

Bimolecular Reactions of the Chromium-Benzyne Ion $\text{Cr}^+-\text{C}_6\text{H}_4$ in the Gas Phase. An FT-ICR Study

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The chromium-benzyne ion $\text{Cr}^+-\text{C}_6\text{H}_4$ was generated in the gas phase by electron-impact-induced loss of 5 CO from $(\eta^6\text{-}1,2\text{-dioxocyclobutabenzene})\text{tricarboxylchromium}(0)$. The gas-phase reactions of the $\text{Cr}^+-\text{C}_6\text{H}_4$ ions with methanol, ammonia, several alkanes, alkadienes, and aromatic species were studied by Fourier transform ion cyclotron resonance spectrometry (FT-ICR) using an external ion source. The results show that the bimolecular reactivity of the $\text{Cr}^+-\text{C}_6\text{H}_4$ cations is determined by the C_6H_4 ligand, exhibiting the high reactivity of benzyne. No reactions due to a primary reaction at Cr^+ are discovered. In most of the reactions, the main product observed for the bimolecular reaction is Cr^+ released from the complex by the great exothermicity of the reaction at the C_6H_4 ligand. However, in the case of less exothermic reactions and if the excess energy is removed from the reaction complex by "evaporating" a neutral leaving group, Cr^+ complexes are observed whose ligands arise from addition reactions of the reactants to C_6H_4 . This is the case for cycloadditions of benzene- d_6 and naphthalene- d_8 to $\text{Cr}^+-\text{C}_6\text{H}_4$, where the adducts still containing Cr^+ as well as ions formed by loss of acetylene- d_2 from the adducts are observed. Thus, in the family of transition-metal-cation-benzyne complexes, the $\text{Cr}^+-\text{C}_6\text{H}_4$ cation is extraordinary in exhibiting reactivity exclusively at the benzyne ligand.

Introduction

The study of the gas-phase reactions of bare transition-metal cations with organic substrates during the last few years has given a wealth of information about organometallic chemistry.¹ A typical gas-phase reaction of a transition-metal ion with a hydrocarbon is the oxidative insertion into C-H and C-C bonds. Besides the investigation of the reactivity of bare metal ions, a study of the modification of the reactivity of the central metal ions of coordinatively unsaturated metal complexes by the ligands is a major field of research in metal-organic chemistry.² Usually the complexation of ligands alters the reactivity of the central transition-metal cation as well as that of the ligand. This is of particular interest if the free ligand is unstable and difficult to handle under the conditions typical of synthetic chemistry. Benzyne (1,2-didehydrobenzene) and other arynes are very reactive intermediates³ which have to be prepared in situ during a chemical synthesis.⁴ However, stable benzyne complexes with transition metals are known,⁵ showing that complexation may markedly attenuate the reactivity of benzyne.

Recently, the transition-metal-benzyne complexes $\text{Fe}^+-\text{C}_6\text{H}_4$ ⁶ and $\text{Sc}^+-\text{C}_6\text{H}_4$ ⁷ were prepared in the gas phase by dehydrohalogenation and dehydrogenation reactions, respectively, between $\text{C}_6\text{H}_5\text{X}$ (X = Cl, Br) and the transition-metal cation and were reacted with a variety of organic substrates. The gas-phase chemistry of these complexes is explained by initial reactions at the metal center followed by intramolecular reactions of benzyne in the ligand sphere.^{6,7} In an extension of this series of coordinatively unsaturated transition-metal-benzyne complexes, the reactions of the Cr^+ -benzyne complex are of special interest. Ground-state Cr^+ does not react with hydrocarbons by the usual C-H/C-C insertion,⁸ and this inability for oxidative insertion is attributed to the large promotion energy $\text{Cr}^+(3d^5) \rightarrow \text{Cr}^+(3d^4s^1)$ of 142 kJ mol⁻¹ necessary to put Cr^+ into a reactive electron configuration. If this inertness of Cr^+ is sustained in complexes of this transition metal, the Cr^+ -benzyne complex should exhibit

benzyne reactivity only. However, because of the unreactive Cr^+ ion, the gas-phase addition-elimination sequence between a transition-metal cation and a suitable benzene derivative^{7,8} cannot be used to prepare $\text{Cr}^+-\text{C}_6\text{H}_4$. Here we present a new technique to generate $\text{Cr}^+-\text{C}_6\text{H}_4$ in the gas phase by electron-impact-induced decomposition of a suitable (arene)tricarboxylchromium(0) complex, which can be used generally to prepare transition-metal-benzyne complexes, and we report on the gas-phase reactions of $\text{Cr}^+-\text{C}_6\text{H}_4$ with a variety of substrates, including alkanes, alkenes, and arenes.

