

## Reactivity of the Uranium–Carbon $\sigma$ -Bond in ‘Silylamido’ Compounds\*

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### Abstract

The uranium–methyl  $\sigma$ -bond of  $(\text{N}(\text{SiMe}_3)_2)_3\text{U-CH}_3$  (**1**) and the uranium–methylene  $\sigma$ -bond of the metallacycle  $(\text{N}(\text{SiMe}_3)_2)_2\text{U-CH}_2\text{SiMe}_2\text{N-SiMe}_3$  (**2**) are very reactive towards insertion reactions and nucleophilic substitution reactions. Their reactivity can be used in organic synthesis.

Compounds **1** and **2** reacted readily with isocyanides, nitriles and carbonyl compounds  $\text{R}_1\text{R}_2\text{C=O}$ . Aldehydes, ketones and esters inserted rapidly in compound **2**, affording quantitatively the six-membered metallacycles:  $(\text{N}(\text{SiMe}_3)_2)_2\text{-UOC(R}_1\text{R}_2)\text{CH}_2\text{SiMe}_2\text{N-SiMe}_3$ . These metallacycles were hydrolyzed leading to methylketones (from esters) and to vinyl compounds (from aldehydes and ketones) in high yields. The insertion reaction was highly stereoselective.

Compound **2** is a very rapid, clean and high yielding methylenation reagent. It can be used instead of ‘Tebbe’s reagent’ to synthesize vinyl compounds from carbonyls.

**1** reacted rapidly with aldehydes, much more slowly with aliphatic, cyclic and aromatic ketones, but did not react with sterically hindered ketones or esters. Hydrolysis of the intermediate alkoxyuranium  $(\text{N}(\text{SiMe}_3)_2)_3\text{UOCR}_1\text{R}_2\text{CH}_3$  gave the corresponding secondary or tertiary alcohols. Compound **1** is a very highly chemoselective reagent of methylation of aldehydes *versus* ketones and a highly stereoselective reagent.

### Introduction

The reactivity of two electron sigma bonds between a metal ion and the carbon atom of organic

moieties plays a major role in both stoichiometric and catalytic chemistry. While for elements of the main groups, the chemistry of this type of linkage has known a fantastic development since the fifties, the chemistry of actinide hydrocarbyls is a recent field and it became apparent only ten years ago that a wide range of kinetically stable actinide hydrocarbyls can be synthesized and that these compounds underwent a variety of unusual reactions with surprising vigor. Therefore the last few years have witnessed a dramatic expansion in areas of both synthesis and reactivity of 5f metal hydrocarbyls.

The synthesis of stable actinide complexes containing only alkyl or aryl groups bonded to the metal has been a challenge since the early 1940s. Since then, many attempts to synthesize stable homoleptic actinide hydrocarbyls have failed and, although Marks *et al.* had isolated a stable heptamethylthorate complex [1], most kinetically stable actinide hydrocarbyls are coordinatively saturated cyclopentadienyls or related anionic species. A great number of thorium and uranium triscyclopentadienyl hydrocarbyls with single [2, 3] or multiple metal–carbon bonds [4] have been synthesized and extensively studied.

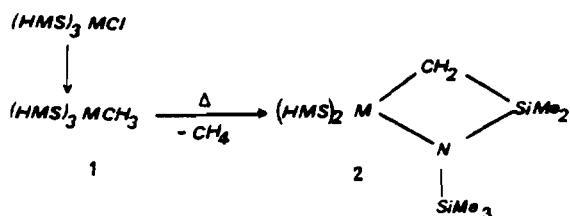
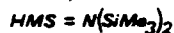
More reactive actinide hydrocarbyls are stabilized by bispentaalkylcyclopentadienyl coligation and a wide range of mono- or bishydrocarbyls have been synthesized [5–7]. Thermolysis of thorium bishydrocarbyls afforded the extremely reactive thoracyclobutanes [8, 9].

