

with the latter reagents.²⁰ In similar studies difluoroethylenes were major products of the C₂H₂ and F₂ matrix photochemical reaction.⁷

Additional support for this assignment is obtained by comparing the absorptions of HFC=NF with those of gas-phase F₂C=NF⁴ in Table II. The frequencies of three stretching modes of HF-C=NF showed the anticipated red shift from those of F₂C=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 F₂CN free radical⁵ 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 F₂CN was unshifted with DCN and observed in previous FCN studies,⁵ which suggests a higher (CN)(F)_n species.

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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 ν₃ and ν₁ 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 F₂ 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 C₂H₂ and F₂ 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.

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Electronic Stability of Metal-Dihydrogen and -Polyhydrogen Complexes

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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 η²-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 (H₂) reduces the extent of back-bonding into σ*(H₂) and stabilizes this arrangement. Extensive analogies are made with main-group species containing close H-H contacts, such as the ²B₂ state of CH₂⁺ and the molecules H₃⁺ and CH₅⁺. The mechanism of the H/D exchange reaction occurring with Cr(CO)₄(H₂)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 (H₄) 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 (H₃) and H ligands (open and closed geometries for the coordinated (H₃) ligand are both calculated to be low-energy structures) and (b) one that involves a coordinated open (H₄) species. Analogies with other molecules lead to studies of species containing a coordinated tetrahedral H₄ unit (both η² and η³).

Introduction

In 1984, Kubas and colleagues¹ reported the characterization of the first isolable transition-metal complexes M(CO)₃(PR₃)₂(H₂) (M = Mo, W; R = Cy, *i*-Pr), in which H₂ was coordinated sideways as an undissociated molecule. The structure of this η²-H₂ moiety (which we will write as (H₂)) was determined by X-ray and neutron diffraction methods and by vibrational spectroscopy.¹ More recently² accurate low-temperature neutron diffraction data gave, for W(CO)₃(PPR₃)₂(H₂), 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 (H₂) species have been reported. A number have been isolated: Mo(CO)(dppe)₂(H₂) (dppe = (diphenylphosphino)ethane);³ [IrH(H₂-

(PPh₃)₂C₁₃H₈N]⁺;⁴ [IrH₂(H₂)₂(PR₃)₂]⁺;⁵ *trans*-[M(H₂)H-(PPh₂CH₂CH₂PPh₂)]⁺ (M = Fe, Ru);⁶ [(η⁵-C₅H₅)Ru(PPh₃)(CN-*t*-Bu)H₂]⁺.⁷ Note that in several of these compounds both dihydrogen (1) and hydride (2) ligands are present and there is strong evidence⁸ for exchange among them, a point to which we

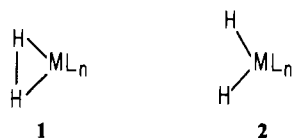
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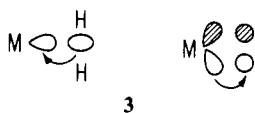
¶ Present address: California Institute of Technology, Pasadena, CA 91125.



shall return later. In addition, with low-temperature techniques a number of much less stable species have been identified. Photolysis of parent carbonyls in H_2 -doped matrices has provided $\nu(C-O)$ IR evidence for $Cr(CO)_5H_2$, $Cr(CO)_4(H_2)_2$,⁸ $\eta^5-(C_5H_5)HMo(CO)_2(H_2)$,⁹ and $Ni(CO)_3(H_2)$.¹⁰ Photolysis of parent carbonyls in liquid xenon under H_2 pressure generates sufficient (H_2) compound to permit identification via $\nu(H-H)$ IR bands as well as $\nu(CO)$ and $\nu(NO)$ IR bands, e.g., $M(CO)_5(H_2)$ ($M = Cr, Mo, W$),^{11,12} *cis*- $Cr(CO)_4(H_2)_2$,¹² $Fe(CO)(NO)_2(H_2)$, and $Co(CO)_2(NO)(H_2)$.¹³ By following the change in $\nu(C-O)$ band intensities with time (over several milliseconds), it has been possible to monitor the decay kinetics of $Cr(CO)_5(H_2)$ at room temperature.¹⁴ The simplest conceivable transition-metal H_2 species would be $M(H_2)$, and it has been possible to identify from the $\nu(Pd-H_2)$ mode the species $Pd(H_2)$ obtained by cocondensing Pd atoms with H_2 -doped Kr or Xe at 12 K.¹⁵ Both sideways (η^2) and endways (η^1) species have been identified.

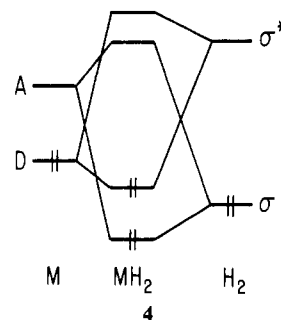
This activity suggests that many species long regarded as conventional hydrides may well be more appropriately described as dihydrogen complexes. Crabtree and Hamilton¹⁶ have argued that NMR relaxation times are sensitive to whether the hydrogen is present as **1** or **2** and have concluded that, whereas $Os(PR_3)_3H_4$ is genuinely a tetrahydride, the Fe and Ru analogues are actually $M(PR_3)_3(H_2)H_2$. In xenon solution, $Cr(CO)_5(H_2)$ exchanges with D_2 to give $Cr(CO)_5(D_2)$ but importantly there is no evidence for $Cr(CO)_5(HD)$. However, $Cr(CO)_4(H_4)_2$ exchanges with D_2 to give the scrambled species $Cr(CO)_5(HD)$ in addition to the non-scrambled species.¹² This exchange is of considerable relevance to an understanding of the interaction of H_2 with the metal center.

There has also been considerable theoretical activity¹⁷⁻²⁴ at varying levels of sophistication. The simplest interpretation of these studies is that the (H_2) structure implies a model in which there is electron donation from the filled σ H_2 molecular orbital into an empty σ orbital on the metal, partially balanced by flow from a filled π orbital on the metal into the σ^* orbitals on the H_2 as shown in **3**. This is of course reminiscent of olefin and CO



bonding to metals. The most significant point in the hydrogen

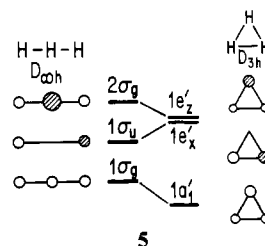
case is that, since there is no underlying supporting framework (actually σ bonding in the cases of olefin and CO), too much back-donation leads to H-H fission and the production of a dihydride MH_2 . Thus, arresting this flow by ensuring that the metal is a poor π donor may stabilize the species at the $M(H_2)$ stage. It is noteworthy that all the (H_2) compounds so far reported achieve this in some way. Three routes that appear to be operative are (i) having the metal in a positive oxidation state, (ii) having a positive metal charge via protonation, and (iii) the presence of strong π -acceptor ligands on the metal, particularly in the position trans to (H_2) . Schematically this can be represented as in **4**, where



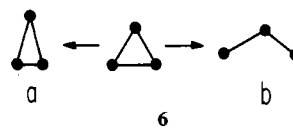
the objective is to lower the energy of D with respect to the H_2 σ^* orbital. Some subtleties have been explained in this way. Hay¹⁸ has shown how replacement of CO by PR_3 as a ligand will lead to hydride rather than (H_2) formation. This helps us understand the observation that $W(CO)_3(PR_3)_2(H_2)$ contains (H_2) but $Mo(PMe_3)_5H_2$ contains hydrides.²⁰ Of interest to us here is the examination of some of the factors that stabilize the η^2 -dihydrogen complex **1** over the dihydride, **2**, and the placement of these complexes in a broader context by making analogues with main-group and organic chemistry.

