Inorg. Chem. **1987**, *26*, 3051–3054

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FTIR Spectra of Photolytic Reactions of HCN with F_2 in Solid Argon

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Received April 7, 1987

Hydrogen cyanide was condensed with fluorine in excess argon at 12 K, and no reaction was observed. Photolysis produced the hydrogen abstraction product complex $FC{\equiv}N{-}{-}HF$ as well as the addition product $HFC{=}NF$. The HF submolecule stretching frequency was observed at 3662 cm^{-1} while the HF librational mode appeared at 553 cm^{-1} for the complex. Three infrared absorptions were observed for the difluoro addition product $HFC{=}NF$. Sample annealing facilitated F atom addition to HCN and produced $HFC{=}N$, which was characterized by four infrared absorptions with deuterium shifts. The carbon–nitrogen bonds for both $HFC{=}N$ and $HFC{=}NF$ are found to possess double-bond character.

Introduction

Fluorine chemistry involving various π systems has been an active research area. Theoretical investigations[1,2] have been performed on fluorine derivatives of $H_2C{=}NH$ while the products from F atom additions to $FC{\equiv}N$ have been examined experimentally.[3-5] Many other experiments have been carried out to study hydrogen abstraction by F atoms.[6] Hydrogen-bonded complexes have been made by photolyzing $HC{\equiv}CH$ with F_2.[7] The $HC{\equiv}N/F_2$ system possesses a unique opportunity since photolysis permits both F atom addition and hydrogen abstraction to be observed in the same sample.

Matrix infrared spectroscopy has proven to be very useful for the characterization of unstable molecules[5] such as F_2CN as well as hydrogen-bonded complexes between HF and small base molecules, such as C_2H_2,[8] HCN,[9] and ClCN.[10] The purpose of this study is to investigate the complex between HF and FCN and the products from F atom addition to HCN. Infrared spectra of the photolytic reactions of HCN with F_2 in solid argon will be described below.

Experimental Section

The vacuum and cryogenic apparatus and FTIR spectroscopic methods have been described in detail previously.[11,12] All spectra were recorded with a Nicolet 7199 Fourier-transform infrared spectrometer at 1.0-cm^{-1} resolution from 4000 to 400 cm^{-1}. A single-beam spectrum of the CsI window at 12 K was recorded and ratioed as a background to a single-beam spectrum of the sample to produce a simulated double-beam spectrum for each experiment. Most of the reported frequency values were rounded to the nearest wavenumber; the accuracy is ±0.3 cm^{-1}.

HCN, prepared by a previously reported method,[9] was purified by evacuation at 77 K to remove volatile impurities. DCN was produced by exchanging HCN in a manifold that had been thoroughly treated with D_2O.

Cyanide samples were diluted between 200/1 and 400/1 mole ratios with argon (Air Products) while F_2 (Matheson) samples were diluted to either 100/1 or 200/1 mole ratios. Approximately 27 mmol of each sample was codeposited at a rate of 7.5 mmol/h onto the cold window at 12 K, and an infrared spectrum was recorded. The matrix was photolyzed for 30 min by the full light of a high-pressure mercury arc (Illumination Industries, Inc., BH-6-1, 1000 W) passed through a water filter. After another spectrum was taken, the matrix was photolyzed for another 45 min with the use of a lens to focus the light on the matrix. Following another spectrum, the resulting matrix was warmed to 29–32 K and then recooled to 12 K, and then the final spectrum was recorded.

Table I. Absorptions (cm^{-1}) Produced from Hydrogen Cyanide and Fluorine in Excess Argon following Photolysis and Sample Warming

HCN + F_2	DCN + F_2	assignt
3707		ν_{sb}
3662	2694	ν_s
3512		ν_{sa}
3016	2252	(1)
2354.8	2356.6	ν_1^c
2318	2318	FCN^a
1778	1755	$(HCN)(F)_n$
1734	1734	F_2CN^b
1672	1651	(1)
1647	$(1624)^c$	(2)
1284	1284	$(CN)(F)_n$
1252	1252	F_2CN^b
1232	1238	$(HCN)(F)_n$
1205	1217	(2)
1107.0	1107.0	ν_2^c
1076	1076	FCN^a
1057	1047	(1)
999		$2\nu_l$
951	968	(2)
553		ν_l
536	530	(1)
459	459	ν_3^c $(456)^a$

[a] Values for uncomplexed FCN in solid argon.[15] [b] Two strongest bands.[5] [c] DFCNF counterpart probably coincident with water at 1624 cm^{-1}.

