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Reactions of Bare and Ligated Chromium(I) Ions with Gaseous Arenes. Role of a "Spectator" Aromatic Ring in Chelate Complex Formation†

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The gas-phase reaction of XCr^+ ($X = C_6H_6$, NH_3) and $(NH_3)_2Cr^+$ with arenes (L) leads to $XCrL^+$, LCr^+, and L_2Cr^+ complexes. The pattern and the efficiency of the two classes of complex formation processes allow a clear distinction between simple arenes, such as toluene and mesitylene, yielding ultimately sandwich-type L_2Cr^+ complexes, and α,ω-diphenylalkanes, yielding only LCr^+ complexes, where a common sandwich-type structure is achieved by simultaneous coordination of the metal cation with the two aryl rings. The critical parameter controlling the extent of chelate coordination is the length of the methylene chain joining the two rings. A different behavior is displayed by ligands such as *trans*-stilbene and [2.2]paracyclophane, where only one aryl ring is involved in the stepwise NH_3 substitution from $(NH_3)_2Cr^+$. Under low pressure, and hence inefficient collisional deactivation, the Cr^+ reaction with the selected arenes is governed by relative binding energies and radiative cooling efficiencies of the ensuing complexes. Insertion of free Cr^+ into the cage of [2.2]paracyclophane may not be excluded.

Introduction

The field of gas-phase organometallic chemistry is expanding at a fast pace.[1] Its growth is sustained by several major spurs such as the effort toward an understanding of the mechanisms of C−H and C−C bond activation and catalytic processes in general, the elucidation of basic properties of metal-containing ions and neutrals and of the effect of complexation on the reactivity of the metal center and the organic residue, and the search for highly specific chemical ionization (CI) reagents. A conspicuous body of knowledge is thus being constructed on the structural and reactivity features of species which are either known in solution but are studied in an isolated environment, void of complicating solvation and ion-pairing phenomena, or are entirely new. Whenever ions collide with neutral molecules in the isolated state, they are especially prone to establish interactions that allow the most effective electrostatic stabilization and frequently the formation of covalent bonds. Hence, an enhanced quest for coordination is expected from bare and partially ligated metal ions. In this perspective, we became interested in the study of reactions of chromium(I) ions with single-ring arenes and α,ω-diphenylalkanes (DPAs: $C_6H_5(CH_2)_nC_6H_5$, $n = 1-4$). The latter can in fact supply two phenyl rings, possibly behaving as the benzene moieties of $(\eta^6\text{-}C_6H_6)_2Cr$ (I) and satisfying the overall coordination demand of Cr(I). Previous studies on the protonation and alkylation of DPAs, effected both by radiolytic[2] and mass spectrometric techniques,[3] demonstrated that the second (spectator) ring interacts with the positively charged (protonated or alkylated) ring, providing electrostatic stabilization. Such interaction requires folding of the methylene chain at the expense of the entropy lost in frozen rotors. Indirect evidence that a similar type of arrangement may be attained in gaseous $(DPA)Cr^+$ ions can be found in the EI and NH_3-CI mass spectra of $(DPA)Cr(CO)_3$, where remarkably abundant $(DPA)Cr^+$ ions are formed and ammonia adducts are not formed, respectively, at variance with other $(arene)Cr(CO)_3$ compounds.[4] $(arene)M(arene')^+$ species of likely sandwich-type structure have been produced in the gas phase by ion−molecule reactions.[5] The intramolecular coordination of two closely spaced phenyl rings to a metal cation was previously invoked,[6] but the effect of systematic structural variation of a diaryl ligand was never explored. The present study reports on the formation and reactivity of complexes of Cr(I) bound to simple arenes (benzene, toluene, mesitylene, and styrene) and to the diaryl compounds listed in Chart 1.

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† Dedicated to Professor Fulvio Cacace on the occasion of his 65th birthday.

