) particularly suitable³.

Dimethyl mercury was not particularly reactive towards $(\text{C}_5\text{Me}_5)_2\text{TiX}$ possibly for kinetic reasons, although oxidative alkylations are known for the former compound (e.g. reaction with lithium metal⁴). In contrast ZnMe_2 was found to react stoichiometrically with $(\text{C}_5\text{Me}_5)_2\text{TiX}$ ($\text{X} = \text{OMe, Cl, Me}$) to form $(\text{C}_5\text{Me}_5)_2\text{TiX(Me)}$ and zinc metal[†]. To the best of our knowledge, the oxidizing capacity

of zinc compounds was unknown prior to this work. Zinc alkyls have been widely used as non reductive

substitution reagents⁵, but reduction to zinc metal has not been reported before.

The oxidative alkylation proceeds smoothly in toluene at room temperature and reactions usually are complete within 24h. Remarkably, the oxidative alkylation is kinetically favoured over substitution. Reaction of (C₅Me₅)₂TiCl with half a mole of ZnMe₂ leads to selective formation of (C₅Me₅)₂TiCl(Me) (**2**). Neither products originating from salt metathesis, like (C₅Me₅)₂TiMe, nor its consecutive oxidation alkylation product (C₅Me₅)₂TiMe₂ (**3**) (*vide infra*) is present in the reaction mixture⁶. In addition, (**2**) is not reduced by zinc metal formed *in situ*, although zinc is reported to be capable of reducing tetravalent titanium halides⁷.

Treatment of (C₅Me₅)₂TiMe with half a mole of ZnMe₂ at room temperature quantitatively yields (**3**) within 2h. However, reactions of ZnMe₂ with other (C₅Me₅)₂TiR (R ≠ Me) are complicated by extensive disproportionation. This presumably results from rapid alkyl exchange between trivalent (C₅Me₅)₂TiR and ZnMe₂, followed by irreversible oxidation to a mixture of tetravalent (C₅Me₅)₂TiR(Me), (C₅Me₅)₂TiMe₂ and (C₅Me₅)₂TiR₂ species. For example, reaction of (C₅Me₅)₂TiPh with ZnMe₂ results in the isolation of a mixture of (**3**), (C₅Me₅)₂TiPh(Me)⁸ and (C₅Me₅)₂TiPh₂⁹. The oxidative alkylation strategy for the synthesis of pure (C₅Me₅)₂TiR¹R² from (C₅Me₅)₂TiR¹ seems to be restricted to the case where R¹ = R² = Me.

We are currently investigating the scope of oxidative alkylations, especially for the preparation of pure mixed (C₅Me₅)₂TiR¹R² compounds. The method of introducing alkyl groups at low-valent (early) transition metal center through the oxidative alkylation pathway reported here is a promising alternative for the preparation of alkyl complexes.

† Reaction of vanadocene with dialkylcadmium complexes has been reported to give Cp₂VR₂. We observed that compounds (C₅Me₅)₂TiX are also oxidatively alkylated by CdR₂. However, the use of CdR₂ has some disadvantages over ZnR₂ owing to the photosensitivity of the former compounds. G.A. Razuvaev, V.N. Latyaeva, L.I. Vishinskaya, V.K. Cherkasov, S.P. Korneva, N.N. Spiridonava, J. Organomet. Chem. **129**, 169 (1977).

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