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Matrix Isolation Investigation of the Interaction of Lewis Acids with $Cr(CO)_6$ and $Mo(CO)_6$

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Abstract

The matrix isolation technique has been employed for the study of the interaction between several Lewis acids and $Cr(CO)_6$ and $Mo(CO)_6$. The twin jet codeposition of ClF with either of the metal hexacarbonyls gave rise to a single product absorption at 1974 cm^{-1}, which is indicative of a perturbed carbonyl stretching mode in a weakly bound molecular complex. No perturbed mode of the ClF subunit was detected, contrary to previous ClF studies. The singlet jet codeposition of either BF_3 or BCl_3 with these metal carbonyls gave no indication of complex formation. These results are discussed, as is the potential implication for Lewis acid-induced alkyl migration reactions.

Introduction

The coordination of a Lewis acid to a carbonyl oxygen is well known for transition metal complexes in which the CO ligand is in a bridging environment [1]. Similarly, trialkyl aluminium reagents coordinate to the carbonyl oxygen of neutral complexes with low (<1900 cm^{-1}) CO stretching frequencies [1]. In contrast, this type of interaction has not been observed in simple metal carbonyl complexes with relatively high CO stretching frequencies (approximately 2000 cm^{-1}). Lewis acid–carbonyl oxygen interactions are believed to be important in facilitating the Lewis acid-induced alkyl migration reaction in $Mn(CO)_5Me$ and related complexes [2]. Since the carbonyl stretching frequencies of $Cr(CO)_6$ and $Mo(CO)_6$ are in the same range as those observed for $Mn(CO)_5Me$, these hexacarbonyls were chosen as model compounds for studies designed to detect Lewis acid–carbonyl interactions. Since preliminary studies showed that the infrared spectrum of $Cr(CO)_6$ is unperturbed in liquid BBr_3 at room temperature, a low temperature (10 K) cryogenic matrix was employed [3, 4], in conjunction with infrared spectroscopy, to study this interaction.

Experimental

The experiments in this study were conducted on two different matrix isolation systems; the key features of which were quite similar [5, 6]. Both employed a closed cycle refrigerator and a stainless steel vacuum line. Single jet experiments with pulsed deposition were employed for the BF_3 and BCl_3/$Cr(CO)_6$ experiments, while twin jet deposition was employed for the ClF/$Cr(CO)_6$ and ClF/$Mo(CO)_6$ experiments. Samples of the metal carbonyl were prepared by using the full vapor pressure of the solid (approx. 0.2 torr), adding matrix gas, and diluting sequentially to obtain the desired ratio. Argon and krypton were employed as the matrix gases in these experiments.

The infrared spectra of the metal hexacarbonyls in argon matrices were quite similar to those obtained by previous workers [7, 8], with a very intense absorption due to the triply degenerate C–O stretch near 1990 cm^{-1}, and a much weaker feature near 1960 cm^{-1} which can be attributed to the singly ^{13}C substituted species in natural abundance. In addition, M–C stretching and M–C–O bending modes were detected in the low energy portion of the spectrum. Blank experiments of ClF, BF_3 and BCl_3 in argon were identical to those recorded previously in this laboratory [9–11] and elsewhere [12–14].

Results and Discussion

When a sample of $Ar/Cr(CO)_6 = 4000$ was codeposited with a sample of $Ar/ClF = 250$, one somewhat broad but distinct new spectral feature was observed repeatedly, at 1974 cm^{-1}, as shown in Fig. 1. While not particularly intense, this band

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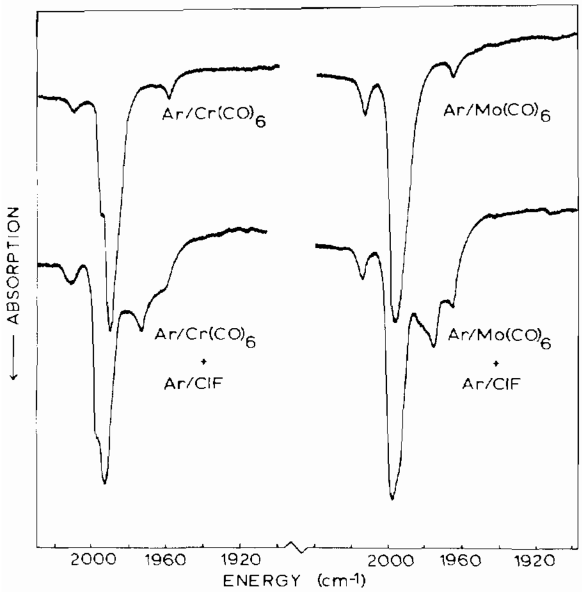

