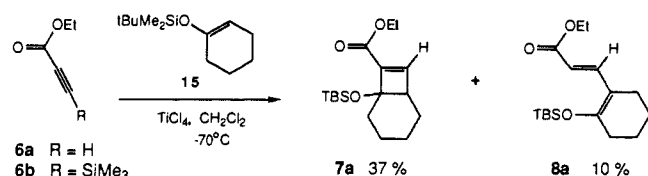


effect of silicon has not been reported for the Lewis acid mediated ene reactions of olefins with either β -silyl-substituted acetylenic esters (such as **6b**) or β -silyl-substituted alkenyl esters.



Three trends of significance can be seen from the data presented in Table I. First, the reactions of alkynyl carbene complexes with silyl enol ethers give mainly ene products while alkyl enol ethers give predominately [2 + 2] cycloadducts. Second, it was found that six-membered-ring enol ethers give a greater proportion of ene products than their five-membered-ring analogues, and this has also been observed in reactions of esters.^{7a} Third, the effect of a β -silyl substituent was not an isolated phenomenon; in each case in Table I the silyl-substituted carbene complexes give a greater proportion of ene product than do the corresponding alkyl complexes. Furthermore, the effect of silicon on these reactions can be judged to be electronic since the steric bulk of R does not affect the product partition between **13** and **14**. This suggests that either (a) silicon stabilizes an intermediate of the type **21** for a period of time sufficient to allow for conformation changes required for proton transfer or (b) silicon destabilizes intermediate **21** relative to a concerted ene reaction.



This issue was probed with the reactions of complexes **2a** and **2b** with the *cis* and *trans* isomers of ethyl propenyl ether. In these reactions, ene products are not possible, but the question of whether silicon stabilizes or destabilizes the zwitterionic intermediate **21** could be approached in a study of the stereospecificity of the [2 + 2] cycloadditions, an issue that has not been previously examined.³ The reactions of both the silyl- and methyl-substituted complexes **2a** and **2b** were stereospecific with *cis*-propenyl ethyl ether giving the *cis*-cyclobutene complex **22** and its ring-opened dienyl complex **23**. The reaction of *trans*-propenyl ethyl ether with the methyl complex **2b** gave only the dienyl complex **25b**. The only reaction where there was crossover in the stereochemistry was that of the trimethylsilyl complex **2a** with *trans*-propenyl ethyl ether, where only the *cis*-cyclobutenyl complex **22a** was observed.⁸ This is the first piece of evidence indicating that the [2 + 2] cycloaddition of alkynyl carbene complexes with enol ethers occurs by a stepwise mechanism. Taken together, the above results suggest that the role that silicon plays in affecting the partition between ene and [2 + 2] cycloaddition product is also played in stabilizing zwitterionic intermediates of the type **21**. Silicon is known to stabilize cationic centers in a variety of situations;⁹⁻¹¹ however, it is not clear how silicon stabilizes **21**, and this issue and the scope of the ene reactions of carbene complexes are currently being investigated.

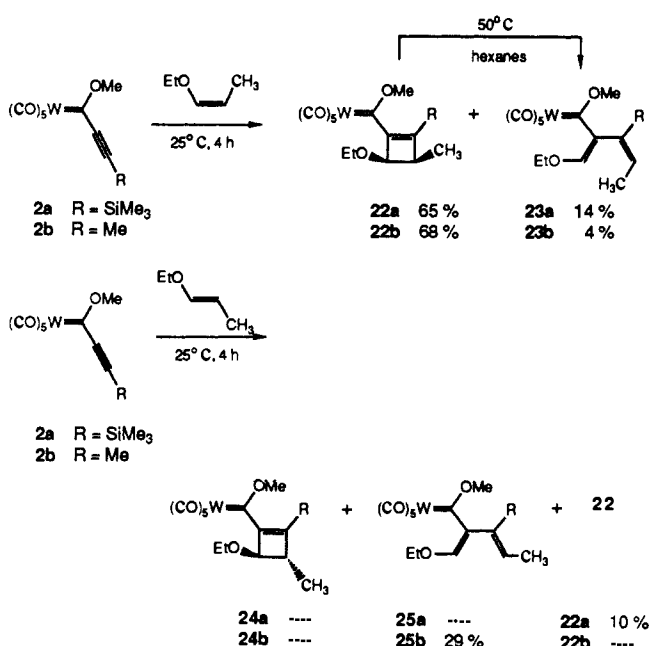
(7) (a) Clark, R. D.; Untch, K. G. *J. Org. Chem.* **1979**, *44*, 248. (b) Clark, R. D.; Untch, K. G. *J. Org. Chem.* **1979**, *44*, 253.

