Transition Metal-Organic Chemistry Physical Methods and Results of General Interest, 1973*

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*Transition Metal-organic Chemistry: Physical Methods and Results of General Interest, 1972 see Organometal. Chem. Rev. B, 10(1972-1974)301.

GENERAL

The plenary lectures of the 14th International Conference on Coordination Chemistry have been published. Topics of of interest to organometallic chemists include the synthesis and properties of transition metal to carbon bonds (1), vitamin B_{12} and model compounds, and reductive cleavage of the cobalt-carbon bond (2), and reactions of carbon dioxide with transition metal compounds (3). The papers presented at the 6th International Conference on Organometallic Chemistry have been listed, with authors' affiliations (4). Procedures have been given for the preparation of cyclic diolefin complexes of palladium and platinum; of species $X_3SiCo(CO)_4$ ($X = Cl, CH_3, F$); triallylchromium and diallylnickel; metal-metal bonded species including $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$; and phosphine and phosphite complexes of low valent metals (5); and of $KPtCl_3C_2H_4$, $(RhCl(cyclo\text{-}octene)_2)_n$, and $(IrCl(cyclo\text{-}octene)_2)_n$ (6). A book about inorganic thermodynamics includes a chapter on organometallic compounds (7).

REVIEWS (See also under individual sections)

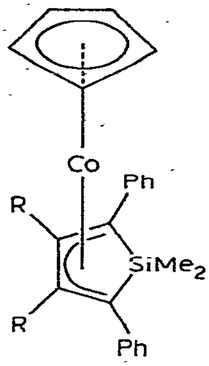
Reviews have appeared on organometallic electro-chemistry (8) and radiochemistry (9); on thermodynamic data for olefin and acetylene complexes of transition metals (10); transition metal hydrides (11), and dinitrogen complexes (12), and dioxygen complexes of Group VIII metals (13); on spectroscopic studies of metal-phosphorus bonding in complexes (14) and stereo-chemical studies of metal carbonyl triphenylphosphine derivatives (15); and on silicon-bonded and silicon-carbon-bonded transitionmetal complexes (16); while transition metal carbene complexes have been reviewed more than once (17, 18). Other classes of transition metal complex reviewed by type of ligand include isocyanide complexes (19), complexes of carbon-cyanide and nitrogen-cyanide ligands (20), 'new organic ligands' (trimethylenemethane, tetramethylene-ethane, pentadienyl and benzyl) (21), and complexes of chelating group V-olefin ligands (22). Organic compounds of cobalt (III) have been reviewed twice (23, 24), and reviews have appeared on the Co_3C cluster (25), on mixed valence ferrocene chemistry (26), on the reactions of cobaltocene and nickelocene (27), and on organo-platinum chemistry, with emphasis on metal-induced carbonium ions (28). Several reviews have concentrated on specific types of reaction such as insertion of carbon monoxide into transition metal-carbon bonds (29), olefin oxidation and related reactions with Group VIII noble metal compounds (30), π-ligand transfer reactions (31), the synthesis of heterocycles via transition metal intermediates (32), conjugated additions of organocopper reagents (33), and the formation of carbon-carbon bonds via nickel π-allyls (34). Other topics reviewed include binuclear compounds in which transition metals are linked through a common unsaturated ligand (35), and 7-membered conjugated cyclic compounds (including a section on metal π-complexes) (36). A general review of stability, reactivity, and orbital correlations in organo-transition metal complexes has appeared (37), and a literature guide has been updated to 1971 (38).