Results

Fourier-transform matrix infrared spectra of HCN and HCN/DCN mixtures with F_2 will be described in turn.

HCN + F_2. Three experiments were performed with HCN and F_2 codeposited at 12 K. The spectrum for the most concentrated sample, displayed in Figure 1a, showed sharp, weak absorptions due to the HF monomer[13] and water (labeled W),[14] weak bands due to the HF- -HCN complex produced from trace HF impurity in the fluorine sample (labeled I)[9] and strong HCN precursor bands. Photolysis for 30 min without the lens produced significant changes in the spectrum, which are shown in Figure 1b. New product absorptions include a sharp band (labeled ν_s) at 3662 cm^{-1} (A = absorbance = 0.31), a sharp absorption (labeled ν_l) at 553 cm^{-1} (A = 0.14), and a weaker band (labeled $2\nu_l$) at 999 cm^{-1}. Two groups of weaker product absorptions (labeled 1 and 2) involving F atom additions are given in Table I. In addition, three perturbed FCN modes (labeled ν^c) due to HF product complex were observed at 2354.8, 1107, and 459 cm^{-1}. A 45-min photolysis using the lens more than doubled the intensity of all the product

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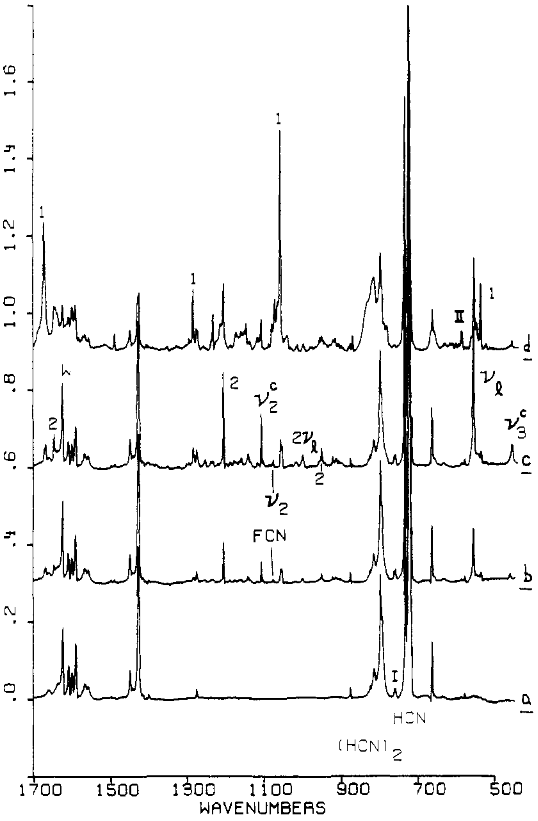

Figure 1. FTIR spectra of hydrogen cyanide/fluorine samples: (a) after codeposition of 27 mmol of Ar/HCN = 200/1 and 25 mmol of Ar/F_2 = 100/1 at 12 K for 3 h; (b) after photolyzing for 30 min without the lens; (c) after photolyzing for 45 min with the lens; (d) after warming to 32 K and recooling to 12 K.

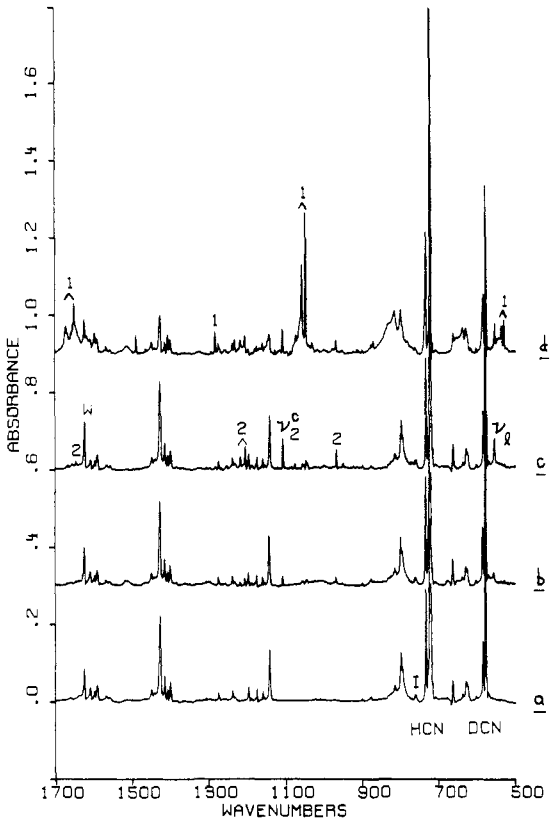

Figure 2. FTIR spectra of deuterium cyanide/fluorine samples in the 1700–500-cm^{-1} region: (a) after codeposition of 27 mmol of Ar/(DCN + HCN) = 200/1 and 29 mmol of Ar/F_2 = 100/1 at 12 K for 3 h; (b) after photolyzing for 30 min without the lens; (c) after photolyzing for 45 min with the lens; (d) after warming to 29 K and recooling to 12 K.

