The redox behavior observed in solution upon extraction (i.e., conversion of the Pt_{12} cluster anion to the Pt_9 cluster anion) may be associated with water introduced in the impregnation step, which was followed by mild drying. Reduction of the cluster might be accompanied by oxidation of CO, presumably by nucleophilic attack of water on coordinated CO groups to form CO_2 and H^+; the CO_2 that was presumably formed could be accounted for by a slight, undetectable decomposition of the Pt cluster.

The nature of the Pt carbonyl clusters present in solution reflects a competition between reduction by water and the reverse oxidation that can take place as a consequence of the increased acidity of the solution.

Reduction by water could also proceed as follows:[14]

$$3[Pt_{12}(CO)_{24}]^{2-} + H_2O \rightarrow 4[Pt_9(CO)_{18}]^{2-} + 2H^+ + \tfrac{1}{2}O_2 \quad (3)$$

Thus, wetting of the acetone with water from the impregnation step would account for the continued reaction observed after filtration. The halide-induced disproportionation of the Pt_{12} carbonyl anion has also been suggested.[20]

Alternatively, the IR spectra assigned to **1** may be attributed to a mixture of compounds converted at comparable rates with the main component being $[Pt_6(CO)_{12}]^{2-}$ (ν_{CO} = 2012 cm^{-1}). Thus Figure 2A may be explained in terms of a redox system in which the main compounds are $[Pt_{12}(CO)_{24}]^{2-}$ (ν_{CO} = 2048, 1862 cm^{-1}), $[Pt_9(CO)_{18}]^{2-}$ (ν_{CO} = 2030, 1799 cm^{-1}), and $[Pt_6(CO)_{12}]^{2-}$ (ν_{CO} = 2012 cm^{-1}). Under these conditions, disappearance of the dodecaplatinum cluster is expected as a result of the well-documented[8] redox reaction between nonconsecutive Pt carbonyl clusters:[21]

$$[Pt_{12}(CO)_{24}]^{2-} + [Pt_6(CO)_{12}]^{2-} \rightarrow 2[Pt_9(CO)_{18}]^{2-} \quad (4)$$

Although the observed redox behavior may involve **1**, this compound was not detected (either on the surface or in solution, after extraction of the surface species) when the Pt(allyl)$_2$ derivative was used as the precursor. The kinetic instability of the Pt_{12} derivative, prepared by the surface-mediated synthesis, is contrasted with the kinetic stability of the same compound obtained by the solution procedure.[8]

The transformations observed upon extraction of the surface species are enhanced in the presence of H_2 and do not appear to be related to the nature of the precursor on the MgO surface.

Conclusions

The MgO surface can be used effectively as a medium for the carbonylation of Pt complexes under mild conditions, with the resulting anionic carbonyl clusters being stabilized by the basic support in the presence of CO. The transformations observed parallel the reductive carbonylation of the Pt^{IV} species in basic solution.[8] The dominant species formed on the surface depend on the nature of the Pt precursor and are controlled by the reductive character of the gas phase.

Acknowledgment. This research was supported by the National Science Foundation (Grants CBT 8605699 and CTS-8910633). The work of R.P. at the University of Delaware was supported by Snamprogetti-RICE.

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(20) One reviewer indicated (on the basis of his own observations) that the halide-induced disproportionation of $[Pt_{12}(CO)_{24}]^{2-}$

$$10[Pt_{12}(CO)_{24}]^{2-} + 9Cl^- \rightarrow 13[Pt_9(CO)_{18}]^{2-} + 3[Pt(CO)Cl_3]^-$$

takes place in methanol, acetone, or THF solutions containing moderate concentrations (0.01–0.1 M) of Cl$^-$. However, the presence of the mononuclear carbonyl anion was not detected in our extraction experiments.

(21) The weaker bands at 2071, 1977, and 2067 cm^{-1} are not assigned. The presence of the band attributed to $[Pt_6(CO)_{12}]^{2-}$ (ν_{CO} = 2012 cm^{-1}) at higher frequency than that reported (ν_{CO} = 1995 cm^{-1}) may be associated with the transient nature of the experiment.