Closed vs. Open Three-Center Bonding

We can make considerable progress in understanding the stability of compounds of type **1** by using simple ideas associated with the stability of three-membered rings. A general rule is that such systems are stable if two electrons are associated with the collection of ring orbitals and unstable if there are three or four. **5** shows the orbital correlation diagram for triangular and linear



H_3 units.²⁵ The energies are written in terms of the Hückel α and β parameters. Clearly the cyclic form is Jahn-Teller unstable for the three- or four-electron case but stable for two electrons, as determined experimentally²⁶ for H_3^+ . However, H_3^- , with four electrons, is Jahn-Teller unstable in the D_{3h} structure. The Jahn-Teller-active mode is of e' symmetry, **6**, one component of



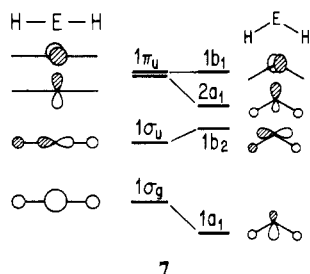
which leads to a lengthening of one side of the equilateral triangle leading eventually to a linear structure. Put simply, electron density in the $1e'_x$ orbital enhances H-H antibonding character and forces apart two of the H atoms. Irrespective of which pathway is followed the regular triangular structure is destroyed.

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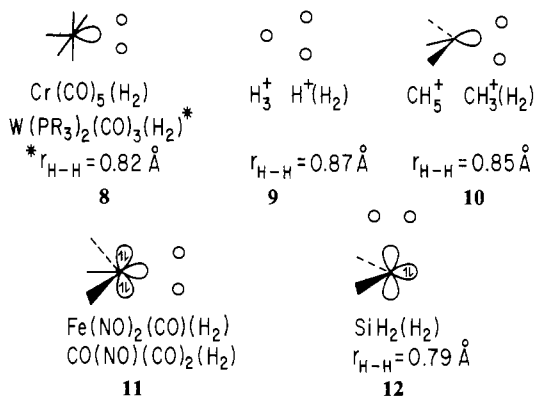
Similar results come too from consideration of Hückel's $4n + 2$ rule (the cyclic structure with two electrons, $n = 0$, is stable) or via an analysis of ring structures using the method of moments.²⁷ In a broader context closed, three-membered rings are a feature of "electron-deficient" borane chemistry and are not often found in molecules with precise electron counts.

Analogous conclusions come from the study of this orbital problem in heterorings such as the ones we will look at in this paper. These are of the type XH_2 where X is some main-group or transition-metal fragment. Here the first-order Jahn-Teller instability of the homoatomic three-membered ring is replaced by a second-order one. For example, the ground state of CH_2^+ has the configuration $(1a_1)^2(1b_2)^2(2a_1)^1$, 2A_1 , with a bond angle of around 140° . (7 shows a correlation diagram linking the levels



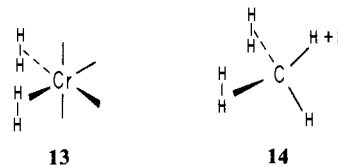
of linear and bent units.) However, in the excited state $(1a_1)^2(1b_2)^1(2a_1)^2$, 2B_2 , the reduced electron density in $1b_2$ and increased electron density in $2a_1$ will both tend to decrease H-H repulsion. In fact, Schaeffer and colleagues²⁸ have concluded from ab initio calculations that the structure of the 2B_2 state of CH_2^+ is $r(\text{C-H}) = 1.41 \text{ \AA}$, $\angle\text{HCH} = 35.2^\circ$, and $r(\text{H-H}) = 0.84 \text{ \AA}$. The latter distance is strikingly similar to that in the coordinated H_2 unit in Kubas' compound.²

Since the H_2 molecule itself will contribute two electrons to bonding, one requirement for a stable species of type 1 is that the fragment ML_x have a vacant, energetically accessible orbital that is geometrically located so as to provide a strong interaction between metal and hydrogen. Thus, instead of constructing diagrams such as that of 7 for each case, we may look at the frontier orbitals of relevant fragments and use the ideas of the isolobal analogy. Many unsaturated transition-metal organometallic fragments and main-group units automatically become candidates. 8-12 show some examples. There is great experimental and



theoretical interest in such loosely bound H_2 species, frequency called "small bond angle states". The examples in 10 and 12 show results from high-quality calculations. The CH_5^+ species²⁹ is a "mass spectrometer molecule"; the species shown in 12 lies³⁰ in a local energy minimum separating silane (the "dihydride") and separated SiH_2 and H_2 units. Similar minima are found³¹ for the

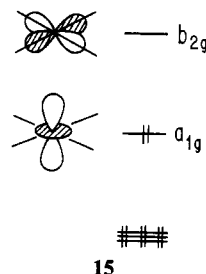
addition of H_2 and HF to the SiF_2 radical. Importantly, no such feature is found³² for similar reactions with CH_2 . The result for H_3^+ is an experimental one.²⁶ Notice that there are two different types of species represented here, those where there is only one (empty) frontier orbital located on the ML_x fragment and those where other frontier orbitals are filled with electrons.³³ Obviously, if there are two empty frontier orbitals, then the possibility exists of coordinating a second H_2 molecule. Such is the case in Crabtree's species $[\text{IrH}_2(\text{H}_2)_2(\text{PR}_3)_2]^+$ ⁵ and the recently identified $\text{Cr}(\text{CO})_4(\text{H}_2)_2$ molecule 13.^{8,12} These species are readily related



to Olah's predicted structure for CH_6^{2+} , 14. The stability of this species and its geometry have been confirmed³⁴ by accurate ab initio calculations. Our discussion emphasizes the result that in the early stages of the addition of an H_2 molecule to a molecular fragment the pathway will be the one that maximizes the overlap between the HOMO of H_2 (the σ -bonding orbital) and the LUMO of the fragment. All of the structures of the systems 8-14 show this feature. Such arguments have lain at the heart of mechanistic and structural organic and inorganic chemistry for years.²⁵

Further Use of Three-Center Model

It is interesting to see how these ideas apply to some other problems involving the reactions of dihydrogen. The classic case of the generation of a dihydride of type 2 is the oxidative addition reaction of H_2 to low-spin d^8 square-planar complexes. 15 shows



a typical orbital diagram for such ML_4 molecules. Bringing up an H_2 molecule along the z axis of such a system and parallel to the square plane will lead initially to a strong interaction between the $a_{1g} z^2/s$ hybrid orbital of the square-planar unit and the orbitals of H_2 . Since this three-orbital problem contains four electrons, the closed three-center arrangement is unstable and the eventual generation of a dihydride encouraged. Jean and Lledos²² have considered this problem in detail using the extended Hückel method and have shown that this four-electron destabilization is minimized when the H_2 lies in the plane of stronger π -acceptor ligands. Notice that the empty orbital of the molecule (b_{2g}) not only is of higher energy but also is inconveniently situated in a geometric sense for good metal-hydrogen overlap. (It is of δ type for an incoming molecule.) We can view the destabilization in another way, in terms of a two-orbital-four-electron destabilization shown in 16. Notice that formation of the dihydride, with consequent oxidation of the metal center and hence loss of the two electrons in the upper orbital, removes this problem. (As we shall see later, such four-electron destabilizations are not always a problem, as long as there are other stabilizing mechanisms in operation.)

We could also envisage coordination of H_2 in an end-on, or η^1 , fashion. For stability of such a structure, the ideas developed here

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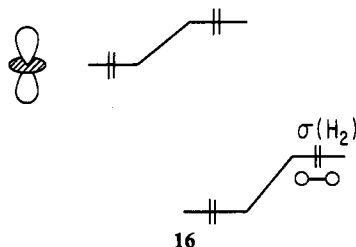
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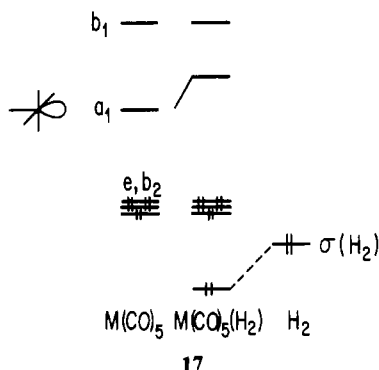
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suggest that we need a filled fragment orbital for interaction with H_2 so as to produce a four-electron-three-orbital picture. A d^8 square-planar ML_4 complex of the type described above would fit this requirement. It would have a linear $M-H-H$ unit (perpendicular to the ML_4 plane) and be isoelectronic with H_3^- . A related species has recently been made.³⁵ It consists of a PtL_4 unit attached to an I_2 molecule such that the $Pt-I-I$ fragment is linear. The electron count is such that it is isoelectronic with I_3^- . Along similar lines, an octahedral $d^8 ML_5(\eta^1-H_2)$ species might also be possible.

