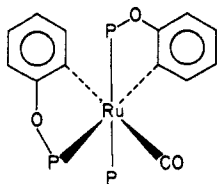
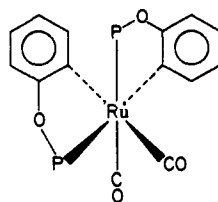


gomers. ^{31}P NMR analysis of the white precipitates from the styrene reactions showed no resonances (no phosphorus in sample). The ^{31}P NMR of V showed a broad resonance at ca. 126 ppm (6-ppm wide). FDMS analysis showed $M = \text{P}(\text{OPh})_3$, m/e 415 (M^+ + styrene), 518 (M^+ + styrene₂), 622 (M^+ + styrene₃), 726 (M^+ + styrene₄), 830 (M^+ + styrene₅).

Reaction of II with CO. Complex II (0.026 g, 0.019 mmol) was dissolved in 10 mL of toluene and placed in a 90-mL thick-walled bottle under N_2 . The bottle was charged with CO (100 psi, 0.025 mol) and then heated to 205 °C for 4 h with stirring. The bottle was cooled to room temperature and vented. The contents of the bottle were completely extracted with THF. LC analysis showed that quantitative conversion of II to two new products had occurred. The prep LC column was used to separate the products.



IR ν_{CO} (CH_2Cl_2) 2044 cm^{-1} .¹⁶ FDMS: m/e 1061 (M^+ , Ru isotope pattern).



IR ν_{CO} (CH_2Cl_2) 2055, 2010 cm^{-1} .¹⁵ FDMS: m/e 776 (M^+ , Ru isotope pattern).

Reaction of X with $\text{P}(\text{OPh})_3$ (Equation 10a). Complex X (0.037 g, 0.14 mmol) was dissolved in 2 mL of C_6D_6 under N_2 in a septum-capped

10-mm NMR tube. $\text{P}(\text{OPh})_3$ (37 mL, 0.14 mmol) was then added by syringe. The solution was analyzed by ^1H , ^{13}C , and ^{31}P NMR (see Table II and eq 10a) and yield established by ^1H and ^{31}P NMR. FDMS analysis showed X m/e 258 (M^+), XI m/e 540 (M^+), and XII m/e 822 (M^+).

Reaction of I and X (Equations 11a-c). A C_6D_6 solution (1 mL) of complex I (0.054 g, 0.039 mmol) was combined with a C_6D_6 solution (1 mL) of X (0.013 g, 0.050 mmol) under N_2 . ^{31}P NMR analysis indicated that I was unchanged and that only trace quantities of XI and XII were produced. Incremental amounts of solid X were added to the solution under N_2 . When the Ru:Rh ratio was 1:3 (eq 11a), the ^{31}P NMR showed resonances for XI and XII (relative intensity of XI:XII was 1:4) as well as resonances for I and VI (see text). There were about equal amounts of I and XII at this point, which indicated about 60-70% unreacted X. An additional equivalent of solid X was added under N_2 (eq 11b). The ^{31}P NMR spectrum at this time showed that the relative ratio of XI to XII was 1:5 while I was consumed; VI and VII grew in intensity. The solution was heated in an oil bath at 85 °C for 2 h. The color of the solution changed from yellow to maroon but no precipitate was observed. ^{31}P NMR showed complete consumption of I had occurred.

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Registry No. I, 25839-18-3; II, 59634-28-5; III₀, 101-02-0; III₁, 100814-87-7; III₂, 100814-86-6; III₃, 100814-84-4; III₄, 100814-82-2; III_{4a}, 100814-93-5; III₅, 100814-83-3; III₆, 100814-85-5; IV₁, 100814-88-8; IV₂, 100814-89-9; IV₃, 100814-90-2; IV₄, 100814-91-3; IV_{4a}, 100814-92-4; VI_b, 100814-96-8; VII_b, 100814-97-9; IX_b, 100839-15-4; X, 12082-47-2; XI, 100814-95-7; XII, 25966-19-2; Ru($\text{P}(\text{OPh})_3$)($\text{P}(\text{OPh})_2(\text{O}-o\text{-C}_6\text{H}_4)$)CO, 100814-94-6; Ru($\text{P}(\text{OPh})_2(\text{O}-o\text{-C}_6\text{H}_4)$)₂(CO)₂, 100897-56-1; C_2H_4 , 74-85-1; PCl_3 , 7719-12-2; $\text{Ph}(\text{H})\text{C}=\text{CH}_2$, 100-42-5; C_3H_6 , 115-07-1; polystyrene, 9003-53-6; 2,6-diethylphenol, 1006-59-3; phenol, 108-95-2; 2-ethylphenol, 90-00-6.

Metal Carbonyl $\nu(\text{CO})$ Force Constants as Predictors of π -Ethylene and π -Benzene Complex Reactivity with Nucleophiles

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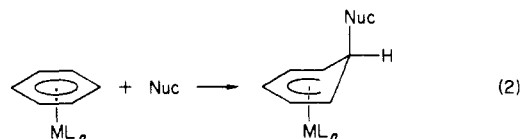
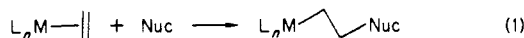
Abstract: Nucleophilic attack on π -ethylene and π -benzene organometallic compounds, resulting in β -substituted ethyl and exo-substituted cyclohexadienyl complexes, respectively, is examined in terms of a new reactivity parameter, k_{CO}^* . This parameter represents the Cotton-Kraihanzel (C-K) C-O stretching force constant of a hypothetical compound in which CO ligands replace the unsaturated hydrocarbon of interest. For example, k_{CO}^* for ethylene in $\text{L}_n\text{M}(\text{C}_2\text{H}_4)$ is simply the C-O force constant of $\text{L}_n\text{M}(\text{CO})$. The C-K force constants may be calculated from available IR data, or they may be conveniently estimated by using the ligand effect constants described by Timney. A survey of reported reactions of nucleophiles with π -ethylene and π -benzene complexes reveals a definite correlation between the magnitude of k_{CO}^* and the likelihood of addition to the hydrocarbon ligand; a reactivity index utilizing k_{CO}^* is established for several nucleophiles. For coordinated ethylene, attack by PPh_3 or most amines is not observed for complexes with $k_{\text{CO}}^* \leq 16.8$ mdyn/Å. Trialkylphosphines react with complexes that have k_{CO}^* values as low as 15.5 mdyn/Å. Attack on coordinated benzene by PPh_3 does not occur for complexes with $k_{\text{CO}}^* \leq 18.3$ mdyn/Å, and trialkylphosphines do not add to benzene in complexes with k_{CO}^* below a value of 17.7 mdyn/Å. Carbanions, such as alkylolithium reagents and CH_2X^- ($\text{X} = \text{CN}, \text{NO}_2$), successfully add to benzene complexes with k_{CO}^* values as low as 16.5 mdyn/Å. The results indicate that the k_{CO}^* parameter provides a simple means of gauging the activation of coordinated ethylene and benzene toward nucleophilic attack.

Nucleophilic attack on unsaturated hydrocarbons which are coordinated to transition metals has been studied extensively and continues to be a subject of considerable interest.¹ Two reactions

of this type involving attack on π -ethylene and π -benzene ligands are shown in eq 1 and 2. Such reactions are important in certain industrial processes, such as the Wacker acetaldehyde synthesis,² and are also useful in a variety of laboratory scale syntheses.³ In

(1) (a) Pauson, P. L. *J. Organomet. Chem.* **1980**, *200*, 207. (b) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047. (c) Kane-Maguire, L. A. P.; Honig, E. D.; Sweigart, D. A. *Chem. Rev.* **1984**, *84*, 525.

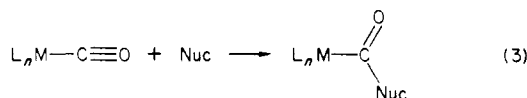
(2) Bäckvall, J. E.; Åkermark, B.; Ljunggren, S. O. *J. Am. Chem. Soc.* **1979**, *101*, 2411.



attempts to understand better the reactivities of unsaturated ligands in these complexes, several theoretical studies have been carried out. Through the application of simple Hückel MO theory, Davies, Mingos, and Green^{1b} developed a useful qualitative scheme for predicting the site of attack on organo-transition-metal cations containing unsaturated hydrocarbon ligands; however, their approach was not designed to determine which complexes were susceptible to attack and which were not. Their simple set of rules has been successfully applied, though not without exception, to a number of organometallic reactions. Several researchers have also applied more quantitative MO techniques to explore the factors which contribute to the activation of alkenes, arenes, and other unsaturated hydrocarbon ligands in various organometallic complexes.⁴

An empirical correlation of reactivity with some readily obtainable experimental quantity would be desirable, yet attempts to do this with various experimental observables have met with little success. For various benzene complexes, there is no useful correlation between ¹³C and ¹H NMR shifts of the arene ligand and its reactivity with nucleophiles.⁵ Similarly, there is no correlation with C(1s) energies from XPS measurements.⁵ However, Sweigart and co-workers^{1c,5} have noted a correlation between the reduction potentials and relative rates of phosphine attack on a series of π -hydrocarbon complexes, but this type of electrochemical data is not routinely obtainable for many compounds. Sweigart^{1c} has also reported parameters, called electrophilic transferability (T_E) numbers, which reflect the activating ability of metal-ligand fragments bound to π -hydrocarbons. The T_E numbers are useful in predicting the reactivity of triene and diene complexes; however, values for only a few ML_n fragments are available.

