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Photochemical strategies for investigating organometallic intermediates relevant to catalysis mechanisms

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Abstract

This paper presents an overview of the use of time resolved spectroscopic techniques for the investigation of reactive organometallic intermediates generated by laser flash photolysis. Specific examples will be drawn from mechanistic studies in these laboratories in which time-resolved IR and time-resolved optical detection have been used to probe the reactivities and structures of intermediates relevant to the homogeneous catalytic activation of dihydrogen and carbon monoxide. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Reactions in organometallic chemistry important to homogenous catalysis schemes include the activation of C–H and H–H bonds, ligand substitution reactions, carbon monoxide migratory insertions reactions, alkene isomerizations and oligomerizations etc. [1,2]. A major problem in elucidating the detailed mechanisms is to characterize the structures and reactivities of intermediates formed along reaction coordinates. Such transient species are elusive under thermal catalytic (or stoichiometric) conditions owing to their low steady state concentrations, which impede direct observation. To this end, flash photolysis can be a tool for preparing high, non-steady state concentrations of reaction intermediates [3]. With some intuition (and luck) suitable precursors may be chosen which, when flashed with the suitable wavelength of light, generate the reactive intermediate of interest and fast detection techniques can be used to probe the decay of such species along the reaction coordinates. Fig. 1 is a cartoon illustrating this strategy for generating such species in non-steady state concentrations. Once these short-lived transients are generated, they can be interrogated with time-resolved optical (TRO) or infrared (TRIR) spectral techniques which provide an ensemble of spectroscopic and kinetic information. Such data and chemical intuition enable the elucidation of their structures and reactivities.

What types of species might one expect to be able to detect in this manner? For a mononuclear metal complex ML_n with a certain subset of ligands L, the most common photoreaction would be simple ligand dissociation (Eq. (1)), since the M–L bonds are usually the weakest in the complex. With molecular ligands such as CO or an alkene, dissociation is heterolytic, but with metal alkyls and similar species homolytic dissociation to radicals is common. In solution, other relaxation processes are sufficiently fast that one normally expects but a single ligand to be labilized; in the gas phase, multiple dissociations are common given sufficient excitation energy. For polynuclear organometallic complexes, metal–metal

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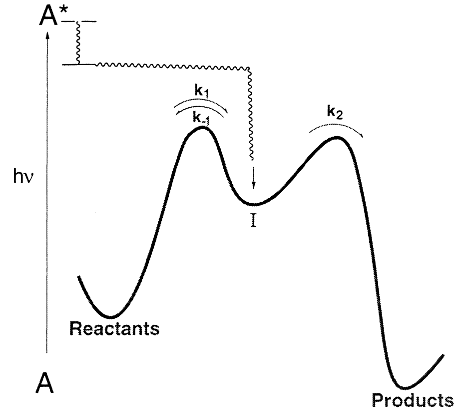


Fig. 1. Cartoon illustrating the use of photochemical techniques to generate reactive intermediates in nonsteady state concentrations from a suitable precursor **A**.

bonds are often the weakest, and homolytic cleavage to metal radicals may compete with ligand dissociation (Eq. (2)). For either mononuclear or polynuclear species, unimolecular processes may occur from very short-lived or even unbound dissociative excited states (ES), but bimolecular reactions (e.g., electron transfers as in Eq. (3)) require longer ES lifetimes.

$$ML_n \xrightarrow{h\nu} ML_{n-1} + L \qquad (1)$$

$$L_nM\text{-}ML_n \xrightarrow{h\nu} \begin{cases} \longrightarrow M_2L_{2n-1} + L \\ \longrightarrow 2L_{n-1}M\cdot \end{cases} \qquad (2)$$

$$ML_n \xrightarrow{h\nu} [ML_n]^* \begin{cases} \xrightarrow{Red} ML_n^- + Red^+ \\ \xrightarrow[Ox]{} ML_n^+ + Ox^- \end{cases} \qquad (3)$$

Organometallic intermediates have been prepared by photochemical pathways in (very) low temperature matrices or solutions of nonreactive solvents or even liquefied noble gases under conditions where their further reactivity is very slow or nonexistent. Such studies have proved especially valuable in identifying types of species prepared by this photochemistry and allowed the characterization of the spectroscopic signatures for further study. For kinetics studies, especially those relevant to homogeneous catalysis, it is desirable to have time resolved methods capable of probing the reactivities under conditions closer to those of the thermal reactions. To do this, it is necessary to employ flash photolysis kinetics. Described briefly here are some of the flash photolysis techniques employed in our laboratory for such studies and several examples of investigations relevant to catalysis mechanisms.

