

# THEORETICAL STUDIES OF REACTIONS AT TRANSITION METAL CENTERS

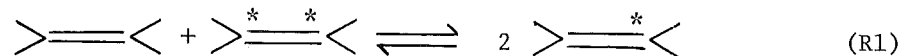
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## I. INTRODUCTION

For normal organic molecules, systematic studies in recent years have established the level of theoretical description\* required to obtain reliable geometries,<sup>1-3</sup> relative energies of isomers,<sup>3-5</sup> excitation energies, and even bond energies.<sup>6-8</sup> Considerations here are the type of basis set<sup>9</sup> (minimal basis or STO-3G *versus* double zeta or 4-31G *versus* inclusion of polarization functions) and the levels of electron correlation (generalized valence bond, configuration interaction, or many-body perturbation theory) or lack of correlation (Hartree-Fock). Some of these considerations are outlined in other chapters in this book. However, for molecules containing transition metals there is yet much uncertainty concerning these matters.

In this paper we will examine the effects of basis and level of electron correlation in describing some prototype systems, Cl<sub>2</sub>M=X, where M=Ti, Cr, and Mo, and X=CH<sub>2</sub>, NH, and O. Using the results of these studies, we examine an interesting chemical system, metathesis of olefins



by related transition metal complexes, and in particular we make

\*We consider only *ab initio* theoretical studies; current semiempirical techniques suffer large deficiencies for transition metal systems.

inferences about W complexes<sup>†</sup> by using general thermochemical comparisons between Mo and W systems. From these studies we have been able to establish a chemical principle (involving spectator metal-oxo bonds) crucial to the mechanism of these reactions.

## II. CALCULATIONAL DETAILS

### A. Basis Sets

For transition metals, minimal basis sets lead to extremely large errors. This occurs because changes in the occupation of d orbitals lead to large changes in the shape of these orbitals. Fixing the shape of the d orbital based upon one d occupation can make errors of 3 to 10 eV in the description of a state having a different occupation. Even for some flexible basis sets there can be serious errors as described below.<sup>10-13</sup>

Using five basis functions optimized for the  $3d^8 4s^2$  configuration of Ni, a double zeta (split valence) or triple zeta contraction leads to basis set errors of 4.1 eV in the description of the  $d^{10}$  state. However, optimizing the basis functions for the  $3d^{10}$  states and using a double zeta contraction leads to errors of only 0.07 eV in describing the  $3d^8 4s^2$ - $3d^{10}$  splitting.<sup>11</sup> For this reason we always use primitive basis sets optimized for the maximum d occupation of the neutral atom.<sup>11</sup>

In general, the basis utilized is a new-style Gaussian basis, somewhat similar to several in the literature for select elements.<sup>10</sup> The primitive basis consists of four Gaussians to describe 1s, 2p, and 3d atomic orbitals and two optimized functions to describe each remaining atomic orbital. This basis is then contracted to a split-valence basis<sup>9</sup> (minimal basis for core orbitals and two contracted functions for valence orbitals). The basis sets for H-Ba and a more detailed discussion will be presented elsewhere.<sup>11b</sup> For reference, this style basis introduces an error of 3.2 kcal (relative to the standard Dunning-Huzinaga VDZ basis<sup>9</sup>) in the C-O bond strength of the CO molecule.

In the calculations reported here, the Cl atoms were described using an effective potential<sup>14</sup> to replace the core electrons, and the basis set was contracted to minimal basis based on molecular calculations on  $TiCl_4$ . Allowing double zeta contraction and

<sup>†</sup>In practice, metathesis of olefins is commonly carried out in systems containing W, but the Mo-containing systems are more amenable to theoretical study. Bond strengths for Mo-ligand and W-ligand bonds generally differ by only on the order of 5 kcal/mol.

polarization functions on the Cl affected the bond energies to X by less than 1.6 kcal/mol.

To describe these basis sets we will use the abbreviations: MBS, minimum basis set; VDZ, valence double zeta; and VDZP, valence double-zeta plus polarization.

### B. Electron Correlation

Three levels of wavefunctions are considered: (i) Hartree-Fock approximation (HF), closed-shell Hartree-Fock for singlet states, restricted open-shell Hartree-Fock for higher spin states; (ii) Generalized valence bond method with the perfect-pairing restriction (GVB-PP), the form of generalized valence bond wavefunctions<sup>15</sup> in which each correlated pair is described as a singlet pair; (iii) Generalized valence bond configuration interaction method (GVB-CI), a full configuration interaction over the generalized valence bond orbitals from the GVB-PP calculations.<sup>5,6</sup> The GVB-PP level leaves out spin-coupling terms often important at saddle points for reactions; the GVB-CI allows general spin coupling, and includes the simultaneous interpair correlation terms often essential for multiply bonded systems.

In the GVB-PP method, one must decide how many and which electron pairs to correlate. In the calculations reported here we consider compounds of the form  $H_2C=X$ , where  $X=O, NH$ , or  $CH_2$ , and also compounds containing a single metal atom and various ligands. In the non-metal-containing compounds, only the two electron pairs in the  $C=X$  bond are correlated. In the metal-containing compounds, all metal-ligand bonds except those to Cl are correlated, thus requiring the correlation of as few as two electron pairs, as in  $Cl_2Ti=X$ , or as many as five, as in structure I (illustrated in section V).

## III. GEOMETRIES

In Tables 1 and 2, we show the variation of  $Ti=X$  bond length and  $ClTiCl$  bond angle for  $Cl_2TiX$  as a function of how much electron correlation is included in the wavefunction. Since there are no experimental values yet for these systems, we compare similar calculations for  $H_2C=X$  in Table 1. The results for  $H_2C=X$  are consistent with the general trends found for other small molecules; that is, HF underestimates bond distances, GVB-PP tends to overestimate bond distances, and proceeding to the GVB-CI level has a small effect on the bond distance (if adjacent bonds are correlated, GVB-CI will significantly shorten GVB-PP bond distances, usually resulting in quite adequate accuracy). Table 2 indicates that correlation of the  $Ti-X$  bond has little effect on the  $Cl-Ti-Cl$  angle. Addition of f functions

Table 1

Effect of electron correlation on the Ti=X bond lengths (Å) of Cl<sub>2</sub>Ti=X and CH<sub>2</sub>=X (basis sets: MBS on Cl, VDZ on Ti, VDZP on CH<sub>2</sub> and X).