Several years ago publications by Darensbourg and Darensbourg^{6a} and from this laboratory^{6b-d} reported correlations between C-O stretching force constants, k_{CO} , and the susceptibility of CO ligands to nucleophilic attack (eq 3). This method was based on the assumption that k_{CO} is a measure of the electron-withdrawing



ability of the ML_n metal-ligands fragment: the higher k_{CO} , the more electron withdrawing the ML_n unit. An electron-withdrawing ML_n group makes the CO carbon more positive and more susceptible to nucleophilic attack. Therefore, the higher k_{CO} , the more susceptible to nucleophilic attack is the CO carbon in the

complex. It was found that primary alkyl amines react with CO groups having k_{CO} values greater than approximately 17.0 mdyn/Å; alkyllithium reagents (LiR) react with CO ligands having k_{CO} values higher than 15.3 mdyn/Å.

In the present paper, we use k_{CO} values to measure the electron-withdrawing ability of the ML_n fragment in complexes with unsaturated hydrocarbon ligands. For example, the electron-withdrawing ability of the ML_n group in the π -ethylene complex $ML_n(C_2H_4)$ is measured by the k_{CO} value of the analogous CO complex, $ML_n(CO)$. As demonstrated in this paper, k_{CO} values are very useful for correlating a large number of literature reports of the reactivity or nonreactivity of π -ethylene and π -benzene complexes with various nucleophiles.

Method

Approach. As noted above, carbonyl stretching force constants, k_{CO} , have been used as an indicator of the positive charge on a CO carbon and the reactivity of a CO ligand with nucleophiles (eq 3).⁶ MO calculations by Fenske and co-workers⁷ have established that k_{CO} can be correlated with the carbonyl lone pair orbital and π^* -antibonding orbital occupations in several metal-carbonyl complexes. Increasing the σ -donor strength of CO results in an increase in k_{CO} and a decrease in electron density at the carbonyl carbon. A decrease in metal-to-carbonyl back-bonding has a similar effect. If one considers the Dewar-Chart model for a π -ethylene bond to a transition metal, the factors that increase positive charge on carbon in CO should also increase positive charge on carbon in ethylene; that is, increased σ -donation from ethylene and decreased back-donation from the metal to the π^* -orbitals both decrease electron density at carbon, resulting in an increased positive charge. These parallels in bonding between CO and π -ethylene suggest that electronic changes in the ML_n group of $ML_n(C_2H_4)$ will be reflected in properties of the CO ligand in the analogous $ML_n(CO)$.

As noted in the introduction (eq 3), k_{CO} for the CO group in $ML_n(CO)$ has been used as a measure of the electron-withdrawing ability of the ML_n fragment. We assume that k_{CO} is also a measure of the electron-withdrawing ability of the ML_n group in the analogous $ML_n(C_2H_4)$ complex and also that k_{CO} is a measure of the susceptibility of the ethylene to nucleophilic attack. Similarly, the k_{CO} of the 3 CO groups in the complex $ML_n(CO)_3$ is a measure of the electron-withdrawing ability of the ML_n group in the analogous $ML_n(C_6H_6)$ π -benzene complex.

EHMO calculations carried out by Hoffmann and Eisenstein^{4a} indicate that ethylene activation is not necessarily due to positive charge buildup on the carbon atoms. Some complexes for which they calculate negative charges on the ethylene carbons nevertheless undergo nucleophilic addition. They propose that the olefin is activated by a slippage toward an η^1 -configuration with concomitant enhancement of the LUMO coefficient on the carbon farthest from the metal. However, they also conclude that the more positively charged η^2 -olefins were more activated in the slipped configuration; thus the use of k_{CO} as a gauge of the relative activation of ethylene could still be valid. However, it should be noted that the present approach cannot and makes no attempt to address the question of whether nucleophilic addition reactions are charge or frontier orbital controlled. We simply note that $\nu(CO)$ force constants are useful predictors of π -ethylene and π -benzene reactivity with nucleophiles.

In this paper, the k_{CO} for the CO group(s) replacing π -ethylene or π -benzene ligands is labeled k_{CO}^* . In the general case, k_{CO}^* is the average k_{CO} for the CO's replacing a π -hydrocarbon ligand maintaining the same formal electron count at the metal and occupying approximately the same coordination sites as the π -hydrocarbon. For ethylene complexes, k_{CO} and k_{CO}^* have the same value. For example, the k_{CO}^* value for $CpFe(CO)_2(C_2H_4)^+$ is equal to k_{CO} for the CO groups in $CpFe(CO)_3^+$. For benzene complexes, k_{CO}^* is an average of the three k_{CO} values. Thus, the k_{CO}^* value for $(C_6H_6)Mn(CO)_3^+$ ($C_6H_6 = \eta^6-C_6H_6$) is equal to the average k_{CO} of the 3 *fac* CO groups in $Mn(CO)_6^+$, which in

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(4) (a) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308. (b) Brown, D. A.; Chester, J. P.; Fitzpatrick, N. J. *Inorg. Chem.* **1982**, *21*, 2723. (c) Clack, D. W.; Kane-Maguire, L. A. P. *J. Organomet. Chem.* **1979**, *174*, 199. (d) Clack, D. W.; Monshi, M.; Kane-Maguire, L. A. P. *Ibid.* **1976**, *107*, C40. (e) Clack, D. W.; Monshi, M.; Kane-Maguire, L. A. P. *Ibid.* **1976**, *120*, C25. (f) Bäckvall, J. E.; Björkman, E. E.; Pettersson, L.; Seigbahn, P. *J. Am. Chem. Soc.* **1984**, *106*, 4369.

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(6) (a) Darensbourg, D. J.; Darensbourg, M. Y. *Inorg. Chem.* **1970**, *9*, 1691. (b) Angelici, R. J.; Blacic, L. J. *Ibid.* **1972**, *11*, 1754. (c) Angelici, R. J. *Acc. Chem. Res.* **1972**, *5*, 335. (d) Angelici, R. J.; Christian, P. A.; Dombeck, B. D.; Pfeffer, G. A. *J. Organomet. Chem.* **1974**, *67*, 287.

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this case are all equivalent. For complexes in which the CO groups are not equivalent, k_{CO}^* is the weighted average of the different k_{CO} values. An example of this situation is the complex *fac*- $\text{RuCl}_2(\text{PPh}_3)(\text{CO})_3$, which has two k_{CO} values, k_{CO}^1 (*trans*-C1) and k_{CO}^2 (*trans*-PPh₃). The k_{CO}^* value for this complex is equal to $(2k_{\text{CO}}^1 + k_{\text{CO}}^2)/3$.

Force Constants. Carbonyl stretching force constants were, wherever possible, either taken from the literature or calculated from literature IR data with use of approximate energy-factored force field methods, such as the Cotton-Kraihanzel (C-K) approximation.⁸ However, in many cases the IR spectrum of the desired carbonyl analogue was unavailable. For these situations, the method outlined by Timney⁹ was employed to estimate force constants. This procedure is based on C-K force constants and involves calculating k_{CO} for the CO ligand in a complex $\text{ML}_n(\text{CO})$ with use of individual ligand and metal contributions. The formula used for these calculations (eq 4) contains a parameter, k_d , that is dependent only on the number of valence d electrons of a

$$k_{\text{CO}} = k_d + \sum_L \epsilon_L^\theta + n\epsilon_c \quad (4)$$

transition metal in a particular row. The ligand effect constant, ϵ_L^θ , gives the contribution of a particular ligand in a given geometry. These constants are calculated from k_{CO} values in a series of complexes and are estimated to have standard deviations of up to ± 0.03 mdyn/Å. The factor $n\epsilon_c$ accounts for charge effects on k_{CO} (n = the net charge of the species, $\epsilon_c = 197 \pm 10$ N/m). The formula is used as shown for pseudooctahedral complexes and for other complexes with carbonyls and only one other type of ligand. Slight modifications are made for other situations.

An example of the use of this equation for *fac*- $\text{Ru}(\text{PMe}_3)_3(\text{CO})_3^{2+}$ is shown in eq 5. Thus, k_{CO} for this compound is equal to 1824 N/m, or 18.24 mdyn/Å. Timney has compiled a list of

$$\begin{aligned} k_{\text{CO}} &= k_d + 2\epsilon_{\text{CO}}^{\text{cis}} + 2\epsilon_{\text{PMe}_3}^{\text{cis}} + \epsilon_{\text{PMe}_3}^{\text{trans}} + 2\epsilon_c \\ &= 1389 + 2(33.5) + 2(-27.7) + 29.8 + 2(197) = \\ &1824 \text{ N/m} \end{aligned} \quad (5)$$

ligand effect constants for over 30 common ligands in different geometries. Others can be calculated by combining his formula with k_{CO} values calculated from IR data. Additional ϵ_L^θ values calculated for use in this study are $\epsilon_{\text{C}_6\text{H}_6} = 40$ N/m and $\epsilon_{\text{C}_5\text{Me}_5}^{\text{d}} = 86$ N/m.

Reaction Data. Information on reactions of π -coordinated hydrocarbon complexes was taken from the literature. In many cases, the adducts resulting from nucleophilic addition to the π -hydrocarbon were isolated and fully characterized. In others, the products were not isolable; then, reasonable spectral evidence for the formation of an adduct was considered sufficient. Some compounds are stated to undergo reactions other than addition to the π -hydrocarbon or they are reported to not react at all. This information is given in the Results and Discussion sections and listed in the tables.

