rically to the triangular face, with a 24° tilt of the least-squares line through the CCO relative to the perpendicular to the metal triangle. The CCO is more nearly perpendicular in the CoFe$_2$ compound than in the Fe$_3$ analogue, III, where a 33.5° tilt is observed. In both structures the CCO ligand tilts toward the metal atom to which the α-carbon of CCO displays the longest distance. Metal replacement reactions similar to that in eq 4 have been observed for several different clusters containing a capping ligand.[16,17] In comparison to these other examples of metal substitution, the reaction observed here is unusually facile.

Compound VI displays a reactivity pattern which is similar to that of the one other anionic ketenylidene, III. Thus protonation generates a methylidyne with simultaneous migration of the ketenylidene CO into a bridging position on the metal framework.[18] The mononegative iron–cobalt cluster, VI, is significantly less reactive than the dinegative Fe$_3$ cluster, III. For example, it shows no reaction with CH$_3$I nor is there any apparent reaction with excess Co$_2$(CO)$_8$ overnight at room temperature.

In summary, the present work provides the first examples of mixed-metal exposed carbide clusters and the first example of a mixed-metal ketenylidene. These were prepared by cluster building and metal substitution reactions on [Fe$_3$(CO)$_9$(CCO)]$^{2-}$. Similar reactions between III and labile transition-metal organometallics are likely to yield a broad class of clusters which have reactive carbon ligands.

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Registry No. II, 74792-04-4; III, 87698-62-2; IVa·2PPN, 88669-42-5; IVb·2PPN, 88657-60-7; IVb·2AsPh$_4$, 88657-61-8; V, 88657-62-9; VI·PPN, 88657-64-1; Fe$_2$(CO)$_9$, 15321-51-4; Cr(CO)$_3$(NCCH$_3$)$_3$, 16800-46-7; W(CO)$_3$(NCCH$_3$)$_3$, 16800-47-8; [HFe$_3$W(CO)$_{13}$C]$^-$, 88657-65-2; Co$_2$(CO)$_8$, 10210-68-1; CoFe$_2$(CO)$_{10}$(CH), 88657-66-3.

Supplementary Material Available: Complete listings of positional parameters, anisotropic thermal parameters, bond angles, bond distances, and observed and calculated structure factors for [PPN][Fe$_2$Co(CO)$_9$(CCO)] and [AsPh$_4$]$_2$[Fe$_3$WC(CO)$_{13}$] (115 pages). Ordering information is given on any current masthead page.

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[18] For [CoFe$_2$(CO)$_{10}$CH]: IR ν_{CO}(hexane) 2051 (vs), 2035 (s), 2013 (m), 1864 (m), 1853 (m) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$ −90 °C) 12.72 ppm; ^{13}C NMR 269.8 (1), 250.3 (1), 207.3 (6), 200.0 (3) (J_{C-H} = 170.5 Hz) ppm.

Oxidation of Alkenes by d^0 Transition-Metal Oxo Species: A Mechanism for the Oxidation of Ethylene by a Dioxochromium(VI) Complex in the Gas Phase

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Summary: Reaction of ClCrO$_2^+$ with ethylene in a selected ion flow tube gives product ions deriving both from oxygen transfer and from cleavage of the alkene. The results are interpreted in terms of the Sharpless–Goddard–Rappê mechanism of oxidation of alkenes by Cl$_2$CrO$_2$ involving oxametallacyclobutane formation followed by reductive elimination of an epoxide (oxygen transfer) or metathesis to give formaldehyde and a Cr(VI)–oxo carbene (cleavage).