The actinide–carbon bond of bispentaalkylcyclopentadienyl actinides is relatively polar and undergoes rapid protonolysis addition to carbonyl groups, halogenolysis and hydrogenolysis [10]. Moreover, the facile activation of saturated hydrocarbons, as in olefinic insertion by thoracyclobutanes, is particularly fascinating [11, 12] but all these very interesting compounds suffer from a very high cost price!

Andersen *et al.* have reported that coordinatively unsaturated, thermally stable and hydrocarbon-soluble actinide methyl compounds are readily synthesized in another way [13]:

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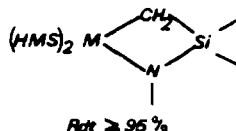
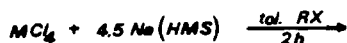
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Thermolysis of the methyl compound **1** proceeds by  $\gamma$ -hydrogen elimination to give the metallacycle **2** [14]. The polarity of the actinide-carbon bond and the ring strain inherent in the four-membered ring enhance significantly the reactivity of the metal-methylene bond [15] and trissilylamido actinide complexes appear to have a rich and complex organometallic chemistry. Therefore, they could be used as reagents in organic synthesis. For this purpose, we have investigated the reactivity of the uranium metallacycle **2** and of the trissilylamidoalkyluranium **1** towards insertion reactions into the metal-carbon bond and towards substitution reactions of the hydrocarbyl ligand.

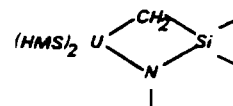
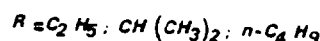
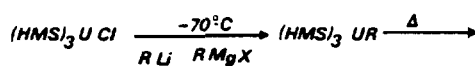
### Insertion Reactions

In the first place, with the aim of using a cheap starting material, the synthesis of the metallacycles **2** (uranium or thorium) has been significantly improved. They are obtained almost quantitatively in an one-step one-pot operation [16] from U or Th tetrachlorides and an excess of hexamethyldisilylamidosodium in boiling toluene, followed by direct recrystallization from the reaction mixture. The yields are more than 95%.



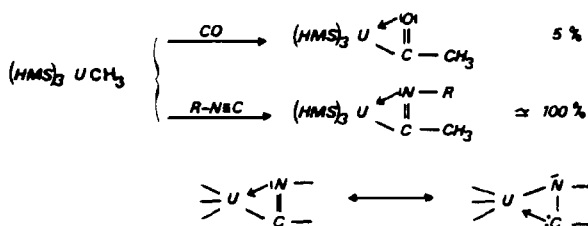
The methyl compounds (uranium or thorium) are obtained in very good yield as described by Andersen [13]. These compounds are stable in the solid state, but in benzenic or hydrocarbon solution the uranium compound undergoes a slow cyclisation reaction affording the metallacycle. At 60°, this reaction is complete within 1 h in benzene. Of course, such

behavior precludes heating and all reactions must be performed at temperatures lower than 25°. At room temperature, the reaction of the chloro compound  $(HMS)_3UCl$  with alkyllithium or alkylmagnesium afforded the metallacycle [14]. Hence, it was impossible to isolate trissilylamido alkyls other than the methyl complex. In fact, these thermally unstable complexes are synthesized and stored for a short period at -70°.



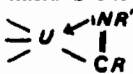
### Carbon Monoxide and Isocyanides

Carbon monoxide and isocyanides insert easily in the uranium-methylene bond of **2** [15]. On the contrary it is very difficult to insert carbon monoxide into the metal-methyl bond of **1** and very small amounts of the insertion compound are obtained at medium pressure, whereas the insertion of isocyanide occurs rapidly and quantitatively at room temperature (heating is precluded, see above). The infrared C=N stretching band appears near 1590 cm<sup>-1</sup>. This low frequency is in good accordance with an important part of the carbenoid form in the molecule. We have previously reported similar behavior for the inserted isocyanides in the triscyclopentadienyl and biscyclopentadienyl series [17].



