Coordination Chemistry Reviews, 55 (1984) 1–29
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

MATRIX ISOLATION STUDIES OF ORGANOMETALLIC INTERMEDIATES

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(Received 17 October 1983)

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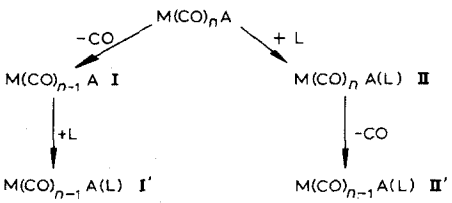
0010-8545/84/$08.70

A. INTRODUCTION

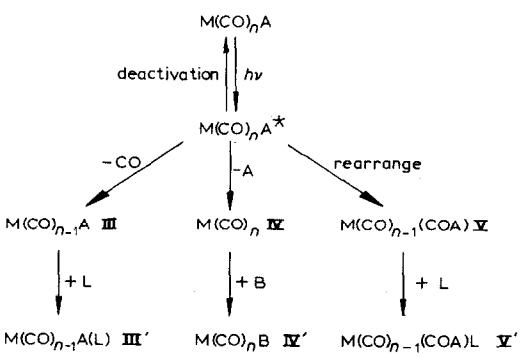
Thermal reactions of organometallic complexes often involve the replacement of bound ligands as steps in the overall reaction processes, e.g. substitution reactions. For such substitution reactions, kinetic studies have established two broad categories of reactions: (i) those reactions which show a dependence solely on the concentration of the metal complex, and (ii) others which show a dependence on the concentrations of the metal complex and of the incoming ligand. The former reactions are described as proceeding by a dissociative mechanism with coordinatively unsaturated species, e.g. **I** in Scheme 1, postulated as reaction intermediates. The latter reactions are



Scheme 1

described as proceeding by an associative mechanism with expanded coordination number species, e.g. **II** in Scheme 1, postulated as intermediates.

Many organometallic compounds are not very thermodynamically stable so that the thermal energy required to effect their synthesis and to carry out reactions with them often leads to decomposition. However, UV–visible irradiation of the reaction mixture at ambient temperatures and/or lower temperatures, i.e. a photochemical reaction, often leads to a good yield of products. In the general photochemical reaction illustrated in Scheme 2, the

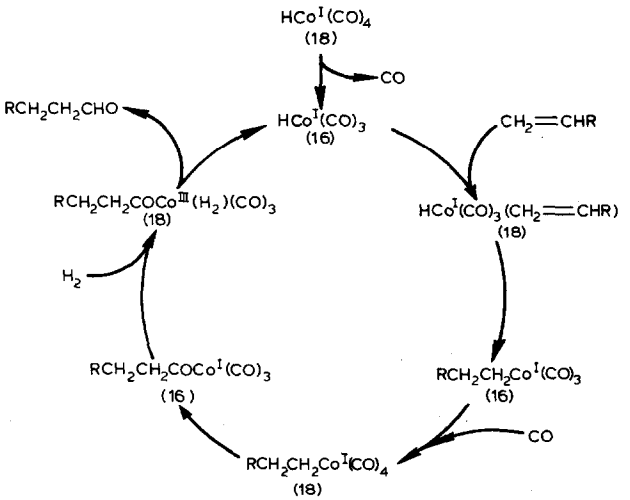


Scheme 2

absorption of energy to give an excited state, $M(CO)_nA^*$ leads to products **III′**, **IV′** and **V′** which may be accounted for by proposing the existence of

coordinatively unsaturated short-lived intermediate species **III–V**.

Mechanisms for thermal and photochemical reactions could be put on firmer bases if evidence could be found for the existence of species such as **I–V**, which have been proposed as reaction intermediates. Furthermore, if precise details of the structure, reactivity and bonding of such species could be determined, it should be possible to develop a better understanding of organometallic reactions. Such an understanding could lead to a rational and predictive approach to the reactions of organometallic complexes and, very importantly, to establishing the validity or otherwise of catalytic cycles. For example, the hydroformylation of olefins (Scheme 3) is proposed to involve a



Scheme 3. (Taken from C. Masters, Homogenous Transition-metal Catalysis, Chapman and Hall, London, 1981.)

number of coordinately unsaturated 16-electron species.

Given that reaction intermediates and transition state species are highly reactive and very unstable, there are basically two ways of studying them:
(a) to observe them in their natural lifetime by rapid detection techniques, e.g. flash photolysis and pulse radiolysis;
(b) to prolong their life by quenching the species, once they have been formed, at low temperatures, e.g. matrix isolation spectroscopy.

For molecules with more than a few atoms approach (a), although capable of giving information about the lifetimes of species down to picoseconds, provides little information about the detailed structures of the species. This is because the very short lifetimes are measured using electronic absorption bands which are generally broad and structureless for organometallic complexes. Approach (b), however, allows more leisure for spectroscopy and

using the matrix isolation technique very detailed information about the structures of unstable species can be obtained.

The essential features of the matrix isolation technique [1] are that: (i) the unstable species are surrounded by large numbers of unreactive host matrix atoms or molecules which form a rigid array so that pairs of unstable species cannot come together for bimolecular reactions, and (ii) at low temperatures, and especially at temperatures in the range 4–25 K, the unstable molecules themselves have very little internal energy and so cannot decompose by unimolecular reactions. Unstable species for matrix isolation spectroscopy are produced primarily either by some gas-phase reaction or process and then quenched on to the cold spectroscopic window, or by decomposing stable molecules already isolated in the matrices using some form of irradiation. In order to generate the types of unstable species which have been proposed in reaction mechanisms, e.g. Schemes 1 and 2, the latter approach has been most widely used.

Some aspects of applications of matrix isolation spectroscopy to metal carbonyls [2] and metal atom co-condensation reactions [3] have been reviewed previously. In this review we survey the use of matrix isolation studies, primarily using gas matrices at 4–30 K, to investigate organometallic species which have been proposed as intermediates in chemical reactions and catalysis cycles together with transition state species proposed in fluxional processes observed by NMR spectroscopy. The principal types of reaction path are illustrated in Section B and examples of paths for various metals, primarily transition metals, are tabulated in Section C.

B. SURVEY OF PRINCIPAL REACTION PROCESSES

(i) CO ejection

Almost all transition metal carbonyls undergo CO loss as the primary photochemical step ($h\nu$) generating coordinatively unsaturated 16-electron fragments (eqn. (1), see Section C). The reactivities of the fragments are demonstrated by the recombination reactions on long wavelength irradiation ($h\nu'$), annealing the host matrices (Δ, warming up the matrix to close to its

$$ML(CO)_n \underset{h\nu',\Delta}{\overset{h\nu}{\rightleftharpoons}} ML(CO)_{n-1} + CO \qquad (1)$$

diffusion point, e.g. ca. 35 K for Ar), and reactions with dopants in the matrices, e.g. N_2 and C_2H_4 forming $ML(CO)_{n-1}(N_2)$ and $ML(CO)_{n-1}(C_2H_4)$ complexes respectively.

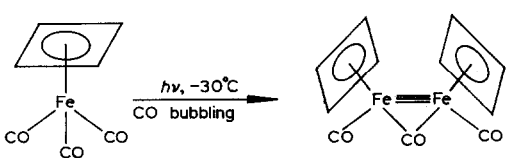
Photosubstitution reactions of $ML(CO)_n$ complexes in solution are proposed to proceed via coordinatively unsaturated intermediates of the type

$ML(CO)_{n-1}$ (Scheme 2). A careful comparison of the electronic absorption bands of $Cr(CO)_5$ species in matrix isolation studies [8–12] with the bands observed for transients in flash photolysis studies of $Cr(CO)_6$ in hydrocarbon solutions [110] has established a correspondence of a species assigned as "solvated" $Cr(CO)_5$ and the matrix species $Cr(CO)_5 \ldots CH_4$ [11,12]. The other flash photolysis transient was assigned as "naked" $Cr(CO)_5$ [110].

The extreme reactivities of species towards recombination ($h\nu'$ and Δ, eqn. (1)) emphasise the importance of working at very low temperatures in order to stabilise and observe the coordinatively unsaturated species. For example, early studies using hydrocarbon glasses at 77 K were able to stabilise $M(CO)_5$ fragments (M = Cr, Mo, W) [111] but were unable to stabilise the $Fe(CO)_4$ fragment, observed later in gas matrices at 20 K [72].

A crucial feature of any matrix isolation study is to determine the structures of any species formed. Fortunately the costs of isotopically enriched gases, e.g. ^{13}CO, $C^{18}O$, ^{15}NO, $^{15}N_2$, have decreased so that various levels of enrichment can be attained in the products and the resulting spectra fitted using an energy-factored force field fitting approach [2,112]. Such an approach affords well-defined geometries for molecular fragments and should always be carried out unless there are good reasons, e.g. extensive overlapping of parent and product bands [2]. Unless there are actually vibrations of other ligands within ca. 150 cm^{-1}, it is not necessary in practice to include CO–ligand interaction force constants in the calculations using $^{13}CO/^{12}CO$ fitting, i.e. inclusion of $k_{CO,NO}$ and $k_{N_2,CO}$ interactions is not crucial to get a good fit for ^{13}CO enriched $M(CO)_n(NO)_m$ and $M(CO)_x(N_2)_y$ complexes.