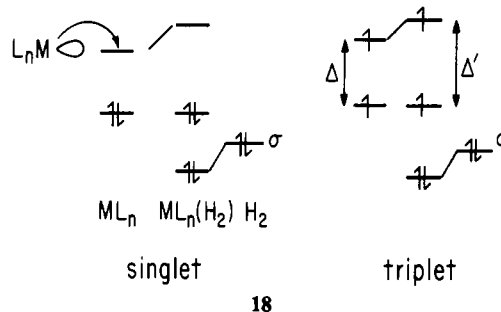
Some theoretical calculations have been performed³⁶ on the PdH_2 molecule, which has been studied experimentally in a matrix. The energy difference between η^1 and η^2 arrangements was found to be small, rationalizing the occurrence of both forms in the matrix.¹⁵ The metal-containing fragments that we have studied here are, of course, very different from an isolated atom in the sense that they have a set of frontier orbitals, well-defined both energetically and spatially. The energy difference between the two forms can be expected to be much larger here as a result. In the molecules we will study, the H_2 unit is attached in a sideways fashion as shown either by crystallographic studies of the relevant solids or via isotopic studies of the vibrational spectrum of the complex in solution.

These three-center arguments allow comment on possible rearrangement processes in the excited state. A simple orbital interaction diagram for $Cr(CO)_5(H_2)$ and the other species of 9 is shown in 17. (We have not forgotten about π bonding; we will

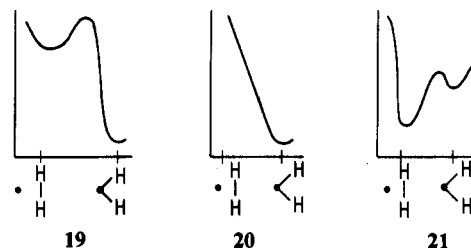


include it later.) Promotion of an electron from the metal-centered e pair of orbitals, or the b_2 orbital, to the a_1 orbital is clearly the lowest energy transition possible. For the related molecules $M(CO)_5 \cdots X$ ($M = Cr, Mo, W$; $X = Ar, Kr, Xe, CH_4$) the visible/near-UV absorption band has been assigned to the $e \rightarrow a_1$ transition by using polarized photolysis/spectroscopy.³⁷ In this series of molecules visible photolysis leads³⁸ to loss of X . H_2 loss certainly occurs on near-UV photolysis of $Cr(CO)_5(H_2)$. The instability of the three-center arrangement with three electrons can lead to similar loss of H_2 via the process in 6a. It might also be possible via the process in 6b to encourage dihydride formation on excitation, but such an event has not yet been observed.

Along similar lines, the availability of a low-lying triplet state may dramatically alter the propensity for dihydrogen complex formation. 18 shows the one-electron energy levels and their



occupancy for the singlet and triplet forms of the complex. Clearly, the singlet form could give rise to a dihydrogen complex, but the triplet form with three electrons in the three-orbital set most certainly will not. $Fe(CO)_4$ and CH_2 are a pair of isolobal species where such arguments may be appropriate. For CH_2 the triplet states lies³⁹ lower in energy than the singlet by about 0.47 eV. $Fe(CO)_4$ is an unusual carbonyl molecule in that it exists as triplet in its ground electronic state, as shown by MCD studies.⁴⁰ As mentioned above, theoretical studies³² on the addition of H_2 to CH_2 show no evidence for the formation of a species akin to 12. We note that, in contrast, for SiH_2 the singlet lies lower³⁹ in energy than the triplet by about 0.8 eV. Experimental studies on the addition of H_2 to $Fe(CO)_4$ in low-temperature matrices⁴¹ show only the formation of the dihydride (the well-known molecule $Fe(CO)_4H_2$) and no evidence for the formation of a dihydrogen complex. Since these experiments are carried out at extremely low temperature, any local well at the dihydrogen complex geometry must be either tiny or nonexistent. We describe later in this paper another effect that may also stabilize the dihydride over the dihydrogen complex for this species. 19-21 show three types



of potential surface for the reaction of H_2 with a suitable fragment. 19 describes the case applicable to species 12, where the dihydrogen complex exists in a local minimum. However, even though predicted by high-level theory, the species $SiH_2(H_2)$ was not detected in a matrix experiment.⁴² 20 represents the barrierless case as found for CH_2 and H_2 , and perhaps too (vide infra) for $Fe(CO)_4$ and H_2 . 21 corresponds to the situation where the dihydrogen complex lies lowest in the energy. In the next section we will examine how this state of affairs is controlled by the electronic nature of the fragment.

We know that Δ in 18 is smaller than the pairing energy in the $Fe(CO)_4$ molecule since the triplet is the lower energy structure, but whether Δ' is large enough to stabilize a dihydrogen complex in a thermodynamic sense is a question that is extremely difficult to answer. The molecules $Fe(CO)_4Q$ ($Q = CH_4, Xe$), which have been studied⁴³ in low-temperature matrices and show a trigonal-bipyramidal geometry with an equatorial substituent, may well exist as singlets. The X group here behaves as a rather weak donor. This observation does not therefore exclude a dihydrogen

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(37) Burdett, J. K.; Perutz, R. N.; Poliakov, M.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1975**, 157.

(38) Burdett, J. K.; Gryzbowski, J. M.; Perutz, R. N.; Poliakov, M.; Turner, J. J.; Turner, R. F. *Inorg. Chem.* **1978**, *17*, 147.

(39) For example, see: Salem, L. *Electrons in Chemical Reactions*; Wiley: New York, 1984.

(40) Barton, T. J.; Grinter, R.; Thomson, A. J.; Davies, B.; Poliakov, M. *J. Chem. Soc., Chem. Commun.* **1977**, 841.

(41) Sweany, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 2410.

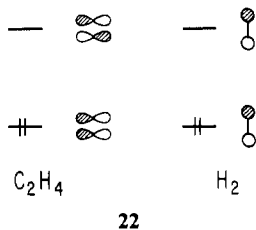
(42) Fredin, L.; Hauge, R. H.; Kafafi, Z. H.; Margrave, J. L. *J. Chem. Phys.* **1985**, *82*, 3542.

(43) Poliakov, M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1974**, 2276.

complex as a viable alternative to the known dihydride. It is possible that the very fluxional nature of the molecule actually samples a part of the space we would call a dihydrogen complex.

Involvement of the $\sigma^*(\text{H}_2)$ Orbital

The analogy between the binding of ethylene and of H_2 as dihydrogen was made soon after the discovery of these nonclassical hydrogen-containing complexes. **22** shows an orbital diagram.



For the case of coordinated ethylene, the metal-carbon σ bonds are strengthened at the expense of π bonding between the two carbon atoms as a result of the mixing of ligand acceptor orbital character into a suitable orbital on the metal. This will be one of the "t_{2g}" set in the $\text{Cr}(\text{CO})_5$ case and one of the other frontier orbitals in the three- or four-coordinate fragments ML_3 and ML_4 , respectively. For the case of dihydrogen, extensive back-bonding, while stabilizing the system as a whole, will result in splitting of the H-H linkage and formation of the dihydride. Stability of the dihydrogen complex **1**, relative to the dihydride **2**, can therefore be encouraged by ensuring that the metal-containing fragment is a poor π donor, as mentioned above. Increasing the oxidation state or the presence of a positive charge will depress the metal-centered levels so that interaction with $\sigma^*(\text{H}_2)$ is reduced. Recall the large and classic variation in CO stretching frequency in the isoelectronic series $\text{V}(\text{CO})_6^-$, $\text{Cr}(\text{CO})_6$, and $\text{Mn}(\text{CO})_6^+$ as a result of the different charge on the metal atoms. Coordination of good π -acceptor ligands will have a similar effect, but via delocalization will also reduce the metal character in orbital D of **4** and hence lower the energy of interaction.

