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Ultraviolet Laser Desorption of Chromium Tricarbonyl Arene Complexes: A Route to Extended Sandwich Complexes

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The positive-ion ultraviolet laser desorption/ionization mass spectra of the benzene complex $Cr(CO)_3(C_6H_6)$ and the [2.2]cyclophane complexes $Cr(CO)_3(C_{16}H_{16}$-1,4), $Cr(CO)_3(C_{16}H_{16}$-1,3), and $\{Cr(CO)_3\}_2(C_{24}H_{24})$ are reported. In each spectrum intense ion signals are obtained which correspond to the decarbonylated chromium arene cation $[Cr(arene)]^+$ and the bis(arene) sandwich cation $[Cr(arene)_2]^+$. The cyclophane complexes also generate ion signals at higher masses which can be attributed to extended polynuclear sandwich complexes. In addition, the ultraviolet laser desorption mass spectrum of a mixture of $Cr(CO)_6$ and [2.2]-paracyclophane is shown to comprise ions containing new metal−ligand bonds, *viz.* the sandwich species $[Cr(C_{16}H_{16}\text{-}1,4)_2]^+$.

Introduction

The chemistry of chromium−arene complexes has been studied in some considerable detail since the pioneering work of Fischer and Hafner in 1954 and is now textbook material.[1] They heated anhydrous $CrCl_3$ with an arene, aluminum powder, and aluminum trichloride to produce $[Cr(arene)_2][AlCl_4]$, the subsequent reduction of which yields the neutral sandwich compound $Cr(arene)_2$. A few years later the first arene tricarbonyl complexes were prepared from the direct thermal reaction between $Cr(CO)_6$ and the arene; a wide range of arenes have since been employed as reagents, and their complexes have been the subject of numerous reviews.[2]

One group of particularly attractive ligands are the cyclophanes.[3] Cyclophane chemistry became a flourishing area of research in the 1950s, and many years later the preparation of the first cyclophane complex, $Cr(CO)_3(C_{16}H_{16}$-1,4) ($C_{16}H_{16}$-1,4 = [2.2]paracyclophane), was achieved;[4] and several years later its X-ray structure was determined.[5] By implementation of the techniques previously developed for other chromium arene complexes, a range of different species have been prepared.[6] The four archetypal chromium-cyclophane complexes are illustrated in Figure 1. There has been much effort devoted toward the synthesis of oligomers containing alternate cyclophanes and chromium atoms, due to their potential as conducting polymers, and while this has not as yet proved possible, some progress has been made where Ru(II) or Os(II) ions are used in place of Cr(0) atoms.[7]

Since the early 1980s considerable advances have been made in the gas-phase chemistry of organometallic systems.[8] The gas-phase properties of bare or ligated transition metals can provide valuable information concerning their reactivity and mechanistic behavior in the condensed phase. Gas-phase studies can also provide information concerning the intrinsic reactivity of the molecules in the absence of solvent effects. Investigations into the gas-phase reactions of organometallic compounds have been undertaken using a variety of mass spectrometers to enable identification of both reagent and product ions.[8] It is well-known that some transition-metal complexes can undergo ion−molecule reactions in the gas phase.[8,9−13] In particular, studies have shown that certain reactions of (arene)chromium complexes, which do not take place in solution, are possible in the gas phase. A notable example is the formation of bis(arene) sandwich complexes, *via* CO substitution, by chemical ionization (CI) of mono(arene)chromium tricarbonyl complexes with free arenes in a double-focusing mass spectrometer.[14]

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(1) Most advanced inorganic and organometallic textbooks have sections dealing with (arene)chromium complexes due to their historic position in the development of organometallic chemistry; for example, see: (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: Chichester, U.K., 1996. (b) Elschenbroich, C.; Salzer, A. *Organometallics*; VCH: Weinheim, Germany, 1989.

(2) There are many reviews on this topic, the most recent being: Morris, M. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol 5, p 471.

(3) Vögtle, F. *Cyclophane Chemistry*; Wiley: Chichester, U.K., 1993.

(4) Cram, D. J.; Wilkinson, D. I. *J. Am. Chem. Soc.* **1960**, *82*, 5721.

(5) Kai, Y.; Yasuoka, N.; Kasai, N. *Acta Crystallogr.* **1978**, *B34*, 2840.

(6) (a) Misumi, S.; Otsubo, T.; *Acc. Chem. Res.* **1978**, *11*, 251. (b) Elschenbroich, C.; Möckel, R.; Zenneck, U. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 531. (c) Elschenbroich, C.; Schneider, J.; Mellinghoff, H. *J. Organomet. Chem.* **1987**, *333*, 37.

(7) For a comprehensive review on (cyclophane)metal complexes see: Schulz, J.; Vögtle, F. *Top. Curr. Chem.* **1994**, *172*, 41.