System	X	HF	GVB-PP	GVB-CI	Exp.
Cl <sub>2</sub> Ti=X	O	1.53	1.57	1.56	...
	NH	--	1.71	1.64	...
	CH <sub>2</sub>	1.84	1.90	1.89	...
CH <sub>2</sub> =X	O	1.183	1.215	1.221	1.2078
	NH	1.251	1.280	1.285	...
	CH <sub>2</sub>	1.327	1.357	1.362	1.339

Table 2

Effect of electron correlation on the ClTiCl bond angle of Cl<sub>2</sub>Ti=X (basis sets: MBS on Cl, VDZ on Ti, VDZP on X).

X	HF	GVB-PP	GVB-CI
O	129.6	131.5	131.8
CH <sub>2</sub>	137.9	143.4	144.4

(zeta = 0.3) to the Ti basis lengthens the Ti=O bond length Cl<sub>2</sub>TiO by 0.004 Å, a negligible effect. Finally, a warning is in order. In spite of the reasonable results presented above for HF geometries, HF may perform disastrously for transition metal systems with more than one covalent ligand (the chlorine bonds in the above system are quite ionic). For example, the geometry for Cl<sub>2</sub>Cr $\begin{smallmatrix} \text{O} \\ \text{<} \\ \text{H} \end{smallmatrix}$  OH optimized at the HF level leads to an error of 15 kcal/mol relative to the GVB-CI optimized geometry!

## IV. BOND STRENGTHS

## A. A Direct Comparison

In Table 3 we compare the bond strengths for Cl<sub>2</sub>Ti=X and H<sub>2</sub>C=X as a function of electron correlation. For double bonds, the differential correlation error between H<sub>2</sub>C=X and Cl<sub>2</sub>Ti=X systems is between about 30 and 40 kcal/mol. Clearly, while HF may be acceptable for some organic applications (at least as a reference configuration<sup>16</sup> for standard CI calculations), it is totally unacceptable for transition metal systems.

The effect of polarization functions (f functions on transition metals, d functions on the ligand X) are indicated in Table 4; f functions on the metal contribute 5 kcal/mol and d functions on the ligand contribute 15 kcal/mol to the bond strength. Our conclusion is

Table 3

Effect of electron correlation on the Ti=X and C=X bond strength (kcal/mol) of Cl<sub>2</sub>Ti=X and H<sub>2</sub>C=X, respectively (basis sets: MBS on Cl, VDZ on Ti, VDZP on CH<sub>2</sub> and X).

System	X	HF	GVB-PP	GVB-CI	Dif. <sup>a</sup>	Exp.
Cl <sub>2</sub> Ti=X	O	20.6	67.7	119.8	99.2	...
	NH	-9.9	50.3	77.9	87.8	...
	CH <sub>2</sub>	-14.6	59.7	51.5	66.1	...
H <sub>2</sub> C=X	O	105.8	138.2	165.0	59.2	180.4
	NH	100.1	130.8	146.2	46.1	...
	CH <sub>2</sub>	123.8	149.2	157.8	34.0	176.7

a. difference between HF and GVB-CI

that polarization functions on the ligand are essential. However, the effect of f functions is 5.2 kcal/mol on



and 5.1 kcal/mol on

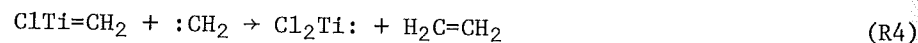


Thus, for reactions retaining comparable bonding at the transition metal, contributions from f basis functions may cancel.

In order to provide a more detailed understanding of the importance of various electron correlation effects, we show in Tables 5 through 10 the dominant correlation terms for several analogous organic and transition metal systems. In these tables, each configuration is indicated by the occupation number for the various GVB orbitals. Here  $\sigma$ ,  $\pi$ , etc., refer to the first GVB natural orbital, while  $\sigma^*$ ,  $\pi^*$ , etc., refer to the second GVB natural orbital. The energy cutoff is 1 kcal/mol in all cases. There are no surprises in the results in these tables; the effects for transition metal compounds are similar to those previously discussed for organic systems. Note the importance of interpair correlation terms\* for systems with double or triple bonds. An interesting point (see Tables 8 and 9) is that molybdenum systems have smaller correlation errors in general than do analogous chromium systems. This is due to the increased overlap of the metal d orbitals with the p orbitals on the ligands.

#### B. Retention of Bondedness

Accurate calculations of the energetics for chemical processes require inclusion of those electronic correlation effects that are different for reactants than products. For less-than-exact wavefunctions, one can improve the accuracy of bond-energy calculations by considering processes involving formation and dissolution of similar bonds, all at the same level of correlation. For example, to obtain the Ti=C bond strength of  $\text{Cl}_2\text{TiCH}_2$ , we calculate the energy difference for the process



\*Interpair terms consist of simultaneous single excitations between pairs of electrons; for example,  $(\sigma_1 \rightarrow \sigma_1^*) \times (\sigma_2 \rightarrow \sigma_2^*)$ , which allows dynamic correlation of the electrons in two sigma bonds.

Table 4  
Effect of polarization basis functions on the Ti=O and C=C bond strengths (kcal/mol) of  $\text{Cl}_2\text{Ti}=\text{O}$  and  $\text{C}_2\text{H}_4$ , respectively (basis sets: MBS on Cl, VDZ on Ti, O, and  $\text{CH}_2$ ).

System	Polarization functions	Bond energy
$\text{Cl}_2\text{Ti}=\text{O}$	None	104.4
	d on O	119.8
	d on O and f on Ti	125.0
$\text{H}_2\text{C}=\text{CH}_2$	None	145.2
	d on C	157.8

Table 5  
Dominant correlation contributions for the GVB-CI wavefunctions of  $\text{Cl}_2\text{TiCH}_2$  and  $\text{C}_2\text{H}_4$ .

System	$\sigma$	$\sigma^*$	$\pi$	$\pi^*$	Energy contribution (kcal/mol)	Correlation
$\text{Cl}_2\text{TiCH}_2$	2	0	2	0	--	HF
	2	0	0	2	29.0	$\pi$ (PP)
	1	1	1	1	14.4	$\sigma\pi$ interpair
	0	2	2	0	9.5	$\sigma$ (PP)
	0	2	0	2	4.0	$\sigma\pi$ (PP)
$\text{H}_2\text{C}=\text{CH}_2$	2	0	2	0	--	HF
	2	0	0	2	15.6	$\pi$ (PP)
	1	1	1	1	9.6	$\sigma\pi$ interpair
	0	2	2	0	5.1	$\sigma$ (PP)

Table 6

Dominant correlation contributions for the GVB-CI wavefunction of  $\text{Cl}_2\text{TiO}$  and  $\text{H}_2\text{CO}$  (molecules in the xz plane).