Our treatment assumes the mechanism of these reactions is direct nucleophilic addition to the coordinated hydrocarbon, and kinetic studies^{1c} indicate that this is the preferred mechanism in the overwhelming majority of such reactions. However, in a few cases the situation may be more complicated than this. Two modes of nucleophilic addition to Pt(II) and Pd(II) olefin complexes have been observed, direct attack on the olefin to give overall *trans* addition and initial attack on the metal followed by insertion to give overall *cis* addition. Recent results^{2,10} indicate that the direct attack mechanism occurs in the reactions of amines with Pd(II) olefin and Pt(II) olefin complexes. MO calculations by Bäckvall et al.^{4f} suggest that insertion of ethylene into the metal-nucleophile bond may occur for nucleophiles with high energy HOMO's (such

as Me^-) but is highly unfavorable for N- and O-donor nucleophiles with lower lying HOMO's.

Results

Results of the investigation are summarized in Tables I and II for ethylene and benzene, respectively. The compounds are listed in order of decreasing k_{CO}^* . References to $\nu(\text{CO})$ data and reactions are also given in these tables. Nucleophiles which are reported to add to the arene or olefin are highlighted in bold type. Those nucleophiles given in regular type do not add to the hydrocarbon; either they react at another site in the complex, which is indicated by a superscript to a footnote, or they do not react at all, in which case there is no footnote superscript.

As will be discussed in greater detail in the next section, a given nucleophile adds to the ethylene (or benzene) ligand only when k_{CO}^* is above a certain value, which we call the threshold value. The threshold value (Table III) is defined as the highest k_{CO}^* corresponding to a complex that was reported *not* to react with a specific nucleophile. Threshold k_{CO}^* values are for cases where no reaction of any kind was reported; examples where side-reactions occurred were not taken as defining a threshold value because the side-reaction could simply be faster than attack at the unsaturated hydrocarbon. For some nucleophiles there are no reports of failed reactions. In these instances, the value corresponding to the lowest k_{CO}^* of a *reacting* complex is listed, in parentheses, in Table III. The following discussion of the tables makes use of force constants calculated from IR data wherever possible; those calculated by Timney's method will be denoted by a "T" superscript.

As noted in the tables, reactions of π -hydrocarbon complexes with nucleophiles may lead to products other than those resulting from nucleophilic addition to the π -hydrocarbon. Reduction, especially with carbon-centered nucleophiles, attack on other ligands, and displacement of the olefin or arene are the predominant side reactions. These processes are often accompanied by extensive decomposition of the starting material as well, and products resulting from these side reactions are in many cases observed concurrently with the desired nucleophilic addition product.

Fairly polar solvents such as MeOH, acetone, MeCN, and MeNO_2 are often used in these reactions. Recent calculations^{4b} for nucleophilic addition to $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ suggest that attack at the hydrocarbon is favored as the solvent polarity increases. Thus, the solvent may play a role in favoring or disfavoring reactions 1 and 2.

These reactions are nearly always performed at or below ambient temperature, with many in the range of -20 to 0°C . Kinetic studies of Sweigart and Kane-Maguire^{1c} show that, in general, activation energies are low (<40 KJ mol⁻¹) and entropies of activation are large and negative. Thus, elevated temperatures would not be very useful in promoting nucleophilic addition to the unsaturated hydrocarbon.

It should be noted that while the force constants calculated from IR data are accurate to approximately ± 0.04 mdyn/Å within the CK approximation, comparisons must be made with larger errors in mind. The spectral data used for the determination of force constants were obtained in several different solvents, and solvent shifts of IR bands could cause variations in k_{CO}^* of up to 0.1 mdyn/Å. Other factors, which are not taken into consideration in this treatment, could play some role. Temperature, concentrations, and solvents vary widely in the reactions that have been reported. Also, steric properties of the attacking nucleophiles and the ligands around the metal are not considered in this treatment. Therefore, the threshold k_{CO}^* values must be considered not as firm cutoffs but as approximate guidelines for predicting which π -ethylene or π -benzene complexes will react with specific nucleophiles and which will not.

Discussion

Nucleophilic Addition to π -Ethylene Complexes. Table I lists data pertaining to reactions (eq 1) involving nucleophilic addition to π -ethylene complexes. References to all literature results are given in the tables.

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(10) (a) Kurosawa, H.; Majima, T.; Asada, N. *J. Am. Chem. Soc.* **1980**, *102*, 6996. (b) Kurosawa, H.; Asada, N. *Tetrahedron Lett.* **1979**, 255. (c) Åkermark, B.; Bäckvall, J. E.; Siirala-Hansén, K.; Sjöberg, K.; Zetterberg, K. *Tetrahedron Lett.* **1974**, *15*, 1363.

Table I. Correlation of k_{CO}^* with Nucleophilic Addition to π -Ethylene Ligands^a

| compound [L _n M(C ₂ H ₄)] | $\nu_{CO}(cm^{-1})$ [L _n M(CO)] | k_{CO}^{*b} | k_{CO}^{*c} | PR ₃ | NR ₃ | carbanions | others | foot- notes |
|---|---|--------------------|---------------|--|--|---|--|----------------|
| (C ₂ H ₄)Ir(H)Cl(CO)(Ph ₃ P) ₂ ⁺ | | | 18.41 | | | | Re(CO) ₅ ⁻ | v |
| <i>trans</i> -(C ₂ H ₄)PtCl ₂ (py) | 2133 ^v | 18.39 | | | py | | | w-y |
| (C ₂ H ₄)Rh(PMe ₃) ₂ Cp ²⁺ | | | 18.26 | Me ₃ P, <i>i</i> -Pr ₃ P, (MeO) ₃ P | Et ₃ N | | SCN ⁻ | z |
| <i>trans</i> -(C ₂ H ₄)PtCl ₂ - (NH ₂ CH(Me)Ph) | 2126 ^k | 18.27 | | | Ph(Me)CHNH ₂ | | | v |
| <i>trans</i> -(C ₂ H ₄)PtCl ₂ (<i>n</i> -PrNH ₂) | 2125 ^k | 18.25 | | | <i>n</i> -PrNH ₂ | | | v |
| (C ₂ H ₄)Pd(Ph ₃ P)Cp ⁺ | 2113 ^l | 18.05 | | | Et ₂ NH, ^d py ^d | CH(COMe) ₂ ⁻ | OMe ⁻ , <i>i</i> -PrO ⁻ | aa |
| <i>cis</i> -(C ₂ H ₄)PtCl ₂ (Ph ₃ P) | 2108 ^m | 17.96 | | | Me ₂ NH, Et ₂ NH, <i>n</i> -Bu ₂ NH, NH ₃ | | | bb, cc |
| <i>cis</i> -(C ₂ H ₄)PtCl ₂ (<i>n</i> -Bu ₃ P) | 2101 ⁿ | 17.84 | | | Me ₂ NH, Et ₂ NH, <i>n</i> -Bu ₂ NH, NH ₃ | | | bb, cc |
| (C ₂ H ₄)Ru(PMe ₃) ₂ (C ₆ H ₆) ²⁺ | | | 17.72 | Me ₃ P, Ph ₃ P, <i>i</i> -Pr ₃ P, (PhO) ₃ P, (MeO) ₃ P | Et ₃ N | | | z |
| (C ₂ H ₄)Fe(CO) ₂ Cp ⁺ | 2125 ^o 2079 | 17.71 ^o | 17.58 | Ph ₃ P, <i>n</i> -Bu ₃ P, (EtO) ₃ P | Me ₂ NH, MeNH ₂ , Me ₃ N, py, NH ₃ , NH ₂ NH ₂ | MeLi ^f , PhLi, MeMgX, ^f PhMgCl, CH ₂ NO ₂ ⁻ , CH(CO ₂ Et) ₂ ⁻ , CMe(CO ₂ Et) ₂ ⁻ , Ph ₃ PCH(CO ₂ Et), Ph ₃ PCH ₂ , ^d various enamines | OMe ⁻ , <i>t</i> -BuS ⁻ , N ₃ ^{-f} , CpFe(CO)(Ph ₃ P)H[H ⁻], CN ⁻ , CpFe(CO) ₂ (σ -allyl) | dd-ii |
| (C ₂ H ₄)Ru(CO) ₂ Cp ⁺ | 2125 ^o 2075 | 17.62 | 17.60 | | NH ₃ | | | jj |
| (C ₂ H ₄)Ni(Me ₂ PhP)Cp ⁺ | 2086 ^l | 17.59 | | R ₃ P ^{d,e} | | | | l |
| (C ₂ H ₄)Rh(Me ₃ P)MeCp ⁺ | | | 17.28 | Me ₃ P | | | | z |
| (C ₂ H ₄)PtCl(acac) | 2066 ^g | 17.25 | | | <i>n</i> -PrNH ₂ , Et ₂ NH | | | x |
| (C ₂ H ₄)Fe(CO)(CNMe)Cp ⁺ | 2078 ^o 2038 | 17.10 ^o | 17.00 | Ph ₃ P ^d | py ^d | | | kk |
| (C ₂ H ₄)W(CO) ₃ Cp ⁺ | 2118 ^r 2034 2010 | 16.88 | | Ph ₃ P | Me ₂ NH, MeNH ₂ , py, Me ₃ N, NH ₃ | | Re(CO) ₅ ⁻ , CpW(CO) ₃ ⁻ | dd, ll |
| (C ₂ H ₄)Fe(PhO) ₃ P ₂ Cp ⁺ | | | 16.82 | Ph ₃ P | NH ₃ , NR ₃ ^e | | CN ⁻ | dd |
| (C ₂ H ₄)Ru(Me ₃ P)Me(η^6 -C ₆ H ₆) ⁺ | | | 16.7 | Me ₃ P | | | | z |
| (C ₂ H ₄)RuCl ₂ (PhMe ₂ P) ₂ (CO) | 2058 ^s 1994 | 16.60 | | PhMe ₂ P, ⁱ Ph ₂ MeP, ⁱ PhMe ₂ As, Ph(MeO) ₂ P | PhCH ₂ NH ₂ , 4-MePy, PhMe ₂ N | | OMe ⁻ , SMe ₂ , CN ^{-h} | mm |
| (C ₂ H ₄)Fe(CO)(Ph ₃ P)Cp ⁺ | 2055 ^o 2010 | 16.68 ^o | | | | Ph ₃ PCH ₂ | OP(OMe) ₂ ⁻ | nn |
| (C ₂ H ₄)Fe(CO) ₄ | 2023 ^t 2000 | 16.56 | | | | CH(CO ₂ Me) ₂ ⁻ | | oo |
| (C ₂ H ₄)W(CO) ₂ (Ph ₃ P)Cp ⁺ | | | | | | | Re(CO) ₅ ⁻ , CpW(CO) ₃ ⁻ | ll |
| (C ₂ H ₄)WMeCp ₂ ⁺ | 1960 ^u | 15.53 | | Me ₃ P, PhMe ₂ P | | | | pp |