Experimental Section

All experiments were performed with a Bruker Spectrospin FT-ICR CMS 47 X equipped with an external ion source. The $\text{Cr}^+-\text{C}_6\text{H}_4$ ions were generated in the ion source from $(\eta^6\text{-}1,2\text{-dioxocyclobutabenzene})\text{tricarboxylchromium}(0)$ by 70-eV electron-impact ionization. The ions were transferred into the ICR cell and thermalized by collisions with argon for about 500 ms.⁹ The ions of interest were isolated by a broad-band ejection of most other ions and by selected single-frequency ejections pulses of low amplitude ("soft single shots") to remove ions of masses close to those studied. This procedure minimizes any kinetic excitation of the isolated ions and ensures that the reactions observed are due to ions of thermal energy. The neutral substrates were introduced into the ICR cell by a leak valve at a pressure of 4×10^{-8} mbar (background pressure 1×10^{-9} mbar). The reaction times were varied from milliseconds to several seconds. The

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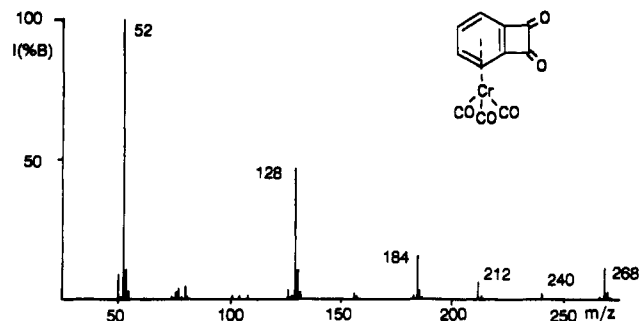


Figure 1. Mass spectrum (70 eV) of (η^6 -1,2-dioxocyclobutabenzene)tricarbonylchromium(0).

collision-induced dissociations (CID) in the ICR cell were achieved by accelerating the ions of interest with a rf pulse into a mixture of argon and the reactant gas (total pressure 1×10^{-7} mbar, pressure of the reactant gas 4×10^{-8} mbar).

The elemental compositions of all ions observed were determined by high-resolution FT-ICR measurements ($m/\Delta m > 300\,000$), and the exact masses agree with the composition given in the text.

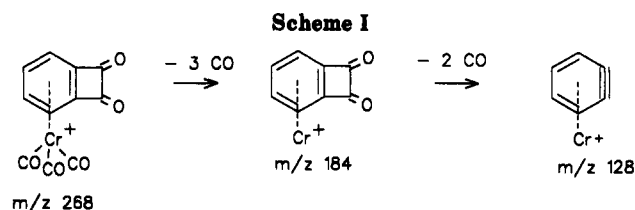
MIKE spectra were measured with a VG ZAB-2F double-focusing mass spectrometer by 70-eV electron impact ionization. The ions of interest were focused into the second field-free region between the electromagnet and the electrostatic analyzer, and the MIKE spectra were obtained by scanning the deflection voltage of the electrostatic analyzer.

(η^6 -1,2-Dioxocyclobutabenzene)tricarbonylchromium(0) (1) and (η^6 -1,2-[^{18}O]-dioxocyclobutabenzene)tricarbonylchromium(0) (1- ^{18}O) were synthesized as described elsewhere.¹⁰ The organic substrates for the reactions are available commercially and were used without further purification. Liquid compounds were subjected to multiple freeze-pump-thaw cycles to remove non-condensable gases before introduction into the ICR cell. 1,3-Pentadiene was prepared by the Grignard reaction of bromoethane with acrolein and dehydration of the resulting pent-1-en-3-ol using standard methods.¹¹

Results and Discussion

Generation of $\text{Cr}^+-\text{C}_6\text{H}_4$. Whereas Fe^+ reacts with chloro- and bromobenzene to yield $\text{Fe}^+-\text{C}_6\text{H}_4$,^{6,12} no reaction of Cr^+ with benzene or chloro-, bromo-, or iodobenzene is observed. It is not known whether this is due to the endothermicity of the total reaction, because the reaction may be blocked at the first insertion step. Thus, any method to generate $\text{Cr}^+-\text{C}_6\text{H}_4$ in the gas phase has to start from another Cr^+-arene complex. Figure 1 shows the 70-eV mass spectrum of (η^6 -1,2-dioxocyclobutabenzene)tricarbonylchromium(0) (1).

The spectrum contains the peak of the molecular ions at m/z 268 and a series of peaks at m/z 240, 212, 184, 156, and 128 due to the successive loss of CO molecules. Consecutive eliminations of CO ligands are a typical mass spectrometric fragmentation pattern of metal carbonyls.¹³ The peculiar feature of the mass spectrum of 1, however, is the elimination of two additional CO molecules besides the three CO losses expected for the tricarbonylmetal fragment. In fact, in this series the relative intensity of the fragment ions reaches a maximum for the ions $[1 - 3 \text{ CO}]^{++}$ and a minimum for the ions $[1 - 4 \text{ CO}]^{++}$, reflecting



the different origin of the first three CO molecules and the last two CO molecules lost. This is corroborated by the mass spectrum of 1- ^{18}O , which exhibits initial loss of three CO groups before eventually two C^{18}O molecules are expelled. The same sequence of CO eliminations is observed in the MIKE spectra and CA spectra of the molecular ions of 1- ^{18}O and of the resulting fragment ions. Hence, an interchange between the CO ligands of the tricarbonylchromium moiety and of the two CO groups of the 1,2-dioxocyclobutabenzene ligand does not occur even for ions of long lifetimes, neither for the molecular ions of 1 nor for the fragment ions $[1 - n \text{ CO}]^{++}$. The latter observation is of special interest because it makes even an insertion of the coordinatively unsaturated chromium into the C-C bonds of the 1,2-dioxocyclobutabenzene ligand unlikely. Thus, the 1,2-dioxocyclobutabenzene ligand is still intact after the loss of three CO groups from 1^{++} and is transformed into a benzyne ligand by the subsequent eliminations of two CO molecules (Scheme I). The exact structure of the resulting $\text{Cr}^+-\text{C}_6\text{H}_4$ ion is not known; the Cr^+ may be bonded "face-on" by the six- π -electron system of the benzyne as in 1 or "side-on" to yield a metallabenzocyclopropene species as shown by the X-ray structure of stable benzyne complexes.⁵ The CA spectrum of the $\text{Cr}^+-\text{C}_6\text{H}_4$ ions exhibits only a small peak for loss of H besides a large peak of Cr^+ ions and gives no additional structure information. The loss of the metal ion in the CA spectrum as the only fragmentation is also observed for $\text{Fe}^+-\text{C}_6\text{H}_4$,⁶ while $\text{Sc}^+-\text{C}_6\text{H}_4$ forms additional fragment ions by cleavage of the benzyne ligand.⁷ C

