Metallacyclobutanes from Central Carbon Alkylation of Early Metal η^3-Allyl Complexes. Nucleophilic Additions to Cationic, Lewis Base-Free Zirconium and Titanium Permethylmetallocene η^3-Allyl Complexes

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Received April 14, 1993

Recent investigations[2,3] have sought to elucidate the principles governing metallacyclobutane formation by the regioselective addition of nucleophiles to the central carbon of transition-metal η^3-allyl complexes.[4] Based on this experimental work, previous molecular orbital calculations,[5] and the potential for developing synthetically practical systems for the alkylative metallacyclobutane formation, we considered cationic, Lewis base-free zirconium and titanium η^3-allyl complexes, $[(C_5R_5)_2M(\eta^3\text{-allyl})]^+X^-$, to be strong candidates for further investigation. Cationic group IV metallocene complexes, however, are strongly electron deficient, lacking the conventional metal–ligand $d \rightarrow \pi^*$ back-bonding thought necessary to direct nucleophiles to the η^3-allyl central carbon.[4a,6] Theory notwithstanding, in this communication we report that permethylmetallocene η^3-allyl cations are converted to metallacyclobutane complexes by the regioselective addition of nucleophiles to the allyl central carbon.

To inhibit competitive nucleophilic addition to the unsaturated and highly electrophilic metal center, the sterically significant bis(pentamethylcyclopentadienyl) series was selected for this investigation. Two previous reports of cationic group IV metallocene allyl complexes have appeared, each involving allene insertion into zirconium hydride or alkyl bonds.[7] Several alternative methods for the synthesis of cationic coordinatively unsaturated metallocene η^3-allyl complexes are included in this report.

Unsolvated permethylzirconocene η^3-allyl cation (**2**)[8,9] is prepared in high yield by either oxidative cleavage[7a,10] or protonolysis[11] procedures, well-precedented methodology for the synthesis of related cationic alkyl zirconocene complexes (Scheme I). Oxidation of bis(allyl) complex **1**[12] using 1,1′-dimethylferrocenium tetraphenylborate[7a] in THF at −35 °C leads to the precipitation of cation **2**, isolated as a red crystalline solid after trituration of the dimethylferrocene with toluene and crystallization from CH_2Cl_2 layered with toluene at low temperature.[13] In contrast to the related 1,1′-dimethylzirconocene η^3-allyl complex,[7a] tetrahydrofuran is not retained by the coordinatively unsaturated metal center. Neither the use of stronger oxidants, such as $AgBPh_4$ or $(C_5H_5)_2Fe^+BPh_4^-$, nor protonolysis of the bis(allyl) complex yields an appreciable quantity of the cationic allyl complex. In contrast, however, protonolysis of the "tuck-in" allyl complex **4**[8] using $Et_3NH^+BPh_4^-$ in THF at low temperature provides complex **2** cleanly, after isolation and crystallization as above. Although the yields are similar, the oxidation of bis(allyl) complex **1** is preferable to the protonolysis route, which is both less direct and requires the separation of cationic complex **2** from residual ammonium salt. The NMR spectroscopic data for complex **2** are consistent with a fluxional allyl ligand at room temperature, with the allyl central proton resonance strongly deshielded and the terminal methylene signal broadened into the baseline. In CD_2Cl_2 at −77 °C, however, the allyl ligand is nearly static and clearly η^3-coordinated.

Nucleophilic addition to cationic allyl complex **2** proceeds regioselectively either to the metal or, as anticipated, to the allyl central carbon, depending on the steric profile of the nucleophile. Thus, addition of MeMgCl, MeLi, or allyl Grignard in THF at low temperature yields $(C_5Me_5)_2Zr(\eta^3\text{-allyl})Me$[12] and bis(allyl) complex **1**, respectively, in high yield, with no detectable zirconacyclobutane formation.

Sterically significant nucleophiles, however, add regioselectively to the allyl central carbon (Scheme I). The addition of diphenylmethylpotassium[8] or 1-phenylethylpotassium[8] to a suspension of cation **2** in THF at low temperature leads to the isolation of β-substituted zirconacyclobutane complexes **5**[8] and **6**.[8] No intermediates or substantial byproducts are observed when the reaction with 1-phenylethylpotassium in THF-d_8 is monitored by NMR spectroscopy at low temperature. At room temperature, however, deprotonation of the C_5Me_5 ligand becomes competitive, returning the "tuck-in" allyl complex **4** as a byproduct. The infrared and NMR spectroscopic data for the bright yellow complexes **5** and **6** are fully consistent with known zirconacyclobutane complexes.[12,14]

Using benzylpotassium, a nucleophile of intermediate steric profile, a kinetic partitioning is observed, leading to mixtures of allyl benzyl complex **7** and β-benzylzirconacyclobutane complex **8**.[12] Although the allyl complex rearranges quantitatively to the zirconacyclobutane slowly above room temperature,[12] the kinetic formation of zirconacyclobutane **8** has been established by ^1H NMR spectroscopy in THF-d_8 at −78 °C, a temperature at which the thermal rearrangement does not proceed. At low temperature, complexes **7** and **8** are formed in an approximately 1.5:1 ratio, shifting at higher temperature in favor of the metal adduct. With

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(6) Davies, S. G.; Green, M. L. H.; Mingos, M. P. *Tetrahedron* **1978**, *34*, 3047.