2. Apparatus for time resolved spectroscopic studies

Most flash photolysis studies involving the measurement of transient absorption behavior of organometallic intermediates are carried out on apparatus with a standard "pump"–"probe" configuration as illustrated in Fig. 2. Pump laser systems are commercially accessible which generate UV/Vis light pulses as short as several hundred fs, and laser systems with ps and ns temporal capabilities are common if not routine. The advent of OPO's and other tunable nonlinear optical devices provide remarkable access to a range of excitation wavelengths. The probes fall into two categories. For the slower systems operating on the ns or longer time frame, continuous probe sources can be used and the timing is done electronically. The timing of ultrafast laser detection systems (sub-nanosecond time resolution) is generally based on an optical delay line. Simplistically, the laser pulse is split and one component serves as the excitation source while the other is allowed to traverse a longer but variable optical path before reaching the sample to serve as the probe. The delay between the excitation and the probe pulses is governed by the finite time required for the probe pulse to travel the longer pathlength (33 ps per cm). For detection in the UV/

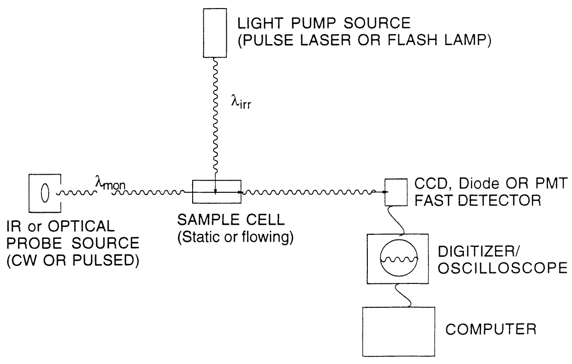


Fig. 2. "Pump–probe" flash photolysis apparatus.

Vis region, the probe pulse is often used to generate a continuum (white) flash by focusing it into a liquid such as D_2O and this continuum is passed through the sample, then a spectrograph, before recording on a multichannel recorder such as a CCD camera. IR detection in this time regime has been reviewed recently [4].

At UCSB, our studies have largely been carried out in the ns to ms regime where continuous IR or UV/Vis sources can be used as probes. The pump sources have been either a XeCl Excimer laser (308 nm) or a Nd/YAG laser operating at the second (532 nm), third (355 nm) or fourth harmonic (266 nm). For UV/Vis detection, the probe is generally white light from a xenon short arc lamp. For kinetics studies this is generally passed through a monochromator to give a (variable) single frequency source which is detected using a PMT. Alternatively, the full visible range spectrum can be recorded using a spectrograph and a CCD camera, with the timing defined by electronic gating.

Infrared detection is attractive for kinetic studies of the reactants, intermediates, and products of certain organometallic reactions, especially if the relevant compounds include groups, such as carbonyls, which are strong IR chromophores. The broad, often featureless, UV/Vis absorptions common to many organometallic compounds in solution generally allow little structural interpretation, and the absorption bands of the various species in solution often overlap. IR bands tend to give much better resolution between individual species and can be probed either by time-resolved laser flash photolysis experiments at ambient temperature or by FTIR under low T conditions where subsequent reactions of the transients are extremely slow. The relatively narrow and, sometimes, structure specific IR bands often allow for direct observation of the temporal decay and appearance of individual species without interference from excessive overlapping. In the ns to ms time regime, kinetics using IR detection are usually explored with (variable) single frequencies using a tunable IR laser source and a fast rise-time solid state detector as shown in Fig. 3 which illustrates the UCSB TRIR apparatus. An alternative

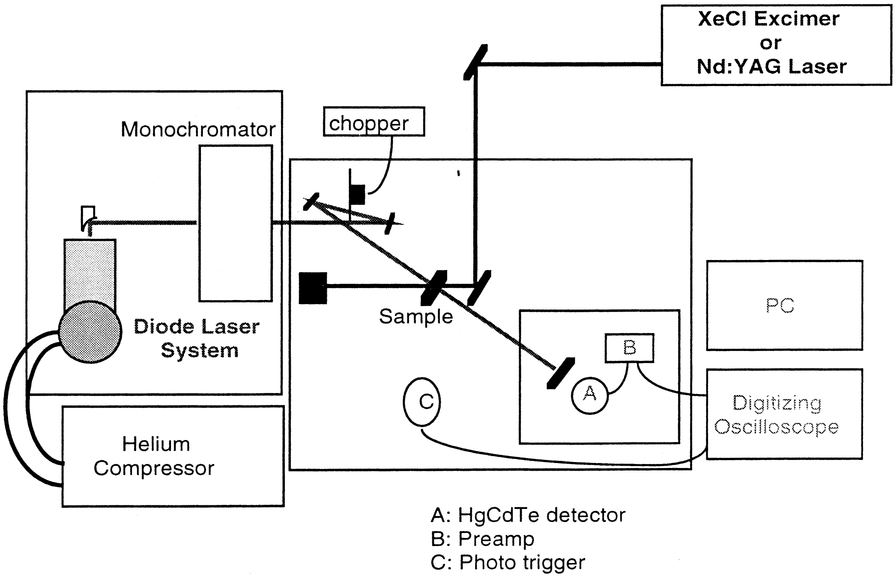


Fig. 3. Diagram of UCSB TRIR system using a lead salt IR diode laser as the probe source. The probe source is based on 3 components available from Laser Photonics Inc., a cold head containing 4 diode lasers cooled by a closed cycle He refrigerator, a collimating assembly which includes a HeNe laser for alignment, and a monochromator to filter unwanted frequencies since at a given *i* and T, the diode lasers may lase at several modes separated by 1–3 cm^{-1}. The IR beam is directed through a chopper (C), then the sample cell to a HgCdTe (PV) detector (A), the signal from which is amplified by a preamplifier (B) and recorded by a digital oscilloscope. (The chopper is used to obtain I_o, then is removed.) The excitation source is either a XeCl excimer laser or a Nd : YAG laser, either of which can be operated with a dye laser. The sample cell is modified from a commercially available (McCarthy) demountable infrared cell with CaF_2 windows. The inlets and outlets of this cell are silver soldered to stainless steel cannula connected to a pump driven flow system designed for constant flow of deaerated solutions under inert or reactive gas atmospheres.