The identities of various $ML(CO)_{n-1}(N_2)$ and $ML(CO)_{n-1}(C_2H_4)$ species characterised in N_2 and C_2H_4 doped matrices have been confirmed in several cases by comparisons with authentic samples prepared conventionally, e.g. $Mn(\eta^5\text{-}C_5H_5)(CO)_2(N_2)$($\nu_{NN}$ at 2169 cm^{-1}, ν_{CO} at 1980 and 1923 cm^{-1}, n-hexane [113]; ν_{NN} at 2175.3 cm^{-1}, ν_{CO} at 1978.7 and 1927.0 cm^{-1}, N_2 at 20 K [31]) and $W(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_4)H$($\nu_{CO}$ at 1961 and 1883 cm^{-1}, n-hexane [114]; ν_{CO} at 1974.2 and 1897.2 cm^{-1}, 5% C_2H_4 doped CH_4 at 12 K [29,36]). The stimulus of new 18-electron species in matrices has not always led to the same species being isolated from solutions, e.g. an attempt to prepare $Fe(\eta^4\text{-}C_4H_4)(CO)_2(N_2)$ [31] led instead to a novel dimer (eqn.



(2)

(2)) [115]. Nevertheless it is to be hoped that the known matrix spectroscopic

data for 18-electron species will increasingly enable them to be detected in solution.

If instead of using UV–visible light for the forward photolysis step ($h\nu$, eqn. (1)), vacuum UV light or electron bombardment is used the result is ejection of CO as CO^+ and the formation of anions, e.g. $[Cr(CO)_5]^-$ [14] and $[Ni(CO)_3]^-$ [14]. Reversal, in this case, does not occur (cf. eqn. (1)).

(ii) Loss of ligand other than CO

An early criticism of matrix isolation studies of transition metal carbonyl compounds and their relevance vis-à-vis solution studies was that only CO was ever ejected. This criticism was answered when it was shown that pyridine and 3-bromopyridine were ejected from $W(CO)_5L$ complexes (L = pyridine, 3-bromopyridine; eqn. (3)) just as in eqn. (1) [48]. Subsequently a

$$W(CO)_5L \underset{h\nu',\Delta}{\overset{h\nu}{\rightleftharpoons}} W(CO)_5 + L \tag{3}$$

variety of $M(CO)_5L$ complexes (M = Cr, Mo, W) were found to give M–L bond rupture on long wavelength photolysis and M–CO bond cleavage on irradiation with higher energy light [48–50]. Photoejection of some π-hydrocarbons from M(π-hydrocarbon)$(CO)_n$ complexes occurs in CO matrices via reduced hapticity (ring slippage) species (see (x) below) and leads to $M(CO)_m$ complexes, e.g. Mo(η^6-C_7H_8)$(CO)_3$ gives $Mo(CO)_6$ via Mo(η^4-C_7H_8)$(CO)_4$ [43].

(iii) Partial dechelation

Substituted transition metal carbonyl complexes with chelating ligands are not as stable on volatilisation as their monodentate analogues and have, therefore, not been so extensively studied. In M(polyene)$(CO)_n$ complexes (M = Cr, Mo, W, Fe) partial decomplexation of the polyene ligand has been found to occur alongside CO ejection (eqn. (4)) [26,43,60]. The formation of η^{m-2} polyene intermediates has been proposed to be responsible for photo-induced isomerisation and rearrangement processes [116].

$$M(\eta^m\text{-polyene})(CO)_n \underset{h\nu'}{\overset{h\nu}{\rightleftharpoons}} M(\eta^{m-2}\text{-polyene})(CO)_n \tag{4}$$

In the case of acetylacetonato (acac) ligands, detachment of one end of this bidentate ligand occurs, i.e. σ,σ-acac → σ-acac, in $M(CO)_2$(acac) complexes (M = Rh, Ir) but to a lesser extent than CO ejection [99,100].

(iv) M–H bond cleavage

The earliest gas matrix isolation study of an organometallic compound, $Mn(CO)_5H$, showed ejection of a CO ligand to give $Mn(CO)_4H$ [52] (cf. the generation of the 16-electron species $Co(CO)_3H$ (Scheme 3)). A later study, however, in CO matrices found evidence for Mn–H bond homolysis and the formation of $Mn(CO)_5^{\cdot}$ and $HCO^{\cdot}$ radicals [53]. In studies of other hydrides, radicals have been observed in rare gas matrices as well as in CO matrices, where the CO traps the ejected $H^{\cdot}$ as HCO, e.g. $Co(CO)_4H \rightarrow Co(CO)_4^{\cdot} + H^{\cdot}$ [91,92] and $W(\eta^5\text{-}C_5H_5)(CO)_3H \rightarrow W(\eta^5\text{-}C_5H_5)(CO)_3^{\cdot} + H^{\cdot}$ [29,36]. The observation of a radical pathway for $Co(CO)_4H$ in addition to the CO ejection pathway, which affords $Co(CO)_3H$, indicates that there may be a hydroformylation cycle based on $Co(CO)_4^{\cdot}$ in addition to that based on $Co(CO)_3H$ (Scheme 3).

In the case of dihydrido complexes, photolysis leads to the ejection of H_2, e.g. $M(\eta^5\text{-}C_5H_5)_2H_2 \rightarrow M(\eta^5\text{-}C_5H_5)_2 + H_2 (M = Mo, W)$ [7].

(v) α-H elimination

Reversible α-H elimination from carbons bonded to transition metals, although less well documented than β-H elimination (see below), is being encountered with increasing frequency and may be important in generating active intermediates in metal catalysed disproportionation reactions [117]. The key in such processes is the equilibrium between metal alkyl and metal–carbene hydride species (eqn. 5). Infrared spectroscopic evidence,

$$M\text{–}CH_3 \rightleftharpoons \overset{H}{\underset{|}{M}}\text{=}CH_2 \qquad (5)$$

including ^{13}CO labelling and energy-factored force-field fitting has established that photolysis of $Cr(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)$ in Ar, CH_4, N_2 and CO matrices results in CO dissociation followed by α-H elimination to yield the carbene hydride complex, $Cr(\eta^5\text{-}C_5H_5)(CO)_2(=CH_2)H$, and that this reaction is reversible [30] (cf. eqn. (5)). This is the first direct evidence for a reversible α-H elimination and sets proposed carbene hydride reaction intermediates on a firmer basis.

(vi) β-H elimination

Reversible elimination of hydrogens from carbons which are in β-positions relative to transition metals has been established to occur widely and to be important in catalytic reactions, e.g. olefin isomerisation [117]. Photolysis

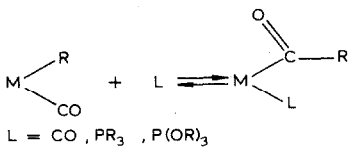
of $M(\eta^5\text{-}C_5R'_5)(CO)_3(R)$ complexes (M = Mo, W; R' = H, CH_3; R = C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, n-C_5H_{11}) in paraffin wax matrices at 77 K [118] and in gas matrices at 12 K [38] has shown that β-H elimination occurs in two steps following the trapping of the 16-electron coordinatively unsaturated species $M(\eta^5\text{-}C_5R'_5)(CO)_2(R)$ and the olefin hydride complexes $M(\eta^5\text{-}C_5R'_5)(CO)_2$(olefin)(H). Crucial features of this process, which were revealed only at the lower temperature, are that *cis* and *trans* isomers can be detected for $W(\eta^5\text{-}C_5R'_5)(CO)_2$(olefin)(H) complexes at 12 K, that these can isomerise thermally and photochemically and that annealing the matrix produces only the *trans* isomer [38], which is observed as the sole product at 77 K [118]. These observations underline the importance of working at the very lowest temperature, which is economically possible (ca. 12 K using a closed-cycle He refrigerator), in order to observe all the potential proposed reactive intermediates.

(vii) Ring-to-metal H and CH_3 migration

Reversible ring-to-metal H and CH_3 migrations have been proposed to occur in fluxional processes observed by NMR spectroscopy in which equalisation of environments is encountered for metal polyene complexes [116]. Evidence from studies at 12 K on $Fe(\eta^4\text{-}C_5H_4(CH_3)_2)(CO)_3$, which undergoes CH_3 migration irreversibly to yield $Fe(\eta^5\text{-}C_5H_4CH_3)(CO)_2(CH_3)$ [82]; $Fe(\eta^4\text{-}C_7H_{10})(CO)_3$, which afforded $Fe(\eta^5\text{-}C_7H_9)(CO)_2(H)$ irreversibly [81]; and $Mo(\eta^6\text{-}C_7H_8)(CO)_3$, which underwent isomerisation in the gas phase to yield the parent compound and $Mo(\eta^7\text{-}C_7H_7)(CO)_3H$ on the cold matrix spectroscopic window [44], reinforce the proposals for ring-to-metal migrations to explain some fluxional NMR processes.

(viii) Alkyl migration

Insertion and decarbonylation reactions of metal carbonyl alkyl complexes (eqn. (6)) are proposed to obey the principal of microscopic reversibil-



(6)

ity and to proceed via migration of the R group [119]. The common intermediate in both reactions is assumed to be the 16-electron coordinatively unsaturated species, M(COR) [119]. Photochemical decarbonylation of metal acyl complexes has indeed shown the initial formation of M(COR)

species, e.g. $Mn(CO)_4(COCH_3)$ from $Mn(CO)_5(COCH_3)$ [55,57,58] and $Fe(\eta^5\text{-}C_5H_5)(CO)(COCH_3)$ from $Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)$ [58,85], and that these species undergo CH_3 migration in a second step to give alkyl species. It is notable that CF_3 [39] and C_7H_7 [60] migrations also occur. In the 16-electron coordinatively unsaturated acyl species the bonding of the acyl ligand appears to be of normal σ-type (η^1-COR) rather than of π-type (η^2-COR) [59]. Reactions of CO with M(CO)R complexes in CO matrices have not yet yielded M(CO)(COR) complexes (eqn. (6)).