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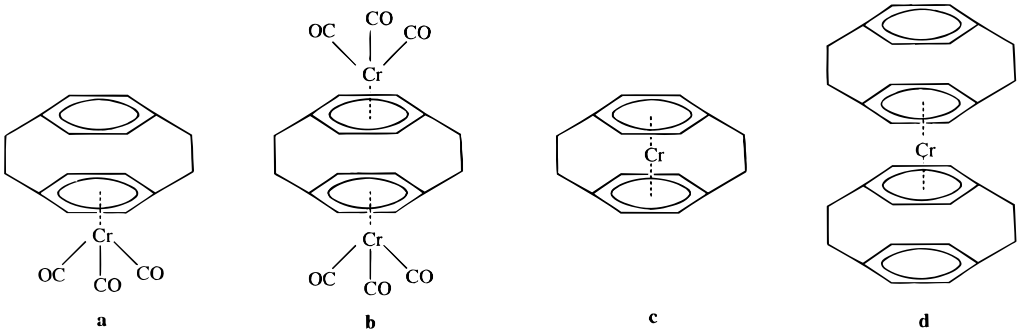

Figure 1. Chromium complexes of [2.2]paracyclophane: (a) $Cr(CO)_3(C_{16}H_{16})$; (b) $\{Cr(CO)_3\}_2(C_{16}H_{16})$; (c) $Cr(C_{16}H_{16})$; (d) $Cr(C_{16}H_{16})_2$.

Laser desorption/ionization has been widely used in mass spectrometry to activate involatile or thermally labile organic molecules.[15] This approach has also been used to investigate a variety of organometallic complexes.[16−20] In a typical experiment, a solid sample is exposed to a desorption laser pulse and the gas-phase product ions analyzed using time-of-flight mass spectrometry. Laser desorption effects both the sublimation of a solid sample and the chemistry required for ion formation. It is interesting to consider the temporal evolution of the desorption/ionization process. Laser irradiation of the solid creates a high-density selvedge region, where intermolecular interaction and reaction can occur. Following the expansion of a desorption plume into the mass spectrometer, bimolecular interactions become unlikely and essentially only unimolecular decay takes place. Thus, it is likely that any reactions will occur during the early stages of plume expansion. It is also worth noting that the reagent density is much higher in the selvedge region than would be typical in a conventional mass spectrometer.

Two major types of product ions can be observed in an LD mass spectrum: (1) molecular and fragment ions which contain analytical information directly relevant to the structure of the target molecule and (2) ions whose "synthesis" occurred during the desorption process. The latter are often regarded as problematic in that they can complicate mass spectral interpretation. However, from an alternative perspective, these provide direct information concerning the reactivity of desorbed ions and neutrals.

A number of previous investigations have demonstrated that UV laser desorption of organometallic compounds can result in the generation of novel product ions. For example, studies of transition-metal arene carbonyl clusters have shown that the UV laser desorption process can result in the aggregation of the metal cores, resulting in the generation of high-nuclearity clusters and the partial stripping of carbonyl ligands from the precursor molecule.[21,22] In addition, it has been observed that ion−molecule reactions, following the UV laser desorption of $[Tl(o\text{-phenan})_2]ClO_4$, can result in ligand replacement and the production of $[Tl(o\text{-phenan})_3]^+$ ions (*o*-phenan = *o*-phenanthroline).[19]

For these reasons we felt that laser desorption/ionization could be used to study the reactivity of species derived from both pure organometallic precursors and arene/organometallic mixtures. In this paper we report the investigation of a number of chromium tricarbonyl cyclophane compounds using ultraviolet laser desorption mass spectrometry. In particular, we note the propensity of the paracyclophane complexes to form high-mass gas-phase polynuclear complexes.

Results and Discussion

The spectra of $Cr(CO)_6$, $Cr(CO)_3(C_6H_6)$ (**1**), $Cr(CO)_3(C_{16}H_{16}\text{-}1,4)$ (**2**), $Cr(CO)_3(C_{16}H_{16}\text{-}1,3)$ (**3**), and $\{Cr(CO)_3\}_2(C_{24}H_{24})$ (**4**) were recorded in the positive-ion mode on a UV laser desorption/ionization time-of-flight mass spectrometer (see experimental Section for details). The spectra of complexes **1**−**4** are shown in Figures 2−5, respectively.

The spectrum of $Cr(CO)_6$ was recorded as a control. The laser desorption/ionization of $Cr(CO)_6$ resulted in only three significant peaks, at 23, 39, and 52 Da, which are readily attributed to Na^+, K^+, and Cr^+. These three peaks were observed in all the spectra discussed herein. Na^+ and K^+ are ubiquitous contaminants in LD experiments, while the Cr^+ can be attributed to ligand stripping from the metal carbonyl. The loss of CO ligands is also a typical fragmentation pattern of metal carbonyls in conventional mass spectrometry.[23] Neither ions corresponding to partial CO loss nor higher mass clusters of chromium were observed on desorbing from a solid crystalline sample of $Cr(CO)_6$. The latter feature is an important consideration with respect to the paracyclophane experiments reported later, as $(C_{16}H_{16}\text{-}1,4)$ and $(C_{16}H_{16}\text{-}1,3)$ have the same nominal mass as the Cr_4^+ ion.

The mass spectrum of the (benzene)chromium tricarbonyl complex (**1**), is shown in Figure 2. The base peak at 52 Da corresponds to the presence of Cr^+. Two intense peaks are also observed at 130 and 208 Da. The former peak corresponds to an ion in which all three

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[23] Chamot-Rooke, J.; Pennequin, F.; Morizur, J.-P.; Tortajada, J.; Rose, E.; Rose-Munch, F. *J. Mass Spectrom.* **1996**, *31*, 199.

