vacuum pyrolysis of **11** at 1000 °C (10^{-3} torr) caused very little conversion to naphthalene (ca. 6.5%). At 1180 °C (10^{-3} torr), the azulene/naphthalene product ratio was 1:5. The labeled naphthalene was separated from azulene by gas chromatography and examined by ^{13}C NMR spectroscopy. The results are collected in Table I. The labeled **11** was also subjected to gas-phase photolysis[15] at 50 °C (ca. 0.07 torr) by using a 450-W medium-pressure Hanovia lamp. After 6 days, 2–3% of naphthalene had formed. The naphthalene and azulene were again separated and examined by ^{13}C NMR (see Table I). A control experiment showed that no detectable amount of naphthalene was formed at 50 °C in the absence of light.

The pyrolysis and photolysis results are remarkably similar (Table I). Notably, both conditions cause partial carbon scrambling in azulene itself, and the extent of scrambling is of the same order of magnitude as the yield of naphthalene. The real problem is now the elucidation of the mechanism of carbon scrambling in azulene, and to this end we plan double-labeling experiments. From the data in Table I, it is clear, however, that the Scott–Agopian mechanism[3] could account at most for 52–57% of the conversion into naphthalene, since this mechanism predicts labeling of C-1 only. By repyrolysis of the labeled naphthalene isolated from the 1180 °C pyrolysis, we established that no further scrambling in naphthalene takes place under our conditions. The mechanism given in Scheme I predicts labeling of C-9 and C-1 only, and in equal amounts. Since C-1- and C-5-labeled azulenes are formed during the reactions, these, too, would rearrange to naphthalenes and thereby increase the amount of label found in positions 1 and 2 in naphthalene. Thus, the experimental data (Table I) are in qualitative agreement with Scheme I.

A further complication arose as we discovered that the azulene–naphthalene rearrangement cannot be wholly unimolecular, even under flash vacuum pyrolysis conditions. Azulene-*4-d* was prepared by adaptation of the method given in Scheme II and pyrolyzed at 1180 °C as described above. The naphthalene formed was examined by ^{1}H NMR and low-voltage mass spectrometry. Yields of 12% d_0, 12% d_2, and 76% d_1 naphthalene-*d* were obtained, with an integrated ratio $H_\alpha/H_\beta \approx 0.9$. The recovered azulene was $\approx$100% d_1. In another experiment, 50 mg of azulene-*4-d* was pyrolyzed statically in a 50-mL Pyrex tube [previously silylated with $(CH_3)_2SiCl_2$] at 400 ± 5 °C for 20 h. Yields of 13% d_0, 14% d_2, and 73 ± 1% d_1 naphthalene-*d* with $H_\alpha/H_\beta \approx 0.87$ were obtained. These results show that at least 25% of the reaction is *inter*molecular under both sets of conditions. This is surprising for low-pressure gas-phase reactions and indicates that an appreciable part of the reaction takes place on the quartz surface in the flash pyrolysis experiments. The mechanisms put forward by Alder[6] involve rearrangements in radical adducts of azulene under static conditions. The similarity of our static and flash pyrolytic results demonstrates that Alder's mechanisms can also contribute in our reactions.[16]

In conclusion, several mechanistic pathways appear to contribute to the azulene–naphthalene rearrangement. One of these is the norcaradiene–vinylidene pathway shown in Scheme I. The possible weights of the various pathways cannot be assessed without a detailed knowledge of the mechanism of carbon scrambling in azulene itself.

