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C25–C26 (119 (2) and 143 (2)°, respectively) are also comparable with those in ref 3 (124.0–135.8°). The dihedral angles between the planes defined by the three-carbon skeleton of the η^3-allyl groups and the plane defined by the metal atom and the two terminal carbon atoms of the η^3-allyl groups are 112 (2)° and 117 (3)°. The high values of the temperature factors of these carbon atoms in the allyl groups mean they are somewhat disordered.

The geometry about the two Mg ions is distorted octahedral with two lengths (2.455 (3) and 2.505 (4) Å) to the bridging atoms Cl1 (or Cl2) and Cl5, two average lengths (2.596 (3) Å) to the two capping atoms, and two average distances (2.236 (7) Å) to the two nitrogen atoms of the tmed molecules. The distances from Mg1 and Mg2 to the bridging chloride atoms Cl1, Cl2, and Cl5 (2.452 (3), 2.458 (4), and 2.505 (4) Å, respectively) and to the two capping atoms Cl3 and Cl4 2.601 (3) and 2.589 (3) Å, respectively) are comparable to those in $[C_2H_5Mg_2Cl_3(THF)_3]_2$[17] (2.47–2.51 and 2.50–2.79 Å, respectively). In addition, the chelating rings Mg–N–C–C–N formed by the tmed molecule and Mg^{2+} bring additional stability to the compound. As shown by their disordered arrangements, these ethylene groups are not rigid. Like some solvent molecules in the lanthanide compounds,[18] they may statistically exist as two conformers.

The appearance of the molecule is quite similar to those of other trinuclear cluster compounds.[19–21] The trianglar conformation of the complex, with full bridging and capping ligands coordinating to the metal atoms, seems to be one of the most favorable schemes in electrostatics.

Further studies of these complexes are ongoing.

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Registry No. **1**, 130095-97-5; **2**, 130063-49-9; **3**, 130063-50-2; **4**, 130063-51-3; **5**, 130063-52-4; **6**, 130063-53-5; **7**, 130063-54-6; C_3H_5MgBr, 1730-25-2; $CeCl_3$, 7790-86-5; $NdCl_3$, 10024-93-8; $PrCl_3$, 10361-79-2; $SmCl_3$, 10361-82-7; C_3H_5MgCl, 2622-05-1; $LaCl_3$, 10099-58-8; 3-butenoic acid, 625-38-7; propylene, 115-07-1.

Supplementary Material Available: Listings of crystal data, thermal parameters, bond distances and angles, least-squares planes, and torsion angles for **1**, **2**, and **4** (56 pages); listings of observed and calculated structure factors (31 pages). Ordering information is given on any current masthead page.

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Gas-Phase Ion Chemistry of Cr(η^6-arene)$(CO)_3$ Complexes by FTMS Techniques

Lorenza Operti and Gian Angelo Vaglio

Dipartimento di Chimica Generale ed Organica Aplicata, Università di Torino, Corso Massimo d'Azeglio 48, 10125 Torino, Italy

James R. Gord[†] and Ben S. Freiser*

Chemistry Department, Purdue University, West Lafayette, Indiana 47907

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The gas-phase reactivities of eight Cr(η^6-arene)$(CO)_3$ complexes (arene = toluene, mesitylene, PhCOOMe, PhCOMe, PhCOEt, PhCO-*n*-Pr, PhCO-*t*-Bu, $PhCH_2COMe$) have been studied by FTMS techniques. Self-condensation processes occur that follow different reaction pathways when the coordinated arene is a hydrocarbon or a phenyl ketone. PhCOOMe and $PhCH_2COMe$ show an intermediate behavior. Reactions with free arenes or propene give substitution of the carbonyl groups, yielding $Cr(arene)(arene')^+$ and $Cr(arene)(propene)^+$, respectively. The extent to which displacement takes place depends on the nature of the original coordinated arene and is higher when it contains a CO group. With suitable free arenes as reagent gases, arene displacement is also observed, producing $Cr(arene')_2{}^+$. The formation of the disubstituted ions depends, once again, on the nature of the coordinated arene as well as on the relative bond energy of Cr^+–arene' with respect to Cr^+–arene. CID experiments have been performed in order to obtain a sequence of relative binding energies of the arenes to Cr^+. The results are consistent with the electronic and steric properties of the arene ligands, which affect the Cr^+–arene bond strength.

Introduction

In the last decade, an increasing number of studies have been reported on gas-phase ion–molecule reactions involving transition-metal complexes and the reactivity of atomic and coordinated metal ions.[1–5] The rapid growth in this area can be attributed to the development of new experimental methodologies involving techniques such as ion beam,[1,2] flowing afterglow,[3] ion cyclotron resonance (ICR),[4] and Fourier transform mass spectrometry (FTMS).[5] This research has mainly focused on atomic metal cations produced by laser desorption, surface ioni-

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[†] National Science Foundation Predoctoral Fellow. Present address: Joint Institute for Laboratory Astrophysics, University of Colorado and National Institute of Standards and Technology, Boulder, CO 80309.

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zation, collision-induced dissociation of selected precursors, and electron impact ionization of volatile inorganic compounds such as metal carbonyls. Recently, the formation and reactivity of bare metal cluster ions in the gas phase has also been receiving a great deal of attention.[6] Generally, the neutral reactant species have been small organic molecules, with a primary interest being to study C–H and C–C activation.

In this paper we report an investigation of the gas-phase behavior of some Cr(η^6-arene)(CO)$_3$ complexes and in particular discuss (a) their self-condensation reactions to form ionic clusters, (b) their reactivity in the presence of free arenes and propene, and (c) the relative binding energies of some arenes to Cr$^+$. (Arene)chromium tricarbonyl complexes have been known as selective hydrogenation catalysts in solution since 1968.[7] Recent papers on the mechanism of arene exchange processes[8] have renewed the interest in the study of this class of complexes, particularly on account of the importance that formation and displacement of transition-metal π bonds display in catalysis. Extensive studies on the gaseous chemistry of Cr$^+$, Cr$^-$, and chromium-containing cations and anions have already been reported.[9–12] Preliminary research on the Cr(η^6-arene)(CO)$_3$ complexes by conventional positive chemical ionization mass spectrometry (CIMS) with benzene, toluene, and propene has shown extensive substitution of the three carbonyl groups by the reagent molecules.[13] For a better understanding of these systems, we have studied the mechanism both of self-condensation reactions and of reactions with free arenes by FTMS techniques. The extent to which secondary reactions take place has been shown to depend upon the nature of the coordinated arene, and this effect will be discussed. The relative stabilities of Cr$^+$–arene ions are obtained by collision-induced dissociation of the (arene)Cr(arene$'$)$^+$ ions. When possible, a cross-check of the results is provided by forming the (arene)Cr(arene$'$)$^+$ ions from different precursors: Cr$^+$, Cr(η^6-arene)(CO)$_3$, or Cr(η^6-arene$'$)(CO)$_3$.

