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Transition Metal Alkane Complexes[†]

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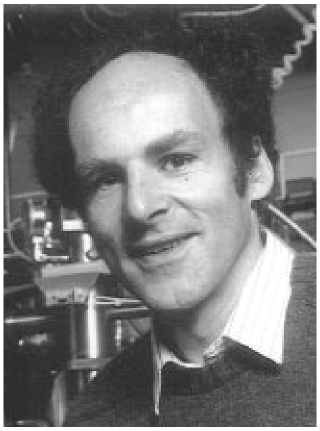
Contents

Chris Hall was born in Barrow-in-Furness, England, in 1966. He studied at the University of York both for his undergraduate and his graduate work. His doctoral research on alkane complexes with Robin Perutz won him the Kathleen Mary Stott Prize and a D. Phil in 1993. He spent a postdoctoral year at the University of Lausanne in Switzerland studying dynamic processes in metal carbonyl clusters by NMR spectroscopy. He is currently working at the University of Nottingham investigating the synthesis of porous polymeric materials derived from silsesquioxanes.



Robin Perutz graduated from the University of Cambridge, England, in 1971 and went on to a Ph.D. with J. J. Turner. The first year of research was spent in Cambridge, the rest in Newcastle upon Tyne. During his Ph.D. he discovered the coordination of chromium pentacarbonyl by methane in low-temperature matrices which forms the starting point of this review. After postdoctoral work in Mülheim, Germany, he took up positions as Demonstrator, first in the University of Edinburgh (1975–1977) and then in Oxford (1977–1983). He moved to the University of York in 1983 where he now holds a full professorship. He has held the Royal Society—British Gas Senior Research Fellowship and been awarded the Tilden Medal by the Royal Society of Chemistry. In 1996, he gave the Seaborg Lectures at the University of California, Berkeley, CA. In his research he applies a wide range of techniques including synthetic and structural methods, time-resolved spectroscopy, and matrix isolation, to problems in the photochemistry of organometallics and coordination compounds. Reductive elimination and oxidative addition reactions involving C–F and C–H bonds form an important theme.

I. Introduction

The coordination of alkanes to transition metals is counterintuitive; they are notoriously unreactive and possess none of the properties associated with good ligands. An example of a good ligand is carbon monoxide: it has orbitals of the correct symmetry and energy available to donate and accept bonding elec-

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[†] Dedicated to the memory of Dr. Andrew McCamley (1965–1996), student, colleague, and friend.

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trons. In contrast, alkanes are poor electron donors and poor acceptors. The alkane C−H σ-bond is both strong and nonpolar, the HOMO σ is low-lying and therefore unsuitable for electron donation, and the LUMO σ^* is high in energy and unsuitable for accepting electron density. The direct coordination of an alkane molecule to a transition metal would seem an unlikely prospect.

Nevertheless, alkane complexes have been detected using a number of methods. Not surprisingly, all the alkane complexes detected so far are unstable at room temperature, and rather specialized methods are required for their detection. Each of the methods used has been the subject of reviews or books and will not be described in detail.[1,2] Matrix isolation is one of the best established methods for the stabilization and characterization of reactive intermediates. The first examples of alkane coordination were found with this technique in the photochemistry of the d^6 metal carbonyls, $M(CO)_6$ (M = Cr, Mo, W). More recently, the coordination of methane to naked transition metal atoms has been detected directly in low temperature matrices. The coordination of alkanes to $M(CO)_5$ fragments has now been observed in solution and in the gas phase by transient absorption techniques. Alkane complexes with transition metal atoms and ions have also been detected in the gas phase. Examples of each of these experiments will also be described.

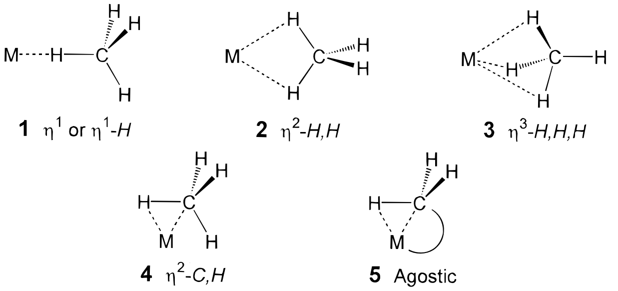
A large number of organometallic complexes are now known to be capable of reacting with alkanes by way of C−H activation.[3] This reaction is also somewhat counterintuitive as the very strong C−H σ-bond must be cleaved. However, the energy gained from the formation of strong metal−hydride and metal−carbon bonds is ample compensation for the energy used in the C−H bond breaking, at least in the case of third row transition metals.[3g] By contrast, the coordination of an alkane does not require the expenditure of energy for bond cleavage (although a small amount of energy may be expended if the alkane needs to distort significantly to coordinate to the metal), but does not reap the reward of strong bond formation.

Experiments on the oxidative addition and reductive elimination of alkanes from transition metal complexes have revealed the presence of alkane complexes as reaction intermediates. This discovery has renewed interest in alkane coordination and prompted a flurry of research activity in the area—a selection of these experiments will also be described.

Alkane complexes have also been subjected to theoretical examination, both as intermediates in C−H activation, and as independent entities−a brief summary of the findings will also be included.

A number of excellent reviews, most notably by Crabtree,[4] have dealt with the general phenomenon of σ-bond coordination, but the intermolecular coordination of C−H σ-bonds has received scant attention. The purpose of this review is to concentrate on this area, with only a brief comparison with intramolecular agostic complexes, and "intermolecular" silane, borohydride, and dihydrogen complexes. These comparisons assist in identifying the possible mode of coordination, and methods of stabilization of alkane complexes.

Scheme 1. Possible Coordination Modes of Methane to Metal Atoms (1−4) with Recommended Nomenclature (Adapted from Ref 75) and *Intra*molecular Agostic Coordination (5)



II. Nomenclature

There are a number of discrepancies in the literature on the naming of alkane complexes. For instance, a complex in which one σ-bond of an alkane is coordinated to the metal has been described as an η^2, tilted end-on, or side-on alkane complex, whereas one with an alkane coordinated through two hydrogen atoms may also be described as an η^2-alkane complex. To avoid confusion, the following nomenclature will be used throughout this review to describe the structure and mode of coordination of alkane complexes—we recommend that it is adopted generally. If the alkane is bound in an end-on fashion through one, two, or three hydrogen atoms the complexes will be termed η^1, η^2-*H,H*, and η^3-*H,H,H* respectively (Scheme 1, **1-3**). Notice that the η^2-*H,H* and η^3-*H,H,H* structures will necessarily involve close contact between metal and carbon (see section VII). Therefore, coordination of two C−H σ-bonds to a metal is equivalent to the η^2-*H,H* description and the coordination of three C−H σ-bonds is equivalent to the η^3-*H,H,H* description. In contrast, an alkane may bind side-on through a single C−H σ-bond, η^2-*C,H*, (Scheme 1, **4**) which would be distinguishable from an end-on η^1 interaction. The four types of alkane coordination of Scheme 1 match those given by Cotton and Wilkinson for metal borohydride complexes.[5a]

These complexes belong to the larger class of σ-complexes, which can be defined as complexes where the donor is a σ-bond, and includes dihydrogen complexes and silane complexes. Such complexes contrast with those in which the donor is an atom with a lone pair or a π-bond. Agostic complexes represent the class of σ-complexes in which the donor is a C−H bond of a group already bound to a metal: an intramolecular C−H−M interaction (Scheme 1, **5**).

Alkanes are often termed *token* ligands, but this carries the implication of a very weak metal−ligand bond which is not supported by experiment.[5b]

III. The Coordination of Alkanes to Metal Complexes without Oxidative Addition

A. $M(CO)_5$(alkane) (M = Cr, Mo, W)

1. Matrices

The elucidation of the photochemistry of $M(CO)_6$ (M = Cr, Mo, W) by Perutz and Turner in the early

1970s still represents the most complete investigation of its kind. UV photolysis of these species resulted in CO expulsion, leaving the unsaturated intermediates $M(CO)_5$. There were two possible structures for $M(CO)_5$, either square pyramidal (C_{4v}) or trigonal bipyramidal (D_{3h}). $Cr(CO)_5$ displayed three IR bands at 2093 (vw), 1965.6 (s), and 1936.1 (m) cm^{-1} in argon matrices. These bands were unambiguously assigned to the a_1, e, and a_1 modes of C_{4v}-$Cr(CO)_5$ with the powerful combination of isotopic labeling and IR frequency prediction by energy-factored force field analysis.[6a]

The UV/vis spectrum of C_{4v}-$Cr(CO)_5$ exhibited an absorption band (e to a_1 transition) whose position was extremely sensitive to the matrix host, appearing at 624 nm in Ne, 547 nm in CF_4, 533 nm in Ar, and 489 nm in CH_4. By comparison, the absorption maxima of related 18-electron complexes shift less than 5 nm from one matrix material to another. Moreover, when $Cr(CO)_5$ was generated in mixed matrices, distinct absorption maxima were observed in positions close to those observed in the pure matrices. For instance, in a matrix of neon doped with 2% argon, an intense band was observed at 533 nm with a shoulder at 630 nm.[6b] The mixed-matrix results were irreconcilable with general solvation of $Cr(CO)_5$, and were ascribed to a specific solvation of $Cr(CO)_5$ by the matrix host. In this model, the matrix host behaved as a weak sixth ligand through interaction with the d_{z^2} orbital, which was both available and of the correct symmetry for chemical bonding.[7] The strength of this interaction was directly proportional to the perturbation of the d_{z^2} (a_1) orbital and hence strongly influenced the energy of the visible absorption band. However, the energy of the e to a_1 transition was also found to be dependent on the axial–equatorial bond angle of the $Cr(CO)_5$ fragment,[7e] thus precluding any estimate of the magnitude of the $Cr(CO)_5$–(matrix) interaction. Nevertheless, indisputable evidence had been obtained that the methane molecule is weakly bound to $Cr(CO)_5$.[8]

The method of choice for demonstrating the interaction of $Cr(CO)_5$ with an alkane is UV/vis spectroscopy. Shifts in the IR spectra due to coordination of the sixth ligand are very hard to distinguish from solvent effects since they are less pronounced than the general solvent shift. The position of the UV/vis maximum on complexation of methane is very similar to that on complexation of xenon and quite different from those for coordination of η^2-H_2 and N_2 (370 and 364 nm respectively).[9a,b] The effects of complexation on the IR ν(CO) bands are more subtle, but can be discerned in mixed matrices of Ar + 2% Xe or Ar + 2% CH_4. $Cr(CO)_5$ exhibits three IR ν(CO) bands with symmetries e + $2a_1$. Xenon causes a down-frequency shift in the high-frequency a_1 mode of 3.8 cm^{-1} and an up-frequency shift in the low-frequency a_1 mode of 2.8 cm^{-1}.[6b] The effect of methane is even smaller. In contrast, complexation of η^2-H_2 or N_2 causes a high-frequency shift in the low-frequency a_1 mode almost an order of magnitude larger. UV/vis and IR spectra indicate that methane is a much poorer acceptor than η^2-H_2 or N_2 with respect to $Cr(CO)_5$. Neither the matrix experiments, nor any others have defined the structure of $Cr(CO)_5(CH_4)$.

Table 1. Enthalpy of $M(CO)_5$–S Bond ($-\Delta H_{M-S}$) in Alkane Solvent (S) (Adapted from Refs 14a and 14c)[a]

M	S	ΔH_{M-S}/kJ mol^{-1}
Cr	pentane	37(13)
Cr	heptane	40(10)
Cr	isooctane	46(9)
Cr	cyclohexane	53(9)
Mo	heptane	71
W	heptane	56(12)

[a] Error bars correspond to 1 σ.

2. Solution

Around the same period, Kelly et al. identified $Cr(CO)_5$ in cyclohexane solution by laser flash photolysis of $Cr(CO)_6$. It displayed a broad absorption band at 503 nm, very similar to that observed in methane matrices at 489 nm. By analogy with the matrix experiments it was proposed that the observed transient was actually $Cr(CO)_5(C_6H_{12})$.[10] If this formulation was correct, the matrix experiments would predict two important phenomena. Firstly, the coordination of cyclohexane would stabilize the transient, implying that generation of $Cr(CO)_5$ in a more weakly coordinating solvent should decrease its lifetime. Secondly, the absorption maximum should shift to lower energy in such solvents, by analogy with the shift observed between methane and neon matrices. As predicted, laser flash photolysis of $Cr(CO)_6$ in weakly coordinating perfluorocyclohexane produced $Cr(CO)_5$ with an absorption maximum at 620 nm and a lifetime that was a factor of 10^3 shorter than that observed in cyclohexane.[11] The position of the absorption maximum is very close to that observed in neon matrices. In addition to the greatly enhanced reactivity, this led to the proposal that $Cr(CO)_5$ in perfluorocarbon solvents was effectively naked (but see later). Direct demonstration of the structure of $Cr(CO)_5$ in cyclohexane solution came in 1985 when isotopic data were obtained by time-resolved infrared spectroscopy (TRIR) following laser photolysis of $Cr(^{12}CO)_5(^{13}CO)$. The axial–equatorial bond angle of C_{4v}-$Cr(CO)_5(C_6H_{12})$ was estimated as 93°, the same as that calculated for $Cr(CO)_5(CH_4)$ in CH_4 matrices.[12,13]

One of the most intriguing questions about $Cr(CO)_5(C_6H_{12})$ was the strength of the chromium–alkane bond. The degree of stabilization afforded by cyclohexane compared to perfluorocyclohexane would suggest the bond energy to be significant. In 1989, Morse et al. reported the direct measurement of the metal–alkane bond strengths for $M(CO)_5(C_6H_{12})$ (M = Cr, Mo, W) with the technique of photoacoustic calorimetry (PAC).[14a] In this experiment the enthalpy of a photochemical reaction may be determined from the amplitude of an acoustic wave measured following laser flash photolysis.[14b] The method assumes that reaction volume changes are small and that the reaction enthalpy is equal to the difference in the metal–carbonyl and metal–alkane bond enthalpies. Knowledge of the metal–carbonyl bond dissociation energy from gas phase experiments thus yields the metal–alkane bond enthalpy.

