Review

Organometallic photochemistry at the end of its first century

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Abstract

The discovery of the light initiated reaction of $Fe(CO)_5$ to yield $Fe_2(CO)_9$ by Dewar and Jones in 1905 ushered in an era of the use of light to drive chemical reactions. This review seeks to examine selective chapters in this story by examining particularly significant reaction types in the context of their historical development.
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1. Introduction

The application of photochemistry to organometallic compounds has its roots deep in the history of the field. The first recorded instance appears to have been the recognition by Dewar and Jones in 1905 that sunlight resulted in the conversion of the very newly discovered $Fe(CO)_5$ into a new substance [1], the correct formula of which was later reported by Speyer and Wolf to be $Fe_2(CO)_9$ [2]. Photolysis remains the preferred method for the preparation of $Fe_2(CO)_9$ and its synthesis is described in *Organometallic Synthesis*, perhaps the single most influential synthesis reference in the field [3].

Shortly after the Ferrocene Renaissance and the veritable flood of new compounds coming from the laboratories of Wilkinson, Fischer, Stone and Nesmeyanov, among others, a paper appeared by Rausch and Schrauzer describing the use of photochemistry to prepare derivatives of $Fe(CO)_5$ and cyclooctatetraene, Scheme 1 [4]. Photochemical studies began in earnest with a series of papers from the Strohmeier laboratory in Würtzburg. These papers examined the application of photochemistry to the substitution of carbonyl ligands in the Group VI carbonyls [5], and $CpMn(CO)_3$ [6]. The first quantum yield and mechanistic study also was reported by the Strohmeier group at this time [7]. Even ferrocene itself was found to undergo oxidation by an irreversible electron transfer when photolyzed in halogenated solvents [8].

The honor of the first photochemistry article in the Journal of Organometallic Chemistry goes to Green and Stear who described the preparation of $CpW(CO)_2$ $(\eta^3\text{-}C_3H_5)$ from $CpW(CO)_3(\eta^1\text{-}C_3H_5)$, Scheme 2, on page 230 of Volume 1. In Volume 2, King and Bisnette reported one of the first examples of alkyl and aryl migration from an acyl group when they photolyzed $CpFe(CO)_2C(=O)C_nF_{2n+1}$ derivatives to prepare the corresponding perfluoroalkyl derivatives, Scheme 3. Having been at the forefront of organometallic photochemistry since its earliest days, it is only fitting that a review of the progress in this field be included in this 40th Anniversary issue.
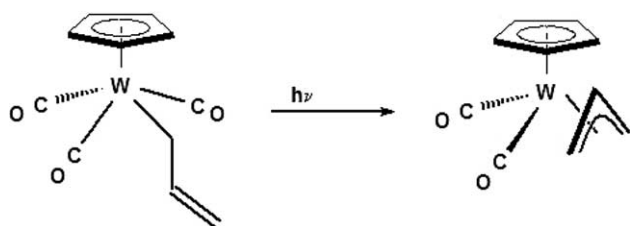
As any review of a topic this large must be selective, if not idiosyncratic, the reader is referred to reviews [9] and books [10] for additional reference.
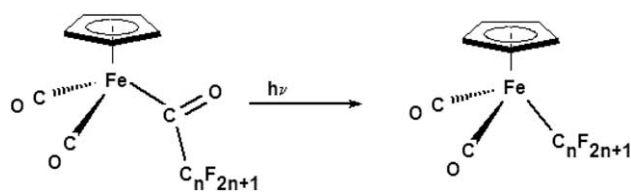
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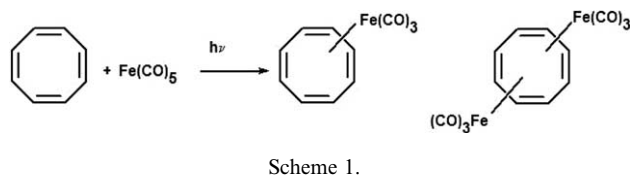
Scheme 1.

Scheme 2.

Scheme 3.

2. CO loss and ligand substitution

As described above, the first applications of photochemistry involved photolysis of metal carbonyl compounds leading to the loss of a carbon monoxide ligand to form an intermediate that can undergo subsequent reaction with other ligands. The reactions described by both Dewar and Rausch proceed by loss of a carbon monoxide from $Fe(CO)_5$ and subsequent reaction of the "$Fe(CO)_4$" intermediate. Closely related to the Rausch reaction is the formation of $Fe(CO)_3(C_8H_{14})_2$, a useful synthon for "$Fe(CO)_3$" [11]. The characterization and chemistry of the photochemical intermediates from $Fe(CO)_5$ continues to be of interest as evidenced by recent reviews [12].

As demonstrated by Green, η^1-allyl complexes may be readily converted to η^3-allyl complexes by photochemical loss of a CO ligand. The mechanism of this reaction for $CpW(CO)_3(\eta^1-C_3H_5)$ was confirmed using Ar matrix photochemistry [13]. Wang and Lai have demonstrated that photolysis of the chelated species, (η^5,κ^1-$C_5H_4C_2H_4PPh_2)Fe(CO)(\eta^1-C_3H_4R)$, where R=H, Me, yields the corresponding η^3-allyl derivatives upon photochemical CO-loss [14]. Similarly, η^1-benzyl ligands have been observed to form η^3-benzyl species upon CO loss [15]. Photolysis of $CpFe(CO)_2(\eta^1-C_5H_5)$ yields ferrocene [16], and this method appears to be an attractive strategy for the synthesis of ferrocene derivatives containing mixed rings.
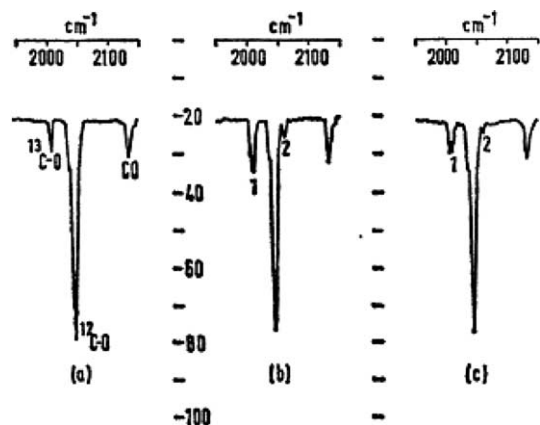

Fig. 1. Photolysis of $Ni(CO)_4$ in an Ar matrix. (a) One hour deposition of Ar:$Ni(CO)_4$ mixture (160:1), (b) one hour photolysis, (c) anneal to 30 K followed by return to 15 K [17].

The first direct observation of a CO-loss intermediate was reported by Rest and Turner in their examination of $Ni(CO)_4$ in Ar, Kr and Xe matrices, Fig. 1 [17]. The photochemistry of a large number of metal carbonyl compounds has now been examined using gas (Ar, Kr, Xe, N_2, CH_4), hydrocarbon (paraffin, Nujol, 3-methylcyclohexane, MCH, and 3-methylpentane, MP), 2-methylTHF, polyvinyl chloride, and ionic (KBr, low melting inert ionic compounds) matrices. Frozen matrix techniques have been reviewed [18]. The close relationship between time resolved methods and matrix studies is nicely illustrated in the early literature by flash photochemical studies (uv/visible detection) of $(C_6H_6)Cr(CO)_3$ that revealed the presence of a short lived photointermediate [19]. Subsequent studies by Rest established the existence of the CO-loss photoproducts for this compound as well as for $CpMn(CO)_3$ and $(C_4H_4)Fe(CO)_3$ using inert gas matrices [20]. Braterman and Black had previously observed the $CpMn(CO)_3$ photoproduct in hydrocarbon glasses [21].

We have noted above the aryl and alkyl migration from acyl ligands observed by King. In an important set of studies establishing the mechanism of these migration reactions, Wojcicki examined the decarbonylation and alkyl migration in enantiomerically pure (1-Me, 3-$PhC_5H_3)Fe(CO)(PPh_3)(C(=O)Me)$ and found complete stereoretention in the products, Scheme 4 [22]. Similarly, decarbonylation of enantiomers of $CpFe(CO)(PPh_3)$-
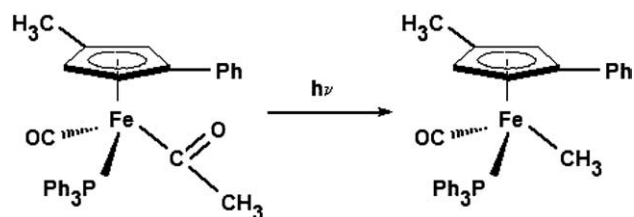
Scheme 4.

$(C(=O)R^*)$ where R^* is a chiral group, established that chirality was retained both at the R^* and at iron [23].

Opening a coordination site by loss of a carbonyl ligand from $CpW(CO)_3(\eta^1$-pentyl) has been shown in paraffin matrix studies to result in β-hydride transfer to the metal forming $CpW(CO)_2(H)(\eta^2$-pentene) [24]. Perhaps more surprisingly, evidence for α-hydride transfer and concurrent carbene formation has been revealed by photolysis of $CpCr(CO)_3CH_3$ in Ar and CH_4 matrices [25]. Very similar reactions have been observed by Pannell upon photolysis of $CpFe(CO)_2(SiMe_3SiMe_3)$ and $CpFe(CO)_2(SiMe_2GePh_3)$, and $CpFe(CO)_2(GeMe_2GePh_3)$ and related silyl oligiomers resulted in the formation of $CpFe(CO)_2MMe_{3-n}Ph_n$ products via what is believed to be a silylene or germylene intermediate [26].

Since photochemical reactions are frequently very selective they are used to prepare derivatives when thermal reactions either do not proceed or produce unwanted side-products. An example of such a reaction is the substitution of $Rh(CO)_2(R_2HN)Cl$ by a second amine ligand. Photolysis of the mono(ammine) complex in the presence of excess amine yields *trans*-$Rh(CO)(R_2HN)_2Cl$, Scheme 5 [27].

Photochemical reactions are particularly useful when the incoming ligand is weakly bound by the metal such as the nitrogen ligand derivatives reported by Strohmeier, the synthesis of reactive intermediates such as $CpM(CO)_2THF$, where $M=Mn$ or Re, or the formation of weakly bound chelated species as reported by Johnson and coworkers [28]. Even dinitrogen complexes can be readily formed under photochemical conditions, thus $CpMn(CO)_2N_2$ is frequently observed as a side product in the formation of $CpMn(CO)_2THF$ [29], and it is very likely that the "$M(CO)_5$" intermediate identified by Strohmeier upon flushing a solution with N_2 during irradiation, was actually $M(CO)_5N_2$.