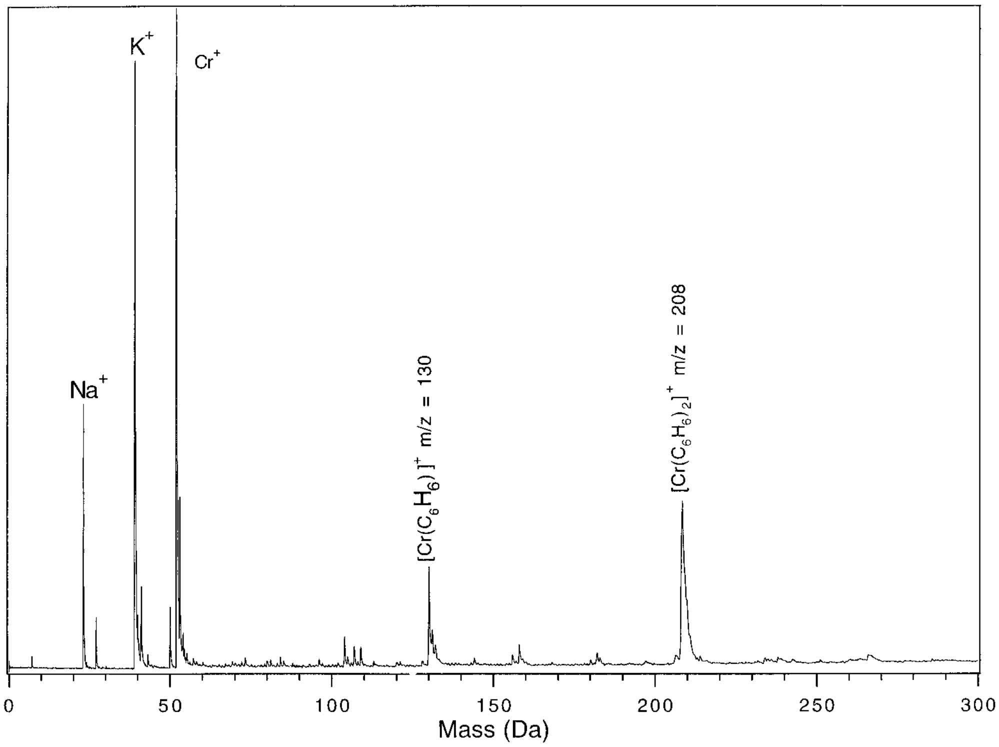

Figure 2. UV laser desorption/ionization mass spectrum of $Cr(CO)_3(C_6H_6)$ (**1**) recorded in the positive ion mode.

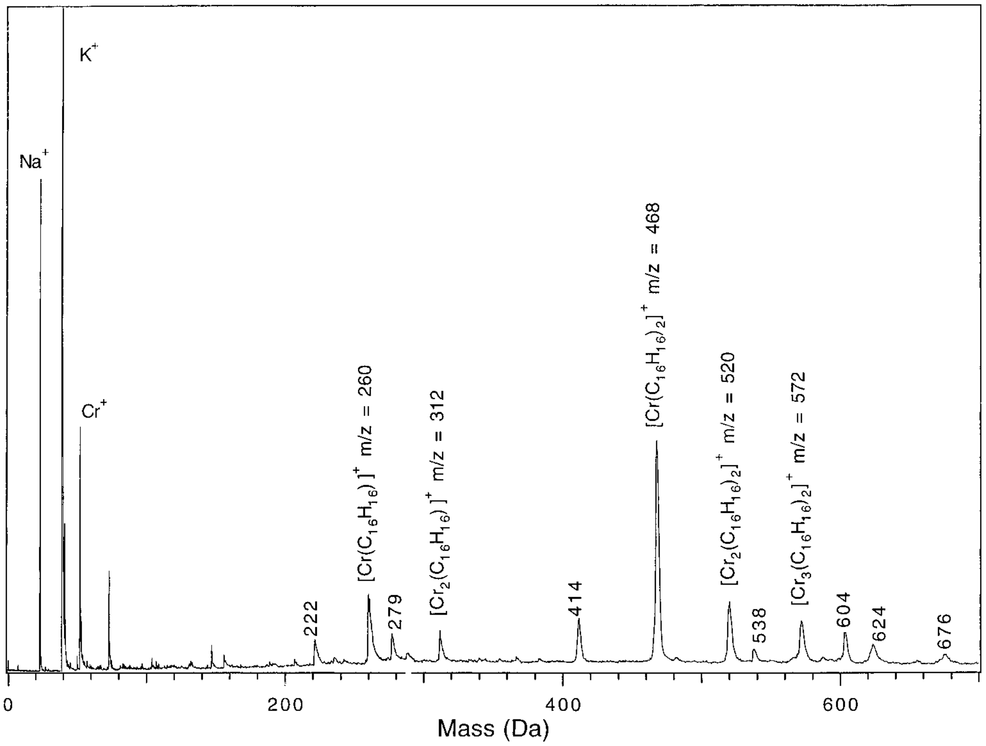

Figure 3. UV laser desorption/ionization mass spectrum of $Cr(CO)_3(C_{16}H_{16}$-1,4) (**2**) recorded in the positive ion mode.

carbonyls have been lost, *viz.* $[Cr(C_6H_6)]^+$, and the latter peak can be attributed to a bis(benzene) sandwich ion, $[Cr(C_6H_6)_2]^+$. It is noteworthy that no peak is observed which corresponds to the intact complex, *viz.* $[Cr(CO)_3(C_6H_6)]^+$. These observations provide information which allow the reactions taking place during the desorption process to be rationalized (see Scheme 1).

