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Review

Organometallic chemistry in the solid state

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Abstract

Synthesis and reactivity studies in organometallic chemistry have traditionally been carried out in the solution (non-aqueous) phase while equivalent studies in the solid state has been little explored. This review attempts to summarise what is known about solid state organometallic chemistry with particular emphasis on the synthetic utility of this area of chemistry. The review focuses on the two types of reactions that constitute this area of chemistry. These are (i) reactions at a surface | molecule interface and (ii) reactions between molecules (identical, different) in amorphous or crystalline materials. As will be seen, numerous solid state reactions that give close to 100% yields and complete conversion between isomers are known. In some instances yields exceed those available by solution routes. Reactions can also give products different to those found in solution. Developments in the related fields of solid state synthetic organic and coordination chemistry (topotactic principle, recaction cavity, phase reconstruction) will be described and the connection between surface supported synthesis and heterogeneous catalysis will be mentioned.

Keywords: Solid state reactions; Isomerisation; Catalysis

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1. Introduction

Organometallic chemistry is regarded as a mature sub-discipline of chemistry [1] and the numerous books, journals and compendia on this topic attest to this state of affairs [2]. This area of chemistry has been largely driven in the past by (i) its interconnection to the field of homogeneous catalysis-many of the principles that underlie homogeneous catalysis were enunciated between 1950 and 1980 [1]; and (ii) the synthesis of new and exotic complexes. In more recent times the extensive use of organometallic complexes in organic synthetic methodology has become apparent and this has required efficient syntheses of numerous organometallic complexes.

Much, if not most, of the preparative work described in the area of organometallic chemistry entails reactions in a solvent (homogeneous solution chemistry), although chemistry in matrices (at low temperature) [3] or at interfaces (e.g. heterogeneous catalysis) [4] has been developed. Reactions in the gas phase have also been described but here the emphasis has not been on synthetic chemistry [5]. The development of synthetic organometallic chemistry in the solid state, as well as reactions on surfaces, by contrast, has been little mentioned in the literature.

Interestingly, solid state organic and coordination chemistry have both been studied for close to 100 years and these two areas of chemistry can be regarded as relatively mature [6–18]. Numerous principles that provide for an understanding of the chemistry associ-

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Abbreviations: AFM, atomic force microscopy; COD, cyclooctadiene; COE, cyclooctene; DRIFTS, diffuse reflectance infra red Fourier transform spectroscopy; DSC, differential scanning calorimetry; ESR, electron spin resonance; GC, gas chromotography; ΔH_f, heat of fusion; ΔH_i, heat of isomerisation; Mes, 1,3,5-trimethylphenyl; STM, scanning tunnel microscopy; Tetraphos, $P(CH_2CH_2PPh_2)_3$; Triphos, $CMe(CH_2CH_2PPh_2)_3$; TriphosN, $N(CH_2CH_2PPh_2)_3$; TGA, thermogravimetric analysis; THF, tetrahydrofuran; TPD, temperature programmed desorption; XRD, X-ray diffraction; XPS, X-ray photoelectron spectroscopy; Xyl, 2,6-dimethylphenyl.

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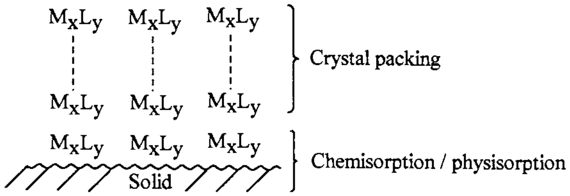

Fig. 1. Two types of solid state reactions are covered in this review. Type (i) reactions are discussed in Sections 2 and 3, and type (ii) reactions are discussed in Section 4.

ated with these fields have been developed. However, the transfer of this information to the field of organometallic chemistry has, to date, hardly occurred. Surprisingly, one of the first notable reports of a solid state reaction in the organometallic chemistry literature is a report by Vaska [19] in 1966 on the reaction between $IrX(CO)(PPh_3)_2$ (e.g. X = Cl, Br, etc.) and HY (e.g. Y = Cl, Br, etc.) to give the oxidative addition reaction products $IrX(H)(Y)(CO)(PPh_3)_2$. However, very little follow up on this, or related reactions, has occurred since this time. The area of surface mediated chemistry has been studied more extensively (see below).

This review attempts to summarise the literature available in the area of solid state transition metal organometallic chemistry. To place the work in perspective, reference will of necessity be made to the appropriate literature that is available in the area of solid state organic and coordination chemistry where applicable.

This review will thus cover:

1. Reactions in the solid state: rearrangement of metal–ligand attachments, ligand rearrangements, reactions with solids or gases as co-reagents, etc.
2. Reactions at the solid surface: cluster rearrangement reactions, reaction with reagents, reaction between particles, etc.

The two types of reactions are shown if Fig. 1. The difference relates to the environment of the molecule. In type (i) reactions, the surrounding M_xL_y molecules are the same as the molecule under consideration while in type (ii) reactions the key interaction relates to a surface–molecule interaction.

The emphasis is thus on the influence of the solid state environment on the chemistry of a fully/partially encapsulated or attached molecule. The review places emphasis on the exploitation of the solid state in the synthesis of new complexes in this environment. The types of reactions that will be considered in this review are shown in Fig. 2.

The above situations provide for both advantages and disadvantages when comparison is made with homogeneous reactions performed in the liquid (or gas) phase. These include:

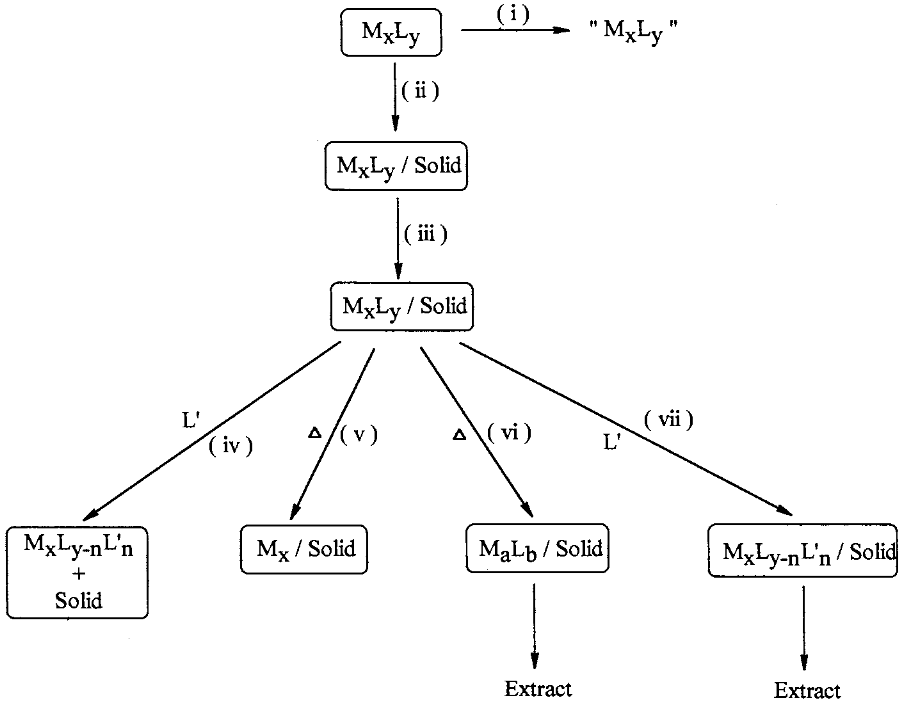

Fig. 2. Scope of the review (M_xL_y = organometallic complex with M = transition metal and L = ligand): (i) solid state reactions involving either metal or ligand loss/addition/rearrangement (Sections 2 and 3), (ii) physisorption of M_xL_y on a solid support e.g. TiO_2, Al_2O_3, SiO_2, etc. (iii) chemisorption, (iv) reaction (catalytic or non-catalytic) in which the solid support acts as a ligand, (v) decomposition reaction in which M_xL_y undergoes loss of L and the formation of metal particles (not covered in this review), (vi) M_xL_y degredation or expansion and (vii) reaction of M_xL_y with L′ (L′ in gas, liquid and solid phase) to generate a new complex.

1. No solvents are needed in the reaction and hence no waste disposal issues associated with the solvent need be considered [9].
2. The constrained environment in a 'reaction cavity' can lead to novel chemical reactions, with product selectivity possibly different from that expected in the liquid phase [8].
3. Enantioselective reactions are feasible in a chiral 'cavity' [11].
4. Crystal engineering using organometallic complexes is possible in the solid state [12].
5. Complexes formed on surfaces must be removable from the surface after reaction [18]. This is not always possible.
6. Reactions on a support surface are limited by available reaction sites on the surface. Loadings of greater than 5% are thus difficult to achieve. Further, typical surface areas are of the order of 200 m^2 g^{-1}, or less, and thus only small amounts of materials (100s of milligrams) are generally produced in a typical reaction at present [18].
7. The range of organometallic complexes that will react in the solid state is limited by the physical properties associated with a particular complex. Thus, not all complexes will undergo a chemical reaction prior to decomposition, and many complexes will melt prior to undergoing any reaction.

Some comments on the coverage are necessary:

1. The boundary between organometallic and coordination compounds can be tenuous and a 'liberal' definition of an organometallic complex will be used in this review. Thus, $IrCl(CO)(PPh_3)_2$ and $Mo(CO)_6$ etc. will be considered for discussion in this review, even though they do not contain classical M–C bonds.
2. The review will be restricted to a discussion of transition metals.
3. No emphasis will be placed on the use of solid state organometallic complexes [20].
4. Neither polymer supported organometallic complexes [21] nor the study of organometallic complexes in matrices at low temperatures [3] will be discussed.
5. Many metal carbonyl complexes, typically under pressure, have been made from the reaction of a metal ([22]a–c) or metal salt ([22]e,f) with CO. These types of reactions will not be discussed in detail here unless the emphasis is on the reaction as a synthetic route.

2. Solid state reactions within a solid

2.1. Molecular rearrangments

Prior to discussing the use of the solid state environment in generating isolable new organometallic complexes, it is necessary to discuss the issues relating to molecular motion in solids. This arises since molecular motion is a pre-requisite for molecular reactivity [23]. An excellent overview of this issue, as it applies to organometallic chemistry, has recently been given by Braga ([24]a).

All atoms in a molecule, independent of the phase, are in a constant state of motion around a molecular centre of mass. In the solid state this vibrational motion can be recognised by the thermal ellipsoids generated in an X-ray crystal structure determination. The molecules can also undergo both inter and intramolecular rotational motion but generally intermolecular motion is not observed in the solid state (excluding liquid crystals). However, intramolecular rotation in the solid state is a common phenomenon. A good example is the rotational behaviour of the methyl group. Here rotation around an $R-CH_3$ bond (R an organic moiety), requires energies of less than 20 kJ mol^{-1} [25]. Clearly R could also be a metal atom!

Molecules of the type $(C_nH_n)ML_x$ in which the cyclic carbon ring, C_nH_n, is π-bonded to the metal, M, can also undergo motion in the solid state. Here ring rotation has been found to be rapid [24]. Rearrangement of CO ligands in $M(CO)_x$ complexes is also known in the solid state [26].

A variant of the above occurs when a molecule can re-orientate itself with respect to surrounding molecules. This gives rise to a polymorph, i.e. 'a solid crystalline phase of a given compound resulting from the possibility of at least two different arrangements of the molecules of that compound in the solid state' [27]. Clearly polymorphism entails molecule–molecule interactions in the solid state. Polymorphism can be induced by means of pressure, irradiation or heat. There is still discussion as to the precise difference between two (or more) polymorphs and compounds [14]. Irrespective of the precise definition it is to be noted that the phenomena arises from intermolecular interactions. Once these forces have been removed (e.g. by dissolving the material in a solvent) only one compound is observed. Polymorphism does not in itself lead to the generation of new molecules. Polymorphism in organometallic chemistry has been extensively studied and classical examples include the studies on ferrocene and related congenors [24,28].