Jürgen Becker, Curt Wentrup*
Department of Chemistry, University of Marburg
Lahnberge, D-3550 Marburg, West Germany

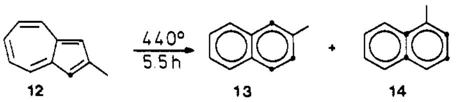
Ellen Katz, Klaus-Peter Zeller*
Department of Organic Chemistry, University of Tübingen
D-7400 Tübingen, West Germany

Received February 21, 1980

---

(15) (a) The photochemical conversion of azulene to naphthalene (quantum yield $\leq 10^{-5}$) has been reported.[15b] The first excited singlet state of azulene (~116 kcal/mol) is near the heat of formation of the transition state for the thermal reaction.[4,13a] (b) J. Olmsted, III, *Mol. Photochem.*, **1**, 331 (1969); M. Comtet and H. D. Mettee, *ibid.*, **2**, 63 (1970).

(16) (a) The vinylidene–acetylene interconversion **7** $\rightleftarrows$ **9** would lead to scrambling of the acetylenic carbon atoms and is thus in excellent agreement with the label distribution in the major product (**13**) of the static pyrolysis[6]



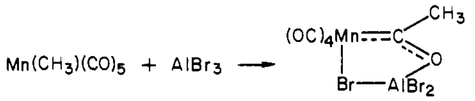
12 13 14

of **12**. However, this mechanism completely fails to explain the minor product (**14**). In general, the norcaradiene–vinylidene mechanism is consistent only with the *major* products obtained in the studies of Alder et al.[4-6] The mechanism is in agreement with the pyrolytic formation of 1,2- and 2,3-dimethylnaphthalenes from 1,2-dimethylazulene.[16b] (b) M. Magon and G. Schröder, *Justus Liebigs Ann. Chem.*, 1379 (1978).

Surface-Induced Alkyl Migration Reactions in Metal Carbonyls

Sir:

The surface chemistry of the reaction between organometallic complexes and such oxides as alumina and silica has provided interesting parallels with homogeneous organometallic chemistry. Initial chemisorptive reaction of the complexes may involve nucleophilic displacement of carbon monoxide by the basic oxide or hydroxide ions of the surface of alumina [for example, in reaction with $Mo(CO)_6$[1]], formation of Lewis acid adducts between the carbonyl oxygen atom and exposed ions of Al^{3+},[2,3] and protonolysis of alkyl or allyl groups in complexes by surface hydroxide ions.[4] In the case of complexes of more electropositive metals in low oxidation states, subsequent activation may liberate hydrogen from surface hydroxide ions with consequent oxidation of the metal atom. In the present research, we investigated the possibility that surface Lewis acid and Lewis base sites could promote the methyl migration reaction in a manner similar to that observed with molecular Lewis acids (eq 1).[5] It will be noted



$$Mn(CH_3)(CO)_5 + AlBr_3 \longrightarrow (OC)_4Mn(Br{-}AlBr_2)C(CH_3){=}O \qquad (1)$$

that $AlBr_3$ displays diphilic properties in this reaction, with the Al serving as a Lewis acid toward the acetyl oxygen and bromide serving as a base toward the Mn atom.

Reactions between metal carbonyls and alumina were monitored by infrared spectroscopy at 25 °C with a Nicolet 7199 FT-IR spectrometer and by analysis of the gases issuing from a microreactor.[1] The infrared spectroscopy was performed on transparent γ-alumina films,[6] onto which a pentane solution of the organometallic complex had been injected. Prior to this injection, the degree of dehydroxylation of the alumina was adjusted by heating the film for 1 h at 500 °C to yield partially dehydroxylated γ-alumina (PDA), the surface of which contained roughly equal proportions of O^{2-}, OH^-, and oxygen vacancies which exposed Al^{3+},[7] or by heating at 1000 °C for 1 h to produce a nearly fully dehydroxylated mixture of γ- and δ-alumina (DA).[6] During the dehydroxylation and the subsequent infrared spectroscopic measurements, a flow of ultrapure helium was maintained through the cell which was sandwiched between two columns of MnO/SiO_2. These served both to protect the sample from oxygen and to detect any leakage of air into the system.[8]

When a pentane solution of $Mn(CH_3)(CO)_5$ or $(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2$ is injected onto PDA or DA, an immediate color

---

(1) A. Brenner and R. L. Burwell, Jr., *J. Catal.*, **52**, 353 (1978).