The synthesis of $Cr(C_6H_6)_2$ by conventional synthetic methods is best achieved by either the Fischer–Hafner method or by metal vapor synthesis.[24] While three carbonyl ligands can be displaced by benzene (or other arene ligands) from $Cr(CO)_6$ to yield $Cr(CO)_3(C_6H_6)$, it has not been possible, in solution, to substitute the remaining carbonyls from $Cr(CO)_3(C_6H_6)$ to yield $Cr(C_6H_6)_2$. In contrast, ultraviolet laser desorption generates coordinatively unsaturated metal-containing fragments by stripping the carbonyl ligands from the chromium tricarbonyl arene precursor complex. The main product is $[Cr(C_6H_6)]^+$, although there is a less intense peak observed at 158 Da, which may be assigned

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[24] Silverthorn, W. E. *Adv. Inorg. Chem.* **1975**, *13*, 47.

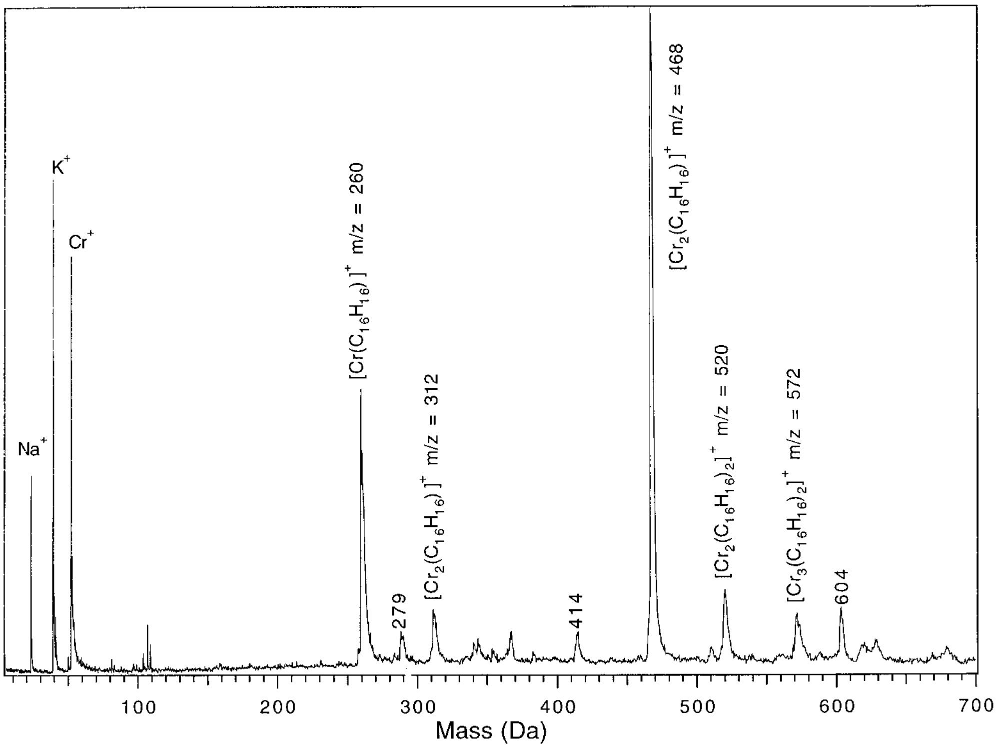


Figure 4. UV laser desorption/ionization mass spectrum of $Cr(CO)_3(C_{16}H_{16}\text{-}1,3)$ (**3**) recorded in the positive ion mode.

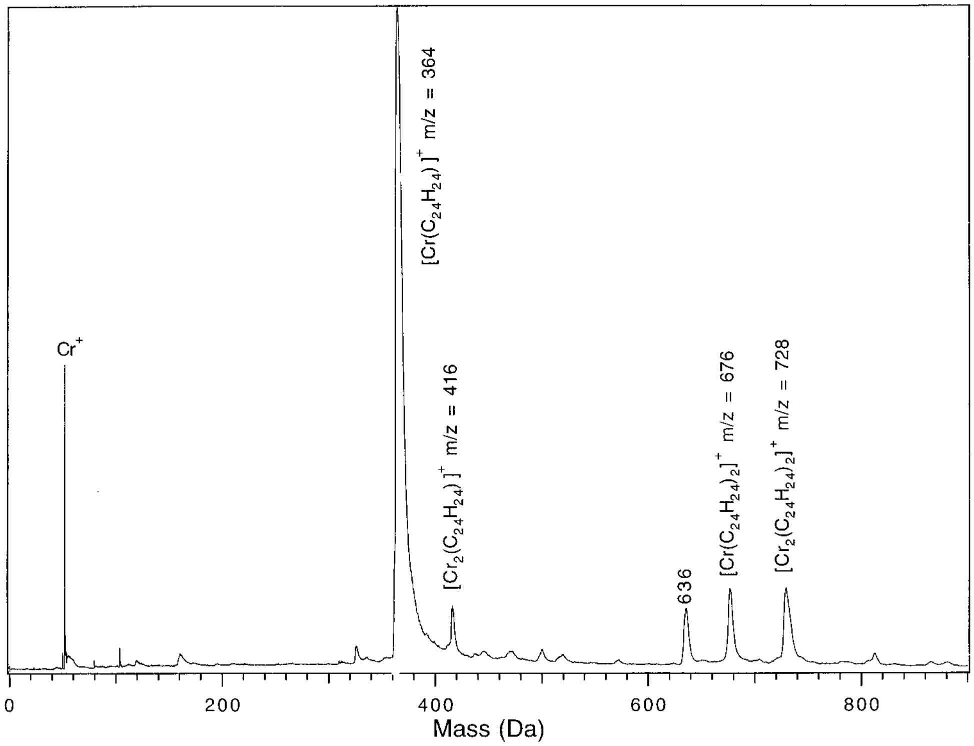
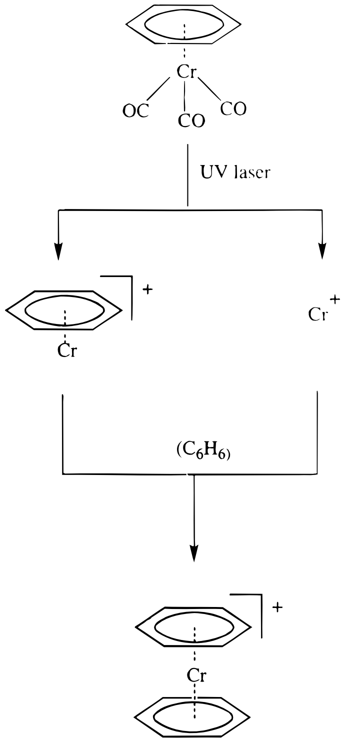


