Title:

Binding of Hydrocarbons and Other Extremely Weak Ligands to Transition Metal Complexes that Coordinate Hydrogen; Investigation of Cis-Interactions and Delocalized Bonding Involving Sigma Bonds

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Submitted to:

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Binding of Hydrocarbons and Other Extremely Weak Ligands to Transition Metal Complexes That Coordinate Hydrogen: Investigation of Cis-Interactions and Delocalized Bonding Involving Sigma Bonds

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Abstract

This is the final report of a three-year Laboratory Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). At the forefront of chemistry are efforts to catalytically transform the inert C-H bonds in alkanes to more useful products using metal compounds. Our goal is to observe binding and cleavage of alkane C-H bonds on metals or to use related silane Si-H bonding as models, analogous to our discovery of hydrogen (H_2) binding to metals. Studies of these unique "sigma complexes" ($M \cdots H-Y$; $Y=H, Si, C$) will aid in developing new catalysts or technologies relevant to DOE interest, e.g. new methods for tritium isotope separation. Several transition metals (Mo, W, Mn, and Pt) were found to reversibly bind and cleave H_2 , silanes, and halocarbons. The first metal-SiH₄ complex was made and its coordinated Si-H bond was shown to cleave on Mo as for H_2 complexes, thus serving as a model for methane reactions. A second goal is to study the dynamics and energetics of H-Y bonds on metals by neutron scattering, and evidence for interactions between bound H-Y and nearby H atoms on metal complexes has been found.

1. Background and Research Objectives

One of the "Holy Grails" in chemistry is the catalytic conversion of alkane hydrocarbons such

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as methane (CH_4) in natural gas to useful products such as gasoline or methanol. An important question is whether metal-containing catalysts can bind (coordinate) these inert alkane molecules to the metal center via their C-H σ bonds at ambient conditions. Equally important is whether the strong C-H bonds can be broken in controlled fashion to provide the *modus operandi* for catalysis. As models for the above, our project has focused on the binding and cleavage of similar σ bonds such as H-H and Si-H on metal complexes [1-12]. Stable metal-alkane complexes held together by $\text{M}\cdots\text{C}-\text{H}$ interaction are unknown despite the best efforts of chemists worldwide. Coordination of methane does occur on highly-reactive photochemically-generated fragments such as $\text{Cr}(\text{CO})_5$ but only at very low temperatures [13]. Very low binding energies are present (5-10 kcal/mol) because the hydrocarbon cannot easily donate and/or accept electrons to/from the metal d-electron orbitals, which is the basis of all metal-substrate binding. Molecules such as methane and dihydrogen (H_2) possess only inert 2-electron sigma (σ) bonds and cannot easily hold onto the metal to be catalytically converted. However, we made the startling discovery that H_2 forms *stable* complexes via a type of nonclassical chemical bonding (two electrons joining together three atoms) that was previously thought to be too unstable to exist [14]. Furthermore we showed [15] that the strength of the nonclassical bonding in $\text{M}-\text{H}_2$ can rival that of classical ligands such as H_2O , *i.e. a metal can coordinate a bonding σ -electron pair (left) as strongly as a nonbonding (lone) electron pair*:

In $\text{M}-\text{H}_2$ binding, backdonation from a filled metal d-orbital (shaded) to the σ^* antibonding H_2 orbital strengthens the interaction as in metal- π bonding. Importantly, this type of bonding is extendible to *any* 2-electron bond such as C-H, Si-H, C-C. Also crucial is the *activation* (weakening) of the σ bonds towards *rupture*, which is the basis of industrial catalysis and biological enzymatic processes. We have demonstrated that side-on bonded H_2 *lies on the reaction*

coordinate for splitting of H_2 to atomically-bound hydride (see Scheme 1 below) [14,16].

Collaboration with Eckert [17] and Hay [18] experimentally and theoretically proved the existence of $M \rightarrow H_2$ backbonding, which ultimately ruptures the strong H-H bond when it becomes extensive (i.e. electron-rich metal centers). By analogy, cleavage of C-H and related bonds should be controllable by similar variation of the electronic properties of the metal center.

