# Reactivity of $(C_5Me_5)_2UMe_2$ and $(C_5Me_5)_2UMeCl$ toward Group 13 Alkyls

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The reactions of group 13 alkyl reagents ($AlMe_3$, $AlEt_3$, $GaMe_3$, $InMe_3$) with the uranium metallocene complexes $Cp^*_2UCl_2$, $Cp^*_2UMe_2$, and $Cp^*_2UClMe$ ($Cp^* = C_5Me_5$) were studied, and similarities to pertinent group 4 and lanthanide chemistry were considered. The methyl derivative $Cp^*_2UMe_2$ exhibits high reactivity toward the alkylaluminum reagents involving C−H bond activation, in contrast to $Cp^*_2UCl_2$, which did not react under similar conditions. The orange-red C−H bond activation product of the $AlMe_3$ reaction, $Cp^*_2MeU(\mu\text{-}Me)AlMe_2(\mu_3\text{-}CH_2)Al_2(\mu\text{-}Me)Me_4$, was identified by X-ray crystallography. It contains a trinuclear aluminum−methyl−methylene moiety, $[Al_3Me_8(CH_2)]^-$, linked to $[Cp^*_2UMe]^+$ via a bridging methyl group. The reaction of triethylaluminum with the orange-red chloro-methyl derivative $Cp^*_2UClMe$ gives reduction to the dark green uranium(III) complex $Cp^*_2U[(\mu\text{-}CH_2CH_3)AlEt_2(\mu\text{-}Cl)]_2UCp^*_2$ as evidenced by an X-ray structural analysis. Reactions of the less Lewis acidic gallium and indium alkyls were not observable by NMR spectroscopy, but the heterobimetallic complex $Cp^*_2U[(\mu\text{-}Me)(InMe_3)]_2$ was obtained by crystallization of a 1:2 mixture of $Cp^*_2UMe_2$ and $InMe_3$ from hexane. As indicated by a rather long $(U-CH_3)\cdots In$ distances in the range of 2.846−2.922 Å, the $InMe_3$ molecules interact only weakly with the dimethyl metallocene unit (no tetramethylindate coordination), which is further substantiated by facile removal of the group 13 alkyl under vacuum.

## Introduction

Alkylaluminum reagents interact synergistically with a wide range of transition metals and lanthanide metals to make combinations active in Ziegler−Natta-type polymerization catalysis.[1,2] Investigations into structure−reactivity relationships have revealed not only the beneficial alkylating and reducing power of the organoaluminum compounds, but also their crucial role as chain transfer reagents and catalyst deactivators.[1,2,4,5] Uranium-based catalyst mixtures also were found to be highly active and efficient polymerization initiators (e.g., $[U(OMe)_4-EtAlCl_2]$, >99% *cis*-polybutadiene), but their applicability is limited due to their radioactive nature.[6] It is therefore not surprising that only a few reports on discrete actinide/aluminum organometallics have appeared in the literature.[7−17] In fact, tetrachloroaluminate complexes constitute the only well-examined organouranium−aluminum(III) derivatives reported to date.[7−10] Already more than 35 years ago, the π−arene complex $(\eta^6\text{-}C_6H_6)U^{III}(AlCl_4)_3$, **A** (Chart 1), was crystallographi-

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(11) Despite the rich structural chemistry of rare-earth[12] and group 4 metal tetrahydroaluminate complexes,[13] uranium(actinide) derivatives remained scarce. Complexes $Cp_2U^{IV}(AlH_4)_2$, $Cp_3U^{IV}(AlH_4)$, and $U^{III}(AlH_4)_3$ were described but not structurally characterized.[14] The latter homoleptic complex was suggested as an active species in hydroalumination reactions.[15]

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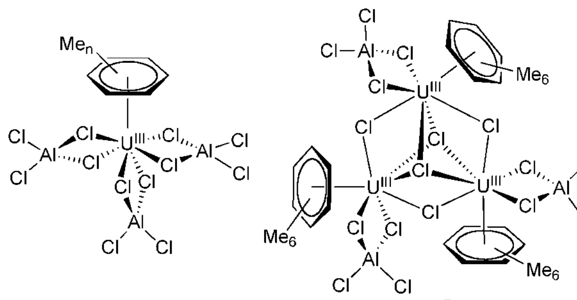
10.1021/om800914w CCC: $40.75

**Chart 1**



**A** (n = 0,1,6) **B**⊕

cally characterized and found to contain three $\eta^2$-coordinated tetrachloroaluminate ligands.[7]

Later on, closely related complexes with hexamethylbenzene[8] and toluene $\pi$-donors[9] were investigated with uranium, and a pronounced similarity to group 3 and 4 transition metals and lanthanides was found. While the synthesis conditions for such tetrachloroaluminate complexes, that is, Fischer's reductive Friedel−Crafts reaction,[18] routinely involved $U^{IV}/U^{III}$ redox couples (cf., $Zr^{IV}/Zr^{II}$ yielding $(\eta^6\text{-}C_6H_6)_2Zr^{II}(AlCl_4)_2)$),[19] structural similarities were found with redox-stable lanthanide metal(III) congeners (e.g., isostructural $(\eta^6\text{-}C_6Me_6)U(AlCl_4)_3$ and $(\eta^6\text{-}C_6Me_6)Sm(AlCl_4)_3$).[8c,20] Higher agglomerated complexes $[U^{IV}_2(\eta^6\text{-}C_6Me_6)_2Cl_4(\mu\text{-}Cl)_3]^+[AlCl_4]$[8b] and $[U^{III}_2(\eta^6\text{-}C_6Me_6)_3(\mu_3\text{-}Cl)_2(\mu_2\text{-}Cl)_3(\mu_1,\eta^2\text{-}AlCl_4)]^+[AlCl_4]^-$ ($[\mathbf{B}]^+[AlCl_4]^-$, Chart 1)[8a] were shown to form separated ion pairs.

