Inorg. Chem. **2003**, *42*, 358–364

Inorganic Chemistry
Article

(Arene)tricarbonylchromium Complexes Synthesized on NaX Zeolite: Solid-State NMR and DRIFTS Studies

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Received August 12, 2002

Various (arene)tricarbonylchromium complexes were synthesized within the confines of NaX zeolite and studied with diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and carbon-13 magic-angle-spinning nuclear magnetic resonance (MAS NMR) spectroscopy. In each case, the surface complex $Cr(CO)_3(O_z)_3$ (O_z represents a framework oxygen of the NaX zeolite) was prepared before a particular arene was added. The arenes benzene, toluene, mesitylene, anisole, and aniline all produce hexahapto π-complexes physisorbed within the zeolite supercage. DRIFTS spectra show three bands in the carbonyl region indicating less than C_{3v} symmetry. The NMR spectra have narrow carbonyl bands near 240 ppm which indicate rapidly reorienting complexes within the zeolite. The (η^6-benzene)tricarbonylchromium complex is physisorbed at two sites as indicated both by the DRIFTS spectra and by two carbonyl resonances at 242.5 and 239.1 ppm at 300 K. Variable-temperature MAS NMR shows these two resonances coalescing near 360 K with an activation energy of 48 ± 6 kJ/mol. When the temperature is decreased to 205 K, the high-frequency carbonyl resonance disappears. The 239 ppm resonance is still narrow at 134 K while MAS sidebands show that the resonance from physisorbed benzene is ca. 200 ppm wide. The complex prepared with pyridine gave a broad resonance as indicated by the spinning sidebands in the MAS NMR spectra. The pyridine complex was identified as $Cr(CO)_3(C_5H_5N)_3$.

Introduction

A compound adsorbed in a zeolite is in an environment that presents a challenge for chemists to understand and exploit. Group 6 metal carbonyls deposited on zeolites have been shown to be catalyst precursors[1,2] and may be precursors of materials for electronic or optical devices.[3] A few studies of the kinetic details of the reaction of group 6 metal carbonyls with other species within the "nanoreactors" provided by the zeolite environment have been carried out.[4,5] There continues to be a need for basic data and understanding that permit more control of the placement of metal-containing species within the zeolite.

While IR spectroscopy provides keys to understanding the location and identity of adsorbed species, NMR spectroscopy often can add information about the dynamic behavior of the adsorbed species. Many organic and inorganic compounds, including group 6 metal hexacarbonyls, are known to move rapidly within the confines of the zeolite so that their NMR spectra differ little from the spectra of the compounds dissolved in a liquid solvent.[6,7] This coincides with a view that a zeolite can behave as a solid solvent.[8] A superficially contradictory observation is that adsorbed species within a zeolite are found at specific locations and often anchored directly to a particular site in the zeolite. Of

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10.1021/ic020512+ CCC: $25.00

course, the time scale of the observation method determines whether the intrazeolite species can be observed as either dynamic or anchored. One example is in spectra of $Cr(CO)_6$ adsorbed in NaX zeolite. The IR spectrum indicates strong interactions with the zeolite,[9] while carbon-13 NMR indicates that the $Cr(CO)_6$ is undergoing rapid, isotropic motion which must occur by jumps between different orientations of the molecule.[10]

X- and Y-type zeolites are synthetic faujasites with eight supercages/unit cell. The supercages have diameters of ca. 1.3 nm/unit cell and admit molecules with kinetic diameters up to ca. 0.8 nm.[11] The considerable number of studies of group 6 metal hexacarbonyls adsorbed on these zeolites have established that a thermally stable surface tricarbonyl species, $M(CO)_3(O_z)_3$ (M = Cr, Mo, or W), can form within the supercage when oxygens of the zeolite framework (O_z) displace three carbonyl ligands.[10,12,13] The reactions of group 6 metal hexacarbonyls with benzene primarily within Y-type zeolites have been studied by Brémard et al. using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and molecular simulations of the energetics and siting locations.[14−16] This work concluded that the reaction on NaY zeolite proceeds through the loss of three CO ligands to produce the $M(CO)_3(O_z)_3$ surface moiety before benzene exchanges with the zeolite oxygens to produce $M(CO)_3(C_6H_6)$.[15] Özkar et al. have studied the reactions between the $M(CO)_3(O_z)_3$ moiety formed in Y zeolites and adsorbed arenes to again produce (arene)tricarbonylmetal complexes physisorbed within the zeolite supercages.[13]

This work represents a continuation of our research in which (η^6-benzene)tricarbonylchromium(0) and (η^6-anisole)tricarbonylchromium(0) were prepared on NaX zeolite and observed by DRIFTS.[17] Additional arenes are used and solid-state carbon-13 NMR adds information about the motion of the adsorbed species. Guidance for understanding the reactions is provided by the earlier work of Brémard et al. and Özkar et al., but their work did not involve carbon-13 NMR spectroscopy and arene complexes were not formed on NaX zeolite.

