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Crystal Structure, Solubility, and Electronic Spectrum of Titanium Tetraiodide

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The two crystalline forms of TiI_4 and the conditions for their appearance have been studied. The cubic modification belonging to the space group $Pa3$-T_h^6 is apparently always formed when TiI_4 crystallizes from the melt or from a supersaturated solution. However, this modification is metastable at room temperature and converts into a less well-defined structure with a considerably more complicated X-ray diffraction pattern within a period which may vary from a few days to some months, depending upon the size and condition of the crystals in the original cubic modification. The unit cell dimensions of the cubic form determined at 23 °C corresponding to $a_0 = 12.055$ Å were found to differ from those reported previously, in one case quite appreciably. The interplanar *d* spacings for the stable modification also differed slightly from those in the literature, but the exact structure could not be determined. Because of the metastable character of the cubic modification, physical properties of TiI_4, such as solubility in organic solvents, reported in the literature have normally been those of the stable modification. Contrary to literature data, the cubic modification of TiI_4 was found to dissolve very readily and to exhibit appreciable solubility in hydrocarbon solvents. In solution, TiI_4 gives a very interesting electronic spectrum, which is undoubtedly of charge-transfer character and is reminiscent of the one reported for $TiCl_4$ but with the absorptions occurring at considerably higher wavelengths as expected from the much more ready oxidizability of I^- in comparison with Cl^-. Thus the first major absorption for TiI_4 occurs at 517 and 514 nm, in benzene and cyclohexane, respectively, and is responsible for the strong color of this compound. With the established molar extinction coefficients at these wavelengths, the solubility of TiI_4 in benzene and cyclohexane at 23 °C could be determined colorimetrically and was found to be 32.7 and 24.4 g/L, respectively.

Introduction

The crystal structure of TiI_4 was first determined by Hassel and Kringstad,[1] who, for a freshly prepared sample, found it to be cubic and to belong to the space group $Pa3$-T_h^6 and thus to be isomorphous with SnI_4, the lattice of which is built up of tetrahedral molecules. However, a crystal transformation to what appeared to be a less symmetrical modification with a rather complicated X-ray diffraction pattern was observed to take place within a few days, but the structure of this modification was not established. A later investigation by Rolsten and Sisler[2] revealed that TiI_4 prepared by three different methods had a structure similar to the second one reported by Hassel and Kringstad. The observed *d* spacings indexed quite well as a hexagonal lattice, but Rolsten and Sisler were not able to establish a definite structure. However, when heated to 125 °C the TiI_4 was found to undergo a crystal transformation to the cubic structure previously established by Hassel and Kringstad but having a larger cell constant (a_0 = 12.21 vs. 12.002 Å) as would be expected from the higher temperature (125 °C vs. room temperature) used for the structure determination.

The solubility of TiI_4 in inert solvents, e.g., hydrocarbons, has not been the subject of much study. However, the few statements in the literature about this property indicate that this compound either is insoluble or has an extremely limited solubility in such solvents.[3-6] The only more definite information on this matter can be found in a paper by Clark and Willis[7] wherein the concentration of a saturated solution in cyclohexane is claimed to be 2.86×10^{-4} M (0.16 g/L) at room temperature. Our interest in TiI_4 developed in connection with Ziegler's discovery of the transition metal containing catalysts now bearing his name, and especially after the disclosure by Zelinski and Smith[8] that TiI_4 in combination with trialkylaluminum will form a very active catalyst for producing high *cis*-1,4-polybutadiene, a novel polymer which exhibited very interesting elastomeric properties. Although an intermediate in the so-called van Arkel–de Boer[9,10] process for purifying titanium, TiI_4 was not at that time a commercially readily available compound, which prompted us to study its synthesis as well as those of its physical properties which could conceivably have a direct bearing on its properties as a polymerization catalyst component. As a result of this study we obtained additional information regarding the conditions under which the two different crystalline modifications of TiI_4 may appear and we also discovered that the solubility of this compound, if properly prepared, may be quite appreciable in hydrocarbons.