A very interesting structural point concerns the chemical shifts of the methyl protons in the inserted compounds of both trissilylamido and triscyclopentadienyl series (Table I).

The chemical shifts of the alkyl groups on the nitrogen atom are of the same order for the triscyclopentadienyls, whereas they are recorded over a range of about 100 ppm for the trissilylamido compounds. This major difference in behavior for two series of similar geometry could be rationalized in terms of electronic factors. For the coordinatively unsaturated

TABLE I.  $^1\text{H}$  NMR Chemical Shifts of the R Protons of the Inserted Compounds:


R'	$\text{Cp}_3\text{U}$	$(\text{C}_5\text{Me}_5)_2\text{U}$	$(\text{HMS})_3\text{U}$	
$\text{C}(\text{CH}_3)_3$	67.8	58.3 <sup>a</sup>	49.5	78.4
$\text{C}_6\text{H}_{11}$		35.7 <sup>a</sup>	42.7	19.7
$\text{C}_6\text{H}_3(\text{CH}_3)_2$		53.4 <sup>a</sup>	33.8	-24.6

<sup>a</sup> $\text{CH}_3$  or  $\alpha\text{-CH}_2$  of  $n\text{-C}_4\text{H}_9$ .

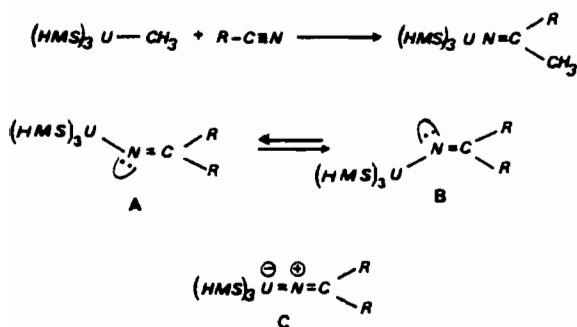
trisilylamido compounds, the value of the contact term in the isotropic chemical shift of these protons is greatly affected by the electronic effects of the substituents on the nitrogen atom, whereas for the coordinatively saturated triscyclopentadienyls, the contact term is weakly dependent on the same effects.

As previously reported, the cyclohexyl protons [17–19] of inserted cyclohexylisocyanides appear within a range of 30–50 ppm in good resolved multiplets, corresponding to a locked chair conformation of the cyclohexyl ring.

### Nitriles

A large difference in reactivity is also observed with nitrile insertion into  $\text{U-CH}_3$  or  $\text{U-CH}_2$  bonds. Andersen had reported the reaction with *t*-butylcyanide giving a six-membered metallacycle [15]. Such a reaction is a general feature and occurs rapidly whatever the nitrile may be. In contrast, the insertion reaction into the uranium methyl occurs slowly with aliphatic nitriles, whereas benzonitrile did not react even after several days at room temperature.

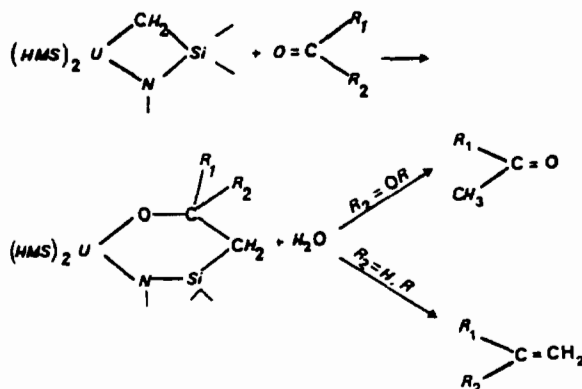
The infrared spectra of the azomethine insertion complexes display a characteristic  $\text{C=N}$  stretching frequency near  $1650\text{ cm}^{-1}$ .  $^1\text{H}$  NMR of  $(\text{HMS})_3\text{UN}=\text{C}(\text{CH}_3)_2$  reveals the equivalence of the two methyl groups, suggesting either a fluxional structure  $\text{A} \rightleftharpoons \text{B}$  or an 'ylid-heteroallene' structure  $\text{C}$ .