^a Bold type denotes successful addition. ^b Calculated by the C-K method. ^c Calculated by Timney approximation. ^d Olefin displacement only. ^e Decomposition or reduction occurs. ^f Attack on other ligand observed. ^g R-group unspecified. ^h Uncharacterized products. ⁱ Final product has one halide displaced by a second molecule of phosphine. ^j Brause, A. R.; Rychek, M.; Orchin, M. *J. Am. Chem. Soc.* **1967**, *89*, 6500. ^k Ellis, R.; Weil, T. A.; Orchin, M. *Ibid.* **1970**, *92*, 1078. ^l Majima, T.; Kurosawa, H. *J. Organomet. Chem.* **1977**, *134*, C45. ^m Anderson, G. K.; Clark, H. C.; Davies, J. A. *Inorg. Chem.* **1981**, *20*, 1636. ⁿ Chatt, J.; Johnson, N. P.; Shaw, B. L. *J. Chem. Soc.* **1964**, 1662. ^o Johnson, B. V.; Ouseph, P. J.; Hsieh, J. S.; Steinmetz, A. L.; Shade, J. E. *Inorg. Chem.* **1979**, *18*, 1796. ^p Kruse, A. E.; Angelici, R. J. *J. Organomet. Chem.* **1970**, *24*, 231. ^q Hulley, G.; Johnson, B. F. G.; Lewis, J. J. *Chem. Soc. A* **1970**, 1732. ^r Jetz, W.; Angelici, R. J. *J. Am. Chem. Soc.* **1972**, *94*, 3799. ^s Barnard, C. F. J.; Daniels, J. A.; Jeffery, J.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1976**, 953. ^t Haas, H.; Sheline, R. K. *J. Chem. Phys.* **1967**, *47*, 2996. ^u Green, M. L. H.; Mahtab, R. J. *Chem. Soc., Dalton Trans.* **1979**, 262. ^v Olgemöller, B.; Beck, W. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 834. ^w Kaplan, P. D.; Schmidt, P.; Orchin, M. *J. Am. Chem. Soc.* **1968**, *90*, 4175. ^x Al-Najjar, I. M.; Green, M. J. *Chem. Soc., Dalton Trans.* **1979**, 1651. ^y Al-Najjar, I. M.; Green, M. J. *Chem. Soc., Chem. Commun.* **1977**, 926. ^z Werner, H.; Freser, R.; Werner, R. *J. Organomet. Chem.* **1979**, *181*, C7. ^{aa} See ref 10a. ^{bb} Panunzi, A.; DeRenzi, A.; Palumbo, R.; Paiaro, G. *J. Am. Chem. Soc.* **1969**, *91*, 3879. ^{cc} DeRenzi, A.; Paiaro, G.; Panunzi, A.; Paolillo, L. *Gazz. Chim. Ital.* **1972**, *102*, 281. ^{dd} Knoth, W. H. *Inorg. Chem.* **1975**, *14*, 1566. ^{ee} Rosan, A.; Rosenblum, M.; Tancrede, J. *J. Am. Chem. Soc.* **1973**, *95*, 3062. ^{ff} Lennon, P.; Rosan, A. M.; Rosenblum, M. *Ibid.* **1977**, *99*, 8426. ^{gg} Bodnar, T.; LaCroce, S. J.; Cutler, A. R. *Ibid.* **1980**, *102*, 3292. ^{hh} Busetto, L.; Palazzi, A.; Ros, R.; Belluco, U. *J. Organomet. Chem.* **1970**, *25*, 207. ⁱⁱ Lennon, P.; Madhavarao, M.; Rosan, A.; Rosenblum, M. *Ibid.* **1976**, *108*, 93. ^{jj} Behrens, H.; Jungbauer, A. Z. *Naturforsch. B* **1979**, *34b*, 1477. ^{kk} Johnson, B. V.; Steinmetz, A. L. *J. Organomet. Chem.* **1980**, *190*, 187. ^{ll} Olgemöller, B.; Beck, W. *Chem. Ber.* **1981**, *114*, 867. ^{mm} Stephenson, M.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1981**, 2112. ⁿⁿ Reger, D. L.; Culbertson, E. C. *J. Organomet. Chem.* **1977**, *131*, 297. ^{oo} Roberts, B. W.; Wong, J. J. *Chem. Soc., Chem. Commun.* **1977**, 20. ^{pp} Green, M. L. H. *Pure Appl. Chem.* **1978**, *50*, 27.

Table II. Correlation of k_{CO}^* with Nucleophilic Addition to π -Benzene Ligands^a

| compound [L _n M(C ₆ H ₆)] | $\nu_{CO}(cm^{-1})$ L _n M(CO) ₃ | $k_{CO}^*{}^b$ | $k_{CO}^*{}^c$ | PR ₃ | R-M ^d and R-MgX | stabilized carbanions | others | foot- notes |
|---|--|--------------------|----------------|--|---|---|---|------------------|
| (C ₆ H ₆)CoCp ²⁺ | | | 19.55 | Ph ₃ P ^e | NaCp, MeLi, ^f MeMgI ^g | LiCH ₂ CN, ^f LiCMe ₂ CN, ^f LiCMe(CO ₂ Et) ₂ ^f | OMe ^e , NaBH ₄ , ^f LiBEt ₃ H, ^f CN ⁻ , OH ⁻ | u |
| (C ₆ H ₆)CoCp ^{*2+} | | | 19.42 | <i>n</i> -Bu ₃ P | | | | v |
| (C ₆ H ₆)IrCp ^{*2+} | | | 19.36 | | MeLi | CH ₂ NO ₂ ⁻ | NaBH ₄ , OMe ^e NEt ₃ , py, ^h NHEt ₂ , Li[AlH(<i>t</i> -BuO) ₃], OMe ^e , CN ⁻ | w |
| (C ₆ H ₆)Rh(C ₃ Me ₄ Et) ₂ ²⁺ | | | 19.27 | <i>n</i> -Bu ₃ P, PhMe ₂ P, (MeO) ₃ P, ^f (EtO) ₃ P, ^f (PhO) ₃ P | | | | v |
| (C ₆ H ₆) ₂ Ru ²⁺ | | | 18.90 | Ph ₃ P, <i>n</i> -Bu ₃ P, (<i>n</i> -BuO) ₃ P | PhLi | | | x, y |
| (C ₆ H ₆) ₂ Fe ²⁺ | | | 18.88 | Ph ₃ P, <i>n</i> -Bu ₃ P, (<i>n</i> -BuO) ₃ P | | | NaBH ₄ | x, z, aa |
| (C ₆ H ₆) ₂ Os ²⁺ | | | 18.82 | Ph ₃ P, <i>n</i> -Bu ₃ P, (<i>n</i> -BuO) ₃ P | | | | x, z |
| (C ₆ H ₆)Mn(CO) ₃ ⁺ | 2101 ^o | 18.33 ^o | 18.44 | <i>n</i> -Bu ₃ P, Ph ₃ P, (EtO) ₃ P | MeLi, PhLi, MeMgCl, MeMgI | CH(CO ₂ Et) ₂ ⁻ | CN ⁻ , N ₃ ⁻ , OH ⁻ , OMe ^e , LiAlH ₄ , NaBH ₄ | bb-ee, rr |
| (C ₆ H ₆)Re(CO) ₃ ⁺ | 2085 ^o | 18.09 | 18.38 | <i>n</i> -Bu ₃ P | | | | z, ee |
| (C ₆ H ₆)Ru- (PMe ₃) ₂ CH ₂ CN ²⁺ ^κ | | | 18.12 | Me ₃ P | | | | ff |
| (C ₆ H ₆)Ru(PMe ₃)- (PPh ₃)Cl ⁺ ^κ | | | 17.71 | Me ₃ P, PhMe ₂ P | | | | ff |
| (C ₆ H ₆)Ru(PMe ₂ Ph)- (bipy) ²⁺ | | | 17.70 | R ₃ P ⁱ | | | NaBH ₄ , OH ⁻ , CN ⁻ | gg |
| (C ₆ H ₆)Co(η-C ₄ Ph ₄) ⁺ | | | 17.69 | | <i>n</i> -BuLi, MeMgBr | | NaBH ₄ , OMe ^e | hh |
| (C ₆ H ₆)Ru(PMe ₃) ₂ Cl ⁺ ^f | | | 17.67 | Me ₃ P | MeLi | | | ff, ii |
| (C ₆ H ₆)FeCp ⁺ | 2125 ^g 2079 | 17.71 ^g | 17.58 | | MeLi, PhLi, EtLi, PhCH ₂ MgCl, PhMgBr | | NaBH ₄ | y, jj, kk, ll |
| (C ₆ H ₆)RuCp ⁺ | 2125 ^g 2075 | 17.62 | 17.60 | R ₃ P, ⁱ (MeO) ₃ P | | | CN ⁻ , OH ⁻ | mm, nn |
| (C ₆ H ₆)Ru(PMe ₃) ₂ Cl/Br ⁺ ^κ | | | 17.67/17.59 | | PhLi | | | ii |
| (C ₆ H ₆)OsCp ⁺ | | | 17.52 | R ₃ P ⁱ | | | H ⁻ , CN ⁻ , OH ⁻ | mm |
| (C ₆ H ₆)Mn(CO) ₂ (PPh ₃) ⁺ | 2141.8 ^h 2063 2052.0 | 17.43 ^h | 17.76 | | | | CN ⁻ | cc |
| (C ₆ H ₆)Os(PMe ₃) ₂ 1 ⁺ | | | 17.38 | | MeLi, PhLi, EtLi, <i>n</i> -BuLi, <i>t</i> -BuLi, <i>n</i> -PrLi | | | ii |
| (C ₆ H ₆)Ru(PPh ₃)Cl ₂ | | | 17.13 | | MeLi ⁱ | | | oo |
| (C ₆ H ₆)Ru(PEt ₃)Cl ₂ | | | 17.04 | Ph ₃ P, <i>n</i> -Bu ₃ P, Et ₃ P, Ph ₂ MeP, PhMe ₂ P, (MeO) ₃ P, (PhO) ₃ P, PhAs | RLi, ⁱ RMgX ⁱ | | | pp |
| (C ₆ H ₆)Cr(CO) ₃ | 1985 ⁱ | 16.49 ⁱ | 16.47 | | <i>t</i> -BuLi, <i>p</i> -tollLi, <i>n</i> -BuLi, ^m <i>t</i> -BuMgCl | LiCHSCH ₂ CH ₂ CH ₂ S, LiCH ₂ CN, LiCH(SPh) ₂ , LiCH ₂ COCMe ₃ , KCH ₂ COCMe ₃ ⁿ | | |