Experimental Section

The theory, instrumentation, and methodology of Fourier transform mass spectrometry (FTMS) have been discussed elsewhere.[14] The experiments on the Cr(η^6-arene)(CO)$_3$ compounds were performed on a Nicolet FTMS-2000 Fourier transform mass spectrometer previously described in detail.[15] The instrument is equipped with a differentially pumped dual analysis cell, which is situated in the bore of a superconducting magnet maintained at 3 T. The two 4.8-cm cubic cells share one common side, which consists of a solid plate with a 2 mm diameter orifice. For this study, however, the system was operated as a single-cell instrument with all of the experiments performed in the "source" cell.

Table I. Percentage of Ion Abundances in 30-eV FTMS Electron Impact Mass Spectra of CrL(CO)$_3$ Complexes

L	ion M$^+$	(M – CO)$^+$	(M – 2CO)$^+$	(M – 3CO)$^+$	Cr$^+$
toluene	16.2	2.6	3.5	18.1	59.6
mesitylene	22.2	1.3	3.7	23.4	49.4
PhCOOMe	11.6	2.0	3.6	19.6	63.3
PhCOMe	12.9	3.7	6.0	16.5	60.9
PhCOEt	8.9	2.8	4.5	25.8	58.0
PhCO-*n*-Pr	7.4	2.7	5.2	29.1	55.6
PhCO-*t*-Bu	6.1	2.5	5.4	29.3	56.7
PhCH$_2$COMe	7.3	14.8	13.5	21.9	42.5

The Cr(η^6-arene)(CO)$_3$ complexes were prepared as described in the literature.[7] They were introduced into the ion source through a direct-insertion probe heated at the minimum temperature necessary to obtain reproducible mass spectra, typically in the range of 20–80 °C, to a pressure of about 2×10^{-7} Torr. Reagent compounds for chemical ionization (CI) experiments were obtained commercially in high purity and were used as supplied. Noncondensable gases were removed from liquids by multiple freeze–pump–thaw cycles. The reagents were admitted to the cell through a modified inlet system with a Varian leak valve to a pressure of about 1×10^{-6} Torr. A Bayard-Alpert ionization gauge was used to measure static pressure without further calibration. Ions were generated by electron impact ionization at 30-eV electron energy, with use of a 5-ms electron beam pulse and a 0.5–1-μA emission current.

In CI experiments, sample ions are expected to be formed only by ion–molecule reactions with the reagent gas ions.[16] In conventional mass spectrometers, this condition is achieved with a relative partial pressure of sample/reagent gas on the order of 1/10 000 at a total pressure of about 0.5 Torr. In contrast, in the FTMS instrument the sample/reagent gas ratio is about 1/100 at a total gas pressure of about (1–2) $\times 10^{-6}$ Torr. CI experiments were performed in the FTMS instrument by first isolating the reagent gas ions with use of double resonance pulses[17] and then allowing them to react with the sample molecules. Argon was used as the collision gas for collision-induced dissociation (CID) experiments at a total pressure of about 5×10^{-6} Torr. Details of the CID experiment have been previously reported.[18] Under CI conditions, primary ions were permitted to undergo thermalizing collisions for 100 ms with the neutral molecules present in the cell at approximately 10^{-6} Torr. However, the presence of a small population of excited ions cannot be completely ruled out.[19]

Experiments on Cr$^+$ ions were performed on a Nicolet prototype FTMS-1000 Fourier transform mass spectrometer previously described in detail.[20] The instrument is equipped with a 5.2-cm cubic trapping cell situated between the poles of a Varian 15-in. electromagnet maintained at 0.9 T. The cell, constructed at Purdue, utilizes two 80% transmittance stainless steel screens as the transmitter plates. Cr$^+$ was generated by focusing the beam of a Quanta Ray Nd:YAG laser (1064 nm) into the center-drilled hole (1 mm) of a chromium rod supported on the transmitter screen nearest to the laser.

Conventional electron impact mass spectra of the Cr(η^6-arene)(CO)$_3$ complexes were obtained on a Kratos double-focusing MS 80 mass spectrometer. Samples were introduced into the source through a direct-insertion probe maintained at room temperature for the most volatile compounds or heated up to 50 °C for the least volatile ones, to a pressure of about 5×10^{-6} Torr.

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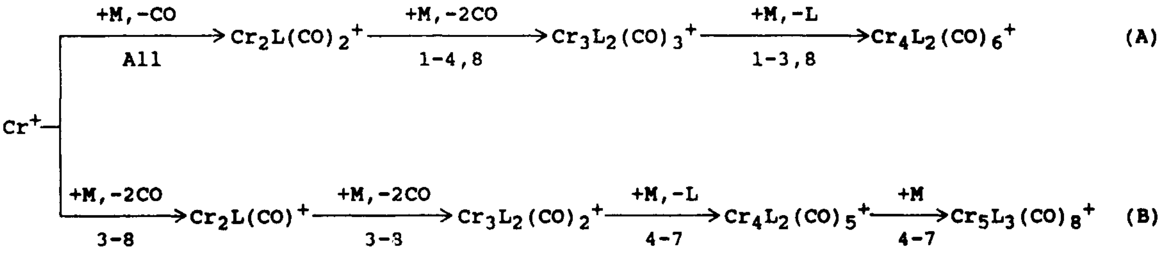
Table II. Percentage of Ion Abundances in 30-eV Electron Impact Mass Spectra of $CrL(CO)_3$ Complexes with a Magnetic Sector Mass Spectrometer

