GENERAL, THEORETICAL AND PHYSICAL INVESTIGATIONS IN TRANSITION METAL ORGANOMETALLIC CHEMISTRY IN 1975*

Antony J. Rest

Department of Chemistry, The University, Southampton SO9 5NH, Great Britain.

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* Transition Metals: Physical Methods and Results of General Interest, 1974 see J. Organometal. Chem., *123* (1976) 75-204.

INTRODUCTION

Previous Annual Surveys have covered the journals arriving in the library of the reviewer during a calendar year but, because of the wide variation in arrival times of different journals in different countries round the world, it has been decided to change over to a system of covering *complete volumes* of journals for the particular calendar year.

A new international English-language journal, *Transition Metal Chemistry*, appeared for the first time in 1975. The new journal sets out to bring under one cover papers which are related by subject matter (doubtless containing papers on transition metal organometallic chemistry) but which otherwise would continue to be scattered over a great variety of journals. To mark the hundredth issue of the *Journal of Organometallic Chemistry* the editors invited some leading research workers to contribute a personal account of their involvement in the field and to discuss its future development. The result is fascinating and accounts are included under appropriate headings.

A unified system of notation for geometric isomers, including central atom symmetry and optical isomers for mononuclear complexes, has been presented for known geometries up to coordination number 6 [1]. This notation system, which makes extensive use of the complimentary features of the Cahn, Ingold and Prelog (CIP) system for tetrahedra and the I.U.P.A.C. system, has been adopted for the Indexes to *Chemical Abstracts*.

A Crystallographic Data Centre has been established at the University of Cambridge, U.K., to help specialists and non-specialists alike to keep up to date with the rapidly increasing literature on organic and organometallic crystal structures [2].

REVIEWS (See also under individual headings)

General reviews of metal carbonyls and their complexes have described *The Life Work of Walter Hieber* [3], the basicity and reactivity of metal carbonyls [4], perspectives in the synthesis of novel organometallic compounds using metal carbonyl anions [5] and the reactivity patterns of metal carbonyl anions and their derivatives [6]. Reviews in specific areas have detailed some new kinetic and mechanistic aspects of the substitution reactions of metal carbonyl complexes of chromium, molybdenum and tungsten [7] and, as part of a survey of the platinum metal carbonyls and their derivatives, ruthenium and osmium carbonyls [8].

Reviews of the nickel group metals have described organometallic reactions involving hydrido-nickel, -palladium and -platinum complexes [9], synthetic applications of d^{10} metal complexes [10] and reactions of Pd(0) and Pt(0) complexes with electronegatively activated small rings [11].

Reviews concentrating on the organic ligand have surveyed the preparation, properties and reactivity of transition metal carbonyl-carbyne complexes [12], polyolefin carbonyl derivatives of iron, ruthenium and osmium [13], the role of $(\eta^4-C_4H_4)Fe(CO)_3$ in the cyclobutadiene problem [14], arene transition metal chemistry [15] and the synthesis of some perfluoroorganometallic types R_f-M [16]. Another basis for classification is the donor atom and reviews have described the coordination chemistry of NO [17], chemical and biological aspects of the fixation and reduction of molecular N_2 [18], recent developments in the chemistry of PF_3 complexes of the platinum metals [19] and S atoms as ligands in metal complexes [20].

Metal to metal bonds continues to be an active area and reviews have appeared on quadrupole bonds and other multiple metal to metal bonds [21], organometallic complexes containing bonds between transition metals and Group IIIB metals [22] and oxidation-reduction and related reactions of metal-metal bonds [23].

The importance of organic synthesis *via* metal reagents has led to reviews on $Na_2Fe(CO)_4$ - a transition metal analogue of a Grignard reagent [24], organic synthesis using transition metal carbonyl compounds [25], industrial reactions using CO with metal carbonyls as catalysts [26], transition metal-carbene complexes in synthetic organic chemistry [27], palladium-catalysed organic reactions [28] and transition metal catalysis of the so-called forbidden pericyclic reactions, including a discussion of the Woodward-Hoffmann rule [29].

Massive Russian-language reviews have appeared on π-complexes of mono-olefins [30], acetylene π-complexes of transition metals [31], mono-π-cyclopentadienyl compounds of transition metals [32], bis-π-cyclopentadienyl compounds of transition metals [33], allyl derivatives of metals and related compounds [34] and also alkylation and arylation of unsaturated compounds using complexes of transition metals [35].

A monograph on *Organochromium Compounds* has been published [36].

THEORETICAL STUDIES (See also Ionisation Studies)

The M.O. methods (see below) for the calculation of the electronic structure of transition metal compounds have been reviewed [37] but in contrast Pauling has described a simpler valence-bond theory [38]. An equation relating the strength, i.e. bond-forming power, of an *spd* hybrid bond orbital to the angle it makes with other bond orbitals is formulated and applied to the structures of transition metal carbonyls and other substances by the valence-bond method. The theory gives results that agree well with those obtained by the complicated and laborious calculation of sets of orthogonal hybrid orbitals with maximum strength.

A Hartree-Fock-Slater method, with a basis set comprised of a double-zeta set of STO's supplemented with two *4p* sets on the central atom, was used to calculate the elelectronic charges (Q) on the metal (when present), C and O atoms in CO, $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$ [39]. Good agreement with available experimental data on the C and O 1s-electron binding-energy shifts (ΔE) in $Fe(CO)_5$ and $Cr(CO)_6$ was obtained in calculations with the relaxation-potential model. Comparison of these results with corresponding Q and ΔE values obtained by other workers in Hartree-Fock calculations with the Koopmans' theorem showed agreement for the Q values, and demonstrated that the failure of Koopmans' theorem calculations to reproduce the experimental ΔE values was due to neglect of the 1s-orbital relaxation energy change in going from free CO to coordinated CO, and not due to deficiencies in the basis sets used. Discrete variational Hartree-Fock-Slater X_α calculations are reported on $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$, $Co(CO)_4^-$, $Fe(CO)_4^{2-}$, $Mn(CO)_5^-$, $Mn(CO)_6^+$ and $V(CO)_6^-$ [40]. The description of complex binding in $Ni(CO)_4$ according to these calculations differs markedly from the one obtained in MSX_α and Hartree-Fock calculations which contradicted one another. It was found that the relative magnitudes of σ-donation and π-back-donation are approximately equal for neutral complexes but large changes in π-back-donation occurred in the anions. The changes are correlated with the observed terminal CO stretching frequencies and force constants, and valence electron ionisation potentials were predicted well by transition-state calculations.

An extension of the CNDO/2 formalism has been proposed for investigating the electronic structure of transition metal complexes [41]. The results for $Ni(CO)_4$ and $Ni(PF_3)_4$ agreed well with those of *ab initio* calculations and with some experimental data. Such a semi-empirical approach may be performed, using *ab initio* results as reference data, in order to interpret the physical and chemical behaviour of large series of complexes in their ground state. In a subsequent paper the approach was extended to $Fe(CO)_5$ and $Cr(CO)_6$ [42]. The validity of the parametrization (parameters are now available for the Cr, Fe and Ni set) was supported by the pretty good agreement which was found between energy level distributions and independent results for $Ni(CN)_4^{2-}$. A parametrization in a CNDO-type M.O. method has been presented for Pt compounds [43]. By the use of this parametrization the electronic spectra of $PtCl_4^{2-}$ were calculated and agreed well experimental spectra in transition energies and assignments and so parametrized calculations were extended to C_2H_4-Pt(II), C_2H_2-Pt(II), C_2H_4-Pt(0) and C_2H_2-Pt(II) complexes, where good agreement was found between calculated and experimental transition energies of Zeise's salt. Some trends emerging from the calculations are: (a) donation of electrons from C_2H_4 and C_2H_2 to the metal, Pt(II) > Pt(0); (b) strength of the π-bonds in the C_2H_4 and C_2H_2 moieties, Pt(II) > Pt(0); (c) strength of the coordination bond between C_2H_4 and C_2H_2 and the metal, Pt(II) < Pt(0) and C_2H_4 < C_2H_2.

Parameter-free M.O. calculations using the Fenske-Hall model have been performed on several d^0, d^1 and d^2 M(IV) (η^5-C_5H_5)ML_2 molecules and the results have been completely compatible with the interpretation of EPR and photoelectron spectral measurements as well as with the crystallographically† acquired bond-length and bond-angle data [45]. The M.O. calculations revealed that the LUMO for d^0 Ti(IV) complexes and the HOMO for the d^1 and non-hydridic d^2 M(IV) complexes possessed analogous orbital characters, principally associated with the metal d_{z^2} and $d_{x^2-y^2}$ A.O.'s with considerable contribution from the $3p$ A.O.'s of the sulphur and chlorine L ligands. Similar calculations have also been carried out on ligand-bridged complexes of the $Fe_2(CO)_6X_2$-type where it was found that variations of the bridging ligands did not markedly affect the nature of the Fe-Fe interactions [46]. The orbital character of the a_1 HOMO in each neutral species was found to correspond closely to the classical "bent" Fe-Fe bond with the b_2 LUMO being its antibonding counterpart. The results of the M.O. study, which provides the first detailed description of the electronic structure and bonding characteristics of this important dimeric metal cluster system, were correlated with spectroscopic and crystallographic data.

Self-consistent charge and configuration molecular orbital (SCCC-MO) calculation results have been correlated with relative reactivities for the isoelectronic series π-AM(CO)$_3$ (AM = (η^6-C_6H_6)Cr, (η^5-C_5H_5)Mn, (η^4-C_4H_4)Fe, (η^3-C_3H_5)Co and (η^2-C_2H_4)Ni) [47]. Variations in 5σ and π^* orbital populations were interpreted as implying a slightly weaker σ and stronger π CO bond across the series and this trend is reflected experimentally by an increase in the frequency of both A_1 and E ν(CO) modes. The decreases in M-C(O) overlap population and π^* population in the series Cr > Mn > Fe > Co were used to predict an increasing S_N1 character across the series since both parameters indicate weakening of the M-CO bond. Gradations in reactivity among the Group VI metallocenes have been studied theoretically by an extended Hückel M.O. analysis of one-electron energy changes associated with the formation of reaction products and intermediates and also by an evaluation of the associated electron-electron repulsion energies in terms of Racah repulsion parameters [48]. A satisfactory accounting was obtained for the different stabilities observed for (η^5-C_5H_5)$_2$Cr(CO) and (η^5-C_5H_5)$_2$Mo(CO) and the formation of the dihydride (η^5-C_5H_5)$_2MoH_2$ from a (η^5-C_5H_5)$_2$Mo intermediate and a H_2 molecule. The formation of (η^5-C_5H_5)$_2$W(H)Ph complexes by insertion into aromatic C-H bonds was discussed in terms of repulsive

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† A note of caution has been struck by the discovery that the long O-O bond length (1.625 Å) reported for $IrO_2(Ph_2PCH_2CH_2PPh_2)^+$ is an artefact caused by crystal decomposition [44]. This means that the widely held and accepted deductions drawn about the bonding between the O_2 moiety and the metal, e.g. the rate and degree of O_2 uptake could be correlated with the O-O bond length in Rh and Ir complexes, are no longer tenable.

ligand interaction and facilitated ring dislocations similar to those held responsible for the unique stability of $(\eta^5\text{-}C_5H_5)_2W(CO)_2$.

It is now recognised that many aspects of chemistry are, in some measure, topologically determined, e.g. fluxional molecules undergoing rapid molecular rearrangements. The various mechanisms for interconversion of isomers are conveniently distinguished by the different shortest-path sequences by which one isomer can be converted into another. The shortest paths are detailed in a so-called *distance matrix* of the system and, to remedy a glaring omission in the chemical literature, a derivation of distance matrices is presented together with some proposals for innovations that will increase the information content of them [49]. A new concept of the symmetry of non-rigid molecules has been put forward [50]. It is based on the fact that the electronic energy of a molecule assumes the same value for all isometric nuclear configurations. The stereochemistry of compounds of the type $Fe(CO)_2(\eta^5\text{-}C_5H_5)Y$, where Y covers a range of univalent groups and includes groups which are capable of forming bridges to the Fe atom, has been shown to be remarkably close to a regular octahedron [51]. By assuming that the presence of octahedral geometry in a wide range of structures indicates a certain rigidity in this arrangement, it was shown that the tautomer-interconversion mechanism for $\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2$ must involve simultaneous making or breaking of two carbonyl bridge systems. A presentation was made of the general interconversion of isomers of $M(\eta^5\text{-}C_5H_5)M'(\eta^5\text{-}C_5H_5)ABCD$, where A,B,C and D are ligands which bridge in pairs, as a basis for explaining the NMR results in cluster molecules. Further insight into how CO ligands might be interchanged between two metals was obtained from calculations of the effect of overlapping filled metal orbitals with π^* orbitals of CO groups on an adjacent metal [52]. The result of such an overlap would be to transfer charge from one metal to another via a "semi-bridging" CO ligand. It seems likely that such interactions are common though incidence of semi-bridging CO ligands might have no appreciable effect on molecular geometry.

A simple model based on the interaction of ligand electron pairs and holes in the central metal charge distribution has been used to rationalise the shapes of binary transition metal complexes with fewer than 18 electrons, e.g. $Fe(CO)_4$, $Pd(N_2)_3$, $Ni(CN)_4^{2-}$ [53]. Only the orbital occupation numbers of the three highest *d* orbitals are important in determining the angular geometry because the deeper-lying *d* orbitals are predominantly involved in π-bonding. Depending upon how different the metal electronic charge distribution is from spherical, the overall geometry is sometimes intermediate between that demanded by these hole-pair forces and the structure with minimum ligand-ligand repulsion energy. The challenge of the novel structures of $M(CO)_n$ and $M(N_2)_m$ species observed by matrix isolation spectroscopy (see below), which prompted the previous work, has also provided the impetus for an alternative approach to the structures of complex molecules by breaking them up into fragments whose orbitals are easily visualised [54]. The energy ordering, symmetry, and extent in space of the valence M.O.'s of a range of geometries of $M(CO)_3$, $M(CO)_4$ and $M(CO)_5$ fragments, where M is a transition metal, are analysed in detail and then the properties of the fragment orbitals are used to examine the ability of the fragments to interact with other ligands as well as the geometrical preference of the isolated fragment. The approach has been used to probe the pyramidality of 5-coordinate fragments, metal-metal bond formation, 7-coordination, stabilisation of "umbrella" distortions of fragments, differences between $M(CO)_n$ and ML_n (L = π-donor) fragments, geometrical distortions in transition metal hydrides, and why $Fe(CO)_3$ favours bonding to conjugated dienes while $Cr(CO)_4$ coordinates preferentially with unconjugated dienes. Two of these topics have been discussed in greater detail e.g. a unified M.O. treatment of ML_5 complexes of transition metals for D_{3h} and C_{4v} geometries [55], stereochemistry of 5-coordinate complexes of the type $M(bidentate)(unidentate)_3^{x\pm}$ [56] and the stereochemistry of 7-coordinate compounds of the type $M(bidentate)_2(unidentate)_3^{x\pm}$ [57].

The consequences of applying the normalised spherical harmonic Hamiltonian to molecules of tetragonal symmetry have been discussed theoretically and illustrated with data from C_{4v} and D_{4h} complexes of Ni(II), Co(II) and Cr(III) together with the use of ground-state energy space diagrams with particular reference to the limits of linear and square-planar bonding [58]. Using the simple angular model described previously [53], the stabilisation energies of square planar, square pyramidal and octahedral d^8 and d^9 complexes were found to be equal when ligand-metal d orbital interactions only were included [59]. This implies that the bond energies between the metal and the fifth and sixth ligands are low, a situation found to be the case in practice,but only a few of the observed distortions may be rationalised by the Jahn Teller formulation. The tetrahedral-square planar isomerism of 4-coordinate complexes of Ni(II) of the L_2NiX_2 type (L = neutral ligand, X = anionic ligand) was discussed in terms of the second-order Jahn-Teller effect [60]. It was shown that, when the ligands L possess π-acceptor orbitals, the isomerization may be facilitated and it was suggested that a ready isomerization may account for the catalytic activity of these and possibly other transition metal complexes with π-bonding ligands. The second-order Jahn-Teller effect has been demonstrated to be a powerful aid to the understanding of the molecular geometry of metallocenes and related analogues in that it predicted the nature of deviations from the idealized geometry without requiring any calculations [61].

The use of n-electron polycentre bonding to hold together clusters, e.g. boron hydrides, metal carbonyls, metal-hydrocarbon π-complexes, has been reviewed [62]. The Wade electron counting scheme has been widely used e.g. the bi-capped tetrahedral arrangement of Os atoms in $Os_6(CO)_{18}$ [63] and the structures of the pyrolysis products of $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ [64], because it enables structures to be predicted and rationalises the reaction products of cluster compounds, e.g. addition of electrons, H_2 molecules, and electron pair donors, provided no ligands are displaced, since addition or removal of electrons will alter the cluster shape. An alternative approach has been to relate the cluster geometry to close hexagonal packing, e.g. the new anions $Rh_{13}(CO)_{24}H_{5-n}^{n-}$ (where n = 2 or 3) [65].

The isolation of new, relatively stable alkyl and aryl complexes $Li_2(NiPh_4).4THF$ and $Li_2(NiMe_4).4THF$ [66], $Li(Pt(Me)_5PPh_3)$ and $Li_2(PtMe_6)$ [67], $Li(AuMe_4)$ [68] and $Cr(i\text{-}C_3H_7)_4$ [69] contradicts the frequently-cited Chatt-Shaw π-bonding effect and requires the factors governing the stability and existence of such complexes to be re-evaluated.

The emergence of the computer as a piece of routine chemical equipment to investigate the nature of intervening transient non-equilibrium states in reactions has been predicted [70]. The applications surveyed were largely in the realm of organic chemistry but the challenge to the organometallic chemist is clear. The possibility for activating CO in square planar $MX(CO)L_2$ complexes (M = Rh, Ir; X = Cl, CN, OH; L = PH_3, NH_3, CO) has been studied by an iterative extended Hückel method [71]. The ability of transition metal atoms and clusters to catalyse olefin isomerisation has been traced to metal *d* orbital stabilisation of the olefin transition-state π-orbital [72] and two elegant investigations of isomerisation promoted by Fe [73] and Rh [74] have tested the validity of the mechanism based on the formation of allyl-metal-hydride intermediates. The concept of triplet instability for conventional Hartree-Fock molecular orbitals was applied to cyclodimerisations of $CH_2=CH_2$ and $CH\equiv CH$ and hydrogenation of $CH_2=CH_2$ catalysed by hypothetical nickel hydride complexes [75]. Rectangular approach of reactants was accompanied by significant bi-radical character and thus concerted one-step reactions were not necessarily energy-favourable processes. The ability of a transition metal to lift symmetry-imposed restrictions on the cycloadditions of organic ligands attached to itself has been probed by a study of the reactions of $CF_3C\equiv CCF_3$ with $BFe(CO)_3$ (B = butadiene or 2,3-dimethylbutadiene) [76]. The fact that such a normally facile concerted process should occur in an unequivocally stepwise fashion under the influence of the transition metal was used to suggest that previously reported examples of concerted 'forbidden' reactions promoted by transition metals should be re-examined with a view to eliminating completely the possibility of stepwise addition.

IONISATION STUDIES

X-ray photoelectron spectra have been reported for compounds of V [77] and Mo [78] spanning a wide range of metal oxidation states. Vanadium $2p_{3/2}$ binding energies were correlated using CHELEQ atomic charges and the "transition-state" point-charge potential equation and an excellent correlation was obtained for compounds which could be represented by a single valence-bond structure, e.g. VF_5 and $(\eta^7\text{-}C_7H_7)V(\eta^5\text{-}C_5H_5)$. In the cases of other compounds, e.g. $(\eta^5\text{-}C_5H_5)V(CO)_4$ and $V(CO)_6$, information was obtained regarding the relative contributions of various resonance structures and the importance of back-bonding by comparison of experimental and calculated binding energies. A plot of the metal binding energy versus calculated charge indicated that a binding energy shift of 1 eV corresponds to a 0.3+ charge unit on Mo. The study of several organometallic compounds showed that the strong σ-donor ligands increase the electron density about Mo producing even lower metal binding energies than those obtained for argon-sputtered metal foil. Configuration interaction calculations of the excited states of core hole ions observed as satellite peaks in the X-ray photoelectron spectra of H_2O, N_2, CO, C_3O_2 and $Ni(CO)_4$ are described [79]. It was concluded that such calculations provide a promising method of interpreting satellite structure and this was particularly gratifying for the chemically interesting molecules C_3O_2 and $Ni(CO)_4$. A survey of the X-ray photoelectron spectra of organotransition metal carbonyls revealed that both C and O 1s ionisation potentials of complexed CO ligands are lower than for free CO [80]. If the shift was taken to represent a change in the charge distribution then the measurement suggests that π-back-donation is the most important part of the M-CO bond. Two groups have found that X-ray photoelectron spectroscopy provides a complimentary method to infrared spectroscopy for distinguishing bent and linear metal nitrosyls [81,82].