^a Bold type denotes successful addition. ^b Calculated by the C-K method. ^c Estimated by Timney approximation. ^d R = alkyl or aryl, M = alkali metal. ^e Decomposition or reduction occurs. ^f Product is that resulting from Michaelis-Arbusov rearrangement of attacking phosphite. ^g Starting material is [(C₆H₆)Ru(CH₃CN)₃]²⁺, assume [(C₆H₆)Ru(PMe₃)₂(CH₃CN)]²⁺ to be the reactive species for ring attack based on author's observations. ^h Starting material is either (C₆H₆)Ru(PPh₃)Cl₂ or [(C₆H₆)Ru(PPh₃)₂Cl]⁺, but [(C₆H₆)Ru(PPh₃)(PMe₃)Cl]⁺ is believed to be the reactive species. ⁱ R-group unspecified. ^j Final product has also undergone chloride substitution by a second molecule of nucleophile after attack on benzene. ^k Starting complex is [(C₆H₆)Ru(PMe₃)₂Cl]⁺. PhLi solution contained LiBr and product isolated was [(C₆H₆)Ru(PMe₃)₂Br]. Authors did not comment on reaction sequence. ^l Displacement of chloride occurs. ^m Lithiation of benzene occurs. ⁿ Reaction carried out in 1:5 THF/HMPA, compare result to LiCH₂COCMe₃ reaction run in THF alone. ^o Sarapu, A. C.; Fenske, R. F. *Inorg. Chem.* **1975**, *14*, 247. ^p Abel, E. W.; McLean, R. A. N.; Tyfield, S. P.; Braterman, P. S.; Walker, A. P.; Hendra, P. J. *J. Mol. Spectrosc.* **1969**, *30*, 29. ^q See footnote m, Table 1. ^r See footnote n, Table 1. ^s Drew, D.; Darendbourg, D. J.; Darendbourg, M. Y. *Inorg. Chem.* **1975**, *14*, 1579. ^t See ref 8. ^u Lai, Y.-H.; Tam, W.; Vollhardt, K. P. C. *J. Organomet. Chem.* **1981**, *216*, 97. ^v Bailey, N. A.; Blunt, E. H.; Fairhurst, G.; White, C. *J. Chem. Soc., Dalton Trans.* **1980**, 829. ^w Grundy, S. L.; Smith, A. J.; Adams, H.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1984**, 1747. ^x See ref 5. ^y Jones, D.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 4458. ^z Chung, Y. K.; Honig, E. D.; Sweigart, D. A. *J. Organomet. Chem.* **1983**, 256, 277. ^{aa} Madonik, A. M.; Mandon, D.; Michaud, P.; Lapinte, C.; Astruc, D. *J. Am. Chem. Soc.* **1984**, *106*, 3381. ^{ab} Mawby, A.; Walker, P. J. C.; Mawby, R. J. *J. Organomet. Chem.* **1973**, *55*, C39. ^{ac} Walker, P. J. C.; Mawby, R. J. *Inorg. Chim. Acta* **1973**, *7*, 621. ^{ad} Evans, D. J.; Kane-Maguire, L. A. P.; Sweigart, D. A. *J. Organomet. Chem.* **1981**, *215*, C27. ^{ae} Kane-Maguire, L. A. P.; Sweigart, D. A. *Inorg. Chem.* **1979**, *18*, 700. ^{af} Werner, H.; Werner, R. *Chem. Ber.* **1984**, *117*, 142. ^{ag} Robertson, D. R.; Robertson, I. W.; Stephenson, T. A. *J. Organomet. Chem.* **1980**, *202*, 309. ^{ah} Efraty, A.; Maitlis, P. M. *J. Am. Chem. Soc.* **1967**, *89*, 3744. ^{ai} Werner, H.; Werner, R. *Chem. Ber.* **1984**, *117*, 152. ^{aj} Nesmeyanov, A. N.; Vol'kenau, N. A.; Shilovtseva, L. S.; Petrovka, V. A. *Bull. Acad. Sci. USSR, Chem. Sci.* **1975**, *24*, 1057. ^{ak} Michaud, P.; Astruc, D.; Ammeter, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 3755. ^{al} Khand, I. U.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc. C* **1969**, 2024. ^{am} Robertson, I. W.; Stephenson, T. A.; Tocher, D. A. *J. Organomet. Chem.* **1982**, *228*, 171. ^{an} Gill, T. P.; Mann, K. R. *Organometallics* **1982**, *1*, 485. ^{ao} Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233. ^{ap} Zelonka, R. A.; Baird, M. C. *Can. J. Chem.* **1972**, *50*, 3063. ^{aq} See ref 3a,d. ^{ar} Chung, Y. K.; Williard, P. G.; Sweigart, D. A. *Organometallics* **1982**, *1*, 1053. ^{as} Displacement of C₆H₆.

Table III. Threshold k_{CO}^* values for Nucleophilic Addition to π -Ethylene and π -Benzene Ligands

| nucleophile | k_{CO}^* thresholds ^a | |
|------------------------------------|------------------------------------|----------------|
| | π -ethylene | π -Benzene |
| PPh ₃ | 16.8 | 18.3 |
| P(OR) ₃ ^b | | 18.3 |
| NR ₃ | 16.8 | |
| CH(COR) ₂ ^{-c} | (16.6) | (18.3) |
| PR ₃ ^b | (15.5) | 17.7 |
| RMgX | | 17.7 |
| CN ⁻ | | 17.5 |
| RLi | | (16.5) |
| CH ₂ X ^{-d} | | (16.5) |

^a Defined as the highest value for which addition was not observed. Values in parentheses refer to the lowest k_{CO}^* at which addition was observed when no examples of no-reaction were reported. ^b R = alkyl. ^c R = alkyl, alkoxy. ^d X = NO₂, CN.

(a) Phosphine Nucleophiles. When PPh₃ is the attacking nucleophile, addition to ethylene has been observed for the following complexes: (C₆H₆)Ru(PMe₃)₂(C₂H₄)²⁺ (C₆H₆ = η -C₆H₆) with k_{CO}^* = 17.72^T, CpFe(CO)₂(C₂H₄)⁺ (17.71), CpW(CO)₃(C₂H₄)⁺ (16.88), and CpMo(CO)₃(C₂H₄)⁺. The reaction does not occur for CpFe[P(OPh)₃]₂(C₂H₄)⁺ (16.82^T). Since we find no reports of successful addition below this value of k_{CO}^* , the threshold value for PPh₃ attack on π -ethylene is 16.8.