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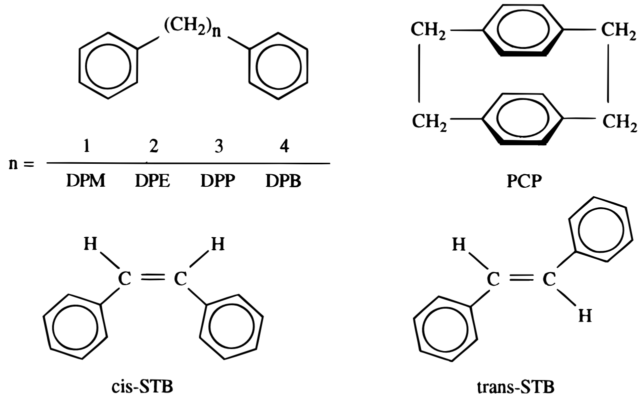
Chart 1



Experimental Section

Materials. (η^6-benzene)Cr(CO)$_3$, benzene, toluene, mesitylene, styrene, [2.2]paracyclophane, *trans*- and *cis*-stilbene, $C_6H_5CH_2C_6H_5$, and $C_6H_5(CH_2)_2C_6H_5$ were purchased from Aldrich and used without further purification. Samples of $C_6H_5(CH_2)_3C_6H_5$ and $C_6H_5(CH_2)_4C_6H_5$ were obtained as previously described.[3e] NH_3 and Ar were research grade gases from UCAR Specialty Gases.

Procedure. FT-ICR[7] experiments were performed on a Bruker Spectrospin Apex TM 47e mass spectrometer equipped with an external ion source and with a cylindrical "infinity" cell of 12 cm length and 6 cm radius situated in the bore of a 4.7 T superconducting magnet. (η^6-benzene)Cr(CO)$_3$ was introduced into the ion source at 2×10^{-6} mbar (1 mbar = 100 Pa) through a direct insertion probe at 84 °C. Ionization was effected by electron impact at 35 eV electron energy, using a 100 ms electron beam pulse and a 10 μA emission current. The resulting ion mixture was transferred into an ICR cell containing a known pressure of the neutral reagent. The ion of interest was selected by broad-band selection and relieved of any excess energy content by collisions with Ar, admitted through a pulsed magnetic valve up to the peak pressure of 10^{-5} mbar. After a suitable pumping time, further isolation from all other fragment or product ions was achieved by a soft selective-ejection technique, using low-energy "single shots". The reactant ion was then allowed to react with the neutral reagent introduced at the pressure of $(1-4) \times 10^{-8}$ mbar by a needle valve from a reservoir thermostated chamber. The whole inlet system was heated to 120−140 °C to allow vaporization of the higher boiling samples, some of them reaching a stationary concentration in the ICR cell only after a time of several hours. The cell was mantained at the room temperature of 25 °C, which is considered as the effective reaction temperature.[3e] Whenever required, a second reagent, NH_3, was admitted by another inlet. Neutral pressures were read from an ion gauge located in front of the high-vacuum turbo pump and calibrated with the reference reaction $CH_4^{\bullet+} + CH_4 \rightarrow CH_5^+ + CH_3$ using the value of $k = 1.1 \times 10^{-9}$ molecule^{-1} cm^3 s^{-1} as its rate constant.[8] Pressure readings for each neutral reagent were further weighted by individual response factors.[9]

Collisional activation experiments[10] on selected product ions, (DPP)Cr$^+$ and (DPM)Cr$^+$, were effected by 10−30 μs radiofrequency pulses at the voltage $V_{p-p} = 80$ V, in the presence of 4.5×10^{-8} mbar of C_6D_6 and 1.0×10^{-8} mbar of DPP or DPM, respectively. The center of mass energy for collisions with C_6D_6 ranged from 3.8 to 0.4 eV.

Kinetic processes were followed in time by recording relative ion intensities with increasing reaction time. Pseudo-first-order rate constants were obtained from the logarithmic decrease of reactant ion intensity and were divided by the neutral concentration to obtain second-order rate constants. Reported values of second-order rate constants are the average of usually three experiments run at different neutral pressures. The error in the rate constants (ca. ±30%) arises largely from the uncertainty of neutral concentration. The product ratio from competitive reaction channels was evaluated from the ion intensities of the product ions extrapolated at initial time, in order to minimize interference by possible further reaction steps.