Experimental Section

Preparation of TiI_4. This compound was prepared by modifications of two established methods: (1) direct combination of the elements[2] and (2) halogen exchange between $TiCl_4$ and dry HI at a temperature between the melting and the boiling points of the mixture.[1,2,11] In the synthesis according to method (1), 7.2 g (0.15 g-atom) of carefully dried and degassed Ti metal powder (Metal Hydrides, Inc.) was

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introduced via an inlet tube into one of the ~150 mm long legs of a U-shaped tube made of 25 mm o.d. Pyrex tubing and 76.2 g (0.6 mol) of dried I_2 (Baker Analyzed) into the other one. The legs of the tube were then cooled with dry ice whereupon the tube was evacuated and sealed at the inlet tube. A small amount of the Ti powder was then transferred to the I_2-containing leg which was heated above the melting point of I_2. A vigorous reaction accompanied by spark formation ensued and a small amount of material sublimed over into the Ti leg. After the reaction had subsided and the I_2 leg cooled down somewhat, more Ti was transferred to this leg, which was then again heated to initiate the reaction. This procedure was repeated until all the Ti had been reacted. (*Note*! The reaction between Ti and I_2 is highly exothermic and great care must be taken not to transfer too much Ti, about 0.5 g is a suitable amount, each time to the I_2 tube. The operation should also be carried out behind a safety shield and safety glasses should be worn.) After the reaction had been completed, both legs were heated above the melting point of TiI_4 (150 °C) whereupon the reaction product was moved back and forth between the two legs several times to ensure complete reaction and homogenization. The tube was then transferred to a muffle furnace where it was heated to 250 °C for several hours and then cooled down slowly, ~4–5 °C/h, to room temperature. The reaction product formed a dark violet hard cake which did not break up easily. It was completely soluble in water and no free Ti or I_2 could be detected. It analyzed Ti 8.60% and I 90.89%, corresponding to $TiI_{3.99}$. In the synthesis according to method (2), the reaction was carried out in a 1-L four-necked round-bottom flask equipped with a stirrer, a gas inlet tube, a condenser cooled with chilled *n*-heptane, and a thermowell. This flask was charged with 189.7 g (1 mol) of $TiCl_4$ (J. T. Baker, Purified) and heated with stirring from room temperature to 290 °C over a period of about 6 h during which time dry HI was introduced at a constant rate, about 130 g (~1 mol)/h. The HI was produced by dropping hydriodic acid (Baker Analyzed, 57% HI) onto P_2O_5 (Baker Analyzed) and then purified and dried in three scrubbers containing in order a saturated aqueous CaI_2 (Matheson Coleman and Bell) solution, P_2O_5, and red phosphorus (Matheson Coleman and Bell). At the termination of the reaction the conversion to TiI_4 was about 98%, not counting losses of $TiCl_4$ by evaporation. The recovered yield of crude product was 518 g.

Purification of TiI_4 by Extraction. The extraction of TiI_4 from various reaction products as well as commercial preparations (when available) was carried out with refluxing dry benzene in a Kumagawa extractor. The TiI_4 (usually 100 g) was charged inside a drybox on top of a 1 cm thick dried Pyrex wool layer in a 57 × 150 mm Pyrex thimble with a coarse (C) fritted glass disk. A 2 cm thick layer of Pyrex wool was then placed on top of the TiI_4 and the thimble transferred to the N_2-blanketed extractor. The use of glass wool between the TiI_4 and the fritted glass disk served to prevent plugging of the latter, and the use of glass wool on top of the TiI_4 served to prevent finely divided undissolved material from getting into the extraction flask either through splashing or through overflowing of the thimble in case of plugging of the disk. The extraction was carried out until the siphoning liquid appeared colorless, which took from about 1 to 4 days depending upon the origin (solubility) of the original preparation.