There are some examples (Table I) in which ethylene is displaced by PPh₃, even though addition might be expected on the basis of the k_{CO}^* value. In these cases, ethylene displacement is presumably faster than nucleophilic addition to the olefin. The present method cannot predict when displacement is faster than addition; it only indicates when addition is a possible pathway. One example of ethylene displacement is the reaction of CpFe(CO)(CNMe)(C₂H₄)⁺ with PPh₃ in refluxing acetone. The k_{CO}^* value for this complex is 17.10, certainly large enough to expect addition based on the threshold value of 16.8. Many of the tetracoordinate Pt complexes with k_{CO}^* values above 16.8 also undergo displacement of ethylene by phosphines. For square-planar Pt(II) and Pd(II) complexes, nucleophilic attack at the metal might be expected to be especially favorable, leading to ethylene-displaced products. It is possible that in some cases addition to the olefin occurs at low temperature, but at higher temperatures only olefin-substituted products are observed. This has been reported for the reaction of CpRu(PMe₃)₂(C₂H₄)²⁺ and SCN⁻, in which an olefin adduct is formed at 25 °C, but warming of the solution results in loss of ethylene. NMR evidence suggests the same behavior for attack by I⁻ as well. Nevertheless, olefin substitution is the end result and is a possible side reaction in all complexes, even when the olefin is susceptible to attack as indicated by its k_{CO}^* value.

The more nucleophilic trialkylphosphines¹¹ also add to several olefin complexes. CpRh(PMe₃)₂(C₂H₄)²⁺ (k_{CO}^* = 18.26^T) and (C₆H₆)Ru(PMe₃)₂(C₂H₄)²⁺ (17.72^T) undergo addition with PMe₃ and P(*i*-Pr)₃; CpFe(CO)₂(C₂H₄)⁺ (17.71) adds P(*n*-Bu)₃; and PMe₃ reacts with CpRh(PMe₃)Me(C₂H₄)⁺ (17.28^T), (C₆H₆)Ru(PMe₃)Me(C₂H₄)⁺ (16.7^T), and Cp₂W(Me)(C₂H₄)⁺ (15.53). The mixed alkyl-aryl phosphine PMe₂Ph is also quite reactive, successfully adding to ethylene in RuCl₂(PMe₂Ph)₂(CO)(C₂H₄) (16.60) and in Cp₂W(Me)(C₂H₄)⁺ (15.53). Since there are no reports of no-reaction with these phosphines, it is not possible to estimate a k_{CO}^* threshold value. Nevertheless, the observed reactivity indicates that the k_{CO}^* threshold is below 15.53.

(b) Amine Nucleophiles. Quite a number of complexes in Table I react with amine nucleophiles. Reactions of aliphatic amines include Et₃N addition to CpRh(PMe₃)₂(C₂H₄)²⁺ (k_{CO}^* = 18.26^T), Ph(Me)CHNH₂ reaction with *trans*-PtCl₂(Ph(Me)-CHNH₂)(C₂H₄) (18.27), *n*-PrNH₂ with *trans*-PtCl₂(*n*-PrNH₂)(C₂H₄) (18.25), and dimethyl-, diethyl-, and dibutylamines with both *cis*-PtCl₂(PPh₃)(C₂H₄) (17.96) and *cis*-PtCl₂(*n*-Bu₃P)(C₂H₄) (17.84). Also, CpFe(CO)₂(C₂H₄)⁺ (17.71) reacts

with Me₃N, Me₂NH, and MeNH₂; Pt(acac)Cl(C₂H₄) (17.25) adds *n*-PrNH₂ and Et₃NH; and CpW(CO)₃(C₂H₄)⁺ (16.88) reacts with tri-, di-, and monomethylamine. Amines do not add to ethylene in CpFe[P(OPh)₃]₂(C₂H₄)⁺ (16.82^T), and benzylamine and *N,N*-dimethylaniline fail to add to RuCl₂(PMe₂Ph)₂(CO)(C₂H₄) (16.60); thus, the k_{CO}^* threshold value for alkylamine reactions is roughly the same as in the PPh₃ reactions, i.e., approximately 16.8. One apparent exception to this threshold value is the failure of (C₆H₆)Ru(PMe₃)₂(C₂H₄)²⁺ (17.72^T) to react with Et₃N. This is the only example in this paper where k_{CO}^* does not correctly predict the reaction or non-reaction of a system. While the bulkiness of Et₃N may account for its lower reactivity, it is remarkable that steric effects need not be considered in any other system, including those involving the sterically dissimilar primary, secondary, and tertiary amines.

Pyridine adds to ethylene in *trans*-PtCl₂(py)(C₂H₄) (18.39), CpFe(CO)₂(C₂H₄)⁺ (17.71), and CpW(CO)₃(C₂H₄)⁺ (16.88) but coordinates to Pt in PtCl(acac)(C₂H₄) to give a five-coordinate complex.¹² The more basic 4-methylpyridine fails to react with RuCl₂(PMe₂Ph)₂(CO)(C₂H₄) (16.60); thus, pyridine and 4-methylpyridine appear to be similar in reactivity to the aliphatic amines (k_{CO}^* threshold = 16.8).

(c) Other Nucleophiles. Most of the other nucleophiles in Table I have not been studied sufficiently to allow an estimate of threshold k_{CO}^* values. Reactions of carbon-centered nucleophiles have been carried out primarily on CpFe(CO)₂(C₂H₄)⁺ (17.71). Although reduction and displacement of the olefin complicate these reactions, Grignard reagents, ester enolates, phosphorus ylides, enamines have all been successfully added to ethylene in this complex. Reactions of ketone and ester enolates show that a threshold value of k_{CO}^* will be relatively low for these nucleophiles, probably below 16.6.

Addition of CH(COMe)₂⁻ occurs for CpPd(PPh₃)(C₂H₄)⁺ (18.05), CH(CO₂Et)₂⁻ and CMe(CO₂Et)₂⁻ add to ethylene in CpFe(CO)₂(C₂H₄)⁺ (17.71), and even the neutral Fe(CO)₄(C₂H₄) complex (16.56) reacts with CH(CO₂Me)₂⁻. Unsuccessful attempts at addition have not been reported for these enolates.

Alkoxide and cyanide reactions have also been investigated for a few different complexes. Methoxide and isopropoxide ions attack ethylene in CpPd(PPh₃)(C₂H₄)⁺ (18.05), and cyanide and methoxide ions react with CpFe(CO)₂(C₂H₄)⁺ (17.71). Cyanide ion also reacts with CpFe[P(OPh)₃]₂(C₂H₄)⁺ (16.82^T). Reaction of OMe⁻ and RuCl₂(PMe₂Ph)₂(CO)(C₂H₄) (16.60) fails, and the product of the CN⁻ reaction with this complex was not characterized. On the basis of these observations, the threshold k_{CO}^* for OMe⁻ is about 16.60, but the CN⁻ value is not as well defined.

Another class of nucleophiles capable of adding to ethylene is the metal carbonyl anions. CpW(CO)₃⁻ and Re(CO)₅⁻ form olefin adducts with CpW(CO)₃(C₂H₄)⁺ (16.88) as well as the mono-phosphine-substituted complex CpW(CO)₂(PPh₃)(C₂H₄)⁺. Instances of no-reaction have not been reported.

In comparing various nucleophiles, one observes that many exhibit threshold k_{CO}^* values in the range of 16.6–16.8; these include PPh₃, various alkyl amines, pyridine, and methoxide ion. Carbon-centered nucleophiles and trialkylphosphines, for which reactions have been observed with complexes with k_{CO}^* values of 16.56 and 15.53, respectively, are more reactive.

Nucleophilic Addition to π -Benzene Complexes. Nucleophilic attack on a π -benzene ligand gives an η^5 -6-exo-substituted cyclohexadienyl complex, as shown in eq 2. Several studies^{1c} have established that the product of kinetically controlled attack is the exo adduct. The reactions being considered in this section are summarized in Table II.

(a) Phosphine Nucleophiles. The reaction of PPh₃ with (C₆H₆)₂Fe²⁺ (k_{CO}^* = 18.88^T) results in the formation of a cyclohexadienylphosphonium complex. The reaction also occurs for the ruthenium and osmium analogues (18.90^T and 18.82^T, respectively). PPh₃ does not add to (C₆H₆)Mn(CO)₃⁺ (18.33) or (C₆H₆)Ru(PEt₃)Cl₂ (17.04^T). Although kinetic studies^{1c} show that PPh₃ is more reactive than alkyl phosphites, there are not

(11) Tolman, C. A. *Chem. Rev.* 1977, 77, 313.

(12) See footnote x, Table I.

sufficient data in the literature to distinguish these nucleophiles by the k_{CO}^* approach. The phosphites, $\text{P}(\text{OMe})_3$ and $\text{P}(\text{OEt})_3$, add to $(\text{C}_5\text{Me}_4\text{Et})\text{Rh}(\text{C}_6\text{H}_6)^{2+}$ (19.27^T), and $\text{P}(\text{OBu})_3$ adds to the $(\text{C}_6\text{H}_6)_2\text{M}^{2+}$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) complexes. $\text{P}(\text{OEt})_3$ fails to react with $(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_3^+$ (18.33), and reaction also fails for $\text{P}(\text{OMe})_3$ with $(\text{C}_6\text{H}_6)\text{RuCp}^+$ (17.62) and $(\text{C}_6\text{H}_6)\text{Ru}(\text{PEt}_3)\text{Cl}_2$ (17.04^T). The threshold k_{CO}^* for the $\text{P}(\text{OR})_3$ and PPh_3 nucleophiles is thus approximately 18.3. Although the benzene ligand in $\text{CpCo}(\text{C}_6\text{H}_6)^{2+}$ (19.55^T) would be expected to add PPh_3 , this reaction gives decomposition products and free benzene presumably by initial displacement of the arene by PPh_3 . The analogous $(\text{C}_5\text{Me}_4\text{Et})\text{Rh}(\text{C}_6\text{H}_6)^{2+}$ (19.27^T) reportedly does not react with PPh_3 ; however, this is likely in error since we have observed that displacement of benzene by PPh_3 in the very similar $\text{Cp}^*\text{Rh}(\text{C}_6\text{H}_6)^{2+}$ complex ($\text{Cp}^* = \text{C}_5\text{Me}_5$) is essentially complete in 50 min at room temperature.