(2) J. M. Basset, Y. Ben Taarit, J. L. Bilhou, J. Bousquet, R. Mutin, and A. Theolier, *Proc. Int. Congr. Catal., 6th*, **1**, 570 (1977).

(3) D. F. Shriver, *J. Organomet. Chem.*, **94**, 259 (1975).

(4) Yu. I. Yermakov, *Catal. Rev.-Sci. Eng.*, **13**, 77 (1976).

(5) S. B. Butts, E. M. Holt, S. H. Strauss, N. W. Alcock, R. E. Stimson, and D. F. Shriver, *J. Am. Chem. Soc.*, **101**, 5864 (1979).

(6) M. Laniecki and R. L. Burwell, Jr., *J. Colloid. Interface Sci.*, **75**, 95 (1980). The IR cell employed in this work was modified to permit direct injection of a pentane solution of complex onto the alumina film.

(7) J. B. Peri, *J. Phys. Chem.*, 69, 220 (1965).

(8) B. Horvath, R. Moseler, E. G. Horvath, and H. L. Krauss, *Z. Anorg. Allg. Chem.*, **418**, 1 (1975).

0002-7863/80/1502-5112$01.00/0

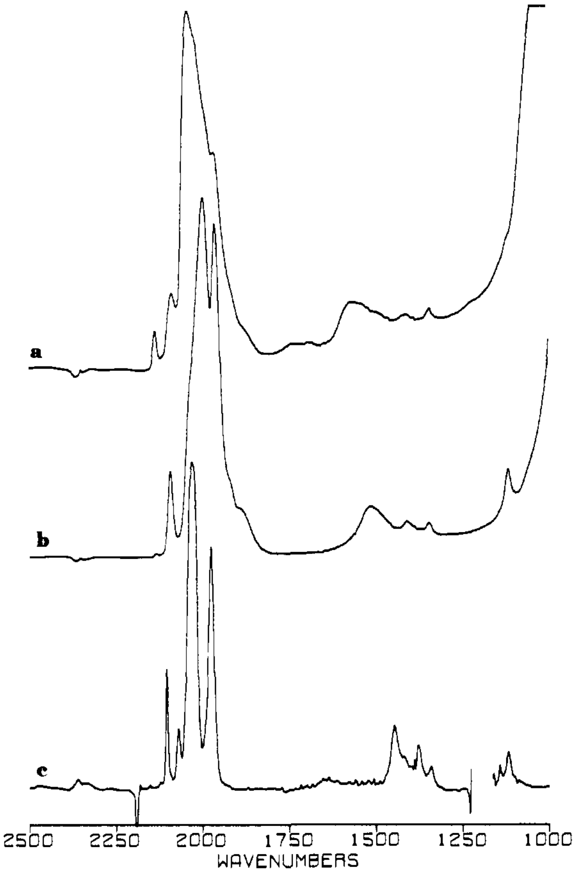
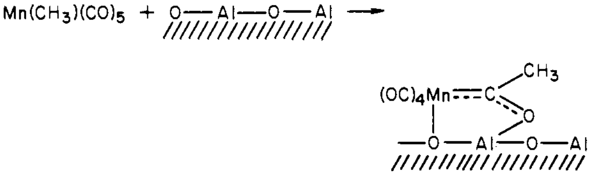


Figure 1. Infrared spectra at room temperature of (a) $\mathrm{Mn[C(O)CH_3](CO)_5}$ on DA, (b) $\mathrm{Mn(CH_3)(CO)_5}$ on DA and (c) molecular adduct $\mathrm{M\overline{n[C(OAlBr}Br_2)CH_3](CO)_4}$ in $\mathrm{CH_2Br_2}$ with solvent spectrum removed by digital subtraction. Spectra a and b when PDA was used were essentially identical with those shown.