(ix) CO insertion into a ring

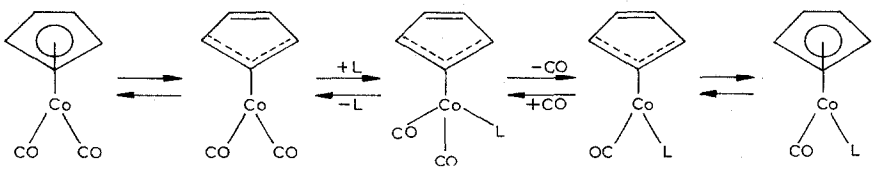
Among the products of reactions between $Fe(CO)_5$ and acetylenes are some with cyclopentadienone and quinone rings bonded to the metal while others contain only hydrocarbon rings [120]. An insight into this matter was afforded by the observation that photolysis of $Fe(\eta^4\text{-}C_4H_4)(CO)_3$ in CO matrices led to the formation of $Fe(\eta^4\text{-}C_4H_4CO)(CO)_3$ rather than decomplexation of the $\eta^4\text{-}C_4H_4$ ligand as is found for $\eta^4\text{-}C_4H_6$ and other η^4-polyenes [80]. Interestingly, the terminal ^{12}CO ligands in $Fe(\eta^4\text{-}C_4H_4CO)(CO)_3$ could be exchanged with ^{13}CO but not the ketonic CO whereas the ^{12}CO ligands in $Fe(\eta^4\text{-}C_4H_4)(CO)_3$ rapidly exchanged with ^{13}CO. The implication of this is that it is a bound CO ligand which enters the ring intramolecularly rather than an unbound CO reacting intermolecularly with some ring-opened species [81].

(x) Hapticity changes ($\eta^n \rightleftharpoons \eta^m$) of polyenes

Not all the olefinic double bonds in polyenes are bound to the central metal and changes in the number of such bound double bonds can occur during chemical reactions, e.g. eqn. (7) [121].

$$W(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)(CO)_3 \rightarrow W(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)(CO)_2 \qquad (7)$$

The change $\eta^1\text{-}C_5H_5 \rightarrow \eta^3\text{-}C_5H_5$ involves a change in the number of polyene carbons bound to the metal from 1 to 3 and this is described as a change in ring hapticity [122]. Such changes in hapticity are usually encountered as changes by ± 2 when CO ligands are lost or gained. Photolysis of $Co(\eta^5\text{-}C_5H_5)(CO)_2$ in CO matrices at 12 K leads to the uptake of a CO ligand and the formation of a $(\eta^n\text{-}C_5H_5)Co(CO)_3$ species which, on the basis of the 18-electron rule, is assigned to be $Co(\eta^3\text{-}C_5H_5)(CO)_3$ rather than the 20-electron species $Co(\eta^5\text{-}C_5H_5)(CO)_3$ [96]. Such a hapticity change has important implications for the substitution reactions of $Co(\eta^5\text{-}C_5H_5)(CO)_2$ which are proposed to proceed via an associative mechanism as demonstrated by the second order kinetics [123]. The pathway for such an association reaction



(8)

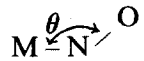
would now seem to be a $\eta^5 \rightleftharpoons \eta^3$ change, followed by uptake of a ligand L, and then ejection of either L or CO (eqn. (8)). Support for such processes was afforded by the observation that the reaction to form $Co(\eta^3\text{-}C_5H_5)(CO)_3$ could be reversed by irradiating the matrix with a different UV–visible source [96]. An extended series of hapticity changes occurs for $Mn(CO)_5(COC_7H_7)$ which, after the initial CO loss to give $Mn(CO)_4(COC_7H_7)$ and migration of the C_7H_7 ring to the metal, gives $Mn(\eta^1\text{-}C_7H_7)(CO)_5 \rightarrow Mn(\eta^3\text{-}C_7H_7)(CO)_4 \rightarrow Mn(\eta^5\text{-}C_7H_7)(CO)_3 \rightleftharpoons Mn(\eta^7\text{-}C_7H_7)(CO)_2$ [60]. The converse of such a sequence is the progressive addition of CO and the ejection of a polyene in a stepwise fashion, e.g. $Mo(\eta^4\text{-}C_7H_8)(CO)_4 \rightarrow Mo(\eta^2\text{-}C_7H_8)(CO)_5 \rightarrow Mo(CO)_6$ [26]. It seems, from the matrix isolation studies, that the possibilities of hapticity changes ($\eta^n \rightleftharpoons \eta^m$) in bound polyenes have received insufficient attention when reaction pathways have been proposed.

(xi) Polyene isomerisation

Polyenes bound to a transition metal are often capable of binding in a number of ways especially if all the olefinic double bonds are not bound to the metal, e.g. $Fe(tub\text{-}\eta^4\text{-}C_8H_8)(CO)_3$ and $Os(chair\text{-}\eta^4\text{-}C_8H_8)(CO)_3$ [116]. An investigation of the fluxional molecule, $Fe(\eta^4\text{-}C_8H_8)(CO)_3$, in matrices at ca. 12 K has resulted in the discovery of *tub* $\rightleftharpoons$ *chair* isomerisation on visible irradiation with the photoisomerisation facilitated by the partial decomplexation process, i.e. $Fe(\eta^4\text{-}C_8H_8)(CO)_3 \rightarrow Fe(\eta^2\text{-}C_8H_8)(CO)_3$ [80,84]. A number of other metal polyene complexes, e.g. Fe(polyene)$(CO)_3$ complexes and Fe(olefin)$(CO)_4$ complexes, undergo isomerisation (see Section C).

(xii) Changes in NO coordination

The NO ligand is most commonly encountered in metal nitrosyl complexes with a linear M–N–O structure in which it contributes 3 electrons to the electron counting associated with the 18-electron rule. Nitrosyls with bent linkages



(θ = ca. 120°) are also encountered and in these the NO ligand is reckoned to contribute 1 electron [122]. The dissociation and exchange of reactions of NO ligands in metal nitrosyl complexes is difficult and slow and the kinetics indicate associative mechanisms. Additionally the substitution and exchange reactions of CO ligands in mixed metal carbonyl nitrosyl complexes are dominated by the associative mechanism although some show a larger contribution from the dissociative mechanism (Scheme 1). Irradiation of $Ni(\eta^5\text{-}C_5H_5)NO$ in matrices at 20 K resulted in the observation of a new band at ca. 1390 cm^{-1} which showed the appropriate shift on replacing ^{14}NO by ^{15}NO [104,105]. The result was initially interpreted in terms of ejecting NO^- to give an ion pair $Ni(\eta^5\text{-}C_5H_5)^+NO^-$ [106] (cf. M^+NO^- ion pairs (M = Na, K, Rb, Cs) [124]). Later, when a variety of other nitrosyl complexes were observed to give low wavenumber NO bands after photolysis e.g. $Mn(CO)_4(NO)$ [62,63], $Mn(CO)(NO)_3$ [62,64], $Cr(NO)_4$ [17], it was recognised that photoelectron transfer could take place to give NO ligands designated as NO* (see Section C). Such an electron transfer would leave the metal centre electron deficient and provide not only the site but also the means whereby a nucleophile could attack in an associative mechanism. At present the extent of electron transfer is unknown; hence the designation NO* rather than NO(1 electron), as for the bent nitrosyls. The validity of this matrix isolation approach for metal nitrosyls is demonstrated by the fact that $Mn(CO)_4(NO)$ shows both CO loss and formation of $Mn(CO)_4(NO^*)$ in matrices [62,63] while the solution photochemical reaction involves contributions from dissociative and associative paths depending on the strength of the incoming nucleophile [127].