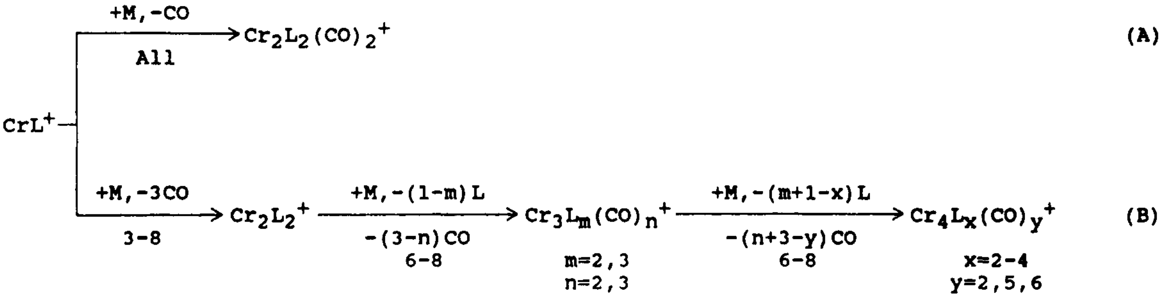
	ion								
L	M^+	$(M - CO)^+$	$(M - 2CO)^+$	$(M - 3CO)^+$	L^+	$PhCO^+$	$PhCH_2^+$	Ph^+	Cr^+
mesitylene	9.9	0.5	6.7	35.3	9.5	10.6[a]			27.5
PhCOOMe	8.9	0.5	2.9	29.2	3.7	12.9		8.8	33.1
PhCOMe	10.0	0.3	5.0	27.8	9.0	17.3		8.3	22.3
PhCOEt	8.1	0.2	4.4	30.0	6.2	19.5		8.8	23.0
PhCO-*t*-Bu	6.2	0.6	5.0	38.8	2.3	15.9		3.9	27.2
$PhCH_2COMe$	4.2	1.0	1.7	21.3	19.5		31.9		20.4

[a] $C_6H_3(CH_3)_2^+$.

Scheme I



Scheme II



Ionizing electrons were generated by a rhenium filament at 30 eV. The trap current was 100 μA.

Results

The FTMS electron impact mass spectra of the eight $CrL(CO)_3$ complexes (L = η^6-arene; arene = toluene (1), mesitylene (2), methyl benzoate (3), acetophenone (4), phenyl ethyl ketone (5), phenyl *n*-propyl ketone (6), phenyl *tert*-butyl ketone (7), benzyl methyl ketone (8)) are reported in Table I. They show a series of chromium-containing ions, formed by sequential losses of the three carbonyl groups and of the arene ligand, whose relative abundances depend on the nature of the coordinated arene. However, all of the complexes, except $Cr(\eta^6\text{-}PhCH_2COMe)(CO)_3$, display a similar trend in which the abundance of ions decreases in the order: Cr^+ (base peak), $(M - 3CO)^+$, M^+, $(M - 2CO)^+$, and $(M - CO)^+$. When L is benzyl methyl ketone, however, $(M - CO)^+$ and $(M - 2CO)^+$ show an abundance higher than that of M^+. As discussed below, we believe this suggests a possible rearrangement of the ketonic CO of the ligand in the coordination sphere of the chromium cation. For comparison, the electron impact mass spectra of some $CrL(CO)_3$ complexes obtained in a conventional mass spectrometer using ionizing electrons at 30 eV are reported in Table II. The main difference observed is the presence of organic ions in the conventional mass spectra. The reasons for this difference are discussed below.

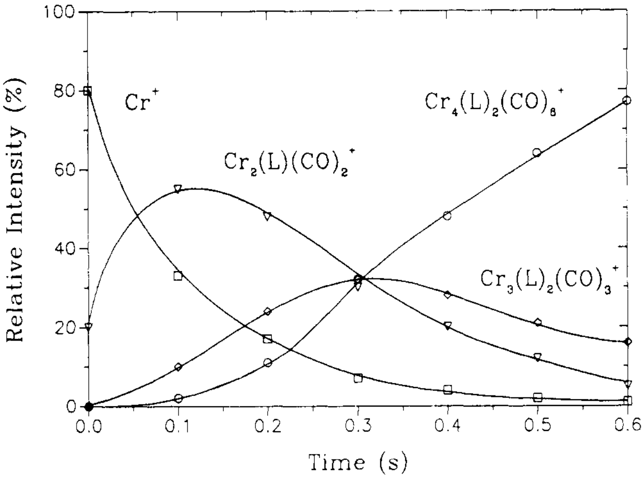
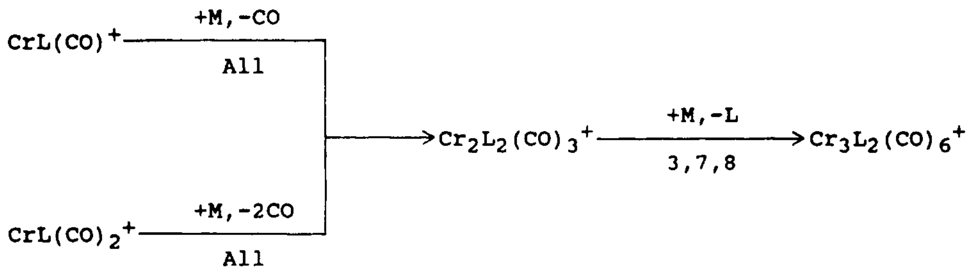


Figure 1. Variation of ion abundances with time of the self-condensation products of Cr^+ with $Cr(\eta^6\text{-mesitylene})(CO)_3$, where L = mesitylene.

In the FTMS experiments, applying a suitable delay time following the ionization event allowed the primary ions to react with their neutral precursors, leading to the formation of several cluster ions. Reaction sequences were determined by isolating one ion at a time, which was readily accomplished with use of double-resonance ejection methods,[17] and monitoring its subsequent reactions. When an ion was too low in abundance to be isolated, it was continuously ejected and its affect on the appearance of the secondary ions was determined. As an example, Figure 1 shows the variation of ion abundances of Cr^+ reacting with its neutral precursor $Cr(\eta^6\text{-mesitylene})(CO)_3$. The largest cluster ion observed in the sequence was $Cr_4(\text{mesitylene})_2(CO)_6^+$. The charge-exchange product, $Cr(\text{mesitylene})(CO)_3^+$, was continuously ejected during the whole experiment. The condensation reaction sequences for all of the complexes with Cr^+ and CrL^+ are summarized