Figure 5. UV laser desorption/ionization mass spectrum of $\{Cr(CO)_3\}_2(C_{24}H_{24})$ (**4**) recorded in the positive ion mode.

to the monocarbonyl ion $[Cr(CO)(C_6H_6)]^+$. Cr^+ and $[Cr(C_6H_6)]^+$ are highly reactive species. Therefore, it is reasonable to expect that we will observe some ion–molecule reactions as the complexes are desorbed into the vacuum. For example, both species can coordinate with benzene to form the bis(benzene) sandwich compound $[Cr(C_6H_6)_2]^+$. The presence of free benzene in the reaction mixture can be inferred from the presence of Cr^+ ions in the mass spectrum. These indicate that stripping of all the ligands has taken place. Peaks which correspond to $[C_6H_6]^+$, or a related fragment, and $[CO]^+$ are not observed, suggesting that these ligands are liberated as neutral molecules. The high density of desorbed material in the selvedge region, combined with the high reactivity of the Cr^+ and $[Cr(C_6H_6)]^+$ species, results in the high-intensity bis(benzene)chromium ion. It is interesting to note that this is a *major* product of the laser desorption process, having a greater intensity than the $[Cr(C_6H_6)]^+$ species.

Further reactions of the bis(benzene) sandwich ion are unlikely, as the compound has returned to a high degree of coordinate saturation. A triple-decker sandwich

Scheme 1

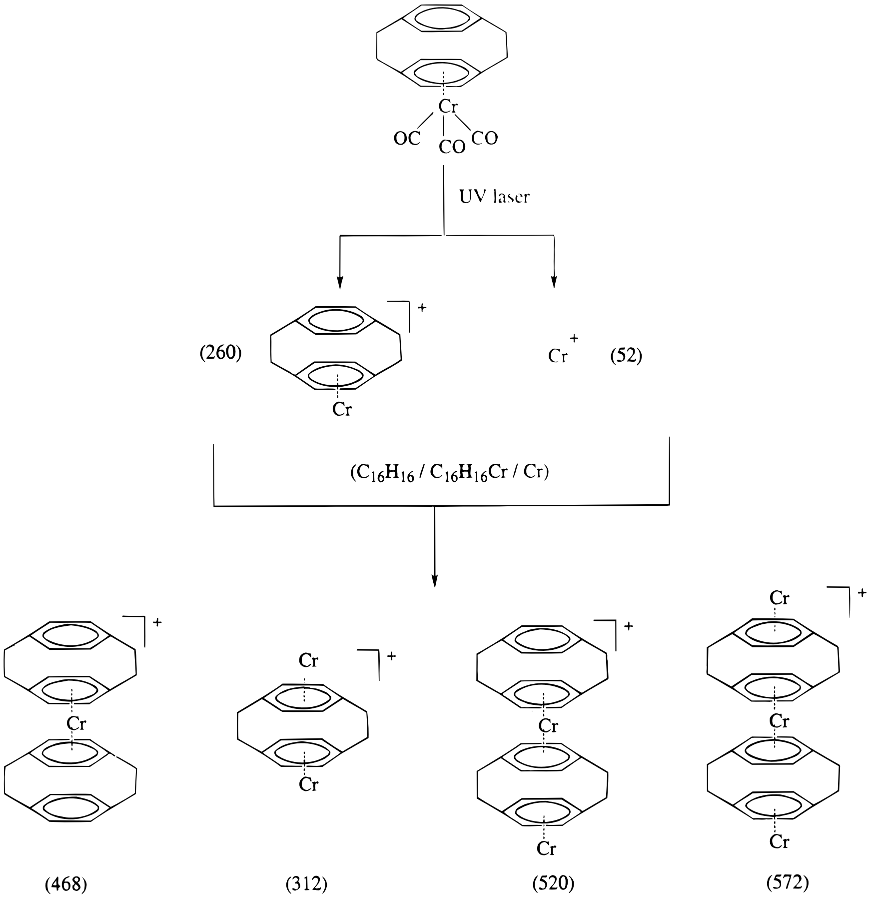


complex, $Cr_2(C_6H_3Me_3\text{-}1,3,5)$, has been prepared by metal vapor synthesis and characterized by X-ray diffraction;[25] however, the analogous benzene species has not been made. Cyclophane complexes, however, contain two or more aromatic centers which are suitable for coordination to metal species. In this case, replacement of the three CO ligands with the arene need not be the ultimate reaction product; *i.e.*, further reactions could occur at the vacant aromatic site on the cyclophanes, generating metal−cyclophane−metal oligomers.