(xiii) Generation of nitrenes

The reaction of $Mo(\eta^5\text{-}C_5H_5)(CO)_2(NO)$ with $P(C_6H_5)_3$ generated, among other products, a complex which X-ray crystallography showed to contain an isocyanate ligand, viz. $Mo(\eta^5\text{-}C_5H_5)(CO)(P(C_6H_5)_2)_2NCO$. The NCO ligand was proposed to arise via a metal nitrene complex which captured a CO ligand [126]. UV–visible photolysis of $M(\eta^5\text{-}C_5H_5)(CO)_2(NO)$ complexes (M = Mo, W) in matrices at 12 K showed the appearance of bands appropriate for M–NCO formation. Careful experiments with the W analogue, whose rate of reaction could be most easily controlled, showed that the C in the NCO came from a bound $CO(^{13}C)$, the O in the NCO came from a bound $CO(^{18}O)$ and that there was ejection of the nitrosyl O because no ^{18}O transferred from $N^{18}O$ to NCO. The observation of $W(\eta^5\text{-}C_5H_5)(NCO)$, which could arise from $W(\eta^5\text{-}C_5H_5)(CO)(NO)$, provides one pathway for the formation of the final matrix product, $W(\eta^5\text{-}C_5H_5)(CO)(NCO)$. An alterna-

C. TABULATION OF REACTION PATHWAYS FOUND FOR VARIOUS METALS

Compound	Reaction pathways	Ref.
$V(CO)_6$	Loss of CO to give $V(CO)_5$	4
$V(\eta^5\text{-}C_5H_5)(CO)_4$	Loss of CO to form $V(\eta^5\text{-}C_5H_5)(CO)_3$, $V(\eta^5\text{-}C_5H_5)(CO)_2$ and $V(\eta^5\text{-}C_5H_5)(CO)$	5
	Substitution of CO by N_2 and C_2H_4 to form $V(\eta^5\text{-}C_5H_5)(CO)_3(N_2)$, $V(\eta^5\text{-}C_5H_5)(CO)_3(C_2H_4)$ and $V(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_4)_2$	
	Association of CO to form $V(\eta^3\text{-}C_5H_5)(CO)_5$	
$V(\eta^5\text{-}C_5H_5)(CO)(NO)_2$	Loss of CO to form $V(\eta^5\text{-}C_5H_5)(NO)_2$	5, 6
	Substitution of CO by N_2 to form $V(\eta^5\text{-}C_5H_5)(N_2)(NO)_2$	
	Change in NO co-ordination from NO(3e donor) → NO*(1e donor) in $V(\eta^5\text{-}C_5H_5)(CO)(NO)(NO^*)$	
	Association of CO to produce $V(\eta^5\text{-}C_5H_5)(CO)_2(NO)(NO^*)$ followed by loss of NO and formation of $V(\eta^3\text{-}C_5H_5)(CO)_5$	
$V(\eta^5\text{-}C_5H_5)_2(CO)$	Loss of CO to form metallocene complex $V(\eta^5\text{-}C_5H_5)_2$	7
$Cr(CO)_6$	Loss of CO to form $Cr(CO)_5$ and $Cr(CO)_4$	8–11
	Observation of $Cr(CO)_5 \cdots$ matrix species	11, 12
	Observation of oriented $Cr(CO)_5$ species	13
	Ejection of CO^+ and formation of anion $[Cr(CO)_5]^-$	14
	Substitution of CO by N_2 to form $Cr(CO)_5(N_2)$ and $Cr(CO)_4(N_2)_2$	15
	Substitution of CO by H_2 to yield $Cr(CO)_5H_2$	16
	Substitution of CO by NO to give $Cr(CO)_3(NO)_2$	17
$Cr(CO)_5(CS)$	Loss of CO to yield $Cr(CO)_4(CS)$ in two isomeric forms	18
$Cr(CO)_5(CSe)$	Loss of CO to yield $Cr(CO)_4(CSe)$ and equilibrium between two isomeric forms	19
	Loss of CSe to form $Cr(CO)_5$	
$Cr(CO)_5PCl_3$	Loss of PCl_3 to form $Cr(CO)_5$	20–22
$Cr(CO)_5(N(CH_3)_3)$	Loss of CO to form $Cr(CO)_4(N(CH_3)_3)$	23
	Loss of $N(CH_3)_3$ to form $Cr(CO)_5$	
	Observation of $Cr(CO)_5 \cdots$ matrix, $Cr(CO)_5 \cdots N(CH_3)_3$, and $Cr(CO)_4(N(CH_3)_3) \cdots$ matrix species	
$Cr(CO)_5$(pyridine)	Loss of CO to form $Cr(CO)_4$(pyridine)	22
	Loss of pyridine to form $Cr(CO)_5$	
$Cr(CO)_5$(pyrazine)	Loss of CO to form $Cr(CO)_4$(pyrazine)	22
	Loss of pyrazine to form $Cr(CO)_5$	
	Observation of *cis* → *trans* isomerisation of $Cr(CO)_4$(pyrazine)	

$Cr(CO)_5$(piperidine)	Loss of CO to form $Cr(CO)_4$(piperidine)	24
	Loss of piperidine to yield $Cr(CO)_5$	
$Cr(CO)_5(C_4H_4N_2)$	Loss of CO to form *cis*-$Cr(CO)_4(C_4H_4N_2)$	25
$Cr(CO)_4(NC_5H_4CH{=}N^iPr)$	Loss of *cis* CO to form *fac*-$Cr(CO)_3(NC_5H_4CH{=}N^iPr)$	25
$Cr(\eta^4\text{-}C_7H_8)(CO)_4$	Loss of equatorial CO to yield $Cr(\eta^4\text{-}C_7H_8)(CO)_3$	26
	Association of CO and stepwise ejection of C_7H_8 to give $Cr(\eta^2\text{-}C_7H_8)(CO)_5$ and $Cr(CO)_6$	
	Substitution of CO by N_2 to form *mer*-$Cr(\eta^4\text{-}C_7H_8)(CO_2)(N_2)$	
Cr(*trans,trans*-2,4-diene)$(CO)_4$	Loss of CO to give Cr(*trans,trans*-2,4-diene)$(CO)_3$	27
$Cr(\eta^5\text{-}C_5H_5)(CO)_3(H)$	Cr–H cleavage to produce $Cr(\eta^5\text{-}C_5H_5)(CO)_3^{\cdot}$ and $HCO^{\cdot}$ radicals in CO matrices and $Cr(\eta^5\text{-}C_5H_5)(CO)_3^{\cdot}$ and $H^{\cdot}$ radicals in Ar matrices	28, 29
$Cr(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)$	CO dissociation and α-H elimination to give $Cr(\eta^5\text{-}C_5H_5)(CO)_2(CH_2)(H)$	30
$Cr(\eta^5\text{-}C_5H_5)(CO)_2(NO)$	Loss of CO to form $Cr(\eta^5\text{-}C_5H_5)(CO)(NO)$	5, 6
	Substitution of CO by N_2 to give $Cr(\eta^5\text{-}C_5H_5)(CO)(N_2)(NO)$	
$Cr(\eta^6\text{-}C_6H_6)(CO)_3$	Loss of CO to yield $Cr(\eta^6\text{-}C_6H_6)(CO)_2$	31
	Substitution of CO by N_2 to form $Cr(\eta^6\text{-}C_6H_6)(CO)_2(N_2)$	
$Cr(\eta^6\text{-}C_7H_8)(CO)_3$	Loss of CO to give $Cr(\eta^6\text{-}C_7H_8)(CO)_2$	32
	Association of CO and ejection of C_7H_8 to yield $Cr(CO)_6$	
	Substitution of CO by N_2 to yield $Cr(\eta^6\text{-}C_7H_8)(CO)_2(N_2)$	
$Cr(NO)_4$	Change in NO co-ordination from NO(3e donor) → NO*(1e donor) in $Cr(NO)_3(NO^*)$	17
	Association of CO and ejection of NO to yield $Cr(CO)_3(NO)_2$	
$Mo(CO)_6$	Loss of CO to form $Mo(CO)_5$, $Mo(CO)_4$ and $Mo(CO)_3$	8–11,33
	Substitution of CO by N_2 to yield $Mo(CO)_5(N_2)$ and $Mo(CO)_4(N_2)_2$	34
$Mo(CO)_5$(piperidine)	Loss of CO to form $Mo(CO)_4$(piperidine)	24
	Loss of piperidine to form $Mo(CO)_5$	
$Mo(\eta^4\text{-}C_7H_8)(CO)_4$	Loss of axial CO to yield $Mo(\eta^4\text{-}C_7H_8)(CO)_3$	26
	Association of CO and stepwise ejection of C_7H_8 to give $Mo(\eta^2\text{-}C_7H_8)(CO)_5$ and $Mo(CO)_6$	
	Substitution of CO by N_2 giving $Mo(\eta^4\text{-}C_7H_8)(CO)_3(N_2)$. Stepwise loss of C_7H_8 to form $Mo(\eta^2\text{-}C_7H_8)(CO)_4(N_2)_2$ and ultimately $Mo(CO)_4(N_2)_2$	
$Mo(\eta^5\text{-}C_5H_5)(CO)_3(H)$	Loss of CO to form $Mo(\eta^5\text{-}C_5H_5)(CO)_2(H)$	28, 35
	Mo–H cleavage to yield $Mo(\eta^5\text{-}C_5H_5)(CO)_3^{\cdot}$ and $HCO^{\cdot}$ radicals in CO matrices	
	Substitution of CO by N_2 to form *cis*-$Mo(\eta^5\text{-}C_5H_5)(CO)_2(N_2)(H)$	29, 36
	Substitution of CO by C_2H_4 to yield *trans*-$Mo(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_4)(H)$ followed by rearrangement to give $Mo(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_5)$	