Oxidation of alkenes by d^0 transition-metal oxo species such as OsO$_4$, RuO$_4$, MnO$_4^-$, and Cr(VI) oxo complexes is of central importance in preparative organic chemistry. Since the relatively recent proposal by Sharpless[2] that metal–carbon bonded intermediates may be involved in these reactions, considerable interest in the mechanism of oxidation of alkenes by these high-valence oxo complexes has also been generated. Chromium oxo oxidation of alkenes gains a special significance in this regard, since the study of reactions of this type has a particularly long history, and the chemistry evidenced is very rich indeed.[2–4]

An understanding of the mechanism of oxidation of alkenes by Cr(VI) oxo species is hindered by the fact that diverse solvents and ligands have been utilized in the various experimental studies reported, and these factors can have a dramatic effect on the course of the reaction. In order to gain a better insight into the intrinsic reactivity of chromium dioxo species with alkenes we undertook a study of the reactions of some chromium oxo cations with ethylene and oxirane in the gas phase.[5] This work represents to our knowledge the first gas phase study of the reactions of any high-valence metal oxo species with alkenes.

Electron impact on chromyl chloride (95 eV) in the low-pressure source of a selected ion flow tube (SIFT) gives large quantities of Cr$^+$, CrO$_2^+$, ClCrO$^+$, and ClCrO$_2^+$. The SIFT technique allows clean injection of any one of these ions into the flow tube for the study of its reactions with neutral reagents. In particular, ClCrO$_2^+$ reacts very rapidly with ethylene to give two product ions resulting from oxygen transfer (C$_2$H$_3$O$^+$, 75%, and ClCrO$^+$, 12%) and one product containing both chromium and carbon (ClCrOCH$_2^+$, 13%).[6]

The mechanistic questions surrounding the reaction of Cr(VI) oxo species with alkenes seem to focus on the topology of the important intermediates or transition states. Specifically, experimental work by Sharpless[2] and very recently by Kochi[4] indicates that a primary process in the oxidation of alkenes by X$_2$CrO$_2$ (X = Cl or ONO$_2$) in solution is formation of the epoxide with retention of configuration. While even the oxidation state of the metal in the oxidant is controversial,[4] an exceedingly interesting mechanistic question, which extends to many oxidation processes, is well illustrated by the mechanistic proposals shown in Schemes I and II for the oxidation of ethylene by ClCrO$_2^+$ (1).

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[1] Alfred P. Sloan Foundation Fellow, 1982–1984. Camille and Henry Dreyfus Teacher–Scholar, 1983–1985.

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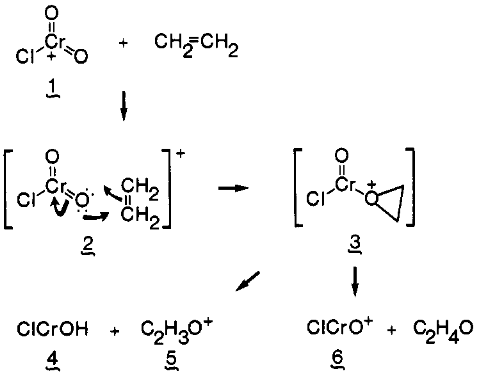
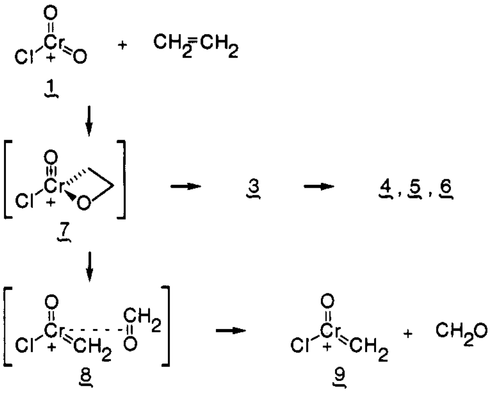
[6] A single measurement of the rate constant for this reaction gave $k = 1 \times 10^{-9}$ cm^3 particle^{-1} s^{-1}. Stevens and Beauchamp (Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 6449–6450) have observed products analogous to ClCrO$^+$ and ClCrOCH$_2^+$ in the reaction of MnO$^+$, a d^4 species, with ethylene.