The research with Eckert and Hay was supported on a previous LDRD program. This work led to several awards for the Principal Investigator including the 1993 ACS Award in Inorganic Chemistry and the 1994 E. O. Lawrence Award in Chemistry. An entire new field of metal- H_2 chemistry evolved from this seminal discovery, involving 60 research groups worldwide that have synthesized and/or theoretically studied over 250 different H_2 complexes. Remarkably, the normal H-H bond distance (0.74 Å), has been found to increase in *near continuum fashion* on binding to various metal complexes to nearly the interatomic distance in hydrides (>1.6 Å) [14c]. Thus splitting of the H-H bond can be followed like taking snapshots along the reaction path ("oxidative addition," below left). Interactions [17d,19] between H_2 and adjacent hydrides have also been identified on H_2 -hydride complexes that lead to atom exchange, a key step in catalysis:

In the right side of Scheme 1, replace any or all of the H atoms by other atoms and one can see the variety of possible reactions by bond breaking/making and elimination of ligands at a metal center. One of our goals has been to study such interligand hydrogen/hydride interactions using techniques such as inelastic neutron scattering (INS) and quasielastic neutron scattering (QNS).

The activation on metals of Si-H bonds in silanes, SiH_xR_{4-x} , which are *analogous to hydrocarbons*, can be studied much like the H-H bonds. Metal-silane complexes are known [7,20] but have not been studied in great detail, especially on our complexes. The objectives of our work thus includes studies of silane activation on the same complexes that coordinate H_2 , and a comparison of Si-H versus H-H σ bond coordination and cleavage. This could lead to valuable information applicable to hydrocarbon activation. As will be discussed below, *we have now observed the first example of reversible cleavage of a sigma bond other than H-H, namely the Si-H bond in SiH_4 , representing a direct model for methane binding and activation.*

2. Importance to LANL's Science and Technology Base and National R&D Needs

Major technical impact would be expected for the development of new conversions of methane-like molecules. For example, reactions of hydrogen are by far the world's largest chemical reactions (all petroleum is treated with hydrogen and 10 billion tons of ammonia are produced annually), wherein the H-H bond is broken on metal catalysts before reaction occurs. However analogous selective catalytic reactions of methane are unknown. A metal-complex system that reversibly and *selectively* binds small molecule substrates could also be valuable in separations technology, analytical/sensor applications, and hydrogen or other gas storage. Our metal-phosphine complexes are excellent performers here, readily binding a wide variety of gases (H_2 , N_2 , SiH_4 , NH_3) and releasing them reversibly in vacuo or above room temperature [10,21]. The bulky phosphines induce remarkable size selectivity, e. g. ethylene binds but not larger olefins. Isotopic exchange is another capability of these complexes, which completely equilibrate $H_2 + D_2 = 2HD$, even in the *solid state*. Lastly, according to our recent calculations, the isotopic forms of H_2 (D_2 , T_2) can conceivably be *separated at room temperature* on dihydrogen complexes, with a better separation factor than the current cryogenic methods. Tritium separation from other hydrogen isotopes is clearly in the interest of the DOE.

3. Scientific Approach and Accomplishments

The complexes that we are continuing to study [1-3,5,9,10,14,16,21-23] are electronically unsaturated complexes such as $M(CO)_3(PR_3)_2$ that are similar to the unstable $M(CO)_5$ systems [13] that bind hydrocarbons at low temperature.

