TRANSITION METALS: RESULTS OF GENERAL INTEREST

ANNUAL SURVEY COVERING THE YEAR 1971

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CONTENTS

Reviews

Reviews have appeared on the structure of compounds with transition metal—carbon σ-bonds[1], and on metal—metal bond lengths and covalent radii in π-allyl and polymeric carbonyl complexes[2]; on optical activity from asymmetric transition metal centres[3] and from complexes of prochiral olefins[4]; on metallocene homoannular electronic effects[5]; on the synthesis and reactivity of metal carbonyls[6] and the uses of metal carbonyl anions in organometallic synthesis[7]; on polyfluoroaromatic derivatives of metals[8], metal—boron compounds[9] and Group IVB derivatives of transition metals[10]; and on oxidative addition to transition metal complexes[11].

Theoretical studies (see also references 300–304)

Interest has continued in calculations, of varying degrees of sophistication, on metal carbonyls and on alkene and enyl complexes. In tetracarbonylnickel, SCFMO calculations give a lower bonding energy for $9t_2$ than for $2e$ ($3d$) electrons, in agreement with experiment. The effect of coordination on CO is to reduce the carbon $2s$ population but to increase that of $2p$. The metal $4p$ orbitals are not greatly populated, but contribute significantly to the overlap population by virtue of their diffuseness[12]. The isoelectronic species $Mn(CO)_6^+$, $Mn(CO)_5CN$, $Mn(CN)_5CO^{4-}$ and $Mn(CN)_6^{5-}$ have been compared. The main variations in the attachment of ligand carbonyl are in the σ-system, while the cyanide groups show variations in both σ- and π-bonding[13]. MO calculations self-consistent in charge and configuration have been carried out on the pentacarbonyl halides of manganese and rhenium; the bond populations indicate that axial carbonyl is more bonded than equatorial, and that metal–carbon bonding increases from chloride to iodide[14]. Similar calculations on dimanganese decacarbonyl show that in this species (though not in its heavy congeners) direct interaction between each metal atom and the axial CO groups attached to the other plays an important part in holding the two halves of the molecule together. The highest filled orbital is calculated to be that of the metal–metal σ-bond[15]. The dipole moment changes calculated for perturbations of simplified models of substituted metal carbonyls have been used to predict relative intensities. The predictions differ markedly from those of an oscillating bond dipole model; in particular the intensity ratio of A_1 to E in species *cis*-$M(CO)_3L_3$ is calculated to be very sensitive to π-bonding between M and L[16].

A semi-empirical SCFMO calculation on Zeise's anion has been carried out with explicit inclusion of electron–electron repulsion energies. The calculated carbon–carbon bond order is 1.5, and the *trans*-influence of the olefin is attributed to a combination of π-*trans*-labilising and σ-*cis*-stabilising effects[17]. Calculations on bis(π-2-methylallyl) complexes of Cr, Fe, Co and Ni relate the greater stability of the nickel complex to the low energy of the Ni($4s$) orbital and its use in bonding[18]. In an all valence electron SCFMO treatment of butadienetricarbonyliron, the electron distribution at the butadiene ligand corresponds to a mixture of free molecule excited states; as might be expected, the π-system is more involved in bonding to metal than is the σ-bonding skeleton[19]. The calculated structure (from an extended Hückel MO treatment) of the cation $(\pi\text{-}C_5H_5)Fe(\pi\text{-}C_5H_4CH_2)^+$ has the methylene group displaced towards the metal, so that all the carbon atoms of the complex are in some sense coordinated[20].

Ionisation studies

A recent review of photoelectron spectroscopy[21] includes a section on metal carbonyls. The high-energy photoelectron spectra of the carbonyls of chromium, tungsten, iron and nickel all show a decrease in the binding energy of carbon $1s$ by between 2.2 and 2.5 eV, while that of oxygen $1s$ falls by between 1.4 and 1.7 eV; thus coordinated CO is a net charge acceptor[22], as predicted by calculations[12]. A curious feature of the chromium carbonyl spectrum is the presence of satellites corresponding to binding energies around 6 eV higher than the main peaks; these are ascribed to configuration interaction in the ground state, which to some extent permits formally forbidden processes leading to formation of ions in excited states[23]. The ionisation potentials and photoelectron spectra of trifluorophosphine-substituted derivatives of chromium, cyclopentadienylmanganese, -iron and -nickel carbonyls show that replacement of CO by PF_3 increases ionisation potentials[24].

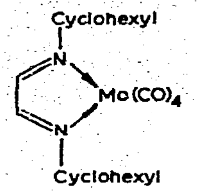
Carbon 1*s* data for chromocene, ferrocene, cobaltocene and nickelocene, together with chromium 2*p* data for chromocene and hexacarbonylchromium, indicate that the cyclopentadienyl groups have acquired a small net positive charge. In $(\pi\text{-}C_5H_5)Mn(CO)_3$, ring carbon is unusually positive and carbonyl carbon unusually negative, indicating a net charge flow between the two types of ligand[25,26]. Separate binding energies for core electrons of iron(II) and iron(III) are found in salts of partially oxidised biferrocene [biferrocene iron(II), iron(III)] ; this indicates that the charge is trapped on one of the ferrocenyl moieties[27]. Signals both from ligand[28] and from metal[29] have been obtained for a range of platinum complexes. The carbon 1*s* electrons of alkene or alkyne complexes of Pt^0 are less tightly bound than those of the free ligands, and the metal 4*f* electrons are more tightly held than in $(Ph_3P)_2Pt$, though less strongly than in $(Ph_3P)_2PtCS_2$ or $(Ph_3P)_2PtCl_2$.

Ultraviolet and visible spectra

The electronic ($f \rightarrow f$) spectra of the tricyclopentadienide complexes of americium and curium show only a small nephelauxetic effect, consistent with mainly ionic bonding[30].

Emission has been observed at low temperature from species $W(CO)_5$ and $W(CO)_5L$ (L = acetone, amine) at longer wavelength than absorption; the intensity of the emission depends on the nature of L[31]. The visible absorption band of imine complexes such as (I) is known to show a marked solvent dependence, with more polar solvents increasing the frequency, but this fact does not distinguish between ground state stabilisation and excited state destabilisation effects. It has now been shown that the ν(CO) bands also show solvatochromism, polar solvents reducing the stretching frequency of those ligands *trans* to nitrogen; thus the visible solvatochromism is a ground state effect, with the relevant transition (metal to ligand charge transfer) reducing or reversing the ground state dipole moment. The visible band solvent effect is reduced and finally reversed on successive replacement of CO by triphenylphosphine, as the donor orbital changes character from being mainly on the metal to being mainly on the nitrogen ligand[32].

The 50000 cm^{-1} band of ferrocene has been assigned to metal to ligand charge transfer. The 22700 cm^{-1} band has two electronic components, detectable in the absorption spectrum at 4.2. K; this is also so for the corresponding bands of ruthenocene and of the cobalticinium cation. The low-energy (16200 cm^{-1}) band of the ferricenium cation (ligand to metal charge transfer; *cf.* AS 1970, p. 3) shows a doubled progression in the a_{1g} vibration at 77 K, attributed to splitting of the ^2E_u excited state[33]. The $d \rightarrow d$ spectrum of nickelocene has been analysed assuming cylindrical symmetry. Five $d \rightarrow d$ bands are found and assigned, the others lying beneath charge transfer bands[34].



I

Photochemistry and photolysis

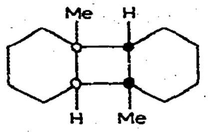
The photochemistry of metallocenes has been reviewed[35].

Photolysis of the $V(CO)_6^-$ anion[36], or of the neutral hexacarbonyls[37], in methyltetrahydrofuran (MeTHF) glasses at 77 K causes replacement of one CO group by MeTHF; for V^{-I} this process is photoreversible. The generation of species $M(CO)_5$ (M = Cr, Mo, W) in argon matrices has been described in detail. Photoreversal is associated with CO exchange and with annealing[38]; for all these reasons it is now agreed to be merely a consequence of local lattice softening. The bands attributed by earlier workers[39] to a trigonal bipyramidal isomer of $Mo(CO)_5$ are in fact of a more complex pattern, and probably belong to a polynuclear species[37]. The flash photolysis of chromium hexacarbonyl in hexane at room temperature gives rise to a short-lived species[40] the electronic spectrum of which corresponds to that[37] of $Cr(CO)_5$ in hydrocarbon glasses; this gives rise to a second species which reacts with CO [to give $Cr(CO)_6$] or with dinitrogen or dihydrogen (to give uncharacterised products); relatedly, $Cr(CO)_6$ shows photocatalysis for the 1,4 hydrogenation of conjugated dienes[41]. The complex $W(CO)_5$(stilbene) shows photocatalysis of the stilbene *cis–trans* isomerisation; this is attributed to isomerisation within the photochemically excited complex[42]. Carbonyl loss on photolysis of matrix isolated $Fe_2(CO)_9$ is a very efficient process; spectra indicate the initial formation of doubly bridged $Fe_2(CO)_8$, followed by rearrangement to a non-bridging form[43]. Coirradiation of iron pentacarbonyl with ethylene in argon at 17 K gives the known $Fe(CO)_4 \cdot C_2H_4$; with acetylene, the product is an iron carbonyl complex of $HC{\equiv}C{-}CH{=}CH_2$ [44].

The polymerisation of styrene by tetrabenzylzirconium shows photocatalysis by a range of mechanisms, depending on the exciting wavelength[45]. Ferrocene is oxidised to the ferricenium cation in carbon tetrachloride or chloroform on irradiation in the charge transfer to solvent band[46]. Absorption of light by methylcobalamine, in the region of π–π^* absorption by the corrin ring, causes homolytic fission of the cobalt–CH_3 bond[47]. Photolysis of the silver(I) complex of methylcyclohexene gives (II); this is quite different from the photolysis of the free ligand, which gives a variety of products[48].

Vibrational spectra

Carbonyls. It has been shown[49] by a detailed analysis of model systems that, at least in symmetrical species, stretching and interaction parameters calculated only from carbonyl



II

stretching frequencies give a very good approximation to true quadratic force constants. These constants must, however, be taken to refer to the MCO unit as a whole and not to the CO group alone, if only because stretching the carbon–oxygen bond causes compression of that between carbon and metal. It is this interaction that is responsible for the anomalous similarity in frequency between $CoCl_2(^{13}CO)(PEt_3)_2$ and $CoCl_2(C^{18}O)(PEt_3)_2$ [50]. It has been pointed out that force constants are a sum of classical and electronic relaxional (orbital following) effects. The latter may be related to specific electronic transitions, and the availability of transitions of the correct symmetry depends among other things on the point group of the molecule. For this reason, comparison of vibrational data for species of different symmetry is dangerous[51]. Dangers in two other areas have been pointed out. The differences between stretching parameters for the chemically distinct CO ligands of substituted complexes are sometimes taken as a measure of metal-substituent π-bonding[52]; it has now been shown that the ranking of such differences depends on the choice of approximations used to derive these parameters[53]. It has also been shown that the apparent angle between carbonyls, as calculated from relative intensities, depends critically on any differences in effective bond dipole change between symmetric and asymmetric stretching modes[54]; such differences may be expected because of orbital following. Furthermore, there is no guarantee that the direction of the oscillating dipole will coincide with that of the CO bond; and indeed one study produces a certain amount of evidence that this is not the case[55].

Jones's monumental investigation of the metal hexacarbonyls has continued with the evaluation of compliance constants and interaction coordinates[56]. Molten molybdenum hexacarbonyl has been obtained, sealed under carbon monoxide, and its Raman spectrum measured; the principal force constants appear to be slightly lower than in carbon tetrachloride solution[57]. The Raman spectrum of $Mn_2(CO)_{10}$ in solution has been examined, and previous assignments reviewed. This study is particularly interesting in its use as an aid to assignment of correlations with single crystal data, to which factor group analysis can be applied[58]. The vibrational (infrared and Raman) spectra of pentacarbonylrhenium chloride and bromide have been reported, and related to the previously discussed spectrum of the iodide[59]. The infrared spectrum of solid $Fe(CO)_5$ in the carbonyl stretching region has been measured at 77 K; Raman-active bands of symmetry A_1' and E'' were observed, as well as a totally inactive (A_2') mode[60]. The spectrum of matrix-isolated $Fe_2(CO)_9$, deposited from the vapour in argon, has been assigned in D_{3h}[43]. The band near 1900 cm^{-1} in the infrared spectrum of $NaCo(CO)_4$ (T_2 in the isolated anion) has been investigated in a variety of solvents. In water, the band is very broad, indicating some kind of special interaction. In other solvents of high polarity, the band envelope is simple, as expected for the tetrahedral anion. In dry tetrahydrofuran, effectively free anions are in equilibrium with tight ion pairs of symmetry C_{3v}, the latter giving rise to three bands between 2005 and 1855 cm^{-1} [61,62]. Infrared and Raman data for normal nickel tetracarbonyl and its all- ^{18}O derivative, combined with force constants calculated for trifluorophosphine-substituted derivatives, confirm[63] the force field of Jones[64]. Carbonyl infrared spectra have been used to detect complex formation between copper (or silver) atoms and carbon monoxide in matrix deposition studies; in each case two bands in the terminal carbonyl region were observed[65].

