

Catalytic Homologation of Vinyltributylstannane to Allyltributylstannane by Mo(IV) Complexes in the Presence of Ethylene

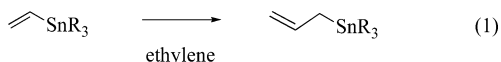
Richard R. Schrock,^{*,†} M. Duval-Lungulescu,[†] W. C. Peter Tsang,[†] and Amir H. Hoveyda[‡]

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and
Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467

Received October 22, 2003; E-mail: rrs@mit.edu

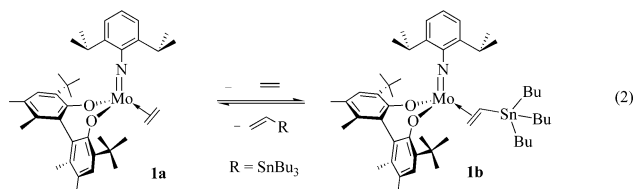
Recently we have been interested in imido alkylidene complexes of (primarily) molybdenum and tungsten that contain an enantiomerically pure biphenolate or binaphtholate ligand.¹ Since ethylene is often a product in metathesis reactions that involve terminal olefins, we have been exploring reactions between these asymmetric imido alkylidene complexes and ethylene. We have found that M(IV) ethylene complexes are formed as end products and that they are in equilibrium with metalacyclopentane complexes.² We have now found that Mo(IV) imido bisalkoxide olefin complexes are catalysts for the conversion of vinyltributylstannane to allyltributylstannane, a one methylene olefin homologation reaction, and propose a mechanism that involves contraction of a metalacyclopentane (MC₄) ring to a metalacyclobutane (MC₃) ring.

The reaction was discovered in the process of exploring potential cross-metathesis reactions³ between vinyltributylstannane and, for example, 1-hexene catalyzed by asymmetric molybdenum imido alkylidene complexes, as well as Mo(NAr)(CHCMe₂Ph)[OC(CF₃)₂Me]₂ (Ar = 2,6-*i*-Pr₂C₆H₃).¹ No cross-metathesis between vinyltributylstannane and 1-hexene or homometathesis of vinyltributylstannane to give Bu₃SnCH=CHSnBu₃ was observed, although 1-hexene was homometathesized to yield 5-decenes. Peculiarly, however, vinyltributylstannane was consumed in these reactions in a catalytic fashion to give largely allyltributylstannane and small quantities of Bu₃SnCH=CHCH₂SnBu₃ (according to comparison with an authentic sample; see Supporting Information) and Bu₃SnCH₂-CH=CHCH₂SnBu₃ (prepared by homometathesis of allyltributylstannane with Mo(NAr)(CHCMe₂Ph)[OC(CF₃)₂Me]₂) and possibly other species that contain two tins. Similar results were obtained in reactions involving vinyltributylstannane and diallyl ether (which is effectively an ethylene source) and in reactions involving vinyltributylstannane and ethylene. Therefore, we proposed that the reaction that produces allyltributylstannane involves ethylene (eq 1) and suspected that the catalyst was *not* an alkylidene complex.



Recently,^{2c} we found that addition of 2 or more equivalents of C₂H₄ to Mo(NAr)(CHCMe₂Ph)[biphen] (where [biphen]²⁻ = 3,3'-di-*tert*-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diolate) yields the ethylene adduct, Mo(NAr)(CH₂=CH₂)[biphen] (**1a**), quantitatively, along with CH₂=CHCMe₂Ph, the metathesis product from the initially formed molybdacyclobutane complex. (The four ethylene resonances were observed at 3.15, 2.30 (area 2), and 3.28 ppm in the proton NMR spectrum.) Addition of 2 equiv of CH₂=CHSnBu₃ to this solution led to **1b** (eq 2) in 80% yield in 1 h at 22 °C in equilibrium with **1a**. The three olefinic proton resonances in **1b** were found at 3.82 ppm (dd), 2.88 (dd) and 3.64

ppm (~triplet) in the ¹H NMR spectrum. Ethylene and vinyltributylstannane were slowly consumed over the next 48 h to give allyltributylstannane in 75% yield and complexes **1a** and **1b** in a 2:3 ratio. Other minor products (e.g., Bu₃SnCH=CHCH₂SnBu₃ and Bu₃SnCH₂CH=CHCH₂SnBu₃) were also observed at the end of the experiment. Complexes **1a** and **1b** are analogous to related hexafluoro-*tert*-butoxide species.⁴