The bulky phosphines in these derivatives confer both stability and stereoselectivity to the system but in some cases (left) at a price, namely the "agostic" interaction [3,21] between an organic C-H

bond on the phosphine and the metal. Although this *internal* σ interaction is weak (binding energy ~5-10 kcal/mol) and easily displaced by external ligands, it is entropically favored over *weak* external ligands such as alkanes. Both the established Cr, Mo, W complexes and newer *positively-charged* cationic complexes such as the manganese-diphosphine [5] and platinum species [9] have been examined for weak-ligand binding. The Mn complex contains an unusual *double* agostic interaction (Figure 2) and is very reactive because it contains an electron-poor metal center that desperately seeks electron donation to it. The anion here and for the Pt cation must be noncoordinating (a fluorinated BPh₄). However, none of these species have been found to bind methane. Nonetheless we have learned much by looking at H₂ and silane σ bond activation. A major strategy is to vary how much the metal wants electrons by changing the metal center and the ligands around it, and examine the effects on σ -bond binding and splitting (e. g. H-X bond distance). Even minor changes in the ligands on the metal can be crucial in whether the H-H or Si-H bond binds as a σ ligand or is cleaved. We have been examining the differences in behavior between X=H and Si to obtain information applicable towards improving alkane (X=C) binding.

To investigate the interligand interactions and rotational dynamics of σ ligands that involve low-energy, highly dynamic processes (as low as 1 kcal/mol activation energies) [25], neutron scattering experiments were carried out by Eckert [4,6,11,12] at Los Alamos and in France. This methodology [17] is well-suited because of fast time-scale, sensitivity, and low-energy resolution (<0.1 kcal). We have been using this to study the dynamics of bound H₂, such as rotation, as a measure of both H-H bond activation and its interaction with adjacently-bound atoms.

Silane Coordination and Activation. Our most significant accomplishment is discovering and characterizing the first examples of silane sigma bonding to Mo [1,2], for which a large series of complexes have been prepared:

The NMR spectra of these complexes in solution indicate that the silane is regarded as *one* ligand with the midpoint of one Si-H bond taking up a coordination site *cis* to the CO ligand. The side-

on bonded silane coordination in is established by the observation of reduced $J_{\text{Si-H}}$ NMR coupling constants for the bound Si-H bonds. The molecular structure was determined by a single crystal X-ray diffraction analysis (Figure 1), and the results confirm the coordination of the Si-H bond. The molybdenum-bound Si-H(1) bond is significantly lengthened (1.78 Å) relative to the terminal Si-H(2) (1.42 Å) and Si-H(3) (1.41 Å) bonds, which suggests substantial Mo to Si-H back-donation leading to Si-H bond lengthening. It is noteworthy that the silane ligand and the CO ligand are *cis* to each other while in the corresponding compounds containing an H_2 ligand or an agostic C-H bond, the CO is *trans* to the H_2 ligand or the agostic C-H bond. This indicates that a silane is better π acceptor (backbonder) than H_2 or an agostic C-H.

This model of Si-H binding and bond activation agrees well with the situation for the prototype H_2 complexes. Importantly, these are the first systems in which *H_2 , silane, and agostic C-H bonding is observed on the same metal fragment..* This allows direct comparison of bond activation and shows that more backbonding is needed to both stabilize and cleave Si-H bonds than H-H bonds. Thermodynamic data for binding of Ph_2SiH_2 to $\text{Mo}(\text{CO})(\text{Bu}^i_2\text{PC}_2\text{H}_4\text{PBu}^i_2)_2$ have been determined by NMR: $\Delta H = -12.8 \pm 1.2 \text{ kcal mol}^{-1}$ and $\Delta S = -40 \pm 4 \text{ cal mol}^{-1} \text{ K}^{-1}$. The binding energy, ΔH , is similar to that for H_2 if the recently found [3] agostic C-H interaction on this complex is taken into account. The large negative entropy is noteworthy since a similar value would be expected for binding of an alkane.

The first examples of stable metal SiH_4 complexes, 4a, were discovered [2]:

X-ray crystallography showed a similar structure to those in Figure 1. Remarkably, in solution **4a** is in equilibrium with its seven-coordinate hydridosilyl tautomer **4b**. The coordination of SiH_4 in **4a** followed by Si-H bond cleavage to give the hydridosilyl species **4b** serves as a model for methane coordination and activation. *This is the first example of such a bond breaking/formation equilibrium other than for the H-H bond.* NMR studies yielded thermodynamic data for the conversion of **4a** to **4b** remarkably similar to that for $\text{W}(\text{CO})_3(\text{PR}_3)_2(\text{H}_2) \rightleftharpoons \text{WH}_2(\text{CO})_3(\text{PR}_3)_2$ [26]. We have recent evidence that the GeH_4 congener may bind like SiH_4 .

