

Connectivity and Reactivity of Gaseous $\text{CrC}_3\text{H}_4\text{O}^+$

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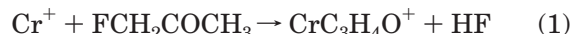
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Gaseous $\text{CrC}_3\text{H}_4\text{O}^+$ is prepared by reaction of Cr^+ with monofluoroacetone and investigated by means of Fourier transform ion-cyclotron resonance mass spectrometry. $\text{CrC}_3\text{H}_4\text{O}^+$ only slowly dehydrogenates alkanes larger than propane, but efficiently reacts with alkenes to afford dehydrogenation, ligand loss, and C–C bond cleavage. These reactions can be explained by assuming the metal carbene structure **1** for $\text{CrC}_3\text{H}_4\text{O}^+$, which reacts with alkenes by an initial [2+2] cycloaddition. Consecutive cycloreversion results in metathesis products that undergo alkylidene-olefin conversion and elimination of the C–C cleaved fragments. For allene, the corresponding vinylidene-acetylene transformation appears to be particularly favorable. In addition, the experimental findings suggest the occurrence of initial hetero-Diels–Alder reactions that involve the carbonyl group of **1**. At elevated energies, such as upon complexation by benzene, **1** can rearrange to form the chromaoxacyclobutene **2** and eliminate propyne.

1. Introduction

Since the first synthesis and description of a metal carbene complex by Fischer and Maasböl in 1964,¹ the chemistry of this intriguing class of compounds has experienced a tremendous rise. Today, metal carbenes form an essential component of organometallic chemistry with applications, inter alia, in olefin polymerization,^{2,3} olefin metathesis,^{4–7} benzoannulation,⁸ and cyclopropanation reactions.⁹ The strong interest in these compounds is also reflected in numerous gas-phase studies. Probing the reactivities of metal carbenes in the gas phase excludes the complicating effects of additional ligands, solvents, counterions, etc., and thereby promises to reveal mechanistic details not easily accessible by other methods. Whereas earlier work focused on simple metal-methylidene species,^{10–17} recent studies have also investigated much more complex carbenes. Thus, realistic gas-phase models for important chemical reactions occurring in solution have been established.^{18–21}

Recently, our group has reported a possible further example of a more complex transition-metal carbene generated in the gas phase. Upon reaction with gaseous Cr^+ , monofluoroacetone loses HF and forms $\text{CrC}_3\text{H}_4\text{O}^+$, reaction 1.²²



Most likely, this process corresponds to a 1,1 elimination, producing the chromium carbene **1** (Scheme 1). Presumably, this species is stabilized by a dative bond between the oxygen atom and the metal cation. This interaction might even lead to an electrocyclic ring closure and formation of the chromaoxacyclobutene **2**, eventually followed by a shift of the double bond to generate **3**.²² Note, however, that the latter species with the double bond in *exo*-position might be thermochemically less favorable than **2**.

Support for the involvement of **2** (and possibly also **3**) comes from collision-induced dissociation (CID) experiments. Upon CID, $\text{CrC}_3\text{H}_4\text{O}^+$ does not lose $\text{C}_3\text{H}_4\text{O}$ only, reaction 2a, but roughly equal amounts of C_3H_4 as well, reaction 2b. The latter process corresponds to an elimination of CrO^+ from **2** (or **3**) with propyne as

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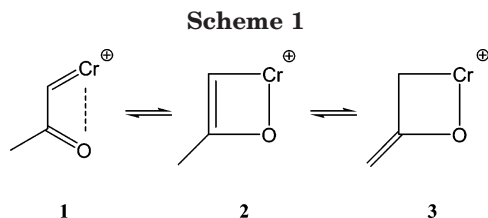
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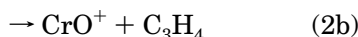
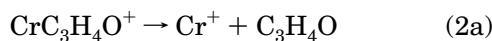
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neutral product (or allene for **3**).²²



The present study aims at a further characterization of $\text{CrC}_3\text{H}_4\text{O}^+$ formed in reaction 1. To this end, the reactions of $\text{CrC}_3\text{H}_4\text{O}^+$ with hydrogen, alkanes, olefins, and other unsaturated hydrocarbons are probed. The evolving patterns in reactivity can then be compared to the behavior of several reference systems such as metal methylidenes, CrO^+ , and Cr^+ . Observed trends in reactivity should correlate with structural similarities and may thus help to confirm or disprove the connectivities suggested for $\text{CrC}_3\text{H}_4\text{O}^+$.

2. Experimental Section

The Spectrospin CMS 47X FT-ICR mass spectrometer employed has been described in detail before.^{23–25} Briefly, Cr^+ ions are generated by focusing the second harmonic of a pulsed Nd:YAG laser onto a rotating chromium target. A system of electrostatic lenses then transfers the Cr^+ ions into the analyzer cell, where they are trapped in the field of a 7.05 T superconducting magnet. After mass selection²⁶ of the $^{52}\text{Cr}^+$ isotope and thermalization by an argon pulse, Cr^+ is allowed to react with pulsed-in monofluoroacetone (**note of caution**: monofluoroacetone is very toxic and should only be handled with appropriate safety precautions). Mass selection of $\text{CrC}_3\text{H}_4\text{O}^+$ concludes the gas-phase synthesis.

$\text{CrC}_3\text{H}_4\text{O}^+$ is then exposed to the neutral reactants at pressures $p \approx 1 \times 10^{-8}$ – 10^{-6} mbar. The identities of the product ions formed are established by measuring their exact m/z ratios in the instrument's high-resolution mode. From the decline of reactant $\text{CrC}_3\text{H}_4\text{O}^+$ and the rise of the product ions in time, bimolecular rate constants k are derived on the basis of the pseudo-first-order kinetic approximation. The data are corrected for contributions of consecutive products resulting from the known reactions of $\text{CrC}_3\text{H}_4\text{O}^+$ with residual traces of the pulsed-in monofluoroacetone.²⁷ The absolute error of the rate constants reported is estimated at 30%.²⁸ Reaction efficiencies $\varphi \equiv k/k_{\text{cap}}$ are calculated according to capture theory.²⁹

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(27) The absolute amount of these unwanted consecutive products could be minimized by increasing the time delay between the monofluoroacetone pulse and the mass selection of $\text{CrC}_3\text{H}_4\text{O}^+$. However, a too long delay is not suitable either, because it leads to loss of $\text{CrC}_3\text{H}_4\text{O}^+$ by reaction with the constantly leaked-in neutral reactant. As a tradeoff, delay times of 3–4 s were chosen.

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For CID experiments, the ions of interest are mass-selected, kinetically excited, and collided with pulsed-in argon. In a few cases, the reactivity of a primary product ion toward a second substrate is probed. To this end, the primary product ion is mass-selected before its reactions with the second substrate (pulsed-in or admitted to the ICR cell simultaneously with the first neutral reactant) are investigated.

3. Results and Discussion

3.1. Reactions with H_2 and Alkanes. $\text{CrC}_3\text{H}_4\text{O}^+$ shows no appreciable reactivity toward H_2 , ethane, and propane. With *n*-butane, isobutane, and cyclohexane, only dehydrogenation of the alkane occurs to afford $\text{CrC}_3\text{H}_6\text{O}^+$ and the corresponding alkene (Table 1). The relative reaction efficiencies observed, $\varphi(\text{propane}) < \varphi(\text{isobutane}) < \varphi(n\text{-butane}) < \varphi(\text{cyclohexane})$, do not strictly follow the trend one would expect on the basis of C–H bond dissociation energies.³⁰ Apparently, other factors such as steric hindrance are important as well.