method which allows recording broad-band spectra of transient species (but currently is less convenient for kinetics studies, especially in the sub μs) regime would be a step scan FTIR spectrometer slaved to the pulsed laser pump source. The general makeup of various TRIR systems has been the subject of several recent reviews [4–6].

It is generally necessary to carry out considerable signal averaging to assure reasonably large signal-to-noise (s/n) ratios. This requires multiple laser pulsing of the sample, sometimes many hundreds of times. Thus, in most cases it is highly desirable to have the sample flowing through the excitation region at a pace such that physical motion is slow relative to the

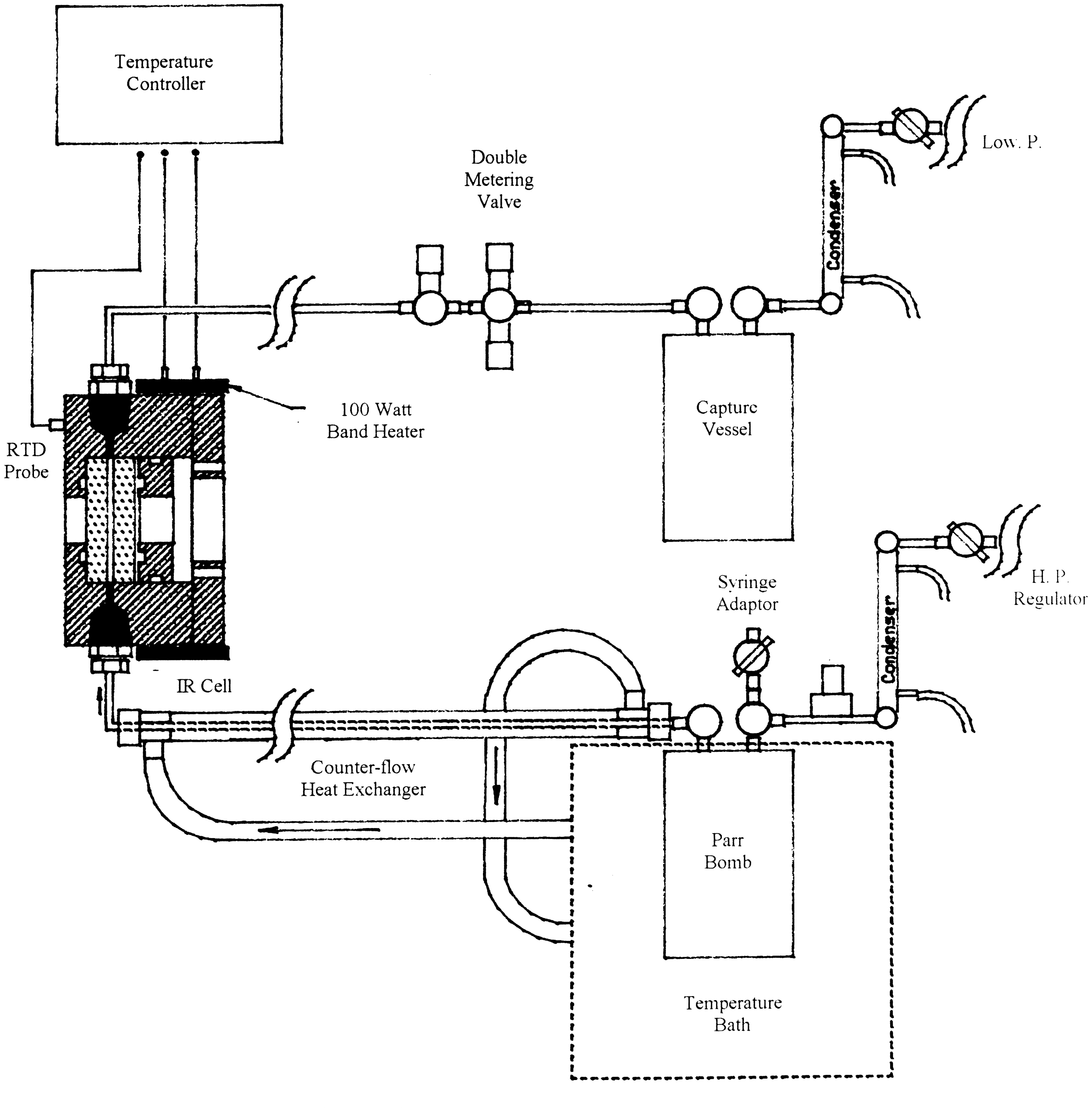


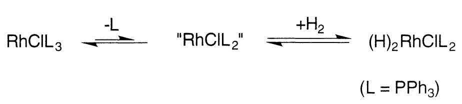
Fig. 4. TRIR flow cell for examining reactions at elevated temperature and pressure.

observation time, but sufficiently rapid that there is sample renewal between laser pulses. It is also desirable to define and control the reaction conditions (temperature, gaseous atmosphere, etc.). In this context, we have recently added to our apparatus a flow system that can operate under gaseous pressure in excess of 100 atm and up to 150°C in order to approach conditions more relevant to certain known industrial catalysts (Fig. 4).