Results and Discussion

Formation of Reactant Ions. (η^6-benzene)Cr(CO)$_3$ was used as the primary source of bare and ligated Cr(I) ions. Ionization by 35 eV electrons yielded the molecular ion and fragment ions from consecutive losses of neutral ligands with the following relative abundances: $(C_6H_6)Cr(CO)_3^+$ (100), $(C_6H_6)Cr(CO)_2^+$ (20), $(C_6H_6)Cr(CO)^+$ (20), $(C_6H_6)Cr^+$ (85), Cr^+ (40). $(C_6H_6)Cr^+$ and Cr^+ were selected as reactant ions with the aromatic compounds of interest. In addition, $(NH_3)Cr^+$ and $(NH_3)_2Cr^+$ to be used as ionic reagents were obtained from reaction of the ion mixture exiting from the ion source with NH_3, introduced at 3×10^{-8} mbar in the ICR cell. The NH_3 ligand was chosen as an example of a lone-pair donor (as opposed to C_6H_6, a π-donor), providing ligated Cr(I) ions of varying coordination and electronic demand. The selected ions underwent several unreactive collisions with Ar, disposing of any excess internal and translational energy, before being allowed to react. The electronic energy state of Cr^+ was checked by testing its reactivity with CH_4. In fact, whereas excited-state Cr^+ is reactive with alkanes, ground-state (3d^5) Cr^+ does not react with hydrocarbons by the usual C−H and C−C insertion.[11] The observed lack of reactivity confirmed the attainment of a ground-state population of Cr^+ ions.

Reactions of Bare Cr(I). The reactions of Cr^+ with gaseous arenes lead to formation of (arene)Cr$^+$ adducts according to reactions whose second-order rate constants (k_{exp}) and efficiencies (Eff) are listed in Table 1. The reported rate constants are effective second-order rate constants, invariant with respect to pressure, at least within the explored pressure range and within the stated experimental uncertainty. It follows that the observed formation of (arene)Cr$^+$ complexes does not experience substantial stabilization by collision with the neutral but is, rather, allowed by a radiative stabilization process.[13] Given the low neutral pressure ($\leq 10^{-8}$ mbar), this finding is in line with reported transition pressures from collisional to radiative association, typically ranging from 10^{-4} to 10^{-7} mbar.[13c,14] As previously reported,[1a,15] Cr^+ is unreactive toward benzene, which apparently contrasts with the abundant formation of

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Table 1. FT-ICR Reactions of Cr^+ with Gaseous Arenes

arene (L)	k_{exp}[a]	Eff[b]
benzene		
toluene[c]	1.6	10
mesitylene[c]	7.36	48
styrene[c]	3.9	26
PCP[c]	8.5	45
cis-STB[d]	2.8	16
trans-STB[d]	12	66
DPM[d]	4.0	23
DPE[d]	1.1	6
DPP[d]	20	≃100
DPB[d]	6.0	28

[a] Units of 10^{-10} cm^3 molecule^{-1} s^{-1}. [b] Eff = $(k_{exp}/k_{coll}) \times 100$. The collisional rate constant, k_{coll}, is calculated according to ref 12. [c] Reaction pattern: $Cr^+ + L \rightarrow LCr^+ (+L) \rightarrow L_2Cr^+$. [d] Reaction pattern: $Cr^+ + L \rightarrow LCr^+$.

stable $(C_6H_6)Cr^+$ fragment ions in the ionization process. The $(C_6H_6)Cr^+$ binding energy amounts to 53 ± 9 kcal mol^{-1},[16] a recent density functional approach estimating it as 41 kcal mol^{-1}.[17] Thus, the lack of formation of $(C_6H_6)Cr^+$ complex by direct association of the two partners is to be ascribed to the inefficient cooling of the adduct ion, excited by the exothermicity of its formation process. This is consistent with the ion−molecule reaction of Cr^+ with small benzene clusters, leading to $(C_6H_6)_nCr^+$ ($n = 1, 2$), by a proposed mechanism in which the evaporation of benzene molecules ensures the necessary cooling of the complex ions.[18] An increase in binding energy of the complex and in the number of degrees of freedom for energy dispersal are predicted to increase the rate of IR radiative stabilization and the association efficiency.[13] Thus, both factors can play a role in the increasing ligation efficiency displayed by toluene and mesitylene, where the increasing number of degrees of freedom parallels the trend in binding energies to Cr^+ (benzene < toluene < mesitylene).[5c]