In contrast to $\text{CrC}_3\text{H}_4\text{O}^+$, bare Cr^+ does not react with alkanes at thermal energies.³¹ The well-known poor reactivity of Cr^+ can be ascribed to the isotropic electron density of its half-filled 3d shell and the spin-forbidden nature of oxidative additions to Cr^+ in its ^6S ground state.^{31,32} Therefore, the distinct behavior observed for $\text{CrC}_3\text{H}_4\text{O}^+$ is a clear indication that the organic fragment in this complex strongly influences the electronic situation at the metal center. Such a strong interaction points to a covalent bond between Cr^+ and the $\text{C}_3\text{H}_4\text{O}$ moiety, rather than to a merely coordinative binding as in the complex $\text{Cr}^+(\text{C}_3\text{H}_4\text{O})$. Possible structures for covalently bound $\text{CrC}_3\text{H}_4\text{O}^+$ are the carbene species **1** and the metallacycle **2** (as well as **3**). As bare CrO^+ is known to dehydrogenate alkanes,³³ involvement of $\text{CrO}^+(\text{C}_3\text{H}_4)$ has to be considered as well. In analogy with the case of CrO^+ ,³³ $\text{CrO}^+(\text{C}_3\text{H}_4)$ should yield the aqua complex $(\text{H}_2\text{O})\text{Cr}^+(\text{C}_3\text{H}_4)$ upon reaction with alkanes.

In contrast, a different product structure is supposed to evolve for the carbene reactant **1**. In the first step, the chromium atom inserts into a C–H bond of the alkane, Scheme 2. Subsequent hydride migration onto the alkylidene leads to the insertion species **4**, which can undergo a β -H elimination; β -H eliminations arguably constitute the most characteristic reaction type for metal-alkyl compounds with β -hydrogen atoms in general³⁴ and for the corresponding gaseous cations in particular.³⁵ The resulting energized complex **5** then loses its olefin ligand and undergoes reductive elimination to yield the chromium acetone complex **6**. The same product results if the cyclic structure **2** is assumed for reactant $\text{CrC}_3\text{H}_4\text{O}^+$, Scheme 2. Here, the alkane first adds to the chromium–oxygen single bond, the orientation suggested in Scheme 2 corresponding to that observed for the addition of alkanes to CrO^+ .³³ After β -H elimination and reductive elimination, the enol complex **7** is formed, which can tautomerize to **6**. Alternatively,

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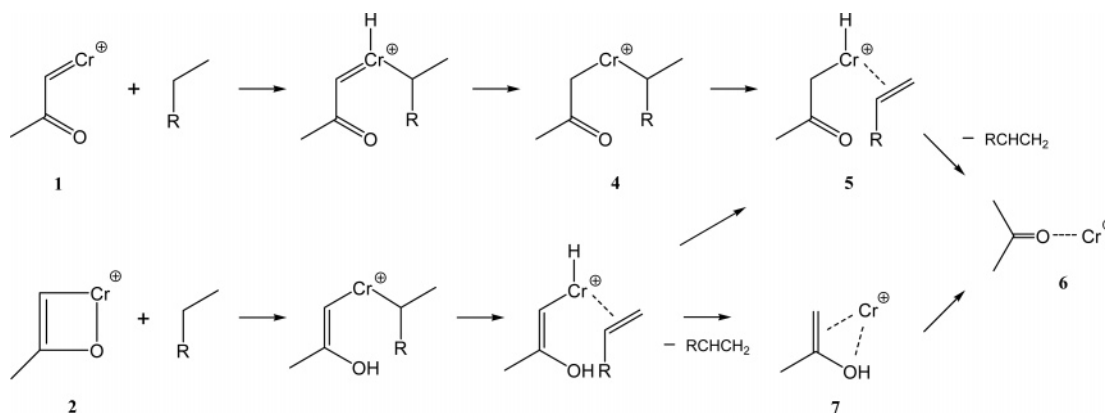
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Table 1. Overall Efficiencies φ and Branchings Ratios (in %) for the Different Product Channels of the Reactions of $\text{CrC}_3\text{H}_4\text{O}^+$ with Hydrocarbons (only the ionic products are given)^a

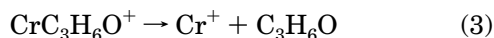
	<i>n</i> -C ₄ H ₁₀	<i>i</i> -C ₄ H ₁₀	<i>c</i> -C ₆ H ₁₂	C ₂ H ₄	C ₃ H ₆	1-C ₄ H ₈	2- <i>E</i> -C ₄ H ₈	2- <i>Z</i> -C ₄ H ₈	<i>i</i> -C ₄ H ₈	allene	1,3-butadiene	C ₆ H ₆
φ	0.007	0.002	0.08	0.25	0.31	0.45	0.32	0.31	0.39	0.38	0.67	0.56 ^b
Cr ⁺				92 ± 3	12 ± 3					17 ± 2	15 ± 2	
CrC ₃ H ₆ O ⁺	100	100	100			5 ± 1	11 ± 3	13 ± 2	5 ± 2		10 ± 2	
CrC ₄ H ₆ O ⁺					11 ± 3	20 ± 3	3 ± 1	3 ± 1	9 ± 3	81 ± 2	3 ± 1	
CrC ₅ H ₆ O ⁺				8 ± 3		10 ± 3	2 ± 1	4 ± 1			45 ± 7	
CrC ₅ H ₈ O ⁺						19 ± 2	12 ± 3	10 ± 2	2 ± 1		4 ± 1	
CrC ₆ H ₆ O ⁺										2 ± 1	4 ± 1	100
CrC ₆ H ₈ O ⁺											4 ± 1	
CrC ₆ H ₈ O ⁺					77 ± 5	6 ± 1	4 ± 1	8 ± 2	20 ± 3			
CrC ₇ H ₈ O ⁺									17 ± 6 ^c			
CrC ₇ H ₈ O ⁺									7 ± 2		15 ± 2	
CrC ₇ H ₁₀ O ⁺						40 ± 8	68 ± 7	62 ± 5	40 ± 8			

^a Only product channels with b.r. ≥ 2% are included. ^b Value given refers to C₆D₆. ^c Quantitative analysis is complicated due to an isobaric interference between CrC₇H₈O⁺ and CrC₃H₅FO₂⁺, which is formed as a byproduct upon reaction of CrC₃H₄O⁺ with residual monofluoroacetone (see Experimental Section for details).

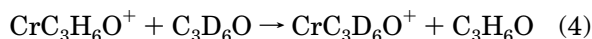
Scheme 2

the tautomerization can occur prior to the reductive elimination, thus yielding complex **5** and, finally, **6** as well. Note that also for **3** as reactant ion an analogous reaction sequence leads to the acetone-chromium complex **6**, which Freiser and co-workers assumed as the energetic minimum for CrC₃H₆O⁺.³⁶

To discriminate between the two possible alternatives for product CrC₃H₆O⁺, a (H₂O)Cr⁺(C₃H₄) species on one hand or the chromium acetone complex **6** on the other, two further experiments were performed. First, CID of CrC₃H₆O⁺ generated from CrC₃H₄O⁺ and *n*-butane was found to solely yield Cr⁺ as ionic fragment over a range of collision energies, reaction 3.



This behavior is not consistent with a (H₂O)Cr⁺(C₃H₄) structure for which sequential ligand losses are expected at low collision energies. Moreover, reaction of CrC₃H₆O⁺ with *d*₆-acetone leads to ligand exchange, reaction 4 (along with formation of protonated *d*₆-acetone and addition products).



These findings provide strong evidence for the formation of a chromium acetone complex **6** upon dehydrogenation of *n*-butane by CrC₃H₄O⁺. Accordingly, a CrO⁺(C₃H₄) structure can be discarded for the reactant ion, whereas

the metal carbene **1** and the metallacycle **2** (or **3**) remain as viable alternatives.

