TRANSITION METALS : PHYSICAL METHODS AND RESULTS OF GENERAL INTEREST (1974)

by P. S. Braterman

Department of Chemistry, University of Glasgow,
Glasgow, G12 8QQ.

CONTENTS:

Transition metal-organic chemistry. Physical methods and results of general interest, 1973 see J. Organometal. Chem., 103(1975)307-419.

REVIEWS (See also under individual headings)

A retrospective account by Chatt ranges over the organic and hydride chemistry of the transition metals (1). Reviews have appeared on metallocarboranes (2), the chemistry of isonitrile complexes (3), dinitrogen complexes (4) and the fixation of dinitrogen in the presence of transition metal complexes (5), and structures, bonding and reactivity of metal nitrosyls (6); stable homoleptic metal alkyls (7), π-allyl (8) and allene (9) complexes, and pseudo-allyl metal carbonyl complexes (covering a range of 3-electron donors) (10). Processes surveyed include the reactions of coordinated pnictogen ligands (11), the insertion of SO_2 and other molecules into transition metal-carbon bonds (11a), and the activation of carbon disulphide by transition metal complexes (12). The growing interest in transition metal compounds as organic reagents is reflected in reviews on applications of organo-iron complexes (13) and on compounds derived from alkynes and cobalt carbonyls (14), together with a spate of reviews on organocopper chemistry (15, 16, 17) with specific coverage of controlled carbon-carbon bond formation (16) and on oxidative coupling in particular (17). The reactions of diynes with transition metal compounds merit a separate review; this 'diyne reaction' is described as a path to a wide new range of compounds, including heterocyclics, seven- and eight-membered rings, and arene quinones (18). More specialised reviews have appeared on the ferrocenophanes (19), applications of ferrocenes (20), the chemistry of nickelocene (21) and vitamin B_{12} and its inorganic models (22). The bibliography of organometallic chemistry has been updated to 1972 (23).

THEORETICAL STUDIES (See also Ionisation Studies)

A general procedure has been developed for predicting the geometries of metal carbonyl fragments $M(CO)_n$ by second order perturbation theory, taking account of both σ- and π-bonding. The known C_{2v} structure of $Mo(CO)_4$ is as expected for a singlet, and the distortion of $Fe(CO)_4$ (presumed triplet) from tetrahedral geometry is correctly predicted (24). A generalised valence bond treatment of TiCO and $[TiCO]^+$ gives the expected fall in back-bonding on ionisation (25). The bonding in $Ni(CO)_4$ and $Ni(N_2)_4$ has been examined in a Hartree-Fock model using a Gaussian basis set. The two species are predicted to be highly similar, but both electronic and geometric effects favour back-bonding to 2π of CO (localised chiefly on C), and the metal-carbonyl average bond strength is calculated to exceed the metal-dinitrogen average by 75kJ/mol (26). Self consistent charge extended Hückel MO calculations on the CO adducts of haemoglobin and coboglobin show the metals as unambiguously d^6(Fe(II)) and d^7(Co(II)) respectively, but the valence formalism breaks down for the nitrosyl adducts (27). Wolfsberg-Helmholtz calculations on the $[Co_6(CO)_{14}]^{4-}$ anion rationalise the 86-electron count in terms of full population of all bonding and weakly antibonding orbitals (28); the formal analogies (29) between carborane and carbonyl cluster compounds can then be explained in terms of the non-population of strongly antibonding orbitals while all others are filled (28). Calculations on the phosphide-bridged species $[Cr_2(CO)_8(PR_2)_2]^{0,-1,-2}$ and the isoelectronic manganese (+2, +1, 0) species lead to the prediction of a simple σ-bond between metals in the neutral chromium species (30), reportedly in disagreement with the predictions of an earlier attempted general model (31).

CNDO/2 calculations on π-complexes of Cr(0) (including Cp_2Cr* and its cation, $(C_6H_6)_2Cr$, $CpCr(CO)_3H$ and $C_4H_4SCr(CO)_3$) indicate the metal-ring bonding to be mainly of 'π' symmetry with little 'δ' contribution. Both 5- and 6-membered rings are net charge donors (32). More precise calculations using a multi-exponent basis set, have been used to determine the success of various theoretical models in predicting the electric dipole matrices for $C_6H_5XCr(CO)_3$ ($X = H, F, NH_2$) (33,34). The preferred input was that of Gray _et al._ (35), while the charge convergence was better using the apportionment procedure of Löwdin (36) than that of Mulliken (37).

Extended Hückel calculations on species of type $M(\text{ethylene})_n$ and $M(\text{allyl})_n$ show steric preference to be dominated by π-bonding. It is predicted that the ligands in $Ni(C_2H_4)_3$ should all lie in a plane. Significant rotational barriers are predicted for $Ni(\text{all})_2$ and

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* Cp = $(h^5-C_5H_5)$; all = $(h^3-C_3H_5)$

$Pt(all)_2$, and the structures of $Co(all)_3$, $Rh(all)_3$ and hypothetical $Ni(C_2H_4)_4$ and $Cr(C_2H_4)_6$ are also discussed (38). Modified CNDO MO calculations on olefin complexes of Pd(II) and Hg(II) predict enhanced rates of attack by hydroxide. This is predicted to be cis to the metal rather than trans, and to occur, in agreement with experiment, at C(1) of propenes rather than C(2) (39). Scattered wave calculations (40) on Zeise's anion show σ-bonding to affect both the d-orbitals of a_1 symmetry while π-back-bonding is assigned relatively little importance. The lowest electronic transition is calculated to be from alkene to a metal-alkene antibonding orbital, purportedly explaining the known (41) photoreaction of Zeise's anion with water to liberate ethylene. A CNDO treatment of $(all)Co(CO)_3$ predicts an asymmetry among the CO groups, related to the asymmetry of the 5-membered ring in CpNi(all) (42) [an hypothesis that it would be of interest to test by CO vibrational and cmr spectroscopy].

The theory for d^4 (43) and d^n (44) systems in an axially symmetric ligand field has been critically applied to the available interpretations of magnetic and photoelectron data (q.v.) on metallocenes. Several other workers have published results that do not always agree, showing the need for caution in the interpretation of data for organometallic complexes. INDO calculations on Cp_2Mn, Cp_2Mn^+, and Cp_2Fe^+ show a ${}^6A_{1g}$ state as the ground state for manganocene and the photoelectron spectrum can be interpreted on this basis. The considerable covalency in the $e_{1g}(xz,yz)$ orbitals leads to redistribution of charge on ionisation, so that Koopmans' theorem cannot be used to predict ionisation potentials (45). Scattered wave calculations on ferrocene lead to the unfashionable conclusion that the first ionisation is from 3d(a_{1g}) rather than 3d(e_{2g}). The greater intensity of the lowest energy photoelectron band is then attributed to differences in the precise natures of the a_{1g} and e_{2g} orbitals, such as the contribution of 4s to the former (46). However, the lowest energy electronic band of ferrocene has been assigned (47) as $e_{2g} \rightarrow e_{1g}$ on a model in which configurational interaction between all singly excited states is included. The electronic structure of nickelocene has been re-investigated, taking into account configurational interaction involving both d–d and charge transfer excited states, and using a fit to the electronic spectrum as a criterion (48). Simplistic interpretations of one-electron energies are dealt yet another severe blow by double exponent calculations on $Ni(all)_2$. It is possible to interpret the photoelectron spectrum by comparing the energy for $Ni(all)_2$ with that for the various states of $Ni(all)_2^+$, but not by using Koopmans' theorem on the data for $Ni(all)_2$ alone [compare also (50, 57) below]. Within $Ni(all)_2$, the chief bonding interaction is between ψ_2 of the allyl group and the appropriate nickel d-orbital, and the barrier to rotation around the carbon–carbon bond is predicted to be too high for it to contribute to the fluxional properties of π-allyls (49).

IONISATION STUDIES (see also Theoretical Studies; Mass Spectrometry).

Photoionisation studies have appeared on a range of species of type $Cr(CO)_5L$ (L = phosphine, amine, $CNCH_3$) and $W(CO)_5$(amine). The first and second ionisations correspond to removal of a 'd'(e) and 'd'(b_2) electron respectively, which order is in accord with naive prediction but not with SCF calculations. It is suggested that the removal of the e electron is facilitated by relaxation somewhat more than that of the b_2 electron, since the orbital involved is calculated to have more metal character (50). The XPE spectrum of $(OC)_5CrC(OCH_3)CH_3$ contains a peak at higher apparent binding energy than that of carbonyl carbon 1s, but this is merely a shakeup satellite. The carbene carbon, together with the methyl carbons, gives rise to a low bonding energy shoulder of the main peak, suggesting that carbene carbon does not really carry much positive charge (51).

In $CH_3Mn(CO)_5$ and $CF_3Mn(CO)_5$, the relative intensities of the lowest binding energy photoelectron bands would suggest that ionisation from d(e) takes place, unexpectedly, at higher energy than ionisation from d(b_2). However, calculations (52) show that ionisation from the manganese-carbon σ-bond should be in the same region, so that the lowest binding energy could correspond to d(e) with the bands for ionisation from d(b_2) and σ(Mn–C) overlapping.
A related problem is the order of ionisation energies in species $M(CO)_5X$ (M = Mn, Re), previously taken (53) as

$$X(\pi) < X(\sigma) < d(e) < d(b_2)$$

The He(I) spectra of the pentacarbonyl halides of rhenium have now been examined, and on the basis of the relative shifts when metal or halogen are changed, a revised order

$$X(\pi) < d(b_2) < d(e) < X(\sigma)$$

is proposed. The first ionisation band of $Re(CO)_5Br$ is split by spin-orbit coupling, showing that the 'ligand' $p(\pi)$-orbital has acquired some metal character.(54).

He(I) photoelectron spectra have been analysed for the species Cp_2M, ($M = V, Cr, Mn, Co, Ni$) and the related $(CH_3C_5H_4)_2M$. The d-electron ionisations from the open shell metallocenes show the expected effects of term-term splitting. Manganocene itself appears to have a high spin ground state, while the methylated analogue exists in the vapour as an equilibrium mixture of high spin and low-spin forms [compare (44) above] (55). The related sandwich compounds $(C_6H_3Me_3)_2M$($M = V, Cr, Mo$), $(C_6H_6)_2Mo$, $(C_6H_5Me)_2Mo$, $(C_7H_7)(C_5H_5)M$($M = Ti, V$) and $(C_5H_5)(C_8H_8)Ti$ have been examined, and trends analysed using simple MO arguments (the explicit assumption being that the deviations from Koopmans' theorem will be fairly similar for any one type of orbital throughout the series). The expected term-term splitting is found in the open shell complexes, and a number of generalisations emerge. In the species $(Arene)_2M$, ionisation potentials fall with increased methylation, and also on going from chromium to molybdenum. The order of ionisation potentials is

$$d(a_{1g}) < d(e_{2g}) \ll (ring)e_{1u} \ll (ring)\ e_{1g}$$

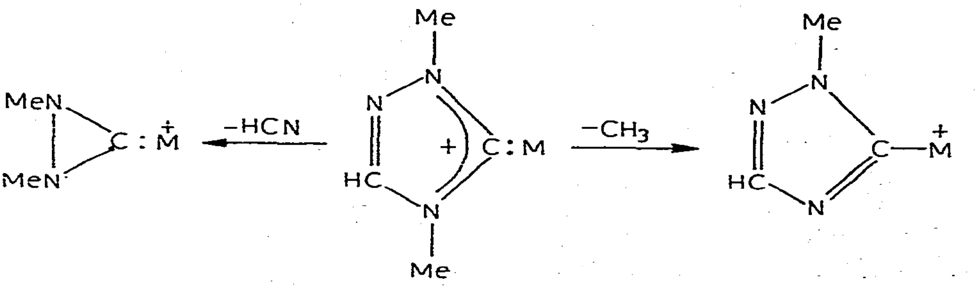
In (mesitylene)$_2$V, the ground state is assigned as $^2A_{1g}$ ($e_{2g}^4a_{1g}$), but the ionised state $^3E_{2g}$($e_{2g}^3a_{1g}$) is lower in energy than $^1A_{1g}$(e_{2g}^4). In (C_7H_7)(C_5H_5)V, however, the first ionisation is from a_1. The ionisation potential from a_1 falls on going from 17- to 18-electron systems, an effect attributed to electron-electron repulsion , and the first ionisation of the (as yet unknown) species (C_5H_5)(C_8H_8)V is predicted to be below 5 volts (56). The He(I) spectra of CpNiNO and $CH_3C_5H_4$NiNO show, as expected, a first ionisation from the metal. The orbital with the lowest Hartree-Fock binding energy is on the ring, but comparison of calculations for CpNiNO and the various states of CpNiNO$^+$ shows that removal of an electron from the metal produces some 6 eV more relaxation energy than ionisation of the ring, and accounts satisfactorily for the observed order (57).

X-ray photoelectron data have been reported for Cp_2Cr, CpCrC_6H_6, CpCrC_7H_7 (C_6H_6)$_2$Cr, [(C_6H_6)$_2$Cr]$^+$I$^-$, C_6H_6Cr(CO)$_3$ and related species. The carbon 1s binding energy is lower in species of type (ring)$_2$M than in (ring)M(CO)$_n$, but independent of ring size (and hence of formal charge)(58). In the sequence CpMC_7H_7 (M = Ti, V, Cr), however, XPE data show the apparent oxidation state of the metal to increase from chromium to vanadium to titanium (59). In the species MR_4 (M = Ti, Zr, Hf; R = trimethylsilylmethyl (tsm), meopentyl (np)), the first ionisation is in all cases at around 8.6 eV, and is attributed to the metal-carbon σ-bonding system. The second, at 10.3 (or 11.3) eV, is attributed to the silicon-carbon (or carbon-carbon) bonds, while the third ionisation, at 12.5 eV in the np complexes but at 13.3 eV in those of tsm, is assigned to the C–H systems (60). In the species trans $Ni(X)(Y)(PEt_3)_2$ (X,Y = alkyl, alkenyl, alkynyl, aryl, halogen), the Ni 2p binding energy correlates as expected with the ionic character of the Ni(X)(Y) bonds, but π-bonding has no detectable effect (61).

MASS SPECTROMETRY

The mass spectra of transition metal π-complexes have been reviewed (62). Negative ion mass spectra have been described as complementary to those of positive ions. For example, the sequence $[W(CO)_n]^-$ is given by $W(CO)_5(C_5H_5N)$, which in the positive ion spectrum shows only CO loss, and formation of halide anions is a characteristic reaction of carbonyl or nitrosyl metal halogen compounds (63,.

In (positive ion) spectra of cyclic amino carbene complexes of pentacarbonylchromium and tetracarbonyliron, the strongest peak corresponds always to $[\text{metal carbene}]^+$. This decomposes further by such processes as methyl loss or HCN elimination, as in Scheme 1 (64). The spectra



Scheme 1

of species $M(CO)_5PR_3$ (R = OMe, OEt, OBu^n, Bu^n, Ph; M = Cr, Mo, W) have been reported. With long chain phosphine substituents, loss of organic fragments competes with CO loss, and for M = W, R = OBu^n or Bu^n, loss of such fragments (principally C_4H_{10}) dominates the 70 eV spectrum, even though appearance potential data show CO loss to be energetically less demanding (65). Ortho-methyl groups block formaldehyde elimination in the mass spectrum of tricarbonylchromium acetanilide, but not in the free ligands themselves. The implication is that in the free ligands rearrangement involves a 1,3-hydrogen shift to give $[Ar-NH_2]^+$, but that in the complexes the rearrangement involves a 1,5-shift of acetyl hydrogen to ortho carbon (not, interestingly enough, directly to metal) (66). Arene tricarbonylchromium complexes (arene = benzene, toluene, biphenyl, chlorobenzene, mesitylene, methyl benzoate) are protonated by chemical ionisation with bombarded methane, but unlike the free arenes do not add ethyl cations. For dibenzene chromium, the most abundant ion corresponds to $[p]^+$, possibly formed by hydrogen atom loss from $[(C_6H_6)_2CrH]^+$ (67). Electron capture by tricarbonylchromium methyl benzoate leads to successive loss of four CO groups, and eventually to formation of Cr^-; the peak $[p-CO]^-$ is intense, and is plausibly assigned to CO loss from the ester grouping (68).

In the positive ion spectra of species $Ph_n(C_6F_5)_{3-n}M.Mn(CO)_5$ (M = Si, Ge, Sn), loss of one or more CO groups is followed by loss of a neutral manganese (carbonyl) fragment. The tin-manganese and tin-iron dissociation energies in $Ph_3SnMn(CO)_5$, $Ph_3SnFe(CO)_2C_5H_5$ are 250 ± 30 and 225 ± 40 kJ/mol (69). The mass spectra of substituted styrene bis(tricarbonyliron) complexes show formation of ions of the type $[styrene\ Fe]^+$, which, unlike the neutral ligands, lose neutral fragments such as methane, acetylene, or hydrogen halide (70). In the spectrum of $Co_3(CO)_9Co.C_{10}H_{12}$ ($C_{10}H_{12}$ = tetralin), loss of more than five carbonyl groups is followed by extensive loss of one or more molecules of dihydrogen. This is said to be a rare example of aromatisation of a ligand in the mass spectrum without increase in its degree of coordination [although it seems possible to the reviewer that it could indeed be experiencing such an increase after migration to an edge or free site of the Co_4 cluster] (71). Bis(triphenylphosphine) platinum bis(aryl) cations show ready loss of biaryl; the analogous bis(methyl) shows either loss of methyl followed by methane, or loss of phenyl followed by methane or benzene (72).

Molecule-ion reactions have been studied by mass spectrometry, not only for the case where both components are generated from the same species, but also for the case where molecule and ion are chemically completely distinct. Reaction between $Ni(PF_3)_4$ and derived cations gives species $Ni_2(PF_3)_n$ (n =2-5) and $Ni_2(PF_2)(PF_3)n$ (n = 2-4). Similarly, pentacarbonylchromium methoxymethylcarbene gives successively $[Cr(CO)_2.COCH_3]^+$, $[Cr_2(CO)_5(CMeOMe)COCH_3]^+$; and, by hydrogen loss, species that may contain coordinated methyl vinyl ether functions (73). Fragments $[CpM(CO)_n]^+$, derived from $CpV(CO)_4$, $CpMn(CO)_3$ and $CpCo(CO)_4$ react in the mass spectrometer with ethers, arenes, or unsaturated hydrocarbons; $[CpCo(CO)_2]^+$ reacts with cyclohexane to give $[CpCo(cyclohexene)]^+$, with loss of dihydrogen and carbon monoxide (74).

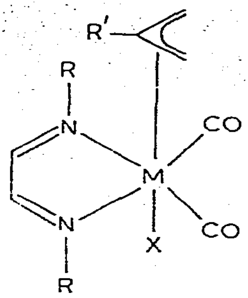
The spectra of the lanthanide(III) cyclopentadienides have been studied and appearance potentials tabulated for fragments. The principle processes are loss of C_5H_5, followed by loss of C_3H_3, C_2H_2 or C_2H_4, and the dissociation energy for the loss of one C_5H_5 decreases with increasing atomic number (75).

ELECTRONIC SPECTRA (see also Theoretical Studies)

The f–f bands of $Cp_2ErCCPh$ are more intense than those of Cp_2ErCl, indicating a greater covalent distortion of the f orbitals, and a large ultraviolet charge transfer band is also present (76). The visible–UV spectra of the species $M(CO)_5X$ (M = Mn, Re, Cr^{-1}, Mo^{-1}, W^{-1}; X = halogen) and $Mn(CO)_5R$ (R = H, CH_3, CF_3) have been compared and discussed, using such criteria as solvent sensitivity, spin–orbit splitting in iodine compounds, and the plausibility of trends, to examine possible assignments. It is concluded that the low energy band of the halides corresponds to transfer from an orbital predominantly $Xp(\pi)$ to an M–X σ-antibonding orbital (77). The pentacarbonylmanganese halides show a positive A term and no C term in the magnetic ORD spectrum in the region of this band. The dipole strength of the absorption band and the ratio A/D both change regularly with the nature of the halogen, consistent with promotion of an $Xe(\pi)$ electron to a non-degenerate orbital (78).

An electronic Raman effect has been found for the ferricenium cation. Bands at 213 and 1580 cm^{-1} correspond to excitations among the spin-orbit terms of the $(a_{1}g^{2}eg\ ^{3})$ ground state, in agreement with EPR data (79). The luminescence of ruthenocene and its decay have been studied between liquid helium and liquid nitrogen temperatures. The pattern is fitted to a $^{3}E_{1}$ (d-d) excited state split by about 500 cm^{-1} through the expected spin-orbit coupling. At 4.2K, the luminescence is well structured and is fitted to the Franck-Condon requirements of an excited state expanded along the long axis (80).