The extraction flask was then allowed to cool to room temperature and the TiI_4, which had come out of solution as a fine crystalline material, filtered off in a Büchner funnel, washed with three 50-mL portions of benzene, and dried in vacuo (~0.5 mmHg) at room temperature. The yield of pure material, analyzing between $TiI_{3.99}$ and $TiI_{3.95}$ for the various preparations, varied between about 70 and 80 g depending upon both the purity of the starting material and the volume of benzene in the extraction flask, which was influenced by losses during the extraction and the volume of benzene remaining in the extractor. The effect of the benzene volume on the recovered yield derived from the appreciable solubility of TiI_4 in cold benzene (see below), but no attempt was made to recover additional, but probably less pure, TiI_4 by evaporation of the solvent. However, the amount of TiI_4 in the filtrate could be estimated from its light absorption at about 517 nm.

X-ray diffraction patterns were obtained on finely powdered samples containing crystalline silicon as an internal standard with a Philips Electronics (Norelco) instrument employing Cu Kα_1 radiation and equipped with a direct recording goniometer. Because of their air and moisture sensitivity the samples were put into special sample holders in which they were protected by a 0.5-mil Mylar film. The samples were also blanketed with dry nitrogen while in the diffractometer. The lattice parameters, where determinable, were refined by the Simplex method.[12]

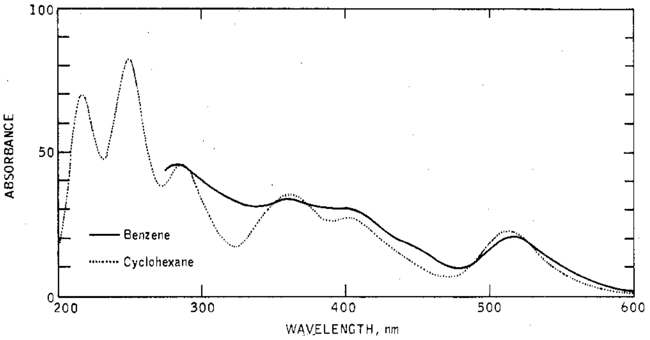

Figure 1. UV and visible spectrum of TiI_4 in benzene and cyclohexane (0.5 mM solutions, 1-mm cell, absorbance full scale = 2.0).

UV–visible spectra were obtained with a Beckman Acta CIII direct-recording spectrophotometer.

Results

The synthesis of TiI_4 according to method (1) gave of course a quantitative yield, and the only possible problem was that of inhomogeneity, but it appeared not to have occurred. The X-ray diffraction pattern obtained several days after the preparation revealed that the crystal structure was the less symmetrical but more stable one first mentioned by Hassel and Kringstad[1] and later described in more detail by Rolsten and Sisler.[2] Because of the equipment used, we were also able to record diffraction peaks corresponding to *d* spacings of 6.62 and 4.87 Å, but the agreement with the data presented by the latter workers was otherwise good.

Our *d* spacings tended to be slightly larger than those reported by Rolsten and Sisler. Thus if a hexagonal structure is assumed, our value for c_0 would be 19.86 Å rather than 19.68 Å as reported earlier.

The synthesis of TiI_4 according to method (2) also gave a high yield but a product purity of about 98%. The conversion could, of course, have been driven further, but this would have required a rather large additional amount of HI for a small additional yield of TiI_4, which was not considered worthwhile, since subsequent purification was contemplated. The crystal structure of this material was not determined until several months had passed and was then found to be isomorphous with the TiI_4 made directly from the elements.

The crystal structure of the benzene-extracted TiI_4, which came out of solution as fine octahedral crystals, was always cubic, exhibiting *d* spacings and hence unit cell dimensions which agreed fairly closely with those reported by Hassel and Kringstad,[1] i.e., $a_0 = 12.055 \pm 0.005$ as compared to $a_0 = 12.002 \pm 0.001$ Å by the earlier workers. However, our experimental method allowed us to observe several *d* spacings which were not reported by these workers.