(7) (a) $[(MeC_5H_4)_2Zr(\eta^3\text{-allyl})(thf)]^+$: Jordan, R. F.; LaPointe, R. E.; Bradley, P. K.; Baenziger, N. *Organometallics* **1989**, *8*, 2892. (b) After completion of this work, the first *unsaturated* zirconocene allyl cations were reported, also using the bis(C_5Me_5) template: Horton, A. D. *Organometallics* **1992**, *11*, 3271.

(8) Complete experimental, spectroscopic, and analytical data are included as supplementary material.

(9) Partial data for complex **2**: IR (CH_2Cl_2) 1580 (m, η^1-allyl), 1480 (s, η^3-allyl) cm^{-1}; ^1H NMR (−77 °C, 300 MHz, CD_2Cl_2) δ 7.73 (m, 1H, H_c), 4.60 (br d, $J = 14.7$ Hz, 2H, H_a), 2.09 (s, 15H, C_5Me_5), 2.05 (signal partially obscured, H_5 2.05 (s, 15H, C_5Me_5); ^{13}C NMR (gated, −77 °C, 75 MHz, CD_2Cl_2) δ 160.7 (br d, $J = 151.0$ Hz, C_c), 82.5 (td, $J = 152.0, 6.0$, C_t).

(10) See: Borkowsky, S. L.; Jordan, R. F.; Hinch, G. D. *Organometallics* **1991**, *10*, 1268, and references therein.

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(12) Tjaden, E. B.; Stryker, J. M. *J. Am. Chem. Soc.* **1993**, *115*, 2083.

(13) Thermally stable but highly air- and moisture-sensitive complex **2** decomposes over several hours in CH_2Cl_2 at 23 °C but is recrystallized without appreciable decomposition at −35 °C in CH_2Cl_2/toluene.

(14) (a) Feldman, J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1. (b) Tikkanen, W. R.; Liu, J. Z.; Egan, J. W.; Petersen, J. L. *Organometallics* **1984**, *3*, 825. (c) Seetz, J. W. F. L.; Van de Heisteeg, B. J. J.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Mol. Catal.* **1985**, *28*, 71.

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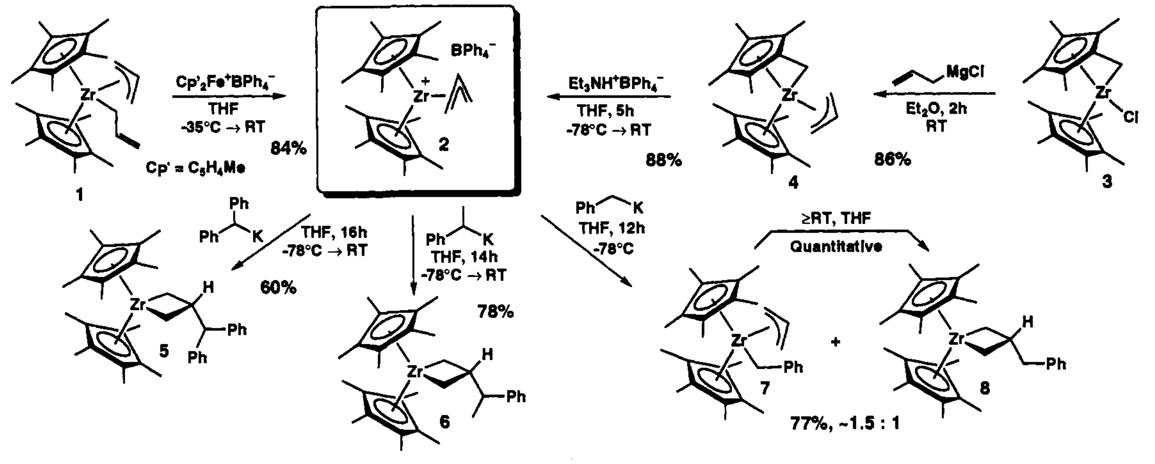
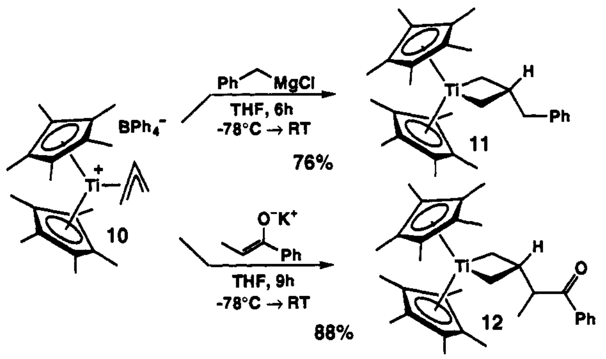
Scheme I

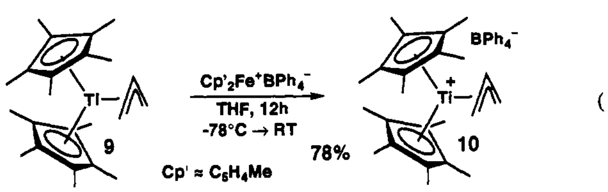


Scheme II



all three anions, the formation of either transient or persistent green solutions is observed, suggesting that electron transfer may be mechanistically relevant to the formation of intermediates and/or side products.