For $Cr(CO)_5$(heptane) the strength of the metal alkane interaction was determined as 40 ± 10 kJ mol^{-1} (Table 1). The corresponding values for the molybdenum and tungsten complexes were 71 (no errors given)[14c] and 56 ± 12 kJ mol^{-1} respectively. Interestingly, the bond strength for $Cr(CO)_5$(cyclohexane) was measured as 53 ± 9 kJ mol^{-1}. The metal−alkane bond was unexpectedly strong, certainly stronger than hydrogen bonding observed in many stable complexes, and suggested that the isolation of stable alkane complexes should be possible. Yang et al. also reported a photocalorimetric study of the photosubstitution of $Cr(CO)_6$ with a range of ligands in heptane solution, and deduced a value for the Cr−alkane bond enthalpy of 41 kJ mol^{-1} (no errors given).[14d]

During the 1980s, another group of researchers was involved in the pursuit of naked $Cr(CO)_5$ in alkane solution, and the associated question of how fast the $Cr(CO)_5$(alkane) bond forms. These experiments were complicated by the formation of electronically and vibrationally excited species and the extremely short time scales involved. The photoejection of CO from d^6-metal carbonyls requires the use of UV radiation. A typical UV laser source is the Nd:YAG third harmonic at 355 nm which corresponds to a photon energy of 337 kJ mol^{-1}, whereas the $Cr(CO)_5$−(CO) bond dissociation energy is approximately 154 kJ mol^{-1}.[15] The excess energy is sufficient to leave the molecule in an excited state. Simon and Xie used laser flash photolysis with UV/vis detection on a picosecond time scale to investigate the photochemistry of $Cr(CO)_6$ in cyclohexane and methanol. They found that $Cr(CO)_5$(cyclohexane) ($\lambda_{max} = 500$ nm) was formed within the experimental rise time (0.8 ps), whereas $Cr(CO)_5$(MeOH) was detected after 2.8 ps (the reaction takes longer in MeOH due to slower solvent reorganization).[16a] In later experiments the upper limit for the formation time of $Cr(CO)_5$(cyclohexane) was placed at 0.5 ps, the rise time of the improved apparatus.[16b]

On an even shorter time scale, Joly and Nelson showed that naked $Cr(CO)_5$ ($\lambda_{max} = 480$ nm!) was formed in about 0.3 ps.[17] The position of the visible band was curious given the position of "naked $Cr(CO)_5$" characterized in neon matrices at 623 nm. The initial species was assigned as an electronic excited state of $Cr(CO)_5$. This species reacted with the MeOH solvent within 1.6 ps, but over the next 70 ps the visible band associated with the electronic ground state of the methanol complex shifted to higher energy. The explanation was that the methanol complex was present in a highly vibrationally excited state, so that the energy of the transition to the electronic excited state was reduced. Similar experiments by Lee and Harris confirmed the shift of absorption maximum for the cyclohexane complex to shorter wavelength as the molecule cooled from its initial hot state.[18]

UV/vis spectra are diagnostic for the coordination of alkanes, but they provide no direct information on the structure of the organometallic fragment. Such information is available from IR spectroscopy.

Spears et al. have recently succeeded in answering some very important questions with IR detection on a picosecond time scale. In the initial experiments, the metal carbonyl fragment was generated in a vibrationally hot state, since short wavelength radiation was needed to photodissociate the metal hexacarbonyls.[19] As a result, the ν(CO) modes in the TRIR spectra were strongly perturbed from those expected for the ground-state organometallic fragments. Spears et al. were able to generate $Cr(CO)_5$ with less excess energy by first producing $Cr(CO)_5$(cyclohexane) from $Cr(CO)_6$ with a UV laser pulse, or then waiting until the solvent complex cooled to its ground vibrational state, and finally inducing cyclohexane ejection with a second visible laser pulse ($\lambda = 532$ nm). Naked $Cr(CO)_5$ was detected from its e mode at 1970 cm^{-1} (Figure 1) with a lifetime of ~15 ps to give $Cr(CO)_5$(cyclohexane).[20] Even this reaction with cyclohexane requires the extremely rapid dissipation of 3−4 quanta of excess energy into the CO modes, otherwise the cyclohexane would be immediately re-expelled (laser pulse of wavelength 532 nm corresponds to a photon energy of 225 kJ mol^{-1}). However, it has also been suggested that the expelled cyclohexane may take some of the excess energy on dissociation, leaving the transition metal fragment vibrationally cooler.[21]

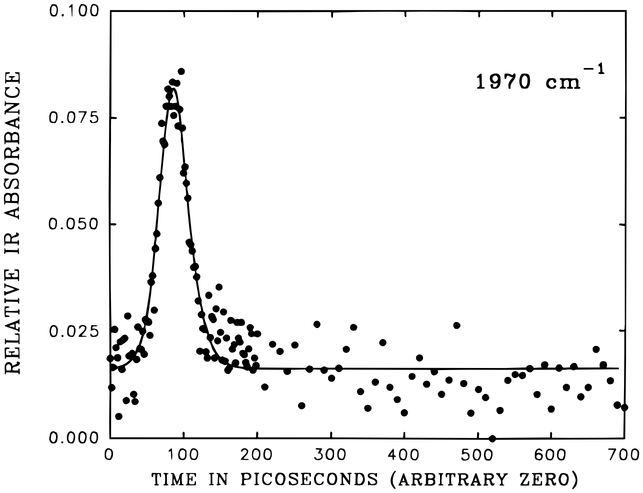


Figure 1. Ultrafast kinetic trace recorded following laser-induced dissociation of C_6H_{12} from $Cr(CO)_5(C_6H_{12})$, showing the reaction of "naked" $Cr(CO)_5$ with C_6H_{12} (IR detection at 1970 cm^{-1}). (Adapted from ref 20.)

3. Gas Phase

Gas-phase work has the considerable advantage of being solvent free, and therefore the production of naked $Cr(CO)_5$ is easier than in solution. Reagents, including alkanes, may be added in order to observe reactions with the transition metal fragments. As there is no general solvent effect to compete with the effect of the sixth ligand coordination on the CO-stretching frequencies, relatively small shifts can be clearly seen. For instance, the ν(CO) modes of $W(CO)_5$ in the gas phase shift from 1980 and 1942 cm^{-1} to 1971 and 1947 cm^{-1} on coordination of ethane.[27]

Breckenridge et al. investigated the gas-phase photochemistry of $Cr(CO)_6$ in the presence of argon or methane as a buffer gas with visible detection.[22,23] They observed absorption maxima between 530 and 500 nm, comparable to the matrix spectra of $Cr(CO)_5(Ar)$ and $Cr(CO)_5(CH_4)$. With He as buffer gas, the transient absorption of naked $Cr(CO)_5$ appeared at 620 nm (cf. $Cr(CO)_5$ in a matrix of neon, 623 nm).

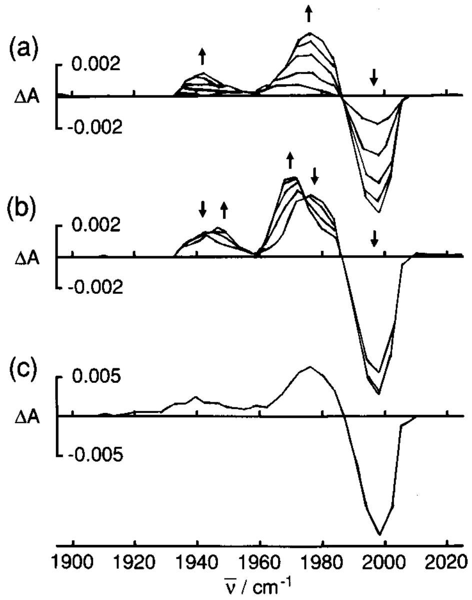


Figure 2. Time-resolved difference absorption spectra following 308 nm photolysis of a mixture of $W(CO)_6$, and i-C_4H_{10} in Ar buffer gas: (a) spectra every 100 ns over 0.1-0.5 μs range, (b) spectra every 500 ns over 0.5-2.5 μs range, and (c) spectrum illustrating the absorption of isolated $W(CO)_5$ at room temperature. (Reprinted from ref 27. Copyright 1990.)

Naked $Cr(CO)_5$ in the gas phase was also identified using TRIR by Weitz et al.[24,25] and exhibited ν(CO) modes at 1980 and 1948 cm^{-1}, consistent with the C_{4v} structure observed in low-temperature matrices. Rayner et al. reported the detection of $W(CO)_5$(ethane) and subsequently a range of other $W(CO)_5$(alkane) complexes by TRIR in the gas phase.[26,27] An equilibrium between unsaturated $W(CO)_5$ and $W(CO)_5$(alkane) complexes was observed (eq 1). Distinct ν(CO) modes were detected for each species (Figure 2).

$$\mathrm{W(CO)_5 + L \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} W(CO)_5L} \qquad K_p = k_1/k_{-1} \quad (1)$$

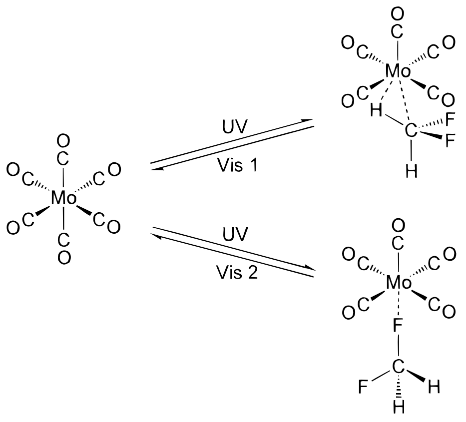
The binding enthalpy ΔH_{300} was determined from the slope of a plot of equilibrium yield $[W(CO)_5(L)]/[W(CO)_5]$ vs temperature. The equilibrium constant K_p was obtained from the slope of a plot of the equilibrium yield vs the alkane pressure. Alkane binding energies were also deduced from K_p by statistical thermodynamics (with various assumptions about the similarity of free and bound alkanes).

Table 2. Equilibrium Constants and Binding Enthalpies for $W(CO)_5$–Alkane with C–H σ-MO Ionization Energy (Adapted from Ref 27)

alkane	K_p (atm^{-1})	$\Delta H°_{300}$ (kJ mol^{-1})	IE (eV of C–H σ-MO)[a]
CH_4	–	<20	14.33
C_2H_6	610 (100)	31(8)	12.35
C_3H_8	1300 (400)	34(8)	11.51
n-C_4H_{10}	1500 (500)	38(13)	11.66
i-C_4H_{10}	1700 (500)	36(8)	11.13
n-C_5H_{12}	2600 (800)	44(13)	10.93
n-C_6H_{14}	5200 (1600)	45(13)	
c-C_3H_6	1300 (400)	37(8)	13.00
c-C_5H_{10}	4600 (1400)	43(13)	11.01
c-C_6H_{12}	7300 (2000)	49(13)	10.32
CH_3F	3500 (1100)	47(13)	13.04
CH_2F_2		>20	13.29
CHF_3		<20	14.80
CF_4		<20	16.23
C_2H_5F	3200 (1000)	51(13)	12.43

[a] These values appear to correspond to the maxima of the first photoelectron bands, but see section VIII.A.

Scheme 2. The Photochemistry of $Mo(CO)_6$ in CH_2F_2 Matrices (Adapted from Ref 28)



The tungsten–hexane bond strength in the gas phase was measured as 45 ± 13 kJ mol^{-1}, in good agreement with the value obtained in heptane solution. A complex between $W(CO)_5$ and CH_4 could not be identified with this apparatus, suggesting that the tungsten–methane interaction was worth less than 21 kJ mol^{-1}. The authors also attempted to address the problem of the mode of coordination of alkanes to transition metal centers by studying the reaction of $W(CO)_5$ with a range of fluoroalkanes. They observed complex formation with CH_3F, CH_2F_2, and C_2H_5F, but not with CHF_3 and CF_4. The binding enthalpies were then compared to the ionization energies of the C–H σ-HOMO of the various alkanes (Table 2), to test the assumption that the alkanes bind purely by σ-donation. There is an inverse relation between $\Delta H°_{300}$ and the energy of the C–H σ-MO within groups of linear, cyclic and fluorinated alkanes, although comparisons between members of different groups are not so good. Therefore, the σ-donating ability of the alkane is important but cannot account for all the observations, and steric or orbital overlap factors must also be involved. The metal–alkane bond strength was also noted to be directly proportional to the size of the alkane. Rayner et al. assumed in their discussion that the alkane would be η^1 bound, but did not obtain direct evidence for this mode of coordination.

Rayner et al. assumed that the interaction of fluoroalkanes with $W(CO)_5$ involved only a C–H σ-bond. However, preliminary experiments in our research group show that the fluorine atom can also interact. Wavelength-selective photolysis of $Mo(CO)_6$ in low-temperature matrices of CH_2F_2 reveals the presence of two forms of $(CH_2F_2)Mo(CO)_5$ with absorption maxima at 426 and 396 nm. By analogy with the photochemistry of $Mo(CO)_6$ in CF_4 and CH_4 matrices, we assign these intermediates to $Mo(CO)_5$(F–CH_2F) and $Mo(CO)_5$(H–CHF_2) (Scheme 2). No information was obtained which could differentiate between η^1 and η^2-*C,H(F)* binding in these species. The intermediates may be interconverted with the appropriate wavelength of visible light.[28] More structural evidence emerged as photolysis of $Cr(CO)_6$ in argon and methane matrices doped with 2% fluoroalkane revealed distinct ν(CO) modes for (fluoroalkane)$Cr(CO)_5$, depending on whether the fluoroalkane was bonded through a hydrogen atom of a C−H σ-bond or a fluorine lone pair.[29] The coordination of fluoroalkanes may have also occurred via the fluorine lone pair in the gas phase work of Rayner et al., but the interaction is probably below their detection limit of 21 kJ mol^{-1}.

Wells et al. have recently used TRIR spectroscopy to probe the reactivity of $Cr(CO)_5$ toward several ligands.[30] At CH_4 pressures of 100 Torr, they report a small decrease in the rate of $Cr(CO)_6$ regeneration, but were unable to determine the dissociation energy of the $Cr-CH_4$ bond. Nevertheless, they estimate the interaction energy as 33 ± 8 kJ mol^{-1}. For comparison, the $Xe-Cr(CO)_5$ bond dissociation energy was determined as 37.7 ± 3.8 kJ mol^{-1} in the gas phase and 35.1 ± 0.8 kJ mol^{-1} in liquid xenon solution.[31] The similarity of the bond enthalpies of xenon and methane complexes is consistent with the observation that shifts in the UV/vis spectra of $M(CO)_5$ species (M = Cr, Mo, W) are of comparable magnitude in matrices of methane and xenon.[6]

B. Other Metal Alkane Complexes

The methods of matrix isolation, laser flash photolysis, and PAC have been used to demonstrate alkane coordination to several other molecules.

Brookhart and co-workers attempted to improve on the stability of the prototypical $Cr(CO)_5(CH_4)$ fragment by increasing the Lewis acidity of a d^6 metal fragment.[32] They found that photolysis of (dfepe)$Cr(CO)_4$ in low-temperature matrices resulted in CO dissociation to form predominantly *fac*-(dfepe)$Cr(CO)_3$, which was characterized with the aid of the Timney ligand effect constant method for predicting IR spectra.[33] Although this intermediate appeared to bind to methane no better than $Cr(CO)_5$, it was also capable of coordinating a fluorine atom of the phosphine ligand in the vacant sixth position. The two intermediates *fac*-(dfepe)$Cr(CO)_3(CH_4)$ and F-coordinated, *fac*-(dfepe)$Cr(CO)_3$(*F*−) had very similar IR spectra, but showed visible absorption bands in quite different positions (Figure 3). In addition, the absorption maximum of the complex, *fac*-(dfepe)$Cr(CO)_3$(matrix), was very dependent on the nature of the host, whereas that of the fluorine coordinated complex was not. Transient photochemistry in solution provided further evidence for the existence of the two intermediates. The F-coordinated species was found to be approximately 50 times more reactive than the corresponding alkane complex. In low-temperature matrices and in hydrocarbon solution, competition was observed between intramolecular F atom and intermolecular CH_4 coordination (Scheme 3).

