The synthetic utility of this methodology is significantly enhanced by our discovery that the cyclopentenylmethyl sulfone anions generated in these rearrangements can be trapped in situ with a variety of organic electrophiles and that desulfonylation can then be conveniently achieved in the same flask under mild conditions. Table I summarizes our results. A number of useful substitution and addition reactions involving α-sulfonyl carbanions[14] can thus be exploited to prepare a wide variety of cyclopentenes bearing functionalized and branched appendages; the transformation of (vinylcyclopropyl)methyl sulfone to the cyclopentene derivative is effected as a single, efficient synthetic operation. Another notable feature of this annulation method is its stereoselectivity (Table I, entries 4–7). As in the case of our earlier [4 + 1] method, the predominant product of the overall annulation process can be viewed as resulting from the effective suprafacial exo cycloaddition of a substituted carbene to the conjugated diene (eq 2).[15]

In summary, we have developed an efficient [4 + 1] annulation strategy for the stereocontrolled synthesis of a wide variety of highly substituted and functionalized five-membered carbocycles. With the feasibility of the carbanion-accelerated vinylcyclopropane rearrangement now solidly established, we are currently investigating more direct, two-step variants of this [4 + 1] annulation strategy.

Acknowledgment. We thank the National Institutes of Health, Firmenich AG, and Eli Lilly and Co. for generous financial support.

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(15) However, our preliminary results suggest that the scope of this stereoselectivity may not prove as impressive as in the previous alkoxy series. Thus, rearrangement of the (vinylcyclopropyl)methyl sulfones derived from (*Z*)-1,3-pentadiene affords a mixture of both cis- and (mainly) trans-substituted cyclopentenes.

Insertion of Iridium into the C–H Bonds of Alkenes: The π-Complex Cannot Be an Intermediate

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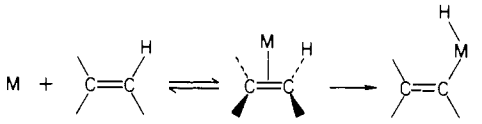
Despite their high bond energies[1], sp^2-hybridized (aromatic and vinyl) carbon–hydrogen bonds are more easily activated by transition metals than are the sp^3-hybridized C–H bonds in alkanes. It has been commonly assumed[2] that this is due at least partly to prior coordination of the metal to the π-electrons in the organic substrate (forming an η^2- or π-complex) followed by the oxidative addition step (eq 1).[3] We have now found that insertion

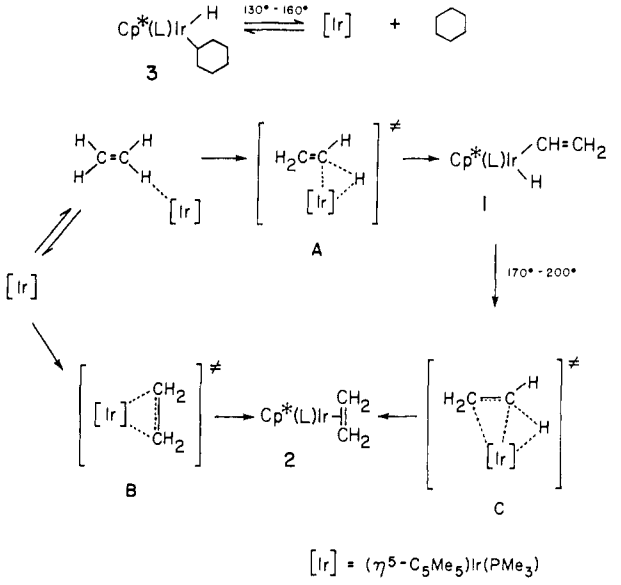


(1)

(1) Benson, S. W. "Thermochemical Kinetics"; Wiley: New York, 1968; p 309.

(2) (a) Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139. (b) Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113. (c) Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980; Chapter 7. (d) Muetterties, E. L.; Bleeke, J. R. *Acc. Chem. Res.* **1979**, *12*, 324. (e) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 4240. (f) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1984**, *106*, 1650. (g) Chatt, J.; Davidson, J. M. *J. Chem. Soc.* **1965**, 843–855. (h) Parshall, G. W. *Catalysis* **1977**, *1*, 334. (i) Fryzuk, M. D.; Jones, T.; Einstein, F. W. D. *Organometallics* **1984**, *3*, 185. (j) Keister, J. B.; Shapley, J. R. *J. Organomet. Chem.* **1975**, *85*, C29. (k) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1984**, *106*, 644–652.

