

Figure 2. Logarithmic plot of the TT rate constants versus ET rate constants for the compounds indicated. Compound key in Table I.

maximum rates among stereoisomers are found for the equatorial-equatorial substituent patterns.

Both long distance ET and TT are nonadiabatic processes and therefore should be describable by the Golden Rule (eq 1), ex-

$$k = 2\pi\hbar^{-1} |V|^2 \text{FCWDS} \quad (1)$$

pressing the rate as a product of an electronic coupling term, V , and the Franck-Condon weighted density of states. Assuming through-bond coupling with an exponential decay of V with the number of intervening σ -bonds as in

$$V = V_0 \exp - [\alpha(\text{no. of bonds} - 1)/2] \quad (2)$$

we can write

$$k = 2\pi\hbar^{-1} \text{FCWDS} |V|^2 \exp - [\alpha(\text{no. of bonds} - 1)] \quad (3)$$

$$k = k_0 \exp - [\alpha(\text{no. of bonds} - 1)] \quad (4)$$

where k_0 contains the Franck-Condon factors and the coupling matrix element when donor and acceptor are separated by one σ -bond. A correlation of a series of compounds with different spacers by eq 4 will only be successful if k_0 is kept constant throughout the series. Using identical donors and acceptors will assure a reasonable invariance of the Franck-Condon factors. However, as has been shown in the electron-transfer work, a constant V_0 can only be expected for a series of compounds with identical stereochemical attachment to the spacer.

Figure 1 shows a logarithmic plot of the rate constants versus numbers of bonds separating donor and acceptor of the cyclic compounds with both donor and acceptor being attached equatorially. The least-squares line has a slope $\alpha = 2.6/\text{bond}$ and an intercept $k_{0TT} \approx 3 \times 10^{13} \text{ s}^{-1}$. A corresponding correlation for electron transfer on the same spacer series gave an exponent of $\beta = 1.15/\text{bond}$ and $k_{0ET} \approx 10^{11} \text{ s}^{-1}$.^{2a} With the aid of eq 4, we can derive the relationship between TT and ET rate constants for any spacer as

$$k_{ET}^{\alpha/\beta} / k_{TT} = k_{0ET}^{\alpha/\beta} / k_{0TT} \quad (5)$$

Figure 2 shows a logarithmic plot of the rates for TT versus ET for all the compounds where both rates are available.⁸ The fact that (5) correlates compounds of different stereochemical attachment with a single line shows that the k_0 's obey the same power dependence as the other points. The least-squares line has a slope of $\alpha/\beta = 2.2 \pm 0.2$.

This slope is close to the slope of 2 predicted from a rather simple model, viewing triplet transfer as simultaneous two-electron transfer. The matrix element determining the rate in electron transfer can be written as a two-center, one-electron resonance integral (6).

$$\langle \psi_{\text{LUMO}}^D(1) | H_{\text{ion}} | \psi_{\text{LUMO}}^A(1) \rangle = H_{\text{DA}} = V_{\text{ET}} \quad (6)$$

The appropriate integral in triplet transfer is a two-center (four orbital) two-electron exchange integral (7).⁹

$$\langle \psi_{\text{LUMO}}^D(1) \psi_{\text{HOMO}}^A(2) | e^2 / r_{1,2} | \psi_{\text{LUMO}}^A(1) \psi_{\text{HOMO}}^D(2) \rangle = K_{\text{DA}} = V_{\text{TT}} \quad (7)$$

The distance dependence of both integrals will parallel the distance dependence of the corresponding overlap integrals. Inspection shows that elimination of the operator converts (6) to a simple two orbital overlap integral, while (7) will become a product of two such integrals. If the overlap for all orbitals falls off with the same exponent $-\gamma R$, the product of two integrals will give an exponent of $-2\gamma R$, remarkably close to the α/β ratio found experimentally.

Besides these similarities between TT and ET, there are important differences. ET rates, involving charged particles, show strong solvent dependencies caused by large changes in the Franck-Condon factors. Triplet transfer occurs in neutral molecules with little solvent reorganization. Preliminary results show rate changes in some of the compounds studied here to be less than a factor of three upon switching from hexane to acetonitrile. In ET the corresponding changes would amount to many orders of magnitude.^{2a} It is therefore much easier to separate electronic coupling from Franck-Condon factors in TT than in ET, and the study of TT may sometimes be a preferred way to learn about electronic coupling in ET.

Acknowledgment. We are indebted to Joseph Alfano and Hilary Arnold who participated in the synthesis of some of the compounds.

(9) This expression is strictly correct only for a direct exchange mechanism. For through bond coupling, it must be replaced by the appropriate superexchange Hamiltonian.