$CpMn(CO)_2Py$, first reported by Strohmeier, along with the analogous bimetallic pyrazine species has been shown to be unusually photolabile and paramagnetic. The magnetic moments of these complexes were found to decrease with decreasing temperature suggesting that the paramagnetism and heightened reactivity arises from low lying ligand field states that may be populated thermally or photochemically at room temperature [30].

Photochemical conditions are ideal for generating complexes with weakly bound ligands. The first observation of a σ-H_2 species was made by Sweany upon photolysis of Group VI carbonyls in an Ar matrix saturated with H_2, Fig. 2 [31]. Previous studies involving
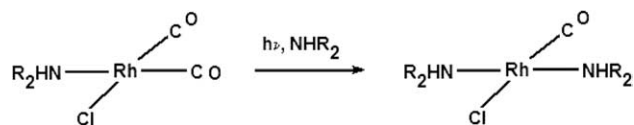
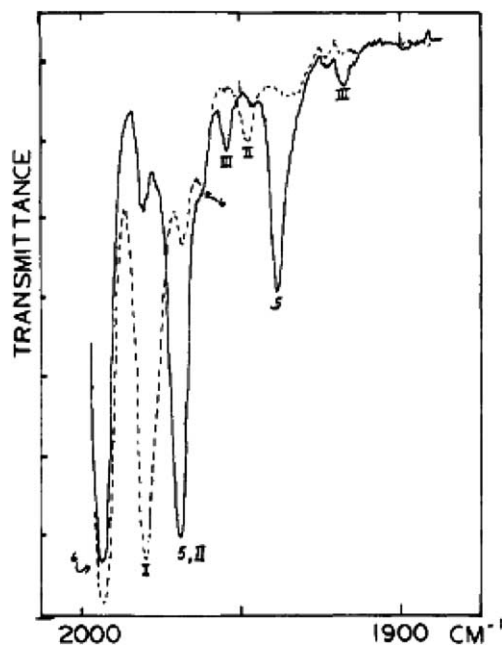Fig. 2. Matrix photolysis of $Cr(CO)_6$ and H_2 in an Ar matrix. I, $Cr(CO)_5H_2$; II, $Cr(CO)_4(H_2)_2$; III, $Cr(CO)_4H_2$, 6, $Cr(CO)_6$; 5, $Cr(CO)_5$ [31].

$Fe(CO)_5$ in H_2 doped Ar matrices established the formation of the oxidative addition product, $Fe(CO)_4H_2$, for which the carbonyl stretching frequencies increase as expected for formal oxidation of the iron. In contrast the carbonyl stretching frequencies of the Group VI hydrogen complexes went down. After publication of the neutron diffraction structure of $W(CO)_3(PCy_3)(H_2)$ by Kubas [32], Sweaney submitted a full paper on his observations and assignment of the Group VI derivatives to a complex of the intact H_2 [33]. Poliakoff has described the use of a flow reactor in which supercritical fluids containing H_2 were used to prepare working quantities of $CpMn(CO)_2(H_2)$ [34]. Dihydrogen and σ-H_2 complexes have been reviewed by Heinekey and Oldham [35], Sweany [36], and Kubas [37]. The Kubas paper also proved to be a watershed in metal-silane chemistry as well, with the recognition that Si–H complexes reported by Graham in 1969 were indeed σ-bound species [38].

Among the most surprising species to have been observed are solvates of noble gases and hydrocarbons. In the course of examining the photochemistry of the Group VI carbonyls in frozen noble gas matrices Turner and Perutz noted that the electronic and IR spectral bands were sensitive to the nature of the matrix gas and proposed that the species were best described as $M(CO)_5S$, where S corresponds to a noble gas atom serving as a ligand [39]. Time-resolved IR studies in supercritical fluids have allowed direct observation noble gas and CO_2 solvates of the Group VI carbonyls [40]. Transition metal-noble gas compounds have been

Scheme 5.

reviewed to 2001 [41], and organometallic photochemistry in liquefied and supercritical noble gases has been reviewed through 1995 [42]. Subsequent studies revealed that hydrocarbons, including methane, also serve as weak ligands under frozen matrix conditions and, as we will see below, these agostically bound species are frequently precursors to C–H oxidative addition. These studies have been reviewed through 1996 [43].
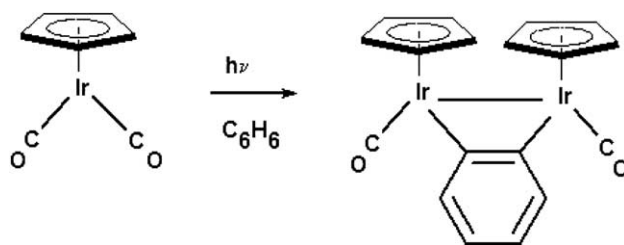

Scheme 7.

3. Oxidative addition of C–H bonds preceded by CO-loss

The insertion of metals into C–H bonds was first directly observed by Chatt and Davidson in 1965 during their examination of the thermal reactions of low-valence ruthenium complexes [44]. Some time later, Green and coworkers noted that photolysis of Cp_2WH_2 in the presence of arenes gave rise to derivatives of the form, $Cp_2W(H)(Ar)$ [45] that appeared identical to products formed when $Cp_2W(H)(R)$, R = alkyl, were heated in arene solvents [46]. Surprisingly, when Cp_2WH_2 was photolyzed in the presence of mesitylene a product was obtained in which oxidative addition of the methyl groups had taken place [47]. Identical products were later reported by Brintzinger and coworkers upon photolysis of $Cp_2W(CO)$ in benzene and toluene [48]. In all cases the putative intermediate was presumed to be "tungstenocene," Scheme 6. The tendency for metal carbonyl and metal dihydride compounds to yield identical photo-intermediates was also observed in the closely related cases of photolysis of Cp_2MH_3 and $Cp_2MH(CO)$ [49].

In 1977 Rausch found that photolysis of $CpIr(CO)_2$ in the presence of benzene resulted in formation of a bimetallic derivative, $[Cp_2Ir(CO)]_2(\mu-\eta^1, \eta^1-C_6H_4)$, that appeared to arise from a double oxidative addition of CpIr(CO) units, Scheme 7. Evidence was presented for the presence of traces of the monosubstituted, CpIr(CO)(H)(Ph), species in the reaction mixture [50].
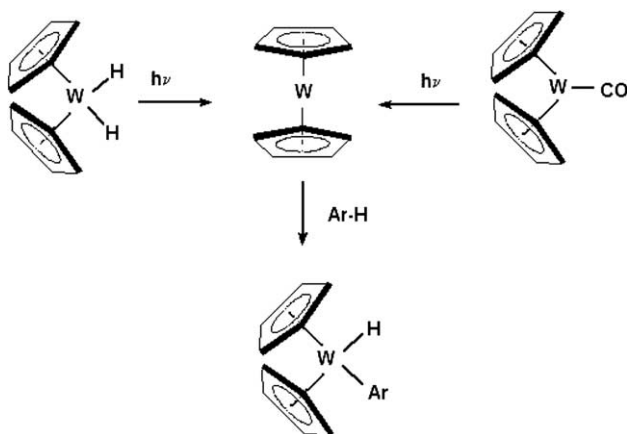
In 1971, Graham and coworkers carried out the photolysis of a number of silane derivatives with $CpMn(CO)_3$, $CpCo(CO)_2$, $(C_6H_6)Cr(CO)_3$ [51], and notably $CpRh(CO)_2$ [52] and recovered products in which Si–H oxidative addition had taken place. Not until after Crabtree reported the first observation of thermal C–H activation of an alkane did Graham return to this reaction. The discovery of photochemical activation of alkane C–H bonds was reported almost simultaneously by Graham [53] and Bergman [54].

Rest provided the first direct evidence for the intermediacy of Cp*M(CO), where M═Rh or Ir, and CpIr(CO) in oxidative addition of C–H bonds with the observation of the C–H activation of methane under matrix conditions [55]. The subsequent observation that $Cp*Ir(CO)H_2$ also activated methane in matrices pointed to a common electron-deficient intermediate for these processes, Scheme 8 [56]. A number of excellent reviews have explored various aspects of this chemistry [57]. The similarities between C–H and Si–H oxidative addition have been examined by Schneider [58].

The spin state of the photochemical intermediate has been shown to play a role in Si–H and C–H oxidative addition processes. Triplet species such as $CpV(CO)_3$, CpCo(CO), and $Fe(CO)_4$ do not form agostic bonds with hydrocarbons and thus tend to react with Si–H bonds to directly form oxidative addition products [59,60]. Perhaps counter intuitively, singlet intermediates such as CpRh(CO) and $CpRe(CO)_2$ on the average take longer
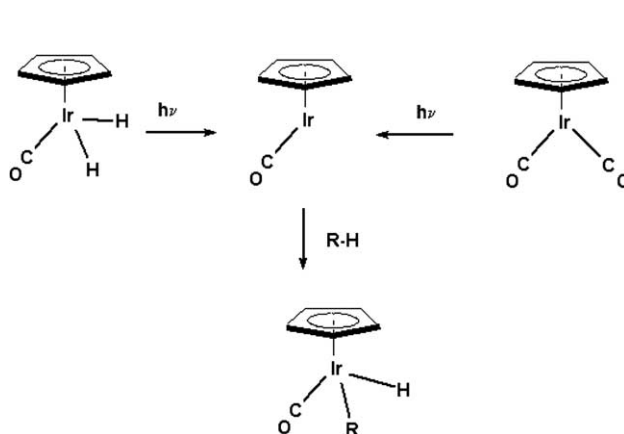
Scheme 6.

Scheme 8.

to form oxidative addition products since they are prone to form modestly stable agostic species with the hydrocarbon moieties in silanes, thus Si–H activation must await rearrangement of these intermediates [61]. $CpMn(CO)_2$ represents something of a middle case in that the initially formed triplet relaxes to a singlet relatively quickly.

The flash photolysis of $Cp^*Rh(CO)_2$ in liquid Kr with neopentane and d^{12}-neopentane as substrates has provided a detailed picture of the oxidative addition reaction mechanism. Upon photolysis an equilibrium is observed between $Cp^*Rh(CO)Kr$ and $Cp^*Rh(CO)(\sigma$-neopentane). The latter undergoes thermal rearrangement to $Cp^*Rh(CO)(H)(C_5H_{11})$ [62]. Additional studies have established that the character of the alkane has an influence on the rate of oxidative addition. While increasing the alkane size shifts the equilibrium toward $Cp^*Rh(CO)(\sigma$-alkane), the rate of conversion to $Cp^*Rh(CO)(H)(alkyl)$ is inversely related to alkane size. It is proposed that the transition states of the alkane oxidative additions are relatively close together in energy and that the activation energies and thus the rates of reactions reflect the stability of the σ-complex [63].