(8) It was determined that the recovered *trans*-propenyl ether had not isomerized and that this was not the source of the stereochemical crossover. The reason for the low mass balance has not been determined.

(9) α -Stabilization: Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1985**, *107*, 2806.

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Supplementary Material Available: Spectral data for all new compounds (11 pages). Ordering information is given on any current masthead page.

Nucleophilic Addition of Enolates to the Central Carbon of Transition-Metal η^3 -Allyl Complexes. Metallacyclobutane Formation, Reversibility of Nucleophilic Addition, and Synthesis of α -Cyclopropyl Ketones

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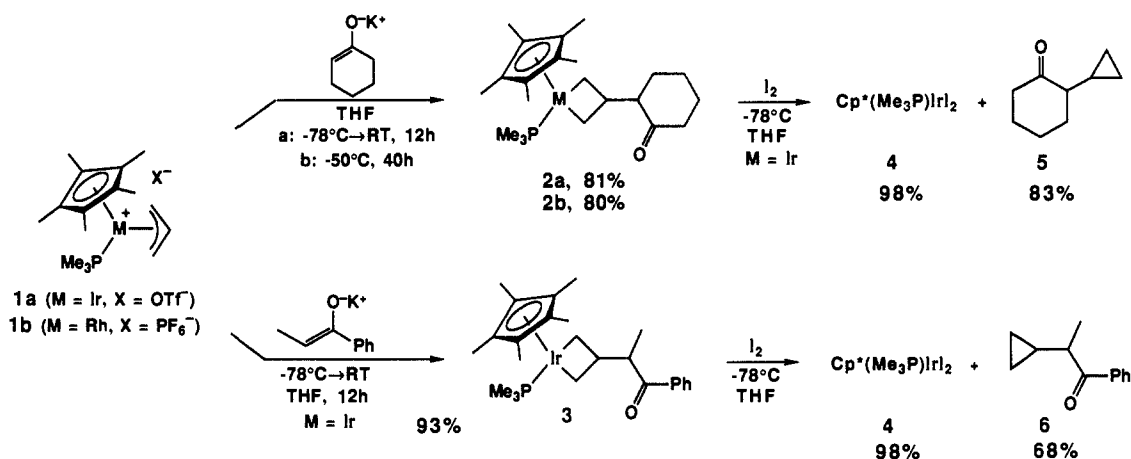
Received March 30, 1990

Nucleophilic addition to the central carbon of the π -allyl ligand has been observed in reactions of a limited class of transition-metal π -allyl complexes, leading to the formation of metallacyclobutane complexes.¹ Originally reported for the addition of hard nucleophiles to $[(C_3H_5)_2M(\eta^3\text{-allyl})]^+PF_6^-$ ($M = Mo, W$),^{1a} this regioselectivity is in marked contrast to the terminal carbon addition generally observed in such reactions.² Two theoretical

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(2) (a) Pd; reviews: Tsuji, J. In *The Chemistry of the Carbon-Carbon Bond, Vol. 3. Carbon-Carbon Bond Formation Using Organometallic Compounds*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1985; Chapter 3, Part 2. Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. (b) Mo; see: Fallner, J. W.; Chao, K. H.; Murray, H. H. *Organometallics* **1984**, *3*, 1231, and references therein. (c) Fe: Whitesides, T. H.; Arhart, R. W.; Slaven, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 5792. Pearson, A. J. *Tetrahedron Lett.* **1975**, 3617. Pearson, A. J. *Aust. J. Chem.* **1976**, *29*, 1841.