Species (arene)Cr(CO)$_3$ form charge transfer complexes with 1,3,5-trinitrobenzene (TNB) and with tetracyanoethylene (TCNE), but not with electron donating species. Comparison of trends in charge transfer band position, with those in the ionisation potential and CO stretching frequencies of the chromium complex, shows up differences in behaviour between TNB and TCNE. These are marked enough to suggest possible differences in electron acceptor coordination site (81). 2,3-Bis(diphenylphosphine)-maleic anhydride displaces two CO groups from the Group VI hexacarbonyls, or from tetracarbonylnickel, to give complexes with a strong band around 17,500 cm^{-1}. The band shows a strong blue shift on changing solvent from carbon tetrachloride to dimethylformamide [as expected here for a metal-ligand charge transfer band] (82). A similar effect is found in the complexes I (83).



(I)

Metal-ligand charge transfer energies increase in the sequence $Et_2Nibipy < Et_2Ptbipy < Me_2Ptbipy <$ MePtClbipy < MePdClbipy, and this order is taken as that of the binding energies of the metal d-electrons. Low binding energy then correlates well with reactivity towards alkenes or alkynes (84). Diferrocenylacetylene undergoes two reversible one-electron oxidations at an electrode, and the monocation shows an intense band at 6,400 cm^{-1} due to intervalence charge transfer (85). Visible spectra have been used to characterise cobalt(II)-alkene complexes formed in anhydrous cobalt(II)-bearing zeolite A, and characterised gravimetrically as 1:1 complexes with a binding energy around 68 kJ/mol (86).

PHOTOCHEMISTRY

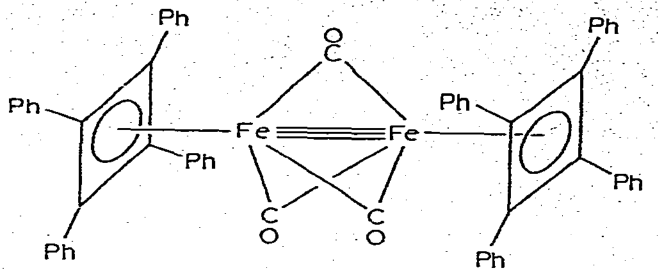
The photochemistry of metal carbonyl derivatives has been reviewed (87). It has been shown that triplet quenching by ferrocene can occur for triplet states as low as 8,000 cm^{-1} from the ground state, although diffusion controlled quenching only sets in above 15,000 cm^{-1}, which is the accepted lowest triplet energy of ferrocene. The phenomenon is attributed to the formation of a charge transfer complex between ferrocene and the substrate in its lowest triplet state (88). Species of type $ClRe(CO)_3(phen)$ (phen = o-phenanthroline) undergo radiative decay from their lowest excited state either in solution at room temperature or in EPA glasses around 77K, with a quantum efficiency of around 0.1. The relevant state is assigned as metal-ligand charge transfer, with considerable triplet character (89).

The photochemistry of a wide range of carbonyl anions $M(CO)_n^-$ of first transition series elements has been studied in the gas phase by ion cyclotron resonance. The dominant reaction is not, as with most gaseous anions, electron loss, but loss of CO. The maximum of the action spectrum increases in general with the number of CO groups and with the atomic number of the metal, and this is consistent with a spectrum dominated by metal to CO charge transfer. $[Ni(CO)_3]^-$ shows an anomalously low frequency maximum, as expected for excitation of a 4s,p electron, and $Fe(CO)_4^-$ shows a subsidiary low energy maximum ascribable to d-d excitations (90,91). $Cr(CO)_5$ has been generated from $Cr(CO)_6$ by flash photolysis in alkane solution in the presence of a variety of donors. Comparison of the rate of association of $Cr(CO)_5$ and L with the rate at which L dissociates from $Cr(CO)_5$ (inferred from the rates at which $Cr(CO)_6$ is generated in the presence of CO) may be combined to give equilibrium constants for the dissociation of L from $Cr(CO)_5$. The order of increasing rate of attack of L on $Cr(CO)_5$ is also the order of increasing equilibrium constant, namely

$C_6H_6 < Et_2O < MeOH < CH_3COOEt < CH_3COCH_3 < CH_3CN$

This is also, interestingly enough, the order of decreasing propensity for the oligomerisation of butadiene by bis(butadiene) iron monocarbonyl in the presence of triphenylphosphine to show solvent-hindered side-reactions (92). The photolysis of ^{13}C-enriched iron pentacarbonyl has been carefully studied by ir in a variety of matrices. Non-donor matrices (SF_6, Ar) give a species $Fe(CO)_4$, distorted from tetrahedral, with opposed CFeC angles of 120° and 145°. $Fe(CO)_4$ reacts further with a dinitrogen matrix to give $Fe(CO)_4N_2$. In xenon or methane, $Fe(CO)_4$ (as described above) is obtained together with species in which the opposed angles are 120° and 180°. These latter are regarded as equatorially substituted derivatives $Fe(CO)_4(Xe)$, $Fe(CO)_4(CH_4)$, of $Fe(CO)_5$ (while the neon-tetrahedral species is presumably (24) a triplet). If the matrix ratio is less than 1,000:1, then $Fe_2(CO)_8$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ are also generated (93). Further photolysis of $Fe(CO)_5$ gives $Fe(CO)_3$ (in which the CFeC angle is estimated, from relative infrared intensity data, as 108°) (94). The same process also gives rise to a small number of iron atoms, which have been studied in nitrogen, argon and methane matrices at 20K by first derivative uv spectroscopy (95).

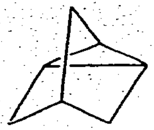
Photolysis of cyclobutadiene complexes $R_4C_4Fe(CO)_3$ (R = Ph, Bu^t) in hexane gives dimeric species for which the structure II has been established crystallographically;



(II)

the iron-iron bond length is 218 pm, consistent with the triple bonded formulation (96). The formation of such species is highly relevant to the suggestion that $Fe_2(CO)_7$ is an intermediate in the reactions of photochemically (or otherwise) generated $Fe(CO)_4$ in solution (97).

In the photolysis of amine-substituted molybdenum and tungsten carbonyls $M(CO)_5L$, the total quantum yields are always less than unity. The dominant process is replacement of L, with replacement of CO becoming more important at higher energies; this result is directly related (87) to the possibilities of populating different ligand field excited states (98). Irradiation of the parent hexacarbonyls with excess olefin gives light sensitive carbonyl alkene complexes of all three Group VIA metals. Light induced rearrangements occur, including cis-trans isomerisation and 1,3-hydrogen shifts, as also do photosubstitution reactions of CO and alkene (99). Irradiation of chromium hexacarbonyl with norbornadiene under hydrogen gives a mixture of nortricyclene (III) and norbornene in the (non-equilibrium) ratio 2.80:1. The

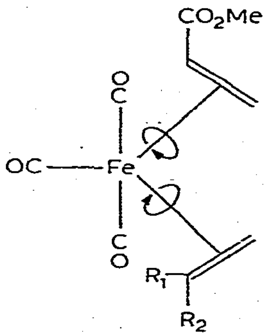


(III)

first photoproduct formed is pentacarbonylchromium norbornadiene, which can either lose CO on further irradiation to give (nbd) $Cr(CO)_4$, or revert thermally to hexacarbonyl and free nbd. It is found that (nbd) $Cr(CO)_4$ is the true photocatalyst. The reaction is first order in nbd at low nbd concentration, approaching at high concentration a limiting quantum yield of 1.9 (with 366 nm light). Using deuterium rather than hydrogen caused no overall rate change but did alter the product ratios; norbornene was formed as the endo,endo dideuterated species, whereas nortricyclene was formed with deuterium in positions 3,5. Interestingly, photolysis of $Cr(CO)_4$ (nbd) with helium purging gives no net reaction, while hydrogen purging leads to decomposition; this result is consistent with an open $Cr(CO)_4$ (nbd) species as the primary product of photolysis of normal $Cr(CO)_4$ (nbd), rather than with $Cr(CO)_3$ (nbd) (100). The relative rates of photohydrogenation of the three isomers of 2,4-hexadiene depend on whether $Cr(CO)_6$ or $Cr(CO)_4$ (nbd) is used as catalyst; the mechanistic implications of this finding are discussed (101). Photochemical exchange between (nbd) $Cr(CO)_4$ and ^{13}CO has been shown by IR spectroscopy to lead preferentially to formation of fac $-(O^{12}C)_3Cr(nbd)(^{13}CO)$, with subsequent dark reaction scrambling. This is explained by assuming a stereochemically rigid intermediate (nbd) $Cr(CO)_3$ since an intermediate $(h^2\text{-nbd})Cr(CO)_4$ would be converted *via* (presumably) *cis*-$(h^2\text{-nbd})(O^{13}C)Cr(^{12}CO)_4$ to a mixture of isomers (102). *trans*-Pentadiene is converted by trimethylsilane, using chromium hexacarbonyl as a photocatalyst, to 1-trimethylsilyl, *cis*-pent-2-ene (90%) and 4-trimethylsilyl, *cis*-pent-2-ene (10%) (103). It is relevant in this context that $Cr(CO)_3(CH_3CN)_3$ is a 1,4-hydrogenation catalyst for dienes even in the dark (104).

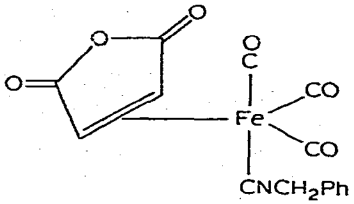
The species $CpFe(CO)_2N_3$, generated by the action of azide on $CpFe(CO)_2(C_2H_4)^+$, may be photolysed under CO in low yield to give $CpFe(CO)_2NCO$ (105); previous claims (106) to have prepared $[CpFe(CO)(C_2H_4)NCO]$ by action of azide on $[CpFe(CO)_2C_2H_4{}^+]$ are disputed.

Photochemical reaction of excess methyl acrylate with iron tetracarbonyl methyl acrylate at −30° gives a mixture of isomers, presumably (IV a,b). The room tempera-

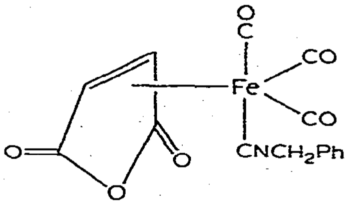


IV (a,b)

(a) R_1 = CO_2Me, R_2 = H
(b) R_1 = H, R_2 = CO_2Me



IV (c)

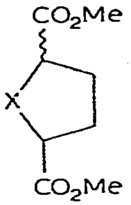


IV (d)

ture ultimate product is, specifically, the ketone V (107). Specific formation may be explained (97) by frontier orbital arguments; the new carbon-carbon bond is formed between those unsaturated carbon atoms at which the population of the lowest unoccupied orbital is highest. Similar specificity is observed in the carbonylative fusion of norbornenes by iron pentacarbonyl to give substituted cyclopentanones. Alkene exchange is required to maintain stereospecificity, and has been independently demonstrated (108), and similar specificity has been established for the related thermal reaction (109). A closely related reaction is the fusion of two norbornene molecules to give the *trans*-cyclobutane on irradiation in the presence of copper(I) triflate; the data are constant with ring formation within an irradiated 2:1 alkene-Cu(I) complex (110). The reaction is also shown by simple cycloalkenes, in which it may be accompanied by *cis*-*trans* isomerisation across the original double bond (111).

By using nitrosodurene as a spin trap for both fragments, homolysis has been demonstrated in the photolysis of compounds of the type alkyl-pentacarbonyl manganese (acyl-pentacarbonylmanganese gives the same products), and also in the dimeric species m_2 for $m = Mn(CO)_5$, $Mn(CO)_4PMe_2Ph$, $Re(CO)_5$, $CpFe(CO)_2$, $CpMo(CO)_3$, and $(EtO)_3PCo(CO)_3$ (112). The photodecomposition of tri-n-butylphosphine silver butyl at -60° gives 39% butane, as expected for a free radical process (113);, for the contrasting thermal decomposition, see under

'Kinetics and Mechanism' below. Photolysis of $[CpMo(CO)_3]_2$ in acetone, acetonitrile or tetrahydrofuran in the presence of chloride, bromide or thiocyanate gives products $CpMo(CO)_3X$ and $CpMo(CO)_3^-$; the quantum yield is much greater for the 500 nm than for the 382 nm band of the starting material (114). Metal-metal bond cleavage characterises two other reported sets of photoreaction. $Mn_2(CO)_{10}$ in pentane gives successively $Mn(CO)_4NO$ and $Mn(NO)_3CO$, while in tetrahydrofuran the ultimate product, $Mn(NO)_3THF$, has not been isolated but may be converted by phosphine or arsine donors to more stable species $Mn(NO)_3L$ (115). Photolysis of triruthenium dodecacarbonyl at 390 nm under carbon monoxide gives pentacarbonylruthenium while in the presence of triphenylphosphine the products are $Ru(CO)_4PPh_3$ and $Ru(CO)_3(PPh_3)_2$, formed in a 2:1 ratio (116).



(a) X = CO
(b) X = $Fe(CO)_4$

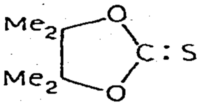
(V)

Photolysis of species Cp_2MMe_2 (M = Ti, Zr, Hf) gives methyl radicals and, apparently, true metallocenes. These are isolable and diamagnetic, and have infrared spectra consistent with the suggested structures. Added tolane gives rise to metallacyclopentadienes, and also to methyl stilbenes by methyl radical capture (117).

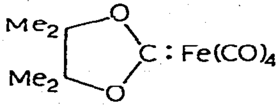
It is known (118) that irradiation of Cp_2WH_2 in benzene gives $Cp_2W(H)Ph$, and toluene behaves similarly, but p-xylene and mesitylene give rise to species of type $Cp_2W(CH_2Ar)_2$ (119). A further, most convenient route to bis(cyclopentadienyl) complexes of molybdenum and tungsten is photolysis of the carbonyls $Cp_2M(CO)$ (120). Irradiation (121) in benzene causes exchange between Cp_2TiCl_2 and $(C_5D_5)_2TiCl_2$. In a presumably related set of reactions, it has been shown that photolysis of Cp_2TiCl_2 in chloroform or carbon tetrachloride gives $CpTiCl_3$; this is also the main product in benzene to which HCl has been added, but the product in the absence of HCl is $CpTiCl_2$ (122).

Photolysis of ferrocene (FcH) in a region where it absorbs by charge transfer to solvent carbon tetrachloride gives, eventually, ferric chloride (123). In the presence of ethanol, however, the presumed intermediate $FcCCl_3$ is converted to Fc.COOEt. Similarly, Fc.CHO, $Fc.CH_2OEt$, $Fc.CH_2Ph$ and $Fc.CH_2CHCH_2$ may be prepared from $CHCl_3$, CH_2Cl_2, $PhCH_2Cl$ and CH_2CHCH_2Br (124). A sublimable 1:1 adduct of ferrocene and lithium chloride has been described; photolysis of this material in acetone gives eventually the ion $[Fe]^{2+}$(125). Ruthenocene also shows a new band (around 285 nm), assignable to charge transfer to solvent, when dissolved in halocarbons; irradiation in this region leads to formation of ruthenicinium cation (126).

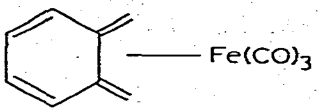
Several groups have described experiments in which iron pentacarbonyl reacts photochemically with organometallics, in some cases themselves most readily prepared photochemically. Thus reaction of chromium hexacarbonyl with 1,3-dioxolan-2-thione (VI), L, gives



(VI)

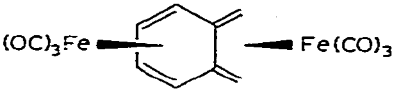


(VII)

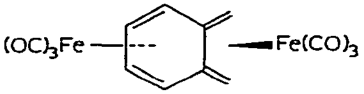


(VIII)

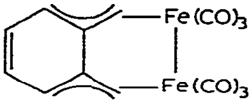
$LCr(CO)_5$; but when this in turn is irradiated with iron pentacarbonyl in THF the product is VII (127). The quinodimethane complex VIII, irradiated with $Fe(CO)_5$, gives a mixture of the two readily predictable products IX and X, together with the less foreseeable product XI



(IX)



(X)



(XI)

(128). Irradiation of $Fe(CO)_5$ with bis(trimethylsilyl) mercury gives a mixture of *cis*-$Fe(CO)_4(SiMe_3)_2$ and [*cis*-$Fe(CO)_4SiMe_3]_2$ Hg (129).

Photolysis of $CpRu(CO)_2SC_6F_5$ gives several different products; the expected $CpRu(CO)SC_6F_5$ as a mixture of isomers, the species CpRu(CO)[CO][SR]Ru(SR)Cp in which there is a metal-metal bond, and $CpRu[CO][SR]_2RuCp$ in which there is a metal-metal bond supported by three bridging groups (130).

Photolysis of $CpMn(CO)_2CS$ in the presence of phosphine, amine or phosphite donors leads to replacement of one or both CO groups, the CS group remaining unattacked (131). Alkylcobaloximes, in which the sixth position round cobalt is occupied by a base, shows light-catalysed insertion of O_2 into the carbon metal bond; the process seems to involve reversible loss of base (132). In the absence of oxygen, photolysis of methyl or benzyl cobaloxime pyridine complexes has been shown by ESR to give Co(II) species, presumably by electron transfer from solvent or from equatorial ligands; but other alkyl groups (isopropyl, isobutyl, n-pentyl, cyclohexyl) are cleaved homolytically (133).

MATRIX STUDIES (see also under Photochemistry)

Claims (134) to have prepared a trigonal bipyramidal form of $Cr(CO)_5$ in argon by co-deposition of metal atoms, carbon monoxide and argon have been hotly disputed (135,136). Nonetheless, atom deposition has led to some important new results in metal carbonyl chemistry. The species $Re(CO)_5$ has been prepared and its infrared spectrum assigned in C_{4v} (137). The species $Rh_2(CO)_8$ and $Ir_2(CO)_8$ have been prepared by atom-carbon monoxide co-deposition, along with some $M(CO)_4$. The dimers are bridge-bonded [like solid $Co_2(CO)_8$] but unstable at room temperature, giving the species $M_4(CO)_{12}$ (138).

Vaporisation of molybdenum or tungsten by electrical resistive heating in vacuo, and co-deposition with arenes, gives species $(Arene)_2M$. The method may be applied to arenes containing nitrogen, oxygen or chloride substituents. Resistive heating is described as cheaper than electron gun heating, and the risk of processes due to secondary electrons is avoided (139). Dibenzene chromium has been prepared in much the same way. With the exception of a line at 432 cm^{-1}, there are no strong features in the spectrum other than those due to free arene and bis(arene) chromium (140). Molybdenum and tungsten atoms when co-deposited with 1,3-butadiene at at a matrix ratio of 1:100 given products $(butadiene)_3M$ (141). The products from the co-condensation of these same metals with cyclopentadiene are, however, Cp_2MoH_2 and Cp_2WH_2; respective yields of 30% and 50% upwards are claimed (142).

Matrix deposition of metal atoms with perfluorobenzene gives rise to reaction complexes of Ti, V, Cr, Fe, Co, Ni and possibly Cu; benzene gives the familiar $Cr(C_6H_6)_2$ and $V(C_6H_6)_2$, as well as less stable complexes of Ti and Fe. Compared with benzene, C_6F_6 seems to give less stable complexes of the early transition metals, but more stable derivatives of the later members (143). Deposition of atoms together with perfluorinated organohalides, followed by treatment with triethylphosphite, gives rise to <u>trans</u> $(Et_3P)_2Pd(COC_3F_7)Cl$. Triethylphosphine treatment of the adduct of palladium atoms and perfluoroacetic anhydride gives some <u>cis</u>$(Et_3P)_2Pd(O.CO.CF_3)_2$, while hexafluorobut-2-yne gives $(Et_3P)_2Pd(C_4F_6)$ (144). The efficiency of the palladium atom insertion into carbon-halogen bonds falls from iodides to chlorides. Stability of species RPdX falls with R along the series

$$C_6F_5 > CF_3 > C_6H_5 > CF_2Br \sim CH_3$$

and species ArPdBr decompose to give palladium, biaryl, and palladium dibromide. Acyl halides react with palladium atoms to give species RCOPdX; the stability of these to decarbonylation falls with R in the order (145)

$$R_F > C_6H_5 > CH_3$$

The reactions of metal atoms collected in mobile solutions bridge the gap between matrix and conventional synthetic methods. The possible working ranges of various solvents are discussed (these must be mobile, non-volatile, and inert to the metal atoms themselves) and the preparation of bis(cyclooctadiene)iron is described (146).