Tri-*n*-butylphosphine adds to $\text{Cp}^*\text{Co}(\text{C}_6\text{H}_6)^{2+}$ (19.42^T), $(\text{C}_6\text{H}_6)\text{Rh}(\text{C}_5\text{Me}_4\text{Et})^{2+}$, and $(\text{C}_6\text{H}_6)_2\text{M}^{2+}$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$, with k_{CO}^* values of 18.88^T, 18.90^T, and 18.82^T, respectively) and to $(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_3^+$ (18.33) and $(\text{C}_6\text{H}_6)\text{Re}(\text{CO})_3^+$ (18.09). Dimethylphenylphosphine reacts with $(\text{C}_5\text{Me}_4\text{Et})\text{Rh}(\text{C}_6\text{H}_6)^{2+}$ and $(\text{C}_6\text{H}_6)\text{Ru}(\text{PPh}_3)(\text{PMe}_3)\text{Cl}^+$ (17.71^T); likewise, PMe_3 reacts with $(\text{C}_6\text{H}_6)\text{Ru}(\text{PMe}_3)_2(\text{CH}_3\text{CN})^{2+}$ (18.12^T), $(\text{C}_6\text{H}_6)\text{Ru}(\text{PPh}_3)(\text{PMe}_3)\text{Cl}^+$, and $(\text{C}_6\text{H}_6)\text{Ru}(\text{PMe}_3)_2\text{Cl}^+$ (17.67^T). Trialkylphosphines do not add to benzene in $(\text{C}_6\text{H}_6)\text{Ru}(\text{PMe}_2\text{Ph})(\text{bpy})^{2+}$ (17.70^T), $\text{CpRu}(\text{C}_6\text{H}_6)^+$ (17.62), and $\text{CpOs}(\text{C}_6\text{H}_6)^+$ (17.52^T). Though the nonreacting complex $(\text{C}_6\text{H}_6)\text{Ru}(\text{PMe}_2\text{Ph})(\text{bpy})^{2+}$ has a k_{CO}^* value slightly greater than that of the reacting $(\text{C}_6\text{H}_6)\text{Ru}(\text{PMe}_3)_2\text{Cl}^+$ species, the magnitude of the difference is well within the error margins of the correlation method. Thus, the threshold value for addition of trialkylphosphines and PMe_2Ph is in the area of 17.7.

(b) Carbanion Nucleophiles. Alkyl- and aryllithium reagents add to the arene in a variety of π -benzene complexes. $(\text{C}_6\text{H}_6)_2\text{Ru}^{2+}$ (18.90^T) reacts with PhLi , $(\text{C}_6\text{H}_6)\text{Co}(\text{C}_4\text{Ph}_4)^+$ (17.69^T) with *n*-BuLi, and $\text{CpFe}(\text{C}_6\text{H}_6)^+$ (17.71) with Me-, Et-, and PhLi. $(\text{C}_6\text{H}_6)\text{Ru}(\text{PMe}_3)_2\text{Br}^+$ (17.59^T) is attacked by PhLi, $(\text{C}_6\text{H}_6)\text{Os}(\text{PMe}_3)_2\text{I}^+$ (17.38^T) by Ph-, *t*-Bu-, *n*-Bu-, *n*-Pr-, Et-, and MeLi, and the neutral $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ complex (16.49) by *p*-tolyl- and *t*-BuLi. One complex that does not follow this trend is $(\text{C}_6\text{H}_6)\text{Ru}(\text{PEt}_3)\text{Cl}_2$ (17.04^T), which was reported not to react with alkyllithium reagents, but this report may not be correct since the PPh_3 complex $(\text{C}_6\text{H}_6)\text{Ru}(\text{PPh}_3)\text{Cl}_2$ (17.48^T) has been shown to undergo displacement of chloride by MeLi. Since no cases of failed reactions have been reported below a k_{CO}^* value of 16.49, the threshold for these very reactive nucleophiles can be assumed to be below this value.

There are few examples of Grignard reagent reactions with π -benzene complexes. The Grignard reagents MeMgX attack benzene in $(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_3^+$ (18.33), and PhCH_2MgCl adds to $\text{CpFe}(\text{C}_6\text{H}_6)^+$ (17.71), but MeMgBr fails to react with $(\text{C}_6\text{H}_6)\text{Co}(\text{C}_4\text{Ph}_4)^+$ (17.69^T). Reaction also fails for *t*-BuMgCl with $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ (16.49); so, for Grignard reagents the k_{CO}^* threshold can be estimated at 17.7. Though $\text{CpCo}(\text{C}_6\text{H}_6)^{2+}$ has a k_{CO}^* value of 19.55^T, reaction with MeMgI results only in decomposition of the complex.

The stabilized carbanion, CH_2NO_2^- , adds to the arene in $\text{Cp}^*\text{Ir}(\text{C}_6\text{H}_6)^{2+}$ (19.36^T), $\text{CH}(\text{CO}_2\text{Et})_2^-$ reacts with $(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_3^+$ (18.33), and $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ (16.49) undergoes attack at benzene by several different reagents, including LiCH_2CN , $\text{LiCH}(\text{SPh})_2$, and $\text{KCH}_2\text{COCMe}_3$. As in the case of alkyl- and aryllithium reagents, a threshold value is not well defined for these nucleophiles but should be lower than 16.49.

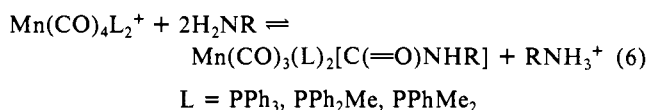
(c) Other Nucleophiles. A number of other common nucleophiles have been successfully added to benzene in transition-metal complexes. Methoxide ion reacts to give 6-*exo*-methoxycyclohexadienyl derivatives with $\text{Cp}^*\text{Ir}(\text{C}_6\text{H}_6)^{2+}$ (19.36^T), $(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_3^+$ (18.33), and gives double addition with $\text{CpCo}(\text{C}_6\text{H}_6)^{2+}$ (19.55^T). There is no reaction with $(\text{C}_6\text{H}_6)\text{Co}(\text{C}_4\text{Ph}_4)^+$ (17.69^T); so, the k_{CO}^* threshold for MeO^- is approximately 17.7.

Cyanide and hydroxide add to $(\text{C}_6\text{H}_6)\text{Mn}(\text{CO})_3^+$ and to $(\text{C}_6\text{H}_6)\text{Ru}(\text{PMe}_2\text{Ph})(\text{bpy})^{2+}$ (17.74^T), but neither reacts with

$\text{CpOs}(\text{C}_6\text{H}_6)^+$ (17.52^T). The threshold value would seem to be 17.52; however, CN^- adds to benzene in $(\text{C}_6\text{H}_6)\text{Mn}(\text{PPh}_3)(\text{CO})_2^+$ (17.43). But in this latter case, there is considerable disagreement between the Timney and IR data force constants with the Timney value equal to 17.76. Uncharacterized products were obtained from the reactions of $\text{CpCo}(\text{C}_6\text{H}_6)^{2+}$ (19.55^T) and $\text{CpRu}(\text{C}_6\text{H}_6)^+$ (17.52) with both CN^- and OH^- .

Comparison of Threshold k_{CO}^* Values for Different Nucleophiles. Because there are insufficient data to establish threshold k_{CO}^* values for many nucleophiles, one can only draw tentative conclusions from the values in Table III. For nucleophilic addition to the π -benzene ligand, the carbanions (RLi , CH_2NO_2^- , and CH_2CN^-) are the most reactive with threshold k_{CO}^* values below 16.5. Next comes a group of nucleophiles ($\text{P}(\text{alkyl})_3$, OMe^- , RMgX , and CN^-) with threshold k_{CO}^* values in the approximate range 17.5–17.7. And finally, the least reactive nucleophiles (PPh_3 and $\text{P}(\text{OR})_3$) have threshold k_{CO}^* values of approximately 18.3. For additions to the π -ethylene ligand there are fewer results available, but $\text{P}(\text{alkyl})_3$ has a lower threshold (<15.5) than PPh_3 , NR_3 , and OMe^- which all fall in the range 16.6–16.8.

Kinetic or Thermodynamic Control of Nucleophilic Addition. Although k_{CO}^* values are useful guidelines for predicting whether or not π -ethylene and π -benzene ligands are susceptible to nucleophilic attack, there is the question of whether this reactivity is determined by kinetic or thermodynamic factors. Studies^{6a} of organolithium addition to CO ligands (eq 3) were discussed in terms of the importance of kinetic factors, but thermodynamic factors were not specifically excluded. In a study¹³ of amine attack on CO ligands (second order in amine), both the rate and equilibrium constants were affected by the electronic (i.e., k_{CO}) and steric properties of L (eq 6).