Although the cubic structure was usually observed as late as a month after they had been made, the benzene-extracted TiI_4 preparations eventually also changed into the more complex structure exhibited by the unextracted preparations. The exact time for the crystallographic change was not determined, but no extracted preparation retained any detectable amount of its cubic structure for more than a year. However, even after the structure change many of the original small crystals seemed to remain intact and to retain their octahedral shape, although with surfaces having a rather pitted structure.

The high and ready solubility of the extracted, cubic TiI_4 in hydrocarbons made it possible to prepare solutions of known concentration and thus to obtain the spectrum of this compound in the UV–visible range between 190 and 600 nm in both benzene and cyclohexane as shown in Figure 1. Once the extinction coefficients for the various absorption bands, and especially the one at 517 nm for benzene and 514 nm for cyclohexane, had been established, it became possible to determine the solubility of TiI_4 in both solvents. For this purpose TiI_4 in excess was dissolved in the solvent at about 75 °C. After the extract had been cooled down to room temperature and allowed to stand for at least 24 h, the absorption spectrum was determined on a properly diluted aliquot. The solubility in benzene was found to be 32.7 g/L (0.059 M) and in cyclohexane 24.4 g/L (0.044 M) at 23 °C.

The solubility of the more stable modification of TiI_4, which went into solution much more slowly, especially at room temperature, was found to vary considerably and occasionally reached levels about half of those for the cubic form.

Discussion

The dimorphic character of TiI_4 first established by Hassel and Kringstad[1] and then by Rolsten and Sisler[2] was confirmed in our study. However, additional light was shed on the conditions under which the two crystalline modifications will appear. Hassel and Kringstad's observation that TiI_4 crystallizes in the cubic form from a melt, combined with our observation that it crystallizes in the same manner from a benzene solution, can be taken as an indication that this modification will normally appear when TiI_4 crystallizes out of a phase in which it is present as discrete molecules. It has also been well established that a transformation to the less symmetrical structure will always take place, but at a rate which will depend upon the character of the original cubic material. Thus, while a microcrystalline material resulting from a melt may change its structure within a few days, a material consisting of well-developed discrete octahedral crystals of a size clearly discernible with the naked eye may not undergo any detectable crystallographic changes for a month or more.

In the case of the cubic modification, the difference in the value for a_0 between our determination and that of Hassel and Kringstad can probably be fully explained by a difference in the temperature for the two determinations. Ours was made at 23 °C, while, considering the place and time of the study (Oslo, 1931), the one by Hassel and Kringstad was probably carried out at a significantly lower temperature. It is, of course, also of interest to note that the determination by Rolsten and Sisler at about 125 °C gave $a_0 = 12.21$ Å. These data actually suggest that the cubic form exhibits an abnormally high coefficient of thermal expansion, corresponding to about $1.3 \times 10^{-4}/°C$ from our data and those of Rolsten and Sisler. The structure of the less symmetric but obviously more stable form of TiI_4 has not been established and can probably not be determined without access to single crystals.

The fact that the more stable form of TiI_4 changes to the cubic structure between 100 and 125 °C, as determined Rolsten and Sisler,[2] which is well below the melting point of TiI_4 (150 °C), combined with the fact that numerous particles retain their octahedral shape after transformation from the cubic to the more stable structure, suggests that the transformation does not involve any highly significant change in the position of the iodine atoms relative to each other. Rather these facts suggest that the transformation involves primarily a rearrangement of the iodine atoms from a regular to a distorted tetrahedral arrangement around the titanium atoms.