Molecule	$\sigma$	$\sigma^*$	$\pi_x^*$	$\pi_x^*$	$\pi_y^*$	$\pi_y^*$	Energy contribution (kcal/mol)	Correlation
$\text{Cl}_2\text{TiO}$	2	0	2	0	2	0	--	HF
	1	1	2	0	1	1	18.8	$\sigma\pi_y$ interpair
	1	1	1	1	2	0	13.9	$\sigma\pi_x$ interpair
	2	0	1	1	1	1	13.3	$\pi_x\pi_y$ interpair
	2	0	2	0	0	2	9.7	$\pi_y - \text{PP}$
	0	2	2	0	2	0	9.5	$\sigma - \text{PP}$
	2	0	0	2	2	0	6.7	$\pi_x - \text{PP}$
	1	1	1	1	0	2	2.0	
	0	2	1	1	1	1	1.8	
	1	1	0	2	1	1	1.5	
$\text{H}_2\text{CO}$	2	0			2	0	...	HF
	2	0			0	2	18.1	$\pi - \text{PP}$
	1	1			1	1	13.5	$\sigma\pi$ interpair
	0	2			2	0	7.2	$\sigma - \text{PP}$

Table 7

Dominant correlation contributions for the GVB-CI wavefunctions of  $\text{Cl}_2\text{TiNH}$  and  $\text{H}_2\text{CNH}$  (molecules in the xz plane).

Molecule	$\sigma$	$\sigma^*$	$\pi_x^*$	$\pi_x^*$	$\pi_y^*$	$\pi_y^*$	Energy contribution (kcal/mol)	Correlation
$\text{Cl}_2\text{TiNH}$	2	0	2	0	2	0	--	HF
	2	0	1	1	1	1	24.1	$\pi_x\pi_y$ interpair
	2	0	2	0	0	2	16.1	$\pi_y - \text{PP}$
	2	0	0	2	2	0	10.5	$\pi_x - \text{PP}$
	0	2	2	0	2	0	5.6	$\sigma - \text{PP}$
	1	1	1	1	2	0	3.9	$\sigma\pi_x$ interpair
	2	0	0	2	0	2	2.6	$\pi_x\pi_y - \text{PP}$
	1	1	2	0	1	1	2.5	$\sigma\pi_y$ interpair
	1	1	1	1	0	2	1.0	
$\text{H}_2\text{CNH}$	2	0			2	0	...	HF
	2	0			0	2	16.6	$\pi - \text{PP}$
	1	1			1	1	10.6	$\sigma\pi$ interpair
	0	2			2	0	6.2	$\sigma$

Table 8a

Dominant correlation contributions for the GVB-CI wave-function of  $\text{Cl}_2\text{CrO}_2$ .

$\sigma_1$	$\sigma_1^*$	$\sigma_2$	$\sigma_2^*$	$\pi_1$	$\pi_1^*$	$\pi_2$	$\pi_2^*$	Energy contribution (kcal/mol)	Correlation
2	0	2	0	2	0	2	0	--	HF
2	0	1	1	2	0	1	1	30.3	$\sigma_2\pi_2$ interpair
1	1	2	0	1	1	2	0	30.3	$\sigma_1\pi_1$ interpair
2	0	2	0	0	2	2	0	29.6	$\pi_1 - \text{PP}$
2	0	2	0	2	0	0	2	29.6	$\pi_2 - \text{PP}$
2	0	0	2	2	0	2	0	14.3	$\sigma_2 - \text{PP}$
0	2	2	0	2	0	2	0	14.3	$\sigma_1 - \text{PP}$
2	0	0	2	2	0	0	2	6.4	$\sigma_2\pi_2 - \text{PP}$
0	2	2	0	0	2	2	0	6.4	$\sigma_1\pi_1 - \text{PP}$
2	0	2	0	0	2	0	2	3.2	$\pi_1\pi_2 - \text{PP}$
2	0	1	1	0	2	1	1	2.9	
1	1	2	0	1	1	0	2	2.9	
1	1	1	1	1	1	1	1	2.4	
2	0	2	0	1	1	1	1	2.0	$\pi_1\pi_2$ interpair
2	0	0	2	0	2	2	0	1.4	$\pi_1\sigma_2 - \text{PP}$
0	2	2	0	2	0	0	2	1.4	$\sigma_1\pi_2 - \text{PP}$
1	1	2	0	2	0	1	1	1.2	$\sigma_1\pi_2$ interpair
2	0	1	1	1	1	2	0	1.2	$\sigma_2\pi_1$ interpair
1	1	0	2	1	1	2	0	1.1	
0	2	1	1	2	0	1	1	1.1	

Table 8b

Dominant correlation contributions for the GVB-CI wave-function of  $\text{Cl}_2\text{MoO}_2$ .

$\sigma_1$	$\sigma_1^*$	$\sigma_2$	$\sigma_2^*$	$\pi_1$	$\pi_1^*$	$\pi_2$	$\pi_2^*$	Energy contribution (kcal/mol)	Correlation
2	0	2	0	2	0	2	0	--	
2	0	1	1	2	0	1	1	23.2	$\sigma_2\pi_2$ interpair
1	1	2	0	1	1	2	0	23.2	$\sigma_1\pi_1$ interpair
2	0	2	0	0	2	2	0	17.3	$\pi_1 - \text{PP}$
2	0	2	0	2	0	0	2	17.3	$\pi_2 - \text{PP}$
2	0	0	2	2	0	2	0	9.9	$\sigma_2 - \text{PP}$
0	2	2	0	2	0	2	0	9.9	$\sigma_1 - \text{PP}$
2	0	0	2	2	0	0	2	2.3	$\sigma_2\pi_2 - \text{PP}$
0	2	2	0	0	2	2	0	2.3	$\sigma_1\pi_1 - \text{PP}$
1	1	1	1	1	1	1	1	1.2	
2	0	1	1	0	2	1	1	1.2	
1	1	2	0	1	1	0	2	1.2	
2	0	2	0	0	2	0	2	1.0	$\pi_1\pi_2 - \text{PP}$

Table 9a  
Dominant correlation contributions for the GVB-CI wave-  
function of  $\text{Cl}_2\text{CrOCH}_2$ .