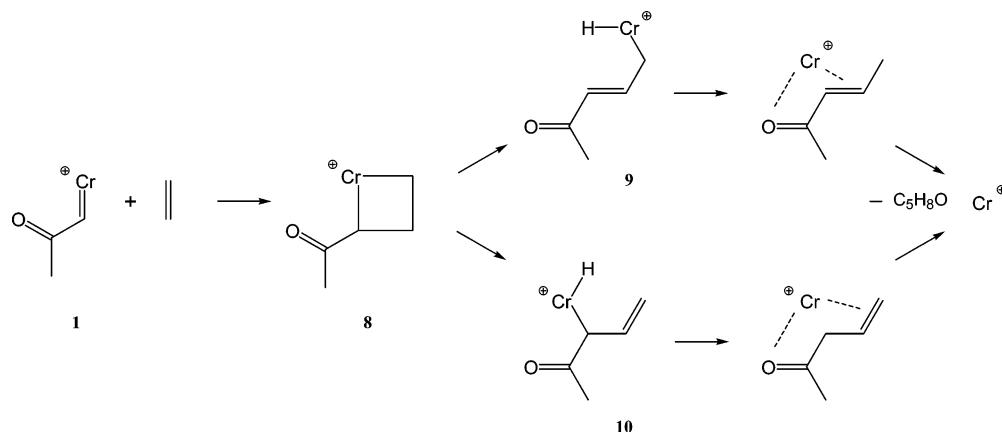
Remarkably, the mechanistic scenario outlined for alkane dehydrogenation by the chromium carbene **1** in Scheme 2 parallels suggestions of Freiser and Jacobson for the reactions of FeCH₂⁺ and CoCH₂⁺ with linear alkanes, although the product distributions found in their study contrast with the present observations.¹⁴ The solution of this seeming contradiction lies in the difference of the alkylidene ligands probed in both experiments. After transfer of two hydrogen atoms onto the methylene moiety of MCH₂⁺, M = Fe and Co, (alkene)M⁺(CH₄) complexes are formed in analogy with species **5** in Scheme 2.¹⁴ Whereas the former lose the only weakly bound CH₄, the corresponding expulsion of acetone does not occur for complex **5**, where the oxygen atom can interact with the metal center. The elimination of the olefin observed instead reflects its lower binding energy compared to acetone, *D*₀(Cr⁺-C₂H₄) = 96 ± 11 (as an estimate for the unknown *D*₀(Cr⁺-C₄H₈)³⁷ versus *D*₀(Cr⁺-C₃H₆O) = 176 ± 14 kJ mol⁻¹.³⁶ Other processes observed for FeCH₂⁺ and CoCH₂⁺ involve C-C cleavage of the alkane and have no counterparts in the reactions of CrC₃H₄O⁺.¹⁴ This difference indicates that the nature of not only the alkylidene ligands but also the metal center matters, as one might expect.

3.2. Reactions with Alkenes. CrC₃H₄O⁺ reacts with alkenes much more efficiently than with alkanes (Table 1). This observation is not surprising because alkenes

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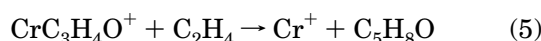
(37) Sievers, M. R.; Jarvis, L. M.; Armentrout, P. B. *J. Am. Chem. Soc.* **1998**, *120*, 1891.

Scheme 3



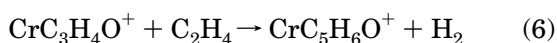
can form much stronger interactions with the cationic metal center than saturated hydrocarbons, thereby increasing the lifetimes of the initial encounter complexes and providing larger amounts of internal energy for the surpassing of activation barriers. As a result, a rather complex chemistry evolves. Again, this behavior is in marked contrast to that of bare ground-state Cr^+ , which does not react with small alkenes at thermal energies.³¹

Ethene. For ethene, the predominant process yields bare Cr^+ as ionic product, reaction 5, implying a rearrangement of bonds that involves the $\text{C}_3\text{H}_4\text{O}$ fragment of the ionic reactant.



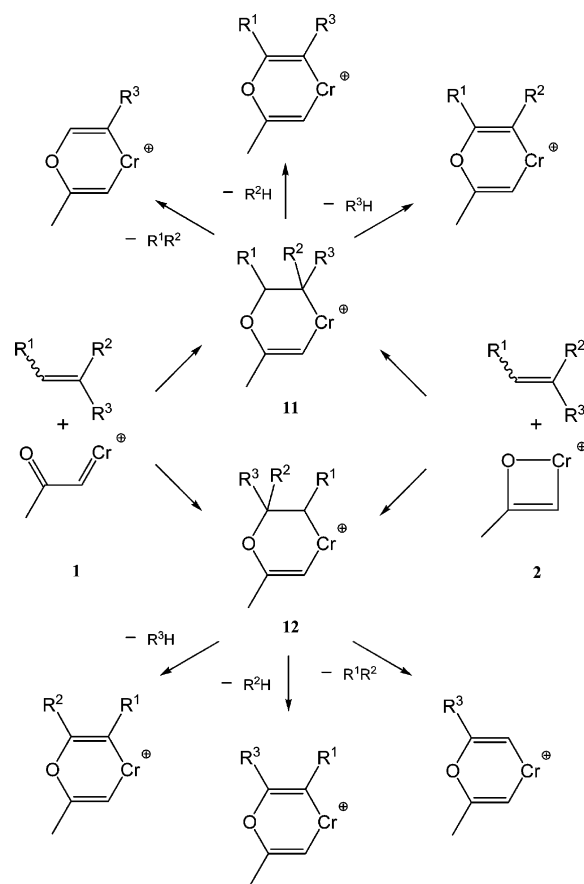
Given the strength of vinylic C–H bonds and the relatively low reactivity of $\text{CrC}_3\text{H}_4\text{O}^+$ toward alkanes, initial insertion of the metal center into one of the C–H bonds of ethene seems unlikely. Rather, the metal carbene structure **1** is suggested to undergo direct coupling in terms of a [2+2] cycloaddition (Scheme 3); analogous processes have been established for the reactions of MnCH_2^+ ,¹¹ FeCH_2^+ , and CoCH_2^+ with olefins.¹³ The resulting metallacycle **8** then has two options for a β -H elimination, generating species **9** or **10**, respectively. Presumably, formation of **9** prevails because its newly formed double bond and the carbonyl double bond are in energetically favorable conjugation. After reductive elimination, the reaction exothermicity leads to the expulsion of the organic ligands. Note that breaking the bonds between the bifunctional ligands and the metal center demands considerable amounts of energy, which have to be provided by the coupling reaction. In total, one new C–C single bond is formed at the expense of the chromium–alkylidene bond. A simple comparison of chromium–alkylidene bond-dissociation energies, $D_0(\text{Cr}^+-\text{CR}_2) \approx 150 \text{ kJ mol}^{-1}$,³⁸ and typical strengths of C–C single bonds, $D_0 \approx 350 \text{ kJ mol}^{-1}$,³⁰ demonstrates that generation of $\text{Cr}^+(\text{C}_5\text{H}_8\text{O})$ should be indeed quite exothermic.

A second product channel yields loss of H_2 (reaction 6).