The scorpionate derivative, $Tp^*Rh(CO)_2$, was found by Graham to activate aromatic and alkyl C–H bonds at visible wavelengths [64]. Subsequent photochemical studies in matrices by Rest [65] and detailed studies by Lees [66] and Bergman [67] have established a mechanism in which CO-loss results in formation of an agostically bound R–H. Subsequent dechelation of one pyrazole arm of the scorpionate forms a species which undergoes ready C–H oxidative addition, Fig. 3.

4. Oxidative addition without CO-loss

While C–H oxidative addition is rightly regarded as one of the great milestones in organometallic chemistry, the frustrating reality is that many alkyl and aryl hydride complexes are chemically dead ends. To become an effective tool in synthesis, C–H oxidative addition must be coupled with other reactions that modify the organic substrate in some productive manner.

One reaction that achieves this elusive goal is the photochemical carbonylation of alkyl and aryl hydrocarbons to aldehydes by photolysis of solutions of $Rh(CO)(PMe_3)_2Cl$ under an atmosphere of CO. This reaction was first observed for the case of benzene by Eisenberg [68]. Since that time, carbonylation reactions have been carried out in a variety of aromatic and hydrocarbon solvents, liquid propane [69], supercritical ethane [70], and in supercritical CO_2 with ethane and methane [71] as substrates. For pentane and toluene a wavelength dependence upon the site of carbonylation has been observed [72]. There is evidence that $Rh(CO)_2(PMe_3)Cl$, or a related species, may be a more effective catalyst for the reaction than $Rh(CO)(PMe_3)_2Cl$ although detailed studies remain to be carried out [73].

Elegant studies carried out by Goldman have established that, contrary to expectation, C–H activation occurs between substrate and an excited state of the intact catalyst [74]. The resulting octahedral species undergoes secondary photolysis to yield products, Fig. 4 [75]. While CO-loss does occur under photochemical conditions,
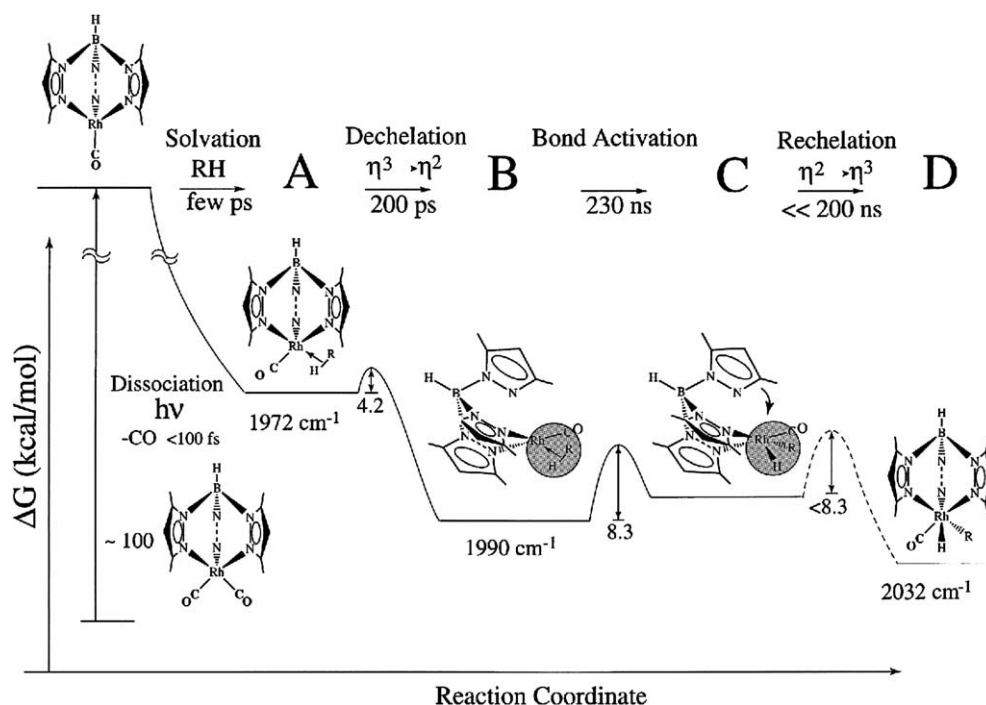

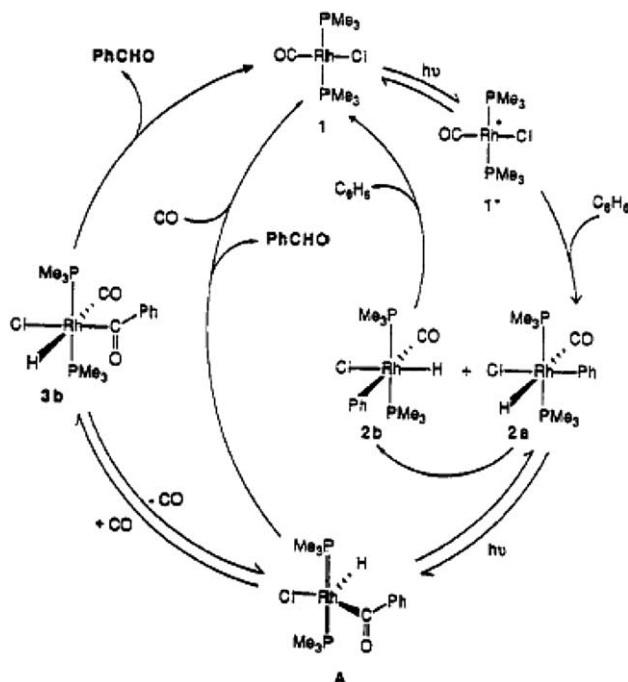Fig. 3. Mechanism of C–H activation by $TpRh(CO)_2$ [67b].

Fig. 4. Proposed mechanism for photochemical carbonylation of alkanes with two photochemical steps [75].

Scheme 9.

and oxidative addition of benzene to this species has been observed, this does not appear to be the primary catalytic pathway [76]. Photolysis of Rh(CO)(PR$_3$)$_2$Cl, where R=Me or Bu, in frozen Nujol results in formation of a species with a carbonyl stretching frequency below that of the parent complex. Theoretical calculations support the possibility that this species is a tetragonally distorted excited state, although possibility that the observed species is a photochemically generated agostic complex with the Nujol solvent cannot be ruled out [77]. A very similar species is observed for Ir(CO)(PMe$_3$)$_2$Cl in Nujol [78], and a recent flash photochemical study has observed a long lived excited species, perhaps the same as that observed in Nujol, with a carbonyl stretching frequency near that of the parent iridium complex [79].

5. Metal–metal bond breaking and radicals

Early photochemical studies of asymmetric metal–metal bonded compounds resulted in the observation that symmetric species were frequently among the products. Speculation quickly centered upon the possibility that radicals might be involved in the rearrangements [80]. In 1973, Wrighton and his coworkers reported in the Journal of Organometallic Chemistry that photolysis of Re$_2$(CO)$_{10}$ in halocarbons such as CCl$_4$ resulted in formation of ClRe(CO)$_5$ and proposed a radical mechanism to account for their observations, Scheme 9 [81].
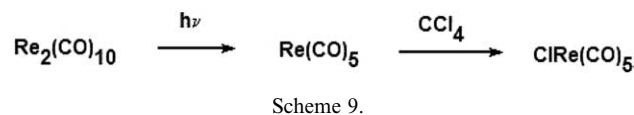
Subsequent studies of a number of metal–metal bonded species including Mn$_2$(CO)$_{10}$ [82], Cp$_2$M$_2$(CO)$_6$, where M=Mo and W [83], and Cp$_2$M$_2$(CO)$_4$, where M=Fe as well as heterobimetallic compounds such as MnRe (CO)$_{10}$ [84], and Cp(CO)$_3$M–M'(CO)$_5$, where M=Mo or W, and M'=Mn or Re [85], established that photochemical bond homolysis was a general reaction for this class of compounds. Photolysis of Mn$_2$(CO)$_{10}$, Re$_2$ (CO)$_{10}$, Cp$_2$Fe$_2$(CO)$_4$, and Cp$_2$Mo$_2$(CO)$_6$ in the presence of spin-traps confirmed the formation of metal radicals [86]. The efficiency of these bond homolysis reactions led Madach and Vahrenkamp to utilize photolysis to prepare a range of heterobimetallic compounds from their homobimetallic precursors [87].

Flash photolysis studies on Mn$_2$(CO)$_{10}$ and other M–M bimetallic compounds were interpreted in terms of M–M bond homolysis in which radicals recombined at nearly the diffusion controlled limit, but it was noted in almost every case that a second, smaller pathway appeared to involve a longer lived intermediate [88]. In order to resolve the identity of the second intermediate, Hepp and Wrighton carried out low temperature hydrocarbon glass photochemical studies and directly observed a Mn$_2$(CO)$_9$ intermediate having a low energy bridging carbonyl band consistent with a 4-electron μ-η^1:η^2-CO, Fig. 5. Various studies established that this species reacted with 2-methyltetrahydrofuran, 2-MTHF, to form Mn$_2$(CO)$_9$(2-MTHF) and with PPh$_3$ doped matrices to form Mn$_2$(CO)$_9$(PPh$_3$) [89]. While the Mn(CO)$_5$ radicals were not observed in these matrix studies (a common feature in frozen matrices due to the rapid recombination of radicals within the solvent cages), they have since been directly observed by time-resolved IR
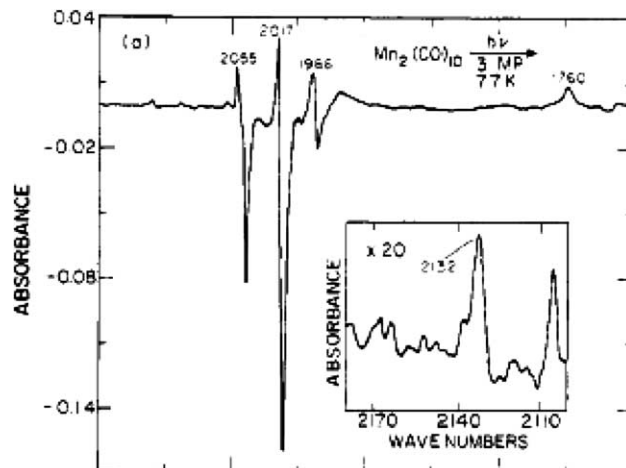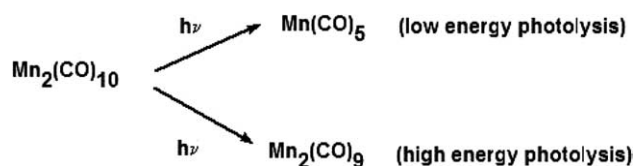

Fig. 5. Photolysis of Mn$_2$(CO)$_{12}$ in 3-MP [89].

$$Mn_2(CO)_{10} \xrightarrow{h\nu} Mn(CO)_5 \quad \text{(low energy photolysis)}$$

$$Mn_2(CO)_{10} \xrightarrow{h\nu} Mn_2(CO)_9 \quad \text{(high energy photolysis)}$$

Scheme 10.

studies [90]. A strong wavelength dependence has been found for the photochemistry of $Mn_2(CO)_{10}$ with Mn–Mn bond breaking dominating at lower energies, while CO-loss is more important at higher energies, Scheme 10. To some extent this wavelength dependence makes it possible to direct the photochemical pathway and thus reactions by controlling the wavelength of irradiation [91].