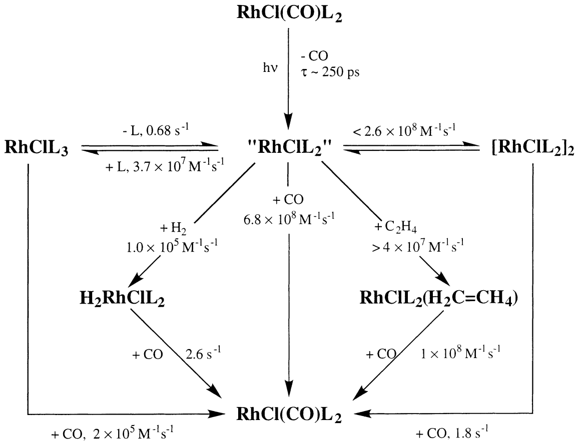
3. Examples of systems investigated at UCSB

3.1. *Rhodium phosphine catalysts and photocatalysts*

The mechanism(s) of dihydrogen activation toward alkene hydrogenation by Wilkinson's catalyst ($RhCl(PPh_3)_3$) and related rhodium(I) phosphine complexes is a subject of continuing interest and investigation. In studies some time ago, Halpern demonstrated that a key step involved PPh_3 dissociation prior to reaction with H_2 (Scheme 1). The reaction presumably proceeds in this manner because the "tricoordinate" species $RhCl(PPh_3)_2$ is orders of magnitude more reactive with H_2 than is Wilkinson's catalyst itself [7]. In this context, D. Wink of this laboratory decided to use flash photolysis techniques to "prepare" the intermediate from the carbonyl complex $RhCl(CO)(PPh_3)_2$ and to probe the reactivity of the $RhCl(PPh_3)_2$ formed thus with a variety of substrates. The initial studies [8], carried out on a conventional xenon flash lamp photolysis train, confirmed that $RhCl(PPh_3)_2$ is indeed reactive with various key reactants including H_2, the latter reaction having a second order rate constant, $1\times10^5\ M^{-1}\ s^{-1}$, nearly five orders of magnitude larger than that for the analogous reaction with $RhCl(PPh_3)_3$. This system has been subsequently reinvestigated using the TRO spectral techniques and instrumentation described above [9,10], and the revised rate constant data for this system are summarized in Scheme 2.



Scheme 1. Simplified scheme for the activation of Wilkinson's Catalyst by dissociation of PPh_3 before reaction with H_2



Scheme 2. Summary of rate data accumulated by flash lamp and laser flash photolysis of *trans*-$RhCl(CO)(PPh_3)_2$ in ambient temperature benzene. [10]

A series of observations reported from the product studies using continuous photolysis techniques have indicated that the photochemistry of the $RhCl(CO)L_2$ complexes ($L = PR_3$) is richer than the reversible CO dissociation described above. Indeed C–H activation products are observed as minor products when $L = PPh_3$ but play a much greater role when $L = PMe_3$ [11–20]. There were hints of these pathways in the earlier flash photolysis studies by Wink et al., but the more recent laser studies [10] show these much more clearly. Fig. 5 illustrates a typical decay profile for the tricoordinate intermediate in benzene with added CO. The decay is first order giving a good fit to exponential decay with a k_{obs} value linearly dependent on [CO]. Notably, this decay did not return immediately to baseline but gave a modest residual absorption which in slower processes, especially under added CO, eventually returned to baseline. The residual spectra are illustrated in Fig. 6. This residual apparently involves at least two processes, formation of dimers by reaction of $RhClL_2$ ($L = PPh_3$) with the starting complex (more of a problem in the laser experiments because of higher concentration requirements) and C–H activation of either solvent benzene or ligand PPh_3 by oxidative addition reactions of the four coordinate electronic excited state $[RhCl(CO)L_2]^*$ or of the tricoordinate species $RhClL_2$ (Scheme 3). We have