C. (continued)

Compound	Reaction pathways	Ref.
$Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)$	Loss of CO to form $Mo(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)$	37
	Substitution of CO by N_2 to afford *cis*-$Mo(\eta^5\text{-}C_5H_5)(CO)_2(N_2)(CH_3)$	
$Mo(\eta^5\text{-}C_5H_5)(CO)_3(C_2H_5)$	Loss of CO to give $Mo(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_5)$	38
	β-H elimination to form *trans*-$Mo(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_4)(H)$ followed by substitution of C_2H_4 by CO to give $Mo(\eta^5\text{-}C_5H_5)(CO)_3(H)$	
$Mo(\eta^5\text{-}C_5H_5)(CO)_3(CF_3)$	Loss of CO followed by α-F elimination to yield $Mo(\eta^5\text{-}C_5H_5)(CO_2)(CF_2)(F)$	39
$Mo(\eta^5\text{-}C_5H_5)(CO)_3(COCF_3)$	Loss of CO to give $Mo(\eta^5\text{-}C_5H_5)(CO)_2(COCF_3)$ followed by CF_3 migration to yield $Mo(\eta^5\text{-}C_5H_5)(CO)_3(CF_3)$	39
$Mo(\eta^5\text{-}C_5H_5)(CO)_3(Cl)$	Loss of CO to form $Mo(\eta^5\text{-}C_5H_5)(CO)_2(Cl)$	40
	Substitution of CO by N_2 and C_2H_4 to yield *cis*-$Mo(\eta^5\text{-}C_5H_5)(CO)_2(N_2)(Cl)$ and *cis*-$Mo(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_4)(Cl)$	
	Mo–Cl bond cleavage in a CO matrix to give $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]^+ Cl^-$	
$Mo(\eta^5\text{-}C_5H_5)(CO)_3(E(CH_3)_2)$ (E=As, Sb)	Loss of CO to give $Mo(\eta^5\text{-}C_5H_5)(CO)_2(E(CH_3)_2)$ and the double-bonded species $Mo(\eta^5\text{-}C_5H_5)(CO)_2(=E(CH_3)_2)$	41
$Mo(\eta^5\text{-}C_5H_5)(CO)_2(NO)$	Loss of CO to form $Mo(\eta^5\text{-}C_5H_5)(CO)(NO)$	42
	Substitution of CO by N_2 to give $Mo(\eta^5\text{-}C_5H_5)(CO)(N_2)(NO)$	
$Mo(\eta^5\text{-}C_5H_5)_2H_2$	Loss of H_2 to give the metallocene complex $Mo(\eta^5\text{-}C_5H_5)_2$	7
$Mo(\eta^5\text{-}C_5H_5)_2CO$	Loss of CO to give the metallocene complex $Mo(\eta^5\text{-}C_5H_5)_2$	43
$Mo(\eta^6\text{-}C_7H_8)(CO)_3$	Loss of CO to form $Mo(\eta^6\text{-}C_7H_8)(CO)_2$	44
	Substitution of CO by N_2 to yield $Mo(\eta^6\text{-}C_7H_8)(CO)_2(N_2)$, $Mo(\eta^6\text{-}C_7H_8)(CO)(N_2)_2$ and ultimately $Mo(N_2)_6$	
	Association of CO and stepwise ejection of C_7H_8 giving $Mo(\eta^4\text{-}C_7H_8)(CO)_4$ and $Mo(CO)_6$	
	Gas-phase ring-to-metal H transfer to afford $Mo(\eta^5\text{-}C_7H_7)(CO)_3(H)$	45
$Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_6$	Loss of CO to form $Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_5$ having two terminal, two semi-bridging and one 4-electron donor bridging CO ligands	46
$W(CO)_6$	Loss of CO to give $W(CO)_5$, $W(CO)_4$ and $W(CO)_3$	9–11, 47
	Substitution of CO by N_2 to yield $W(CO)_5(N_2)$ and $W(CO)_4(N_2)_2$	34

$W(CO)_5(CS)$	Loss of CO to form $W(CO)_4(CS)$ in two isomeric forms	18, 48
$W(CO)_5PCl_3$	Loss of PCl_3 to give $W(CO)_5$	20, 23
$W(CO)_5$(piperidine)	Loss of CO to give $W(CO)_4$(piperidine) Loss of piperidine to yield $W(CO)_5$	24
$W(CO)_5(L)$ (L = H_2S, pyridine, 3-bromopyridine, $N(CH_3)_3$ and pyrazine)	Loss of CO to give $W(CO)_4(L)$ Loss of L to form $W(CO)_5$	24, 49–51
$W(\eta^5\text{-}C_5H_5)(CO)_3(H)$	Same processes as for $Mo(\eta^5\text{-}C_5H_5)(CO)_3(H)$ with exception that $W(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_4)(H)$ exists as *cis* and *trans* isomers	28, 35 29, 36
$W(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)$	Same processes as $Mo(\eta^5\text{-}C_5H_5)(CO)_3(CH_3)$	52
$W(\eta^5\text{-}C_5R'_5)(CO)_3(R)$ (R′=H; R=C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9) (R′=CH_3; R=n-C_3H_7)	Loss of CO to give $W(\eta^5\text{-}C_5R'_5)(CO)_2(R)$ followed by β-H elimination to afford *cis*- and *trans*-$W(\eta^5\text{-}C_5H_5)(CO)_2$(olefin)(H)	38
$W(\eta^5\text{-}C_5H_5)(CO)_3(\eta^1\text{-}CH_2C_6H_5)$	Loss of CO to give $W(\eta^5\text{-}C_5H_5)(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ followed by $\eta^1 \rightarrow \eta^3$ conversion affording $W(\eta^5\text{-}C_5H_5)(CO)_2(\eta^3\text{-}CH_2C_6H_5)$	38
$W(\eta^5\text{-}C_5H_5)(CO)_3(C_6H_5)$	Loss of CO to give $W(\eta^5\text{-}C_5H_5)(CO)_2(C_6H_5)$ Substitution of CO by N_2 and C_2H_4 to give $W(\eta^5\text{-}C_5H_5)(CO)_2(N_2)(C_6H_5)$ and $W(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_4)(C_6H_5)$	38
$W(\eta^5\text{-}C_5H_5)(CO)_3(\eta^1\text{-}C_3H_5)$	Loss of CO to give $W(\eta^5\text{-}C_5H_5)(CO)_2(\eta^1\text{-}C_3H_5)$ followed by $\eta^1 \rightarrow \eta^3$ rearrangement to form $W(\eta^5\text{-}C_5H_5)(CO)_2(\eta^3\text{-}C_3H_5)$	52
$W(\eta^5\text{-}C_5H_5)(CO)_3Cl$	Loss of CO to yield $W(\eta^5\text{-}C_5H_5)(CO)_2Cl$ Substitution of CO by C_2H_4 but not N_2 to give *cis*-$W(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_4)Cl$ W–Cl bond cleavage in CO matrix to form $[W(\eta^5\text{-}C_5H_5)(CO)_3]^+ Cl^-$	40
$W(\eta^5\text{-}C_5H_5)(CO)_3(ER_2)$ (E = As, Sb; R=CH_3, i-C_3H_7, t-C_4H_9)	Loss of CO to yield $W(\eta^5\text{-}C_5H_5)(CO)_2(ER_2)$ and the double-bonded species $W(\eta^5\text{-}C_5H_5)(CO)_2(=ER_2)$	41
$W(\eta^5\text{-}C_5H_5)(CO)_2(NO)$	Loss of CO to form $W(\eta^5\text{-}C_5H_5)(CO)(NO)$ followed by intraligand rearrangement to yield $W(\eta^5\text{-}C_5H_5)(CO)(NCO)$ and $W(\eta^5\text{-}C_5H_5)(NCO)$ via a nitrene intermediate Substitution of CO by N_2 to give $W(\eta^5\text{-}C_5H_5)(CO)(N_2)(NO)$	42
$W(\eta^5\text{-}C_5H_5)_2(CO)$	Loss of CO to yield the metallocene complex $W(\eta^5\text{-}C_5H_5)_2$	43

C. (continued)

Compound	Reaction pathways	Ref.
$W(\eta^5\text{-}C_5H_5)_2H_2$	Loss of H_2 to form the metallocene complex $W(\eta^5\text{-}C_5H_5)_2$	7
$W(\eta^4\text{-}C_7H_8)(CO)_4$	Loss of axial CO to give $W(\eta^4\text{-}C_7H_8)(CO)_3$	26
	Substitution of CO by N_2 to yield *fac*-$W(\eta^4\text{-}C_7H_8)(CO)_3(N_2)$	
	Association of CO and stepwise loss of C_7H_8 forming $W(\eta^2\text{-}C_7H_8)(CO)_5$ and $W(CO)_6$	
$Mn(CO)_5H$	Loss of CO to give $Mn(CO)_4H$ in two isomeric forms	53, 54
	Mn–H bond cleavage in CO matrices yielding $Mn(CO)_5^{\cdot}$ and $HCO^{\cdot}$ radicals	55
$Mn(CO)_5CH_3$	Loss of CO to form $Mn(CO)_4CH_3$	56–58
$Mn(CO)_5CF_3$	Loss of CO followed by α-F elimination to give $Mn(CO)_4(CF_2)(F)$	39
$Mn(CO)_5(COR)$ ($R=CH_3$, CF_3)	Loss of terminal CO to form $Mn(CO)_4(COR)$ followed by R migration to give $Mn(CO)_5R$ complexes	39, 56, 58, 59
$Mn(CO)_5(COC_7H_7)$	Stepwise loss of CO forming $Mn(CO)_4(COC_7H_7)$, $Mn(CO)_5(\eta^1\text{-}C_7H_7)$, $Mn(\eta^3\text{-}C_7H_7)(CO)_4$, $Mn(\eta^5\text{-}C_7H_7)(CO)_3$ and $Mn(\eta^7\text{-}C_7H_7)(CO)_2$	60
$Mn(CO)_5(\eta^1\text{-}C_3H_5)$	Loss of CO followed by $\eta^1 \rightarrow \eta^3$ rearrangement affording $Mn(CO)_4(\eta^3\text{-}C_3H_5)$	61
$Mn(CO)_4(\eta^3\text{-}C_3H_5)$	Loss of CO to yield $Mn(CO)_3(\eta^3\text{-}C_3H_5)$	61
	Substitution of CO by N_2 to produce $Mn(CO)_3(N_2)(\eta^3\text{-}C_3H_5)$	
$Mn(CO)_5(X)$ ($X = Cl, Br, I$)	Loss of CO to form $Mn(CO)_4(X)$	62
$Mn(\eta^5\text{-}C_5H_5)(CO)_3$	Loss of CO to yield $Mn(\eta^5\text{-}C_5H_5)(CO)_2$	31
	Substitution of CO by N_2 to give $Mn(\eta^5\text{-}C_5H_5)(CO)_2(N_2)$	
$Mn(CO)_4(NO)$	Loss of CO to give $Mn(CO)_3(NO)$	63, 64
	Substitution of CO by N_2 to yield $Mn(CO)_3(N_2)(NO)$	
	Change in NO coordination from NO(3e donor) → NO*(1e donor) in $Mn(CO)_4(NO^*)$	
$Mn(CO)(NO)_3$	Loss of CO to give $Mn(NO)_3$	63, 65
	Substitution of CO by N_2 to afford $Mn(N_2)(NO)_3$	
	Photoelectron transfer changing NO(3e donor) → NO*(1e donor) in $Mn(CO)(NO)_2(NO^*)$	
$Mn_2(CO)_{10}$	Loss of CO in Ar and CH_4 matrices to give presumably $Mn_2(CO)_9$	66
	Mn–Mn bond cleavage in CO matrices to yield $Mn(CO)_5^{\cdot}$ radicals	