It is now known that most, if not all, M–M bonded bimetallic carbonyl compounds have both M–M bond homolysis and CO-loss photochemical channels and that the rearrangements and subsequent reactions of these CO-loss intermediates may be exceedingly complex. For example, later photochemical studies by Brown [92] of $Mn_2(CO)_{10}$ in hydrocarbon glasses established that CO-loss leads initially to the formation of a solvated species that subsequently gives rise to the bridging carbonyl complex observed by Wrighton [93]. $MnRe(CO)_{10}$ also yields an initial solvated species that slowly converts to a bridged species, while $Re_2(CO)_{10}$ forms a stable solvated species with no evidence of bridging carbonyl formation [94]. Extended photolyses in frozen matrices frequently give rise to multiple CO-loss, such as in the case of $Mn_2(CO)_{10}$, where $Mn_2(CO)_8$ is observed [95]. The photochemistry of $Cp_2M_2(CO)_6$, where M=Cr, Mo, and W, and $Cp_2Fe_2(CO)_4$, where M=Fe, Ru, and Os, have been extensively studied and have been recently reviewed [96].

6. In flagrante delicto: probing photochemical reactivity at high speeds

For those of us interested in the most intimate details of photochemical reaction mechanisms, advances in spectroscopic techniques over the last two decades have driven our sense of time from observations of reactions of photochemical fragments taking place in ms, to direct observations of vibrationally hot species within fs of interaction with a photon.

While there is a tendency to think of photochemistry in terms of ultraviolet irradiation, it should be remembered that even visible light has sufficient energy to initiate many processes. For example, the energy necessary to break a typical metal–carbonyl bond is ca. 190–210 kJ/mol [97], while 400 nm light corresponds to ca. 300 kJ/mole. In principle 570 nm light should be capable of initiating decarbonylation reactions. The "extra" energy appears initially in the form of vibrationally excited states and is eventually dissipated to the solvent. In studies conducted in the gas phase, where there is no opportunity to transfer this energy to a solvent, multiple CO-loss is often observed. Not surprisingly the extent of CO-loss is often a function of the energy of the incident photons as in the case of $CpMn(CO)_3$ which yields a mixture of $CpMn(CO)_2$ and $CpMn(CO)$ at 355 nm, but mostly $CpMn(CO)$ at 266 nm [98].

Frozen matrix studies, as we have seen, are excellent for the examination of photochemical intermediates and in certain circumstances may even permit detection of photochemical and thermal transitions between isomeric forms of an intermediate. The photochemical transformation from triplet (terminal) to singlet (bridged) forms of $Cp_2Fe_2(CO)_2$ observed by Bursten and his coworkers is one such example [99]. Matrix studies unfortunately tell nothing about the lifetimes of observed species or their possible role in observed reactions. For these questions time-resolved methods must be employed.

Beginning in the mid-1970s the use of flash photolysis, typically using xenon flash lamps with UV/vis detection, began moving the temporal resolution of detection into the ms range, Fig. 6 [100]. Improvements in detectors and the introduction of pulsed lasers as light sources quickly drove these times to the μs [101] and ps range, Fig. 7 [102]. One particularly impressive example of the use of these high speed methods is the examination of the effect of molecular mass on the rate of cooling of vibrationally hot $M(CO)_5S$ species, M = Group VI metal, S = solvent, at the low ps time scale [103].

While extremely fast, UV/vis detection lacks definition leaving the identity of an observed intermediate to either speculation or to the matrix photochemist to resolve. Because of challenges with the response rate of detectors, IR spectroscopy lagged behind UV/visible spectroscopy.

The first strategies for conducting time-resolved IR studies utilized low temperature solutions in which the life-times of intermediates could be extended making detection by conventional spectrometers possible. The study by Brown of $Cp_2Fe_2(CO)_4$ in low temperature hydrocarbon solution is an excellent example of the use of reduced temperature to slow the rate of molecular rearrangements, thus permitting routine IR detection, Fig. 8 [104]. These studies constitute a bridge between matrix methods and high speed time-resolved methods, and it is surprising that greater use had not been made of this strategy.

Early time-resolved IR instruments employed pulse/probe methods utilizing point by point detection in the mid-IR. These provided good temporal resolution and fair spectral resolution, not to mention requiring enormous devotion and patience by the scientists actually collecting the data. An indication of the speed
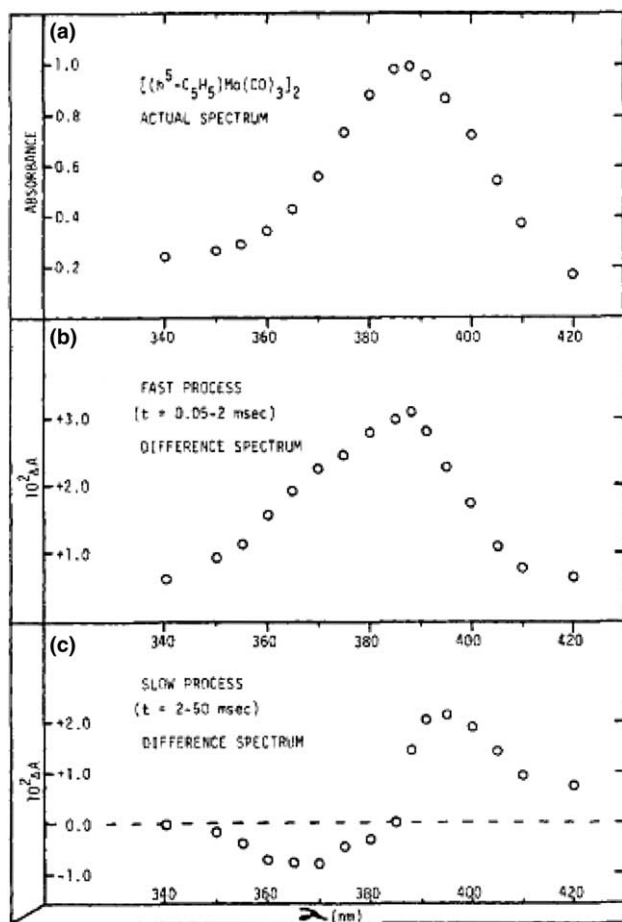
Fig. 6. Flash photolysis of $Cp_2Mo_2(CO)_6$ in cyclohexane. (a) Electronic spectrum of $Cp_2Mo_2(CO)_6$, (b) fast process, radical, 0.5–2 ms, (c) slow process, CO-loss species, 2–50 ms [100].
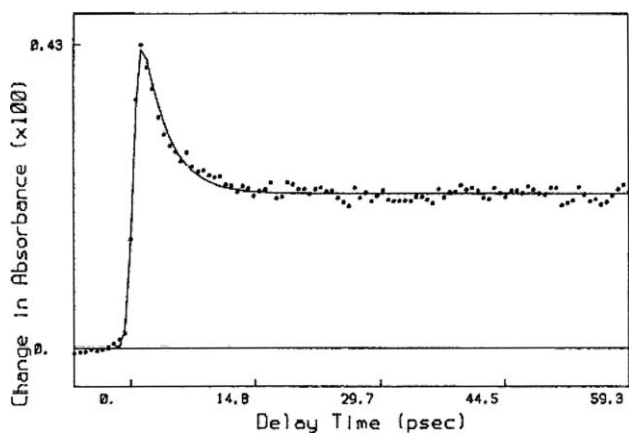

Fig. 8. Photolysis of $Cp_2Fe_2(CO)_4$. (a) Room temperature in hexane after 7 flashes, 1, 60, and 150 min, respectively; (b) −25 °C, methylcyclohexane (90%) and 3-methylpentane under Ar or CO 1 min after 7 flashes; (c) −75 °C, methylcyclohexane (90%) and 3-methylpentane under Ar, before 1 flash and 1 min and 36 min after flash [104].