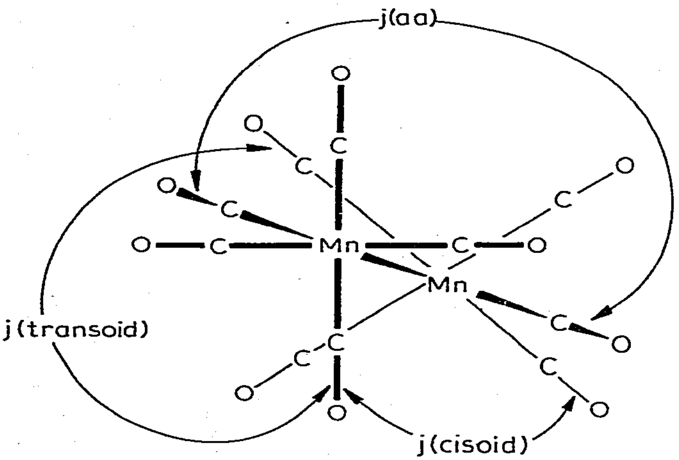
VIBRATIONAL SPECTRA

The changes in infrared frequency and intensity of carbonyl groups in metal complexes can successfully be mimicked, according to calculations, by attachment to a negatively charged metal (147).

The carbonyl vibrations of $LiMn(CO)_5$ and $NaMn(CO)_5$ in ethereal solvents have been assigned to trigonal ion-paired species, with in THF an equilibrium between solvent-separated and contact ion pairs. When $NaMn(CO)_5$ in THF is treated with magnesium ions, there is evidence for Mg^{++}–OC– Mn interaction (148). Rather similar effects are shown by the anion $[Ph_3PFe(CO)_3C(O)Ph]^-$

in the presence of Li^+ or, even more markedly, $MgCl^+$ in ether; in more strongly complexing solvents (such as dimethylformamide) the effects disappear. The effects are ascribed to perturbation by cation of an equatorial CO ligand. [Data for the acyl CO region would be of obvious interest, if obtainable, but are unfortunately not given] (149). Ion pairing in such poor solvents as THF is well known for $NaCo(CO)_4$ (150), but in better solvents (dimethylsulphoxide, dimethylformamide, nitromethane, hexamethylphosphoramide) no distortion from tetrahedral number averaged geometry could be detected even by a computer analysis searching enough to detect the ^{13}CO satellite beneath the wings of the main broad anion band (151). Pyrazolylboratomanganese carbonyls $RB(Pz)_3Mn(CO)_2L$ (R = Pz, H; L = Phosphorus ligand) have been subjected to a study of relative intensities, from which bond angles are calculated. An interesting feature is that the size of the carbonyl local oscillating dipole is allowed to depend on the symmetry mode in which it is taking part, and with the help of compounds of known structure the value of μ'_s/μ'_a is found to be 0.8-0.9 (152).

The 2107 cm^{-1} band of $Co_2(CO)_8$ has been shown, by enrichment, to be a ^{13}CO satellite band, probably of the bridged isomer, and not an all-^{12}CO band of the unbridged isomer; thus there is no longer any need to assign the latter a symmetry lower than D_3 (153). The vibrational spectra of the species $(OC)_4CoM(CO)_5$ (M = Mn, Tc, Re) have been analysed in terms of a 'free rotation' model, i.e. one in which the total effect of interactions across the metal-metal bond is independent of the angle of twist (154). The Raman and infrared spectra of $[Mn(CO)_6]PF_6$ have been analysed. The CO force constants for this cation and its rhenium analogue are not very different, but the metal-carbon force constant is lower for manganese (155). The spectra of the species $M_2(CO)_{10}$ (M = Mn, Tc, Re) have been carefully re-examined with emphasis on the ^{13}CO satellite bands and in the case of $Mn_2(CO)_{10}$ using ^{13}CO enrichment. The highest CO force constants are found with technetium (an example of the familiar alternation effect). The data do not permit separate optimisations of the couplings in the A_1 and B_2 modes, but do permit quite accurate determination of the coupling constants. In all cases j (cisoid) (see XII) and j(aa) are of the same order as the interaction constants linking CO groups on the same metal, while j(transoid) and j (ea) are far smaller.



(XII)

Electronic coupling is held responsible for j(aa), while j(cisoid) is presumed to arise by a through-space mechanism (156).

The Raman spectrum of $Mn(CO)_5Br$ has been observed down to 15K; there is no phase change from room temperature. ^{13}CO satellites are reported for the first time in the Raman spectrum, a feat much more difficult than in infrared spectroscopy because of the absence of a high concentration levelling of detector signals (157). High pressure infrared spectroscopy has been used to follow steps of the hydroformylation process, the spectra of reaction mixtures being discussed in detail. It is concluded that in the hydroformylation of terminal alkenes, hydrogenolysis of the acylcobalt tetracarbonyl intermediate is rate-determining, while for internal olefins, or using the tributylphosphine modified catalyst, the slowest step under the conditions studied is interaction of alkene with the cobalt hydride (158). The spectra of isonitrile derivatives of the Group VI hexacarbonyls have been studied, applying the Cotton-Kraihanzel (159) approximations both to CO and to CN stretching modes. Increased incorporation of isonitrile lowers both CO and (to a smaller extent) CN frequencies, and interaction constants linking CO groups are greater than the analogous constants for CN vibrations (160). Polarised Raman spectra in solution have been obtained for a range of monosubstituted derivatives of chromium and tungsten hexacarbonyls. There is a clear inverse relationship between axial MC and CO stretching frequencies, as required by a simple π-bonding model, but the situation regarding equatorial CO groups is less clear (161). A range of closely related compounds, the species $Ar_3E\ Cr(CO)_5$ (162) and $Ar_3ENi(CO)_3$ (163) (Ar = 3- or 4- chloro or fluorophenyl, E = P, As, Sb) have been examined in both high and medium frequency regions. Comparison of the effects of 3- and 4-substitution on CO stretching frequencies suggest that mesomeric effects are detectable but smaller than inductive effects. In the species trans $ML_2[Mn(CO)_5]_2$ (M = Pd, Pt; L = pyridine, methylpyridine) the CO stretching frequencies clearly support the contention that the manganese carries an appreciable negative change (164) [although the reported intensities are, in the reviewer's opinion, inconsistent with the proposed assignments, and obvious alternatives exist]. The CO stretching frequencies (and ^{13}C shifts) in the cations $[CpFe(CO)_2L]^+$ correlate well (165) with those for the neutral manganese analogues (166) (see below, under Mössbauer Spectra, for further discussion of these series).

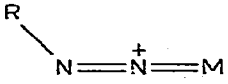
Force constants have been calculated for mono-substituted derivatives of iron pentacarbonyl (substituents being axial phosphines, phosphites or carbenes, or equatorial alkenes) using ^{13}CO data. For the axially substituted species, the axial stretching parameter is some 50 Nm^{-1} greater than the equatorial parameter, while for the alkene derivatives the force constants are on the whole greater but their order is reversed. Group dipole derivatives are calculated from the infrared intensities

(167). The infrared and Raman spectra have been compared of species $Fe(CO)_4L$ (L = PMe_3, $AsMe_3$, $SbMe_3$) and $Co(CO)_4Y$ (Y = $SiCl_3$, $GeCl_3$, $SnMe_3$, $PbMe_3$). Of the cobalt species, the trichlorosilyl and -germyl derivatives are monoclinic, four molecules in each unit cell, and the spectra are readily interpreted by the factor group method. The others belong to the trigonal space group R_3, which contains one molecule in each (optically active) unit cell; too many bands are found to be accommodated to standard theory, and it is proposed that the crystallographic unit cell is but a portion of the spectroscopic unit cell (168).

This is one of several studies on Group IV derivatives of metal carbonyls; the others are directed to the determination of force constants, on which there is not complete unanimity even on trends. The infrared spectra of the species $Mn(CO)_5MX_3$ (M = Si, X = Cl; M = Ge, X = Cl, Br; M = Sn, X = I) have been analysed using for the environment of M a modified Urey-Bradley field. The Mn-M force constant found falls on descending the periodic table for either M or X (169). The Raman intensity of the metal-metal band has been made as a measure of bond order in the series $(Cl, Me)_3(Ge, Sn)-(Mn,Re)(CO)_5$; the order found is roughly the mean of the corresponding homonuclear values and fails to show any π-bonding effects. Force constants are also calculated (170). The infrared and laser Raman spectra have been obtained of the species $[X_3MFe(CO)_4]^-$ (X = Cl, M = Ge, Sn; X = Br, M = Sn) and compared with those of the isoelectronic species $X_3MCo(CO)_4$. Force constants calculated using a uniform set of assumptions show (a) k(M–Fe) > k(M–Co) (this is taken as evidence for π-bonding) (b) k (MM′) falls with atomic weight of halogen (a result that commands general acceptance) and (c) k(SnM′) > k(GeM′) (171) [contrast results of (172,173) below]. Infrared and Raman spectra (including depolarisation data) have independently been reported for many of the species $X_3MCo(CO)_4$ ($X = H, D, F, Cl, Br, I$; $M = C, Si, Ge$) and force constants calculated. Metal-metal force constant is again found to fall with atomic weight of halogen, with hydrogen (deuterium) giving results similar to bromine while k(Sn–Co) < k(Si–Co) < k(Ge–Co) (contrast (171) above). The importance of π-bonding on metal-metal bond strength is stressed (172,173) [although the reported CO force constants are lower for the hydrogen (deuterium) compounds than for those of iodine, as expected from simple inductive effects].

Solid state Raman polarisation data have been obtained for a series of compounds of type (arene)$Cr(CO)_3$, and assignments made using the full factor group. Some corrections are proposed to earlier assignments, particularly for bending modes in the middle frequency region. Ring frequencies are generally shifted on complexation in the same sense as on electronic excitation of free benzene, but some exceptions, notably for the CH bending modes, arise through kinematic coupling (174). The infrared and Raman spectra of $C_4H_4NMn(CO)_3$ and $C_4D_4NMn(CO)_3$ have been compared with those of $CpMn(CO)_3$. The assignments for the latter compound agree in general with earlier studies (175), and the substitution of N for one CH group hardly affects the properties of the ring, although some bands that appear only in the Raman spectrum of $CpMn(CO)_3$ become observable in the infrared (176). However, in a study of $CpMn(CO)_3$ and $[CpMo(CO)_3]_2$ under various conditions, deviations from the selection rules for C_{5v} have been detected even for $CpMn(CO)_3$ itself (177).

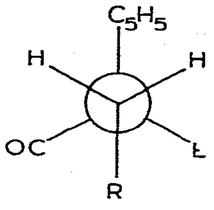
In diazonium complexes such as $HB(Pz)_3Mo(CO)_2NNPh$, which are known to have structures (XIII), the NN stretch



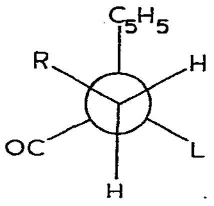
(XIII)

has been ascribed on the basis of ^{15}N shifts and of Raman intensities, to a band in the region 1530-1580 cm^{-1}; a band some 50 cm^{-1} higher is reassigned as an asymmetric coupled motion of the (N-N-Ph) grouping (178). A fall occurs in the C=C frequencies in N-methylmaleimide (179) and in maleic anhydride(180, 181) from 1585 and 1595 cm^{-1} to 1370 and 1352 cm^{-1} respectively on complexation to the $Fe(CO)_4$ grouping; a lowering of intensity in the C-H deformation modes in the latter case has been discussed in terms of bonding changes (181). A valence force field has been calculated for cyclobutadiene iron tricarbonyl. The high ring breathing frequency (1234 cm^{-1}) arises from large positive interaction constants linking the CC bonds, and some reassignments are proposed for the $Fe(CO)_3$ fragment in the medium frequency range (182).

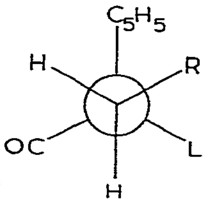
In species of the type $CpFe(CO)(L)CH_2R$, two CO stretching frequencies are found, indicating some kind of isomerism. The protons of the CH_2 group are diastereotopic, and the results are interpreted in terms of rapid equilibration between conformers XIV (a,b,c) (183).



XIV (a)



XIV (b)



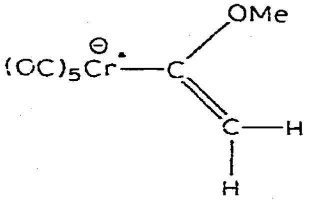
XIV (c)

Raman and infrared spectra have been obtained for the species $S_2Fe_2(CO)_6$ and the two isomers of $(MeS)_2Fe_2(CO)_6$ A simple force field has been solved for the S_2Fe_2 unit of the former compound, the Raman modes of which show pre-resonance enhancement, and the calculated iron-iron force constant of 130±20 Nm^{-1} is described as satisfactory for a single metal-metal bond (184). The dark brown $(OC)_2Rh.C_7H_7.Fe(CO)_3$ shows resonance enhancement of a band at 172 cm^{-1}, assigned to the Fe-Rh stretch (185). The spectra of species $[(Ru,Os)(NH_3)_5(CO,N_2)]X_2$ have been investigated mainly in order to investigate the N_2 ligand; solid state splitting was observed for the CO stretching mode (186). The vibrational spectrum of the novel tetrabenzylthorium has been compared with that of tetrabenzylzirconium (187). Infrared spectra have been reported for the bis(cyclooctatetraene) complexes of Ti, V, Th, U. Assignments are proposed for the Th, U compounds, which are highly symmetrical sandwich compounds, but the others are of lower symmetry and their spectra could not be analysed in any detail (188). The infrared spectrum of $CpFeC_5H_4HgCl$ shows bands not present in ferrocene, for example at 1148 and 873 cm^{-1}, due to coupled symmetric C-C and C-Hg modes; similar effects are known in haloferrocenes and halobenzenes (189). The spectra of a range of complexes $(Ph_3P)_2(Ni,Pd)(C_6Cl_5)X$ have been compared with that of hexachlorobenzene itself: the skeletal E_u mode is split and A_{2g} activated in the infrared, while A_{2u} is little altered (190). CN and CO frequencies in species $NC.C_6H_4.Ni(PR_3)_2X$ and $CH_3-CO-C_6H_4.Ni(PR_3)_2X$ show nickel to be strongly electron-donating, more so than palladium and platinum (191). The infrared spectra of species $C_5H_5AuPPh_3$ and $CH_3C_5H_4AuPPh_3$ are characteristic of σ-bonded (methyl)cyclopentadienyl. The NMR spectra show time-averaging and coupling between phosphorus and ring carbon. This coupling is lost in the presence of excess phosphine indicating exchange by an associative mechanism (192). Palladium- and platinum-halogen frequency has been used as a probe of trans-influence, in carbene complexes: by this criterion, and that of phosphorus-platinum coupling in NMR, carbenes are assigned a trans-influence similar to that of triethylphosphine (193). The spectra of species $(Ph_3P)_2Pt(HCCR)$ have been assigned in the region 300-600 cm^{-1}, and tentative assignments proposed for the platinum-phosphorus and platinum-carbon stretching modes (194).

NMR: STATIC SYSTEMS (See also (165, 166, 193) above; NMR; Dynamic Systems, below)

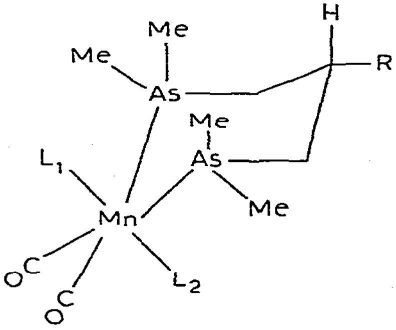
Carbon nmr (cmr) shifts, and carbon-metal coupling constants, have been reviewed in general (195) and with particular reference to metal carbonyls (196). It has been argued that no simplistic interpretation of cmr shifts is, or should be, possible. The atomic orbitals of the normal treatment are not gauge invariant, and the conventional separation of diamagnetic and paramagnetic terms is an artefact of the method of calculation; moreover, the usual discussions [which proceed regardless; see below] in terms of such isolated effects as metal-carbon π-bonding do not fit the known facts (197). The theory of (natural abundance) carbon to phosphorus coupling in species continuing two phosphorus atoms has been described. When the phosphorus atoms are <u>trans</u>, so that J(PP') is large, a 1:2:1 triplet is expected. If the phosphines are mutually <u>cis</u>, and J(PP') is small but not zero, a second order 5-line spectrum is observed which may be observed as a triplet but not with ratio 1:2:1. If J (PP') is zero, the carbon spectrum is a doublet (for J (PC') zero) or a first order quartet (for J(PC') detectably non-zero). The extraction of coupling constants is discussed (198).

Relative to tetracyanoethylene or $(NC)_2C = CHCl$, species $(NC)_2C{=}C(CN)m$ and $(NC)_2C{=}C(H)m$ show a 50 ppm low field shift of the α carbon. Relaxation is fast, unlike that in carbonyls, so a relaxing agent is not necessary (199). Methyl exchange between tetramethyltitanium and trimethylaluminium has been followed by nmr, using deuteriated materials. In hexane, there is rapid exchange. Addition of one mole of ether leads to formation of a species formulated as $Me_3Ti\cdot AlMe_4$, followed by slow reversal and eventual scrambling. When the individual etherates are mixed, a new species is formed, regarded as a solvent-separated ion pair $[Me_3Ti]^+[AlMe_4]^-$ (200). Cmr and pmr data have been obtained for the species $C_5H_5MC_7H_7$ (M = Ti, Zr, Cr, Mo) and, for M = Ti, for some methylated derivatives (compare (59) above). In the Ti, Zr derivatives, the seven-membered ring occurs at higher field: The opposite is true for Cr, and in the molybdenum complex both signals are close together. The proton signals indicate hindered rotation (!) for the chromium and molybdenum complexes but not for those of Ti, Zr, and the proton chemical shifts parallel those of carbon (201). In the species $Cp_2Nb(Et)C_2H_4$ and $Cp_2Nb(H)C_2H_4$, the ethylene carbon atoms lie in the mirror plane, and exchange between the ends is slow at room temperature (202). Methoxy-methylcarbene chromium pentacarbonyl is readily deprotonated by butyllithium to give a species formulated as XV, in which the methylene hydrogens are non-equivalent up to



(XV)

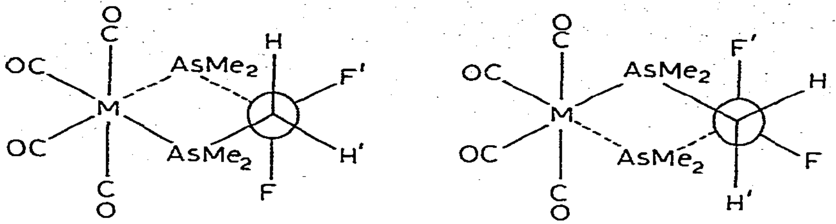
120°C; the ease of deprotonation, and the low CO stretching frequencies of the product, also support the proposed assignment (203). In the Group VI tetracarbonyl derivatives of the ligands $Me_2As.CH_2.CHR.CH_2.CH_2AsMe_2$, the metal chelate ring adopts a chair conformation; this rapidly inverts when R=H, but when R = Bu^t the chair is locked in the conformation in which R is equatorial (204). A very similar situation exists for the manganese tricarbonyl halide derivatives of these same ligands, except that the tert-butyl species is (205) now a mixture of isomers XVI (a,b). Similar studies



XVI (a) $L_1 = CO, L_2 = X$
XVI (b) $L_1 = X, L_2 = CO$

have been carried out using substituted derivatives of 1,2-bisdimethylphosphino- and arsinoethane, obtaining proton and (where appropriate) fluorine spectra and using heteronuclear decoupling of H, F and P. In the metal tetracarbonyl derivatives of $Me_2AsCH_2CH(SiMe_3)AsMe_2$, the $SiMe_3$ group is always equatorial, while in complexes of $Me_2As.CH_2CHF.AsMe_2$ and $Me_2As.CF_2.CHFAsMe_2$ the fluorine prefers the axial position. In complexes of

$Me_2As.CF_2.CH_2.AsMe_2$, there is some time-averaging between conformations XVII (a,b), and the effects of changing



(a) (b)

(XVII)

metal, and the differences between phosphorus and arsenic donors, are discussed in terms of geometry (206). Similar studies have been carried out on complexes of the type (chelate) $Mn(CO)_3X$, in which the nature of X affects conformational preferences (207).