[2 + 1] versus [4 + 2] Cycloadditions of Fischer Carbene Complexes with 1,3-Dienes. Evidence for a Zwitterionic Intermediate in a Cyclopropanation Reaction[†]

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Received August 27, 1987

Revised Manuscript Received February 12, 1988

The reactions of transition-metal carbene complexes with alkenes are known to occur under the proper conditions to give cyclopropane products in a formal [2 + 1] cycloaddition.² We report herein the first examples of the cyclopropanations of 1,3-dienes with isolable transition-metal carbene complexes,^{3,4} the first nonstereochemical evidence for the intermediacy of a zwitterion in a reaction in which a cyclopropane is formed from a carbene complex in a stoichiometric reaction,^{2a,5,6} and a dramatic example

[†] Dedicated to Professor Gerhard L. Closs on the occasion of his 60th birthday.

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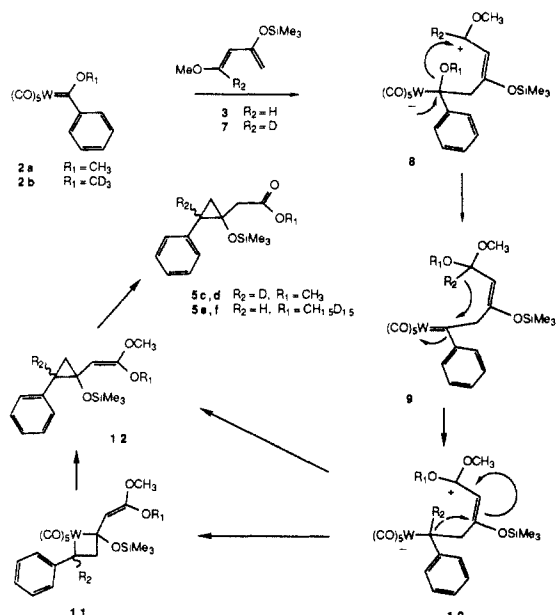
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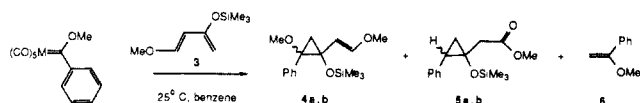
(8) To assure minimum variation in the Franck-Condon factors, the experimental ET rate constants have been corrected to a constant reorganization energy throughout the series.^{2a}

Scheme I



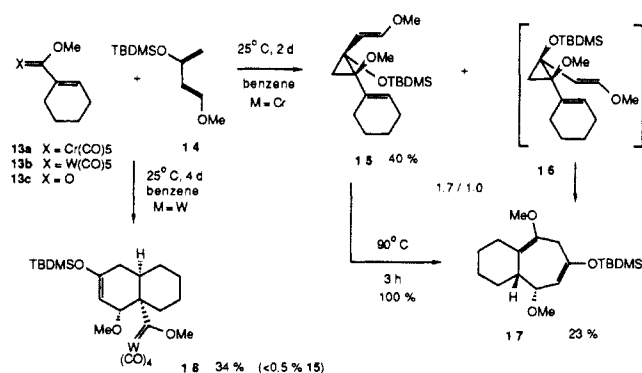
of chemoselectivity in an organometallic reaction.

The reaction of the phenyl-substituted chromium carbene complex **1**⁷ with Danishefsky's diene in benzene went to completion in 5 days at room temperature to give a 52% yield of the vinyl cyclopropanes **4** as a 1.3:1 mixture of diastereomers.^{12b} The cyclopropanes **4** are the result of the regioselective transfer of the carbene ligand to the more electron-rich double bond^{2a,8} of the diene. Also produced in this reaction are α -methoxystyrene **6** (36%), which is the metathesis product resulting from the fragmentation of a metallacyclobutane intermediate² and the very interesting cyclopropanes **5a** and **5b** in 12% yield. The cyclopropanes **5a** and **5b** are formally related to the expected products **4a** and **4b** by an internal oxidative/reductive disproportionation which is unprecedented in cyclopropanation products from the reactions of transition-metal carbene complexes. The reaction of the tungsten complex **2** gave a high selectivity for these novel cyclopropanes **5a** and **5b**. The metathesis product **6** is not produced from the tungsten reactions or from the chromium reaction carried out under carbon monoxide.