The valence (He(I)) photoelectron spectra of $HMn(CO)_5$, $CH_3Mn(CO)_5$ and $H_2Fe(CO)_4$ were found to be incorrectly interpreted using Koopmans' theorem in conjunction with *ab initio* wave functions [83]. The relative ordering of the ionic states arising from metal 3*d* and Mn-X (X = H, CH_3) σ-bonding orbitals given by Koopmans' theorem was opposite to that observed experimentally and the breakdown in Koopmans' theorem was discussed in terms of orbital relaxation accompanying ionisation from the metal and from the ligand orbitals. These compounds provide a further illustration of the need for caution in using photoelectron spectroscopy to infer details of the electronic structure of the molecular ground state of metal complexes because of the shortcomings in Koopmans' theorem and it may be necessary to revise the assignments for $SiH_3Mn(CO)_5$ and $GeH_3Mn(CO)_5$ [84], $SiF_3Mn(CO)_5$ [85], and $Fe(CO)_4X_2$ (X = Br, I) [86]. Through a study of the spin-orbit coupling in $LRe(CO)_5$ complexes (L = H, CH_3, $COCF_3$, $Re(CO)_5$, Cl, Br, I) it has been possible to establish a complete assignment of the lower ionisation potentials obtained from the He(I) photoelectron spectra of these compounds [87]. The analysis of spin-orbit coupling has been shown to be a powerful technique in establishing the assignments and characterising molecular orbitals and their bonding. The failure of Koopmans' theorem which was also noted in this work [87] was attributed in part to the size of the basis set used. The sometimes striking intensity changes observed under different ionising radiation and on changing the metal atom have led to a new approach to assigning photoelectron spectra and this has been applied to the He(I) and He(II) photoelectron spectra of $M(CO)_5X$ and $M_2(CO)_{10}$ complexes ($M = Mn, Re$; $X = Cl, Br, I$) [88]. From observations of intensity changes it was deduced that for $Mn(CO)_5I$ and $Re(CO)_5Br$ the orbital ionisation sequence for the low ionisation potential region is $e(X) < b_2(M) < e(M) < a_1$ (M–X, σ-bonding) but that in $Mn(CO)_5Cl$ and $Mn(CO)_5Br$ the sequence of e orbital ionisation potentials is reversed [88]. These assignments remove several inconsistencies which existed between earlier assignments. Yet another approach to making assignments is to use the results of discrete X_α variational calculations and this has been applied to the He(I) photoelectron spectra of $Fe(CO)_5$ and $Fe(CO)_4(C_2H_4)$ where the electronic structure of the coordinated $CH_2{=}CH_2$ was of particular interest [89].

The He(I) and He(II) photoelectron spectra of $(\eta^6\text{-}C_6H_6)_2Cr$ and $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ were interpreted by all-electron *ab initio* SCF MO calculations and the change in intensity between He(I) and He(II) spectra was correlated with the AO character of the molecular orbitals [90]. Koopmans' theorem enabled the ionisation potentials to be interpreted for ionisation due to ligand M.O.'s [90] but where there was a low lying ligand orbital, as for $\eta^4\text{-}C_4H_4$ in $(\eta^4\text{-}C_4H_4)Fe(CO)_3$ [91], an incorrect ordering was again predicted for the lowest mainly metal and cyclobutadiene orbitals. A linear correlation was obtained between the calculated eigenvalues and the observed ionisation potentials for a series of ring whizzers, $(\eta^5\text{-}C_6H_7)Mn(CO)_3$, $(\eta^5\text{-}C_7H_9)Mn(CO)_3$ and $(\eta^5\text{-}C_7H_7)Mn(CO)_3$, and this was taken to suggest that deviations from Koopmans' theorem in these complexes are small so that the 7–14 eV photoelectron spectroscopy data can be adequately assigned by the results of calculations [92]. Two conclusions which emerged were: (1) the principal bonding interaction between the organic ligand and the metal is due to that of the a' (e_1'') level of the pentadienyl moiety with the metal d_{xz} orbital, and this interaction is considerably more important than the a''(e_1'')–d_{yz} interaction; (2) calculations indicate a low lying virtual level in $(\eta^5\text{-}C_7H_7)Mn(CO)_3$ resulting from the interaction of the π* level with a''(e_2'') which may play an important role in the fluxional degenerate rearrangement of this molecule.

There have been a number of reports on the He(I) photoelectron spectra of complexes containing two $\eta^5\text{-}C_5H_5$ ligands and their analogues. A study of

$(\eta^5\text{-}C_5H_5)ReH$, $(\eta^5\text{-}C_5H_5)MH_2$ (M = Mo, W), $(\eta^5\text{-}C_5H_5)_2TaH_3$, $(\eta^5\text{-}C_5H_5)MMe_2$ (M = Mo, W), $(\eta^5\text{-}C_5H_5)_2MoL$ (L = CO, $CH_2{=}CH_2$), $(\eta^5\text{-}C_5H_5)_2WL$ (L = $CH_2{=}CH_2$, C_3H_6), and $(\eta^5\text{-}C_5H_5)_2Nb(\eta^3\text{-}C_3H_5)$ has obtained a bonding model which accounts for the observed spectra and in particular a molecule within molecule approach, i.e. taking out $(\eta^5\text{-}C_5H_5)_2M$ bonding and then looking at how this unit could combine with other ligands, was found useful [93]. Spectra of $(\eta^5\text{-}C_5H_5)_2MCl_2$ complexes (M = Ti, Zr, Hf) [94] and $(\eta^5\text{-}C_5H_5)MCl_2$ and $(\eta^5\text{-}C_5H_4Me)MCl_2$ complexes (M = Ti, V) [45] were assigned using approximate CNDO and approximate non-parametrized (Fenske-Hall)-type calculations respectively. The spectra of $(\eta^5\text{-}C_5H_5)_2Fe$ and $Fe(CO)_5$ were used as a basis for the assignment of $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ compounds (X = Me, Cl, Br, I) and $\{(\eta^5\text{-}C_5H_5)Fe(CO)\}_4$ [95] and comparisons were drawn. It was found particularly useful to note that although the $(\eta^5\text{-}C_5H_5)Fe(CO)_2X$ complexes have low overall symmetry, some of the bonding features could be treated by higher symmetry methods, e.g. $(\eta^5\text{-}C_5H_5)Fe$ in terms of C_{5v}. Above 11 eV it was found that the spectra of $(\eta^5\text{-}C_5H_5)M(\pi\text{-}C_7H_7)$ complexes (M = Zr, Nb, Mo) were very similar to those of the corresponding 3*d* transition metals, but that there were considerable differences below 11 eV [96].

The He(I) photoelectron spectra of the complexes $M(PF_3)_6$ (M = Cr, Mo, W), $M(PF_3)_5$ (M = Fe, Ru), $HM(PF_3)_4$ (M = Co, Rh, Ir) and $HMn(PF_3)_5$ were assigned by analogy with those of PF_3 and the analogous metal carbonyl complexes [97]. It was concluded that: (i) PF_3 has a greater overall electron withdrawing effect than CO; (ii) *d* orbital ionisation potentials generally increase across a series and down a vertical group; (iii) M-P σ-bonding increases across a series and down a vertical group; (iv) the degree of π-bonding is not readily ascertained from the photoelectron spectra. However, using photoelectron spectra in conjunction with CO stretching frequencies and force constants, ligands were classified according to their π-bonding ability within the series of *cis* $Mo(CO)_4L_2$ complexes (L = $PR_{3-n}X_n$, where R = Me, *t*-Bu; X = H, F, Cl; n = 0-3; and L = $P(Me_2N)_{3-n}X_n$ where X = F, Cl; n = 0-2) and their relative σ donor ability was proposed to be related to the first vertical ionisation potentials [98].

The He(I) and He(II) photoelectron spectra of authentic samples of Me_6W and Me_5Ta were found to be consistent with O_h symmetry for the former and D_{3h} symmetry for the latter [99] and the spectra were so different from those of previous workers (S. Cradock and W. Savage, Inorg. Nucl. Chem. Letters, *8* (1972) 753) that the authors concluded that previous work was of a different compound! The metal-carbon bonding appeared to be mainly *d + s* in character with little *p* contribution and there was evidence for steric interaction between the Me groups of Me_6W.

A chapter on negative ion mass spectrometry of organic, organometallic and coordination compounds is of particular interest in a volume about *Mass Spectrometry* which is part of the International Review Science series [100].

The scope of mass spectrometric investigations has been considerably increased by a new technique, Field Desorption Mass Spectrometry, which is particularly valuable for non-volatile, ionic and thermo-labile compounds. The present state of the theoretical understanding of the ionisation of such compounds has been described and the special problems of the technique and prospective developments in the apparatus have been outlined [101]. Applicati of field desorption mass spectrometry to inorganic cations [102] and anions [1 and the first examples of organometallic salts [104] have been described. In the field desorption spectra of $LM(CO)_3{}^+BF_4{}^-$ (M = Fe, L = cyclo-C_6H_7, cyclo-C_7H_9, cyclo-$C_{10}H_{11}$, 2-MeO-cyclo-C_6H_7; M = W, L = cyclo-C_7H_7), $(\eta^6\text{-Ar})Fe(\eta^5\text{-}C_6H_5)^+PF_6{}^-$ (Ar = C_6H_6, C_6H_5Me, $C_6H_3Me_3$), (cyclo-C_8H_{11})Co-$(\eta^5\text{-}C_5H_5)^+BF_4{}^-$ and $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ the molecular ions or quasi-molecular ions for the cations were present in all cases usually as the base peaks in the spectra and fragment ions corresponding to metal-ligand cleavage were also formed in most cases [104].

A technique which permits the experimental detection of the consecutive formation of molecular fragments, i.e. fragment genesis, is of potential value to organometallic chemists. The technique, direct analysis of daughter ions (DADI) (equivalent to mass analysed ion kinetic energy spectrometry (MAIKES)) can be carried out with commercial mass spectrometers embodying the Nier-Johnson inverse geometry [105]. Knowledge of fragment genesis enables the chemist to clarify the fragmentation processes of molecule-ions and provides information on the structures of fragments formed in the mass spectrometer. In combination with classical mass spectrometry, DADI measurements make it easier to determine the structure of compounds, to analyse mixtures, to determine the sequences in periodically constructed molecules and to study rearrangement reactions occurring in the mass spectrometer [105]. Under suitable measuring conditions binuclear secondary ions appeared in the mass spectra of $(\eta^5\text{-}C_5H_5)Cr(\eta^6\text{-}C_6H_6)$, $(\eta^5\text{-}C_5H_5)Mn(\eta^6\text{-}C_6H_6)$, $(\eta^5\text{-}C_5H_5)V(\eta^7\text{-}C_7H_7)$ and $(\eta^5\text{-}C_5H_5)Cr(\eta^7\text{-}C_7H_7)$ in addition to a great number of ion-molecule reaction which occurred between molecular or fragment ions and neutral σ- or π-donors in the ion source of the mass spectrometer [106]. The formation and fragmentation processes of the secondary ions were discussed [106] and would presumably have considerable insight shed on them by DADI measurements.

Another technique for studying ion-molecule reactions is ion cyclotron resonance spectroscopy and, although few papers on organometallic compounds have appeared, two reports serve to illustrate the potential. The ion molecule reaction of $Fe(CO)_5$ alone resulted in the formation of polynuclear clusters containing up to four Fe atoms [107]. In mixtures with other species, substitution reactions were observed in which CO was replaced by a wide variety of σ- and π-bonding ligands resulting in unusual organometallic complexes. The basicity of $Fe(CO)_5$ in the gas phase was determined by examining H^+ transfer reactions and it was found that $Fe(CO)_5$ was only slightly less basic than NH_3 [107]. In an ion cyclotron resonance study of the gaseous ion chemistry observed in mixtures of alkyl halides and transition metal complexes the formation of M–C bonds has been reported [108]. From observation of the process

$$M^+ + CH_3X \rightarrow MCH_3^+ + X$$

limits on the gas-phase M–C bond strengths were inferred: 284 kJ mol^{-1} > $D(M^+-CH_3)$ > 234 kJ mol^{-1} (M = Fe, Co) and from HX elimination reactions, limits on several metal-ion-olefin bond strengths were inferred. The concept of molecular ions and metal-containing fragment ions formed in the mass spectra of the mononuclear carbonyls $M(CO)_6$ (M = Cr, Mo, W), $Fe(CO)_5$ and $Ni(CO)_4$ containing the metal in an excited state appeared to violate the quasi-equilibrium theory [109]. Calculations, using the simplified form of the theory, showed that the high heat of formation values for metal ions, as determined by mass spectrometry, were consistent with the excess energies representing kinetic shifts.

In mass spectral fragmentation patterns of transition metal compounds complexed to organic rings it has been suggested that H_2 is lost more readily than H• because only low activation energy fragmentation processes can compete with metal decarbonylation. While agreeing that activation energies must be of major importance, Davis has suggested [110] that, in certain cases, rationalisation of the mass spectral behaviour can only be achieved by also considering the stability of the products of the possible decomposition paths and particularly among these, the ability of the metal atom to participate in decompositions involving rearrangement, e.g. the stereoselective migration of the *endo*-hydrogen of the cyclohexadienyl ring to the Fe atom in the fragmentation of $(\eta^5-C_5H_5)Fe$(cyclohexadienyl) derivatives [111]. Two further examples describe taking into account the effect of the R and R' groups to explain the different breakdown pathways of $(\eta^5-C_5H_5)_2Ni_2{}^{RC\equiv CR'}$ complexes [112] and the facile CO loss and EPh_3 (E = P, As, Sb) elimination from benzocyclobutadienetricarbonyliron where ions corresponding to free and coordinated benzocyclobutadiene and benzyne were detected [113].

Bond dissociation energies have been calculated from the mass spectrometric appearance potential data for a range of complexes, e.g. D(W–W) for $\{(\eta^5-C_5H_5)W(CO)_3\}_2$ [114], $D(M^1-M^2)$ for $Me_3M^1M^2(CO)_x$ (M^1 = Si, Ge, Sn; M^2 = Co, x = 4; M^2 = Re, x = 5) [115], and D(Mn–CS) versus D(Mn–CO) for $(\eta^5-C_5H_4R)Mn(CO)_2(CX)$ (R = H, Me; X = S, O) [116].

ELECTRONIC SPECTRA (See also Photochemistry)

The theory has been presented for the activity of electronic Raman transitions between electronic states arising from the ground electronic configuration of some sandwich compounds containing transition metals [117].

Absorption and emission spectral studies of $M(CO)_4L$ complexes (M = Cr, Mo, W; L = 2,2'-bipyridine, 1,10-phenanthroline and substituted phenanthrolines) have been carried out and reveal that the lowest excited state in every case is charge-transfer in character (M → LCT in absorption) and in no case do the ligand field excited states cross below the charge-transfer state [118]. Minimum energies of the ligand field states were established by the spectroscopic study of *cis* bis(pyridine)- and *cis* bis(aliphatic amine)$M(CO)_4$ complexes (M = Mo, W) which all have ligand field lowest excited states. Emission was detectable for the $M(CO)_4L$ complexes (M = Mo or W) and occurred in the range 14,400-15,660 cm^{-1} (638-694 nm) with lifetimes of 7.9-13.3 μsec and quantum yields of 0.02-0.09, with all of these measurements taken in EPA solution at $77^{o}K$. Only the $W(CO)_4(py)_2$ and $W(CO)_4(amine)_2$ simple complexes gave rise to emission [118]. The visible and near ultraviolet spectra of $W(CO)_5L$ complexes (L = quinuclidine, cyclohexylamine, piperazine, piperidine, dabco) were obtained and assigned by using the results of molecular orbital calculations [119].

The results of a semi-empirical M.O. calculation for $Mn_2(CO)_{10}$ and an electronic spectral investigation of $M_2(CO)_{10}$ (M = Mn, Te, Re) and $MnRe(CO)_{10}$ have been reported [120]. The calculation was fully consistent with the assignment of the electronic absorption band at 29,400 cm^{-1} (340 nm) in $Mn_2(CO)_{10}$ to a transition between σ and σ* orbitals associated with the metal-metal bond. The energy of the σ → σ* band maximum for each of the four complexes increases with decreasing temperature and with increasing metal-metal stretching force constant. Metal-to-ligand charge-transfer (M → LCT) bands were assigned within the derived M.O. framework. Absorption bands attributed to σ → π*(CO) and *d*π → π*(CO) transition were observed between 33,000 and 38,000 cm^{-1} (263-303nm) in all four complexes and an extremely intense band near 50,000 cm^{-1} (200 nm) in each case was assigned to the *d*π → π*(CO) transitions $6e_1 \rightarrow 2a_2$ and $6e_3 \rightarrow 2b_1$. Electronic spectra of related complexes $MnCr(CO)_{10}^{-}$, $Cr_2(CO)_{10}^{2-}$, $Mn_2(CO)_9PPh_3$ and $Mn_2(CO)_8(PPh_3)_2$ were also reported and discussed [120].

The absorption and magnetic circular dichroism (MCD) spectra of $Mn(CO)_5Br$ in a solution of 2-methyltetrahydrofuran were measured at various temperatures in the 22,220-28,570 cm^{-1} (350-450 nm) region [121]. Within experimental error, the MCD spectra were not temperature dependent and, in addition to a negative B term, exhibited a positive A term which is indicative of a degenerate excited state. Following the irreducible tensor method, it was concluded that the transition would be $e(\pi,Br) \rightarrow a_1(\sigma^*,3d_{z^2})$ and for the excited state a magnetic moment was calculated which agreed quite closely with the experimental value.

The electronic spectra of a series of alkyl- and aryl platinum complexes of the type $R_2Pt(2,2'$-bipyridine) contain charge-transfer (M → LCT) bands whose energy is dependent on the nature of the substituents on platinum and also on the solvent [122]. It was suggested that π-bonding is important in the Pt-Ph bond.

VIBRATIONAL SPECTRA (See also Matrix Studies)

A second volume of the *Index of Vibrational Spectra of Inorganic and Organometallic Compounds* covers information published during the period 1961-63 [123]. The *Index* lists the compounds alphabetically together with brief details of experimental conditions, the type of spectrum and the frequency range covered. A forthcoming volume, Volume III, will complete the set and form a comprehensive index from 1935-66 and provide an efficient tool for searching the literature. The *Index* could form the basis of a computer retrieval and identification, a possibility which has been investigated for organic compounds [124]. A new monograph on the interpretation of infrared and Raman spectra has been published [125].

The field of metal carbonyl vibrational spectroscopy has been surveyed in terms of what's been done and what's left to do [126] and *Metal Carbonyl Spectra* is a monograph dealing with vibrational spectra of metal carbonyl compounds [127]. The major part of the book consists of a general discussion of infrared and Raman spectroscopy in both its theoretical and practical aspects and is followed by a more detailed discussion of the carbonyl group. There is a full theoretical treatment, much of which has not appeared elsewhere, of the vibrational patterns to be expected from species with CO ligands in various possible environments and detailed advice, deriving from the author's wide experience, on sample manipulation and handling. Current bonding interpretations and approximate calculations using CO vibrational data, e.g. force constants, are critically discussed. Force constant calculations in molecules havebeen reviewed [128] and a general method for calculating force constants for polyatomic molecules from their vibrational spectra without needing the energy matrix reduction with respect to symmetry was developed using a computer [129]. The force constants of $M(CO)_6$ (M = Cr, Mo, W) calculated by the new method agreed with those obtained with consideration to molecular symmetry during the calculations. A method was proposed for determining the importance of anharmonicity corrections to the Cotton-Kraihanzel stretching force constants of substituted octahedral metal carbonyls [130]. From an analysis of experimental data it was shown that, if the comparisons are limited to compounds of similar geometry whose frequencies and force constants occur within a narrow range in keeping with the original intentions of the Cotton-Kraihanzel method, the neglect of anharmonicity is entirely valid. During the last twenty years "local symmetry" arguments have been widely used in the interpretation of the vibrational spectra of metal carbonyls without a clear definition of the limits of the applicability of the method. This situation has been rectified by some observations on $(\eta^5\text{-}C_5H_5)V(CO)_4$ derivatives and it has been suggested that the method is applicable until the molecular orbitals of the carbonyl become sufficiently deformed to produce observable spectroscopic effects such as e-splitting or appearance of "inactive" bands which are governed not by the "local symmetry" but by the overall symmetry of the molecule [131]. A simple rule, which is applicable to all commonly encountered point groups, has been presented for the Jahn-Teller activity of a vibrational mode [132].