One possible rationalization for this process might be hydrogen elimination from the [2+2] adduct **8**. However,

Scheme 4



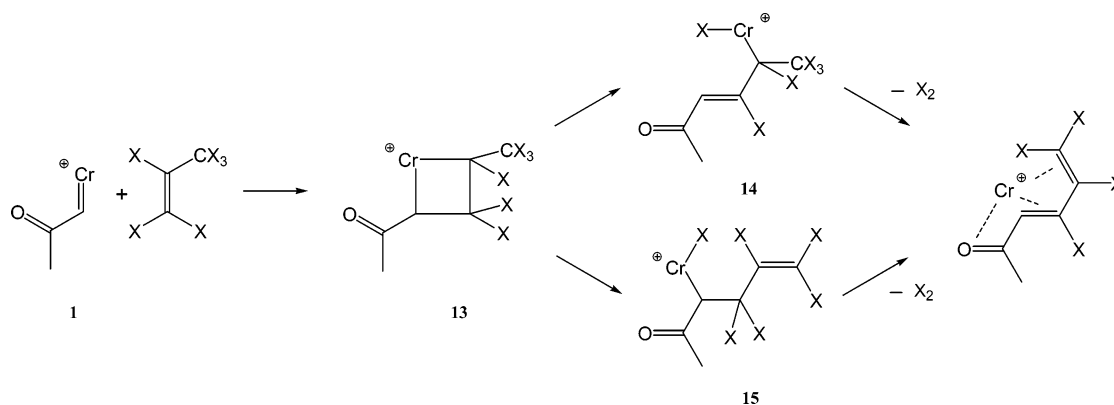
the metal carbene **1** could also react with ethene in a [4+2] addition, i.e., a hetero-Diels–Alder type reaction, Scheme 4, with $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$.³⁹ The resulting six-membered ring **11** (identical with **12** for ethene), which is presumably less strained than its four-membered counterpart **8**, can then stabilize by dehydrogenation. Alternatively, a sequence of β -H elimination and reductive elimination analogous to the mechanism proposed in Scheme 3 could lead to the loss of divinyl ether as another possible contribution to reaction 5.

The metallacycles **11** and **12** can also be formed by addition of the olefin to the chromium–oxygen bond of

(38) Fisher, E. R.; Armentrout, P. B. *J. Am. Chem. Soc.* **1992**, *114*, 2039.

(39) For a recent review focusing on cycloadditions of metal-free ions in the gas phase, see: Eberlin, M. N. *Int. J. Mass Spectrom.* **2004**, *235*, 263.

Scheme 5



the cyclic structure **2**, Scheme 4. This is the case because **2** can be considered as the electrocyclic ring-closure product of **1** and because the outcome of a series of a four-electron ring closure and a [2+2] cycloaddition equals that of the corresponding direct [4+2] addition.

Propene. The dehydrogenation channel strongly gains in importance for the reaction with propene, Table 1. Jacobson and Freiser found a similar trend for FeCH_2^+ and CoCH_2^+ , which induce H_2 elimination from propene but not from ethene. However, dehydrogenation of propene by FeCH_2^+ and CoCH_2^+ does not account for more than 6 and 15%, respectively,¹³ of all product channels, whereas the branching ratio (b.r.) amounts to 77% for $\text{CrC}_3\text{H}_4\text{O}^+$. A comparison between the reactivities of $\text{CrC}_3\text{H}_4\text{O}^+$ with those of FeCH_2^+ and CoCH_2^+ is particularly interesting because the mechanism involving a Diels–Alder type reaction (Scheme 4) obviously cannot apply for the simple metal methylidenes. The higher amount of dehydrogenation observed for the reaction of $\text{CrC}_3\text{H}_4\text{O}^+$ might therefore directly reflect the contribution of the Diels–Alder channel. The alternative mechanism for H_2 elimination, which Jacobson and Freiser inferred for the dehydrogenation of propene by FeCH_2^+ and CoCH_2^+ ,¹³ proceeds by initial [2+2] cycloaddition of the metal carbene and alkene, Scheme 5, with $\text{X} = \text{H}$. Of the two different orientations of the addition, only the one yielding intermediate **13** with its linear C_6 chain can lead to dehydrogenation. Similarly, only two of the three possibilities for β -H elimination from **13** are relevant with respect to sequential loss of H_2 . Note that one of the products of these β -H eliminations, namely, complex **14**, is perfectly analogous to intermediate **9** in Scheme 3. Like the latter, complex **14** and its counterpart **15** can undergo reductive elimination followed by expulsion of $\text{C}_3\text{H}_3\text{O}$, thus generating bare Cr^+ . Formation of Cr^+ is indeed observed, but to a much smaller extent than for ethene (b.r. = 12 versus 92%). Apparently, this difference originates from competition by dehydrogenation in the case of propene. Dehydrogenation permits a stabilization of the energized intermediates **14** and **15** without cleaving the dative bonds between the bifunctional organic ligand and the metal center and may therefore be thermodynamically favored. The dehydrogenation step itself can be regarded as another β -H elimination followed by a reductive elimination of H_2 from the chromium atom.

In addition, the reactions of $\text{CrC}_3\text{H}_4\text{O}^+$ with deuterated propene were investigated. Overall reaction rate and b.r. for the dehydrogenation channel agree with the

values determined for the reaction with C_3H_6 within experimental uncertainties. This finding implies a kinetic isotope effect $\text{KIE} \approx 1$ and thus rules out activation of a C–H/C–D bond in the rate-limiting step. Neither the dehydrogenation mechanism starting with a Diels–Alder reaction (Scheme 4) nor that proceeding via the four-membered metallacycle **13** (Scheme 5, with $\text{X} = \text{D}$) is affected by this argument as, for both, the initial addition step is expected to be rate-determining. Moreover, both mechanistic scenarios predict elimination of D_2 and thus formation of $\text{CrC}_6\text{H}_4\text{D}_4\text{O}^+$ as ionic product. Experiment matches well these expectations and finds generation of $\text{CrC}_6\text{H}_4\text{D}_4\text{O}^+$ (loss of D_2) and $\text{CrC}_6\text{H}_3\text{D}_5\text{O}^+$ (loss of HD) in a ratio of ca. 20:1. The small amount of isotopic scrambling can be rationalized by a reversible reductive elimination. CID of product $\text{CrC}_6\text{H}_4\text{D}_4\text{O}^+$ generates Cr^+ as sole ionic fragment and thus does not provide additional information, except supporting the proposed coupling of the organic ligands.

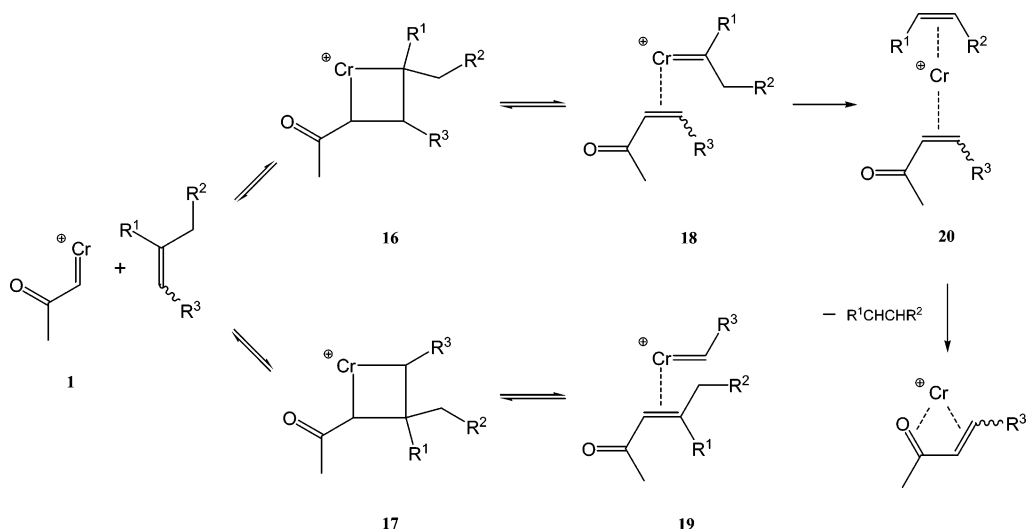
Although the experiments performed do not allow a discrimination between the possible pathways for dehydrogenation, two observations indicate that actually both mechanisms are operative. First, H_2 loss is much more efficient for propene than for ethene, which suggests an additional reaction channel for the former, such as the sequence outlined in Scheme 5. Second, $\text{CrC}_3\text{H}_4\text{O}^+$ dehydrogenates ethene and propene significantly faster than FeCH_2^+ and CoCH_2^+ (the two metal methylidenes do not dehydrogenate ethene at all).¹³ As pointed out above, this difference can be attributed to the inability of FeCH_2^+ and CoCH_2^+ to react via an initial Diels–Alder reaction (Scheme 4), which vice versa appears to be operative for $\text{CrC}_3\text{H}_4\text{O}^+$.