The infrared spectra of a number of phosphine ligand-substituted carbonyls of Group VI have been reported. The order of ligand π-acceptor strength inferred from the CO stretching frequencies is[66] $P(OMe)_3 > MeP(OMe)_2 > Me_3P > MeP(NMe_2)_2 > P(NMe_2)_3$; these results would indicate that nitrogen is π-donating to phosphorus. Similar studies on pentacarbonylchromium stibine (prepared by an indirect photochemical method) indicate it to be a better π-acceptor than triphenylstibine; this result parallels those for phosphorus and arsenic ligands[67]. The bonding between phosphorus and the Group IVB elements has been studied by comparing infrared, ultraviolet, proton NMR and phosphorus NMR data for chromium, molybdenum and tungsten carbonyl derivatives of species PR_3 (R = t-Bu, $SiMe_3$, $GeMe_3$, $SnMe_3$)[68]; these studies have also been extended to the series $(\pi\text{-}C_5H_5)Mn(CO)_2PR_3$ and $(\pi\text{-}C_5H_4CH_3)Mn(CO)_2PR_3$ [69]. Bridged–non-bridged and in one case axial–equatorial isomerism have been observed in the IR spectra of phosphine- and arsine-substituted derivatives of the compounds $YCCo_3(CO)_9$ [70] (Y = Me_2Ph). The frequency of the out-of-plane Rh—C—O bend in the species *trans*-$RhX(CO)(PPh_3)_2$ decreases from X = Cl to X = I, but also on oxidative addition of halogen[71].

Below 248 K, the *E* bands of tricarbonylnitrosylcobalt appear as doublets; the loss of structure at this temperature is assigned to an order–disorder transition. A band at 313 cm^{-1}, previously thought to be a "hot band", does not lose intensity down to 100 K, and is reassigned as an out-of-plane bending mode[72].

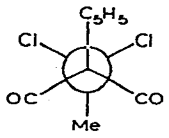
In a series of *para*-substituted phenylmethoxycarbene complexes $(OC)_5CrC(OMe)C_6H_4X$, carbonyl force constants correlate with σ-parameters for X. *Cis–trans* ratios and coalescence temperatures for rotation about the C—OMe bond are measured, and electronic spectra reported. The lowest band (20000–28000 cm^{-1}) depends on the nature of the carbene and is assigned as metal to carbene charge transfer. These methoxycarbenes may be converted into aminocarbenes, for which the relationship between carbonyl force constant and substituent σ still holds[74]. Related studies on ferrocenylmethoxycarbene and pentachlorophenylmethoxycarbene complexes confirm the electron-withdrawing nature of C_6Cl_5, while ferrocenyl is electron-releasing[75]. Such phenylmethoxycarbene complexes as $C_6H_6Cr(CO)_2C(OMe)Ph$ show a temperature-independent four-band spectrum in the carbonyl stretching region, attributed to restricted rotation of the carbene[76].

The Raman and infrared spectra of a range of arene tricarbonylchromium compounds have been represented and a full assignment proposed for the toluene complex, in which the splitting of the carbonyl *E* mode is clearly resolved in cyclohexane[77]. Factor group analyses have been carried out for the carbonyl modes of solid cyclopentadienyltricarbonylmanganese and methyl-substituted benzenetricarbonylchromium complexes; the complex 1, 2, 3-$(CH_3)_3C_6H_3Cr(CO)_3$, undergoes polymorphic changes during incorporation into a KBr disc[78]. The symmetric carbonyl stretch of $(\pi\text{-}C_5H_5)Mn(CO)_3$ is much more strongly polarised than that of $C_6H_6Cr(CO)_3$[79]; the reviewer suggests this may be due to changes in chromium to benzene π-bonding during the vibration. Carbonyl frequencies, as well as cyanide frequency changes, ring proton chemical shifts, and frequencies of electronic transitions, correlate with substituents' σ_p in *para*-substituted cyclopentadienylbenzonitriledicarbonylmanganese[80]. Carbonyl stretches and bends, as well as the metal–ring frequency, have been reported for the metal cyclopentadienyldicarbonylphosphine fragment in derivatives of molybdenum and tungsten; the metal–ring frequencies are assigned near 300 cm^{-1}, while metal–phosphorus frequencies are in the range 200–240 cm^{-1} [81].

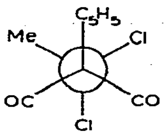
Comparison of Raman and infrared spectra for the species $[Cr(CO)_5]_2Hg^{2-}$ and $[Fe(CO)_4]_2M^{2-}$ (M = Zn, Cd, Hg) shows these species to have regular linear structures[82]. The complex $(THF)_3Al[W(CO)_3(\pi\text{-}C_5H_5)]_3$ (THF = tetrahydrofuran), formed by reaction between aluminium metal and $Hg[W(CO)_3(\pi\text{-}C_5H_5)]_2$ in THF, has been shown crystallographically to contain aluminium coordinated to the organometallic groupings through carbonyl oxygen; this explains the presence of very low carbonyl frequencies (around 1600 cm^{-1}) in the infrared spectrum[83]. However, the carbonyl spectra of species $R_2AlW(CO)_3$-$(\pi\text{-}C_5H_5)$, formed by elimination of hydrogen between R_2AlH and $HW(CO)_3(\pi\text{-}C_5H_5)$, indicate the presence both of oxygen- and of tungsten-coordinated aluminium[84].

The skeletal stretches of $Fe(CO)_4(GeH_3)_2$, formed by the reaction of the $Fe(CO)_4{}^{2-}$ anion with bromogermane, confirm the expected *cis*-octahedral structure; the Raman spectrum shows the symmetric iron–germanium stretch to lie at 229 cm^{-1}, higher than the asymmetric stretch (at 217 cm^{-1}); this is contrary to what is usually found[85] and would thus seem to indicate an appreciable positive interaction between the bonds. It has been known for some time that $(\pi\text{-}C_5H_5)Fe(CO)_2SiCl_2CH_3$ exists as a mixture of the two rotamers (III) and (IV); for this reason two pairs of carbonyl stretching bands are observed, but it is not apparent which bands belong to which rotamer. This problem has now been solved. (III) gives rise to only one ^{13}CO satellite band, while (IV), in which the carbonyl groups are chemically distinct, gives rise to two. Enough information is then available to determine separate stretching parameters for these two groups, as well as their interaction constant, and comparison of these data with the unique stretching parameter for (III) shows the more rigid carbonyl group in IV to be that *transoid* to methyl[86].

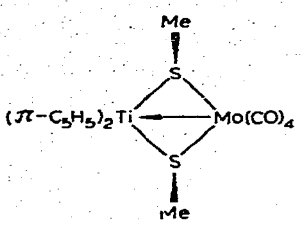
The carbonyl stretching modes of trichlorosilyltetracarbonylcobalt and the triphenyl-



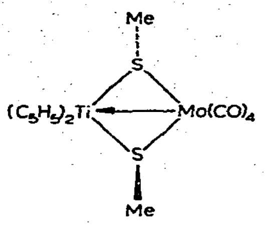
III



IV



Va



Vb

silyl analogue have been carefully analysed, and compared with those of isoelectronic triphenylphosphinetetracarbonyliron[54]. The fundamental and combination infrared spectra and laser Raman spectra of trichloro- and triiodostannyltetracarbonylcobalt and of the germanium analogues have been analysed and compared with those of the trichloro derivatives; the cobalt–metalloid force constants fall from the chlorine to the iodine compounds[87].

The infrared spectra of $(\pi\text{-}C_5H_5)_2Ti(SMe)_2Mo(CO)_4$ (V) and related species show the reality of the molybdenum to titanium dative bonding[88,89]; this contrasts with the situation in such species as $(Ph_2PCH_2CH_2PPh_2)Pt(SMe)_2Mo(CO)_4$, where the platinum dithiolate complex is acting merely as a bidentate sulphur ligand[90]. Infrared and Raman data for $Mn_2Fe(CO)_{14}$ and the rhenium analogue in the CO stretching region have been assigned, and the frequencies fitted to an approximate force field[91]. The infrared spectrum of $(\pi\text{-}C_5H_5)Fe(CO)_2Co(CO)_4$ has been examined; in the solid, there are two bridging carbonyls and the FeC_2Co ring is probably puckered. In solution, a non-bridged form and two bridged forms are in equilibrium; for the ruthenium analogue, only the non-bridged isomer is observed[92]. Similarly, $(\pi\text{-}C_5H_5)Ni(CO)_2Ni(\pi\text{-}C_5H_5)$ possesses a puckered NiC_2Ni ring, but the corresponding ring in $(\pi\text{-}C_5H_5)Fe(CO)(CO)_2Ni(\pi\text{-}C_5H_5)$ is thought to be almost planar[93].

Other groups. The spectra of variously deuterated analogues of dimethylbis(triphenylphosphine)platinum have been used to identify the resonances associated with the methyl groups[94]. Vibrational data for species of type Me_3RAuPR_3 show the strong *trans*-weakening influence of the methyl ligand[95]. In species $[Me_2AuX]_2$, the order of Raman intensities is $Cl \ll Br < I$; this is also the expected order of increasing covalency and the observed order of decreasing metal–carbon frequency[96].

In cobalt(III) acyls of macroscopic ligands, the acyl CO stretching frequency is sensitive to the nature of the other ligand but varies little from one acyl to another[97]. In the anions $[RC{\equiv}C{-}M(CO)_5]^-$, prepared from the Group VI hexacarbonyls by the indirect photochemical route, the carbon–carbon frequency is high, showing efficient net charge donation from the alkynyl group to the metal[98]. In the diacetylidebis(triphenylphosphine) complexes of nickel, palladium and platinum, $(Ph_3P)_2M(C{\equiv}C{-}R)_2$, electron-withdrawing groups R lower the frequency; the suggested interpretation is in terms of variations in the degree of π-back-bonding[99].

The carbon–carbon frequencies of vinyl alcohol and ether complexes of palladium and platinum dichlorides are shifted by conjugation with the oxygen lone pairs despite coordination. Metal–ligand frequencies are assigned; the alkenes form stronger bonds to platinum than to palladium[100].

The Raman spectra of mixtures of bis(π-allylpalladium chloride) with donors (triphenylphosphine or dimethylsulphoxide) show the presence of species (π-allyl)Pd(Cl)L, but not of any σ-allyl groups[101]; this does not of course preclude the occurrence of such groups in intermediates. The Raman spectrum of perdeuteroferrocene has been obtained; results support[102] the assignment[103] of the ring breathing frequency in ferrocene to 1105 cm^{-1}, with the 1356 cm^{-1} band being assigned to an e_{2g} carbon–carbon stretch. The symmetrical metal–ligand frequencies observed in the Raman spectra of diindenyl complexes of iron and ruthenium are depressed relative to the corresponding dicyclopentadienyl species. This is an electronic rather than a simple mass effect, since in the tetrahydroindenyl derivatives these frequencies are raised[104].

A series of very full reports have appeared on the vibrational spectra of dibenzene complexes of the transition metals in oxidation states 0 and +1 and of dibenzene-d_{12}-chromium (the work has also been extended to ferrocene). The shift in the 673 cm^{-1} benzene A_{2u} frequency to higher values in the complexes (794 cm^{-1} in dibenzenechromium) is the result of purely kinematic rather than of bonding effects; the vibrational amplitudes are such as to rule out the reality of any distortion of the six-fold symmetry of the rings of dibenzenechromium; and the force constants for different complexes are very similar, though there are some differences in the interaction constants[105–109].

The technique of inelastic neutron scattering may be used to detect, not only the motion of hydrogen atoms, but also the motion of metal atoms to which hydrogen is attached. The method has been applied to the tetrahedral species $HFeCo_3(CO)_{12}$, and to the trigonal species $H_3[Mn(CO)_4]_3$ and $H_3[Re(CO)_4]_3$. Data for the former are taken to support the view that here the hydrogen atom is inside the tetrahedron of metal atoms, while the force constants of the latter are estimated at around half of those in $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ [110].

Paramagnetism and electron paramagnetic resonance

Linewidth effects have been investigated in the EPR spectra of a range of species $(\pi\text{-}C_5H_5)_2Ti(H)_2M$ (M = Na, Li, MgBr, $AlCl_2$, AlH_2). It is inferred that the coordination around titanium is approximately tetrahedral, with the odd electron in an orbital bisecting the HTiH angle, and that this angle decreases from the sodium to the aluminium complexes. Contrary to earlier suggestions[111], the hydrogen bridges in the static structures are thought to be symmetrical[112]. The EPR spectrum to tetrabenzylvanadium is well resolved, and indicates appreciable distortion from ideal tetrahedral coordination[113]; this distortion is possibly related to that found crystallographically in tetrabenzyltitanium[114,115].

The paramagnetic properties of the ferricinium cation continue to attract interest. The controversy over the EPR spectrum[116,117] appears to have been resolved; the purported 77 K spectrum is due to an impurity, and the true spectrum can only be obtained at lower temperatures[118]. The appreciable orbital contribution to the magnetic moment of the cation confirms a split ^2E_g $(a_{1g}{}^2\, e_g{}^3)$ configuration; however, the failure of the moment to vary as expected with temperature indicates, either that the splitting itself increases with temperature, or else that the ${}^2A_{1g}$ state becomes thermally populated[119]; for biferrocene iron(II) iron(III) salts, at least, the former alternation is preferred after comparison of the temperature variability of both the magnetic moments and the EPR spectrum[120].

The EPR spectrum of cobalt(II)-tetraphenylporphyrin carbonyl indicates the electronic configuration $(xy)^2\ (yz)^2\ (zx)^2\ (z^2)$; not surprisingly, the hyperfine coupling to carbonyl ${}^{13}C$ is extensive[121]. The spectrum of $Co_3(CO)_9Se$ has been obtained in a $Co_2Fe(CO)_9Se$ host matrix; the extra electron in addition to those required to satisfy the 18-electron rule is in an a_2 (cobalt–cobalt antibonding) orbital, but a comparison of bond lengths shows the antibonding influence to be less than in the sulphur analogue[122].

Nuclear magnetic and quadrupole resonance: static systems

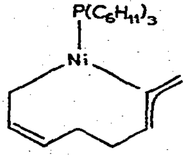
Two groups have extended the use of europium shift reagents to organometallic compounds. Results on troponetricarbonyliron and related complexes of seven-membered rings are in accord with assignments based on spin decoupling[123]. Since europium(III) is a hard acid, it coordinates to some species of type $(\pi\text{-}C_5H_5)Fe(CO)_2X$ but not to others. Thus where X is F, Cl, or N_3 there is a shift, where X is Br, I or CH_3 there is not, and the cyanide complex shows an equilibrium between coordinated and uncoordinated species. Cyclopentadienyldicarbonyliron does show a shift, implying coordination through the bridging carbonyl groups; however, terminal carbonyls of sufficiently low frequency can also coordinate, as in the case of (phenanthroline)$(Ph_3P)_2Mo(CO)_2$. The spatial selectivity of the shift can also give structural information, distinguishing between triphenylphosphine groups *cis* and *trans* to halogen[124].