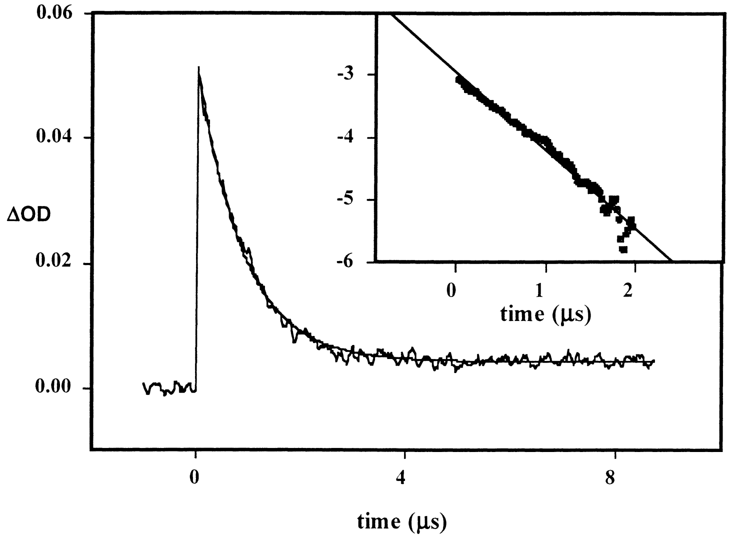


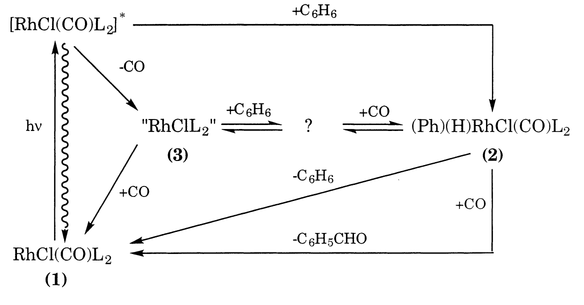
Fig. 5. Temporal decay of the transient formed after 355 nm flash photolysis of RhCl(CO(PPh$_3$)$_2$ in benzene with [CO]=1.3 mM. The first order fit to the data is shown in the inset. $k_{obs}=1.2\times10^6$ s^{-1}.

recently described TRIR experiments which concluded that both pathways, i.e., "prompt" reaction of the excited state as well as the slower oxidative addition of the RhClL$_2$ may each be contributing to the C–H activation products when L = PMe$_3$ [21]. Ongoing studies are examining these reactions in careful detail for several L [10].

3.2. Intermediates generated by CO photodissociation from Mn(CO)$_5$CH$_3$

Application of the TRIR technique for the characterization of reactive intermediates is nicely illustrated by studies of the flash photolysis of Mn(CO)$_5$CH$_3$ (**M**) [22]. Fig. 7 shows the TRIR spectrum resulting from the flash photolysis of **M** in cyclohexane solution under CO. The notable features are the prompt formation of a transient species **X** with new ν_{co} absorptions at 1992, 1986 and 1952 cm^{-1}, which decay exponentially within a few μs. A plot of k_{obs} versus [CO] proved to be linear with slope k_{co} of 4.5×10^8 M^{-1} s^{-1} (295°C) and a zero intercept consistent with the rate law

$$-\frac{d[\mathbf{X}]}{dt} = k_{obs}[X] = k_{co}[CO][X] \qquad (4)$$



Scheme 3. Scheme showing two possible pathways for the photoactivation of the C–H bonds in benzene by RhCl(CO)L$_2$.

Notably, reformation of **M** occurred at the same rate as the decay of **X**; however, some permanent bleaching was observed owing to competing photochemical cleavage of the Mn–Me bond. The TRIR spectra of **X** proved to be strongly dependent on the nature of the solvent medium; for example, the ν_{co} bands shifted to lower frequency (1974, 1964 and 1921 cm^{-1}) in the much stronger donor solvent tetrahydrofuran. Furthermore, the decay of **X** proved to be strongly solvent dependent, k_{co} ranged from a nearly diffusion limited value in perfluoro-methylcyclohexane (PFMC) solution to a value eight orders of magnitude smaller in THF (Table 1). The kinetics data and TRIR spectra can be interpreted in terms of the photodissociation of

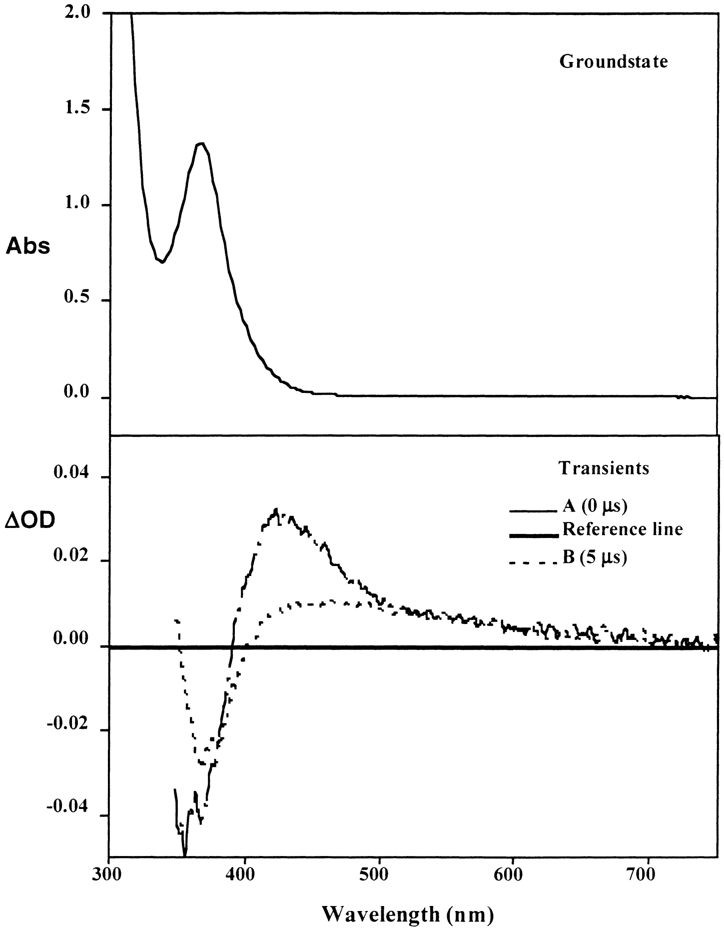
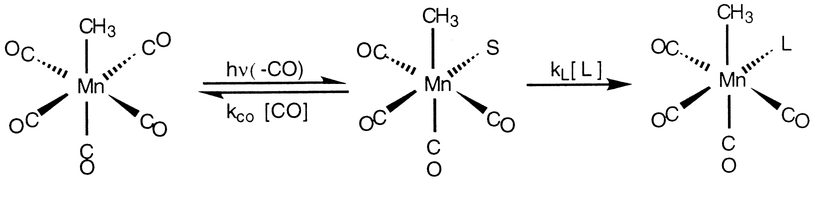