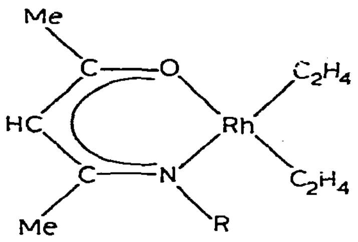
While solid $Cp_2Cr_2(NO)_4$ is known to adopt the transoid conformation (with two nitrosyl bridges), the proton nmr spectrum shows two signals, of which the weaker, attributed to the cisoid isomer, increases with solvent polarity, as does a weak infrared band attributed to ν_4 (cisoid) (208). Several thiophene chromium tricarbonyl complexes have been investigated by proton mmr; α-hydrogen shows a larger upfield shift on complexation than does β-hydrogen, and the two differenct vicinal coupling constants become more similar to each other (209). The cmr spectra of a range of arene chromium tricarbonyl complexes have been reported and compared with existing data; it is agreed that carbon shifts are influenced both by ligand-metal and by metal-ligand donations involving ligand π or π^* orbitals, and that no simple generalisation can cover the observed shifts (compare (197) above) (210). Cmr data have been reported for both ring (211) and carbonyl (212) carbons of a wide range of species of type $PhX.Cr(CO)_3$, and for species $(Ph_3P)Cr(CO)_5$, $(PhO)_3PCr(CO)_5$, $[(PhO)_3P]_2Cr(CO)_4$, $CpM(CO)_3$ (M = Cr^{-1} Mn^o, Fe^+ (212, 213). It is concluded, from the shifts of C(1) and C(4) in free and complexed PhX, and from C-H coupling constants, that complexation does not interfere with the transmission of effects but does cause net withdrawal of electrons from the ring σ framework. Higher back-donation to carbonyl causes greater deshielding, and trends in the arene complexes are dominated by inductive effects.

In $CpMn(CO)_2CS$, CO is less deshielded than in $CpMn(CO)_3$, suggesting that CS is a better π-acceptor than CO, and indeed the thiocarbonyl carbon is the most intensely deshielded yet reported (213). Species of type $[(arene)Mn(CO)_3]^+$ have been studied by cmr, pmr, ^{55}Mn nqr, and CO stretching frequency. It is found, not totally surprisingly, that there is much more electron migration from ring to metal in complexes of Mn(I) than in those of Cr(0), and that $[C_5H_5]^-$ is a much better electron donor than a neutral arene. The efg at manganese increases linearly with the number of methyl groups on the ring (214).

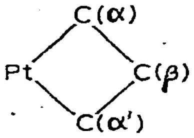
Species $CpMn(CO)_2L$, $CpMn(CO)L_2$ (L = e.g. PPh_3, L_2 = e.g. $(PPh_3)_2$, dppe) are reversibly protonated by trifluoroacetic acid in methylene chloride, and the process has been studied by both pmr and ^{31}P nmr. Protonation is at the metal, as shown by the large proton phosphorus coupling constant, and the appearance of a hydride signal in the region $\tau = 14-16$. The protonated species adopt a 4-legged stool structure; in $[CpMn(CO)(PPh_3)_2H]^+$ and $[CpMn(CO)[Ph_2P(CH_2)_3PPh_2]H]^+$, the proton is trans to CO (since the phosphorus atoms are mutually trans), while protonation of CpMn(CO)(dppe), CpMn(CO)(dppm), and (judging by phosphorus-proton coupling constant) $CpMn(CO)_2PPh_3$ gives species where phosphorus and proton are mutually cis (215,216). The cmr spectra of $PhCH_2Mn(CO)_5$, $Re_2(CO)_{10}$, $Re(CO)_5Br$, $Ph_2C_2Co_2(CO)_6$ and $CpIr(CO)_2$ have been studied at room temperature and below; lowering the temperature reduces quadrupolar broadening by metal of the carbonyl carbon signals. In the cobalt complex, even at -67°C, only one carbonyl carbon signal is detected, but at this temperature in the manganese and rhenium species, the signals from equatorial and axial CO are resolved and distinguishable (217).

The pmr spectra of the substituted cyclobutadiene complexes $(C_4H_3X)Fe(CO)_3$ ($X = Cl, Br, CH_3$) have been carefully examined and all the different $^1H-^{13}C$ coupling constants measured. It is inferred that, despite the influence of the substituents, bond orders in the C_4 ring remain almost uniform (218).

Pmr and cmr data have been reported for species $[Co_3(CO)_9CCHR]^+$. The apical carbon signal in this cation is little shifted from that in the parent alcohol, indicating charge delocalisation onto the Co$_3$ ring (219). The reaction between Rh(CO)$_4^-$ and carbon tetrachloride, which gives $[Rh_6(CO)_{15}C]^{2-}$, has been investigated by ^{13}C labelling followed by cmr. A label on the tetrachloride carbon appears at carbide carbon in the product; this carbon is highly deshielded and its coupling to metal is small. A ^{13}C label on the anion does not appear at carbide carbon. All the different types of carbonyl carbon give separate signals at 25°C, showing interchange to be slow on the nmr time-scale (220). Relatedly, the species $[Rh_{12}(CO)_{30}]^{2-}$, which may be formulated as $[Rh_{12}(CO)_{20}\mu_2(CO)_2\mu_3(CO)_8]^{2-}$, shows a spectrum essentially unaltered from -70°C to + 52°C. There are three signals from terminal CO and one from doubly bridging CO, while the triply bridging groups give a complex pattern (221). The methylene proton signal in CpRh[P(OEt)$_3$]$_2$ shows the effects of strong phosphorus-phosphorus ('virtual') coupling (222). In the complexes XVIII, the two types of ethylene give distinct proton signals; that trans to nitrogen is more strongly affected by electron-withdrawing groups R, and more labile to exchange (223).



(XVIII)

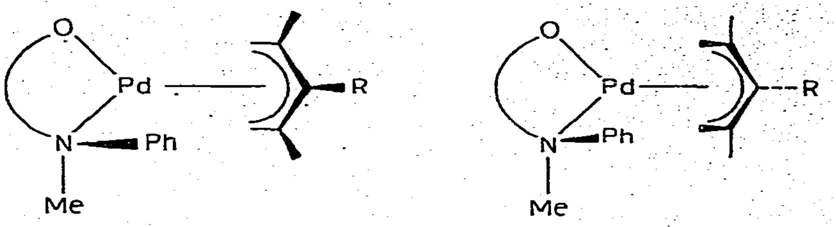


(XIX)

Both cmr and pmr spectra have been obtained for species Cp_2Ni_2RCCR'; the results, in conjunction with those from ir spectroscopy, indicate that the central bond of the μ-alkyne is very similar to that in a free alkene (224). The pmr, cmr, and ^{195}Pt nmr spectra of platinum cyclopropane complexes conform with the metallacyclobutane formulation XIX, but there appears to be a degree of specific Pt–C(β) interaction (225). The cmr spectra of seven different species of the types cis-Me_2PtL_2 and cis-Me_2PtL–L have been compared. Trans-influences appear to be much more powerful than cis-influences,while carbon hydrogen coupling within the methyl groups is insensitive to the nature of the other ligands (226). A comparison of species of type (pdma) Pt(Me)X, $[(pdma)Pt(Me)L]^+$ (pdma = o-phenylenebisdimethylarsine) gives further information about cis-influences on J(Pt–C); these do not correlate well with trans-influences, and appear to be related in part to ligand bulk (227). The cmr and pmr of thirteen different di- and trimethylplatinum(IV) species have been examined, and it is found that cis and trans influences on carbon chemical shift, and on platinum-carbon and platinum-methyl hydrogen coupling constants, resemble these in Pt(II) compounds (228); it has independently been shown that, as would then be expected, in cis-dimethylplatinum(IV) Schiff's base complexes, the trans-influence of nitrogen is stronger than that of oxygen (229). These results suggest that, at the least, much of what is known about the trans-influence must be explained without invoking π-bonding, and this has been shown to be true even for the Pt(II)-phenyl bond. For in species trans-$Pt(AsMe_3)_2(Ph)L^+$, the phenyl α-carbon chemical shift, and coupling to platinum, appear subject to the same trans-influences as those found for Pt(II) methyls, while meta and para carbon chemical shifts vary in a similar manner, although the former is not directly accessible to mesomeric influences (230).

The large upfield shift of carbon in alkene complexes of copper(I) has been interpreted in terms of extensive back-donation (231). In 1-butene complexes of Ag(I), C(1) shows a much greater upfield shift than does C(2), indicating that the bond between silver and the alkene is not symmetrical; the 2-butene complex, on the other hand, is symmetrical (232). Cmr changes in alkenes on being adsorbed on Ag(I)-rich zeolites are similar to those on complex formation in solution, but at low Ag(I) content the observed spectra are an average of those for adsorption at Ag(I) and Na^+ sites (233).

Pmr and cmr spectra of ferrocenes bearing chiral substituents show the results of magnetic non-equivalence (234), while diastereotopy in $CpFe(CO)_2CH(Me)Ph$ has been observed directly by cmr (235). In the diastereomers of π-allyls of (N-α-phenylethylsalicylaldiminato)palladium, the phenyl ring causes anisotropic shielding, making it possible to distinguish between XX(a) and XX(b) (236). Cmr has been used to follow the deprotonation of cobalaminacetic acid. The remarkably high pK_a value of 7.2 is attributed to hydrogen bonding between the carboxylic



(a) (b)

(XX)

acid function and acetamide side-chains, an effect relevant to the general question of z-axis ligand influence on corrin ring conformation (237). The severely overlapping proton resonances of trans(pyridine)(C_2H_4)$PtCl_2$ in nematic solution have been analysed using intensities rather than frequencies; the calculated ratio of gem to cis proton-proton coupling constants is described as reasonable (238).

The ^{19}F resonance spectra of 3- and 4-fluorodiazometals lead to the conclusion that ArN_2^+ is a poorer π-acceptor than NO^+(239). In 3- and 4-fluorobenzylcobaloximes $C_6H_4FCH_2Co(dmgH)_2X^-$ (X= CN, N_3, NCO, halogen, NO_2, NCS) and related species, the variations in fluorine resonances with X reflect changes in the donor power of the CH_2Co grouping (240). Similar studies on complexes 3- and 4- $FC_6H_4M(PEt_3)_2X$ (M = Ni, Pd, Pt) show the metal to be electron-releasing; the three metals are quite similar in their effects but nickel appears to be the best π-electron donor (241).

Tungsten-ligand phosphorus coupling constants in species of type $W(CO)_5$ PPh_2-(bridge)-PPh_2 change on quaternisation of the free phosphorus atom. Surprisingly, the size of the change does not depend on the degree of saturation of the bridging group, the effect varying with the nature of the bridge in the order (242)

cis-CH=CH $<$ CH_2-CH_2 $<$ $C \equiv C$ $<$ trans-CH=CH $<$ CH_2

In complexes of the type trans-$L_2Rh(CO)X$ (L = PR_3, $P(OR)_3$, PPh_3, $P(OPh)_3$), the shift in the ^{31}P resonance on coordination varies with the acceptor strength of L in parallel with changes in ν(CO) (243).

Comparison of ^{59}Co chemical shifts in series of compounds of the type $R_nX_{m-n}Sn[Co(CO)_4]_{4-m}$ led to the conclusion that the chemical shift of cobalt depends mainly on π-bonding effects in the tin-cobalt bond (244). In an independent but relevant study of species of type $XCo(CO)_3L$, $XCo(CO)_2L_2$ (X = e.g. Ph_3Sn; L = phosphine or phosphite) it was concluded that the quadrupole coupling constant at cobalt depends on both the σ and the π bonding effects of X (245). In cobaloxime-type complexes, the cobalt chemical shift increases with ligand, and the inferred ligand field decreases, on going from $(dmgH)_2$ to N,N',ethylenebis(salicylaldiminato) to N,N',ethylenebis-(acetylacetonato). This is also the order of falling stability of cobalt-carbon and cobalt-group IV bonds in such compounds (246).

The isotropic ^{11}B and ^{13}C nmr shifts in metallacarboranes $CpM(C_2B_nH_{n+2})$, $M(C_2B_nH_{n+2})_2$ (M = Cr(III), Fe(III), Ni(III), Co(II); n = 6-9) show delocalisation effects. These are confined to the metallated face, and attributed to L → M, or for Co(II), M → L, charge transfer processes (247). The proton spectra of species $(RC_5H_4)_2Fe^+$ have been examined between -60 and +60°C, and α and β resonances reassigned. The signals from the ferricenium cation itself obey a Curie law, but alkyl substituents give rise to deviations connected with ring signal splitting. Neither pmr Fermi contact nor pure dipolar interaction alone can account for the observed paramagnetic shifts (248).

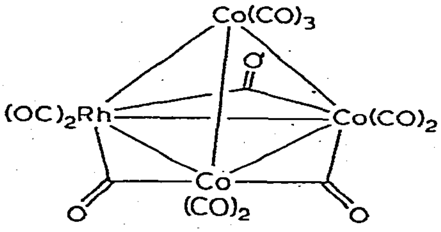
NMR: DYNAMIC SYSTEMS

The possible rearrangement mechanisms of octahedral species L_4MH_2, with 0, 1, or 2 chelating rings in the L_4 system, have been discussed (249). The broad line spectra of a range of solid metallocenes and dibenzene complexes in the range 178-381 K fit a model in which organic groups rotate essentially freely about their principal axes; but in $(C_8H_8)_2U$ there is evidence for distinct rotamers (250).

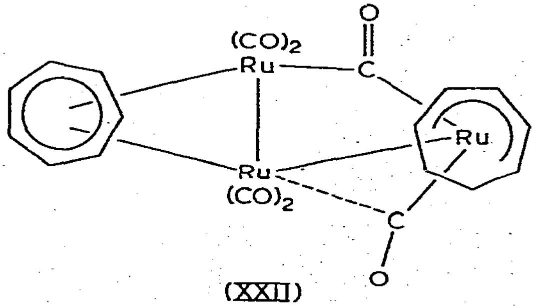
The ^{13}C chemical shift tensor in $Ni(CO)_4$ and $Fe(CO)_5$ has been separated into parallel and perpendicular components by using relaxation narrowing studies to determine the anisotropy (for $Fe(CO)_5$, the average anisotropy) of the shift. In $Fe(CO)_5$, there is a large paramagnetic contribution to the perpendicular component, which is evidence for π-bonding, but the corresponding effect in $Ni(CO)_4$ is within the error limits (251). The cmr spectra of trifluorophosphine-substituted iron carbonyls also show time-averaging. There is the further complication of the presence of different isomers, the relative concentrations of which have been followed by ir as a function of temperature, and used to explain the observed temperature dependence of the averaged phosphorus-carbon coupling constants. The chemical shift difference between axial and equatorial carbonyl carbon is calculated to be 17.7 ± 1.5 ppm, and using information from relaxation time studies (252) leads to an axial-equatorial exchange rate of 1.1×10^{10} sec^{-1} at -20°C (253). The cation $[(p\text{-tolyl.NC})_5Co]^+$ shows only one methyl proton signal at room temperature, but $[(p\text{-tol.NC})_4CoPPh_3]^+$ shows separate signals for the axial and equatorial methyl groups of a trigonal bipyramidal structure (254). The crystal structure of $(NBD)(PhMe_2P)_2IrSnCl_3$ has been determined; the $SnCl_3$ group is equatorial, in contrast to related iridium methyls, in which the methyl is always axial. This explains the finding (255) that chelation of phosphine ligands hinders axial-equatorial interchange in iridium trichlorostannyl complexes, but facilitates it in the related methyls (256). In complexes of type $[M(all)_2L_2]^+$ (M = Rh, Ir; all = π-allyl, π-2-methallyl; L = phosphine, phosphite, arsine, pyridine, acetonitrile), the related $M(all)_2$ (tropolonate), and $Rh(All)_2$ (pyridine-2-carboxylate), the asymmetry in bonding of the allyls is detectable by pmr. The neutral species show concomitant syn-anti and left-right interchange, as expected on the familiar π-σ-π mechanism. The cations, however, show left-right interchange without syn-anti interchange, and this is inhibited by excess neutral ligand; these results are explained by pseudorotation in a 5-coordinate intermediate (257).

The cmr spectrum of $Fe_3(CO)_{12}$ is time-averaged down to -160°C (258). $Os_3(CO)_{12}$, by contrast, gives two signals +10°, coalescing at +70°. $Fe_2Ru(CO)_{12}$, $Ru_3(CO)_{12}$, and $[MnFe_2(CO)_{12}]^-$ all show averaging, with carbonyl exchange between metals as well as between sites. By contrast $Ru_3(CO)_{10}(NO)_2$ from −50° to +40° gives three signals, in the ratio 4:4:2; this implies exchange within the $Ru(CO)_4$ unit but not between the various units. Axial-equatorial exchange also occurs in $Fe(CO)_4(AuPPh_3)_2$ (but not in $Fe(CO)_4Br_2$). $[HFe_3(CO)_{11}]^-$ gives signals in the ratio 1:10 at −30°, averaged at +40°. The unique signal is attributed to the carbonyl of the Fe(CO)(H)Fe bridged unit, which cannot be averaged with the others by carbonyl pairwise scrambling, but only by a ring opening process that requires charge separation and hence, reasonably enough, higher temperature (259). Intramolecular scrambling occurs above room temperature in species $Ir_4(CO)_8L_4$ ($L = Ph_2PMe$, $PhPMe_2$, Ph_2AsMe, and L_2 = dppe), causing changes in carbonyl cmr and also in ligand pmr (260).

The −85° cmr spectrum of $RhCo_3(CO)_{12}$ suggests the structure XXI. Between −85° and + 10°, averaging takes place involving all groups except those on Rh, which become equivalent because of a mirror-plane in the time-averaged structure. Above 10°, complete scrambling sets in (261). In $(C_7H_7)(C_7H_9)Ru_3(CO)_6$ (XXII), the C_7H_7

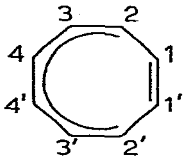


(XXI)

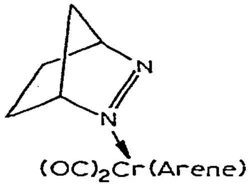


(XXII)

ring shows time-averaging down to −100°C. At room temperature, the C_7H_7 unit appears as a symmetrical pentadienyl, showing that the fully and partly bridging CO groups are exchanging roles, but the interchange is quenched at lower temperatures (262). The cmr spectrum of $C_8H_8Mo(CO)_3$ shows four separate ring carbon signals at 0° in chloroform-toluene; these all collapse at the same rate, whereas a 1,2-shift mechanism would lead to less rapid exchange of C(1) and of C(4) in the instantaneous structure (XXIII). A suggested explanation is that in the



(XXIII)

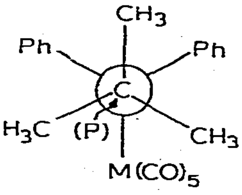


(XXIV)

transition state molybdenum becomes equally coordinated to all carbons (263), or alternatively that averaging occurs by 1,3- or by random shifts. The spectra of $C_8H_8Cr(CO)_3$ and $C_8H_8W(CO)_3$ pose similar problems, but that of $1,3,5,7\text{-}Me_4H_4C_8\ Cr(CO)_3$ can be explained by single, reversible, 1,2-shifts only (264).

The coordinated carbene groups in $Rh(:\overline{C\text{-}N(Et).CH_2.CH_2.N}(Et)]_2(CO)Cl$ show restricted rotation which has been followed by pmr. The activation energy for rotation is less than 40 kJ mol^{-1}, and the entropy of activation is negligible (265). The spectrum of tetrapyrrolyluranium shows, in addition to the expected isotropic paramagnetic shift, fluxional processes attributed to rotation and at higher temperatures h^1-h^5 interchange of the ligands (266). Complexes XXIV, prepared photochemically from (arene)$Cr(CO)_3$ in THF and the nitrogen ligand, show rapid interchange at room temperature of free and coordinated ligand nitrogen (267).