There are a few studies of reactions 1 and 2 which have some bearing on the question of whether k_{CO}^* is related to equilibrium or rate. Equilibrium studies of amine attack on several Pt(II) ethylene complexes do not show a direct relationship between k_{CO}^* and K_{eq} . For example, at 25 °C *n*-PrNH₂ adds to *trans*-PtCl₂(*n*-PrNH₂)₂(C₂H₄) (18.25) with $K_{\text{eq}} = 20$, yet its reaction with PtCl(acac)(C₂H₄) (17.25) has $K_{\text{eq}} \sim 73$.

Kinetic studies of the reaction of PPh_3 with $(\text{C}_6\text{H}_6)_2\text{M}^{2+}$ complexes of Fe, Ru, and Os show that the Fe complex is more reactive than either the Ru or Os analogue,⁵ although their k_{CO}^* values are very similar. The second-order rate constants at 20 °C are $3.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for $(\text{C}_6\text{H}_6)_2\text{Fe}^{2+}$ (18.88^T), 8400 for $(\text{C}_6\text{H}_6)_2\text{Ru}^{2+}$ (18.90^T), and 1500 for $(\text{C}_6\text{H}_6)_2\text{Os}^{2+}$ (18.82^T). The equilibrium constants parallel this trend, with values of 139, 2.0, and 1.1 for Fe, Ru, and Os, respectively, since the reverse rate constants are comparable for all three reactions. Neither the rate nor the equilibrium constants are reflected in the k_{CO}^* values. The problem could be in the estimation of k_{CO}^* using the Timney method, but the method seems to work well for many other Ru(II) complexes of the type $\text{RuX}_2\text{L}(\text{CO})_3$, and comparison of analogous Fe and Ru complexes does not reveal a large difference in CO stretching frequencies. A possible, but incomplete, explanation is that the well-known unusually strong back-bonding abilities of Ru(II) and Os(II) are not, for some reason, reflected in the $\nu(\text{CO})$ values. It appears k_{CO}^* values are not able to predict trends in reactivity where k_{CO}^* differences are small, as in this series of complexes.

The k_{CO}^* parameters are available from IR data for the complexes $(\text{C}_6\text{H}_6)\text{M}(\text{CO})_3^+$ ($\text{M} = \text{Mn}, \text{Re}$), and the kinetics of their reactions with $\text{P}(\textit{n}\text{-Bu})_3$ have also been studied.¹⁴ The second-order rate constant for the Mn complex (18.33) is $2000 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C in nitromethane and 1800 for $(\text{C}_6\text{H}_6)\text{Re}(\text{CO})_3^+$ (18.09) under the same conditions. The equilibrium constants are 400

(13) Angelici, R. J.; Brink, R. W. *Inorg. Chem.* 1973, 12, 1067.

(14) See footnote ee, Table II.

for $(C_6H_6)Mn(CO)_3^+$ and 450 for $(C_6H_6)Re(CO)_3^+$. Thus, the k_{CO}^* values predict the relative rate order, but not the K_{eq} order, though the differences in both the rate and equilibrium constants may be too small to yield a substantial conclusion. The $(C_6H_6)_2M^{2+}$ complexes ($M = Fe, Ru, Os$), which all have higher k_{CO}^* s than the Mn and Re compounds, react rapidly to give quantitative yields of the $P(n-Bu)_3$ adducts, and neither $(C_6H_6)Mn(CO)_3^+$ nor $(C_6H_6)Re(CO)_3^+$ forms an adduct with PPh_3 . Therefore, while k_{CO}^* apparently reflects large qualitative differences in reactivity, it appears not to be sensitive to small differences in closely related compounds.

On the basis of the above studies, one must conclude that it is not clear whether k_{CO}^* is related to kinetic or thermodynamic factors and that k_{CO}^* is useful primarily for predictions when fairly large differences in reactivity are involved.

Conclusions

Results of this paper show that k_{CO}^* is a very useful parameter for predicting the susceptibility of π -ethylene or π -benzene ligands

to nucleophilic addition. The k_{CO}^* values of the π -ethylene or π -benzene complexes may be calculated from experimental $\nu(CO)$ values of the analogous metal carbonyl complexes or by Timney's method⁹ using known, additive parameters. This latter method is a particularly useful and simple way to obtain k_{CO}^* values. Threshold k_{CO}^* values establish approximate lower limits for reaction of π -ethylene and π -benzene ligands with different nucleophiles; these threshold values should be of particular value in designing syntheses where nucleophilic addition to the π -ligands is involved. The usefulness of k_{CO}^* values for predicting nucleophilic addition to CO^6 and the π -hydrocarbon ligands reported herein suggests that k_{CO}^* may be helpful for predicting reactions of other ligands and correlating properties of complexes which depend upon the electron density on the metal.

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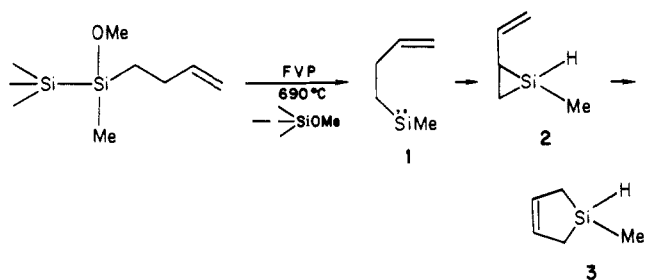
Silylene-to-Silanone Thermal Isomerization

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Abstract: Thermal generation of (allyloxy)methylsilylene, C_3H_5OSiMe , by flash vacuum pyrolysis of 1,1-bis(allyloxy)-tetramethyldisilane unexpectedly produced products strongly suggestive of the intermediacy of allylmethylsilanone, $C_3H_5MeSi=O$. Alternative routes were probed through the pyrolysis of model systems, and the silanone was apparently trapped with $Me_2Si(OMe)_2$. It is proposed that this silanone arises from isomerization of the initially formed silylene via a [2,3] sigmatropic allyl migration, although a stepwise process proceeding through the intermediacy of an oxasilabicyclo[2.1.0]pentane ring cannot be ruled out. Thermal generation of (allyloxy)(trimethylsilyl)silylene, $C_3H_5OSiSiMe_3$, initiated an apparent silylene \rightarrow silanone \rightarrow silylene rearrangement sequence culminating in the formation of a silacyclobutene. Here consideration of an oxasilabicyclo[2.1.0]pentane intermediate reveals the possibility that the reaction actually involves a silylene-to-silylene rearrangement without silanone intermediacy.

Recently we reported that butenylmethylsilylene (**1**), generated by flash vacuum pyrolysis (FVP), isomerized to silacyclopentene (**3**) and have suggested that this isomerization proceeds through the intermediacy of vinylsilane (**2**) followed by a 1,3-migration of silicon.¹

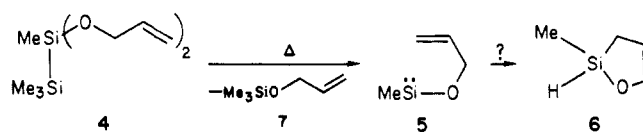


We now report an attempt to extend this reaction to the synthesis of a dihydrosilafuran and the unexpected chemistry to which this approach led.

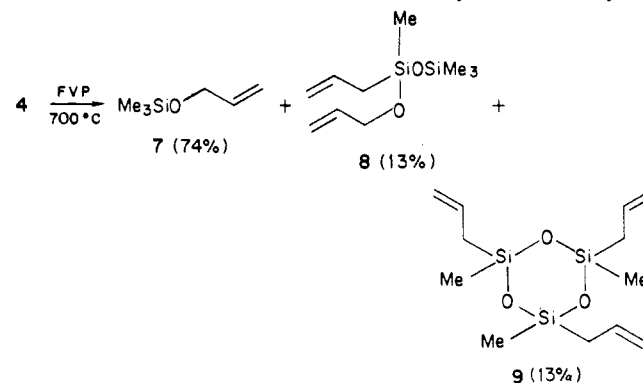
Results and Discussion

The obvious precursor, at least from a synthetic viewpoint, to the silylene **5** required for the proposed dihydrosilafuran synthesis is 1,1-bis(allyloxy)tetramethyldisilane (**4**). One confidently anticipates² that thermolysis of **4** would induce reductive elimination of (allyloxy)trimethylsilane (**7**) to produce silylene **5** for which

cyclization to dihydrosilafuran **6** was a reasonable expectation based on the known chemistry of silylene **1**. Synthesis of **4** was easily accomplished in 53% yield from coupling of the lithium salt of allyl alcohol and 1,1-dichlorotetramethyldisilane.



FVP of **4** was performed by slowly distilling neat **4** through a quartz-chip-packed tube at 700 °C ($\sim 10^{-5}$ torr) with an 81% mass recovery. Three major products were isolated by preparative GC: (allyloxy)trimethylsilane (**7**, 74%), 1-allyl-1-allyloxy-1,3,3,3-tetramethyldisiloxane (**8**, 13%), and 2,4,6-trimethyl-2,4,6-tri(2-propenyl)cyclotrisiloxane (**9**, 13%). No evidence for **6** even in trace amounts could be found by GCMS analysis.



(1) Barton, T. J.; Burns, G. T. *Organometallics* 1983, 2, 1.

(2) Weyenberg, D. R.; Atwell, W. H. *Pure Appl. Chem.* 1969, 19, 343.