Rather distinct reactivity patterns have been discovered with lanthanide and group 4 metal complexes with organoaluminum reagents and in particular with trimethylaluminum. While the lanthanides form a variety of thermally stable homo- and heteroleptic tetraalkylaluminate complexes,[2b,21] the isolation of corresponding group 4 derivatives seems to be hampered by their intrinsic instability.[22] The complex $[Ti(NtBu)(Me_3[9]\text{-}aneN_3)(\mu\text{-}Me)_2AlMe_2][BAr^F_4]$ appears to be the only crystallographically authenticated tetraalkylaluminate derivative.[23] It is noteworthy that C−H bond activation is a common reaction pathway in such heterobimetallic complexes, with the "Tebbe reagent", $Cp_2Ti(\mu\text{-}Cl)(\mu\text{-}CH_2)AlMe_2$, being the most prominent example.[3,24−28] To the best of our knowledge, well-characterized alkylated heterobimetallic complexes of uranium and group 13 metals have not been reported so far.[17] Herein we present the initial results of a study aiming at the reactivity of known metallocenes $Cp^*_2UCl_2$,[29] $Cp^*_2UMe_2$,[30] and $Cp^*_2UMeCl$[31] toward organoaluminum reagents, as well as trimethylgallium and -indium.

## Results and Discussion

The orange-red precursor compounds $Cp^*_2UCl_2$ (**1a**),[29] $Cp^*_2UMe_2$ (**1b**),[30] and $Cp^*_2UMeCl$ (**1c**)[31] were synthesized according to literature procedures. Such discrete organoactinide(IV) complexes have been subjected to a number of X-ray crystallographic investigations with bulky cyclopentadienyl ligands $C_5R_5$ stabilizing mononuclear complexes with terminally bonded methyl and chloro ligands (Table 1),[32−35] but surprisingly $Cp^*_2UMeCl$ (**1c**) has never been structurally characterized by X-ray diffraction. Compound **1c** crystallizes from toluene in space group $P2_1$ with unit cell parameters that are very close to those of crystals of **1a** obtained in this study from toluene/hexane solution in the monoclinic space group $P2_1/n$ (Figure 1). Previously, single crystals of **1a** obtained by sublimation were reported to crystallize in a different crystal system (orthorhombic *Fmm*2).[29] Although the structure of **1c** had disorder between the Me and Cl ligands, the crystal data suggest that this is $Cp^*_2UMeCl$ and not a cocrystallization of **1a** and **1b**, the latter of which crystallizes in $I_1/a$. Metrical parameters cannot be discussed for **1c** due to the disorder. A model in which the Me and Cl ligands were 50% disordered at each position gave the best results. The overall rigidity and chemical robustness of the well-shielded metallocene environment is anticipated to facilitate reactivity studies involving U−X moieties and group 13 reagents. Additionally, comparisons to the corresponding well-investigated metallocene chemistry of the group 4 and rare-earth metals can be drawn.

**Reactivity of $Cp^*_2UCl_2$.** The metallocene bis(chloride) complex **1a** did not react with any of the group 13 reagents under study (trimethylaluminum, triethylaluminum, trimethylgallium, and trimethylindium) in hexane at ambient temperature. After 2 d, only unreacted **1a** was recovered. Neither chloro/alkyl ligand exchange occurred, nor did adduct complexes of type $[Cp^*_2UCl_2(MR_3)_x]$ (M = Al, Ga, In) form upon crystallization. For comparison, in group 4 chemistry, $AlR_3$ addition and chloro/alkyl ligand exchange is commonly observed when complexes $Cp'_2MCl_2$ (M = Ti, Zr, Hf) are treated with

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**Table 1. Selected Metrical Parameters of Uranium Metallocenes $(C_5R_5)_2UX_2$ (X = Me, Cl)**

| compound | U−X (Å) | U−Cnt (Å) | X−U−X (deg) | Cnt−U−Cnt (deg) | ref |
|---|---|---|---|---|---|
| $(C_5Me_5)_2UMe_2$ | 2.424(7), 2.414(7) | 2.456 | 94.5(3) | 140.5 | 30a,b |
| $[1,3\text{-}(Me_3Si)_2C_5H_3]_2UMe_2$ | 2.42(2) | 2.44 | 105.0(7) | 130.8 | 33 |
| $(C_5Me_4H)_2UMe_2$ | 2.426(2) | 2.444 | 100.76(13) | 134.3 | 32c |
| $(C_5Me_4H)_2UMeCl$ | C, 2.653(6); Cl, 2.38(2) | 2.429 | 101.5(15) | 133.6 | 32c |
| $(C_5Me_5)_2UMeCl$ (**1c**) | C, 2.34(2), 2.35(2); Cl, 2.679(4), 2.650(4) | 2.393, 2.501 | 98.0(4), 98.4(5) | 139.2 | this work, 31a |
| $(C_5Me_4H)_2UCl_2$ | 2.5909(7) | 2.42 | 99.79(3) | 133.1 | 32b |
| $(C_5Me_5)_2UCl_2$ (**1a**) | 2.583(6) | 2.47 | 97.9(4) | 132 | 29b |
| $(C_5Me_5)_2UCl_2$ (**1a**) | 2.953(8) | 2.44 | 98.31(3) | 138 | this work |
| $[1,3\text{-}(Me_3Si)_2C_5H_3]_2UCl_2$ | 2.579(2) | 2.44 | 95.3(1) | 124.7 | 33, 34 |
| $[1,3\text{-}tBu_2C_5H_3]_2UCl_2$ | 2.577(4) | 2.49 | 91.0(2) | 128.1 | 33 |
| $[1,2\text{-}tBu_2C_5H_3]_2UCl_2$ | 2.591(4), 2.576(4) | 2.43 | 97.66(14) | 123 | 35 |