In the complexes $Bu^tPh_2PM(CO)_5$ (M = Cr, Mo, W), the high temperature limiting phosphine pmr spectrum consists of one doublet, but this resolves at lower temperature into two overlapping doublets of different intensities, due to the different methyl environments in the structure (XXV). The hydrogen-phosphorus coupling constants for trans and gauche methyl have the same sign, the values being 10 and 17 Hz respectively, and the free energy of activation for interchange is in all cases around 35-36 kJ mol^{-1} (268). The ring carbon spectra of species $RC_6H_5Cr(CO)_3$ are temperature dependent; for R = Et, carbons 2,4,6 shift upfield with increasing temperature while for R = CH_3CO and even more strongly for R = Bu^t, the reverse is the case. These results are explained by equilibria between instantaneous states of type (XXVI a, b), with the bulkier substituent presumably favouring (a) (269).



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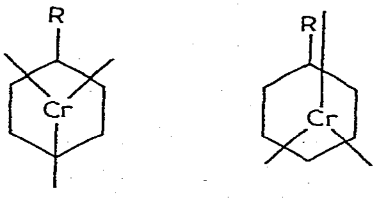
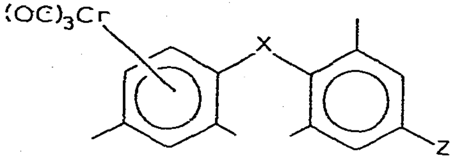


(a) (b)

(XXVI)

The spectra of species XXVII have been used to study the kinetics of the restricted rotation of the uncomplexed ring (270). Butadiene tricarbonyliron complexes show at low temperature two carbonyl cmr signals in the ratio 2:1;

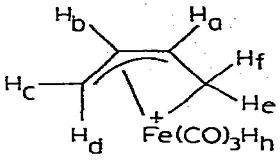


(XXVII)

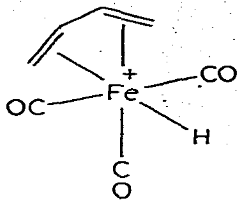
these coalesce on heating (271). In the low temperature spectra of tricarbonyliron complexes of the dienes $CH_3CHOH.CH:CH.CH:CH.CH_3$ and $CH_3CO.CH:CH.CH:CH.CH_3$ it is possible to distinguish all three ligand carbonyl carbons; the coalescence temperatures in the two complexes are very similar, but 50° higher than that in butadiene tricarbonyliron (272). The spectra of tricarbonyliron diene complexes in strong acid have been re-interpreted in terms of an asymmetric tetrahapto ligand, as in the structure XXVIII. Then a fast 1,2 shift of the iron-bond proton to the 'purely σ-bonded' carbon would account for fast interchange of protons e,f,h, while conversion of the C_4Fe skeleton to its mirror-imaged valence tautomer would lead to a slower left-right interchange (273).

The reviewer is tempted to re-write XXVIII as XXIX; the slow process could then be a steric rearrangement at iron.

Rotation around the metal-metal bond in $[CpCr(CO)_3]_2$, and the equilibrium between trans and gauche rotomers,



(XXVIII)

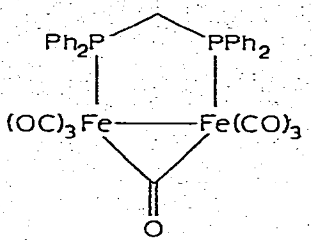


(XXIX)

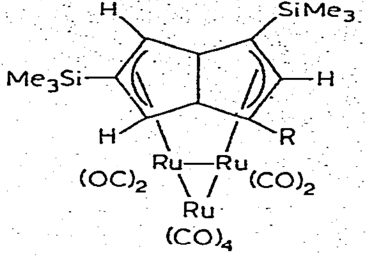
have been studied as a function of solvent and of temperature; the barrier to rotation is around 51 kJ mol^{-1}, and line broadening, which sets in reversibly above -10°C, is attributed to the formation of some paramagnetic species (274). The barrier to rotation is higher in the molybdenum compound, and much higher in that of tungsten; it may be relevant that the metal-metal distance is shorter for tungsten than for molybdenum (275). In $Cp_2Fe_2(CO)_3P(OPh)_3$, which has been studied both by pmr and by cmr, cis-trans and bridge-terminal interchanges occur at the same rate at all temperatures; this result supports the proposal (276) that interchange in species of this kind occurs by pairwise bridge opening followed by rotation in the non-bridged intermediate. The detailed permutations are shown to be consistent with that rotation being hindered, and the slower exchange in $Cp_2Fe_2(CO)_3P(OPh)_3$ than in $Cp_2Fe_2(CO)_4$ is then ascribed to steric hindrance by the bulky phosphite (277). In $Cp_2Fe_2(CO)_3(GeMe_2)$, which is known to contain a germylene bridge, interchange sets in only above 90°C. This implies an unusually high activation energy, which can be explained on the pairwise opening hypothesis by the relative instability of terminal germylene as a ligand (278).

Nmr analysis shows that $Cp_2Fe_2(CO)(CNMe)_3$ and $Cp_2Fe_2(CO)_2$-$(CNMe)_2$ both contain two bridging (CNMe) groups. The former is predominantly a mixture of anti and one syn isomer which interconvert rapidly at 25°C but give separate sharp spectra at −100°C. The latter is known to exist as a mixture of a cisoid species with two isonitrile bridges (the structure found (279) crystallographically) and a transoid species with both carbonyl and isonitrile bridges. This last shows a temperature dependent nmr spectrum due to inversion at the bridge, which is estimated to be five orders of magnitude faster than bridge-terminal rearrangements (280). On the other hand, pmr and ir show that $Cp_2Fe_2(CO)_3(CNBu^t)$ is primarily a mixture of cisoid and transoid doubly carbonyl bridged species; these exchange rapidly down to − 120°C, while exchange of isonitrile between ends of the molecule, causing coalescence of the ring signals, is a much slower process (281). The carbonyl cmr spectrum of heptacarbonyldi-iron bis(diphenylphosphino)-methane, which is shown crystallographically to have the structure XXX in the solid, is a 1:2:1 triplet at 25°C, implying rapid interchange of carbonyls over all available sites (282). The structure XXXI(a) has been established in the solid for $Ru_3(CO)_8[C_8H_4(SiMe_3)_2]$, and there is no evidence for fluxional behaviour, but the symmetrical species XXXI(b) shows left-right interchange (283).

The pmr spectra of $CpMn(CO)_2C_2H_4$ and $CpCr(CO)(NO)C_2H_4$ give evidence of hindered rotation about the metal-alkene axis. Deuteriated derivatives have also studied, and free energies of activation of 34 and 47.8 kJ mol^{-1}



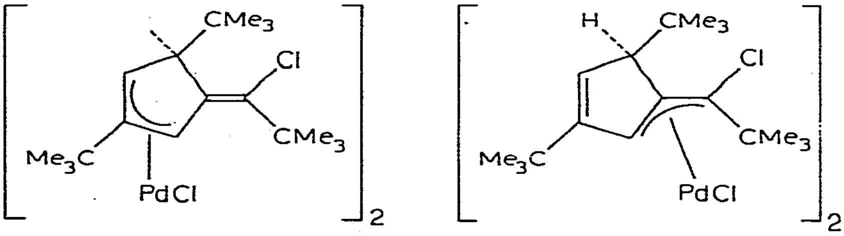
(XXX)



(XXXI)

(a) R = H
(b) R = SiMe$_3$

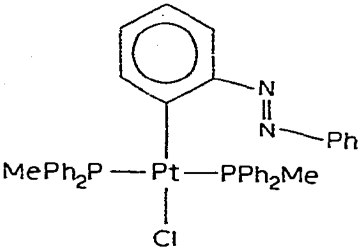
respectively inferred (284). The in-plane preference of alkenes in their tetracarbonyliron complexes has been used to increase the barrier to pseudorotation at iron so that the low-temperature limit becomes observable. The averaging process appears to be a true intramolecular pseudorotation; rates are independent of solvent or of the presence of added alkene, and are slower for complexes of electronegative alkenes, while axial-equatorial interchange always accompanies any other kind of exchange of CO between distinguishable sites (285). There is, however, evidence that rotation even of an electronegative alkene can at times be more rapid than axial-equatorial interchange. The complex (maleic anhydride) (benzylisonitrile)tricarbonyliron can exist as two isomers (IV c,d). At -30°C, these give two distinct sets of carbonyl carbon signals, each in the ratio 2:1. At 25°C, only one 2:1 pattern is observed, showing that (c) and (d) are interconverting while axial and equatorial CO are not (286). The variable temperature cmr spectra of tricarbonylruthenium diene and tetracarbonylruthenium alkene complexes have, however, been discussed in terms of the coupled olefin rotation - Berry pseudorotation mechanism (287). In isoelectronic Rh(I) complexes, the facility of the exchange process depends as might be expected on the degree of metal-alkene back-bonding. Thus the spectra of species $Rh(CNR)_2PPh_3.TCNE.I$ and $[Rh(CNR)_2(PPh_3)_2.TCNE]^+$ (TCNE = tetracyanoethylene) fit a rigid structure but the fumaronitrile analogues, and $[Rh(CNR)_4TCNE]^+$, all give temperature dependent spectra interpreted in terms of ligand rotation (288). The species $[Pd[(HC_2CMe_3)_3Cl]Cl]_2$, formed from palladium(II) chloride and t-butylacetylene, is fluxional at room temperature, but at -30° gives separate signals assigned to the isomeric dimers XXXII (a, b). Triphenylphosphine gives a product shown crystallographically to be its adduct with the monomer of XXXII(a), while thallous acetylacetonato gives a species related to XXXII(b) (289).



(a) (b)

(XXXII)

The pmr and cmr spectra of $(Me_5C_5)_2TiN_2$ at low temperature both show two distinct signals; these interconvert rapidly above -60°C (on the pmr timescale; -45°C on the cmr timescale). The ^{15}N nmr spectra of the $^{15}N_2$ species at low temperature show two equal signals (attributed to end bonded N_2) and a third signal (attributed to side-bonded N_2); this linkage isomerism in the TiN_2 unit then explains the pmr and cmr results (290). In $TaH(CO)_2(dmpe)_2$, shown crystallographically to be 7-coordinated in the solid, the low temperature ^{31}P nmr spectrum fits an $[AB]_2$ model, as required for such a structure; the hydride pmr signal, however, gives evidence for a scrambling process involving a second isomer (291). The pmr spectra of the cations $[M(CO)_2(dmpe)_2I]^+$ (M = Mo, W) are temperature-dependent in the range 220-320K, with the low temperature spectra again fitting a 7-coordinate (mono capped trigonal prismatic) structure (292). In $Rh_2[P(OMe)_3]_8$, the room temperature spectrum is as expected for a non-fluxional species. At 100°C, the axial phosphorus signal collapses to a doublet (due to coupling to rhodium) while that for equatorial phosphorus becomes a singlet. This indicates an intermolecular exchange process which is confirmed by scrambling at 100°C with added free phosphite (293); it is remarkable that axial and equatorial phosphite retain their separate identities throughout this process. Reversible phosphorus ligand loss, this time presumably assisted by an S_Ni process, has been invoked to explain the variable temperature pmr spectrum of XXXIII (294).



(XXXIII)

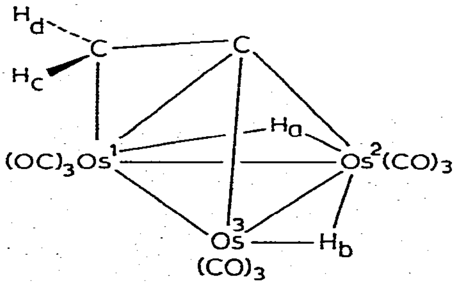
The isomerisation of σ-allyls in species of the type (allyl)Co(dmgH)$_2$L has been studied in such solvents as deuteriochloroform-deuteriomethanol. Good ligands L inhibit the isomerism, for which a σ-π-σ process following loss of L is the suggested mechanism (295).

The spectrum of (2,3-dimethylbutadiene)(bistriphenylphosphine) cobalt hydride shows temperature variation in its pmr spectrum between -50°C and -10°C, with loss of the hydride signal. This is attributed to reversible conversion of diene hydride to σ-allyl, although no π-allyl can be isolated in this case in the absence of added ligand (296). It had been suggested (297) that the equivalence of the proton nmr signals in (acac)Ni(PPh$_3$)Et was due to a rapid equilibrium between metal ethyl and metal alkene hydride; but the cmr spectrum clearly distinguishes C(α) from C(β), showing the true explanation of the simple pmr spectrum to be a fortuitous coincidence (298).

In CpFe(CO)(PPh$_3$)CF$_2$CF$_3$, the coupling between F(α) and phosphorus shows only a small degree of temperature variation, consistent with the existence of a single rotamer, but the coupling is temperature-dependent in CpFe(CO)(PMePh$_2$)CF(CF$_3$)$_2$. The failure of CpNi(PPh$_3$)CF(CF$_3$)$_2$ and CpNi(PPh$_3$)$_2$CF$_2$CF$_3$ to show temperature variation are attributed in the former case to the presence of a single conformer, in the latter, to essentially free rotation. Rotation of the phenyl rings is also restricted, coalescence temperatures increasing over a range of iron, cobalt and nickel complexes in the manner expected for steric control.

The iron carbonyl species, including $CpFe(CO)(PPh_3)CF_3$, show two CO stretching frequencies; in this last case at least rotation about the iron-carbon bond cannot give rise to distinct rotamers, and it is suggested that chirality both at iron and at densely packed phosphorus (phenyl ring packing being propeller-like, and rigid on the ir timescale) leads to the existence of diastereomers (299). Results for species of type $CpCo(PR_3)R_FI$ and for $[CpCo(CO)(PPh_3)C_2F_5]^+$ are similar (300).

The temperature-dependence of the complexes $(i\text{-}PrSe.C_2H_4.Se.i\text{-}Pr)M(CO)_4$ (M =Cr, Mo, W) could be due to inversion either at ligand selenium or throughout the ring; the latter explanation was preferred since rates vary little between the chromium and molybdenum complexes (301). The methyl pmr signal in the complex $[Cr(CO)_4]_2[As_2Me_4]_2$, which contains a crystallographically established chair-like $CrAs_2CrAs_2$ ring, broadens on cooling; this is attributed to slowing down of the chair inversion, and the coalescence temperature is estimated to be -90°C, with an activation energy of around 40 kJ mol^{-1} (302).



(XXXIV)

The species $H_2Os_3(CH_2C)(CO)_9$, formed by reaction of ethylene with $Os_3(CO)_{12}$, has the structure XXXIV. The methylene proton signals coalesce at 72°C, while the hydride signals fail to coalesce up to 115°C; this finding is explicable if H(α) migrates between the Os(1)-Os(2) and Os(1)-Os(3) bonds, while H(β) remains restricted (303).

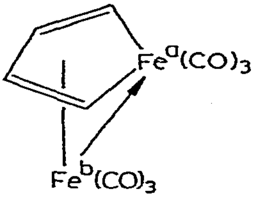
MÖSSBAUER SPECTRA

In species $[CpFe(CO)_2L]^+$, the $^{57}Fe^*$ quadrupole splittings are positive, strongly suggesting the same to be the case for the ^{55}Mn splittings in the isoelectronic neutral manganese complexes. The Mössbauer centre shifts, which are taken to measure the sum of ligand σ (donor) and π (acceptor) behaviour, increase with L in the order

$$MeCN \ll C_2H_4 < C_5H_5N < PPh_3 < CO < CS$$

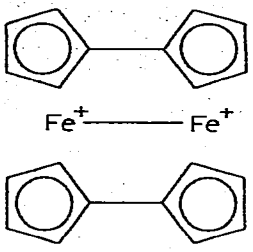
This differs from the order of CO stretching frequencies (166); a most useful finding if the latter are taken to measure the difference between the π (acceptor) and σ(donor) properties of L. Such arguments may explain the finding (304) that in allyl nitrosyldicarbonyliron complexes, CO and NO stretching frequencies are sensitive to substituents in the allyl grouping, but the iron centre shift is not. Mossbauer and nqr studies have been used to evaluate the field gradient in species $M(CO)_{5-x}L_x$ ($M = Mn^{-1}$, Fe, Co^{+1}; $L = PPh_3$, $P(OMe)_3$) and compared with the contributions calculated for uneven population of p and d orbitals. It is concluded that the populations of the planar d-orbitals increase with increasing atomic number relative to that of $d(z^2)$, but the effects of substitution follow no simple trend (305).

In species $Fe(dmgH)_2(CO)L$ (L = pyridine, substituted pyridine) the centre shift varies with ligand pK_a, while the quadrupole splitting varies with $\nu(CO)$; it is suggested that delocalisation of d(xz,yz) orbitals onto CO dominates this splitting (306). The Mössbauer spectrum of ^{57}Fe-enriched carboxymyoglobin has been studied at liquid helium temperature in a magnetic field; the field gradient is positive. Results are fitted to a model in which the iron atom lies in the haem plane, while the Fe–C–O unit is bent with an angle of about 135° at carbon; this is consistent with crystal structures cited (307). Spectra of tricarbonylferrole-iron tricarbonyl complexes (XXXV) have been obtained in glassy n-butylbenzene at 85K,



(XXXV)

in which the expected two doublets can be resolved although they cannot be recognised as such in the spectra of the neat solids (308). Spectra have been obtained for a range of substituted ferrocenes. The centre shift is relatively insensitive to substitution, while the quadrupole splitting is said to accord better with the model of Shustorovich and Dyatinka (309) than with that of Dahl and Ballhausen (310) (311). In the ferrocenophane dication XXXVI, obtained as



(XXXVI)

its diamagnetic hexafluorophosphate, magnetic field perturbation studies show the electric field gradient to be negative, in accord with the expected effects of iron-iron e$_{2g}$ bonding (312). Spectra have been obtained for [CpFe(CO)]$_4$ and its monocation in a magnetic field. The cation spectrum develops hyperfine structure, attributed to the removal of an electron delocalised mainly over iron, as in the model of Dahl _et al._ (313), and in contrast to the case of [Fe$_4$S$_4${S$_2$C$_2$(CF$_3$)$_2$}$_4$]$^-$, in which the unpaired electron is mainly on the ligands (314)

The ^{129}I spectrum of [Cp$_2$RuI]I$_3$ shows the electric field gradient tensor in the ruthenium-iodine bond to be almost exactly axially symmetrical; e^{2}qQ is negative. It is inferred that the 5p population is higher in iodine p(x,y) than in p(z), as expected from the nature of the bond to metal; the I$_3^-$ spectrum is also analysed (315).

The ^{119}Sn shifts in Cr(CO)$_5$SnCl$_3^-$ and the molybdenum and tungsten analogues are 2.04, 2.12 and 1.87 mm s^{-1} relative to SnO$_2$; this is regarded as within the upper limit for Sn(IV) (316). The isomer shift of ^{119}Sn in species [Co(CO)$_3$L]$_n$SnX$_{4-n}$ is lower than in the related manganese derivatives; the authors attribute this result to the greater electronegativity of cobalt causing more s-character in the tin-halogen bonds. Replacement of CO by phosphorus ligands increases the shift, as expected if the change in metal-tin σ-bonding is much more important than any π-bonding effects (317). The bonding in cations of type $SbX_n[CpFe(CO)_2]_{4-n}^+$ has been studied by ^{57}Fe and ^{121}Sb spectroscopy. The antimony shift is intermediate between the values expected for Sb(III) and Sb(V), in accord with a more significant degree of Fe-Sb π-bonding than occurs in the neutral tin analogues. The iron spectrum, however, varies little between the antimony cations and the related neutral tin species, showing that the positive charge is not much delocalised onto the iron fragments (318).

EPR AND MAGNETISM

The epr spectrum of $OReMe_4$, obtained from $OReCl_4$ on treatment with methyllithium, is consistent with a single unpaired spin in a system of near axial symmetry and with a complex belonging to C_{4v}. The hyperfine splitting is lost above −150°C (319). Single crystal studies of Cp_2VS_5 in Cp_2TiS_5, and the solution epr spectra of Cp_2VS_5 and $Cp_2V(SPh)_2$, clearly show the unpaired electron to be in an orbital concentrated at right angles to the bisector of SVS angle; this is in accord with the model of Alcock (320) rather than that of Dahl and Ballhausen (310b) (321). The spin state equilibria of manganocene and dimethylmanganocene [see (44), (55) above] have been studied by epr. $(Mecp)_2Mn$ has a low spin doublet ($^2E_{2g}$) ground state in toluene solution, in a glass at 4.2 K, or in $(Mecp)_2Mg$. The situation with Cp_2Mn itself is slightly more complicated. It was not possible to obtain satisfactory results from glasses, presumably because of precipitation. The spectrum in Cp_2Mg is assigned to the high spin, $^6A_{1g}$, species, but in Cp_2Fe or Cp_2Ru the compound is low spin (322, 323).

