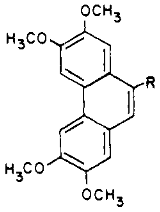
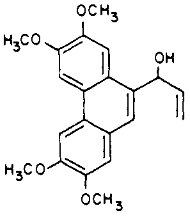
alcohol **11** and oxidized with pyridinium chlorochromate[15] to afford aldehyde **12** (78% from **10**; mp 218–219 °C).[7] Addition of vinyllithium to aldehyde **12** in THF at room temperature produced the allylic alcohol **13** (82%; mp 151–152 °C),[7] which underwent the orthoester Claisen rearrangement[8] ($CH_3C(OEt)_3$-propionic acid, 130–135 °C, 2 h) to afford ester **14** (84%; mp 97–98 °C).[7] Amide **15** was formed in 80% yield by treatment of ester **14** with 3.5 equiv of dimethylaluminum amide[9] in refluxing methylene chloride (mp 213–214 °C; IR ($CHCl_3$) 3550, 3425, 1680 cm^{-1}). This amide was treated first with a mixture of 37% aqueous formaldehyde–5% NaOH–glyme at room temperature and then with acetic anhydride–pyridine to afford crystalline acetate **16** in 60% isolated yield (mp 155–156 °C; IR ($CHCl_3$) 3540, 1740, 1695 cm^{-1}). Pyrolysis of this acetate in bromobenzene at 220 °C for 5 h yielded the known[6a] pentacyclic lactam **17**[17] (50%; mp 263 °C, lit.[6a] mp 273 °C).[7] The lactam carbonyl of **17** was reduced with $LiAlH_4$ in THF at room temperature to produce racemic tylophorine (**2**, 64%) identical with an authentic sample[15] (IR, UV, MS, ^{1}H NMR).



10 R=COOCH3
11 R=CH2OH
12 R=CHO



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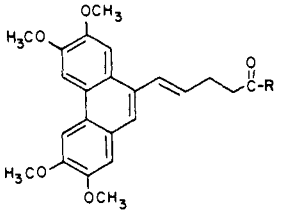
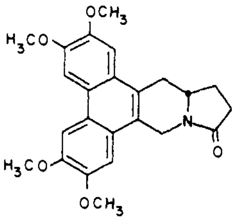


14 R=OEt
15 R=NH2
16 R=NHCH2OAc



17

We are currently exploring the scope of the intramolecular imino Diels–Alder reaction for synthesis of other alkaloids and are also actively investigating the stereochemical parameters of the reaction. This work will be reported shortly.

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(15) We thank Dr. N. B. Mulchandani for a generous sample of natural tylophorine.
(16) Fellow of the A. P. Sloan Foundation, 1975–1979. Recipient of a Research Career Development Award (HL00176) from the National Institutes of Health. Address correspondence to The Pennsylvania State University.
(17) NOTE ADDED IN PROOF. Our lactam **17** was identical with an authentic sample provided by Dr. R. E. Summons. We also thank Dr. A. J. Liepa for providing spectra of compound **17**.

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Titanium-Catalyzed Olefin Metathesis

Sir:

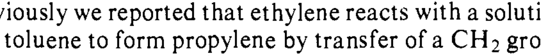
The methylenetitanium complex, $Cp_2TiCH_2AlClMe_2$ (**1**),[1] catalyzes a metathesis process in which the methylene groups of isobutene and methylenecyclohexane exchange (eq 1). This

(1)

catalyst is selective for exchange of terminal methylene groups and provides strong evidence for an alkylidene/metallacycle mechanism like that now generally accepted for olefin metathesis with conventional catalysts.[2]

Previously we reported that ethylene reacts with a solution of **1** in toluene to form propylene by transfer of a CH_2 group from titanium to the olefin.[1] In contrast, isobutene did not seem to interact with **1** under these conditions other than apparently to stabilize it against decomposition at elevated temperatures. Now, labeling studies indicate that the methylene group of **1** *exchanges* with isobutene and that this exchange provides the mechanism for the metathesis reaction described above.