trimethyl(alkyl)aluminum.[1,5,25] Moreover, subsequent reaction of these M−methyl(alkyl) moieties with an excess of the organoaluminum compound can lead to C−H bond activation (cf., Tebbe reagent).[3] Mixtures of $[Cp^*_2LnCl]_x/AlR_3$ (R = Me, Et, *i*Bu) neither undergo a fast chloride exchange, nor is C−H bond activation a common reaction pathway. Instead the formation of adducts with the alkylaluminum reagents seems to be favored as shown recently for complexes $Cp^*_2Y(\mu\text{-Cl})(\mu\text{-Me})AlMe_2$[36] and $[Cp^*_2Sm(\mu\text{-Et})(\mu\text{-Cl})AlEt_2]_2$.[37]

**Reactivity of $Cp^*_2UMe_2$.** Instant reaction of the dimethyl complex $Cp^*_2UMe_2$ (**1b**) with trialkyl aluminum reagents ($AlMe_3$, $AlEt_3$) was observed at ambient temperature in deuterated benzene as indicated by methane/alkane evolution and a considerable chemical shift of the $C_5Me_5$ proton resonance to higher field (Figures S1 and S2, Supporting Information). Variation of the $Cp^*_2UMe_2/AlR_3$ ratios gave different mixtures of products as determined by NMR spectroscopy, but the paramagnetism of the uranium precluded a more detailed interpretation of these reactions. Moreover, a highly fluxional nature of the alkylaluminum groups is anticipated to contribute to signal broadening.[21] For comparison, $Cp_2ZrMe_2$ undergoes facile methyl exchange with $AlMe_3$ in toluene solution,[25] while complexes $[Cp^*_2LnMe]_x$ and $[Cp^*LnMe_2]_3$ add $AlMe_3$ to form tetramethylaluminate complexes $[Cp^*_2Ln(AlMe_4)]_n$[4] and $Cp^*Ln(AlMe_4)_2$, respectively.[27a]

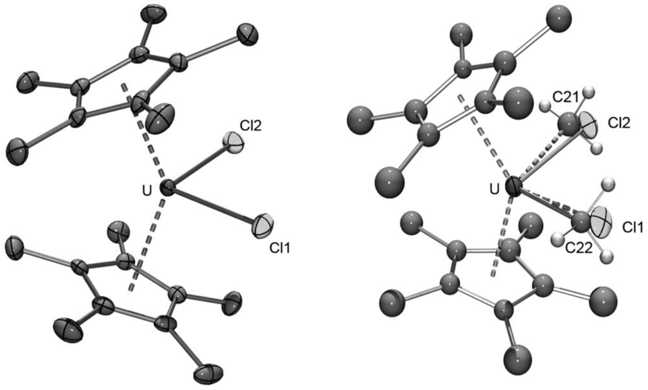

**Figure 1.** Molecular structure of $Cp^*_2UCl_2$ (**1a**, left) and partial ball-and-stick figure of $Cp^*_2UMeCl$ (**1c**, right) with the atomic displacement parameters set at the 50% level; for clarity, only hydrogen atoms are shown for the methyl ligands of **1c**.

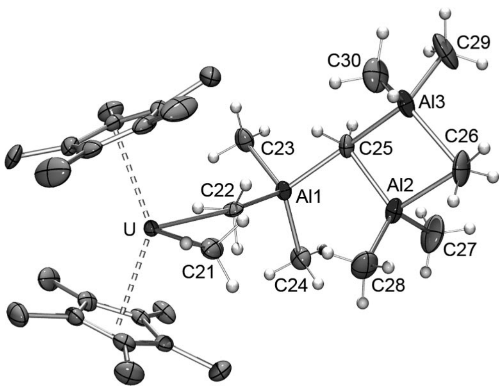

**Figure 2.** Molecular structure of $Cp^*_2UAl_3(\mu_3\text{-}CH_2)(\mu_2\text{-}CH_3)_2(CH_3)_7$ (**2**) with the atomic displacement parameter drawn at the 50% probability level. Hydrogen atoms of the Cp* ligands have been omitted for clarity.

Fortunately, we were able to identify the product of the reaction of **1b** with an excess (8 equiv) of $AlMe_3$ in hexane by X-ray crystallography (Scheme 1). At −35 °C, the reaction mixture produced red single crystals of $Cp^*_2UAl_3(\mu_3\text{-}CH_2)(\mu_2\text{-}CH_3)_2(CH_3)_7$, **2**. The molecular structure of the $UAl_3$ heterobimetallic complex provides the first structural evidence of an alkylaluminum induced C−H bond activation in actinide chemistry. Single-crystalline **2** showed a rather complicated $^1H$ NMR spectrum (benzene-$d_6$; >20 signals at 25 °C; Figure S2, Supporting Information). For group 4 organometallics, such hydrogen abstraction from alkyl ligands is a well-documented reaction pathway with several reaction products fully defined by X-ray crystallography.[24−26,38] Also, in the organolanthanide area, several examples of organoaluminum-assisted transformations of methyl ligands into cluster-embedded methylene ($CH_2^{2-}$), methine ($CH^{3-}$), and carbide ($C^{4-}$) moieties have been observed.[27,28] The latter monocyclopentadienyl complexes, however, involve direct $Ln^{3+}-CH_2^{2-}$ interaction. Heating complex **2** with an excess of trimethylaluminum led to further C−H bond activation as indicated by methane formation, but the attempted crystallization of these products was unsuccessful.