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Matrix Isolation Spectroscopic Studies of Hydrogen-Bonded Complexes of Titanocene Dihalides with HCl

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Received July 23, 1990

The matrix isolation technique has been combined with infrared spectroscopy to characterize the interaction between Cp_2TiF_2 and Cp_2TiCl_2, and HCl. Isolated 1/1 complexes were observed for each pair of reactants; the $Cp_2TiF_2 \cdot HCl$ complex was characterized by a red shift of the HCl stretching mode to 2440 cm^{-1} and a dramatic broadening of this absorption. In addition, strongly perturbed Ti–F stretching modes were observed near 536 and 556 cm^{-1}. The spectral data collectively indicate formation of hydrogen-bonded complexes, from the HCl subunit to both of the halogens on the titanocene dihalide in a bidentate structure.

Introduction

Transition-metal centers serve as Lewis acids, accepting electron density from the ligand or Lewis base during complex formation. On the other hand, ligands attached to metal centers can exhibit basic character and undergo acid catalyzed reactions. An important example of this is the acid-catalyzed hydrolysis of transition-metal halides; for example, the rate of hydrolysis of [*trans*-Co(en)$_2$F$_2$]$^+$ shows a distinct hydrogen ion dependence.[1,2] Also, the formation of adducts between transition-metal halides and strong Lewis acids points to the basic character of the metal halide.[3,4] Several studies have examined the Lewis acid chemistry of titanocene difluoride, Cp_2TiF_2, and presented evidence for complex formation.[4–6] In the most recent study, evidence was obtained for a hydrogen-bonded complex between Cp_2TiF_2 and 4-chlorophenol in chloroform from NMR and IR spectra.[6] Unfortunately, the infrared data consisted of only a single band, the O–H stretching mode, due to spectral limitations.

Related studies[7a–d] have been carried out by Lokshin and coworkers in which they examined the interaction of perfluorobutanol and HCl with a range of transition-metal carbonyls in liquid-xenon

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solution at 175 K. The O–H stretching frequency of perfluorobutanol shifted approximately 100 cm^{-1} to lower energies, characteristic of hydrogen-bond formation. The shifts for the analogous HCl complex were somewhat less. These workers also characterized the hydrogen-bonded complexes of perfluoro-*tert*-butanol with the π-electron system of ferrocene and its derivatives under similar experimental conditions and observed somewhat greater shifts. These studies demonstrate the capability of transition-metal complexes to form hydrogen bonds in a manner analogous to that proposed for titanocene difluoride.

The matrix isolation technique was developed for the isolation and characterization of reactive chemical intermediates and has proven very effective in this regard.[8,9] In particular, many hydrogen-bonded complexes have been characterized over the years in a well-defined environment, free from solvent perturbations and interference.[10–12] In addition, the low temperatures employed may lead to sharp spectral features and the opportunity to resolve product absorptions from the precursor spectrum. Since the titanocene dihalides are known to sublime without decomposition at moderate temperatures, deposition of these species with a suitable proton donor into inert matrices is readily accomplished. Consequently, a study was undertaken to characterize hydrogen-bonded complexes of the titanocene dihalides with a prototypical Bronsted acid, HCl, in an inert environment.

Experimental Section

The experiments in this study were carried out on conventional matrix isolation equipment that has been described.[13] HCl (Matheson) was introduced into the vacuum line from a lecture bottle and purified by freeze–thaw cycles at 77 K prior to dilution with argon. DCl (MSD Isotopes, 99% D) was handled in a similar manner. The vacuum line was exposed to 500 Torr of DCl repeated to exchange with hydrogen-containing impurities in the line. During a given DCl experiment, some residual HCl was noted due to exchange; a D/H ratio of 4/1 was typical. Cp_2TiF_2 and Cp_2TiCl_2 were placed (in different experiments) in a Pyrex Knudsen cell, which was then inserted into a resistively heated oven within the matrix vacuum vessel. The oven was then heated gently until a steady effusive beam of the material was generated, approximately 90 °C for both materials, and directed at the 14 K cold window. This beam was codeposited with a sample of Ar/HCl, at dilutions between 1000/1 and 200/1. Final spectra were recorded at 1-cm^{-1} resolution after 20–24 h deposition on an IBM 98 FTIR or Perkin-Elmer 983 infrared spectrophotometer. In some experiments, the matrix was then warmed to as high as 45 K to allow some diffusion and then recooled and additional spectra were recorded. In other experiments, the closed-cycle refrigerator was turned off and the sample allowed to warm slowly to room temperature. Spectra were recorded at regular intervals during the warm-up process at 4-cm^{-1} resolution, averaging 100 scans so that the temperature rise during a given collection interval did not exceed 8 K.