Besides dehydrogenation and formation of bare Cr^+ , the reaction of $\text{CrC}_3\text{H}_4\text{O}^+$ with propene yields $\text{CrC}_4\text{H}_6\text{O}^+$ as a third product (Table 1), reaction 7.



Unlike all other processes discussed so far, this reaction involves cleavage of a C–C bond. As insertion of chromium into the strong vinylic C–C bond appears energetically unfavorable, it is not considered a viable mechanism for reaction 7. Instead, it has been demonstrated above that [2+2] cycloadditions between the carbene structure **1** and propene can account for most of the reactions observed. Strictly speaking, the addition step is reversible although the reverse reaction just regenerates the reactants and therefore is of no further

Scheme 6



interest. However, a different situation arises if the orientation of the cycloreversion is opposite to that of the initial cycloaddition. In this case, metathesis products are formed, which have been observed in the reactions of gaseous MnCH_2^+ ,¹¹ FeCH_2^+ , and CoCH_2^+ with olefins.¹³ As shown in Scheme 6 ($\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$), metathesis can also rationalize occurrence of reaction 7. Depending on the orientation of the initial [2+2] addition, two different metallacycles, structures **16** and **17**, are formed. Cycloreversion then yields the metal carbene complexes **18** and **19**; all these species are assumed to be interconvertible. Whereas **19** does not give rise to any further intermediates in the case of propene ($\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$), **18** can undergo a hydrogen shift that produces the bis-alkene complex **20**. The latter loses exclusively ethene ($\text{R}^1 = \text{R}^2 = \text{H}$), as it binds to the Cr^+ ion less strongly than the bidental α,β -unsaturated ketone. The entire mechanism is fully consistent with the formation of $\text{CrC}_4\text{H}_4\text{D}_4\text{O}^+$ (and neutral C_2D_4) observed upon application of d_6 -propene. The key step of the reaction sequence is the conversion of the metal alkylidene **18** to the bis-alkene complex **20**. Jacobson and Freiser postulated analogous transformations in the reactions of FeCH_2^+ and CoCH_2^+ with propene and concluded that these were facile and irreversible; thus, this reaction step shifts the whole equilibrium to the product side.¹³ A similar situation is assumed for $\text{CrC}_3\text{H}_4\text{O}^+/\text{C}_3\text{H}_6$. The importance of the alkylidene-olefin conversion can be recognized from the complete lack of the corresponding metathesis products in the reactions of FeCH_2^+ , CoCH_2^+ ,¹³ and $\text{CrC}_3\text{H}_4\text{O}^+$ with ethene, which does not have an allylic hydrogen necessary for the conversion step. Alkyldiene-olefin rearrangements have also been observed for cationic metal alkylidenes in solution.⁴⁰

Concluding the discussion of the reactions of $\text{CrC}_3\text{H}_4\text{O}^+$ with propene, we note that no abstractions of atomic hydrogen from the neutral substrate are observed. Such radical-like behavior occurs in the reaction of CrO^+ with propene.⁴¹ Hence, it is confirmed once again that $\text{CrC}_3\text{H}_4\text{O}^+$ does not resemble CrO^+ in its reactivity and that it most certainly does not correspond to a $\text{CrO}^+-(\text{C}_3\text{H}_4)$ complex.

Table 2. Branching Ratios (b.r., in %) for the Different Product Channels of the Reaction of $\text{CrC}_3\text{H}_4\text{O}^+$ with 1,1- d_2 -1-Butene

products	b.r.	products	b.r.
$\text{CrC}_3\text{H}_6\text{O}^+ + \text{C}_4\text{H}_4\text{D}_2$	7 ± 2	$\text{CrC}_5\text{H}_8\text{O}^+ + \text{C}_2\text{H}_2\text{D}_2$	2 ± 1
		$\text{CrC}_5\text{H}_7\text{DO}^+ + \text{C}_2\text{H}_3\text{D}$	2 ± 1
		$\text{CrC}_5\text{H}_6\text{D}_2\text{O}^+ + \text{C}_2\text{H}_4$	10 ± 2
$\text{CrC}_4\text{H}_6\text{O}^+ + \text{C}_3\text{H}_4\text{D}_2$	2 ± 1	$\text{CrC}_6\text{H}_7\text{DO}^+ + \text{CH}_3\text{D}$	2 ± 0.5
$\text{CrC}_4\text{H}_5\text{DO}^+ + \text{C}_3\text{H}_5\text{D}$	3 ± 2	$\text{CrC}_6\text{H}_6\text{D}_2\text{O}^+ + \text{CH}_4$	2 ± 0.5
$\text{CrC}_4\text{H}_4\text{D}_2\text{O}^+ + \text{C}_3\text{H}_6$	20 ± 5		
		$\text{CrC}_7\text{H}_{10}\text{O}^+ + \text{D}_2$	1.5 ± 0.5
$\text{CrC}_5\text{H}_6\text{O}^+ + \text{C}_2\text{H}_4\text{D}_2$	3 ± 2	$\text{CrC}_7\text{H}_9\text{DO}^+ + \text{HD}$	19 ± 3
$\text{CrC}_5\text{H}_5\text{DO}^+ + \text{C}_2\text{H}_5\text{D}$	3 ± 2	$\text{CrC}_7\text{H}_8\text{D}_2\text{O}^+ + \text{H}_2$	23 ± 5

Butenes. The reactions of $\text{CrC}_3\text{H}_4\text{O}^+$ with 1-butene, 2-*E*-butene, 2-*Z*-butene, and isobutene are similarly or slightly more efficient than its reaction with propene (Table 1). A comparison of the products observed for the different butenes shows far-reaching parallels. Particularly, as in the case of the reaction with propene, H_2 elimination represents the predominant product channel, reaction 8.

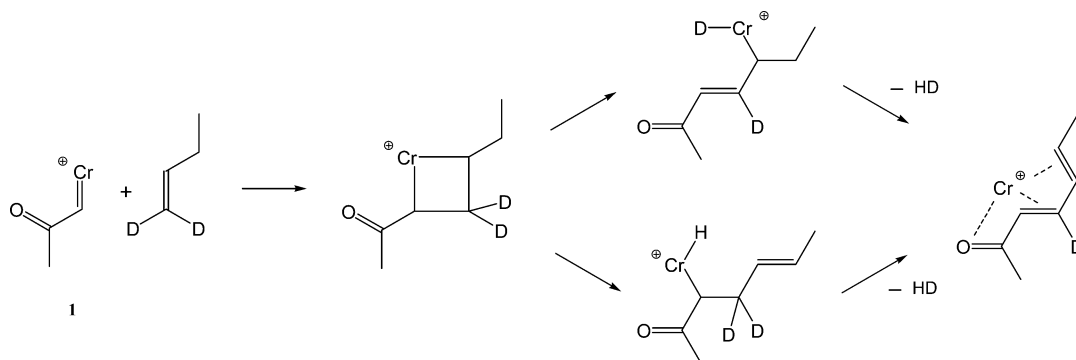


To address this aspect in more detail, the behavior of 1,1- d_2 -1-butene was studied exemplarily. The overall reaction efficiency ($\varphi = 0.42$) and the combined b.r. of the products that just differ by the distribution of the isotopic label (Table 2) are similar to the values found for unlabeled 1-butene; thus, operation of particularly large KIEs can be ruled out. With respect to hydrogen elimination, losses of H_2 and HD strongly prevail. Assuming an initial Diels–Alder type reaction (Scheme 4 with $\text{R}^1 = \text{C}_2\text{H}_5$, $\text{R}^2 = \text{R}^3 = \text{D}$), one would expect solely loss of HD. Obviously, this cannot be the only mechanism operative. In analogy with the situation for propene (Scheme 5), hydrogen elimination could also occur after initial formation of a metallacyclobutane. However, this pathway should again only yield HD (Scheme 7). In contrast, loss of H_2 can be rationalized if chromium initially inserts into the allylic C–H bond. C–H insertion is supposed to be facile for 1-butene because of the activating effect of the allyl group and the considerable amount of complexation energy released, which is available for surmounting reaction barriers. The inser-

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(41) Kang, H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 5663.