The molecular structure of complex **2** is shown in Figure 2, and selected bond lengths and angles are listed in Table 2. The most striking structural feature is the negatively charged trimetallic aluminum ligand $[Al_3(CH_3)_6(\mu_3\text{-}CH_2)(\mu_2\text{-}CH_3)_2]^-$, which is linked to the $[Cp^*_2UMe]^{1+}$ entity via one of the bridging methyl groups. The $U-C_{Me}$ bond length of 2.658(5) Å of the latter bridging methyl group is markedly elongated compared with the terminally bonded one (2.395(6) Å). For comparison, complexes $(C_5R_5)_2UMe_2$ show $U-C_{Me}$ bond lengths

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**Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for [$Cp^*_2UAl_3(\mu_3\text{-}CH_2)(\mu_2\text{-}CH_3)_2(CH_3)_7$] (2)**

| Bond Distances (Å) | | | |
|---|---|---|---|
| U−C21 | 2.395(6) | Al1−C23 | 1.983(6) |
| U−C22 | 2.658(5) | Al2−C25 | 2.018(6) |
| U−Cp(Cnt1) | 2.431 | Al2−C26 | 2.219(8) |
| U−Cp(Cnt2) | 2.429 | Al3−C25 | 2.104(6) |
| Al1−C22 | 2.099(5) | Al3−C26 | 2.219(8) |
| Al1−C25 | 2.076(6) | | |
| **Bond Angles (deg)** | | | |
| C21−U−C22 | 93.4(2) | C25−Al3−C26 | 103.6(3) |
| Al1−C22−U | 170.3(3) | C25−Al2−C26 | 102.2(3) |
| C22−Al1−C25 | 107.5(2) | C25−Al3−C28 | 114.8(3) |
| Al1−C25−Al3 | 166.3(3) | C26−Al3−C28 | 103.1(3) |
| Al1−C25−Al2 | 98.4(3) | C27−Al3−C28 | 123.0(4) |

in the range of 2.404(5)−2.426(2) Å (Table 1).[30,32] The angle $C_{Me}$−U−$C_{Me}$ of 93.4(2)° is only slightly more acute than the one found in $Cp^*_2UMe_2$ (94.5(3)°) consistent with no interaction of the "$Al_3$" ligand with the terminal methyl group (C21). Each aluminum atom is surrounded by four carbon atoms in a distorted tetrahedral fashion and is attached to two terminally bonded methyl groups (Al−C, 1.968(7)−1.986(6) Å). Although one has to be careful with the localization of hydrogen atoms on the basis of X-ray structure data only, the $Al_3$ coordination of carbon atom C25 is very supportive of a five-coordinated methylene unit in this position.[28]

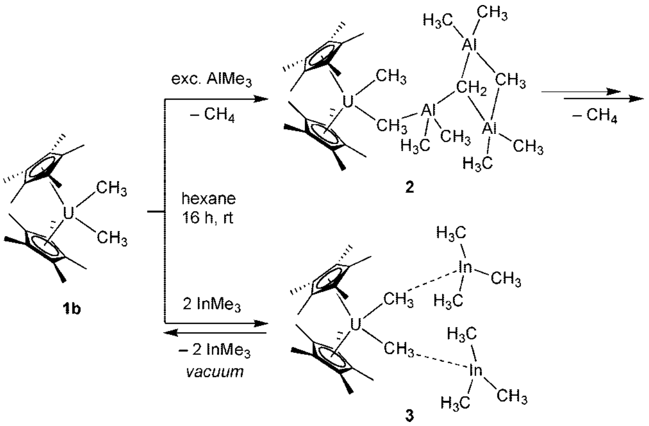
The Al−$CH_2$ bond distances average 2.066 Å being comparable to those found for the $Al_3$−$CH_2$ moiety in complexes $(Cp^*M)_3Al_6(CH_3)_8(\mu_3\text{-}CH_2)_2(\mu_4\text{-}CH)_4(\mu_3\text{-}CH)$ (M = Zr, Hf) (2.047(8)−2.071(8) Å).[38a,b] The Al1 atom is linked to the $Cp^*_2UMe_2$ entity via a bridging methyl group (Al1−C22, 2.099(5) Å), whereas the other two aluminum atoms complete their coordination sphere by sharing an asymmetrically bridging methyl group (Al2−C26, 2.219(8); Al3−C26, 2.094(7) Å). The distinct coordination chemistry of Al2 and Al3 is also revealed by almost linear and rather acute Al1−C25−Al3 (166.3(3)°) and Al1−C25−Al2 (98.4(3)°) bonding angles, respectively. Due to the significantly longer Al−C bond lengths of the linear Al1−C25−Al3 array (2.076(6) and 2.104(6) Å) compared with the 2.018(6) Å of Al2−C25 at right angles, one might postulate an inverse trans influence.

No visible reaction occurred when $Cp^*_2UMe_2$ (**1b**) was treated with less Lewis acidic trimethylgallium or trimethylindium, and the unreacted uranium compound **1b** could be recovered upon evaporation of the solvent and the group 13 alkyl reagent. However, from mixtures of **1b** and 2 equiv of $InMe_3$ in toluene/hexane, the complex $Cp^*_2U[(\mu\text{-}Me)(InMe_3)]_2$ (**3**) could be obtained as red crystals (Scheme 1, Figure 3). The weakly coordinated $InMe_3$ molecules dissociate and sublime under vacuum, and the proton NMR spectrum of complex **3** only shows the unshifted signals of **1b** and $InMe_3$.

