



Group-13 carbenoid ligands at tungsten: Coordination and C–H activation



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ABSTRACT

Reactions of zero valent tungsten complexes with AlCp^* and GaCp^* (Cp^* = pentamethylcyclopentadienyl) are presented. The treatment of $[\text{W}(\text{C}_2\text{H}_4)_2(\text{PMe}_3)_4]$ with 2 equiv of GaCp^* or AlCp^* leads to the formation of *cis*- $[\text{W}(\text{GaCp}^*)_2(\text{PMe}_3)_4]$ (**1**) or *trans,cis,cis*- $[\text{W}(\text{AlCp}^*)_2(\text{C}_2\text{H}_4)_2(\text{PMe}_3)_2]$ (**2**) under cleavage of ethylene or PMe_3 ligands, respectively. Treatment of either $[\text{W}(\text{C}_2\text{H}_4)_2(\text{PMe}_3)_4]$ or **2** with 4 or 6 equiv of AlCp^* leads to the C–H activated species of over-all composition $[\text{W}(\text{AlCp}^*)_6(\text{C}_2\text{H}_4)_2]$ (**3**), which features terminal W–H as well as bridging W–H–Al hydride ligands and C–H activated C_2H_4 resulting in Al–C bonds. All new compounds are characterized by solution NMR, IR, elemental analyses (EA), liquid injection field desorption ionization mass spectrometry (LIFDI-MS) as well as single crystal x-ray crystallography.

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1. Introduction

Carbenoid group 13 metal organyls $\text{E}^{\text{I}}\text{R}$ ($\text{E} = \text{Al}, \text{Ga}, \text{In}$; $\text{R} =$ steric demanding organic residue) and their coordination chemistry have been in the focus of research for two decades [1–6]. The first synthetic routes to transition metal complexes of these exotic, very strong 2e donor ligands have been the CO/ $\text{E}^{\text{I}}\text{R}$ substitution reactions of transition metal carbonyls like $[\text{Ni}(\text{CO})_4]$ or $[\text{Co}_2(\text{CO})_8]$. For example, a certain amount of GaCp^* could be introduced in the coordination sphere of the transition metal leading to the selective formation of defined substitution products such as $[\text{Ni}_4(\text{GaCp}^*)_4(\text{CO})_6]$ or $[\text{Co}_2(\text{GaCp}^*)_2(\text{CO})_6]$ under evolution of CO. However, coordination of GaCp^* leads to an increase of the M–CO bond strength in the resulting products, i.e. the number of CO ligands which can be substituted by ECp^* is intrinsically limited and homoleptic complexes $[\text{M}(\text{ECp}^*)_n]$ ($n \geq 4$) cannot be obtained from the respective homoleptic carbonyls [7,8]. This intrinsic limitation is not given when homoleptic olefin complexes are used as starting materials [7,9–11], and various mono- and multinuclear complexes $[\text{M}_a(\text{ECp}^*)_b]$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$; $\text{E} = \text{Ga}, \text{Al}$) could be obtained [9,10,12–

14]. Compounds $\text{E}^{\text{I}}\text{R}$ as well as their interactions with transition metal centres were thoroughly investigated on the density functional level of theory (DFT), revealing the M– ECp^* dissociation energies to follow the order $\text{B} > \text{Al} > \text{Ga} > \text{In} > \text{Tl}$ with a major contribution of the electrostatic attraction $\text{M}^{\delta-}-\text{E}^{\delta+}$ to the total bond dissociation energies [15,16]. Different from the heavier homologues Ga and In, the enhanced Lewis acidic character of the aluminium site in AlCp^* complexes of electron rich metal centres has been shown to enable C–H and Si–H activation reactions, e.g. $[\text{M}(\text{AlCp}^*)_5]$ ($\text{M} = \text{Fe}, \text{Ru}$) reveal C–H activated CH_3 -groups and M–H–Al and Al–C bonds. [9,17]

We have been particularly interested to expand the series of $[\text{M}(\text{ECp}^*)_n]$ compounds with $n > 5$ and were aiming to achieve $[\text{M}(\text{ECp}^*)_6]$ compounds as analogues to the classic hexacarbonyl complexes $[\text{M}(\text{CO})_6]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$). Recently, we reported on the successful synthesis of the homoleptic MoGa_6 complex $[\text{Mo}(\text{GaCp}^*)_6]$ prepared by hydrogenolysis of $[\text{Mo}(\eta^4\text{-butadiene})_3]$ in the presence of GaCp^* [18]. However, the AlCp^* analogous complex of MoAl_6 composition is not accessible using this hydrogenolytic route, since AlCp^* readily reacts with H_2 under very mild conditions. Also, the homologous WGa_6 complex $[\text{W}(\text{GaCp}^*)_6]$ has been inaccessible due to the low reactivity of $[\text{W}(\eta^4\text{-butadiene})_3]$ towards H_2 [19]. Despite numerous complexes featuring W– $\text{Al}^{\text{III}}\text{R}_3$ interaction (with or without bridging hydrides), the number of

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tungsten complexes with E¹R ligands is quite small and only a few examples with unsupported W–E¹R bonds are known [8,20–24]. Herein, we would like to give an account on some new results on our way to [M(ECp*)_n] (n > 5) and in particular we will discuss the reactivity of the tungsten complex *trans*-[W(C₂H₄)₂(PMe₃)₄] towards AlCp* and GaCp* and discuss characterization and the structural properties of the products isolated from these reactions.