$\sigma_c$	$\sigma_c^*$	$\sigma_0$	$\sigma_0^*$	$\pi_c$	$\pi_c^*$	$\pi_0$	$\pi_0^*$	Energy contribution (kcal/mol)	Correlation
2	0	2	0	2	0	2	0	--	HF
2	0	1	1	2	0	1	1	29.5	$\sigma_0\pi_0$ interpair
2	0	2	0	0	2	2	0	28.4	$\pi_c$ - PP
1	1	2	0	1	1	2	0	24.2	$\sigma_c\pi_c$ interpair
2	0	2	0	2	0	0	2	23.6	$\pi_0$ - PP
0	2	2	0	2	0	2	0	14.9	$\sigma_c$ - PP
2	0	0	2	2	0	2	0	13.6	$\sigma_0$ - PP
0	2	2	0	0	2	2	0	8.8	$\sigma_c\pi_c$ - PP
2	0	0	2	2	0	0	2	4.2	$\sigma_0\pi_0$ - PP
2	0	1	1	0	2	1	1	3.3	
2	0	2	0	0	2	0	2	3.2	$\pi_c\pi_0$ - PP
2	0	2	0	1	1	1	1	2.8	$\pi_c\pi_0$ interpair
1	1	1	1	1	1	1	1	2.4	
1	1	2	0	1	1	0	2	2.2	
2	0	2	0	1	1	2	0	1.6	$\pi_c$ - readjust
1	1	2	0	2	0	1	1	1.5	$\sigma_c\pi_0$ interpair
2	0	0	2	0	2	2	0	1.5	$\sigma_0\pi_c$ - PP
0	2	1	1	2	0	1	1	1.4	
2	0	1	1	2	0	0	2	1.4	
2	0	1	1	1	1	2	0	1.3	$\sigma_0\pi_c$ interpair
0	2	2	0	2	0	0	2	1.3	$\sigma_c\pi_0$ - PP
1	1	1	1	2	0	2	0	1.3	$\sigma_c\sigma_0$ interpair
1	1	0	2	1	1	2	0	1.1	
1	1	2	0	0	2	1	1	1.0	

Table 9b  
Dominant correlation contributions for the GVB-CI wave-  
function of  $\text{Cl}_2\text{MoOCH}_2$ .

[illegible]

Table 10  
Dominant correlation contributions for the GVB-CI wavefunction of  $\text{Cl}_4\text{CrO}$ .

$\sigma$	$\sigma^*$	$\pi_x$	$\pi_x^*$	$\pi_y$	$\pi_y^*$	Energy contribution (kcal/mol)	Correlation
2	0	2	0	2	0	--	
2	0	1	1	1	1	23.4	$\pi_x \pi_y$ interpair
2	0	2	0	0	2	20.8	$\pi_y$ - PP
2	0	0	2	2	0	20.8	$\pi_x$ - PP
1	1	2	0	1	1	16.0	$\sigma \pi_y$ interpair
1	1	1	1	2	0	16.0	$\sigma \pi_x$ interpair
0	2	2	0	2	0	7.2	$\sigma$ - PP
1	1	1	1	0	2	5.4	
1	1	0	2	1	1	5.4	
2	0	0	2	0	2	5.1	$\pi_x \pi_y$ - PP
1	1	2	0	2	0	3.4	$\sigma$ - readjust
1	1	0	2	0	2	2.3	
0	2	1	1	1	1	2.1	
0	2	2	0	0	2	1.3	$\sigma \pi_y$ - PP
0	2	0	2	2	0	1.3	$\sigma \pi_x$ - PP
2	0	0	2	1	1	1.1	
2	0	1	1	0	2	1.1	

Table 11  
Errors in directly calculated bond energies (kcal/mol)  
for organic reactions.

Process	$\Delta H$ HF	$\Delta H$ GVB-CI	$\Delta H$ Exp	Error HF	Error GVB-CI
$\text{CH}_2\text{O} \rightarrow \text{CH}_2 + \text{O}$	105.8	165.0	180.4	74.6	15.4
$\text{C}_2\text{H}_4 \rightarrow 2\text{CH}_2$	110.4	157.8	176.7	66.3	18.9
$\text{H}_2 \rightarrow 2\text{H}$	80.1	92.3	109.5	29.4	17.2
$\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$	86.7	96.7	112.1	25.4	15.9
$\text{C}_2\text{H}_6 \rightarrow 2\text{CH}_3$	77.8	82.4	96.2	23.4	13.8
$\text{CH}_3\text{OH} \rightarrow \text{CH}_2 + \text{OH}$	63.6	77.4	98.7	35.1	21.3
$\text{CH}_3 \rightarrow \text{CH}_2 + \text{H}$	86.5	98.2	114.4	27.9	16.2
$\text{CH}_4 \rightarrow \text{CH}_2 + \text{H}_2$	93.1	102.5	117.0	23.9	14.5

Because the residual correlation errors on both sides of (R4) will be comparable, GVB-CI calculations should yield accurate theoretical values for the  $\Delta H$  of (R4). The most accurate value for the  $\Delta H_f$  of  $\text{Cl}_2\text{TiCH}_2$  or of the  $\text{Ti}=\text{C}$  bond strength can then be obtained from experimental (or more accurate theoretical) values for  $\Delta H_f$  of  $\text{Ti}(\text{Cl})_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{CH}_2$ . By considering processes with constant bondedness, even HF calculations may yield moderately reliable bond energies for organic systems.<sup>17</sup> However, since HF leads to much larger correlation errors in pi bonds than in sigma bonds and much larger errors for transition metal systems than for organics, the use of HF would lead to very large errors for cases of interest herein. This is exemplified in Table 11 where the error in bond energies for HF ranges from 23 to 75 kcal/mol, while the error in GVB-CI ranges from 14 to 21 kcal/mol. Thus, use of GVB-CI with the retention-of-bondedness principle can lead to very accurate relative bond energies, even for transition metal systems.