Scheme III



Scheme IV

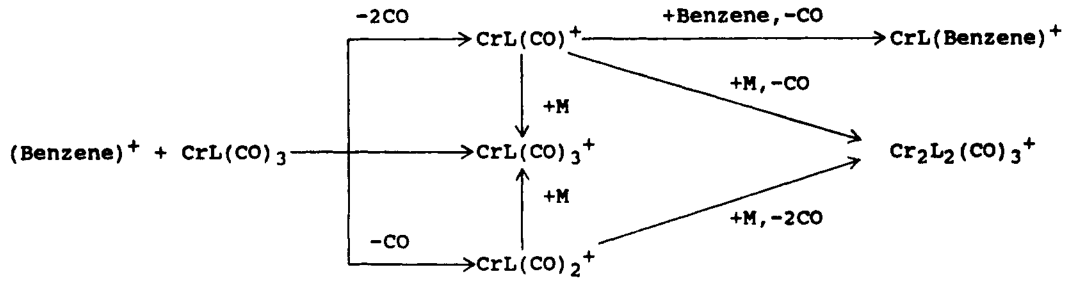


Table III. Relative Percentage[a] of Self-Condensation Products of Cr(η^6-PhCOR)(CO)$_3$ Complexes Formed through Pathway B in Scheme I[b,c]

	condensation products			
R	$Cr_2L(CO)^+$	$Cr_3L_2(CO)_2^+$	$Cr_4L_2(CO)_5^+$	$Cr_2L_2^+$[d]
Me	37	86	100	29
Et	49	100	100	38
n-Pr	63	100	100	52
t-Bu	98	100	100	86

[a] (B/(A + B)) × 100. [b] Total pressure about 2 × 10^{-7} Torr. [c] Reaction times are chosen corresponding to the highest concentration of the products of each condensation step. [d] Formed through pathway B in Scheme II.[b,c]

in Schemes I and II, respectively. Cr^+ and CrL^+, which are the two fragments exhibiting the highest degree of coordinative unsaturation, each show two different and competitive reaction pathways, A and B. These pathways differ mainly in the first condensation step, in which one (A) or more (B) carbonyl groups are displaced. When L is a hydrocarbon, the complexes react by pathway A exclusively, but they react by both pathways when L is a ketone or an ester. Table III reports the abundances of products arising from self-condensation via pathway B for the complexes containing a phenyl ketone, PhCOR, ligand. It is evident that, as the size of the alkyl group R increases, there is a corresponding increase in the yield of pathway B. Moreover, as the condensation reactions proceed to form clusters containing three and four chromium atoms, an enhanced selectivity for pathway B is observed, eventually accounting for 100% of the condensation products. When L is PhCOOMe or $PhCH_2COMe$, an intermediate behavior is observed, yielding products via both pathways A and B in the first self-condensation steps, but forming only $Cr_4L_2(CO)_6^+$ as the highest mass ion. Scheme III reports the condensation reaction sequences of both $CrL(CO)^+$ and $CrL(CO)_2^+$, which lead to the same condensation product. The molecular ion, $CrL(CO)_3^+$, is always unreactive and is continuously formed from its fragment ions by charge-exchange reactions. Charge exchange from fragment ions to the neutral precursor Cr(PhCOOMe)(CO)$_3$ yields an abundant Cr(PhCO)(CO)$_3^+$ ion.

Scheme IV shows the reaction sequence of the benzene molecular ion with the neutral complexes. The three primary products M^+, $(M - CO)^+$, and $(M - 2CO)^+$ are formed by charge-exchange processes, while $(M - 3CO)^+$ and Cr^+ are not observed. Figures 2 and 3 show the behavior of Cr(mesitylene)(CO)$^+$ and Cr(mesitylene)(CO)$_2^+$,

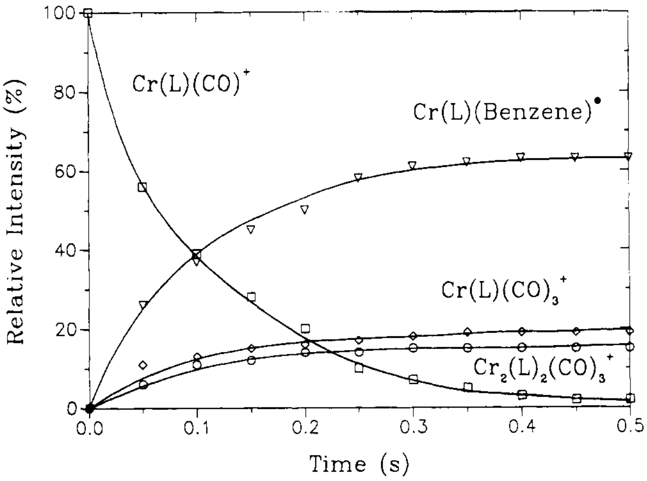


Figure 2. Variation of ion abundances with time of the products of reaction of Cr(L)(CO)$^+$ (L = mesitylene) in the presence of its neutral precursor Cr(η^6-mesitylene)(CO)$_3$ and benzene.

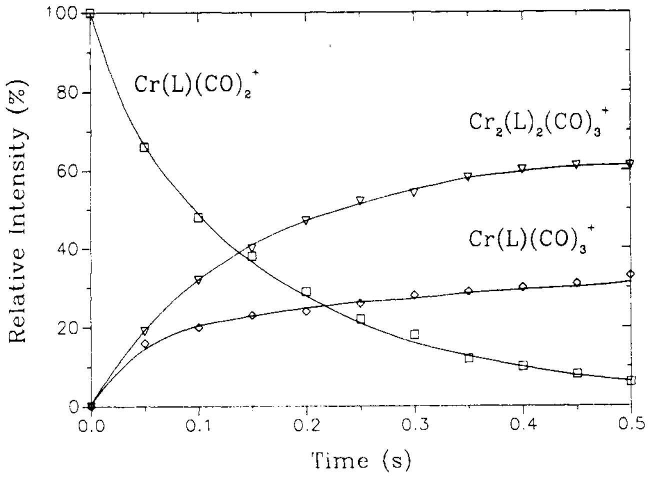


Figure 3. Variation of ion abundances with time of the products of the reaction of Cr(L)(CO)$_2^+$ (L = mesitylene) in the presence of its neutral precursor Cr(η^6-mesitylene)(CO)$_3$ and benzene.