2. Results and discussion

2.1. Synthesis

According to Scheme 1, *cis*-[W(GaCp*)₂(PMe₃)₄] (**1**) and *trans*,*cis*-[W(AlCp*)₂(PMe₃)₂(C₂H₄)₂] (**2**) can be obtained in good yields by ligand exchange reactions from *trans*-[W(C₂H₄)₂(PMe₃)₄] and 2 equiv of ECp* (E = Al, Ga). Complex **1** represents the tungsten analogue of the previously reported complex [Mo(GaCp*)₂(PMe₃)₄], obtained by substitution of N₂ and 1 equiv of PMe₃ by GaCp* from [Mo(N₂)(PMe₃)₅]. In both cases the use of an excess of GaCp* does not lead to further substitution of phosphine ligands and the reaction stops at the MoGa₂ and WGa₂ stoichiometry, respectively.

The use of AlCp* instead of GaCp* leads to a different reaction pathway. Thus, heating a solution of *trans*-[W(C₂H₄)₂(PMe₃)₄] and AlCp* to 60 °C for 1 h leads to the selective substitution of two PMe₃ by AlCp* giving [W(C₂H₄)₂(PMe₃)₂(AlCp*)₂] (**2**). Treatment of **2** with four additional equivalents of AlCp* results in the formation of the desired compound **3** of WAl₆ stoichiometry and a formal composition of [W(AlCp*)₆(C₂H₄)₂]. As shown in Scheme 1 and discussed below in Section 2.2.3 only three intact ligands AlCp* are coordinated to the W centre, while another set of three AlCp* units are bound quite differently. Interestingly, both ethylene units remain in the coordination sphere of the complex in the course of the reaction. However, three C–H bonds are cleaved forming one terminal W–H as well as two bridging W–H–Al units. One C₂-fragment

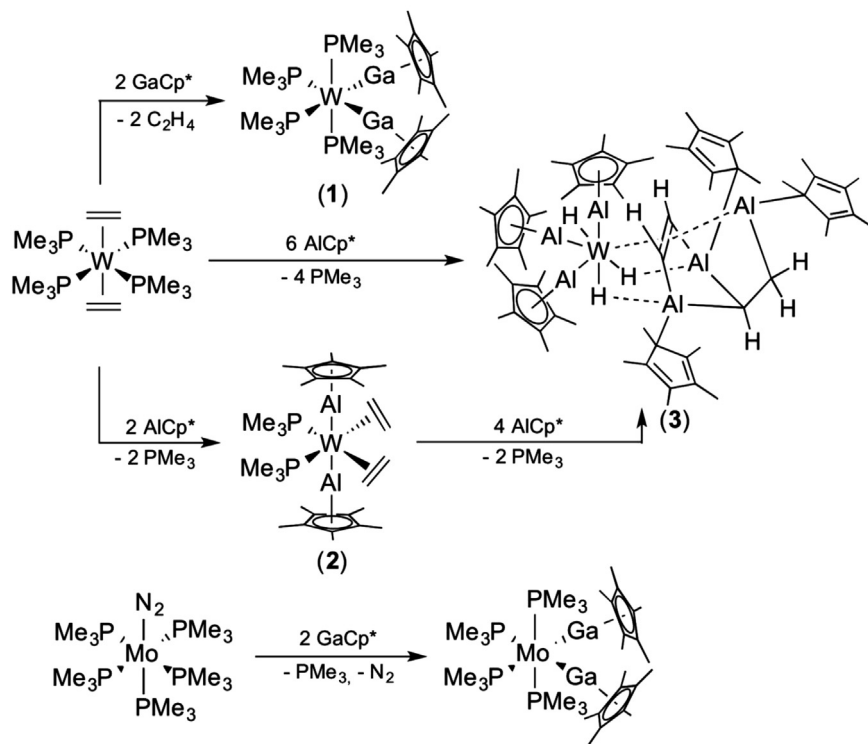
remains coordinated to the tungsten centre and interacts with one AlCp* unit, while the second C₂-fragment is bound to all the other three aluminium centres only. Compound **3** proves to be inert upon further treatment with AlCp*. It should be noted that complex **3** can be directly prepared from **1** and 6 M equiv of AlCp*. All new compounds **1–3** are air sensitive, both in solution and in solid state. They are stable for several weeks when stored under an inert atmosphere at low temperatures (e.g. –30 °C). Compounds **1** and **2** dissolve well in non-polar solvents like hexane or toluene, while compound **3** is moderately soluble in hot toluene. Suitable single crystals for molecular structure determination in the solid state were obtained by slow cooling of saturated toluene solutions of **1** and **2** to –30 °C or from hot toluene in the case of **3**. Finally we like to note that *trans*-[W(C₂H₄)₂(PMe₃)₄] does not react with InCp* at all, matching with the lesser donor strength of InCp* with respect to GaCp* and AlCp*. Also, *trans,trans,trans*-[W(CO)₂(C₂H₄)(PMe₃)₂] did not yield defined products upon reaction with AlCp* or GaCp*, respectively.

2.2. Analytical, spectroscopic and structural characterization

Mass spectrometric analyses were obtained for all complexes using liquid injection field desorption ionization mass spectrometry (LIFDI-MS). The molecular ion peaks are all in agreement with the proposed sum formulae (see Experimental part and Supplementary material for details). Fragmentation is observed in complex **1** by loss of GaCp* ligands [M – (GaCp*)⁺]: 695.2 and [M – (GaCp*)₂]²⁺: 489.1 m/z. Fragmentation was also observed in **3** with peaks for [WH₃(AlCp*)₃C₃H₃⁺]: 850.4 and [Al₃₂Cp₂C₃H₃⁺]: 389.3 m/z.

2.2.1. *cis*-[W(GaCp*)₂(PMe₃)₄] (**1**)

Compound **1** crystallizes in form of orange prismatic single crystals in the orthorhombic space group P2₁2₁2₁ as an inversion



Scheme 1. Synthesis of compounds **1–3**, as well as previously reported *cis*-[Mo(GaCp*)₂(PMe₃)₄].

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