Experimental Section

Samples were prepared as described previously under conditions in which air was rigorously excluded.[17] About 0.25 g of NaX zeolite (Strem Chemicals, 600 mesh powder) was calcined at 773 K for 1 h in O_2 and 0.5 h under vacuum before it was dry-mixed with ca. 5.5 mg of $Cr(CO)_6$ (Aldrich 99%). The mixture was agitated and heated at 403 K in a 30 cm^3/min flow of helium for about 1 h to produce the surface species, $Cr(CO)_3(O_z)_3$. Up to 43 mg of the appropriate arene was then distilled into the evacuated reactor, and the mixture was held at 403 K for 2 h for most samples. The samples were sealed in glass tubes to await IR studies.

Samples prepared for NMR studies were enriched in carbon-13 by exchange with ^{13}CO (90 atom %, BOC Limited). The ^{13}CO gas (about 30 kPa) was admitted to the reactor containing the $Cr(CO)_3(O_z)_3$ sample, and exchange was allowed to continue for 0.5 h at 373 K. The sample was again flushed with helium and heated to 403 K until CO evolution became negligible and the enriched $Cr(CO)_3(O_z)_3$ surface species was apparently formed. Enrichment of the carbonyl carbons is to 70 ± 10 atom %. The arene was then added and treated as described for the nonenriched samples. The enriched sample was divided and flame-sealed in a glass tube for IR analysis and a glass insert (Wilmad DWGSK2356) that fits inside 7 mm rotors for solid-state NMR studies.

DRIFTS studies used a Mattson Research Series FTIR spectrometer with an MCT detector and a "Praying Mantis" diffuse reflectance attachment (Harrick Scientific Corp., DRA-3C5). Inside a glovebox with a nitrogen atmosphere, the IR sample was transferred to a Harrick vacuum chamber (HVC-DRP) designed for the DRA. All DRIFTS spectra were obtained at room temperature with a resolution of 2 cm^{-1} using 500 scans. The spectra were obtained as single-beam spectra and ratioed against the spectrum from a separate sample of calcined NaX zeolite. Mattson software was used to present the spectra in either "absorption units" or as baseline-corrected "Kubelka−Munk units".[18] Below ca. 1350 cm^{-1}, strong absorbance by the zeolite makes the spectra unusable. The OH spectral bands above 3500 cm^{-1} are not of high quality since they are affected by slight variations in the different zeolite samples used in the single beam and background spectra.

The NMR spectra were made using either a 4.7 T Bruker MSL spectrometer at the NAWCWD or a 7.05 T Bruker DPX spectrometer at PSU. Both spectrometers were equipped with broad-band, cross-polarization/magic-angle-spinning (CP/MAS) probes using 7 mm ZrO rotors. High-power proton decoupling (without CP) was used on most samples although decoupling effects on carbonyl carbons were minimal. Chemical shifts are reported relative to TMS but were determined using adamantane as an external reference (38.56 ppm). Uncertainty in the chemical shifts are about ±0.2 ppm (unless otherwise indicated), while uncertainty in the temperature for NMR measurements is thought to be ±2 K (but perhaps higher at very low temperatures).

Results

Details of the preparations for samples of (arene)tricarbonylchromium(0) complexes absorbed within NaX zeolite are given in Table 1. Samples B (with benzene) and C (with anisole) were used in a previous investigation, and preparation conditions for these samples were optimized in the earlier study.[17] While mesitylene required a higher temperature than benzene or anisole to react significantly with the surface chromium tricarbonyl complex on NaX, pyridine reacted with the surface complex at room temperature to give a yellow sample.