The solid-state structure of complex **3** revealed an unusual interaction of two $InMe_3$ molecules with the $Cp^*_2UMe_2$ unit (Figure 3; selected bond lengths and angles are listed in Table 3; two independent molecules in the unit cell). The U−C(methyl) bond distances average 2.451 Å and appear only slightly elongated compared with those in **1b** (2.404(5) and 2.414(7) Å), whereas the $C_{Me}$−U−$C_{Me}$ angle of average 98.8° is marginally wider (**1b**, 94.5(3)°).[27] The coordination geometry of the indium metal centers is close to trigonal planar with In−C distances of 2.158(5)−2.184(6) Å and the In atoms displaced 0.164−0.221 Å out of the ligand plane in the direction toward the bridging methyl group and the uranium center.

For comparison, the In−C distances in the two different polymorphs of $InMe_3$ range from 2.149(5) to 2.173(3) Å with the In atoms located only 0.0701(2) Å above the ligand plane.[39] Interestingly, the In···C(μ-Me) distances of the U−$CH_3$···In linkages average 2.890 Å, which is considerably shorter than the intermolecular In···C contacts in pure $InMe_3$ (3.028(3)−3.409(4) Å).[39] This shorter contact might indeed be the driving force for the formation and crystallization of compound **1b**. Homoleptic tetramethylaluminate complexes $Ln(AlMe_4)_3$ tend to cocrystallize with trimethylaluminum forming 2:1 inclusion compounds $[Ln(AlMe_4)_3]_2[Al_2Me_6]$ with no additional close Ln···C or Al···C contact.[21a] However, it is clear from the Al−C distances of the $\eta^1$-coordinated tetramethylaluminate ligand in $[2,6\text{-}\{(2,6\text{-}iPr_2C_6H_3)NCMe_2\}_2C_5H_3N]Ln[(\mu\text{-}Me)(AlMe_3)](THF)$ (Al−$C_{\mu\text{-}Me}$, 2.024(7); Al−$C_{Me}$, avg 1.974 Å),[40] that the In−methyl coordination in **3** does not make up a tetramethylindate ligand. For indium, only the alkali metal tetramethylindates $MInMe_4$ (M = Li, Na, K, Cs) have been structurally investigated by X-ray diffraction, each showing four equal In−C bond lenghts (Li, 2.223(4); Na, 2.195(4); K, 2.239(3); Cs, 2.26(2) Å).[41] The two trimethylindium molecules

**Scheme 1. Reaction of $Cp^*_2UMe_2$ (1b) with Trimethylaluminum and Trimethyindium**



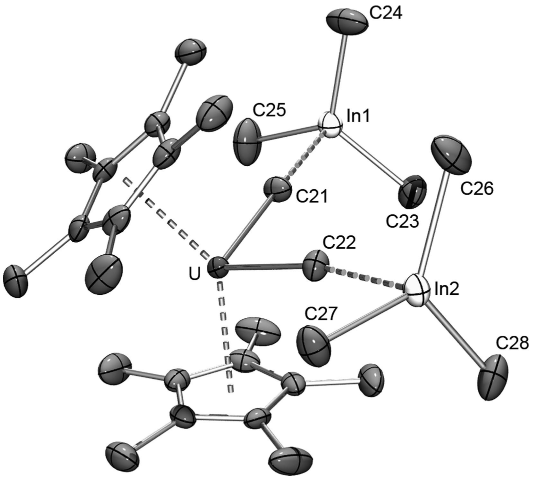


**Figure 3.** Molecular structure of $Cp^*_2U(\mu\text{-}Me)_2(InMe_3)_2$ (**3**) with the atomic displacement parameter drawn at the 50% level. Hydrogen atoms have been excluded for clarity.

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**Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for Cp*$_2$U($\mu$-Me)$_2$(InMe$_3$)$_2$ (3)**

| molecule 1 | | molecule 2 | |
|---|---|---|---|
| Bond Distances (Å) | | | |
| U1−Cp(Cnt1) | 2.455 | U2−Cp(Cnt3) | 2.458 |
| U1−Cp(Cnt2) | 2.455 | U2−Cp(Cnt4) | 2.459 |
| U1−C21 | 2.448(4) | U2−C49 | 2.448(4) |
| U1−C22 | 2.448(4) | U2−C50 | 2.458(4) |
| In1···C21 | 2.876 | In3···C49 | 2.922 |
| In2···C22 | 2.915 | In4···C50 | 2.846 |
| In1−C23 | 2.164(5) | In3−C51 | 2.184(6) |
| In1−C24 | 2.152(5) | In3−C52 | 2.158(5) |
| In1−C25 | 2.161(6) | In3−C53 | 2.158(5) |
| In2−C26 | 2.160(5) | In4−C54 | 2.176(6) |
| In2−C27 | 2.167(5) | In4−C55 | 2.164(6) |
| In2−C28 | 2.167(5) | In4−C56 | 2.164(5) |
| Bond Angles (deg) | | | |
| C21−U1−C22 | 97.32(16) | C49−U2−C50 | 100.33(16) |
| U1−C21−In1 | 169.3 | U2−C49−In3 | 162.5 |
| U1−C22−In2 | 164.7 | U2−C50−In4 | 175.8 |
| C23−In1−C24 | 117.5(3) | C51−In3−C52 | 121.3(3) |
| C25−In1−C23 | 119.9(3) | C51−In3−C53 | 117.3(3) |
| C24−In1−C25 | 119.5(3) | C52−In3−C53 | 119.2(3) |
| C26−In2−C27 | 118.6(2) | C54−In4−C55 | 115.7(3) |
| C26−In2−C28 | 122.0(2) | C54−In4−C56 | 120.7(3) |
| C27−In2−C28 | 117.7(2) | C55−In4−C56 | 120.6(2) |