At low temperature, the two methyl groups appear to be anisochronous favoring the  $\text{A} \rightleftharpoons \text{B}$  equilibrium. (The structure  $\text{C}$  had been postulated in scandium chemistry [20].)

### Carbonyl Compounds

A very important reaction is the insertion of carbonyl compounds into uranium-carbon bonds. When a stoichiometric amount of aldehyde, ketone or ester is added to a benzenic solution of the metallacycle, a fast and quantitative insertion reaction occurs (even at  $-70^\circ\text{C}$ ) and six-membered metallacycles with uranium atom bonded both to nitrogen and oxygen atoms are obtained:



A wide range of carbonyl compounds has been tested and the resulting insertion products have been isolated and identified. Six-membered metallacycles are cleaved very cleanly by aqueous diluted  $\text{HCl}$  or a saturated solution of ammonium fluoride. From inserted compounds of esters, the methyl ketones are obtained; from inserted aldehydes or ketones, the vinyl hydrocarbyls are almost quantitatively obtained. In the first case, the uranium metallacycle acts as an organocadmium compound. The second reaction is a Wittig-like reaction and the Andersen metallacycle can be used concurrently with the Tebbe reagent [21] ( $\text{Cp}_2\text{TiClCH}_2\text{Al}(\text{CH}_3)_2$ ) to synthesize vinyl compounds from carbonyls.

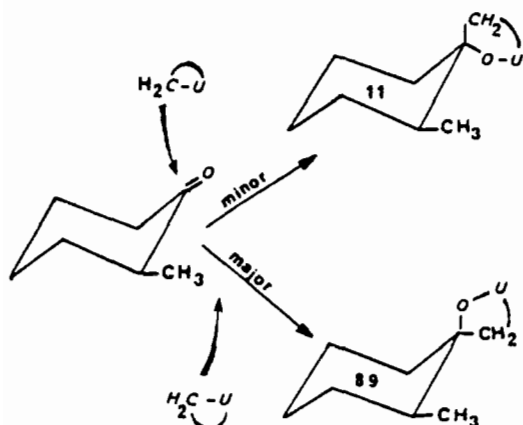
Table II reports some significant results. The yields are given for isolated olefinic products. Entries C, E, F and G illustrate the important point that no

TABLE II. Representative Reactions of Aldehydes and Ketones with the Metallacycle **2** (1:1 mol. equiv.) in Pentane at Room Temperature for 2 min

Entry	Substrate	Yield of vinyl compound (%)
A	aliphatic, aromatic aldehyde	75–92
B	aliphatic, aromatic ketones	85–90
C	cyclohexanones	90–92
D	fluorenone	85
E	$\alpha$ -tetralone	88
F	ferrocenocyclohexanone	90
G	camphor, (1R)-(-)-fenchone	85, 88

olefinic isomerization occurs in any of these reactions. Entries E and F show that the reaction can be extended to easily enolisable ketones without noticeable formation of intermediate addition *enol* compound. (Less than 3% of the E and F starting ketones providing of the cleavage of the *enol* addition compound were recovered after working up. *Enol* addition compounds have been identified by NMR in the crude mixture.)