The issue of bond-stretch isomerism also relates to a solid state phenomenon. In this instance two crystallographically stable isomers differ only in the bond length of a single bond (in this case a metal–ligand bond). An overview of work in this area has been well summarised by Parkin ([29], [30]a,b) and it appears that no isomers of this type have as yet been isolated. A recent report

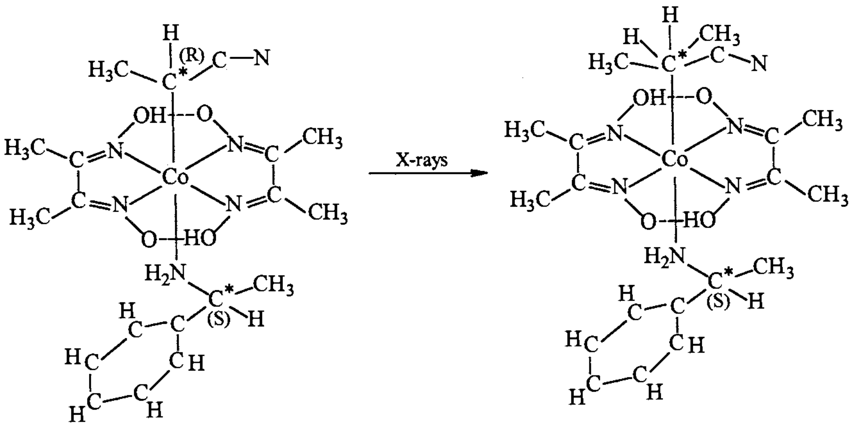

Fig. 3. Racemization of the cyanoethyl group in [(*R*)-1-cyanoethyl][(*S*)-α-methylbenzylamine]bis(dimethylglyoximato)cobalt(III).

on the characterisation of two isomers of $Co_3(dpa)_4^{2+}$ (dpa = dipyridyl anion) is suggestive of the identification of two bond-stretch isomers ([29], [30]c) but given the earlier history of this form of isomerism other factors may turn out to be responsible for the observation of variable bond lengths in the complex.

The discussion above suggests that the shape of the molecule will have a bearing on the possibility of either inter- or intra-molecule rearrangements in the solid state. Those molecules that are spherical will more readily undergo motion, while molecules with protuberances are more likely to undergo restricted motion. Crystal packing thus imposes constraints on molecular motion and hence introduces issues that are unique to the solid state and in principle can be exploited to synthesise new molecules. Hindered rotation of ligands attached to the metal can also be achieved by varying the electronic and steric parameters associated with the molecule.

2.2. Isomerisation reactions

Isomerisation reactions in the solid state are well known in the fields of coordination and organic chemistry. While reactions of coordination complexes in the solid state have been known since 1904 ([31]a), the simplest isomerisation reaction, racemisation, was studied first in the 1930s ([31]b). The early work in this area has been summarised by O'Brien ([16]a). *Cis–trans* isomerisation reactions around carbon–carbon double bonds [6,32], and the isomerisation reactions of ligands around the metal in coordination complexes have also been reported [10,33]. The reactions are typically induced by thermal means or by irradiation, either with X-rays or visible light [6,11].

Isomerisaton reactions involving organometallic complexes are listed below.

2.2.1. Isomerisation at the ligand

Very few examples are known in which a ligand attached to a metal atom undergoes isomerisation in the solid state. The best studied complexes are the cobaloximes. Ohashi and co-workers discovered that the cyanoethyl group in crystalline chiral [(*R*)-1-cyanoethyl][(*S*)-ethylbenzylamine] bis(dimethylglyoximato)cobalt(III) was racemized on exposure to X-rays in a diffractometer (Fig. 3). As the crystal did not degrade the reaction could be monitored by X-ray crystallography [34]. In later studies a wide range of cobaloximes were prepared in which the axial ligand was varied. Crystal structure analyses showed that the packing around the cyanoethyl group was important in determining the degree of reactivity [15]. This led to the concept of a measurable 'reaction cavity' [15,35] which will be discussed in more detail below (Section 6). Visible light has also been shown to induce the above racemization reaction [35]. ESR data were consistent with a radical process in which the Co–C bond was cleaved homolytically [35,36]. Irradiation (X-rays, visible light) of racemic mixtures of the cobaloximes have resulted in a racemic-to-chiral reaction, i.e. a reverse reaction to those described above [37].

A *β*-*α* photoisomerisation reaction in the presence of visible light, a reaction that only proceeds in the solid

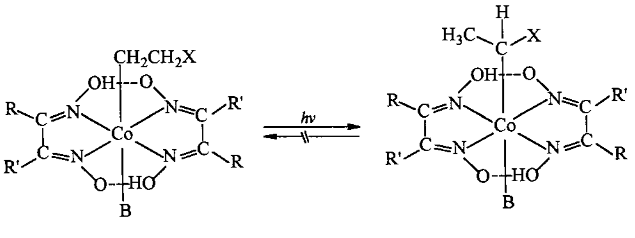

Fig. 4. *β*-*α* isomerisation of a cobaloxime complex (B = base; X = CN; R = R′ = Me, Ph).

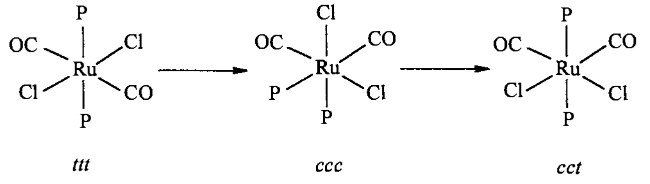

Fig. 5. Isomers of $RuCl_2(CO)_2(PR_3)_2$ [41].

state, has also been observed for the cobaloximes [38] (Fig. 4). Recently a single crystal-to-crystal study of this reaction has been reported [39]. The results indicate that asymmetric synthesis is possible in a crystal that has a chiral space group. The ratio of the enantiomers produced varied with the axial base and this was correlated with the size of the reaction cavity. The method presently does not permit quantitative assessment of the asymmetry of the reaction.

2.2.2. Isomerisation of ligands around the metal

Studies have revealed that solution state fluxional behaviour is a common phenomenon and that the energy barrier for the rearrangement of ligands around a metal can be quite low. Further, the more ligands attached to a metal the more facile the movement of ligands around the metal. These findings suggest that similar observations should be expected in the solid state, and to date isomerisation reactions have been detected for 4, 5, 6 and (pseudo) 7 coordinate complexes. As more studies are performed to investigate this process a better understanding of the mechanism of the reaction in the solid state will be forthcoming.

One of the earliest recorded thermodynamic measurements of an isomerisation reaction of an organometallic complex in the solid state was that obtained (indirecly; the reaction entailed fusion/isomerisation/resolidification) for the reaction shown below [40]:

cis-$PtCl(Me)(PMePh_2)_2 \rightarrow$ *trans*-$PtCl(Me)(PMePh_2)_2$

An investigation of the solid phase reactions of some Ru(II) complexes, $Ru(Cl)_2(PR_3)_{3-x}(CO)_x$,($PR_3$ = $PMePh_2$, PMe_2Ph, PMe_3, $P(CH_2C_6H_5)_3$; $x = 1$, 2) revealed ligand isomerisation reactions in the temperature range 140–180°C (Fig. 5) [41]. DSC and TGA studies showed that no mass loss occurred at the (exothermic) phase change, which corresponded with the isomerisation reaction. Attempts were made to correlate ΔH_i and ΔH_f with the properties of the phosphine ligands but no clear trends were noted.

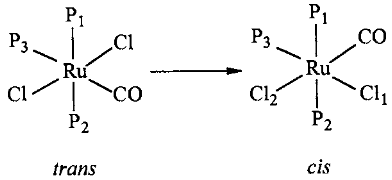

Fig. 6. Isomers of $RuCl_2(CO)(PMePh_2)_3$ [41].

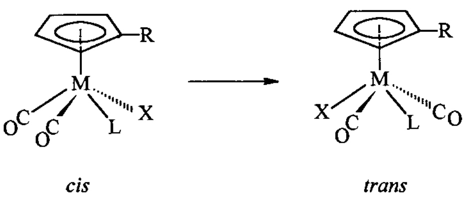

Fig. 7. Isomers of pseudo 7-coordinate complexes (M = Mo, W, Re; X = halide; R = H, Me, etc. L = PR_3, CO) [44–47].

X-ray analysis indicated that only a small volume difference (0.7%) existed between the isomers of $RuCl_2(CO)(PMePh_2)_3$ (Fig. 6) and that no fragmentation of the crystalline material was apparent after the isomerisation reaction. In most instances the *cis* to *trans* isomerisation entailed movement of small groups. The exception was *c,c,c*-$RuCl_2(CO)_2(PMePh_2)_2$ which isomerised to the *c,c,t* isomer. However 'considerable compression' of the sample was noted and it is possible that the reaction took place in the melt [41]. No comment was made on the solid state reaction mechanism, although isomerisation in solution was consistent with a ligand dissociative process.

More recently a study on related complexes, $RuCl_2(RNC)_{4-x}(PR'_3)_x$ (R = Xyl, Mes, etc. PR'_3 = PPh_3, $P(4\text{-}MeC_6H_5)_3$; $x = 0{,}2$), revealed similar *trans* to *cis* ligand isomerisation reactions [42]. It was noted that even complexes that contained both bulky phosphine and bulky isonitrile ligands underwent the isomerisation reaction, but no comment was made on the mechanism of the reaction. The authors commented on the measured values of ΔH_i—the isocyanide complexes isomerised more readily than the phosphine complexes. Without crystallographic information it is not possible to ascertain whether this arises from intermolecular interactions or from the electronic/steric effects associated with the molecule.

In a recent communication Caulton and co-workers [43] have noted that the reaction of $Ru(H)(Cl)(CO)L_2$ (L = bulky phosphine; H *trans* to a vacant coordination site) with acetylene gave the η^1-vinyl complex without observation of an intermediate Ru–acetylene complex. This, as suggested by the authors, almost certainly implies an isomerisation/rearrangement step in the solid state (Section 3.1.1).

A range of piano stool complexes of the type $CpML_4$ (M = Re, Mo, W) have been synthesised and shown to undergo *trans*/*cis* (*diag*/*lat*) isomerisation in the solid state (Fig. 7) [44–47]. Variation of the Cp ring, the metal and the ligands, L, have provided a wide range of complexes for study (Table 1).

This study has revealed the following:

1. No prediction, to date, can be made as to whether a complex will or will not undergo isomerisation based on an analysis of molecular properties.
2. The isomerisation reaction in the solution phase, the melt and the solid state are not related in an obvious way. Examples have been found in which the solid