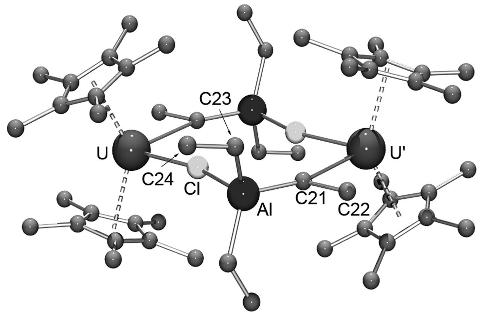
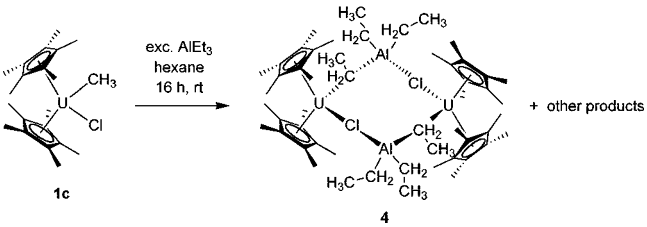


**Figure 4.** Ball-and-stick figure of Cp*$_2$U[($\mu$-CH$_2$CH$_3$)AlEt$_2$($\mu$-Cl)]$_2$UCp*$_2$ (**4**).

in **3** are bent away from each other in such a way that they form obtuse U−C$_{\mu\text{-Me}}$−In angles ranging from 162.5° to 175.8°.

**Reactivity of Cp*$_2$UMeCl.** As with Cp*$_2$UMe$_2$ (**1b**), treatment of Cp*$_2$UClMe (**1c**) with trimethylgallium and trimethylindium in hexane for 48 h led to the isolation of unreacted **1c** after evaporation of the solvent (and group 13 alkyls). Surprisingly, also trimethylaluminum did not show any reactivity toward **1c** within 3 d at ambient temperature in deuterated benzene or hexane. On the other hand, triethylaluminum reacted instantly with **1c** in aliphatic solvents (pentane, hexane) as indicated by a color change from red to dark green. Upon crystallization from hexane solution at −35 °C, dark green single crystals of complex **4** could be obtained in reasonable yields (59%; thicker crystals appear black). The crystals could be redissolved in a hexane/toluene mixture. The overall structure of **4** was determined by X-ray crystallography as Cp*$_2$U[($\mu$-CH$_2$CH$_3$)AlEt$_2$($\mu$-Cl)]$_2$UCp*$_2$ (Figure 4); however, the quality of the crystals (examined from different batches and reactions) precluded a detailed discussion of metrical parameters. The formation of a U$^{III}$ compound, **4**, with this molecular composition/connectivity (Scheme 2) is consistent with the observed color changes, microanalytical data, mass spectrum (peak assignable to [Cp*$_2$UCl]$_3$),[42] and $^1$H NMR data (Figure S3, Supporting Information). Moreover, the reducing action of organoaluminum compounds is well-established in Ziegler−Natta catalysts, and the enhanced reducing capability of AlEt$_3$ toward chlorinated hydrocarbons has been first reported 45 years ago.[43]

**Scheme 2. Reaction of Triethylaluminum with Cp*$_2$UMeCl (1c)**



Complex **4** crystallizes in the space group $P2_1/c$ showing a centrosymmetric dinuclear metallocene structure with two [Cp*$_2$U]$^{1+}$ units connected by $\mu_2$−$\eta^1$(Et):$\eta^1$(Cl) heterobridging [AlEt$_3$Cl]$^{1-}$ ligands to form an eight-membered metallacycle. The solid-state structure is isomorphous to that of the samarium(III) complex Cp*$_2$Sm[($\mu$-CH$_2$CH$_3$)AlEt$_2$($\mu$-Cl)]$_2$SmCp*$_2$, which was obtained by addition of AlEt$_3$ to [Cp*$_2$Sm($\mu$-Cl)]$_3$.[37]

## Conclusion

Reactions of the known uranium(IV) metallocene complexes Cp*$_2$UMe$_2$ and Cp*$_2$UClMe with organoaluminum compounds AlR$_3$ (R = Me, Et) reveal similarities to both group 4 and lanthanide metal complexes. Comparable to well-established zirconocene chemistry, the dimethyl complex engages in C−H bond activation reactions and aluminum−methyl−methylene clustering as evidenced by the formation of Cp*$_2$U$^{IV}$Al$_3$($\mu_3$-CH$_2$)($\mu_2$-CH$_3$)$_2$(CH$_3$)$_7$. Under the same conditions, the less Lewis acidic GaMe$_3$ and InMe$_3$ interact only weakly with these cyclopentadienyl-supported U$^{IV}$−CH$_3$ moieties. The approach of two group 13 metal alkyls as structurally identified in adduct Cp*$_2$U[($\mu$-Me)$_2$InMe$_3$]$_2$ can be seen as the first possible reaction intermediate prior to C−H bond activation and formation of the UAl$_3$ cluster. In contrast, mixed chloride/methyl coordination as in Cp*$_2$UClMe favors an AlEt$_3$-promoted reduction and formation of [Cp*$_2$U$^{III}$Al($\mu$-CH$_2$CH$_3$)(Et)$_2$($\mu$-Cl)]$_2$. Such dimerization via $\mu_2$−$\eta^1$(Et):$\eta^1$(Cl) heterobridging [AlEt$_3$Cl]$^{1-}$ ligands involving the larger uranium(III) is a known structural motif in trivalent lanthanide chemistry.

## Experimental Procedures

**General Remarks.** This chemistry was performed under argon with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. Solvents were sparged with UHP argon (airgas) and dried over columns containing Q-5 and molecular sieves. NMR solvents (Cambridge Isotopes) were dried over benzophenone-ketyl, degassed, and vacuum transferred before use. Cp*$_2$UCl$_2$ (**1a**) and Cp*$_2$UMe$_2$ (**1b**) were prepared according to the literature procedures.[29,30] The synthesis of Cp*$_2$UMeCl (**1c**) was slightly modified[31] by stirring an equimolar mixture of **1a** and **1b** overnight at ambient temperature. HCp* (Aldrich) was distilled before use. Trimethylaluminum, triethylaluminum, trimethylgallium, and trimethylindium were used as received from Aldrich. $^1$H and $^{13}$C NMR spectra were recorded on Bruker 500 and 600 MHz spectrometers. Infrared spectra were recorded as Nujol mulls between CsI plates on a NICOLET Impact 410 FTIR spectrometer. Elemental analyses were performed on an Elementar Vario EL III.