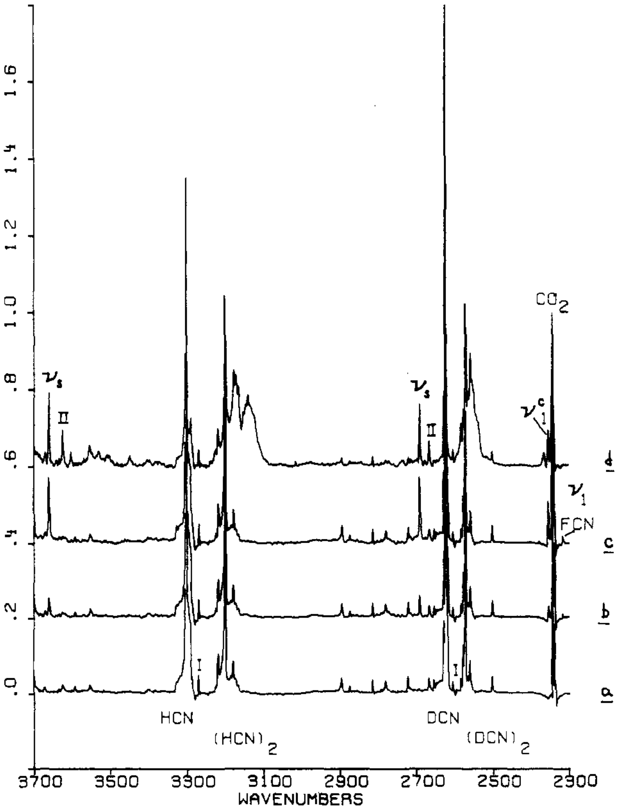

Figure 3. FTIR spectra in the 3700–2300-cm^{-1} region for the deuterium cyanide/fluorine sample described in Figure 2.

absorptions, as shown in Figure 1c, and made possible observation of weak FCN bands[15] at 2318 and 1076 cm^{-1}. Sample warming to 28 K and then recooling to 12 K also produced considerable changes in the spectrum, which are presented in Figure 1d. Sample annealing reduced the ν_s, ν_l, ν^c, and 2-band product absorptions by approximately 40% and dramatically increased (factor of 7) the 1-bands. In addition, the ν_s and ν_l bands of HCN- -HF were observed at 3626 and 586 cm^{-1} (labeled II)[9] along with weak new bands at 3707 and 3512 cm^{-1} (ν_{sb} and ν_{sa} in Table I). The other experiments with HCN and F_2 had a growth and decay pattern similar to the one shown in Figure 1.

DCN/HCN + F_2. Three additional F_2 experiments were performed with DCN/HCN mixtures, and the product absorptions from these experiments are also listed in Table I. The spectrum for the most concentrated sample, displayed from 1700 to 500 cm^{-1} in Figure 2a, revealed a 60% deuterium enrichment of the HCN as well as the sample impurity bands seen in the HCN and F_2 experiments. The photolyses with and without the lens, illustrated in Figure 2b,c, produced counterpart absorptions to those observed in the HCN experiments. All of the 2-absorptions exhibited small shifts from their corresponding bands in the HCN experiments. Once again, sample annealing to 29 K, displayed in Figure 2d, dramatically increased the 1-bands while the other product bands were slightly reduced. Most of the new 1-bands were red shifted from their hydrogen cyanide counterparts. The 3700–2300-cm^{-1} region from this experiment is illustrated in Figure 3; the very strong C–H and C–D stretching absorptions of precursor monomer and weaker bands for dimer are indicated. Photolysis produced the ν_s(HF) and ν_s(DF) bands at 3662 and 2694 cm^{-1}, a weak isolated FCN band at 2318 cm^{-1}, and a stronger $\nu_1{}^c$ band at 2356.6 cm^{-1}. Annealing the sample to allow diffusion