Table 1
Reactions of organometallic complexes in the solid state

Reactant	Reagent	Product	Yield (%)	Ref.
Isomerisation reactions				
t-$RuCl_2(CO)(PMePh_2)_3$		*c,c,t*-$RuCl_2(CO)(PMePh_2)_3$	100[a]	[41]
t,t,t-$RuCl_2(CO)_2(PR_2)_2$ ($R = PMePh_2$, PBz_3)		*c,c,t*-$RuCl_2(CO)_2(PR_3)_2$	100[a]	[41]
c,c,t-$RuCl_2(CO)_2(PMePh_2)_2$		*c,c,t*-$RuCl_2(CO)_2(PMePh_2)_2$	100[a]	[41]
diag-(η^5-$C_5H_{5\text{-}n}R_n$)$Re(CO)LX_2$ ($n =$ 0, 1, 2; R = Me, Et, ^{i}Pr, ^{t}Bu, $SiMe_3$; X = Cl, Br, I; L = CO, R″NC, PR'_3,$P(OR')_3$) [b]		*lat*-(η^5-$C_5H_{5-n}R_n$)$Re(CO)LX_2$	70–96	[44,45]
diag-(η^5-$C_5H_{5-n}R_n$)$Mo(CO)_{3-n}L_nI$ ($n = 0, 1$; R = Me; L = PR'_3) [b]		*lat*-(η^5-$C_5H_{5-n}R_n$)$Mo(CO)_{3-n}L_nI$	70–82	[46]d,e, [90]
lat-(η^5-C_5H_4Me)$W(CO)_2L$ [$P(O^iPr)_3$]I		*diag*-(η^5-C_5H_4Me) $W(CO)_2L$ [$P(O^iPr)_3$]I	80	[46]d
diag-(η^5-$C_5H_{5-n}R_n$)$W(CO)_{3-n}L_nX$ ($n = 0, 1$; R = Me, ^{t}Bu, $SiMe_3$; L = R″NC, PR'_3, $P(OR')_3$)[b]		*lat*-(η^5-$C_5H_{5-n}R_n$)$W(CO)_{3-n}L_nX$	50–80	[46]d, [90]
Ligand linkage reactions				
$NiBr_2[P(CH_2CH_2CN)_3]_2$		See Fig. 9	100	[49]
(η^5-C_5H_5)$Co(S_2C_6H_4)$		See Fig. 10	100[c]	[50]
$PtCl_2(P_2C_{24}H_{26})$		See Fig. 11A	100	[51]
Thermal conversion reactions				
$[Pt(PR_3)_2(H)(CH_3CN)]_3[PW_{12}O_{40}]$ (R = Ph,Et)		$[Pt(PR_3)_2(H)]_3[PW_{12}O_{40}]$, $[Pt_2(PEt_3)_3(\mu\text{-}PEt_2)(\mu\text{-}H)]_3PW_{12}O_{40}$	?	[57]a,d,e
$[Rh(PPh_3)_2(CO)(CH_3CN)]_4SiW_{12}O_{40}$		$Rh(PPh_3)_2(CO)]_4SiW_{12}O_{40}$	?	[57]c
Reductive elimination reactions[d]				
Ligand rearrangement reactions				
$Pt(PPh_3)_2Cl(COR)$ [e]		$Pt(PPh_3)_2Cl(R)$	?	[64]
$Ir(PPh_3)_2(COR)Cl_2$ [f]		$Ir(PPh_3)_2(CO)(R)Cl_2$	?	[65]
$RhCl(P^iPr_3)_2[\eta^2\text{-}C(H)CC(H)CH_2]$		$RhCl(P^iPr_3)_2[CC(H)C(H)CH_2]$	100	[66]
$Rh(H)Cl(P^iPr_3)_2(CCSiR_3)$ (R = Me, Ph)		$RhCl(P^iPr_3)_2(CC(H)SiR_3)$	100	[66]
$RhCl(P^iPr_3)_2[CC(H)C(Me)_2NH_2]$		$RhCl(P^iPr_3)_2[CC(H)C(Me)CH_2]$	100	[66]
$[(\eta^5\text{-}C_5Me_5)Ru(dippe)H(CCR)]^+$ (R = $SiMe_3$, Ph)		$[(\eta^5\text{-}C_5Me_5)Ru(dippe)(CC(H)R)]^+$	?	[67]
$[Co(tetraphos)(H)(CCR)]^+$ (R = H, Ph, $SiMe_3$, CMe_3)		$[Co(tetraphos)(CC(H)R)]^+$	100(?)	[68]
Reactions of organometallic complexes with reagents in the solid state				
Reaction with gases				
Ligand replacement reactions				
$[Co(tetraphos)(N_2)]^+$	H_2, CO, C_2H_4	$[Co(tetraphos)L]^+$ (L = CO, CH_2CH_2, η^2-H_2 or $(H)_2$ [g])	100 (?)	[70,71]
	C_2H_2, HCHO, MeCHO	$[Co(tetraphos)CCH_2]^+$, $[Co(tetraphos)(CO)]^+$, $[Co(tetraphos)(COMe)]^+$	100 (?)	[71]
$[Ir(COD)L(PhCN)]$ (L = $AsPh_3$, PPh_3)	CO	$[Ir(COD)(CO)_2(L)]^+$,	77 (PPh_3), 86 ($AsPh_3$),	[72]
		$[Ir(COD)(CO)(L)_2]^+$,	100 (?)	
		$[Ir(CO)_3(PPh_3)_2]^+$	?	
$Ru(H)_2Cl_2(P^iPr_3)_2$	CO	$RuCl_2(P^iPr_3)_2(CO)_2$ and $Ru(H)Cl(P^iPr_3)_2(CO)_2$	?	[43]
$RuCl_2(\eta^2\text{-}{}^iPr_2PCH_2CH_2O\ Me)_2$	CO	$RuCl_2(\eta^2\text{-}{}^iPr_2PCH_2CH_2O\ Me)_2(\eta^2\text{-}{}^iPr_2PCH_2CH_2O\ Me)(CO)$	100	[66]
$[RhCl(P^iPr_3)_2]_n$	CO, C_2H_4, C_2H_2	$RhCl(P^iPr_3)_2L$	Quant	[66]
$[Ir(triphos)(H)_2(C_2H_4)]^+$	H_2	$[Ir(triphos)(H)_2]^+$ and dimer (Fig. 15)	Quant, 1:1 mix[h]	[73]
	H_2, C_2H_4	Dimer (Fig. 15)	70	
$[Ir(triphos)(C_6H_6)]^+$	C_8H_6S, H_2	See Fig. 17	100	[74]
$Os_3(CO)_{11}L$ (L = CH_3CN, C_2H_4)	CO, NH_3, H_2	$Os_3(CO)_{11}(L')$ (L′ = CO, NH_3), $Os_3(CO)_{10}(H_2)$ and $Os_3(CO)_{12}$	Quant[i]	[75]
Addition and oxidative-addition reactions				
$IrY(CO)(PPh_3)_2$ [j]	HX	$IrY(H)(X)(CO)(PPh_3)_2$	Quant(?)	[19,77]
$M(OH)(CO)(PPh_3)_2$ (M = Ir, Rh)	CO_2	$M(CO_2)(OH)(CO)(PPh_3)_2$	Quant	[78]
$Rh(PPh_3)_3Cl$	CO	$Rh(CO)(PPh_3)_2Cl$	Quant (?)	[79]

Table 1 (Continued)

Reactant	Reagent	Product	Yield (%)	Ref.
$Ru(PPh_3)_3Cl_2$	CO	$Ru(PPh_3)_2(CO)_2Cl_2$	Quant (?)	[79]
$IrCl(H)_2(PR_3)_2$ (R = ^{i}Pr, Cy)	H_2	$IrCl(\eta^2\text{-}H_2)(H)_2(PR_3)_2$	Near quant	[81]
$Ru(CO)_2(PBu_2Me)_2$	H_2, O_2, Cl_2, CO, C_2H_2	$Ru(CO)_2(PBu_2Me)_2(A/B)$ (AB = H_2, O_2, Cl_2, CO, C_2H_2) [k]	25–100	[43]
$[Pt(AuPPh_3)_8]^{2+}$	H_2	$[Pt(H)_2(AuPPh_3)_8]^{2+}$	?	[82]
Ni(triphosN)	CO	$Ni(triphosN)(CO)_2$ (Fig. 18)	?	[83]
$H_2Os_3(CO)_{10}$	CO, NH_3, H_2S	$H_2Os_3(CO)_{10}L$ (L = CO, NH_3, H_2S)	High yield	[84]
$[Ir(COD)(L)_2]^+$ (L = PPh_3, $AsPh_3$)		$[Ir(COD)(CO)(L)_2]^+$, $[Ir(CO)_3(PPh_3)_2]^+$	High yield	[72]
$[Ir(PPh_3)_2(C_8H_{12})]_3PW_{12}O_{40}$	H_2	$[Ir(PPh_3)_2H_2]_3PW_{12}O_{40}$	Quant	[57]b
$[Ir(PPh_3)_2H_2]_3PW_{12}O_{40}$	PF_3, CO	$[Ir(PPh_3)_2(PF_3)H_2]^+$, $[Ir(PPh_3)_2(CO)_2H_2]^+$	90, 49,	[57]b
	$SiMe_3H$	$[Ir(PPh3)_2(SiMe_3)H]^+$	50	
Elimination and reductive elimination				
$[Ir(PPh_3)_2H_2]_3PW_{12}O_{40}$	CO	$[Ir(PPh_3)_2(CO)_3]_3PW_{12}O_{40}$	49	[57]b
	CF_2CF_2	$[Ir(PPh_3)_2(CF_2CF_2)_2]_3^+$	10	[57]b
$[Ir(triphos)(H)_2(C_2H_4)]^+$	CO, C_2H_4	$[Ir(triphos)(L)_2]^+$ (L = CO, C_2H_4)	Quant, 8	[73]
Ligand reactions				
$[Ir(triphos)(H)_2(C_2H_4)]^+$	C_2H_2	Fig. 21	Variable	[86,87]
$[Ir(triphos)(C_2H_4)_2]^+$	C_2H_4	Fig. 21D,E	Quant (3:1)	[87]
	C_2H_2	Fig. 21B	Quant	
$[Ir(triphos)(H)_2(THF)]^+$	C_2H_2	Fig. 21B,C	8, 92	[87]
Fig. 21 D and E	C_2H_2	Fig. 21B	Quant	[87]
$[Ir(PPh_3)_2H_2]_3PW_{12}O_{40}$	CF_2CF_2	$[Ir(PPh_3)_2(H)(CF_2CF_2H)_2]^+$	30	[57]b
	C_3F_6	$[Ir(PPh_3)_2(H)(CF_2CFHCF_3)_2]^+$	33	
	C_3H_6	$[Ir(PPh_3)_2(H)(C_3H_7)]^+$	70	
	C_2H_4	$[Ir(PPh_3)_2(C_2H_5)_2]^+$ [l]	?	
	$c\text{-}C_5H_8$	$[(\eta^5\text{-}C_5H_5)Ir(PPh_3)_2(H)]^+$	70	
	C_2H_2	$[(\eta^5\text{-}C_6H_6)Ir(PPh_3)_2]^+$	60	
	1,3-diene	$[(\eta^3\text{-}C_6H_{11})Ir(PPh_3)_2(H)]^+$	95	
Reaction with solids				
$(\eta^5\text{-}C_5H_4Me)M(CO)_2LBr$ (M = Re, Mo, W; L = Br, CO)	NaI	$(\eta^5\text{-}C_5H_4Me)M(CO)_2LI$	Near quant.	[46]d, [90]
$(\eta^5\text{-}C_5H_4Me)W(CO)_3Br$	[m]	$(\eta^5\text{-}C_5H_4^tBu)W(CO)_3Br$ and $(\eta^5\text{-}C_5H_4Me)W(CO)_3I$	1:1 Mixture	[46]d, [90]
$[Ir(triphos)Cl(C_4H_4)]^+/TlPF_6$	C_2H_4,	Fig. 21B, [n]	20	[87]
	C_2H_2	Fig. 21B	Quant	

[a] By DSC.

[b] Wide range of R′, R″ used.

[c] Single crystal study.

[d] See text. Reactions not performed for synthetic reasons.

[e] RCO, range of benzoyl derivatives.

[f] R, range of phenyl derivatives.

[g] Counter-ion effect.

[h] See also reaction of mixture with CO and C_2H_4; see Fig. 16.

[i] 1:1 Mixture of reaction from H_2.

[j] X = Y = F, Cl, Br, I, SCN, HS.

[k] AB cleaved when AB = H_2, Cl_2.

[l] Other products also formed in the reaction.

[m] $(\eta^5\text{-}C_5H_4^tBu)W(CO)_3I$.

[n] Product similar to Fig. 21C also formed (80%).

state and solution phase isomerisation reaction occur in the same and in different directions. Clearly, the reaction is influenced by both intramolecular and intermolecular forces, but the relative weightings of the forces are still unknown.

3. The isomerisation reaction goes from the low melting point isomer to the high melting point isomer. If the melting point of the reactant isomer and the temperature of the isomerisation reaction are too close, then the isomerisation can take place in the melt.
4. The methodology provides for a facile procedure for the synthesis of pure isomers in high yield. In some instances these isomers are only available in high yield when synthesised in the solid state.

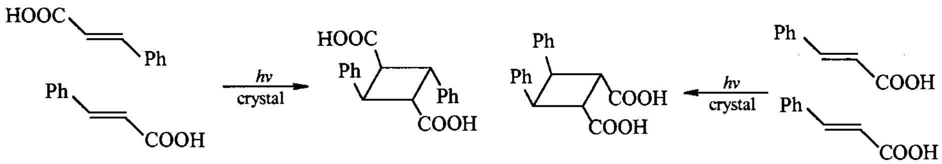

Fig. 8. Irradiation of cinnamic acid in the solid state; different packing arrangements give different dimer products [8,12].