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**Table 4. X-ray Data Collection Parameters for Cp*$_2$UCl$_2$ (1a), Cp*$_2$UClMe (1c), [Cp*$_2$UAl$_3$($\mu_3$-CH$_2$)($\mu_2$-CH$_3$)$_2$(CH$_3$)$_7$] (2), and Cp*$_2$U[($\mu$-Me)(InMe$_3$)]$_2$ (3)**

| compound | **1a** | **1c** | **2** | **3** |
|---|---|---|---|---|
| empirical formula | $C_{20}H_{30}Cl_2U$ | $C_{21}H_{33}ClU$ | $C_{30}H_{59}Al_3U$ | $C_{28}H_{54}In_2U$ |
| FW | 579.37 | 558.95 | 738.74 | 858.38 |
| temp (K) | 148(2) | 163(2) | 163(2) | 163(2) |
| cryst syst | monoclinic | monoclinic | orthorhombic | triclinic |
| space group | $P2_1/n$ | $P2_1$ | $P2_12_12_1$ | $P\bar{1}$ |
| $a$ (Å) | 8.6224(12) | 8.1602(13) | 9.5861(14) | 10.5446(16) |
| $b$ (Å) | 16.960(2) | 17.039(3) | 12.0189(17) | 16.071(3) |
| $c$ (Å) | 13.919(2) | 8.3283(13) | 30.141(4) | 18.994(3) |
| α (deg) | 90 | 90 | 90 | 88.303(2) |
| $\beta$ (deg) | 91.340(2) | 116.735(3) | 90 | 89.779(2) |
| $\gamma$ (deg) | 90 | 90 | 90 | 83.912(2) |
| vol (Å$^3$) | 2034.9(5) | 1034.2(3) | 3472.7(9) | 3199.1(8) |
| $Z$ | 4 | 2 | 4 | 4 |
| $\rho_{calcd}$ (mg/mm$^3$) | 1.891 | 1.795 | 1.413 | 1.782 |
| $\mu$ (mm$^{-1}$) | 8.237 | 7.976 | 4.765 | 6.491 |
| R1[a] ($I > 2.0\sigma(I)$) | 0.0288 | 0.0226 | 0.0308 | 0.0262 |
| wR2[b] (all data) | 0.0349 | 0.0355 | 0.0438 | 0.3568 |

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

**Cp*$_2$UAl$_3$($\mu_3$-CH$_2$)($\mu_2$-CH$_3$)$_2$(CH$_3$)$_7$, 2.** Cp*$_2$UMe$_2$ (150 mg, 0.279 mmol) was dissolved in 5 mL of hexane, and AlMe$_3$ (161 mg, 2.236 mmol) dissolved in 3 mL of hexane was added under stirring. The solution was filtered after 1 h and transferred into a vial, and the solvent was reduced by evaporation at ambient temperature for several hours. Overnight crystallization at −35 °C afforded red crystalline **2** in 49% yield (104 mg). The synthesis of **2** is also possible in pentane. Anal. Calcd for $C_{30}H_{59}Al_3U$ (741.796 g/mol): C, 48.58; H, 8.42. Found: C, 50.16; H, 7.80. $^1$H NMR (500 MHz, toluene-$d_8$, 25 °C): $\delta$ = 9.17, 7.09, 6.21, −1.33, −2.09, −3.06, −3.75, −5.00, −7.38, −7.94, −9.58, −14.07 ppm (see Figures S1 and S2 of Supporting Information). IR (Nujol): 1308 m, 1152 w, 971 w, 919 w, 888 w, 842 w cm$^{-1}$.

**Cp*$_2$U[($\mu$-Me)InMe$_3$]$_2$, 3.** Cp*$_2$UMe$_2$ (100 mg, 0.19 mmol) was dissolved in 10 mL of pentane. InMe$_3$ (2.5 eq., 74 mg, 0.46 mmol) was added, and the reaction mixture was stirred for 2 h. The solvent was reduced to ca. 4 mL under vacuum. Cooling the red solution to −35 °C produced colorless crystals of InMe$_3$ overnight. The red supernatant was decanted and filtered, producing orange crystals (thicker crystals appear red) of **3** overnight at −35 °C. The X-ray crystal structure was confirmed by checking the cell constants of a second crystal. The InMe$_3$ was easily removed under vacuum, making follow-up characterization difficult. After drying under vacuum, only Cp*$_2$UMe$_2$ (**1b**) could be recovered in quantitative yield. A $^1$H NMR spectroscopic examination of a solution of Cp*$_2$UMe$_2$ and InMe$_3$ in $C_6D_6$ did not reveal any significant chemical shifts of the adduct signals.