DRIFTS. The DRIFTS spectra from the nonenriched samples (B−G) are shown in Figure 1 using absorbance units. Spectral bands arise from both the synthesized intrazeolite

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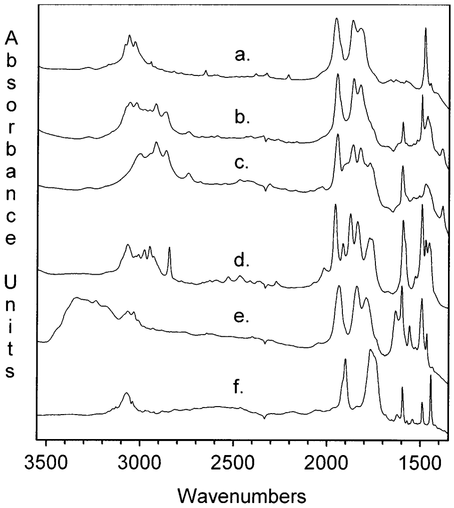

Figure 1. Room-temperature DRIFTS spectra of nonenriched samples prepared from $Cr(CO)_6$, NaX zeolite, and an arene. The spectra are of the following samples: (a) sample B (benzene); (b) sample D (toluene); (c) sample E (mesitylene); (d) sample C (anisole); (e) sample F (aniline); (f) sample G (pyridine).

Table 1. Samples Prepared with Hexacarbonylchromium and 0.25 g of Calcined NaX Zeolite

sample	$Cr(CO)_6$ (mg)	CO/Cr ratio	^{13}C enriched?	arene	arene (mg)	*T* used (K)
A	5.80	2.82	no	none		
AE	5.99	3.06	yes	none		
B	5.24	2.87	no	benzene	34.5	403
B2	5.77	3.03	no	benzene	42.6	403
BE	5.83	3.13	yes	benzene	27.9	403
B2E	5.87	2.71	yes	benzene	26.6	403
C	6.62	2.95	no	anisole	40.2	403
CE	5.81	3.12	yes	anisole	40.2	403
D	5.61	3.15	no	toluene	34.7	403
DE	5.79	3.00	yes	toluene	37.0	403
E	6.63	3.01	no	mesitylene	36.0	443
EE	6.11	3.06	yes	mesitylene	35.8	443
F	6.49	3.15	no	aniline	42.1	403
FE	5.43	2.57	yes	aniline	38.8	403
G	6.47	3.19	no	pyridine	10.9	(300)
GE	6.42	3.00	yes	pyridine	37.1	403

(arene)tricarbonylchromium and the excess arene physisorbed in the NaX zeolite. The physisorbed arene bands generally overwhelm bands from the complexed arene. The (benzene)tricarbonylchromium spectrum (Figure 1a) shows a sharp band at 1477 cm^{-1} from the physisorbed benzene and a very small band at 1452 cm^{-1} from the complexed benzene as noted previously.[17]

In the region between 1700 and 2000 cm^{-1} are carbonyl stretching vibrations. Figure 2 shows the DRIFTS spectra of the carbonyl region from the nonenriched samples using Kubelka−Munk units. Five of the spectra of the (arene)tricarbonylchromium complexes in Figure 2 show three main bands. The spectrum (f) of the pyridine complex is significantly different from the others in this region with just two main bands. Spectra of the anisole (d) and mesitylene (c) complexes have additional bands at ca. 1918 and 1774 cm^{-1} which are identified with excess $Cr(CO)_3(O_z)_3$.[17] These bands indicate that the reactions to form the anisole and mesitylene complexes did not go to completion under the conditions used. Sample B prepared with benzene has turned out to be somewhat unusual since other samples prepared with benzene under nominally the same conditions tend to show a second, usually less intense, set of carbonyl bands. In a previous publication, the carbonyl bands seen in the DRIFTS spectrum of sample B were referred to as "site 1" bands while the second set of bands is from a "site 2" complex.[17] Included in Table 1 is preparation data for a sample (B2) whose DRIFTS spectrum shows site 1 and site 2 bands of almost equal intensity as judged by the 1958 and 1930 cm^{-1} bands. While the preparation of sample B2 is considered inferior to that of sample B, perhaps due to inadequate mixing, the exact cause of sample differences is not known. Of the present samples, the benzene samples were the only ones to show two different types of carbonyl bands.