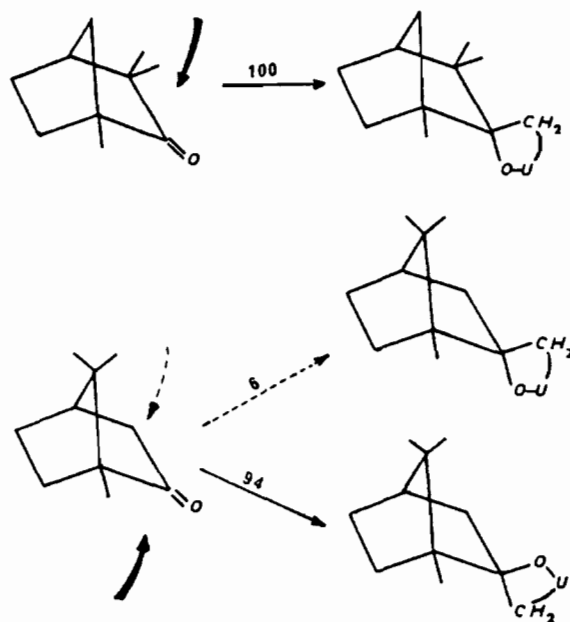
An interesting question concerns the stereochemistry of the insertion: two diastereoisomeric metallacycles are expected after reaction of 2 with substituted cyclic ketones. Only 2-methylcyclohexanone leads to important stereoselectivity (89/11), whereas 4-substituted cyclohexanones show lower selectivity (67/33). In the cyclohexanone series, it is well known that the major isomer obtained after reaction of organometallic compounds results from equatorial attack [22]. Both methyl and methylene substituents of the major diastereoisomer occupy equatorial positions. Much more important selectivity was expected and it is surprising that the dramatically bulky entering group has a so poor effect on the stereospecificity of the reaction.



About 6% of the unexpected minor isomer was formed with camphor. Here, the methyl group bonded to C<sub>7</sub> on camphor encounters such severe steric strain with groups attempting to enter the molecule from the *exo* direction that essentially 100% *endo* attack is currently observed.

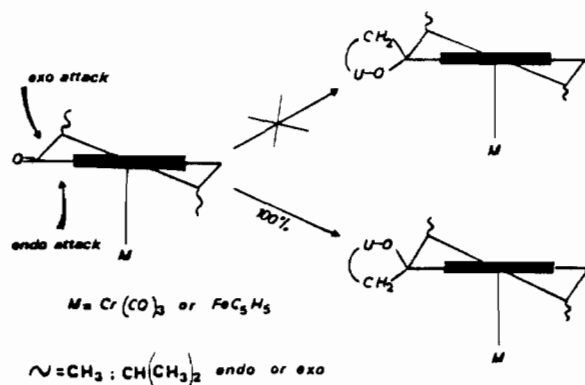
In contrast, fenchone is known to undergo attack 100% from the *exo* side (*endo* attack is precluded by combined steric strain and torsional strain) and only one diastereoisomeric alcohol is generally obtained. Indeed, (1R)-(-)-fenchone reacts readily with 2 and the diastereoisomer resulting from the *exo* attack is exclusively obtained.

The attack of organometallic alkylating reagents occurs preferentially from the *exo* side of ferrocenyl or benchtrotrenotetralones and a mixture of major OH *endo* and minor OH *exo* diastereoisomeric alcohols is



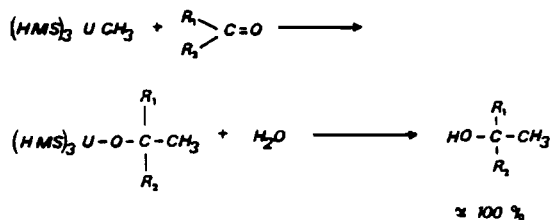
generally obtained. Otherwise, an  $\alpha$  *exo* substituent favors the *exo* attack, whereas a  $\beta$  substituent favors the *endo* attack [23].

In every case, the steric hindrance of silylamido groups precludes the *endo* attack and starting from both *endo* or *exo*  $\alpha$  or  $\beta$  substituted metallocenotetralones, the 'O-U' *endo* diastereoisomer is exclusively obtained.