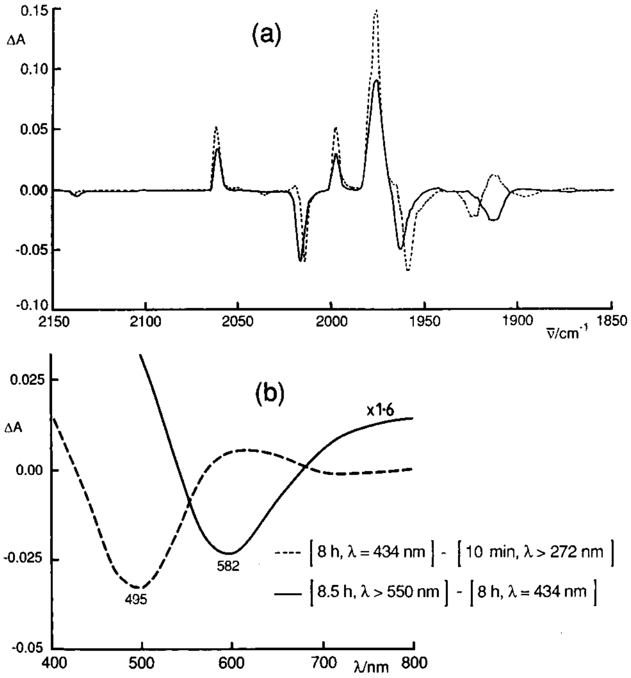
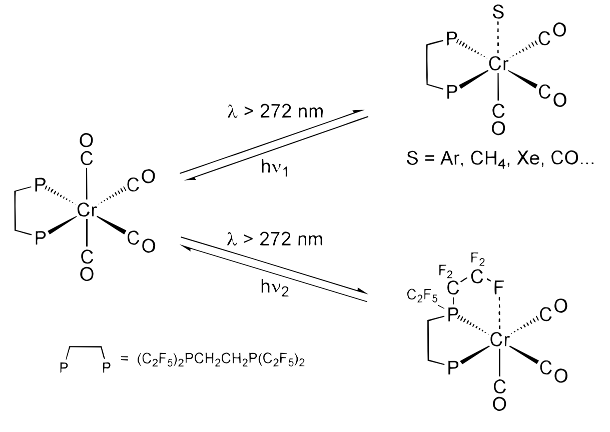


Figure 3. (a) IR difference spectra in the ν(CO) region showing the conversion of Cr(dfepe)$(CO)_3(CH_4)$ to Cr(dfepe)$(CO)_4$ (broken line) and the conversion of Cr(dfepe)$(CO)_3$(*F*−) to Cr(dfepe)$(CO)_4$ (solid line) with selective visible irradiation. (b) UV/vis difference spectra showing the conversion of Cr(dfepe)$(CO)_3(CH_4)$ to Cr(dfepe)$(CO)_4$ (broken line) and the conversion of Cr(dfepe)$(CO)_3$(*F*−) to Cr(dfepe)$(CO)_4$ (solid line) with selective visible irradiation. (Adapted from ref 32.)

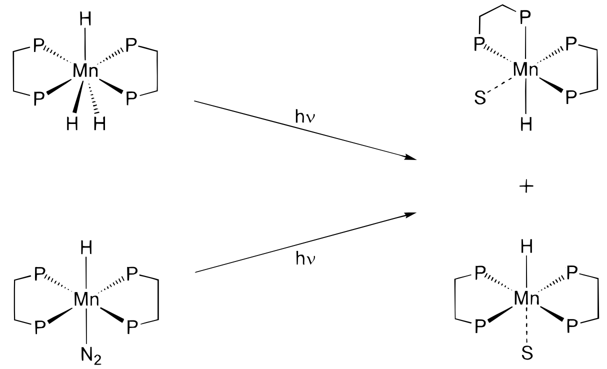
Scheme 3. The Matrix Photochemistry of $Cr(CO)_4$(dfepe) (Reprinted from Ref 32. Copyright 1992 American Chemical Society)



The d^6 intermediates $MeMn(CO)_4$ and $HMn(CO)_4$ were characterized in low-temperature matrices following the photolysis of the pentacarbonyl precursors.[34,35] Each intermediate was present in C_S and C_{2v} isomeric forms and all of the fragments showed a strong interaction with the matrix hosts. The magnitude of the shifts in visible absorption maxima was greater than observed for $Cr(CO)_5$. For instance, C_s-$HMn(CO)_4$ displayed a visible absorption band at 445 nm in argon shifting to 400 nm in methane (a shift of 2528 cm^{-1} compared to 1688 cm^{-1} for $Cr(CO)_5$ in argon and methane[6]). Belt et al. used TRIR to detect $MeMn(CO)_4$(alkane) complexes as intermediates in methyl migration reactions in hydrocarbon solution.[36]

Further evidence for the coordination of alkanes to manganese carbonyl fragments was reported by Hop and McMahon in 1991 with the observation of a weakly bound $[Mn(CO)_5(CH_4)]^+$ complex.[37a] They detected an ion $MnC_6O_5H_4^+$ by high-pressure mass spectrometry of $Mn_2(CO)_{10}$ in the presence of methane. This ion was formulated as $[Mn(CO)_5(CH_4)]^+$

Scheme 4. The Matrix Photochemistry of $(dmpe)_2MnH_3$ and $(dmpe)_2MnH(N_2)$ (Adapted from Ref 28)



on the basis of fragmentation to CH_4 and $Mn(CO)_5^+$ and analogous behavior of H_2 and H_2O adducts. The Mn−CH_4 bond dissociation energy was estimated to be less than 30 kJ mol^{-1}. The behavior of $[Mn(CO)_5(CH_4)]^+$ is distinct from that of $[Mn(CO)_5(CH_3)(H)]^+$ which undergoes CO loss. The latter ion may be observed by ion cyclotron resonance, but not $[Mn(CO)_5(CH_4)]^+$.[37b]

Unpublished observations from our research group on the coordination of methane to electron-rich transition metal fragments such as $Mn(dmpe)_2H$ and $Re(dmpe)_2H$ indicate that methane coordination is not confined to metal carbonyls.[28] These studies assume further significance as both of the reactive intermediates are capable of catalytic H/D exchange between arenes and alkanes.[38] Characterization of non-carbonyl complex intermediates in low-temperature matrices is difficult as their infrared spectra are weaker and less predictable than those of metal carbonyls. An unambiguous assignment can only be made if the intermediates are generated from more than one precursor molecule. On photolysis of either $Mn(dmpe)_2H(H_2)$ or $Mn(dmpe)_2H(N_2)$ in a matrix of argon two very intense visible absorption bands appeared at 644 and 798 nm, assigned to the C_S and C_{2v} isomers of the 16-electron intermediate $Mn(dmpe)_2H$ (Scheme 4). When $Mn(dmpe)_2H(H_2)$ was photolyzed in a methane matrix the absorption maxima shifted to 544 and 654 nm respectively ($\Delta\nu = 2850$ and 2760 cm^{-1}). Clearly, both isomers were specifically coordinated to methane. Similarly, the alkane complexes C_S- and C_{2v}-$Re(dmpe)_2H(CH_4)$ were characterized from the photolysis of $Re(dmpe)_2H_3$ and $Re(dmpe)_2H(C_2H_4)$ in argon and methane matrices.

Unsaturated d^6 half-sandwich complexes have also been shown to coordinate methane. Photolysis of $CpW(CO)_3(Et)$ in low-temperature matrices, hydrocarbon glasses, and solution produces the alkane complex $CpW(CO)_2(Et)(S)$ and the β-agostic ethyl complex $CpW(CO)_2(CH_2CH_2{-}\mathbf{H})$.[39] As usual the intramolecular agostic interaction was significantly stronger than the intermolecular alkane interaction. Photolysis of the related complex $Cp^*Re(CO)_2(Et)_2$ in a methane matrix also formed a mixture of the intermolecular methane complex $Cp^*Re(CO)(Et)_2(CH_4)$ and the intramolecular agostic complex $Cp^*Re(CO)(Et)(CH_2CH_2{-}\mathbf{H})$.[40]

The (arene)chromium intermediate $(C_6H_6)Cr(CO)_2$ was characterized in low temperature matrices by Rest and co-workers.[41] Long et al. with laser flash photolysis, showed that the intermediate was present as (arene)$Cr(CO)_2$(alkane) in solution. The variation with alkane in the rate of reaction of (arene)$Cr(CO)_2$(alkane) + CO was not associated with a change in the enthalpy of activation for metal−alkane dissociation, but a change in entropy of activation.[42] They proposed that longer chain alkanes have greater freedom of motion than shorter chain alkanes and cyclic alkanes and that this was the origin of the greater binding energy of cyclohexane (hence lower reactivity) than linear alkanes to carbonyl fragments. Comparison of the reactivity of $(\eta^6\text{-}C_6R_6)Cr(CO)_2$(alkane) species with CO revealed that the steric rather than electronic nature of the R group was key (Table 3). It was suggested that the bulkier substituents increase the freedom of motion of the bound solvent molecule ($\Delta S^\ddagger$ less negative).

Table 3. Activation Parameters (290−320 K) and Rate Constant Data at 298 K, Obtained by UV/Vis Flash Photolysis, for the Reactions of $(\eta^6\text{-Arene})Cr(CO)_2{-}(S)$ with CO (From Ref 42)

arene	$\Delta H^{\ddagger\,a}$	$\Delta S^{\ddagger\,b}$	$10^{-6}\,k_3\,^c$	solvent (S)
chlorobenzene	23	−38	5.7	cyclohexane
p-chlorotoluene	25	−34	4.0	cyclohexane
benzene	22	−37	9.8	cyclohexane
	24	−18	13	*n*-pentane
	26	−16	23	*n*-heptane
	26	−12	28	*n*-decane
	26	−10	34	*n*-dodecane
toluene	23	−35	9.4	cyclohexane
ethylbenzene	24	−31	6.6	cyclohexane
p-xylene	24	−28	8.3	cyclohexane
o-xylene	25	−28	6.8	cyclohexane
1,3,5-mesitylene	24	−27	13	cyclohexane
hexamethylbenzene	25	−26	15	cyclohexane
hexaethylbenzene	22	−23	59	cyclohexane
	23	−12	110	*n*-heptane

[a] ±2 kJ mol^{-1}. [b] ±10 J mol^{-1} K^{-1}. [c] M^{-1} s^{-1}, ±10%.

$CpMn(CO)_2$ was also studied in low-temperature matrices[41] and by TRIR in solution. The TRIR study on the reaction of $(\eta^5\text{-}C_5R_5)Mn(CO)_2(S)$ species with CO in alkane solutions, had previously shown that steric factors controlled reactivity.[43,44]

There is also photoacoustic evidence for alkane coordination to $CpMn(CO)_2$.[45] A Mn−heptane bond dissociation energy of up to 37.7 kJ mol^{-1} was estimated. This value is comparable to that determined for $Cr(CO)_5$(heptane) (42 kJ mol^{-1}).

The evidence presented above shows that d^6 16-electron fragments have little if any existence in solution since they coordinate solvent molecules in their vacant sites within 1 ps of formation. The implication is that solution reaction mechanisms must always include the solvent as a specific ligand because it can have an enormous kinetic impact (eqs 2 and 3): NOT eq 2 BUT eq 3.

$$Cr(CO)_6 \xrightarrow[-CO]{h\nu} Cr(CO)_5 \xrightarrow{L} Cr(CO)_5L \qquad (2)$$

$$Cr(CO)_6 \xrightarrow[-CO]{h\nu,\,S} Cr(CO)_5S \xrightarrow{L} Cr(CO)_5L + S \qquad (3)$$

The free metal carbonyl fragment has a negligible existence in solution. Therefore, the displacement of an alkane by other ligands is unlikely to proceed via a dissociative mechanism, but probably proceeds by a type of interchange mechanism. Experimental support is found from determination of volumes and entropies of activation for reaction of $Cr(CO)_5$(alkane) and (arene)$Cr(CO)_2$(alkane).[42,46]

Alkane complexes of d^8 metal carbonyl fragments have also been detected. In 1974, Poliakoff and Turner reported the characterization of reaction intermediates on photolysis of $Fe(CO)_5$ in low-temperature matrices by infrared spectroscopy with isotopic labeling.[47] In a matrix of argon, the principal photoproduct was the 16-electron species $Fe(CO)_4$. In contrast to the matrix photochemistry of $Cr(CO)_5$ where a molecule of matrix host is always coordinated with the metal, $Fe(CO)_4$ did not bind a molecule of the matrix. This was probably a result of the proposed triplet ground state of C_{2v}-$Fe(CO)_4$. However, in matrices of methane or xenon, $Fe(CO)_4$ was present in two forms. One of these was triplet C_{2v}-$Fe(CO)_4$ observed in argon matrices, but the other had IR spectra consistent with singlet C_{2v}-$Fe(CO)_4$(S) (S = CH_4, Xe). These two forms of $Fe(CO)_4$ could be interconverted by irradiation with UV or near-IR light. The authors proposed that the interaction of methane with $Fe(CO)_4$ stabilized the singlet state, whereas the interaction of argon with the metal was too weak and therefore only the “naked” triplet state of $Fe(CO)_4$ was present. The axial–axial CO bond angle was determined as 145° in free triplet $Fe(CO)_4$ and 174° in singlet $Fe(CO)_4(CH_4)$. It also appears that the interaction of methane with $Fe(CO)_4$ is weaker than with $Cr(CO)_5$.

In the gas phase, $Fe(CO)_4$ reacts with CO about 600 times more slowly than $Cr(CO)_5$.[24] In solution, however, the lower reactivity of the iron fragment with hydrocarbons may render it more reactive with other molecules than $Cr(CO)_5$, as the latter is always present as $Cr(CO)_5$(solvent). Detection of $Fe(CO)_4$ in solution has been thwarted by rapid formation of $Fe_2(CO)_9$ and other insoluble polynuclear species, although $Fe(CO)_4(C_6D_6)$ has been detected using TRIR in C_6D_6 solution.[48] TRIR experiments in the gas phase revealed $Fe(CO)_4$ with a C_{2v} triplet ground state very similar to that found in low-temperature matrices.[49]

Burkey et al. recently employed laser flash photolysis and photoacoustic calorimetry to study the solution photochemistry of some iron(phosphine)(carbonyl) complexes.[50] Their primary conclusion was that the intermolecular iron–alkane bonds were significantly weaker than previously observed with the d^6 metal carbonyls. The possibility of a large decrease in alkane binding energies between the fragments $Fe(CO)_2(PMe_3)_2$ and $Fe(CO)_3(PMe_3)$ was dismissed in favor of a variation in Fe–P and Fe–CO bond strengths with degree of phosphine substitution.