In the cubic modification the close-packed iodine layers are parallel to the (111) plane and the *d* spacing for (222), 3.48 Å, gives the distance between equivalent points on two adjacent layers. As pointed out by Rolsten and Sisler,[2] the *d* spacings for the more stable modification index rather well as a hexagonal lattice, with $c_0 = 19.68$ Å, while, on the same assumption, we find $c_0 = 19.86$ Å. Since the *d* spacing for (006) would correspond to the distance between equivalent positions on adjacent layers, we find a contraction in the packing of the layers to have taken place from 3.48 to 3.31 Å. Such a contraction would be possible if the iodine atoms separate slightly from each other within parallel layers. If this happens, the close packing and the cubic symmetry disappear, even though the stacking of the remaining expanded layers may remain cubic. Such a structure could exhibit hexagonal or pseudohexagonal character in a manner analogous to that encountered in γ-$TiCl_3$.[13,14]

Like $TiCl_4$ and $TiBr_4$, which have been studied exhaustively,[15] TiI_4 is, of course, a highly covalent compound in the gaseous, molten, and dissolved states, and it remains so also in the cubic modification. The latter is strongly indicated by the Ti–I distance of only 2.61 Å, which agrees well with the sum of the covalent radii calculated or determined for these elements ($r_{Ti} = 1.28$ Å[14] and $r_I = 1.33$ Å[16]). The sum of the ionic radii ($r_{Ti^{4+}} = 0.64$–0.68 Å and $r_{I^-} = 2.16$–2.20 Å[17]) on the other hand is considerably greater than this distance.

The covalent character of TiI_4 in the cubic modification is further indicated by the softness of this material, which, when crushed in a mortar, produces a smooth purplish brown coating of the mortar surface. By contrast, after transformation to the stable modification TiI_4 is a very hard blackish violet material which does not coat the mortar surface. This suggests a more ionic character for this form which in turn may explain the cause of the crystallographic transformation. Of course, it is not known whether the transformation is a consequence of a change in the character of bonding or the latter is a consequence of the structural changes. However, it appears certain that the cubic structure will not be compatible with a high degree of ionic character of the Ti–I bonds, since the length of these bonds would be much shorter than the sum of the ionic radii.

Although the Ti–I distance for gaseous or dissolved TiI_4 does not appear to have been determined, it seems reasonable to assume, especially in view of similar data reported for $TiBr_4$,[15] that little change in the molecular dimensions occurs when cubic TiI_4 is formed from the gaseous or dissolved states. However, intermolecular forces now enter into the picture, probably derived from interaction between the closest packed iodine atoms, since the shortest Ti–Ti distance, about 5.8 Å, appears much too long for significant metal–metal interaction. In particular, interaction could be expected between the nonbonding p orbitals of the iodines in neighboring TiI_4 molecules.

A similar phenomenon is observed for $TiBr_4$, which crystallizes with the same cubic structure as TiI_4[1] and also undergoes a crystallographic transformation at room temperature. Brand and Schmidt[18] established that the structure of the stable modification is monoclinic and belonging to the space group C_{2h}^5-$P2_1/c$. The lattice retains a molecular character, but the $TiBr_4$ tetrahedra have become slightly distorted and have separated from each other in such a manner that the intermolecular Br–Br distances are about 6% longer than the intramolecular ones. As a result the arrangement of the Br atoms has changed from cubic to deformed hexagonal closest packing. It appears likely that the crystallographic transformation in TiI_4 is of a similar nature, but a comparison of the two diffraction patterns does not reveal an easily detectable similarity.