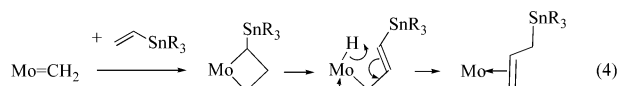


Conversion of CH₂=CHSnBu₃ to CH₂=CHCH₂SnBu₃ was found to be catalytic when 31 equiv of CH₂=CHSnBu₃ were added to **1a** under 1 atm of ethylene. Complex **1b** was the major molybdenum complex observed in the first 60 h, with a mixture of **1a** and **1b** being observed thereafter. Allyltributylstannane was obtained in 80% yield (3% Mo catalyst). The reaction was first-order with respect to CH₂=CHSnBu₃ in the first 60 h (*t*_{1/2} ≈ 40 h) with a plot of ln[CH₂=CHSnBu₃] versus time yielding an observed rate constant (*k*_{obs}) of 4.70 × 10⁻⁶ s⁻¹ with R² = 0.9969.

When 2 equiv of CH₂=CHSnBu₃ were added to **1a** prepared in a reaction between Mo(NAr)(CHCMe₂Ph)[biphen] and 2 equiv of ¹³C₂H₄, the allyltributylstannane that was formed in the first 12 h was selectively ¹³CH₂=CHCH₂SnBu₃ (δC = 110.17 ppm with ¹J_{CH} = 157.9 and 152.5 Hz and ³J_{SnC} = 44.8 Hz); the α and β carbons (at 16.72 and 138.57 ppm, respectively) were not labeled. After 56 h, ~15% of CH₂=CH¹³CH₂SnBu₃ was observed. Therefore, it appears that CH₂=CH¹³CH₂SnBu₃ is formed in a secondary reaction which we attribute to a 1,3 migration of the tributylstannane fragment in ¹³CH₂=CHCH₂SnBu₃; the mechanism is not known. Therefore, we propose that the primary catalytic reaction being observed is that shown in eq 3, i.e., each methylene from ethylene is appended to the vinyl group (with the accompanying migration of a proton from a β to an α carbon atom) to form an allyl group.



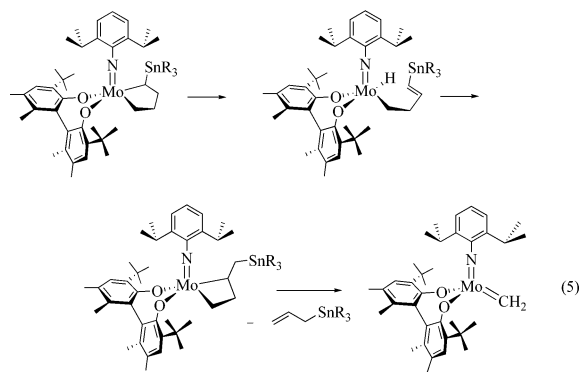
We have been able to think of only two possible mechanisms for this reaction. The first is that ethylene is literally split by two Mo(IV) species (possibly in a dimer) to give two Mo=CH₂ species. Formation and rearrangement of an α-substituted molybdacyclobutane complex (eq 4) would then produce the allyl tin product and a Mo(IV) species again.



[†] Massachusetts Institute of Technology.

[‡] Boston College.

The other possibility is that the molybdacyclopentane complex formed from ethylene and vinyltributylstannane shown in eq 5 undergoes a “ring-contraction” to a molybdacyclobutane complex, which then does not continue to rearrange (because a carbon-based group is in the α position at that point), but metathesizes to yield allyltributylstannane and a methylene complex. A methylene complex that is generated in *this* fashion then reacts as shown in eq 4 to yield more allyltributylstannane or decomposes to form ethylene and/or a Mo(NAr)[biphen](olefin) complex such as **1a** or **1b**.