Metal carbonyl and related radical anions have been characterised by epr. In species $[(RN{:}CR'.CR'{:}NR)M(CO)_4]^-$ (M = Cr, Mo, W), formed by potassium metal reduction of the neutral complexes in dimethoxyethane, the epr signal is split by coupling to ligand hydrogen, to ligand nitrogen, and to metal (324). Other species reduced to radical monoanions by alkali metals or electrochemically in ethereal solution include $Fe(CO)_5$, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $RuFe_2(CO)_{12}$, $[(PhO)_3P]_2PtFe_2(CO)_8$, $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, $Ir_4(CO)_{12}$ and $Ru_6(CO)_{17}C$. The parent carbonyls are quantitatively regenerated by methyl iodide, and the g values are independent of the particular choice of ethereal solvent. In many cases, more than one epr signal is observed and relative intensities are temperature dependent; this effect is attributed to temperature-variable equilibria between isomers with different degrees of bridging (325).

In such compounds as $Cp_2TiCl_2ZnCl_2TiCp_2$, there is coupling between the two Ti(III) centres; the ground state is a singlet lying some 20 cm^{-1} below the triplet state (326).

POLAROGRAPHY AND ELECTROCHEMISTRY

Polarographic reduction of species $Cp_2V(IV)LL$, where LL is a bidentate sulphur, oxygen or other ligand, led in all cases studied to reversible formation of $[Cp_2V(III)LL]^-$ (327). In acetonitrile, chromium hexacarbonyl is oxidised reversibly by a 1-electron process, but the molybdenum and tungsten analogues, and iron pentacarbonyl, all show irreversible 2-electron processes, as does $Mn_2(CO)_{10}$, which is converted to $[Mn(CO)_5NCMe]^+$ (328). Oxidation of the anions $[Cr(CO)_5X]^-$ gives neutral $Cr(CO)_5X$ (reversibly at room temperature) and $[Cr(CO)_5X]^+$ (stable at -75°C); the neutral molybdenum and tungsten analogues disproportionate, or react by an ECE process, to give eventually divalent metal derivatives (329). A variety of species $[M(CO)_2(dppe)_2]^n$ ($M = Cr, Mo, W$; $n = 0, +1, +2$) has been studied polarographically at mercury or platinum electrodes, and the range of known cis and trans isomers extended (330). Complexes (arene) $Cr(CO)_2$(alkyne) (arene = benzene, methylated benzene; alkyne = tolan, 4,4'-dimethoxytolan) undergo reversible 1-electron oxidation electrochemically as well as chemically; the products were further investigated by epr (331). Ferrocene, ruthenocene, and osmocene all undergo 1-electron oxidation at a platinum anode; ferrocene behaves similarly at mercury, but the other species give $[(Cp_2M)_2Hg]^{2+}$ (332).

Allyltricarbonylcobalt undergoes irreversible 2-electron reduction at the dropping mercury electrode; propene and $Co(CO)_4^-$ are the identifiable products, and allyl anion and $Co(CO)_3^-$ are suggested intermediates (333). The electrochemical reduction of the cobalticenium cation in acetonitrile or in glyme takes place by two reversible 1-electron steps, thus giving evidence for the existence of $[Cp_2Co]^-$. Further reduction in acetonitrile proceeds by ECE mechanism, which may involve a bis(cyclopentadienyl)-cobalt hydride (334).

MISCELLANEOUS PHYSICAL METHODS

Nqr (^{35}Cl, ^{81}Br and ^{127}I) spectra have been obtained for a range of cyclopentadienyltitanium(IV) halides. The quadrupole coupling constant for each halide increases with the number of cyclopentadienyl ligands; this effect is attributed to a fall in the degree of $Xp(\pi) \rightarrow Ti(d)$ donation (335).

Neutron irradiation of $Cp_2Fe_2(CO)_4$ or of $CpFe(CO)_2I$ gives $Cp^{59}Fe(CO)_2$ radical, $^{59}Fe(CO)_5$, and $^{59}FeCp_2$. The radical is stable in the solid but is rapidly scavenged by iodine in solution (336).

The reaction between pentacarbonyltungsten ammines and phosphorus ligands had been described as an equilibrium process, with, surprisingly, positive ΔS° and ΔH° values for the forward reaction (337). It has now been shown that excess amine, used to study the 'equilibrium', suppresses the exchange which proceeds (in part at least) by a dissociative mechanism, and which eventually proceeds to completion (338).

For reactions of the type

$$L_2IrCl_2.COR \rightarrow L_2IrCl_2(CO)R$$

in solution, ΔH° values (in the solid) lie in the range -13 to -80 kJ mol^{-1}, while $\Delta H^\ddagger$ in solution is in the range $+60$ to $+80$ kJ mol^{-1} (339). The enthalpies of thermal decarbonylation of species of type $(Ph_3P)_2Pt(Cl).CO.Ar$ fall from 34 kJ mol^{-1} for Ar = Ph to 20 and 19 kJ mol^{-1}

for Ar = tolyl and Ar = nitrophenyl respectively. The platinum acyl bond strength is in excess of 180 kJ mol^{-1} (340). Heats of formation for methylpentacarbonylmanganese and rhenium have been found from heats of iodination. The inferred values for the metal–methyl bond energy depend on the value chosen for the metal–metal bond energy in the dimetal decacarbonyls, but are around 125 kJ mol^{-1} for CH_3–Mn and 225 kJ mol^{-1} for CH_3–Re (341). Enthalpies for loss of C_2F_4 or hexafluorobut-2-yne from solid $IrX(CO)(PPh_3)_2(ene)$ indicate that the metal–ene bond energy falls from X=F through X = Br, but increases for X = I (342). The replacement of ethylene in $(Ph_2P)_2PtC_2H_4$ by TCNE is exothermic to the extent of 156 ± 8 kJ mol^{-1} (343). The thermolysis of complexes containing the unit $\overline{PtCH_2CH_2CH_2}$ has been followed by DSC/TGA, with quantitative monitoring of the products (cyclopropane and propene). It is inferred that the mean platinum–carbon bond energy is around 115 kJ mol^{-1}. This is low, presumably because of ring strain (344).

CHEMICAL RESULTS OF GENERAL INTEREST

X-ray fluorescence spectrometry of discs pressed in borax has been commended as a method of quantitative analysis for transition metals in organometallic and other complexes, especially where combustion analysis is likely to prove unreliable (345). Cathodic reduction is a novel route of some generality to alkene complexes; thus tris(acetylacetonato)iron can be converted in the presence of dienes and triphenylphosphine to species of the type $(\text{diene})_2\text{FePPh}_3$ (346), while cobalt salts in the presence of butadiene and phosphines give products $(C_4H_6)(C_4H_7)\text{CoPR}_3$ or, interestingly, $(C_4H_6)[C_4H_6-(C_4H_7)]\text{CoPR}_3$ (347).

It has been suggested that carbonyl bridging only occurs in association with a metal-metal bond. An apparent exception, '$\text{Cp}_2\text{Rh}_2(\text{CO})_4$' (348) is shown to correspond to the known $\text{Cp}_2\text{Rh}_2(\text{CO})_3$' (349), and notification of other apparent exceptions is solicited (350). The ease of metallation falls from $C_5H_5\text{TiC}_7H_7$ through the vanadium to the chromium complex. Substitution occurs preferentially in the 5-membered ring for vanadium and chromium complexes but in the 7-membered ring for that of titanium; an explanation in terms of very simple MO theory is offered (351). The equilibrium

$$3\text{Tlm} \rightleftharpoons \text{Tlm}_3 + 2\text{Tl}$$

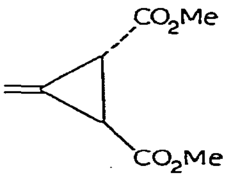
lies to the right with more strongly basic groups m (e.g. $\text{Mn}(\text{CO})_5$, $\text{CpM}(\text{CO})_3$, $\text{Co}(\text{CO})_3\text{PPh}_3$, $\text{CpFe}(\text{CO})_2$) but not with less strongly basic groups such as $\text{Fe}(\text{CO})_4\text{R}^-$, $\text{Fe}(\text{CO})_3\text{NO}^-$, and $\text{V}(\text{CO})_6^-$ (352). The very hindered alkyl group bis(trimethylsilyl)methyl, $(\text{Me}_3\text{Si})_2\text{CH}$, gives rise to stable compounds of the types MR_3 (M = Y, Ti, V), $\text{MR}_3.2\text{THF}$ (M = Sc, Y), Cp_2TiR, R_3MCl (M = Zr, Hf), and $C_6H_6\text{CrR}_3$ (353).

The rates of insertion of SO_2 into metal-methyl bonds in neat liquid SO_2 follow the sequence

$$m = \text{CpFe}(\text{CO})_2 > \text{Re}(\text{CO})_5 > \text{CpRu}(\text{CO})_2 \sim \text{Mn}(\text{CO})_5 \gtrsim \text{CpMo}(\text{CO})_3 \gg \text{CpW}(\text{CO})_3$$

but for metal-benzyl bonds the sequence becomes

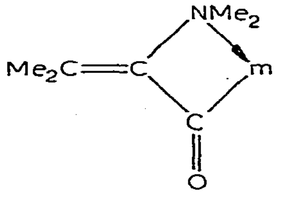
m = $CpMo(CO)_3 \gtrsim CpFe(CO)_2 \gtrsim Mn(CO)_5 > CpRu(CO)_2 \gg CpW(CO)_3$
Generally, methyls react faster than benzyls; derivatives of $CpCr(NO)_2$ react far faster than all others; and the reaction of $CpW(CO)_3$ derivatives is immeasurably slow. The order is quite different from that for CO insertion, and is consistent with the suggested (354) pathway of electrophilic attack by SO_2 on metal (355). A number of metal hydrides ($FeH_2(N_2)PPh_2Et$, $CoH(N_2)(PPh_3)_3$, $RuHCl(PPh_3)_3$, $RuH_2(PPh_3)_4$, $RhH(PPh_3)_4$, $PdH_2[P(C_6H_{11})_3]_2$) release ethylene or propene from vinyl or allyl acetate, the metal itself being converted into an acetate complex; this reaction is in a sense the reverse of the conversion of ethylene and acetic acid to vinyl acetate by Pd(II) (356). The unusual alkene XXXVII forms stable complexes with



(XXXVII)

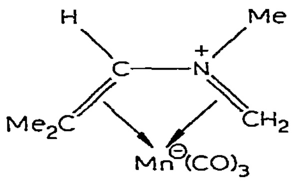
Rh(I), Ir(I) and Pt(0), without ligand rearrangement or ring opening. Subsequent nucleophilic attack on the alkene, and ring opening reactions, are described for the Pd(II) complexes (357).

Reaction of chloroaminoalkenes $Me_2C{=}C(NR_2)Cl$ with strong nucleophiles ($[CpFe(CO)_2]^-$, $[Re(CO)_5]^-$) leads to simple displacement of chlorine by organometal. Reaction with $[Co(CO)_4]^-$ or $[CpMn(CO)_3]^-$ gives species $Me_2C{=}C{=}\overset{+}{N}Me_2\overset{-}{Co}(CO)_3$ and $Me_2C{=}C{=}\overset{+}{N}Me_2\overset{-}{Mo}(CO)_2Cp$; of these the former is thought, on spectroscopic evidence, to contain a metal-bonded alkene, and the latter a metal-bonded iminium group. The moderate nucleophiles $Mn(CO)_5^-$, $CpW(CO)_3^-$ react with chloroaminoalkenes to give products XXXVIII(a,b); in XXXVIII(a) the terminal methyl groups are equivalent, but not in XXVIII(b). Uv irradiation



(a) m = $Mn(CO)_4$
(b) m = $CpW(CO)_2$

(XXXVIII)



(XXXIX)

of XXXVIII(a) in heptane gave the azabutadiene complex XXXIX (358). Reaction of anions or trimethylsilyl derivatives m^- or $mSiMe_3$ ($m = CpCr(CO)_3$, $CpMo(CO)_3$, $CpW(CO)_3$, $CpFe(CO)_2$) with chlorodimethylarsine gives monomeric $m{-}AsMe_2$; this may be 'quaternised' at arsenic by alkyl halides to give species $[m{-}AsMe_2R]^+$ (359).

The reactions of the polypyrazolylborate anions $[X(n)]^- = [(C_3H_3N_2)_nBH_{4-n}]^-$; n = 2,3,4) with a range of organometallic halides have been studied. $CpCo(CO)R_fI$ gives $CpCo(R_f)X(n)$, in which X(n) is bidentate; $[X(4)]^-$ also gives boron-free $CpCo(R_f)(C_3H_3N_2)_2H$. $Fe(CO)_4(C_3F_7)I$ gives $C_3F_7Fe(CO)_3X(2)$ (as a mixture of fac and mer isomers) and $C_3F_7Fe(CO)_2X(3)$ (360). $[Me_3PtI]_4$ and $CpPtMe_3$ both give species $Me_3PtX(n)$; for n = 4, free and bound pyrazolyl are scrambled on the nmr timescale down to -60°C, while for n = 2, the coordination octahedron of Pt(IV) is completed by Pt-H-B bridging, a new, lowered, B-H stretching frequency appearing at 2039 cm^{-1} ; addition of trimethylphosphite leads, as expected, to cleavage of this bridge (361). The reaction of $C_3H_5Fe(CO)_3I$ with KX(2) gives $[X(2)]_2Fe(CO)_2$. KX(3) gives at least five products; the ferrocene analogue $[X(3)]_2Fe$, the pyrazolyl bridged species $[C_3H_3N_2Fe(CO)_3]_2$, the pyrazolyl allyl $(C_3H_5)(N_2C_3H_3)Fe(CO)_3$, the σ-vinyl trans-$CH_3CH{:}CHFe(CO)_2X(3)$, and its carbonyl insertion product $CH_3CH{:}CH.CO{-}Fe(CO)_2X(3)$ (362). The self-addition reaction of coordinated β-hydroxyethyl isonitrile has been used to prepare carbene complexes $m{:}\overline{C{-}O{-}CH_2{-}CH_2{-}N}H$ where m = Pd(II), Pt(II), Au(III); Zn(II) gives $Zn(II) \leftarrow \overline{N{=}CH{-}O{-}CH_2{-}C}H_2$, which is the expected rearrangement product of an initial unstable carbene complex (363).

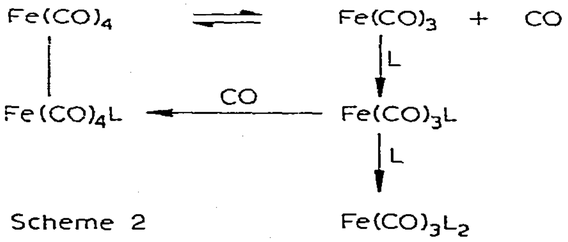
KINETICS AND MECHANISM

The mechanisms of transition metal to carbon σ-bond scission have been reviewed (364).

Displacement of coordinated nitrogen from species $M(CO)_4(PPh_2(CH_2)_3NMe_2)$ by ^{13}CO always gives the product in which the ^{13}CO is specifically cis to the coordinated phosphorus atom; likewise fac $Mo(CO)_3(PPh_2.C_2H_4.NEt.C_2H_4.PPh_2)$ gives a product in which the two phosphorus atoms and the ^{13}CO are all mutually cis. It follows, either that dissociation of ligand nitrogen gives a stereochemically stable square pyramidal intermediate, or else (less plausibly in the reviewer s opinion) that a trigonal bipyramid is formed with one phosphorus always axial and

CO always entering cis to equatorial phosphorus where this is present (365). The cis–trans isomerisations of $(OC)_4Cr[C(OMe)Me]PR_3$ complexes are first order, independent of added CO or phosphine, and show an entropy of activation close to zero; all these data indicate truly intramolecular process (366).

Reaction of tetracarbonyliron alkene complexes with certain ligands ($SbPh_3$, $AsPh_3$, pyridine) gives $Fe(CO)_4L$ and alkene as the only products; the kinetics of the process are consistent with reversible loss of alkene from substrate to give a reactive $[Fe(CO)_4]$ fragment. With other ligands (such as PPh_3), the rate of disappearance of $Fe(CO)_4$ (alkene) is the same, but $Fe(CO)_4L$ and $Fe(CO)_3L_2$ are both produced from the beginning of the reaction (367). The ratio of mono- to disubstituted species is not greatly affected by the nature of the solvent, provided this is not itself too good a potential ligand (368). The effects of added carbon monoxide have been studied. and the results fitted to the model of Scheme 2 (369). The conversion of dicobalt



Scheme 2

octacarbonyl to tetracobalt dodecacarbonyl in heptane is second order in starting material and of order −2 in carbon monoxide; it is suggested that the rate determining step might be the encounter of two $Co_2(CO)_7$ fragments formed in a fast pre-equilibrium (370).

The rate of thermal decarbonylation of species $CpMo(CO)_2L.COMe$ from acetyl to methyl is independent of the solvent. Rates increase with L from tri-n-butylphosphine to triarylphosphines to tricyclohexylphosphine, showing dominance by steric effects (371). Racemisation of $CpMn(NO)(PPh_3)COPh$ is inhibited by excess phosphine, and exchange with excess tris-p-methoxyphenylphosphine occurs with retention; thus the intermediate formed by loss of phosphine from starting material has some conformational stability (372).

The photochemical decarbonylation of $CpFe(CO)(PPh_3).CO.Et$ has been shown to proceed with inversion at iron. The simplest explanation is ethyl migration into the gap left by departing CO; thus the natures of the ligands change but the individual bonds to iron retain their conformation (373). The same effect has independently been established for $CpFe(CO)(PPh_3).CO.Me$. This complex can conveniently be prepared in optically active form by the action of methyllithium on a resolved diastereomer of the 1-menthyl ester $CpFe(CO)PPh_3.CO.OC_{10}H_{19}$. An interesting point is that this last reaction also proceeds with inversion at iron (as shown unequivocally by comparison of iodinolysis products) (374); again, a possible mechanism is methyl attack on one CO while menthoxy is eliminated from the other (374). The photochemical decarbonylation of 1-Me, $3\text{-Ph-}C_5H_3Fe(CO)(PPh_3).COMe$ has also been shown to be stereospecific; the reaction proceeds at the same rate of both epimers. There is also a slow photochemical epimerisation, probably due to reversible loss of triphenyl phosphine (375).

The rate of thermal reaction of $CpFe(CO)_2R$ with added ligands to give $CpFe(CO)(L).COR$ is independent of solvent, even in the extreme care of dimethylsulphoxide which gives rise to a definite complex $CpFe(CO)(DMSO).COR$. The rate-limiting step is intramolecular and of low polarity, the key step no doubt being alkyl migration to ligand CO leaving an unsaturated intermediate (376), identical with that invoked above (373) in the discussion of photochemical decarbonylation. The insertion of sulphur dioxide into the iron-methyl bond of 1-Me, $3\text{-}PhC_5H_3Fe(CO)(PPh_3)Me$ is stereospecific; but the reactions with mercuric iodide, iodine, or most particularly hydrogen iodide are accompanied by a degree of epimerisation. The suggested mechanism is oxidative addition of A^+ from AI to the iron complex, to give an intermediate which can rearrange to some extent when A is small (e.g. H) before undergoing a possibly iodide-assisted reductive elimination of A-Me (377).

The alkyl migration reaction of species $(Ph_3P)_2RhCl_2.COR$ (R = aryl, substituted benzyl), with subsequent reductive elimination to give $(Ph_3P)_2Rh(CO)Cl$ and RCl, has been studied for a range of species R. The form of the free energy relationships obtained shows that the reaction involves little charge separation (378). Optically active $PhCH(CF_3)COCl$ is decarbonylated by $(Ph_3P)_3RhCl$ to give, predominantly, racemic $PhCH(CF_3)Cl$, although removal of SO_2 from active $PhCH(CF_3)SO_2Cl$, gives predominantly inversion. Thus the racemisation would appear in this case to occur at the decarbonylation stage (379). However, the related decarbonylations of erythro and threo $CH_3CHPh.CHPh.COCl$ lead exclusively to trans and cis methylstilbene respectively. Thus the acyl-alkyl conversion would in this case appear to occur stereospecifically with retention, or else the mechanism is cis β-hydride elimination. The overall elimination of metal hydride is shown to follow Saytzeff's rule, and to exhibit a marked primary isotope effect (380).