Scheme I



of the iridium center in Cp*Ir(L) (Cp* = η^5-Me$_5$C$_5$; L = PMe$_3$) into the C–H bonds of ethylene occurs with concurrent, but *not* prior, formation of a π-complex. In addition, the chemistry of this system has allowed us to identify three distinct transition states having the formula [Cp*(L)Ir(C$_2$H$_4$)] and has provided the first X-ray structure of a mononuclear transition-metal hydrido vinyl complex.

Heating Cp*(L)Ir(C$_6$H$_{11}$)(H) (**3**; cf. Scheme I)[4] in cyclohexane-d_{12} under 20 atm of H$_2$C=CH$_2$ at temperatures between 130 and 160 °C resulted in an essentially quantitative reductive elimination of cyclohexane,[5] leading to a solution containing 66% of the vinyl hydride **1** and 34% of the olefin complex **2**. Both products were prepared independently, **2** in a procedure based on Maitlis' preparation of the corresponding triphenylphosphine complex[6] and **1** by treatment of Cp*(L)IrCl$_2$[7] with H$_2$C=CH-MgBr in THF at room temperature, followed by reduction with NaBH$_4$ in isopropyl alcohol. Chromatography of **1** at −80 °C followed by recrystallization yielded crystals suitable for an X-ray diffraction study. An ORTEP diagram of the molecular structure of **1** is illustrated in Figure 1; details of the structural study are included as supplementary information. To our knowledge this is the first structure determination of a mononuclear hydrido vinyl complex.

Significantly, the ratio of hydrido vinyl complex **1** to alkene complex **2** was invariant during the reaction of **3** with ethylene.[8]

(3) For the insertion of rhodium into arene C–H bonds, both kinetic and comparative inter- and intramolecular isotope effect studies (ref 2f; Jones, W. D., private communication) implicate η^2-arene complexes as true intermediates.

(4) (a) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 3929. (b) Bergman, R. G. *Science (Washington, D.C.)* **1984**, *223*, 902.

(5) The reductive elimination is reversible, and cyclohexane-d_{12} is incorporated into the iridium complex as the reaction proceeds. However, conversion to **1** and **2** is complete at the end of the reaction. On thermolysis in mixed benzene/alkane solvents, hydridocyclohexyliridium complex **3** is converted cleanly and quantitatively to cyclohexane and the benzene C–H activation product Cp*(L)Ir(C$_6$H$_5$)(H). In studies parallel to those reported here (Buchanan, J. M.; Stryker, J. M.; Bergman, R. G., manuscript in preparation), we have demonstrated that this reaction proceeds by kinetics that are first order in **3** and zero order in benzene. The rates are inhibited at high concentration of added cyclohexane. These data are consistent with a mechanism involving reversible, rate-determining reductive elimination of cyclohexane to give Cp*IrL, followed by trapping of this intermediate by benzene in a subsequent fast step. We assume the same type of mechanism operates with ethylene in place of benzene as the trap.

(6) Moseley, K.; Kang, J. W.; Maitlis, P. M. *J. Chem. Soc. A* **1970**, 2875.

(7) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.

(8) At 160 °C, upon extended thermolysis, a slow conversion of **1** to **2** occurs. If the reaction was stopped immediately after all Cp*(L)Ir(C$_6$H$_{11}$)(H) was consumed, however, the amount of conversion of **1** to **2** was so small that it had no significant effect on the ratio.

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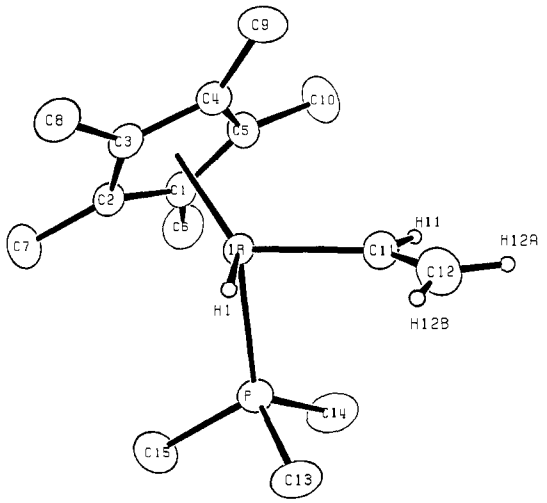

Figure 1. ORTEP diagram of Cp*(L)Ir(CH=CH_2)(H) (**1**). Selected distances and angles: Ir–C_{11}, 2.054 (4); Ir–H_1, 1.61 (5); C_{11}–C_{12}, 1.296 (6); Ir–Cp*, 1.899 Å; H_1–Ir–C_{11}, 86.2 (17)°; P–Ir–C_{11}, 85.8 (1)°.