That π interaction is important can be inferred from both UV/vis data and $\nu(\text{CO})$ vibrational frequencies, as pointed out by both Sweany and Andrea et al.⁴⁴ The visible band of $\text{Cr}(\text{CO})_5\text{H}_2$ is at 364 nm in an argon matrix⁸ and at 370 nm in liquid xenon.¹¹ These values are to shorter wavelengths than those for pure σ ligands and in fact are almost identical with that found for $\text{Cr}(\text{CO})_5\text{N}_2$ (365 nm).⁴⁵ The position of the $\nu(\text{CO})$ bands of $\text{M}(\text{CO})_5\text{L}$ species are sensitive in general to the nature of L.⁴⁶ It has been pointed out previously¹¹ that the $\nu(\text{CO})$ bands of $\text{Cr}(\text{CO})_5\text{H}_2$ are close in frequency to those of $\text{Cr}(\text{CO})_5\text{N}_2$ and the force constants are correspondingly similar. By analogy with N_2 , H_2 is both a σ donor and a π acceptor. We do not feel that a numerical quantification is justified, given the nature of the data and the pitfalls associated with detailed interpretation of CO force constants.

23 shows the results of calculations on some 18-electron carbonyl dihydrogen complexes and their substituted nitrosyl analogues.

Computed H-H bond overlap populations (bop) and extent of involvement of the H_2 σ and σ^* orbitals in metal-hydrogen bonding for some $\text{M}(\text{H}_2)$ complexes

bop	0.57	0.57	0.54	0.54	0.57	0.57	0.58
σ	1.85	1.79	1.81	1.81	1.85	1.84	1.82
σ^*	0.11	0.09	0.15	0.12	0.11	0.10	0.08

23

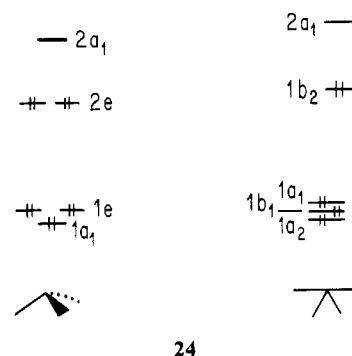
In all of these species the dihydrogen is coordinated in an η^2 fashion. Notice how the population of $\sigma^*(\text{H}_2)$ in the complex is

influenced by the presence of the better π acceptor (nitrosyl) coordinated to the metal. Recently Jean²³ has reached similar conclusions on the effect of NO as a ligand.

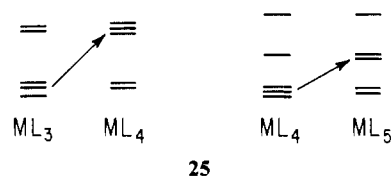
Electronic Structure of Pyramidal d^{10} $\text{ML}_3(\text{H}_2)$ and Butterfly d^8 $\text{ML}_4(\text{H}_2)$ Complexes

Except for the matrix evidence¹⁰ for $\text{Ni}(\text{CO})_3(\text{H}_2)$ and the characterization in liquid xenon¹³ of $\text{Fe}(\text{CO})(\text{NO})_2(\text{H}_2)$ and $\text{Co}(\text{CO})_2(\text{NO})(\text{H}_2)$, most of the reported (H_2) species are nominally d^6 . We have already commented on the reasons behind hydride rather than dihydrogen complex formation at d^8 square-planar centers. Here we examine the possibilities for a butterfly d^8 species and pyramidal three-coordinate, d^{10} fragments. As we have noted above, for the two well-characterized molecules with an $\{\text{MNO}\}^{10}$ configuration (recall that this notation contains as a superscript the number of metal "d" electrons plus the electrons associated with the NO π^* level) a part of the explanation¹³ must lie in the strong π -acceptor nature of the NO ligand, which lowers the π -donor capability of the metal toward the H_2 ligand. This effect is seen in calculations on some 18-electron carbonyl dihydrogen complexes and their substituted nitrosyl analogues as shown in **23**.

We now describe these calculations in more detail. As examples of species that illustrate some of the points we have made above, but which in detail are more complex, we derive here the orbital interaction diagram between H_2 and trigonal-pyramidal ML_3 d^{10} and butterfly ML_4 d^8 units. The frontier orbitals of the pyramidal ML_3 and butterfly ML_4 fragments are well-known and are shown in **24** for the relevant d^n (or $\{\text{MNO}\}^n$) configuration. The vacant



a_1 orbitals in this simple picture are the empty orbitals responsible for the coordination of dihydrogen in **11** and the, as yet unknown, ML_4 analogue. There is however another effect that is important. In contrast to the situation in **17** for the formation of $\text{Cr}(\text{CO})_5(\text{H}_2)$, in these species one of the occupied orbitals of **24** is also raised in energy on formation of $\text{ML}_{3,4}(\text{H}_2)$. This is easy to see in **25**,



where we show the movement of the d orbitals on going from pyramidal ML_3 to tetrahedral ML_4 ($\text{Ni}(\text{CO})_4$ is an example here) and on going from butterfly ML_4 to trigonal-bipyramidal ML_5 ($\text{Fe}(\text{CO})_5$ is an example). In $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_4$ such a destabilization is offset by the stabilization of the orbital that is largely a lone pair on the entering CO and by π back-bonding with the π^* levels of the same unit. In these H_2 complexes recall that we do not wish to encourage extensive back-bonding.

Figure 1 shows molecular orbital diagrams for the coordination of H_2 to give dihydrogen complexes with these fragments. (Details of the computations are given in the Appendix.) The degeneracy of the levels of **24** and **25** has been removed as a result of the loss of symmetry on coordination of the ligand, but the general picture is clear. Two metal fragment centered levels of a_1 symmetry are destabilized. The higher energy orbital is associated with the larger movement, is empty, and represents the donor-acceptor interaction

(44) Andréa, R. R.; Vuurman, M. A.; Stufkens, D. J.; Oskam, A. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 372.

(45) Turner, J. J.; Simpson, M. B.; Poliakoff, M.; Maier, W. B.; Graham, M. A. *Inorg. Chem.* **1983**, *22*, 911.

(46) Dobson, G. R.; Brown, R. A. *Inorg. Chim. Acta* **1972**, *6*, 65.

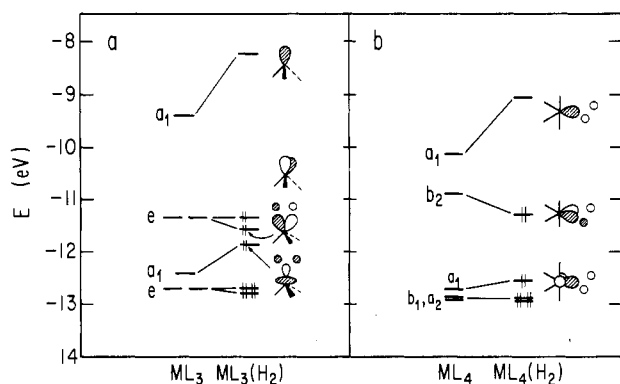


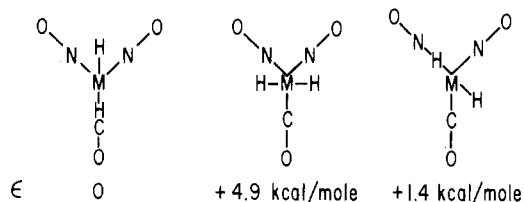
Figure 1. Results of molecular orbital calculations on (a) $ML_3(H_2)$ and (b) $ML_4(H_2)$ complexes showing their assembly from fragments.

with the H_2 molecule. The lower energy one is associated with a four-electron-two-center repulsion. There is also a stabilization of two of the occupied d orbitals in ML_3 and one in ML_4 as a result of π back-bonding with $\sigma^*(H_2)$. The larger interaction occurs with the HOMO, of the metal-containing fragment, one component of the e pair and the b_2 orbital in ML_3 and ML_4 , respectively. Such back-bonding is calculated to be much more important energetically than that occurring on coordination of H_2 to $Cr(CO)_5$. Here (17) there is no strategically located orbital to provide such an interaction, but simply one of the "t_{2g}" orbitals. We find numerically that this interaction in ML_5 is comparable to the weaker of the two interactions in ML_3 . It would clearly be nice to be able to calculate a critical π -back-donation parameter that would give rise to H-H bond fission. This is not a worthwhile numerical exercise at present.