change is observed, indicating very fast reaction with the surface. During the several additional minutes required to purge pentane from the surface, no further color change is seen. As shown in Figure 1, the infrared spectrum of $\mathrm{Mn(CH_3)(CO)_5}$ on alumina displays a medium-intensity, low-frequency band in the vicinity of 1510 $\mathrm{cm^{-1}}$ and a shift of the absorptions due to terminal CO stretching to slightly higher frequency. This pattern of frequency shifts is very similar to that seen for the CO insertion reaction induced by a molecular Lewis acid which is depicted in reaction 1.[5] Of particular importance in this comparison is the low-frequency mode which has been assigned to the CO stretch of the acyl oxygen coordinated to an electron acceptor.[5,9] The weaker features which accompany this band on the low-frequency side are also seen in the molecular adducts and presumably arise from $\mathrm{CH_3}$ deformation modes.[5,9]

The amounts of gas liberated during the passage of helium over Mn complexes on alumina at 25 °C were determined. The liberation of CO from $\mathrm{Mn(CH_3)(CO)_5}$ on PDA (CO/Mn liberated was ~0.5 at 0.5 h and 1.0 at 3 h) was distinctly faster than for that on DA (CO/Mn = 0.2 at 0.5 h and 0.4 at 3 h). The liberation of $\mathrm{CH_4}$ from $\mathrm{Mn(CH_3)(CO)_5}$ on PDA corresponded to $\mathrm{CH_4/Mn} \simeq 0.01$ at 3 h and that of $\mathrm{H_2}$ corresponded to $\mathrm{H/Mn} \simeq 0.01$ at 3 h. The $\mathrm{CH_4}$ and $\mathrm{H_2}$ liberations were negligible from the complex on DA, as one would expect since the content in $\mathrm{OH^-}$ is very low on DA. Thus, methyl migration is fast compared to protonolysis of the $\mathrm{CH_3}$ ligand, and negligible oxidation of Mn(I) to Mn(II) occurs at 25 °C. The first infrared spectra obtained after evaporation of pentane were essentially identical for DA and PDA. The spectra changed slowly with time, presumably because of loss of CO. The gas liberation and IR data indicate that the initial adsorption of $\mathrm{Mn(CH_3)(CO)_5}$ involves methyl migration (eq 2).



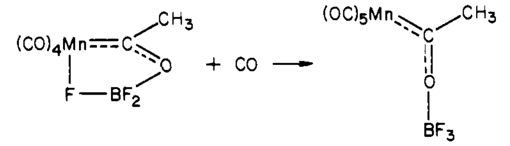
(2)

The similarity between the infrared spectra for the adsorbed species and the molecular species $\mathrm{M\overline{n[C(OAlBr}Br_2)CH_3](CO)_4}$ is evident in Figure *1*.

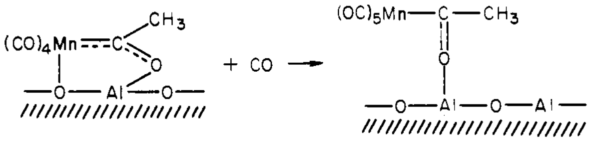
Further evidence for the infrared assignment of surface-bound acetyl was obtained from the spectrum of $\mathrm{Mn[C(O)CH_3](CO)_5}$ adsorbed on PDA and DA, where a band at 1570 ± 10 $\mathrm{cm^{-1}}$ is assigned to the acetyl ligand bound to the surface (Figure 1). Gas-evolution data show that the adduct between the simple acetyl $\mathrm{Mn[C(O)CH_3](CO)_5}$ and the alumina surface evolves CO much more slowly (CO/Mn ratio = 0.2 in 3 h on PDA and 0.3 in 3 h on DA) than does the surface-promoted insertion product shown in eq 2. The similarity between infrared spectra of surface species and molecular complexes is remarkably close. For example, the CO stretch for the acetyl group is 57 $\mathrm{cm^{-1}}$ higher in frequency for $\mathrm{Mn[C(OBF_3)CH_3](CO)_5}$ than for $\mathrm{M\overline{n[C(OBF}F_2)CH_3](CO)_4}$ while the difference in frequency between $\mathrm{Mn[C(O)CH_3](CO)_5 \cdot Al_2O_3}$ and $\mathrm{Mn[C(O)CH_3](CO)_4 \cdot Al_2O_3}$ is ca. 65 $\mathrm{cm^{-1}}$.