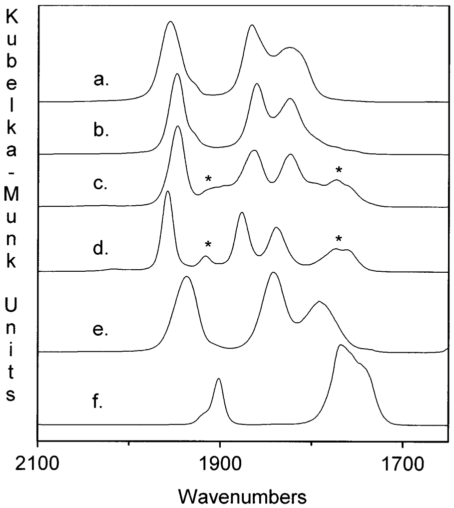

Figure 2. Room-temperature DRIFTS spectra of nonenriched samples prepared from $Cr(CO)_6$, NaX, and an arene. The spectra are in the same order as those of Figure 1. Asterisks mark bands identified with the surface complex, $Cr(CO)_3(O_z)_3$.

Wavenumbers obtained from the major carbonyl bands of the DRIFTS spectra of all samples are listed in Table 2. The DRIFTS spectra of samples that had been carbon-13 enriched generally show the formation of the same complexes indicated in the spectra of the nonenriched samples. The three largest carbonyl bands of each of the enriched samples are shifted about 40 cm^{-1} lower in wavenumber relative to those of the natural abundance samples while bands involving the arene are not shifted. Figure 3 gives a comparison of the DRIFTS spectra of an enriched sample (BE) and a nonenriched sample (B) prepared with benzene.

Room-Temperature NMR Spectroscopy. MAS NMR spectra of the carbon-13 enriched samples show at least one isotropic carbonyl resonance near 240 ppm. Values of the chemical shifts found for the carbonyls are given in Table 2. In the samples (CE and EE) with anisole and mesitylene, the presence of the unreacted $Cr(CO)_3(O_z)_3$ complex is indicated by an additional resonance at 246.7 ppm in agreement with DRIFTS results on samples C and E.[10] The benzene-containing samples (BE and B2E) are the only samples whose NMR spectra show two isotropic carbonyl resonances coming from the (arene)tricarbonylchromium complex. These two samples, while nominally prepared under identical conditions, show different relative intensities

Table 2. DRIFTS and Carbon-13 MAS NMR Carbonyl Spectral Data from Samples Prepared with $Cr(CO)_6$, NaX, and an Arene

sample	arene	DRIFTS (cm^{-1})			NMR (ppm)[a]
A	none	1919	1776		
AE	none	1892	1757		246.7
		1875	1735		
B	benzene	1957	1867	1825	
B2	benzene	1958	1866	1832[c]	
		1930[b]			
BE	benzene	1918	1820	1792[c]	242.5[b]
					239.1
B2E	benzene	1917	1818	1792[c]	242.5[b]
		1908			239.2
		1888[b]			
C	anisole	1959	1878	1840	
CE	anisole	1926	1839	1798	236.2
		1917			
D	toluene	1949	1862	1825	
DE	toluene	1913	1822	1788	239.0
E	mesitylene	1949	1865	1825	
EE	mesitylene	1910	1830	1787	239.1
F	aniline	1940	1843	1793	
FE	aniline	1904	1807	1759	241.6
G	pyridine	1902	1768		
			1746		
GE	pyridine	1874	1737		237
		1857	1722		

[a] For comparison, the following chemical shifts of the dissolved complexes have been reported in refs 19 and 20: (benzene)tricarbonylchromium in $CHCl_3$, 233.3 ppm; (anisole)tricarbonylchromium in $CHCl_3$, 233.2 ppm; (toluene)tricarbonylchromium in $CHCl_3$, 233.6 ppm; (aniline)tricarbonylchromium in CH_2Cl_2, 234.6 ppm; (mesitylene)tricarbonylchromium in CH_2Cl_2, 234.5 ppm. [b] Identified with site 2. [c] Significant contributions from both site 1 and site 2.

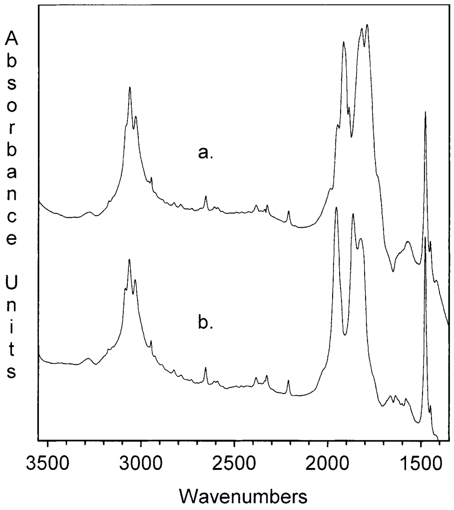

Figure 3. Room-temperature DRIFTS spectra of samples prepared from $Cr(CO)_6$, NaX zeolite, and benzene: (a) carbon-13 enriched sample BE; (b) nonenriched sample B.