The homologous series of DPAs is expected to give a uniform trend of rather similar efficiency values if the Cr^+ complexation involves only one phenyl ring and the second one behaves as a more or less remote substituent on the alkyl chain. On the contrary, the efficiency ranges from 6% to 100% in a way which is only apparently erratic, since it actually fits into a model viewing the simultaneous interaction of the two phenyl rings with the metal ion (eq 1). Such a model is

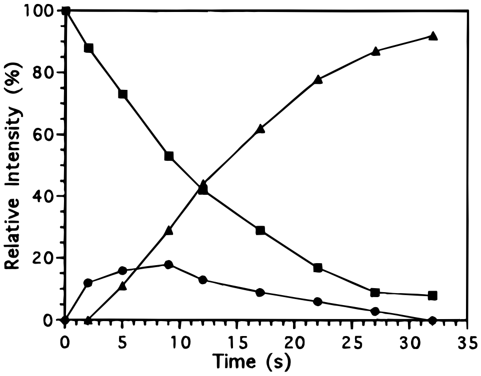
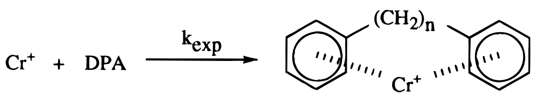


Figure 1. Relative ion intensities of Cr^+ (■), (toluene)Cr^+ (●), and $(toluene)_2Cr^+$ (▲) as a function of reaction time (eq 2). The toluene pressure was 2.1×10^{-8} mbar.



(1)

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supported by the different reaction patterns shown by toluene and mesitylene, where formation of the primary (arene)Cr^+ complex is followed by a consecutive, irreversible addition process to give $(arene)_2Cr^+$ ions (eq 2 and Figure 1 for arene = toluene), and by DPAs, where

$$Cr^+ + \text{arene} \xrightarrow{k_{exp}} (\text{arene})Cr^+ \xrightarrow{\text{arene}} (\text{arene})_2Cr^+ \quad (2)$$

addition of a second ligand is never observed. If the sandwich-type structure of $(\eta^6\text{-benzene})_2Cr$ (I) in the solid state[19] can be taken as a model for **1**, a Cr−C_6-(ring centroid) distance of ca. 1.6 Å should confer the best bonding interaction. Therefore, it is not surprising that the least effective DPA ligand (DPE) corresponds to the one where the two phenyl ring centroids are separated by ca. 5 Å, based on the C−C bond lengths and bond angles of a standard hydrocarbon. On the other hand, the most efficient DPA ligand (DPP) is the one best suited to attain the parallel sandwich type geometry[3e] that allows the closest proximity of the phenyl rings.

It is worth noting that none of the aromatic hydrocarbons included in this study showed any evidence of C−H and C−C activation processes. The alkane portion of DPAs appeared unreactive toward Cr^+, just like simple linear and branched alkanes, which showed no exothermic C−H or C−C activation pathway upon reaction with ground-state Cr^+.[11] Ionic products involving unimolecular H_2, C_2H_4, and C_7H_8 loss have instead been observed in the metastable decomposition of the Fe^+ complexes with $Ph(CH_2)_nPh$ ($n = 4, 6, 8$), showing regio- and stereoselective products depending on the chain length of the diphenylalkane chain and suggesting a sandwich type structure for the dissociating complex.[20]

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(14) The kinetics of complex formation have been analyzed within the framework of the *standard hydrocarbon model*,[13a] in an attempt to obtain semiquantitative binding energies. Application of the generic model to the present systems unfortunately did not give a meaningful trend. The model may fail seriously when one of the reactants is an atomic ion, as in the present case.[13d] The general formalism of this useful approach has been recently implemented by combining ab initio quantum-chemical calculations of structures, frequencies and intensities with estimates of rate constants based on variational transition state theory.[13e] Such treatment was, however, beyond the scope of this study.