Scheme V

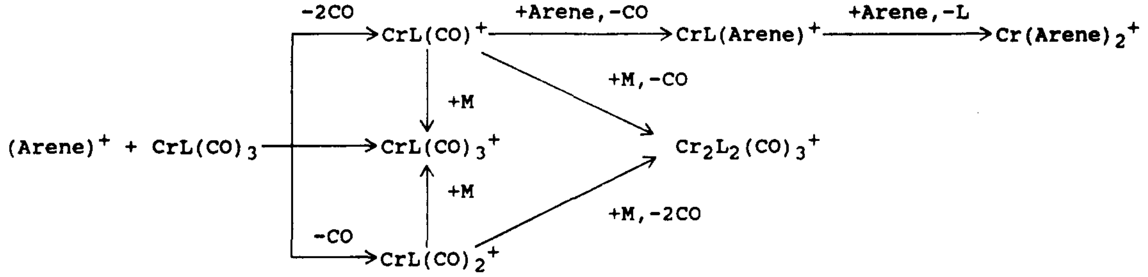


Table IV. FTMS Chemical Ionization Mass Spectra of $CrL(CO)_3$ Complexes with Benzene (B)[a,b]

	ion, %			
L	M^+	$(M - CO)^+$	$(M - 2CO)^+$	$(M - 3CO + B)^+$
toluene	100.0	34.2	1.9	43.2
mesitylene	100.0	27.4	10.5	64.8
PhCOOMe	37.4	1.8	4.6	100.0
PhCOMe	25.6	4.4	5.8	100.0
PhCOEt	49.3	2.4	9.5	100.0
PhCO-*n*-Pr	12.2	1.1	3.4	100.0
PhCO-*t*-Bu	28.4			100.0
$PhCH_2COMe$	16.0	43.8	0.7	100.0

[a] Total pressure about 1 × 10^{-6} Torr. [b] Reaction time 0.5 s.

Table V. FTMS Chemical Ionization Mass Spectra of $CrL(CO)_3$ Complexes with Propene (P)[a,b]

	ion, %				
L	M^+	$(M - CO)^+$	$(M - 2CO)^+$	$(M - 3CO)^+$	$(M - 3CO + P)^+$
mesitylene	100.0	6.5	1.1	4.4	3.5
PhCO-*t*-Bu	100.0	2.9	7.1	11.3	34.7
$PhCH_2COMe$	46.3	100.0	2.5	9.3	12.8

[a] Total pressure about 1 × 10^{-6} Torr. [b] Reaction time 0.1 s.

respectively, when they are isolated and permitted to react for 0.5 s with benzene and their neutral precursor. Both ions react by self-condensation and charge-exchange processes, leading to $Cr_2(mesitylene)_2(CO)_3^+$ and M^+, respectively. Moreover, $Cr(mesitylene)(CO)^+$ also reacts with neutral benzene by CO displacement to give $Cr(mesitylene)(benzene)^+$. As in the EI experiments, M^+ is unreactive. Similar behavior is observed for all of the $CrL(CO)_3$ complexes examined, with the only differences being the relative abundances of the ions. The FTMS chemical ionization mass spectra obtained by permitting the benzene cation to react for 0.5 s in the presence of the complexes and benzene at a total pressure of about 1 × 10^{-6} Torr are reported in Table IV. The cluster ions that do not involve reaction with benzene are not shown. In accordance with spectra obtained by conventional CIMS methods,[13] when L is a hydrocarbon, the base peak is the molecular ion, M^+, and condensation with a benzene molecule occurs to an intermediate extent, while $(M - 3CO + benzene)^+$ is the base peak when the coordinated ligand contains a carbonyl group.

Table V shows the FTMS chemical ionization mass spectra of some $Cr(\eta^6\text{-arene})(CO)_3$ compounds with propene at 1 × 10^{-6} Torr as the reagent gas. Ions in which a propene molecule has substituted three carbonyl groups are less abundant than in the corresponding benzene CI spectra, as is expected due to the lower binding energy of propene versus that of benzene. It is noteworthy that $(M - CO)^+$ is more abundant than M^+ when L = $PhCH_2COMe$ even under chemical ionization conditions, despite the fact that benzene and propene CI are softer forms of ionization than EI and should give molecular ions with lower internal energies and greater stability with respect to electron impact ionization.[16]

The FTMS chemical ionization mass spectra of $Cr(\eta^6\text{-toluene})(CO)_3$ and $Cr(\eta^6\text{-PhCOOMe})(CO)_3$ with some free arenes as reagent gases (benzene, mesitylene, anisole, and benzaldehyde) are reported in Tables VI and VII, respectively. When the reagent gas is other than benzene, $Cr(A)_2^+$ ions are also observed in which a second arene molecule, A, has substituted the coordinated ligand, L, (Scheme V). The mass spectra recorded at 0.1- and 0.5-s reaction times generally show a decreasing relative abundance of $Cr(L)(A)^+$ and a corresponding increasing abundance of $Cr(A)_2^+$ ions, as expected.

Table VI. FTMS Chemical Ionization Mass Spectra of the $Cr(\eta^6\text{-toluene})(CO)_3$ Complex with Arenes (A)[a]

	ion, %									
	M^+		$(M - CO)^+$		$(M - 2CO)^+$		$(M - 3CO + A)^+$		$(M - 3CO - L + 2A)^+$	
arene	0.1 s	0.5 s	0.1 s	0.5 s	0.1 s	0.5 s	0.1 s	0.5 s	0.1 s	0.5 s
benzene	100.0	100.0	75.9	34.2	16.0	1.9	31.2	43.2		
mesitylene	100.0	100.0	5.4		12.7		5.9	3.2	3.4	6.4
PhOMe	100.0	100.0	3.0		2.3		10.9	8.4	3.3	4.6
PhCHO	100.0	100.0	3.6		4.9		12.0	5.4	12.9	15.8

[a] Total pressure about 1 × 10^{-6} Torr.

Table VII. FTMS Chemical Ionization Mass Spectra of the $Cr(\eta^6\text{-PhCOOMe})(CO)_3$ Complex with Arenes (A)[a]

	ion, %									
	M^+		$(M - CO)^+$		$(M - 2CO)^+$		$(M - 3CO + A)^+$		$(M - 3CO - L + 2A)^+$	
arene	0.1 s	0.5 s	0.1 s	0.5 s	0.1 s	0.5 s	0.1 s	0.5 s	0.1 s	0.5 s
benzene	57.9	37.4	16.8	1.8	37.9	4.6	100.0	100.0		
mesitylene	100.0	100.0	5.9		2.1		29.0	20.2	9.4	16.5
PhOMe	100.0	100.0	4.9		2.0		45.3	15.7	4.7	5.6
PhCHO	100.0	100.0	3.8	1.5			45.5	7.6	17.5	16.4

[a] Total pressure about 1 × 10^{-6} Torr.