of the two carbonyl resonances with the 242 ppm resonance being less intense than the 239 ppm resonance in sample BE but more intense in sample B2E. Sample B2E also has a small resonance at 247 ppm indicating that unreacted $Cr(CO)_3(O_z)_3$ is also present. The 239 and 242 ppm resonances in the enriched benzene-containing samples appear to correspond to the site 1 and site 2 sets of DRIFTS bands found with samples B and B2. Carbon resonances from the excess, physisorbed arene are also seen in the carbon-13 NMR spectra although the arenes were not enriched with carbon-13. Carbon resonances from the arene complexed to chromium are apparently too weak to be seen in these NMR spectra.

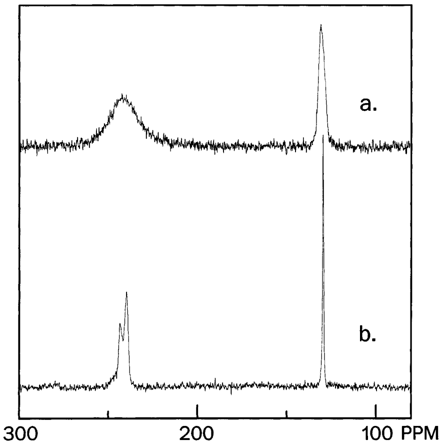

Figure 4. Room-temperature carbon-13 solid-state NMR spectra at 7.05 T of the enriched sample prepared with $Cr(CO)_6$, NaX zeolite, and benzene (sample BE). The following parameters were used: 0.040 s acquisition time; 4 μs pulse (90°); 2.0 s repetition time; 8 Hz line broadening. In (a) the sample is in a 7 mm MAS rotor but it is not spinning; 1200 scans are used without decoupling. In (b) the sample is in the MAS rotor spinning at 3000 Hz, and 600 scans are used with high-power decoupling.

The MAS NMR spectrum of the ^{13}C-enriched benzene sample (BE) is seen in Figure 4b. There are no clear spinning sidebands for either the benzene resonance or the carbonyl resonances. The resonances broaden somewhat when the NMR spectra are run without MAS (Figure 4a), but the line widths are relatively narrow for non-MAS carbon-13 solid-state NMR. In Figure 4a, the two carbonyl peaks have merged into one 1300 Hz wide resonance and the benzene resonance is 320 Hz wide. The resonances from samples with toluene, mesitylene, anisole, and aniline also have no clear spinning sidebands with MAS and are observable without MAS.

The complex prepared with $Cr(CO)_6$, pyridine, and NaX zeolite has an MAS NMR spectrum unlike the other five complexes (Figure S5 in the Supporting Information). The carbonyl resonance cannot be found without MAS. The isotropic resonance for sample GE is at 237 ± 1 ppm while spinning sidebands are seen over the range from 440 ppm to -30 ppm with an MAS rate of 5000 Hz. Despite the heating of the sample to 353 K while the MAS NMR spectrum was obtained, no narrowing of the carbonyl resonance was observed.

Variable-Temperature NMR Spectroscopy. Variable-temperature carbon-13 NMR spectra were carried out on the benzene-containing sample BE. This is the same sample used in the Figure 4 spectra, but the variable-temperature studies were made at a lower field (4.7 T) and at a MAS rate of ca. 2000 Hz. Figure 5 shows the carbonyl resonances obtained from 205 to 380 K. The two carbonyl peaks at room temperature appear to coalesce near 360 K. As the temperature is decreased below room temperature, the high-frequency resonance seems to disappear so that at 205 K there is again only one carbonyl peak.

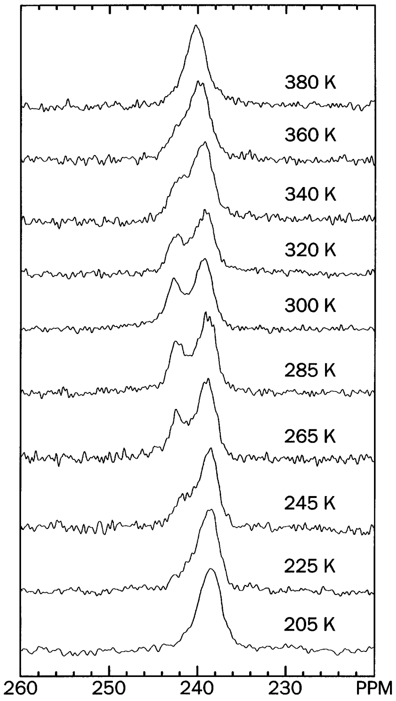

Figure 5. Carbon-13 solid-state NMR spectra at various temperatures for the enriched sample prepared with $Cr(CO)_6$, NaX zeolite, and benzene (sample BE). The field is 4.7 T, the MAS rate is 2000 Hz, the acquisition time is 51.2 ms, the repetition time is 5 s, the pulse length is 4.5 μs (90°), the number of scans is from 320 to 450, and high-power decoupling is used.