5. Initial mechanistic studies were consistent with an intermolecular rearrangement process [47]. However, recent studies on some related Mo and W complexes are suggestive of facile movement of ligands (Cl, Br, etc.) between different molecules in the solid state ([46]d).

2.3. Ligand linkage reactions

Irradiation of olefins such as cinnamic acid, in the solid state, yields dimer products [48], and the type of product obtained is determined by the arrangement of the monomers in the solid phase [8,12] (Fig. 8). Very few examples of organometallic complex ligand linkage reactions, i.e. reactions in which a metal bonded ligand links to a neighbouring ligand or metal, to give dimers or oligomers, have been reported. In principle this could provide for the synthesis of unusual materials.

Foxman and co-workers synthesised the complexes $NiX_2[P(CH_2CH_2CN)_3]_2$ (X = Cl, Br) and these complexes underwent a solid state reaction (< 130°C) with neighbouring nickel centres to yield polymeric materials bridged by the phosphine ligands (Fig. 9).The reaction is only product specific in the solid state [49]. The polymerisation occurs in only one crystal plane and this leads to a polymer with no cross-linking.

An unusual monomer–dimer solid state reaction of an organometallic complex that involves Co–S bonds has been reported (Fig. 10) [50]. The reaction is made possible by the 'head-to-tail' arrangement of the monomers. The space group is unchanged in the reaction while the density increases (6%) in the dimer. This density change is proposed to be the driving force in the reaction.

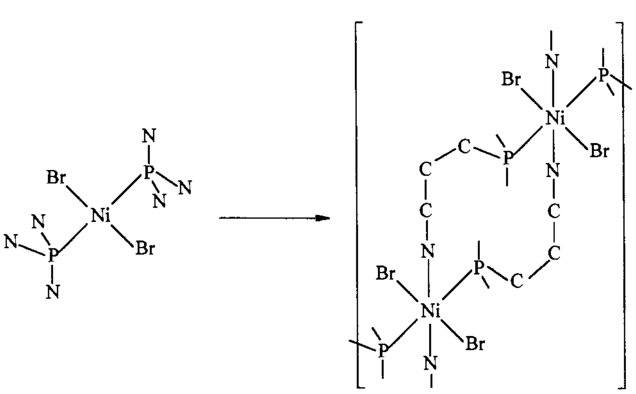

Fig. 9. Solid state reaction of $NiBr_2[P(CH_2CH_2CN)_3]_2$ [49].

Reaction of PtX_2L_2 (L = 1-phenyl-3,4-dimethylphosphole) at 140°C in the solid state has been observed. A mixture of products in which ligand dimerisation occurred was obtained, with product ratios different to those found in solution studies. The final product (Fig. 11 (A)) was obtained in 100% yield after extensive heating. A common mechanism involving bi-radicals was proposed (Fig. 11) [51].

2.4. Thermal decomposition/conversion reactions

In this type of reaction the reactant is generally heated in an inert atmosphere and the reaction monitored by DSC, TGA, colour change, etc. Post-reaction analysis by conventional procedures typically provides information on the course of the reaction. This must be the most common type of solid state reaction that has been described in the literature. However, in very few cases has the technique been exploited for synthetic (or mechanistic) purposes.

Rather the procedure has been used to generate thermochemical information [52], e.g. for the reactions shown below:

$PtX(CH_3)A_2L + heat \rightarrow PtX(CH_3)A_2 + L$

(X = Cl, Br; A = arsine; L = C_2F_4, C_4F_6) [53]

$IrX(CO)(PPh_3)_2L + heat \rightarrow IrX(CO)(PPh_3)_2 + L$

(X = F, Cl, Br; L = C_2F_4, C_4F_6, C_2H_3CN [54]

Some recent examples from the organometallic chemistry literature in which aspects of synthesis have been described are given below.

Thermal decomposition of $Ru(H)_2(\eta^2\text{-}H_2)_2[P(C_6H_{11})_3]_2$ was studied using TPD. In the reaction the bound hydrogen as well as hydrogen from the phosphine was lost in a two-step process to give phosphines with hydrogenated rings [55].

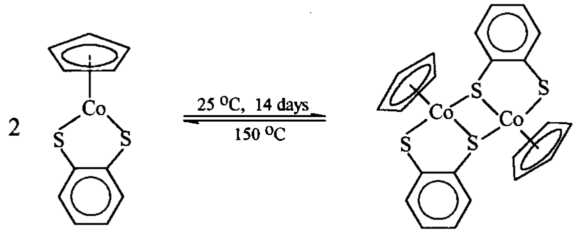

Fig. 10. Ligand dimerisation reaction of $(\eta^5\text{-}C_5H_5)Co(S_2C_6H_4)$ [50].

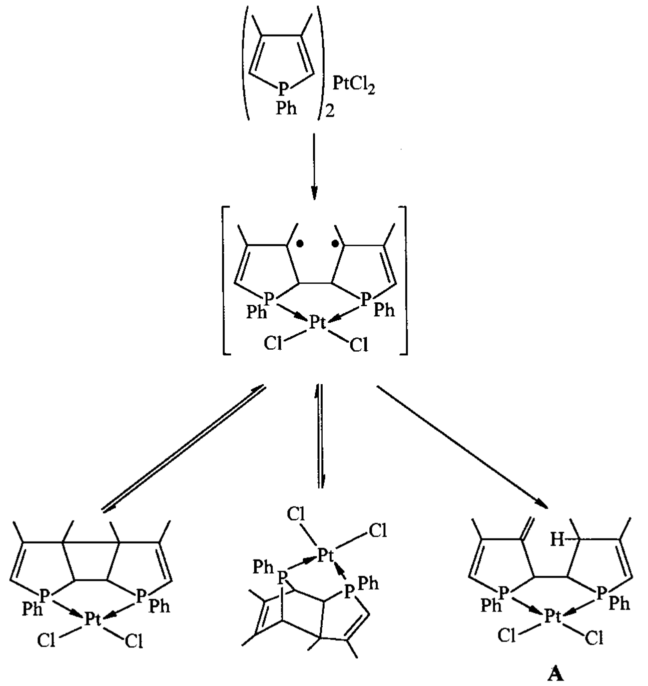

Fig. 11. Ligand dimerisation reaction of $PtCl_2L_2$ (L = 1-phenyl-3,4-dimethylphosphole) [51].

The reaction of a range of iridium complexes (e.g. $[Ir(COD)(CO)_2L]^+$, L = PPh_3) with H_2 resulted in reactant decomposition but more importantly the hydrogenation of the COD ligand gave COE. The products found were different from those obtained from the equivalent solution reaction [56].

An interesting approach to the modification of a solid by heating is indicated in the work of Siedle and co-workers [57]. The philosophy underlying this work has been the synthesis of metal atoms that are well separated from each other, the modification of the metal environment by thermal procedures, and then the determination of the reactivity patterns of the new solid state materials. Specifically, the study has entailed the reaction of Keggin ions, $XM_{12}O_{40}^{(8-n)-}$ (X = P,Si; M = Mo, W) with metal ions such as $[Pt(PR_3)_2(H)(CH_3CN)]^+$ ([57]a), $[Ir(PPh_3)_2(C_8H_{12})]^+$ ([57]b) or $[Rh(PPh_3)_3(CO)]^+$ ([57]c). Thermal reaction of the solid materials results in elimination of one (or more) of the ligands bound to the metal centre which gives a coordinatively unsaturated metal center. The Keggin ion ensures poor interaction with the metal and in principle keeps the reactive centers apart. Thus, after heating, $[Pt(PPh_3)_2(H)(CH_3CN)]_3PW_{12}O_{40}$ gives $[Pt(PPh_3)_2(H)]_3PW_{12}O_{40}$ in which the coordinatively unsaturated Pt atoms are well separated. However, the choice of ligands surrounding the metal can influence the metal mobility and recent work suggests that at high temperatures these metal centers can also become mobile. For example, thermal reaction (180°C) of, $[Pt(PEt_3)_2(H)(CH_3CN)]_3PW_{12}O_{40}$ gave the expected $[Pt(PEt_3)_2(H)]^+$ as well as $[Pt_2(PEt_3)_3(\mu\text{-}H)(\mu\text{-}PEt_2)(Et)]^+$ ([57]a). Numerous addition and oxidative–addition reactions have been performed with these 'encapsulated' metal ions and the reactions are discussed below (Section 3.1.2).

2.5. Reductive elimination reactions

Reductive elimination reactions in the solid state, mainly on Pd and Pt complexes, have been investigated to provide thermochemical and kinetic information, rather than provide a means to new complexes. From the early studies of Ruddick and Shaw [58] to the more recent studies of Goldberg and co-workers [59] the emphasis on heating complexes of the type $PtMe_3XL_2$ (X = halide ion, $L = \frac{1}{2}$ diphos, PMe_2Ph, $AsMe_2Ph$, etc. has been on (i) assessing the reaction mechanism and (ii) obtaining accurate Pt–C and Pt–X bond strengths. In the various studies by the above authors and others [40,60,61] a wide range of Pt (and Pd [62]) complexes have been investigated in which the ligands surrounding the central Pt atom have been varied. The approach has also been used to assess the strength of Pt–Ge, Pt–Si and Pt–Sn bonds in complexes of the type $PtMe_2(MMe_3)X(bipy)$ (M = Si, Ge, Sn; X = Cl, Br, I; and bipy = a bipyridine type ligand) [63].

2.6. Ligand rearrangement reactions

The migration reaction provides a facile pathway for converting a metal bonded ligand into another metal bonded ligand. This is exemplified by the solid state reaction [64]:

$$PtCl(PPh_3)_2(COR) + \text{heat} \rightarrow PtCl(PPh_3)_2R + CO$$

(R = substituted benzoyl ligand)

for which thermodynamic data were measured by DSC procedures. By judicious choice of metal and ligand it is possible to carry out the decarbonylation reaction without mass change; this provides for a facile measurement of heat changes in the reaction. Blake et al. [65] monitored the reaction

$$Ir(Cl)_2(L)_2COR + \text{heat} \rightarrow Ir(Cl)_2(L)_2(CO)R$$

($R = CF_3$, $p\text{-}XC_6H_4Me$; $L = PPh_3$)

by calorometric means and in this way established that the reaction rate was inversely related to the enthalpy change for the above reaction.

A facile solid state reaction appears to be the conversion of an η^1-alkyne into a vinylidene ligand, e.g. the room temperature conversion of $Rh(H)Cl(P^iPr_3)_2(CCSiR_3)$ into *trans*-$RhCl(P^iPr_3)_2(CC(H)SiR_3)$ (R = Me, C_6H_5) [66]. A similar reaction was reported for a Ru complex (Fig. 12) [67]. The first example of this type of solid state rearrangement reaction was, however, reported by Bianchini and co-workers [68]. A chance

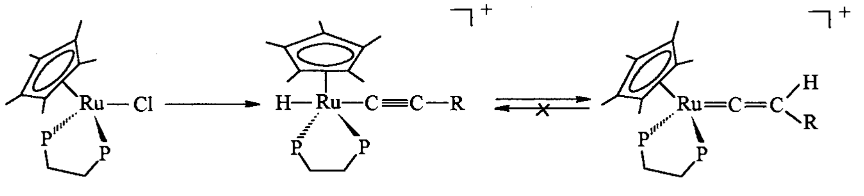

Fig. 12. Conversion of η^1-alkyne into a vinylidene ligand (R = COOMe, $SiMe_3$, Ph) [67].

discovery indicated that the complex $[Co(tetraphos)(H)(CCR)]^+$ (R = H, Ph, $SiMe_3$, CMe_3) converted to $[Co(tetraphos)(CC(H)R)]^+$ in the solid state. The ease of the irreversible reaction was found to be related to the R group viz. $SiMe_3 > Ph = H \gg CMe_3$ with a reaction sequence which is similar to that found in solution studies and said to be determined by electronic effects. This would suggest that inter-molecular interactions do not play a significant role in determining the ease of the reaction.