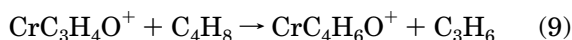
Scheme 7



tion itself is analogous to the first part of the mechanism for alkane dehydrogenation (Scheme 2). If subsequent β -H elimination takes place before the hydrogen shift from the metal onto the alkylidene can occur, a dihydrido species is formed that loses H_2 . Compared to the dehydrogenation of alkanes, the β -H elimination in the reaction of $\text{CrC}_3\text{H}_4\text{O}^+$ with 1-butene is facilitated by the conjugation of the double bonds in the 1,3-butadiene ligand generated. Nevertheless, formation of some $\text{CrC}_3\text{H}_6\text{O}^+$ (Table 2) indicates that, at least to a minor extent, hydrogen shift from the metal to the alkylidene also takes place. In analogy with alkane dehydrogenation (Scheme 2), β -H elimination and expulsion of the olefin follow.

Together, the mechanisms starting with a hetero-Diels–Alder reaction, [2+2] cycloaddition, and allylic C–H insertion, respectively, can satisfactorily explain the labeling distribution of the products, except for the small amount of D_2 lost, which evidently involves more complex rearrangements. Whereas the first two pathways should also apply for the other butenes, a C–H insertion pathway is impossible for isobutene and not necessarily likely for 2-*E*- and 2-*Z*-butene, as it would generate energetically unfavorable 1,2-butadiene. Nonetheless, the latter two substrates do exhibit increased degrees of H_2 elimination (Table 1). This observation and the formation of significant amounts of $\text{CrC}_3\text{H}_6\text{O}^+$ for 2-*E*- and 2-*Z*-butene could indicate that allylic C–H insertion and formation of 1,2-butadiene actually are feasible for these two reactants. In light of these findings, an analogous allylic C–H insertion and consecutive H_2 elimination might potentially also contribute to the dehydrogenation of propene by $\text{CrC}_3\text{H}_4\text{O}^+$. CID of $\text{CrC}_7\text{H}_{10}\text{O}^+$ generated from the different butenes yields Cr^+ as predominant or exclusive ionic fragment and thus does not provide specific structural information.

The second most important product channel in the reaction of $\text{CrC}_3\text{H}_4\text{O}^+$ with 1-butene is generation of $\text{CrC}_4\text{H}_6\text{O}^+$, reaction 9.

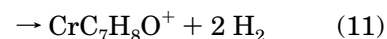
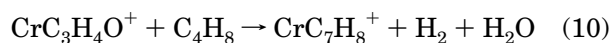


This process corresponds to olefin metathesis followed by alkylidene-alkene conversion and final expulsion of an olefin, Scheme 6, with $\text{R}^1 = \text{R}^3 = \text{H}$ and $\text{R}^2 = \text{CH}_3$. In line with expectation, the isotopic label predominantly remains in the ionic product although some H/D-exchange processes occur as well (Table 2). An analogous mechanism also accounts for the formation of

$\text{CrC}_4\text{H}_6\text{O}^+$ from isobutene (Scheme 6, with $\text{R}^1 = \text{CH}_3$ and $\text{R}^2 = \text{R}^3 = \text{H}$). The lower b.r. of this channel probably reflects a reduced tendency toward metathesis because of increased steric hindrance. For 2-*E*- and 2-*Z*-butene, metathesis should lead to $\text{CrC}_5\text{H}_8\text{O}^+$ and C_2H_4 (Scheme 6, with $\text{R}^1 = \text{R}^2 = \text{H}$ and $\text{R}^3 = \text{CH}_3$). Indeed, formation of $\text{CrC}_5\text{H}_8\text{O}^+$ is observed in these reactions, whereas only very little $\text{CrC}_4\text{H}_6\text{O}^+$ is produced (Table 1), as expected.

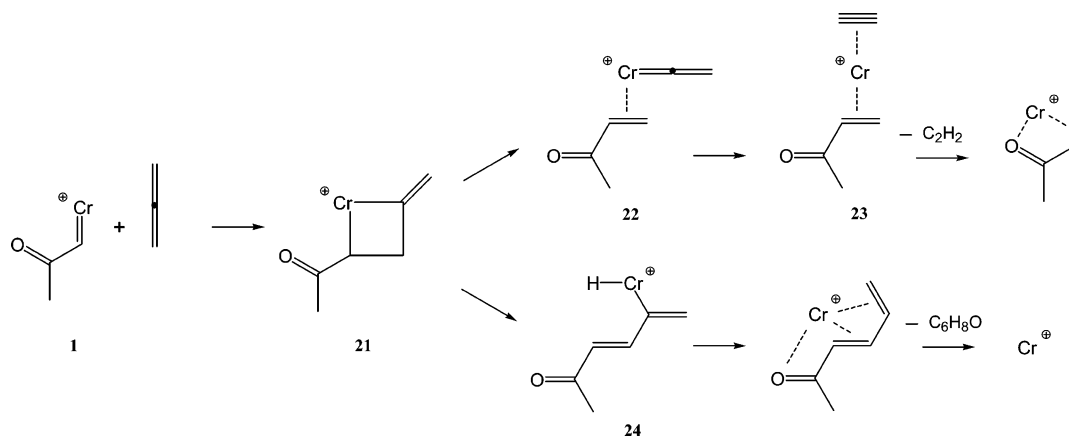
Note that also the reaction of $\text{CrC}_3\text{H}_4\text{O}^+$ with 1-butene yields significant amounts of $\text{CrC}_5\text{H}_8\text{O}^+$, though apparently not as a result of metathesis. Predominant incorporation of the isotopic label in the ionic product suggests cleavage of the C(2)–C(3) bond of the C_4 chain. Whereas cleavage of the vinylic C–C bond of 1-butene appears energetically less favorable, the situation alters after ring formation via [2+2] or [4+2] cycloadditions. Additionally, the energy released by these processes may help to overcome the barriers associated with C–C bond cleavage. A possible way for C–C cleavage is a 1,2-elimination. While generation of $\text{CrC}_5\text{H}_8\text{O}^+$ and expulsion of C_2H_4 corresponds to the formation of the double bond in the neutral product, the double bond could also be placed in $\text{CrC}_5\text{H}_6\text{O}^+$ as product ion accompanied by neutral ethane (Scheme 4, with $\text{R}^1 = \text{C}_2\text{H}_5$ and $\text{R}^2 = \text{R}^3 = \text{H}$). This reaction channel is in fact observed as well. However, the reaction with labeled 1,1-*d*₂-1-butene yields not only the expected products $\text{CrC}_5\text{H}_5\text{DO}^+ + \text{C}_2\text{H}_5\text{D}$ but also $\text{CrC}_5\text{H}_6\text{O}^+ + \text{C}_2\text{H}_4\text{D}_2$, which shows that additional pathways must be operative as well. For the other butenes, analogous processes lead to $\text{CrC}_6\text{H}_8\text{O}^+$ and CH_4 . The relatively high tendency toward CH_4 elimination for isobutene might reflect steric overload at the quaternary carbon atom in the cyclic adduct. CID of $\text{CrC}_6\text{H}_8\text{O}^+$ formed from isobutene yields only Cr^+ in detectable amounts.

The reaction of $\text{CrC}_3\text{H}_4\text{O}^+$ with isobutene reveals two additional product channels, which are not operative for the other butenes, reactions 10 and 11.