Most of the fundamental vibrations of $M(CO)_5(PH_3)$ complexes (M = Cr, Mo and W) were assigned from their infrared and Raman spectra and a normal coordinate analysis gave the normal modes description and force constants for a general quadratic valence potential field [133]. The Cotton-Kraihanzel force constants for some *s*-trithiane complexes of the type $M(CO)_5(RCHS)_n$ (M = Cr, Mo, W); R = H, Me, n = 3; R = H, n = 4) indicated that the sulphur ligands are slightly more basic than PPh_3 [134]. The trimethylthiane complexes (R = Me, n = 3) exhibited rapid intramolecular exchange of the $M(CO)_5$ group along the three coordination centres of the ligand. The solid-state and solution infrared and laser Raman spectra of $W(CO)_4(NO)Br$ are consistent with a *trans* C_{4v} symmetry and assignments are proposed which were verified by an energy-factored force field calculation, including the weak satellite peaks of $W(^{12}CO)_3(^{13}CO)(NO)Br$, on the basis of the C_{4v} geometry [135]. The Raman spectrum of $Mn(CO)_5Br$ in CCl_4 did not obey C_{4v} selection rules for the terminal CO stretching modes [136]. This was attributed to the axial CO differing only slightly from the equatorial CO groups so that some modes of vibration displayed the symmetry of both geometric groups M and H instead of only one of the groups. The theory of the general phenomenon of dual symmetry (hidden symmetry) and the derivation of selection rules was presented. The exchange of ^{13}CO with $Mn(CO)_5Br$ and $Re(CO)_5Br$ in hexane has been measured by infrared spectroscopy on the basis of a detailed force constant analysis of the various isotopically labelled species [137]. A complete accounting of the time dependence of all isotopically labelled species and comparison with the results of phosphorus ligand substitution rates led to the conclusions: (a) the rate determining process is CO dissociation; (b) the rate constant for *cis* dissociation is at least ten times that for *trans*; (c) the five-coordinate intermediate formed on dissociation of CO is fluxional; (d) the rate constant for *cis* dissociation for Mn is 2.8×10^{-5} sec^{-1} at $23^{\circ}C$ and for Re it is 5.0×10^{-7} sec^{-1} at $30^{\circ}C$. The reaction of *cis* $Mn(CO)_4(L)Br$ complexes (L = PPh_3, $AsPh_3$, $SbPh_3$) with 96%

$C^{18}O$ in cyclohexane solution at 35°C has been investigated by infrared spectroscopy and the vibrational modes of the parent molecule and the various $C^{18}O$-substituted species have been assigned with the aid of approximate force field calculations for the energy-factored CO stretching blocks of the FG matrices [138]. The infrared data for the reaction with the PPh_3 complex indicate that while all four CO ligands are exchanged there is an initial preference for the axial CO substitution while for As and Sb complexes both CO and L substitution takes place. The gas-phase infrared and liquid-phase infrared and Raman spectra of $(CF_3)_2EMn(CO)_5$ complexes (E = P, As) have been recorded and the spectra were assigned on the basis of a normal coordinate analysis using a transferred force field [139]. It has been shown that a simultaneous fit of infrared or Raman spectra on the one hand and NMR spectra on the other can make possible the determination of the ligand exchange frequency (v_e) for "very fast" exchange and can also facilitate the determination of v_e in "slow" and "medium" exchange processes considerably [140a]. The consequences of the surprisingly high ligand exchange frequency for $Fe(CO)_5$ (1.1×10^{10} sec^{-1}) were discussed with respect to infrared band assignments for molecular fragments of the type $M(CO)_n$ (n = coordination number; M = transition metal, lanthanoid or actinoid). Raman spectra have been obtained at *ca* 90°K for $H_2M(CO)_4$ complexes (M = Fe, Ru, Os) in which the bands due to ν(M-H) vibrations are very intense, contrasting with the weakness of the corresponding infrared absorptions, and are consistent with a *cis* configuration in the solid state for all three molecules and moreover the *cis* geometry persists into the liquid-phase for $H_2Os(CO)_4$ [140]. The value of using solid solutions for carrying out force constant determinations in solids has been explored through a study of the infrared and Raman spectra of $Mo(CO)_4(PEt_3)_2$, $Fe(CO)_3(P(OMe)_3)_2$ and $Ni(CO)_4$ in solution, the solid state and a solid solution of EtOH + Et_2O + Me_2CHEt (1:5:5) [141]. The force constants obtained from the crystalline solids and the solid solutions were approximately equal and, interestingly, intermolecular interaction constants were also determined from isotopic studies without requiring a knowledge of the crystal structure. Despite the considerable effort which has been expended on studying the vibrational spectra of metal carbonyls there appears to be no data on their Raman spectra in the ν(CO) overtone region and very little infrared solid-state work either [142]. The Raman spectra of polycrystalline transition metal hexacarbonyls in the 4000 cm^{-1} region have been reported and, in marked contrast to the spectra in the 2000 cm^{-1} region, factor-group effects appear to be negligible so that the spectra are much simpler than might be expected from the wealth of peaks in the fundamental region [142].

Empirical correlations between the absolute infrared intensity of CO stretching modes and ionisation energy and MC and CO bond polarisability derivatives and ^{13}C chemical shifts and charge-transfer spectra and calculated 2π-bond populations on the CO groups in $M(CO)_6$ complexes were discussed and rationalisations of bonding sequences were suggested [143]. The results support the suggestion that the absolute intensity should be a more sensitive measure of the importance of π-bonding in complexes of this type than the CO stretching force constants. The square root of the absolute infrared intensity of E mode CO stretching vibration increased with increasing 2π orbital population on the CO groups in $M(CO)_{6-n}X_n$ complexes (M = Cr, Mn, Fe; X = Cl, Br, I; n = 1,2) [144]. The trend in orbital occupancies reflects the trend in $M(d\pi)$-$CO(2\pi)$ interaction that occurs in bond stretching and an approximate linear dependence of the M-CO bond reactivities or the 2π orbital populations in these complexes was also indicated. The infrared band intensities of $Ni(CO)_3(PMe_3)$ were determined and used with L_{kp} eigen vectors of the GF matrix to calculate the bond moment derivatives and their signs [145]. The results accounted for the near-zero value of the A_1 band intensities of the ν(Ni-P) and ν(Ni-C) and for the enhancement of the ν(P-C) and A_1 ν(C-P-C) band intensities compared with the free ligand. The values of the bond dipole moment derivatives were discussed in relation to electron transfer. The results of absolute integrated infrared band intensities of the ν(CO) and ν(CS) modes in $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$ showed that the dipole moment μ'(MnCS) was significantly greater than μ'(MnCO) and this was taken as direct evidence, because the intensities were compared in the same complex, for the greater π-acceptor ability of the CS versus CO ligand [146]. It will be interesting to see how CSe compares as a ligand in this respect in the new CSe complexes $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CSe)$ and $(\eta^6\text{-}C_6H_5CO_2Me)Cr(CO)_2(CSe)$ [147]. Caution was urged when infrared band intensities are used to determine isomerisation enthalpies and entropies because of the influence of temperature dependence on the absorptivities of reference bands [148].

The resolution of metal isotopic structure in the ν_7 infrared bands of $Cr(CO)_6$ (670 and 700 cm^{-1} respectively) was only possible because of the extreme sharpness of the bands and the lack of rotational coupling which was afforded by the matrix isolation technique (Ar, N_2, O_2 matrices at 20^oK) [149]. The matrix isolation work (see also later section) is significant because it shed new light on the characteristics of the lower wavenumber vibrations, e.g. ν_7 was previously considered to be a bending mode while ν_8 ($\sim$450 cm^{-1}) was ascribed to M-C stretching but the present study where isotope effects were seen in ν_7, confirms that ν_7 contains significant M-C stretching motion. The new data enabled the force field to be refined and with a predicted shift of 1.2 cm^{-1}/amu for ν_8 the question of isotope splittings or matrix site effects, which were also noted in the matrix isolation infrared spectrum of $Fe(CO)_5$ in the ν(Fe-C) region [150], to be settled.

A special type of infrared solution cell, equipped with stopcocks to permit filling with a syringe outside a glove box but with essentially complete exclusion of air, has been developed to obtain spectra of metal carbonyl anions [151]. The success of the exclusion of air was demonstrated by keeping a solution in the cell of $(\eta^5\text{-}C_5H_5)Fe(CO)_2^-$ in THF for over 30 minutes without significant oxidation to dimer, as monitored by the infrared spectrum. The cells were used to characterise the first non-cluster binary transition metal carbonyl trianions, $Mn(CO)_4^{3-}$ and $Re(CO)_4^{3-}$, which resembled strongly those of the series $Fe(CO)_4^{2-}$, $Co(CO)_4^-$ and $Ni(CO)_4$, i.e. tetrahedral structure [152]. Treatment of hexamethylphosphoramide solutions of $M(CO)_4^{3-}$ with Ph_3ECl (E = Ge, Sn or Pb) or Ph_3PAuCl provided colourless salts of the type $(Ph_3E)_2M(CO)_4^-$ and the complex $(Ph_3PAu)_3M(CO)_4$. Infrared spectra of the Et_4N^+ salts were consistent with *cis* $(Ph_3E)_2M(CO)_4$ for Sn and Pb and *trans* for Ge [152].

An approximate vibrational analysis of the complete $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ molecule and its deuteriated analogue has been presented in which kinetic coupling effects were, in most cases, insufficient to explain the frequency shifts which are observed in coordination of the benzene moiety [153]. The effects of ligation on the force constants of the C_6 ring are evaluated, a description of the normal modes is given and inactive molecular frequencies are calculated. The infrared and Raman spectra of the crystalline solid and of a solid solution of $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ in EtOH + Et_2O + Me_2CHEt (1:5:5) at 85°K (c.f. [141]) and the vapour-phase infrared spectrum at 500°K were observed and the CO force constants calculated [154]. The two methods of calculation based on infrared band intensities and the molecular force constants derived from ^{13}CO species were generally more applicable than that using fundamental band frequencies. In the case of $(\eta^6\text{-}C_6H_6)M(CO)_3$ complexes (M = Cr, Mo, W) studied by infrared (250-4000 cm^{-1}) and Raman spectroscopy, the force constants for the M-ring bond increased in the order Mo < Cr < W whereas for the M-CO bond they changed in the order Cr < Mo < W [155]. The symmetric and degenerate CO stretching frequencies were found to correlate linearly with the σ_p^o parameter which was interpreted as demonstrating that transmission of the substitution electronic influence through the metal atom was an inductive effect. This was supported by the establishment of a correlation of substituent parameters (σ_I, σ_p, σ_R^p σ_p^o, σ_R^o) with the value for the CO stretching force constant for twenty eight mono- and poly-substituted arenetricarbonylchromium complexes [156]. A valence force field of $(\eta^6\text{-}C_6H_5CO_2Me)Cr(CO)_3$ has been determined from a consideration of the force fields of $C_6H_5CO_2Me$ and $Cr(CO)_6$ [157]. Single crystal Raman studies of $(\eta^6\text{-}C_6H_{6-n}Me_n)Cr(CO)_3$ (n = 5 or 6) have shown that, whilst a vibrational factor-group method offers the simplest explanation of the vibrations of the $Cr(CO)_3$ unit at ~2000 cm^{-1}, some features were unexplained and it appeared that an explanation for them lay outside any simple harmonic oscillator/factor group approach [158]. Vibrational spectra of the π-thiophene complexes (π-SC_4H_2RR')-$Cr(CO)_3$ (R = R' = H, [159]; R,R' = H, Me, OMe, Br, CO_2Me, [160]) are interpreted by comparison with (η^6-C_6H_6)$Cr(CO)_3$. A new assignment of the (η^5-C_5H_4Me) modes, on the basis of C_s symmetry, was given from an infrared and Raman study of (η^5-C_5H_4Me)$Mn(CO)_3$ and its deuteriated derivative and of $\{(\eta^5\text{-}C_5H_4Me)Mo(CO)_3\}_2$ [161]. A detailed normal coordinate analysis has been carried out for $(CH_2)_3CFe(CO)_3$ [162].

The currently accepted idea that the high Raman intensity of ν(M-M) leads to an unequivocable assignment in the spectra of metal-metal bonded complexes has been questioned, e.g. $Re_2(CO)_{10}$ has had ν(ReRe) assigned to a band at 125 cm^{-1} however $Re_2(CO)_8Br_2$ and $Re_2(CO)_8Cl_2$ have also intense Raman bands at ∿125 cm^{-1} but these cannot be ν(MM) because these halide complexes have halide bridges [163]. High Raman intensity for ν(MM) arises from the fact that the sample is often irradiated near or within an electronic transition involving the metal framework and while this leads to enhanced scattering this may occur *via* resonance or pre-resonance mechanisms and also from sample decomposition. The authors suggest that Raman data on coloured organometallic compounds should be collected using inert-atmosphere sealed samples in conjunction with sample spinning, because spinning alone was not able to eliminate decomposition for $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$, and additionally, spurious features should be sought by obtaining spectra for laser-damaged material [163].

Two groups have reported independently on the assignment of the CO stretching bands of $MnRe(CO)_{10}$ [164,165]. One group used ^{13}CO enrichment and a CO-factored force field calculation [164], while the other interpreted the weak natural abundance bands and calculated force and interaction constants in a CO-factored force field by a parametric rotational method applied for the presence of a species of fourth order with constraints in the eigen-vector matrix [165]. The two groups reached a broad consensus of agreement but some of the assignments are still a matter of contention [166]. The Raman spectra of $(CO)_5Re\text{-}M'(CO)_5^-$ complexes (M' = Cr, Mo, W) have been assigned on the basis of C_{4v} symmetry and normal coordinate analyses have been performed which showed that k(Re-M') followed the order k(ReW) > k(ReMo) > k(ReCr) [167]. The infrared spectrum of $Mn_2(CO)_5(Ph_2PCH_2CH_2PPh_2)_2$ exhibits an unusually low CO stretching band at 1645 cm^{-1} and this has been shown by x-ray crystallography to be associated with a bridging CO ligand in which the second Mn interacts strongly with the O as well as the C atoms with a short Mn-O contact distance (2.29 Å) [168]. An earlier method of calculating CO stretching force fields for mono- and binuclear metal carbonyl compounds with the help of infrared intensities has been extended to incorporate Raman data [169]. The solution Raman spectrum of $Hg(Co(CO)_4)_2$ in the CO stretching region has been obtained, including measurements of intensities and depolarization ratios, and comparison with previous work suggests that two Raman bands should be reassigned. On the basis of experimental evidence it seems that Raman intensity data may be more directly applicable to the evaluation of CO stretching force constants than infrared data. Infrared stretching frequencies are reported for new linear metal-metal bonds in $(M''-Au-M'')^-$ complexes (M'' = $Mn(CO)_5$, $Co(CO)_4$, $(\eta^5-C_5H_5)Mo(CO)_3$, $(\eta^5-C_5H_5)Fe(CO)_2$) and correlations are established between the oxidation state and coordination number of M' in linear M"-M'-M" systems (M' = Pd(II), Pt(II), Hg(II), Au(I)) and the corresponding $\nu(M'M'')$ stretching frequencies [170]. Infrared and Raman spectra have been described for some $X_3MM'(CO)_4$ complexes (X = H, F, Cl; M = C, Si; M' = Fe, Co), complete vibrational assignments have been made on the basis of force field calculations for these compounds and for $CF_3Co(CO)_4$ and evidence for π-interaction in the M-M' bond has been considered [171]. The effect of the nature of the bridging ligands on the CO stretching force constants in $(\mu-Y)_2M_2(CO)_6$ complexes (Y = S, SR, Se, PRR', Br, I for M = Fe; Y = CO, P, As, CR for M = Co) has been investigated [172]. A normal coordinate analysis of *cis* and *trans* $\{Rh(CO)_2Cl\}_2$, $\{Rh(CO)_2Br\}_2$ and $\{Rh(CO)(PMe_3)Cl\}_2$ complexes has given the first description of their normal modes of vibration [173]. Enrichment using ^{13}CO has enabled the terminal CO stretching bands of $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$ and $HFeCo_3(CO)_{12}$ to be assigned and in all three cases the wavenumbers follow the scheme $A_1 > A_1 > E > E > A_1 > E$ [174]. Several facile routes are reported for the syntheses of $B_xMg(M)_2$ complexes (B = Lewis base e.g. THF; M = $(\eta^5-C_5H_5)Fe(CO)_2$, $Co(CO)_3(P(C_4H_9)_3)$) and the variability of the number of Lewis bases coordinated to the Mg atom leading to coordination numbers 4 (x = 2) or 6 (x = 4) can be related to the nucleophilicity of the transition metal carbonyl anion [175]. In the 6-coordinate complexes Mg-O≡C-M bridges invariably occur and these are characterised by extremely low ν(CO) values, ∿ 100 cm^{-1} below bands found for transition metal anions. For 4-coordinate complexes, depending on the nucleophilicity of the metal carbonyl anion, evidence was presented for direct Mg-M bonds as an alternative to Mg-O≡C-M bridges.

A good account has been given of the high pressure infrared spectroscopic studies of the carbonylation reactions of olefins in the presence of Co, Rh and Ir metal carbonyls as a means of determining the mechanism of the hydroformylation of olefins [176]. In such studies, e.g. the reaction between $Co_2(CO)_8$ and $P(\underline{n}-Bu)_3$ in heptane with variable temperature (100-150°C), variable pressures of H_2 and CO (11-74.5 atm. and 3-54 atm. respectively) and variable P:Co ratios from 0 to 13.7 [177], species are observed which enable kinetic data and thermodynamic parameters to be determined for a series of equilibria.

Approximate force fields have been calculated for the fragments $(CH_2{=}CH_2)Fe$ and $(CH_2{=}CH_2)Pt$ from the vibrational data of $(C_2H_4)Fe(CO)_4$ and

$(C_2H_4)PtCl_3^+$ [178]. The metal-ligand bonding is much stronger in the latter case, as shown by the larger value of the M-C stretching force constant and the smaller value of the C=C stretching force constant, but many of the normal modes were shown to be derived from more than one type of internal coordinate and hence vibrational wavenumbers themselves are of limited value in discussions of bonding [178]. The relation between the vibrational spectra of methylenes coordinated to Pt and the electronic spectra of free methylethenes has been reviewed [179]. Infrared and electric dipole moment studies of (olefin)$Fe(CO)_4$ complexes (olefin = *trans* PhCH=$CHCOCH_3$, *trans* PhCH=CHCOPh, *trans* PhCH=CHO, CH_2=CHCHO and CH_2=CHCN) have found that the ligand plane is never parallel to the axis of the trigonal bipyramid [180]. A general scheme, utilising both energetic and kinetic data, has been derived for the classification of allyl-metal complexes such that, on the basis of infrared spectral data, three categories are formulated as π, σ, and $\pi + \sigma$ and these are futher subdivided into dynamic and static on the basis of ^1H NMR spectra [181]. Vibrational studies of Zr- and Hg- [181] and Fe-allyls [182] have been reported. The solution Raman spectra of $(\eta^5\text{-}C_5H_5)_2M$ (M = Fe, Ru, Os) complexes have been reinvestigated with the aid of polarisation measurements and, although the work in general supports previous assignments for $(\eta^5\text{-}C_5H_5)_2Fe$, the unexpected polarisation of the 1186 cm^{-1} band (usually assigned as $\nu_{24}(E_{2g})$ an in-plane C-H bending mode) led the authors to suggest that this band should be reassigned as an overtone of ν_{28} (out-of-plane $\eta^5\text{-}C_5H_5$ mode) at ∿ 600 cm^{-1} [183]. From a study of the infrared and Raman spectra of norbornadiene complexes of Pd, Pt, Rh and Fe, an assignment of the normal modes is given and the ligand variations are compared with those of the free ligand, e.g. $\Delta\nu(C{=}C)$ ∿ 175 cm^{-1} on complexation [184]. The strength of the metal-ligand bond increased in the series Pd < Pt < Rh.

Evidence for hydrogen-bonded intermediates, from a shift of ν(NH) to lower wavenumbers on the addition of R_3PO, in amine substitution reactions involving $M(CO)_5$(amine) (M = Cr, Mo, W) derivatives with phosphorus ligands has been produced [185]. The addition of R_3PO to hexane solutions of $M(CO)_5(NHC_5H_{10})$ also shifts the infrared bands of the CO ligands to lower wavenumbers (2066, 1930 and 1906 cm^{-1} as against 2073, 1939 and 1921 cm^{-1}) and the dissociation of the amine ligand was found to be considerably faster in the hydrogen-bonded adduct than in the absence of such hydrogen-bonding interaction.

The infrared (2000-250 cm^{-1}), far infrared (350-150 cm^{-1}) and laser Raman (2000-150 cm^{-1}) spectra of the tetradentate ligands $C\{CH_2EPh_2\}_4$ (E = P, As) and of complexes of the type *cis* $M(CO)_3\{Ph_2ECH_2\}_3C(CH_2EPh_2)$ (M = Cr, Mo, W) have been assigned fully for all the ligand vibrations using the assumption of C_{3v} symmetry for the polyhedra *cis* $M(CO)_3E_3$ [186]. The infrared spectra of PF_3-substituted butadienetricarbonylion complexes show no evidence for more than one of the possible isomers, for each value of $(\pi\text{-}C_4H_6)Fe(CO)_{3-n}(PF_3)_n$, in a square-based pyramidal structure [187].

A force constant analysis has been presented for the series of complexes $Mn(CO)_{5-n}(CNCH_3)_nBr$ (n = 0–4), $Mn(CO)_{6-n}(CNCH_3)_n{}^+$ (n = 0–6) and $Fe(CNCH_3)_6{}^{2+}$ which shows, in conjunction with an approximate M.O. calculation, that both σ- and π-bonding changes in the metal-isocyanide bond can influence observed stretching frequencies [188]. The antibonding behaviour of the $7a_1$ orbital, the carbon "lone pair" in methylisocyanide, helps explain the observed increase in ν(CN) values for bound CNMe *versus* free ligand in many metal complexes even though there is significant back-bonding to the ligand.