Thermochemical Considerations. A necessary, but not sufficient, condition for an ion-molecule reaction of thermal ions to occur in the diluted gas phase of an ICR spectrometer is exothermicity. Unfortunately, the enthalpy of formation, ΔH_f , of the $\text{Cr}^+-\text{benzyne}$ complex is not known. Hence, the reaction enthalpies of its reactions are difficult to estimate. Recently, the $\Delta H_f(\text{o-benzyne})$ value of $442 \pm 10 \text{ kJ mol}^{-1}$ was determined independently by two groups,¹⁴ and the $\Delta H_f(\text{Cr}^+)$ value of 1049 kJ mol^{-1} is well-known.¹⁵ However, neither the bond dissociation energy $D(\text{Cr}^+-\text{benzyne})$ nor the related $D(\text{Cr}^+-\text{benzene})$ is known. $\text{Cr}^+-\text{C}_6\text{H}_4$ is not formed by a reaction of Cr^+ with benzene, suggesting $D(\text{Cr}^+-\text{benzyne}) < 260 \text{ kJ mol}^{-1}$. Furthermore, if the failure of Cr^+ to yield $\text{Cr}^+-\text{C}_6\text{H}_4$ and HI by the reaction with $\text{C}_6\text{H}_5\text{I}$ is due to endothermicity, the bond dissociation energy $D(\text{Cr}^+-\text{benzyne})$ is even below 210 kJ mol^{-1} . $\text{Cr}^+-\text{C}_6\text{H}_4$ is hydrogenated by $i\text{-C}_4\text{H}_{10}$ to yield $\text{Cr}^+-\text{C}_6\text{H}_6$ and free Cr^+ and C_6H_6 (see below), resulting in $D(\text{Cr}^+-\text{benzyne}) < 240 \text{ kJ mol}^{-1}$. This shows that $D(\text{Cr}^+-\text{benzyne})$ is considerably less than $D(\text{Fe}^+-\text{benzyne}) = 318 \text{ kJ mol}^{-1}$ ⁶ and $D(\text{Sc}^+-\text{benzyne}) = 368 \text{ kJ mol}^{-1}$.⁷ A bond dissociation energy $D(\text{Cr}^+-\text{benzyne})$ of $235 \pm 25 \text{ kJ mol}^{-1}$ is close to values expected for a purely electrostatic bond between a metal cation and benzene¹⁶ and to the

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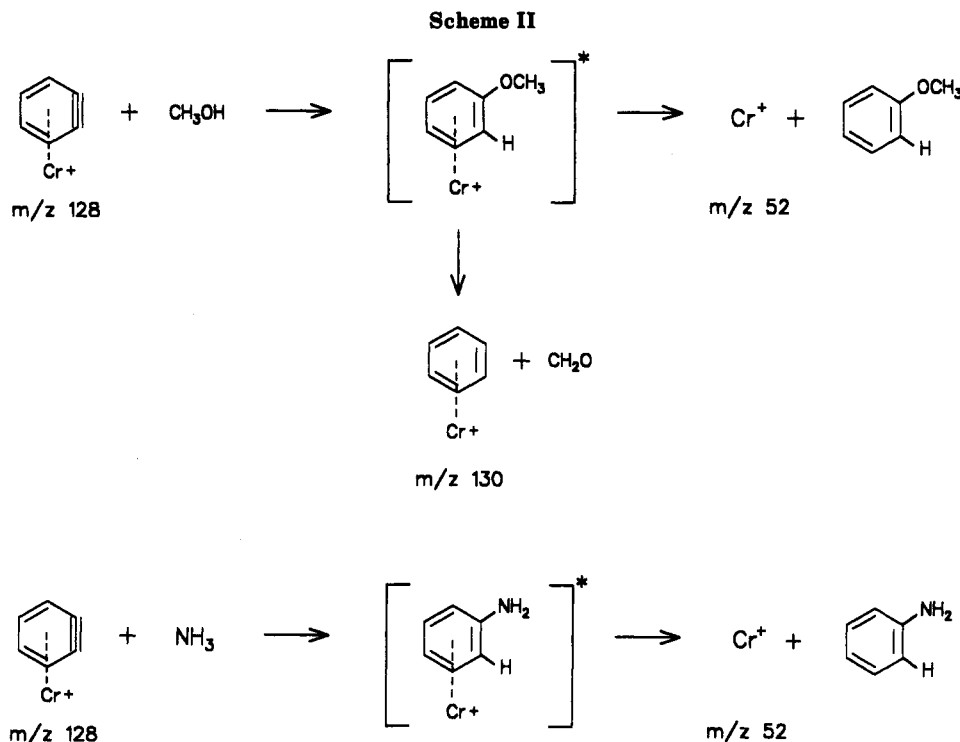
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values of 230 and 205 kJ mol^{-1} reported for $D(\text{Fe}^+-\text{benzene})^{17}$ and $D(\text{Sc}^+-\text{benzene})$,⁷ respectively. Therefore, it is likely the bond dissociation energy of Cr^+ in the complexes does not change greatly if the benzyne ligand of $\text{Cr}^+-\text{C}_6\text{H}_4$ reacts to form a benzene derivative. This would allow us to estimate to a first approximation the reaction enthalpy for the ion-molecule reactions of $\text{Cr}^+-\text{C}_6\text{H}_4$ by taking into account only the changes of the ΔH_f value of benzyne and the resulting benzene derivative and those of the other reactants. The ΔH_f values of reactants and products for the estimation of the reaction enthalpies were taken from the compilation of Lias et al.,¹⁵ with the exception of the ΔH_f values of the alkylbenzocyclobutenes, which were estimated using Benson's incremental method.¹⁸