$Mn_2(CO)_6(DAB)_2$ (DAB=1,4-diaza-1,3-butadiene)	Loss of CO to give presumably $Mn_2(CO)_5(DAB)_2$	67
$Re(CO)_5H$	Re–H bond cleavage in CO matrices to afford $Re(CO)_5^{\cdot}$ and $HCO_5^{\cdot}$ radicals	55
$Re(CO)_5(X)$ (X = Cl, Br)	Loss of CO to give $Re(CO)_4(X)$, cf. $Mn(CO)_4(X)$	68
$Re(\eta^5\text{-}C_5H_5)(CO)_3$	Loss of CO to form $Re(\eta^5\text{-}C_5H_5)(CO)_2$	69, 70
	Substitution of CO by N_2 to yield $Re(\eta^5\text{-}C_5H_5)(CO)_2(N_2)$	
$Re(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_5H_6)(CO)_2$	Loss of CO to give $Re(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_5H_6)(CO)$	69, 70
	Loss of C_5H_6 to yield $Re(\eta^5\text{-}C_5H_5)(CO)_2$	
	Ring-to-metal H migration to form $Re(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)(CO)_2(H)$	
$Re(\eta^5\text{-}C_5H_5)_2H$	Re–H bond cleavage to give $Re(\eta^5\text{-}C_5H_5)_2^{\cdot}$ and $HCO^{\cdot}$ radicals in CO matrices followed by association of CO, $\eta^5 \rightarrow \eta^1$ conversion, metal-to-ring H transfer and C_5H_6 ring ejection affording $Re(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)(CO)$, $Re(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_5H_5)(CO)_2$, $Re(\eta^5\text{-}C_5H_5)(CO)_3$ and additionally $Re(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)(N_2)(H)$ in N_2 matrices	69, 70
$Fe(CO)_5$	Loss of CO to form $Fe(CO)_4$ and $Fe(CO)_3$	71, 72
	Observation of $Fe(CO)_4 \cdots$ matrix species	72
	Ejection of CO^+ and formation of charged species $[Fe(CO)_4]^-$	73
	Substitution of CO by N_2 and C_2H_4 to give $Fe(CO)_4(N_2)$ and $Fe(CO)_4(C_2H_4)$	72, 74
	Substitution of CO by H_2 to yield $Fe(CO)_4(H)_2$	75
	Substitution of CO by NO affording $Fe(CO)_2(NO)_2$	76
$Fe(CO)_4(L)$ (L = $N(CH_3)_3$, pyridine)	Loss of CO to give $Fe(CO)_3(L)$ which can exist in two isomeric forms $C_{3v} \rightleftharpoons C_s$	77
$Fe(C_2H_4)(CO)_4$	Loss of CO to form $Fe(C_2H_4)(CO)_3$	78
$Fe(\eta^2\text{-}C_4H_6)(CO)_4$	Loss of CO to form $Fe(\eta^2\text{-}C_4H_6)(CO)_3$ which rearranges to $Fe(\eta^4\text{-}C_4H_6)(CO)_3$	78
$Fe(\eta^2\text{-}C_6H_8)(CO)_4$	Loss of CO to give $Fe(\eta^4\text{-}C_6H_8)(CO)_3$	78
$Fe(\eta^4\text{-}C_4H_4)(CO)_3$	Loss of CO to form $Fe(\eta^4\text{-}C_4H_4)(CO)_2$	31, 79, 80
	Substitution of CO by N_2 to afford $Fe(\eta^4\text{-}C_4H_4)(CO)_2(N_2)$ and $Fe(\eta^4\text{-}C_4H_4)(CO)(N_2)_2$	
	Partial dechelation of ring yielding $Fe(\eta^2\text{-}C_4H_4)(CO)_3$ followed by $\pi \rightleftharpoons \sigma$ rearrangement to form metallocyclic species $Fe(\eta^2, \sigma, \sigma\text{-}C_4H_4)(CO)_3$ and $Fe(\sigma,\sigma\text{-}C_4H_4)(CO)_3$	
	Insertion of CO into ring to give $Fe(\eta^4\text{-}C_4H_4CO)(CO)_3$	80, 81

C. (continued)

Compound	Reaction pathways	Ref.
$Fe(\eta^4\text{-}C_4H_6)(CO)_3$	Loss of CO to form $Fe(\eta^4\text{-}C_4H_6)(CO)_2$ Substitution of CO by N_2 to yield $Fe(\eta^4\text{-}C_4H_6)(CO)_2(N_2)$ Partial dechelation to give $Fe(\eta^2\text{-}C_4H_6)(CO)_3$ followed by s-*cis* ⇌ s-*trans* isomerisation Association of CO and stepwise ejection of C_4H_6 affording $Fe(\eta^2\text{-}C_4H_6)(CO)_4$ and $Fe(CO)_5$	78, 80
$Fe(\eta^4\text{-}C_4H_4(CH_3)_2)(CO)_3$	Loss of CO to give $Fe(\eta^4\text{-}C_4H_4(CH_3)_2)(CO)_2$ Substitution of CO by N_2 to afford $Fe(\eta^4\text{-}C_4H_4(CH_3)_2)(CO)_2(N_2)$	78
$Fe(\eta^4\text{-}spiro[4,4]$nona-1,3-diene$)(CO)_3$	Loss of CO to form $Fe(\eta^4\text{-}spiro[4,4]$nona-1,3-diene$)(CO)_2$ followed by C–C single bond cleavage to yield $Fe(\eta^5$-butylcyclopentadien-1,4′-diyl$)(CO)_2$	82
$Fe(\eta^4\text{-}C_5H_4(CH_3)_2)(CO)_3$	Loss of CO to give $Fe(\eta^4\text{-}C_5H_4(CH_3)_2)(CO)_2$ Ring-to-metal alkyl migration affording $Fe(\eta^5\text{-}C_5H_4(CH_3))(CO)_2(CH)_3$	82
$Fe(1\text{-}\sigma\text{-}4\text{-}6\text{-}\eta^3$-organo$)(CO)_3$ (organo = methyl acrylate, 2,3-dimethyl-butadiene)	Loss of CO to form $Fe(1\text{-}\sigma\text{-}4\text{-}6\text{-}\eta^3$-organo$)(CO)_2$	83
$Fe(\eta^4\text{-}C_4H_4CO)(CO)_3$	Loss of CO to give $Fe(\eta^4\text{-}C_4H_4CO)(CO)_2$ Substitution of CO by N_2 to form $Fe(\eta^4\text{-}C_4H_4CO)(CO)_2(N_2)$	80
$Fe(\eta^4\text{-}C_7H_{10})(CO)_3$	Loss of CO to yield $Fe(\eta^4\text{-}C_7H_{10})(CO)_2$ followed by ring-to-metal H migration to give $Fe(\eta^5\text{-}C_7H_9)(CO)_2(H)$ Ring flipping isomerisation Substitution of CO by N_2 to form $Fe(\eta^4\text{-}C_7H_{10})(CO)_2(N_2)$ Substitution of C_7H_{10} by CO in CO matrices giving $Fe(CO)_5$	80
$Fe(\eta^4\text{-}C_8H_8)(CO)_3$	Loss of CO to form $Fe(\eta^4\text{-}C_8H_8)(CO)_2$ Substitution of CO by N_2 to give $Fe(\eta^4\text{-}C_8H_8)(CO)_2(N_2)$ Partial dechelation to yield $Fe(\eta^2\text{-}C_8H_8)(CO)_3$ followed by *tub* ⇌ *chair* isomerisation Association of CO followed by C_8H_8 ejection forming $Fe(\eta^2\text{-}C_8H_8)(CO)_4$ and $Fe(CO)_5$	80, 84
$Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)$	Association of CO and $\eta^5 \rightleftharpoons \eta^3$ conversion forming $Fe(\eta^3\text{-}C_5H_5)(CO)_3(CH_3)$	85