Raman spectra and polarisation measurements provided definitive proof of the structure of the new alkyl complexes of Pt, and in particular that $PtMe_6{}^{2-}$ has octahedral symmetry [67], and also that the $Au(CH_3)_2{}^-$ ion has a linear structure with active vibrations correlating with $Hg(CH_3)_2$, $Tl(CH_3)_2{}^+$ and $Pb(CH_3)_2{}^{2+}$ [68]. The infrared spectra of $ReO(R)_4$ complexes (R = Me, CH_2SiMe_3) are consistent with a square-based pyramidal structure, which was confirmed by a separate matrix isolation study of $ReO(Me)_4$ in argon, while the dimer $Re_2O_3(CH_2SiMe_3)_6$ is consistent with a linear Re-O-Re bridge and the Re=O groups in a *cis* configuration [189].

A full structural and spectroscopic study of the bonding of CO_2 to Ni in $Ni(CO)_2(PCy_3)_2$ shows considerable similarity to that of CS_2 in $Pt(CS_2)(PPh_3)_2$ with the CO_2 coordinated through the C and one of the O atoms and with infrared-active $\nu(CO)_2$ bands at 1740 (vs), 1698 (vw) and 1150 (s) cm^{-1} in a nujol mull spectrum [190].

NMR STUDIES OF STATIC SYSTEMS (See also NMR Studies of Dynamic Systems)

It has become common practice to correlate NMR parameters with Cotton-Kraihanzel stretching force constants for CO groups and to go on from there to discuss σ- and π-bonding in complexes, but the authors of a ^{13}C NMR study on some $Re(CO)_5X$ derivatives have sounded a note of caution [191]. For example, in the series of neutral compounds $Re(CO)_5X$ the carbonyl carbon *trans* to X is more shielded than the CO carbons *cis* to X whereas in the cationic complex $(CH_3CN)Re(CO)_5{}^+PF_6{}^-$ the carbonyl carbon *trans* to CH_3CN is less shielded than those in the *cis* positions and although there is a linear relation between ^{13}C chemical shifts and stretching force constants for *cis* carbonyls there is no apparent correlation of force constants with other features of the ^{13}C NMR spectra. The authors go on to point out that one can make no prediction of whether *cis* or *trans* carbonyl carbon will be more shielded on the basis of Cotton-Kraihanzel CO stretching force constants [191]. Nevertheless several correlations based on ^{13}C chemical shifts $^1J(^{13}C\text{-}^{31}P)$ and $^2J(^{13}C\text{-}^{31}P)$ have been reported, e.g. for $L_nNi(CO)_{4-n}$ complexes [192], $L_nM(CO)_{6-n}$ complexes [193] and $(\eta^5\text{-}C_5H_5)Mn(CO)_2L$ [194] where L is a phosphine or phosphite ligand, so that only time and a more thorough theoretical understanding of NMR parameters, particularly for heavy nuclei, will tell whether these correlations are chemically useful. The controversy over the relationship between ^{13}C coordination shifts and π-back-bonding is also mentioned in some work on the ^{13}C NMR spectra of (olefin)Ni(P(O-*o*-tol)$_3$)$_2$ complexes [195]. The equilibrium constants of olefin complex formation increase in the series C_2H_4 < methylacrylate < dimethylmaleate ∿ acrylonitrile < fumaronitrile ∿ maleic anhydride and a good correlation between the upfield shift of the olefinic carbons on coordination and log K was found i.e. larger back donation to π* associated with larger shift, but no correlation was observed for $^1J(^{13}C\text{-}H)$ with other measures of back-bonding [195]. The ^{13}C NMR spectra for three series of π-1,5-cyclooctadiene (COD) derivatives of the types (COD)Pt(CH$_3$)R, (COD)Pt(CH$_3$)L$^+$PF$_6^-$ and (COD)PtRR' (R,R' = anionic substituents; L = neutral donor) have shown that ^{13}C shielding and $^nJ(^{13}C\text{-}^{195}Pt)$ trends for π-bonded carbons generally parallel those trends for σ-bonded carbons [196]. In a series of anionic, neutral and cationic platinum carbonyl complexes of the type Pt(CO)(X)LL' with the X ligand trans to the ^{13}CO decreases in the ^{13}C shift for constant X have been observed for the carbonyl carbon with increasing negative charge on the complex but little variation occurred with changes in the *cis* ligand [197]. Two ranges of $^1J(^{13}C\text{-}^{195}Pt)$ have been observed for variation of the *trans* group X such that for ligands with a high *trans*- influence, e.g. H, CH$_2$Ph, the value is in the range 960-990 Hz while for ligands with low *trans*-influence, e.g. NO$_3$, Br, I, the value falls in the range 1658-1817 Hz [197].

^{13}C NMR spectroscopy has been shown to be a valuable analytical tool, which offers considerable advantages over other physical methods, for investigating the site and in some cases the degree of deuterium incorporation in several simple alkenes and also in various tertiary phosphine complexes of Pt(II) [198]. The location of hydride ligands and the measurement of M-H bond lengths are two problems which nematic phase NMR spectroscopy in conjunction with X-ray crystallography can solve in favourable cases e.g. $H_3Ru_3(CO)_9(CCH_3)$ [199], where a detailed x-ray structure has enabled the ^1H NMR nematic phase spectrum to be re-interpreted to give calculated values for Ru-H (1.81 Å) and Ru-H-Ru (103°) which are probably more accurate than calculated only from X-ray data. A nematic phase ^1H NMR study has also been carried out on (η^3-C$_3$H$_5$)Re(CO)$_4$ [200] and it was concluded that the protons do not all lie in one plane.

^{11}B NMR has been used as the main basis for structural characterisation of the metalloborane products of the reaction of $B_9H_{12}^-$ and (η^5-C$_5$H$_5$)$_2$Ni with Na amalgam [201]. The ^{31}P NMR spectra of a number of Rh complexes have been investigated with Rh in different oxidation states and it has been shown that structural elucidation is possible on the basis of $^1J(^{31}P\text{-}^{103}Rh)$

[74]. ^{31}P NMR parameters have also been found to be diagnostic of the distinction between metalated and unmetalated phosphite ligands [202] the distinction between *mer* and *fac* isomers of $L_3Mo(CO)_3$ [203] and the position of phosphorus ligands ($^2J(^{31}P-^{31}P)$) in trigonal bipyramidal Ir(I) complexes [204]. The $^1J(^{31}P-^{195}Pt)$ coupling constants in the complexes *cis* $PtCl_2(R_2PCH_2CH_2PPh_2)$ (R = CF_3, C_6F_5) and the bond lengths in the CF_3 complex were interpreted as indicating that the metal-ligand bonding is strongly influenced by the substituents on the phosphorus [205]. A study of the ^{119}Sn chemical shifts in thirty five complexes with tin-transition metal bonds has shown that whereas with light transition metal species exceptionally low field field shifts were observed, which were attributed to a large paramagnetic contribution arising from small average excitation energies associated with $d\pi$-$d\pi$ bonding, heavier metals increased the ^{119}Sn shielding but there was no apparent correlation between the shifts and the *s* electron density on the Sn atom [206].

A new method of measuring relative Lewis acidities involves measuring the coupling constant $^1J(^1H-^{195}Pt)$ in complexes of the type *trans* $Pt(PEt_3)_2(H)CN \rightarrow L$ because the coordination of the cyanide to the Lewis acid weakens the Pt-CN and thereby changes the electron density on the Pt atom [207].

All previously known Co(III) alkyl complexes have been diamagnetic and have given satisfactory NMR spectra but the new complexes of the type $Co(C_{10}H_{14}N_8)(L)R$ (L = py, CN^-, MeCN, MeNHNH ; R = Me, Et, Ph) have anomalous NMR spectra, although they are virtually diamagnetic, and this has been ascribed to paramagnetic contact shifts arising from a thermally populated triplet state [208].

The influence of a chiral group on the ^{1}H and ^{13}C NMR parameters of ferrocenes and titanocenes has been studied and it has been observed that differences of screening due to the diastereotopy of the cyclopentadienyl carbon nuclei is usually larger than the non-equivalence of corresponding ^{1}H chemical shifts [209]. If the chiral group is the titanium atom itself a diasterotopy is also induced into the cyclopentadienyl ring. The results were used to give information about stereochemistry, e.g. preferred conformations. In contrast to other η^1-C_5H_5 rings which are fluxional (see below), those in $(\eta^5-C_5H_5)Mo(CO)_2(\eta^1-C_5H_5)_3$ did not undergo rapid 1,2 shifts on the NMR time scale as judged by observations of σ-type inequivalence [210].

NMR STUDIES OF DYNAMIC SYSTEMS

A comprehensive progress report on the study of molecular processes which are rapid on the NMR time scale has appeared in the form of a book entitled *Dynamic Nuclear Magnetic Resonance Spectroscopy* [211]. Chapters on dynamic molecular processes in inorganic and organometallic compounds [212], stereochemical non-rigidity in organometallic compounds [213], bonding, movements of the allyl group and proton exchange in metal-allyl complexes and stereochemical non-rigidity in metal carbonyl compounds [215] are of particular interest to the practising organometallic chemist. The topic c fluxionality in organometallic and metal carbonyls has been reviewed elsewhere [216] and a contribution on the flipping of CO ligand groups in meta carbonyl compounds and its frequency in Fe(CO)$_5$ was given at the Darmstadt symposium on metal atoms [140a] (see Matrix Studies for other contributions

The temperature dependence of the ^{13}C NMR spectra of metal cluster compounds, in situations where the static structures obtained from X-ray crystallography or predicted by cluster electron counting [62] show inequivalence, have been interpreted in terms of two distinct CO site-exchange processes, one of which interchanges environments on the same metal and th other, usually with a higher barrier, involves movement of CO ligands from one metal to another and here a bridging CO intermediate is commonly invol Most complexes show the former process, e.g. Os$_6$(CO)$_{18}$ [63], but some show more than one process including the latter process, e.g. Rh$_6$(CO)$_{15}$$^{2-}$ [217]. The type of scrambling process has been claimed to depend on the type of bridging CO for clusters in which bridging CO ligands occur, e.g. Co$_4$ clust [218]. In the "butterfly" structure of the Co$_4$(CO)$_{10}$RCCR series there is nc exchange because the bridging groups have a shorter and probably stronger bond to the Co while exchange does occur in the skeletal type represented b Co$_4$(CO)$_{12}$ where the authors infer that the cluster has a D$_{2d}$ structure in solution in contrast to the C$_{3v}$ structure in the crystal [218]. The D$_{2d}$ structure for Co$_4$(CO)$_{12}$ in solution has been challenged on the basis of a study of ^{13}CO-enriched Co$_4$(CO)$_{11}$P(OMe)$_3$, which shows a pattern of resonance derived from a C$_{3v}$ parent and a new ^{59}Co NMR study of Co$_4$(CO)$_{12}$ in solution which shows resonances in the ratio 1:3 [219]. The combined evidence was interpreted as favouring a C$_{3v}$ geometry for Co$_4$(CO)$_{12}$ unless there was a D$_{2}$ C$_{3v}$ ratio 1:3, but this evidence is contrary to infrared data, though the anomalous D$_{2d}$ result may have arisen from problems with relative intensitie of resonances as a result of scalar relaxation of ^{13}C spins caused by ^{59}Co quadrupolar relaxation [219]. It has been suggested the CO exchange betwee metals in clusters should be enhanced if there is an intermediate which involves minimal changes in symmetry, coordination numbers of the metal atoms, and total back-bonding compared with the solid-state structure [217]. On this basis the observed behaviour of Rh carbonyl clusters was explained, i.e. Rh$_6$(CO)$_{15}$$^{2-}$ has good pathways for terminal, edge- and face-bridging CO interchange, Rh$_7$(CO)$_{16}$$^{3-}$ for terminal and edge-bridging interchange while no pathway exists for Rh$_6$(CO)$_{16}$. For these Rh clusters there was a good correlation between the average charge for CO and the weighted average of the ^{13}CO chemical shift and this correlation should aid structural assignments of unknown carbonyl clusters and is directly related to the correlatio of shifts: terminal < edge-bridging < face-bridging [217]. The variable temperature studies of $H_2FeRu_3(CO)_{12}$ showed that intramolecular CO exchange occurred in three distinguishable stages, i.e. the first for CO groups localised on the Fe, the second for the CO groups localised at the three Ru atoms and the last, a general interchange, over the cluster [220]. An investigation of the ^{13}C and ^{31}P NMR spectra of $(CH_3C)Co_3(CO)_8PR_3$ showed that interchange was occurring without transfer of CO from one Co to another, i.e. an axial-equatorial interconversion *via* a twist mechanism [221]. In the acetylenic cluster complexes $HM_3(CO)_9C_2CMe_3$ (M = Ru, Os) both Ru and Os complexes showed axial-equatorial CO exchange of CO ligands localised in the metal atom which is σ-bonded to the acetylene but only the Ru complex showed exchange between metal atoms [222]. The fact that the coalescent temperature for the slow-exchange limit for $Fe_3(CO)_{12}$ may be below −160°C has so far precluded a determination of the structure of this cluster in solution, e.g. $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ give one sharp ^{13}C signal down to −100°C [222]. An alternative approach to $Fe_3(CO)_{12}$ has been sought in a ^{13}C NMR study of $(\eta^5\text{-}C_5H_5)MFe_2(CO)_9$ (M = Co, Rh) and $(\eta^5\text{-}C_5H_5)_2Rh_2Fe(CO)_6$ where it was demonstrated for the dirhodium complex that facile terminal-bridging CO exchange took place *via* pairwise opening and closing of bridges [223]. The variable temperature ^{31}P NMR spectrum of $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_2P(OPh)_3$ showed that the phosphite ligand stayed on the same Rh throughout the process which exchanged terminal and bridging CO ligands and on the basis of these results it was suggested that single bridge-terminal exchange, possibly occurring as a one-step process, must now be considered as a viable alternative in other systems, e.g. $(\eta^5\text{-}C_5H_5)Rh_2Fe(CO)_6$ [223], unless there is definitive evidence to the contrary [224]. The importance of localised CO scrambling was stressed in a study of the ^{13}C NMR spectra of (acenaphthylene)$Fe_2(CO)_5$ and (cycloheptatriene)-$Fe_2(CO)_6$ [225] while simultaneous twitching of the polyene moiety and localised CO scrambling occurred for (1,3,5-cyclooctatetriene)$Fe_2(CO)_6$ [226]. The ^1H and ^{13}C NMR spectra of some heteroatom-bridged complexes $(CO)_3M(\mu\text{-}ER_n)_2M(CO)_3$ (M = Fe, ER_n = PMe_2, AsMePh, $AsMe_2$, SMe, SEt; M = Co, ER_n = $GeMe_2$, $SnMe_2$) identified (1) localised CO scrambling as the lowest barrier process followed by (2) axial-equatorial R group exchange in a concerted fashion such that it occurred in both ER_n groups simultaneously with (3) axial-equatorial R group exchange in such a way that isomers of an ERR' bridged species were interconverted having the highest barrier [227]. The high activation energy needed for (3) was consistent with the need for inversion of the configuration of the pyramidal bridging ligand in a bridge-opened intermediate but the mechanism of (2) may not require bridge-opening. The ^1H and ^{13}C NMR results for $(\mu\text{-}SnMePh)_2$-$Fe_2(CO)_7$ indicated that permutation of the axial and equatorial substituents on Sn by a flapping (deformation) mechanism was facilitated by or occurred in concert with rapid bridge-terminal interchange of CO ligands without MM' bond cleavage while the higher temperature exchange processes were best explained by MM' cleavage [228].

^1H NMR spectroscopy has demonstrated that the acetylene ligand rotates about the M-acetylene bond in cationic complexes of osmium of the type $Os(CO)(NO)(A)L_2^+PF_6^-$ (A = C_2H_2, C_2HPh, C_2Ph_2, $C_2(CO_2Me)_2$, L = PPh_3; A = C_2H_2, L = $P(C_6H_{11})_3$) [229] and ^{13}C NMR spectroscopy has shown that the acetylene ligand of $(\eta^5\text{-}C_5H_5)_3Rh_3(CO)(Ph^{13}C{\equiv}CPh)$ is fluxional at room temperature but static at $-87^\circ C$ [230]. Variable temperature ^{13}C NMR data has provided direct experimental evidence that the ethylene ligand rotates about the M-olefin bond in $Os(CO)(NO)(C_2H_4)(PPh_3)_2^+PF_6^-$ [231]. The authors note that a turnstile mechanism might also need to be considered, i.e. interchange of CO and NO ligands, but this would probably be energetically unfavourable and would not explain all the other instances where rotation occurs, e.g. C_2H_4 in $Pt(C_2H_4)_2(C_2F_4)$ [232], $C(OMe)_2{=}C(OMe)_2$(ol) in $(\eta^5\text{-}C_5H_5)Mn(CO)_2$(ol) [233], ol in $(\eta^5\text{-}C_5H_5)Mn(CO)_2$(ol) and $(\eta^5\text{-}C_5H_5)Cr(CO)(NO)$(ol) (ol = dimethylmaleate, dimethyl fumarate) [234], *trans*-fumaronitrile(ol) in $Rh(p\text{-}CH_3OC_6H_4NC)_2(P(OPh)_3)$-(ol)I [235], in a series of cyclopentadienyl- and indenyliron olefin complexes where the barrier to rotation about the metal-olefin bond was determined as $\sim$ 33 kJ mol^{-1} [236]. Olefin rotation has also been invoked to explain the variable temperature ^1H and ^{13}C NMR spectra of $H_2M_3(CO)_9(RR'C_2)$ (M = Ru, Os) in addition to two separate hydride migration processes [237]. A combination of rotation about the metal-olefin bond and an orthogonal 1,2-shift of the organometallic ligand was used to explain how the four Me resonances of the allene ligand in $(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_7H_{12})Fe(CO)_2^+BF_4^-$ could become equivalent [238].

Rotation about the $Ta\text{-}CH_2$ bond has been observed for the first methylene complex of a transition metal, $(\eta^5\text{-}C_5H_5)_2Ta(CH_3)(CH_2)$, and $\Delta G^{\ddagger}$ for methylene rotation was determined as $\geq$ 89.5 kJ mol^{-1} [239]. Although scrambling processes of CO ligands bound to metal clusters are well documented, reports of intracluster motion of hydrocarbon ligands are relatively rare. A further example is afforded from a ^{13}C NMR study of $HOs_3(CO)_{10}(CH{=}CHR)$ where it has been established that the σ- and π-bonds binding the vinylic group are rapidly interchanged between the bridged Os atoms [240]. The addition of good nucleophiles, e.g. $PMePh_2$, to otherwise static, symmetrically-bonded η^3-allyl complexes of the form $(L\text{-}L)Pt(2\text{-}Me\text{-}allyl)^+$ produces 1:1 adducts which are dynamic in solution at ambient temperature [241]. The low temperature limiting spectra of the adducts appeared to correspond to η^1-allyl groups and the mechanism of the base-induced fluxionality and reactivity was discussed. A series of $(\eta^5\text{-}C_5H_5)Fe(CO)(L)CH_2R$ complexes (L = CO, phosphorus donor; R = Ph, $SiMe_3$, 1-naphthyl, for which infrared spectroscopy in the ν(CO) region indicates rotational isomerism about the Fe-alkyl bond, have been shown to undergo rapid interconversion on the ^1H NMR time scale

[242]. Variable temperature measurements suggest that steric considerations determine the rotamer preference with the stablest rotamer having the bulky (η^5-C_5H_5) group *gauche* to both methylene hydrogens. Preferred conformational studies have commonly employed PR_3 ligands to influence population distributions, e.g. [242], but a new technique, which uses lanthanide shift reagents, has been developed [243]. Addition of the shift reagent $Eu(fod)_3$ to solutions of (η^5-C_5H_5)Fe(CO)(CN)L complexes (L = PPh_3, PPh_2Me, $PPhMe_2$ and PMe_3) produces downfield shifts and first order coupling patterns in ^1H and ^{13}C NMR spectra and allows determination of conformation effects and rotational barriers in addition to providing a method of assigning resonances of diastereotopic nuclei to particular nuclei [243]. Broad line NMR measurements on crystalline (η^6-C_6H_6)$Cr(CO)_3$ at various temperatures has located two narrowings of the ^1H absorption line-width centred at about −165°C and −45°C and the lower temperature narrowing has been attributed to rotation of the arene groups with rotational hindrance caused by packing forces rather than intramolecular forces [244]. ^{13}C NMR studies of cyclopolyene complexes of the type (η^6-cyclopoly)$M(CO)_3$ (M = Cr, Mo, W; cyclopoly = 1,3,5-cycloheptatriene, 1,3,5-cyclooctatriene, 1,3,5,7-cyclooctatetraene) have detected two novel ligand movements: (a) a hindered motion of the polyene about the prolonged 3-fold axis of the $M(CO)_3$ fragment, and (b) the 1,3,5-cyclooctatriene ligand in (η^6-C_8H_{10})$Cr(CO)_3$ can be frozen out at −120°C into a chiral conformation [245]. The reaction of $Ru_3(CO)_{12}$ with cycloheptatriene affords a product $Ru_3(CO)_6(C_7H_7)(C_7H_9)$ which has been described as the most spectacularly non-rigid metal cluster yet discovered [246]. A crystal structure determination has been used to unravel the temperature dependent ^1H NMR spectrum of $(C_9H_{10})Fe_2(CO)_6$ [247]. Although the $(C_5H_5)Cr(C_8H_8)$ complex was paramagnetic, NMR data was obtained to show that the C_8H_8 ligand undergoes quick rotation [248].