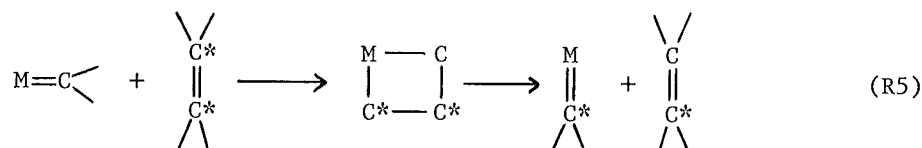


## C. General Procedure

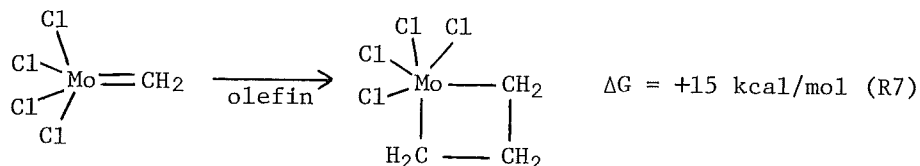
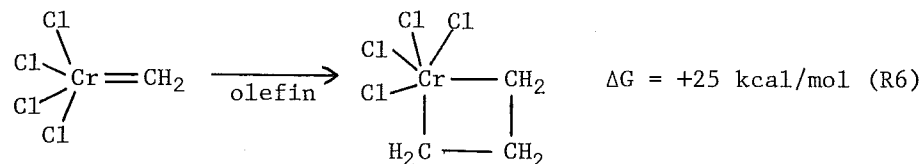
We use the following scheme for determining accurate energetics for chemical processes. Using the GVB-CI method, we calculate the energy differences for reactions where the number and type of bonds are as similar as possible. To calculate the enthalpy changes at 0 K for these processes, one must add the differential zero point corrections to the calculated energy differences. The resulting  $\Delta H_{f,0}$  are combined with previously obtained  $\Delta H_{f,0}$  for the other species in the idealized reactions to calculate  $\Delta H_{f,0}$ 's for the molecules of interest. These  $\Delta H_{f,0}$ 's are combined with vibrational frequencies (experimental, calculated, or estimated) and moments of inertia to obtain  $\Delta H_{f,300}$  and  $S_{300}$ . Finally,  $\Delta G_{r,300}$  for the reactions of interest are calculated. As is apparent, this technique is analogous to the standard experimental techniques for obtaining free energies.

## V. APPLICATIONS TO REACTIONS

The mechanism of metathesis has been established to involve a carbene as the active catalyst and to involve formation of a metallocycle intermediate,<sup>18,19</sup>

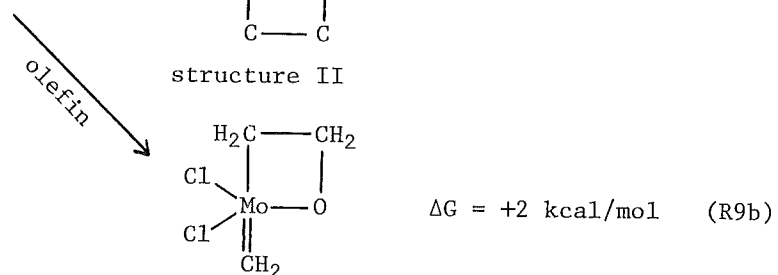
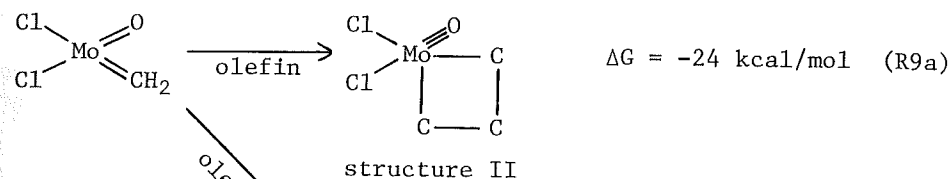
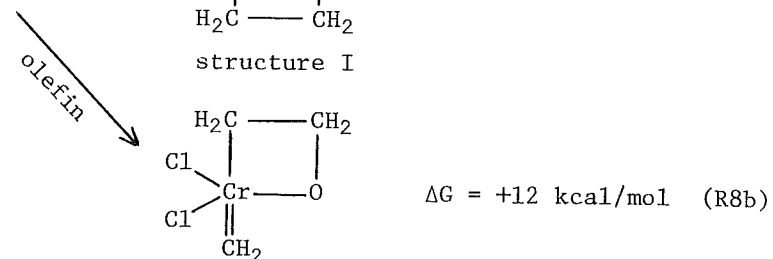
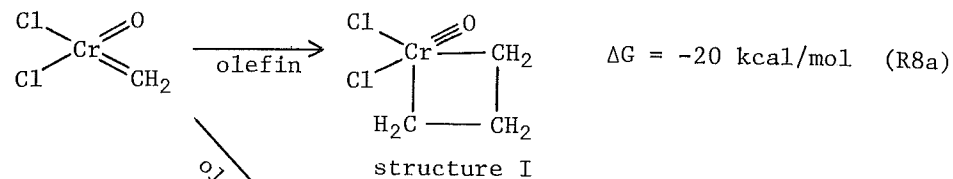


However, we find that the formation of the metallocycle intermediate is unfavored for normal Cr(VI) and Mo(VI) carbenes, *e.g.*,

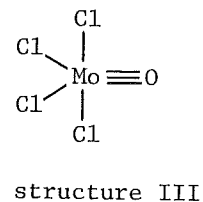


## TRANSITION-METAL REACTIONS

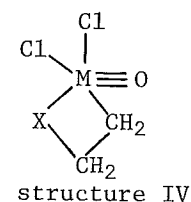
On the other hand, considering related Cr(VI) and Mo(VI) systems, we found<sup>19,20</sup> that carbene species containing an extra or spectator metal-oxo bond lead to facile formation of metallocyclobutane intermediates (but without side reactions involving metallocyclo oxetane intermediates),



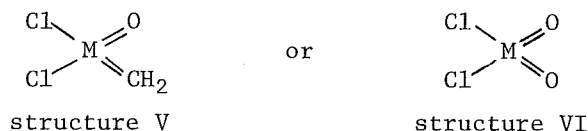
Thus, the presence of a spectator metal-oxo bond drives the formation of the metathesis intermediate (metallocyclobutane) without introducing side reactions involving the oxo bond. The origin of this remarkable change [(R6) to (R8a) or (R7) to (R9a)] has to do with the character of metal-oxo bonds. For species such as