Coordination of H_2 to either of these units as a dihydrogen complex could therefore be unfavorable unless both the superlative π -donor nature of the ML_n units and the four-electron repulsion are moderated. Substitution of CO by NO is one way to do this. The nitrosyl ligand is a better π acceptor than CO and will reduce the weight of the d-orbital contribution to the metal valence orbitals. Our calculations show that for $M(XO)_3$ the coefficient of z^2 in the lower energy a_1 orbital has been reduced from 0.90 ($X = C$) to 0.78 ($X = N$). Substitution of CO by NO reduces both of the unfavorable interactions described above. The π -acceptor stabilization has dropped from 0.32 to 0.22 eV, and the destabilization of the a_1 orbital has been dramatically reduced from 0.52 to 0.31 eV. Overall then, there has been a gain in stabilization energy of around 0.2 eV. Interestingly, there is only evidence for the species $Ni(CO)_3H_2$ from matrix isolation spectroscopy.¹⁰ It will be interesting to see whether this molecule may be made under less extreme conditions and how its stability compares with that of one of the $\{MNO\}$ ¹⁰ nitrosyl-containing examples known from liquid-xenon studies.

Similar results are found for the ML_4 case. Replacement of an equatorial CO by NO for example leads to a reduction of the stabilization of the HOMO by 0.08 eV and of the destabilization of the occupied metal a_1 orbital by 0.03 eV. These effects show up nicely in the computed populations of $\sigma(H_2)$ and $\sigma^*(H_2)$ shown in 23. Notice that the lowest H-H populations are associated with the molecules with the larger contributions from $\sigma^*(H_2)$.

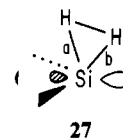
26 shows the calculated energy differences between the most stable conformer and two other possibilities for the molecule $Fe(NO)_2(CO)(H_2)$. Notice that the H_2 molecule has a quite



26

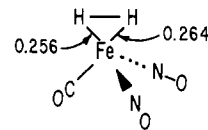
strong energetic preference to lie in the same plane as the CO

ligand, a direct result of the stronger π -acceptor nature of the NO ligand. An exactly analogous effect has been observed¹ and described theoretically^{18,27} in the structure of $W(CO)_3(PR_3)_2(H_2)$, where the H_2 molecule lies along the PWP axis. Notice that there is a similar orientational preference for the coordinated dihydrogen in the molecule 12. The H_2 unit is oriented so that there is maximal overlap with the HOMO (the "lone pair" of 12) shown in 27. The H_2 molecule is even tilted to maximize the overlap



27

with the larger lobe of the hybrid. The distances are calculated to be $a = 1.86 \text{ \AA}$ and $b = 1.79 \text{ \AA}$. Along similar lines we would predict from the overlap populations in 28 that in $Fe(NO)_2(C-$



28

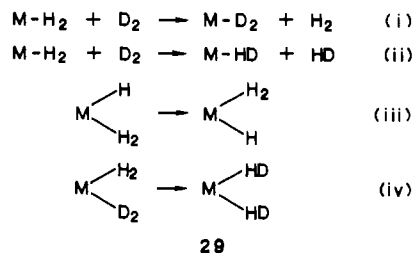
$O)(H_2)$ the molecule should be slipped toward the NO ligands.

Dihydrogen Complexes Containing More Than One Coordinated H_2 Unit

The compound $[IrH_2(H_2)_2(PCy_3)_2]^+$ has been isolated,⁵ and there is both matrix⁸ and liquid-xenon-solution¹² evidence for $Cr(CO)_4(H_2)_2$. By analogy with the many $[IrH_2S_2(PR_3)_2]^+$ complexes that are known, it is suggested^{5a} that in the bis (H_2)₂ iridium complex the two (H_2) units are cis with respect to each other. There is stronger evidence¹² for the structure of $Cr(CO)_4(H_2)_2$ from the $\nu(C-O)$ band pattern, which clearly distinguishes the cis from the possible trans structure. It has not been possible, however, to identify the conformation of the (H_2) units from the vibrations of these ligands. Our calculations on this species show a small orientational effect with 13 being the lowest energy structure. We find an energy difference of 0.7 kcal/mol between 13 and the structure where one H_2 molecule has been rotated by 90° about the line joining its midpoint to the metal. The energetic availability of other geometries for the four hydrogen atoms in this molecule is of interest in the light of increasing evidence of exchange in (H_2) species, a topic to which we now turn.

Exchange in Dihydrogen Species of Transition Metals

Exchange can be of several different sorts, as shown in 29. Type i is simply the replacement of an (H_2) unit by (D_2). Many of



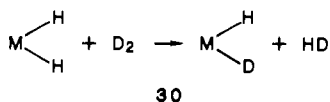
29

the (H_2) species are only stable under an atmosphere of H_2 , which indicates low-energy pathways for exchange. More direct evidence is the H_2/D_2 exchange in Kubas' original compound⁴⁷ and is also demonstrated for $Cr(CO)_5(H_2)$ even in liquid xenon at $-70^\circ C$ over 3 h.¹³

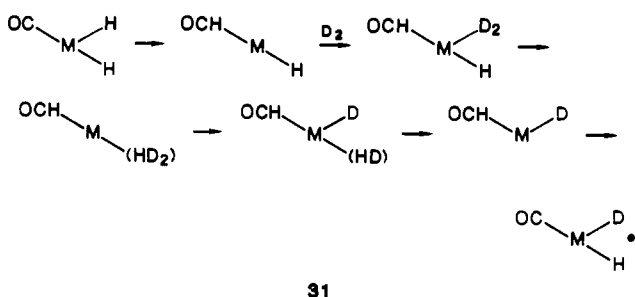
The only published evidence for type ii exchange also comes from experiments on Kubas' compound.^{3,47} Isotope exchange occurs between $W(CO)_3(PR_3)_2(H_2)$ and D_2 in both solution and solid state at $20^\circ C$, giving within a few days a statistical mixture

(47) Kubas, G. J.; Unkefer, C. J.; Swanson, B. I.; Fukushima, E. *J. Am. Chem. Soc.* 1986, 108, 7000.

of H₂, HD, and D₂ species. This exchange does not involve the phosphine ligands, which therefore precludes a mechanism in which both H₂ and D₂ are coordinated to two empty coordination sites (but see later for Cr(CO)₄(H₂)₂). Very significantly NMR and IR evidence³ suggests that room-temperature solutions of W(CO)₃(P-*i*-Pr)₂(H₂) contain some 15–20% of a hydridic species, presumably the seven-coordinate W(CO)₃(P-*i*-Pr)₂(H)₂. On the other hand, there was no spectral evidence for any M–H linkage in solutions of Mo(CO)(dppe)₂(H₂) and no evidence was presented for isotopic scrambling. Similarly,¹² liquid-xenon solutions of Cr(CO)₅(H₂) give no evidence for Cr(CO)₅(H)₂. Also in the presence of added D₂ only, the only species observed are Cr(CO)₅(H₂) and Cr(CO)₅(D₂), with no evidence for any Cr(CO)₅-(HD). These results suggest that type ii exchange involves fission of the H–H bond to give a hydridic species as an intermediate. It is thus promoted by ligands that are less electron withdrawing than CO (see above). It is still not clear how the step in **30** occurs

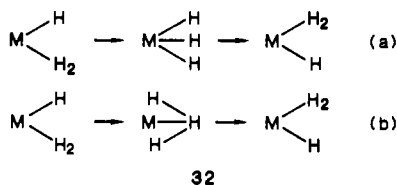


without access to another coordination site. One possibility would involve an intermediate containing a coordinated trihydrogen species as in the mechanism of **31**. This mechanism also involves



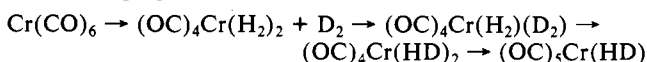
formation of a formyl species. The other obvious mechanism is loss of H as proton and exchange of this proton with D₂ in solution before recoordination of the deuteron. The scrambling of hydrogen and deuterium in the trihydrogen unit may occur independent of the geometry (linear or triangular) of the fragment. Below we will comment more on the electronic structure of such coordinated units.