Variable temperature ^1H NMR studies of $\{HMo(C_2H_4)_2(diphos)_2\}^+CF_3COO^-$ have shown that at −85°C a hydride resonance can be observed which at +7°C exchanges rapidly with half of the bound ethylene protons [249]. This is the first case where an insertion-de-insertion process, fundamental to many catalytic mechanisms, has been observed directly with the intermediate formation of an ethyl derivative. Another Mo complex, HMo(η^3-C_3H_5)$(diphos)_2$ shows exchange of hydride with the terminal hydrogens of the allyl group and this provides direct evidence for the π-allyl-hydride exchange mechanism proposed for 1,3-hydride shifts found in many metal-catalysed olefin reactions [249]. For the allyl-type complexes $M(CPh_3)(acac)$ (M = Pd, Pt) three independent types of fluxional motion of the α,1,2-triphenylmethyl ligand have been observed by ^1H and ^1H-decoupled ^{13}C NMR spectroscopy [250]. In the lowest energy process the metal (Pd or Pt) remains associated with one particular ring but the third carbon can be either C(2) or C(6) while at higher energy the Pd becomes associated with all three rings, i.e. the Ph_3C system rotates somewhat in the manner of a 3-bladed propeller and ultimately the acetylacetonate resonances are scrambled. A mechanism involving a three-coordinate complex as an intermediate in the lowest energy process was eliminated [250].

It has been shown by ^1H NMR that at ∿100°C the isonitrile ligands in $Mn_2(CO)_7(CH_3NC)_3$ are rapidly exchanged between the two Mn atoms [251]. A variable temperature ^{13}C NMR study of $(\eta^5\text{-}C_5H_5)Fe_2(CO)_3(CNR)$ (R = *t*-Bu, Ph) has shown that for the complex with the terminally bonded isonitrile ligand (R = *t*-Bu) bridge-terminal CO exchange and isonitrile exchange occur while the complex with the bridging CNPh group undergoes no exchange processes [252]. The ^{13}C chemical shift was also shown to be diagnostic for the presence of a bridging or terminal CNR group [252].

Intramolecular exchange of PF_3 ligands in (Me-butadiene)$Fe(PF_3)_2CO$ complexes has been observed in the variable temperature ^1H, ^{13}C and ^{31}P NMR spectra and it has been explained using a Berry pseudorotation mechanism [253]. Stereochemical non-rigidity has been demonstrated for derivatives of $Fe(CO)_5$ containing bidentate ligands [254] and in the case of Fe(diars)$(CO)_3$ (diars = *o*-phenylenebisdimethylarsine) this overturns previous work. ^{31}P NMR has been used to study the rapid interconversion of some diene and dienyl complexes of Mn, Re, Fe and Ru containing phosphite ligands in a series of complexes of the type (diene)$M(CO)_n(EPTB)_{3-n}$ (diene = cyclohexadiene, cycloheptadiene; M = Fe, Ru; n = 0,1,2) and (dienyl)$M(CO)_n(EPTB)_{3-n}$ (dienyl = cyclopentadienyl, cyclohexadienyl, cycloheptadienyl; M = Mn, Re, Fe^+, Ru^+; n = 1,2), where EPTB is 4-ethyl-1-phospha-2,6,7-trioxabicyclo(2,2,2)-octane [255]. ^{31}P NMR spectroscopy has also been used to follow the exchange of phosphine ligands (L) in PdL_n (n = 2-4) complexes where the kinetics are consistent with a dissociative mechanism and the authors suggest that the 14e complexes may be stabilised by Pd-H bonds from side-chains or the phosphorus ligands [256]. The temperature dependent ^1H NMR spectra of some new chelated $M(CO)_4$(msdp) (M = Cr, Mo, W; msdp = $MeSCH_2CMe_2CH_2SMe$) were interpreted by considering total inversion of the 6-membered chelate ring system and thermodynamic parameters for the ring inversions, obtained by line-shape fitting techniques, are reported [257].

Currently there is much interest in homolytic reactions of organometallic compounds and, whereas mechanistic studies of these reactions have mainly centred on Group III and IV metals, transition metals have remained unexplored and evidence for radical mechanisms is circumstantial, e.g. reactions of C_6H_5SH with methyl derivatives of Pt(II), Au(I) and Au(III) [258]. A CIDNP study of the homolytic substitution reactions of metal alkyls has shown that $Au(PPh_3)Me$ is much more prone to these reactions than *cis* $Pt(PPh_3)_2Me_2$ [259].

^{13}C spin-lattice relaxation times (T_1) have been shown to reflect the inter- and intramolecular mobility of a molecule and thus compliment the results of temperature-dependent NMR spectroscopy. The T_1 differences within a molecule show, for instance, whether the molecular motion is anisotropic in solution, whether the internal motion of groups is subject to steric hindrance, the extent to which strong intermolecular or interionic interactions affect the flexibility of the molecule and which parts of a molecule are rigid and which are flexible. Applications of ^{13}C spin-lattice relaxation times to the problems outlined above have been reviewed [260] and, although the examples are drawn from organic chemistry, the potential for the organometallic chemist is clear.

MÖSSBAUER SPECTRA

A new source, consisting of an Os-Nb alloy suitable for repeated neutron irradiation, has been developed which makes ^{193}Ir Mössbauer studies a routine practical proposition [261]. Well resolved quadrupole-split spectra have been obtained even from organometallic compounds which might have been expected to give very low recoil-free fractions [262,263]. ^{193}Ir Mössbauer appears to be an extremely powerful means of studying electron distribution in these otherwise rather intractable Ir complexes.

A ^{57}Fe Mössbauer investigation of $Fe(CO)_3L_2$ complexes indicated that the σ-bond strength decreased in the series of L-ligands: CNPh > $P(OMe)_3$ > PBu_3 > $P(NMe_2)_3$ and $P(OPh_3)_3$ > PPh_3 > $AsPh_3$ ∿ $SbPh_3$ but it was not possible to calculate qualitative values for π-bond strengths [264]. The experimental data showed rather large variations in quadrupole splitting which were explained by differences in the bonding properties of the ligands, whereas the variations in the isomer shifts were very small [264]. In the ^{57}Fe Mössbauer spectra of π-allyliron carbonyl complexes variations in isomer shifts were explained qualitatively in terms of forward coordination and back donation while quadrupole splitting values seemed to depend on the localised electron density and on the geometry of each system [265]. Data from ^{57}Fe Mössbauer spectra of some carbene complexes $\{Fe(CNMe)_5(carbene)\}(PF_6)_2$ and $\{Fe(CNMe)_4(carbene)_2\}(PF_6)_2$ is consistent with the X-ray and ^1H NMR conclusion that carbenes are better σ-donors but poorer π-acceptors than isocyanides [266]. A combination of X-ray diffraction and Mössbauer studies has been used to solve the structure of $HFe_3(CO)_9SR$ complexes (R = *i*-Pr, *t*-Bu) [267]. The Mössbauer spectra contained two quadrupole-split doublets of relative intensity 2:1 but there seemed to be no correlation of M-M distances with the location of the bridging hydride ligand. ^{57}Fe Mössbauer data showed that in the reactions of $HFeCo_3(CO)_{12}$ with phosphorus donors to give $HFeCo_3(CO)_{12-n}L_n$ complexes (L = PPh_2, $PMePh_3$, PEt_3, $P(OPh)_3$, P(OPr); n = 1-3 depending on L) substitution took place preferentially at the Co atom with up to one CO per Co being replaced [268].

In the series of complexes $HFeCo_3(CO)_{12-n}(PMePh_2)_n$ ($n = 0-3$) the change in the quadrupole splitting showed that a large distortion of the electric field gradient had occurred for $n = 1$ or 2 but that the symmetry about the Fe was restored in some way for $n = 3$. The authors commented that it was surprising that substitution at Co should affect the Fe atom so much but it was noted that substitution does remove the pseudo-octahedral symmetry overall for $n = 1$ or 2 and that this symmetry is restored for $n = 3$.

Trends in ^{119}Sn Mössbauer isomer shifts and quadrupole splitting values in a series of complexes with Cl-bridged Sn-Mo and Sn-W bonds of the type $(LL)M(CO)_3Sn(R_{3-n}Cl_n)Cl$ (LL = α,α'-bipyridyl, *o*-phenanthroline, dithiahexane; M = Mo, W; R = Me, Ph; $n = 1-3$) indicated that W is a better σ-donor than Mo [269]. New ^{119}Sn and ^{57}Fe Mössbauer data for $SnX_3\ M(CO)_3(\eta^5\text{-}C_5H_5)$, $SnX_2\ M(CO)_3(\eta^5\text{-}C_5H_5)_2$, and $SnX_2\ M(CO)_3(\eta^5\text{-}C_5H_5)\ Fe(CO)_2(\eta^5\text{-}C_5H_5)$ has been examined for correlations with other physical parameters [270]. It was concluded that the point-charge model, which assumes partial quadrupole splittings are independent of the ligands, made assumptions which are not valid so that it would seem unwise to attempt to give chemical significance to small differences in partial quadrupole splitting value. However; good linear correlations were found between the electric field gradient at the Sn nucleus and the carbonyl stretching frequencies of the M' group, with the highest frequencies corresponding to most negative electric field gradient values. The correlation showed that the transition metal M' is functioning as the most-effective donor to Sn, but overall the electric field gradient changes, though real, were rather small so again caution was urged [270].

EPR AND MAGNETISM

The controversy over the EPR detection of the radical $Mn(CO)_5\cdot$ has been fuelled by matrix infrared spectroscopic evidence for $Mn(CO)_5$ following reactions of Mn atoms with CO and CO-argon mixtures at 10-15°K [271] (see Matrix Studies). The 350 nm irradiation of $Mn_2(CO)_{10}$ in thoroughly dried and degassed THF in the EPR cavity gave a spectrum which was interpreted as due to a solvated(S) Mn(II) species: $3Mn_2(CO)_{10} + 12S \rightarrow 2MnS_6^{2+} + 4Mn(CO)_5^- + 10CO$ so that, although evidence from spin-trapping and mechanistic studies supports the initial formation of $Mn(CO)_5\cdot$, the authors conclude that the EPR spectrum has not yet been observed [272]. This conclusion was challenged in a later study which assigned the EPR spectrum obtained during the photolysis of $Mn_2(CO)_{10}$ in THF to a quartet state species, which is more consistent with Mn(0), i.e. $Mn(CO)_5\cdot$, than Mn(II), and chemical studies were cited to support this conclusion [273]. Exposure of $Tl\{Co(CO)_4\}$ to ^{60}Co γ-rays at 77°K gave a high-field resonance identified as a Tl(II) centre and two lower-field resonances which were assigned to two distinct $Co(CO)_4^{2-}$

species [274]. One species, which had unusually large hyperfine coupling to ^{59}Co corresponding to ∿ 38% spin density in the outer *4s* orbital with some *4p* character implied from the low g-value, was assigned as due to $Co(CO)_4{}^{2-}$, which is probably distorted, and the other, which had a rather small hyperfine coupling to ^{59}Co and a higher g-value, was tentatively identified as $Co(CO)_4{}^{2-}$ with the unpaired electron confined to a CO ligand. At room temperature the EPR signal corresponded to a species with the properties expected for a peroxide, i.e. $Co(CO)_4(O_2)\cdot$ [274]. A combination of EPR spin densities at the coordination sites, ^{31}P coupling constants, and solvatochromism of the absorptions in the electronic spectra of the complex series $LMo(CO)_4$, $LMo(CO)_3(PBu_3)$ and $LMo(CO)_2(PBu_3)_2$ (L = *t*-Bu-N=CH-CH=N-*t*Bu(DAB), 2,2'-bipyridyl(bipy) and their paramagnetic monoanions revealed that the π-acceptor quality of bipy is only about half of that of DAB [275].

Metal-metal bonds of a variety of binuclear transition metal carbonyl complexes can be readily cleaved by the action of one-electron oxidising agents and the single electron transfer from a neutral diamagnetic organometallic compound must necessarily lead, in the primary mechanistic step, to a cationic paramagnetic intermediate which can undergo fragmentation into a diamagnetic cation and a reactive metal- or carbon-centred radical. EPR evidence for the formation of radicals from a variety of organometallic compounds containing M-M or M-C bonding, using tetracyanoethylene (TNCE) as the 1e oxidising agent, has been reported [276]. For example, reaction of a 10^{-3} M THF solution of $Mn_2(CO)_{10}$ with TCNE gave an EPR spectrum which was the superposition of the spectra of the TCNE radical anion ($TCNE^{\overline{\cdot}}$) and a radical eventually identified as $(CO)_5Mn\text{-}N{=}C(CN)\text{-}C(CN)_2\cdot$, an iminotricyanoallyl radical, formed by the addition of $Mn(CO)_5\cdot$ to a neutral TCNE molecule. Similar radicals were obtained with $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (M = Cr, Mo W) and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ but not with $Re_2(CO)_{10}$, $Co_2(CO)_8$ and $\{(\eta^5\text{-}C_5H_5)Ni(CO)\}_2$ which gave $TCNE^{\overline{\cdot}}$ as the only radical [276]. EPR in conjunction with selective deuteriation [277] and spin trapping [278] has been used to study radicals formed in the photolysis of some alkylcobaloximes and arising from Co-C bond cleavage. A useful method to probe for transient species present during the reactions of paramagnetic complexes with olefins, involving the application of careful temperature modulation of EPR signals, has been reported [279]. The method was applied to paramagnetic Nb(IV) and Ta(IV) hydrides interacting with olefins because the metals have large nuclear magnetic and nuclear spin moments and hence give rise to well resolved spectra.

Room temperature magnetic susceptibility measurements on a series of new σ-bonded organolanthanide complexes of the type $(\eta^5\text{-}C_5H_5)_2L_nR$ (R = Me, Ph, C≡CPh) are in agreement with theoretical values but as the temperature was lowered values also decreased [280,281]. This behaviour is in sharp contrast to other cyclopentadienyllanthanide complexes, where values of μ_{eff} are temperature invariant, and has been tentatively attributed to enhanced quenching of the *f*-orbital angular momentum by the electric field and/or ligand field of the R moiety, i.e. some degree of covalency in the Ln–R σ bond. New EPR measurements on $(\eta^5\text{-}C_5H_5)_2Mn$ and $(\eta^5\text{-}C_5H_4Me)_2Mn$ have shown that the complexes exist as high spin $^6\Sigma^+$ or low spin $^2\Delta$ depending on molecular environment and this has enabled previous anomalous properties to be explained as a consequence of a thermal equilibrium between HS (high spin and LS (low spin) states [282]. The results of EPR studies and extended Hückel M.O. calculations on the radical anions of benzocyclopentadienyltricarbonylmanganese and in mono- and dimethyl derivatives have shown that there is extensive delocalisation of electrons over the molecules with spin density localised mainly on the Mn atom, the ketonic group and the phenyl ring [283]. The nominal electron configuration in (1-phenylborabenzene)$_2$Co has been proposed as $(d_{x^2-y^2})^2\ (d_{xy})^2\ (d_{yz})^2\ (d_{z^2})^1$ on the basis of EPR measurements at 77°K [284]. Analysis of the quadrupole coupling constant suggests that the bonding is very similar to that in $(\eta^5\text{-}C_5H_5)_2Fe$ with ∿ 0.7 electron back-donated to each borabenzene ring. A dilute single-crystal EPR investigation of $(\eta^5\text{-}C_5H_5)_2V(S_5)$ doped in a crystal lattice of the diamagneti $(\eta^5\text{-}C_5H_5)_2Ti(S_5)$ host has provided the first quantitative determination of the relative metal orbital character and the directional properties of the unpaired electron in a V(IV) $(\eta^5\text{-}C_5H_5)_2VL_2$ complex [285]. A detailed analysi of the anisotropy of the hyperfine interaction of the unpaired electron with the ^{51}V nucleus shows clearly that the electron resides primarily on the vanadium in an a_1-type M.O. mainly comparised of $3d_{z^2}$ with a small but significant amount of $3d_{x^2-y^2}$and no $4s$ character. These EPR results thereby provide convincing evidence that the widely utilised Ballhausen-Dahl (qualitative) model is not valid for d^1 and d^2 M(IV) $(\eta^5\text{-}C_5H_5)_2ML_2$ compounds and additionally indicate that the subsequent Alcock (qualitative) model, which arbitrarily assumes the d^1 and d^2 electrons occupy a d_{z^2} A.O., is also inadequate. An EPR study of $(\eta^5\text{-}C_5H_4Me)_2VCl_2$ in $(\eta^5\text{-}C_5H_4Me)TiCl_2$ extended and confirmed the above conclusions [286]. Two studies of the magnetic susceptibilities of organometallic complexes involving *f*-electrons have noted temperature dependence in $(\eta^8\text{-}C_8H_8)_2U$ [287] and in a series of $(C_8H_8)_2M$ complexes (M = lanthanide, actinide) [288].

The ^{13}C pulse Fourier transform NMR spectra of selected phenyl- and ethyl-substituted paramagnetic metallocenes (M = V, Cr, Co, Ni) have been recorded [289]. Appropriate instrumental conditions, to resolve the multiple structure of such spectra and to carry out not only selective proton decoupling but also selective off-resonance experiments as a means to ascertain formerly ambiguous assignments of ^{13}C and ^1H resonances, have been demonstrated.

EPR spectroscopy has been used to study catalysts obtained by supporting $Mo_2(CH_3CO_2)_4$, $M_2(CH_2SiMe_3)_6$ (M = Mo, W), $W(CO)_6$, $W(CH_3)_6$, $Cr(CO)_6$ and $Cr(CH_2CMe_3)_6$ on high surface area silica [290]. The supported Mo complexes, activated at sufficiently high temperature, gave rise to EPR signals identical to those observed previously from silica-supported $Mo(CO)_6$ and MoO_3 catalysts, i.e. square pyramidal Mo(V) and O_2^-, while W complexes gave only O_2^- and Co complexes gave only Cr(V) signals identical with those observed from silica-supported CrO_3.

POLAROGRAPHY AND ELECTROCHEMISTRY

The background to the use of electrochemistry as a preparative technique in organometallic chemistry has been reviewed [291-3]. Most examples are taken from organic and main group organometallic chemistry but there are some stimulating new applications using transition metals [291] and the importance of electrosynthesis for industry is clear [291].

The relationship between structure and the formal electrode potential (E^o) for the oxidation of substituted metal carbonyls of the type $\{M(CO)_{6-n}L_n\}^{y+}$ has been investigated [294]. A significant quantitative relationship between the formal electrode potential and the structure of a metal carbonyl, in terms of net charge on the species and the degree and type of ligand substitution, has been established and this means that electrochemical measurements provide additional and complimentary information to that obtainable from spectroscopic studies [294]. The electrochemical reduction of $Cr(CO)_6$ in DMF on a Hg electrode has been shown to yield $Cr_2(CO)_{10}^{2-}$ and $HCr_2(CO)_{10}^-$ [295]. One disadvantage of Hg electrodes is the formation of Hg-M bonds but this can be overcome by using Pt electrodes [296] and this has enabled metal carbonyl anions, e.g. $M_2(CO)_{2n-2}^{2-}$ (M = Cr, Mo, W, n = 6; M=Fe, n = 5), $V(CO)_6^-$ and $M(CO)_5^-$ (M = Mn, Re), and cations, e.g. $Cr(CO)_6^+$ and $M(CO)_5(NCMe)^+$ (M = Cr, Mo, W) to be prepared. In addition the electrochemical experiments showed that there are often quasi-stable intermediates and these may be useful both for the synthesis of organometallic compounds and in the construction of new organic reaction routes, e.g. $M(CO)_5^{-\cdot}$ (M = Cr, Mo, W) [296]. Electrochemical studies have demonstrated that a series of $\{M(CO)_2DPM_2\}^{0,+,2+}$ complexes (M = Cr, Mo, W; DPM = $Ph_2PCH_2PPh_2$) exist however, thermodynamically, the equilibria for the reactions

$$\mathit{cis}^{o} + \mathit{trans}^{+} \rightleftarrows \mathit{cis}^{+} + \mathit{trans}^{o}$$

$$\mathit{trans}^{+} + \mathit{cis}^{2+} \rightleftarrows \mathit{trans}^{2+} + \mathit{cis}^{+}$$

lie to the left so that only *cis*^{o}, *trans*$^+$ and *cis*$^{2+}$ species are thermodynamically stable, with *cis*$^+$, *trans*^{o} and *trans*$^{2+}$ readily isomerising. Electrochemical oxidation pathways were characterised by equations of the kind:

$$\mathit{cis}^{o} \underset{+e}{\overset{-e}{\rightleftarrows}} \mathit{cis}^{+} \rightarrow \mathit{trans}^{+}$$

$$\mathit{trans}^{+} \underset{-e}{\overset{+e}{\rightleftarrows}} \mathit{trans}^{o} \rightarrow \mathit{cis}^{o}$$

$$\mathit{trans}^{+} \underset{+e}{\overset{-e}{\rightleftarrows}} \mathit{trans}^{2+} \rightarrow \mathit{cis}^{2+}$$

and the authors commented on claims to have made various bis-DPM complexes, e.g. *trans*^{o}, by a direct route [297]. A series of Vaska's complexes of the type $Ir(CO)XL_2$ (X = monanionic ligand, $L = PR_3$) have been studied using a rotating Pt electrode and electrochemical oxidation has been shown to proceed as a diffusion-controlled, irreversible one-electron process, indicating that in the redox addition process atom transferability plays a more important role than the redox properties of the complex [298]. The electrochemical behaviour of Re dinitrogen complexes and analogues has been described in detail and the results have been discussed in terms of criteria for a correlation between redox potentials and X-ray photoelectron spectroscopic measurements [299].