or



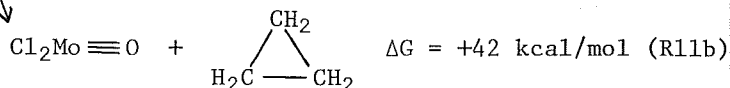
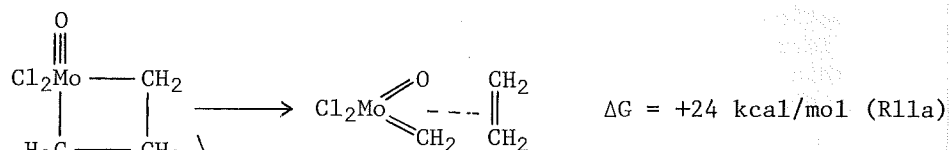
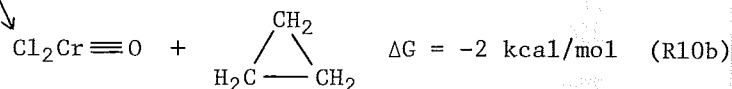
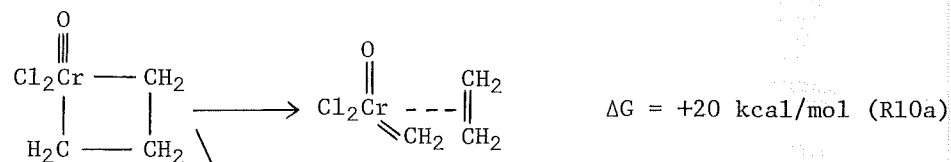
(where  $M = \text{Cr}$  or  $\text{Mo}$  and  $X = \text{O}$  or  $\text{CH}_2$ ), the metal-oxo bond forms an effective triple bond much like that in  $\text{CO}$  diatomic, whereas in species such as



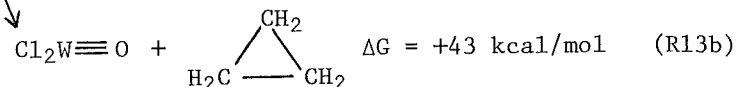
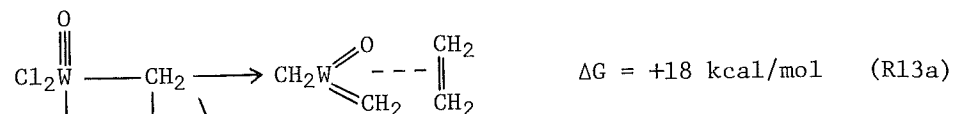
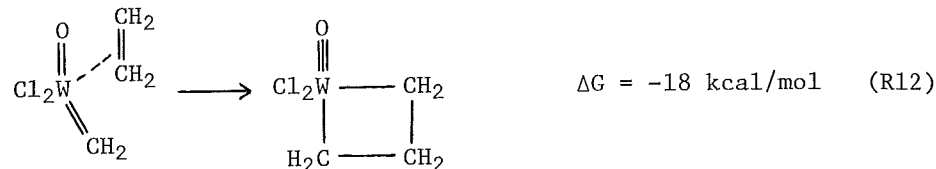
the metal-oxo bond is a double bond much like that in  $\text{CO}_2$  or ketones. From calculations of the (first) metal-oxo bond energy of  $\text{Cl}_4\text{MO}$  and  $\text{Cl}_2\text{MO}_2$ , we find that the  $\text{M}=\text{O}$  triple bond, structure III, is 31 kcal/mol stronger than the  $\text{M}=\text{O}$  double bond, structure VI, for Cr and 22 kcal/mol stronger for Mo. Thus the formation of the metallocycle intermediates, structures I and II, is stabilized by about 30 kcal/mol, converting an endothermic reaction (R6) or (R7) into an exothermic reaction (R8a) or (R9a). On the other hand, for the side reactions (R8b) and (R9b) there is no such stabilization, leaving rather endothermic reactions.

Of course it is not enough just to form the intermediate, we must also examine various pathways for decomposition.

Decomposition of the metallocycle butane, structures I and II, can lead to the metathesis product; however, it can also reductively eliminate a cyclopropane. The energetics are as follows:\*

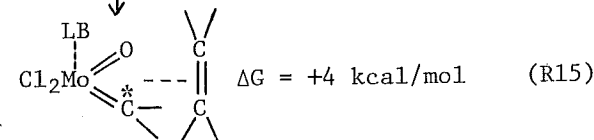
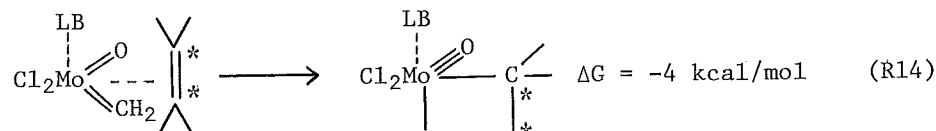


For Cr the reductive elimination process (R10b) is overwhelmingly favored, whereas for Mo the metathesis process is favored. We have not carried out calculations for W systems; however, general thermochemical comparisons between Mo and W systems suggest that



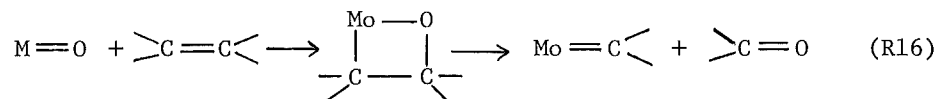
Thus, for both W and Mo, the oxo-carbene leads to metathesis.

These theoretical results are for gas-phase reactions. In order to discuss the real metathesis processes (in solution in solvents like  $\text{CCl}_4$ ,  $\text{HCCl}_3$ , and  $\text{C}_6\text{H}_6$ ), we must estimate the role of solvation effects. Some important effects are (i) an olefin can form a  $\pi$ -complex with a species such as structure V or VI, leading to a stabilization (about 5 kcal/mol) on the left side of (R8), (R9), and (R12) and the right side of (R10a), (R11a), and (R13a); (ii) Lewis bases present in solution (e.g.,  $\text{Cl}^-$  alcohols,...) should stabilize tetracoordinate species such as structures V and VI with respect to pentacoordinate metallocycle species (by about 15 kcal/mol). The net result is that in solution the metathesis processes for Mo and W are nearly thermoneutral, e.g.,

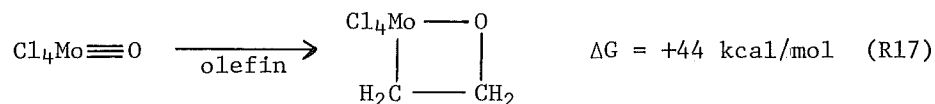


\*In reactions (R10b), (R11b), and (R13b), the energetics are based on the spin-allowed process.