Reaction 10 is the only process observed that corresponds to dehydration. It is not clear why this reaction exclusively occurs for isobutene. Similarly, it is not evident either why double dehydrogenation takes place only for this substrate. In the opposite, one would expect such a process for linear rather than branched butenes.

Scheme 8

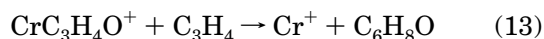


3.3. Reactions with Polyunsaturated Hydrocarbons. Allene. As the prototypical cumulene, allene was included in the reactivity studies. Efficient reaction with $\text{CrC}_3\text{H}_4\text{O}^+$ predominantly yields $\text{CrC}_4\text{H}_6\text{O}^+$ as ionic product, reaction 12.



This reaction corresponds to metathesis (Scheme 8). Dissociation of the initially formed cycloadduct **21** leads to the vinylidene **22**. The latter then rearranges to the acetylene-olefin complex **23** and finally loses C_2H_2 . Interestingly, coordinatively saturated transition-metal complexes in solution generally undergo reverse acetylene-vinylidene transformations.⁴² Quantum-chemical calculations revealed higher thermochemical stabilities of metal vinylidenes compared to the corresponding isomeric acetylene complexes; however, the relative stabilities of the latter increase for more electron-deficient metal centers because acetylene is a stronger donor than vinylidene.^{42,43} Hence, the occurrence of a vinylidene-acetylene rearrangement in the present case does not appear implausible in light of the considerable electron deficiency of the cationic, highly unsaturated $\text{CrC}_6\text{H}_8\text{O}^+$ species. Nevertheless, the high efficiency of the overall process for $\text{CrC}_3\text{H}_4\text{O}^+$ is remarkable given the scarcity of examples of metathesis reactions involving allenes.⁴⁴

Metallacyclobutane **21** can alternatively undergo a β -H elimination to produce intermediate **24**. Subsequent reductive elimination yields an energized chromium complex, which stabilizes by expulsion of $\text{C}_6\text{H}_8\text{O}$, reaction 13.



In addition, small amounts of $\text{CrC}_6\text{H}_6\text{O}^+$ and H_2 are formed. This reaction can be rationalized by a second β -H elimination of **24** and a consecutive reductive elimination of H_2 from the metal center.

1,3-Butadiene. While the reaction of $\text{CrC}_3\text{H}_4\text{O}^+$ with allene is already fast, that with 1,3-butadiene is even more efficient (Table 1). Probably, the high reactivity of the conjugated diene largely results from its superior

Table 3. Branching Ratios (b.r., in %) for the Different Product Channels of the Reaction of $\text{CrC}_3\text{H}_4\text{O}^+$ with 1,1,4,4-*d*₄-1,3-Butadiene

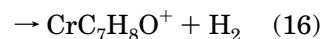
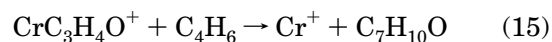
products	b.r.	products	b.r.
$\text{Cr}^+ + \text{C}_7\text{H}_6\text{D}_4\text{O}$	16 ± 2	$\text{CrC}_5\text{H}_5\text{D}_3\text{O}^+ + \text{C}_2\text{HD}$	1 ± 1
$\text{CrC}_3\text{H}_6\text{O}^+ + \text{C}_4\text{D}_4$	2 ± 0.5	$\text{CrC}_6\text{H}_5\text{DO}^+ + \text{CHD}_3$	3 ± 1
$\text{CrC}_3\text{H}_5\text{DO}^+ + \text{C}_4\text{HD}_3$	2.5 ± 0.5	$\text{CrC}_6\text{H}_3\text{D}_3\text{O}^+ + \text{CH}_3\text{D}$	3 ± 1
$\text{CrC}_3\text{H}_4\text{D}_2\text{O}^+ + \text{C}_4\text{H}_2\text{D}_2$	1 ± 1	$\text{CrC}_6\text{H}_2\text{D}_4\text{O}^+ + \text{CH}_4$	1 ± 1
$\text{CrC}_3\text{H}_3\text{D}_3\text{O}^+ + \text{C}_4\text{H}_3\text{D}$	1 ± 1		
$\text{CrC}_4\text{H}_6\text{O}^+ + \text{C}_3\text{D}_4$	2 ± 1		
$\text{CrC}_5\text{H}_6\text{O}^+ + \text{C}_2\text{D}_4$	3 ± 2	$\text{CrC}_7\text{H}_6\text{D}_2\text{O}^+ + \text{D}_2$	6 ± 1
$\text{CrC}_5\text{H}_5\text{DO}^+ + \text{C}_2\text{HD}_3$	24 ± 3	$\text{CrC}_7\text{H}_5\text{D}_3\text{O}^+ + \text{HD}$	9 ± 1
$\text{CrC}_5\text{H}_4\text{D}_2\text{O}^+ + \text{C}_2\text{H}_2\text{D}_2$	18 ± 2	$\text{CrC}_7\text{H}_4\text{D}_4\text{O}^+ + \text{H}_2$	6 ± 1
$\text{CrC}_5\text{H}_3\text{D}_3\text{O}^+ + \text{C}_2\text{H}_3\text{D}$	2 ± 2		

coordination properties, which initially enable the formation of a long-living collision complex $\text{CrC}_3\text{H}_4\text{O}^+$ -(C_4H_6). Also note that the presence of two double bonds in 1,3-butadiene and allene may result in increased reaction path degeneracies, compared to the simple olefins.⁴⁵ The main process gives rise to $\text{CrC}_5\text{H}_6\text{O}^+$ as ionic product, reaction 14.



Like most of the other product ions investigated, $\text{CrC}_5\text{H}_6\text{O}^+$ yields only Cr^+ as ionic fragment upon CID. In analogy with ethane loss in the reaction of $\text{CrC}_3\text{H}_4\text{O}^+$ with 1-butene, a possible mechanism for reaction 14 might be a 1,2-elimination from the product of [2+2] or [4+2] cycloadditions. In the reaction with 1,1,4,4-*d*₄-1,3-butadiene, $\text{CrC}_5\text{H}_5\text{DO}^+$ is formed as main ionic product (Table 3), which is indeed consistent with the cycloaddition/elimination mechanism (Scheme 4, with $\text{R}^1 = \text{CHCD}_2$, $\text{R}^2 = \text{R}^3 = \text{D}$). However, also $\text{CrC}_5\text{H}_4\text{D}_2\text{O}^+$ is formed in appreciable amounts, indicating involvement of additional pathways.

Besides loss of ethene, generation of bare Cr^+ and H_2 elimination are most prominent, reactions 15 and 16.



Dehydrogenation could proceed from the same cycloadduct that is assumed to also lose C_2H_4 . In agreement with the mechanism proposed in Scheme 4, mainly

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(43) Silvestre, J.; Hoffmann, R. *Helv. Chim. Acta* **1985**, *68*, 1461.

(44) Ahmed, M.; Arnauld, T.; Barrett, A. G. M.; Braddock, D. C.; Flack, K.; Procopiou, P. A. *Org. Lett.* **2000**, *2*, 551.

(45) Holbrook, K. A.; Pilling, M. J.; Robertson, S. H. *Unimolecular Reactions*; Wiley: New York, 1996.

expulsion of HD is observed in the reaction with 1,1,4,4-*d*₄-1,3-butadiene. Again, considerable isotopic scrambling occurs as well (Table 3). Reaction 15 can be explained by a sequence of [2+2] cycloaddition, β -H elimination from the resulting chromacyclobutane, reductive elimination, and loss of the organic ligand (compare Scheme 3 for the analogous reaction of ethene).