An NH_2 displacement in a vinylidene compex has also been reported viz. *trans*-$RhCl(P^iPr_3)_2(CC(H)C(Me)_2NH_2)$ converted into *trans*-$RhCl(P^iPr_3)_2(CC(H)C(Me)CH_2)$ in the solid state at room temperature (Fig. 13) [66]. In the same paper the conversion of an η^2-alkyne ligand into a vinylidene ligand was reported (Fig. 14)[66].

Ligand conversion via a de-insertion type reaction has led to a complex reaction mixture when $CpM(CO)_3(SO_3H)$ (M = Mo, W) was heated in the solid state. Products formed included $[CpMS_xO_y]_n$, $[CpM(O)(\mu\text{-}S)]_2$, etc. [69]. Undoubtedly there are many more potential synthetic reactions of this type that have been reported in the literature and that will be studied by a new range of techniques in the future.

3. Solid state reactions between a solid and a reagent

3.1. Reaction with gases

3.1.1. Ligand displacement reactions

One of the simplest reactions that can take place between a solid and a gas is a ligand displacement reaction. Many reactions of this type have been reported and typically the incoming (gas) ligand is a small molecule such as H_2, CO, etc.

For example, the reaction between $[Co(tetraphos)(N_2)]^+$ and H_2 led to a reversible replacement of the N_2 to give $[Co(tetraphos)(\eta^2\text{-}H_2)]^+$. In solution the equivalent reaction gives the classical di-hydride complex indicating that the reaction phase influences the product outcome. Even the counterion (PF_6^-, BPh_4^-) has an effect on the bonding mode of the hydrogen ligand in the solid state [70]. Bianchini and co-workers have also investigated the replacement reaction of N_2 in $[Co(tetraphos)(N_2)]^+$ with other ligands, L (L = C_2H_2, C_2H_4, CO, HCHO and MeCHO) [71]. Only for L = CO and C_2H_4 was the displacement reaction product, $[Co(tetraphos)L]^+$, observed. Reaction with HCHO gave $[Co(tetraphos)CO]^+$ and with MeCHO gave $[Co(tetraphos)(MeCHO)]^+$ (and H_2). Interestingly, the reaction with C_2H_2 gave the vinylidene product $[Co(tetraphos)CC(H)H)]^+$ (see Section 2.5) without detection of the intermediate oxidative addition η^1-alkyne product. Reactions do not have to give single products. Thus, the addition of CO to $Ru(H)_2Cl_2(P^iPr_3)_2$ results in the displacement of either H_2 (to give *c,c,t*-$RuCl_2(CO)_2(P^iPr_3)_2$) or HCl (to give $RuHCl(CO)_2(P^iPr_3)_2$) [43]. These reactions reveal the simplicity of the solid state route available in organometallic synthesis.

The differences between solid state and solution state displacement reactions are shown by the addition of CO to $RuCl_2(\eta^2\text{-}^iPr_2PCH_2CH_2OMe)_2$. Reaction in solution gives the dicarbonyl complex $RuCl_2(CO)_2(\eta^1\text{-}^iPr_2PCH_2CH_2OMe)_2$ while in the solid state the monocarbonyl complex, $RuCl_2(CO)(\eta^1\text{-}^iPr_2PCH_2CH_2OMe)(\eta^2\text{-}^iPr_2PCH_2CH_2OMe)$ is obtained [66]. In the same publication the reaction of $[RhCl(P^iPr_3)_2]_n$ with L (L = CO, C_2H_2, C_2H_4) was reported to give $RhCl(P^iPr_3)_2L$. As the solid state structure is expected to involve Rh–Cl bonds between different molecules, this reaction can be viewed as a displacement reaction of Cl by a L group.

The reaction of $[Ir(COD)(PhCN)L]^+$ (L = PPh_3, $AsPh_3$) with CO gives an addition/displacement reaction in which the final product is $[Ir(COD)(CO)_2L]^+$ [72]. A similar reaction with $[Ir(COD)(PhCN)_2]^+$ gave a complex reaction in which small amounts of $Ir_4(CO)_{12}$ were formed [56].

The reaction of $[Ir(triphos)(H)_2(C_2H_4)]^+$ with L (L = CO, C_2H_4) results in the formation of $[Ir(triphos)L_2]^+$ and some ethane formation [73]. Thermal heating of the starting material gives the dimer shown in Fig. 15. This suggests that a dimerisation occurred in the solid state, presumably after the loss of the ethene from the momomeric starting material. A series of displacement/addition reactions of the starting material with H_2/CO or C_2H_4/H_2 were carried out in the solid state and a summary of this work is shown in Fig. 16.

Hydrodesulfurization reactions, well documented in the solution state ([74]a), have also been reported in the solid state. Thus, the reaction of $[Ir(triphos)(C_6H_6)]^+$

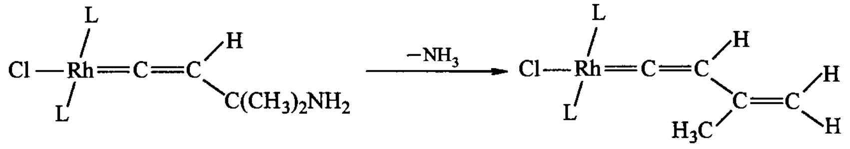

Fig. 13. Ligand rearrangement reaction in the solid state ($L = P^iPr_3$) [66].

with 2,3-dihydrobenzo[b]thiophene, results in a two step process to give [Ir(triphos)$(H)_2$(o-SC_6H_4Et)] via the isolable intermediate [Ir(triphos)(η^2-C,S-C_8H_6S)]$^+$ ([74]b). The structures of the thiophene complexes are shown in Fig. 17. The reaction involves the displacement of the C_6H_6 ligand with ring opening/hydrogenation of the thiophene.

Another facile displacement reaction involves the reaction of $Os_3(CO)_{11}L$ (L = MeCN, C_2H_4) with H_2, NH_3 and CO [75]. Significantly, the displacement of either MeCN, which occupies an axial position, or C_2H_4, which occupies an equatorial position on the osmium cluster, by NH_3, gave the same axially substituted product (80°C). Similarly, the reaction with ^{13}CO gave a product with CO scrambled throughout both axial and equatorial positions. Thus, fluxional behaviour has occurred at some stage in the reaction. The reaction with H_2 gave an equimolar mixture of readily separable $Os_3(CO)_{12}$ and $H_2Os_3(CO)_{10}$, both of which were shown to be formed from the intermediate, (μ-H)(H)$Os_3(CO)_{11}$.

The displacement of olefins from metal complexes in the solid state has been performed to provide enthalpies of reaction. Thus,

$$M(acac)(olefin)_2 + 2CO \rightarrow M(acac)(CO)_2 + 2olefin$$

$$(M = Ir, Rh;\ olefin = C_2H_4, C_3H_6, C_2H_3Cl, etc.)$$

indicated stronger Ir–C_2H_4 than Rh–C_2H_4 bonds [76]. The reactions were monitored by both TGA and DSC techniques.

3.1.2. Addition and oxidative-addition reactions

One of the earliest of the solid state reactions to be studied was the oxidative-addition reaction [19]:

$$IrY(CO)(PPh_3)_2 + HX \rightarrow Ir(H)(X)(Y)(CO)(PPh_3)_2$$

$$(X = F, Cl, Br, I, HS, Y = Cl, Br, I, SCN).$$

A solid state kinetic investigation was carried out (see below) on the complex with X = Y = Cl [77]. The product obtained was the *trans* di-chloro complex. Both *cis*- and *trans*-$IrCl_2(H)(CO)(PPh_3)_2$ complexes gave the original starting material on heating in the solid state, suggestive of a common transition state in the reaction. In a later study the reaction of $M(OH)(CO)(PPh_3)_2$ (R = Ir, Rh) with CO_2 was also investigated by Vaska [78]. The solid state reaction was shown to instantaneously give a product formally written as $M(CO_2)(OH)(CO)(PPh_3)_2$ [78].

More recently the reaction of both $RhCl(PPh_3)_3$ and $RuCl_2(PPh_3)_3$ with CO in the solid state has been reported [79]. This comprehensive study used a range of techniques (IR, TGA, XPS) to determine the reaction pathway which generated the known products, $RhCl(CO)(PPh_3)_2$ and $RuCl_2(CO)_2(PPh_3)_2$. The data are suggestive of the formation of 18 electron complexes in the solid state, but these complexes disproportionate in solution.

An early study on the reaction of η^2-H_2 complexes performed in the solid state was the reaction of $W(CO)_3(P^iPr_3)_2(\eta^2\text{-}H_2)$ with D_2 which resulted in H_2/D_2 exchange via an unknown H–H bond cleavage mechanism [80]. The H_2 ligand is also readily lost from the molecule on standing in the solid state, in keeping with the weakness of the W–H bond. The reaction of the unsaturated complexes $IrCl(H)_2(PR_3)_2$ (R = PCy_3, P^iPr_3) with H_2 gave the product $IrCl(H)_2(\eta^2\text{-}H_2)(PR_3)_2$ [81]. The solid state reaction favoured the six coordinate complex, while in solution the five coordinate complex predominated. The reversible reaction was also studied in the presence of H_2 and D_2 by IR spectroscopy in KBr.

Reaction of the 16 electron complexes $Ru(CO)_2(P^tBu_2Me)_2$ with AB (AB = H_2, O_2, Cl_2, CO or C_2H_2), readily gave the expected 18 electron complexes of the type $Ru(CO)_2(P^tBu_2Me)_2(AB)$ (AB cleaved for H_2 and Cl_2), identical to the complexes prepared in solution [43]. The unusual feature of the reaction was the relative reaction rates. A very slow reaction was

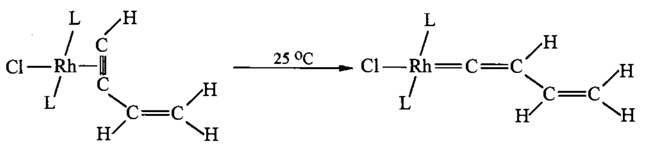

Fig. 14. Conversion of an η^2-alkyne ligand into a vinylidene ligand [66].

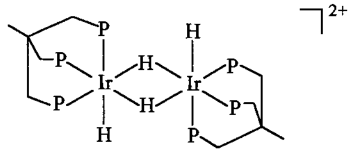

Fig. 15. Dimer formed in the solid state reaction from [Ir(triphos)$(C_2H_4)(H)_2$]$^+$ [73].

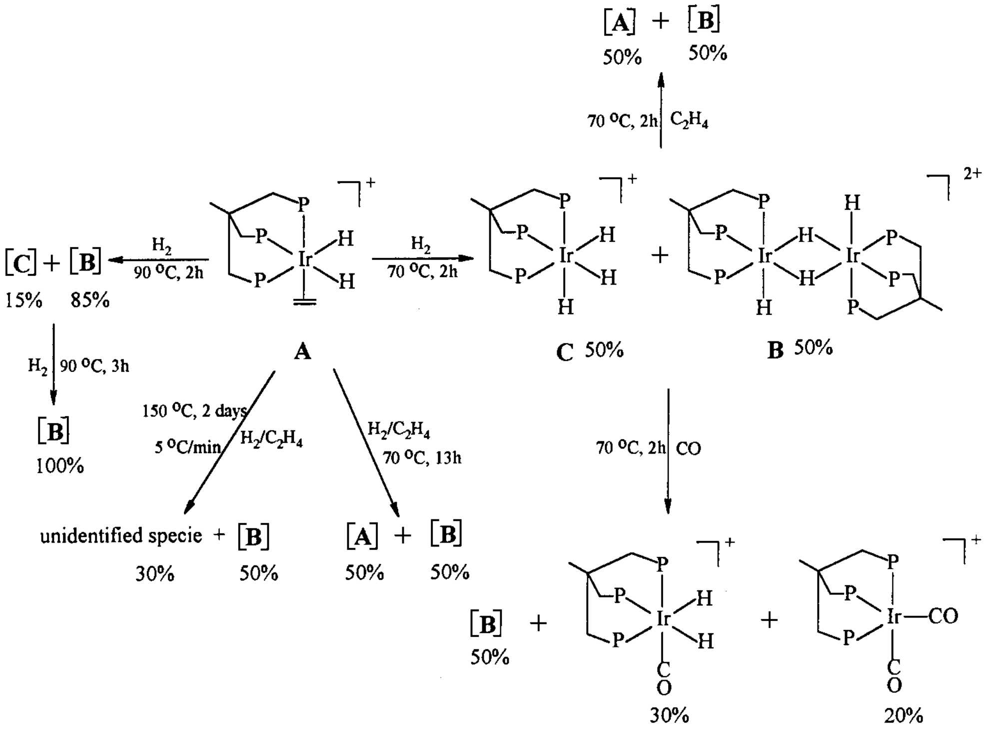

Fig. 16. Reaction of $[Ir(triphos)(C_2H_4)(H)_2]^+$ with H_2, H_2/C_2H_4, $H_2 + C_2H_4$ or $H_2 + CO$ [73].

observed when L = CO. The slow reaction was said to correlate with the size of the product formed in the reaction. If the reactant and product have dissimilar solid state structures then crystal 'cracking' occurs as the reaction proceeds and this permits facile access of further gas phase reagents into the solid structure for further reaction. In the case of AB = CO the structures of the reactant and product are said to be similar and hence the reaction is slow.