A different type of reactivity, *oxidative addition* of silanes, occurred with $\text{W(CO)}_3(\text{PR}_3)_2$ [10].

In contrast, H–H cleavage did not occur for H_2 addition, except in solution equilibrium. The table below summarizes the results of reactions of H_2 and silanes (OA = Oxidative Addition):

Precursor Complex	Complex with: H_2		PhSiH ₃
	$J(\text{HD}), \text{Hz}$	H–H, Å	$J(\text{SiH}), \text{Hz}$
$\text{Cr(CO)}_3(\text{PR}_3)_2$	35	0.85	no reaction
$\text{W(CO)}_3(\text{PR}_3)_2$	34, equil OA	0.89	OA
$\text{Mo(CO)(Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2$	34	0.88	57
$\text{Mo(CO)(Bz}_2\text{PC}_2\text{H}_4\text{PBz}_2)_2$	30	0.87	41
$\text{Mo(CO)(Et}_2\text{PC}_2\text{H}_4\text{PEt}_2)_2$	OA		39
$[\text{Mn(CO)(Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2]^+$	33	0.89	weak
$[\text{Mn(CO)(Et}_2\text{PC}_2\text{H}_4\text{PEt}_2)_2]^+$	32		weak
$[\text{PtH(P-}i\text{-Pr}_3)_2]^+$	weak, 34		

Lower values of the NMR parameters $J(\text{HD})$ and $J(\text{SiH})$ and larger H–H distances correspond to more activated sigma bonds (stretched towards oxidative addition). Thus there are subtle differences in the reaction coordinates between H_2 and silanes, and it is now apparent that the *relative ease of oxidative addition of silanes versus dihydrogen depends on the metal/ligand system*. [10]. H_2 oxidatively adds to the more electron-rich $\text{Mo(CO)(Et}_2\text{PC}_2\text{H}_4\text{PEt}_2)_2$ congener, but PhSiH_3 does *not*. This would qualitatively indicate that PhSiH_3 is more difficult to oxidatively add than H_2 *even though the silane appears to be the better backbonder*. However, the results for H_2 versus PhSiH_3 addition to $\text{W(CO)}_3(\text{PR}_3)_2$ are the reverse: the silane completely oxidatively adds while H_2 does so only partially. Obviously there is a fine balance of electronic forces involved here.

Unlike for the uncharged Mo complexes, the cationic Mn complexes bind H_2 as a σ ligand for *both* the R = Ph and Et phosphines, indicative of a more electron-poor metal. Backbonding appears to be weak and the main interaction here is “forward” donation of H_2 electrons to the metal [5]. Surprisingly, the $J(\text{HD})$ and H–H distance parameters are similar to those for the more electron-rich Mo and W complexes. Silane binding is weak and complexes have not yet been

isolated. For the cationic $[\text{PtH}(\text{PR}_3)_2]^+$ fragment, H_2 binds very weakly and only below room temperature [9]. However, *halocarbon* binding was discovered and rare examples of dichloromethane and iodobenzene complexes were isolated and characterized (Figure 3). Although these are not hydrocarbon complexes (methane did not bind), halocarbons are weak ligands and this Pt center may give silane complexes. These complexes are *air-stable*, a rare feature for weak-ligand complexes that may be valuable in hydrogen isotope separations and sensor applications. We have found that the Mn complex can be supported on the surface of alumina and reversibly binds H_2 as indicated by blue to yellow color changes. This should make H_2 complexes more efficient for isotope separations, and color changes can be correlated with H_2 concentration for sensors.