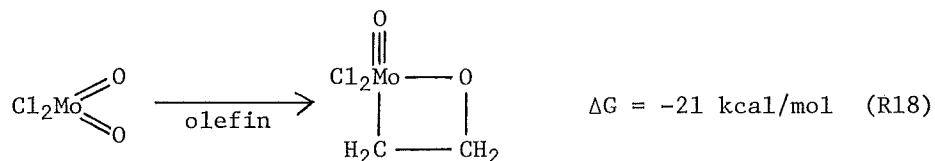
The above studies indicate that an oxo-carbene of Mo or W can catalyze metathesis. The remaining major question is how one might form this intermediate. One suggestion is that they are formed by reaction of the olefin with metal-oxo bonds,<sup>20</sup>



We have also investigated this process with the following results

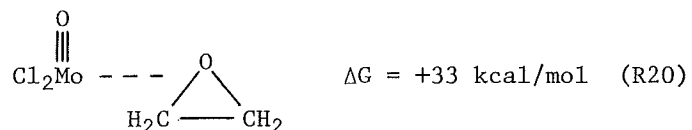
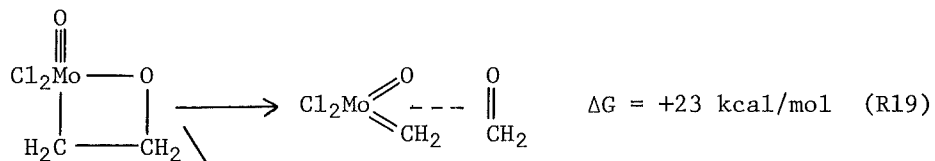


This process is far too endothermic to play any role. However,



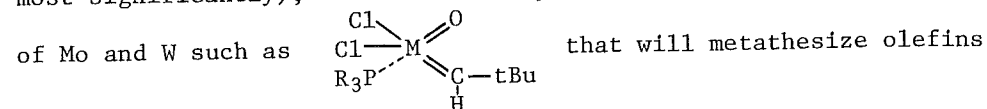
Again, the formation of the metallocyclo intermediate is driven by the spectator oxo bond (converting from a double to a triple bond).

Decomposition of the metallocyclo oxetane can lead to metal-carbene formation or to reductive elimination,



Including differential effects in the solution due to  $\pi$ -complexation and Lewis bases, the process (R18) + (R19) should be approximately thermoneutral, thus providing a mechanism for forming the oxo-carbene postulated as the catalyst for metathesis.

Several experiments tend to confirm our finding that the stable high-valent metathesis catalyst is an oxo-carbene. First, Basset *et al.*<sup>21</sup> found that oxygen-containing compounds ( $\text{O}_2$  or alcohols) accelerate the metathesis reaction. Second, Muettterties and co-workers<sup>22</sup> have shown that oxygen and perhaps chlorine are essential for the generation of active, stable metathesis catalysts for high-valent tungsten. We feel that the chlorine serves the role of a Lewis base and could probably be replaced by other electronegative ligands such as alkoxides. More recently Osborn and coworkers<sup>23</sup> have generated Mo and W complexes that will metathesize olefins without standard co-catalysts; we believe that these experiments could generate an oxo-carbene complex through a straightforward ligand exchange<sup>24</sup> followed by an alpha abstraction<sup>25</sup> process. Finally (and most significantly), Schrock<sup>26</sup> has synthesized high-valent complexes

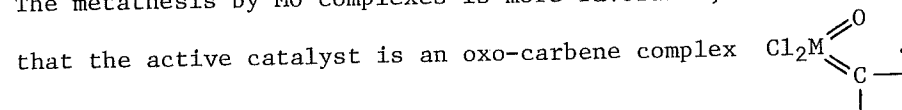


without co-catalysts. As discussed above, the Lewis base should decrease the energy gap between the carbene and metallocyclic complexes and should decrease the importance of the bimolecular decomposition pathway for homogeneous systems. The general accelerating effect of Lewis bases (amines) is well documented for heterogeneous catalysts.<sup>27</sup>

To verify the energetic similarity of dioxo- and oxo-carbene complexes, we suggest that reaction of ketones with Schrock's oxo-carbene complex should generate olefins and a dioxo complex. If isolated, this dioxo complex should react with olefins to regenerate an oxo-carbene complex.

## VI. SUMMARY

We consider the various factors (basis set, level of electron correlation) governing the accuracy of theoretical calculation of bonds to transition metals. The lessons of these studies are utilized in examining metathesis by high-oxidation-state Cr and Mo complexes. Metathesis of olefins by the Cr complexes is unfavorable because of a competing reaction involving cyclopropane elimination. The metathesis by Mo complexes is more favorable, and we conclude



Based on the thermochemical comparisons we conclude that an oxo-carbene complex is also the stable metathesis catalyst for high-valent W complexes. For both Mo and W complexes, the oxygen ligand is intimately involved in the catalytic process.

## VII. ACKNOWLEDGMENT

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## VIII. REFERENCES

1. S. Bell, The effects of basis set and configuration interaction on the predicted geometries of  $AH_2$  molecules, *J. Chem. Phys.* 68: 3014 (1978).
2. D. Cremer, Theoretical determination of molecular structure and conformation. I. The role of basis set and correlation effects in calculations on hydrogen peroxide, *J. Chem. Phys.* 69: 4440 (1978).
3. C. A. Parsons and C. E. Dykstra, Electron correlation and basis set effects in unimolecular reactions. A study of the model rearrangement system  $N_2H_2$ , *J. Chem. Phys.* 71: 3025 (1979).
4. J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, Electron correlation theories and their application to the study of simple reaction potential surfaces, *Int. J. Quantum Chem.* 14: 545 (1978).
5. C. J. Casewit and W. A. Goddard III, Thermochemistry of *trans*-diimide and 1,1-diazene. *Ab initio* studies, *J. Amer. Chem. Soc.* 102: 4057 (1980).
6. J. H. Davis, W. A. Goddard III, and L. B. Harding, Theoretical studies of the low-lying states of vinylidene, *J. Amer. Chem. Soc.* 99: 2919 (1977).
7. L. B. Harding and W. A. Goddard III, Intermediates in the chemiluminescent reaction of singlet oxygen with ethylene. *Ab initio* studies, *J. Amer. Chem. Soc.* 99: 4520 (1977).
8. M. L. Steigerwald and W. A. Goddard III, unpublished results; R. A. Bair and W. A. Goddard III, unpublished results.
9. T. H. Dunning, Jr. and P. J. Hay, Gaussian basis sets for molecular calculations, in: "Methods of Electronic Structure Theory", H. F. Schaefer III, ed., Plenum, New York (1977), p. 1.
10. E. L. Mehler and C. H. Paul, Small Gaussian basis sets for *ab initio* calculations on large molecules, *Chem. Phys. Lett.* 63: 145 (1979); H. Tatewaki and S. Huzinaga, A systematic preparation of new contracted Gaussian-type orbital set. 1. Transition metal atoms from Sc to Zn, *J. Chem. Phys.* 71: 4339 (1979); D. F. Feller and K. Reudenberg, Systematic approach to extended even-tempered orbital bases for atomic and molecular calculations, *Theoret. Chim. Acta* 52: 231 (1979); M. W. Schmidt, and K. Ruedenberg, Effective convergence to complete orbital bases and to the atomic Hartree-Fock limit through systematic sequences of Gaussian primitives, *J. Chem. Phys.* 71: 395 (1979).