Scheme I



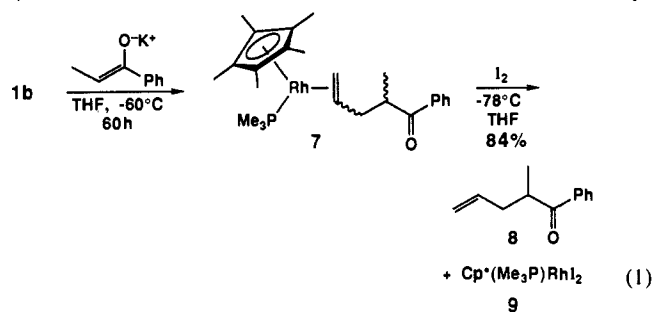
investigations were subsequently undertaken, rationalizing the regioselectivity of this unusual reaction.³ More recently, metallacyclobutane formation was reported for addition of hydride and methyl lithium to the complexes [(C₅Me₅)(Me₃P)M(η³-allyl)]⁺BF₄⁻ (M = Rh, Ir),^{1b,c} a system for which central carbon attack was predicted to be potentially favorable.^{3b} Theory, however, fails to provide adequate explanation for the contradictory results obtained from two closely related complexes: neither [(C₅H₅)(¹Pr₃P)Rh(1-methylallyl)]⁺PF₆⁻ nor [(C₅Me₅)Ir((1,3)-η³-(5,6)-η²-cyclooctadienyl)]⁺PF₆⁻ gives central carbon addition on reaction with hydride.⁴ More unusual is the cyclopropanation of branched ester enolates reported for a π-allyl palladium complex,⁵ the only example of central carbon addition known in this extensively studied system.^{2a}

To determine experimentally the factors controlling the regioselectivity of nucleophilic addition to π-allyl complexes, we have undertaken a program designed to probe this problem in considerably more detail. In addition, this investigation provides the basis for evaluating the development of synthetically interesting organic chemistry based on alkylative metallacyclobutane formation. From this perspective, in contrast to common allylic electrophiles and most transition-metal π-allyl complexes, selection of the appropriate coordination environment leads to a reversal of the natural polarization of the allyl moiety, directing nucleophilic addition to the normally nonelectrophilic central position. For this initial investigation, cationic rhodium and iridium complexes and synthetically relevant enolate nucleophiles were examined for regioselective addition.

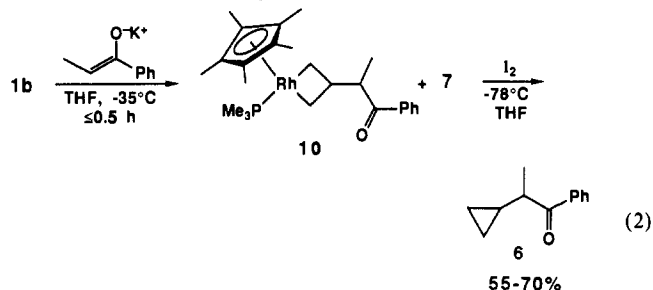
Treatment of iridium complex 1a^{1c} with the potassium enolate of either cyclohexanone or propiophenone gave crystalline metallacyclobutane complexes 2a and 3 in high yield (Scheme I).⁶ The more soluble triflate complexes are preferred over use of PF₆⁻ or BF₄⁻ and the use of lithium enolates resulted in minor amounts of terminal carbon adducts, particularly in the rhodium series. The metallacyclobutane complexes were identified by characteristic upfield resonances in both the ¹H and ¹³C NMR spectra for the α-hydrogen and carbon atoms.⁶ Interestingly, the carbonyl absorptions in the infrared spectra are shifted to lower energy, appearing at 1680 and 1675 cm⁻¹ for the cyclohexanone and propiophenone adducts, respectively.⁷ Release of the organic fragment by iodinolysis⁸ results in quantitative recovery of diiodide

complex 4⁹ and cyclopropanated ketones 5¹⁰ and 6,¹¹ providing an overall alkylative cyclopropanation protocol.⁵