Summarizing, sigma bond activation follows a relatively simple model yet offers a wealth of opportunity for study. There are at least four primary variables in $\text{M}(\text{X}-\text{H})$ systems influencing the electronics: M, X, and the substituents at both M and X. The bonding of σ ligands to metals has two components: "forward" and "back" bonding. It now appears to be possible to sort out and isolate these effects by suitable manipulation of metal/ligand sets. Correlations should hopefully be valuable in defining electronic structure requirements for the optimal design of metal fragments for σ bond activation, especially hydrocarbon coordination.

Dynamics of Bound Hydrogen. We have recognized the potential of quasielastic neutron scattering (QNS) to investigate the details of the rapid H_2 -hydride atom exchange that occurs in virtually all compounds with H_2 adjacent to (cis to) H atoms on a metal (Scheme 1 above). A complex with the hydride ligand cis to the H_2 should show increasingly strong interaction between the two as a function of temperature, including possibly exchange. This might affect the rate of rotation of the H_2 ligand as it becomes increasingly "aware" of the neighboring hydride's electrons and could be reflected in non-Arrhenius like behavior of the quasielastic linewidth. We have now analyzed QNS data collected at temperatures up to 325K on instruments in France on several H_2 compounds, including (1) $[\text{FeH}(\text{H}_2)(\text{dppe})_2]\text{BF}_4$; (2) $\text{FeH}_2(\text{H}_2)(\text{PEtPh}_2)_2$; (3) $\text{IrClH}_2(\text{H}_2)(\text{P}^i\text{Pr}_3)_2$ [17h]; and (4) $\text{RuH}_2(\text{H}_2)_2(\text{PCy}_3)_2$ [12]. The temperature dependence of the spectral linewidth can be fitted to an Arrhenius law which gives an activation energy for the rotation of the H_2 ligand. For compounds 1-3 we obtained values that were 30-50% of the experimentally determined barriers to rotation. This is very surprising as one would expect that at these temperatures the rotation would be essentially classical, i.e. thermally activated rotational hopping over the barrier. It is therefore apparent that even at room temperature the rotational motion of the dihydrogen ligand is at least in part quantum mechanical. Similar effects are known

for the translational diffusion of hydrogen in metals, where activation energies can be substantially lower than potential well depths. The dynamics of H_2 in **2** and **3** differ substantially from that of **1**, where the H_2 and H are *not* *cis*. This may be due to interaction with the *cis*-hydride in **2** and the very rapid exchange between hydride and H_2 ligands that is known to occur in **3**. At this stage it is necessary to devise and test possible models for the H_2 -hydride dynamics in **2** and **3**. Some qualitative conclusions can nonetheless be reached. The data for **3** are remarkable in that they show nearly free rotation of the H_2 ligand that appears to be broadened by a distribution of potentials much like that for disordered systems, e.g. methane impurities in solid rare gas matrices. This is likely to arise from the rapid H_2 -hydride exchange in which the H_2 may rotate at various points of the exchange process [17h].

The INS spectrum of **4** at temperatures below 75K consists of the usual pair of bands from the rotational transitions [17] within the librational ground state at $\pm 4.7\text{ cm}^{-1}$ (Figure 4) [12]. These can be interpreted in terms of planar rotation in a double-minimum potential well to yield a barrier to rotation of 1.1 kcal/mol. The structure of these bands may be attributed to the effect of interactions between the two dihydrogen ligands. As the temperature is increased (Figure 5) the tunneling peaks shift to lower energy and broaden in the usual manner where the width shows an Arrhenius type temperature dependence with an activation energy of only ~ 0.4 kcal/mol. In addition, a broad quasielastic feature appears below the inelastic peaks at $< 75\text{ K}$. The rotational tunneling peaks coalesce into a broad quasielastic line below the elastic peak at $< 150\text{ K}$. The width of this line continues to increase with temperature up to 250 K, the highest temperature reached in this experiment. The activation energy derived from the temperature dependence of the width of this quasielastic line is 0.25 kcal/mol. In addition, a second, more narrow quasielastic component (Figure 6) is evident at 250K with a width of approximately 4 cm^{-1} . The increase in width of the rotational tunneling transition lines as a function of temperature is the result of inhomogeneous broadening from coupling to the phonon bath and of the incoherent H_2 exchange processes that we recently described [11]. The observed non-Arrhenius behavior (i.e. the two different activation energies for different temperature regimes reported above) is consistent with superposition of these processes. It should be noted that both of these activation energies are well below the height of the barrier to rotation. It is also interesting that at the temperature at which the rotational tunneling lines coalesce into a quasielastic line ($\sim 150\text{ K}$), NMR data demonstrate the existence of rapid intramolecular hydrogen exchange even though the activation energy for the latter process is much higher than those observed by INS for the rotational motions. It is therefore reasonable to assume that in this interconversion of hydride and H_2 ligands the latter are subject to a variety of