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Table 2. FT-ICR Reactions of XCr^+ ($X = NH_3$, C_6H_6) with Gaseous Arenes

arene (L)	reactant ion XCr^+	k_{exp}[a]	Eff[b]	product ions[c] $LCr^+/XCrL^+$
C_6D_6	$(C_6H_6)Cr^+$	4.6	41	0.8/0.2
toluene	$(C_6H_6)Cr^+$	8.6	75	0.8/0.2
mesitylene	$(C_6H_6)Cr^+$	12	100	0.8/0.2
styrene	$(C_6H_6)Cr^+$	7.8	65	0.9/0.1
cis-STB	$(C_6H_6)Cr^+$	17	100	1.0/0.0
trans-STB	$(C_6H_6)Cr^+$	18	≈100	0.7/0.3
DPM	$(C_6H_6)Cr^+$	9.7	75	1.0/0.0
DPP	$(C_6H_6)Cr^+$	20	≈100	1.0/0.0
mesitylene	$(NH_3)Cr^+$	11	79	1.0/0.0
styrene	$(NH_3)Cr^+$	4.1	30	0.8/0.2
PCP	$(NH_3)Cr^+$	4.5	30	0.8/0.2
cis-STB	$(NH_3)Cr^+$	1.7	10	1.0/0.0
trans-STB	$(NH_3)Cr^+$	16	100	1.0/0.0
DPM	$(NH_3)Cr^+$	16	100	1.0/0.0
DPP	$(NH_3)Cr^+$	17	100	1.0/0.0
DPB	$(NH_3)Cr^+$	11	67	1.0/0.0

[a] See footnote *a* in Table 1. [b] See footnote *b* in Table 1. [c] Abundance ratio extrapolated at initial time.

In recent years complexes of Cr(0) with [2.2]paracyclophane-type ligands have been actively studied in the condensed phase.[21] It was found possible to introduce a chromium atom into the [2.2]paracyclophane cavity by means of cocondensation techniques, although the resulting (η^{12}-[2.2]paracyclophane)chromium(0/I) shows the features of a rather compressed sandwich complex. The rigid chelate ligand cage shields the metal from solvolytic attack, rendering the chromium(I) complex remarkably inert. The same kind of structure can be conceivably obtained from the gas-phase reaction of Cr^+ with PCP, supported by the lack of reactivity of the $(PCP)Cr^+$ complex toward further ligand addition. The double bond of styrene does not seem to play a major role in the ligation reaction, which proceeds to L_2Cr^+ species. The same does not occur for the Cr^+ reaction with *cis*- and *trans*-STB, which yield only LCr^+ complexes, as do the DPA ligands. This raises the questions whether the rigid double-bond geometry may still allow coordination to the two phenyl rings of *cis*-STB and whether trans → cis isomerization may occur from *trans*-STB upon activation by the exothermicity of ligation. Further information was sought by utilizing the less exothermic reactions of various ligated Cr(I) species as an alternative route to LCr^+ species.

Reactions of XCr^+ ($X = C_6H_6$, NH_3) and $(NH_3)_2Cr^+$. The reaction of $(C_6H_6)Cr^+$ with gaseous arenes (Table 2) proceeds by exchange and addition pathways, as shown by the ion intensity profiles as a function of time of the C_6D_6 reaction (eq 3, Figure 2). Reaction 3a represents a prototypical arene exchange process[22] and occurs with fair efficiency (33%), despite being nearly thermoneutral.[23] Once again the addition reaction (3b) (Eff = 8%) stands in contrast to the apparent unreactivity of the Cr^+−benzene pair. The addition complex $(C_6H_6)Cr(C_6D_6)^+$ is unreactive as well, being unable to yield the ligand exchange product $(C_6D_6)_2Cr^+$. The inertness toward ligand exchange was found to be a general feature of (arene)Cr(arene′)$^+$ complexes and prevented the study of arene-exchange equilibria. The same holds for the DPA complexes of Cr^+, proven to be inert both toward arene addition and arene exchange. For example, the upper limit for the efficiency of the $(DPM)Cr^+ + DPP \rightarrow (DPP)Cr^+ + DPM$ reaction is 0.5%. This finding demonstrates the chelate interaction of the DPA ligands, which react with $(C_6H_6)Cr^+$ exclusively by the exchange route. An attempt to activate $(DPA)Cr^+$ ions toward further ligand addition has been tried by a radio-frequency excitation pulse delivering 0.4−3.8 eV center of mass energy upon collision of $(DPP)Cr^+$ with C_6D_6. It was reasoned that, given a certain amount of energy, the organized sandwich-type structure would eventually break and the ensuing coordinatively unsaturated metal ion would add a second DPP or C_6D_6 molecule. The fact that no further addition processes are observable suggests that radiative cooling of the excited complex may occur before the first collision with a neutral ligand. The same experiment was performed with $(DPM)Cr^+$ ions, where the chelate interaction of the two phenyl rings is believed to be less efficient. Once again, addition of a second aromatic ligand was not observed. The only product ion appearing at excitation energies above 1.6 eV (center of mass) was the naked Cr^+ ion. It thus appears that translationally excited $(DPA)Cr^+$ ions are unable to undergo translational to internal energy conversion, cleavage of coordination to one phenyl ligand, and adduct formation with a second aromatic molecule within the same first collision event.