**[Cp*$_2$UAl($\mu$-CH$_2$CH$_3$)(Et)$_2$($\mu$-Cl)]$_2$, 4.** Cp*$_2$UClMe (200 mg, 0.36 mmol) was dissolved in 15 mL of hexane, and AlEt$_3$ (200 mg, 1.75 mmol) in 5 mL of hexane was added under stirring. After the color had changed from red to dark green within 1 h, the mixture was reduced to ca. 2 mL. The dark green solid, which crystallized upon evaporation of the solvent under vacuum, was redissolved by addition of 1 mL of toluene to the mixture. After filtration, the product was recovered by crystallization at −35 °C as dark green almost black crystals. Three crystallization steps within 3 days yielded 138 mg (59%) of a single-crystalline product. The crystals could be stored in glass ampules at ambient temperature over weeks without decomposition. Anal. Calcd for $C_{52}H_{88}Al_2Cl_2U_2$ (1314.198 g/mol): C, 46.90; H, 6.56. Found: C, 47.52; H, 6.75. $^1$H NMR (500 MHz, toluene-$d_8$, 25 °C): $\delta$ = −2.77, −9.90, −11.83 ppm (see Figure S3 of Supporting Information). IR (Nujol): 1303 m, 1240 w, 1194 m, 1168 m, 1152 m, 1080 w, 1023 w, 971 w, 935 w, 888 w, 847 w, 811 w, 681 s, 547 m cm$^{-1}$.

**X-ray Data Collection, Structure Determinations, and Refinement.** A typical procedure is given for **2**. All other structures were done similarly except as noted. Table 4 presents the crystallographic data.

**Cp*$_2$UAl$_3$($\mu_3$-CH$_2$)($\mu_2$-CH$_3$)$_2$(CH$_3$)$_7$, 2.** A red plate of approximate dimensions 0.06 × 0.18 × 0.21 mm$^3$ was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[44] program package was used to determine the unit-cell parameters and for data collection (30 s/frame scan time for a sphere of diffraction data). The raw frame data were processed using SAINT[45] and SADABS[46] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[47] program. The diffraction symmetry was *mmm*, and the systematic absences were consistent with the orthorhombic space group $P2_12_12_1$, which was later determined to be correct.

The structure was solved by direct methods and refined on $F^2$ by full-matrix least-squares techniques. The analytical scattering factors[48] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. At convergence, wR2 = 0.0689 and GOF = 1.121 for 352 variables refined against 7678 data (0.78 Å), and R1 = 0.0294 for those 7231 data with $I > 2.0\sigma(I)$ (GOF = $S = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$ where $n$ is the number of reflections and $p$ is the total number of parameters refined). The structure was refined using the SHELXTL[47] TWIN command, BASF = 0.328(7).

**Cp*$_2$UCl$_2$, 1a.** A red crystal of approximate dimensions 0.04 × 0.13 × 0.23 mm$^3$ was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The diffraction symmetry was 2/*m*, and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/n$, which was later determined to be correct. Hydrogen atoms were located from a difference-Fourier map and refined ($x$, $y$, $z$, and $U_{iso}$). At convergence, wR2 = 0.0477 and GOF = 1.071 for 328 variables refined against 5004 data (0.75Å); R1 = 0.0201 for those 4095 data with $I > 2.0\sigma(I)$.

**Cp*$_2$UCl(CH$_3$), 1c.** A red crystal of approximate dimensions 0.07 × 0.10 × 0.23 mm$^3$ was mounted on a glass fiber and transferred to a Bruker SMART1K diffractometer. For data collection, 40 s/frame scan time was used for a hemisphere of diffraction data. The diffraction symmetry was 2/*m*, and the systematic absences were consistent with the monoclinic space groups $P2_1$ and $P2_1/m$. It was later determined that the noncentrosymmetric space group $P2_1$ was the better choice. The structure was solved in space groups $P2_1$ and $P2_1/m$ and was disordered in both. Refinement in space group $P2_1/m$ was not satisfactory and resulted in the pentamethylcyclopentadienyl rings adopting an eclipsed orientation due to the mirror plane. The chloro and methyl ligands were also disordered. Space group $P2_1$ yielded a better refinement, and a reasonable disorder for the chlorine and methyl ligands was observed (each was included as two components with site-occupancy factors = 0.50, Cl1/Cl2 and C21/C22). It was necessary to refine all carbon atoms with isotropic thermal parameters. While neither space group gave an entirely satisfactory refinement, it was determined that refinement using the noncentrosymmetric space group $P2_1$ resulted in the best model. Least-squares analysis yielded wR2 = 0.0719 and GOF = 1.070 for 129 variables refined against 4425 data (0.78Å); R1 = 0.0286 for those 4068 data with $I > 2.0\sigma(I)$. The structure was refined as a twin with BASF = 0.514(14).

**Cp*$_2$[($\mu$-Me)InMe$_3$]$_2$, 3.** A red crystal of approximate dimensions 0.20 × 0.23 × 0.25 mm$^3$ was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. For data collection, 25 s/frame scan time was used for a sphere of diffraction

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(44) SMART Software Users Guide, version 5.1, Bruker Analytical X-Ray Systems, Inc.; Madison, WI, 1999.

(45) SAINT Software Users Guide, version 6.0, Bruker Analytical X-Ray Systems, Inc.; Madison, WI, 1999.

data. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The pentamethylcyclopentadienyl ring defined by atoms C39−C48 was disordered and included using multiple components, partial site-occupancy factors, and isotropic thermal parameters. At convergence, wR2 = 0.0661 and GOF = 1.085 for 591 variables refined against 15540 data (0.75Å), R1 = 0.0280 for those 13853 data with $I > 2.0\sigma(I)$.

**Acknowledgment.** We thank the program Nanoscience@UiB and the Chemical Sciences, Geosciences, and Biosciences Division of the Office of Basic Energy Sciences of the U.S. Department of Energy for financial support.

**Supporting Information Available:** $^1$H NMR spectra showing the progress of the reaction of **1b** with trimethylaluminum, $^1$H NMR spectrum of single-crystalline **2**, VT $^1$H NMR spectra of complex **4**, and full crystallographic data for complexes **1a**, **1c**, **2**, **3**, and **4** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

OM800914W

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(46) Sheldrick, G. M. SADABS, version 2.10, Bruker Analytical X-Ray Systems, Inc.; Madison, WI, 2002.

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