The NMR spectrum has been obtained of cyclopentadienyltricarbonylmanganese aligned in a nematic solvent; this permits measurements of all the direct and indirect coupling constants linking the identical ring protons[125].

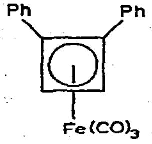
The chemical shift of ligand methyl in methylcobaloxime complexes $CH_3Co(DMG)_2L$ is sensitive to the nature of L (DMG = dimethylglyoxime); there is a downfield shift for L = CO relative to cobaloxime dimer, in accord with IR evidence that CO is acting, even though attached to cobalt(III), as a π-acceptor[126].

The NMR spectra of $[trans\text{-}(Et_3P)_2Pt(Cl){=}C(NHPh)_2]^+$ and related carbene complex cations show the existence of isomers, assigned to restricted rotation about the carbon–nitrogen bond within the carbene ligand[127]. In addition, the presence of four magnetically non-equivalent phosphorus-bonded methyl groups in related species $[trans\text{-}(PhMe_2P)_2Pt(NCR){=}C(NHR)OEt]^{2+}$ etc. demonstrates that the rotation of the carbene ligand as a whole round the metal–carbon bond is restricted[128].

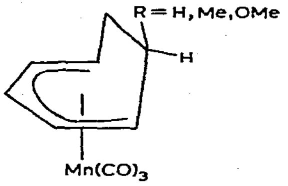
There are large shifts in the position of the allyl protons of π-allyl-π-indenyldicarbonylmolybdenum relative to those of the π-allyl-π-cyclopentadienyl complex; these are attributed to the effect of ring currents in the benzenoid ring of the indenyl ligand[129]. Structure VI has been established from the solution NMR spectrum for the complex $[(C_6H_{11})_3P]Ni(C_8H_{12})$ (C_6H_{11} = cyclohexyl), formed by the reaction either of $(C_6H_{11})_3PNi$ (cyclododecatriene)



VI



VII



VIII

or of $[(C_6H_{11})_3P]_4Ni_2N_2$ with butadiene; comparison of IR spectra shows this structure to persist also in the solid[130].

The complete proton NMR spectrum of the complex VII has been obtained, including all the ring ^{13}C—^1H coupling constants; it is inferred that the bond orders within the cyclobutadiene ring are uniform[131]. There is evidence for charge localisation between C(1) and C(2), and between C(4) and C(5), of the unsubstituted and of the C(7)-*exo*-substituted cycloheptadienyltricarbonylmanganese species VIII; the substituents cause a marked disturbance of conformation within the ring[132]. Studies on the proton NMR spectra of specifically deuterated aminoferrocenes show that the electron-donating nature of the substituent causes increased shielding mainly at positions 3 and 4[133]. 1-Amino-, 1-dimethylamino- and 1-methoxy-2-isopropylbenzene are prochiral; the isopropyl methyl groups in the tricarbonylchromium complexes are magnetically non-equivalent, and the 1-methoxy complex has in fact been partly resolved on lactose[134].

The proton NMR spectrum of the nickelocinium(III) cation shows the effect of first order delocalisation of the unpaired electron over the π-systems of the rings[135]. Paramagnetic effects also arise in the spectrum of dicyclooctatetraeneuranium; but in this case since the spin and orbital moments of the unpaired electrons are antiparallel, the ligand proton shift is to higher field[136].

A preliminary survey has been published of ^{13}C shifts in organometallic compounds. In species $(\pi\text{-}C_5H_5)Fe(CO)_2X$, carbonyl carbon is shifted increasingly upfield along the series X = CN, Cl, Br, I; the behaviour of cyclopentadienyl carbon is the reverse. $(\pi\text{-}C_5H_5)Fe(CO)_2CH_3$ and $(\pi\text{-}C_5H_5)W(CO)_3CH_3$ show methyl carbon shifted to high field relative to tetramethylsilane. By contrast, the phenyl rings in $(\pi\text{-}C_5H_5)_2Ti(C_6H_5)_2$ are shifted to low field relative to toluene; this is attributed to the existence of low-lying electronic excitations in the complex causing an increase in the paramagnetic shielding term. In substituted carbonyls, the position of the coordinated carbon is sensitive to the nature of the ligand *trans* to it, so that *cis* and *trans* carbonyl signals can be resolved. Arenes show an upfield shift on formation of their tricarbonylchromium complexes, and coordinated carbene appears electron-deficient[137]. In the Group VI hexacarbonyls and their monosubstituted derivatives, the ^{13}CO chemical shifts correlate well with stretching parameters[138] The changes in ring carbon of arenes on formation of their tricarbonylmetal complexes correlate well with the changes in mobile π-bond order at carbon as estimated from bond lengths[139]. While the ^{13}C NMR signals of α-diimines are generally shifted to low field on coordination, there is a high field shift in $(t\text{-BuN=CH–CH=NBu-t})Mo(CO)_4$ [140]. The spectrum of $(CH_3C{\equiv}CCH_3)Co_2(CO)_6$, enriched in ^{13}C, has been interpreted in terms of ethylene-like hybridisation in the coordinated alkyne[141].

In methyl complexes of platinum(II), the platinum–^{13}C coupling constant is sensitive to the σ-influence of the *trans* ligand, in the same way as the platinum–methyl hydrogen coupling; this observation validates the use of the latter [142] as a measure of $\sigma(\text{Pt } s)$ character in the platinum–methyl bond. Noteworthy also is the similarity between the NMR *trans*-influences of CO and CNR, and of CH_3 and CF_3 [143]. Relatedly, replacement of phosphorus in $(PhMe_2P)_2PtMe_2$ by arsenic increases both the platinum–methyl carbon and platinum–methyl hydrogen coupling constants, while the methyl carbon–hydrogen coupling falls[144].

The ^{13}C resonances of C(1) and C(3) in allylpalladium complexes are intermediate between those of C(1) and C(3) in iridium σ-allyls, while C(2) is in the region appropriate for the $-CH{=}CH_2$ grouping. The asymmetry in $(\pi\text{-allyl})Pd(PPh_3)Cl$ is detectable; the carbon split by and therefore presumably *trans* to phosphorus is also, as expected, the more olefinic (higher field absorption)[145].

Fluorine NMR spectra have been reported for a range of complexes of type $L_2Pt(C_2F_4)$. The phosphorus–fluorine coupling constants fall on going from phosphorus to nitrogen supporting ligands; the interpretation offered is that nitrogen is a poorer σ-donor to platinum, and thus increases the σ component in the fluoroolefin–metal bond[146].

In the complexes *trans*-$(R_3P)_2Rh(CO)Cl$, there is a linear relationship between the chemical shift of the phosphorus ligand and the change in this shift on coordination. Surprisingly, there is no such clear correlation between the phosphorus–rhodium coupling constant and CO stretching frequency[147]. Heteronuclear decoupling has been used to find the chemical shift of tungsten in the complexes *cis*- and *trans*-$(Bu_3P)_2W(CO)_4$ [148].

The quadrupole coupling constant of deuterium has been determined in $(\pi\text{-}C_5H_5)_2MoD_2$, and the tungsten analogue; the compounds follow the general relationship found for post-transition metal deuterides between coupling constant and $\nu(M{-}D)$[149].

The room temperature ^{55}Mn NQR spectra of a range of compounds of type $(\pi\text{-}C_5H_4R)Mn(CO)_3$ have been measured; the resonance frequency correlates both with ring proton NMR shifts and with shifts in the UV maximum, and is lowered by π-conjugating groups (e.g. COOH or, even more so, CHO and COMe); this is as expected[150]. Quadrupole coupling constants (for both metal and halogen) have been extracted from the broad line NMR spectra of the pentacarbonylmanganese halides[151]; the low anisotropy of the manganese chemical shift is consistent with calculations[152] in placing the highest filled orbital (8*e*) mainly on halogen $p(\pi)$; but it is thought the calculations overestimate the extent of halide to metal σ-donation. The halide NQR spectra of Zeise's salt[153] and its bromide analogue[154] show the expected *trans*-influence of the coordinated olefin. The broad line ^{59}Co NMR spectrum of crystalline dicobalt octacarbonyl at 77 K has been analysed; the results are taken to favour a direct cobalt—cobalt bond rather than a "bent" bond[155].

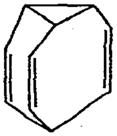
Nuclear magnetic resonance: dynamic systems (see also reference 300)

This topic has been reviewed in general[156] and with special reference to allyl complexes[157].

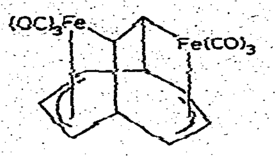
The room temperature ^{13}C and ^{31}P spectra of $Fe(CO)_5$ and $Fe(CO)_4PEt_nPh_{3-n}$ (n = 1, 2, 3) have been reported and the coupling to ^{57}Fe measured. Unfortunately, even in the substituted derivatives the signals from axial and equatorial CO groups are averaged[158].

In derivatives of type $(C_3H_5)Ti(NMe_2)_3$, assessible by Grignard reactions, the allyl group is σ-bonded to the metal but exhibits fluxional behaviour with interchange of C(1) and C(3)[159]. Fluxionality in a σ-bonded organic residue is also shown by $(\sigma\text{-}C_5H_5)_2Ge[Fe(CO)_2\text{-}(\pi\text{-}C_5H_5)]_2$; here relative peak broadening rates indicate a 1, 2-shift for the migration of the germanium—carbon bond[160]. The NMR spectra of tolyl and other substituted phenyl—copper compounds have been studied, and the observed shifts related to paramagnetic anisotropy in the copper—carbon bond; the signal from an *ortho* methyl group is temperature-variable, indicating restricted rotation below 250 K[161]. The ligand tris(*ortho*-vinylphenyl)phosphine, and the arsenic and antimony analogues, give complexes of type $LPtBr_2$; in these, infrared and Raman spectroscopy show the existence both of free and of coordinating vinyl groups, but the proton NMR signals from these are averaged at room temperature[162]. The kinetics of interchange of $(acac)Pt(Cl)(C_2H_4)$ (acac = acetylacetonato) with free ethylene have been studied by NMR; the rate is first-order in each component, and solvent-independent. The entropy of activation is negative, suggesting 5-coordination of platinum in the transition state, and there is retention of configuration[163]. The NMR spectra of silver—olefin complexes are averaged with those of free ligand down to 220 K; equilibrium constants depend on the nature both of olefin and of solvent, but little on temperature[164].

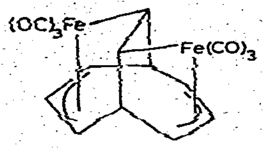
A range of products[165,166] have been isolated from the reaction of bullvalene (IX) and its isomers with iron carbonyls; of particular interest are the enantiomeric pairs (Xa, Xb)[167] and (XIa, XIb)[168]; in each of these pairs, degenerate valence isomerisation leads to racemisation, detected by time-averaging of allyl protons in (X) and by double resonance experiments in (XI).



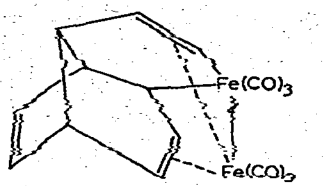
IX



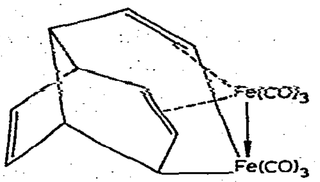
Xa



Xb



XIa



XIb

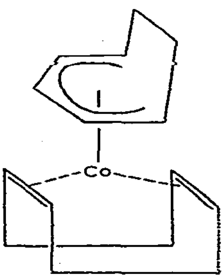
The temperature-variable NMR spectrum of $(\pi\text{-}C_3H_5)Ni(H)PF_3$, which is stable up to 245 K, indicates that it is in equilibrium with $(h^2\text{-}CH_3CH{=}CH_2)NiPF_3$; the deuterium atom in $(\pi\text{-}C_3H_5)Ni(D)PF_3$ interchanges with the protons at C(1) and C(3) of the organic ligand, but not with that at C(2)[169]. Allene and butadiene both cause rapid *syn—anti* interchange in π-allylpalladium halide dimers, doubtless by coordination to the metal and the π—σ—π process; formation of insertion products (in which the entering ligand contributes the skeleton of a new allylic ligand, while the former ligand is incorporated into a side-chain) is a slower process, and so it follows that the initial coordination is not the slow step in the insertion[170].

A range of phosphorus—ligand complexes of type $L_2Ru(\pi\text{-}2\text{-methallyl})_2$ have been prepared by displacement of cyclooctadiene. Proton NMR shows the methallyl groups to be asymmetrically bonded, as expected if the L groups are mutually *cis*. Left-right interchange may be detected at room temperature by double irradiation, and is ascribed to an intramolecular twist at the metal; at higher temperatures *syn—anti* interchange also occurs[171].