The spectrum of $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CH_3)(CO)_2}$ in toluene solution displays two intense bands at 2007 and 1951 $\mathrm{cm^{-1}}$ which represent the symmetric and asymmetric stretches for the two CO ligands. When this compound is adsorbed on PDA or DA, only one strong band remains in the terminal CO stretching region, at 1960 $\mathrm{cm^{-1}}$ with a medium sideband of 2003 $\mathrm{cm^{-1}}$, and a low-frequency feature at ca. 1470 $\mathrm{cm^{-1}}$ (PDA) appears which is characteristic of the surface-coordinated acetyl ligand. Again, the pattern for the strong terminal bands and the frequency shifts is consistent with that of a surface-bound species similar to that shown for the manganese compound in eq 2. As with the manganese system, the infrared spectrum of the acetyl $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)_2[C(O)CH_3]}$ on PDA and DA confirms the nature of the methyl migration product. Thus, as indicated by the immediate color change consequent to adsorption, both PDA and DA promote the methyl migration in the two complexes investigated with the same potency as $\mathrm{AlBr_3}$. The methyl migration reaction so promoted is at least 10^3 times faster for $\mathrm{Mn(CO)_5(CH_3)}$ than the reaction in the presence of CO alone, and $>10^6$ times faster for $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CO)_2(CH_3)}$.

As illustrated in eq 3, cyclic insertion products, which result with molecular Lewis acids, add CO to form Lewis acid adducts of the simple acetyl. This same reaction occurs on an alumina surface, but it is much more sluggish. For example, the CO addition illustrated in eq 3 is nearly complete in 1 h at room temperature and with ca. 0.5 atm of CO. By contrast, reaction 4 on PDA occurs to roughly 40% conversion after 1 h at 100 °C in 1.0 atm of CO. Similarly, the addition of CO to adsorbed $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CH_3)(CO)_2}$ is much slower than for the molecular analogue, $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{F\overline{e(C(OAlBr}Br_2)CO}$.



(3)



(4)

In summary, alumina surfaces greatly increase the rate of the methyl migration reaction in $\mathrm{Mn(CH_3)(CO)_5}$ and $(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Fe(CH_3)(CO)_2}$ to form cyclic addition products (eq 2) for which the surface Lewis acid and base sites are essential. The subsequent uptake of CO is much slower on the alumina surface, eq 4, than

---

(9) R. E. Stimson and D. F. Shriver, *Inorg. Chem.*, **19**, 1141 (1980).

for the analogous molecular reaction, eq 3.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, NATO, and the Ipatieff Fund of Northwestern University.

F. Correa, R. Nakamura, R. E. Stimson
R. L. Burwell, Jr.,* D. F. Shriver*
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

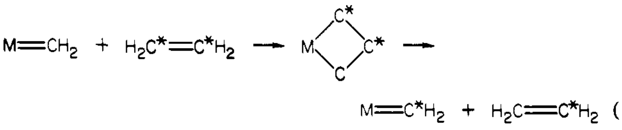
Received April 4, 1980

Mechanism of Metathesis and Epoxidation in Chromium and Molybdenum Complexes Containing Methyl-Oxo Bonds