In the cubic form, TiI_4 has a limited but significant solubility in both benzene and cyclohexane. Since concentrations of the order of 0.1–0.5 mM are usually employed in diene polymerizations involving this compound,[3,4,6] no solubility problems should be encountered if the cubic modification is used, and the catalyst most certainly cannot be characterized as insoluble *by virtue* of the *insolubility of TiI_4* as will be reported elsewhere.[19] The solubility of the less symmetrical form of

Table I. Absorption Peaks of TiI_4 in Benzene and Cyclohexane Solutions

benzene		cyclohexane	
wavelength, nm	$10^{-3}\epsilon$	wavelength, nm	$10^{-3}\epsilon$
517	8.15	514	8.9
449	5.8		
400	12.15	402	10.7
361	13.45	362	14.0
282	18.2	287	18.1
		249	32.8
		217	28.1

TiI_4 is considerably lower and exhibits some irregularities. These may partly be of kinetic origin owing to the fact that the particle size and shape of an originally cubic TiI_4 which has changed into the more stable modification can vary considerably. Another important factor is the tendency of the more stable form of TiI_4 to change into the cubic modification somewhere above 100 °C, as shown by Rolsten and Sisler.[2] If the TiI_4 is heated together with the hydrocarbon solvent to a temperature above the transition temperature but below the melting point of TiI_4, then, obviously, the TiI_4 will go into solution as the cubic modification and exhibit appreciable solubility even if originally present in the more stable form. What actually happens when the same mixture is heated to slightly below the transition temperature for solid TiI_4, e.g., 80 °C, is not known, but it seems reasonable to expect that the solubility of the more stable form should increase rapidly as the transition temperature is approached. If all the TiI_4 in the system goes into solution at the elevated temperature, the solubility of this compound at room temperature will, of course, again be that of the cubic modification. However, all TiI_4 preparations exhibit some solubility in benzene and cyclohexane at room temperature, even if the rate of solution at times may be very low for the more stable modification.

The electronic spectrum of TiI_4 was reported some years ago by Clark and Willis.[7] However, only part of the spectrum was shown and, while the reported positions of the six maxima in cyclohexane are close to those found by us, the extinction coefficients reported by these investigators are considerably in error. They were apparently dealing with the stable modification of TiI_4 when preparing their cyclohexane solutions and thus obtained a supposedly saturated solution which was only 2.86×10^{-4} M. The small volume, about 1 mL (approximately 0.16 mg of TiI_4) of this solution available for analyses probably resulted in an erroneous estimation of the concentration, which was apparently judged too high. Thus the molar extinction coefficient for the absorption at 514 nm which we found to be 8900 was reported to be 5400 at 515 nm by Clark and Willis. About the same relative intensity was reported for the following three maxima, but for the fifth peak at about 249 nm the value reported by these workers was considerably closer to that reported by us, while no intensity was given for the final maximum at about 217 nm. Since iodine begins to absorb strongly at about 260 nm, we must conclude that the TiI_4 preparation used by Clark and Willis was contaminated by this element despite the great effort (quadruple sublimation) to remove any iodine impurity. This observation also suggests that extraction with benzene is a much more effective means of purifying TiI_4 than repeated sublimation.

Obviously a minor error is also possible in our determination of the extinction coefficients for TiI_4 in cyclohexane solutions, but on the basis of the results from close to 100 determinations (carried out before each polymerization experiment as will be reported separately[19]) we conclude that our extinction coefficients are well within the accuracy range of ±3% and ±5% for cyclohexane and benzene solutions, respectively. It should be noted, however, that even a small amount of moisture in the solvent, on the order of a few parts per million, may cause the absorption maximum to decrease significantly, especially for more dilute solutions, e.g., 0.5 mM or less. From the very high intensity of the absorptions one can conclude, as did Clark and Willis, that the TiI_4 spectrum is of charge-transfer character in both cyclohexane and benzene. While there are definite similarities between the two spectra obtained in these solvents, there are also significant differences. The spectrum for the benzene solution is, of course, limited in range by the strong benzene absorption beginning at about 280 nm. Thus two of the main absorption peaks of TiI_4 can be seen only in the cyclohexane solution. However, beyond this we find that minor shifts occur in the positions of the absorption maxima as well as in the relative intensities of the peaks when one solvent is exchanged for the other as shown in Table I.