Fig. 6. Spectra of $RhCl(CO)(PPh_3)_2$ in benzene (upper) and transient spectra generated immediately and 5 μs after 355 nm flash photolysis. (Conditions [Rh]=0.16 mM, [CO]=1.5 mM)

CO leading (eventually) to formation of a reactive solvento species *cis*-$CH_3Mn(CO)_4S$ (**X**), which reacts with CO to regenerate the starting complex (Eq. (5), L = CO). These kinetics observations parallel those made previously for the "isoelectronic" chromium carbonyl, i.e., $Cr(CO)_5S$ [23]



M X ML (5)

3.3. Migratory insertion of CO into metal alkyl bonds

Another mechanism which has attracted the attention of this group has been the formation of carbon–carbon bonds via CO "migratory insertion" into metal

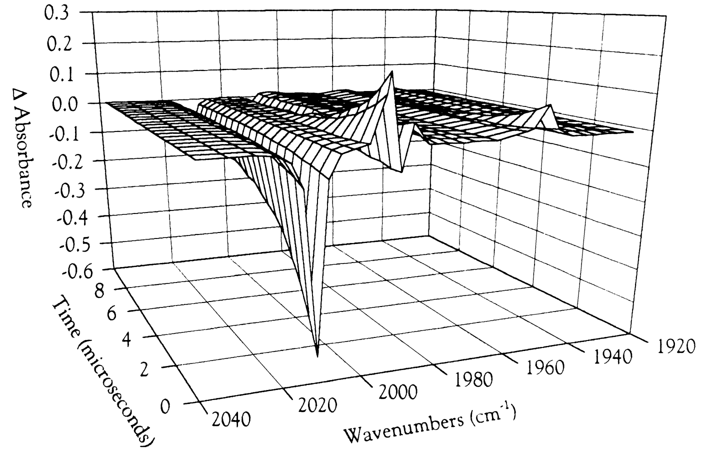
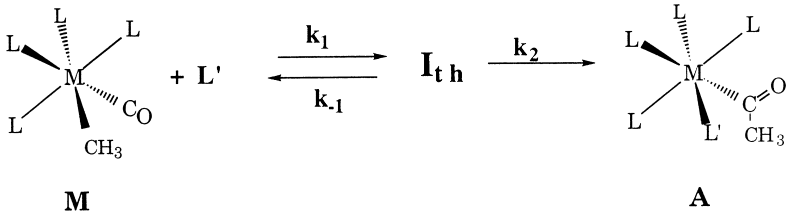


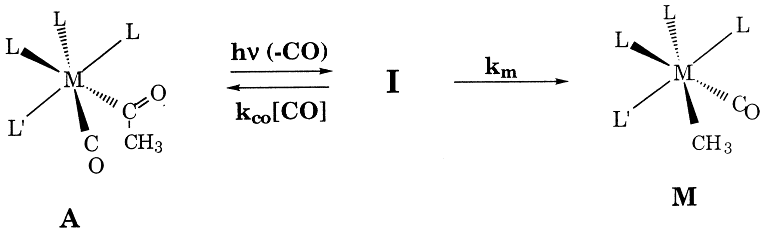
Fig. 7. IR spectral changes following 308 nm laser flash photolysis of Mn(CO)$_5$CH$_3$ in 295 K cyclohexane under 10% CO (500 ns intervals) adapted from [13].

alkyl bonds (Eq. (6)), a key step in catalytic schemes for methanol carbonylation to acetic acid, alkene hydroformylation, etc. [24,25].



(6)

Our strategy for characterizing the structure and reactivity of intermediate $\mathbf{I}_{th}$ involves the preparation of relevant key intermediates by photolytic decarbonylation of a coordinated CO of the metal acetyl to form the "coordinatively unsaturated" transient species **I** (Eq. (7)). The alkyl migration to form the metal alkyl and competitive trapping of I by CO or other ligands are then monitored [26].