In contrast to the reactions of CrC₃H₄O⁺ with propene, the different butenes, and allene, metathesis appears to be less pronounced for 1,3-butadiene. In fact, the putative metathesis product CrC₄H₆O⁺ (compare Scheme 6) does not show the expected incorporation of two deuterium atoms if 1,1,4,4-*d*₄-1,3-butadiene is applied, thereby questioning the occurrence of metathesis at all (Table 3). This lack of metathesis reactivity can be explained by a reduced tendency toward the alkylidene-olefin conversion that follows the actual metathesis step. For 1,3-butadiene, this rearrangement would form allene and thus no longer be thermochemically favorable enough to shift the whole equilibrium toward the products. This demonstrates again the crucial importance of the alkylidene-olefin conversion step for the occurrence of metathesis altogether.¹³

The remaining reactions of CrC₃H₄O⁺ with 1,3-butadiene are all rather inefficient (b.r. \leq 0.10, Table 1). Analysis of the distribution of the isotopic label in the products for the reactions with 1,1,4,4-*d*₄-1,3-butadiene is complicated by isobaric interferences (the intense peaks for CrC₅H₅DO⁺ and CrC₅H₄D₂O⁺ may overlap with those expected for possibly formed CrC₆H₅D₃⁺ and CrC₆H₄D₄⁺ and prevent detection of the latter, Table 3) and consecutive H/D exchange reactions.

Benzene. Finally, the reactivity of CrC₃H₄O⁺ toward *d*₆-benzene was investigated. The efficient reaction affords addition of C₆D₆ accompanied by loss of C₃H₄, reaction 17.⁴⁶



CID of the product ion generates both Cr⁺ and CrO⁺ as ionic fragments. This behavior contrasts that of all the other product ions studied, as it indicates preformation of the CrO unit in CrC₆D₆O⁺. Further support for this interpretation and the presence of a CrO⁺(C₆D₆) structure is provided by the occurrence of ligand exchange with C₆H₆, eq 18.



Reaction 17 resembles the reaction of CrC₃H₄O⁺ with monofluoroacetone, which also leads to addition of the neutral substrate and simultaneous loss of C₃H₄.²² Apparently, the complexation energies released from coordination of these ligands to CrC₃H₄O⁺ (compare *D*₀(Cr⁺–C₆H₆) = 170 \pm 10 kJ mol⁻¹)⁴⁷ are sufficiently high to cause major rearrangements of the C₃H₄O entity. These processes are therein similar to collisional activation of CrC₃H₄O⁺, which also yields CrO⁺ besides Cr⁺, reactions 2a and 2b.²² Expulsion of C₃H₄ can be under-

stood as elimination of CrO⁺ from the chromaoxacyclobutene **2** (or its isomer **3**), which can form from the metal carbene **1** by electrocyclic ring closure. The fact that the reactivity of benzene differs drastically from those of all other hydrocarbons studied reflects the arene's particular stability, which disfavors the occurrence of cycloadditions or C–H bond activation processes.

4. Conclusions

The reactions of CrC₃H₄O⁺ with the hydrocarbons studied can be divided into six different categories:

(1) C–H Bond Insertion. This reaction mechanism applies to alkanes larger than propane. After initial insertion of the metallic center of the carbene **1** into the C–H bond of the alkane, migration of the H atom yields a dialkyl species, which undergoes β -H elimination (Scheme 2). Subsequent reductive elimination generates an acetone-olefin complex that exclusively loses the olefin as the less strongly bound ligand. A similar reaction sequence starts with the addition of the alkane to the Cr–O bond of the metallacycle **2**. There is also evidence that insertion of chromium into the allylic C–H bond of 1-butene takes place.

(2) Ligand Loss by Reductive Elimination. This reaction forming bare Cr⁺ is observed for ethene, propene, allene, and 1,3-butadiene. [2+2] cycloaddition of **1** and the olefin is followed by β -H elimination, reductive elimination, and expulsion of the organic ligand (Scheme 3). Different orientations of the cycloaddition and/or the β -H elimination step give rise to different isomers of the neutral product.

(3) H₂ Loss by β -H Elimination. This reaction occurs for propene and the butenes. Like the previous reaction channel, it involves [2+2] cycloaddition of **1** and the olefin with subsequent β -H elimination. A second β -H elimination can then compete with reductive elimination and produces a dihydrido complex, which loses molecular hydrogen (Scheme 5).

(4) Metathesis. Metathesis reactivity is observed for propene, the butenes, and allene. Again, [2+2] cycloaddition of **1** and the olefin is postulated for the initial step. Cycloreversion yields an olefin-alkylidene species as direct product of metathesis. Irreversible alkylidene-olefin conversion forms a bis-alkene complex, which loses the less strongly bound of its two ligands (Scheme 6). The importance of the alkylidene-olefin rearrangement is reflected in the fact that no metathesis products are detected for ethene and 1,3-butadiene, for which this conversion is either impossible or energetically unfavorable. In contrast, the efficient metathesis reaction of allene points to a remarkable facility of the vinylidene-acetylene conversion operative in this case (Scheme 8).

(5) 1,2-Elimination after Cycloaddition. This reaction mechanism is proposed to rationalize some findings difficult to explain by other processes. After a hetero-Diels–Alder reaction between **1** and an olefin, H₂ or a simple hydrocarbon is expelled in a 1,2-elimination (Scheme 4). This reaction appears to occur for the simple alkenes and 1,3-butadiene. In a variant of this process, the double bond can also form in the neutral byproduct (ethene) in the case of 1-butene. Alternatively, the initial cycloadduct could result from

(46) Additionally, traces of CrC₆D₆⁺ were observed. However, it could not be established unequivocally whether this species arises from direct reaction of CrC₃H₄O⁺ or rather consecutive processes involving residual monofluoroacetone.

(47) Meyer, F.; Khan, F. A.; Armentrout, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 9740.

reaction of the chromaoxacyclobutene **2** with the olefin (Scheme 4).

(6) Rearrangement and C_3H_4 Loss. This reaction takes place for benzene and, as previously inferred, monofluoroacetone.²² Complexation by these substrates releases enough energy to induce rearrangement within $\text{CrC}_3\text{H}_4\text{O}^+$ and to eliminate C_3H_4 . The elimination itself probably starts from the metallacycle **2** and generates propyne as neutral product (or allene if alternatively structure **3** is assumed as direct precursor).

On the basis of these reactivity patterns, the question of the structure of $\text{CrC}_3\text{H}_4\text{O}^+$ can be re-addressed in a more conclusive manner. The reactivity of $\text{CrC}_3\text{H}_4\text{O}^+$ differs significantly from that of either Cr^+ or CrO^+ , which most likely rules out the complexes $\text{Cr}^+(\text{C}_3\text{H}_4\text{O})$ and $\text{CrO}^+(\text{C}_3\text{H}_4)$, leaving the chromium carbene **1**, the chromaoxacyclobutene **2**, and the related metallacycle **3** as possible structures for $\text{CrC}_3\text{H}_4\text{O}^+$. Except for rearrangement reactions in category 6, all other processes can be explained by assuming the metal carbene **1** as direct reactant. In particular, the occurrence of metathesis provides compelling evidence for the presence of **1**. The alternative structures **2** and **3** appear to be involved only at elevated energies (CID and rearrangement reactions in category 6).

Although the oxygen does not covalently bind to the chromium ion in **1**, it can nonetheless form a dative bond

to the metallic center. This interaction controls the outcome of several reactions, as it prohibits loss of the oxygen-containing ligand from transient bis-alkene complexes. However, even in these processes the carbonyl group is confined to the role of an internal spectator ligand. Moreover, the high efficiencies of the reactions between **1** and olefins indicate that coordination of the metal center by oxygen does not significantly impede the reactivity of the metal carbene. This behavior possibly mirrors the fact that most of the reactions between **1** and olefins start by cycloadditions, which involve the whole carbene unit rather than just the chromium ion; therefore, changes of the positive charge density at the metal center need not necessarily strongly affect these reactions. Whereas the vast majority of cycloadditions observed are of the [2+2] type, there is also evidence for occurrence of hetero-Diels–Alder reactions, in which the carbonyl group actively participates.

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