Methyl compound 1 is also reactive toward carbonyl compounds. With aldehydes a very fast reaction occurs at room temperature and at a reasonable rate (5 to 10 min) at  $-70^\circ\text{C}$ . Aliphatic ketones or cyclohexanones react much more slowly: 30 min to 6 h; whereas only 30% of alkoxyuranium is obtained after 3 days with acetophenone; benzoylferrocene did not react. Sterically hindered ketones, camphor or fenchone, are very poorly reactive, giving about 5% yield after 60 h.

The intermediate alkoxyuranium compounds were hydrolysed and the reaction products analysed by gas



or thin layer chromatography. In most cases, the pure secondary or tertiary alcohols are obtained in high yield.

### Chemoselective Reactions

The high selectivity of **1** to the carbonyl group of aldehydes *versus* ketones has been tested in intermolecular competition experiments. Treatment of a 1:1 mixture of benzaldehyde and acetophenone in benzene with **1** equivalent of **1** followed by hydrolysis affords exclusively the secondary alcohol, and unreacted acetophenone is quantitatively recovered. Comparative results are reported in Table III. It is worth noting that the uranium compound **1** is at least as selective as titanium compounds [24].

Competition reactions between aliphatic aldehydes and ketones have been performed; an essentially complete chemoselectivity is also observed and high yields of secondary alcohols are obtained (Table IV). The observed selectivity is independent of the solvent and comparable rates are obtained in aliphatic,

TABLE III. Results of the Addition of  $\text{CH}_3\text{M}$  ( $\text{M} = \text{Li}, \text{MgBr}, \text{Ti}(\text{O}i\text{Pr})_3, \text{U}(\text{HMS})_3$ ; 1 mol. equiv. of  $\text{CH}_3\text{M}$ ) to a 1:1 Mixture of Benzaldehyde and Acetophenone at Room Temperature

M	Sec. alcohol	Tert. alcohol	Benzylic alcohol
Li	32	23	8
MgBr	8	30	5
Ti(O <i>i</i> Pr) <sub>3</sub>	1	44	0
U(HMS) <sub>3</sub>	0	46	0

TABLE IV. Results of the Addition of  $(\text{HMS})_3\text{U-CH}_3$  (1 mol. equiv.) to a 1:1 Mixture of Aliphatic Aldehydes and Ketones at Room Temperature

Aldehyde	Ketone	Sec. alcohol	Tert. alcohol
Propanal	propanone	81 (98) <sup>a</sup>	2 (2)
Hexanal	propanone	85 (96)	3 (4)
Hexanal	3-pentanone	91 (99.8)	0 (0.2)
Heptanal	4-heptanone	92 (100)	0 (0)

<sup>a</sup>Rates of  $(\text{HMS})_3\text{UOC}(\text{R}_1\text{R}_2)\text{CH}_3$  were calculated by NMR integration on the reaction mixture before hydrolysis.

TABLE V. Reaction of Alkyluranium (RM) ( $\text{M} = (\text{HMS})_3\text{U}; \text{Cl}_3\text{U}; \text{CpCl}_2\text{U}$ )<sup>a</sup>

R	$(\text{HMS})_3\text{U-}$	$\text{Cl}_3\text{U-}$	$\text{CpCl}_2\text{U-}$
$\text{CH}_3$	99/1	70/30	65/35
$\text{C}_2\text{H}_5$	85/15	70/30	70/30
$\text{CH}(\text{CH}_3)_2$	80/20		
<i>n</i> - $\text{C}_4\text{H}_9$	80/20	80/20	70/30

<sup>a</sup>Conditions: 1 mol. equiv.  $\text{CH}_3\text{M}$  to a 1:1 mixture of heptanal and 4-heptanone in pentane at  $-70^\circ\text{C}$ ; reaction time = 2 h; relative rates, secondary/tertiary alcohols.

aromatic hydrocarbons, diethyl ether or THF. Moreover, esters do not react in the same conditions.