Very recently, Mawby et al. reported the photochemistry of $Ru(CO)_3(PMe_3)_2$ in low-temperature matrices.[51] Photolysis in argon, methane, or xenon matrices resulted in CO expulsion leaving the trigonal-bipyramidal d^8 16-electron fragment $Ru(CO)_2(PMe_3)_2(S)$ (S = Ar, CH_4, Xe). This species exhibited an intense UV absorption band which shifted from 423 nm in Ar to 385 nm in CH_4 ($\Delta\nu = 2330$ cm^{-1}) and 352 nm in Xe ($\Delta\nu = 4770$ cm^{-1}). The intermediate was also generated by photolysis of $Ru(CO)_2(PMe_3)_2(H)_2$, although both reductive elimination of H_2 and dissociation of CO occurred, complicating the analysis. This is the first time that such shifts in visible absorption spectra have been observed for a d^8 metal fragment. In addition, the shifts are greater in magnitude than those produced on coordination of methane or xenon to d^6 metal carbonyl fragments.

Variation in stability of alkane complexes with electronic character of metal and ancillary ligands is intriguing. The above work from our research group suggests that metal–alkane interactions may be favored by high electron density at the metal.

Although there are other examples of the coordination of alkanes to d^8 and d^4 metal complexes, the complexes are C–H activators, and the alkane complexes are intermediates on the reaction pathway to C–H activation which will be covered in the next section.

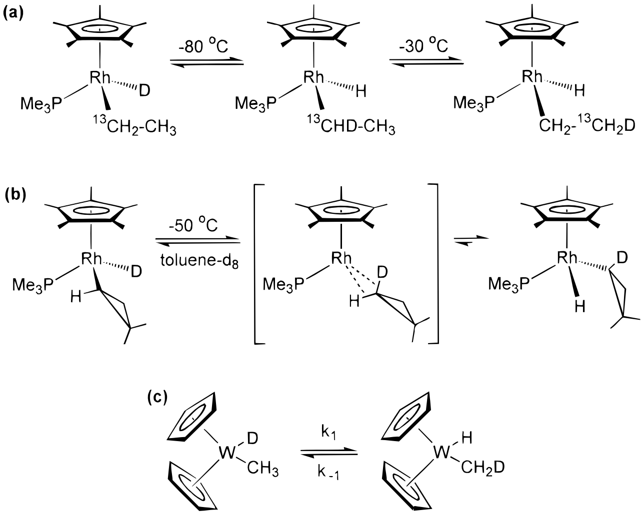
IV. Alkane Complexes as Intermediates in Oxidative Addition and Reductive Elimination

A. Hydrocarbon Solutions

A growing body of evidence supports the intermediacy of transition metal alkane complexes in solution C–H activation (and reductive elimination) reactions. The first example was obtained in 1986 by Bergman et al. in a study of the oxidative addition and reductive elimination of cyclohexane to and from the unsaturated fragment Cp^*IrPMe_3.[52] In this work the authors employed well-designed experiments with conventional NMR methods and isotopic labeling. Two important phenomena indicated the presence of a metal σ-alkane intermediate in these reactions. Firstly, H/D scrambling was observed between the hydride and α-cyclohexyl positions of $Cp^*IrPMe_3(C_6H_{11})D$. Virtually no deuterium was incorporated into the other positions in the cyclohexyl ring, yet if the H/D exchange occurred via simple reductive elimination and oxidative addition of $C_6H_{11}D$, the deuterium should appear in all possible positions. Thermolysis of a mixture of $Cp^*IrPMe_3(C_6D_{11})D$ and $Cp^*IrPMe_3(C_6H_{11})H$ produced only d^0 and d^{12} cyclohexane, proving that the reductive elimination was completely intramolecular. Secondly, the reductive elimination exhibited an inverse isotope effect of $k_H/k_D = 0.7$. The authors argue that an inverse isotope effect cannot result from a single step elimination and requires an intermediate between the alkyl hydride and free alkane, proposed as the σ-alkane complex $Cp^*IrPMe_3(C_6H_{12})$.

A similar study on the analogous rhodium complexes Cp^*RhPMe_3(alkyl)H provided further evidence for the intermediacy of alkane complexes.[53a] A combination of ^{13}C and ^2H labeling revealed the presence of two exchange processes in this system (Scheme 5a). The specific H/D exchange occurring at −80 °C was also accompanied by a large inverse isotope effect (0.5). Additional information has been obtained in both the rhodium and iridium systems by the introduction of a dimethylcyclopropyl group. Exchange of H for D (Scheme 5b) is then linked to interconversion of diastereomers. With iridium, but

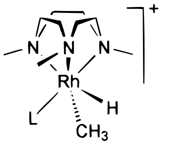
Scheme 5. (a) Exchange Processes in Cp*RhPMe$_3$(C$_2$H$_5$)H, (b) H/D Exchange at Secondary Carbon Atoms via a σ-Alkane Complex Intermediate (Reprinted from Ref 53. Copyright 1996) American Chemical Society), and (c) H/D Exchange in Cp$_2$W(CH$_3$)(H)



not with rhodium, the diastereomers have been isolated and the kinetics of exchange studied independently.[53b] These observations provide further evidence for the intramolecular nature of the H/D exchange process and the involvement of a metal σ-alkane intermediate in the reductive elimination/oxidative addition pathway.

In 1989, compelling evidence was presented for the presence of metal σ-methane complexes in the reductive elimination of methane from Cp$_2$W(CH$_3$)H (Norton et al.), Cp*$_2$W(CH$_3$)H (Bercaw and Parkin), and [Cp$_2$Re(CH$_3$)H]$^+$ (Heinekey and Gould).[54-56] All the investigations employed experiments similar to those described by Bergman et al. H/D exchange between the hydride and methyl positions of Cp$_2$W(CH$_3$)D was found to be faster than reductive elimination of methane (Scheme 5c), and experiments with Cp$_2$W(CH$_3$)H and Cp$_2$W(CD$_3$)D yielded only d^0 or d^4 methane, as expected for an intramolecular process. In each case oxidative addition of methane does not occur, ruling out an elimination/insertion mechanism and providing further evidence for the intramolecular nature of the reactions. The isotope effect for the reductive elimination of methane from Cp$_2$W(CH$_3$)H was measured as 0.7. By analogy with the experiments of Bergman et al., the findings were rationalized by the presence of a metal σ-methane intermediate (Figure 4).

Wang et al. recently prepared the complexes [(Cn)Rh(PR$_3$)(H)(CH$_3$)][BAr$_4$], **6**, (Cn = 1,4,7-trimethyl-1,4,7-triazacyclononane; R = Me, OMe; BAr$_4$ = B[C$_6$H$_3$-3,5-(CF$_3$)$_2$]$_4$) and reported a detailed study of the reductive elimination of methane in the presence of isotopically labeled methane or benzene.[57] The rhodium alkyl hydride complexes were unusually stable, possibly a consequence of the cationic nature of the complexes and the hard environment provided by the Cn ligand. Thermolysis of [CnRh(PMe$_3$)(H)(CH$_3$)]$^+$ and [CnRh(PMe$_3$)(D)(CD$_3$)]$^+$ at 50 °C induces unimolecular elimination of CH$_4$ and CD$_4$ respectively with an inverse isotope effect $k_H/k_D = 0.74 \pm 0.02$, also consistent with the formation of a rhodium σ-methane complex prior to reductive elimination.



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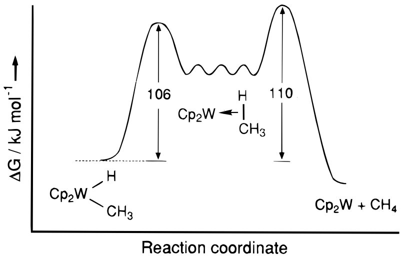


Figure 4. Reaction profile for H/D exchange in Cp$_2$W(CH$_3$)(H). (From ref 54.)

Wolczanski and co-workers carried out a similar study of a σ-bond metathesis, involving methane elimination from d^0 (^{t}Bu$_3$SiNH)$_3$ZrCH$_3$, but found no conclusive evidence for a methane complex at any stage.[58]

B. Liquified Noble Gases

Bergman has obtained evidence for the intermediacy of alkane complexes in C−H activation from TRIR experiments.[59,60] Liquified rare gas solvents are highly desirable for this kind of study for a number of reasons.[61] Since they are monatomic they are completely transparent to infrared radiation; they can be used (at only moderate pressures) at very low temperatures if the requirement is to stabilize reactive intermediates and slow down reactions. Alternatively, a large temperature range can be employed assisting detailed kinetic analyses. Although there is plenty of evidence that noble gases can bond to reactive intermediates,[31,62] they cannot be activated in the same way as conventional hydrocarbon or fluorocarbon solvents. Photolysis of Cp*Rh(CO)$_2$ in liquid xenon resulted in CO expulsion and the formation of a reactive intermediate, characterized from its ν(CO) mode. The band was shifted little in liquid krypton, but the intermediate was found to be considerably more reactive than in xenon. This observation led to the assignment of the transients as Cp*Rh(CO)(Xe) and Cp*Rh(CO)(Kr). In the presence of a small amount of cyclohexane these species were rapidly transformed into the insertion product Cp*Rh(CO)(C$_6$H$_{11}$)H. The kinetics of formation of Cp*Rh(CO)(C$_6$H$_{11}$)H in liquid krypton were inconsistent with a dissociative mechanism, but could be reconciled with an equilibrium between krypton and cyclohexane complexes prior to oxidative addition. A distinct ν(CO) mode due to Cp*Rh(CO)(C$_6$H$_{12}$) could not be detected, probably because of overlap with that of Cp*Rh(CO)(Kr).[63]

Bergman and co-workers have recently described the reaction of Cp*Rh(CO)$_2$ with C$_6$H$_{12}$ and C$_6$D$_{12}$ in Kr$_{(l)}$ and Xe$_{(l)}$.[64] The observed rate of reaction saturated at high alkane concentrations, indicative of a two-step mechanism in which the first step is an equilibrium (eqs 4−6). Although the authors were

$$\mathrm{Cp^*Rh(CO)_2} \xrightarrow[\text{Kr liq}]{h\nu} \mathrm{Cp^*Rh(CO)(Kr) + CO} \quad (4)$$

$$\mathrm{Cp^*Rh(CO)(Kr) + C_6X_{12}} \underset{X = H, D}{\overset{K_{eq}}{\rightleftharpoons}} \mathrm{Cp^*Rh(CO)(C_6X_{12}) + Kr} \quad (5)$$

$$\mathrm{Cp^*Rh(CO)(C_6X_{12})} \xrightarrow[X = H, D]{k_2} \mathrm{Cp^*Rh(CO)(C_6X_{11})X} \quad (6)$$

able to measure the equilibrium constant for the interconversion of Cp*Rh(CO)(Kr) and Cp*Rh(CO)(C_6H_{12}) (K_{eq}) and the rate constants for the alkane activation step (k_2), they were unable to observe distinct ν(CO) bands for the krypton and alkane complexes.

The effect of deuterium substitution was markedly different for the two stages of the reaction. The activation step was easier for C_6H_{12} ($\Delta H^{\ddagger}(\mathrm{CH}) = 17.6 \pm 2.1$ kJ mol^{-1} and $\Delta H^{\ddagger}(\mathrm{CD}) = 22.2 \pm 2.1$ kJ mol^{-1}), entirely as expected from the difference in zero-point energies of the C–H and C–D bonds. However, there was an inverse equilibrium isotope effect for the interconversion of krypton and alkane adducts, i.e. C_6D_{12} binds more strongly to the metal than C_6H_{12}, contrary to expectations on zero-point energy arguments.[65,66] The greater stability of Cp*Rh(CO)(C_6D_{12}) compared to Cp*Rh(CO)(C_6H_{12}) originates in the greater change in entropy on binding C_6D_{12} over C_6H_{12}.

Bergman and co-workers showed that the reaction of Cp*Rh(CO)$_2$ with neopentane proceeded similarly to that with cyclohexane.[67] However, with neopentane-d_{12} they observed two distinct transient absorption bands at 1946 cm^{-1} (Cp*Rh(CO)(Kr)) and 1947 cm^{-1} (Cp*Rh(CO){$(CD_3)_4C$}). They monitored the equilibrium between the krypton and alkane complexes and the direct conversion of the neopentane-d_{12} complex to the neopentyl deuteride (2009 cm^{-1}), both from the rise of the product IR signal and the decay of the alkane complex (Figure 5). Complete reaction profiles of each step of the alkane activation reaction of Cp*Rh(CO)$_2$ were obtained—excellent evidence for the intermediacy of alkane complexes in the oxidative addition of alkanes.[67,68] These experiments indicate that the electronic effect on Cp*RhCO of an alkane is similar to that for Xe, as for Cr(CO)$_5$.

C. Gas Phase

Indirect evidence for alkane coordination to CpRh(CO) in the gas phase has recently been presented.[69] Reaction with a range of alkanes occurred at every collision, implying a minimal barrier to C–H activation. The remarkable ease of the reaction was ascribed to the formation of alkane complexes before C–H activation. It was proposed that the conversion of the alkane complexes to alkyl hydride complexes would be exothermic, with an activation energy of less than 21 kJ mol^{-1} (Figure 6).

The evidence presented in this section strongly supports the presence of alkane complexes as intermediates in C–H activation reactions.