A solution of 0.25 mmol of **1** and 0.5 mmol of $^{13}CH_2{=}CMe_2$[3] in benzene-d_6 (0.6 mL) was examined periodically by ^{1}H and ^{13}C NMR. The spectra show depletion of $^{13}CH_2{=}CMe_2$ with growth of $^{12}CH_2{=}CMe_2$ and $Ti^{13}CH_2$. Carbon-13 enrichment is limited to the $TiCH_2$ group (eq 2).



$$\underset{\mathbf{1}}{Cp_2TiCH_2AlClMe_2} + {}^{13}CH_2{=}CMe_2 \rightleftharpoons Cp_2Ti{}^{13}CH_2AlClMe_2 + CH_2{=}CMe_2 \quad (2)$$

The exchange of CH_2 groups approaches equilibrium in 30 h at 52 °C. Under these conditions, the solution seems stable for 4 days. Approximately 20% of the organometallic decomposes over 8 days, but the amount of isobutene is constant during this time. Methylene exchange catalysis persists beyond 8 days.[4]

Similar experiments were carried out with deuterium-labeled reagents and were monitored by ^{1}H and ^{2}H NMR. In the reaction of $(C_5H_5)_2TiCD_2AlCl(CD_3)_2$[5] with $CH_2{=}C(CH_3)_2$, or $(C_5H_5)_2TiCH_2AlCl(CH_3)_2$ with $CD_2{=}C(CH_3)_2$,[3] exchange is limited to hydrogens connected

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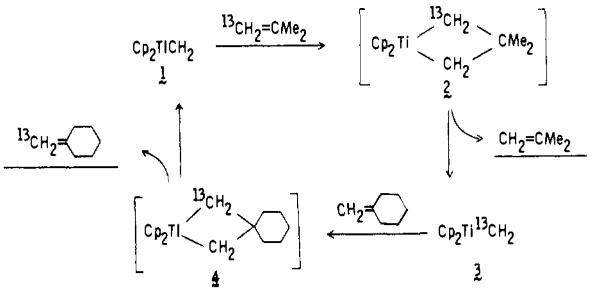
Scheme I. The ClAlMe$_2$ Group Is Omitted for Clarity. Each step is Considered Reversible



to metal and olefin methylene groups (eq 3). Since methylene hydrogen and methylene carbon equilibrations take place on

$$(C_5H_5)_2TiCD_2AlCl(CD_3)_2 + CH_2{=}CR_2 \rightleftharpoons (C_5H_5)_2TiCH_2AlCl(CD_3)_2 + CD_2{=}CR_2 \quad (3)$$

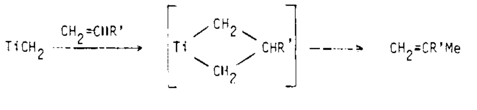
$$R_2 = (CH_3)_2 \text{ or } -CH_2(CH_2)_3CH_2-$$

the same time scale, it is likely that the CH$_2$ groups exchange as units. Methylenecyclohexane undergoes the analogous exchange reaction with (C$_5$H$_5$)$_2$TiCD$_2$AlCl(CD$_3$)$_2$ at approximately the same rate as isobutene.

In the metathesis experiment, a mixture of isobutene and methylenecyclohexane, supplied as ^{13}CH$_2$=CMe$_2$ (0.4 mmol) and CH$_2$=C$_6$H$_{10}$ (0.4 mmol), was combined with Cp$_2$TiCH$_2$AlClMe$_2$ (0.1 mmol) in benzene-d_6 solution (0.6 mL). Metathesis is indicated by the appearance of CH$_2$=CMe$_2$, ^{13}CH$_2$=C$_6$H$_{10}$, and Cp$_2$Ti^{13}CH$_2$AlClMe$_2$ and the disappearance of ^{13}CH$_2$=CMe$_2$, CH$_2$=C$_6$H$_{10}$, and Cp$_2$TiCH$_2$AlClMe$_2$. Reaction is extensive after 47 h at 51 °C and is limited to methylene group exchange (^{1}H NMR). Decomposition or byproduct formation are not detected under these conditions. This system thus performs the "degenerate"[7,8] olefin metathesis reaction with chemical and isotopic selectivity.