0276-7333/84/2303-0498$01.50/0

Scheme I



Scheme II



Thus, as shown in Scheme I, the $C_2H_3O^+$ (**5**) and $ClCrO^+$ (**6**) ions may derive from a "classical" direct oxygen transfer to the alkene, affording the complex **3** via an intermediate or transition state represented by structure **2**. Hydride transfer in **3** may then give the chromium hydride species **4** and the major observed ion **5**. Alternatively, dissociation of C_2H_4O from complex **3** would give the Cr(IV) oxo species **6**. Experimentally, the pathway leading from **6** and oxirane to the ion **5** is established, since oxirane reacts rapidly[7] with $ClCrO^+$ (**6**) in the flow tube to give $C_2H_3O^+$ (**5**) as the only observed ionic product. This scheme, however, does not readily explain the formation of the carbon-containing ionic product.

A topologically distinct mechanistic framework in which carbon–metal-bonded intermediates are involved is shown in Scheme II. Thus, on the basis of the elegant speculations of Sharpless and the pioneering theoretical work of Goddard and Rappê,[8] epoxide may derive from initial stereospecific insertion of the alkene into an oxo bond in a formal 2 + 2 process to give the oxametallacyclobutane **7**.[9] In structure **7**, the "spectator oxo" bond is drawn as a triple bond analogous to the CO bond in carbon monoxide, according to the Goddard–Rappê theory. A reductive elimination with retention of configuration then results in the Cr(IV) complex **3**. However, the ion **7** may fragment in an alternative manner by retro "2 + 2" to afford the complex **8**. Loss of formaldehyde would then give the chromium oxo carbene species **9**. The latter mechanism links the Cr oxo oxidation of alkenes with the mechanistically and commercially important olefin metathesis process,[10] which is known to involve d^0 oxo carbene complexes of tungsten and molybdenum exactly analogous to complex **9**, at least in some cases.[11]

While other interpretations of these data are certainly possible, we believe that the observed agreement with the theoretical predictions of Goddard and Rappê argues in favor of the mechanism shown in Scheme II. It must be pointed out that if the Goddard–Rappê calculations are basically correct, then the gas-phase chemistry of $ClCrO_2^+$ in the SIFT is an excellent model, since the CrX bonds of X_2CrO_2 species are expected to be highly ionic and the theory applies to reactions of gas-phase species at room temperature.

Thus, in the reaction of $ClCrO_2^+$ with ethylene, both oxygen transfer and cleavage are indeed observed, with the primary channel for reaction being oxygen transfer and a minor channel being cleavage, as predicted by Goddard and Rappê. Further studies aimed at experimental verification of the structure of the ion **9** and at exploration of the reactivity of other d^0 transition-metal oxo species in the gas phase are under way.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grants CHE 82-03110 (C.H.D. and V.M.B.) and CHE 80-11391 (D.M.W.)) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. 1, 88610-58-6; 6, 88610-59-7; ethylene, 74-85-1; oxirane, 75-21-8.

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(7) $k = 1 \times 10^{-9}$ cm^3 particle^{-1} s^{-1} (one determination).

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Stereochemically Nonrigid Molybdenum Alkyne Complexes Studied by 2-D NMR Spectroscopy

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Summary: Intramolecular exchange processes in the molybdenum complexes $[Mo(CO)(HC{\equiv}CR)_2(Cp)]^+$ (R = *t*-Bu, Ph, CO_2Me, Me) were studied by using 2-D NMR exchange techniques in which kinetic parameters for the two independent alkyne rotations are derived from the intensities of the off-diagonal cross peaks. The exchange rates were largely governed by the steric bulk of the alkyne ligands. The 2-D NMR technique was very effective for thermally sensitive compounds in slow exchange.

Two-dimensional NMR spectroscopy[1] provides an elegant new technique for the study of chemical exchange which has not been previously applied to organo-

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