The importance of the role of hydride ligands is well demonstrated for type iii exchange. New observations on species that contain both hydride and (H₂) (i.e., Fe(H)(H₂)-(PPh₂CH₂CH₂PPh₂)₂⁺⁶ and [Ir(H)(H₂)(bq)L₂]⁺⁴) prove that rapid scrambling takes place. Crabtree^{4,5} has suggested two ways in which such an exchange might occur, **32**. Path a involves



oxidative addition and, in view of Kubas³ observations on W(CO)₃(PR₃)₂(H₂), might be expected (but see below); path b involves proton transfer, promoted by the acidic nature of the H₂ ligand. As Crabtree points out,⁵ an intermediate involving an H₃ unit (either open or closed) as in **32** cannot be excluded, a point to which we shall return later. Of course there is always the possibility, which cannot be discounted, that some of these observations concerning the generation of HD arise because of trace amounts of water.

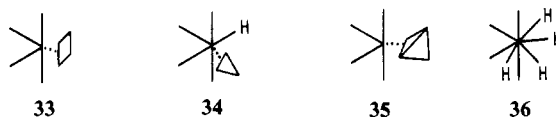
The evidence for type iv exchange comes from the liquid-xenon experiments on Cr(CO)₆/H₂ species. It should be emphasized that in the proposed scheme¹²



the scrambled species Cr(CO)₄(HD)₂ is inferred and not positively identified. However, no scrambling occurs with Cr(CO)₅(H₂)/D₂ (see above), and a possible implication of this is that for Cr(CO)₄(H₂)₂ scrambling only occurs when both H₂ and D₂ are coordinated to the metal. We will examine theoretically some of the structures geometrically feasible for the case of four hydrogen atoms, in order to cast some light on these various possibilities.

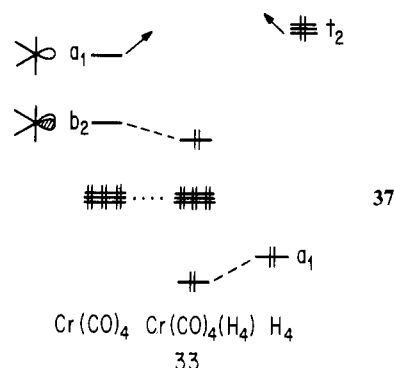
Polyhydrogen Structures

We will begin by looking at some species that could be intermediates for the scrambling reaction in Cr(CO)₄(H₂)₂, on the basis that the mechanism has to be consistent with the lack of observation of a similar reaction in Cr(CO)₅(H₂). We shall exclude intermolecular processes such as that which could arise via attack of a hydride on coordinated (H₂), since these will not be likely in the liquid-xenon medium, which was used for the experimental studies. Some possible intermediates containing four hydrogen atoms are shown in **33–36**. There are clearly orientational isomers

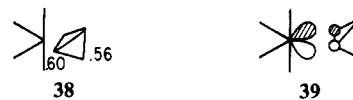


for all of them. Three of them contain polyhydrogen units. Although such clusters of atoms H_n⁺ are known⁴⁸ up to quite large *n* in the mass spectrometer and have received some theoretical attention,⁴⁹ Here we suggest their use as potential ligands. At the level of theory used in this paper we will not be able to accurately rank the species **33–35** energetically, but we will be able to comment on their structural stability by making analogies with polyene chemistry, as we have earlier in this paper, and by making use of simple ideas of electron counting.

33, of interest because of the existence^{50,51} of similar compounds with coordinated P₄, is readily dismissed. The H₄ tetrahedron requires a total of two electrons for stability, and generation of a molecule containing such a coordinated unit places two electrons in a high-energy metal located orbital (**37**). **38** shows our cal-



culated charge distribution, which is in accord with these ideas. (Notice that the electron-counting rules for these polyhydrogen systems are different from Wade's rules. Only one radial orbital per site is present.) There is an orientational preference for the conformation of **33** via overlap of one component of the H₄ t₂ orbital with the Cr(CO)₄ b₂ orbital, as shown in **39**. This



stereoelectronic control is identical with the mechanism that controls the orientational preference of the olefin in Fe(CO)₄-

(48) Clampitt, R.; Gowland, L. *Nature (London)* **1969**, 223, 815.

(49) Yamaguchi, Y.; Gaw, J. F.; Schaefer, H. F. *J. Chem. Phys.* **1983**, 78, 4074.

(50) Lindsell, W. E.; McCullough, K. J.; Welch, A. J. *J. Am. Chem. Soc.* **1983**, 105, 4487.

(51) These P₄ complexes have been analyzed in theoretical terms by: Kang, S. K.; Albright, T. A.; Silvestre, J. *Croat. Chem. Acta* **1984**, 57, 1355.

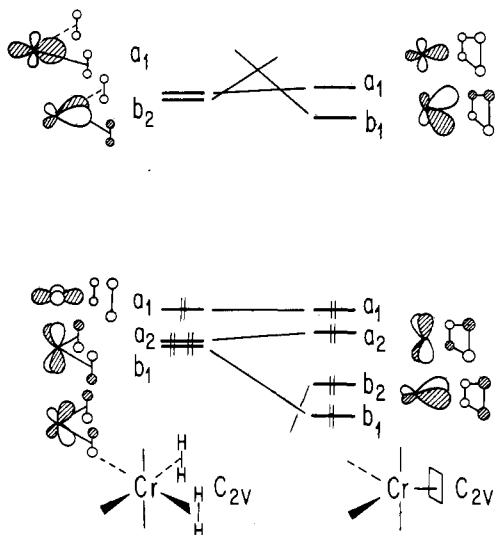
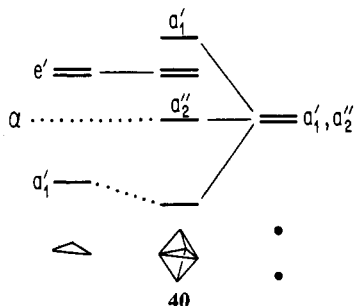


Figure 2. Results of molecular orbital calculations showing the symmetry-allowed nature of the interconversion of the bis(dihydrogen) and square tetrahydrogen complexes of d^6 $\text{Cr}(\text{CO})_4$.

(olefin) complexes⁵² and of course in the analogous dihydrogen complex of the previous section. There are similar problems for the coordination of the tetrahedron via a face. The trigonal-bipyramidal unit so formed (with the metal at one of the axial vertices) has one bonding and one nonbonding orbital. (40 shows



the assembly of the molecular orbital diagram for an H_5 unit from those of smaller fragments.) Two pairs of electrons occupy these orbitals in the tetrahydrogen complex. One pair has clearly been moved from a deep-lying MH bonding level in the bis(dihydrogen) complex to a higher energy level in the tetrahydrogen molecule. (We note that the most stable conformation calculated⁴⁹ for H_5^+ , a "mass spectrometer molecule", is one where an H_2 moiety is coordinated to one H atom of H_3 , thus generating a distorted "spiropentahydrogen".)