This degenerate metathesis is nicely explained by the mechanism of Scheme I, which is derived from the currently accepted mechanism for more typical olefin metatheses.[2] As in the conventional mechanism, a methylene complex **1** reacts with olefin (^{13}CH$_2$=CMe$_2$) to form a metallacyclobutane, **2**. Cleavage of the metallacycle in the proper sense yields a new olefin and a new metal alkylidene. With this mechanism, coordination of only one olefin at a time is required to produce exchange of alkylidene units between two olefins.

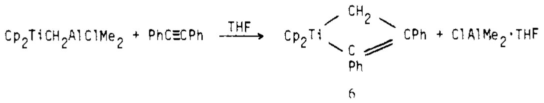
This scheme is thoroughly consistent with that proposed for homologation of ethylene and propylene.[1] With these olefins, which contain a hydrogen substituent at both ends of the double bond, the metallacycle **5** undergoes facile β-hydrogen transfer and olefin elimination before methylene exchange can occur (eq 4). Olefins of the type CH$_2$=CR$_2$ do not yield analogous products because they preferentially produce metallacycles with alkyl groups substituted in the β position (**2** and **4**, Scheme I).



(4)

5, R' = H or CH$_3$

Metallacyclobutanes thus seem plausible intermediates in the three known reactions of olefins with **1**, metathesis, homologation, and the cyclopropanation reported previously.[1] Although there is no direct evidence for the metallacyclobutane, we have isolated a metallacyclobutene (**6**) from the reaction of **1** with diphenylacetylene in tetrahydrofuran (THF)[9] (eq 5). The metallacyclobutene is probably more stable toward carbon–carbon bond breaking or coupling reactions than the related cyclobutanes because the formation of acetylenes or cyclopropenes is energetically less favorable.



(5)

6

The role of aluminum in these reactions is not yet clear. Aluminum coordinated to the methylene group in **1** is responsible for its long-term stability, and aluminum bonding may affect the interactions of **1** with CH$_2$=CR$_2$ in aromatic solvents.[1] This question will be explored further because compounds such as C$_2$H$_5$AlCl$_2$ are important for the activity of some of the best conventional olefin metathesis catalysts.

Acknowledgment. We thank D. K. Babcock for skilled experimental assistance.

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(3) Labeled isobutenes were purchased from Merck Sharp and Dohme, Canada, Ltd.
(4) After 8 days, the olefin was separated from the reaction mixture and was found by the mass spectrum to be isobutene, ^{12}C enriched. Isotopically normal isobutene was then charged to the ^{13}C-enriched organometallic. As the reaction mixture was heated overnight, metal and olefin methylene exchange occurred as expected.
(5) Trimethylaluminum-d_9, prepared from dimethylmercury-d_6 (Orgmet) and aluminum,[6] was reacted with Cp$_2$TiCl$_2$ to produce (C$_5$H$_5$)$_2$TiCD$_2$AlCl(CD$_3$)$_2$.
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Pentamethylcyclopentadienyl Organoactinides. Trivalent Uranium Organometallic Chemistry and the Unusual Structure of Bis(pentamethylcyclopentadienyl)uranium Monochloride

Sir:

A conspicuous and important property of transition metal organometallic compounds is the tendency for the metal ions to exist in a number of formal oxidation states and to pass facilely between them. In contrast, the vast majority of organothorium and organouranium compounds contain the metal in the tetravalent oxidation state.[1,2] The known trivalent[3-5] compounds consist largely of triscyclopentadienyls, M(η^5-C$_5$H$_5$)$_3$,[3,4] and their Lewis base (L) adducts, M(η^5-C$_5$H$_5$)$_3$-L.[3,4] Owing to low solubility, what appears to be coordinative saturation, and nonroutine syntheses, the chemistry of these trivalent complexes has not been investigated in detail. Thus, there is very little known about the kinds of organometallic compounds which may exist for actinides in the +3 oxidation state and the reaction patterns which they undergo. In this communication we report that trivalent uranium, when complexed by the pentamethylcyclopentadienyl ligand,[6] possesses an extensive organometallic chemistry which includes, among