Solid state metal clusters have also been reported to react with H_2 and D_2 without cluster fragmentation [82], e.g. reaction of $[Pt(AuPPh_3)_8]^{2+}$ resulted in H–D scrambling, similar to that observed in the solution state.

The complex Ni(triphosN) reacted with CO in the solid state to give two complexes of Ni(tiphosN)$(CO)_2$ (Fig. 18) [83]. The five coordinate structure was based on DRIFTS and ^{31}P-NMR spectra and the complex reversibly lost CO under reduced pressure. In solution the complex converted to the four coordinate complex.

Addition reactions to an osmium cluster have been reported by Aime et al. [84]. Thus, the reaction of $H_2Os_3(CO)_{10}$ with L (L = CO, NH_3, H_2S) in the solid state has led to the production of $H_2Os_3(CO)_{10}L$ in high yield. Indeed the solid state route provides complexes that are not available by solution routes.

The reaction of $[Ir(COD)L_2]^+$ (L = PPh_3, $AsPh_3$) with CO results in formation of $[Ir(COD)(CO)L_2]^+$ in high yield under mild conditions [72]. In a slow reaction $[Ir(COD)(CO)(PPh_3)_2]^+$ reacts further with CO to give $[Ir(CO)_3(PPh_3)_2]^+$, and the slow reaction allows for the facile separation of the mono CO species from the reactant and final product.

The reactions of [Co(tetraphos)(N_2)] with HCHO, MeCHO and C_2H_2 have already been discussed above [71] (Section 3.1.1) and will not be discussed here.

As mentioned above (Section 2.5) Siedle and coworkers have studied the reaction of numerous gas molecules with coordinatively unsaturated metal ions in the solid state. For example, addition of CH_3CN to $[Rh(PPh_3)_2(CO)]_4SiW_{12}O_{40}$ gave $[Rh(PPh_3)_2(CO)(CH_3CN)]_4SiW_{12}O_{40}$ ([57]c). Both of the above Keggin ion complexes have been shown to activate CO and H_2 ([57]c,f).

The reaction of $[Ir(PPh_3)_2(C_8H_{12})]_3PW_{12}O_{40}$ with Q_2 ($Q_2 = H_2$ or D_2) gave $[Ir(PPh_3)_2Q_2]_3PW_{12}O_{40}$ ([57]d–f). A detailed analysis revealed that H/D exchange involving the cyclooctene was necessary to explain the D content of the final Ir complex. Finally a comprehensive study of the reaction of $[Ir(PPh_3)_2H_2]_3PW_{12}O_{40}$ with a wide range of ligands, L, has been reported ([57]b). In some instances high yields (> 70%) of the new complexes were formed. Some examples, shown in Figs. 19 and 20, are listed below.

1. Reaction with PF_3. This yielded the complex $[Ir(PPh_3)_2(PF_3)H_2]_3PW_{12}O_{40}$.
2. Reaction with CO. The major product obtained was $[Ir(PPh_3)_2(CO)_2H_2]_3PW_{12}O_{40}$, with $[Ir(PPh_3)_2(CO)_3]_3PW_{12}O_{40}$ also being observed (Fig. 19).

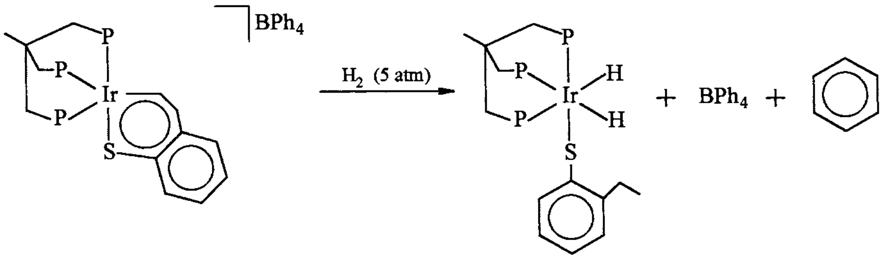

Fig. 17. Hydrodesulfurization reaction monitored in the solid state [74].

3. Reaction with hydrocarbons. Reaction with cyclopentene (liquid) gave > 90% $[(\eta^5\text{-}C_5H_5)Ir(PPh_3)_2H]^+$ in the presence of a hydrogen acceptor. Reaction with propene gave a propylallyl complex.

Solid state reactions involving oxidative addition of Ir across a RH bond, addition of IrH to a C=C bond, addition of a ligand to a metal and reductive elimination of hydrogen from Ir have been known for many years [57]. This work gives a clear indication of the possibilities that exist in this area of chemistry.

3.1.3. Reactions with CO

One of the first reported reactions between a metal and CO entailed the passage of CO over Ni ([22]a–c). This important reaction not only provided a means for the purification of Ni, but also provided an excellent high yield route to $Ni(CO)_4$. Other early developments in the synthesis of metal carbonyl chemistry entailed the reaction of metal salts with CO. Numerous of these reactions involved reduction of the metal in the absence of a solvent. For example reaction of $OsCl_3$ with CO (65 atm./155°C) gave $Os(CO)_4Cl_2$ in 60% sublimed yield [85]. Further examples can be found in the literature. These reactions will not be discussed further here as in many instances these reactions were performed under very high pressures and temperatures and little is known about the reactions.

3.1.4. Ligand reactions

Reaction of a ligand with an organometallic complex can result in the synthesis of new ligands. For example, reaction of acetylene with $[Ir(PPh_3)_2H_2]_3PW_{12}O_{40}$ gave a cyclotrimerization product while reaction with ethene gave a mix of products (Fig. 20) ([57]b). A diverse reactivity pattern has also been observed for the reaction of $[Ir(triphos)(H)_2(C_2H_4)]^+$ with C_2H_2 [86,87]. Thus, the reaction of the starting material with ethyne at 4 atm. and 70°C for 3 h gives the five products shown in Fig. 21. Various solid state reactions of these products with ethyne permitted the reaction mechanism to be determined. Of significance was the finding that ligand dimerisation (i.e. C–C bond forming reactions) can readily occur in the solid state.

3.2. Reaction with solids

Two types of reactions can be envisaged here. The first is the physical mixing of two different complexes in the solid state. This is a procedure commonly used in metallurgical preparations (e.g. ball milling) and entails the synthesis of fine particles to ensure as much surface–surface interaction as possible [9,88]. Microwave techniques can occasionally be used to advantage in this synthetic route [9,89]. The second reaction type would entail co-crystallistion procedures to not only ensure thorough mixing of reactants but also to set up the correct alignment of the reactants for further reaction [9].

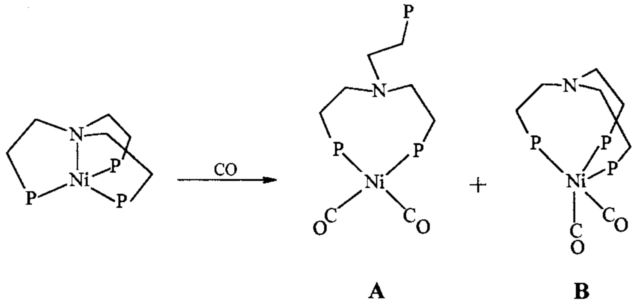

Fig. 18. Possible structures for the two $Ni(triphosN)(CO)_2$ complexes formed in the solid state [83].

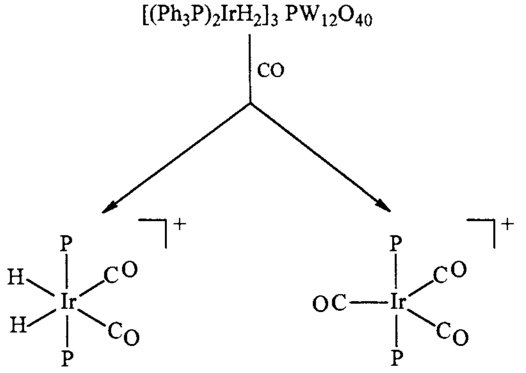

Fig. 19. Reaction of $[Ir(H)_2(PPh_3)_3]_2PW_{12}O_{40}$ with CO [57]b.

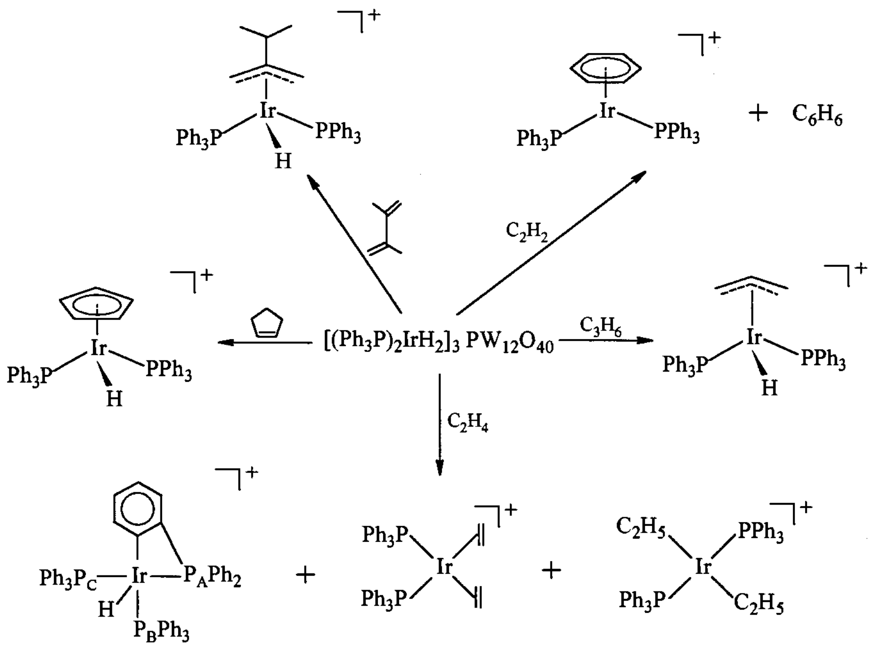

Fig. 20. Reaction of $[Ir(H)_2(PPh_3)_3]_2PW_{12}O_{40}$ with hydrocarbons [57]b.

Recently, the thermal (50°C) solid state reaction of co-crystallised $(\eta^5$-$C_5H_4Me)W(CO)_3I$ with$(\eta^5$-$C_5H_4^tBu)W(CO)_3Br$ has been studied (in the dark) and halogen exchange was noted in the products formed in the reaction ([47]b). Similar results were noted for related Re and Mo complexes, suggesting a very general and facile solid state reaction type. Halogen exchange in the solid state, e.g. by mixing of $(\eta^5$-$C_5H_4Me)Re(CO)_2Br_2$ with NaI resulted in the synthesis of $(\eta^5$-$C_5H_4Me)Re(CO)_2I_2$ [90]. The numerous literature reports of reactions that entailed halogen exchange during the recording of IR spectra of solids dispersed in KBr could also be of this reaction type.

Host-guest reactions in the solid state would also fit this category of reaction. The work of Toda and coworkers on the exploitation of this concept in organic chemistry is to be noted [17,91]. Enantioselective reactions in the constrained environment are also possible [11,15].