We prefer the second proposal for two reasons. First, $M=CH_2$ species have long been known to decompose to yield ethylene or ethylene complexes,⁵ and there is no precedent for this reaction being reversible. Second, there is considerable precedent for the ring-contraction mechanism in the chemistry of $Cp^*Cl_2Ta(olefin)$ and tantalacyclopentane complexes made from them by adding an olefin⁶ and in the rearrangement of a rhenacyclopentane complex, $Cp^*(CO)_2Re(C_4H_8)$, in the presence of a phosphine to yield methylcyclopropane.⁷

Perhaps the most surprising feature of this Mo ring-contraction mechanism is that a methylene complex is generated from ethylene. In fact, the possibility of generating alkylidene complexes from reduced metal complexes in the manner shown in eq 5 (for ordinary olefins) was recognized in a paper in 1979 that was concerned with ring contraction of tantalacyclopentanes.⁸ Replacing the tributyltin group in the α position with a methylene group when the MC_4 ring contracts to an MC_3 ring (eq 5) appears to trigger this phenomenon. The second surprising feature is that only molybdacyclobutane and molybdacyclopentane species that contain a tin in the α position, i.e., only those with a proton that is β with respect to *both* tin and molybdenum, rearrange rapidly by a β hydride migration process, one that can be viewed in an alternative manner (eq 4 and ref 6) to a traditional “reductive elimination” step. All other molybdacycles either do not form to a substantial degree (in some cases for steric reasons) or do not rearrange rapidly relative

to the rate of loss of an olefin from the metalacyclopentane. As mentioned above, two of the minor products formed in these reactions have been identified as $Bu_3SnCH=CHCH_2SnBu_3$ and $Bu_3SnCH_2CH=CHCH_2SnBu_3$. It is not yet known whether these species are formed via rearrangement of molybdacyclobutane or molybdacyclopentane complexes or whether they are formed in metathetical reactions.

We could find no example in the literature of a homogeneous catalytic one methylene homologation of an olefin in which ethylene is the methylene source, although heterogeneous examples (e.g., conversion of ethylene to propylene) are known.^{9a} Reactions are also known that involve methylene sources such as diazomethane.^{9b-d} In some cases, only olefins are involved and mixtures of many products are obtained.^{9d} These new findings suggest (inter alia) that contraction of an MC_4 ring to an MC_3 ring may be a more common mode, perhaps even the dominant mode, of decomposition of metalacyclopentane rings of d^0 complexes. In addition to exploring further mechanistic details, we are curious whether other vinyl compounds (e.g., silicon) behave similarly, whether tungsten(IV) complexes^{2b} are also catalysts for such reactions, and whether certain *ordinary* olefins could ever be homologated in this manner under some conditions.

Acknowledgment. We thank the National Science Foundation (CHE-0138495 to R.R.S.) and the National Institutes of Health (GM-59426 to R.R.S. and A.H.H.) for supporting this research.

Supporting Information Available: Experimental details for the synthesis of $Bu_3SnCH=CHCH_2SnBu_3$ (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Schrock, R. R.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4592.
- (2) (a) Tsang, W. C. P.; Schrock, R. R.; Hoveyda, A. H. *Organometallics* **2001**, *20*, 5658. (b) Tsang, W. C. P.; Hultzsck, K. C.; Alexander, J. B.; Bonitatebus, P. J., Jr.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 2652. (c) Tsang, W. C. P.; Jamieson, J. Y.; Aeilts, S. L.; Hultzsck, K. C.; Schrock, R. R.; Hoveyda, A. H. *Organometallics*, in press.
- (3) Chatterjee, A. K. In *Handbook of Metathesis*; Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, Germany, 2003; Vol. 2, p 246.
- (4) Robbins, J.; Bazan, G. C.; Murdzek, J. S.; O'Regan, M. B.; Schrock, R. R. *Organometallics* **1991**, *10*, 2902.
- (5) (a) Schrock, R. R. In *Reactions of Coordinated Ligands*; Braterman, P. R., Ed.; Plenum: New York, 1986. (b) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1. (c) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145.
- (6) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 5610.
- (7) Yang, G. K.; Bergman, R. G. *Organometallics* **1985**, *4*, 129.
- (8) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5451.
- (9) (a) Imamura, H.; Konishi, T. *Lanthanide Actinide Res.* **1991**, *3*, 387. (b) Adnadevic, B. K.; Agabalyan, L. G. *J. Serb. Chem. Soc.* **1997**, *62*, 409. (c) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (d) Leconte, M. *J. Mol. Catal.* **1994**, *86*, 205. (e) Leconte, M.; Theulier, A.; Rojas, D.; Basset, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 1141.

JA039173P