In the titanium series, the unsaturated permethyltitanocene allyl cation (**10**)[8] is prepared by oxidation of the Ti(III) allyl complex **9**[15] using the 1,1'-dimethylferrocenium cation (eq 1).[16]



(1)

Complex **10**, isolated by extraction into CH_2Cl_2 after trituration of the ferrocene with toluene, is purified by crystallization from CH_2Cl_2/toluene at −35 °C, giving dark purple crystals in 78% yield. As observed for zirconium, the use of stronger oxidants is not effective. In contrast to the zirconocene cation, the fluxional allyl ligand in complex **10** rigidifies to static η^3-coordination at just −18 °C but is otherwise spectroscopically very similar.[8]

Nucleophilic addition to the titanocene cation **10** proceeds regioselectively to the central allyl position (Scheme II). The smaller ionic radius and the lower electrophilicity associated with titanium mitigates competitive addition to the metal, giving titanacyclobutane complexes **11**[8] and **12**[8] as exclusive products on addition of benzyl Grignard and the enolate of propiophenone, respectively.[17] In contrast to the zirconium series, the use of benzylpotassium returns an intractable product mixture containing significant amounts of both titanacycle **11** and 1,2-diphenylethane, the latter presumably arising from reduction at titanium and dimerization of benzyl radicals. Complexes **11** and **12** are thermally stable and spectroscopically analogous to previously reported examples of this structural class.[18]

Thus, highly reactive cationic permethylmetallocene η^3-allyl complexes undergo regioselective nucleophilic addition to the allyl central position, with addition to the unsaturated metal center observed only for nucleophiles of low steric demand in the sterically less shielded zirconocene series. Competitive addition to the allyl terminal position is not observed in this series, suggesting that pseudotetrahedral η^3-allyl complexes are, in general, strong candidates for kinetic central carbon alkylation, regardless of d-orbital occupancy.[19] Although these results tend to support the dominance of molecular orbital control in determining the position of kinetic nucleophilic addition to η^3-allyl complexes, bonding in the early metal–allyl fragment may be significantly polarized, resulting in anionic character at the terminal allyl positions and consequent charge-controlled nucleophilic attack at the relatively electron deficient central position.

A comprehensive investigation of the coordination chemistry and reactivity of cationic η^3-allyl metallocene complexes[20] and further investigation of metallacyclobutane formation and reactivity in synthetically promising early metal systems are currently in progress.

Acknowledgment. We thank Professor R. F. Jordan for insightful discussions. Financial support from the National Science Foundation (U.S.), an American Cyanamid Faculty Award, and the University of Alberta is gratefully acknowledged.

Supplementary Material Available: Experimental procedures and complete data for all new compounds (7 pages). Ordering information is given on any current masthead page.

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(16) Oxidation of Ti(III) to cationic Ti(IV) using Ag(I): Bochmann, M.; Jagger, A. J.; Wilson, L. M.; Hursthouse, M. B.; Motevalli, M. *Polyhedron* **1989**, *8*, 1838.

(17) Nonstabilized alkyl nucleophiles (e.g., ^{t}BuMgCl and ^{i}PrMgCl) also yield titanacyclobutane complexes under similar conditions: Carter, C. A. G.; Stryker, J. M., unpublished results.

(18) See refs 14a,c and the following: Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6878. Lee, J. B.; Gajda, G. J.; Schaefer, W. P.; Howard, T. R.; Ikariya, T.; Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 7358. Beckhaus, R.; Thiele, K.-H.; Ströhl, D. *J. Organomet. Chem.* **1989**, *369*, 43.

(19) No overriding preference for central carbon addition is observed in this series: preliminary results indicate that addition of PhCHMeK to the electronically and geometrically perturbed complex $(C_5Me_5)_2Zr(\eta^3\text{-allyl})Cl$ results in substantial formation of $(C_5Me_5)_2ZrH(\eta^1\text{-}CH_2CH{=}CHCH(Me)\text{-}Ph)$, a product derived from *terminal* allyl addition followed by allylic activation of the unstable olefin complex.

(20) Cationic η^3-allyl complex **2**, *inter alia*, functions as a catalyst for ethylene polymerization: Tjaden, E. B.; Stryker, J. M., unpublished results.