The complexes $Cr(CO)_2L(\eta^6\text{-}C_6Me_6)$ ($L = PPh_3$, $PMePh_2$, $P(OPh)_3$, $P(OMe)_3$) have been found to react with $NO^+PF_6^-$ to afford $\{Cr(CO)L(\eta^6\text{-}C_6Me_6)NO\}PF_6$ and $\{Cr(CO)_2(\eta^6\text{-}C_6Me_6)NO\}PF_6$ where as $PhN_2^+PF_6^-$ yields paramagnetic $\{Cr(CO)_2L(\eta^6\text{-}C_6Me_6)\}PF_6$ or $\{Cr(CO)L(\eta^6\text{-}C_6Me_6)N_2Ph\}PF_6$ and $\{Cr(CO)_2(\eta^6\text{-}C_6Me_6)N_2Ph\}PF_6$ and electrochemical studies confirmed that the oxidation of $Cr(CO)_2L(\eta^6\text{-}C_6Me_6)$ to $Cr(CO)_2L(\eta^6\text{-}C_6Me_6)^+$ is a reversible le process [300]. The factors determining whether NO^+ or PhN_2^+ oxidise organometallic complexes or cause substitution are discussed and it was concluded that the course of the reaction depends on the relative metal-ligand bond strengths in the proposed intermediate $\{Cr(CO)_2L(\eta^6\text{-}C_6Me_6)X\}^+$ (X = NO or PhN_2) rather than the reduction potentials of NO^+ and PhN_2^+. Various transition metal complexes of the types $(\eta^5\text{-}C_5H_5)FeL_2X$, $(\eta^5\text{-}C_5H_5)Mn(CO)L_2$ and MnL_5X (L = isocyanides, phosphines, phosphites; X = halides, Me, SnX_3) have been found to undergo either facile le oxidations to give isolable 17e species or they lost X^- to yield intermediates which went on to react either with other added ligands or with ligands produced by degradation of complexes [301]. The authors suggested that mixed ligand complexes might be prepared in high yield by electrochemical routes. The relative case of oxidation of several diindenyliron and cyclopentadienyl(indenyl)iron sandwich compounds, as measured by cyclic voltammetry, decreased in the series $(Ind)_2Fe$ > $(Ind)(Cp)Fe$ > $(Cp)_2Fe$ and $(1,3\text{-}Me_2Ind)Fe$ > (1-MeInd) > $(Ind)_2Fe$ [302].

Polarography was able to differentiate between π-arene bis{$(\eta^5\text{-}C_5H_5)Fe\}^{2+}$ ions and π-arene{$(\eta^5\text{-}C_5H_5)Fe\}^+$ ions, whereas electronic absorption and ^{57}Fe Mössbauer spectroscopy were not, because the dications exhibited two iron reduction waves in addition to reduction waves for the arene [303]. Electrochemically generated cobaltocene and cobaltocene anion were found to react in high yield with alkyl halides [304]. Electro-oxidation of organo-Co(III) and organo-Rh(III) chelates yielded fairly stable species retaining the σ-bonded organic group, which behaved as a carbonium ion and was readily transferred to nucleophiles [305].

PHOTOCHEMISTRY (See also Matrix Studies)

A monograph entitled *Concepts of Inorganic Photochemistry* gives a comprehensive account of developments which have been achieved through emphasis on the application of summarising principles to a wide variety of coordination compounds and includes a chapter on the photochemistry of metal carbonyl complexes [306]. Progress is beginning to be made in studying the excited states responsible for photoreactions and spectroscopic investigations of excited states of transition metal complexes have been reviewed [307]. M.O. calculations are increasingly being carried out to facilitate assignments of excited states [308] and to rationalise photosubstitution quantum yields, allow predictions of the labilised ligand, and the reactivities of ligand field states [309]. The contribution which the matrix isolation technique can make to photochemical studies has been reviewed in a contribution to the Darmstadt Symposium on "Metal Atoms in Chemical Synthesis" (see Matrix Studies) [310].

The most widely cited quantum yield in the photochemistry of metal carbonyls is that for the photodissociation of CO from $M(CO)_6$ (M = Cr, Mo, W) and it has been repeatedly reported that the quantum yield is 1 for all three metal hexacarbonyls. On the other hand, the quantum yields for photosubstitution in $M(CO)_5L$ complexes (M = Cr, Mo, W) are all appreciably less than unity and this has prompted a reexamination which found $\Phi_{CO} = 0.67 \pm 0.02$ for $[Cr(CO)_6] = 3 \times 10^{-4}$ mol l^{-1} and [pyridine] = 10^{-2} mol l^{-1} [311]. The authors noted that overlap of electronic absorption bands of parent and products made completely selective photolysis impossible with a consequence of secondary photolysis for long irradiation times and it was undetected secondary photolysis which led to early values of $\Phi_{CO} = 1$. The fact that $\Phi_{CO} < 1$ demonstrates that there are radiationless processes competing with photodissociation and photosubstitution and also suggests that other early values of Φ_{CO} and Φ_L should be treated with caution [311]. Kinetic studies of the reaction of $W(CO)_5$(aniline) with PPh_3 have given irreproducible results and the origin of the problem has been sought [312]. It was shown that no reaction occurred in the dark under the conditions of the original report but when the experiment was carried out on the bench a reaction took place. The bench reaction was arrested in the darkness of the spectrometer so that the kinetics reflect, in part at least, a photochemical reaction. Even taking all reasonable precautions irreproducibility still occurred and this was traced to Ph_3PO which accelerates the reaction, possibly via hydrogen bonding (see [249]). The authors urged the need for the highest purity of materials and solvents for quantitative thermal and photochemical studies and the cognizance of the possibility of photochemical contributions to thermal reactions [312]. Photosubstitution of pyridine has been described as efficient in *cis* $W(CO)_4(py)_2$ ($\Phi_{436} = 0.23$; $\Phi_{405} = 0.27$; $\Phi_{366} = 0.23$) [118]. The $M(CO)_4L$ complexes (M = Cr, Mo, W; L = 2,2'-bipyridine, 1,10-*o*-phenanthroline) have strongly wavelength dependent, but modest, quantum yields for CO substitution, e.g. values for $W(CO)_4$(*o*-phen) are: $\Phi_{436} = 1.6 \times 10^{-4}$, $\Phi_{405} = 1.2 \times 10^{-3}$, $\Phi_{366} = 9.2 \times 10^{-3}$, $\Phi_{313} = 2.2 \times 10^{-2}$, and show that the lowest charge-transfer state is unreactive [118]. Photochemical studies of $W(CO)_5L$ complexes in solution at room temperature have shown that $\Phi_L >> \Phi_{CO}$ and infrared spectroscopy has provided evidence that 366 nm photolysis of $W(CO)_5L$ (L = pyridine or 3-bromopyridine) in an argon matrix at $12^{\circ}K$ produces $W(CO)_5$ and free ligand [313]. This is the first report of photodetachment of a bulky ligand in a matrix experiment and it suggests that matrix studies can provide valuable information about the reactions under more usual conditions [313]. The photochemical reaction of (norbornadiene)$Cr(CO)_4$ with PPh_3 has been described [314]. The unusual photostability of (norbornadiene)$Cr(CO)_4$ led the authors to the conclusion that the primary photoprocess does not consist of CO dissociation but M-olefin bond rupture followed by a rapid thermal return to full coordination and this concept was extended to (diene)Cr(CO where dienes were non-cyclic. It has been demonstrated that the decarbonylation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(^{13}COCH_3)$ either photochemically or in the mass spectrometer occurs with loss of a terminal CO group and that the intermediate resulting from the photochemical process undergoes nucleophilic attack by PPh_3 faster than methyl migration [315]. The first evidence for a radical chain pathway for transition metal carbonyls has been reported and it is claimed that such a pathway may prove of considerable generality and importance. The observation suggesting a chain pathway were supported by photochemical reactions of $HRe(CO)_5$ [316]. Once again the authors noted that kinetic studies with $HRe(CO)_5$ have been erratic (see [312] above) but after extreme care for purity and light exclusion no reaction took place after 60 days at 25°C whereas exposure to light, failure to purify and various other circumstances led to a rapid reaction. A photochemically generated radical has been shown to be responsible for the activation of molecular hydrogen [317] according to the proposed series of reactions:

$$Re_2(CO)_{10} \overset{h\nu}{\rightleftarrows} 2Re(CO)_5\cdot$$

$$Re(CO)_5\cdot \rightleftarrows Re(CO)_4 + CO$$

$$Re(CO)_4 + H_2 \rightleftarrows H_2Re(CO)_4$$

$$H_2Re(CO)_4 + Re(CO)_5\cdot \rightarrow HRe(CO)_5 + HRe(CO)_4$$

The quantum efficiency of photosubstitution of (η^6-Ar)Cr(CO)$_3$ complexes (Ar = C_6H_6, $C_6H_3Me_3$) has been shown to be independent of irradiating wavelength (Φ_{CO} = 0.72 ± 0.07 at 313, 366 and 436 nm) and of the concentration of pyridine in the range 0.008-0.17 mol l^{-1} [318]. The complexes were observed to quench triplet-excited benzil at the diffusion-controlled rate and the quenching was accompanied by reaction to give (η^6-Ar)Cr(CO)$_2$(py). The reaction product, which presumably arises from CO release, i.e. (η^6-Ar)Cr(CO)$_2$, was the same in the sensitised and direct irradiation experiments but the triplet sensitised reaction occurred with a much lower quantum efficiency (Φ = 0.15 ± 0.05) than on direct irradiation (Φ = 0.72 ± 0.07). In C_6H_6 a mathematical treatment of the data, which is necessary because of overlapping absorption bands (see [311] above), for the photosubstitution of a CO ligand in (η^6-$C_6H_3Me_3$)Cr(CO)$_3$ by N-dodecylmaleimide, gave a quantum yield Φ_{CO} = 0.90 ± 0.09 for irradiation at 313 nm with no evidence for labilisation of the arene ligand [319]. The origin of the 0.1 ± 0.1 deficit in the quantum yield measurements was not clear but the operation of some radiationless processes was suggested because no luminescence has been observed even at 77°K.

Quenching of electronically excited benzil and Ru(bipy)$_3^{2+}$ by metallocenes (Fe, Ru, Os, Co) has been investigated [320, 321]. The quenching behaviour is that expected for "non-vertical" electronic energy transfer to the geometrically distorted lowest triplet state of the metallocene and from the marked fall in quenching efficiency for organic molecules with triplet state having energies less than 14,000 cm^{-1} the absorption maximum of the lowest triplet state of (η^5-C_5H_5)$_2$Fe was deduced to lie at ∿ 14,000 cm^{-1} (714 nm) [321]. Luminescence from pure solids at 25°K set the emission maximum for ruthenocene and 1,1'-diacetylruthenocene at ∿ 1700 cm^{-1} (588 nm) which corresponds to a red shift of ∿ 10,000 cm^{-1} from the first singlet-triplet absorption maximum [320]. The structured emission of (η^5-C_5H_5)$_2$Ru showed two vibrational progressions separated by 162 ± 10 cm^{-1} with vibrational spacings of 327 ± 10 and 340 ± 10 cm^{-1} associated with the metal-ring stretching vibration found at 330 cm^{-1} in the Raman spectrum. The emission lifetimes (127 μsec at 28°K) and quantum yields (0.027 ± 0.05 at

28°K) for $(\eta^5\text{-}C_5H_5)Ru$ were temperature dependent and this was interpreted as revealing that the decreasing emission efficiency at higher temperatures is due to a faster rate of non-radiative decay [320]. The photolysis and naphthalene-photosensitised reaction of the charge-transfer complex between $(\eta^5\text{-}C_5H_5)_2Ru$ and CCl_4 has been shown to form $(\eta^5\text{-}C_5H_5)_2Ru^+$ in the primary photoprocess ($\Phi_{313} = 0.72$; $\Phi_{366} = 0.52$) [322]. By studying the partial inhibition of the reaction with $SnCl_3$, O_2 and acrylamide, it was possible to show that at 313 nm the quantum yield for the decomposition is made up of contributions from the singlet (0.24) and triplet (0.40) states while the naphthalene-photosensitised reaction proceeds through a triplet state. An electronic spectrum for $(\eta^5\text{-}C_5H_5)_2Ru^+Cl^-$ in 0.1 M HCl has been recorded (λ_{max}: 250 nm(shoulder , $\varepsilon = 9400 \pm 400$ l mol cm^{-1}); 330 nm, ($\varepsilon = 4360 \pm 200$ l mol cm^{-1})) [322].

The observed photochemistry of $Mn_2(CO)_{10}$, $Mn_2(CO)_9(PPh_3)$, $Mn_2(CO)_8(PPh_3)_2$, $Re_2(CO)_{10}$ and $MnRe(CO)_{10}$ [323] and $\{(\eta^5\text{-}C_5H_5)Mo(CO)_3\}_2$ [324] has been interpreted as arising from homolytic metal-metal bond cleavage occurring from an excited state derived from a $\sigma \rightarrow \sigma^*$ one electron transition associated with the M-M bond and each of the complexes exhibits a near ultraviolet absorption corresponding to this absorption. Flash photolysis of $(CO)_5M'\text{-}M(CO)_3(\eta^5\text{-}C_5H_5)$ (M' = Mn, Re; M = Mo, W) in degassed isooctane yields $M'_2(CO)_{10}$ and $\{(\eta^5\text{-}C_5H_5)M(CO)_3\}_2$ in a nearly 1:1 ratio and with a high chemical yield (≥ 65%) [325]. It is interesting that the $\sigma \rightarrow \sigma^*$ absorption results in efficient homolytic cleavage in these mixed metal complexes because heterolytic cleavage would have given two diamagnetic species $M'(CO)_5^+$ and $M(CO)_3(\eta^5\text{-}C_5H_5)^-$ of the stable d^6 configuration. Another flash photolysis study of $\{(\eta^5\text{-}C_5H_5)Mo(CO)_3\}_2$ found direct evidence for loss of CO with the formation of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_5$ in addition to metal-metal bond cleavage to give $(\eta^5\text{-}C_5H_5)Mo(CO)_3\cdot$ [326].

In addition to the report of the photoejection of pyridine or 3-bromopyridine from $W(CO)_5L$ complexes in low temperature matrices [313], there have been two other novel low temperature studies which have important implications for solution photochemistry. Recently $Fe(CO)_4(THF)$ has been proposed as an intermediate in the chemistry of $Fe_2(CO)_9$ in THF and this proposal has been strengthened by the photolytic generation of $Fe(CO)_4(MeTHF)$, $Fe(CO)_3(MeTHF)_2$(2 isomers) and $Fe(CO)_4(NEt_3)$ from $Fe(CO)_5$ in doped glassy matrices at 77°K. Interestingly the authors note that there is evidence for pre-photolytic L ..... $Fe(CO)_5$ interactions [327]. The authors also noted that lighting conditions can seriously affect work on substitution reactions of metal carbonyls and suggested that *lighting conditions should be specified*, particularly in quantitative studies, in all work on substitution reactions. Plane-polarised has been used to produce oriented $Cr(CO)_5$ in CH_4 matrices and this has enabled the symmetry of the 489 nm transition to be determined, i.e. $^1A_1(b_2{}^2e^4) \rightarrow {}^1E(b_2{}^2e^3a_1{}^1)$ has transition moment of E [328]. Photo-orientation has also been demonstrated for the first time and this has implications for matrix photochemistry [328].

There have been a number of synthetic applications where a photochemical pathway for a reaction exists in situations where a thermal pathway does not exist or gives very different products. The photoinduced carbonylation of $(\eta^5\text{-}C_5H_5)_2TiMe_2$ and $(\eta^5\text{-}C_9H_7)_2TiMe_2$ in pentane resulted in cleavage of Ti-Me bonds and the formation of $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ and $(\eta^5\text{-}C_9H_7)_2Ti(CO)_2$ [329]. Photolysis of $M(CO)_6$ (M = Cr, Mo, W) in the presence of adamantanethione, ethylenetrithiocarbamate or $Ph_2C{=}S$ gave new thione complexes, e.g. $Ph_2C{=}S\text{-}M(CO)_5$ [330]. Photochemically-generated $M(CO)_5(THF)$ (M = Cr, Mo, W) has been used to prepare $M(CO)_5(NO_3)^-$ by reaction with Et_4NNO_3 [331]. Several (arene-chelate) metal complexes were prepared in fair yield by the photolysis in ether of the corresponding (arene) metal tricarbonyl complexes, e.g. $(\eta^6$-benzonorbornadiene$)Cr(CO)_3$ gave $(\eta^8$-benzonorbornadiene$)Cr(CO)_2$ [332]. Insertion of W into CH_3OH, to give a W-Me derivative, took place on the photolysis of $(\eta^5\text{-}C_5H_5)_2WH_2$ in CH_3OH and the formation of $(\eta^5\text{-}C_5H_5)_2WH(OMe)$ and $(\eta^5\text{-}C_5H_5)_2W(Me)(OMe)$ has been proposed to take place *via* a tungstenocene intermediate [333]. The photochemical decomplexation of glycols from $(\eta^6\text{-}(CHOHCH_3)_2C_6H_4)Cr(CO)_3$ is a specific route for the preparation of the two corresponding benzenic glycols [334]. Ultraviolet irradiation of an equimolar mixture of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ and $Ph_2PCH_2CH_2PPh_2$ at 20°C in C_6H_6 or C_6H_{12} gave the bidentate complex $(\eta^5\text{-}C_5H_5)Mn(CO)(Ph_2PCH_2CH_2PPh_2)$ but infrared spectra of the solution indicated some monosubstituted complex $(\eta^5\text{-}C_5H_5)Mn(CO)_2\text{-}(Ph_2PCH_2CH_2PPh_2)$ was formed and this indicated that the substitution proceeded stepwise [355]. The stepwise process was supported by the isolation of $(\eta^5\text{-}C_5H_5)Mn(CO)_2(Ph_2PCH_2CH_2P(O)Ph_2)$. Cycloheptatrienes reacted photochemically with $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ or its derivatives to produce neutral diamagnetic $(\eta^6$-cycloheptatriene$)(\eta^5\text{-}C_5H_5)Mn$ compounds *via* $(1,2\text{-}\eta^2$-cycloheptatriene$)\text{-}(\eta^5\text{-}C_5H_5)Mn(CO)_2$ intermediates [336]. The carbonylrhenium clusters $\{Re(CO)_4H\}_3$ and $\{Re(CO)_3OH\}_4$, the latter having Re atoms at opposite corners of a cube with bridging OH groups, were produced by the photoreaction of $Re_2(CO)_{10}$ with H_2O in ether [337]. When $Mn(CO)_4NO$ was photolysed in the presence of 1,3-butadiene it was expected that one of the products would be (1,3-butadiene)$_2$MnNO but surprisingly (1,3-butadiene)$_2$MnCO, the first paramagnetic butadiene complex, was formed in addition to (1,3-butadiene)$Mn(CO)_2(NO)$ [338]. Following the successful replacement of CO by N_2 in matrix isolation experiments to form $(\eta^4\text{-}C_4H_4)Fe(CO)_2(N_2)$ and $(CH_2)_3CFe(CO)_2(N_2)$, a low temperature (-40°C) irradiation of $(\eta^4\text{-}C_4H_4)Fe(CO)_3$ in THF with passage of N_2 gave $(\eta^4\text{-}C_4H_4)Fe(CO)\text{-}(\mu\text{-}CO)Fe(\eta^4\text{-}C_4H_4)CO$, a compound containing an Fe-Fe triple bond [339]. Photolysis of (2,3-Mebuta-1,3-diene)$Fe(\eta^6\text{-}C_6H_5PPhEt)$ in the prescence of excess diene resulted in replacement of the aromatic ligand by the diene to give (2,3-Mebuta-1,3-diene)$_2$Fe(PPh$_2$Et$_2$) [340]. It is known that ultraviolet irradiation of transition metal acyl complexes leads to elimination of CO in complexes which do not eliminate CO thermally and an interesting example is the isocyanide complex (η^5-C_5H_5)Fe(CO)(CNC$_6$H$_{11}$)-(COCH$_3$) which on photolysis gave the heterocyclic ring compound (η^5-C_5H_5)Fe(CO)-{(C=NC$_6$H$_{11}$)$_2$(CH$_3$)} involving N-coordination to the Fe atom [341]. The linkage isomers (η^5-C_5H_5)M(CO)$_n$SCN and (η^5-C_5H_5)M(CO)$_n$NCS (M = Fe, n = 2; M = Mo, n = 3) were interconverted by 366 nm radiation in THF at 30°C and, under similar irradiation, the halide complexes (η^5-C_5H_5)M(CO)$_2$(PPh$_3$)X (M = Mo, W; X = halogen) underwent *cis* → *trans* isomerisation and disproportionation to (η^5-C_5H_5)M(CO)$_3$X and (η^5-C_5H_5)M(CO)(PPh$_3$)$_2$X complexes in benzene solution [342]. The photochemical reaction of Fe(CO)$_5$ with a series of bidentate phosphine ligands Ph$_2$P(CH$_2$)$_n$PPh$_2$ (n = 1, 2, 3 and 4) yielded complexes of the type Ph$_2$P(CH$_2$)$_n$PPh$_2${Fe(CO)$_4$}$_2$ for n = 1-4 and additionally gave a metal-metal bonded complex with a bridging CO ligand (Ph$_2$PCH$_2$PCH$_2$)-Fe$_2$(CO)$_7$ [343]. A new simple synthesis has been described for {(η^5-C_5H_5)Fe(CO)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)}$^+$PF$_6^-$ which has been photochemically converted to the dinitrogen complex {(η^5-C_5H_5)Fe(Ph$_2$PCH$_2$CH$_2$PPh$_2$)}$_2$N$_2^{2+}$ which has a Fe-N-N-Fe bridge [344]. The photolysis of (η^5-C_5H_5)Co(CO)$_2$ has been found to produce a new reactive (η^5-C_5H_5)Co$_2$(CO)$_3$ cluster as a primary photoproduct [345]. The new cluster is very labile and readily decomposes to give {(η^5-C_5H_5)Co(CO)}$_3$ which in turn decomposes to give (η^5-C_5H_5)$_4$Co$_4$(CO)$_2$.