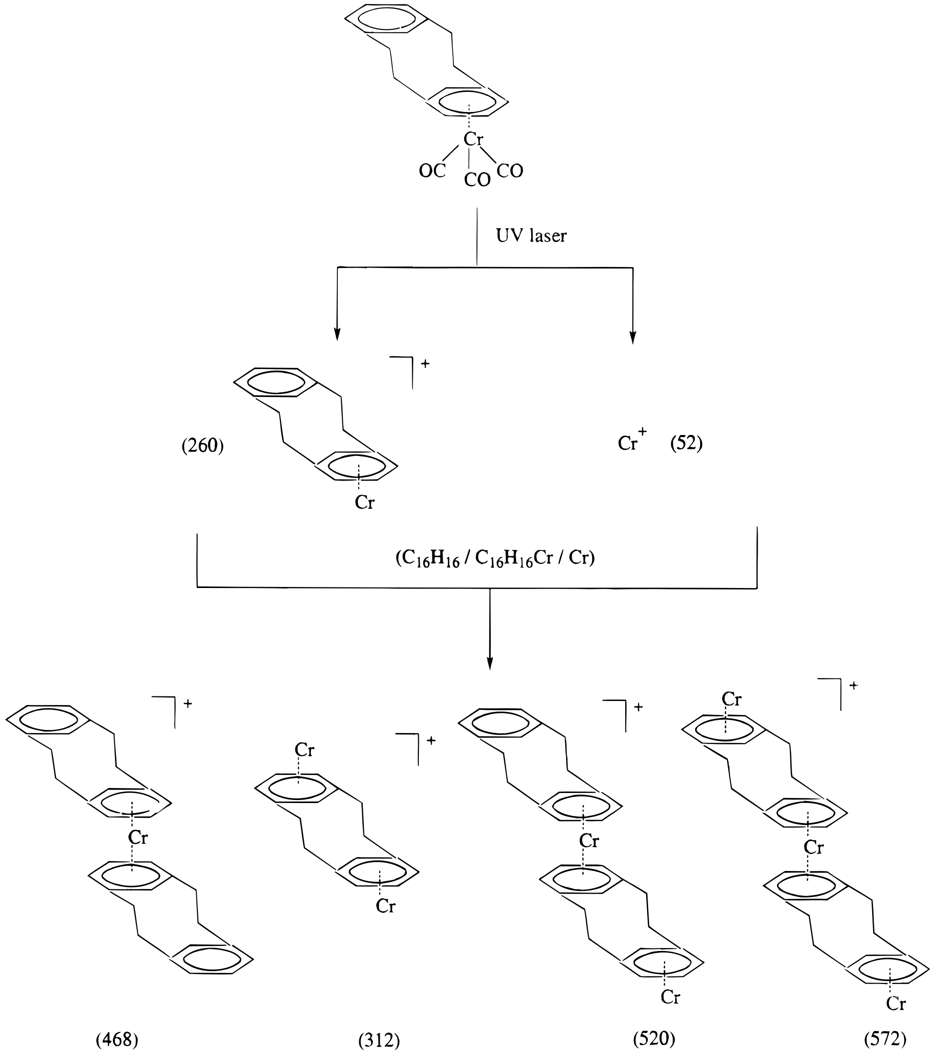
The laser desorption mass spectra of the isomeric (paracyclophane)- and (metacyclophane)chromium tricarbonyl complexes (**2** and **3**) are shown in Figures 3 and 4. As for **1**, no peaks corresponding to the molecular weights of the parent ions are observed, but the triply decarbonylated ion $[Cr(C_{16}H_{16})]^+$ is observed at 260 Da for both compounds. Also, as anticipated from the spectrum of **1**, the most intense high-mass peak observed in the spectra of **2** and **3** can be attributed to the formation of a sandwich complex, $[Cr(C_{16}H_{16})_2]^+$, at 468 Da. However, a number of additional intense signals are observed in both spectra at higher masses than this sandwich complex. Their masses and assignments are summarized in Schemes 2 and 3, for **2** and **3**, respectively.

The peak at 312 Da in each spectrum can be assigned to the dinuclear species, with formula $[Cr_2(C_{16}H_{16})]^+$. This product, along with $[Cr(C_{16}H_{16})_2]^+$, can be thought of as a building block from which higher, alternating metal−ligand oligomers can be constructed (see Scheme 2). It is this process to which we attribute the generation of a number of the higher mass ions. The peaks at 520 and 572 Da may be attributed to the molecular formulas $[Cr_2(C_{16}H_{16})_2]^+$ and $[Cr_3(C_{16}H_{16})_2]^+$, respectively. The addition of a further paracyclophane ligand would result in a peak at 780 Da. This is not observed with significant intensity for either of the isomers.