Reaction of $\text{Cr}^+-\text{C}_6\text{H}_4$ with CH_3OH and NH_3 . In the mass spectra obtained after a 2-s reaction time for the reaction of $\text{Cr}^+-\text{C}_6\text{H}_4$ with CH_3OH and NH_3 , respectively, the signal of $\text{Cr}^+-\text{C}_6\text{H}_4$ at m/z 128 has nearly disappeared and Cr^+ (m/z 52) is observed as the predominant product ion of both reactions. No adduct ions of the nucleophiles to the reactant ion are observed. The ions $[\text{Cr}^+-\text{CH}_4\text{O}]$ (m/z 84) and $[\text{Cr}^+-\text{NH}_3]$ (m/z 69) observed in rather low abundance, arise from a reaction of free Cr^+ with methanol and NH_3 , respectively, as shown by independent experiments. The only other reaction product observed is a small amount of $\text{Cr}^+-\text{C}_6\text{H}_6$ (m/z 130) in the reaction with CH_3OH . The abundant formation of Cr^+ is not due to collision-induced decomposition, because no dissociation of $\text{Cr}^+-\text{C}_6\text{H}_4$ is observed if the ICR cell is filled with an unreactive neutral gas under otherwise identical condi-

Table I. Relative Intensity (%) of the Ionic Products of the Reaction of $\text{Cr}^+-\text{C}_6\text{H}_4$ with Alkanes^a

product ion	CH_4	$i\text{-C}_4\text{H}_{10}$	$n\text{-C}_5\text{H}_{12}$	$n\text{-C}_6\text{H}_{14}$	$c\text{-C}_6\text{H}_{12}$
Cr^+	4	17	19	17	17
$\text{Cr}^+-\text{C}_6\text{H}_6$		28	36	39	39
$\text{Cr}^+-\text{alkene}$		2	2	2	5
alkenyl ion		3	2	3	2
$\text{Cr}^+-\text{C}_6\text{H}_4$	96	50	41	40	37

^a Conditions: total pressure of the ICR cell (c), 4×10^{-8} mbar; reaction time, 2 s.

tions. Clearly, the activation for the release of Cr^+ comes from a chemical reaction of the benzyne ligand with CH_3OH or NH_3 . Benzyne is known to add CH_3OH and NH_3 , forming anisole and aniline, respectively,³ by reactions which are exothermic by 308 and 309 kJ mol^{-1} . Similar exothermic reactions are expected for $\text{Cr}^+-\text{C}_6\text{H}_4$, and certainly they release enough energy to dissociate the complex.

In the case of the reaction with CH_3OH , the chemically activated $\text{Cr}^+-\text{anisole}$ complex may also dissociate by elimination of CH_2O , a fragmentation observed for the analogous $\text{Fe}^+-\text{anisole}$ complex.¹⁹ However, a direct hydrogenation of $\text{Cr}^+-\text{C}_6\text{H}_4$ by CH_3OH also appears possible ($\Delta H_f = -266 \text{ kJ mol}^{-1}$).

Reaction of $\text{Cr}^+-\text{C}_6\text{H}_4$ with Alkanes. $\text{Fe}^+-\text{C}_6\text{H}_4$ and $\text{Sc}^+-\text{C}_6\text{H}_4$ exhibit a rich gas-phase chemistry in their reaction with alkanes^{6,7} which is explained by initial insertion of the transition-metal cation into a C-H or a C-C bond. The ionic products of the reaction of $\text{Cr}^+-\text{C}_6\text{H}_4$ with some linear alkanes and cyclohexane are shown in Table I. No reaction is observed for CH_4 as in the case of the Fe and Sc complexes. The other alkanes studied react rapidly with $\text{Cr}^+-\text{C}_6\text{H}_4$ with estimated reaction efficiencies of >60%, yielding mainly Cr^+ and $\text{Cr}^+-\text{C}_6\text{H}_6$ as the ionic products and minor amounts of the respective alkyl cations and $\text{Cr}^+-\text{alkene}$ complexes. This is in complete contrast to the reactions of the analogous Fe and Sc complexes, which react with alkanes mainly by the incorporation of