Results

Prior to any codeposition experiments, blank spectra were recorded of each of the reagents alone in argon, at several different concentrations. Spectra of HCl in solid argon agreed well with literature spectra[14] and with spectra recorded previously in this laboratory.[15] One of these experiments was subjected to repeated scans during slow warm-up. Monomer absorptions were seen to disappear by 40 K and were replaced by aggregate bands of $(HCl)_x$. By 83 K, all of the argon had been pumped off and a film of solid HCl remained. At 123 K all traces of HCl has disappeared as the sample vaporized and was pumped off.

Deposition of Cp_2TiF_2 into an argon matrix gave rise to quite sharp bands of moderate intensity, which overall matched the Nujul mull spectrum of this material.[5,16–18] In the 550–650-cm^{-1} region, five bands were observed, at 573 (m), 592 (w), 602 (w), 610 (s), and 623 cm^{-1} (s). Mull spectra[16–18] showed two strong Ti–F stretches, at 539 and 564 cm^{-1}, while another reference[5] lists an additional weak band at 606 cm^{-1}. A shift to higher energy is anticipated for argon matrix spectra relative to Nujol or solution spectra, since the argon matrix is significantly less interacting and more similar to the gas phase. The magnitude of the blue shift is somewhat surprising but may simply reflect the very basic nature of the Ti–F bonds and, hence, relatively strong intermolecular interactions. That more than two bands were observed in this region may be attributed to either matrix site splitting or combination/overtones of the numerous low-energy vibrational modes of this species in Fermi resonance with the blue-shifted Ti–F stretching modes. The spectra in other regions agreed very well with the literature spectra (e.g. the ring mode at 812 cm^{-1}), and no additional bands were observed that could be indicative of decomposition upon heating (indeed, sublimation has been used[6] to purify Cp_2TiF_2). Most importantly, the spectral region below 560 cm^{-1} was free of any parent absorption in these blank experiments. In one experiment, Cp_2TiF_2 was deposited onto the cold window without added argon, creating a thin film of the material. Infrared spectra of this thin film resembled the mull and matrix spectra, with some shifting of band positions.

Table I. Band Positions and Assignments for the $Cp_2TiF_2 \cdot HCl$ Hydrogen-Bonded Complex

band position[a]			
parent	Cp_2TiF_2 + HCl	Cp_2TiF_2 + DCl	assgnt
[b]	536	536	symmetric TiF_2 stretch
[b]	556	556	antisymmetric TiF_2 stretch
812	815	815	out-of-plane deformation, Cp ring
2880[c]	2440	1790	H(D)–Cl stretch

[a] Band positions in cm^{-1}. [b] A multiplet was observed at 573, 592, 602, 610, and 623 cm^{-1}; see text for detailed discussion. [c] For DCl, the analogous band was observed near 2050 cm^{-1}.

The spectrum of Cp_2TiCl_2 in solid argon agreed moderately well with mull spectra;[5,16–18] several low-energy modes (below 410 cm^{-1}) were observed here; one Ti–Cl stretch has been reported at 400 cm^{-1}, which agrees well with a band recorded here at 403 cm^{-1}. The second Ti–Cl mode has not been conclusively identified, as other low-frequency modes absorb in this region. In addition, all of these bands were somewhat overlapped by rotational bands from atmospheric H_2O due to imperfect purge.

Cp_2TiF_2 + HCl. Titanocene difluoride was codeposited with samples of Ar/HCl in approximately 15 experiments, over a wide range of concentrations and experimental conditions. In an initial experiment, with Ar/HCl = 500 and a cold window temperature of 18 K, a very broad product absorption was noted centered near 2440 cm^{-1}, with submaxima at 2360, 2440, and 2520 cm^{-1}. The full width at half-maximum of this absorption was approximately 200 cm^{-1}. In addition, distinct new absorptions were observed at 536 and 556 cm^{-1}. Finally, a shoulder at 815 cm^{-1} was observed on the high-energy side of the parent mode at 811 cm^{-1}. These product bands were observed only when both reagents were present and are listed in Table I. When the Ar/HCl concentration was increased to 200/1, all of the above bands were more intense and distinct; in addition, weak features were noted at 520 and 831 cm^{-1}. When the concentration of Ar/HCl was reduced to 1000/1 and the level of Cp_2TiF_2 increased (by increasing the oven temperature), the above product bands were again very apparent (the 2440-cm^{-1} feature was more intense than the residual parent HCl absorptions and still very broad). In this experiment, the weak absorptions near 520 and 830 cm^{-1} were not observed. In additional experiments, further variation of the concentration of the two reagents was examined, and the above absorptions were noted