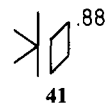
34 and **35** are much more serious contenders for a low-lying geometrical alternative to the bis(dihydrogen) complex. H/D exchange is symmetry allowed for pathways involving either species. Figure 2 shows a calculated orbital correlation diagram for the pathway via the square. H/D exchange may occur in geometrical terms via making and breaking perpendicular linkages of the coordinated unit. If H_2 is analogous to ethylene, then square H_4 and triangular H_3 are analogous to cyclobutadiene and cyclopropenium, respectively, two ligands with well-established transition-metal chemistry.

However, there are quite clear indications that, although there is nothing wrong with species **34** from the point of view of the formal application of the 18-electron rule, this species will not be particularly stable. Elian and Hoffmann³³ have analyzed this problem in some detail for the case of coordinated cyclobutadiene. Their arguments are eloquently detailed elsewhere and are similar to the ones extracted from an analysis of our own computations on the tetrahydrogen problem. By a comparison of the interaction

Table I. Calculated Energy Differences between Tetrahydrogen Complexes

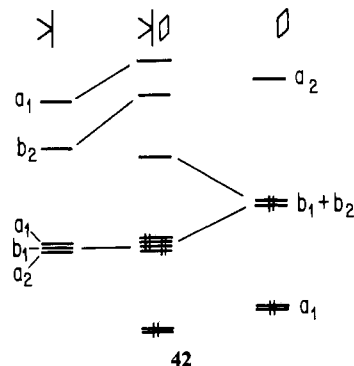
structure	molecule	energy, eV
13	$\text{Cr}(\text{CO})_4(\text{H}_2)_2$	0
33	$\text{Cr}(\text{CO})_4(\text{H}_4)$	6.94
34	$\text{Cr}(\text{CO})_4(\text{H}_4)$	3.73
35	$\text{Cr}(\text{CO})_4(\text{H}_3)\text{H}$	1.51
47	$\text{Cr}(\text{CO})_4(\text{H}_3)\text{H}$	0.97
36	$\text{Cr}(\text{CO})_4\text{H}_4$	1.55
51	$\text{Cr}(\text{CO})_4(\text{H}_4)$	0.72

of the orbitals of a single C_4H_4 molecule or two ethylene moieties with the orbitals of the isolobal fragments $\text{Fe}(\text{CO})_3$ and $\text{Cr}(\text{CO})_4$, it is clear why the former species prefers to interact with a conjugated four-electron donor (such as cyclobutadiene) but the latter with two isolated (unconjugated) double bonds. It comes about via the relative energies of the π levels of the C_nH_n units and their interaction with the frontier orbitals on the metal. There is experimental evidence, in addition to the relative abundance of examples of the two sorts of species (both sorts are known for $\text{Cr}(\text{CO})_4$), to support such a proposition. It includes the observation^{53,54} that whereas $\text{Fe}(\text{CO})_5$ catalyzes the isomerization of nonconjugated 1,5-cyclooctadienes to their conjugated 1,3-analogues, the converse is true for the corresponding reactions involving $\text{Mo}(\text{CO})_4$ and $\text{W}(\text{CO})_4$ fragments. A part of the explanation for the striking difference lies in the direction of the charge transfer between metal and ligand in the two species. Whereas in $\text{Fe}(\text{CO})_5\text{C}_4\text{H}_4$ the organic ligand is well represented as $\text{C}_4\text{H}_4^{2-}$, in the $\text{Cr}(\text{CO})_4$ analogue charge transfer occurs in the opposite direction, namely from ligand to metal. Exactly the same result is found for the tetrahydrogen complex **41** shows a population



analysis of the molecular orbital results of a calculation on a complex with the geometry **34**. The coordinated ligand is adequately represented as $\text{H}_4^{0.5+}$, indicating charge transfer to the metal.

Although according to Hückel's rule the ligand should be stable irrespective of the direction of charge transfer, i.e. $\text{C}_4\text{H}_4^{2-}$ or $\text{C}_4\text{H}_4^{2+}$, donation to the metal results in population of high-energy orbitals. The region of the molecular orbital diagram where the octahedral " t_{2g} " levels are found consists of a group of four occupied levels (see **42** and **43**), whereas that for the bis(dihydrogen)



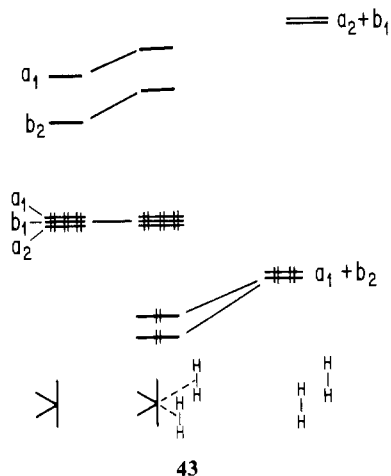
complex only contains three such levels. Clearly in **42** a characteristic feature of the levels of square H_4 is a pair of degenerate levels ($E = \alpha$) lying close to the metal " t_{2g} " set ($a_1 + a_2 + b_1$). Both components ($b_1 + b_2$) may interact with the relevant orbitals on the metal tetracarbonyl fragment, leading to a package of orbitals ($a_1 + a_2 + b_1 + b_2$) in the " t_{2g} " region. The level of b_2 symmetry is of high energy here because of the large contribution

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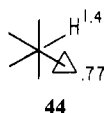
(52) Hoffmann, R.; Albright, T. A.; Thorn, D. L. *Pure Appl. Chem.* **1978**, *50*, 1.



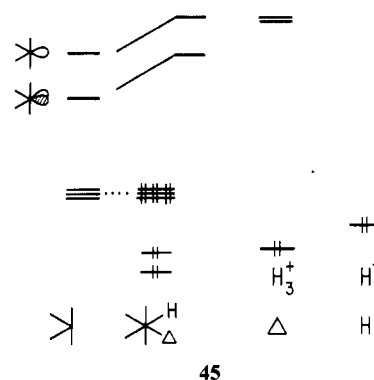
from the nonbonding H_4 level of the free ligand. Electrons have to occupy high-energy orbitals in the tetrahydrogen-containing species rather than low-energy ones in the bis(dihydrogen) molecule (43), and so the relative instability of the former molecule is understandable. The energy differences we report in Table I are certainly not realistic, but because of this reasoning we feel that the pathway via a square tetrahydrogen geometry is energetically unlikely.

Of course, a species that could lead to H/D exchange via one of the processes described earlier, and contains no novel coordinated H_n units, is the conventional tetrahydride 36. Just as we noted the competition between a dihydrogen complex and a dihydride earlier, so will there be a similar competition here. As a general rule of thumb, reduction of the interaction of antibonding (H_n) levels with the metal center, by ensuring the coordination of good π acceptors will similarly encourage stability of the polyhydrogen compound relative to the polyhydride.⁵⁶ Our calculations are not at all good enough to determine numerically the relative thermodynamic stabilities of MH_n and $M(H_n)$ possibilities. The theoretical model is not at all reliable in these linkage isomerization problems where bonds are made and broken. For comparison, however, the energy of 36 is shown in Table I along with the other values. Recent *ab initio* calculations⁵⁷ on the hypothetical species CrH_6 show that a distorted trigonal-prismatic geometry of the hydridic type is the electronic ground state. Such calculations are difficult to do, and to produce reliable results is not a simple matter.