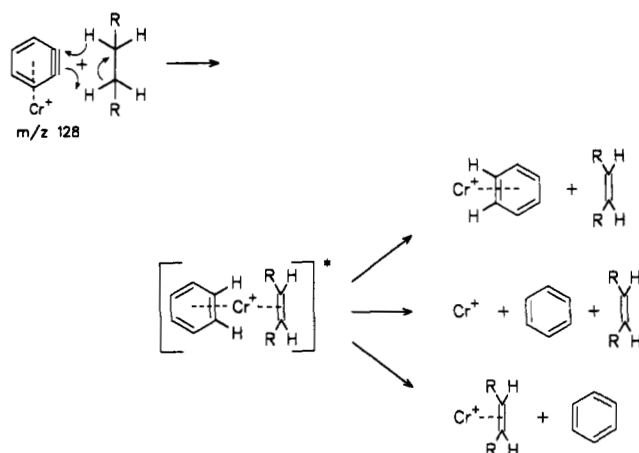
(16) Distances r from 1.73 to 2.14 Å between Cr and the plane of the benzene ring have been observed in stable arene complexes (Silverthorn, W. E. *Adv. Organomet. Chem.* 1975, 13, 47). Thus, 2.0–2.5 Å is a reasonable distance between Cr^+ and benzene in a complex. Using the equation for the classical potential for ion/dipole and ion/induced-dipole interactions (Su, T.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Phys.* 1973, 12, 347) the following electrostatic bond energies (kJ mol^{-1}) are obtained: $r = 2 \text{ Å}$, 415; $r = 2.2 \text{ Å}$, 308; $r = 2.4 \text{ Å}$, 218; $r = 2.6 \text{ Å}$, 158.

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Scheme III

Table II. Relative Intensity (%) of the Ionic Products of the Reaction of $\text{Cr}^+-\text{C}_6\text{H}_4$ with Alkenes^a

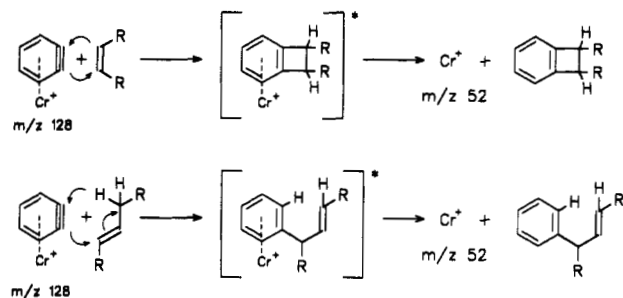
product ion	<i>i</i> -C ₄ H ₈	2-C ₅ H ₁₀	<i>c</i> -C ₆ H ₁₀
Cr ⁺	71	48	33
Cr ⁺ -C ₆ H ₆		19	27
Cr ⁺ -alkadiene		5	3
alkadienyl ion		2	3
Cr ⁺ -C ₆ H ₄	29	26	34

^a Conditions are as given in Table I.

alkane fragments.^{6,7} Obviously, the central Cr⁺ of Cr⁺-C₆H₄ does not cleave the alkane molecule by C-H or C-C insertion, in agreement with the lack of these reactions of free Cr⁺ with alkanes. Thus, the two H atoms are very likely transferred directly from the alkane to the benzyne ligand in the reaction complex. Although the hydrogenation of free benzyne is well-known from pyrolytic processes,²⁰ the hydrogenation by alkanes has not strictly been studied, and it appears that the Cr⁺ "catalyzes" this process in Cr⁺-C₆H₄, which is exothermic by 234–244 kJ mol⁻¹ for the alkanes studied. Such a catalysis of reactions by cations attached to a reactant has been predicted specifically for addition reactions.²¹ The excess energy of the reaction complex can be used to dissociate the resulting Cr⁺-C₆H₆ if it is not carried away by the departing alkene molecule. Interestingly, a ligand exchange for the alkene formed is observed in some of the reaction complexes, suggesting the intermediate complex Cr⁺-(C₆H₆)(alkene). This type of complex is expected to dissociate mainly by loss of the alkene ligand.

Reaction of Cr⁺-C₆H₄ with Alkenes and Alkadienes. Generally Fe⁺-C₆H₄ and Sc⁺-C₆H₄ react with alkenes by addition/dehydrogenation, by addition of fragments of the alkane, and by ligand exchange, but the individual course of the reaction depends on the central transition-metal ion. This is illustrated by the reactions of the Fe and Sc complexes, respectively, with isobutene. The former complex gives Fe⁺-toluene as the sole ionic product, while the latter one gives rise to addition-dehydrogenation and exchange products [ScC₁₀H₁₀]⁺, [ScC₁₁30H₈]⁺, and [ScC₄H₈]⁺. The reactions of Cr⁺-C₆H₄ with alkenes occur again with a large reaction efficiency, but the reaction routes are different from those of the Fe- and Sc-benzyne complexes (Table II). Cr⁺ is the sole reaction product with isobutene, while

Scheme IV

Table III. Relative Intensity (%) of the Ionic Products of the Reaction of Cr⁺-C₆H₄ with 1,3-Dienes^a

product ion	C ₄ H ₆	<i>i</i> -C ₅ H ₈	<i>n</i> -C ₆ H ₈	<i>c</i> -C ₆ H ₈
Cr ⁺	67	65	77	73
[CrC ₉ H ₇] ⁺	11	8 ^b	1 ^b	
other			2 ^c	4 ^d
Cr ⁺ -C ₆ H ₄	22	27	20	23

^a Conditions are as given in Table I. ^b [CrC₁₀H₉]⁺. ^c [CrC₆H₈]⁺. ^d *c*-C₆H₈⁺.