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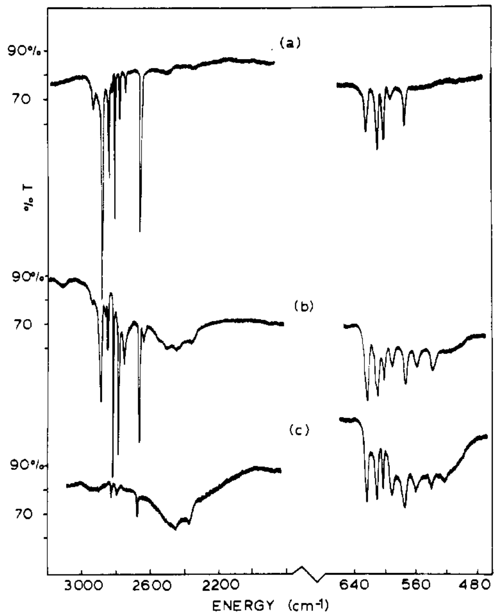

Figure 1. Infrared spectra, over selected regions, of the reaction products arising from the codeposition of samples of Ar/HCl with Cp_2TiF_2. Trace a in the 1800–3200-cm^{-1} region is a blank spectrum of a sample of Ar/HCl = 500, while trace a in the 440–660-cm^{-1} region is a blank spectrum of Cp_2TiF_2 at moderate concentration. Trace b is the spectrum resulting from codeposition of a sample of Ar/HCl = 500 with Cp_2TiF_2 at moderate concentration, while trace c is the spectrum of a sample of Ar/HCl = 1000 codeposited with a somewhat high level of Cp_2TiF_2.

in each experiment, with an approximately constant intensity ratio. Representative spectra are shown in Figure 1.

Several experiments were conducted in which the temperature of the cold window was varied over the range 15–23 K. When a sample of Ar/HCl = 500 was codeposited with Cp_2TiF_2 at a window temperature of 15 K, the same product bands were observed but with substantially reduced intensities. When this sample was annealed stepwise to 32, 40, and 45 K slowly, and each time recooled to 15 K, significant growth of these new absorptions was observed; the 520- and 831-cm^{-1} bands grew more rapidly than those at 536, 556, and 815 cm^{-1}. These same reagents at the same concentration were subsequently codeposited at a cold window temperature of 23 K, and a distinct increase in product yield was noted.

Cp_2TiF_2 was codeposited with a sample of Ar/HCl = 500 with a window temperature of 16 K in an additional experiment, and a good yield of the bands reported above was obtained. After final, high-resolution scans were obtained, the closed-cycle refrigerator was turned off, and the cold window allowed to warm slowly to room temperature without added heat from the temperature controller. Scans were recorded of the sample over the entire temperature range, averaging 100 interferograms at 4-cm^{-1} resolution. Collecting each set of scans took approximately 2.5 min, so that the temperature changed 2–8 °C during the scan process. Nonetheless, changes in the sample could be monitored as a function of window temperature (the indicated temperature is the average temperature from beginning of collection of the 100 interferograms to the end). At 41 K, significant intensification of the product absorptions listed in Table I was noted. At 59 K, absorptions due to parent Cp_2TiF_2 had nearly disappeared and great enhancement in the product absorption intensities was observed. The bands at 536 and 556 cm^{-1} disappeared, and a strong feature at 520 cm^{-1} appeared. The 2440-cm^{-1} band was still broad and intense but appeared to shift upward somewhat, to 2550 cm^{-1}. Bands due to aggregated parent HCl were also quite apparent. At 83 K, aggregated HCl was still present, along with the above product absorptions. At 122 K, all traces of parent HCl, monomer and aggregate, were gone while the product absorptions remained with approximately the same intensity. At 157 K, the product absorptions had all disappeared completely. Instead, absorptions due to parent Cp_2TiF_2 as a thin film were observed. From 157 K to room temperature, no changes were observed. Figure 2 shows the spectra obtained during this slow warm-up sequence over the range 1800–3200 cm^{-1}.