The poorly stable alkylhexamethyltrissilylamido-uranium compounds [25] react at low temperature with an equimolar mixture of heptanal and 4-heptanone. Much lower selectivity is observed (Table V). This result is not surprising if we compare the exceedingly reactive metal-carbon bond of these compounds to the relatively stable uranium-methyl bond of **1**. In the same way, in an alkylation aldehyde *versus* ketone competitive reaction performed in THF solution at  $-70^\circ\text{C}$ , alkyltrichlorouranium (**3**) and alkyl-dichlorocyclopentadienyluranium [25] (**4**) are very poorly selective (Table V).

### Diastereoselective Reactions

2- and 4-substituted cyclohexanones are known to react with organometallic reagents; equatorial attack occurs preferentially giving the major axial alcohol [22].

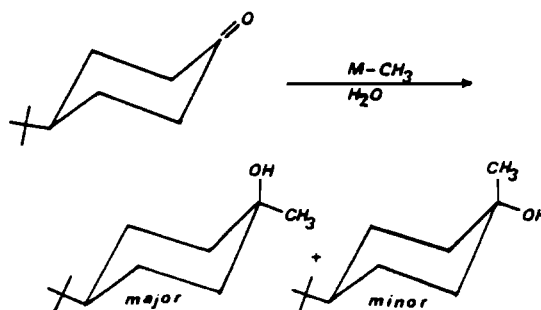


Table VI reports the rates obtained from **1** and substituted cyclohexanones. The reactions appear to be highly stereoselective; nevertheless, the best results were obtained starting from titanium reagents.

A widely quoted example of asymmetric induction in the addition of organometallic compounds to carbonyls is the addition to 2-phenylpropanal (hydrotropic aldehyde) to form the diastereoisomeric alcohols. From Grignard or alkyllithium reagents [27], a ratio of about 2/1 is generally obtained. However, a much higher diastereoselectivity is observed

TABLE VI. Diastereoselective Methylation of 2- and 4-Substituted Cyclohexanones with Methyluranium and Methyltitanium Reagents<sup>a</sup>

Substituent	(HMS) <sub>3</sub> U-CH <sub>3</sub>	(OiPr) <sub>3</sub> Ti-CH <sub>3</sub>
4-t-Butyl	85/15	94/6
4-Methyl	85/15	88/12
2-Methyl	89/11	94/6

<sup>a</sup>Conditions: 2 mol. equiv.; room temperature; relative rates, axial alcohol/equatorial alcohol.

when using organotitanium [27] or organozirconium reagents [27], the best ratios of Cram to anti-Cram product being 93/7.

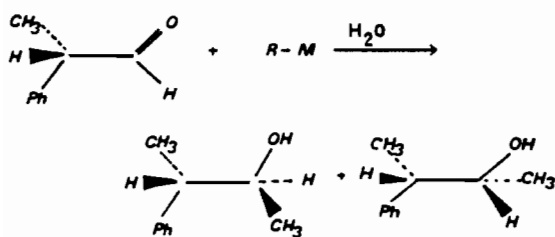


TABLE VII. Diastereoselective Reaction of Alkyluranium and Alkyltitanium (R-M)<sup>a</sup>

R	Cl <sub>3</sub> U	(HMS) <sub>3</sub> U	(OiPr) <sub>3</sub> Ti
CH <sub>3</sub>	90/10	88/12	93/7
C <sub>2</sub> H <sub>5</sub>	84/16	80/20	
CH(CH <sub>3</sub> ) <sub>2</sub>	96/4	95/5	
n-C <sub>4</sub> H <sub>9</sub>	88/12	90/10	89/11

<sup>a</sup>Conditions: 1:1 mol. equiv. with 2-phenylpropanal in pentane at -70 °C; 2 h; relative rates, major alcohol/minor alcohol.

These two sets of reactions show that both methyl and methylene silylamidouranium derivatives appear to be potentially usable reagents in organic synthesis. In some cases, they could be used in preference to titanium reagents and we are pursuing our investigations in this area.

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