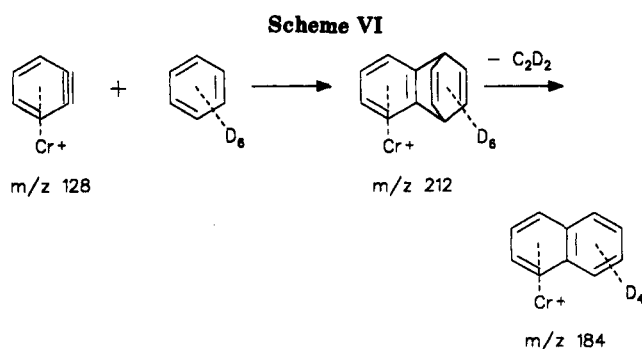
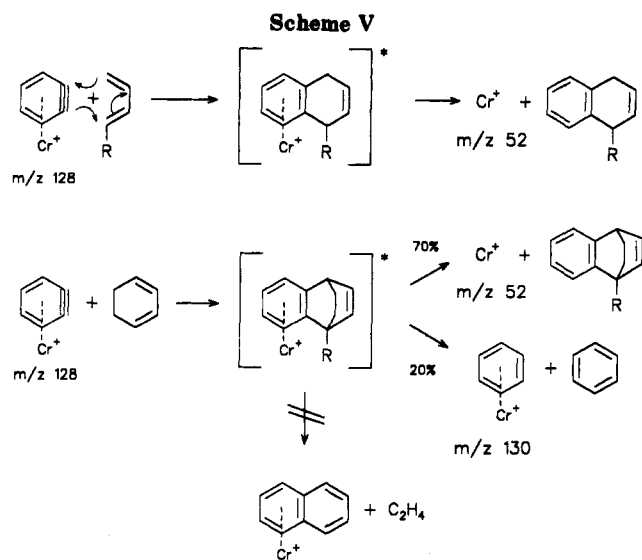
in the case of 2-pentene and cyclohexene Cr⁺ and Cr⁺-C₆H₆ are the main products besides small amounts of alkenyl cations and Cr⁺-alkadiene complexes, in absolute correspondence to the reactions with alkanes. These results are most easily rationalized by again assuming inert Cr⁺ and reactions exclusively at the benzyne ligand, either by abstraction of two hydrogen atoms or by [2 + 2] cycloaddition and an ene reaction, respectively, of the complete alkene (Scheme IV). However, the large efficiency of the reactions may point again to an "electrostatic catalysis"²¹ of the Cr⁺ attached to the benzyne.

In the case of 2-pentene and cyclohexene as reactants, the hydrogen transfer producing Cr⁺-C₆H₆ and a conjugated diene is exothermic by more than 250 kJ mol⁻¹. A hydrogen transfer yielding a diene is not possible in the case of isobutene. The only other dehydrogenation product formed from isobutene without rearrangement of the carbon skeleton would be methylenecyclopropene. This hydrogen transfer to Cr⁺-C₆H₄ is again exothermic by about 140 kJ mol⁻¹ but very likely has to occur in two steps via single H atom transfers. The absence of this process supports a concerted [2_r + 2_r + 2_e] cycloaddition mechanism for the transfer of the two H atoms to Cr⁺-C₆H₄ observed for the other alkenes. As in the case of alkane reactants, the alkadiene formed by this process may stay with the Cr⁺ to a certain extent and the benzene molecule is lost instead from the reaction complex.

The other reactions expected between benzyne and alkenes are the formation of a benzocyclobutene derivative by a [2 + 2] cycloaddition and the ene reaction generating an alkenylbenzene. Both processes are strongly exothermic by more than 300 kJ mol⁻¹. In the reaction between Cr⁺-C₆H₄ and the alkene, the excess energy cannot be released from the reaction complex by ejecting a neutral fragment generated during the process. Thus, the reaction product is strongly chemically activated and dissociates into Cr⁺ and the benzocyclobutene and alkenylbenzene, respectively. Since addition of the alkene is the only process possible for isobutene, Cr⁺ is the only ionic product observed in this case, while Cr⁺ and Cr⁺-C₆H₆ are formed from other alkenes.

A concerted [4_r + 2_r] cycloaddition of Cr⁺-C₆H₄ is also expected for the reactions with 1,3-dienes, if the reactivity is controlled by reactions of the benzyne ligand. In the case of Fe⁺-C₆H₄ the reaction with 1,3-butadiene releases mainly Fe⁺ from the reaction complex, but abundant

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$[\text{FeC}_{10}\text{H}_8]^+$ is also formed, corresponding to a Fe^+ -naphthalene complex.⁶ $\text{Sc}^+-\text{C}_6\text{H}_4$ also generates a considerable amount of $[\text{ScC}_{10}\text{H}_8]^+$, but the main product is $[\text{ScC}_9\text{H}_7]^+$, likely a Sc^+ -indenyl complex.⁷ Large efficiencies approaching the collision limit are estimated for the reactions of $\text{Cr}^+-\text{C}_6\text{H}_4$ with the 1,3-dienes studied, and the distribution of the ionic species in the mass spectra obtained after a 2-s reaction time are shown in Table III.