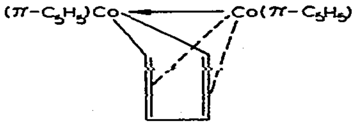
The stereochemistries and interconversion mechanisms of substituted allylpalladium chloride amine complexes have been studied. A single substituent at C(1) is generally found predominantly in the *syn* configuration, but a bulky substituent at C(2) may make the C(1)-*anti* configuration preferred. The interconversion of *syn* and *anti* groups occurs by the π—σ—π mechanism, and each substituent at the carbon atom that remains σ-bonded increases the activation energy for interconversion by between 1 and 3 kcal·mole^{-1}. Thus the interconversion at C(3) of the *syn* and *anti* protons of 1-acetyl-2-methallylpalladium chloride complexes of optically active amines occurs with interconversion of diastereomers but without *syn–anti* interchange at C(1). The latter process, which requires σ-bonding of the organic ligand to metal at C(1), is slower, but can be detected by the double resonance method. Possible restrictions on the range of interconversions of multiply-substituted complexes are discussed[172]. An apparent exception to the above findings is the substituted π-allyl complex $\{CH_2{=}CCl{-}CH_2CH_2{-}h^3{-}C(CH_3)CHCH_2PdCl\}_2$, in which *syn–anti* interchange occurs preferentially at the substituted ligand carbon atom [which we label C(1)]; here the sidechain alkene group can displace C(2) and C(3), allowing free rotation around the C(1)–C(2) bond, but displacement of C(1) and C(2) by this mechanism would not allow rotation[173]. In the 2-isopropyl-π-allylpalladium chloride triphenylphosphine complex, *syn–anti* interchange of protons occurs at the carbon atom *trans* to chlorine (but not that *trans* to phosphorus) at the same time as interchange of the magnetically nonequivalent methyl groups of the isopropyl group; this is as expected for the π–σ–π mechanism, with the carbon *trans* to phosphorus being more readily detached from the metal. The 2-isobutyl and 2-isopentyl analogues are not observed to undergo the rearrangement, presumably because of steric effects. Left–right interchange can be observed and is probably due to anion exchange. Phosphine exchange also occurs, and causes left–right interchange, when this ligand is in excess. Both these processes, accordingly, cause the collapse of magnetic non-equivalence in the substituent methylene groups, and broadening of the signals from all four terminal allyl protons[174]. Both *cisoid* and *transoid* isomers can be identified in the low-temperature NMR spectrum of π-2-methallylplatinum chloride dimer[175].

The complex cycloheptatrienylcyclooctadienecobalt gives a temperature-variable proton NMR spectrum; the low-temperature spectrum (below 250 K) is assigned to a static system XII, and the simplification at higher temperatures, which is independent of concentration, to rotation of the cyclooctadiene ligand[176].

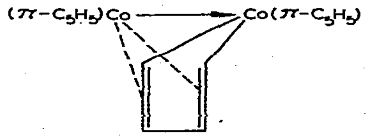
The phosphorus–phosphorus angle in the complex bis(diphenylphosphino)ethane-$Ir(CH_3)$(1,5-cyclooctadiene) is 85°, while that in the bis(dimethylphenylphosphine) complex is 101°; this may be relevant to the more rapid averaging among the cyclooctadiene protons in the former compound[177]. $(PhMe_2P)_2Rh(CH_3)$(norbornadiene) and the arsenic analogue resemble Ir^I compounds[178] in showing coalescence of the vinyl signals without loss of coordinated methyl–phosphorus coupling or of non-equivalence of phosphorus-bound methyls; but in the cyclooctadiene analogue and in $(Ph_3P)_2Rh(CH_3)$ (norbornadiene),



XII



XIII a



XIII b

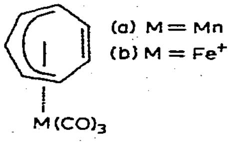
such coalescence does not occur even under conditions leading to intermolecular exchange of phosphines[179].

Photochemical reaction of (π-cyclopentadienyl)(π-cyclobutadiene)cobalt with (π-cyclopentadienyl)cobalt dicarbonyl leads to the formation of XIII; the cyclopentadienyl resonances collapse at 415 K, but H(α) and H(β) remain distinct, suggesting a degenerate valence isomerism of the type (XIIIa $\rightleftharpoons$ XIIIb)[180]. The spectrum of $(h^5\text{-}C_5H_5)_2(h^1\text{-}C_5H_5)_2Ti$ (the solid state structure of which has been confirmed crystallographically[181]) shows the effects of two different averaging processes. Up to 225 K there is increasingly rapid migration of the metal—titanium bond in the σ-bonded rings; between 225 and 310 K there is interchange of the two kinds of ring. The activation energy for this latter process is 16.1 kcal·mole^{-1}; the facility of the interchange is ascribed to back-attack by π-electrons of the σ-bonded ring on vacant orbitals of the metal. The proton spectrum of $(C_5H_5)_3TiCl$ consists of a single sharp peak down to 175 K or below[182]. Failure to show peak broadening at low temperature is also observed in $(C_5H_5)_2Mo(NO)I$ and $(C_5H_5)_2Mo(NO)CH_3$, while $(h^5\text{-}C_5H_5)_2(h^1\text{-}C_5H_5)_2Mo$ exhibits averaging within the σ-bonded ring (but not interchange between rings) at 300 K[183].

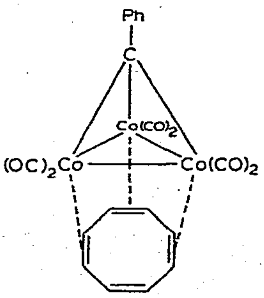
Fluxional behaviour is exhibited by h^5-cycloheptatrienyltricarbonylmanganese (XIVa), but the rate of averaging is lower than in the isoelectronic iron species (XIVb); there is evidence from the low-temperature spectrum for a ring current[184]. The complex formed by reaction of $PhCCo_3(CO)_9$ with cyclooctatetraene has a crystal structure and low-temperature limiting structure XV. The spectrum collapses to a singlet over the range 250—290 K; the relative rates of peak broadening imply, on a first-order analysis, a 1,2-shift averaging process[185].

The simplicity of the NMR spectra of the complexes $H_4Ru_4(CO)_{12-n}[P(OMe)_3]_n$ (n = 0, 1, 2, 3, 4) suggests that only one isomer is formed for each value of n. The hydrogen atoms are thought to bridge four edges of the Ru_4 tetrahedron; nonetheless, all the hydrogens are equivalent and all equally coupled to all the phosphorus atoms on the NMR timescale[186].

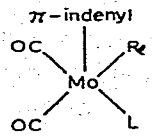
The spectrum of $(\pi\text{-}C_5H_5)W(CO)_3H$ in a nematic solvent implies some degree of alignment. The hydrogen is off-axis, but pseudorotation is fast enough to make all the ring protons equivalent[187]. A similar pseudorotation is presumed to occur in the isoelectronic ca-



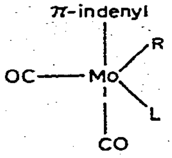
XIV



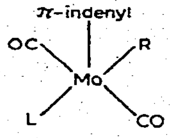
XV



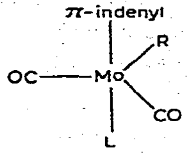
XVI



XVII



XVIII



XIX

tions $C_6H_6MoL_3H^+$ (L = PMe_2Ph or $PMePh_2$), but cannot be frozen out down to 175 K; the coordinated proton chemical shifts are around 10–12 ppm, which is unusually low for metal-bound hydrogen[188]. Steric factors may be responsible for the speed of pseudorotation in this case since it has been reported that the coalescence temperature in (π-C_5H_5)Mo(CO)($PMePh_2$)$_2$Cl is 210 K, 150 degrees lower than in complexes of type (π-C_5H_5)Mo(CO)$_2$(L)Cl, while that of (π-C_5H_5)Mo(CO)(PMe_2Ph)$_2$Cl is lower still[189]

The *cis* isomers XVI of species (π-indenyl) Mo(CO)$_2$(L)R are chiral, as are the possible rearrangement intermediates XVII; but the *trans* isomer XVIII and the transition state XIX are both achiral. Thus racemisation of XVI via XVII must be accompanied by *cis–trans* interconversions, but racemisation via XIX need not be. In *cis*-(π-indenyl)Mo(CO)$_2$(PMe_2Ph)I, the averaging of the hydrogens attached to C(1) and C(3) occurs at the same rate as that of the diastereotopic methyl groups. The free energy of *cis* racemisation depends on the nature of the halide, but that of *cis–trans* isomerisation does not[190].

Phosphine exchange in methyl gold(I) trimethylphosphine is fast enough to be followed by ligand proton NMR. The kinetics indicate an associative mechanism. The observed hydrogen–phosphorus coupling in the ligand goes through zero at intermediate free ligand concentrations, demonstrating a change in sign on complexing[191–193]. Proton NMR studies show rapid exchange of the supporting ligand in Me_2AuCl-(pyridine) and $Me_2Au(SCN)$-$AsPh_3$, but not in $Me_2AuClAsPh_3$ or $Me_2Au(SCN)PPh_3$. Exchange between the $Me_2Au(PPh_3)_2^+$ cation and free ligand in chloroform is fast, in contrast to the situation in the isoelectronic Pt^{II} analogue[194]. The NMR spectrum of species Mo(CO)$_2$(dam)$_2$X$_2$ (dam = bis(diphenylarsino)methane), known from X-ray crystallography to be seven-coordinate, shows freezing out below room temperature of the distinction between ligands, and, at yet lower temperature, of the particular ligand conformations[195].

The triply bridged species $(OC)_3Fe(SiMe_2)_2(CO)Fe(CO)_3$ shows fluxional behaviour[196]. The cyclopentadienyl proton resonances of the species (π-C_5H_5)$_2$Ti(SS) (SS = ethylenedithiolate, *o*-benzenedithiolate) show equivalence of the cyclopentadienyl rings at high temperature only, while the sulphur ligand NMR is temperature-independent; this indicates an up-down flip of buckled TiS_2C_2 rings[197]. The ring proton NMR spectra of (π-C_5H_5)$_2$Ti(SMe)$_2$Mo(CO)$_4$ and related species show high-temperature equivalence of all ring protons; at low temperatures, *cisoid* and *transoid* isomers (Va and Vb), and the chemically non-equivalent "up" and "down" cyclopentadienyl rings of the former, became distinct[88,89].

Mössbauer spectra

The spectrum of the dicarbollyliron(III) salt $Me_4N[Fe(C_2B_9H_{11})_2]$, is an asymmetric doublet of broad lines; this effect is attributed to spin–spin relaxation[198]. Bonding between tin and transition metals continues to arouse interest[199–201]. Magnetic field experiments show the sign of the quadrupole coupling constant of tin to be positive in a wide range of pentacarbonylmanganese and cyclopentadienyldicarbonyliron complexes. The chemical shifts are characteristic of tin(IV), and the relative chemical shift values show $(\pi\text{-}C_5H_5)Fe(CO)_2$ to be a more powerful σ-donating group than $Mn(CO)_5$. Substitution of CO by other groups in compounds $(\pi\text{-}C_5H_5)Fe(CO)_2SnR_3$ decreases the *s*-electron density at the iron nucleus (as expected) but increases that at tin; the latter effect is not what would be expected if iron–tin π-bonding were an important variable. The *s*-electron density at iron is taken as a measure of the π-accepting ability of the substituent ligands, giving an order for the trimethyltin complexes differing in detail from that found for the triphenyltin analogues or[202] for complexes of the type $L_2Fe(NO)_2$ and $LFe(NO)_2CO$.

Mössbauer spectra have been used to elucidate the varying stereochemistry of substitution into $Fe_2(CO)_6(SMe)_2$ and $Fe_2(CO)_6(SPh)_2$ by phosphine[203]. Two separate groups[204,205] have used the method to determine the nature of the solids $ZnFe(CO)_4$, $CdFe(CO)_4$ and $HgFe(CO)_4$. The small, but non-zero, quadrupole coupling shows the iron–metal bonds to be mutually *cis* and highly covalent.

Mass spectra

Deconvolution of ionisation efficiency curves for the formation of species $M(CO)_n^+$ from the Group VI hexacarbonyls reveals steps involving effectively simultaneous loss of more than one CO, from parent or from daughter ions[206]. Appearance potentials in the spectra of species of type $(\pi\text{-}C_5H_5)M(CO)_3M'Me_3$ (M = Cr, Mo, W; M′ = Si, Ge, Sn) combined with thermochemical data indicate the bond dissociation energies to fall from chromium to tungsten complexes, and from silicon through germanium to tin[207].

Several reports (see also ref. 215 below) have appeared of ion–molecule reactions. Such reactions are presumably responsible for the formation of polynuclear cations in the spectra of the Group VI carbonyls[208], and have been shown from pressure and voltage dependence experiments to be responsible for the formation of species $Ar_2Cr_2(CO)_3^+$[209]. Such reactions also occur when the spectra of $(\pi\text{-}C_5H_5)Cr(NO)(CO)_2$ and $(C_5H_5)_2Cr$ are observed at sufficiently high pressure, and the products generated have their own characteristic fragmentation patterns[210]. Ion–molecule reactions between $(\pi\text{-}C_5H_5)Mn(CO)_3^+$ and the potentially basic fluorides AF_n of phosphorus(III), arsenic(III), antimony(III) or sulphur(IV), occur to give $(\pi\text{-}C_5H_5)Mn(CO)AF_n^+$ and $(\pi\text{-}C_5H_5)MnAF_n^+$; NF_3 was not observed to react[211]. In the fragmentation of the species $(Me_2N)_3AsM(CO)_5$ (M = Cr, Mo, W), loss of Me_2N is more marked than it is from $(Me_2N)_3P$ complexes; tungsten even gives series of ions $Me_2NAsW(CO)_n^+$ and $AsW(CO)_n^+$; there is metastable peak evidence for loss of AsH_3 from the $(Me_2N)_2AsFeH^+$ ion[212]. Both loss of carbonyl and loss of X have been observed for iron–allyl complexes $RC_3H_4Fe(CO)_2X$; the dependence of the spectra on the nature of X is discussed[213]. In the spectra of chlorinated ferrocenes, peaks observed include [parent $-FeCl_2]^+$, and, where hydrogen and chlorine are present on different rings, [parent $-HCl]^+$ [214].