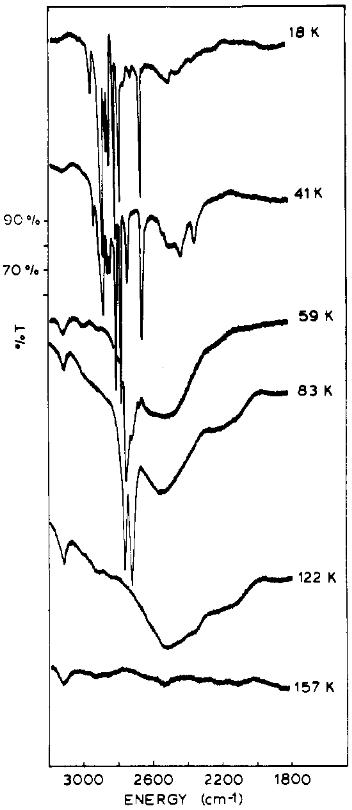

Figure 2. Spectra taken during the slow warm-up of a matrix sample of Ar/HCl = 500 and Cp_2TiF_2. Spectra were recorded as the cryogenic surface warmed from 16 K to room temperature; the indicated temperature of each trace is the mean temperature during the interferogram collection interval (see text). The ordinate scale is specifically for the 41 K trace and is representative of the scales for all of the spectra.

Cp_2TiF_2 + DCl. Titanocene difluoride was codeposited with samples of Ar/DCl = 100 and 200 in a series of experiments. In all experiments, a very broad intense band was noted centered at 1790 cm^{-1}, along with distinct product bands of moderate intensity at 536, 556, and 814 cm^{-1}. When one of these samples was annealed to 44 K and recooled, a significant increase was noted in all of the product band intensities. When the closed-cycle refrigerator was turned off and scans were recorded during the warm-up process, results essentially identical with those described above for the HCl experiments were obtained.

Cp_2TiCl_2 + HCl. Titanocene dichloride was evaporated and codeposited with samples of Ar/HCl in several experiments. In the first, with Ar/HCl = 200, a single weak product absorption was noted at 2496 cm^{-1}. This band was relatively sharp, with a width at half-maximum of 10 cm^{-1} and an optical density of approximately 0.05. When this sample was annealed to 33 K and recooled, this product absorption grew somewhat. The closed-cycle refrigerator was then turned off, and the window was warmed slowly, while spectra were recorded. At 41 K, the 2496-cm^{-1} absorption was distinctly more intense but remained relatively sharp. Some additional, weak features were observed between 2500 and 2600 cm^{-1}. At 60 K, the band had broadened to a full width at half-maximum of 200 cm^{-1} and shifted upward and was now centered at approximately 2575 cm^{-1}. The Cp_2TiCl_2 parent absorption at 826 cm^{-1} appeared to shift upward, to 843 cm^{-1}. At 84 K, all traces of parent HCl had disappeared, while the product band near 2575 cm^{-1} persisted. This band was still observed at a window temperature of 122 K but with significantly diminished intensity and was gone at 170 K.

This experiment was repeated with Ar/HCl = 200. Before warm-up, the product absorption at 2496 cm^{-1} was again present, with a slightly increased intensity relative to the above experiment.

After high-resolution scans were recorded, the refrigerator was again turned off and the sample slowly warmed. The results were very similar to the above experiment, with an intensification around 40 K and a shifting and broadening by 58 K. The band center was measured to be 2590 cm^{-1}, with a full width at half-maximum of 200 cm^{-1}. Growth of the absorption at 843 cm^{-1} was also noted at this temperature. At 74 K, product was present, along with aggregated HCl. At 94 K, most of the HCl had been pumped off and the product remained. At 175 K, the product bands had also disappeared.

Cp_2TiCl_2 + DCl. The codeposition of these two reagents in two experiments led to the observation of a broad feature of medium intensity centered at 1875 cm^{-1}, to the red of the parent D–Cl stretching mode near 2100 cm^{-1}. In the low-energy region, a single medium-intensity product absorption was noted at 235 cm^{-1}.