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(15) Jacox, M. E., unpublished results. Fawcett, F. S.; Lipscomb, R. D. *J. Am. Chem. Soc.* **1964**, *86*, 2574. Matrix and gas-phase FCN bands agree very well except for the broad ν_1 gas-phase band at 2290 cm^{-1}, which has not been analyzed. The present and Jacox matrix results suggest that analysis of the gas-phase band will produce a band center near 2318 cm^{-1}.

of small species produced the ν_s bands of HCN--HF and HCN--DF (labeled II)[9] and increased precursor aggregates. Another DCN/HCN experiment with F_2 had 80% deuterium enrichment, and the HCN and DCN product band populations changed accordingly.

Discussion

The product absorptions listed in Table I were not seen in argon matrix samples of hydrogen cyanide or fluorine. However, these bands were observed in high yields when the reagents were photolyzed and warmed following condensation. These products are most likely due to the photolytic reaction of the F_2--HCN complex even though no definitive spectroscopic evidence was found for this complex. The structures and bonding of three photolysis products will be determined, in part, by comparison with similar complexes and molecules, and their absorptions will be identified and assigned.

FC≡N:--HF. Two different groups of product absorptions can be identified and assigned to this complex on the basis of deuteriation effects and band positions. First, the sharp, primary product absorption labeled ν_s has a similar DF counterpart with a HF/DF ratio of 1.359, which is characteristic of the fundamental vibration of the H–F ligand in a 1:1 product complex. These absorptions are appropriately red shifted from the 3919-cm^{-1} HF fundamental in solid argon[13] due to the hydrogen-bonding interaction. The single ν_l band at 553 cm^{-1} is assigned to the two degenerate librational motions of the HF submolecule in the 1:1 complex arising from the two rotational degrees of freedom of the diatomic; the DF counterpart expected at 409 ± 3 cm^{-1} was not observed due to the low-frequency limit of the instrument.

In addition to the HF submolecule absorptions, three product bands can be identified for perturbed submolecule modes of cyanogen fluoride. The perturbed FCN modes are compared in Table I with modes for isolated FCN.[15] A considerable blue shift (31 cm^{-1}) was observed for the C–F stretching mode while a slightly larger blue shift (37 cm^{-1}) was found for the C≡N stretching mode. In addition the C≡N mode was perturbed slightly more by DF (to 2356.6 cm^{-1}) than HF (2354.8 cm^{-1}). This arises because of the smaller librational amplitude of DF and the closer average distance, which results in a larger perturbation for DF, as has been observed for a number of complexes.[16] In addition, the bending mode was blue shifted by only 3 cm^{-1} from the FCN matrix value. The amount of perturbation of these vibrational modes in the complex reveals the structure of the complex. The large blue shift in the C≡N mode is typical of complexes with HF bonded to the nitrile lone pair;[10] for example, the C≡N mode was blue shifted by 28 cm^{-1} in HCN--HF and by 37 cm^{-1} in ClCN--HF. A red shift would be expected in the C–F stretching mode if HF were bonded to a fluorine lone pair, on the basis of the CH_3F--HF complex.[17]

It is interesting to note that the C–Cl stretching mode in ClCN--HF was not shifted, although a blue shift was found for the C–F mode in FCN--HF. The fluorine substituent has a substantial effect on the C≡N mode, resulting in a 124-cm^{-1} blue shift from the HCN value, whereas ClCN is only 15 cm^{-1} above the HCN value. This means that fluorine interacts more with the C≡N bond, and it is therefore not surprising that the perturbing effect of HF on the C≡N stretching mode is shared with the C–F stretching mode.

On the basis of the positions of the ν_s and ν_l modes, the ν_l splitting, and the perturbations of the FCN submolecule modes, the structure of this 1:1 complex is similar to those of the HCN--HF (ν_s = 3626 and ν_l = 586 cm^{-1})[9] and ClCN--HF (ν_s = 3597 and ν_l = 602 cm^{-1})[10] complexes. Similar spectra for these complexes provide evidence for HF bonding to the lone pair on the nitrile nitrogen instead of the lone pair on the fluorine or the π system.[9,10] The ν_s and ν_l modes for FCN--HF are very close to those of ClCN--HF, and the difference in the halogen inductive effects can easily explain the small differences in the HF modes.