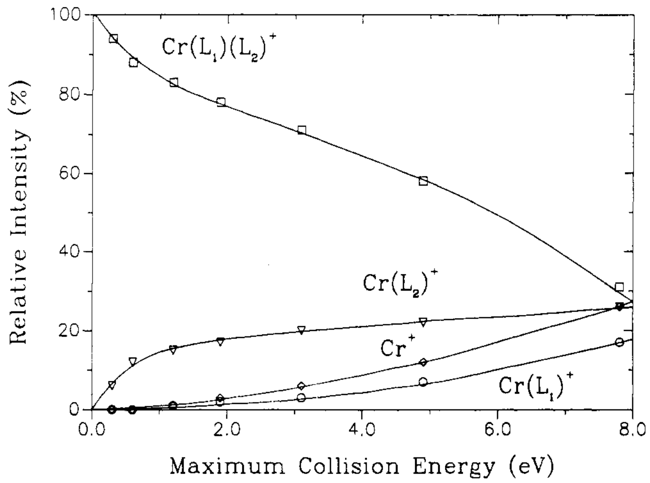


Figure 4. Variation of ion abundances with increasing kinetic energy from CID of the parent ion $Cr(L_1)(L_2)^+$, where L_1 = mesitylene and L_2 = $PhCH_2COMe$.

In all of the FTMS chemical ionization experiments with arenes as reagent molecules, at reaction times longer than 0.5 s, the substituted ions gradually react away, probably by charge-exchange reactions, and the final products are M^+ and $Cr_2L_2(CO)_3^+$. Similar behavior is observed with propene after 0.1-s reaction time.

Collision-induced dissociation (CID) experiments on (arene)Cr(arene′)$^+$ ions provide qualitative information on the relative bond strengths of arenes to Cr^+.[18,21] These ions were formed in the cell by reaction of $Cr(\eta^6\text{-arene})(CO)_3$ complexes with free arene molecules, arene′, through substitution processes illustrated in Schemes IV and V. Different pairwise combinations of arene/arene′ were examined. When both arenes were sufficiently volatile to be introduced as reagent gases, a cross-check was performed by forming the (arene)Cr(arene′)$^+$ ion from the two systems $Cr(\eta^6\text{-arene})(CO)_3$/arene′ and $Cr(\eta^6\text{-arene}')(CO)_3$/arene. Figure 4 shows the variation of ion abundances with increasing kinetic energy from the CID of $Cr(mesitylene)(PhCH_2COMe)^+$. At low energies the abundance of $Cr(PhCH_2COMe)^+$ is greater and increases faster than that of $Cr(mesitylene)^+$. At higher energies, Cr^+ also appears. This behavior suggests that $D(Cr^+\text{–}PhCH_2COMe) > D(Cr^+\text{–mesitylene})$. CID results indicate that the arene binding energies to Cr^+ are as follows: benzene < toluene < PhOMe < PhCOOMe ≃ PhCHO < PhCOMe < mesitylene < PhCOEt < PhCO-*n*-Pr < PhCO-*t*-Bu < $PhCH_2COMe$.

Discussion

A comparison of the mass spectra recorded on a Fourier transform mass spectrometer (Table I) with those obtained with a magnetic sector mass spectrometer (Table II) at the same electron beam energy (30 eV) shows a difference in relative ion abundances. In particular L^+ and its fragments are generally abundant in conventional electron impact mass spectra, as has been reported earlier,[22] but they are weak or undetectable by FTMS. This behavior can be ascribed to the different experimental conditions of the two methods. In the conventional mass spectrometer, the sample pressure was $\sim 5 \times 10^{-6}$ Torr, and ions formed in the source were detected after a flight time of about 10^{-5} s between the source and the detector, while in the FTMS instrument the pressure was $(1\text{–}2) \times 10^{-7}$ Torr and the spectra were recorded 3 ms after a 5-ms ionization event. During this delay, bimolecular processes can begin to occur, as evidenced by the observation of $Cr_2L(CO)_n^+$ (n = 1, 2) (not reported in Table I), and it is likely that charge-exchange reactions also take place. Support for this hypothesis is given by the higher abundance of the molecular ion, M^+, and of its first dissociation product, $(M - CO)^+$, in the FT mass spectra, as is expected in charge-exchange processes with respect to electron impact ionization. As a check, the electron impact mass spectra of some complexes were recorded on the FTMS instrument without any delay following a 100-μs ionization event. Under these experimental conditions, in which the reaction time is still 50–100 times longer than in a magnetic sector instrument, organic ions could be detected, although their abundance was never higher than ≃3%. Therefore, the observed mass spectra are likely to be a combination of ions formed by electron impact and by some bimolecular processes that involve fast charge exchange.

In the self-condensation processes, Cr^+ reacts with $CrL(CO)_3$ molecules by two competitive pathways in which $Cr_2L(CO)_2^+$ is formed by loss of one CO molecule (A) and $Cr_2L(CO)^+$ is formed by loss of two CO molecules (B), as reported in Scheme I. When L is a hydrocarbon, $Cr_2L(CO)_2^+$, formed through pathway A, is the only dimer species observed in the reaction of Cr^+ with $CrL(CO)_3$. In contrast, formation of $Cr_2L(CO)^+$ through pathway B is observed only for complexes in which L contains a carbonyl group. As has been pointed out in the Results, these differences in behavior are enhanced as the self-condensation reactions proceed, eventually leading to the exclusive formation of $Cr_4L_2(CO)_6^+$ through pathway A for complexes 1, 2, 3, and 8 (L = toluene, mesitylene, PhCOOMe, and $PhCH_2COMe$) and to $Cr_4L_2(CO)_5^+$ formation through pathway B for L = PhCOR.

There are several conceivable explanations why pathway A is followed when L is a hydrocarbon and pathway B is followed when L is a ketone. It is possible that the initial complexation energy of Cr^+ with $CrL(CO)_3$ is larger when L is a ketone, resulting in the elimination of two carbonyls (pathway B) as opposed to one carbonyl (pathway A). Alternatively, the CO bond energies may be somewhat weaker in the complex when L is a ketone, again favoring pathway B. Unfortunately, these hypotheses cannot be evaluated because of the paucity of thermochemical data available for the $Cr(\eta^6\text{-arene})(CO)_3$ complexes. An additional factor may be that the stabilization of the $Cr_2L(CO)^+$ ion and its self-condensation products is achieved through the coordination of the carbonyl group of the arene ligand to the incoming Cr^+. The occurrence of this coordination is consistent with the dependence of the relative rate of dimer formation on the length of the alkyl group, R, in the PhCOR ligands. Table III shows that the relative abundance of the condensation products obtained through pathway B increases with increasing size of the alkyl substituents, from methyl to butyl, in agreement with their increasing inductive effect, which enhances the coordinative ability of the ketonic CO of the ligand and also increases complexation energy.