A mechanism to account for the formation of these novel products is presented in Scheme I. Nucleophilic attack of the diene on the carbene carbon would produce the zwitterion **8**^{2,5,6} which is followed by methoxyl transfer⁹ to the cationic center to generate the neutral unstabilized carbene complex **9**. At this point it would be necessary to evoke an unprecedented hydride abstraction by the carbene carbon to generate the new zwitterion **10** which can then collapse to the cyclopropane **12** directly or in two steps via the metallacyclobutane **11**. The ¹H NMR of the crude reaction mixture is complicated by the presence of excess diene and products derived therefrom; however, methoxyl absorptions can be identified ($\delta = 3.35, 3.48$) which can be attributed to the ketene acetal **12** since upon treatment with water the disappearance of

Scheme II

Table I. Cyclopropanation of Complexes 1 and 2 with Diene 3^a

complex	CO atm	time (days)	% yield 4a,b	% yield 5a,b	% yield 6
1, M = Cr	none	5	52 (1.3:1) ^b	12 ^b	36 ^b
1, M = Cr	800 psi	3	67 (2.0:1) ^c	1.2 (5:1) ^d	<0.5 ^d
2, M = W	none	3	<3 ^e	33 (2.4:1) ^c	<0.5 ^e
2, M = W	1250 psi	2.5	10 ^{f,g}	38 (1.9:1) ^f	<1.0 ^e

^a All reactions were run at 0.4 M in carbene complex at 1 mmol scale in benzene with 4 equiv of **3** at 25 °C. ^b NMR yield with added **4a** as standard. ^c Isolated yield (silica gel). ^d NMR yield relative to **4a** in the crude reaction mixture. ^e NMR yield relative to **5a** in the crude reaction mixture. ^f **4** and **5** were purified as a mixture on silica gel in 48% total yield. ^g **4** was obtained as three isomers: **4a** and **4b** (1.7:1) plus a third (**4c**) that could not be separated, but which could tentatively be assigned as the olefin isomer of **4a** (**4c**:**4a** = 3.1:2) from the ¹H NMR.

these absorptions is concurrent with the appearance of those for the reduced cyclopropanes **5a,b**. The two labeling experiments indicated in Scheme I provide evidence to support this mechanism. The reaction of the deuterated complex **2b** produced **5e** and **5f** in which the deuterium content of the methyl group of the ester was found to be 50%, consistent with the formation and hydrolysis of the ketene acetal **12**. The hydride shift evoked for **9** to **10** is supported by the reaction of the unlabeled carbene complex **2a** and the labeled diene **7**. The products of this reaction were **5c** and **5d** where the deuterium label was incorporated exclusively at the benzylic cyclopropane carbon. These labeling studies are consistent with the mechanism in Scheme II but do not definitively rule out other possibilities. One possibility that can be ruled out is the conversion of **4** to **5**. It was established that **5** is a primary product of the reaction when the third reaction in Table I was spiked with 0.24 equiv of **4a**. This reaction gave a 28% yield of **5** and an 80% recovery of **4a** (67% recovery if it is assumed that **4a** is produced in 3% yield). Also there is not a mechanism that scrambles the label prior to reaction since recovery of **2b** after the reaction had gone to 87% completion reveals no loss in deuterium (>99%).

The cyclopropanation of alkenes by Fischer carbene complexes and other types of carbene complexes has been extensively investigated, and the mechanisms that have been proposed vary between and including the two extremes involving zwitterions of the type **8** and metallacyclobutanes of the type **11**.^{2,5,6,10} All of the evidence that has previously been presented to differentiate between these two extremes in the stoichiometric reaction of carbene complexes involves the stereochemistry of the cyclopropane product and comes mainly from the work of Brookhart, Casey, and Doyle.^{2,10} Thus the results discussed above provide the first nonstereochemical evidence for a zwitterionic intermediate in a reaction in which a cyclopropane is formed in the stoichiometric reaction of a Fischer carbene complex.^{5,6} The above evidence for the intermediacy of a zwitterion in the mechanism for the formation of the reduced cyclopropane **5** does not necessarily com-

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ment on the mechanism for the formation of the cyclopropanes **4a** and **4b** nor on the cyclopropanation reactions of simple olefins, since the very electron-rich diene **3** would be expected to favor the formation of the zwitterionic intermediate **8** compared to less activated olefins.

The Diels–Alder reactions of α,β -unsaturated carbene complexes are known and occur with 1,3-dienes via a [4 + 2] cycloaddition at the unsaturated carbon–carbon bond of the carbene carbon substituent.¹¹ Thus on the basis of the reactions observed for complexes **1** and **2**, one would anticipate the possibility that both [2 + 1] and [4 + 2] cycloadditions could occur for the reaction of the diene **14** and the complex **13**; however, to date only Diels–Alder products have been observed for the reactions of α,β -unsaturated complexes and 1,3-dienes.¹¹ The reaction of the tungsten complex **13b** gives the Diels–Alder adduct **18** in 34% yield,^{12a} whereas, the chromium complex **13a**¹³ reacts to give two products, the cyclopropane **15** and the seven-membered ring silyl enol ether **17**. The stereochemical assignment of **17** was made considering that it has been determined that *cis*-divinylcyclopropanes undergo Cope rearrangement via a boat transition state.¹⁴ Since *cis*-divinylcyclopropanes undergo Cope rearrangement much faster than their corresponding *trans* isomers, it can be deduced that the ratio of the *trans*-cyclopropane product **15** and the Cope product **17** from the reaction of the chromium cyclohexenyl carbene complex **17a** and diene **14** is a reflection of the stereoselectivity of the cyclopropanation reaction. The *trans*-divinylcyclopropane **15** will undergo the Cope rearrangement to give **17** at 90°C, and since this rearrangement is essentially quantitative, this tandem cyclopropanation/Cope rearrangement could be utilized for an efficient preparation of highly functionalized fused seven-membered rings.⁴