Fig. 7. Transient decay dynamics of $Mn_2(CO)_9$ probed at 480 nm following photolysis of $Mn_2(CO)_{10}$ at 295 nm in cyclohexane [102].

with which temporal resolution was improving contrasts the photochemical examination of $Cp_2Fe_2(CO)_4$ in cyclohexane carried out at ca. ms resolution using a tunable CO laser as a probe [105], with the examina-
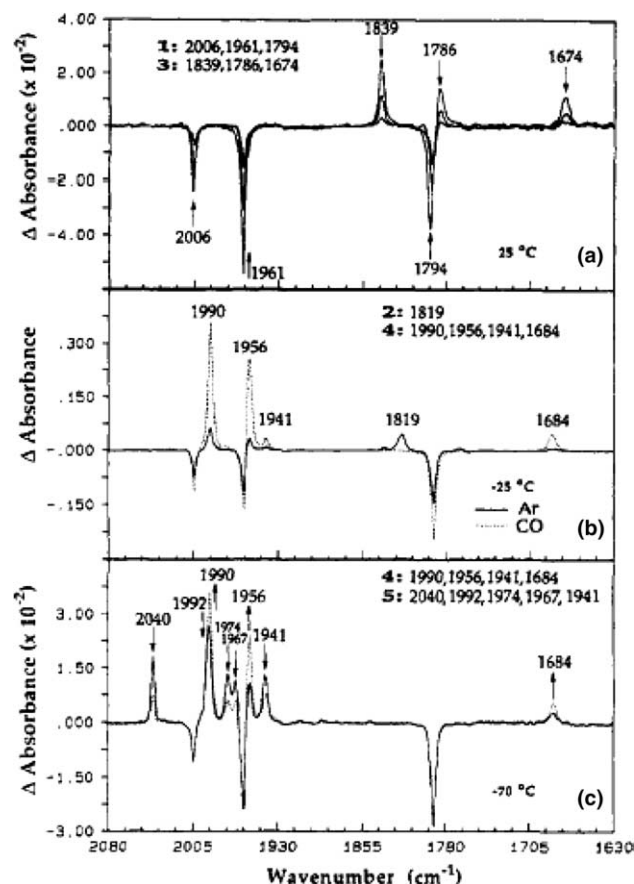
tion of the reaction of the $CpFe(CO)_2$ radical with phosphite only three years later that probed the decay of the radical at ps times [106]. The introduction of step-scan FT-IR instruments in the 1990s permitted spectra to be collected over a modest range of frequencies and averaged over a number of experiments giving excellent temporal (ns) and spectral (4–8 cm^{-1}) resolution. An example of the use of step-scan IR is the examination of the photochemical homolysis of the Mo–Mo bond of $Cp_2Mo_2 (CO)_6$ and recombination of the radicals to form trans and gauche rotamers of the starting material, Fig. 9 [107]. Even faster times (ps) are now possible with excellent resolution. In an example of the latter, the photolysis of $Mn_2(CO)_{10}$ was carried out using a 400 nm pump, IR probe apparatus and observed the vibrationally hot radical as it cooled over the course of 500 ps, Fig. 10 [108]. An upper limit to bond homolysis in $Mn_2(CO)_{10}$ has been determined to be 2–3 ps [109].

Coppens and his coworkers are pioneering the use of extremely fast crystallographic data collection coupled
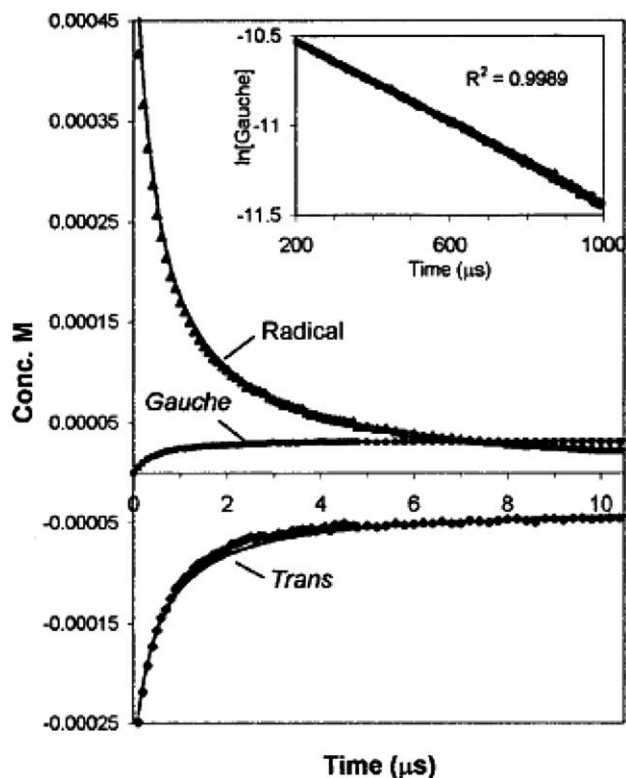
Fig. 9. First 10 μs of the photolysis of (BuCp)$_2$Mo$_2$(CO)$_6$ following the recombination of radicals to form the gauche and trans rotamers [107].
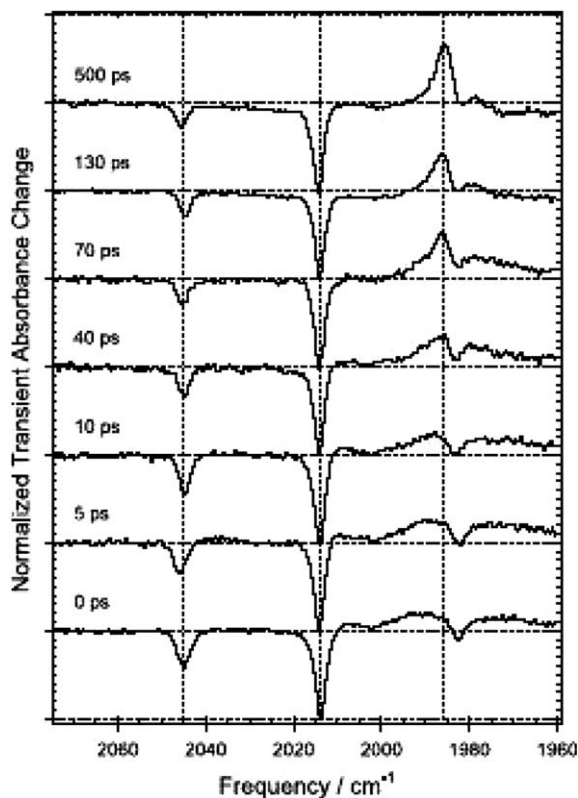

Fig. 10. Normalized time-resolved IR spectra of 400 nm photodissociation of Mn$_2$(CO)$_{10}$ in cyclohexane. Vibrational cooling of the Mn(CO)$_5$ radical is complete by 70 ps [108].

Fig. 11. Ortep diagram of [Pt$_2$(P$_2$O$_7$)$_4$]$^{4-}$ ion [110].

with the flash photolysis of a crystal using a synchrotron light source as a stroboscope to excite molecules followed immediately by X-ray data collection. In the case of [Pt$_2$(P$_2$O$_7$)$_4$]$^{4-}$ the excited state lifetime is ca. 50 μs, and the X-ray data collection pulse length is 33 μs, Fig. 11 [110]. Comparison of the photodifference map between the unphotolyzed and photolyzed data sets permits analysis of the structure of the excited state species. In the case of the Pt compound, a decrease of the Pt–Pt bond length observed in the excited state molecular structure was consistent with predictions of Raman studies of the same compound [111]. While this technique is still very much in its infancy, it is clear that it holds remarkable promise for the examination of short lived excited states.

7. Applications to synthesis

Perhaps the most familiar application of photochemistry in organometallic chemistry has been to the synthesis of new compounds by photochemical substitution of ligands, most commonly carbonyl groups. For example, recent papers appearing in the Journal of Organometallic Chemistry have described the photochemical reaction of the Group VI carbonyls with terminal alkynes [112] and vinyl ferrocenes [113] to yield M(CO)$_5$L derivatives. In an article in press as of this writing, Özkar and coworkers have described the synthesis and molecular structure of Cr(CO)$_5$(2,5-diaminopyridine), Fig. 12 [114]. Tilset and coworkers have recast the King and Wojiciki acyl decarbonylation reactions in a new light with the photochemical synthesis of TpFe(CO)(PMe$_3$)Me from TpFe(CO)(PMe$_3$)(C(=O)Me), Fig. 13 [115].

In some cases an entering ligand such as an alkene or an alkyne can undergo secondary chemistry with a π-bound ligand. For example, Kreiter and coworkers have explored the reaction of (η^5-C$_6$H$_7$)Cr(CO)$_3$ with alkynes and have observed [5+2] cycloaddition via a (η^5-C$_6$H$_7$)Cr(CO)$_2$(R$_2$C$_2$) intermediate [116]. The proposed stepwise mechanism of this reaction is illustrated in Fig. 14.
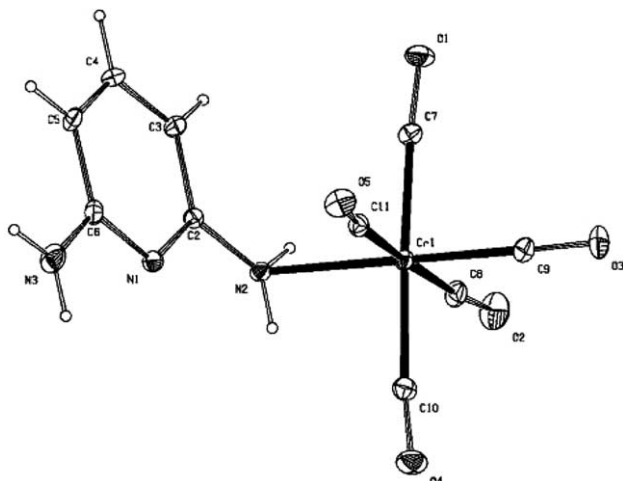
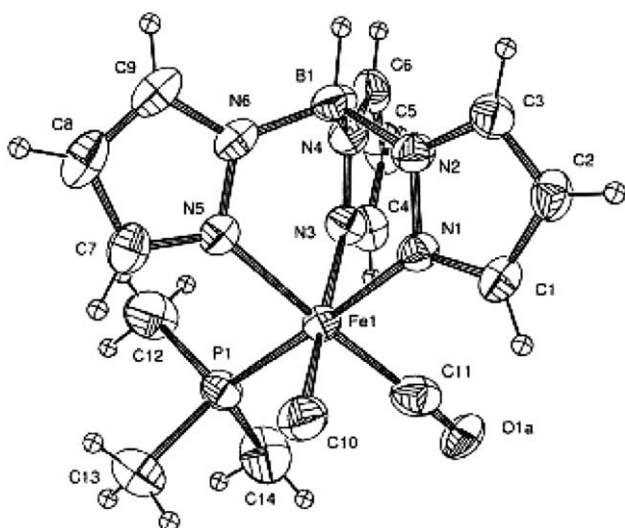Fig. 12. Molecular structure of Cr(CO)₅(2,5-diaminopyridine) [114].

Fig. 13. Molecular structure of TpFe(CO)(PMe₃)Me [115].

One of the more broadly utilized organometallic photochemical reactions is the photolysis of Fischer carbenes in the presence of doubly bonded substrates to yield cycloaddition products in which the metal complex is a de facto ketene source. For example, reactions with immines yield β-lactams [117], aldehydes yield lactones [118], alkenes yield cyclobutanones [119], and alcohols and amines yield substituted acids and amides, respectively [120]. These reactions have been extensively reviewed [121].