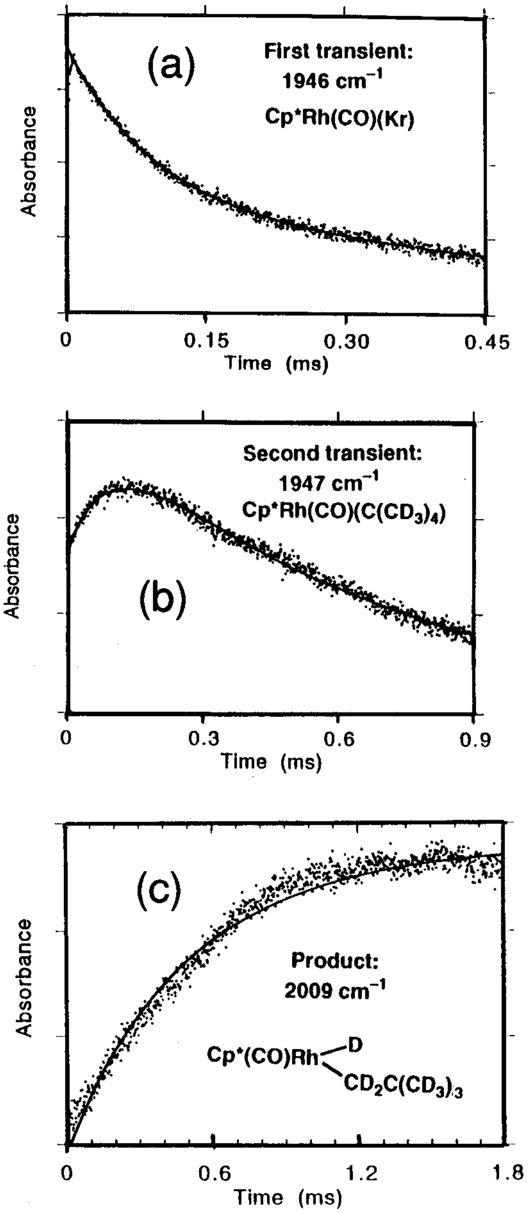


Figure 5. Infrared kinetic traces showing C–D activation of neopentane-d_{12} following UV laser photolysis of Cp*Rh(CO)$_2$ in liquid Kr solution. The initial transient Cp*Rh(CO)Kr (a) is converted to the intermediate alkane complex Cp*Rh(CO)[$C(CD_3)_4$] (b), before C–D insertion to yield Cp*Rh(CO)[$CD_2C(CD_3)_3$]D (c). (Reprinted from ref 59.)

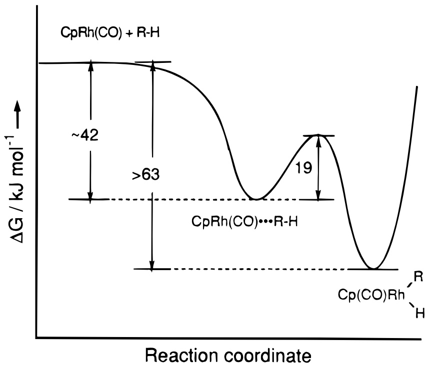


Figure 6. Reaction profile for the gas-phase reaction of CpRh(CO) with alkanes. (Reprinted from Wasserman, E. P.; Moore, C. B.; Bergman, R. G. *Science* 1992, *255*, 315. Copyright 1992 American Association for the Advancement of Science.)

V. The Interaction of Alkanes with Metal Atoms, Ions, and Small Molecules

A. Low-Temperature Matrices

The developments in the study of metal atom−alkane complexes parallel those of the metal carbonyl−alkane complexes. Structural characterization of metal atom−alkane adducts in low-temperature matrices with IR, UV/vis, and ESR spectroscopies was followed by gas-phase studies that provided kinetic and thermodynamic information on the metal−alkane bond.

In 1981, Ozin et al. communicated the photochemistry of copper atoms in methane matrices.[70] UV photolysis of Cu(^{2}S) resulted in the formation of excited Cu(^{2}P) atoms which inserted into the C−H bonds of methane, yielding Cu(CH_3)(H). The methyl hydride underwent further reaction to give CuH and Cu(CH_3). The methane cage complex Cu(^{2}P)(CH_4) was implicated as an intermediate before C−H insertion, but not detected directly. A subsequent publication reported the simulation of the growth kinetics of the ESR signals due to Cu, Cu(CH_3)(H), and CH_3 in this photoreaction. The successful modeling required the presence of a copper atom−methane complex in the reaction pathway.[71] A much stronger interaction between Cu and CH_4 was postulated in the excited state than in the ground state, i.e. Cu*-(CH_4) exciplex. Ozin et al. reported similar chemistry when Ag atoms were isolated in methane matrices.[72]

Prior to the work on copper atoms, Billups et al. had studied the photolysis of a series of transition metal atoms in methane matrices and discovered C−H insertion chemistry for all the second half of the first transition series.[73] Kafafi et al. reported the photochemistry of iron atoms in CH_4 and CD_4 matrices, in which they assigned IR bands to the mononuclear and dinuclear methane adducts Fe(CH_4) and Fe_2(CH_4).[74] The detection of these species in pure methane matrices is hampered by the intense absorption bands of unligated methane.

An elegant solution to the problem of excess methane in these reactions was recently devised by Billups et al. with a route to a 1:1 complex of Co atoms and CH_4 in low-temperature matrices.[75,76] They co-condensed Co atoms with a mixture of diazomethane and hydrogen, which produced Co(CH_3)(H). Subsequent UV photolysis converted this product to the methane adduct Co(CH_4) which was characterized from its IR spectrum (Figure 7, eqs 7 and 8). The shift and splitting of the IR modes of

$$\mathrm{Co} + \mathrm{H_2} + \mathrm{CH_2N_2} \xrightarrow[-\mathrm{N_2}]{\mathrm{Ar/12\ K}} \mathrm{CH_3CoH} \qquad (7)$$

$$\mathrm{CH_3CoH} \underset{280\ \mathrm{nm} < \lambda < 360\ \mathrm{nm}}{\overset{\lambda > 400\ \mathrm{nm}}{\rightleftharpoons}} \mathrm{Co(CH_4)} \qquad (8)$$

methane on coordination is small (<7 cm^{-1} shift and ≤4 cm^{-1} splitting, Table 4). The IR spectrum for the methane adduct was consistent with C_{3v} symmetry. Both the η^1 and η^3-*H,H,H* adducts satisfy this requirement, but the η^3-*H,H,H* geometry was preferred on the grounds that it would be more stable. We will return to the question of mode of coordination in the theory section (section VIII).

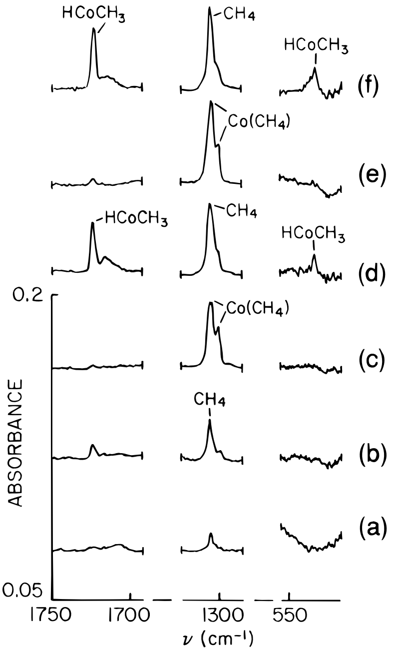


Figure 7. Partial FTIR spectra of CH_4, Co(CH_4), and Co(CH_3)(H) formed by the cocondensation of Co, CH_2N_2, and H_2 in an argon matrix (a) without H_2, (b) with H_2, (c) after 10 min photolysis of b ($\lambda \geq 400$ nm), (d) after 10 min photolysis of c ($360 \geq \lambda \geq 280$ nm) (e) after 10 min photolysis of d ($\lambda \geq 400$ nm), (f) after 10 min photolysis of e ($360 \geq \lambda \geq 280$ nm). (Reprinted from ref 75. Copyright 1993 American Chemical Society.)

The infrared spectra of isotopically labeled complexes, such as Co(CH_2D_2) and Co(CH_3D) provided further evidence for the existence of cobalt methane σ-complexes. In the photochemical isomerization of the methyl hydride and methane complexes, the σ-complexes were shown not to be stereochemically rigid. For instance, visible photolysis of Co(CH_2D)(D) formed the methane complex Co(CH_2D_2), which when subjected to UV photolysis yielded a 2/1 mixture of Co(CHD_2)(H) and Co(CH_2D)(D). The authors concluded that methane must be "loosely bound" in the σ-complex.

Curiously, the corresponding reaction of Cr with diazomethane and hydrogen did not lead to formation of the methyl hydride and methane complexes, but produced only free methane.[77] Presumably, the interaction between Cr and CH_4 was too weak to prevent elimination of methane.

A complex between RhH_2 and CH_4 was reported recently by Van Zee et al.,[78] who used ESR spectroscopy to identify the adduct in a methane-doped argon matrix at 4 K (Figure 8). The complex was formed even when the concentration of CH_4 was as low as 0.01%. No firm conclusions could be drawn regarding the mode of coordination of the methane. Small changes in the hyperfine splitting of RhH_2 and a significant shift in *g* value was observed on methane coordination. No clear evidence was reported for coupling of the electron spin to the protons of CH_4.

B. Gas Phase

1. Atoms

Weisshaar and co-workers studied the gas-phase reaction of neutral transition metal atoms with a

Table 4. Absorption Frequencies (cm^{-1}) for $Co(CH_4)$, $Co(CH_2D_2)$, $Co(CD_4)$, and $Co(CH_3D)$ (From Ref 76)

CH_4	$Co(CH_4)$	vibration mode	CD_4	$Co(CD_4)$	vibration mode	CH_2D_2	$Co(CH_2D_2)$	vibration mode	CH_3D	$Co(CH_3D)$	vibration mode
1305.8	1303.4 1299.3	CH_3 d-def[a]	993.6	992.9 989.8	CD_3 d-def[a]	3020.2	3015.4	CH_2 a-str	3026.5	3019.3	CH_3 d-str[a]
						2981.9	2974.0	CH_2 s-str			
						1431.4	1430.0	CH_2 scis	1302.4	1303.1 1298.6	CH_3 s-def
						1232.3	1229.3	CH_2 wag	1155.4	1155.1 1151.8	CH_3 rock
						1028.6	1026.5	CD_2 scis			

[a] d = degenerate.

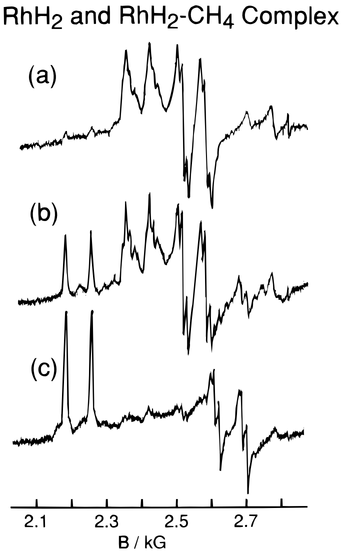


Figure 8. ESR spectra of the RhH_2 molecule and the RhH_2-CH_4 complex in an argon matrix at 4 K: (a) RhH_2 in argon plus a trace of CH_4, (b) in argon plus 0.01% CH_4, and (c) in argon plus 0.1% CH_4. (Reprinted from ref 78. Copyright 1993 American Chemical Society.)

range of linear alkanes and alkenes, by laser-induced fluorescence and mass spectrometry.[79a] Strangely, given the reactivity with methane in low-temperature matrices, none of the 3d transition metal atoms reacted with alkanes in the gas phase.[79b] However, $Pd(^1S_0)$ did react with ethane, propane, and *n*-butane at 300 K in the gas phase (methane was unreactive).[80a] The dependence of these rates on helium pressure provided indirect evidence that the reaction products were collisionally stabilized Pd(alkane) adducts. The activation barrier for adduct formation was less than 21 kJ mol^{-1} and the Pd−alkane binding energies exceeded 33 kJ mol^{-1}. The authors proposed an η^2-*H,H* structure for the alkane adducts, which was further supported in an experimental and theoretical study of the reaction of second row transition metal atoms, by Weisshaar, Siegbahn, and co-workers.[80b] A very weakly stabilized $Pt-CH_4$ σ-complex has been detected recently, again with supporting PCI-80 calculations.[80c]

2. Ions

Over a number of years, alkane complexes have been implicated as intermediates in the gas-phase dehydrogenation of alkanes by transition metal ions. A comprehensive discussion of the reaction of transition metal ions with alkanes is beyond the scope of this review, but the reader is referred to recent papers by Eller and Schwarz[81] and by Armentrout and Beauchamp[82] for further details. However, several papers have appeared over the last five years which deal explicitly with the *coordination* of alkanes.

The gas-phase study of transition metal ions is considerably easier than that of neutral atoms, as mass spectrometric methods permit extensive characterization of reaction intermediates and products. As a consequence, the reactivity of transition metal ions with alkanes is well studied. In general, the transition metal ions are much more reactive with alkanes than the corresponding neutral atoms.

Weisshaar and co-workers have studied the reaction of ground-state first row transition metal cations (M^+) with alkanes in a multicollisional environment of 0.75 Torr He, with a fast flow reactor coupled to a quadrupole mass spectrometer.[83] Under these conditions, collisionally stabilized metal ion alkane adducts were detected for all the first row transition metal ions (except Mn^+ with CH_4). The rate constants for reaction with alkanes were highest for the late transition metal ions (Co^+, Ni^+, and Cu^+) and also higher for those ions with $3d^n$ electronic ground states. The authors obtained no direct evidence for the structure of the adduct ions, but proposed that $M(\sigma\text{-alkane})^+$ and $M(alkyl)(hydride)^+$ complexes were most easily reconciled with the observed trends in reactivity. Metal ion−alkane dissociation energies determined for $Mn(alkane)^+$ and $Zn(alkane)^+$ all exceeded 42 kJ mol^{-1}.

Hill et al. reported the gas-phase reactivity of Y^{2+} with alkanes and alkenes using Fourier transform mass spectrometry.[84] Adduct ions $Y(alkane)^{2+}$ and $Y(alkene)^{2+}$ were detected and their reactivity probed with a series of displacement reactions. Surprisingly, free alkanes were able to displace shorter chain bound alkenes from Y^{2+}. The authors ascribed this behavior to a purely electrostatic interaction between Y^{2+} and hydrocarbons (i.e. no $M-\pi^*$-back donation in Y^{2+}(alkene) complexes), the magnitude of which is governed solely by the size and polarizability of the hydrocarbon. In contrast, Cu^+ displayed the expected preference of a transition metal for alkenes. The authors supported their proposals with MCPF calculations.

A number of studies have used the technique of threshold collisional activation to probe the thermochemistry of transition metal ion reactions. This involves varying the energy of the ions to determine a minimum "threshold" energy at which reactions may occur. These experimentally determined values may be directly converted to bond dissociation energies.