Miscellaneous physical methods

Ion cyclotron resonance has been used to study the vapour phase reactions of iron carbonyls and related ionised species. Thus $Fe(CO)_5$ reacts with iron carbonyl ions to give species $Fe_2(CO)_4^+$ and $Fe_2(CO)_5^+$; with Me_2F^+ to give $MeFe(CO)_5^+$ and $MeFe(CO)_4^+$, and with F^- and EtO^- to give $Fe(CO)_3F^-$ and $Fe(CO)_3OEt^-$. Iron carbonyl cations react with benzene to give $C_6H_6Fe(CO)_2^+$, and (with the exception of $Fe(CO)_5^+$) exchange with water[215]. The cocondensation of metals with CO and $C^{18}O$ in argon matrices has been used to generate species $Ni(CO)_n$ ($n = 1$–4), and at least five tantalum carbonyl species[216]. The range of ^{56}Mn species generated by neutron irradiation of various manganese carbonyl complexes has been determined. Some $H^{56}Mn(CO)_5$ is formed from a wide range of species with hydrogen-containing ligands, including $(\pi\text{-}C_5H_5)Mn(CO)_3$ and $(\pi\text{-}CH_3C_5H_4)Mn(CO)_3$; in this last case $CH_3{}^{56}Mn(CO)_5$ is also formed. $Mn_2(CO)_{10}$ gives rise to $^{56}Mn(CO)_5$ radicals; these have been trapped with I_2 [217,218].

Dipole moment measurements, compared with carbonyl stretching frequencies, indicate that PPh_3 is at once a better σ-donor and a better π-acceptor than $AsPh_3$ [219]. The principal polarisabilities of ferrocene have been determined[220]. A variety of optically active iron carbonyl complexes of prochiral olefins have been prepared, and circular dichroism spectra related to absolute configuration[221].

The vapour pressures of $(\pi\text{-}C_5H_5)_3UCl$ and of the tricyclopentadienides of Pr, Nd, Ho and Tm have been determined; the enthalpies of sublimation quoted are 27.7, 31.3, 32.2, 28.6 and 26.1 kcal·mole^{-1} respectively[222]. The enthalpy of formation of allylpalladium chloride dimer has been determined by differential scanning calorimetry, and a minimum value of 57 kcal·mole^{-1} calculated for the palladium–allyl bond dissociation energy[223]. The effect of a double bond on the thermodynamics of complexation of silver(I) in water by sulphur or selenium donors has been determined. In all cases, the coordination of the double bond is exothermic, but leads to a decrease in entropy. This is unusual for chelation and is attributed to solvent ordering effects[224]. The basicities of *p*-butadienylaniline and its tricarbonyliron complex in ethanol–water mixtures have been compared; complexation reduces the electron-withdrawing character of the butadienyl group[225].

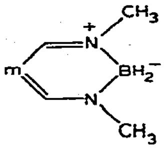
Electrochemical studies have been carried out on a wide range of organometallic species. It has been shown that chromium complexes are capable of reversible 1-electron oxidation; the more strongly π-accepting the ligands, the more difficult the complex is to oxidise[226]. Data for the polarographic reduction of $(\pi\text{-}C_3H_5)Fe(CO)_2(NO)$ and substituted derivatives suggest an initial 2-electron reduction to ions $[Fe(CO)_2(NO)]^-$ and $C_3H_5^-$; the eventual products include $Fe(CO)_3NO^-$ and alkenes. The half-wave potential is more sensitive to substituents at C(1) of the allyl than to those at C(2)[227]. In the polarographic reduction of species $Co(CO)_2(NO)L$, the half-wave potential correlates with NO stretching frequency[228].

The electrochemical behaviour has been studied of derivatives of the bridged cyclopentadienyliron dicarbonyl dimer in which both terminal carbonyls have been replaced by a bridging phosphine; reactions observed include reversible 1-electron oxidation, further oxidation to a dication in which the carbonyl bridges are intact, and disproportionations of the monocation with uptake of solvent acetonitrile[229]. The electrochemical reduction of phenylcobalt(III) complexes of polydentate ligands to cobalt(II) and cobalt(I) complexes is reversible, but further reduction leads to cleavage of the metal–carbon bond[230]. The oxidation of ferrocene, ruthenocene and osmocene at the dropping mercury electrode occurs by a reversible 1-electron step, the ease of oxidation increasing down the periodic table. For ruthenocene derivatives, as for those of ferrocene, there is a linear relationship between half wave potential and the inductive effect of substituents. At the rotating platinum disc, an irreversible 2-electron oxidation occurs[231]. The species $[(\pi\text{-}C_5H_5)FeS]_4{}^n$ can be oxidised or reduced intact through all steps from $n = -1$ to $n = 4$; $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2{}^n$ can be formed for $n = -1$ to $+2$ (ref. 232). In donor solvents, oxidation of the latter gives a general route to species $(\pi\text{-}C_5H_5)Fe(CO)_2L^+$ [233]. The oxidation of nickelocene to the mono- and (at the platinum electrode) di-cation, and the reduction of the cobalticinium cation to cobaltocene, are reversible processes. Further reductions to the diene complex $(\pi\text{-}C_5H_5)CoC_5H_6$, and the allyl $(\pi\text{-}C_5H_5)NiC_5H_7$, are irreversible[234]. There is evidence for polarographic reduction of carbollide complexes to give Co^I and Ni^I complexes[235].

Chemical results of general interest

A variety of carbonyl hydrides have been generated by the reaction of one atmosphere of hydrogen gas with carbonyls or lower hydrides in hydrocarbon solution at between 265 and 475 K; species generated include $H_3Re_3(CO)_{12}$, $H_4Re_4(CO)_{12}$, $H_4Ru_4(CO)_{12}$, $H_4Os_4(CO)_{12}$ and the unstable $H_4FeRu_3(CO)_{12}$ [236]. Dimethylformamide has been used as a source of CO in the preparation of a range of carbonyl halide and carbonyl phosphine complexes of rhodium and platinum[237]. The complexes $Mn(CO)_3(PMe_2Ph)_2Br$ and $Mn(CO)_2(dppe)Br$ (dppe = bis(diphenylphosphino)ethane) are oxidised to monocations by $NOPF_6$, while $(C_5H_5)_2Fe_2(CO)_4$ gives the $(\pi\text{-}C_5H_5)Fe(CO)_3^+$ cation[238]. The reactions of *cis*-1,2-bis(dimethylarsino)ethylene (edas) and *o*-phenylenebis(dimethylarsine) (das) with a range of carbonyl and carbonyl nitrosyls have been reported; compounds described include $Cr(CO)_4$-edas and the molybdenum and tungsten analogues, $Ni(CO)_2$-edas, $Fe(NO)_2$-das and $Co(CO)(NO)$-das, while the substitution of edas into the carbonyl nitrosyls gives unstable products[239]. Reaction of the potentially tetradentate ligand $(Ph_2PCH_2)_4C$ with manganese or cobalt carbonyls causes disproportionation to give products $Ph_2PCH_2C(CH_2PPh_2)_3m^+\ m(CO)_2^-$ (m = $Mn(CO)_3$, $Co(CO)_2$), in which one phosphine group of each ligand is uncoordinated[240].

Cyanogen reacts with phosphine complexes of Ni^0, Pd^0 and Pt^0, to give oxidative addition products; with $RhCl(PPh_3)_3$, coordination of cyanogen without reaction has been observed at 200 K; on warming to room temperature, the oxidative addition reaction occurs. Phosphine chlorides of Pt^{II} and Au^I fail to react, as do $RhCl(CO)(PPh_3)_2$ and the iridium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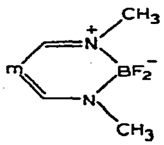
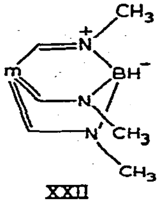
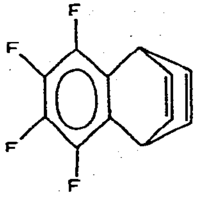

XXI


XXII


XXIII

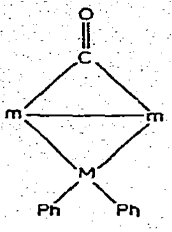
analogue[241]. The isonitrile complexes $m(CNMe)_2^+$ [m = (π-C_5H_5)Fe(CO), (π-C_5H_5)$Mo(CO)_2$, (π-$CH_3C_5H_4$)Mn(NO)] add borohydride to give the species XX; these exchange with fluoroborate to give XXI. The reaction of the (π-C_5H_5)$Fe(CNMe)_3^+$ cation with borohydride involves all three isonitrile groups, giving XXII[242].

The novel ligand tetramethoxyethylene (TME) reacts with diiron enneacarbonyl to give $Fe(CO)_4$TME, and photochemically with (π-C_5H_5)$Mn(CO)_3$ to give (π-C_5H_5)$Mn(CO)_2$TME; the carbonyl stretching frequencies in these species are higher than in the analogous ethylene complexes[243]. A range of complexes of Rh, Ir, Ni, Pd and Au have been prepared from dicyanoacetylene (C_4N_2); species characterised include $RhCl(CO)(C_4N_2)(PPh_3)_2$ and the iridium analogue, NC–CH=C(CN)–$Ir(CO)(C_4N_2)(PPh_3)_2$, and $Pd(C_4N_2)_2(PPh_3)_2$. C_4N_2 is less effective at raising the CO stretching frequency in iridium complexes than is tetracyanoethylene or even maleonitrile[244]. The diene XXIII, formed by the addition of tetrafluorobenzyne to benzene, acts as a bidentate ligand in complexes of Co^I, Rh^I, Pd^{II} and Pt^{II} [245].

The study of pentamethylcyclopentadienyl complexes has been hampered by synthetic problems. It has now been reported that acetylpentamethylcyclopentadiene reacts with a range of metal carbonyls to give such complexes. Materials accessible by this route include $C_5Me_5Co(CO)_2$, $C_5Me_5Mn(CO)_3$, $[C_5Me_5Cr(CO)_2]_2$, $C_5Me_5W(CO)_3CH_3$, $[C_5Me_5Fe(CO)_2]_2$ [from $Fe(CO)_5$] and both $C_5Me_5Fe(CO)_2COCH_3$ and the tricarbonyliron complex of the starting material [from $Fe_2(CO)_9$][246]. While trimethylstannylcyclopentadiene reacts with metal carbonyls with cleavage of the tin–carbon bond[247], the silicon–carbon bond generally survives the reactions of $Me_3SiC_5H_5$. Materials prepared include $[Me_3SiC_5H_4M(CO)_3]_2$ (M = Mo, W); $Me_3SiC_5H_4Mn(CO)_3$ and the rhenium analogue, $[MeSiC_5H_4Fe(CO)_2]_2$, and $Me_3SiC_5H_4Co(CO)_2$ [248]. Not surprisingly, therefore, the elimination of trimethyltin halides between (trimethylstannyl)(trimethylsilyl)cyclopentadiene and metal carbonyl halides also leaves the silicon ring carbon bond intact[249].

The reaction of perfluorophenylmercury bromide with metal carbonyl anions gives species C_6F_5Hgm [m = (π-C_5H_5)$Mo(CO)_3$, $Mn(CO)_5$, (π-C_5H_5)$Fe(CO)_2$] [250]. Indium–metal compounds are formed by the insertion of indium(I) halides into metal–metal bonds, or by the displacement of mercury from its metal derivatives; species of type m_2InX [m = e.g. (π-C_5H_5)$Mo(CO)_3$, (π-C_5H_5)$Fe(CO)_2$, $Co(CO)_4$] have been prepared by one or both of these routes[251].

Photochemical decarbonylation, followed by insertion into a silicon–hydrogen bond,



XXIV

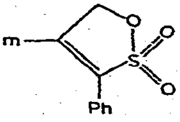
(a) m = $Co(CO)_3$, M = Ge
(b) m = $(\pi\text{-}C_5H_5)Fe(CO)_2$, M = Si
(c) m = $(\pi\text{-}C_5H_5)Fe(CO)$, M = Sn

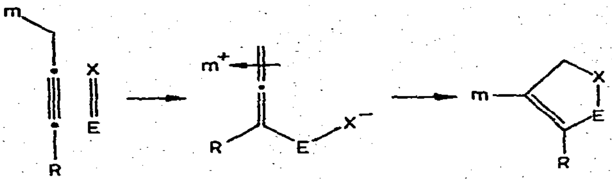
has been used to prepare a wide range of metal silyl compounds, such as $(\pi\text{-}C_6H_6)Cr(CO)_2(H)SiCl_3$, $(\pi\text{-}C_5H_5)Mn(CO)_2(H)SiX_3$, $Fe(CO)_4(H)(SiX_3)$, $(\pi\text{-}C_5H_5)Fe(CO)(H)(SiCl_3)_2$, and $(\pi\text{-}C_5H_5)Co(CO)(H)SiCl_3$ (X = Cl, Ph); infrared intensity measurements show that where there is a choice, it is the *cis* isomer that is formed[252]. Hexamethylditin also replaces CO, giving $Fe(CO)_4(SnMe_3)_2$ and $(\pi\text{-}C_5H_5)Co(CO)(SnMe_3)_2$, as well as *cisoid* and *transoid* isomers of $[(\pi\text{-}C_5H_5)Co(CO)]_2(SnMe_2)_2$; rhodium behaves similarly to cobalt[253]. The reaction of diphenylgermanium dibromide with metal carbonyl anions $m^- = [Fe(CO)_3NO^-, (\pi\text{-}C_5H_5)Fe(CO)_2^-, Co(CO)_4^-]$ gives the bridged species Ph_2Gem_2 ; Ph_2GeCl_2, however, generally gives $Ph_2Ge(m)Cl$, only the strongly nucleophilic $(\pi\text{-}C_5H_5)Fe(CO)_2^-$ anion displacing both chlorides[254]. Of these, $Ph_2Ge[Co(CO)_4]_2$ can be photochemically decarbonylated to give XXIVa; $Ph_2Si[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$ and the tin analogue behave similarly to give XXIVb and XXIVc[255]. In trichlorosilyl and trichlorogermyl derivatives of molybdenum, manganese, iron and cobalt, chloride may be exchanged for fluoride on reaction with $AgBF_4$ [256].