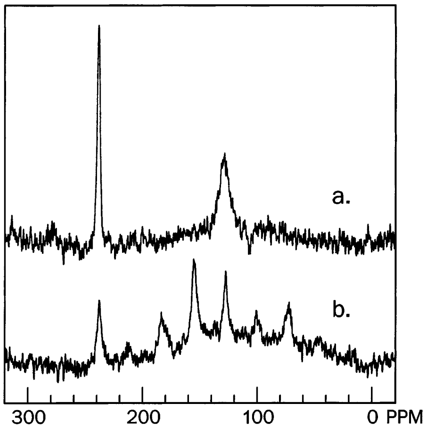

Figure 6. Carbon-13 solid-state NMR spectra at 4.7 T for the enriched sample prepared with $Cr(CO)_6$, NaX zeolite, and benzene (sample BE): (a) 205 K, 320 scans, 5 s repetition, and 2000 Hz; (b) 134 K, 1000 scans, 4 s repetition, and 1300 Hz. Other parameters are as given in Figure 5.

Figure 6 shows the NMR spectra of sample BE at low temperatures. The carbon MAS NMR resonance from the physisorbed benzene of this sample begins to broaden substantially as the temperature is lowered below 205 K. At 134 K, the benzene resonance is seen as an isotropic resonance at 129 ppm with spinning sidebands between about 50 and 220 ppm. It is striking that although the benzene resonance broadens, the carbonyl resonance remains relatively narrow with no sidebands appearing. The intensity of the carbonyl peak decreases relative to the benzene on going from 205 to 134 K perhaps partly because the carbonyl resonance is entering a low-temperature region of broadening below 134 K.

Discussion

The reaction between the chromium tricarbonyl surface species and an arene such as benzene can be represented as the exchange of σ-bonded framework oxygen atoms with π-bonded benzene

$$\mathrm{Cr(CO)_3(O_z)_3 + C_6H_6 \rightarrow Cr(CO)_3(\eta^6\text{-}C_6H_6) + 3O_z}$$

with O_z indicating a zeolite oxygen. Qualitative observations indicate that this reaction occurs more readily on NaY than NaX zeolite. On NaX, an elevated temperature and excess arene is required[17] while Özkar et al. indicated that the reaction occurs at room temperature on NaY.[13] The higher aluminum content of NaX compared to NaY is thought to increase the basicity of the O_z atoms and give a more stable $M(CO)_3(O_z)_3$ surface species (M = Cr, Mo, or W) on NaX.[21] There is considerable evidence that the surface tricarbonyl and the synthesized arene complexes are formed within the X or Y zeolite supercages with Özkar et al. demonstrating the size-exclusion effects of reactions with surface tricarbonyls on NaY and Brémard et al. calculating positions of the complexes within the supercages of NaX and NaY.[13,16]

The DRIFTS spectra of Figures 1 and 2 show evidence of only one type of adsorbed complex being produced for each different arene used in this study. With the exception of the pyridine-containing sample, the arene-containing samples have DRIFTS spectra in the CO region (Figure 2) which correspond to "site 1" spectra of refs 13 and 17 with no second site indicated. In this study, only benzene-containing samples showed evidence of a "site 2" pattern as indicated in Table 2 primarily with a band at 1930 cm^{-1} for sample B2. The (η^6-anisole)tricarbonylchromium complex adsorbed in NaX showed both site 1 and site 2 patterns under some conditions in ref 17, but the site 2 pattern was not found here. The presence of three carbonyl bands in site 1 patterns indicates that the symmetry of the adsorbed complex is lower than the approximate C_{3v} point group of the free complex. The DRIFTS spectrum of the pyridine-containing sample (sample G) shows two main carbonyl bands at 1902 and 1768 with a shoulder at 1746 cm^{-1}. This is strikingly similar to bands at 1902, 1760, and 1736 cm^{-1} reported for $Mo(CO)_3(C_5H_5N)_3$ on NaY zeolite.[22] That the pyridine complex prepared on NaX is $Cr(CO)_3(C_5H_5N)_3$ seems clear given the known difficulty of synthesizing the π-complex (η^6-pyridine)tricarbonylchromium.[23]