Addition of the same potassium enolates to the analogous rhodium π-allyl complex 1b^{1b} led to dramatically disparate results. The cyclohexanone enolate gave predominantly central carbon attack, resulting in a metallacyclobutane complex 2b in high yield (Scheme I), accompanied by minor amounts (≤5%) of olefin isomers 13 (vide infra).⁶ The enolate of propiophenone, however, gave exclusively olefin complexes 7 from terminal addition (eq 1). This mixture of four stereoisomers was characterized by



iodinolysis, giving allylated organic 8¹² and diiodide complex 9⁹ in high overall yield. The origin of this divergence was revealed by repeating the experiment at higher temperature to ensure homogeneity and for shorter reaction time. Under these conditions, the metallacyclobutane complex 10 became the major product, characterized spectroscopically,⁶ accompanied by the previously observed olefin isomers. The metallacyclobutane complex can be trapped prior to substantial rearrangement: reaction at -35 °C for 10–15 min followed by addition of iodine at -78 °C resulted in the isolation of cyclopropane 6 and olefin 8 (eq 2) in a somewhat



variable ratio favoring the cyclopropane (ca. 5–10:1, 55–70% overall yield). Thus, we propose that the kinetic product is indeed

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(4) (a) Rh: Wolf, J.; Werner, H. *Organometallics* **1987**, *6*, 1164. (b) Ir: White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 1305.

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(6) Complete spectroscopic and analytical data is provided as supplementary material.

(7) The shift in carbonyl absorption is general, possibly indicating a polarization of the new carbon-carbon bond, in turn perturbing the carbonyl bond strength.

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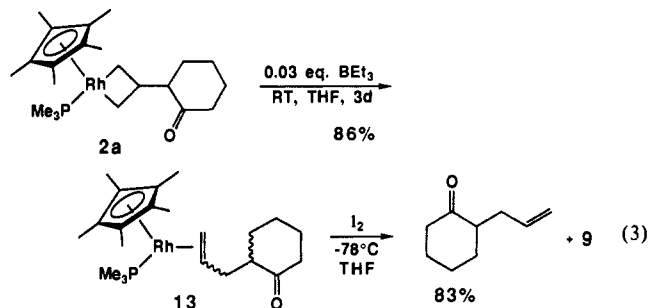
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(12) Marvell, E. N.; Li, T. H.-C. *J. Am. Chem. Soc.* **1978**, *100*, 883.

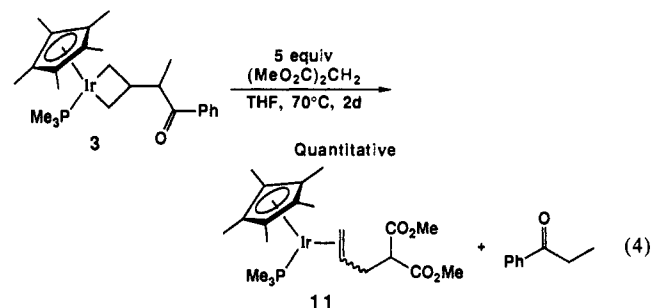
the metallacyclobutane, but the reaction is reversible, leading ultimately to the thermodynamically more stable olefin isomers.

For both iridium and rhodium, addition of the softer dimethyl malonate anion resulted in exclusively terminal carbon addition, giving the corresponding olefin complexes **11** and **12** exclusively,⁶ each as a mixture of isomers. These reactions are impractically slow at low temperature, and no evidence for the intermediacy of a metallacyclobutane has been obtained.

Further supporting the hypothesis of reversible nucleophilic addition, treatment of metallacyclobutane complexes **2a** and **2b** with excess $\text{BF}_3 \cdot \text{OEt}_2$ in Et_2O led to quantitative regeneration of the starting η^3 -allyl complexes **1a** and **1b**.¹³ More significantly, the mild Lewis acid Et_3B catalyzes the rearrangement of metallacyclobutane **2b** to olefin complexes **13**,¹⁴ a mixture of four stereoisomers obtained quantitatively and characterized by iodolysis (eq 3). Under similar conditions, the iridium metalla-



cyclobutane complexes do not rearrange, presumably reflecting stronger metal-carbon bonding for iridium. Heating the iridium complex **3** in the presence of excess dimethyl malonate, however, affords quantitative formation of malonate terminal adducts **11**⁶ and propiophenone (eq 4), strongly supporting reversible disso-



ciation to free ions as the mechanism for metallacyclobutane to olefin isomerization.