Phosphorus trifluoride can be introduced into a wide range of organometallics, with, in some cases, concomitant dehalogenation, by $Ni(PF_3)_4$; products obtained include $(\pi\text{-}C_5Me_5)Rh(PF_3)_2$ [from $[(\pi\text{-}C_5Me_5)RhCl_2]_2$] ; $(\pi\text{-}C_5Me_5)IrPF_3(PF_2)F$; and $Mn_2(CO)_{10}$, $Mn_2(CO)_9PF_3$, and $Mn_2(CO)_8(PF_3)_2$ [from $Mn(CO)_5Br$; but $Re(CO)_5Br$ gives $Re(CO)_3(PF_3)_2Br$]. $(\pi\text{-}C_5H_5)Fe(CO)_2I$ undergoes substitution of one carbonyl, as does the methyl derivative $(\pi\text{-}C_5H_5)Mo(CO)_3Me$; but the corresponding chloride gives $(\pi\text{-}C_5H_5)_2Mo_2(CO)_5PF_3$ [257].

$(OC)_5Cr\text{--}SMe\text{--}SnMe_3$, accessible photochemically from the hexacarbonyl, reacts with a wide range of halides including organometallic halides to eliminate trimethyltin chloride. $(\pi\text{-}C_5H_5)Fe(CO)_2SMeCr(CO)_5$ and $Ph_3PAuSMeCr(CO)_5$ may be prepared in this way, but $Mn(CO)_5Br$ reacts to give Me_3SnBr, $Cr(CO)_6$, and $[Mn(CO)_4SMe]_2$ [258]. A range of metal complexes $mCH_2C{\equiv}CPh$ [m = $(\pi\text{-}C_5H_5)Mo(CO)_3$, $Mn(CO)_5$, $(\pi\text{-}C_5H_5)Fe(CO)_2$] react with sulphur trioxide to give sultones, XXV; it is suggested that this is an example of a general reaction pathway (XXVI) of 2-alkynyl complexes[259].

A range of metal vinyl and related derivatives react with diiron enneacarbonyl. Thus $(\pi\text{-}C_5H_5)Fe(CO)_2CH{=}CHR$ gives XXVII, while $(\pi\text{-}C_5H_5)W(CO)_3CH{=}CH\text{--}CO\text{--}Ph$ gives a mixture of products (XXVIII–XXX). $MeCOCH{=}CHRe(CO)_5$ coordinates an $Fe(CO)_4$ fragment (to give XXXI), as does $(\pi\text{-}C_5H_5)Fe(CO)_2\text{--}CO\text{--}CH{=}CHPh$ which gives XXXII; this

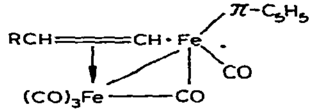

XXV



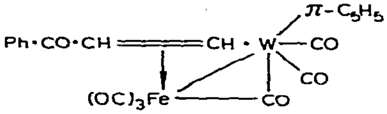
XXVI

may be decarbonylated thermally to give (XXVII, R = Ph), or photochemically to XXXIII[260]. Cyclopentadienyl nickelcarbonyl dimer reacts with dicobalt octacarbonyl to give a product of composition $C_5H_5NiCo_3(CO)_9$, and with $Fe_2(CO)_9$ and $Mn(CO)_5^-$ respectively to give products $(C_5H_5)_2Ni_2M(CO)_5$ ($M = Fe, Mn^-$). The structures XXXIV and XXXV are suggested for the solids; the complexity of the carbonyl stretching spectra suggests the presence of isomers in solution[261].

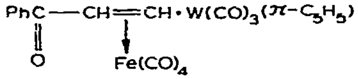
Reaction of dimanganese decacarbonyl with $Ru_3(CO)_{12}$ gives $(OC)_5MnRu(CO)_4Mn(CO)_5$; the related manganese–osmium and rhenium–osmium compounds have been prepared. The reactions with $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ and $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ do give metal–metal bonded products, but the chief species formed is $(\pi\text{-}C_5H_5)Mn(CO)_3$[262]. Elimination of methylamine between $(\pi\text{-}C_5H_5)_2TiNMe_2$ and hydrides is a general route to products $(\pi\text{-}C_5H_5)_2TiR$; among species so generated is $(\pi\text{-}C_5H_5)Mo(CO)_3Ti(C_5H_5)_2$. Reaction of the amide with *trans*-$(Ph_3P)_2PtHCl$ leads to formation of Pt^0 species, presumably by reductive elimination of $(\pi\text{-}C_5H_5)_2Ti\text{–}Cl$[263]. The elimination of hydrogen halides between complexes of diphenyl-



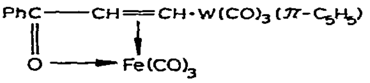
XXVII



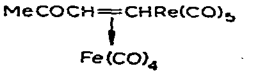
XXVIII


$\underset{\underset{O}{\|}}{PhC}—\underset{\underset{Fe(CO)_4}{\downarrow}}{CH{=}CH}\cdot W(CO)_3(\pi\text{-}C_5H_5)$

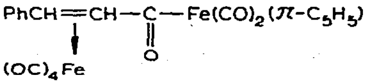
XXIX


$\underset{\underset{O\,\longrightarrow}{\|}}{PhC}—\underset{\underset{Fe(CO)_3}{\downarrow}}{CH{=}CH}\cdot W(CO)_3(\pi\text{-}C_5H_5)$

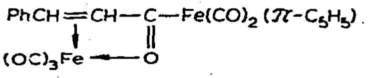
XXX


$MeCO\underset{\underset{Fe(CO)_4}{\downarrow}}{CH{=}CH}Re(CO)_5$

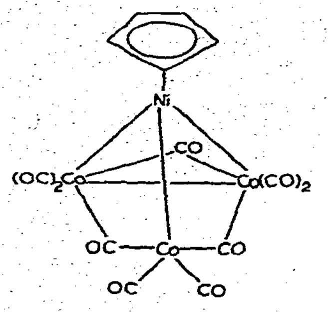
XXXI


$Ph\underset{\underset{(OC)_4Fe}{\downarrow}}{CH{=}CH}—\underset{\underset{O}{\|}}{C}—Fe(CO)_2(\pi\text{-}C_5H_5)$

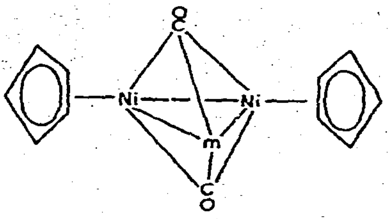
XXXII


$Ph\underset{\underset{(OC)_3Fe\,\longleftarrow}{\downarrow}}{CH{=}CH}—\underset{\underset{O}{\|}}{C}—Fe(CO)_2(\pi\text{-}C_5H_5)$

XXXIII



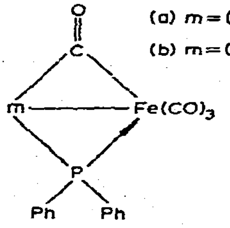
(XXXIV)



(XXXV)

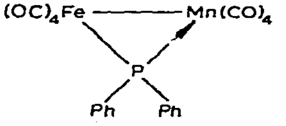
(a) m=Fe(CO)$_3$
(b) m=Mn(CO)$_3$

phosphine and metal halides leads to a variety of products. Thus tetracarbonyliron diphenylphosphine reacts with (π-C_5H_5)Ni(CO)I to give XXXVIa, and with (π-C_5H_5)Fe(CO)$_2$Cl to give (π-C_5H_5)Fe(CO)$_2$PPh$_2$Fe(CO)$_4$; this condenses further to give XXXVIb. Tricarbonylnickel diphenylphosphine reacts with (π-C_5H_5)Ni(CO)I to give (π-C_5H_5Ni)$_2$(PPh$_2$)$_2$. With (π-C_5H_5)Fe(CO)$_2$Cl, the product formed is, as expected, (π-C_5H_5)Fe(CO)$_2$PPh$_2$Ni(CO)$_3$; this does not, however, condense further. The iron diphenylphosphine reacts with BrMn(CO)$_5$ or (π-allyl)Mn(CO)$_4$, to give XXXVII, and with (π-C_5H_5)Co(CO)I to give XXXVIII[264].

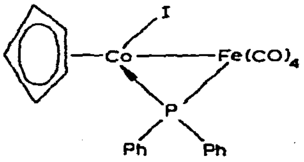


(a) m=(π-C_5H_5)Ni
(b) m=(π-C_5H_5)Fe(CO)

XXXVI



XXXVII



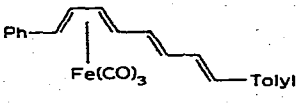
XXXVIII

Kinetics (see also NMR: Dynamic systems, mechanism, catalysis)

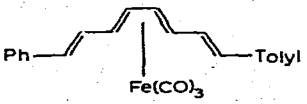
While the replacement of CO in the tetrahydroindenyl complex C_9H_{11}Mo(CO)$_3$Cl is unimolecular, resembling that of the cyclopentadienyl, the indenyl complex reacts more rapidly, with a second-order component. Thus the π-indenyl ligand stabilises the associative transition state[265] (the reviewer suggests this might happen through the ligand acting as a π-allyl). The replacement of acetone by alkenes from the species W(CO)$_5$-acetone occurs by a dissociative pathway[266]. The reactions between tungsten carbonyls and Grignard reagents are measurably slow, unlike the corresponding reactions involving organolithium compounds; it is found that W(CO)$_6$ reacts more rapidly than W(CO)$_5$PPh$_3$, as expected for nucleophilic attack at coordinated carbon[267]. The kinetics of the reaction of species M(CO)$_4$LL (M =

Mo, W; LL = bipyridyl, phenanthroline) with mercuric halides [to give $M(CO)_3(LL)(HgX)X$] imply intermediates of composition $M(CO)_4(LL)\cdot 2HgX_2$ in acetone and both $M(CO)_4(LL)\cdot HgX_2$ and $M(CO)_4(LL)\cdot 2HgX_2$ in ethylene chloride[268]. The exchange of ^{13}CO with $Mn(CO)_5H$ is, contrary to earlier reports[269], a slow process. The exchange is also non-random, the specific rate constant for replacement of axial CO being roughly two to four times as great as that for radial replacement[270]. Reaction of $Ph_3GeMn(CO)_5$ with phosphines in decalin gives *trans* substitution, with competing unimolecular and bimolecular pathways. Since the reaction with dipyridyl gives *cis* substitution, it is suggested that the dissociation step in unimolecular substitution is loss of *cis* carbonyl. This may be replaced directly by a ligand of low steric demand, but a bulkier ligand can attach itself only after the vacancy has migrated to the *trans* position[271]. The kinetics of the replacement of triphenylsilane from $(\pi\text{-}C_5H_5)Mn(CO)_2(SiPh_3)H$ by such ligands as triphenylphosphine have been studied in a variety of solvents. Rate-determining is loss of the silane; this is reversible, excess silane retarding the reaction, but competition experiments show that thriphenylphosphine is more reactive than triphenylsilane towards the unsaturated intermediate. There is a small but significant kinetic isotope effect in both forward and back reactions[272]. The rate of exchange of radioactive manganese between $Mn(CO)_5I$ and other species has been studied; exchange with the pentacarbonyl hydride is complete at room temperature within thirty seconds, but the phenyl, methyl or parent decacarbonyl do not exchange within ten minutes[273]. The rates of substitution of triphenylphosphine into rhenium pentacarbonyl halides decrease from chloride to bromide to iodide; the reactions are[274] much slower than for the manganese analogues, for which the same order is established[275]. The kinetics have been studied of the reaction of the bridged dimer $[Re(CO)_2(NO)Cl_2]_2$ with such ligands as substituted pyridines to give $Re(CO)_2(NO)Cl_2L$; the reaction is first order both in dimer and in the entering ligand[276].

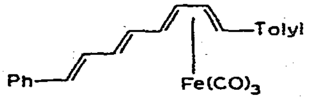
The interchange of XXXIX and XL has been shown to proceed directly, as well as via the intermediate XLI, and to be first order, unaffected by added triphenylphosphine, and little changed between diglyme and toluene as solvents[277]. The reaction of cyclooctatetraeneruthenium tricarbonyl with phosphines to give diphosphineruthenium tricarbonyl compounds is first order in complex and phosphine, even at high phosphine concentrations, and the entropy of activation is negative. The reaction is faster for ruthenium than for iron, and for more basic phosphines, but is not shown by amines. Thus the slow step of the reaction involves attack by phosphine at a soft electron-accepting site in the complex[278]; the reviewer notes that in addition to the central metal atom, the organic ligand and coordinated CO present such sites. Carbonyl exchange in $Co(CO)_2(NO)PPh_3$ obeys a two-term law, being $S_N1 + S_N2$ in poor donor solvents (the influence of solvent being small), while better donors increase the apparent unimolecular rate, no doubt by the $S_N1(S)$ mechanism[279]. The reac-



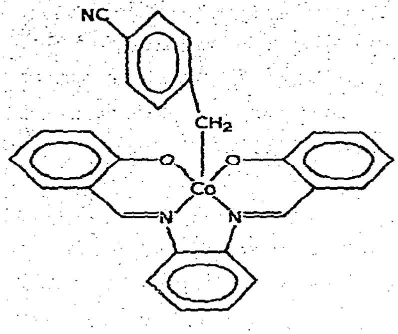
XXXIX



XLI



XL



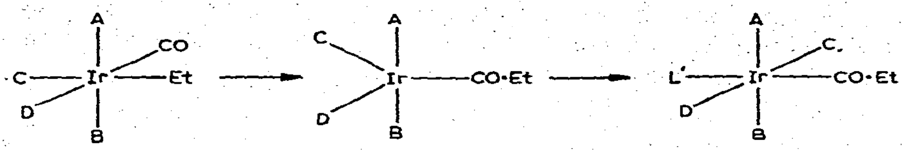
XLII

tion of $(\pi\text{-}C_5H_5)_2Ni_2(CO)_2$ with phosphines, to give nickelocene and $Ni(CO)_2L_2$, is generally first order in both reagents; with tri-n-butylphosphine, there is spectroscopic evidence for intermediates, and it is suggested that the rate-determining step is asymmetrical bridge cleavage[280].