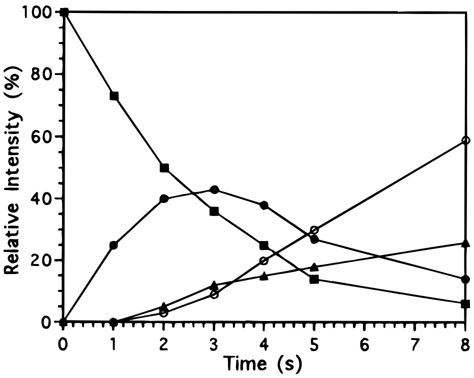
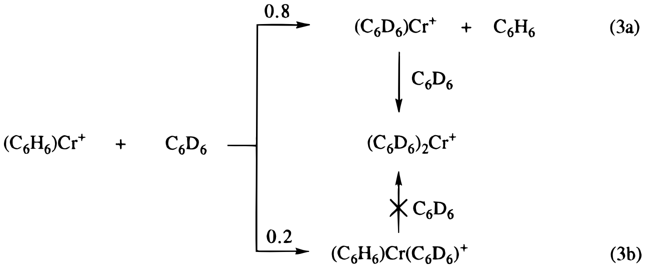


Figure 2. Relative ion intensities of $(C_6H_6)Cr^+$ (■), $(C_6D_6)Cr^+$ (●), $(C_6D_6)_2Cr^+$ (○), and $(C_6H_6)Cr(C_6D_6)^+$ (▲) as a function of reaction time (eq 3). The C_6D_6 pressure was 3.7×10^{-8} mbar.



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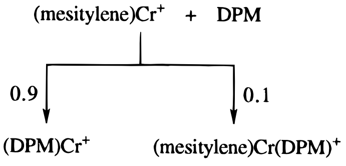
(23) Stöckigt, D.; Hrusàk, J.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1995**, *149/150*, 1. It is found by FT-ICR that BDE(Al^+−(C_6D_6)) > BDE(Al^+−(C_6H_6)). However, this result cannot be directly extrapolated to the Cr^+ complexes, where the arene−metal bond is qualitatively different from the dominating electrostatic interaction of Al^+−(C_6H_6): Dougherty, D. A. *Science* **1996**, *271*, 163.

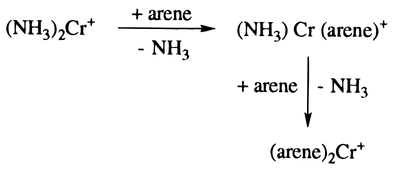
Given enough energy, the system evolves by the entropically favored splitting of Cr^+. The finding that, within the given range of excitation energy, cleavage of Cr^+ is observed from $(DPM)Cr^+$ but does not occur from $(DPP)Cr^+$ is consistent with the superior binding properties of DPP with respect to DPM.