8. Theoretical underpinnings: an understanding in transition

Chemists are an inherently conservative lot as evidenced by vestiges of 19th century, not to mention alchemical, nomenclature that lurks in or language. In descriptions of bonding in metal complexes the language of crystal field theory must still be taught although it has long been displaced by ligand field theory and molecular orbital theory. So too with recent advances in quantum mechanical modeling, notably time dependent density functional theory (TDDFT), we acknowledge a more nuanced approach to bonding than earlier models may have suggested. This section is described as an understanding in transition since very high level theory is only just now becoming capable of modeling excited states of molecules and there have already been surprises and there will certainly be more in the future.

As a case in point, the common model of bonding in the Group VI carbonyl compounds is presented in Fig. 15(a). This model, based on early work of Beach and Gray [122], predicts that the lowest excitation, and one presumes the one responsible for CO loss, to be a ligand field transition between the largely metal based t_2g and eg^* orbitals. In fact, extrapolating from this simple case ligand loss is frequently attributed to ligand field transitions.

Recent studies by Baerends and coworkers using TDDFT methods have established that these ligand field transitions are much higher in energy than previously realized. The one electron energies and percentage composition of the various orbitals is presented in Table 1. In contradiction to long held beliefs, it appears that the low lying excitations responsible for CO-loss are spin forbidden, charge transfer states involving the ligand $2\pi^*$ orbitals. The revised molecular orbital description is presented in Fig. 15(b). The observed dissociations arise from strongly avoided crossings of the CT and LF states as the M–CO bond elongates [123].

Metal–metal bond homolysis is generally regarded as arising from excitation of an electron in the M–M σ bond (which is almost always the HOMO orbital) to a σ* orbital, and even in the most sophisticated modern treatments this is still the picture that emerges, Fig. 16 [124]. This model also serves to explain why CO-loss is also observed from the relatively low energy excitations typically associated with metal–metal bond breaking. Detailed examination of the potential energy curves
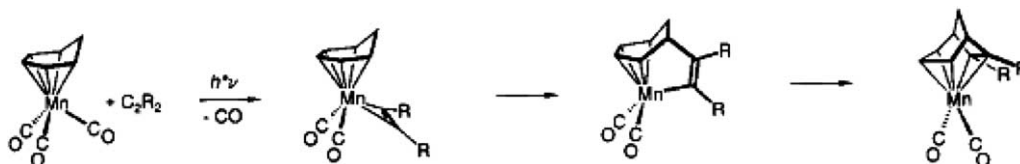

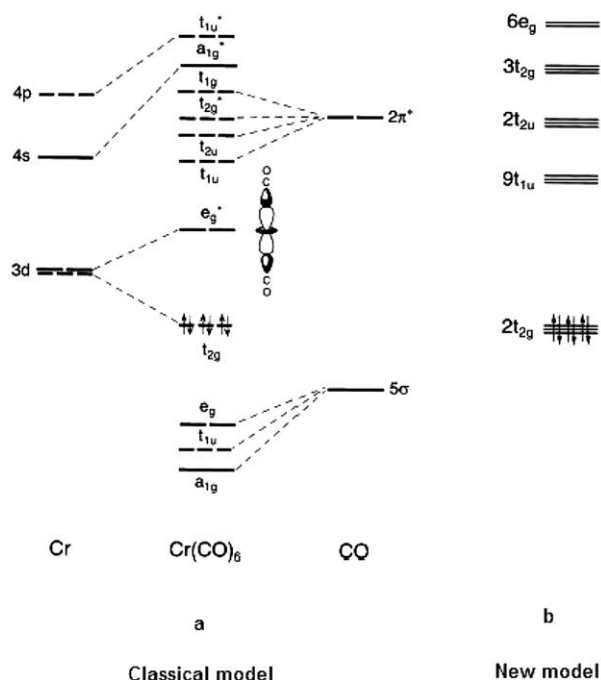Fig. 14. Mechanism of cycloaddition of alkyne to (η⁵-C₆H₇)Cr(CO)₃ [116].

Fig. 15. Qualitative molecular orbital diagram for Cr(CO)$_6$ [123d].

Table 1
One electron energies and percentage compositions of Cr(CO)$_6$ MO's in terms of Cr and CO fragments

MO	ε (eV)	Orbital occupancy	Cr	CO
9a$_{1g}$	0.003	0	77(5s), 23(4s)	
2t$_{1g}$	−0.951	0		100(2π^*)
6e$_g$	−1.127	0	61(3d$_{z^2}$, 3d$_{x^2-y^2}$)	59(5σ)
3t$_{2g}$	−1.574	0	39(3d$_{xy}$, 3d$_{xz}$, 3d$_{yz}$)	61(2π^*)
2t$_{2u}$	−2.165	0		100(2π^*)
9t$_{1u}$	−2.593	0	6(4p$_x$, 4p$_y$, 4p$_z$)	7(5σ), 88(2π^*)
2t$_{2g}$	−6.591	6	59(3d$_{xy}$, 3d$_{xz}$, 3d$_{yz}$)	41(2π^*)

Fig. 16. Molecular orbital diagram for Mn$_2$(CO)$_{10}$ [124].

for elongation of the Mn–CO$_{ax}$ bond establish that excitations from the HOMO-1 (8e$_3$) to the 10b$_2$(σ^*) orbital yields a ^{3}E$_1$ surface that intersects with the ^{1}B$_2$ surface created by 10a$_1$(σ) to 10b$_2$(σ^*) excitations. The result of this overlap is to permit both M–M bond breaking and M–CO bond breaking in the same energy range.

Metal to ligand charge transfer (MLCT) transitions arise when ligands possess low lying π^* orbitals. The prototypical species in this regard is [Ru(bipy)$_3$]$^{2+}$ in which excitation results in a ^{1}MLCT state that transforms to a ^{3}MLCT state with a half life of about 100 fs [125].

Recent detailed examinations of metal carbonyl and carbonyl, nitrosyl compounds containing diimine or DAB (diazabutadiene) ligands have cast new light on the nature of the excited states of these compounds. As expected, high intensity absorptions have been shown to be associated with MLCT transitions to ligand π^* orbitals, while ligand field transitions that were once regarded as important contributors to the photophysics of these compounds [126] have now been shown to be too high in energy to contribute significantly [127]. Instead, M–CO MLCT transitions are seen as accounting for spectral features once assigned to ligand field transitions.

The picture that is emerging from a suite of spectral studies and theory is less intuitive and more nuanced than the traditional models for the photophysical behavior of metal complexes. While these details are probably irrelevant to someone utilizing photochemistry for simple ligand substitutions (after all, atoms were still a hypothesis when Dewar discovered the photochemical synthesis of Fe$_2$(CO)$_9$), those of us who are concerned with the details of mechanisms of photochemical reactions find ourselves having to learn a whole new language of theory in order to interpret our results. The prospect is both exciting and daunting.

9. Conclusion

As described above an understanding of a photochemical system arises not from any one study

or method, but from an orchestra of techniques brought to bear on excited state phenomena. Solution chemistry, matrix and flash studies, theoretical insights, and now the possibility of crystallography on excited states themselves come together over time to yield harmonies and understanding.

Acknowledgement

References

[1] (a) J. Dewar, H.O. Jones, Chem. News J. Indust. Sci. 95 (1907) 109;
(b) J. Dewar, H.O. Jones, Proc. Royal Soc., London 79 (1907) 66;
(c) J. Dewar, H.O. Jones, Proc. Royal Soc., London 76 (1905) 558.

[2] E. Speyer, M. Wolf, Chem. Ber. 60 (1927) 1424–1425.

[3] R.B. King, in: J.J. Eisch, R.B. King (Eds.), Organometallic Synthesis, vol. 1, Academic Press, New York, 1965, p. 93.

[4] M.D. Rausch, G.N. Schrauzer, Chem. Ind. (1959) 957–958.

[5] (a) Cr(CO)$_6$: W. Strohmeier, K. Gerlach, Z. Naturforsch. 15b (1960) 413;
(b) W. Strohmeier, K. Gerlach, Z. Naturforsch. 15b (1960) 622;
(c) W. Strohmeier, K. Gerlach, Z. Naturforsch. 15b (1960) 1346–1349;
Mo(CO)$_6$:W. Strohmeier, K. Gerlach, Chem. Ber. 93 (1960) 2087–2088;
W(CO)$_6$:W. Strohmeier, K. Gerlach, G. Matthias, Z. Naturforsch. 15b (1960) 621–622.

[6] W. Strohmeier, K. Gerlach, Z. Naturforsch. 15b (1960) 675–676.

[7] W. Strohmeier, K. Gerlach, Chem. Ber. 94 (1961) 398–406.

[8] (a) T.E. Bitterwolf, A.C. Ling, J. Organomet. Chem. 40 (1972) C29–C32;
(b) A.M. Tarr, D.R. Wile, Canad. J. Chem. 46 (1968) 2725–2731;
(c) J.C.D. Brand, W. Snedden, Trans. Faraday Soc. 53 (1957) 894–900.

[9] T.E. Bitterwolf, Enc. Inorg. Chem., second ed., J. Wiley and Sons, in press.

[10] (a) M.D. Roundhill, Photochemistry and Photophysics of Metal Complexes, Plenum Press, New York, 1993;
(b) G.L. Geoffroy, M.S. Wrighton, Organometallic Photochemistry, Academic, New York, 1979.

[11] H. Fleckner, F.-W. Grevels, D. Hess, J. Am. Chem. Soc. 106 (1984) 2027–2032.

[12] (a) N. Leadbeater, Coord. Chem. Rev. 188 (1999) 35–70;
(b) M. Poliakoff, J.J. Turner, Angew. Chem., Int. Ed. 40 (2001) 2809–2812;
(c) M. Poliakoff, E. Weitz, Acc. Chem. Res. 20 (1987) 408–414.

[13] R.B. Hitam, K.A. Mahmoud, A.J. Rest, J. Organomet. Chem. 291 (1985) 321–333.

[14] T.-F. Wang, C.-Y. Lai, J. Organomet. Chem. 545–546 (1997) 179–184.

[15] R.G. Severson, A.J. Wojicicki, J. Organomet. Chem. 157 (1978) 173–185.

[16] J.A. Belmont, M.S. Wrighton, Organometallics 5 (1986) 1421–1428.

[17] A.J. Rest, J.J. Turner, J. Chem. Soc., Chem. Commun. (1969) 1026.

[18] (a) A.J. Downs, T.M. Greene, Adv. Inorg. Chem. 46 (1998) 101–171;
(b) R.N. Perutz, NATO ASI Series C 483 (1996) 95–124;
(c) T.E. Bitterwolf, in: J.M. Chalmers, P.R. Griffiths (Eds.), Handbook of Vibrational Spectroscopy, vol. 4, Wiley, West Sussex, 2002, pp. 3137–3151.