4. Reactions at surfaces

4.1. Reactions of metal complexes with surfaces

The deposition of reagents onto solids, either via addition of the reagent in the gas phase or by solution procedures, provides the basis for the synthesis of supported catalysts. Indeed, it was to gain a better understanding of the solid–reactant interaction that the area of surface mediated synthesis evolved. While still in its early stages of development this technique can now be used to synthesize complexes that are difficult to produce by traditional 'wet' procedures and in many instances in high yield (> 90%).

Below are described some of the developments that have taken place when the reagent deposited on a surface is an organometallic complex.

The reaction of an organometallic complex with a surface (e.g. metal, metal oxide, carbon, etc.) provides a facile means of adding a 'metal' to a surface. The initial reaction entails a van der Waals interaction with the surface (physisorption) and these materials can easily be re-extracted back into a solvent (Fig. 2(ii)) [18]. More significant is the chemisorption reaction which entails an ionic or covalent interaction with the surface, to yield a generic M_xL_y/surface complex (Fig. 2(iii)). In this reaction the surface acts like a ligand to the metal coordination sphere. Thermolysis of the M_xL_y/surface material provides a route to the formation of metal particles with some or no ligands L attached to M (Fig. 2(v)). Many studies have been reported on the synthesis of materials of this type for catalytic and other purposes (see [92–99] for some examples). However, in general the emphasis in these studies has not been on re-generating/re-extracting the organometallic complex into solution for further study. These types of reactions, as well as reactions that occur in zeolite cages [100–103], will hence not be discussed further here.

The emphasis in this section is rather on steps (vi) and (vii) shown in Fig. 2. In these reactions the M_xL_y/surface complex either undergoes reaction with an external ligand and/or undergoes metal core expansion (or degradation if M_xL_y is a metal cluster). The facile surface reactions imply easy movement of metal fragments on surfaces. New organometallic complexes at-

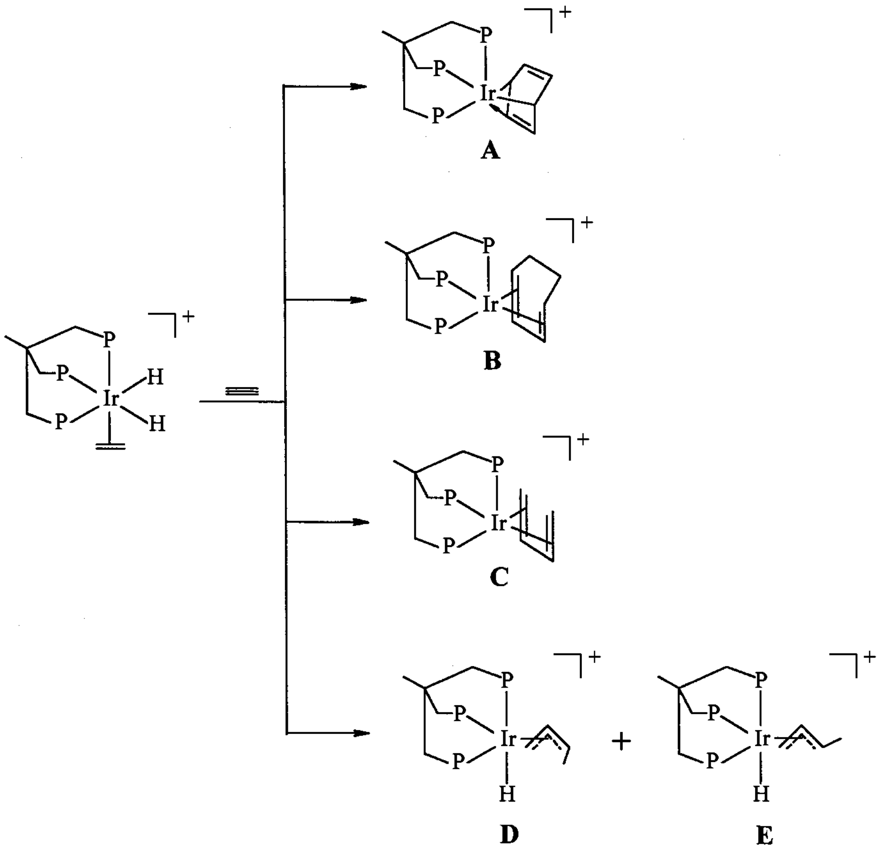

Fig. 21. Reaction of $[Ir(triphos)(C_2H_4)(H)_2]^+$ with C_2H_2 under different reaction conditions [86,87].

tached to the support are formed in the process, and provided that extraction procedures are possible, the new organometallic complexes can be isolated and characterized. Excellent reviews of this synthetic strategy are now available [4,18,104–106] and only developments that have occurred recently will be commented on in any detail here. Table 2 lists many of the new complexes that have been synthesised by these procedures.

Following on from the work of Mond on the synthesis of $Ni(CO)_4$ from Ni and Co [29,30], surface mediated organometallic reactions were studied in earlier work on metal carbonyl synthesis by Fisher [107]. In these reactions both $[Ir(CO)_3Cl]_n$ and $[Rh(CO)_2Cl]_2$ were synthesised by passage of CO and Cl_2 gas over the respective metal chloride salts deposited on SiO_2. However, the synthetic utility of a surface mediated reaction was first exploited in 1986 [108] when the Os and Ru clusters listed below were synthesised in 'quantitative yield'.

$$H_2OsCl_6/MgO + H_2/CO \rightarrow [Os_{10}C(CO)_{24}]^{2-}$$

and

$$RuCl_3/MgO + H_2/CO \rightarrow [Ru_6C(CO)_{16}]^{2-}$$

In work performed prior to this time the extraction of an organometallic complexes into solution (or by sublimation), from M_xL_y/surface complexes was only used as a procedure to identify the surface complex [109–116]. However since then, numerous reports have appeared on the synthesis of Pt, Ru, Rh, Ir, and Os cluster complexes (Table 2) [117–131].

Recent studies have also revealed that irradiation of surface supported $CpRe(CO)_2X_2$ complexes can lead to high yield isomerisation reactions, typically in the opposite direction to that found in the solution state (Table 2) [45]. Only a monolayer of Re reactant supported on SiO_2 underwent the isomerisation reaction suggesting that the support was acting as a 'modifying' ligand in the reaction.

4.2. Reactions of supported materials in the solution phase

The ability to synthesise M_xL_y/surface complexes and then react the complex with ligands in the liquid phase has been reported (Fig. 2(iv)). For example, reaction of $Rh(\eta^3\text{-}C_3H_5)_2/SiO_2$ with PMe_3/H_2 followed by extraction of the cation into solution gave *cis*-$[Ru(H)_2(PMe_3)_4]^+$ in > 90% yield [132]. In a similar manner reaction of $(C_5Me_5)Ir(PMe_3)(Ph)OH/SiO_2$ with

Table 2
Reactions of organometallic complexes on surfaces

Reactants	Surface material	Product extracted	Yield (%)	Ref.
Reaction with gases				
Na_2PtCl_6/CO	MgO	$[Pt_{15}(CO)_{30}]^{2-}$	75 [a]	[131]a
$Pt(C_3H_5)_2/CO(H_2)$	MgO	$[Pt_3(CO)_6]_n^{2-}$ ($n = 3,4$)	30	[131]b
$Pt(acac)_2/CO$	MgO	$[Pt_9(CO)_{18}]^{2-}$	50 [a]	[131]c
$Pt(acac)_2/CO/Re_2(CO)_{10}$	MgO	$[Pt_6(CO)_{12}]^{2-}$	—	[131]c
$Co_2(CO)_8$	SiO_2	$Co_4(CO)_{12}$	?	[109]
$Os_3(CO)_{12}/CO$	MgO	$[Os_5C(CO)_{14}]^{2-}$	65	[117,118]
$H_2OsCl_6/CO/H_2$	MgO	$[Os_{10}C(CO)_{24}]^{2-}$	65	[118]
$Os_3(CO)_{12}$	SiO_2	$HOs(CO)_{10}(OH)$ [b]	56	[119,116]
$Os_3(CO)_{12}$	SiO_2	$H_4Os_4(CO)_{12}$	68	[115]
$OsCl_3/CO$	SiO_2	$[Os(CO)_3Cl_2]_2$	80–90	[120]
$OsCl_3/CO$ (H_2O)	SiO_2	$[Os(CO)_3Cl_2]_2$	28	[121]
		cis-$[Os(CO)_4Cl_2]$	45	
$[Os(CO)_3Cl_2]_2/CO/H_2O$	SiO_2	$HOs_3(CO)_{12}Cl$	[c]	[121]
$[Os(CO)_3Cl_2]_2$ (or $OsCl_3$, $Os_3(CO)_{12}$))$/CO/CO_3^{2-}$	SiO_2	$Os_3(CO)_{12}$	90	[121,125]
		$[Os_5C(CO)_{14}]^{2-}$	88	[126]
		$[Os_{10}C(CO)_{24}]^{2-}$	81	
		$H_4Os_4(CO)_{12}$	83	
		$H_2Os_4(CO)_{12}^{2-}$	92	
		$[H_3Os_4(CO)_{12}]-$	99	
$[Os(CO)_3Cl_2]_2/CO/K_2CO_3$	SiO_2	$K[H_3Os_4(CO)_{12}]^-$	91	[122,125]
$[Os(CO)_3Cl_2]_2/CO$	MgO	$[Os_{10}C(CO)_{24}]^{2-}$	33	[122]
$OsCl_3/CO/K_2CO_3$	SiO_2	$K[H_3Os_4(CO)_{12}]^-$	92	[122]
$Os_3(CO)_{12}/ROH$	SiO_2	$H_4Os_4(CO)_{12}$	94	[127]
		$HOs_3(CO)_{10}Y$ [d]	52–91	
$RuCl_3/CO$	MgO	$[Ru_6C(CO)_{16}]^{2-}$	65	[108,118]
$RuCl_3/CO$	SiO_2	$[Ru(CO)_3Cl_2]_2$	60-93	[120]
$RuCl_3/CO$	SiO_2	$Ru_2(CO)_6Cl_2(H_2O)$	High	[113]
$[H_3Ru_4(CO)_{12}]^-/CO$	MgO	$[HRu_3(CO)_{11}]^-$	Quan [e]	[128]
$[HRu_3(CO)_{11}]^-/H_2$	MgO	$[H_3Ru_4(CO)_{12}]^-$	Quan [e]	[128]
$RuCl_3/CO_3^{2-}/CO$	SiO_2	$Ru_3(CO)_{12}$	93	[129]
$RuCl_3/CO_3^{2-}/CO$	SiO_2	$Ru_3(CO)_{10}Cl_2$	75	[129]
$Ru_3(CO)_{12}$	SiO_2	$H_4Ru_4(CO)_{12}$	78	[115,123]
$Ru_3(CO)_{12}$	MgO	$[H_3Ru_4(CO)_{12}]^-$	[f]	[112]
$Ru_3(CO)_{12}/CO/H_2$	MgO, Al_2O_3	$[Ru_6(CO)_{18}]^{2-}$, $[HRu_3(CO)_{11}]^-$	?	[111]
$H_4Ru_4(CO)_{12}$	MgO, Al_2O_3	$[H_3Ru_4(CO)_{12}]^-$	?	[110,111]
$RuCl_3/CO_3^{2-}/CO$	SiO_2	$[Ru_6C(CO)_{16}]^{2-}$	95	[129]
		$[HRu_3(CO)_{11}]^-$	42	
		$[HRu_6C(CO)_{18}]^-$	65	
$RuCl_3/CO_3^{2-}/CO/H_2$	SiO_2	$H_4Ru_4(CO)_{12}$	94	[129]
$RuCl_3/CO/H_2$ (H_2O)	SiO_2	$[H_3Ru_4(CO)_{12}]^-$	81	[129]
		$H_4Ru_4(CO)_{12}$	10	
$[Ru_3(CO)_9(\mu_3\text{-CCO})]^{2-}$	SiO_2, MgO	$[HRu_3(CO)_9(\mu_3\text{-CCO})]^-$	94	[130]
	SiO_2/Al_2O_3	$H_2Ru_3(CO)_9(\mu_3\text{-CCO})$	90	
$Ir_6(CO)_{16}$	SiO_2	$Ir_4(CO)_{12}$	83	[124]
$IrCl_3/CO$	SiO_2	$[Ir(CO)_3Cl]_n$ [g]	76–83	[120,123]
$IrCl_3/CO/H_2O$	SiO_2	$Ir_4(CO)_{12}$	68	[120,123]
$Ir(CO)_2(acac)/CO$	MgO	$[HIr_4(CO)_{11}]^-$, $[Ir_8(CO)_{22}]^{2-}$	High	[114]a
$Ir(CO)_2(acac)/CO$	Al_2O_3	$Ir_4(CO)_{12}$, $[HIr_4(CO)11]^-$	High	[114]b
$Ir_4(CO)_{12}/H_2O$	MgO	$[Ir_6(CO)_{15}]^{2-}$	High	[114]a
$RhCl_3/CO$	SiO_2	$[Rh(CO)_2Cl]_2$ [g]	80–84	[120,123]
$[Rh(CO)_2Cl]_2/CO(H_2O)$	SiO_2	$Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$	47, 73	[120,123]
$Rh(CO)_2(acac)$	MgO, Al_2O_3	$[Rh(CO)_{30}]^{2-}$, $[Rh_5(CO)_{15}]^-$	?	[114]c
diag-$(\eta^5\text{-}C_5H_{5\text{-}n}R_n)Re\ (CO)_2X_2$ ($n = 0, 1, 2$; R = Me, Et, ^{i}Pr, ^{t}Bu, $SiMe_3$; X = Br, I)	SiO_2/hv	*lat*-$(\eta^5\text{-}C_5H_{5n}R_n)Re\ (CO)_2X_2$	70–85	[45,46]