This investigation thus confirms a kinetic preference for nucleophilic addition to the central carbon of the η^3 -allyl ligand in this system, even for some reactions that give exclusively terminal carbon adducts. In addition, this work also demonstrates unequivocally that despite the highly electron rich metal center, the lower valent olefin complexes are thermodynamically more stable than the nominally higher valent metallacyclobutane complexes.^{1a} The facility of thermal and Lewis acid catalyzed rearrangements in this system suggests a previously unrecognized and potentially critical role that reversibility and (adventitious) Lewis acids may play in determining product distributions in related systems. Facile β -hydride abstraction has been reported in homologous metallacyclopentane complexes using $\text{BF}_3 \cdot \text{Bu}_2\text{O}$,¹⁵ suggesting that milder

Lewis acids may be capable of catalyzing rearrangements even in metallacyclobutane complexes lacking an identifiably Lewis basic site. These possibilities are under investigation.

Acknowledgment. Financial assistance from the NIH-BRSG Program and the Union Carbide Innovation Recognition Award Program is gratefully acknowledged.

Supplementary Material Available: Complete spectroscopic and analytical data for compounds **2a**, **2b**, **3**, **11**, and **12**, and NMR spectral data for thermally unstable **10** (3 pages). Ordering information is given on any current masthead page.

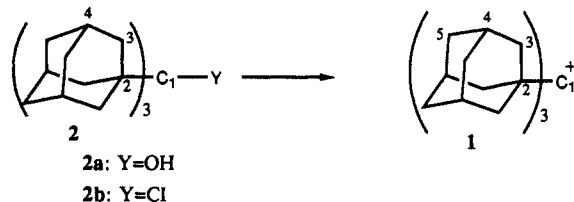
Tris(1-adamantyl)methyl Cation: A Most Highly Crowded Persistent Carbocation¹

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Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry University of Southern California Los Angeles, California 90089-1661 Received April 16, 1990

Highly hindered tris(*tert*-alkyl)methyl systems (R_3CX) are well suited for the study of steric crowding/strain energy relationships as well as the variation of the C-X bond length as a function of the steric bulk and strain energy of the R groups. Lomas² has synthesized and examined by molecular mechanics (MM2) calculations a series of tertiary alcohols containing combinations of *tert*-butyl, 1-adamantyl, 1-bicyclo[2.2.2]octyl, and 1-norbornyl ligands. However, MM2 theory is unable to predict the kinetic stability of tris(*tert*-alkyl)methyl cations. Earlier work by Dubois et al.³ indicated that highly hindered trialkylmethyl cations are formed more slowly than less crowded systems. Two effects working against each other are to be considered: the relief of steric strain associated with a change in hybridization from sp^3 to sp^2 is opposed by an increase of strain resulting from shortening of the C-C bond in the carbocation. We have earlier⁴ been successful in generating under stable ion conditions highly hindered trivalent carbocations, such as the bis(1-adamantyl)methyl cation.

We now report the preparation of tris(1-adamantyl)methyl cation (**1**), possibly the most hindered trialkyl(or cycloalkyl)methyl cation that has yet been observed as a persistent (long-lived) ion.



Its acyclic analogue, the tris(*tert*-butyl)methyl cation, cannot be observed due to its extremely low kinetic stability leading to rearrangement-cleavage reactions.^{7,8} Elimination of **1** to olefinic products is not favored as this would entail the formation of a bridgehead olefin. Thus **1** not unexpectedly has sufficient kinetic stability to allow its observation at low temperatures under stable ion conditions.

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(13) The counterion was not identified, but is presumably BF_4^- from disproportionation of excess BF_3 .

(14) The cyclohexanone-metallacyclobutane complex is thus only marginally more stable toward rearrangement than the propiophenone adduct in the rhodium series, presumably reflecting the greater stability (by 2 $\text{p}K_a$ units) of the propiophenone enolate compared to the cyclohexanone enolate; see: Bordwell, F. G. *Pure Appl. Chem.* 1977, 49, 963. Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* 1975, 97, 7006.

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