$Cr_4L_2(CO)_5^+$ reacts further with a fourth molecule of the complex, leading to $Cr_5L_3(CO)_8^+$, while no products are observed from $Cr_4L_2(CO)_6^+$. This difference in reactivity of the two ions does not arise due to differences in either their reduced mass[23] or their electron deficiency. In fact, the reduced masses, μ = 181 and μ = 178, calculated for

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$Cr_4(mesitylene)_2(CO)_6^+$ and $Cr_4(PhCOMe)_2(CO)_5^+$, respectively, clearly give a negligible effect on the reaction rate. Electron deficiencies (ED) have been determined for the same ionic species on the basis of the 18-electron rule,[24] assuming that the cluster fragment is a tetrahedron in which each chromium atom has three Cr–Cr bonds. ED = 3.25 is calculated for $Cr_4(mesitylene)_2(CO)_6^+$, while ED = 3.25–3.75 is calculated for $Cr_4(PhCOMe)_2(CO)_5^+$, depending on the extent to which a ketonic CO is involved in the coordination sphere (i.e. from two-electron donor to zero-electron donor). According to previously reported data,[25] these ED values should correspond to very reactive species, while their difference is, again, negligible. Therefore, we suggest that $Cr_4L_2(CO)_6^+$ does not react further because, assuming a tetrahedral structure for the metal cluster, the coordination sphere is full.

CrL^+ reacts with $CrL(CO)_3$ in self-condensation processes at a lower reaction rate than Cr^+. This is due mainly to the fact that CrL^+ exhibits a more diffuse charge and in part to its lower degree of coordinative unsaturation (ED = 3.5 for CrL^+ compared to ED = 6.5 for Cr^+), as well as to the higher reduced mass of CrL^+ (i.e. 103 for CrL^+ with L = mesitylene and PhCOMe vs 43 for Cr^+). For all of the complexes, CrL^+ reacts with $CrL(CO)_3$ via displacement of a CO molecule, leading to $Cr_2L_2(CO)_2^+$ (Scheme II). Moreover, complexes **3**–**8**, whose arene ligands contain a CO group, also proceed in a parallel fashion, leading to the formation of $Cr_2L_2^+$ with elimination of three CO molecules. As in the self-condensation reactions of Cr^+, it can be suggested that stabilization of $Cr_2L_2^+$, formed from CrL^+, is achieved by coordination of the carbonyl group of each arene ligand to each chromium atom, resulting in a symmetric structure.

The condensation reactions of $CrL(CO)^+$ and $CrL(CO)_2^+$, which are characterized by a still lower unsaturation than CrL^+, occur at a very low rate. As shown in Scheme III, $Cr_2L_2(CO)_3^+$ is the only product of the first condensation step. All of the complexes react by the same reaction pathway, since it is likely that the low unsaturation of the reagent ions prevents the ketonic CO from interacting with the metal center.

Under benzene chemical ionization conditions, all of the complexes examined give charge-exchange products with $C_6H_6^+$ (Scheme IV), in accordance with their lower ionization potentials.[26] The primary products are the molecular ion, $CrL(CO)_3^+$, and its fragments, $CrL(CO)_2^+$ and $CrL(CO)^+$. These fragment ions react with their neutral precursors both by charge-exchange processes, to give the molecular ion, and by condensation reactions, leading to $Cr_2L_2(CO)_3^+$, which has already been described above. In addition, $CrL(CO)^+$ also takes part in a substitution reaction with neutral benzene, yielding $CrL(C_6H_6)^+$, which has been previously observed by conventional chemical ionization.[13] Results reported in Table IV indicate that the extent to which substitution reactions take place depends upon the nature of the ligand, L. When L is a hydrocarbon (toluene and mesitylene), M^+ shows a higher relative abundance with respect to that of $(M - 3CO + benzene)^+$. The opposite behavior is displayed when the ligand is a ketone (PhCOMe, PhCOEt, PhCO-*n*-Pr, PhCO-*t*-Bu, and $PhCH_2COMe$) or an ester (PhCOOMe). This trend points out the importance of the Cr–CO binding energy, which is stronger when L is a hydrocarbon and weaker when it contains a carbonyl group (ketones and ester), as has previously been reported.[27]

Table VIII. Polarizability of Arene Ligands

arene[a]	polarizability,[b] Å^3	arene[a]	polarizability,[b] Å^3
benzene	10.4	mesitylene	15.9
toluene	12.2	PhCOEt	16.4
PhOMe	12.9	PhCO-*n*-Pr	18.2
PhCOOMe	14.8	PhCO-*t*-Bu	20.1
PhCHO	12.6	$PhCH_2COMe$	16.4
PhCOMe	14.6		

[a] Arenes are listed in order of increasing binding energy to Cr^+. [b] Calculated as described in ref 28.

Table V shows that the substitution reactions of the $CrL(CO)_3$ compounds with propene as reagent gas follow the same overall behavior as that observed with benzene as reagent gas. For example, complexes containing a hydrocarbon ligand undergo substitution reactions to a lesser extent than those containing a ketone. The $(M - 3CO + P)^+$ ions display a lower relative abundance than $(M - 3CO + B)^+$, which can be ascribed to the lower coordination energy of propene with respect to that of benzene.

Reactions of $Cr(\eta^6\text{-toluene})(CO)_3$ with a number of different arenes (Table VI) show that substitution of the coordinated arene can also take place when a suitable reactant is used. Results are in agreement with the relative binding energy order obtained by CID experiments. For example, toluene is not substituted by benzene but is displaced by mesitylene, PhOMe, and PhCHO. The concomitant decrease of the relative abundance of the monosubstituted species and increase of abundance of the disubstituted species with time suggest that $Cr(A)_2^+$ ions are formed directly from $Cr(L)(A)^+$ by displacement of the ligand L. This hypothesis has been confirmed by double-resonance experiments and is illustrated in Scheme V. For each of the reagent gases used, the base peak is always the molecular ion, while the relative abundance of the monosubstituted ions depends on the nature of the free arene, A. Surprisingly, using benzene as the reagent gas gives the most abundant $Cr(toluene)(A)^+$ ion, even though the Cr^+–benzene bond has been shown to be the weakest, and mesitylene, which is supposed to form a stronger Cr^+–A bond than benzene, PhOMe, and PhCHO, gives the least abundant monosubstituted ion. This behavior is ascribed to the different concentration of the precursor ion, $CrL(CO)^+$, in the presence of different reagent gases.