From the point of view of the synthetic methodological development of transition-metal organometallics, the two reactions indicated in Scheme II represent an ideal situation. The reaction of the carbene complex **13** with diene **14** can be fine tuned to give either the tandem cyclopropanation/Cope product **17** or the Diels–Alder product **18** by judicious choice of the metal in the complex. These reactions are remarkably chemospecific in their reactions with the 1,3-diene **14** as the chromium complex **13a** gave no detectable amounts of the Diels–Alder product, and the tungsten complex **13b** gave less than 0.5% of the cyclopropane **15**.^{12a} The rate of the Diels–Alder reaction of the tungsten complex **13b** with diene **14** is also remarkable when compared to the reaction of its closest carbon analogue, the cyclohexenyl ester **13c**, which occurs with **2** in 30 h at 190 °C.¹⁵ Further studies will be needed to determine how the nature of the metal can so dramatically affect the product distribution in these reactions.

Acknowledgment. This work was supported by the National Science Foundation under Grant CHE-8517103 and by the National Institutes of Health (PHS-GM 33589). The National Institutes of Health has provided a predoctoral training grant for

D.C.Y. (No. GM 07151). The NMR instruments used were funded in part by the NSF Chemical Instrumentation Program and by the NCI via the University of Chicago Cancer Research Center (CA-14599).

Supplementary Material Available: Spectral and physical data for compounds **2b**, **4a,b**, **5a–f**, **5a'–f'**, **7**, **15**, **17**, and **18** (4 pages). Ordering information is given on any current masthead page.

Bimetallic Catalysis. A New Method for the Activation of Chloroarenes toward Palladium-Catalyzed Coupling with Olefins

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Received December 14, 1987

Palladium-catalyzed olefin arylation, developed primarily by Heck, is a well-established method for the coupling of activated olefins with aromatic halides (Scheme I).¹ The reaction is general for a broad range of substituents both on the arene and the olefin and is useful for the preparation of a wide array of elaborated arenes from relatively simple starting materials.

A serious limitation to this method is its failure with aryl chlorides. A method for the activation of chloroarenes toward olefin arylation is desirable because of the ready availability and relative inexpense of these materials. For example, bromobenzene undergoes palladium-catalyzed coupling with ethyl acrylate to give ethyl cinnamate in 78% yield² but performing the reaction with chlorobenzene lowers the yield to 4%.³ Only in the presence of styrene or stoichiometric amounts of preformed **1** ($X = Cl$) has successful coupling of olefins with chlorobenzene been observed.^{4,5} Chloroarenes substituted with electron-withdrawing groups undergo olefin coupling but rarely in yields above 30%. An indirect method based on palladium-catalyzed CO extrusion from aroyl halides has been reported.⁶ We wish to report a new method of coupling chloroarenes and olefins in excellent yield by means of a novel bimetallic nickel/palladium catalyst system. To our knowledge, this is the first demonstration of chloroarenes participating in the Heck arylation reaction in a synthetically useful fashion.

In a typical experiment, the chloroarene (10 mmol) is treated with NaI (11 mmol) and NiBr₂ (2 mmol) in DMF at 140 °C for 4–5 h. Gas chromatographic and mass spectral analysis at this point indicates that approximately 5% of the starting chloroarene has been converted to the corresponding iodoarene. The mixture is cooled and treated with the olefin (11 mmol), Pd₂(dba)₃ (0.05 mmol), P(*o*-tol)₃ (4 mmol), and Et₃N (11 mmol). The mixture is heated overnight at 140 °C (usually 16–18 h). The salts are precipitated from the cooled reaction mixture upon addition of Et₂O. Filtration and removal of DMF by washing of the organic fraction with small amounts of saturated NaCl followed by

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(12) (a) The cycloadduct **18** is the major product of the reaction, and the small amounts (<5%) of the many other products formed have not yet been identified. Cyclopropane **15** is absent (<0.5%) by crude ¹H NMR, but GCMS indicates the presence of isomers of **15** which may prove to be five-membered ring compounds and/or small amounts of **17**. (b) The diastereomers of **4a** and **4b** (also **5a** and **5b**) can be separated and characterized (stereochemistry not determined) in each case by hydrolytic cleavage of the trimethylsilyl group to give the corresponding hydroxycyclopropanes (see Supplementary Material).

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