[19] A. Gilbert, J.M. Kelly, M. Budzwait, E.S. Koerner von Gustorf, Z. Naturforsch. 31b (1976) 1091–1095.

[20] A.J. Rest, J.R. Sodeau, D.T. Taylor, J. Chem. Soc., Dalton (1978) 651–656.

[21] P.S. Braterman, J.D. Black, J. Organomet. Chem. 39 (1972) C3–C4.

[22] (a) T.G. Attig, A.J. Wojcicki, J. Organomet. Chem. 82 (1974) 397–415;
(b) T.G. Attig, P. Reich-Rohrwig, A.J. Wojcicki, J. Organomet. Chem. 53 (1973) C21–C23.

[23] P. Reich-Rohrwig, Inorg. Chem. 13 (1974) 2457–2464.

[24] R.J. Kazlauskas, M.S. Wrighton, J. Am. Chem. Soc. 102 (1980) 1727–1730.

[25] R.H. Hooker, K.A. Mahmoud, A.J. Rest, H.G. Alt, J. Organomet. Chem. 419 (1991) 101–112.

[26] (a) K.H. Pannell, S. Sharma, Organometallics 10 (1991) 1655–1656;
(b) K.H. Pannell, J.M. Rozell Jr., C. Hernandez, J. Am. Chem. Soc. 111 (1989) 4482–4485.

[27] T.E. Bitterwolf, W.B. Scallorn, J.T. Bays, C.A. Weiss, J.C. Linehan, J. Franz, R. Poli, J. Organomet. Chem. 652 (2002) 95–104.

[28] Z. Pang, R.F. Johnson, D.G. VanDerveer, J. Organomet. Chem. 526 (1996) 25–32.

[29] D. Sellmann, Angew. Chem., Int. Ed. Eng. 13 (1974) 839–849.

[30] W. Kaim, T. Roth, B. Olbrich-Deussner, R. Gross-Lannert, J. Jordanov, E. Roth, K.H. Eberhard, J. Am. Chem. Soc. 114 (1992) 5693–5697.

[31] R.L. Sweany, Evidence for a Complex of Molecular Hydrogen. The Reaction of Matrix-Isolated Pentacarbonyl Chromium and Its Congers with Dihydrogen, paper given at the Inorganic Chemistry Symposium, Bloomington, IN, May, 1982.

[32] G.J. Kubas, R.R. Ryan, B.I. Swanson, P.J. Vergamini, H.J. Wasserman, J. Am. Chem. Soc. 106 (1984) 451–452.

[33] R.L. Sweany, J. Am. Chem. Soc. 107 (1985) 2374–2379.

[34] P.D. Lee, J.L. King, S. Seebald, M. Poliakoff, Organometallics 17 (1998) 524–533.

[35] D.M. Heinekey, W. Oldham, Chem. Rev. 93 (1993) 913–926.

[36] R.L. Sweany, Trans. Met. Chem. (1992) 65–101.

[37] G.J. Kubas, Metal Dihydrogen and σ-bond Complexes, Kluwer Academic/Plenum Publishers, New York, 2001.

[38] A.J. Hart-Davis, W.A.G. Graham, J. Am. Chem. Soc. 91 (1969) 3375–3376.

[39] R.N. Perutz, J.J. Turner, J. Am. Chem. Soc. 97 (1975) 4791–4800.

[40] X.-Z. Sun, M.W. George, S.G. Kazarian, S.N. Nikiforov, M. Poliakoff, J. Am. Chem. Soc. 118 (1996) 10525–10532.

[41] D.C. Grills, M.W. George, Adv. Inorg. Chem. 5 (2001) 113–150.

[42] M. Poliakoff, J.J. Turner, Adv. Spectrosc. 23 (1996) 275–306.

[43] C. Hall, R.N. Perutz, Chem. Rev. 96 (1996) 3125–3146.

[44] J. Chatt, J.M. Davidson, J. Chem. Soc. (1965) 843–855.

[45] C. Giannotti, M.L.H. Green, Chem. Commun. (1972) 1114–1115.

[46] (a) M.L.H. Green, P.J. Knoles, J. Chem. Soc. A (1971) 1508–1511;
(b) R.B. Francis, F.W. Benfield, M.L.H. Green, Chem. Commun. (1971) 1290.

[47] K. Elmitt, M.L.H. Green, R.A. Forder, I. Jefferson, K. Prout, Chem. Commun. (1974) 747–748.

[48] K.L. Tang Wong, J.L. Thomas, H.H. Brintzinger, J. Am. Chem. Soc. 96 (1974) 3694–3695.

[49] (a) R.F.G. Baynham, J. Chetwynd-Talbot, P. Grebenik, R.N. Perutz, M.H.A. Powell, J. Organomet. Chem. 284 (1985) 229–242;
(b) D.F. Foust, R.D. Rogers, M.D. Rausch, J.L. Atwood, J. Am. Chem. Soc. 104 (1982) 5646–5650;
(c) E.K. Barefield, G.W. Parshall, F.N. Tebbe, J. Am. Chem. Soc. 92 (1970) 5234–5235.

[50] M.D. Rausch, R.G. Gastinger, S.A. Gardner, R.K. Brown, J.S. Wood, J. Am. Chem. Soc. 99 (1977) 7870–7876.

[51] W. Jetz, W.A.G. Graham, Inorg. Chim. 10 (1971) 4–9.

[52] A.J. Oliver, W.A.G. Graham, Inorg. Chem. 10 (1971) 1–4.

[53] J.K. Hoyano, W.A.G. Graham, J. Am. Chem. Soc. 104 (1982) 3723–3725.

[54] A.H. Janowicz, R.G. Bergman, J. Am. Chem. Soc. 104 (1982) 352–354.

[55] A.J. Rest, I. Whitwell, W.A.G. Graham, J.K. Hoyano, A.D. McMaster, J. Chem. Soc., Chem. Commun. (1984) 624–626.

[56] (a) P.E. Bloyce, A.J. Rest, I. Whitwell, W.A.G. Graham, R. Holmes-Smith, J. Chem. Soc., Chem. Commun. (1988) 846–848;
(b) P.E. Bloyce, A.J. Rest, I. Whitwell, J. Chem. Soc., Dalton Trans. (1990) 813–821.

[57] (a) S.A. Blum, K.L. Tan, R.G. Bergman, J. Org. Chem. 68 (2003) 4127–4137;
(b) J.A. Labinger, J.E. Bercaw, Nature 417 (2002) 507–514;
(c) A.E. Shilov, G.B. Shul'pin, Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes, Kluwer, Dordrecht, Boston, 2000;
(d) A.J. Lees, J. Organomet. Chem. 554 (1998) 1–11;
(e) A.E. Shilov, G.B. Shul'pin, Chem. Rev. 97 (1997) 2879–2932;
(f) A.J. Lees, A.A. Purwoko, Coord. Chem. Rev. 132 (1994) 155–160;
(g) R.G. Bergman, Adv. Chem. Ser. 230 (1992) 211–220.

[58] J.J. Schneider, Angew. Chem., Int. Ed. Engl. 35 (1996) 1068–1075.

[59] P.T. Snee, C.K. Payne, K.T. Kotz, H. Yang, C.B. Harris, J. Am. Chem. Soc. 123 (2001) 2255–2264.

[60] P.T. Snee, H. Yang, K.T. Kotz, C.K. Payne, C.B. Harris, J. Phys. Chem. A 103 (1999) 10426–10432.

[61] H. Tanachat, M.C. Asplund, K.T. Kotz, M.J. Wilkens, H. Frei, C.B. Harris, J. Am. Chem. Soc. 120 (1998) 10154–10165.

[62] A.A. Bengali, R.H. Schultz, C.B. Moore, R.G. Bergman, J. Am. Chem. Soc. 116 (1994) 9585–9589.

[63] B.K. McNamara, J.S. Yeston, R.G. Bergman, C.B. Moore, J. Am. Chem. Soc. 121 (1999) 6437–6443.

[64] C.K. Ghosh, W.A.G. Graham, J. Am. Chem. Soc. 109 (1987) 4726–4727.

[65] P.E. Bloyce, J. Mascetti, A.J. Rest, J. Organomet. Chem. 444 (1993) 223–233.

[66] (a) A.A. Purwoko, A.J. Lees, Inorg. Chem. 34 (1995) 424–425;
(b) A.A. Purwoko, A.J. Lees, Inorg. Chem. 35 (1996) 675–682;
(c) A.A. Purwoko, S.D. Tibensky, A.J. Lees, Inorg. Chem. 35 (1996) 7049–7055.

[67] (a) T. Lian, S.E. Bromberg, H. Yang, R.G. Bergman, C.B. Harris, J. Am. Chem. Soc. 118 (1996) 3769–3770;
(b) S.E. Bromberg, H. Yang, M.C. Asplund, T. Lian, B.K. McNamara, K.T. Kotz, J.S. Yeston, M. Wilkens, H. Frei, R.G. Bergman, C.B. Harris, Science 278 (1997) 260–263;
(c) J. Yeston, B. McNamara, R.G. Bergman, C.B. Moore, Organometallics 19 (2000) 3442–3446;

(d) M.C. Asplund, P.T. Snee, J.S. Yeston, M.K. Wilkens, C.K. Payne, H. Yang, K.T. Kotz, H. Frei, R.G. Bergman, C.B. Harris, J. Am. Chem. Soc. 124 (2002) 10695–10712.

[68] (a) E.M. Gordon, R. Eisenberg, J. Organomet. Chem. 306 (1986) C53–C57;
(b) A. Kunin, R. Eisenberg, Richard, J. Am. Chem. Soc. 108 (1986) 535–536.

[69] T. Sakakura, K. Ishiguro, M. Okano, T. Sako, Chem. Lett. (1997) 1089–1090.

[70] T. Bitterwolf, D.L. Kline, J. Linehan, C.R. Yonker, R.S. Addleman, Angew. Chem., Int. Ed. 40 (2001) 2692–2694.

[71] J.-C. Choi, Y. Kobayashi, T. Sakakura, J. Org. Chem. 66 (2001) 5262–5263.

[72] (a) T. Sakakura, K. Sasaki, Y. Tokunaga, K. Wada, M. Tanaka, Chem. Lett. (1988) 155–158;
(b) T. Sakakura, M. Tanaka, Chem. Lett. (1987) 1113–1116.