(7)

The resulting TRO and TRIR spectra as well as the reaction dynamics of the systems under various conditions are then interpreted in terms of potential mechanisms. Comparisons of rates obtained in this manner for **I** to the competitive reactivities deduced for $\mathbf{I}_{th}$ based upon steady state kinetics methods can also be employed to further analyze whether **I** and $\mathbf{I}_{th}$ are indeed the same species. The majority of our studies to date have been with the model systems Mn(CO)$_5$(COR) and (η5-C$_5$H$_5$)Fe(CO)(COR) [22,27,28], but ongoing studies are probing analogous

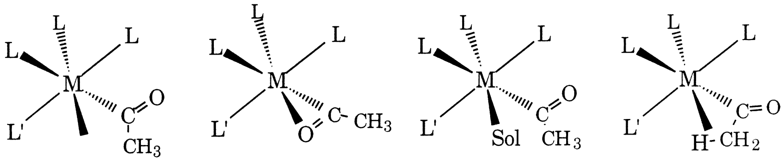
Table 1
The reactivity of the $CH_3Mn(CO)_4(Sol)$ intermediate **X** and of the acetyl analog **I** with CO in cyclohexane, PFMC and THF. Comparison with the reactivity of $P(OMe)_3$

Solvent	Ligand	k_L for **I** (M^{-1} s^{-1}) [a]	k_L for **X** (M^{-1} s^{-1}) [b]
PFMC	CO	1.5×10^4	$\sim1\times10^{10}$
Cyclohexane	CO	6.5×10^3	4.5×10^8
THF	CO	$<5\times10^2$	1.4×10^2
Cyclohexane	$P(OMe)_3$	1.4×10^6	1.1×10^9
THF	$P(OMe)_3$	1.7×10^3	–

[a] Ref. [22].
[b] Ref. [26].

intermediates generated from known cobalt and rhodium catalysts.

What types of intermediates might be generated by flash photoexcitation of a parent acetyl complexes such as $Mn(CO)_5(COCH_3)$? The initial excitation leads to CO dissociation at a rate too fast to observe directly from the excited state using the fastest time resolution (10 ns) of our present systems. Although some acetyl–metal bond fragmentation is also apparent from the products as is some "prompt" formation of M, the principal photoprocess observed is CO dissociation to give **I**. Shown below are some possible forms **I** might take: the fully unsaturated species **U**, the chelated structure **C** with an η^2-carbonyl group, the solvated intermediate **S** and the bidentate **B** with agostic bonding between the methyl group and the metal. **U** seems quite unlikely on this time scale given that analogous d^6 complexes such as $Cr(CO)_5$ bind even alkanes with dissociation energies as large as 10 kcal/mol [29,30]. With regard to **C** and **B**, NMR evidence has been used to argue for an equilibrium between agostic and η^2-CO in a molybdenum acetyl complex [31]; however, theoretical calculations on the manganese system [32–34] point to **C** having a significantly lower energy than **B**.



U **C** **S** **B**

If L and/or L' are carbonyls, the ν_{co} bands are a fairly sensitive probe of the electronic environment around the metal. For **S**, these should shift to lower frequencies as the donor strength of the solvent increases as we have seen for $Mn(CO)_4(Sol)(CH_3)$ above. Furthermore, the lability of **S** in subsequent reactions with other ligands including CO should be especially sensitive to the solvent donicity. In contrast, the spectral and kinetics properties of the chelated species **C** or **B** should be but modestly solvent sensitive. Some TRIR spectral data obtained for **I** in different solvents are summarized in Table 2 while

Table 2
Carbonyl bands (ν_{co} values in cm^{-1}) for **I** formed by 308 nm excitation of **A** in various solvents at ambient T and at 195 K as measured by TRIR and FTIR, respectively [26]

Solvent	ν_{co} (296 K) [a]	ν_{co} (195 K) [b]
PFMC	1997, 1959	2083 (w), 1998, 1958
Cyclohexane	1990, 1952, 1607(w)	–
Methylcyclohexane	1990, 1952	2080(w), 1988, 1941, 1607(w)
Dichloromethane	1987 (br), 1940 (br)	–
THF	1981 (br), 1931 (br)	2077(w), 1977, 1928, 1602(w)

[a] Ambient T data taken from TRIR spectra 100 µs after 308 nm flash excitation.
[b] Low T data recorded on a Bio-Rad FTS-60 FTIR spectrometer immediately after excitation.

Table 3
Rate constants for CO addition (k_{co}) and methyl migration (k_m) reactions of $\mathbf{I}_{Mn}$ in various solvents determined from optical flash photolysis experiments [26]

Solvent	k_{co} [a] (M^{-1} s^{-1})	k_m (s^{-1})
PFMC	1.5×10^4	<1.0
Benzene	3.3×10^3	6.7
Cyclohexane	6.5×10^3	9.0
Dichloromethane	5.3×10^3	30
1,2 Dichloroethane	7.0×10^3	47
THF	$<5\times10^2$	8.8

[a] Concentrations of CO in various solvents were corrected for differences in solubility: IUPAC Solubility Data Series: Carbon Monoxide, vol. 43, R.W. Cargill (Ed.), Pergamon Press, New York, 1990.

the kinetics of the reaction of **I** with CO with several solvents are compared in Table 1 to those for **X**. The k_L values in Table 1 show that the k_{co} values for **I** are not as sensitive to solvent as are those of **X**. Furthermore, the comparative sluggishness with which **I** undergoes ligand substitution in weakly coordinating solvents (Table 3) relative to **X** suggests that **I** is not a solvento species except in stronger donor solvents where the rates of ligand substitution are similar. Thus it is our view that the spectral and kinetic data for **I** are most consistent with the η^2 chelate **C** in weakly coordinating solvents but with **S** in more strongly donating solvents.