$Fe(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_5)$	Loss of CO and β-H elimination affording $Fe(\eta^5\text{-}C_5H_5)(CO)(C_2H_4)(H)$ and $Fe(\eta^5\text{-}C_5H_5)(CO)_2(H)$	86
	Association of CO and $\eta^5 \rightleftharpoons \eta^3$ conversion to give $Fe(\eta^3\text{-}C_5H_5)(CO)_3(C_2H_5)$	
$Fe(\eta^5\text{-}C_5H_5)(CO)_2(COCH_3)$	Loss of terminal CO to give $Fe(\eta^5\text{-}C_5H_5)(CO)(COCH_3)$ followed by CH_3 migration to metal to form $Fe(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)$	85
$Fe(\eta^5\text{-}C_5H_5)(CO)_2Cl$	Loss of CO to yield $Fe(\eta^5\text{-}C_5H_5)(CO)(Cl)$	40
$Fe(CO)_2(NO)_2$	Loss of CO to form $Fe(CO)(NO)_2$	87
	Substitution of CO by N_2 to yield $Fe(CO)(N_2)(NO)_2$ and $Fe(N_2)_2(NO)_2$	
	Association of CO and ejection of NO yielding $Fe(CO)_5$	76
$Fe_2(CO)_9$	Loss of terminal CO to form $Fe_2(CO)_8$	88
$Fe(\eta^5\text{-}C_5H_5)_2(CO)_4$	Loss of CO to form D_{3h} CO-bridged dimer $Fe_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CO)_3$	89
$Ru(\eta^5\text{-}C_5H_5)(CO)_2(CH_3)$	Loss of CO to form $Ru(\eta^5\text{-}C_5H_5)(CO)(CH_3)$	86
	Substitution of CO by N_2 and C_2H_4 to give $Ru(\eta^5\text{-}C_5H_5)(CO)(N_2)(CH_3)$ and $Ru(\eta^5\text{-}C_5H_5)(CO)(C_2H_4)(CH_3)$	
	Association of CO and $\eta^5 \rightleftharpoons \eta^3$ conversion to give $Ru(\eta^3\text{-}C_5H_5)(CO)_3(CH_3)$ and ultimately $Ru(CO)_5$	
$Ru(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_5)$	Loss of CO and β-H elimination yielding $Ru(\eta^5\text{-}C_5H_5)(CO)(C_2H_4)(H)$ and $Ru(\eta^5\text{-}C_5H_5)(CO)_2(H)$	86
	Substitution of CO by N_2 to give $Ru(\eta^5\text{-}C_5H_5)(CO)(N_2)(H)$ and $Ru(\eta^5\text{-}C_5H_5)(N_2)_2(H)$	
	Association of CO, $\eta^5 \rightleftharpoons \eta^3$ conversion and C_5H_5 ejection giving $Ru(\eta^3\text{-}C_5H_5)(CO)_3(C_2H_5)$ and ultimately $Ru(CO)_5$	
$Ru(\eta^5\text{-}C_5H_5)(CO)_2Cl$	Loss of CO to give $Ru(\eta^5\text{-}C_5H_5)(CO)Cl$	40
$Os(CO)_5$	Loss of CO to form $Os(CO)_4$	72
	Substitution of CO by NO to yield $Os(CO)_2(NO)_2$	76
$Co(CO)_4H$	Loss of CO to form $Co(CO)_3H$	90, 91
	Co–H bond cleavage to give $Co(CO)_4^{\cdot}$ and $H^{\cdot}$ radicals together with CO loss in rare gas matrices; $Co(CO)_4^{\cdot}$ and $HCO^{\cdot}$ radicals in CO matrices	91, 92
	Substitution of CO by H_2 to yield $Co(CO)_3H_3$	93
$Co(\eta^3\text{-}C_3H_5)(CO)_3$	Loss of CO to form $Co(\eta^3\text{-}C_3H_5)(CO)_2$	94
	Substitution of CO by N_2 to give $Co(\eta^3\text{-}C_3H_5)(CO)_2(N_2)$	
	Association of CO and stepwise replacement of C_3H_5 giving $Co(\eta^1\text{-}C_3H_5)(CO)_4$ and $Co(CO)_4$	

C. (continued)

Compound	Reaction pathways	Ref.
$Co(CO)_3(NO)$	Loss of CO to give $Co(CO)_2(NO)$	95
	Substitution of CO by N_2 to give $Co(CO)_2(N_2)(NO)$ and $Co(CO)(N_2)_2(NO)$	
	Substitution of NO by CO to afford $Co(CO)_4$	76
$Co(\eta^5\text{-}C_5H_5)(CO)_2$	Substitution of CO by N_2 to give $Co(\eta^5\text{-}C_5H_5)(CO)(N_2)$	96
	Association of CO and $\eta^5 \rightleftharpoons \eta^3$ conversion affording $Co(\eta^3\text{-}C_5H_5)(CO)_3$	
	Loss of CO and dimerisation in more concentrated matrices yielding $Co_2(\eta^5\text{-}C_5H_5)_2(CO)_2$	
$Co_2(CO)_8$	Loss of CO to give presumably $Co_2(CO)_7$	97
	Co–Co cleavage in CO matrices giving $Co(CO)_4$	65
$Rh(CO)_2(L\text{–}L')$	Loss of CO to form Rh(CO)(L–L')	98, 99
(L = acetylacetonato, trifluoroacetylacetonato and hexafluoroacetylacetonato)	Chelate ring opening to form unidentate L–L' bonding in $Rh(CO)_2(L\text{–}L')$	
$Ir(CO)_2(L\text{–}L')$ (L = as Rh)	As for $Rh(CO)_2(L\text{–}L')$	99
$Ni(CO)_4$	Loss of CO to form $Ni(CO)_3$	100
	Loss of CO^+ to form charged species $[Ni(CO)_3]^-$ and CO^+	14
	Substitution of CO by N_2 to give $Ni(CO)_3(N_2)$	101
	Substitution of CO by C_2H_4 and C_2H_2 to yield $Ni(CO)_3(C_2H_4)$ and $Ni(CO)_3(C_2H_2)$	102
	Substitution of CO by SO_2 and O_2 to yield presumably $Ni(CO)_3(SO_2)$ and $Ni(CO)_3(O_2)$	103
$Ni(\eta^5\text{-}C_5H_5)(NO)$	Change in NO coordination from NO(3e donor) → NO*(1e donor) yielding $Ni(\eta^5\text{-}C_5H_5)(NO^*)$	104, 105
	Substitution of NO and C_5H_5 by CO to yield $Ni(\eta^5\text{-}C_5H_5)(CO)$, $Ni(\eta^5\text{-}C_5H_5)(CO)_2$ and $Ni(CO)_4$	
$Cu(CO)_3$	Dimerisation of fragments at 40–45 K affords $Cu_2(CO)_6$	9, 106
$Ag(CO)_3$	Dimerisation of fragments at 20–35 K produces $Ag_2(CO)_6$	108
MeX (X = Cl, Br, I)	Insertion of M atoms (M = Mg, Ca, Sr) into C–X bond produces unsolvated Grignard species $M(CH_3)X$	109

tive pathway via a nitrene species, e.g. $W(\eta^5\text{-}C_5H_5)(CO)(\equiv N)$, cannot be ruled out but could not be substantiated by the IR study [42].

(xiv) Insertion of metal atoms into C–halogen bonds

One of the earliest organometallic compounds to be made, and certainly the ones which were found to have the most widespread applications in synthetic procedures, were those discovered by Grignard and known as Grignard reagents, i.e. RMgX (R = alkyl; X = Cl, Br, I) [127]. The nature of these reagents and the active species in their chemistry has long been a subject of speculation. A recent co-condensation of M atoms (M = Mg, Ca, Sr, Zn) with CH_3Br and CH_3I at 20 K afforded evidence that the M atoms inserted into the C–X bond to form $M(CH_3)X$ (M = Mg, Ca, Sr; X = Br, I) but that Zn atoms were unreactive. The $M(CH_3)X$ species were described as "unsolvated" and different from the solvated species in solutions [109]. The lack of reaction with Zn atoms is surprising because another very early transition metal complex is $Zn(CH_3)_2$, the Frankland reagent [128].

C. TABULATION OF REACTION PATHWAYS FOUND FOR VARIOUS METALS — SEE TABLE p. 12

D. PERSPECTIVES AND CONCLUSIONS

It is obvious from the wealth of general reaction pathways (Section B) and the large numbers of investigations carried out (Section C) that the gas matrix isolation technique affords a very powerful tool for characterising unstable species. The relation of these unstable species to intermediates proposed in solution reaction pathways (Schemes 1 and 2) is more problematical, but it is one which must be faced and overcome if the matrix isolation technique is to achieve widespread credibility with chemists and if the results are to be accepted, trusted and used to understand reaction mechanisms and to formulate catalytic cycles (Scheme 3).

Several aspects of matrix isolation experiments may call into question the results on unstable species vis-à-vis postulated reaction intermediates: the ultra-low temperatures; the relevance of gas matrices, especially the rare gas matrices, to normal solvents; the types of compounds which can be used as precursors; the geometries of the fragments; and the types of reactions which can be observed because of the "cage effect".