11. (a) T. A. Smedley, A. K. Rappé, and W. A. Goddard III, Flexible D basis sets for Sc through Cu, *J. Phys. Chem.*, submitted for publication; (b) A. K. Rappé and W. A. Goddard III, Flexible double zeta Gaussian basis sets for H-Ba, manuscript in preparation.
12. P. J. Hay, Gaussian basis sets for molecular calculations. The representation of 3d orbitals in transition-metal atoms, *J. Chem. Phys.* 66: 4377 (1977).
13. B. R. Brooks and H. F. Schaefer III, A model transition metal-carbene system  $MnCH_2$ , *Mol. Phys.* 34: 193 (1977).
14. A. K. Rappé, T. A. Smedley, and W. A. Goddard III, The shape and Hamiltonian consistent (SHC) effective potentials, *J. Phys. Chem.*, submitted for publication.
15. F. W. Bobrowicz and W. A. Goddard III, The self-consistent-field equations for generalized valence bond and open-shell Hartree-Fock wavefunctions, in: "Methods of Electronic Structure Theory", H. F. Schaefer III, ed., Plenum, New York (1979), p. 79.
16. I. Shavitt, The method of configuration interaction, in: "Methods of Electronic Structure Theory", H. F. Schaefer III, ed., Plenum, New York (1977), p. 189.
17. For a review on the HF calculation of the energetics of "isodesmic" reactions, see W. J. Hehre, *Ab initio* molecular orbital theory, *Acc. Chem. Res.* 9: 399 (1976).
18. P. Schlotter, J. A. Ibers, M. Lenarda, and M. Graziani, Structure and mechanism of formation of the metalloxacyclobutane complex  $Pt[C_2(CN)_4O][As(C_6H_5)_3]_2$ , the product of the reaction between tetracyanooxirane and  $Pt[As(C_6H_5)_3]_4$ , *J. Amer. Chem. Soc.* 96: 6893 (1974); R. H. Grubbs and A. Miyashita, Metallocycles in organotransition metal chemistry, *Fundamental Research in Homogeneous Catalysis* 2: 207 (1977); R. H. Grubbs and A. Miyashita, The relationship between metallacyclopentanes and bis-olefin-metal complexes, *J. Amer. Chem. Soc.* 100: 1300 (1978); S. J. McLain and R. R. Schrock, Selective olefin dimerization *via* tantalocyclopentane complexes, *J. Amer. Chem. Soc.* 100: 1315 (1978); I. M. Al-Najjar, M. Greene, S. J. S. Kerrison, and P. J. Sadler, Platinum complex containing a four-membered ring, *J. Chem. Soc. Chem. Commun.* 311 (1979); J. L. Harrison and Y. Chauvin, Catalyse de transformation des oléfines par les complexes du tungstène. II. Télémérisation de oléfines en présence d'oléfines acycliques, *Makromol. Chem.* 141: 161 (1970); R. H. Grubbs, The olefin metathesis reaction, *Prof. Inorg. Chem.* 24: 1 (1978); N. Calderon, J. P. Lawrence, and E. A. Ofstead, Olefin metathesis, *Advan. Organomet. Chem.* 17: 449 (1979).
19. For a preliminary account of this work, see A. K. Rappé and W. A. Goddard, Bivalent spectator oxo bonds in metathesis and epoxidation of alkenes, *Nature* 285: 311 (1980); Mechanism of metathesis and epoxidation in Cr and Mo complexes containing oxo bonds, *J. Amer. Chem. Soc.* 102: 5114 (1980).
20. A. K. Rappé, Ph.D. thesis, California Institute of Technology, Pasadena, 1980.

21. J. M. Basset, G. Coudurier, R. Mutin, H. Proliaud, and Y. Trambouze, Effect of oxygen on metathesis of cis-2-pentene by a binary catalyst system of  $W(CO)_5P(C_6H_5)_3$  and  $(C_2H_5)AlCl_2$ , J. Catal. 34: 196 (1974).
22. M. T. Mocella, R. Rovner, and E. L. Muetterties, Mechanism of the olefin metathesis reaction. 4. Catalyst precursors in tungsten(VI) based systems, J. Amer. Chem. Soc. 98: 1689 (1976).
23. J. R. M. Kress, M. J. Russell, M. G. Wesolek, and J. A. Osborn, Tungsten (VI) and molybdenum (VI) oxo-alkyl species. Their role in the metathesis of olefins, J. Chem. Soc. Chem. Commun. 431 (1980).
24. R. A. Walton, Halides and oxyhalides of the early transition series and their stability and reactivity in nonaqueous media, Prog. Inorg. Chem. 16: 1 (1972).
25. R. R. Schrock, Alkylidene complexes of niobium and tantalum, Acc. Chem. Res. 12: 98 (1979).
26. R. Schrock, S. Rocklage, J. Wengrovius, G. Rupprecht, and J. Fellmann, Preparation and characterization of active niobium, tantalum, and tungsten metathesis catalysts, J. Mol. Catal. 8: 73 (1980); J. H. Wengrovius, R. R. Schrock, M. R. Churchill, J. R. Missert, and W. J. Youngs, Tungsten-oxo alkylidene complexes as olefin metathesis catalysts and the crystal structure of  $W(O)(CHCMe_3)(PEt_3)Cl_2$ , J. Amer. Chem. Soc. 102: 4515 (1980).
27. J. Fathiakalajaji and G. B. Willis, Effects of ammonia upon propylene metathesis over a  $WO_3-SiO_2$  catalyst, J. Mol. Catal. 8: 127 (1980).