A marked difference is seen to emerge from the study of the $(C_6H_6)Cr^+$ reaction with DPAs and *trans*-STB (=L), the latter yielding both LCr^+ and $(C_6H_6)CrL^+$ in comparable amounts. However, it should be noted that the branching between substitution and addition pathways is a sensitive function of the electron-donating ability of the arene unit in the (arene)Cr^+ reactant ion. The outcome of the $(C_6H_6)Cr^+$ reaction with DPM (Table 2) may be compared with the branching ratio of the (mesitylene)Cr^+ reaction (eq 4), showing that the mesitylene ligand is not completely displaced by the second phenyl ring of DPM. The better chelating DPP ligand reacts with (mesitylene)Cr^+ to give $(DPP)Cr^+$ as the exclusive product. The reactivity of $(NH_3)Cr^+$ is not dramatically different from that of $(C_6H_6)Cr^+$, in spite of the different character of the two ligands. It is possible that the better binding ability of the lone-pair donor compensates for the greater electron deficiency of $(NH_3)Cr^+$. It is interesting to note that LCr^+ ions show the same reactivity toward further ligand addition, no matter whether they derive from the Cr^+ or the $(NH_3)Cr^+$ reaction with L. In particular, LCr^+ ions with L = *cis*- and *trans*-STB, DPM, DPP, and DPB do not form L_2Cr^+. Thus, the two formation processes, starting from different reactants and associated to different reaction exothermicities, seemingly lead to the same product ions.



(4)

$(NH_3)_2Cr^+$ represents the milder and most selective reagent in the selected series of ligated Cr(I) ions. The reactant arenes show two distinct reaction patterns. In the first class, comprising toluene, mesitylene, PCP, and *trans*-STB, the $(NH_3)_2Cr^+$ reaction proceeds by consecutive ligand substitution steps (eq 5), with time-dependent relative ion intensities exemplified by the PCP reaction (Figure 3). To the second class belong typical DPAs, namely DPP and DPB, which replace the two NH_3 molecules in a single reactive event. Both reaction patterns are operative in the DPM reaction, as shown by the ion intensity profiles plotted in Figure 4. The conclusion can thus be strengthened that DPA compounds establish a chelate interaction in $(DPA)Cr^+$ complexes whenever the linking methylene chain allows a proper arrangement of the two phenyl rings. This occurs when the number of methylene units exceeds 2, though a certain extent of chelate effect in $(DPM)Cr^+$ seems ensured.



(5)

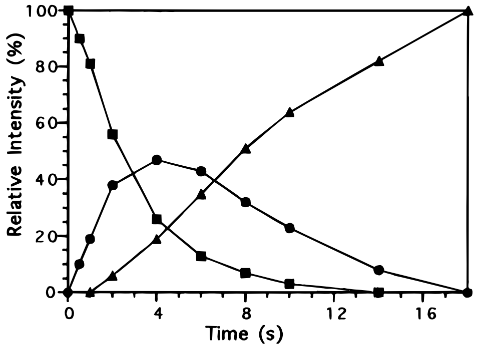


Figure 3. Relative ion intensities of $(NH_3)_2Cr^+$ (■), $(NH_3)Cr(PCP)^+$ (●), and $(PCP)_2Cr^+$ (▲) as a function of reaction time (eq 5). The PCP pressure was 1.1×10^{-8} mbar.

Table 3. FT-ICR Reactions of $(NH_3)_2Cr^+$ with Gaseous Arenes

arene (L)	k_{exp}[a]	Eff[b]
benzene		
toluene[c]	0.2	2
mesitylene[c]	1.1	8
styrene		
PCP[c]	13	86
cis-STB		
trans-STB[c]	1.0	7
DPM[c,d]	7.3	55
DPP[d]	16	100
DPB[d]	9.6	52

[a] See footnote *a* in Table 1. [b] See footnote *b* in Table 1. [c] Reaction pattern: $(NH_3)_2Cr^+ + L \rightarrow (NH_3)CrL^+ + NH_3$, then $(NH_3)CrL^+ + L \rightarrow L_2Cr^+ + NH_3$. [d] Reaction pattern: $(NH_3)_2Cr^+ + L \rightarrow LCr^+ + 2NH_3$.

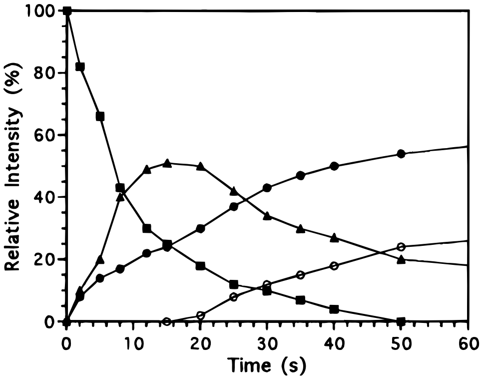


Figure 4. Relative ion intensities of $(NH_3)_2Cr^+$ (■), $(NH_3)Cr(DPM)^+$ (▲), $(DPM)_2Cr^+$ (○), and $(DPM)Cr^+$ (●) as a function of reaction time. The DPM pressure was 4.1×10^{-9} mbar.