Particularly interesting is the appearance of a weak but clearly discernible absorption peak at about 450 nm for the benzene solution. The appearance of an absorption somewhere fairly close to this location is suggested also in the cyclohexane spectrum, but only the benzene spectrum makes the existence of this peak certain.

The TiI_4 spectrum in cyclohexane solution has many similarities with the spectrum of $TiCl_4$ discussed in numerous articles.[20–23] However, the absorptions start at considerably higher wavelengths for TiI_4 than for $TiCl_4$, as would be expected from the much more ready oxidizability of I^- in comparison with Cl^-. For this reason many more absorption peaks occur in the spectrum of TiI_4 than in that of $TiCl_4$ in the range of wavelengths studied.

Clark and Willis interpreted part of the TiI_4 spectrum and concluded that the separation between the two longest wavelength peaks, 5290 cm^{-1}, corresponded to the energy difference between the two subshells of the Ti d orbitals in tetrahedral coordination. We agree with this interpretation but find the separation, often also expressed as $10Dq$, to be 5420 cm^{-1} on the basis of our data.

It is our intent to discuss the TiI_4 spectrum more fully together with the spectra of several other hydrocarbon-soluble tetraiodides in a subsequent publication.

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Relative Bonding Characteristics of Cationic Isocyanide, Carbonyl, and Related Complexes of Iron as Determined by Mössbauer and Infrared Spectroscopy[1]

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Mössbauer-effect isomer shifts in cationic cyclopentadienyliron complexes identify ligand ($\sigma + \pi$) bonding capacities to increase in the order $PPh_3 < CNMe \simeq C(NHMe)_2 < CO$. An analysis of substitution effects on isomer shifts in varying ligand environments illustrates the compensating effect of both carbonyl and isocyanide groups on metal electron density. In contrast, infrared force constants for carbonyl stretching modes decrease uniformly for a given substitution in each metal environment. Consideration of both isomer shifts and stretching force constants for isocyanides and diaminocarbenes distinguishes enhanced σ-donor capacities for the carbene that are paralleled by increased π acceptance on the part of the isocyanide. Both σ and π bonding are reduced in indenyl analogues of the cyclopentadienyl complexes since isomer shifts increase despite negligible differences in carbonyl stretching frequencies.

Introduction

Although Mössbauer spectroscopy is frequently used to characterize iron carbonyl complexes, care must be exercised in interpreting isomer-shift variations, particularly when correlations with carbonyl stretching force constants are made. Complexes containing three or more carbonyls have been shown to exhibit minimal differences in δ due to the capacity of these ligands to absorb excess metal electron density via π back-bonding.[3-5] It is therefore not unusual for significant differences in C≡O stretching frequencies to be accompanied by nearly identical Mössbauer δ values.[3,4] Further, a change in the overall charge of the iron complex complicates isomer-shift comparisons and often prohibits meaningful correlation with other spectroscopic data.[6] However, Mössbauer studies of several closely related series of neutral or cationic cyclopentadienyliron complexes have been reported[7-10] and have permitted comparisons of relative ($\sigma + \pi$) effects for a variety of ligands in specific carbonyl-containing metal environments.

Research in our laboratory has been concerned with isocyanide and diaminocarbene complexes of iron[11,12] for which no Mössbauer data have been reported. Recent photochemical investigations of cationic species have extended this system to include complexes in which all carbonyls have been replaced.[13] As a result, Mössbauer data for these complexes have the potential of not only characterizing ligand ($\sigma + \pi$) effects but also of comparing more subtle bonding differences in analogous isocyanide and carbonyl systems.

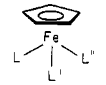
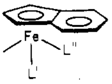
Infrared stretching frequencies are also sensitive to the σ-donating and π-accepting abilities of accompanying ligands, but, unlike the isomer shift, the two factors oppose each other in their effect on carbonyl stretching.[14] Thus, whereas each technique is incapable of an independent assessment of relative donor–acceptor effects, the two in concert offer the possibility of qualitatively separating these factors—particularly where overall differences in structure are minimized.