Fig. 1. Infrared spectra of the matrices produced by the codeposition of a sample of Ar/ClF with a sample of either Ar/Cr(CO)$_6$ or Ar/Mo(CO)$_6$ (lower traces), compared to infrared spectra of argon matrices containing only the parent carbonyl (upper traces), in the region 1900–2080 cm^{-1}.

was present over a wide range of concentrations in subsequent experiments. Moreover, as the concentration of the metal carbonyl was held constant, and the concentration of the ClF sample varied, the intensity of the 1974 cm^{-1} band followed directly. This absorption also appeared to increase in intensity as the concentration of the metal carbonyl was increased, but the 1990 cm^{-1} parent band quickly became sufficiently intense that the 1974 cm^{-1} peak appeared only as a shoulder on the parent absorption. In these experiments, the Cl–F stretching region was monitored as well, since previous studies have shown that the vibrational frequency of complexed ClF occurs at an energy lower than that of the parent. Unfortunately, no new absorptions were seen in this spectral region, which is always somewhat cluttered due to the presence of dimeric ClF [9, 12].

Similar experiments were conducted with Mo(CO)$_6$ and ClF, again in argon matrices. The results were almost identical, in that a new absorption was noted near 1974 cm^{-1} which increased with increasing concentration of either reagent; further, no new absorptions were seen in the ClF stretching region or elsewhere in the spectrum.

Additional experiments were conducted with Cr(CO)$_6$ and the strong Lewis acids BF$_3$ and BCl$_3$, and the Bronsted acid HCl. These were carried out in the single jet mode with pulsed deposition, and were examined over a range of concentrations (including using BF$_3$ as the matrix gas in one experiment). In all of these experiments, no infrared absorptions were noted which could be attributed to an interaction or complex formation between Cr(CO)$_6$ and the acid. Annealing the matrix likewise provided no such spectral features; rather, some additional indication of acid dimerization was observed.

The infrared spectra obtained in this study provide some evidence for the interaction of ClF with both Cr(CO)$_6$ and Mo(CO)$_6$, in that a perturbed carbonyl stretching mode was detected near 1974 cm^{-1} in both of these systems. This shift to lower frequency for the parent carbonyl is consistent with a Lewis acid–carbonyl oxygen interaction [1]. However, both the magnitude of the shift from the parent, and the lack of observation of a perturbed ClF stretching mode indicate that the interaction between the acid and base subunits is quite weak. ClF complexes have been observed with a variety of electron donors, including ethers, ketones [9] and cyclopropane [15], and substantial (20–100 cm^{-1}) shifts of the ClF stretching mode were noted for these complexes. The lack of a detectable shift in the present study suggests that the complexes with Cr(CO)$_6$ and Mo(CO)$_6$ are the weakest studied to data, and that the lone pairs on the carbonyl oxygen must be only very weakly basic at best, for the terminal carbonyls studied here.

The boron trihalide studies gave no perceptible indication of interaction or complex formation. Since BF$_3$ and BCl$_3$ are considered to be very strong Lewis acids [16], more so than ClF, it is surprising that no interaction was detected. However, recent matrix studies of the complexes of cyclopropane found similar results, namely that complex fomation with the boron trihalides at low temperatures is quite difficult [17]. This result was rationalized in terms of steric effects, since the acid center of the boron trihalides is the central boron atom, which is small and surrounded by larger halogens. At room temperature, however, there is some thermal activation of the out-of-plane deformation mode of the boron trihalide, making the central boron more accessible. Regardless, in the current studies no indication of complex formation between the Cr(CO)$_6$ and BF$_3$ or BCl$_3$ was observed.

The implications for Lewis acid-induced alkyl migration reactions from the present work are not clear. These reactions are known for the more reactive alkyl metal carbonyls, and the metal hexacarbonyls employed here may not be suitable models. Alternatively, the low temperatures employed may limit complex formation, particularly for the boron trihalides. Finally, the solvent system may play a role; the inert matrices do not stabilize polar species nearly as well as do more polar solvents, which may also promote formation of ionic species.

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