The chemical ionization mass spectra of $Cr(\eta^6\text{-PhCOOMe})(CO)_3$ with benzene, mesitylene, PhOMe, and PhCHO as reagent gases are very similar to those of $Cr(\eta^6\text{-toluene})(CO)_3$. The main difference is the higher abundance of the substituted ions in the $Cr(\eta^6\text{-PhCOOMe})(CO)_3$ system. This behavior can be ascribed to the lower energy of the Cr–CO bonds,[27] which fragment more readily to give $(M - 2CO)^+$, the precursor ion of the $Cr(PhCOOMe)(A)^+$ species.

The relative binding energy sequence of the arenes to Cr^+, as reported in the Results, can be ascribed in part to their inductive effect when the arene is a hydrocarbon (benzene, toluene, and mesitylene) or an ether (PhOMe). For arenes containing a carbonyl group (ester, aldehyde, and ketones), the Cr^+–arene bond can be stabilized by interaction between the CO of the ligand and the metal center. This effect is enhanced by increasing the size of the R group in phenyl ketones, PhCOR, and by decreasing the steric constraint in $PhCH_2COMe$. The ion-induced dipole effects of the ligands can be evaluated from their

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polarizabilities, which have been calculated[28] for all the arenes examined here. The results are reported in Table VIII and are in general agreement with the observed relative binding energy sequence. Thus, both the inductive effects and the induced dipole effects reinforce each other, leading to the observed bond energy order.

In solution, reactions between $Cr(\eta^6\text{-arene})(CO)_3$ molecules and free arenes give arene-exchange processes[8] (reaction 1), while the CO groups are displaced only under UV light irradiation.[7] The different behavior observed

$$Cr(\eta^6\text{-arene})(CO)_3 + \text{arene}' \rightleftharpoons Cr(\eta^6\text{-arene}')(CO)_3 + \text{arene} \quad (1)$$

may occur because a positive charge on the chromium atom affects the Cr–CO bond strength more than that of the Cr–arene bond, as it lowers the retro-donation contribution in the Cr–CO bond. Interestingly, the equilibrium constants of reaction 1 in solution have been reported for a number of arenes[29] and the stability of the $Cr(\eta^6\text{-arene})(CO)_3$ species has been observed to increase in the order benzene, toluene, *p*-xylene, mesitylene which is in agreement with the gas-phase results.

Conclusion

The mechanisms of self-condensation and displacement processes for eight $Cr(\eta^6\text{-arene})(CO)_3$ (arene = hydrocarbons, ester, and ketones) complexes have been determined by FTMS methods. Different reaction pathways have been observed for self-condensation reactions, which depend upon the nature of the coordinated arene. The extent to which substitution of the carbonyl groups and of the coordinated arene occurs has been shown to depend on the nature of both the coordinated arene ligand and the reactant arene. From CID experiments, the relative binding energy sequence of a number of arenes to Cr^+ has been obtained and correlates well with the relative stabilities of the $Cr(\eta^6\text{-arene})(CO)_3$ complexes in solution.

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Registry No. $Cr(toluene)(CO)_3$, 12083-24-8; $Cr(mesitylene)(CO)_3$, 12129-67-8; $Cr(PhCOOMe)(CO)_3$, 12125-87-0; $Cr(PhCOMe)(CO)_3$, 12153-11-6; $Cr(PhCOEt)(CO)_3$, 58535-55-0; Cr(PhCO-*n*-Pr)$(CO)_3$, 68786-02-7; Cr(PhCO-*t*-Bu)$(CO)_3$, 58482-51-2; $Cr(PhCH_2COMe)(CO)_3$, 12153-79-6; PhOMe, 100-66-3; PhCHO, 100-52-7; PhCOOMe, 93-58-3; PhCOMe, 98-86-2; PhCOEt, 93-55-0; PhCO-*n*-Pr, 495-40-9; PhCO-*t*-Bu, 938-16-9; $PhCH_2OMe$, 103-79-7; benzene, 71-43-2; propene, 115-07-1; mesitylene, 108-67-8; toluene, 108-88-3.

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Structural Systematics. 2.[1] Metal Framework Rearrangements in Cluster Compounds Containing the Au_2Ru_3 Fragment

A. Guy Orpen*,[†] and Ian D. Salter[‡]

Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS, U.K.,
and Department of Chemistry, University of Exeter, Exeter EX4 4QD, U.K.

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It has been postulated that the reaction path for site exchange of gold atoms in cluster compounds containing Au_2Ru_3 fragments involves a partial Berry pseudorotation in which the geometry of the Au_2Ru_3 fragment changes from trigonal bipyramidal (tbp) to square pyramidal (sp) and then back to tbp with exchange of gold atom environments. This hypothesis is tested against data derived from 16 crystal structures of compounds containing such fragments. The Berry-like mechanism is shown to be fully consistent with the structural evidence. The observed geometries map the full range of the reaction coordinate. There is some evidence supporting the existence of an edge-cleavage mechanism, although only the initial stages of this pathway may be observed in the data set. Other mechanisms, such as the turnstile, are shown to be incompatible with the structural data presented.

We have shown,[2,3] in a series of studies by ^{31}P and/or ^{109}Ag NMR spectroscopy, that metal clusters containing trigonal-bipyramidal M_2Ru_3 fragments (M = Cu, Ag, Au) exhibit dynamic behavior in solution that involves intramolecular exchange between Group Ib metal atoms in axial and equatorial sites. We have further postulated[3] that this process occurs by a partial Berry pseudorotation mechanism in which the geometry of the M_2Ru_3 fragment changes from trigonal bipyramidal (tbp) to square pyramidal (sp) and then back to tbp, thereby exchanging the M atoms (see Scheme I (top), A → B → C). The integrity of the Ru_3 triangle is apparently maintained in the process, typically as a consequence of a μ_3 ligand (e.g. S, COMe, or $Ru(CO)_3$) that caps this unit. We now report that analysis of 16 crystal structures of cluster compounds

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[†] University of Bristol.

[‡] University of Exeter.

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