Table 5.

a. Sequential Bond Dissociation Energies (kJ mol^{-1}) of FeL_n^+ Complexes (Adapted from Ref 86)

L	$n = 1$	$n = 2$	$n = 3$	$n = 4$
H_2O	128(5)	164(4)	76(4)	82(5)
CH_4	57(3)	97(4)	99(6)	74(6)

b. Sequential Bond Dissociation Enthalpies (kJ mol^{-1}) of Titanium Ions (Adapted from Ref 87)

ion	$n = 1$	$n = 2$	$n = 3$	$n = 4$
$Ti(CH_4)_n^+$	70(3)	73(3)	28(6)	
$Ti(CH_4)_n(CH_3)(H)^+$			41(3)	21(3)
$Ti(CH_4)_n(CH_2)^+$	>100	80(4)	30(2)	

c. Experimental and Calculated Co−CH_4 Bond Dissociation Energies (kJ mol^{-1}) of $Co(CH_4)_n^+$ Complexes (Adapted from Ref 88)

	$n = 1$	$n = 2$	$n = 3$	$n = 4$
experiment	90(6)	96(5)	40(5)	64(6)
theory	72	85	24	53

Work by Schultz and Armentrout involved measurements of the relative stability of $Fe(C_2H_6)^+$ and $Fe(CH_3)_2^+$ in the gas phase.[85a] The alkane adduct and dimethyl complex were formed from the reaction of Fe^+ ions with C_2H_6 and CH_3COCH_3, respectively. They deduced that $Fe(C_2H_6)^+$ was more stable than $Fe(CH_3)_2^+$, by 14.6 ± 7.1 kJ mol^{-1}, and that it was stable with respect to free Fe^+ and C_2H_6 by 64.0 ± 5.9 kJ mol^{-1}. Rosi et al. had previously predicted by ab initio calculations that the alkane adduct would be more stable than the dimethyl complex by ca. 18 kJ mol^{-1}.[85b] The Fe^+−ethane interaction had been assumed to be purely electrostatic. A study of Fe^+ reactivity toward propane allowed direct detection of $Fe(C_3H_8)^+$ and determination of the Fe^+−propane binding energy of 80 ± 8 kJ mol^{-1}.[85c]

Schultz and Armentrout also employed the technique of collision-induced dissocation (CID) in a guided-ion beam mass spectrometer to obtain bond dissociation energies for $Fe(CH_4)_x^+$ and $Fe(H_2O)_x^+$ clusters ($x = 1-4$) (Table 5a).[86a] The bond dissociation energies of $[(CH_4)Fe-(CH_4)]^+$ and $[(CH_4)_2Fe-(CH_4)]^+$ were significantly higher than that of $[Fe-(CH_4)]^+$. Most surprisingly, the bond dissociation energy of $[(CH_4)_2Fe-(CH_4)]^+$ was higher than that of $[(H_2O)_2Fe-(H_2O)]^+$. These trends were ascribed to a change in the electronic structure of the metal ion with successive coordination of ligands of varying field strength (i.e. $[(CH_4)_2Fe-(CH_4)]^+$ and $[(H_2O)_2Fe-(H_2O)]^+$ have different electronic ground states). Further details of the $Fe^+ + CH_4$ potential energy surface have been explored very recently.[86b]

A study of the mechanism of gas-phase methane dehydrogenation by Ti^+ with quadropole mass spectrometry has been described by van Koppen and coworkers,[87] who obtained reaction enthalpies for the successive reaction of molecules of CH_4 with Ti^+ (Table 5b). The reactions of CH_4 with Ti^+ and $[Ti(CH_4)]^+$ yield metal ion σ-alkane complexes, but with $[Ti(CH_4)_2]^+$ C−H bond activation to give $[Ti(CH_4)_2(CH_3)(H)]^+$ is more exothermic than σ-alkane complex formation. The binding of methane to $Ti{=}CH_2^+$ was stronger than to Ti^+, consistent with a higher positive charge on the metal (the metal ion−methane interaction was assumed to be purely electrostatic).

Haynes et al. used CID with guided ion beam mass spectrometry to determine successive bond energies for the binding of methane to $[Co(CH_4)_x]^+$ ($x = 0-3$) (Table 5c).[88a,b] The bond energies for the first two molecules of methane were the same within experimental error, whereas the third molecule bound very weakly. The authors were able to model the structure of the metal−methane adducts using ab initio calculations. They concluded that all the ligands would bind in an η^2-*H,H* fashion and their predicted bond energies were in excellent agreement with the experimental data. The trend in bond energies was explained by a change in hybridization at the metal on coordination of the third molecule of CH_4. The metal is sd hybridized in $[Co(CH_4)]^+$ and $[Co(CH_4)_2]^+$ (deshielding the positively charged nucleus and resulting in a stronger interaction with CH_4), but not in the higher nuclearity clusters. The binding energy of $Co(C_2H_6)^+$ has recently been determined as 100 ± 5 kJ mol^{-1}.[88c]

Schwarz and co-workers studied the chemical ionization of $Fe(CO)_5$ with a variety of organic molecules, observing four distinct isomers of the ion $[Fe,C,H_4,O]^+$.[89a] One of these, generated from a mixture of $Fe(CO)_5$, CH_4, and N_2O, was only observed when collisionally stabilized. Under other conditions it decomposed to FeO^+ and CH_4, suggesting an FeO^+-CH_4 adduct structure. Ab initio MO calculations support this assignment, with CH_4 bound η^3-*H,H,H* to FeO^+. This adduct was predicted to be approximately 50 kJ mol^{-1} more stable than FeO^+ and CH_4. More details of the reactivity of transition metal oxide cations with alkanes in the gas phase are given by Schröder and Schwarz.[89b]

Metal−propane adduct ions have also been detected in a number of studies on the gas-phase dehydrogenation and demethanation of propane by Co^+, Ni^+, and Fe^+ ions.[90]

VI. Experimental Criteria for the Characterization of Transition Metal Alkane Complexes

In the preceding sections, we have reviewed a variety of experiments in which alkane complexes have been detected. Here we summarize the key experimental approaches and comment on their strengths and weaknesses.

A. In Matrices

Very large shifts (>1500 cm^{-1}) in the positions of UV/vis absorption maxima of coordinatively unsaturated complexes between argon and methane matrices provide prima facie evidence for complexation by the alkane. Confirmation should be sought by demonstrating that two different species are present in CH_4-doped argon matrices corresponding to the methane complex and the argon (or naked) complex. Even larger shifts should be detectable by comparing methane and neon matrices. The absorption maxima observed for methane matrices are usually comparable to those for xenon matrices. Although the UV/vis criteria have proved to be the most widely applicable, they are far from universal.

Shifts may also be observed in IR spectra of matrix-isolated complexes on complexation of an alkane.

However, there are several factors which conspire to make this a difficult criterion to apply: (i) general solvent effects are usually larger than the shifts on complexation so comparisons cannot be made between different matrices; (ii) any two molecules isolated in the same matrix cage undergo a vibrational interaction; (iii) the alkane is usually present in large excess (but see refs 75 and 76); (iv) bands in mixed matrices are broader than in pure matrices. It follows that it is usually necessary to work in methane-doped matrices and to search for two species close together, one of which is complexed by the methane. Even then, a perturbation does not provide evidence of a *significant* interaction.

The effect of methane complexation on a ν(CO) frequency may be contrasted with the effect of oxidative addition. If methane acts as a weak σ-donor it will cause a small shift to low frequency. If it acts as a σ-donor, σ*-acceptor like H_2 it would cause a moderate high-frequency shift. In contrast, oxidative addition should cause a large high-frequency shift. For the low-frequency a_1 ν(CO) mode of $Cr(CO)_5$, methane complexation causes a shift to high frequency relative to argon of $\sim$3 cm^{-1},[6b] compared to a high-frequency shift for H_2 coordination of $\sim$30 cm^{-1}.[9b] Oxidative addition of methane to CpRh(CO) causes a high-frequency shift of $\sim$60 cm^{-1}.[91a] For (η^6-arene)Os(CO) the corresponding figure is close to 80 cm^{-1}.[91b] The ν(CO) modes of $Cp^*Rh(CO)[(CD_3)_4C]$ and $Cp^*Rh(CO)[CD_2C(CD_3)_3]D$ are separated by 62 cm^{-1}.[67,92]

Complexation may also be detected by ESR. In favorable cases, it should be possible to observe a significant shift in the g value and hyperfine coupling to the hydrogen atoms of methane or to ^{13}C in labeled methane. In the example of RhH_2, only the first criterion was achieved.[78]

Matrix isolation has been used most successfully to demonstrate alkane coordination when the UV criteria can be met. When the complex has no suitable UV/vis bands and is diamagnetic (e.g. (η^6-arene)$Cr(CO)_2$), it has not proved possible to establish alkane coordination by matrix methods.[41]

B. In Solution

In principle, it should be possible to monitor the disappearance of a reaction intermediate on addition of alkane and the appearance of the alkane complex. This has not been achieved so far. The nearest comparison is to be found in the reactions of $Os(PP_3)$ ($PP_3 = P(CH_2CH_2PPh_2)_3$). Flash photolysis of $Os(PP_3)H_2$ in cyclohexane yields $Os(PP_3)$. The rate of disappearance of the $Os(PP_3)$ transient increases linearly with concentration of dissolved methane.[93] However, the product is thought to be a methyl hydride complex rather than a methane complex. The obstacles to measurements of this type are numerous: a lack of inert solvents, the rapidity of reaction in liquid alkanes (often < 1 μs), the similarity of the spectrum of the alkane complex to that of the “naked” fragment.

Complexation by an alkane can be established by other kinetic measurements, involving time-resolved visible or IR spectroscopy (section III.A.2). The complexation should reduce the rate constants for reaction of a transition metal species with substrates such as CO or N_2. This criterion poses operational problems once more: (i) an inert solvent is required for comparison, yet such species are so reactive that the notion of an inert solvent is suspect, (ii) if comparison is made between solvents, the effect of the alkane should be outside the bounds of normal solvent effects, (iii) a distinction must be made between the presence of an alkane complex and that of an alkyl hydride complex which may also be very labile (see matrix criteria, A above). Such criteria have been met successfully for $Cr(CO)_5$(alkane) by employing perfluoroalkanes as the inert solvent, and by making comparisons with matrix spectra to establish that an alkane complex is formed.[11] Perfluoroalkanes have not proved widely applicable as solvents because the precursor complexes are often too insoluble. Liquid krypton, but not liquid xenon, has been used successfully for Cp*Rh(CO) with all the concomitant experimental difficulties (section IV.B). Matrix spectra suggest that any interaction with xenon is likely to be comparable in magnitude to interaction with methane. In the case of Cp*Rh(CO), complexation with xenon does indeed prove too strong to study interaction with an alkane in the same medium.[62−64] The choice of spectroscopic method for these measurements should be based on the same criteria as for the matrix spectra. One of the attractions of liquified noble gases is that they dissolve huge quantities of simple alkanes, whereas the solubility of gaseous alkanes such as methane in liquid alkanes is very low ($\sim 10^{-2}$ mol dm^{-3} atm^{-1}). The use of a mixed alkane/liquified noble gas may also enhance the solubility of the complex.[3m]

The low temperatures required for liquified noble gases may be overcome by the use of supercritical noble gases. The latter may be employed at or round room temperature (for Xe, $T_c = 290$ K, $P_c = 57$ bar)[61] and have the attraction that alkanes are continuously miscible in them.

One of the most effective methods for establishing the existence of an alkane complex in solution is photoacoustic spectroscopy (section III.A.2). If the sample meets the requirements of PAC,[14] it may be possible to establish alkane coordination when the matrix spectra leave it uncertain (e.g. $CpMn(CO)_2$(alkane)).[45]

Evidence for alkane coordination has also been obtained by steady-state spectroscopy (especially NMR) when the system includes a stable metal alkyl hydride. Two methods, involving deuterium labeling have been adopted: testing for isotopic scrambling and measurements of kinetic isotope effects. Observation of isotopic scrambling in complexes of type $M(CH_2R)D$ provides some of the best indirect evidence for an alkane complex when scrambling is faster than reductive elimination, or when reductive elimination is irreversible (section IV.A).[52−57]

Kinetic isotope effects (kie) of less than unity on the rate of reductive elimination from a metal alkyl hydride have been found on several occasions.[52−57] The usual interpretation of such an effect is that an equilibrium with an alkane complex precedes reductive elimination (eq 9).

$$[M](CX_2R)X \overset{K_{eq}}{\rightleftharpoons} [M](CX_3R) \qquad X = H, D \quad (9)$$

$$[M](CX_3R) \xrightarrow{k} [M] + CX_3R$$

As far as we are aware, this interpretation has not been justified by a full ab initio calculation of the kie. Recent ab initio calculations of kie on oxidative addition of H_2 have been most instructive. The simple-minded analysis in terms of zero-point energies associated with stretching vibrations has been shown to be misleading.[94a] There is no substitute for a full examination of the contributions of rotational and vibratonal partition functions in the ground and transition state, together with the term arising from excitation. The kie may be calculated via eq 10:

$$\frac{k_H}{k_D} = \frac{Q_H{}^{\ddagger} Q_D}{Q_D{}^{\ddagger} Q_H} e^{-\Delta\Delta ZPE/RT} \qquad (10)$$

where $Q_H{}^{\ddagger}$ is the partition function (pf) for the protiated molecule in the transition state, etc., and $Q_H{}^{\ddagger} = Q_{Hrot}{}^{\ddagger} Q_{Hvib}{}^{\ddagger} Q_{Htrans}{}^{\ddagger}$. The difference in zero-point energy between ground and transition state is defined as ΔZPE, and ΔΔZPE is $(\Delta ZPE_H - \Delta ZPE_D)$. The rotational pf contributes significantly to oxidative addition of H_2 or CH_4 since the moments of inertia of these small molecules are isotope dependent. It will not contribute to reductive elimination. The vibrational pf is dominated by low-frequency vibrations since only they are significantly populated (at 300 K, $kT \approx 200$ cm^{-1}). For a dihydride complex, there are four isotope-sensitive deformation modes at low frequency. For a methyl hydride complex, there are only two such modes. The vibrational pf term in eq 10 is typically less than unity. In contrast, the activation term ΔΔZPE is dominated by high-frequency modes and is typically greater than unity.

Notably, the calculations show that the kie does not increase as the transition state moves further along the reaction coordinate for oxidative addition of H_2. The problems of low frequency vibrations are certainly less acute for a metal alkyl hydride than for a metal dihydride. The mechanism of eq 9 requires calculation both of a kie and an equilibrium isotope effect (eie). Bender has recently calculated and measured the eie for binding of C_2H_4 to $Os_2(CO)_8(C_2D_4)$ and shown both to be close to $K_H/K_D = 0.7$.[94b] In conclusion, we see an urgent requirement for validation of the interpretation of eq 9 via calculations of kie's and eie's.

Since an alkane complex has yet to be observed by NMR in solution, we cannot provide full criteria for its detection. Moreover, such observations are likely to be complicated by rapid exchange with excess alkane. However, we anticipate similar behavior to that observed in host–guest complexes, an example of which is shown in the final section of this review. It may be advantageous to use methane dissolved in liquid xenon as an NMR solvent just as has been employed for observation of $Fe(dmpe)_2(CH_3)H$.[3m]

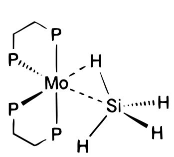
C. Gas Phase

Many of the same principles apply to the gas phase as to solution or matrices. For time-resolved spectroscopy, there are a few significant differences (i) there is no solvent so any shift observed on addition of alkane is more readily attributed to complexation, (ii) IR bands are usually broader in the gas phase than in solution because of rotational contours, hampering measurement of shifts, (iii) it is easier to measure bond dissociation energies in the gas phase (section III.A.3). Measurement of time-resolved visible spectra in the gas phase remains an underused method.