environments in addition to that of the coordination sites. This may account for the INS observations at 75 and 100 K, i.e. that the sharp rotational tunneling bands arise from rotational transitions of H₂ located in their well-defined potential wells while the broad quasielastic component below the rotational peaks may be due to H₂ affected by the rapid exchange of hydride and H₂ ligands.

INS studies on TpRhH₂(H₂) (Tp= tris-(3,5-dimethylpyrazolyl)borate) gave a low rotational barrier of 0.56 kcal/mol and an H-H distance of 0.94 Å [6]. These values indicate that backbonding is relatively weak and/or an interaction between the H₂ and the cis-hydride ligands lowers the barrier for H₂ rotation. IrIH₂(H₂)(PPrⁱ₃)₂ (H-H= 0.86 Å) also had a small barrier of only 0.98 kcal/mol similar in magnitude to the barrier to interconversion of the H₂ and hydride ligands, raising the possibility that these two processes are coupled [4].

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Fig. 1. Molecular structures of $\text{Mo}(\text{SiPhH}_3)(\text{CO})(\text{Et}_2\text{PC}_2\text{H}_4\text{PEt}_2)_2$ (top) and $\text{Mo}(\text{SiPh}_2\text{H}_2)(\text{CO})(\text{Et}_2\text{PC}_2\text{H}_4\text{PEt}_2)_2$ (bottom). The bond distance for the coordinated Si-H in the former is longer (1.78 Å vs 1.60 Å) because electronic changes at the Si (brought about by two phenyl (Ph) substituents vs one) activates the SiH bond more.

Fig. 2. Molecular structure of $[\text{Mn}(\text{CO})(\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2)_2]^+$ showing double agostic interaction (dotted lines from the H atoms of the CH groups interacting with the metal).

P_2PtHL^+	Pt-H	P-Pt-P	Pt-P
L = CH ₂ Cl ₂	1.68(9)	165.77(9)	2.307(2), 2.310(2)
L = THF	1.351	166.50(11)	2.304(3), 2.310(3)
L = PhI	1.68(16)	163.75(11)	2.311(2), 2.314(2)

Fig. 3. Molecular structures of $[\text{PtH}(\text{P-}i\text{-Pr}_3)_2(\text{CH}_2\text{Cl}_2)]^+$ showing dichloromethane bound via only one of its Cl atoms, and also THF (tetrahydrofuran) and PhI (iodobenzene) complexes.

Fig. 4. Inelastic neutron scattering (INS) spectrum of $\text{RuH}_2(\text{H}_2)_2(\text{PCy}_3)_2$ at $T = 5\text{ K}$. The signals of interest lie on either side of the intense elastic scattering line at zero.

Fig. 5. Temperature dependence of the INS spectrum of $\text{RuH}_2(\text{H}_2)_2(\text{PCy}_3)_2$: 5K (+), 50K (*), 75K (◊) and 100K (△).

Fig. 6. Quasielastic scattering from RuH₂(H₂)₂(PCy₃)₂ at T = 150K (solid line), 200K (- - -) and 250K (- . -).