The conversion of phenylmethoxycarbenepentacarbonylchromium to the phenylalkylaminocarbene is described as first order in each of the reagents, but also in proton acid and proton base. This is consistent with a rate-determining attack by base-activated amine on a substrate the methoxy group of which is hydrogen bonded to acid; and there is NMR evidence for such hydrogen bonding[281]. Five-coordinate cobalt(II) Schiff's base complexes react with *p*-cyanobenzyl halides, RX, to give such products as XLII, according to the scheme

$$\text{Co(saloph)L} + \text{RX} \longrightarrow \text{Co(saloph)LX} + \text{R}\cdot \text{ (slow)}$$
$$\text{Co(saloph)L} + \text{R}\cdot \longrightarrow \text{Co(saloph)LR (XLII)}$$
$$\text{Co(saloph)LX} + \text{L} \longrightarrow \text{Co(saloph)L}_2^+ + \text{X}^-$$

Among amines L, basicity causes faster reaction, but where L is a phosphine there is no such simple ordering[282]. The kinetics of the isomerisation of *cis*-$Pt(PEt_3)_2$(*o*-tolyl)Cl suggest chloride loss, and rearrangement of the resultant *cis*-like species to a *trans*-like form, as intermediate steps[283]. The decarbonylation of pyruvoylpentacarbonylmanganese is first order, and far too slow for pyruvoyl derivatives to be intermediates in the reactions of acetylpentacarbonylmanganese with nucleophiles. Such reactions are therefore not strictly analogous to those of methylpentacarbonylmanganese, which involve methyl migration to give acetyl derivatives[284]. The oxidative addition of benzyl halides to $(\pi\text{-}C_5H_5)Rh(CO)PPh_3$, to give arylacetyl derivatives, is first order in each component, the rate increasing from chloride to bromide to iodide. The related reaction of allyl iodide is apparently similar, but in fact involves the equilibrium formation of the cation $(\pi\text{-}C_5H_5)Rh(CO)(PPh_3)(\sigma\text{-}C_3H_5)^+$, which slowly reacts with iodide to give the final allylacyl product[285]. The analogous reaction with methyl and ethyl iodides have been studied, for complexes of all three metals of the cobalt group. The reactions resemble those of the benzyl halides, being first order in each



component; they are much faster for the methyl than the ethyl iodide, more rapid in more polar solvents, and faster for iridium than for the other metals[286]. Carbonyl ethyls of the type $EtIr(CO)_2Cl_2L$ react with donors to give acyls Et–CO–$Ir(CO)Cl_2LL'$. The kinetics of this reaction show the first step to be ethyl migration, and its stereochemistry implies the sequence XLIII, since L′ enters between ligands initially *trans* to ethyl and to CO[287]. Relatedly, the kinetics, and solvent dependence of the reaction of $EtPt(CO)(Cl)AsPh_3$ with triphenylarsine, are consistent with an initial equilibrium formation of Et–CO–$Pt(Cl)AsPh_3$ and the subsequent addition of the incoming ligand to this species[288]. Both steps in the carbonyl–carboxyl equilibrium are first-order in each of the components[289].

$$PtCl(PPh_3)_2CO^+ + ROH \rightleftharpoons PtCl(PPh_3)_2\cdot COOR + H^+$$

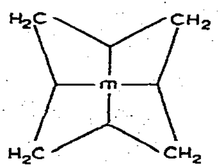
Several reports have appeared of reactions in which the mechanism of displacement of metal from an organic residue is bimolecular electrophilic attack at coordinated carbon. Such reactions include those of Hg^{II} and Tl^{III} with pyridylmethyl compounds of pentacarbonylmanganese[290], and more rapidly, of cyclopentadienyldicarbonyliron[291], and of Hg^{II} with alkylcobalamines and alkylcobaloximes[292,293].

The isomerisation of the tricarbonylchromium complex of benzyl thiocyanate to the isothiocyanate is a relatively rapid process, in accord with the known ability of the coordinated metal to stabilise the benzyl cation[294].

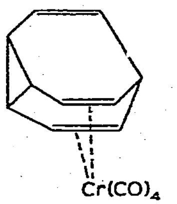
The thermal insertions of stannous halides into the dimers of cyclopentadienyldicarbonyliron[295] and cyclopentadienylcarbonylnickel[296] have been studied; in the first case the kinetics (in tetrahydrofuran) appear to imply an activated (*e.g.* mono-bridged) isomer as intermediate, while the latter reaction is first order in each component. The kinetics of the reversible displacement of triphenylphosphine from $IrH(CO)(PPh_3)_3$ by dihydrogen imply a dissociative mechanism[297]. The racemisation of $(\pi\text{-}C_5H_5)Mn(COOR)(PPh_3)NO$ is first order; the entropy of activation is positive, as expected for a dissociative mechanism[298]. The reaction of nickelocene with thiols is first in each component, is relatively insensitive to changes in solvent, and shows a primary isotope effect for deuteration of the sulphur–hydrogen bond. The proposed mechanism is 1,2-elimination of $H\text{–}C_5H_5$ from an intermediate $(\pi\text{-}C_5H_5)Ni(RSH)(\sigma\text{-}C_5H_5)$, followed by dimerisation of the resultant fragment to give the final product, $[(\pi\text{-}C_5H_5)Ni]_2[SR]_2$ [299].

Mechanistic studies (see also Kinetics, above)

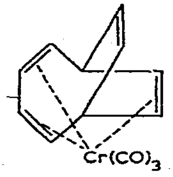
Several theoretical studies have appeared of organic reactions at metal centres; these studies are not all in agreement. Energy level correlation diagrams indicate that the thermal rearrangement pathways of fluxional organometallics are governed by the highest occupied molecular orbital, and that such processes as migration in cyclopentadienyls are expected to proceed by a 1,2-shift mechanism[300]. The removal of symmetry restrictions on $2\pi + 2\pi$ suprafacial cyclo-addition reactions is described as depending on a rearrangement of the metal electrons; this in some cases would imply a decrease in ligand field stabilisation energies and hence an activation energy barrier. The results are related to olefin metathesis, considered to proceed through a cyclobutane-like transition state[301,302]. It has independently been suggested that promotion of a metal to an excited state as a result of metathesis may not preclude reaction and indeed may in some cases play an important role in catalyst regeneration[303]. However, mechanisms involving a cyclobutane intermediate have been criticised on the grounds that free cyclobutane is not formed under thermodynamically favourable conditions, and it is suggested that the intermediate may be a tetramethylene complex XLIV; a molecular orbital description is given[304].



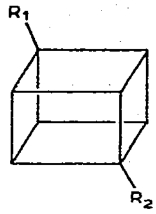
XLIV



XLV

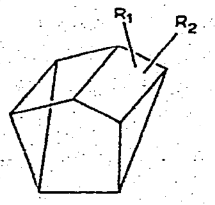


XLVI

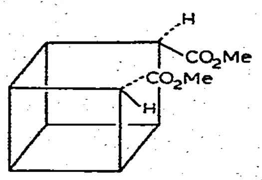


XLVII

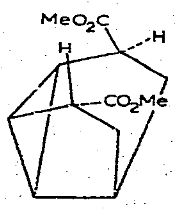
There has been an upsurge of interest in the mechanisms of Woodward–Hoffmann forbidden skeletal rearrangements of organic polycyclic systems under the influence of transition metals. One such process in which a discrete metal complex is implicated is the thermal rearrangement of the bullvalene-containing species XLV to XLVI on heating[305]. Often, the coordination of the metal is inferred indirectly. Thus the silver ion-catalysed isomerisation of disubstituted cubanes [XLVII] to cuneanes [XLVIII] is facilitated by electron-donating groups R_1, R_2 [306]. The rearrangement of XLIX and its isomers to L is stereospecific; thus



XLVIII

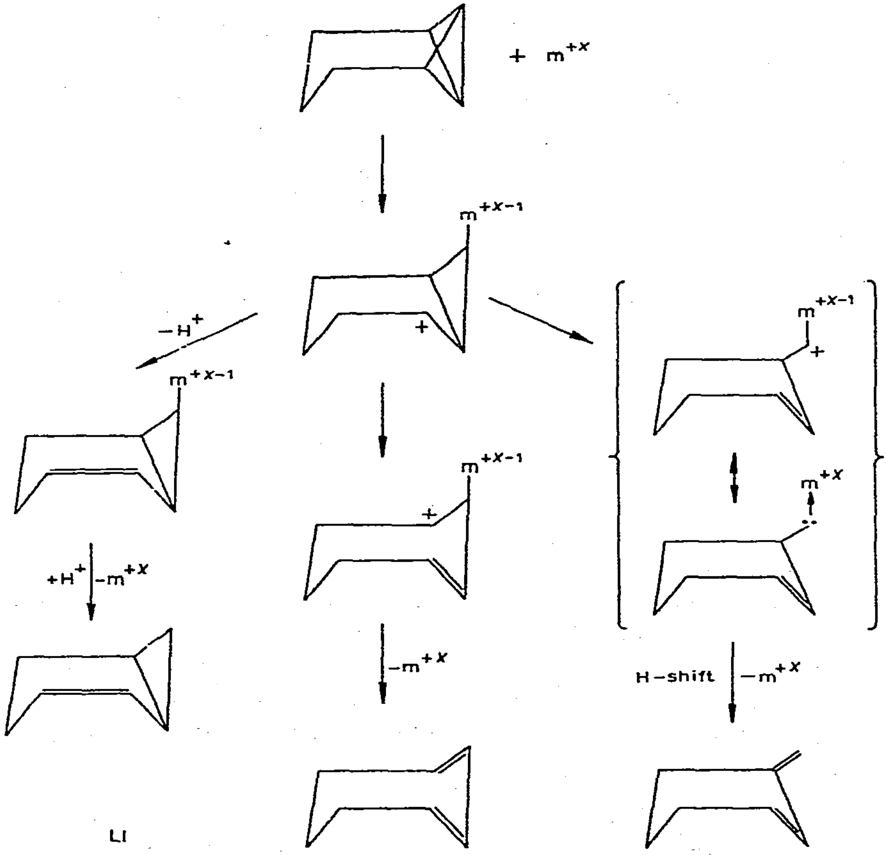


XLIX



L

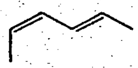
the *endo,endo* starting material shown gives the *endo,endo* product. However, the resultant relief of steric strain peculiar to this isomer does not affect the rate, suggesting that coordination of starting material by Ag^I, rather than skeletal rearrangement, is rate-determining[307]. The extreme formulation of the complex between silver(I) and a strained polycyclic species would be as a silver(III) species; the behaviour of model Tl^{III} compounds suggests that in these, heterolysis of silver—carbon bonds would generate carbonium derivatives, which would indeed show skeletal rearrangements of the type observed[308]. An alternative formalism is electrophilic attack by the metal-ion catalyst on a strained carbon—carbon bond. This process, which has the same effect as insertion followed by heterolysis, could be followed by a variety of rearrangements, as illustrated for tricycloheptane in scheme LI[309].



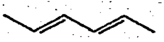
LI

LII

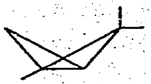
LIII



LIV

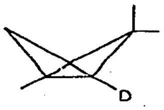


LV

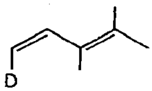


LVI

The kinetics of the rearrangements of bicyclobutanes by silver(I) ions indicate reversible formation of complexes which are the reactive species. The reactions are highly stereospecific, LII and LIII giving LIV and LV respectively, while on heating in the absence of catalyst LII gives LV and LIII gives LIV[310,311]. However, it is not the case that the rearrangements are symmetry controlled, since LVI is rearranged by silver ions to a mixture of 4-*cis*- and 4-*trans*-2-methyl-2,4-pentadienes[312]. The isomerisations of LIII by $(PhCN)_2PdCl_2$, $[Rh(CO)_2Cl]_2$, $HgBr_2$ and CuCl, unlike that catalysed by Ag^I, give a mixture of dienes, including one that can only be formed by hydrogen migration[313]. It has been suggested that the higher specificity of silver-catalysed rearrangements is a general phenomenon, associated with the formation of three-centre bonds at silver but of complete insertion intermediates at, for instance, rhodium(I)[314]. However, even the latter can be a fully specific catalyst, converting LVII quantitatively to LVIII[315]. The precise rearrangement pathway depends not only on the catalyst metal but on the attached ligands, bis(benzonitrile)palladium chloride giving different products in the rearrangement of LVI than does allylpalladium chloride dimer[316]. Moreover, there are hidden complexities even in apparently simple cases. Specifically deuterated bicyclopentane is isomerised by rhodium carbonyl chloride dimer to cyclopentene with statistical scrambling of the position of the deuterium label, although the catalyst does not cause randomisation in specifically labelled cyclopentene[317]. The rhodiumcarbonyl chloride-induced rearrangement of tricycloheptane gives 1-methylene-2-cyclohexene, as required by the carbene elimination (the authors call this process retro-carbene addition) route of scheme LI[318]. The final stage of this route is a 2,1 hydrogen shift, which is not possible in the similarly-catalysed rearrangement of the tetramethylbicyclobutane LIX, since the intermediate LX lacks a hydrogen atom at C(2), and vinyl migration is invoked to explain the observed product LXI[319]. Of course, the occurrence of

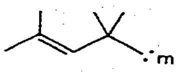


LVII

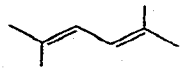


LVIII

LIX



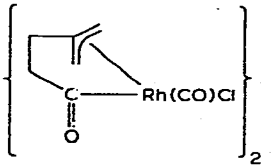
LX



LXI

carbene intermediates in specific cases does not imply their general necessity. Thus both bis(benzonitrile)palladium dichloride and silver ion convert 1-diazomethyl-2-cyclohexene to 1-methylene-2-cyclohexene, which is also the product from the reaction of tricycloheptane with the palladium catalyst, but the silver ion-catalysed rearrangement of this hydrocarbon proceeds by one of the different routes of LI to give cycloheptadiene[320]. The silver ion-catalysed rearrangement has been studied in further detail, the effects of deuteration on rates and product ratios in the rearrangements both of tricycloheptane and of methylated species being determined. The evidence is that the primary step is indeed, as required by scheme LI, cleavage of an *exo*, rather than the central, carbon—carbon bond of the bicyclobutane system[321].