Experimental Section

The following compounds were synthesized by literature methods: $CpFe(CO)_3^+PF_6^-$,[15] $CpFe(CO)_2(CNMe)^+I^-$,[16] $CpFe(CO)(CNMe)(PPh_3)^+I^-$,[17] $CpFe(CO)(PPh_3)[C(NHMe)_2]^+I^-$,[17] $CpFe(CO)(CNMe)_2^+PF_6^-$,[18] $CpFe(CO)(CNMe)[C(NHMe)_2]^+PF_6^-$,[17] $CpFe(CNMe)_3^+I^-$,[16] $InFe(CO)(CNMe)_2^+I^-$.[11]

$CpFe(CO)_2(PPh_3)^+PF_6^-$ was conveniently prepared by combining $CpFe(CO)_3^+PF_6^-$ with an excess of triphenylphosphine in dry acetone for 15 min. Concentration of the solvent followed by addition of ethyl ether resulted in an 81% yield of the product. This method of synthesis offers a savings in time and an increased yield over that reported previously.[19]

Table I. Mössbauer-Effect Parameters[a]

	L	L′	L″	δ, mm/s	ΔE_Q, mm/s
	CO	CO	CO	−0.006	1.85
	CO	CO	PPh_3	0.014	1.81
	CO	CO	CNMe	−0.004	1.84
	CO	PPh_3	PPh_3	0.146	1.85
	CO	PPh_3	CNMe	0.056	1.88
	CO	PPh_3	$C(NHMe)_2$	0.053	1.91
	CO	CNMe	CNMe	0.024	1.87
	CO	CNMe	$C(NHMe)_2$	0.018	1.93
	CNMe	PPh_3	PPh_3	0.204	1.90
	CNMe	CNMe	$C(NHMe)_2$	0.062	1.90
	CNMe	CNMe	PPh_3	0.100	1.93
	CNMe	CNMe	CNMe	0.059	1.92
	CO	CO	CO	0.029	1.85
	CO	CNMe	CNMe	0.045	1.96
	CNMe	CNMe	PPh_3	0.125	2.03

[a] Relative to natural α-iron foil.

$CpFe(CO)(PPh_3)_2^+PF_6^-$ was synthesized by irradiation of $CpFe(CO)_2(PPh_3)^+PF_6^-$ and excess triphenylphosphine in dichloromethane for 4 h. The reaction mixture was chromatographed on alumina, the product eluting with CH_2Cl_2 as a broad orange band. The nonoptimized yield was approximately 63%. The synthesis of this complex has been reported previously by Treichel,[19] with $CpFe(CO)(PPh_3)I$ and excess PPh_3 in the presence of $AlBr_3$. The photolysis reaction, however, requires considerably less time in addition to increased yield.

$CpFe(CNMe)_2[C(NHMe)_2]^+I^-$ was synthesized by the reaction of methylamine with $CpFe(CNMe)_3^+I^-$ as described for analogous compounds.[20]

$InFe(CO)_3^+PF_6^-$ was prepared in the same manner as $CpFe(CO)_3^+PF_6^-$ by using $[InFe(CO)_2]_2$.

$CpFe(CNMe)_2(PPh_3)^+PF_6^-$, $CpFe(CNMe)(PPh_3)_2^+PF_6^-$, and $InFe(CNMe)_2(PPh_3)^+PF_6^-$ were prepared by irradiation of the appropriate carbonyl complex in the presence of triphenylphosphine.[13]

A Mössbauer drive in the constant-acceleration mode was used for the experiments; the system was calibrated by using natural α-iron foil. All spectra were recorded at room temperature. Isomer shifts and quadrupole splittings were obtained by a least-squares fit to the Lorentzian.

Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer calibrated in the CO region with gaseous DCl.

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