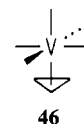
The view of the molecule 35 as containing a coordinated hydride (H^-) and a triangular H_3^+ entity is supported by the results of a population analysis shown in 44. Both hydride and H_3^+ are



two-electron-donor ligands that readily satisfy an 18-electron count at the metal. 45 shows a molecular orbital diagram for this species. It is apparent that in contrast to the picture for the tetrahydrogen species 34, the orbital structure of the complex does not result in the population of high-energy metal-centered orbitals. The energy of this species relative to the bis(dihydrogen) molecule is shown in Table I and is a low-energy structural alternative. (Parenthetically we note that the geometry of the hydrogen atoms in $Cr(CO)_4(H_2)_2$ has yet to be pinned down. There is always a chance that in fact structure 35 might actually be the ground state.) Notice that the metal- H_3 part of the interaction is isolobal with that of the H_4 tetrahedron and overall needs two electrons for stability. We could speculate on the existence of other



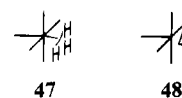
molecules that would satisfy this rule. 46 shows the predicted



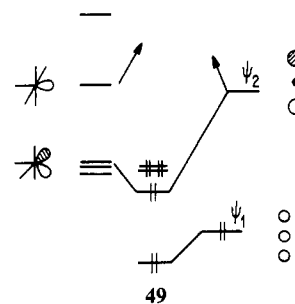
structure for $V(CO)_5(H_3)$, where two electrons are provided by the H_3 unit and the vacant frontier orbital on the metal. In the light of our comments concerning the stability of the $Ni(CO)_3(H_2)$ species earlier, a better example might be an isoelectronic species containing one or more nitrosyl groups. We could also imagine species where more than one H atom site has been replaced by a metal-containing fragment. We investigate the electronic links between these species elsewhere.⁵⁶

Polyhydrogen Species: Open vs. Closed Geometries

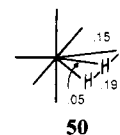
As mentioned above, Crabtree^{5a} has suggested the possibility of a coordinated H_3 unit as an intermediate in the H/ H_2 exchange in $[Ir(H)(H_2)qL_2]^{2+}$. Here we examine the stability of open (47) vs. closed (48) coordinated H_3 units. Either, on geometrical



grounds, can allow scrambling of the type shown in 31. The possibility of a triangular unit follows, as we have described above, from the presence of a single empty frontier orbital on the metal-containing fragment, which can make the species isoelectronic with H_4^{2+} . However, there are other occupied metal orbitals that may also be important. 49 shows a molecular orbital diagram



for the hypothetical species $Cr(CO)_5(H_3)^+$ with a coordinated open H_3 molecule. Here the nonbonding level of the ligand (5) interacts with one of the " t_{2g} " levels of the metal fragment, giving rise to a strong stabilization. The charges on this open unit (50) are only



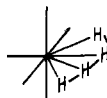
a little different from those of the closed one (48). There has not therefore been very much back-donation to the ligand. There is, however, an orientational preference for the H_3 fragment that has exactly the same origin as that in coordinated H_2 itself. We

(56) Burdett, J. K.; Pourian, M. R. *Organometallics*, in press.

(57) Sweany, R. L. *Abstracts of Papers*, 190th National Meeting of the American Chemical Society, Chicago, IL; American Chemical Society: Washington, DC, 1985.

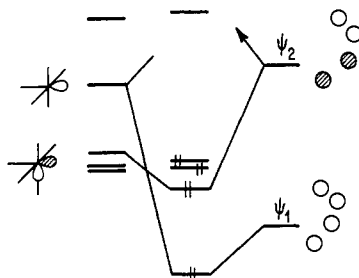
calculate a barrier of about 2 kcal/mol for rotation about the axis linking the metal and the central hydrogen atom of the ligand. Since this orbital is σ nonbonding, such back-donation does not result in weakening of the H-H bonds. The computed H-H bond overlap populations are a little larger than for the cyclic system and indicate stronger bonds to the end atoms of the unit than to the central ones, a result directly traceable to the two interactions in **49**. Our calculations place this isomer at a lower energy than that of the closed trihydrogen species. Table I shows numerical results for the analogous isomers for the species $\text{Cr}(\text{CO})_4\text{H}(\text{H}_3)$, where the orbital picture is very similar to that of **47**. We need to be a little careful in relying heavily on these numerical results since the species **47** and **48** have different coordination numbers, but our conclusion is clearly that both species represent possible rearrangement pathways leading to H/D scrambling. From the qualitative form of the orbital diagrams it is clear that there are occupied low-energy orbitals in both cases. This is in contrast to the result shown in **42** for the species **34**. We have performed similar calculations for the $\text{Co}(\text{CO})_3(\text{H}_3)$ species with analogous results.⁵⁶ There is a preliminary report of such a species⁵⁷ but as yet no definitive publication.

This result leads us to ask a similar question concerning the open form of **34**, namely **51**. In contrast to possible H/D ex-



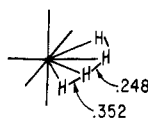
51

change via **34**, there is no obvious geometrical process that could lead to $\text{Cr}(\text{CO})_4(\text{HD})_2$ from $\text{Cr}(\text{CO})_4(\text{H}_2)(\text{D}_2)$ solely via a geometry of this type. However, **52** shows the assembly of an orbital



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diagram for this molecule. A prominent feature in the strong interaction of the $\text{M}(\text{CO})_4 b_2$ orbital with the orbital Ψ_2 of the open tetrahydrogen. (This species is analogous to butadiene of course.) The large interaction arises via a good overlap match and small energy separation of the fragment orbitals. It also provides a strong orientational effect on the ligand coordination, just as described earlier for **33**. As a result, this species is the second lowest energy structure in Table I. **53** shows the computed



53

bond overlap populations for the species, compared with those of the free H_4 unit. Notice the weaker central linkage compared to the outer ones for the coordinated molecule, suggesting that the molecule could distort to one containing two dihydrogen species, i.e. **13**.

Conclusions

We have emphasized in this paper some electronic considerations that may be important in stabilizing dihydrogen and polyhydrogen ligands when coordinated to a transition-metal center. In all cases there is competition between hydride and polyhydrogen complex formation, which appears to influence quite strongly the possible mechanisms for isotopic exchange. In the first part of the paper we stressed the relationship of these $\text{M}(\text{H}_2)$ complexes to some main-group and organic molecules. This was not possible in the context of polyhydrogen complexes since the number of analogues is somewhat restricted. In addition, rearrangement of the hydrogen atoms in such systems is an area that has received virtually no attention. Another competing arrangement for the polyhydrogen units is between open and closed forms. Our results suggest that there are several structures that may be of quite low energy for these unusual molecules but that our theoretical method is not competent to handle. High-quality computations on the CrH_6 molecule show⁵⁸ an interesting series of local minima. The problems discussed in this paper are of the linkage isomerism type, and do require sophisticated theoretical methods for their numerical investigation. In this sense they are similar to the agostic hydrogen and carbene/metallacyclobutane problems of the organometallic chemist, where good calculations are difficult but qualitative ideas useful. In this light we do not feel that it is useful to mimic the barriers separating hydride and dihydrogen complex geometries of **19-21**. One-electron calculations of the type used in this paper are not at all reliable in accurately reproducing energetic features of this type. Experimental effort that could lead to the isolation of a molecule containing a coordinated H_3 moiety is clearly an important step in further understanding of this area.

Acknowledgment. This research was made possible by a grant from NATO. The computational studies were supported by NSF Grant DGR 8414175. We thank Gordon Miller for his help and hospitality.

Appendix

The molecular orbital calculations were of the extended Hückel type. Geometrical and electronic parameters for the metal (chromium was used) carbonyl fragments were those of ref 33. The M-H distances were kept fixed in all of the calculations (except those associated with species **33**) at 1.75 Å. The molecular geometry was then defined by changing the H-H distances. In the dihydrogen complexes it was set to 0.84 Å, and in molecules **33-36**, it was set to 1.0 Å. The general trends reported in the paper are insensitive to the actual values within a range of these. We emphasize the inadequacy of our theoretical model in numerical terms for problems of this type. In **22** the same orbital parameters were used throughout the series. The number of electrons was varied so as to maintain an 18-electron count.

(58) Kang, S.-K.; Albright, T. A., unpublished results.