A review on photochemical activation of transition metal catalysts [346] provides the basis for the expanding area of photocatalysis, e.g. under weak ultraviolet irradiation butynediol is selectively hydrogenated to butenediol with Ir(CO)(Cl)(PPh$_3$)$_2$ as the photoactivating selective hydrogenation catalyst [347], (diene)Cr(CO)$_4$ complexes are effective for the photo-induced hydrogenation of the free dienes [314] and both photoactivated and photoinduced catalysis of the hydrogenation of cyclo-octene in the presence of Rh(Cl)(PPh$_3$)$_3$ has been reported [348]. The ferrocene-sensitised isomerisation of *trans*-ClCH=CHCl and *cis*- and *trans*-2-butene was studied as a function of irradiation time, frequency and temperature and the reaction mechanism, including triplet-triplet energy transfer from ferrocene to the olefin, was discussed [349]. Photolysis of Fe(CO)$_5$ in the presence of alkenes and alkynes (e.g. cyclopentene and EtC≡CEt) and H$_2$ (1 atm.) resulted in hydrogenation and intramolecular isomerisation [350]. The mechanism of both reactions included initial formation of a Fe(CO)$_4$(alkene) complex followed by Fe(CO)$_3$(alkene) production and the discussion was extended to the catalytic properties of other compounds, e.g. Mn$_2$(CO)$_8$(PPh$_3$)$_2$ and {(η^5-C_5H_5)M(CO)$_3$}$_2$ (M = Mo, W), and other processes, e.g. photoisomerisation of styrylpyridines and hydrosilation of 1,3-dienes. The *trans-cis* isomerisation of coordinated styrylpyridine was the subject of a separate report describing the photochemistry of $XRe(CO)_3L_2$ complexes (X = Cl, Br; L = *trans*-3-styrylpyridine, *trans*-4-styrylpyridine) [351]. The photorearrangement (254 nm) of 1,5-cyclooctadiene in the presence of Rh(I) to give 1,4-cyclooctadiene has been shown by deuterium labelling to involve an intramolecular (1,3) shift of a hydrogen [352]. The mechanism for the photorearrangement of olefins catalysed by Rh(I) was proposed to involve an initial photodissociation of one of two Rh(I) coordinated carbon-carbon double bonds and this results in an increase in the coordinative unsaturation of Rh(I) and enhances the proclivity of this d^8 metal towards oxidative addition of an allylic C-H bond. A η^3-allylrhodium intermediate then gives the rearranged olefin by reductive elimination. A novel Rh(I) catalysed hydrogen transfer has been reported which gives cyclooctene from cyclooctadiene under unprecedentedly mild conditions [352]. Photochemical metathesis of olefins occurs readily with $W(CO)_6$ e.g. metathesis of *cis*- and *trans*-2-hexene at room temperature in the presence of $W(CO)_6/Me_2ChCH_2AlCl_2$ catalyst [353], metathesis of hept-3-ene, pent-2-ene and E,E-deca-2,8-diene in the presence of $W(CO)_6/CCl_4$ [354], and metathesis of *trans*-C(H)Et=C(H)Me also in the presence of $W(CO)_6/CCl_4$ [355], and the active species has been proposed to be $W(CO)_5Cl$ [355]. The combination of a transition metal complex and C_2F_4 has provided two systems capable of photoinitiation of polymerisation, e.g. $Re_2(CO)_{10}$ + C_2F_4 for methylmethacrylate [356] and Me_2Pt(2,2'-bipyridyl) + C_2F_4 for methylmethacrylate [357].

Photochromism in the $\{(\eta^5\text{-}C_5H_5)Mo(CO)_3\}_2 + Br^-$ system has been studied and although the authors failed to put together an efficient photochromic system some useful criteria are outlined [358].

MATRIX STUDIES

An introductory monograph on *Matrix Isolation: A Technique for the Study of Reactive Inorganic Species* [359] provides a background to spectroscopic studies of reactive species in matrices but the book has one serious omission, in the opinion of this reviewer, namely that there are no references at all to take the interested reader further into the subject. However, this omission can be remedied by consulting a review on matrix isolation [360] and a detailed study has described the experimental conditions for obtaining matrix isolation Raman spectra routinely [361].

As a curtain-raiser to the Darmstadt Symposium (May 1974) on "Metal Atoms in Chemical Synthesis", Pimentel reviewed the contribution of matrix isolation to studies of metal atom reactions and linked the spectroscopic studies of metal atom reactions with preparative applications of the of the matrix isolation technique in terms of co-condensation of metal atoms with substrates on a large scale [362]. Contributions on preparative applications included the reaction of transition metal atoms with organic substrates [363], synthetic reactions of metal atoms at temperatures of 10 - 273°K [364], laser-evaporation of metals and its application to organometallic synthesis [365] and reaction of metal atoms with fluorocarbons [366]. Spectroscopic applications included transition metal atoms in the synthesis of binuclear complexes [367], spectral evidence for lanthanoid and actinoid carbonyl compounds ($M(CO)_{1-6}$; M = U, Pr, Nd, Gd, Ho) [368] and photochemistry in matrices an its relevance to atom synthesis [310]. Other preparative-based reviews have covered metal vapours as reagents [369], organic chemistry of metal vapours [370], chemistry of transition metal vapours [371] and vapour synthesis - a new technique in synthetic chemistry [372] while a review o cryogenic inorganic chemistry [373] deals with mainly spectroscopic studie

Co-condensation of Ti atoms with C_6H_6, $C_6H_5CH_3$ and $C_6H_3Me_3$(mesitylen afforded bis-arene complexes which were proposed to have symmetrical sandwich structures on the basis of ^1H NMR, infrared, mass and photoelectron spectroscopy [374]. The catalytic activity of these zero-valent (η^6-aren Ti(0) compounds towards butadiene oligomerisation has been investigated a this entailed co-condensation of the vapours of metal atoms (Ti, V, Cr, Mn Fe, Co, Ni) with butadiene in benzene [375]. Oligomerisation was catalyse by all the metals except Ti. The work also included studying the effects of added co-catalysts, e.g. alkylaluminium halides, and added ligands, e.g PPh_3, and it was shown that both of these factors could change the nature of the oligomerisation product [375]. Vapours of V and Cr were condensed with arene substrates, including halogenated arenes and CF_3-substituted arenes to yield bis-arene complexes [376]. The presence of two CF_3 groups caused failure of the preparation for V but gave good yields of extremely air- and temperature-stable Cr complexes. Infrared studies suggested that the ring-metal bonding is weaker in $(\eta^6-C_6H_5CF_3)_2Cr$ than in $(\eta^6-C_6H_6)_2Cr$ [376]. Metal atom syntheses have provided a spur to chemists to re-invest gate conventional routes, e.g. refluxing the pyridine heterocyclic arene complex $(\eta^6-C_5NMe_3R_2)Cr(CO)_3$ (R = CH_3, H) with PF_3 afforded a trisubstitut PF_3 complex $(\eta^6-C_5NMe_3R_2)Cr(PF_3)_3$ [377] analogous to the complex reported from the co-condensation of Cr atoms with PF_3 and pyridine. Synthetic reaction of Mo and W atoms with cyclopentadiene and cycloheptatriene gave $(\eta^5-C_5H_5)_2MH_2$, $(\eta^5-C_5H_5)(\eta^6-C_6H_6)MH$, $(\eta^5-C_5H_5)_2M$, and $(\eta^7-C_7H_7)M(\pi-C_7H_9)$ [378]. Benzylpalladium chloride has been proposed as an intermediate in the palladium acetate catalysed reaction of benzyl chloride with methyl acrylate and the compound has been prepared by the co-condensation of Pd atoms with $C_6H_5CH_2Cl$ at -196°C followed by warming to room temperature [37 The η^3-allyl complex was surprisingly stable and moreover when substituted for palladium acetate it gave the same products in the reaction of benzyl chloride with methyl acrylate [379]. The reactions of Pd atoms with olefi have been studied by low temperature infrared spectroscopy and the most stable compounds observed, (cyclo-octa-1,5-diene)$_2$Pd and (bicyclo[2,2,1]-heptene)$_3$Pd, have been prepared from Pd atoms on a gram scale [380]. Interestingly, (bicyclo[2,2,1]heptene)$_3$Pt has been prepared conventionally [232].

Reactions of Mn atoms, i.e. Mn and Mn$_2$ species, with CO and CO-argon mixtures at 10-15°K have been investigated by matrix isolation infrared spectroscopy [271]. For isolated Mn atoms the infrared data was interpreted as establishing the existence of Mn(CO)$_5$ with C_{4v} stereochemistry but, bearing in mind the controversy elsewhere over the existence or non-existence of Mn(CO)$_5$· [272,273], it is the opinion of this reviewer that the case for Mn(CO)$_5$ in this work is not proven, e.g. why was $^{12}C^{18}O$ isotopic substitution used to determine the structure of Mn$_2$(CO)$_n$ and yet not used to determine both n and the molecular geometry in Mn(CO)$_n$? Besides its reactions in the monoatomic form, Mn has also been shown to react as dimers Mn$_2$, formed as a result of a surface diffusion occurring in the quasi-liquid phase during matrix deposition. The relative concentrations of mononuclear and binuclear species depend on the concentration of metal in a matrix and on the CO:Ar ratios. Using low $^{12}C^{16}O$:Ar ratios, which favour Mn$_2$ formation, binuclear species Mn$_2$(CO)$_n$ have been synthesized and using $^{12}C^{16}O$-$^{12}C^{18}O$ labelling experiments evidence is presented to establish the species formed as Mn$_2$(CO^b), Mn$_2$(CO^b)$_2$ and Mn$_2$(CO^t) where b and t stand for bridging and terminal CO ligands respectively [271]. The products of the co-condensation reaction of Cu atoms with CO at 10-15°K have been investigated by matrix infrared and ultraviolet/visible electronic spectroscopy and have been shown, on the basis principally of $^{12}C^{16}O$, $^{12}C^{16}O$-$^{13}C^{16}O$, $^{12}C^{16}O$-Ar, $^{12}C^{16}O$-$^{13}C^{16}O$-Ar and $^{12}C^{16}O$-$^{13}C^{16}O$-$^{12}C^{18}O$-Ar mixed matrix experiments, to have the stoichiometries Cu(CO), Cu(CO)$_2$, Cu(CO)$_3$ and Cu$_2$(CO)$_6$ [381]. Cu$_2$(CO)$_6$ could also be synthesised by the matrix dimerisation of Cu(CO)$_3$ at 45-50 K or by the reaction of Cu$_2$ molecules and/or Cu$_2$(CO)$_n$ complexes with CO at 10-15°K. Isotopic frequencies were computed for the CO stretching modes of triangular planar Cu(CO)$_3$ and linear Cu(CO)$_2$ on the basis of Cotton-Kraihanzel force-field approximations and were found to be in close agreement with observed values. Qualitative M.O. schemes consistent with ultraviolet/visible spectra are presented for Cu(CO)$_3$ and Cu$_2$(CO)$_6$ and it is proposed that an extremely intense absorption at 417 nm in the electronic spectrum of Cu$_2$(CO)$_6$ is associated with the $\sigma \rightarrow \sigma^*$ transition between orbitals of the Cu-Cu bond [381]. In the co-condensation reactions of Co atoms with CO at 6-15°K the products Co(CO)$_n$ ($n = 1$-4) were characterised using a variety of matrices, isotope studies and spectroscopic techniques (infrared, Raman, ultraviolet/visible and EPR spectroscopy) [382]. In CO, vibrational and EPR studies gave C_{3v} symmetry for Co(CO)$_4$ in agreement with Co(CO)$_4$ generated from Co(CO)$_3$NO in CO matrices by photolysis but the EPR data for Co(CO)$_4$ in argon matrices was interpreted as involving two species, i.e. C_{3v} and D_{2d} geometry from infrared spectroscopy. However, in the opinion of this reviewer, in making this assignment the authors did not consider mixed matrix effects adequately, i.e. one Co(CO) might have a predominance of argon atoms in the nearest-neighbour cage while the other may have a higher proportion of CO molecules (see [383] below for $Cr(CO)_5$ ..... Ar versus $Cr(CO)_5$ ..... CO). Vibrational data for the lower carbonyls was in accordance with planar D_{3h} $Co(CO)_3$ (EPR suggested distortion towards C_{3v}) and linear $D_{\infty h}$ and $C_{\infty v}$ for $Co(CO)_2$ and Co(CO) respectively. The Co atoms reaction with CO was also investigated at high Co concentrations and, by comparison with matrix isolated $Co_2(CO)_8$, was shown to yield a mixture of Co-Co and CO-bridged isomers of $Co_2(CO)_8$ [382]. Low frequency vibrations have been observed for the binary transition metal dinitrogen complexes $M(N_2)_n$ (M = Ni, n = 1-4; M = Pd, Pt, n = 1-3) and these were assigned to metal-dinitrogen stretching modes [384]. Data from detailed isotopic substitution, together with the low frequency modes, made it possible to calculate accurate force constants for the $M(N_2)$ species and also reconciled the controversy over $Pt(N_2)_2$ [384]. The products of the co-condensation reactions of Ni, Pd and Pt atoms with mixtures of O_2, N_2 and argon at 6-10°K have been investigated by matrix isolation infrared spectroscopy and shown to be mixed complexes of the form $(O_2)_xM(N_2)_y$ [385]. From the number and positions of the N-N and O-O stretching modes compared to parent molecules $M(N_2)_n$ and $M(O_2)_m$ (M = Ni, n = 1-4; m = 1 or 2; M = Pd, Pt, n = 1-3, m = 1 or 2) and mixed isotope studies the reaction products were established to be $(O_2)M(N_2)$ and $(O_2)M(N_2)_2$(i.e. x = 1 and y = 1 or 2 above) containing "side-on" bonded O_2 and "end-on" bonded N_2. Isotopic frequencies computed for the ligand stretching and metal-ligand stretching modes, using a Modified Valence Force-Field approximation, were found to be in clear agreement with the observed values. The reaction of Ag atoms with ethylene has been studied by matrix isolation EPR spectroscopy and from a co-condensation of Ag + C_2H_4 + Ne (1:10:1000) at 4°K a new spectrum was obtained which was assigned, using C_2D_4 and computer fitting, to a molecular complex $Ag(C_2H_4)$ randomly oriented within the matrix [386]. Interestingly Cu atoms gave $Cu(C_2H_4)$ but Au atoms failed to form a molecular complex [386].

The infrared spectra of the ^{13}CO-enriched $M(CO)_6$ and $M(CO)_5$ species (M = Cr, Mo, W) have been studied in argon and CH_4 matrices at 20°K [387]. The $M(CO)_6$ spectra can be fitted very accurately in frequency and intensity using a CO-factored force-field and the spectra of $M(CO)_5$ species are inconsistent with a D_{3h} structure but can be fitted accurately using a C_{4v} structure. Using intensity data, axial-radial bond angles between 90° and 95° were calculated for the C_{4v} structure. The structures and force constants are almost independent of matrix material [387]. $Cr(CO)_5$, $Mo(CO)_5$ and $W(CO)_5$ may be generated in a variety of matrices by ultraviolet photolysis of $M(CO)_6$ but the visible band of the $M(CO)_5$ species is extremely sensitive to the matrix, e.g. Cr/Ne (624 nm) and Cr/Xe (490 nm) [388]. Mixed matrix experiments and comparison with spectra of stable species show that the shift in the visible band is due to stereospecific interaction between $M(CO)_5$ and the matrix species occupying the sixth coordination site. In the mixed matrices the different $M(CO)_5$ – matrix species, e.g. $Cr(CO)_5$ ..... Ne and $Cr(CO)_5$ ..... Ar, can be interconverted photochemically. The changes in the infrared spectra reveal differences in the frequency and intensity of the infrared bands of the $M(CO)_5$ – matrix species which indicate a significant change in bond angles between different $M(CO)_5$ – noble gas species in the same matrix (hence the criticism of the $Co(CO)_4$/CO/Ar work [382] above). The shifts in the visible band are interpreted in terms of a weak metal-matrix bond and the implications of such an interaction for solution and matrix photochemistry are discussed [388]. Ultraviolet photolysis of $Mo(CO)_6$ in CH_4 matrices at 20°K produces $Mo(CO)_5$ and two new secondary photolysis products, which grow sequentially, with spectra and growth patterns which are consistent with assignment to $Mo(CO)_4$ and $Mo(CO)_3$ [389]. The assignment was proved by detailed ^{13}CO-substitution studies which showed that the $Mo(CO)_4$ species adopts a C_{2v} structure (angles 174° and 107°) and the $Mo(CO)_3$ species adopts a C_{3v} structure (angle 105°). The spectra of $Mo(CO)_4$ and $Mo(CO)_3$ in CH_4 were sufficiently similar to the spectra in argon and to spectra of Cr and W systems, for a preliminary assignment to be made for these systems. The origins of the asymmetric structures for $Mo(CO)_4$ and $Mo(CO)_3$ was discussed in relation to recent theories of bonding in carbonyl fragments (see [53] and [54]). Two groups [390,383] have challenged the claim (E. P. Kündig and G. A. Ozin, J. Amer. Chem. Soc., 96 (1974) 3820) to have made trigonal bipyramidal D_{3h} $Cr(CO)_5$ as the new more stable isomer formed by vapour deposition followed by annealing. One group [390] showed that all the bands assigned to D_{3h} $Cr(CO)_5$ can be assigned to other known species, i.e. a mixture of $Cr(CO)_4$ and $Cr(CO)_5$, and noted that the observed isotope pattern for "D_{3h} $Cr(CO)_5$", though matching qualitatively, does not show a good enough fit. The other group [383], working independently, showed that ultraviolet photolysis of $Cr(CO)_6$ in argon matrices doped with CO provides ultraviolet/visible and infrared evidence for the weakly interacting $Cr(CO)_5$ ..... Ar and $Cr(CO)_5$ ..... CO molecules. Infrared spectra obtained by reacting Cr atoms with CO in argon matrices are shown to be a mixture of these two C_{4v} species together with $Cr(CO)_6$ and $Cr(CO)_4$. Photolysis experiments in concentrated matrices ($Cr(CO)_6$–Ar, 1:150) indicated that interaction can take place between carbonyl fragments. The implications of these two challenges are that metal atom co-condensation reactions in matrices must be interpreted with caution and where possible one or more of the possible products should be synthesised by the alternative photolysis route, e.g. $Co(CO)_3NO + CO \xrightarrow{h\nu} Co(CO)_4 + NO$. On the basis of these conclusions, the results for $Mn(CO)_5$ [271] and $Co(CO)_4$ (particularly the mixed matrices) [382] should be re-examined in the opinion of the reviewer.

Two innovations in matrix studies, namely the photoejection of bulky ligands (L = py, 3-bromo-py) from $W(CO)_5L$ [313] and the use of plane-polaris light to produce oriented $Cr(CO)_5$ [328], considerably extend the scope of th matrix isolation technique and increase its relevance for photochemical studies in solution at ambient temperatures.

THERMOCHEMISTRY

The thermochemistry of organometallic compounds has been reviewed [391] and a report has been produced in which compounds of B, Si, P and some of the other Group III and Group IV elements as well as transition metals were studied by thermochemical and spectroscopic methods to derive basic parameter such as standard heats of formation and M.O. binding energies [392]. Experimental methods used calorimetry, computer analysis of thermochemical data, mass spectroscopy, ultraviolet and X-ray excitation photoelectron spectroscop and NMR, EPR and Mössbauer spectroscopy. Thermochemical and spectroscopic studies of bonding in organotransition metal carbonyls has also been reviewed [80].