We now turn to the effect of solvent on the rate of methyl migration, the microscopic reverse of the first step in the thermal carbonylation reaction. The k_m values in various solvents, determined by TRO spectroscopy both directly via the first order decay of **I** in the absence of added ligands and by competitive trapping experiments in accord with Eq. (7), are summarized in Table 3. *Notably, the trends observed for k_m do not parallel those of the ligand substitution reactions.* Although CO reaction with **I** is much faster in cyclohexane than in THF, methyl migration rates are nearly identical in the two solvents, although the similarity must be coincidental given the different structures in the two solvents. What is remarkable about the data in Table 3 is that the rates of methyl

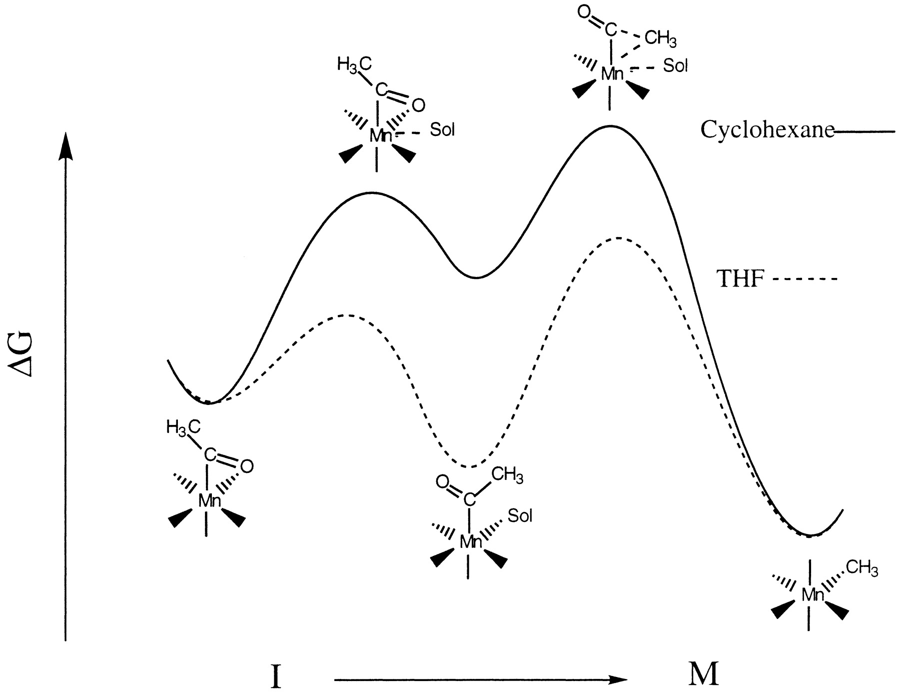


Fig. 8. Free energy profile for methyl migration pathway from **I**.

migration increase with relative solvent donor strength among those solvents where the structure of **I** is almost assuredly that of the η^2 chelate **C**.

Fig. 8 illustrates the role of the solvent in promoting methyl migration in a schematic free energy diagram. Upon inspection of the η^2 acyl structure, it is difficult to imagine a one-step process by which it could rearrange to **M**. We propose that the trend of increasing k_m with donating ability of the solvent is the result of **C** reacting first to form the solvento species, which then undergoes methyl migration with concerted loss of solvent. This is the microscopic reverse of the "solvent assisted" methyl migration proposed for the thermal reaction mechanism. In THF, the lowest energy form of **I** is already the solvento species. Thus, stabilization of S by Mn-THF bonding offsets stabilization of the k_m transition state by solvent–metal interactions giving the fortuitous similarity of the $\Delta G^{\ddagger}_{m}$ values in cyclohexane and THF.

4. Summary

We have demonstrated that when employed in a rigorous mechanistic study of an organometallic reaction, TRIR and TRO spectroscopies provide valuable, otherwise unobtainable, structural and kinetic information about intermediates in the reaction sequence. In one example, it was shown that formation of the tricoordinate intermediate $RhClL_2$ greatly facilitates the activation of dihydrogen enroute to the hydrogenation of alkenes by Wilkinson's catalyst. The same and related species turn out to participate also in the activation of hydrocarbon C–H bonds. When such techniques were applied to the mechanism of C–C bond formation in the carbonylation of $Mn(CO)_5CH_3$, it was found that in weakly coordinating solvents the intermediate is stabilized intramolecularly, presumably via η^2 chelation, but in strong donor solvents the solvento species predominates. However, the methyl migration step is found to involve concerted migration of the methyl group and formation of an Mn–solvent bond, irrespective of the most stable structure of **I**. Similar techniques are now being adapted to the study of active hydroformylation catalysts under conditions more realistically approximating those of industrial catalysis.

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