Interestingly, $\text{Cr}^+-\text{C}_6\text{H}_4$ also yields $[\text{CrC}_9\text{H}_7]^+$ from a reaction with 1,3-butadiene by loss of CH_3 , but no $[\text{CrC}_{10}\text{H}_8]^+$ is formed and the ionic main product is Cr^+ . Similarly, 2-methyl-1,3-butadiene reacts with $\text{Cr}^+-\text{C}_6\text{H}_4$ also by loss of CH_3 , yielding $[\text{CrC}_{10}\text{H}_9]^+$, and by formation of Cr^+ . However, 1,3-pentadiene rarely loses CH_3 and no C_2H_5 on its reaction with $\text{Cr}^+-\text{C}_6\text{H}_4$ but yields Cr^+ in great abundance. Cr^+ is almost exclusively the only ionic product of the reaction with cyclopentadiene. 1,3-Pentadiene and cyclopentadiene can undergo an ene reaction with $\text{Cr}^+-\text{C}_6\text{H}_4$, in contrast to the case for 1,3-butadiene, but it is not known whether this is the origin of the different reaction routes. While the release of Cr^+ from the reaction complex of $\text{Cr}^+-\text{C}_6\text{H}_4$ and a 1,3-diene is again undoubtedly a consequence of the large exothermicity of the cycloaddition of $>400 \text{ kJ mol}^{-1}$, the mechanism of the formation of $[\text{MC}_9\text{H}_7]^+$ ($\text{M} = \text{Sc}, \text{Cr}$) is not clear. Huang et al.⁷ have suggested in the case of the Sc^+ complex a reaction sequence starting with the insertion of Sc^+ into a C-H bond of 1,3-butadiene and involving eventually also a C-C insertion step. The inability of Cr^+ for C-H and C-C insertion cast some doubt on this mechanism, but it may be that Cr^+ exhibits unusual reactivity under the conditions of a strong chemical activation.

Among the 1,3-dienes studied, cyclohexa-1,3-diene is a special case because of the possibility of a concerted transfer of two H atoms as well as cycloaddition to $\text{Cr}^+-\text{C}_6\text{H}_4$ (Scheme V). Indeed, the other abundant ionic reaction product besides Cr^+ is $\text{Cr}^+-\text{C}_6\text{H}_6$. Again, neither Cr^+ -naphthalene, which was expected to arise from cycloaddition and subsequent elimination of C_2H_4 , nor $[\text{CrC}_9\text{H}_7]^+$ is observed as the product.

Reaction of $\text{Cr}^+-\text{C}_6\text{H}_4$ with Arenes. The reaction pathways of $\text{Cr}^+-\text{C}_6\text{H}_4$ with alkanes, alkenes, and alkadienes can be followed only indirectly because Cr^+ is always the main product, released from the reaction complex owing to the certainly large exothermicity of the hydrogenation and cycloadditions at the benzyne ligand. However, less exothermic cycloadditions of benzyne to arenes and heteroarenes are also possible.³ Typically, furan and

furan derivatives are used for these reactions, but 1,2- and in particular 1,4-cycloaddition of benzyne to benzene and other arenes are known also, sometimes followed by elimination of acetylene to restore the aromatic system. The 1,4-cycloaddition of benzyne and benzene, yielding benzobarrelene, is exothermic by 132 kJ mol^{-1} , and the total reaction, including the subsequent fragmentation to naphthalene and acetylene, is exothermic by 147 kJ mol^{-1} . This is distinctly less than the values calculated for the cycloadditions of alkenes and alkadienes. Furthermore, some of the excess energy may be removed from the reaction complex by the departing acetylene molecule. Thus, we hoped to detect the addition product of these reactions directly as an ionic species. These expectations are borne out by the experiment.

If furan reacts with $\text{Cr}^+-\text{C}_6\text{H}_4$ in the gas phase, again only Cr^+ is observed as the ionic product. Furan is a good diene for Diels-Alder reactions, and obviously its cycloaddition to the benzyne ligand is still rather exothermic. However, benzene reacts with a distinctly reduced efficiency with $\text{Cr}^+-\text{C}_6\text{H}_4$, and the reactions can be followed by using C_6D_6 .

The mass spectrum obtained after a reaction time of 5 s and a partial pressure of C_6D_6 of 4×10^{-8} mbar in the ICR cell still exhibits a rather large signal for $\text{Cr}^+-\text{C}_6\text{H}_4$ at m/z 128, persisting even after this long reaction time. New peaks of product ions are observed at m/z 52 (Cr^+), 136 ($[\text{CrC}_9\text{D}_6]^+$), 184 ($[\text{CrC}_{10}\text{H}_4\text{D}_4]^+$), 212 ($[\text{CrC}_{12}\text{H}_4\text{D}_8]^+$), and 268 ($[\text{CrC}_{16}\text{H}_4\text{D}_{10}]^+$). In particular the ions at m/z 52 and 184 are abundant, while the peaks at m/z 136 and 268 are quite small. The ions m/z 212 correspond to the expected cycloaddition product of C_6D_6 to the benzyne ligand of $\text{Cr}^+-\text{C}_6\text{H}_4$, and this assignment is corroborated by CID of the ions at m/z 212, resulting in ions at m/z 184 (loss of C_2D_2) and 52 (Cr^+) as the only products. Similarly, CID of the ions at m/z 184 yield exclusively Cr^+ , as expected for a Cr^+ -tetra-deuterionaphthalene complex. It is important to note, that no H/D scrambling is observed during the reaction, neither during the formation of $[\text{CrC}_{12}\text{H}_4\text{D}_8]^+$ nor during the final elimination of acetylene. Thus, there is no doubt that the reaction occurs *localized* at the benzyne ligand, as depicted in Scheme VI. Apparently, Cr^+ is only a "spectator" of this process but catalyzes the reaction, probably by electrostatic interaction with the reactants.²¹