Thermolysis of titanocene diaryls or dibenzyls in the solid state or in hydrocarbon solution gives arene or methylarene by an intramolecular abstraction, but THF and CCl_4 take part in the reaction when used as solvents (381). The cleavage of Cr(III)-carbon σ-bonds by aqueous bromine in $[(H_2O)_5CrR]^{2+}$ gives $[Cr(H_2O)_6]^{3+}$, RBr, and free bromide. The reaction is first order in each component, and the failure to form a chromium(III) bromo complex, together with the effects of varying R, indicate an S_E2 attack at ligand carbon, probably with inversion (382). The form of the linear free relationship derived on varying R is consistent with this interpretation, as are the corresponding results using iodine (383). The exchange between $[(H_2O)_5Cr(III).CH_2.C_5H_4\overset{+}{N}H]^{3+}$ (C_5H_4N = pyridyl) and labelled Cr(II) is unimolecular in each component, and appears to be either a rare example of a bimolecular free radical (S_H2) process, or else a carbonium (or carbanion) transfer coupled to a forward (or reverse) electron transfer (384). The same results are found for the pH-independent alkyl group transfer between aqueous Cr^{2+} and methyl (or ethyl) cobalamin to give $[(H_2O)_5Cr(III)R]^{2+}$ and vitamin B_{12r} (385).

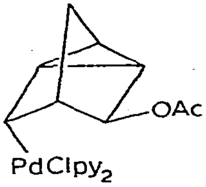
Thermolysis of $C_2H_5.CHCH_3.C_2H_4COMn(CO)_5$, or of either diastereomer of $C_2H_5.CHCH_3.CHCH_3.COMn(CO)_5$, gives the same mixture of 3-methylpentenes. It is inferred that an initial decarbonylation is followed by a reversible β-elimination which is more rapid than alkene loss (386). Decomposition of $PhCH_2Mn(CO)_5$, either on its own, or in hydrocarbon at 140°C, leads to dimanganese decacarbonyl and bibenzyl; polymers of type $(poly).C_6H_4.CH_2Mn(CO)_5$, which are obtainable by chloromethylation of polystyrene followed by reaction with $[Mn(CO)_5]^-$, give rise to cross links of the type $(poly)C_6H_4.CH_2CH_2.C_6H_4(poly)$ (387). $PhCH_2Fe(CO)_2Cp$ decomposes according to first order kinetics to give bibenzyl, $Cp_2Fe_2(CO)_4$, some $(PhCH_2C_5H_4)(C_5H_5)Fe_2(CO)_4$, and tar, said to arise from homolysis. In the decompositions of $PhCH_2Mo(CO)_3Cp$ and the tungsten analogue, benzylation of the 5-membered ring is so extensive that attack by coordinated benzyl on the coordinated ring is thought to be the dominant process (388).

It is possible to distinguish erythro from threo diastereomers R(e)X, R(t)X of type t-Bu-CHD.CHD.X by deuterium-decoupled nmr. The bulk of the tert-butyl group imposes a specific conformation, and the two situations are then distinguished by the size of their vicinal hydrogen coupling constants. Diastereomeric materials may be obtained by sequences starting with deuteration over platinum of cis and trans 2-tert-butyl vinyl acetates. R(t) brosylate reacts with the cyclopentadienyldicarbonyliron anion to give the R(e) organometallic, implying that the reaction is normal nucleophilic attack on C(α) of R; it also follows that the organoiron species is conformationally stable. Oxidative cleavage of the iron-carbon bond by bromine in solvents of high or low polarity, or by iodine in carbon disulphide, occurs with erythro-threo conversion, as does sulphur dioxide insertion. The conversion of $CpFe(CO)_2R$ to $CpFe(CO)(PPh_3).CO.R$, and subsequent photochemical decarbonylation to $CpFe(CO)(PPh_3).R$, all occur with retention, as does oxidation by oxygen, ceric ion, bromine, or chlorine in methanol to give RCOOMe or by chlorine in $CDCl_3$ to give RCOCl. Insertion of bis(carbomethoxy)acetylene into the iron-carbon bond occurs with retention. All these results are consistent with the view that electrophilic attack at C(α) always occurs with inversion, while transfer of R between iron and a coordinated electrophile takes place with retention. The view (389) that 1-electron oxidation of species $CpFe(CO)_2R$ leads to rapid carbonylation of R by alkyl migration thus receives support. Thermolytic elimination of alkene from $CpFe(CO)_2R(e)$ leads to scrambling, with formation of several percent of undeuteriated, dideuteriated and double bond migrated materials (390). Reaction of $CpFe(CO)_2R(t)$ with mercuric chloride gives RHgCl with retention, as expected if attack is at metal rather than carbon; however, the reactions of R(t) brosylate or triflate with

$[Co(dmgH)_2(pyridine)]^-$ or $[CpMo(CO)_3]^-$ give the expected R(e) metal compounds (391), and the Co-R bond is cleaved by mercuric chloride with inversion (392). The reactions of threo-PhCHDCHDFe$(CO)_2$Cp present an interesting comparison with those discussed above, in that cleavage of the iron-carbon bond by bromine or mercuric chloride is accompanied by racemisation. Treatment with $PdCl_2(NCPh)_2$ leads to a range of products including $PhCH{=}CD_2$; this is evidence for alkyl transfer to palladium from iron, followed by rapid reversible β-elimination within the palladium alkyl. Reaction with the triphenyl methyl cation gives $[CpFe(CO)_2alkene]^+$, the labelling of which shows it to be predominantly derived by hydride abstraction from the gauche rotamer (393). The differences between the behaviour of the apparently quite similar β-phenylethyl-iron and β-tert-butylethyl-iron bonds towards electrophilic cleavage has very recently been explained by a study of electrophilic cleavage in $CpFe(CO)_2CD_2{-}CH_2{.}Ph$, which is found to proceed with 50% 1,2-phenyl migration (394).

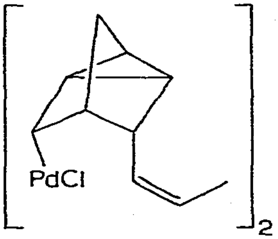
Methyl transfer between methyl cobalamin and $[PdCl_4]^{2-}$ has been shown by kinetic studies, including studies of the effects of chloride ion concentration, to take place between the reagents as written. The kinetics are complicated by reversible formation of an unreactive species [(methylcobalamin)(palladium(II)trichloride]$^-$, which is presumably held together by coordination of benzimidazole to palladium rather than to cobalt, since the electronic spectrum resembles that of the 'base off' form of methylcobalamin (395). Thermolysis of $(Ph_3P)_2Ir(CO)(octyl)$, in the absence of added phosphine, gives 33% octane, but octene is the only product in the presence of added phosphine. β,β-d^2-Octyl gives d^3-octane, and there is no exchange with $HIr(PPh_3)_3$. It is argued that in the absence of added phosphine binuclear elimination occurs between the octyliridium starting material and a fragment $Ir(H)(PPh_3)_2$ (or, in the labelling experiment described, the corresponding deuteride) but that excess phosphine traps this fragment and renders it inert (396). It has further been established that β-elimination from the alkyliridium(I) complex shows a primary isotope effect ($k_H/k_D = 2.31$), in accord with the description of β-elimination as oxidation insertion of metal into the carbon-hydrogen bond (397).

The pyrolysis has been described of a range of platinum(IV) alkyls of the type $PtR_2R'(PMe_2Ph)_2X$ ($R = CH_3$, $R' = PhCH_2$ or σ-allyl; $R = CD_3$, $R' = CH_3CO$; $R = Et$, $R' = Me$). The benzyl and acetyl derivatives give respectively ethylbenzene-ethane mixtures and acetone, while the diethyl compound loses ethylene as the first step. Thermolysis of $PtMe_2Br(PMe_2Ph)_2$-σ-allyl gave a mixture of methane, ethane, propylene, but-1-ene and hexadiene; this was taken as evidence for a free radical pathway, although the residue was described as almost pure trans-$PtBrMe(PMe_2Ph)_2$ (398). The rate of insertion of ethylene into the platinum-hydrogen bond of trans-$[Pt(H)(acetone)PEt_3)_2]^+$ accords with a pre-equilibrium in which acetone is reversibly displaced by ethylene, followed by a slow insertion step. The intermediate has been observed by nmr at low temperature (399). The oxidative hydrolysis of alkenes by palladium(II) salts is also, in general, an insertion reaction; comparison of $[Pd(dien)H_2O]^{2+}$ with $[Pd(en)(H_2O)_2]^{2+}$ (dien = diethylenetriamine) shows that attack is by coordinated rather than free hydroxide wherever possible; indeed, attack by free hydroxide only occurs when formation of a cis(hydroxide)-(alkene) complex cannot occur (400). Reaction of XL



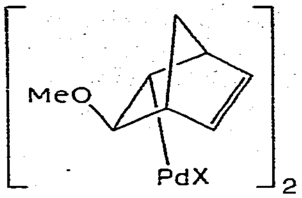
(XL)

with di(cis-propenyl)mercury gives XLI, presumably by

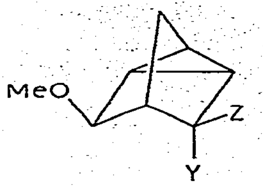


(XLI)

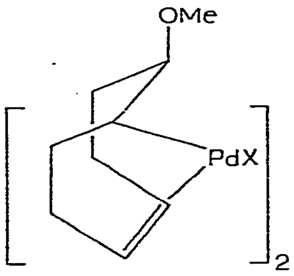
propenyl transfer (with retention of geometry) from mercury to palladium, followed by nucleophilic attack of coordinated propenyl on the other organic ligand (401). Halogenolysis of methoxynorbornenylpalladium halides XLII in methylene chloride gives XLIII (a,b); in methanol, XLIII(c) is also produced. The related reactions of the cyclo-octenyl complex XLIV give, in methylene chloride, specifically XLV(a), while the products in methanol are XLV(b,c). These reactions



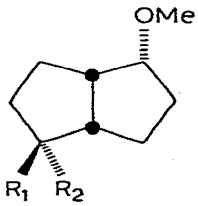
(XLII)



(a) Y = X ; Z = H
(XLIII) (b) Y = H ; Z = X
(c) Y = H ; Z = OMe

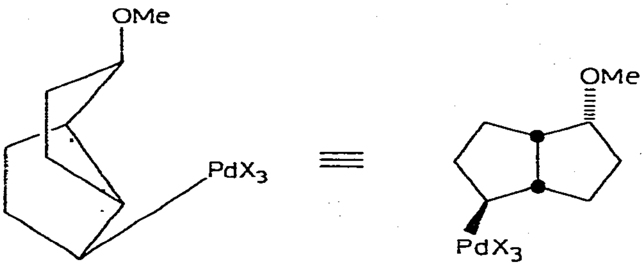


(XLIV)



(a) $R_1 = X ; R_2 = H$
(XLV) (b) $R_1 = H ; R_2 = OMe$
(c) $R_1 = H ; R_2 = X$

are thought to proceed by a common underlying mechanism, which is alkene insertion into a coordinated σ-bond to give, for example, XLVI, which can undergo reductive elimination with retention of stereochemistry at C(α), or, alternatively, nucleophilic attack by methanol or halide causing inversion (402).



(XLVI)

The reaction of methyl iodide with tris- or tetrakis-triphenylphosphine complexes of platinum(0) appears to occur by oxidative addition to an intermediate $Pt(PPh_3)_2$ species; the product is trans-$Pt(Me)I(PPh_3)_2$ (403). The corresponding addition to methylgold(I) triphenylphosphine is more complicated. The first step is again oxidative addition, but the resultant dimethylgold triphenylphosphine iodide reacts with the gold(I) starting material to give an isolable trimethylgold phosphine complex and the triphenylphosphine complex of gold(I) iodide. The trimethylgold complex then slowly evolves methane, no doubt by reductive elimination, and a sequence of this type is presumably responsible for the formation of n-butane in the reaction of ethylgold(I) triphenylphosphine with methyl iodide. Further redistribution can occur; for example, the formation of Me_3AuPMe_3 and $IAuPMe_3$ from $Me_2IAuPMe_3$ and $MeAuPMe_3$ is to some small degree reversible, and since methyl iodide adds to the gold(I) methyl but not to the gold(I) iodide, the eventual product is $Me_2IAuPMe_3$ (404). The mechanisms available to organogold compounds can be strongly solvent-dependent in non-obvious ways. Thus t-$BuAuMe_2PPh_3$ reacts in dimethoxyethane to give $Me_2CH.CH_2CH_2AuMe_2L$ by a first order reaction, suppressed by added phosphine, and attributed to a reversible β-elimination following phosphine loss. In benzene, the observed reaction is cis-trans isomerisation, favouring the trans isomer, at a rate independent of phosphine. In tert-butylbenzene, reductive elimination occurs;

this is cis, intramolecular, and suppressed by added phosphine, although there is no spectroscopic evidence for association (405).

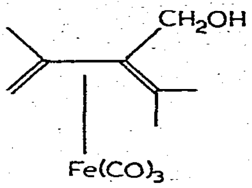
The role of free radical processes in the formation and cleavage of transition metal-carbon bonds remains an area of interest and dispute. There is much evidence that free radical processes occur, but they are far from general. Some processes that might have been assumed to follow this path in fact take place by α-elimination, and some free radical processes identified by using traps or scavengers may not take place in the absence of such reagents. Moreover, traces of oxygen, and photochemically generated halogen, initiate free radical processes that might not occur in their absence. The accounts quoted here of work in this difficult area should be read with these considerations in mind.

Tris(triphenylphosphine)nickel(0) methylmethacrylate reacts with halocarbons to give free radicals, which initiate methylmethacrylate polymerisation, and nickel(II), the appearance of which can be followed by uv. Bromocarbons are more effective than chlorocarbons, and polysubstitution and the presence of charge-withdrawing groups both increase the reaction rate (406). Similar results are found for methylmethacrylate pentacarbonylmolybdenum, and in the presence of carbon tetrachloride each molybdenum(0) appears to give rise to one free radical (407). It has been shown that α-phenylethyl bromide reacts with tetrakis(triphenylphosphine)palladium under carbon monoxide to give $Ph.CHMe.CO.Pd(PPh_3)_2Br$

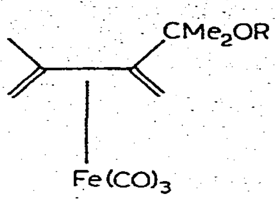
with inversion at C(α). The natural assumption is that alkyl migration with retention (compare e.g. (390)) has followed an S_N2-like oxidative addition (408). However, the alkylpalladium intermediate was not isolated and the reaction of methyl or ethyl iodide, or benzyl bromide, with tris(triphenylphosphine)platinum(O) in the presence of the radical trap tert-butylnitrosyl had given t-BuN(R)O radicals, suggesting for the phosphine complexes a free radical mechanism (409); the results of (408) could then have been taken as peculiar to pre-formed metal carbonyl complexes, with perhaps CO as the true site of attack. However, the reaction of α-phenylethyl chloride with tetrakis(triphenylphosphine)palladium in the absence of CO or of radical traps has now been shown to give the expected alkylpalladium species with inversion, although in the presence of t-BuNO, the radical (t-Bu)(PhCHMe)NO is duly formed. It follows from the first of these new results that the oxidative addition is an S_N2-like process, and from the second, that the formation of detectable radicals in the <u>presence</u> of t-BuNO need not imply that the reaction proceeds by a free radical mechanism in its <u>absence</u> (410). There is further evidence that generalisations about the importance of radical or electron pair processes may be unwarranted even within a group of very closely related reactions. It appears from side-product analysis, inhibition by radical scavengers, and the occurrence of racemisation, that the reactions of the palladium(O) and platinum(O) tris(triethylphosphine) complexes with ethyl and longer chain bromides and iodides, and their substituted derivatives such as neopentyl bromide, β-phenylethyl bromide (contrast α-phenylethyl bromide above), or cyclohexyl or cyclopentyl bromide, proceed by free radical mechanisms. On the other hand, in the reactions of methyl bromide and iodide, phenyl halides, and benzyl, vinyl, or cyclopropyl chlorides or bromides (for $PhCH_2Br$, contrast (412) below), there is no evidence for free radical participation (411). CIDNP is of course a sensitive probe for radical formation, and has been demonstrated in the oxidative addition of isopropyl iodide to $Pt(PEt_3)_3$, which gives as detectable products $HPt(PEt_3)_2I$, $Pt(PEt_3)_2I_2$, a trace of i-$PrPt(PEt_3)_2I$, and propene, propane, and 2,3-dimethylbutane. CIDNP effects are observed only in those cases where metal dihalo complexes are produced rapidly in the initial stages of the reaction, including the reactions of benzyl bromide, (contrast (411) above), but not benzyl chloride, methyl iodide, or allyl bromide (412). There is evidence for aryl radical trapping by Cu(I) and Cu(II) in succession, followed by reductive elimination of biaryl from a Cu(III) complex, in the Cu(I)-modified decomposition of nitrophenyldiazonium cations (413). The reactions of thiophenol with methylgold(I) triphenylphosphine to give $PhS.AuPPh_3$ and methane, and with cis-$(Ph_3P)_2PtMe_2$ to give trans-$(Ph_3P)_2Pt(SPh)Me$ and methane, are inhibited by galvanoxyl and accelerated by azobis(isobutyronitrile), suggesting a free radical chain mechanism, but galvanoxyl does not affect the reaction with Me_3AuPPh_3, which gives cis-$Me_2Au(SPh)PMe_3$(414).

The decomposition of methylcobalt tris(triphenylphosphine) in an atmosphere of deuterium was at first reported to produce some more than singly deuteriated methane, indicating α-exchange and a carbenoid intermediate (415). Unfortunately, the peaks were later reassigned to adventitious (deuteriated) water. Carbene complexes have been invoked more reliably to explain the decomposition products of the complex $FeMe_2(dppe)_2$. This gives methane, ethylene, and ethane when heated on its own, while on standing in CD_2Cl_2 it also generates CD_2CH_2 (416). The carbene $Cp_2W(CD_2)D$ is a postulated intermediate in the equilibrium between species $[Cp_2W(PR_3)(CD_3)]^+$ and $[Cp_2W(D).CD_2.PR_3]^+$ (417).

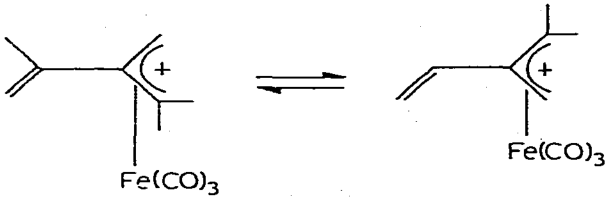
The reactions of cations related to tricarbonyliron diene complexes involve some rather surprising rotations within apparently conjugated systems. Thus dehydroxylation of either XLVII or XLVIII(a) in fluorosulphonic acid – sulphur dioxide at −65°C, followed by methanolysis at −78°C, gives XLVIII(b), presumably by way of a common intermediate XLIX. The free rotation shown by this intermediate supports its formulation as a 2-vinyl-π-allyl complex, which is a 16-electron system. The organic ligand could plausibly have acted as a carbonium-substituted butadiene or trimethylene methane; this would have produced a rigid complex, formally an 18-electron system, but without making use of the lowest empty orbital of the organic unit (418). The reviewer notes that a 1-vinylallyl representation of the pentadienyl tricarbonyliron cation could account for the rearrangements of L(a) in the course of reaction with 1,3-dimethoxy-



(XLVII)

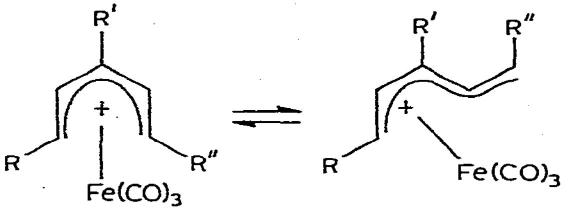


(XLVIII)
(a) R = H
(b) R = Me



(XLIX)

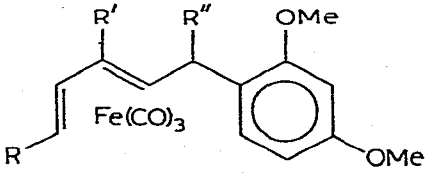
benzene to give LI; in some cases the existence of an activated intermediate such as L(b) is also supported by kinetics (419).