This demonstrates that both products are completely stable to the reaction conditions. Above 170 °C, however, in either cyclohexane or benzene solvent, **1** was completely converted to **2** without any formation of solvent C–H insertion products. These observations require the following conclusions: (a) the invariant 66:34 mixture of **1** and **2** represents the true kinetic product ratio for the thermal reaction of **3** with ethylene; (b) the η^2-ethylene complex **2** is the thermodynamic product of the reaction; (c) because **2** is stable to the ethylene reaction conditions, *the olefin complex* **2** *cannot be an intermediate in the formation of C–H insertion product* **1**—i.e., there must be two independent transition states leading to these two products;[9] (d) given that the transient intermediate "Cp*IrL" reacts with ethylene and benzene at similar rates,[10] the absence of Cp*(L)Ir(Ph)(H) (which control experiments demonstrated was completely stable under these conditions) in the conversion of **1** to **2** above 170 °C requires that this reaction proceeds without reversion to ethylene and the reactive intermediate—i.e., it must proceed through a third transition state distinct from those leading from the intermediate to **1** and **2**.

To account for our results we propose the reaction mechanism illustrated in Scheme I. The separate transition states required for the formation of hydrido vinyl complex **1** and π-complex **2** from the reactive intermediate Cp*Ir(L) and ethylene are suggested to have structures similar to A and B. The third transition state, required for thermal conversion of **1** to **2** at temperatures above 170 °C, should have a structure similar to C, intermediate between A and B. It is startling that the rate of formation of C–H insertion transition state A is so similar to that (B) required for simple coordination of the metal center to the loosely held π-electrons of the alkene. The C–H insertion process may be assisted by prior coordination of the metal to the C–H bond in some way, perhaps in the linear fashion suggested by Hoffmann.[11] This possibility is illustrated in Scheme I but further studies will be required to determine whether such "σ-complexes" are truly involved as intermediates in these and other[12] C–H insertion reactions.

(9) Another possibility is that interaction of Cp*IrL with ethylene leads to only one transition state, and partitioning to **1** and **2** occurs at a branch located beyond this point on the reaction energy surface (for an example of the use of this type of surface, see: Salem, L. "Electrons in Chemical Reactions"; Wiley-Interscience: New York, 1982; p 55). These two alternatives are very difficult to distinguish, but we hope to obtain some information on this question by using deuterium isotope effects.

(10) Thermolysis of **3** in cyclohexane-d_{12} in the presence of known amounts of benzene and ethylene gives both **1** and Cp*(L)Ir(C_6H_5)(H) (in addition to **3**-d_{12} and **2**). The relative yield of these two products can be used to estimate that the rate of attack on one C-H bond in benzene, relative to that in ethylene, is ca. 1.0.

(11) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006–2026.

(12) Periana, R. A.; Stryker, J. M.; Buchanan, J. M.; Bergman, R. G., unpublished results.

As pointed out earlier, it has been almost universally assumed that π-complexes are intermediates in the many known reactions of alkenes with transition metals.[13] Our results demonstrate that in at least one case, even though π-coordination occurs, the coordinated complex does *not* lie on the pathway for activation of the alkene. It must be concluded that prior coordination in other processes cannot be taken for granted, even when the coordinated complex is isolated or detected spectroscopically. Evidence must be provided which demonstrates that complex formation is not simply a "dead end" but actually lies on the pathway for reaction.

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Supplementary Material Available: ^{1}H NMR, ^{13}C NMR, IR, MS, melting point, and elemental analysis data for complexes **1**, **2**, and (η^5-C_5Me_5)(PMe_3)Ir(CH=CH_2)(Br) and experimental details of the X-ray diffraction study, including tables of crystal and data collection parameters, intramolecular distances and angles, and general temperature factor expressions (*B*'s) and a table of positional parameters and their esd's (32 pages). Ordering information is given on any current masthead page.

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Formation of Novel, Dimeric Epidioxides from the Lewis Acid Catalyzed Oxygenation of 1-*tert*-Butylcyclohexa-1,3-diene

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1,1-Diarylethylenes are converted into 3,3,6,6-tetraaryl-1,2-dioxanes by O_2 and $SbCl_5$ in CH_2Cl_2 at −78 °C.[1] In these and related[2] reactions, the lifetime of the cation radical formed from the ethylene and the Lewis acid is presumably too short to allow reaction with O_2, and it is the longer lived, hindered dimer cation radical derived from the monomer cation radical and the ethylene which gives the dioxane.[1] If we consider a 1-alkylcyclohexa-1,3-diene cation radical, it will react through C-4 with the parent

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