The same evidence, based on the characteristic stepwise NH_3 substitution pattern, speaks in favor of external coordination to PCP, at least when this ligand displaces NH_3 from $(NH_3)_2Cr^+$. The stepwise NH_3 displacement from $(NH_3)_2Cr^+$ by PCP, leading ultimately to $(PCP)_2Cr^+$, contrasts with the lack of formation of this ion from the reaction of PCP with Cr^+, giving $(PCP)Cr^+$ ions unreactive toward further PCP addition. It is suggested that whereas the $(NH_3)_2Cr^+$ ligand displacement reaction involves exclusively external coordination to PCP, the highly exothermic addition reaction of the naked Cr^+ ion may overcome the kinetic barrier to the inclusion of Cr(I) within the PCP cage. However, one cannot exclude the alternative possibility that externally coordinated (PCP)Cr^+ ions, where the second aryl ring may exert an electron-donating effect on the ligated one, are simply unreactive toward further PCP addition at the low pressure of the ICR cell.

In the stepwise reaction of eq 5, the NH_3 departure allows both the disposal of the excess internal energy arising from the exothermicity of the ion−molecule reaction and a gross balance of the reaction entropy, at least with regard to translational degrees of freedom. Thus, the efficiencies of this ligand exchange reaction can be qualitatively related to the binding ability of the reactant arene. The observed trend mesitylene > toluene > benzene follows the order of increasing aromatic electron density. In this view, the remarkable efficiency of the PCP reaction suggests an electron-donating effect of the second aromatic ring on the ligated one. The inertness toward styrene may be explained once more by the depleted aromatic electron density due to the electron withdrawing effect of the double bond.[24] When, instead, the double bond allows conjugative electron release from a second phenyl ring (*trans*-STB: Eff = 7%), it exerts a certain positive effect. Such a conjugative interaction should be most effective with a coplanar arrangement of the *trans*-STB carbon skeleton, which instead is inhibited in the *cis* isomer by steric hindrance between the ortho hydrogens of the adjacent phenyl rings, explaining why *cis*-STB is unreactive toward $(NH_3)_2Cr^+$, as is styrene. The reactivity behavior toward $(NH_3)_2Cr^+$ ions may thus be used to differentiate the two isomeric stilbenes.

Conclusions

This study was aimed to test if and to what extent a transition-metal cation, such as Cr^+, would exert its quest for η^{12} coordination to benzene-type rings belonging to the same DPA molecule. The exclusive formation of LCr^+ complexes and the high efficiency of the formation process from both bare and selected ligated Cr(I) ions point to a chelate structure for (DPA)Cr^+ complexes. This conclusion holds particularly for DPA = DPP and DPB. However, the use of various reactant ions allows us to reveal some differences between individual DPAs. For example, DPM reacts with $(NH_3)_2Cr^+$ with a mixed reaction pattern leading to both LCr^+ and L_2Cr^+, the latter by a two-step NH_3 displacement route. Clearly, intervention of the second ring is dependent upon chain length, as this will affect the stability and the entropy of the ensuing chelate complex. When the two aryl rings are separated by a double bond, as in *trans*-STB, simultaneous complexation to the metal ion is inhibited and reaction with $(NH_3)_2Cr^+$ yields L_2Cr^+, the same ultimate product of the toluene and mesitylene reaction. The $(NH_3)_2Cr^+$ reaction with PCP, giving $(NH_3)Cr(PCP)^+$ and $(PCP)_2Cr^+$, shows that metal coordination occurs externally with respect to the PCP cage.

A general feature which characterizes the reactivity of both (arene)Cr(arene′)$^+$ and (DPA)Cr^+ complexes, pointing once again to a common sandwich-type structure and to sizable kinetic barriers, is their remarkable inertness to undergo arene exchange in a thermoneutral or even exothermic direction. This finding is of relevance in the study of catalysis by displacement of transition metal π-bonds[22] and will be the topic of further research.

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