Discussion

The codeposition of HCl with either Cp_2TiF_2 or Cp_2TiCl_2 into argon matrices led to the observation of one or more product absorptions that cannot be attributed to either parent species and must be assigned to a reaction product. For the Cp_2TiF_2/HCl reaction pair, for distinct absorptions were noted, near 536, 556, 815, and 2440 cm^{-1}, the last being quite broad and moderately intense. The growth of these absorptions over a range of reactant concentrations suggests that all four belong to a single absorber. In the DCl experiments, the bands at 536, 556, and 815 cm^{-1} were observed unshifted, while the 2440-cm^{-1} band showed a large shift, to 1790 cm^{-1}. The absorptions at 520 and 831 cm^{-1} in some experiments are likely due to a higher aggregate in as much as they were observed predominantly in experiments with excess HCl. For the Cp_2TiCl_2/HCl reaction pair, only a single absorption near 2500 cm^{-1} was observed (although in the DCl experiments, an additional product band was noted at 235 cm^{-1}). The product bands in the Cp_2TiF_2/HCl experiments all were observed relatively near parent absorptions; the 536- and 556-cm^{-1} bands fell to the red of the parent Ti–F stretching modes between 570 and 625 cm^{-1} and the 815-cm^{-1} band was observed just to the blue of a deformation mode of the Cp rings, while the 2440-cm^{-1} band fell to the red of the parent HCl stretching mode near 2880 cm^{-1}. These observations are characteristic of the formation of a molecular complex, where certain modes of the parent are perturbed and shifted but the reactant species have not lost their chemical identity (e.g. no bond ruptures and rearrangements have occurred). The deuterium shifts (or lack thereof) shown in Table I strongly support assignment as perturbed parent modes in a molecular complex. Given the relatively low concentrations employed in these experiments, the observation of an aggregate at higher concentrations suggests that the stoichiometry of the initially formed complex is 1/1. This is also consistent with many previous matrix isolation studies of acid/base reaction pairs.[10–12,19] Consequently, the initial product absorptions near 536, 556, 815, and 2440 cm^{-1} for the Cp_2TiF_2/HCl reaction pair, and the 2496-cm^{-1} absorption for the Cp_2TiCl_2/HCl reaction pair, are best assigned to an isolated 1/1 molecular complex between the two reactants.

The structure and nature of this 1/1 complex is of particular interest, and all of the spectral features point to a hydrogen-bonded complex. A substantial red shift and a broadening of the HCl stretching mode (ν_s) are the primary diagnostics for hydrogen-bond formation,[20] and both were observed here; shifts from 100 to 1000 cm^{-1} or more have been observed for hydrogen-bonded complexes of HCl in inert matrices.[10–12] Intensification and broadening of the HCl stretch is also a common feature of hydrogen-bonded complexes, and this was likewise observed here. The deuterium shift of the 2440-cm^{-1} band, to 1790 cm^{-1}, confirms the assignment of this band to the HCl (DCl) stretch. The ν_H/ν_D ratio of 1.36 is appropriate for a somewhat anharmonic hydrogen oscillator, as has been seen many times previously in hydrogen-bonded complexes.[20]

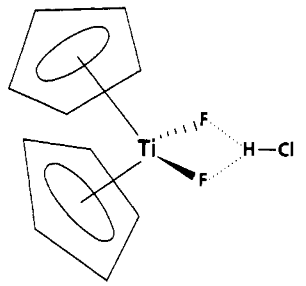

Figure 3. Proposed structure for the hydrogen-bonded complex between Cp_2TiF_2 and HCl.

The results of Lokshin and co-workers[7a–d] are in general agreement with the results obtained here. They were able to observe hydrogen-bonded complexes of HCl and perfluoro-*tert*-butanol with transition-metal carbonyls in liquid Xe; shifts on the order of 100 cm^{-1} to lower energies were observed for the O–H and H–Cl oscillators. The shifts observed here are somewhat larger, probably reflecting the higher basicity of the fluorines on titanocene difluoride relative to carbonyl groups on a variety of transition-metal carbonyls. Nonetheless, the results of Lokshin demonstrate the feasibility of such hydrogen bonding in transition-metal complexes and support the results presented here.

A red shift is anticipated as well for the proton acceptor molecule, and red shifts of 50–70 cm^{-1} were observed for both of the parent Ti–F stretching modes. A single low-energy product absorption was observed for the $Cp_2TiCl_2 \cdot DCl$ complex at 235 cm^{-1}, red shifted from the parent modes between 300 and 400 cm^{-1}. It is tempting to assign this to a shifted Ti–Cl stretching mode, but given the several parent modes in the region,[16,18] such an assignment must be considered tentative at best. The final product absorption, at 815 cm^{-1} for the Cp_2TiF_2/HCl reaction pair, is assigned to the symmetric out-of-plane C–H deformation of the cyclopentadienyl ring, blue shifted 4 cm^{-1} from its parent band position. This shift may arise either from a slight geometry change in the hydrogen-bonded complex or from a slight rearrangement of electron density due to hydrogen-bond formation.