Mass spectrometry provides a wealth of information in gas-phase studies of transition metal ions. However, alkane coordination cannot be proved directly from these studies; rather it must be inferred from fragmentation patterns, reactivity, and variations in the degree of collisional stabilization. Similarly, LIF studies of transition metal atoms are not a direct probe of alkane complexation, but a means of following the reactions of metal atom adducts.

VII. Comparisons of Alkane Complexes with Other σ-Complexes

The various modes of coordination of alkanes all have precedents in other σ-complexes. The BH_4^- ion is isoelectronic with methane, and forms many stable transition metal complexes. Most commonly, it coordinates in the η^2-*H,H* mode although there are a great many isolable η^1, η^2-*B,H* and η^3-*H,H,H* borohydride complexes.[95] The complex, $Ti(BH_4)_3(PMe_3)_2$, allows comparisons of η^2-*H,H* and η^2-*B,H* bonding within the same molecule. Both coordination modes bring the metal within bonding range of boron (r(TiB) = 2.40(1) and 2.27(1) Å, respectively), but the η^2-*B,H* mode brings the boron significantly closer.[95c] All the structures of silane-type complexes determined so far have involved η^2-*Si,H* coordination (typically involving X_3SiH, X = alkyl, aryl, Cl).[96−98] The coordination mode has been proved by neutron diffraction.[96] The link between dihydrogen, η^2-*Si,H* and agostic complexes is demonstrated by Kubas et al. in their study of $Mo(CO)(Ph_2PCH_2CH_2PPh_2)_2$.[98a] Most recently, SiH_4 itself has been found to bind in this way (**7**).[98b]



7 η^2-*Si,H*

The heavy atom skeleton of the SiH_4 complex $Mo(CO)(\eta^2\text{-}SiH_4)(R_2PCH_2CH_2PR_2)_2$ ($R = CH_2CHMe_2$) has been defined crystallographically. The η^2-*Si,H* coordination is demonstrated by the solution $^1H\{^{31}P\}$ NMR spectrum which shows the coordinated η^2-*Si,H* group at high field with $J_{SiH} = 31$ Hz and the remaining SiH_3 protons at low field with $J_{SiH} = 163$ Hz. In contrast, silyl hydride complexes typically have $J_{SiH} < 20$ Hz.

The η^1 and η^2-*C,H* coordination modes of alkanes resemble those found in *intra*molecular "agostic" alkyl complexes (see Scheme 1),[99a] lending credibility to these structures for alkane complexes. Recently, *inter*molecular agostic interactions have been observed in the solid state.[99b,c]

Dihydrogen is now accepted as a prototype for coordination of σ-bonds. Its occupied σ-orbital acts as a donor and its empty σ^* acts as an acceptor, leading to a synergic bonding model akin to CO. Coordination lengthens the H−H bond and reduces ν_{HH} and J_{HD}. It is the possibility of back-bonding that explains the isolation of stable dihydrogen complexes such as $(PPr^i_3)_2W(CO)_3(H_2)$.[101] Of the two components of the bond, σ-donation weakens the hydrogen σ-bond, but is unable to break it as there is still an attraction between the two hydrogen nuclei. The back-donation both stabilizes the metal−hydrogen bond and, if too strong, splits the H−H σ-bond. Dihydrogen complexes are now known with a wide range of H−H bond lengths and values of ν_{HH} and J_{HD}.[100−102]

Thus, electron-deficient metal fragments such as $Cr(CO)_5$ form only unstable dihydrogen complexes,[103] fragments of intermediate electron density form stable dihydrogen complexes (e.g. $(PPr^i_3)_2W(CO)_3$), whereas a very electron-rich fragment such as $Ru(dmpe)_2$ will cleave the H−H bond, yielding a dihydride complex.[104] In contrast, the stabilizing back-bonding to methane and other alkanes is thought to be strongly disfavored for steric reasons. The experimental evidence on $Cr(CO)_5(CH_4)$ and Cp*Rh(CO)(alkane) demonstrates that, in these molecules, alkanes act as weak σ-donors like xenon and not as acceptors like dihydrogen (see section VI).[6a,62−64]

The subject of σ-complexes in general has been reviewed elsewhere.[4b,100]

VIII. Theory of Alkane Coordination: How, Why, and Why Not?

A. Alkane Complexation to 14 and 16 Electron Fragments

1. Coordination to d^6 and d^8 Fragments and the Role in C–H Oxidative Addition

The first theoretical investigation of the role of alkane complexes in C−H activation was undertaken by Saillard and Hoffmann[105a] with extended Hückel methods. They compared the approach of hydrogen and methane to the unsaturated fragments $Cr(CO)_5$ and CpRh(CO). The HOMO of methane is a t_2 C−H bonding orbital, with an experimental IE of 12.54 eV (cf. H_2 σ-orbital 15.45 eV).[105b] The LUMO of methane is the t_2 antibonding counterpart and lies at a similar energy to the σ^*-orbital of H_2 (Figure 9). In the case of hydrogen, the approach to the metal fragment was more attractive for a parallel arrangement due to the possibility of back-bonding from the metal to the σ^*-orbitals of hydrogen. However, in the case of methane, this parallel arrangement is disfavored. The methyl group causes steric repulsion with the metal fragment, disallowing stabilizing back-bonding interactions. The binding of methane was therefore proposed to be η^1, although the possibility of an η^2-*C,H* tilted coordination mode was also explored, which permitted some back-bonding, with less steric repulsion. The end-on geometry was predicted to be the most stable for $Cr(CO)_5(CH_4)$.

Ziegler et al. reached similar conclusions in their density functional study of the reaction of CH_4 with

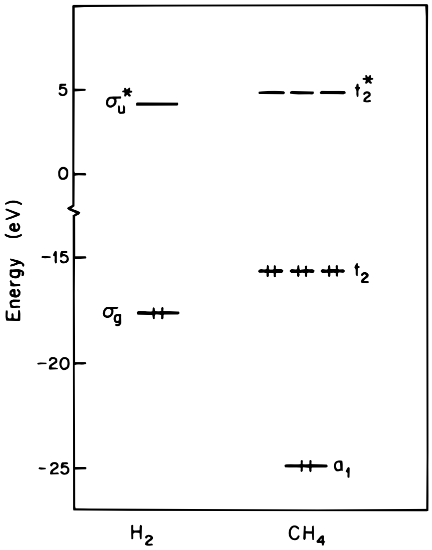


Figure 9. Comparison of the frontier orbital energies of H_2 and CH_4. (Reprinted from ref 105a. Copyright 1984 American Chemical Society.)

a range of transition metal fragments of the type CpML (M = Rh, Ir; L = CO, PH_3) and $M(CO)_4$ (M = Ru, Os).[106] They calculated the relative stability of the intermediate metal alkane adducts, concluding that methane should bind most strongly to $CpIr(PH_3)$—entirely consistent with the trend in C−H activating ability of the modelled fragments.

Ab initio calculations by Song and Hall predicted the structure of the intermediate alkane complex,[107] $CpRh(CO)(CH_4)$, implicated in the liquid krypton and gas-phase kinetics of Bergman et al. They were also able to model the activation parameters for alkane insertion, giving good agreement with experiment. The structure they predicted for the alkane complex is very similar to the crystallographically characterized agostic complex $[Cp^*Rh(C_6H_{11})][BF_4]$,[108] with an η^2-*C,H* interaction showing the beginning of C−H bond cleavage.

Musaev and Morokuma utilized MP2 level ab initio MO calculations to investigate the mechanisms of σ-bond activation of H_2, CH_4, NH_3, H_2O, and SiH_4 by CpRhCO.[109a] They calculated the energy of intermediates, transition states, and final products for each substrate. Of particular interest for our purposes are the structures (Figure 10) and stability of the molecular adducts. For CH_4, NH_3, and H_2O these are true intermediates, the lone pair ligands NH_3 and H_2O being more strongly bound. Interestingly, the barrier to CH_4 oxidative addition is much lower than for NH_3 and H_2O—no point on the reaction profile lies at higher energy than the reactants CpRhCO and CH_4. The molecular adducts for SiH_4 and H_2 do not exist as true intermediates, although these reactions are the most exothermic. Further calculations on CpRhCO and CH_4 are discussed at the end of this section.[109b]

An ab initio study by Koga and Morokuma on the binding of methane to $RhCl(PH_3)_2$ revealed that an η^2-*H,H* coordination of methane would be the most stable.[110] Both donation from methane and back-donation to methane are shown to contribute to interaction with $RhCl(PH_3)_2$. In a later paper Koga and Morokuma reported ab initio calculations com-

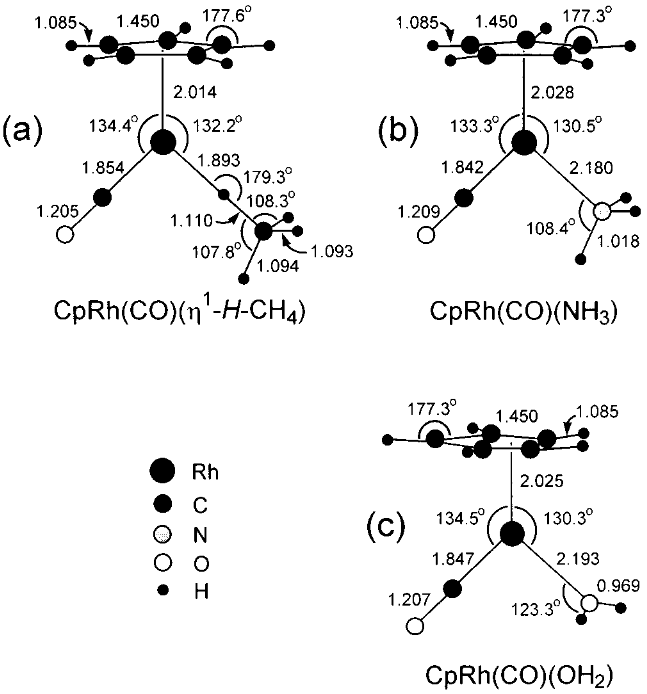


Figure 10. The calculated geometries (distance in Å, angles in deg) of the molecular complexes CpRh(CO)(HR) where HR is (a) CH_4, (b) NH_3, and (c) H_2O. (Reprinted from ref 109a. Copyright 1995 American Chemical Society.)

paring C−H and Si−H bond activation by $RhCl(PH_3)_2$.[112a] Although the η^2-*Si,H* SiH_4 complex was, not surprisingly, much more stable than the corresponding η^2-*C,H* CH_4 complex, it was found to be a transition state on the way to the product silyl hydride, not a potential minimum. By contrast, the η^2-*C,H* CH_4 complex was predicted as an actual intermediate state. A similar study by Re et al.[111] of the fragment $Ni(PH_3)_2$ also predicted the η^2-*H,H* coordination mode as the most stable. Most recently, Ziegler et al. returned to $RhCl(PH_3)_2$ and combined density functional calculations with molecular dynamics calculations to study the carbonylation of methane. These calculations provide a tantalizing glimpse of vibrational frequencies.[112b] Like the 14-electron fragment $RhCl(PH_3)_2$, the 16-electron species $Rh(Cl)(CO)(PH_3)_2$ is predicted to undergo oxidative addition of methane. However, the 16-electron species should react without forming an intermediate methane complex.[112c]

Siegbahn and Svensson studied the activation of methane by RhCl(CO) and RuH_2, which have triplet ground states, and $RhH(NH_3)$ and RhH(CO), which have singlet ground states, using PCI-80 ab initio calculations.[113] Their results indicated that a singlet ground state, which can easily sd hybridize, was required for strong bonding in a σ-alkane complex. On the other hand, a triplet ground state (or low-lying triplet excited state) resulted in a low barrier to oxidative addition. In addition, the π-accepting CO ligand competes with CH_4 bonding in the σ-alkane adduct and replacement of CO with a pure σ-donor such as NH_3 also enhances the Rh−CH_4 bonding (Table 6). When optimized, the methane adducts adopted the η^3-*H,H,H* structure. A consequence of these results is that a low barrier to oxidative addition is possible without a strongly bound σ-alkane complex precursor, and conversely, a strongly bound σ-alkane complex may exist with a high barrier to oxidative addition. The latter scenario offers hope for the ultimate isolation of a stable metal σ-alkane complex!

Table 6. Calculated Energies (D_o, kJ mol^{-1}) on Singlet Potential Energy Surface for Reactions of CH_4 with Substrates (Adapted from Ref 113)

substrate	precursor	transition state	product
RhCl(CO)[a]	−14	−30	−92
RhH(CO)	−45	+18	−12
$RhH(NH_3)$	−60	−62	−104
RuH_2[a]	+17	−28	−49

[a] Triplet state reactant.

Cundari presented density functional calculations on the reaction of methane with prototypical 14-electron C−H activating fragments $IrH(PH_3)_2$ and $IrCl(PH_3)_2$.[114] He predicted the precoordination of methane to iridium in an η^2-*H,H* fashion: $\Delta H_{add} = -65.3$ kJ mol^{-1} to $IrCl(PH_3)_2$ and $\Delta H_{add} = -28.5$ kJ mol^{-1} to $IrH(PH_3)_2$. The “coordinated” C−H bonds of methane were predicted to be weaker than the “spectator” bonds. Thus, the calculated intrinsic stretching frequencies for “coordinated” and “noncoordinated” C−H bonds of methane were 2873 and 3014 (±16) cm^{-1} in the hydride complex, compared to 2680 and 3032 (±17) cm^{-1} in the chloride complex. Replacement of H by Cl results in a more strongly bound methane complex, due to the increase in σ_{CH} acceptor capability of the resulting fragment. Analysis of the electron density on methane throughout the alkane activation reaction confirms that donation from the σ_{CH} occurs first, and is important in adduct formation, but that significant back-donation is required for the fission of the C−H bond. Finally, the authors commented on the reaction trajectories of oxidative addition by low-valent late transition metal complexes and σ-bond metathesis at the hands of high valent early transition metal complexes. It seems that the early part of the reaction profiles are very similar with donation from the σ_{CH}-orbital of methane producing η^2-*H,H* CH_4 adducts with remarkably similar structure.

Since theoreticians employ a variety of methods and study hypothetical molecules, it is often difficult to assess the validity of their calculations. It is not clear either how to compare the density functional methods favored by Ziegler to the ab initio MP2 calculations employed by Morokuma. Siegbahn has now compared the results of six different methods including ab initio and density functional schemes on the CpMCO + CH_4 (M = Co, Rh, Ir) system.[109b] Siegbahn's preferred method, PCI-80, makes the stability order of the methane complexes with respect to methane loss Rh > Ir ≈Co, and those of the methyl hydride complexes Ir > Co > Rh. However, density functional methods make the CpCoCO−(CH_4) complex unbound and CpIrCO−(CH_4) more strongly bound than the corresponding Rh complex. The PCI-80 method makes the binding energies of the cobalt and rhodium methyl hydride complexes very high. The density functional method makes CpCoCO−(CH_3)(H) unbound, and the rhodium methyl hydride bound by only about 25 kJ mol^{-1}. The variations in these results are worrying, especially for cobalt, but the comparisons are most welcome.