Scheme 2



Scheme 3



Two further peaks are observed with significant intensity in Figure 3 at 624 and 676 Da. These can be assigned to the formulas $[Cr_4(C_{16}H_{16}\text{-}1,4)_2]^+$ and $[Cr_5(C_{16}H_{16}\text{-}1,4)_2]^+$. While it is easy to envisage the structure of the trichromium complex, $[Cr-(C_{16}H_{16})-Cr-(C_{16}H_{16})-Cr]^+$, the tetra- and pentachromium species are more problematic. It is noteworthy that the intensity of the latter peaks decreases steadily as additional chromium atoms are added to the complex. In the case of the metacyclophane complex these species are not present in the mass spectrum.

The formation of the product ions discussed above is believed to take place by a mechanism similar to that described for **1**, *viz.* generation of the highly reactive coordinatively unsaturated species $[Cr(C_{16}H_{16}\text{-}1,4)]^+$ and Cr^+ which subsequently interact with neutral species to generate higher molecular weight species. The formation of the tetra- and pentachromium species can be explained if the chromium atoms enter intercalation sites between the decks of the rings within the [2.2]-paracyclophane ligand. This could account for their absence in the spectrum of [2.2]metacyclophane, which cannot accommodate additional chromium atoms in this fashion without prior rotation of one of the rings by 180°. However, it cannot be ruled out that a product which contains metal−metal interactions may be responsible for the species with high metal concentrations in the spectrum of paracyclophane. It is also possible that $[Cr(C_{16}H_{16}\text{-}1,4)]^+$ could be generated from the reaction between Cr^+ and $C_{16}H_{16}$-1,4 with the chromium atom in the resulting product lying in the central cavity of the ligand; however, mass spectrometry cannot distinguish whether this has actually occurred. Nor can one rule out that reactions take place between the primary ion products and the neutral parent molecule followed by decarbonylation.

The spectra in Figures 3 and 4 contain additional peaks which have not been discussed above. These include signals at 222, 279, 538, and 604 Da. These do not conform to any of the Cr−[2.2]cyclophane condensation products described above and at present have not been identified. A peak at 414 Da has also proved difficult to assign. This peak was also observed in the laser desorption mass spectrum of a chromium hexacarbonyl and [2.2]paracyclophane mixture (see later).

The spectrum of the dinuclear complex $\{Cr(CO)_3\}_2(C_{24}H_{24})$ (**4**), is shown in Figure 5. This can largely be interpreted with reference to the arguments outlined above. For example, a low-intensity peak at 416 Da corresponds to the decarbonylated but otherwise intact ion $[Cr_2(C_{24}H_{24})]^+$; of much higher intensity is the monometallic ion $[Cr(C_{24}H_{24})]^+$ at 364 Da, and the peak

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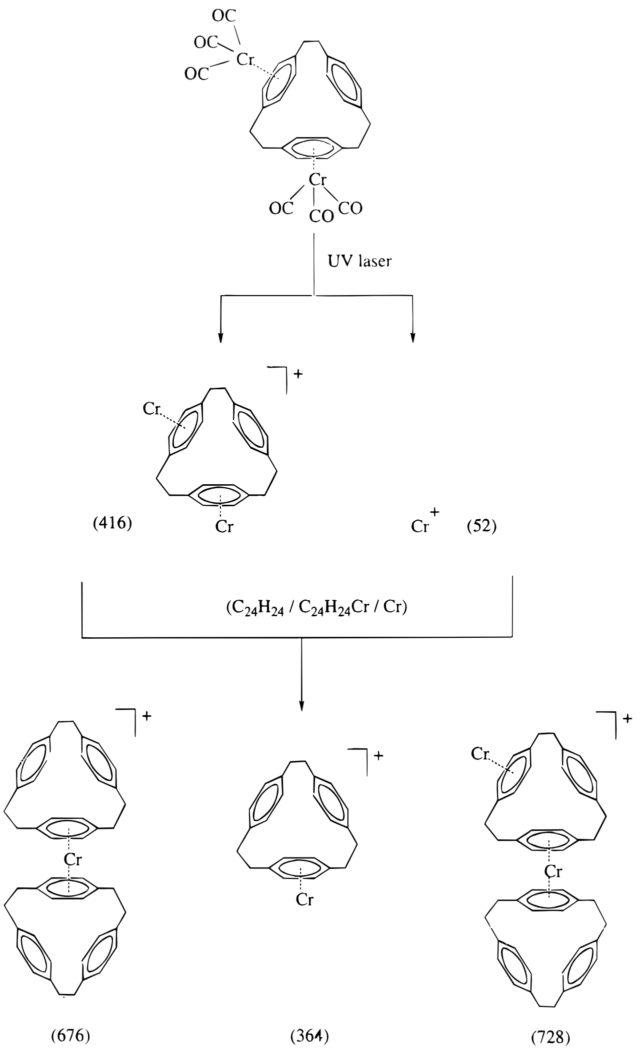
(25) Lamanna, W. M.; Gleason, W. B.; Britton, D. *Organometallics* **1987**, *6*, 1583.

Scheme 4



at 676 Da can be assigned to the sandwich species $[Cr(C_{24}H_{24})_2]^+$. An additional peak is observed at 728 Da and can be assigned to the species $[Cr_2(C_{24}H_{24})_2]^+$; *i.e.*, extended metal−ligand−metal−ligand species are again observed. These products are shown in Scheme 4. The use of the ($C_{24}H_{24}$) ligand suggests some interesting possibilities. For example, the formation of polynuclear sandwich chains from each benzene functionality would result in the dendrimer-like outward growth of the complex.