Buffin and Richmond[6] have obtained infrared spectra of the hydrogen-bonded complex of Cp_2TiF_2 with 4-chlorophenol in solution at room temperature. They observed the O–H stretching mode of the phenol in the complex near 3320 cm^{-1}, shifted from the parent at 3600 cm^{-1}. This shift of 280 cm^{-1} or 7.8% of the parent frequency is distinctly smaller than the results obtained here with HCl as the proton donor. For the $Cp_2TiF_2 \cdot HCl$ complex, a shift of 440 cm^{-1} was observed, or over 15% of the parent frequency. This suggests a stronger interaction in the HCl complex, which is consistent with the higher acidity of HCl compared to 4-chlorophenol.

The fact that both of the Ti–F stretching modes were significantly red shifted upon hydrogen-bond formation indicates the involvement of the Ti–F bond in the hydrogen bond. This is consistent with the known basicity of the Ti–F bond in solution studies.[4–6] The interaction might either be monodentate, involving a single fluorine, or bidentate to both fluorines. the two Ti–F stretching modes of the parent, of course, are coupled and combine into symmetric and antisymmetric stretching modes. In the monodentate geometry, one Ti–F stretching would be expected to shift significantly, and the other very little if at all. In the bidentate arrangement, both modes should shift, although it is difficult to predict the magnitude. The observation of two new Ti–F stretches clearly points toward a bidentate geometry for the hydrogen bonded complex, as depicted in Figure 3.

An alternative structure for the product species would be the product of protonation of the Ti center, with formation of a Ti–H bond. However, such a bond should show[21] a stretching mode between 1700 and 2200 cm^{-1}, as well as a bending mode between

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600 and 800 cm^{-1}. No evidence for either band was obtained. Moreover, the evidence suggests strongly that the H–Cl bond was not ruptured and that hydrogen-bond formation instead occurred. Finally, the protonation reaction would have given rise to ionic (ion pair) products; these have only rarely been observed in matrices for Bronsted acid/base pairs and are disfavored by the very nonpolar nature of the argon matrix.

The slow warm-up experiments provide some additional evidence for hydrogen-bond formation. At 41 K, the argon matrix is very slushy, and diffusion can occur to increase the yield of the isolated 1/1 complex, as observed. By 59 K, the argon matrix material was vaporizing, leaving behind both unreacted HCl and Cp_2TiF_2 as well as product. Since there is likely no barrier to complex formation, all of the Cp_2TiF_2 reacted, leaving no parent Cp_2TiF_2. The strong absorptions at 520 and 831 cm^{-1} indicate that aggregation had occurred by this temperature, and the isolated 1/1 complex was no longer present. However, since HCl was present in excess, some residual $(HCl)_x$ was observed. By 122 K, all of the residual $(HCl)_x$ had vaporized and been pumped off, but the HCl bound to Cp_2TiF_2 remained. By 157 K, the aggregated complex had dissociated and the HCl vaporized and pumped off, leaving behind a thin film of Cp_2TiF_2. It is interesting that the HCl stretching mode shifted to higher energy upon warming and aggregation, from approximately 2440 to 2550 cm^{-1} near 60 K. A smaller red shift is generally interpreted to mean a weaker interaction,[20] which suggests that the hydrogen-bonded HCl molecules in the aggregate are less strongly bound than the single HCl in the 1/1 complex. One explanation is that the 1/1 complex is bidentate and upon aggregation a monodentate 2/1 complex is formed (one HCl with each fluorine). However, given the large bandwidths of these bands, this must be regarded as tentative. The slow warm-up sequence with Cp_2TiCl_2 gave quite similar results, with initially increased product formation and then shifting and broadening of the product absorption, before decomposition of the product. It is noteworthy that, at 122 K, most of the $Cp_2TiCl_2{\cdot}HCl$ complex had dissociated, while, at the same temperature, most of the $Cp_2TiF_2{\cdot}HCl$ complex remained, suggesting stronger binding in the latter complex. This conclusion must be tempered by the fact that the warm-up process was continuous taking between 20 and 60 s for the temperature to increase by one degree, so that it is possible that slow processes might not have reached equilibrium at a given temperature (kinetic rather than thermodynamic control). In this case, comparing the temperatures needed for decomposition would not be valid.

The halogen-exchange reaction between Cp_2TiF_2 and HCl to yield Cp_2TiClF and HF is known to occur in solution[22] and might occur during the slow warm-up experiments conducted here. However, monomeric HF absorbs near 3940 cm^{-1} and was not observed. If the HF product were hydrogen bonded to the Ti–Cl or Ti–F bond, then a distinct absorption red shifted from 3940 cm^{-1} should have been observed and was not. Also, no perceptible decrease in the Ti–F absorptions was seen, indicating little if any reaction. Consequently, there is no evidence that the halogen-exchange reaction occurred under these experimental conditions. Of course, the reaction would have had to occur prior to the decomposition of the complex and vaporization of the HCl, which took place between 122 and 157 K.