Table II. Comparison of Vibrational Frequencies (cm^{-1}) for HFC=N and HFC=NF with Those of Similar Molecules

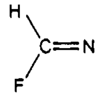
HFC=N (argon)	HFC=O (gas)[a]	HFC=NF (argon)	F_2C=NF (argon)[b]	assignt
1672	1837	1647	1740	ν(C=N)(C=O)
3016	2981			ν(C-H)
1057	1065	1205	1379	ν(C-F)
		951	1016	ν(N-F)
536	633			δ(F-C-N)(O)

[a] Reference 19. [b] Reference 5.

The order-of-magnitude-greater yield of complexed relative to isolated FCN band absorbances is also of interest. This indicates that most of the HF produced by abstraction (or elimination from excited HFCNF) is trapped in the matrix cage with the FCN coproduct. Similar results have been found in fluoroethylene systems.[7,8] These observations underscore the stability of the HF complexes and the ability of the matrix cage to relax photofragments so that complexes can be formed and trapped.

In addition to the absorptions assigned to the 1:1 complex, a second group of HF product bands was observed after sample annealing, which promotes diffusion and aggregation of HF species.[13] These HF absorptions at 3707 (ν_{sb}) and 3512 (ν_{sa}) cm^{-1} thus exhibited a higher order HF concentration dependence, which is characteristic of 1:2 complexes. These HF frequencies are very similar to the frequencies of XC≡N--$(HF)_2$[10] complexes. The probable cyclic structure of this 1:2 complex, which arises from the small amount of HF impurity in the fluorine sample, is discussed in detail elsewhere.[10]

HFC=N:. Four product absorptions can be identified and assigned to the HFC=N free radical (**1**) on the basis of the rate of F atom addition and band positions. The absorptions of this radical have the same growth pattern as O_2F (1498 cm^{-1}),[18] which serves as an useful indicator of F atom diffusion and addition reactions. This growth pattern strongly suggests that this new species is due to a single F atom addition to HCN. Since fluorine forms a stronger bond with carbon than with nitrogen, the most likely structure for this F atom addition product is **1**. Further evidence supporting these assignments is found in comparison with the absorptions[19] of gas-phase HFC=O in Table II. The vibrational modes that involve nitrogen in place of oxygen show the expected red shifts, while the frequencies for the C–H and C–F stretching modes are very close. The 1672-cm^{-1} absorption, which is assigned to the carbon–nitrogen stretching mode, indicates that the C=N bond possesses double-bond and not triple-bond character. The 1672-cm^{-1} band and the 1057-cm^{-1} absorption, assigned to the C–F stretching mode, exhibit deuterium shifts indicating interaction with H–C–N and D–C–N deformation modes intermediate in position that were too weak to observe here.



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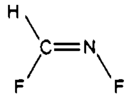

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***cis*-HFC=NF.** Three product bands can be identified and assigned to the difluoro derivative of methylene imide **2** on the basis of growth and decay rates, absorption positions, and deuterium shifts. The absorptions for HFC=NF have the same growth rate as the bands assigned to the HF product complex. This growth rate strongly indicates that the new product is formed by reacting HCN with two fluorine atoms from one F_2 molecule, as in the case of the FCN--HF complex. Since this group of absorptions exhibits deuterium shifts, this new species must be formed by fluorine addition to HCN, and the most probable structure for this addition product is **2**. Presumably **2** results from photolysis of the HCN--F_2 complex, which was not detected in these experiments, but a similar NH_3--F_2 complex was observed

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with the latter reagents.[20] In similar studies difluoroethylenes were major products of the C_2H_2 and F_2 matrix photochemical reaction.[7]

Additional support for this assignment is obtained by comparing the absorptions of HFC=NF with those of gas-phase F_2C=NF[4] in Table II. The frequencies of three stretching modes of HFC=NF showed the anticipated red shift from those of F_2C=NF since an electron-withdrawing fluorine is replaced with an electron-donating hydrogen. Furthermore, these modes show deuterium shifts for interaction and mixing with H–C–N or D–C–N bending motions. In addition, theoretical calculations[1,2] have shown the cis geometric isomer to be more stable than the trans isomer. Finally, the carbon–nitrogen bond was found again to possess double-bond character.

Other Products. Additional weaker absorptions were identified in these samples that point to other minor reaction products. The two strongest bands of the F_2CN free radical[5] were detected here at 1734 and 1252 cm^{-1}. Weak bands produced on annealing at 1778 and 1232 cm^{-1} exhibit deuterium shifts and are due to the addition of more than two F atoms to HCN. Finally, the sharp 1284-cm^{-1} band produced on annealing at the expense of F_2CN was unshifted with DCN and observed in previous FCN studies,[5] which suggests a higher $(CN)(F)_n$ species.