The absence of significant spinning sidebands in the carbon-13 MAS NMR spectra for all samples except the one with pyridine (sample GE) indicates that both the complexes and the physisorbed arenes undergo rapid isotropic motion

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at room temperature. The presence of rapid motion is also indicated by the relatively narrow line widths observed in the static spectra (e.g., Figure 4a). In solid (η^6-benzene)tricarbonylchromium at 293 K, the carbonyl carbon resonance is over 400 ppm wide with reported shielding parameters $\delta_{11} = \delta_{22} = 379$, $\delta_{33} = -51$, and $\delta_{iso} = 235.7$ ppm.[24] The motions of the complexes must be occurring at 30 kHz or more to get a collapse of the powder pattern at 7.05 T. While the motion includes arene rotation and reorientational motion of the $Cr(CO)_3$ moiety as found in solid $Cr(CO)_3(C_6H_6)$,[24] isotropic reorientation of the whole complex must be occurring within the zeolite. The pyridine-containing complex (sample GE) is clearly not as dynamic a species in the zeolite as the other complexes studied here. The spinning sidebands of sample GE seem compatible with an axially symmetric powder pattern approximately 400 ppm wide as expected for static carbonyls although some obscured sidebands make a more detailed analysis questionable. The hindered motion of the pyridine complex lends support to the identification of this complex as $Cr(CO)_3(C_5H_5N)_3$ and not the smaller π-complex.

Since the DRIFTS results indicate that there is lower than C_{3v} symmetry for the complexes in the NaX zeolite, at least one carbonyl carbon is expected to be inequivalent to the other two. Rapid exchange of the carbonyl ligands must be averaging out any inequivalence and resulting in only one carbonyl carbon resonance in the room-temperature MAS NMR spectra for all enriched samples except the ones containing benzene (BE and B2E). This averaging by intramolecular CO exchange probably is also occurring in the (benzene)tricarbonylchromium samples (BE and B2E) despite the appearance of two carbonyl resonances (Figures 4b and 5). The ratio of the intensities of the 242 ppm resonance relative to the 239 ppm resonance is ca. 1 to 2 for sample BE and ca. 1.3 to 1 for sample B2E at room temperature. It appears that, in similar benzene-containing samples, the amount of the (benzene)tricarbonylchromium located at one site compared to the second site can be different. Thus, the 1 to 2 ratio found for sample BE is not an indication that one carbonyl carbon in the complex is inequivalent to the other two.

If we are to conclude that the 239 ppm resonance from sample BE corresponds to the complex located at site 1 and the 242 ppm resonance is for the complex at site 2, then the two sites should be indicated in the DRIFTS spectrum of enriched samples BE (Figure 3a) and B2E. One problem with the DRIFTS spectra of our enriched samples is that the carbon-13 enrichment is incomplete and mixed isotope complexes such as $Cr(C_6H_6)(^{13}CO)_2(^{12}CO)$ can be expected to obscure the bands of the fully labeled complex.[25] The spectrum of enriched sample BE in Figure 3a shows clear distortions of the site 1 spectrum from nonenriched sample B in Figure 3b that are thought to come from the presence of site 2 bands. While comparisons of DRIFTS spectra from the enriched (BE and B2E) and nonenriched samples (B and B2) are not conclusive, the enriched samples are compatible with samples containing the carbonyl complexes in the two sites. It should be recognized that the (benzene)tricarbonylchromium/NaX samples used here (B, B2, BE, and B2E) represent the extremes in the range of site 1 to site 2 ratios found in our benzene-containing samples, and the site 1 complex is generally favored by our reaction conditions.