Related to the rearrangements of polycyclic systems are the reactions of methylenecyclobutane with palladous chloride and with $[Rh(CO)_2Cl]_2$. The former reaction gives a mixture of the dimers of 2-(β-chloro)ethylallylpalladium chloride and 1-methyl-2-chloromethylallylpalladium chloride, while the latter gives LXII; thus in all cases the products are consistent with cleavage of the C(2)—C(3) bond, with or without hydrogen migration[322] The converse of catalysed ring opening is the silver ion modified addition of benzyne to cyclic polyenes. The products can be interpreted in terms of addition of $C_6H_4Ag^+$ to the polyene and of silver ion loss, with concomitant ring closure; this may be preceded or followed by allowed sigmatropic rearrangements[323].



LXII

A second topic in which interest has rapidly expanded is the mechanism of cleavage of metal—carbon bonds (see also references[290–293]); a possible reason for this is the undermining of views concerning the inherent lability of such bonds[324,325] by such developments as the extension[326] of the range of metal trimethylsilylmethyl derivatives.

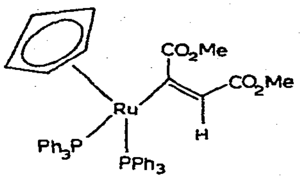
The thermolysis of species $(\pi\text{-}C_5H_5)_2Ti(Cl)R$ has been studied; in one case at least ($R = PhCH_2CH_2$) decomposition obeys the same Arrhenius law above and below the melting point. It is inferred that the rate-determining step is unimolecular; the product-determining steps are not, involving disproportionation, hydrogen abstraction, or ligand combination. The activated organic species is described as radical- or carbonium-like, but still in the coordination sphere of titanium[327]. The fragmentation patterns of organic groups attached to chromium(III) include homolytic cleavage, α-hydride and β-hydride elimination[328]. The reaction of β-deuterated chromium and iron derivatives with olefins demonstrates migration of the β-atom[329]. The bromolysis of the carbon—metal bonds in t-Bu —CHD—CHDFe$(CO)_2$-$(\pi\text{-}C_5H_5)$[330] and in (*cis*-4-bromocyclohexyl)cobaloxime pyridine[331] give the inversion products t-Bu—CHD—CDHBr and *trans*-1,4-dibromocyclohexane. It thus[330] appears plausible that the overall retention of configuration, in the bromolysis of the product from oxidative addition of Ir^I to α-bromopropionic acid[332], should be reinterpreted in terms of inversion, rather than retention, both at the formation of the metal–carbon bond and at its cleavage. Alkylcobaloximes and alkylcobalamines with electron-withdrawing β-groups undergo reversible deprotonation to give olefin complexes of cobalt(I)[333]. The ready decomposition of β-hydroxyethylcobaloxime by HCl proceeds via an ethylene complex of Co^{III}; relatedly, the β-acetatoethyl complex undergoes ready solvolysis in alcohols to give the corresponding β-alkoxy species[334]. Formal carbonium ion transfer between cobalt(I) and alkylcobalt(III) species is first order in each component, and shows a low energy and negative entropy of activation. This is consistent with strong steric compression of the alkyl in the transition state of an S_N2 reaction. Cobalt(II) acts as an equimolar mixture of Co^I and Co^{III}, this disproportionation being extensive under the conditions studied[335]. Thus the apparent methyl radical transfer from Co^{III} to Co^{II} species[336] may be of this type, and the reaction of Co^{III} methyl cations with Co^I methyl anions to give dimethylcobalt(III) species[337] may be nucleophilic capture of methyl by Co^I, rather than electrophilic capture by Co^{III}. While methyl transfer from methyl vitamin B_{12} to Hg^{II} or Tl^{III} is regarded as a simple acid-base process (compare ref. 290), transfer to Pt^{III} or Au^I requires the presence of Pt^{IV} or Au^{III} and is regarded as a 2-electron switching process[338]:

$$Pt^{IV} + Pt^{II} + Me{-}Co^{III} \rightarrow Pt^{II} + Pt^{IV}{-}Me + Co^I.$$

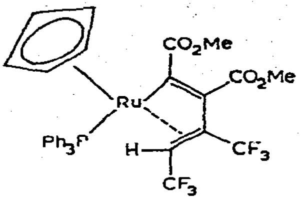
The deuterogenation of cyclooctene (but not of cyclohexene or of octene) catalysed by $(Ph_3P)_3RhCl$ involves exchange of hydrogen throughout the ring. The probable mechanism is reversible elimination of cyclooctene from an intermediate cyclooctyl complex, this loss being facilitated by steric repulsions within a saturated C_8 ring[339].

Thermal decomposition of *cis*- or *trans*-1-propenylcopper(I) or its tributylphosphine complex gives copper(0) and 2,4-hexadienes with retention of configuration; this excludes radical mechanisms[340]. The reaction of ethylcopper with n-propylcopper gives ethane and propene, while that with isopropylcopper gives ethylene and propane. This is not as expected from a hydride elimination–hydride reduction[341] process, and bi- or polynuclear alkyl systems are invoked[342]. Product analysis and kinetic studies of the catalytic decomposition of Grignard reagents by silver ions point to the intermediacy of alkylsilver compounds; these do not decompose by radical loss, but by coupling reactions, although radicals can be generated by the attack of alkyl halides on silver atoms in the reaction mixture[343].

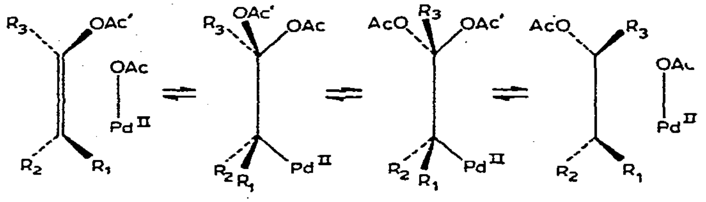
Photochemical substitution of ^{13}CO into piperidinepentacarbonylmolybdenum occurs mainly at the equatorial position; conversion by unimolecular reaction to $Mo(CO)_5AsPh_3$ leads to randomisation of the position of the label, showing that the pentacarbonylmolybdenum intermediate is long enough lived for axial–equatorial interchange[344]. The attempted preparation of stereospecifically labelled pentacarbonylmanganese bromide by bromolysis of *cis*-$Mn(CO)_4(^{13}CO)CH_3$ gives a statistical mixture of *cis*- and *trans*-labelled products[34]. The reduction of 1-haloalkylcobaloximes to the 1-deuteroalkyl species by borohydride in



LXIII



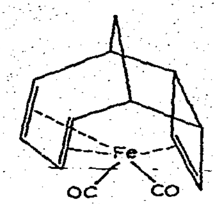
LXIV



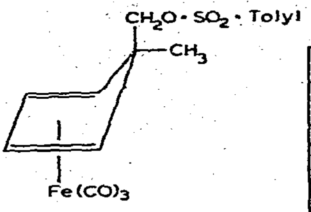
LXV

O-deuteromethanol is attributed to deuteron addition to an intermediate cobaloxime(I) carbene species[346]. The insertion of hexafluoro-2-butyne into LXIII gives LXIV; a suggested mechanism is initial deprotonation of the β-carbon of LXIII[347]. Product analysis in the exchange reaction of perdeuteropropene with tetracarbonylcobalt hydride shows protonation to occur mainly at C(2), consistent with a predominantly Markovnikov 1,2-addition–elimination mechanism[348]. The addition of allyls of nickel and palladium to norbornene[349,350] or norbornadiene[351] is specifically *cis,exo*. Addition–elimination is responsible for the palladous chloride and palladous acetate catalysed *cis–trans* isomerisations of vinyl esters. In particular, the reaction is not shown by cyclic enol acetates, and isomerisation is accompanied by exchange with labelled acetate, as in mechanism LXV[352,353]. The insertion of C_2F_4, hexafluoro-2-butyne or CO into one or both platinum–carbon bonds of complexes L_2PtMe_2 is promoted by electron-donating ligands L; thus coordination of the electron-demanding entering group is the crucial step[354]. In contrast, the facility of the insertion of ethylene into the platinum–hydrogen bond of *trans*-$PtH(PMePh_2)_2$ acetone$^+$ indicates that displacement of the ligand *trans* to hydride, with formation of a four- rather than five-coordinate intermediate, is in this case rate-determining[355]. A cyclisation mechanism involving as intermediates cyclobutadiene dicarbonyliron bis(carbomethoxy)acetylene and an iron carbonyl complex of bis(carbomethoxy)-Dewar benzene has been put forward for the generation of dimethylphthalate from butadieneiron tricarbonyl and bis(carbomethoxy)acetylene; the mechanism is verified by the preparation of LXVI from butadieneiron tricarbonyl and cycloheptatriene[356]. The *exo*-tosylmethyl cyclopentadiene complex LXVII is readily hydrolysed by acid to LXVIII; the *endo* isomer is inert under the conditions used[357].

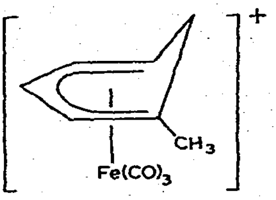
Allyltrimethyltin reacts with the pentacarbonyl halides of manganese and rhenium to give the tetracarbonyl π-allyls; σ-allyls are not intermediates as the rhenium pentacarbonyl σ-allyl does not decarbonylate under the conditions used[358].



LXVI

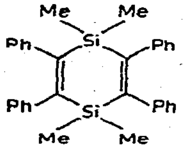


LXVII



LXVIII

Protonation in the conversion of butadieneirontricarbonyls into allylirontricarbonyl cations has been shown by elegant labelling experiments to be stereospecific, opposite in sense to hydride abstraction, and therefore *endo*[359]. Arenetricarbonylmanganese cations add cyanide initially to the ring as an *exo* substituent; heat causes rearrangement to arenedicarbonylmanganese cyanide[360]. The base-catalysed exchange at the methylene group between cycloheptatriene tricarbonyliron and *O*-deuteromethanol is immeasurably fast; $C_7H_7Fe(CO)_3^-$, the presumed intermediate, can be isolated when the substrate is deprotonated by butyllithium[361]. The platinum-catalysed disproportionation of methylsilicon hydrides involves silene complexes, since LXIX can be trapped by addition of diphenylacetylene to the system[362].



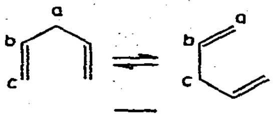
LXIX

Catalysis

Homogeneous catalysis by Ru^{II} has been reviewed[363], as have the carbonylation of monoenes and mono-ynes[364], the influence of ligands on the activity and specificity of metal complex catalysts[365], and the use of organometallics as polymerisation catalysts[366,367].

Platinum(II) catalyses exchange between hydrocarbons and deuterium acetate; platinum metal does not show the reaction, which presumably involves oxidative addition of alkyl hydride to the platinum [368,369]. Toluenetungstentricarbonyl is an efficient catalyst for the disproportionation of nonene to octenes and decenes only in an open system (from which CO loss is possible); this is consistent with the postulated tetramethylene intermediate[304] which is an eight-electron donor[370]. The arenetricarbonyl complexes of the Group VI metals are effective Friedel–Crafts catalysts (presumably through an activation-exchange mechanism) and it is proposed that they be used as such in preference to conventional Lewis acids[371].

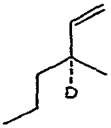
It has been suggested that the vinylation of benzene (or arylation of alkenes), catalysed by palladium(II), proceeds via vinylpalladium complexes as intermediates, and it has been-



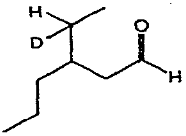
LXX

demonstrated that such species can indeed vinylate benzene[372,373]. The arylation shows an isotope effect as between benzene and deuterobenzene, but not as between proto- and deutero-alkenes; thus aryl–hydrogen bond breaking is part of the slow step, while vinyl hydrogen bond breaking is not[374].

Labelling experiments establish the stereochemistry LXX for the rearrangement of dienes by reduced nickel; this is in accord with an allylnickel alkene complex as intermediate[375]. The complexes $(Ph_3P)_2Ni(Ar)Br$ (Ar = aryl) dimerise ethylene. Exchange between ethylene and C_2D_4 is also catalysed and indeed proceeds more rapidly. Only one hydrogen is exchanged at a time; thus this is a hydride transfer rather than a dismutation reaction[376]. Butadiene reacts with water and carbon monoxide under the influence of palladous acetate and triphenylphosphine to give 1-hydroxy-2,7-octadiene[377], while a similar catalyst converts butadieneammonia into tris(2,7-octadienyl)amine[378]. Deuterium labelling experiments have shown that addition–elimination processes, rather than direct hydroformylation of an alkyl group, are responsible for the conversion of LXXI to LXXII[379]. It has been suggested that the principal differences between cobalt carbonyl itself as a hydroformylation catalyst and its phosphine derivatives are due to differences in the working pressure of CO used; and it is further suggested that cobalt hydrides could act as direct hydrogenation catalysts[380]. Molybdenum thioglycerol complexes in the presence of a trace of iron catalyse the reductions of dinitrogen to ammonia and of acetylene to ethylene by borohydride; these processes are stimulated by ATP, a probable function of which is to phosphorylate a hydroxy group attached to molybdenum, thus facilitating its loss from the coordination sphere of the metal[381,382].



LXXI



LXXII

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