(i) Ultra-low temperatures

Coordinatively unsaturated 16-electron species are highly reactive, e.g. a rise in temperature of the matrix by only a small amount is sufficient to

cause a reaction to take place. This is best illustrated from an experiment with Ni atoms co-condensed with 0.2% CO in Ar when the species formed at 4 K is Ni(CO). On warming this matrix CO ligands add successively to give $Ni(CO)_2$ (ca. 15 K), $Ni(CO)_3$ (ca. 18 K) and $Ni(CO)_4$ (ca. 30 K) [129]. Had that experiment been carried out at 20 K the only species to be isolated would have been $Ni(CO)_3$ and such an observation would not have led to a true understanding of the reaction pathway. It is crucial, therefore, to work at as low a temperature as is economically viable and convenient. The limitations of organic glasses at 77 K are thus obvious although such matrices do serve their purposes.

(ii) Relevance of gas matrices

As noted above, the unstable species are highly reactive even towards N_2 at 8–20 K and it is essential for meaningful results to work with very high purity materials. The gas matrices used are specified as 99.9999% pure whereas organic solvents are rarely better than 99.9% pure. The level of impurities in such solvents would put at risk experiments with unstable species, cf. the exhaustive and extensive purification stages needed for the solvents used in flash-photolysis studies on $Cr(CO)_6$ [110]. One of the more commonly used matrices is now CH_4 which relates directly to hydrocarbon solvents at ambient temperatures. Matrix studies are carried out in a variety of gas matrices and the products are characterised not only by IR spectroscopy but also by UV–visible spectroscopy to check whether the host matrix is perturbing the unstable species, e.g. $Cr(CO)_5 \cdots$ matrix [11,12]. Flash-photolysis studies on $Cr(CO)_6$ identified a very short-lived transient, "naked" $Cr(CO)_5$, and a solvated species $Cr(CO)_5$ (solvent) [110] whose UV–visible spectrum correlated exactly with $Cr(CO)_5 \cdots CH_4$ [11,12]. The matrix isolation data was vital in the identification of the flash-photolysis transient.

(iii) Limitations of precursors

The most serious limitation on the suitability of compounds as precursors in gas matrix isolation studies is that the compound must sublime unchanged at 10^{-5}–10^{-6} Torr; a good test for this is a parent molecular ion peak in a mass spectrum. This criterion rules out very many compounds but there are alternative experiments, e.g. organic glasses (77 K), polymer films (10–293 K, see below) and alkali halide discs (10–293 K, see below).

(iv) Geometries of fragments

If the structures of unstable species have been established as a result of isotopic enrichment (^{13}CO, $C^{18}O$, ^{15}NO, $^{15}N_2$) together with energy-factored

force field fitting of bands [2,112] then the stoichiometries and geometries of fragments can be accepted with a high degree of confidence. The geometries of coordinatively unsaturated species are generally assumed to be those the fragment would adopt if "free" in vacuum in the gas-phase; a point which can be checked by generating the unsaturated species in different host matrices (see Section D(ii)). Such geometries agree well with theoretical calculations [130,131] and have recently been used to systematise the structures and bonding of organometallic compounds via the very important and wide-ranging "isolobal" approach [132].

(v) Limitations of the "cage effect"

Gas matrix isolation studies were criticised because it was felt that the cage of host matrix gas molecules would restrict the movement of ejected species and thus distort the picture of the reaction obtained [133], e.g. only CO ligands were ejected in early studies. This criticism was very effectively answered by the reversible ejection of pyridine and 3-bromopyridine from $W(CO)_5$(pyridine) and $W(CO)_5$(3-bromopyridine) [48]. Since then many more bulky ligands have been ejected (see Section C). In solutions the products of reactions of mononuclear compounds are dinuclear, trinuclear and polynuclear complexes. There is little that can be done to model such reactions because matrix isolation experiments are designed to isolate monomeric compounds. However, successive annealing and photolysis can lead to dimeric products, e.g. $2Co(\eta^5\text{-}C_5H_5)(CO)_2 \rightarrow Co_2(\eta^5\text{-}C_5H_5)_2(CO)_2$ [96]. Reactions in solution are frequently ascribed to a radical pathway. An examination of Section C reveals a dearth of radicals and this does seem to be genuinely ascribable to the proximity of two very highly reactive species in the same cage; in contrast ejection of CO heterolytically generates a stable neutral molecule. The one exception is the ejection of $H^{\cdot}$ which is known to diffuse freely through matrices at 4–30 K and thereby escape from the matrix cage containing its radical partner, e.g. $Co(CO)_4^{\cdot}$ from $Co(CO)_4H$ [91,92]. A device which enhances the observation of radicals is to use a CO matrix, e.g. $Co(CO)_4H \rightarrow Co(CO)_4^{\cdot} + HCO^{\cdot}$ [91,92]. If the matrix cage was having an adverse effect on the chemistry of species as has been claimed, then some of the recently observed isomerisations of $Fe(\eta^4\text{-polyene})(CO)_3$ complexes would not have taken place. It can, therefore, be concluded that the "cage effect" is not a general limitation.

Three recent developments complement the gas matrix isolation experiments discussed above: studies in liquid rare gases, e.g. Kr and Xe; the use of polymer film matrices; and the use of alkali halide disc matrices.

(vi) Liquid rare gases

Metal carbonyl complexes dissolve in liquid rare gases, e.g. in Kr (ca. 114 K) and Xe (ca. 194 K) and will react with dopant molecules, e.g. N_2. In this way N_2 complexes have been synthesised and their thermal stabilities evaluated. For example, $Ni(CO)_3(N_2)$ undergoes a back reaction with CO to form $Ni(CO)_4$ at ca. 114 K whereas $Cr(CO)_5(N_2)$ is stable up to ca. 194 K [133,134]. While such studies do act as a bridge between 10–35 K gas matrices and solutions at 293 K, the temperatures of the liquid rare gases are insufficiently low to stabilise coordinatively unsaturated 16-electron species and so the approach may be of limited usefulness.

(vii) Polymer film matrices

A number of polymers are capable of being cast as film and blocks from normal solutions. If such a solution contains a small amount of substrate compound then the resulting film will have the substrate dispersed through it, cf. a dilute gas matrix sample. Films can be clamped in cryostats and are then useful over the whole range 10–293 K, e.g. polyvinylchloride (pvc) films cast from tetrahydrofuran (thf) or 1,2-dichloroethane (dce) [135]. Methylmethacrylate polymers were used for the initial experiments on $Cr(CO)_6$ at ambient temperatures in either air or vacuum when the yellow colour generated by photolysis was proposed to be due to $Cr(CO)_5$ [136]. The photoreaction was reversed by heating to 100°C, i.e. the system was photochromic. These films were originally set aside in preference to organic glasses at 77 K [137], and then gas matrices at 4–20 K [2] on the basis of possible reactivity of the polymer films, the unknown concentrations of additives, the presence of unspecified amounts of reactive solvent molecules and dissolved O_2, and the broadness of IR bands [2]. These limitations have been recently re-evaluated and have been found not to be serious [135]. More positively, the fact that the film can be warmed from ca. 10 K, where species are formed, all the way to ambient temperatures allows the temperatures at which recombination and isomerisation reactions occur to be evaluated, e.g. $Mo(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_5)$ reacts slowly at 90 K with photoejected CO, or with thf in the film regenerating the parent complex $Mo(\eta^5\text{-}C_5H_5)(CO)_3(C_2H_5)$ or $Mo(\eta^5\text{-}C_5H_5)(CO)_2(thf)C_2H_5$ respectively [138]. Another advantage of solvent cast polymer films is that compounds which decompose on subliming (see Section D(iii) above) can now be studied by matrix isolation techniques, e.g. $Fe(\eta^5\text{-}C_5H_5)(CO)(P(C_6H_5)_3)(COCH_3)$ in pvc(dce) gives $Fe(\eta^5\text{-}C_5H_5)(CO)(P(C_6H_5)_3)(CH_3)$ at 12 K [139].

(viii) Alkali halide disc matrices

If a substrate is insoluble in the solvents used to cast polymer films an alternative is to disperse the substrate in alkali halide powder and press a disc. Such a disc can be mounted between two spectroscopic windows, e.g. CsI, and cooled to an appropriate low temperature. Such a technique has many of the advantages found above for polymer films. For example, the recombination of $Cr^{III}(CN)_5^{2-}$ with CN^- at 200 K gives $Cr^{III}(CN)_6^{3-}$ [140].

In conclusion, it seems that matrix isolation studies constitute a valid approach to providing structural evidence for unstable species and that these may be related to intermediates proposed in solution reactions at ambient temperatures (Schemes 1 and 2). Additionally such matrix isolation studies may be used to model the pathway proposed for catalytic cycles (Scheme 3). For example, with the recent observation of CO substitution by C_2H_4 followed by C_2H_4 insertion into a W–H bond in $W(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_4)(H)$ [35], all the steps except for two have been modelled for the hydroformylation cycle shown in Scheme 3. Future work at Southampton will aim to model the H_2 addition and RCH_2CH_2CHO ejection processes.

ACKNOWLEDGEMENTS

We thank the Universiti Teknologi Malaysia for a Studentship (to R.B.H.), the Lebanese University Faculty of Science for a Studentship (to K.A.M.) and the S.E.R.C. for support (to A.J.R.).

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