Conclusions

In summary, hydrogen cyanide and fluorine were photolyzed to form a well-defined 1:1 hydrogen-bonded complex of the form FCN--HF in solid argon. The matrix ν_s and ν_l modes are quite similar with HCN--HF observations,[9] which provides spectral evidence for the 1:1 product's being a cyanide nitrogen lone pair complex with a linear structure. Blue shifts were observed for all three FCN submolecule fundamentals in the complex. In addition, *cis*-HFC=NF is formed during photolysis, and three predominantly bond stretching modes were observed. The primary photochemical reaction of HCN and F_2 is probably fluorine addition to form excited HFCNF, which eliminates HF to give the FCN--HF complex or relaxes in the matrix cage. Similar yields of the C–F stretching bands at 1205 and 1107 cm^{-1} suggest that these two processes make major contributions to the overall reaction mechanism. Analogous C_2H_2 and F_2 photolysis studies gave similar results.[7] Sample annealing promoted single F atom addition to HCN, which produced HFC=N. Four infrared absorptions were observed for this free radical, which shifted appropriately for DFC=N. The carbon–nitrogen bonds for both fluorine addition products are found to have double-bond character by comparison to spectra of similar compounds.

Acknowledgment. The authors gratefully acknowledge financial support from National Science Foundation Grant CHE 85-16611 and argon matrix data on FCN from M. E. Jacox.

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Electronic Stability of Metal–Dihydrogen and –Polyhydrogen Complexes

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Received January 25, 1987

Molecular orbital ideas, especially those associated with the stability of three-membered rings, and analogies with unsaturated hydrocarbon chemistry are used to investigate the electronic features that stabilize η^2-dihydrogen complexes relative to their dihydride analogues. One crucial result is that the presence of more than two electrons in the collection of three-center frontier orbitals disfavors the dihydrogen complex. The presence of good π acceptors trans to the coordinated (H_2) reduces the extent of back-bonding into $\sigma^*(H_2)$ and stabilizes this arrangement. Extensive analogies are made with main-group species containing close H–H contacts, such as the $^2B_2$ state of CH_2^+ and the molecules H_3^+ and CH_5^+. The mechanism of the H/D exchange reaction occurring with $Cr(CO)_4(H_2)_2$ in liquid xenon solution is also investigated and leads to a study of possible polyhydrogen complexes. Exchange via the topologically simple intermediate containing a coordinated square (H_4) molecule is suggested to be a high-energy process, as a result of the direction of charge flow between ligand and metal in the intermediate. If the process via a tetrahydride species is ignored, the most promising routes from a theoretical point of view appear to be (a) one that involves coordinated (H_3) and H ligands (open and closed geometries for the coordinated (H_3) ligand are both calculated to be low-energy structures) and (b) one that involves a coordinated open (H_4) species. Analogies with other molecules lead to studies of species containing a coordinated tetrahedral H_4 unit (both η^2 and η^3).

Introduction

In 1984, Kubas and colleagues[1] reported the characterization of the first isolable transition-metal complexes $M(CO)_3(PR_3)_2(H_2)$ (M = Mo, W; R = Cy, *i*-Pr), in which H_2 was coordinated sideways as an undissociated molecule. The structure of this η^2-H_2 moiety (which we will write as (H_2)) was determined by X-ray and neutron diffraction methods and by vibrational spectroscopy.[1] More recently[2] accurate low-temperature neutron diffraction data gave, for $W(CO)_3(PPr_3)_2(H_2)$, H–H and W–H distances of 0.82 and 1.89 Å, respectively. This work generated a considerable flurry of activity, and several other dihydrogen (H_2) species have been reported. A number have been isolated: $Mo(CO)(dppe)_2(H_2)$ (dppe = (diphenylphosphino)ethane);[3] $[IrH(H_2)(PPh_3)_2C_{13}H_8N]^+$;[4] $[IrH_2(H_2)_2(PR_3)_2]^+$;[5] *trans*-$[M(H_2)H(PPh_2CH_2CH_2PPh_2)]^+$ (M = Fe, Ru);[6] $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(CN\text{-}t\text{-}Bu)H_2]^+$.[7] Note that in several of these compounds both dihydrogen (**1**) and hydride (**2**) ligands are present and there is strong evidence[8] for exchange among them, a point to which we

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