The temperature dependence of the carbonyl carbon NMR resonances from (benzene)tricarbonylchromium on NaX offers the possibility of obtaining dynamic information about the adsorbed complex. We note that the single resonance in the 380 K spectrum of Figure 5 is centered at 240.1 ppm and is thus consistent with a coalescence of the two resonances found at 242.5 and 239.1 ppm at 300 K. The single resonance at 205 K is centered at 239.1 ppm and seems to be the low-frequency carbonyl resonance after the high-frequency resonance has disappeared. The low signal-to-noise ratio of the spectra and the complexity of the system limit the analysis. The standard equation for exchange between two inequivalent positions A and B has 7 parameters (the static frequencies, ν_A and ν_B; relaxation times, T_{2A} and T_{2B}; population fraction, p_A; rate constant, k_A; normalization constant, C) with $p_B = 1 - p_A$ and $k_B = k_A(p_A/p_B)$.[26] While this is too many parameters for a meaningful fit if all parameters are allowed to vary, satisfactory fits of the 300−360 K spectra from Figure 5 were obtained by allowing k_A and C to vary while keeping the following parameters constant: $\nu_A = 12.220$ kHz (242.7 ppm); $\nu_B = 12.036$ kHz (239.1 ppm); $T_{2A} = 0.0030$ s; $T_{2B} = 0.0024$ s; $p_A = 0.333$; $p_B = 0.667$. These parameters are reasonable estimates but are not based on precise line shape analysis. In this manner, the following rate constants were found: $k_A(300\ K) = 37 \pm 7\ s^{-1}$; $k_A(320\ K) = 75 \pm 8\ s^{-1}$; $k_A(340\ K) = 274 \pm 18\ s^{-1}$; $k_A(360\ K) = 890 \pm 54\ s^{-1}$. An Arrhenius plot of $\ln(k_A)$ vs $1/T$ for these four rate constants is fairly linear and gives an activation energy of 48 ± 6 kJ/mol. A free energy of activation of 70 ± 5 kJ/mol has been reported for the rotation of the $Cr(CO)_3$ unit in solid $Cr(CO)_3(C_6H_6)$.[24] A lower activation energy is probably expected for the complex adsorbed in the zeolite as opposed to the solid complex; however, until more is known about what motion gives rise to the coalescence, comparisons do not seem warranted.

In the present samples, the excess physisorbed arene is a key factor in interpreting motions of the adsorbed complex. Much is presently known about the behavior and location of benzene in a zeolite.[27,28] Neutron diffraction indicates that benzene in NaX zeolite coordinates to Na^+ ions located at the faces of 6-rings in the supercages (the SII cation) but, in contrast to the situation in NaY, benzene is not found in the plane of the 12-ring opening of the supercage.[29,30] The low-

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temperature spectra of Figure 6 demonstrate that benzene has a strong affinity for sites within the zeolite, presumably the sodium ions. At 134 K, benzene shows spinning sidebands tracing out a powder pattern about 200 ppm wide and in agreement with the powder pattern of solid benzene at low temperature.[31,32] At the same temperature, the (benzene)tricarbonylchromium complex is still quite mobile on the NMR time scale with no spinning sidebands apparent. The benzene may in fact be blocking access to the Na^+ sites and preventing the complex from finding an anchored position at the sodium ions. In calculations by Brémard et al. on $Mo(CO)_3(\eta^6\text{-}C_6H_6)$ adsorbed in NaY, three low-energy absorption sites were found with the lowest energy site facially coordinated at the C_6H_6 to an SII sodium ion.[14] The calculations also indicate that $Mo(CO)_3(\eta^6\text{-}C_6H_6)$ will not adsorb on NaX when benzene is present.[14] A final speculation is that the presence of excess benzene is responsible for the low-temperature loss of the high-frequency carbonyl resonance in Figure 5. By blocking access to a site, the benzene may force the complex into a second site.

Conclusion

NMR and infrared spectroscopies have provided much complementary information about chromium complexes formed within NaX zeolite supercages. The DRIFTS spectra indicate that the arene π-complexes which form interact with the zeolite in a way that disrupts the symmetry of the free complex. The NMR spectra give a picture of very mobile π-complexes within the zeolite. Separate carbonyl NMR resonances from the (η^6-benzene)tricarbonylchromium in NaX zeolite indicate two sites within the supercage for the complex and allowed a temperature-dependence NMR study showing an exchange between the sites with an activation energy of 48 ± 6 kJ/mol. Further experimental and computational work will be needed to determine the positions of the two sites and to obtain details about their exchange mechanism.

Acknowledgment. The Bruker DPX-300 NMR spectrometer was purchased with the help of National Science Foundation Award No. 9751497. W.M.S. wishes to thank the U.S. Navy ONR/ASEE Sabbatical Leave Program for support during a sabbatical at the NAWCWD. The work was partially supported by a National Science Foundation-Sponsored Research Experiences for Teachers grant at PSU.

Supporting Information Available: Figures S1−S5, showing additional DRIFTS spectra and carbon-13 solid-state NMR spectra of samples described in Table 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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