In conclusion, calculations have established the plausibility of methane adducts, especially as intermediates on the pathway to oxidative addition. At this stage it would be helpful if theoreticians addressed (i) the question of how to maximize the stability of a methane adduct, (ii) the nature of the balance between donor and acceptor properties, (iii) the vibrational frequencies of the coordinated methane unit, and (iv) the impact of methane coordination on vibrational frequencies of the remainder of the molecule.

2. Coordination to d^0 Fragments and the Role in σ-Bond Metathesis

Ziegler and co-workers performed a density functional study of the σ-bond metathesis of methane by Cp_2ScH, and of hydrogen by Cp_2ScCH_3, invoking η^2-*H,H* CH_4 adducts as intermediates early in the reaction pathway (Figure 11).[115]

With ab initio calculations, Cundari predicted the binding energy of methane to a range of transition metal imido complexes in order to model σ-bond metathesis.[116] The binding was favorable for d^0 complexes (by 46−67 kJ mol^{-1}), but unfavorable for d^2 complexes due to repulsion between σ_{CH} and metal a_1 orbitals. He proposed that $W(NH)_3(\eta^2\text{-}H,H\text{-}CH_4)$ should be the most stable, and could be detected by a lowering of ν_{CH} frequencies as for agostic complexes. In a later paper, Cundari demonstrated (using Hartree−Fock calculations) the impossibility of oxidative addition of d^0-imido(alkane) intermediates, but found that it may be possible for corresponding d^2-imido complexes.[117a] Most recently, Cundari et al. presented effective core potential and molecular mechanics calculations in which the stability of σ-alkane adducts of $[Ta({=}NH)_3]^-$, $[W({=}NH)_3]$, and $[Re({=}NH)_3]^+$ were examined.[117b] The predicted magnitude of the metal-methane interaction increased with increasing positive charge on the metal, being greatest for the Re cation ($\Delta H_{add} = -110$ kJ mol^{-1}). Finally, the authors proposed that an alkane adduct of $[Tc(NAr)_3]^+$ or $[Re(NAr)_3]^+$ ought to be isolable.

B. Alkane Complexes in the Reactions of Transition Metal Atoms and Ions

1. Atoms

Anderson and Baldwin modeled the activation of methane by Fe atoms as studied in methane matrices by Margrave and co-workers. Their results showed that η^1 and η^3-*H,H,H* σ-methane coordination to ground-state Fe atoms would be favorable and predicted binding energies of 10 and 11 kJ mol^{-1}, respectively.[118]

The theoretical work of Blomberg et al. has probed the activation of methane by transition metal atoms using ab initio calculations.[119−120] They explored the possibility that methane may first coordinate intact to second series transition metals prior to C−H insertion. For rhodium atoms they calculated that an η^2-*H,H* complex would be more stable than other modes of alkane coordination, but present only as an intermediate on the way to C−H insertion, while for the palladium atom the η^2-*H,H* complex was predicted to be more stable than the methyl hydride and 16.7 kJ mol^{-1} more stable than ground-state Pd atoms and CH_4 reactants. For most of the metals, a slight net transfer of charge from methane to the metal is predicted in the η^2-*H,H* complex. The reaction of Pd atoms with CH_4 was recently studied by experiment and theory (section V.B.1).[80a,b]

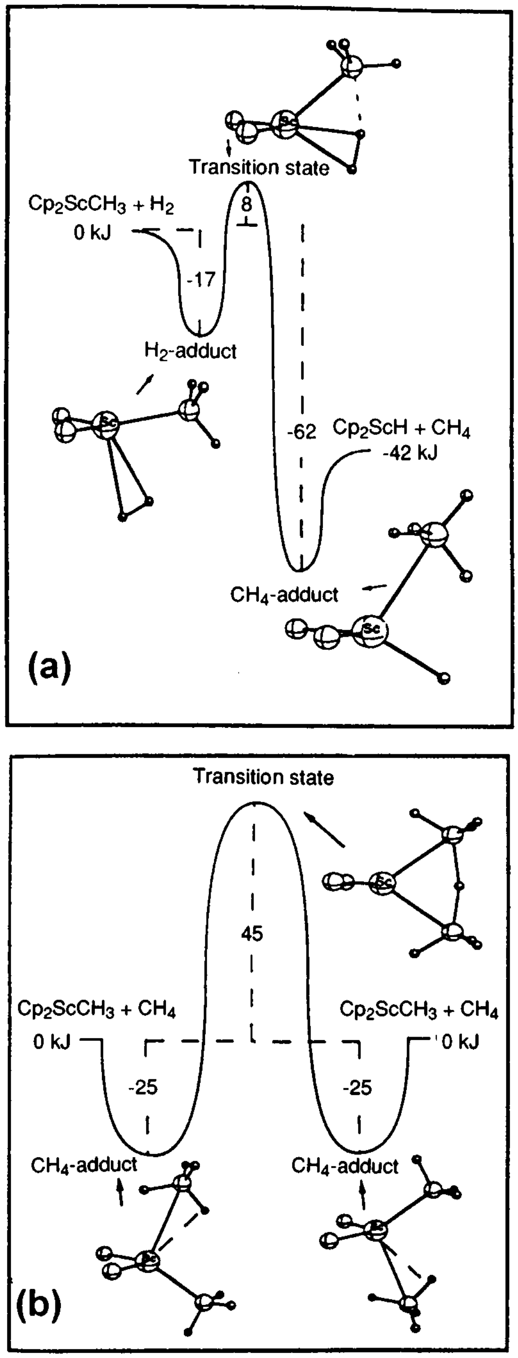


Figure 11. Energy profiles for σ-bond metathesis reactions (kJ mol^{-1}): (a) Cp_2ScCH_3 and H_2, (b) Cp_2ScCH_3 and CH_4. (Reprinted from ref 115. Copyright 1993 American Chemical Society.)

2. Ions

Extensive calculations have shown that alkanes form complexes with singly charged metal ions. Some of the most illuminating calculations were performed by Blomberg et al. who investigated the

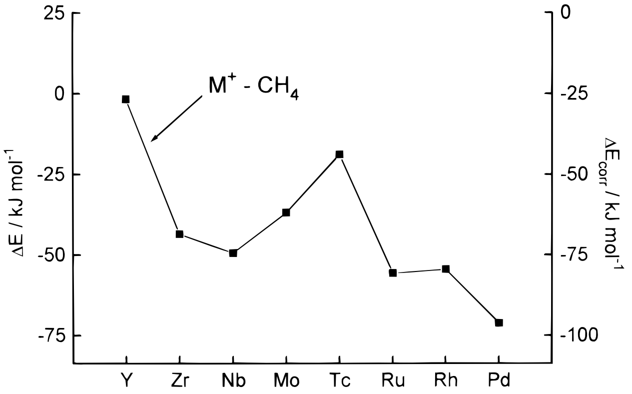


Figure 12. Energies for the $M(CH_4)^+$ molecular complexes, calculated relative to M^+ and free CH_4 using the ground state of each system. The right-hand ordinate scale, ΔE_{corr}, introduces a 21 kJ mol^{-1} correction for the zero-point energy of the complex. (Reprinted from ref 121. Copyright 1994 American Chemical Society.)

reaction of CH_4 with all the second row transition metal cations (M^+) by ab initio methods.[121] They found that η^2-*H,H* metal ion σ-alkane complexes were intermediates in all the reactions and that these species were more stable than the free ions and methane by between 1.7 kJ mol^{-1} (Y^+) and 71.1 kJ mol^{-1} (Pd^+) (Figure 12). Blomberg et al. demonstrated the very strong stabilization of M^+-CH_4 complexes compared to their neutral analogues. The stabilization arises principally from the charge−dipole effect which dominates the binding. The smaller ionic radii of the late transition metals increases the electrostatic stabilization relative to the early transition metals. In addition, a lower 5s population increases the binding energy, leading to some additional stabilization of late transition metal ions over early, and ions over neutrals.

Among first row transition metal ions, ab initio calulations have been reported for the interaction of Fe^+ and Co^+ with methane and for all ions with ethane. Musaev and Morokuma predict (CASSCF method with configuration interaction) that $Fe(CH_4)^+$ with a $^6A_2$ ground state may be formed either by reaction with $Fe(CH_2)^+$ with H_2 or by reaction of Fe^+ with CH_4.[122] At the highest level of calculation, $Fe(CH_4)^+$ is more stable than $Fe(CH_3)H^+$. The behavior of the Co^+ analogues proved very similar.[123] Goddard et al. predicted an η^2-*H,H* geometry for $Co(CH_4)^+$ with a binding energy in agreement with experiment. They showed that the binding of a second molecule of methane to Co^+ should be stronger than for the first (compare Table 5).[124] The ethane complex $Co(C_2H_6)^+$ was also predicted to adopt an η^2-*H,H* structure bound through two hydrogen atoms either from the same or different carbon atoms. The calculations of Haynes et al. on $Co(CH_4)^+$ have already been summarized in the context of their experiments[88] (section V.B.2).

Rosi et al. calculated the binding energies (MCPF method) of ethane complexes, $M(C_2H_6)^+$, and insertion products, $M(CH_3)_2{}^+$, for all first and second row metal ions. They predicted that the ethane complexes would be more stable for group 6 and 11 ions, the dimethyl complexes would be more stable for group 3 and 4 ions and Nb^+. For the remaining metal ions the two structures are almost equienergetic.[85b]

Morokuma and co-workers have calculated that the intermediate in the reaction of $RhCH_2{}^+$ with H_2 should be η^2-*H,H* $Rh(CH_4)^+$ ($^3A'$), which was predicted to be 71.1 kJ mol^{-1} more stable than Rh^+ (^3F) and CH_4.[125] Goddard et al. identified an iridium methane complex η^2-*H,H* $Ir(CH_4)^+$ with a $^3B_2$ state bound by 88 ± 8 kJ mol^{-1} with respect to Ir^+ (^5F) + CH_4.[126] However, $Ir(CH_4)^+$ proved unstable with respect to $Ir(CH_3)H^+$ which was itself less stable than $Ir(CH_2)(H)_2{}^+$. The superior effectiveness of Ir^+ in activating methane was associated with the ease of changing spin state and the strength of the Ir−C and Ir−H bonds.

As for the larger molecules, better correlation with experiment could be achieved if theoreticians were to calculate a full set of vibrational frequencies for the $M(CH_4)$ unit.

IX. Future Perspectives

In conclusion, the existence of transition metal alkane complexes is unambiguous, but the mode of coordination of alkanes to transition metals has yet to be proved. Although the work of Rayner et al. attempted to address this problem experimentally,[27] it remains the province of the theoreticians. In contrast, the stabilization of complexes is popular among experimentalists. The work of Rayner et al. showed that stronger bonds were formed with longer chain hydrocarbons,[27] but the properties of transition metal fragments which stabilize the metal alkane complexes have not yet been addressed. There are no calculations on d^6 complexes analogous to the Kubas dihydrogen complexes, although the majority of alkane complexes detected so far have that configuration. The most stable dihydrogen complexes are those containing bulky phosphine ligands capable of shielding the dihydrogen ligands. It may be that the use of such bulky ligands could also increase the stability of transition metal alkane complexes, although they would need to be designed to avoid competing agostic interactions. Calculations predict enhanced stabilization for cationic complexes but in practice coordination of the counterion may dominate.[127]

It has long been known that methane may be encapsulated within the crystal lattice of ice, viz. methane hydrate. The complexation of methane within a successfully designed host was described recently.[128] The binding was so strong that CH_4 could be trapped even at room temperature, and observed, albeit in rapid exchange with free methane, using conventional NMR spectroscopy ($\Delta G° = -12.1$ kJ mol^{-1}, $\Delta H° = -6.7$ kJ mol^{-1}, $\Delta S° = +16.7$ kJ mol^{-1}) (Figure 13). Other small molecules such as CH_2Cl_2, and most remarkably CF_2Cl_2, were also trapped. These experiments provide the first NMR criteria for establishing methane coordination.

This work suggests that if a ligand shell could be suitably arranged to trap or hold an alkane in the correct place for binding to the metal center, the resulting complex would be stabilized (in the same way that intramolecular agostic complexes are stabilized by the chelate effect of the strong ligand in question). The incorporation of a transition metal

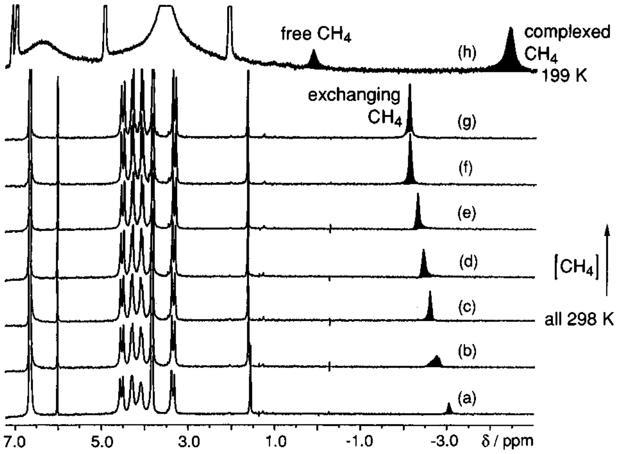


Figure 13. ^{1}H NMR spectra of cryptophane-A in $(CDCl_2)_2$ at 298 K in the presence of increasing amounts of CH_4 (from 0.33 equiv in a to 1.35 equivalents in g); (h) spectrum recorded at 199 K in the presence of 0.9 equivalents of methane (~40% of [D_8]toluene was added to prevent freezing). The resonance due to exchanging CH_4 is shaded in spectra a−g. In spectrum h, the exchange is frozen out and the resonances of free and complexed methane are both shaded. (Reprinted from ref 128. Copyright 1993 VCH.)

may permit subsequent activation or functionalization of an encapsulated alkane.

X. Abbreviations

CASSCF	complete active space self-consistent field
CID	collision-induced dissociation
Cn	1,4,7-trimethyl-1,4,7-triazacyclononane
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
dfepe	1,2-bis[(pentafluoroethyl)phosphino]ethane
dmpe	1,2-bis(dimethylphosphino)ethane
eie	equilibrium isotope effect
IE	ionization energy
kie	kinetic isotope effect
LIF	laser-induced fluorescence
MCPF	modified coupled pair functional
PAC	photoacoustic calorimetry
PCI	parameterized configuration interaction
pf	partition function
TRIR	time-resolved infrared spectroscopy

XI. Acknowledgments

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