Table 2 (Continued)

Reactants	Surface material	Product extracted	Yield (%)	Ref.
Reaction with ligands				
diag-(η^5-C_5H_4Me)Re $(CO)_2Br_2$/NaI	SiO_2/hv	*diag*-(η^5-C_5H_4Me)Re $(CO)_2I_2$	99	[45]
diag-(η^5-C_5H_4Me)Re (CO)$[P(OPh)_3]Br_2$/NaI	SiO_2/hv	*diag*-(η^5-C_5H_4Me)Re $(CO)_2I_2$	50	[45]
Rh(η^5-$C_5H_5)_3$/PMe_3	SiO_2	$[Rh(PMe_3)_4H_2]^+$	?	[132]
$Ru(CO)_3Cl_2$/$[Co(CO)_4]^-$ or bipy	Al_2O_3, SiO_2	$[RuCo_3(CO)_{12}]^-$, $Ru(CO)_2Cl_2$(bipy)	?	[134]
(η^5-C_5Me_5)Ir(PMe_3)(Ph) (OH)/*p*-$NO_2C_6H_4OH$	SiO_2	(η^5-C_5Me_5)Ir(PMe_3) (Ph)(p-$NO_2C_6H_4$)	78	[133]
(η^5-C_5Me_5)Ir(PMe_3)(Ph) (OH)/acetylenes [h]	SiO_2	(η^5-C_5Me_5)Ir(PMe_3) (Ph)(CCCOOEt) and iridacycle (Fig. 22)	44 97	[133]

[a] Uv/vis spectroscopy.
[b] Extracted with HF.
[c] Major product.
[d] Y = OH, OR, Cl, Br, I, OOCR, SCN.
[e] IR spectroscopy.
[f] IR and NMR spectroscopy.
[g] By sublimation.
[h] HCCCOOEt, $(CCOOEt)_2$.

$C_6H_2XY_2OH$ (X = H, OMe, Cl, NO_2; Y = H, Me) gave varying amounts of the product $C_5Me_5Ir(PMe_3)(Ph)(OC_6H_2XY_2)$ [133]. The equilibrium constants for the above reaction were measured and were found to be related to the acidity of the phenol ligands. Reaction of the silica bound Ir complex above with dimethyl acetylenedicarboxylate gave the iridacyclic complex, shown in Fig. 22, in high yield (92%). It is clear from the above study that the ability to synthesise new substituted organometallic complexes will relate to the various bond strengths of the supported/unsupported materials. This is also highlighted by the ready interconversion between MgO supported $[HRu_3(CO)_{11}]^-$ and $[H_3Ru_4(CO)_{12}]^-$ [128].

Addition of 2,2′-bipyridyl to $Ru(CO)_3Cl_2(OH)/SiO_2$ (or $Ru(CO)_3Cl_2(OH)$/NaY) resulted in the expected formation of $Ru(CO)_2Cl_2$(bipy) [134]. Interestingly, reaction of the above two supported Ru complexes with $[Co(CO)_4^-]$ gave $HRuCo_3(CO)_{12}$ after proton addition, but in spectroscopic yields.

The possibility of using the above ideas to synthesise new organometallic complexes in a catalytic reaction is also suggested. Thus, interaction of M_xL_y with a surface to give M_xL_y/surface, followed by reaction with L', could yield $M_xL_{y-n}L'_n$. If the reaction is performed in the liquid phase, and in the presence of M_xL_y, then the process could be made catalytic. Numerous reactions have been reported in which solid state materials have been used to induce catalytic substitution reactions of metal carbonyl complexes and it is possible that the principles described above may have bearing on these reactions [135].

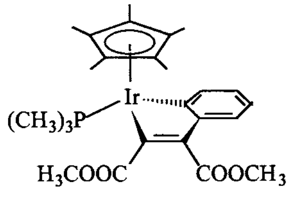

Fig. 22. Structure of the iridacycle complex [133].

4.3. Reactions at surfaces with co-deposited ligands

Reaction with a co-ligand (deposited on the support) with M_xL_y/surface complexes has been reported also. Thus, the reaction of $Ru_3(CO)_{12}$ with 2,2′-bipyridine on SiO_2 has led, after surface extraction with conc. HCl, to the synthesis of $Ru(bipy)(CO)_2Cl_2$. While the yield of the product was not reported the procedure should in principle lead to the synthesis of new complexes [136]. Further reactions of this type, for synthetic purposes, can be predicted.

In an attempt to ascertain the mechanism of the solid state isomerisation reaction of $CpRe(CO)_2Br_2$ complexes (see Fig. 7 [45]), SiO_2 was loaded with excess I^-. Exchange of the halide ion as well as isomerisation (room temperature) was observed on photolysis, revealing that homolytic reactions may be responsible for both reaction types.

In an elegant series of solid state reactions the routes to a wide range of Os and Ru carbonyl cluster complexes have been established. One of the key factors in determining the direction of the reaction was found to be the basicity of the support. This could be varied, for example, by adding different amounts and types of carbonate salts [122,125,129]. The latest studies suggest, however, that the carbonate ion not only reacts with the silanol groups but can also act as a (basic) surface reagent in the reaction [129].

5. Techniques

The exploration of chemistry in the solid state is made accessible by the many developments in instrumental analysis. DRIFTS, ESR, TGA, DSC, solid state NMR, as well as GC instruments and microscopes (light), are readily available for use in this area of chemistry. Techniques not commonly used at present in solid state reactions are AFM [6], STM and various other microscopies. XRD (single crystal, powder) studies permit analysis at the beginning and end of a reaction; in situ studies during a reaction have also been reported (e.g. see [15]).

Post reaction analysis of solid state reactions by solution state procedures is typically carried out by the classical NMR and IR spectroscopic techniques.

Thermodynamic data have been obtained by DSC procedures, typically on milligram quantities of reagents, and this procedure has been reported extensively in the literature.

Kinetic analysis is not straightforward [137], and reactions with orders greater than one are difficult to model. The paucity of data in this area is a reflection of the state of affairs.

6. Principles

6.1. Reactions in the solid state

The work of Schmidt and Cohen [8] on the concept of the topological principle and a reaction cavity provided the first ‘model’ for the interpretation of chemical reactions in the solid state. In this model the concept of least motion was enunciated. The topological principle states that a ‘reaction in the solid state occurs with a minimum amount of atomic or molecular movement’ [8]. In the model a fixed reaction cavity is envisaged in which the reaction occurs. The model was particularly successful in establishing the products expected from a $(2\pi-2\pi)$ photoassisted reaction and a maximum bond separation of 4.2 Å was established.

Attempts to quantify this ‘hard sphere’ model by Ohashi [15,34,35,37,39], in particular, has permitted correlation of a quantified reaction cavity with reaction rates. In this approach the reaction cavity is defined ‘as the space limited by a concave surface of the spheres of the surrounding atoms around the reactive group in the crystal’, with appropriate radii chosen for the measurements [15]. Remarkably, good correlation was obtained for the X-ray induced crystal-to-crystal reactions of a series of cobaloximes.(see Section 2).

Zimmerman and Zhu [138] have attempted to generate transition state molecules in solid state cavities and have proposed a ‘lock and key’ model for quantifying atom–atom interactions in the cavity.

While further refinement of the topological model has occurred there have been reports of many reactions that do not fit the ‘model’. This has led to alternative proposals to rationalise synthesis in solid materials.

(i) Local Stress. In this approach the cavity is not regarded as a ‘passive cradle but as a press’ [139] Thus, a reaction will not necessarily follow the path of least resistance but the reaction path will be determined by the mechanical properties of the surrounding molecules. This model predicts that enormous local stress fields will be produced in a cavity. A 10% radial expansion of the cavity would require a cavity pressure of 10 kbar [140]. While the concept is qualitatively useful it is only recently that a theory to quantify the process has been given [140]. In this theory elastic multipoles are introduced. The model permits for the quantification of both a reaction cavity and steric compression.

(ii) Phase rebuilding. This approach, which treats the whole crystal as a unit, has been championed by Kaupp [6,13,14]. In a solid state chemical reaction ‘reactions work themselves from the surface down into the crystal’ [6] with the reaction movement determined by crystallographic faces and reconstruction occurring over thousands of angstroms. AFM studies have revealed that eight different types of surface structures can be generated in the process and these have been classified according to their shape and kinetics of formation. In this model the strain released in a solid state reaction is crystal face dependent and will be released in the easiest way permitted by the crystal packing. An important feature of the model is ‘the need of the new molecules for immediate accommodation with the crystal lattice, after their formation in solid-state chemical reactions’ [6].

6.2. Reactions at the surface

The principles that apply here are classical principles that relate to the interaction of a surface hydroxyl (or other) group with an organometallic complex. The various complexes formed in solution, prior to addition of a support, will determine the types of complexes formed at the surface. Numerous reviews [4,18,104–106] can be consulted for further details.

7. Catalysis

The emphasis in this review has not been on the use of identifiable supported M_xL_y complexes in the area of catalysis. Reviews can be found elsewhere on this topic [4,104–106]. However, numerous of the complexes described above have been used in catalytic reactions. Clearly if control of surface species can be controlled by classical chemical procedures to produce identical catalytic sites, then better control of supported catalysts will be possible.

Catalysis, involving organometallic complexes in the solid state, is however an unexplored area of chemistry.

8. Conclusions

This review has attempted to give an overview of the current state of synthetic solid state organometallic chemistry. What is clear is that, in general, studies of organometallic complexes in the solid state have not had as their main objective synthetic strategies. Typically studies have been dominated by attempts to obtain thermodynamic data, or to indicate that solution and solid state procedures can give rise to different reaction products.

Two regimes can be identified in this area of solid state organometallic chemistry.

(i) Reactions at the molecule | surface interface. This area of chemistry, although still new, has been delineated. This has been driven by interest in the synthesis of supported heterogeneous catalysts. The high yield synthesis of specific metal carbonyl cluster complexes under controllable reaction conditions attests to the success of this approach to chemical synthesis.

(ii) Reactions in the solid state. This new area of organometallic chemistry has already revealed that high yield syntheses are possible, but to date very few comprehensive synthetic studies have been reported. By contrast, the area of synthetic solid state organic chemistry is an area that has been studied for many years and has a theoretical underpinning. The extension of the principles to solid state organometallic chemistry will most certainly take place in the next decade. Given the 'exotic' nature of the complexes produced in the area of organometallic chemistry due to the presence of the metal d orbitals, a rich solid state chemistry awaits the synthetic organometallic chemist.

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