Other interesting details of the reaction of $\text{Cr}^+-\text{C}_6\text{H}_4$ with C_6D_6 are the observations of $[\text{CrC}_9\text{D}_6]^+$ (m/z 136) and $[\text{CrC}_{16}\text{H}_4\text{D}_{10}]^+$ (m/z 268) as reaction products. A $\text{C}_6\text{H}_4/\text{C}_6\text{D}_6$ ligand exchange is difficult to accept, and more likely the Cr^+ released during the reactions is attached to C_6D_6 , present in great excess in the gas phase. Similarly, the reaction product $\text{Cr}^+-\text{C}_{10}\text{H}_4\text{D}_4$ obviously adds a C_6D_6 to form the sandwich complex $\text{Cr}^+-\text{(C}_6\text{D}_6\text{)}_2\text{(C}_{10}\text{H}_4\text{D}_4\text{)}$. A direct attachment of "bare" Cr^+ has not been reported before, but the Cr^+ released by exothermic reactions from $\text{Cr}^+-\text{C}_6\text{H}_4$ may behave differently because of a chemical

activation. However, free Cr^+ reacts easily with some heteroaromatic compounds.²² Finally, naphthalene- d_8 reacts with $\text{Cr}^+-\text{C}_6\text{H}_4$ in the ICR spectrometer in a fashion analogous to that for benzene. The cycloaddition product $[\text{CrC}_{16}\text{H}_4\text{D}_8]^+$ (m/z 264) and its fragmentation product $[\text{CrC}_{14}\text{H}_4\text{D}_8]^+$ (m/z 236), due to elimination of C_2D_2 , are observed with about the same intensity, besides Cr^+ . However, instrument problems frustrated a more detailed study of this process. Nevertheless, it is clear that cycloaddition of $\text{Cr}^+-\text{C}_6\text{H}_4$ to arenes is a general reaction of this species.

Conclusion

The Cr^+ -benzyne complex $\text{Cr}^+-\text{C}_6\text{H}_4$ was prepared in the gas phase by electron-impact-induced decomposition of the stable complex (η^6 -1,2-dioxocyclobutabenzene)tricarboxylchromium(0). This is a new and general method to generate ionic transition-metal complexes of less reactive transition-metal cations with unstable ligands, and its application to other transition-metal-benzyne complexes is currently under study.

$\text{Cr}^+-\text{C}_6\text{H}_4$ exhibits a unique chemistry with the neutral reaction partners used in this study which can be perceived by the combination of an unreactive central transition-metal cation, a highly reactive ligand, and a weak bond between the central Cr^+ and the benzyne ligand. As a consequence and in comparison with the related complexes $\text{Fe}^+-\text{C}_6\text{H}_4$ and $\text{Sc}^+-\text{C}_6\text{H}_4$, the reactions of $\text{Cr}^+-\text{C}_6\text{H}_4$ with alkanes, alkenes, and 1,3-alkadienes are more straightforward, with no indication of a fragmentation of the carbon skeleton of the hydrocarbon reactant. Certainly,

the reason for this is the inability of Cr^+ to insert into C-H and C-C bonds. On ubiquitous and abundant product of the reactions of $\text{Cr}^+-\text{C}_6\text{H}_4$ in the ICR spectrometer is Cr^+ . This is to be expected, owing to the weak bond of Cr^+ in Cr^+ -arene complexes and the large exothermicity of the addition reactions at the benzyne ligand. The excess energy of the isolated reaction complex leads to strongly chemically activated products which dissociate rapidly.

Alkanes and certain alkenes efficiently transfer two H atoms to $\text{Cr}^+-\text{C}_6\text{H}_4$. In these reactions the excess energy of the reaction complex is carried away by the alkene or alkadiene and abundant $\text{Cr}^+-\text{C}_6\text{H}_6$ is observed. No hydrogenation reaction with CH_4 , $i\text{-C}_4\text{H}_8$, and other hydrocarbons is observed, which cannot transfer two H atoms by forming a C-C double bond. Thus, the hydrogenation of $\text{Cr}^+-\text{C}_6\text{H}_4$ by alkanes and other hydrocarbons very likely corresponds to a concerted $[2_x + 2_x + 2_c]$ cycloaddition mechanism which is "electrostatically catalyzed" by Cr^+ .

The reaction of $\text{Cr}^+-\text{C}_6\text{H}_4$ with benzene and naphthalene is of particular interest. The cycloaddition of benzyne to arenes is distinctly less exothermic than a hydrogenation or the addition of alkenes and alkadienes. Thus, the Cr^+ -benzyne adduct complex is directly observed in the ICR spectrometer and is shown to behave as expected during CID.

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