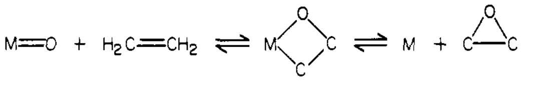
Sir:

Transition-metal metallocycle complexes are recognized as crucial intermediates in a variety of homogeneous and heterogeneous catalytic processes. There is no doubt that metallocycles[1] are intermediates in such reactions as olefin metathesis,[2] epoxidation,[3] and deepoxidation;[4] however, even a qualitative understanding of the energetics of their formation and decomposition is lacking. In this communication, we use the results of ab initio theoretical studies to examine the thermochemistry and mechanism for epoxidation and metathesis of olefins by Cr and Mo complexes. As described below, the theoretical calculations are ab initio (including the core electrons of the Cr and Mo), using a good basis set and including electron correlation [generalized valence bond (GVB) and configuration interaction (CI)].

Consider Scheme I. If X is a carbene (and M = Mo or W), the energetics are of relevance to the Herrison-Chauvin mechanism[2] for olefin metathesis (eq 1). If X is an oxo group, the

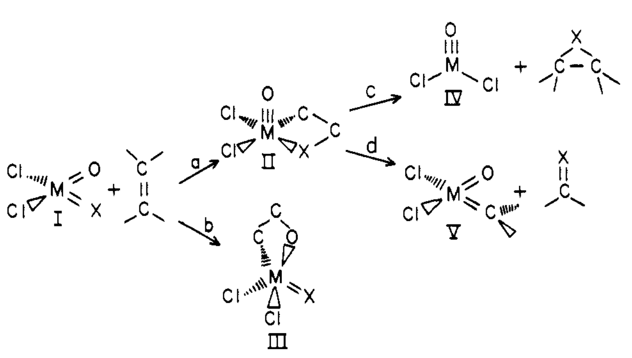

(1)

energetics are relevant for olefin epoxidation and deepoxidation. Indeed, Sharpless and co-workers have suggested that olefin epoxidation by chromyl chloride[3] (Cl_2CrO_2) might occur by the forward reaction (eq 2) and that deepoxidation[4] might occur by the reverse reaction.


(2)

Using energy changes from extensive ab initio calculations and estimated zero-point vibrational energies, we obtained ΔH for these steps at 0 K. Using standard methods[5] and analogy to similar systems, we estimated the ΔS for 25 °C and corrected ΔH from 0 K to 25 °C to obtain ΔG at 25 °C (most reactions are run at this temperature or lower).

Scheme I



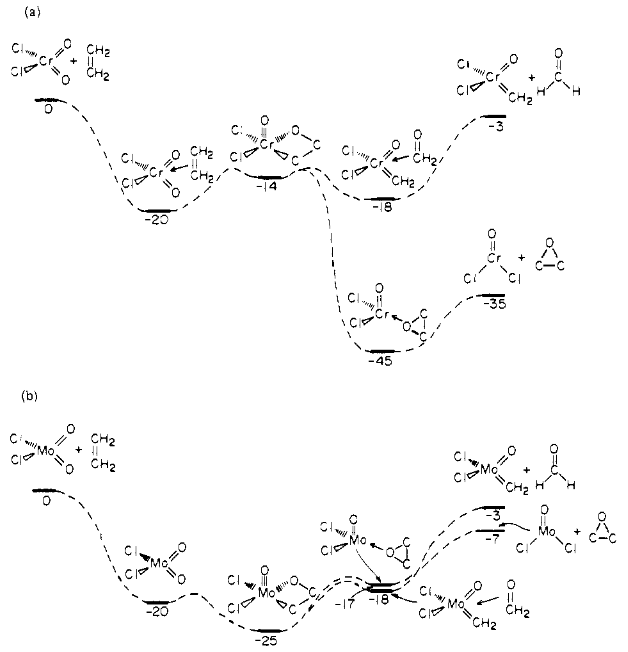


Figure 1. Schematic potential curves for (a) the reaction of Cl_2CrO_2 with C_2H_4 and (b) the reaction of Cl_2MoO_2 with C_2H_4 (energy in kcal/mol).