Acknowledgment. The National Science Foundation is gratefully acknowledged for support of this research through Grant CHE 87-21969. Professor Tom Richmond is gratefully acknowledged for supplying samples of the titanocene dihalides, as well as for helpful discussions and providing results prior to publication.

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Synthesis and Structural Characterization of Manganese(II) Derivatives of the Bulky, Chelating Bis(amido) Ligands $[(NMes)_2SiMe_2]^{2-}$ and $[DippNCH_2CH_2NDipp]^{2-}$, Their Neutral Amine Precursors, and Their Lithium Salts (Mes = $2,4,6\text{-}Me_3C_6H_2$; Dipp = $2,6\text{-}i\text{-}Pr_2C_6H_3$)

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Received October 29, 1990

The synthesis of three new bulky bidentate diamines, the compounds $Me_2Si(NHMes)_2$ (**1**), $Mes(H)NCH_2CH_2N(H)Mes$ (**2**) (Mes = $2,4,6\text{-}Me_3C_6H_2$), and $Dipp(H)NCH_2CH_2N(H)Dipp$ (**3**) (Dipp = $2,6\text{-}i\text{-}Pr_2C_6H_3$ is described. The addition of 2 equiv of *n*-BuLi to **1** or **3** results in almost quantitative yields of the novel dimeric solvent-free dilithium derivatives $[\{Li(Mes)N\}_2SiMe_2]_2$ (**4**) and $[Li(Dipp)NCH_2CH_2N(Dipp)Li]_2$ (**5**). The reaction of **1** with $Mn\{N(SiMe_3)_2\}_2$ in the presence of $LiN(SiMe_3)_2$ gives the unusual product $[Li(Mn\{NMes\}_2SiMe_2)_2N(SiMe_3)_2]$ (**6**), which features a dimeric Mn salt of the dianion of **1** and, in addition, a Li^+ ion sandwiched between two mesityl rings. The reaction of the bulky amine **3** affords the monomeric manganese(II) amide $Mn[N(Dipp)CH_2CH_2N(H)Dipp]_2$ (**7**), which has a very distorted geometry at Mn as a result of the steric requirements and bonding of ligand **3**. Compounds **1** and **3**–**7** have been characterized by X-ray crystallography. Crystallographic data with Cu Kα radiation (λ = 1.541 78 Å) for **1** and **4**–**6** and Mo Kα radiation (λ = 0.710 69 Å) for **3** and **7** at 130 K: **1**, a = 16.401 (10) Å, b = 6.386 (2) Å, c = 9.244 (2) Å, Z = 2, orthorhombic, space group $P2_12_12$: **3**, a = 10.968 (3) Å, b = 11.859 (4) Å, c = 20.455 (7) Å, α = 93.61 (3)°, β = 103.41 (3)°, γ = 109.22 (3)°, Z = 4, triclinic, space group $P\bar{1}$; **4**, a = 9.360 (3) Å, b = 10.052 (2) Å, c = 11.313 (3) Å, α = 77.08 (2)°, β = 85.49 (2)°, γ = 73.50 (2)°, Z = 1, triclinic, space group $P\bar{1}$; **5**, a = 12.758 (4) Å, b = 12.828 (5) Å, c = 19.085 (8) Å, β = 103.23 (3)°, Z = 4, monoclinic, space group $P2_1/c$; **6**, a = 12.918 (5) Å, b = 14.552 (5) Å, c = 13.395 (6) Å, β = 90.35 (3)°, Z = 2, monoclinic, space group $P2_1$: **7**, a = 21.713 (12) Å, b = 13.927 (6) Å, c = 17.764 (11) Å, β = 117.51 (4)°, Z = 4, monoclinic, space group $C2/c$.

Introduction

Amide ($-NR_2$) derivatives of the transition metals are an interesting and varied class of compounds that exhibit a very broad range of structures and reaction types.[1] The combination of high M–N bond strength and steric flexibility has ensured that these ligands have played a pioneering role in the synthesis of numerous low- (two- or three-) coordinate transition-metal complexes.[2,3] In many instances, amide complexes have provided the first examples of these unusual transition-metal coordination numbers.[4] In

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