(a)

(b)

(L)



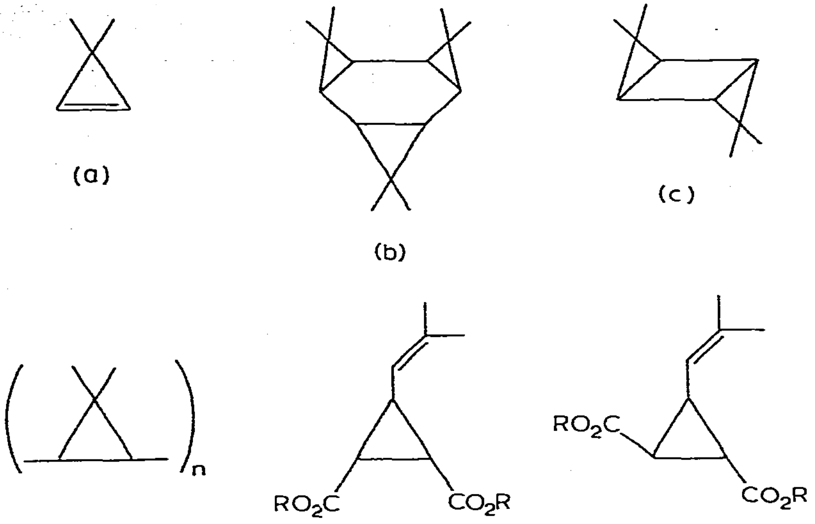
(LI)

The reaction of $Cp_2Ni_2(CO)_2$ with tolan has been re-investigated in n-heptane at 80°C. There is a genuine two-term rate-law as suggested earlier (420); despite criticisms (421) the effects of decomposition are too slight to effect the argument (422).

Complexation to tricarbonylchromium is strongly facilitating, both in unimolecular solvolysis of cumyl chloride (423) and in the alkaline methanolysis of phenylacetylidotriethylgermane (424). The electron-releasing role of $Cr(CO)_3$ is confirmed by the lowering on complexation of the carbonyl frequency of acetophenone (423). The rate of reaction of $PdCl_4^{2-}$ and isoprene in methanol, to give a 1-methoxymethyl,2-methallyl complex, contains terms in $[Cl^-]^{-1}$ and $[Cl^-]^{-2}$; thus, the authors infer, the slow step can be attack of methanol either on $[Cl_3Pd.isoprene]^-$ or $[Cl_2Pd.isoprene]$, containing one and two coordinated double bonds respectively, both formed in rapid pre-equilibria (425). Ring exchange between nickelocene and LiC_5D_5 in THF occurs by two pathways, one unimolecular in each of the reagents as written, the other in nickelocene and $(LiC_5D_5)_2$. Complexation of lithium with tetramethylethylenediamine greatly accelerates the monomer reaction (426). The rates of dioxygen uptake by the complexes trans-$Ir(CO)X(PPh_2R)_2$ increase with X from fluoride to iodide, and with R from phenyl to ethyl to methyl; this is different from the order of electron availability at the metal as measured by carbonyl stretching frequency lowering (427).

The removal of orbital symmetry restrictions on organic reactions by transition metal ions has been reviewed in general twice (428, 429), while promotion by transition metals is among the topics of a review on alkene cyclodimerisation (430). Metal-complex catalysis of homogeneous hydrogenation as such (431) and of asymmetric homogeneous hydrogenation (432) have been reviewed, as has the catalysis of hydrogen transfer from one organic species to another (433). The isomerisation of pent-1-ene to pent-2-ene, catalysed by $Co(H)(N_2)(PPh_3)_3.Et_2O$ in toluene, is said actually to be promoted by a nitrogen atmosphere; since such an atmosphere is commonly taken as inert, this is a point of some consequence (434). Polystyrenes containing the coordinating groups $-C_6H_4PPh_2$ or $-C_6H_4CH_2PPh_2$ have been used to support or modify a variety of metal carbonyl catalysts. For example, cobalt carbonyl combines with the support while remaining an active hydroformylation catalyst, while $Ni(CO)_2(PPh_3)_2$, which trimerises propiolate on its own, reacts with propiolate in the presence of the support to give a tetramerisation catalyst (435). Atoms of V, Cr, Fe, Co, Ni or (in the presence of diethylaluminium chloride) Ti or Mn react with butadiene to give cyclo-oligomers or other polymers; the exact products depend on the presence and nature of the added aluminium compound and of added ligands (436).

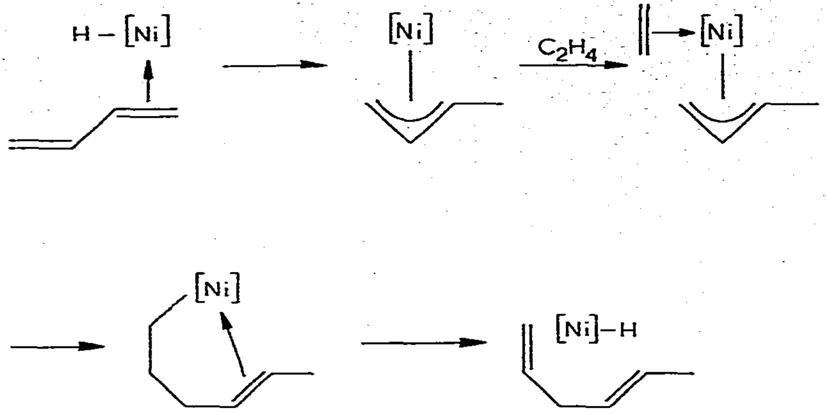
Polymerisation of 3,3-dimethylcyclopropene (LIIa) with $Pd(PPh_3)_4$ gives specifically the trimer (LIIb), while nickel(0)-triphenylphosphine catalysts give (LIIc)



(a) (b) (c) (d) (e) (f)

(LII)

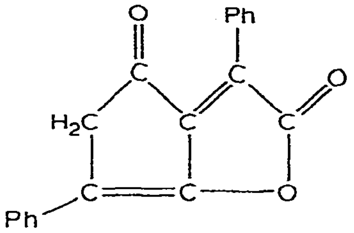
(437). Ni(COD)$_2$ favours oligomerisation to (LIId), or, in the presence of maleic or fumaric esters, co-dimerisation to (LIIe,f) respectively (438). Co-dimerisation of styrene with ethylene in the presence of a $(Ph_3P)_2Ni(Ar)Br/BF_3.Et_2O$ catalyst (Ar = e.g. 1-naphthyl) gives $PhCH_2CH_2CH:CH_2$. It is suggested that the catalyst acts as a source of nickel hydride which adds to styrene. Insertion of olefin into the nickel-carbon σ-bond, and β-elimination of nickel hydride, then complete the catalytic cycle (439). The same catalyst co-dimerises butadiene and ethylene to 1,4-hexadiene, the isomerisation of which by the catalyst (giving the 2,4-diene) is suppressed by excess butadiene. Again, it is suggested that nickel hydride is the catalyst, according to Scheme 3 (440). Proton acids can modify the reaction of metal catalysts with norbornadiene. Thus



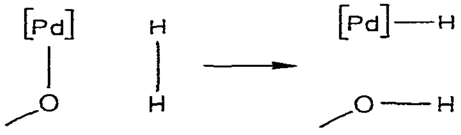
Scheme 3

in the absence of acid, norbornadiene is converted by $Ni(COD)_2/PBu^n_3$ to the cis-cyclobutane dimer, but in the presence of acid and morpholine (or pyrrolidine) the products obtained are exo-4-(o-tolyl)norbornene and N-(exo-4-norbornenyl)morpholine (or -pyrrolidine). It is suggested that in a more oxidising environment the metal is more likely to catalyse polar additions rather than electrocyclisations (441). The polymerisation of vinyls by $CoH(N_2)(PPh_3)_3$ is characterised by a slow initiation (said probably to be insertion of monomer into the cobalt-hydrogen bond) and rapid propagation and termination. The effects of co-polymerisation experiments can be explained in terms of competition between vinyl groups, and the polymerisation of methyl methacrylate gives product rich in syndiotactic fraction (442). Co-condensation of phenylacetylene with carbon-monoxide using rhodium dicarbonyl chloride dimer as catalyst gives LIII, presumably by initial formation of a rhodium acetylide hydride, followed by insertions of carbon monoxide and phenylacetylene (443).

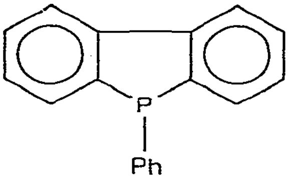
Pd(II)(salen) acts as a catalyst for alkene hydrogenation. The proposed initiation step is formation of a palladium hydride according to Scheme 4, and the important general point is made that this scheme gives ligand loss at palladium, as well as hydride formation, thus providing a site for activity (444). Cobaloximes also act as hydrogenation catalysts to 1,1-disubstituted ethylenes, provided the substituents are electron-withdrawing or only weakly electron-donating; alkylcobalt intermediates are isolable (445). $RhCl(PPh_3)_3$ catalyses a stoicheiometric hydrogen transfer from dioxane to alkenes, producing dioxene and alkanes. There is a large primary isotope effect, indicating that oxidative insertion of rhodium into a C-H bond is rate-determining (446). The sterically hindered catalyst $RhH(DBP)_4$ (DBP is the dibenzophosphole LIV) catalyses selectively the hydrogenation of terminal double



LIII

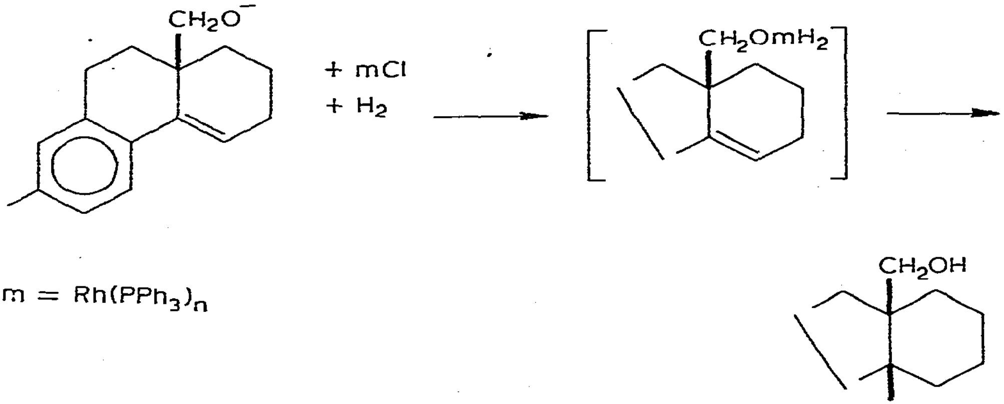


Scheme 4



LIV

bonds. The kinetics of the reaction in benzene indicate a transition state of the composition $RhH(DBP)_2.H_2.alkene$, but it is suggested that this is an alkylrhodium dihydride complex rather than an alkene trihydride, since the catalyst appears inert to hydrogen in the absence of alkene (447). Steric control of hydrogenation can be modified by complex formation at sites other than that to be reduced, as in Scheme 5 (448).

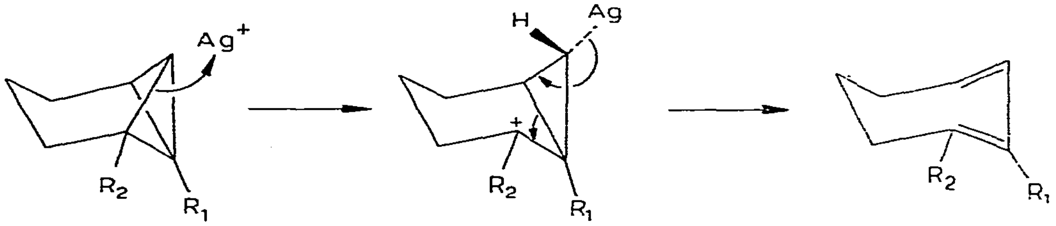


$m = Rh(PPh_3)_n$

Scheme 5

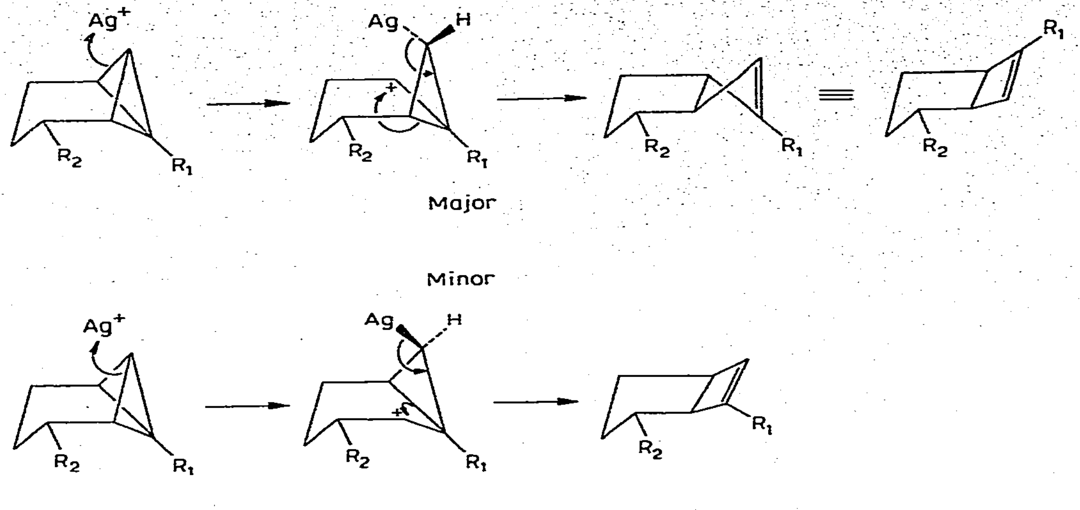
The nature of hydroformylation mixtures has been studied by infrared spectroscopy. Cobalt hydrides and acyls are both detected, in a ratio depending on the pressures of hydrogen and carbon monoxide. If the catalyst dicobalt hexacarbonyl bis(tri-n-butylphosphine) is used instead of the simple carbonyl, then hydrides dominate and acyls are not detectable. Acyl hydrogenolysis is regarded as being rate-determining in simple hydroformylation of terminal alkenes, but in the reaction of internal alkenes, or using the phosphine-substituted catalyst, the rate-determining step may be alkene coordination (449). The rate expression for the oxidation of ethylene by Pd(II) contains, as well as the familiar term in $[(PdCl_4)^{2-}][Cl^-]^{-2}[(H_3O)^+]^{-1}[C_2H_4]$, a term in $[(PdCl_4)^{2-}]^2[Cl^-]^{-3}[(H_3O)^+]^{-1}[C_2H_4]$, attributed to a binuclear (presumably chloride-bridged) active species (450).

The detailed studies by Zon and Paquette of the silver ion-catalysed rearrangements of tricycloheptanes have been extended by kinetic isotope effect studies. The rearrangements are classified as α-type (producing cycloheptadienes), β-type (producing methylenecyclohexenes), and γ-type (producing bicyclo[2.3.0.]heptenes). All the processes depend on formation of an argentocarbonium ion and its subsequent rearrangements, in the case of the α- and γ-type processes by sigmatropic shifts (Schemes 6, 7),

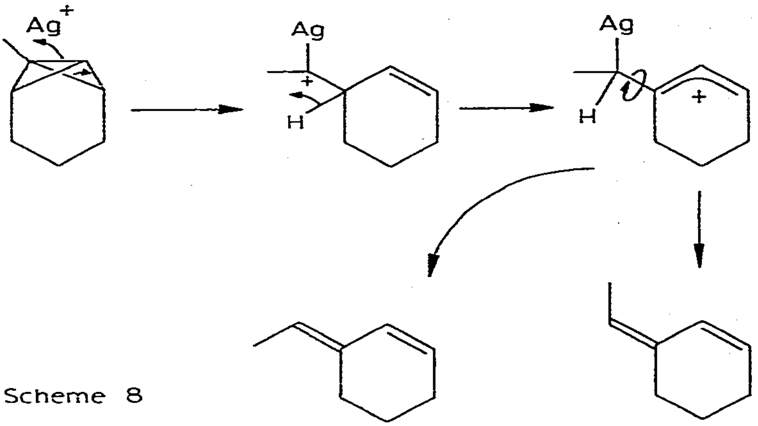


Scheme 6

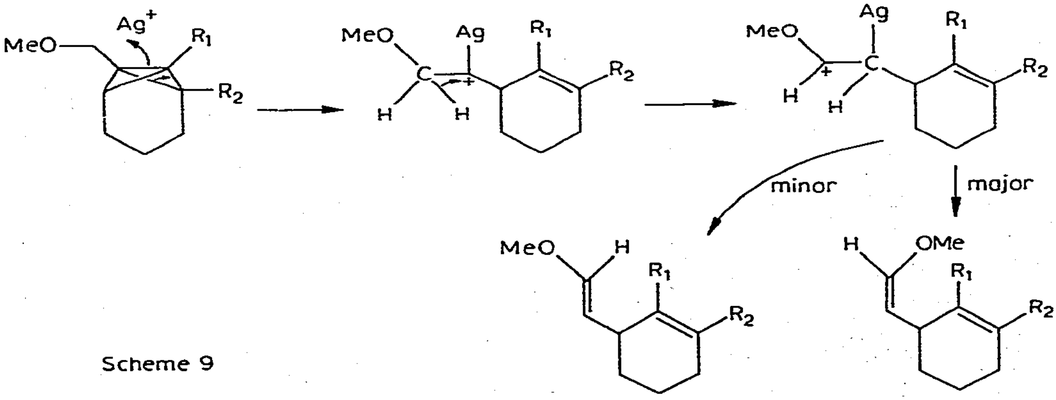
while in the case of the β-mechanism migration occurs either of an allylic ring hydrogen (β-shift, Scheme 8), or of a side-chain activated hydrogen (β'-shift, Scheme 9). In the latter case, the main product is the thermodynamically less stable isomer; this is a consequence of steric effects in the β'-shift process (451, 452, 453). Silver cation catalyses



Scheme 7

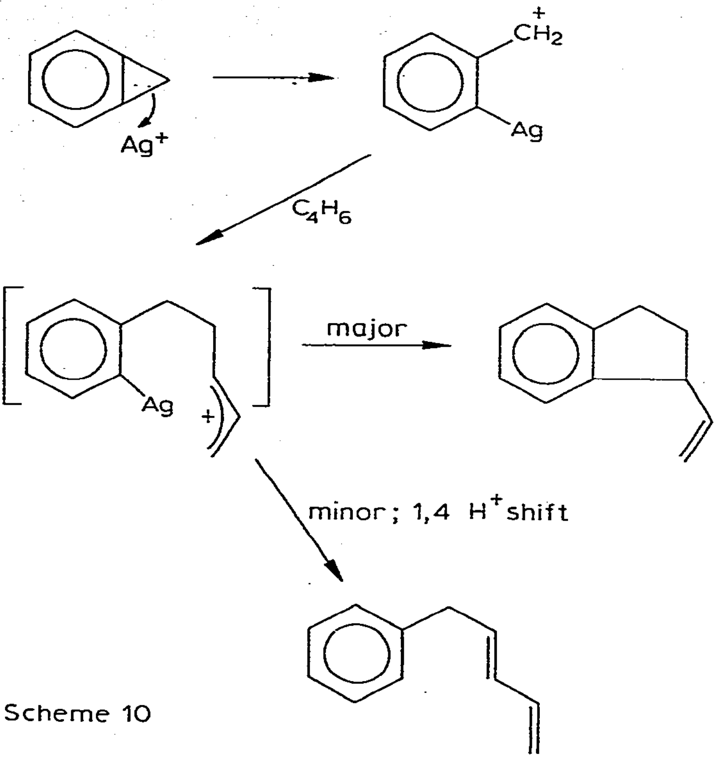


Scheme 8



Scheme 9

modified reactions of benzocyclopropene, for example with butadiene; again the products can be explained by invoking a carbonium ion intermediate (Scheme 10)(454). Nickel



Scheme 10

complex catalysed rearrangements of dienes and vinylcyclopropanes have been the subject of an extended study (455–458). Ring-opening in bicyclo[3.1.0.]hex-2-enes by $Rh(PPh_3)_3Cl$ or $Rh(PPh_3)_3Cl$ or $Rh(PPh_3)_2(CO)Cl$ requires activation of the catalyst by oxygen, which thus seems to be an essential component of the catalyst or catalyst precursor (459).

The hypothesis that olefin metathesis occurs by way of carbene complexes receives support from the reaction of $W(CO)_5{:}CPh_2$ with $CH_2{:}C(OMe)Ph$, which gives, in addition to $\overline{CH_2.C(OMe)Ph.CPh_2}$, the metathesis products $W(CO)_5:C(OMe)Ph$ and $CH_2:CPh_2$ (460). It is tempting to suggest a carbyne mechanism for alkyne metathesis, which generates Ph.CC.Tol from a mixture of diphenyl-and ditolylacetylenes, especially since the catalyst used was a mixture of molybdenum hexacarbonyl and resorcinol (461).

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