The energetics[6] of these two processes for Cr are shown in Figures 1a and 2a, and relevant observations are described below. First, the metal-oxo bond is very different for Cl_2R_2CrO and Cl_2CrO_2. We find that the metal-oxygen bond of Cl_4CrO (and the metallocyclic species II) is essentially a triple bond (analogous to the bond in $C{\equiv}O$) whereas the metal-oxygen bonds in Cl_2CrO_2 are double bonds (analogous to the C—O bond in O=C=O or a ketone). The origins of this effect will be discussed in detail elsewhere, but basically, $Cl_4Cr{\equiv}O$ has available two low-lying, singly occupied d orbitals that can participate in π bonds to the same oxygen whereas in Cl_2CrO_2 the corresponding orbitals are each involved in a single π bond to different oxygens. The result is that the oxo bond in $Cl_4Cr{\equiv}O$ is 31 kcal stronger than an oxo bond in Cl_2CrO_2 (82 vs. 51 kcal, respectively). Similarly, the oxo bond in the metallocycle II is a triple bond, and hence the second oxo group in I is not a spectator but actually drives the formation of the metallocycle. Secondly, bond energies for the oxo bond in Cl_2CrO_2 and the carbene bond in Cl_2CrOCH_2 are similar[7] (51 and 48 kcal, respectively), thus explaining the extraordinary

---

(1) (a) P. Schlodder, J. A. Ibers, M. Lenarda, and M. Graziani, *J. Am. Chem. Soc.*, **96**, 6893 (1974); (b) R. H. Grubbs and A. Miyashita, *Fundam. Res. Homogeneous Catal.*, **2**, 207 (1977); (c) R. H. Grubbs and A. Miyashita, *J. Am. Chem. Soc.*, **100**, 1300 (1978); (d) S. J. McLain and R. R. Schrock, *ibid.*, **100**, 1315 (1978); (e) I. M. Al-Najjar, M. Green, S. J. S. Kerrison, and P. J. Sadler, *J. Chem. Soc., Chem. Commun.*, 311 (1979).

(2) (a) J. L. Herisson and Y. Chauvin, *Makromol. Chem.*, **141**, 161 (1970); (b) M. T. Mocella, R. Rovner, and E. L. Muetterties, *J. Am. Chem. Soc.*, **98**, 4689 (1976); (c) R. H. Grubbs, *Prog. Inorg. Chem.*, **24**, 1 (1978); (d) N. Calderon, J. P. Lawrence, and E. A. Ofstead, *Adv. Organomet. Chem.*, **17**, 449 (1979).

(3) K. B. Sharpless, A. Y. Teranishi, and J. E. Bäckvall, *J. Am. Chem. Soc.*, **99**, 3120 (1977).

(4) K. B. Sharpless, M. A. Umbreit, M. T. Nieh, and T. C. Flood, *J. Am. Chem. Soc.*, **94**, 6538 (1972).

(5) S. W. Benson, "Thermochemical Kinetics", Wiley, New York, 1976.

(6) (a) The relevant heats of formation at 300 K are $Cl_2CrO_2 = -123.9$,[10] $Cl_2OCrCH_2 = -87.7$, $Cl_2OCrC_2H_4O = -137.9$, $Cl_2OCrC_3H_6 = -98.4$, and $Cl_2CrO = -132.5$ kcal/mol. The energetics for the π complexes were estimated from related experimental energetics. (b) The energetics for the Cl_2MoO_2, Cl_2MoOCH_2, and related compounds are estimated from Cl_2MoO_2 and relevant chromium compounds.

(7) This should be compared with the 6-kcal difference in bond energy between $H_2C{=}O$ and $H_2C{=}CH_2$ (179 and 173 kcal, respectively).