Each of the spectra shown so far represents the outcome of ion−molecule interactions and reactions following the desorption of a single analyte. Primary fragmentation reactions, followed by collisions between the desorbed species within the selvedge region of the desorption plume, result in the production of secondary ions with masses higher than the analyte. A similar phenomenon was observed on laser desorbing a mixture of target species. It has been observed previously that UV laser desorption of $Cr(CO)_6$ results in the production of Cr^+ ions. Under the same conditions no ion signals could be observed for a sample of [2.2]paracyclophane. However, when these two species were deposited on the sample probe as a mixture, two high-mass peaks could be observed at 413 and 468 Da. These are the same peaks as were observed in the spectrum of **2** (see Figure 3), and the peak at 468 Da can be assigned to $[Cr(C_{16}H_{16}\text{-}1,4)_2]^+$. In this case, however, the primary reactant species are Cr^+ and neutral desorbed [2.2]paracyclophane. One may anticipate that such a methodology could be used to generate a variety of novel gas-phase complexes. Furthermore, the use of Cr^+, ligated chromium ions, or alternative transition metals may be a useful strategy for the soft ionization of hydrocarbon analytes in ultraviolet laser desorption mass spectrometry.

Concluding Remarks

The ultraviolet laser desorption mass spectra of chromium tricarbonyl arene complexes contain fragment ions which correspond to the products of ligand stripping from the precursor chromium complex and higher mass species which can be attributed to the products of ion−molecule reactions in the selvedge region of the laser desorption plume. In the case of chromium-cyclophane precursors, the high-mass species can be assigned to the formation of extended polynuclear sandwich compounds. The mass spectra indicate that the production of highly unsaturated and reactive ions in the high-density desorption plume can be used as a strategy for gas-phase synthesis. Similarly, the desorption of *mixtures* can also result in the formation of novel gas-phase complexes. The generation of highly reactive Cr-containing ions in the desorption process, and their subsequent reaction with codesorbed species, suggests that such a strategy may also facilitate the LD mass spectrometry of problematic unsaturated analytes.

In the current study only ionic products of laser desorption have been determined. However, it is well-established that the ion yield in laser desorption is several orders of magnitude lower than that for neutral species. While the desorbed ions are expected to be more reactive than their neutral counterparts, future studies will be directed toward a complementary investigation of the neutral product yield.

Experimental Section

Complexes **2**−**4** were prepared under dry nitrogen gas using dried and degassed dioxane and the Strohmeier reflux method to ensure that the $Cr(CO)_6$ was not lost from the reaction mixture by sublimation.[26] The apparatus consists of two reflux condensers connected in series: the lower one without cooling water and the upper one with cooling water. Any $Cr(CO)_6$ which sublimes onto the lower condenser is then washed back into the reaction vessel by the solvent which condenses on the upper condenser. Chromium hexacarbonyl ($Cr(CO)_6$), (benzene)chromium tricarbonyl ($Cr(CO)_3(C_6H_6)$). and [2.2]paracyclophane ($C_{16}H_{16}$-1,4) were purchased from Aldrich Chemicals and used without further purification. [2.2]Metacyclophane ($C_{16}H_{16}$-1,3) and [2.2.2]paracyclophane ($C_{24}H_{24}$) were prepared according to the literature procedures.[27] The complexes were characterized spectroscopically and were in excellent agreement with the published data.[4, 28]

In a typical preparation $Cr(CO)_6$ (100 mg) and the appropriate cyclophane (1 mol equiv for **2** and **3**, 0.5 mol equiv for **4**) were heated to reflux in 1,4-dioxane (50 mL) (24 h for **2** and **3**, 72 h for **4**). During this time the solution became bright yellow and infrared spectroscopy indicated complete consump-

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[26] Strohmeier, W. *Chem. Ber.* **1961**, *94*, 2490.

[27] (a) Baker, W.; McOmie, J. F. W.; Norman, J. M. *J. Chem. Soc.* **1951**, 1114. (b) Tabushi, I.; Yamada, H.; Yoshida, Z.; Oda, R. *Tetrahedron* **1971**, *27*, 4845.

[28] Elschenbroich, C.; Schneider, J.; Wünsch, M.; Pierre, J.-L.; Baret, P.; Chautemps, P. *Chem. Ber.* **1988**, *121*, 177.

tion of $Cr(CO)_6$ had taken place. The solvent was removed *in vacuo* and the yellow solid washed with acetone.

Mass Spectrometry. The samples were deposited onto the sample probe as solutions in dichloromethane. The solvent was allowed to evaporate, leaving a thin layer of pure sample. These were then analyzed without further treatment using a home-built laser desorption time-of-flight mass spectrometer.[29] Desorption was performed using the 337 nm output from a Laser Science Inc. VSL-337ND-T nitrogen laser. The instrument was operated in the linear mode with a typical resolution of *ca.* 200. Ions were extracted with an acceleration voltage of 25 kV and detected using a two-stage chevron microchannel plate detector. All mass spectra were obtained using positive ion mode. Typically, the data from between 50 and 100 laser shots were averaged to improve the signal-to-noise ratio.

Acknowledgment. We wish to thank the Royal Society for a University Research Fellowship (P.J.D.) and a European Exchange Fellowship (M.J.D.) and the EPSRC for financial support (P.S.).

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