The thermodynamic properties C_p^o, S^o, $-(G^o-H_o^o)/T$, $H^o-H_o^o$, ΔH_f^o, ΔG_f^o an $\log K_p$ have been reported for $M(CO)_6$ (M = Cr, Mo, W) in the gaseous state from 100-600°K [393]. For $Mo(CO)_4L$ (L = PhN=CPh-CPh=NPh) the thermogravimetric and differential thermal analysis data indicated three regions for the decomposition: (i) at 20-200°C CO was evolved, (ii) at 200-500°C the azomethine ligands were cleaved from the complex, and (iii) at 500-800°C sintering of the residue occurred [394]. Similar regions of decomposition were also observed on the thermographs for NiL_2 and $NiL(PPh_3)_2$, indicating that the thermal stabilities of these azomethine complexes are independent of the central metal atom and the coordination environment. Thermal decomposition studies on $M(CO)_n(L)_2Cl$ complexes (M = W, Mo; n = 2,3; L = PPh_3, $AsPh_3P(O)Ph_3$) showed that the tricarbonyl complexes first lose 2 then 1 mole of CO and then L is liberated in a multistep process [395]. The thermal stability of the complexes follows the order: W > Mo, $Ph_3P > Ph_3As$, and $n = 2 > n = 3$. The substitution of CO into $W(CO)_5(CH_3CN)$ has been studied on a thermobalance under isobaric conditions [396]. From macrocalorimetric measurements at elevated temperatures of the heats of thermal decomposition and iodination, values of the standard enthalpies of formation of $(\eta^6\text{-arene})Cr(CO)_3$ compounds were determined [397]. A microcalorimetric vacuum sublimation technique is described from which enthalpies of sublimation were obtained. Values for the arene-Cr bond enthalpy in the gas-phase decreas in the series $(\eta^6\text{-}C_6Me_6)Cr > (\eta^6\text{-}C_6H_3Me_3)Cr > (\eta^6\text{-}C_6H_5Me)Cr = (\eta^6\text{-}C_6H_6)Cr >$

(η^6-C_6H_5Cl)Cr > (cyclo-C_7H_8)Cr [397]. While stable metal-carbene complexes have attracted much interest as potential sources of free carbenes, no reaction of these complexes has been shown to involve free carbene and the thermolysis of (2-oxacyclopentylidene)$Cr(CO)_5$ is no exception [398]. The complex was considered to be a definitive test for a carbene mechanism because free 2-oxacyclopentylidene, generated by thermolysis of the corresponding tosylhydrazone, has been shown to rearrange to dihydrofuran and cyclobutanone but in the thermolysis of the Cr complex the major product was the dimer, di-2-oxacyclopentylidine, with a small amount of dihydrofuran. Pyridine-induced decomposition gave a quantitative yield of dihydrofuran but, significantly, no cyclobutanone and it was the absence of cyclobutanone which ruled out intervention of the free carbene. A bimolecular mechanism for decomposition was proposed on the basis of kinetic studies [398]. The thermal decomposition of (η^5-C_5H_5)$Mn(CO)_3$ between 410 and 460°C followed 1st order kinetics and gave CO, Mn and cyclopentadiene [399]. The thermal stability of some Ru hydride complexes, α-$H_4Ru_4(CO)_{12}$, $H_4Ru_4(CO)_{10}L_2$, $H_4Ru_4(CO)_9L_3$, and $H_4Ru_4(CO)_8L_4$ (L = PPh_3) was investigated by differential scanning calorimetry and by thermogravimetric analysis under a dynamic atmosphere [400]. The thermogravimetric curves of the PPh_3-substituted derivatives suggested that the release of CO and PPh_3 groups occurred but the patterns were not well-defined, i.e. there were overlapping decomposition reactions, and P was retained in the residue. The decomposition heat of α-$H_4Ru_4(CO)_{12}$ and the isomerisation heat of $H_4Ru_4(CO)_8L_4$ were evaluated. The enthalpies of thermal decomposition of (C_2H_4)$Fe(CO)_4$, $(C_4H_6)_2Fe(CO)$ and (C_4H_6)$Fe(CO)_3$ have been determined using a Calvet high temperature calorimeter and thermograms were obtained for the iodination of the two 1,3-butadiene complexes [401]. The enthalpies of combustion and of formation and the mean bond dissociation energies of some 3*d*-row dicyclopentadienyl compounds have been measured and data for Cr, Mn, Fe, Co and Ni is tabulated [402]. Using a solution calorimetric method at 298.15°K, the standard enthalpies of formation of crystalline $Co_3(CO)_9(CBr)$, $Co_3(CO)_9(CCl)$ and $Co_2(CO)_8$ have been determined as -1189.5 ± 9.2, -1186.2 ± 10.0, and 1250.6 ± 5.0 kJ mol^{-1} [403]. The enthalpies of sublimation of the compound were determined by effusion manometry as 99.6 ± 1.7, 117.6 ± 2.5 and 65.3 ± 3.3 kJ mol^{-1} respectively. Bond energies have been determined from gas-phase enthalpies of formation and the structural implications of the data were discussed [403].

Some results on the enthalpies (ΔH) of Pt-L bond formation for the reaction of a variety of Group V donor ligands L with *trans*{$CH_3PtQ_2(THF)$}PF_6 (Q = PMe_2Ph) have been reported [404] which clearly illustrate the importance of steric effects on metal-phosphorus bond strengths. The authors concluded: (a) enthalpy is clearly dependent on size and decreases in the series PMe_3 >

$PMe_2Ph > PMePh_2 > PPh_3$: (b) electronic effects cannot be neglected if substituents have high electronegativity; (c) displacement energy decreases in the series $PPh_3 > AsPh_3 > SbPh_3$; (d) phosphites are slightly weaker ligands than phosphines of a similar size; (e) there is an inverse correlation between $^2J(^{195}Pt-^1H)$ (i.e. coupling to Me) and $-\Delta H$(see NMR studies of Static Systems): (f) calorimetric titrations indicate that 5-coordinate complexes do not form at 25°C on adding excess ligand; (g) in cases where the reaction can be followed it is 1st order in Pt and added ligand. The enthalpies of the solution reaction

$$L_2Pt(olefin)[solid] + nC_6H_6[liquid] \rightarrow L_2Pt(olefin)[solv.]$$

$$(L = PPh_3;\ olefin = \textit{cis}\ and\ \textit{trans}\ 1,2\text{-diphenylethene})$$

when combined with other data, led to the conclusion that the differences in the relative strengths of the Pt-olefin bonds, i.e. *trans*-1,2 > *cis*-1.2 > phenylethene, arises mainly from steric effects of the olefins [405]. The enthalpy of the reaction

$$Pt(PPh_3)_2(CH_2{=}CH_2)[cryst] + PhC{\equiv}CPh[cryst] \rightarrow Pt(PPh_3)_2(PhC{\equiv}CPh)[cryst] + CH_2{=}CH_2[gas]$$

has been determined as $\Delta H_{296} = -82 \pm 12$ kJ mol^{-1} from solution calorimetry and this led to the conclusion that the Pt-PhC≡CPh bond is stronger than the $Pt-CH_2{=}CH_2$ bond [406]. The enthalpies of the reactions [407]

$$Pt(PPh_3)_2(PhC{\equiv}CPh)[cryst] + HCl[gas] \rightarrow Pt(PPh_3)_2(CPh{=}CHPh)[cryst]$$

and $$Pt(PPh_3)_2(PhC{\equiv}CPh)[cryst] + 2\ HCl[gas] \rightarrow \textit{cis}\ Pt(PPh_3)_2Cl_2[cryst] + \textit{trans}\ CHPh{=}CHPh[gas]$$

have been determined as $\Delta H = -90.2 \pm 6.0$ and -139.0 ± 16.0 kJ mol^{-1} respectivel and dissociation energies of bonds involving Pt have been expressed by the relationships:

$$41\ kJ\ mol^{-1} + D(Pt\text{-tolane}) = 2D(Pt\text{-}CPh{=}CHPh)$$
$$= \{D_1(Pt\text{-}Cl) + D_2(Pt\text{-}Cl)\} - 350\ kJ\ mol^{-1}.$$

The bond dissociation energy has been shown to be slightly greater for $D(Pt-CS_2)$ than for $D(Pt-CH_2{=}CH_2)$ from a calorimetric determination [408] of the enthalpy of the reaction

$$Pt(PPh_3)_2(CH_2{=}CH_2)[cryst] + CS_2[gas] \rightarrow Pt(PPh_3)_2(CS_2)[cryst] + CH_2{=}CH_2[gas]$$

The enthalpies of reactions of CS_2 with Pt compounds

$$L_2Pt[solid] + nCS_2[liquid] \rightarrow L_2Pt(CS_2)[solv.] + (n - 1)CS_2[liquid]$$

and for

$$L_2Pt(olefin)[solid] + nCS_2[liquid] \rightarrow L_2Pt(CS_2)[solv.] + olefin[solv.] + (n - 1)CS_2[liquid]$$

where L = PPh_3, when combined with other data, showed that the relative strengths of the Pt-olefin bonds decrease in the order *trans*-1,2-diphenylethylene > *cis*-1,2-diphenylethylene > phenylethylene > ethylene [409] (see [405]).

MISCELLANEOUS PHYSICAL METHODS

The stereochemistry of the reactions of optically active organometallic transition metal compounds has been reviewed [410] and the potential of optical activity at metal centres in mechanistic studies has been emphasised. The first examples of resolved, stable Cr(0) complexes, e.g. $(\eta^6\text{-}o\text{-}C_6H_4(Me)(CO_2Me))Cr(CO)(CS)P(OPh)_3$, which owe their optical activity to the chiral Cr centre, have been reported [411] and the work is related to the use of Cr(0) complexes containing chiral Cr centres in possible catalytic asymmetric syntheses under mild conditions. The decomplexation of $Cr(CO)_3$ fragments from optically active (arene)$Cr(CO)_3$ complexes, where the optical properties were associated with the arene ligand, prepared while part of the metal complex under mild conditions, has provided two examples of synthetic routes to optically active organic compounds [334,412] and the ability of a $Cr(CO)_3$ fragment to exchange between arene ligands has also been noted and applied synthetically [413]. The X-ray structure analysis of $(+)_{579}\text{-}\{(\eta^5\text{-}C_5H_5)Mo(CO)_2NN'\}PF_6$ (NN' = Schiffs base derived from 2-pyridinecarbaldehyde and *S*-(−)-α-phenylethylamine) has been reported [414] and represents the first determination of the absolute configuration of an organometallic compound of Mo where the metal atom constitutes the asymmetric centre. In the reaction of $(+)_{579}\text{-}\{(\eta^5\text{-}C_5H_5)Mn(NO)(PPh_3)(CO)\}PF_6$ with LiMe, LiPh and Li-*p*-C_6H_4X respectively, the complexes $(+)_{579}$-(5-*exo*-R-cyclopentadiene)Mn(NO)(PPh_3)CO and the acyl complexes $(+)_{579}\text{-}(\eta^5\text{-}C_5H_5)Mn(NO)(PPh_3)COR$ were formed [415]. Contrary to the configurationally stable cyclopentadiene complexes, the acyl complexes racemise in solution, as determined by polarimetry, according to a 1st order reaction, i.e. reversible process involving PPh_3 ligand without disturbance of the acyl group [415] and an analogous process was observed for the racemisation of resolved $(\eta^5\text{-}C_5H_5)Mn(COOR)(NO)(PR_3)$ complexes [416]. The preparation of the optically pure alkylating agent $(+)\text{-}(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)CH_2Cl$ and its reactions with Grignard and alkyllithium reagents has provided a general route to iron alkyls whose enantiomeric purity may be shown by the ^1H NMR spectra of their SO_2 insertion products [417]. The use of the lanthanide shift reagent Eu(fod)$_3$ to assign resonances of diastereotopic nuclei to particular nuclei has provided a new method for sorting cut conformational isomers [243] and may prove to be important for optical isomers. In an effort to learn more about the intricacies of β-elimination the thermal decomposition reaction of (*threo*-α,β-dideuteriophenylethyl)$MCl_2(CO)(PPh_3)_2$ (M = Rh, Ir) and the catalytic decarbonylation of *threo*-PhCHD-CHD-COCl by $RhCl(PPh_3)_2$ have been studied and the alkyl migration reaction has been shown to proceed with retention of configuration [418]. Alkyl transfer from Hg to Pd proceeds with retention of configuration of the alkyl ligand in the reactions of *threo*- and *erythro*-$MeCH(NMe)_2CH(HgCl)Me$ with $PdCl_2(PhCN)_2$ as demonstrated by deuteration and degradation of the product amines to olefins [419].

Gas-phase electron diffraction is being increasingly used to determine the structures of organometallic compounds and the current state of the art has been reviewed [420]. Some applications of the technique to transition metal complexes are: the structure of $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ with particular reference to internal rotation [421], the structure of $(\eta^5\text{-}C_5H_5)V$ and $(\eta^5\text{-}C_5H_5)Cr$ in relation to their electronic structures [422], the structure of $Mn(CO)_5SiF_3$ (to assess evidence for $d\pi\text{-}d\pi$ bonding as shown by shortening of the Mn-Si bond compared with $Mn(CO)_5SiH_3$) [423], the structure of $(\eta^5\text{-}C_5H_5)_2Co$ [424] and the structure of $(\eta^5\text{-}C_5H_5)NiNO$ [425].

A new method, described as the "Three Phase Test" for the detection of reaction intermediates, has been presented [426]. The technique involves the generation of an intermediate from an insoluble, polymer-bound precursor and its trapping by a second solid phase suspended in the same reaction mixture. The preparation of a polymer-bound *o*-phenthroline derivative of $(\eta^4\text{-}C_4H_4)Fe(CO)_3$ and a polymer-bound maleimide derivative are described. Oxidation of the former to the presence of the latter is shown to proceed with 98% transfer of "free" C_4H_4 between the two phases.

The techniques for studying the kinetics of fast reactions in solutions, e.g. continuous flow, accelerated flow, stopped flow, temperature-jump and pressure-jump, have been reviewed [427] and a more detailed review has been published on temperature-jump techniques [428]. New instrumental developments for commercial Fourier transform NMR spectrometers have been described, one of which uses a Fourier difference spectroscopy technique [429] and the other enables two solutions to be rapidly and efficiently mixed inside a spinning 5 mm NMR tube [430]. A stopped-flow ultraviolet/visible spectrophotometric study of the cleavage of the Sn-M bond in Me_3SnM complexes (M = $(\eta^5\text{-}C_5H_5)Cr(CO)_3$, $(\eta^5\text{-}C_5H_5)Mo(CO)_3$, $(\eta^5\text{-}C_5H_5)W(CO)_3$, $Mn(CO)_5$, $(\eta^5\text{-}C_5H_5)Fe(CO)_2$) by I_2 in CCl_4 shows deceptively simple kinetics, but this probably masks the complexity of the reaction, and schemes involving charge-transfer complexes and intermediates are proposed [431]. The kinetics of decarbonylation of $\{Ir(CO)(Ph_2PCH_2CH_2PPh_2)_2\}Cl$ and $Ir(CO)_2(Cl)(PPh_3)_2$ have been studied in different solvents at temperatures between $-25^{o}C$ and

+70°C by means of reactor of defined fluid dynamics which allows a separation to be made between "physical" and "chemical" rate constants [432]. Chemical rate constants were found to depend markedly on the diffusion coefficient of CO in the various solvents. The process of decarbonylation was described, for both complexes, by the sequence: structural isomerisation, characterised by a very low pre-exponential factor; decomposition of the less stable isomer against the solvent barrier; diffusion of CO to the gas-liquid interface. The kinetic problems involved in the determination of rate constants and their implications were emphasized [432].

A reversible pressure-dependent equilibrium has been detected [433] in the system

$$(\eta^5\text{-}C_5H_5)Mn(CO)_2(N_2) + THF \rightleftarrows (\eta^5\text{-}C_5H_5)Mn(CO)_2THF + N_2.$$

Reversible CO_2 insertion, as demonstrated by cycles of CO_2 gas absorption-evolution during alternate heating and cooling of the system, has been described for the acetylide complex $PhC{\equiv}CCu(P\textit{n}\text{-}Bu_3)_3$ [434]. The complex, which behaves as a reversible CO_2 carrier under mild conditions, is the first example of reversible CO_2 into an organotransition metal complex.

The electric dipole moments of the π-heterodiene complexes $(\pi\text{-}L)Fe(CO)_4$ (L = *trans* PhCH=CHCHO, *trans* PhCH=CHOMe, *trans* PhCH=CHOPh *etc.*) have been measured and a vectorial analysis of the moments leads to the conclusion that the aldehyde and ketone ligands bond to the Fe *via* the olefinic and carbonylic groups and do not involve O lone pairs [435]. The metal-ligand bonding appeared to be stronger in the aldehyde and ketone complexes than in the butadiene ones. The molecular electric dipole moments have been reported for the series of complexes $R_nY_{m-n}Sn\{Co(CO)_4\}_{4-m}$ ($m = 1\text{-}3$, $n \leq m$; R = alkyl, Ph; Y = halogen) [436]. The effect of substituents at the Sn atom on the nature of the Sn-Co bond was established by the calculation of the $Sn\text{-}Co(CO)_4$ group dipole moment and this showed that charge transfer in the Sn-Co bond is mainly determined by the inductive properties of the ligands attached to Sn. Dipole moment studies were among a range of measurements, including X-ray photoelectron spectroscopy and electrochemical (redox) studies, which were evaluated as a means of determining charge distributions in complexes but it was concluded that they were of limited value because of the inability to determine individual bond moments [437]. Incidentally it was concluded that X-ray photoelectron spectroscopy is the most generally applicable but it is limited by lack of sensitivity while redox measurements can only be interpreted clearly where there are no π-bonding ligands. The data is consistent with PR_3 and Cl^- ions being good electron donors, Cl and N atoms as being strongly electron withdrawing, and the so-called "electron donor" ligands N_2, CO, NO (even formal NO^+) being in fact electron withdrawing. On the other hand, the formally anionic H^- ligand is very strongly electron donating, being only slightly negative in its complexes.

An inelastic neutron scattering study of $CH_2=CH_2$ adsorbed by Ag-exchanged 13X zeolite has shown that the C_2H_4 molecules on the zeolite surface vibrate with frequencies dependent on the coverage [438]. At low coverage the spectra corresponding to neutron counts plotted as a function of scattered neutron time-of-flight, show a single feature at 40 cm^{-1} while at higher coverage two features are observed at 56 cm^{-1} and 22 cm^{-1}. The 22 cm^{-1} feature was interpreted as due to weakly bound C_2H_4 and that at 56 cm^{-1} to more strongly bound C_2H_4 with the change 40-56 cm^{-1} as the coverage increases being explained by steric crowding.

A direct determination of the quadrupole coupling constant at deuterium in solid $DMn(CO)_5$ has been reported [439] by the use of the nuclear spin-echo double resonance technique (SEDOR). The experiment provides not only the quadrupole coupling constant at deuterium but also gives a direct measure of the Mn-D bond distance with an accuracy comparable with that obtained from an X-ray diffraction experiment. The calculated Mn-D distance is 1.61 Å ± 0.01 which is excellent agreement with the value of 1.601 Å for Mn-H obtained by a combined X-ray and neutron diffraction study. The authors comment that, in addition to observing terminal M-D bonding in species such as $DRe(CO)_5$, $DCr(CO)_5^-$, $DCo(CO)_4^-$ and other mononuclear hydrides, the technique may be useful in more precisely defining the nature of bridge-bonding situations, e.g. in $H_3Mn_3(CO)_{12}$.

^{55}Mn, ^{185}Re, ^{187}Re and ^{127}I NQR spectra of derivatives of $(\eta^5\text{-}C_5H_5)M(CO)_3$ (M = Mn, Re) depended more on the conjugation characteristics of the substituents than on inductive effects and in this respect Re was a more sensitive probe than Mn [440]. The higher NQR frequency of ^{127}I in $(\eta^5\text{-}C_5H_4I)Re(CO)_3$ than in $(\eta^5\text{-}C_5H_4I)Mn(CO)_3$ suggested that the $(\eta^5\text{-}C_5H_4)Re(CO)_3$ group was a stronger electron acceptor than the Mn group. The ^{59}Co NQR spectra of a number of derivatives of $Co_2(CO)_8$ have been reported, e.g. $(RC{\equiv}CR')Co_2(CO)_6$ $(R{\neq}R')$, $(\pi\text{-}C_7H_8)Co_2(CO)_6$ and $(\pi\text{-}C_7H_8)_2Co_2(CO)_4$ [441]. The parameters obtained from the spectra of the alkyne complexes were related to the electronegativities of R and R' with e^2Q_q being inversely proportional to η and the sign of e^2Q_q different from that in $Co_2(CO)_8$. The two chemically different Co atoms in $(\pi\text{-}C_7H_8)Co_2(CO)_6$ did not have very different NQR parameters. These parameters are similar to those derived for other complexes with a non-planar $Co_2(CO)_2$ bridging system but are different from those of $(\pi\text{-}C_7H_8)_2Co_2(CO)_4$ which reinforces the belief that this complex has a planar $Co_2(CO)_2$ arrangement. The authors conclude that for $(RC{\equiv}CR')Co_2(CO)_6$ a dependence of e^2Q on the electronegativities of R and R' has been detected and this has been useful in determining directions of axes and signs of e^2Q_q but, while substantial differences were found in coupling constants with gross structural changes, further work is necessary to systematize the changes.

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