[73] N.K. Khannanov, G.N. Menchikova, E.A. Grigorjan, Kinet. Katal. 34 (1993) 63–67.

[74] G.P. Rosini, W.T. Boese, A.S. Goldman, J. Am. Chem. Soc. 116 (1994) 9498–9505.

[75] (a) G.P. Rosini, K. Zhu, A.S. Goldman, J. Organomet. Chem. 504 (1995) 115–121;
(b) G.P. Rosini, W.T. Boese, A.S. Goldman, J. Am. Chem. Soc. 116 (1994) 9498.

[76] (a) J.S. Bridgewater, T.L. Netzel, J.R. Schoonover, S.M. Massik, P.C. Ford, Inorg. Chem. 40 (2001) 1466–1476;
(b) J.S. Bridgewater, B. Lee, S. Bernhard, J.R. Schoonover, P.C. Ford, Organometallics 16 (1997) 5592–5594.

[77] T.E. Bitterwolf, W.B. Scallorn, J.T. Bays, C.A. Weiss, J.C. Linehan, J. Franz, R. Poli, J. Organomet. Chem. 652 (2002) 95–104.

[78] T.E. Bitterwolf, B. Wong, Inorg. Chim. Acta, in press.

[79] R.H. Schultz, J. Organomet. Chem. 688 (2003) 1–4.

[80] (a) G.O. Evans, R.K. Sheline, J. Inorg. Nuc. Chem. 30 (1968) 2862–2863;
(b) T. Kruck, M. Höfler, M. Noack, Chem. Ber. 99 (1966) 1153–1167;
(c) W. Hieber, W. Beck, G. Zeitler, Angew. Chem. 73 (1961) 364–368;
(d) W. Heiber, W. Schrapp Jr., Z. Naturforsch. 15b (1960) 271.

[81] M.S. Wrighton, D. Bredesen, J. Organomet. Chem. 50 (1973) C35–C38.

[82] S.A. Hallock, A. Wojcicki, J. Organomet. Chem. 54 (1973) C27–C29.

[83] M.S. Wrighton, D.S. Ginley, J. Am. Chem. Soc. 97 (1975) 4246–4251.

[84] M.S. Wrighton, D.S. Ginley, J. Am. Chem. Soc. 97 (1975) 2065–2072.

[85] D.S. Ginley, M.S. Wrighton, J. Am. Chem. Soc. 97 (1975) 4908–4911.

[86] A. Hudson, M.F. Lappert, B.K. Nicholson, J. Chem. Soc., Dalton Trans. (1977) 551–554.

[87] T. Madach, H. Vahrenkamp, Chem. Ber. 113 (1980) 2675–2685.

[88] (a) J.Z. Zhang, C.B. Harris, J. Chem. Phys. 95 (1991) 4024–4032;
(b) J.L. Hughey IV, C.P. Anderson, T.J. Meyer, J. Organomet. Chem. 125 (1977) C49–C52.

[89] A.F. Hepp, M.S. Wrighton, J. Am. Chem. Soc. 105 (1983) 5934–5935.

[90] J.C. Owrutsky, A.P. Baronavski, J. Chem. Phys. 105 (1996) 9864–9873.

[91] (a) S.K. Kim, S. Pedersen, A.H. Zewail, Chem. Phys. Lett. 233 (1995) 500–508;
(b) D.A. Prinslow, V. Vaida, J. Am. Chem. Soc. 109 (1987) 5097–5100;
(c) T. Kobayashi, H. Ohtani, H. Noda, S. Teratani, H. Yamazaki, K. Yasufuku, Organometallics 5 (1986) 110–113.

[92] H.-T. Zhang, T.L. Brown, J. Am. Chem. Soc. 115 (1993) 107–117.

[93] S. Zhang, H.-T. Zhang, T.L. Brown, Organometallics 11 (1992) 3929–3931.

[94] T.L. Brown, S. Zhang, Inorg. Chem. 34 (1995) 1164–1171.

[95] F.A. Kvietok, B.E. Bursten, Organometallics 14 (1995) 2395–2399.

[96] (a) Group VI: T.E. Bitterwolf, Coord. Chem. Rev. 211 (2001) 235–254;
(b) Group VIII:T.E. Bitterwolf, Coord. Chem. Rev. 206–207 (2000) 419–450.

[97] J.K. Klassen, M. Selke, A.A. Sorensen, G.K. Yang, J. Am. Chem. Soc. 112 (1990) 1267–1268.

[98] Y. Zheng, W. Wang, J. Lin, Y. She, K. Fu, J. Phys. Chem. 96 (1992) 7650–7656.

[99] (a) F.A. Kvietok, B.E. Bursten, J. Am. Chem. Soc. 116 (1994) 9807;
(b) M. Vitale, M.E. Archer, B.E. Bursten, J. Chem. Soc., Chem. Commun. (1998) 179.

[100] J.L. Hughes IV, C.R. Bock, T.J. Meyer, J. Am. Chem. Soc. 97 (1975) 4440–4441.

[101] R.W. Wegman, R.J. Olsen, D.R. Gard, L.R. Faulkner, T.L. Brown, J. Am. Chem. Soc. 103 (1981) 6089–6092.

[102] J.C. Zhang, C.B. Harris, J. Chem. Phys. 95 (1991) 4024–4033.

[103] J.C. King, J.Z. Zhang, B.J. Schwartz, C.B. Harris, J. Chem. Phys. 99 (1993) 7595–7601.

[104] S. Zhang, T.L. Brown, J. Am. Chem. Soc. 114 (1992) 2723–2725.

[105] B.D. Moore, M.B. Simpson, M. Poliakoff, J.J. Turner, Chem. Commun. (1984) 972–974.

[106] A.J. Dixon, S.J. Gravelle, L.J. van de Burgt, M. Poliakoff, J.J. Turner, E. Weitz, Chem. Commun. (1987) 1023–1024.

[107] J.C. Linehan, C.R. Yonker, R.S. Addleman, S.T. Autry, J.T. Bays, T.E. Bitterwolf, J.L. Daschbach, Organometallics 20 (2001) 401–407.

[108] D.A. Steinhurst, A.P. Baronavski, J.C. Owrutsky, Chem. Phys. Lett. 361 (2002) 513–519.

[109] J.C. Owrutsky, A.P. Baronanski, J. Chem. Phys. 105 (1996) 9864–9873.

[110] (a) I.V. Novozhilova, A.V. Volkov, P. Coppens, J. Am. Chem. Soc. 125 (2003) 1079–1087;
(b) C.D. Kim, S. Pillet, G. Wu, W.K. Fullagar, P. Coppens, Acta Crystallogr. A 58 (2003) 133.

[111] K.H. Leung, D.L. Phillips, C.-M. Che, V.M. Miskowski, J. Raman Spectrosc. 30 (1999) 987–993.

[112] M.M. Abd-Elzaher, B. Weibert, H. Fischer, J. Organomet. Chem. 669 (2003) 6–13.

[113] S. Özkar, C. Kayran, N. Demir, J. Organomet. Chem. 688 (2003) 62–67.

[114] I.A. Morkan, K. Güven, S. Özkar, J. Organomet. Chem. 689 (2004) 2319–2323.

[115] O. Grazani, L. Toupet, J.-R. Hamon, M. Tilset, J. Organomet. Chem. 669 (2003) 200–206.

[116] C.G. Kreiter, C. Fielder, W. Frank, G.J. Reiß, J. Organomet. Chem. 490 (1995) 133–141.

[117] M.A. McGuire, L.S. Hegedus, J. Am. Chem. Soc. 104 (1982) 5538–5540.

[118] P.-J. Colson, L.S. Hegedus, J. Org. Chem. 59 (1994) 4972–4976.

[119] (a) B. Brown, L.S. Hegedus, J. Org. Chem. 63 (1998) 8012–8018;
(b) A.G. Riches, L.A. Wernersbach, L.S. Hegedus, J. Org. Chem. 63 (1998) 4691–4696;
(c) S. Koebbing, J. Mattay, G. Raabe, Chem. Ber. 126 (1993) 1849–1858;
(d) S. Koebbing, J. Mattay, Tetrahedron Lett. 33 (1992) 927–930.

[120] (a) J. Zhu, C. Deur, L.S. Hegedus, J. Org. Chem. 62 (1997) 7704–7710;
(b) L.S. Hegedus, Acc. Chem. Res. 28 (1995) 299–305.

[121] (a) L.S. Hegedus, Tetrahedron 53 (1997) 4105–4128;
(b) H.G. Schmalz, Nachricht. Chem., Tech. Labor. 42 (1994) 608–612;
(c) L.S. Hegedus, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Pergamon, Oxford, UK, 1991, pp. 549–576.

[122] (a) N.A. Beach, H.B. Gray, J. Am. Chem. Soc. 90 (1968) 5713–5721;
(b) H.B. Gray, N.A. Beach, J. Am. Chem. Soc. 85 (1963) 2922–2927.

[123] (a) A. Rosa, E.J. Baerends, S.J.A. van Gisbergen, E. van Lenthe, J.A. Grownsveld, J.G. Snijders, J. Am. Chem. Soc. 121 (1999) 10356–10365;
(b) C. Pollak, A. Rosa, E.J. Baerends, J. Am. Chem. Soc. 119 (1997) 7324–7329;
(c) K. Pierloot, E. Tsokos, L.G. Vanquickenborne, J. Phys. Chem. 100 (1996) 16545–16550;
(d) E.J. Baerends, A. Rosa, Coord. Chem.Revs. 177 (1998) 97–125.

[124] A. Rosa, G. Ricciardi, E.J. Baerends, D.J. Stufkens, Inorg. Chem. 34 (1995) 3425–3432.

[125] (a) N.H. Damrauer, G. Cerullo, A. Yeh, T.R. Boussie, C.V. Shank, J.K. McCusker, Science 275 (1997) 54–57;
(b) A. Vlcek Jr., Chemtracts 11 (1998) 621–625.

[126] K.A. Rawlins, A.J. Lees, Inorg. Chem. 28 (1989) 2154–2160.

[127] (a) S. Záliš, I.R. Farrell, A. Vlèek Jr., J. Am. Chem. Soc. 125 (2003) 4580–4592;
(b) I.R. Farrell, F. Hartl, S. Záliš, A. Vlèek Jr., J. Chem. Soc., Dalton Trans. (2000) 4323–4331;
(c) I.R. Farrell, J. van Slageren, S. Záliš, A. Vlèek Jr., Inorg. Chim. Acta 315 (2001) 44–52.