THEORETICAL STUDIES

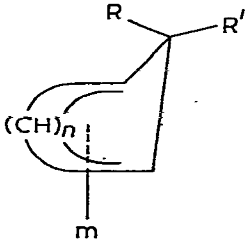
SCCC-MO calculations have appeared on species $C_6H_6Cr(CO)_{3-n}(N_2)_n$ and $C_5H_5Mn(CO)_{3-n}(N_2)_n$. Carbon monoxide is always a better π-acceptor than is dinitrogen, but in the species for which n=1, N_2 is a better overall ($\sigma + \pi$) donor then is CO (39). Similar calculations have been carried out on $h^3(C_3H_5)Co(CO)_3$ and on $h^5(C_5H_5)Co(CO)_2$. The Mulliken metal-carbon bond population is higher in the latter compound, for two reasons; C_5H_5 is a net donor to the metal while C_3H_5 is a net acceptor and orbital overlap geometry is also more favourable. This is consistent with the observed higher metal-carbon and lower carbon-oxygen stretching frequencies (40). The electric dipole moment matrix has been calculated, using a multi-exponent basis set, for benzene-chromium tricarbonyl. Three-centre integrals must be taken into account, since their omission leads to a reversed, and presumably incorrect, sign (41). Closed shell SCF-MO CNDO calculations have been carried out for complexes of Ag(I) and olefins. Methylation of the double bond is calculated to increase the ligand-metal bond energy. The largest single bonding interaction is calculated to be that between the olefin π-orbital and the vacant 5σ orbital on silver, and the forward donation described by this interaction does more to reduce the carbon-carbon π-bond order than does back-bonding (42). Two studies have used an LCAO-SCF-MO Gaussian basis treatment to explore the consequences of excitation and ionisation in transition metal complexes. In the former, it is found from studies on $Ni(CO)_4^+$ that Koopman's approximation gives the correct ordering for the ionisation potentials of $Ni(CO)_4$. The extension of one-electron energy levels to excited states does, however, lead to error in other situations. Thus in $Ni(CN)_4^{2-}$, one-electron energy differences are smallest for $\pi \rightarrow \pi^*$ transitions, but d-d transitions nonetheless occur at lower energy; however, one-electron energies do appear to give the correct order for the possible d-d transitions. The failure of the simple model is attributed to the effects of Coulomb and exchange integrals, and the changes in these on excitation (43). Relatedly, calculations on the cation $Ni(C_3H_5)_2^+$ compared with $Ni(C_3H_5)_2$ show severe breakdown of Koopmans' assumptions, thus explaining differences between the observed ordering of ionisation potentials and those inferred from calculations on the neutral species alone (44). Calculations have been performed on a range of iron compounds including $Fe(CO)_5$ in order to interpret their Mossbauer spectroscopic parameters. Isomer shift relates satisfactorily to calculated electron density at the iron nucleus, which is sensitive both to the Fe 4s population and to overlap effects on the normalisation of the Fe 3s orbital (45). The ligand field treatment has been given of the configurations d^1, d^2 and d^3 in strong axially symmetrical fields, including the effect of spin-orbit coupling, and the results applied to available data on visible esr spectra and magnetic properties of sandwich complexes (46).

IONISATION STUDIES AND MASS SPECTRA

Major routes in the mass spectroscopic fragmentation of titanocene dihalides are loss of halogen to give $(C_5H_5)_2TiX^+$, which in turn loses C_5H_5 either directly or after further halogen loss, and loss of C_5H_5 followed by acetylene and halogen to give in turn $C_5H_5TiX_2^+$, $C_3H_3TiX_2^+$, and $C_3H_3TiX^+$. Species $C_5H_5TiX_3$ show similar routes, and also formation of $C_5H_5^+$ (loss of TiX_3) and TiX_2^+ (loss of C_5H_5X) from the parent ion. HX loss occurs in the spectrum $CH_3C_5H_4TiX_3$, indicating presumably formation of a fulvene complex (47). The spectrum of silacyclopentadiene cyclopentadienylcobalt,I, shows a strong peak for loss of CH_3, and no lower peaks. Presumably $(p - 15)^+$ corresponds to the silacobalticenium ion (48). The fragmentation of cyclo-octatetraene derivatives is modified in their tricarbonyliron derivatives. Thus $C_8H_7CH_2OCH_3^+$ shows α- cleavage to give $C_8H_7CH_2OCH_2^+$ and $CH_2OCH_3^+$, but $C_8H_7CH_2OCH_3Fe^+$ shows loss of CH_2O. This is thought to be a McLafferty rearrangement of what may now be regarded on a neutral, even-electron species complexed to Fe^+ (49). Free radical loss from cyclopentadienes complexed to iron in the mass spectra of species (II, $n = 2$, $m = Fe(CO)_3$) is confined



(I)



(II)

(R = H,Ph)

to the exo substituent; this appears to be a general characteristic of species of type (II) (50).

The ionisation potentials of arenechromium tricarbonyl complexes correlate well with the CO stretching parameter, and with the parameter of the substituent. The same is true for the energy required to remove one or two CO groups from the parent ion, but the correlation for loss of the third CO is less good (51). In $Me_3SiMn(CO)_5$ and species $Me_3SiMn(CO)_{5-x}(PF_3)_x$ (x = 0 - 3), loss of methyl competes with loss of CO and of PF_3. The ionisation potentials are higher than expected from the properties of the Me_3Si radical, presumably because of π-bonding. The metal-hydrogen bond in $HMn(CO)_5$ is very weak (D = 30 ± 50 kJ mol^{-1}) (52). Appearance potential studies on the species $Me_3MMn(CO)_5$ (M = Si, Ge, Sn) lead in each case to approximate values of 250 kJ mol^{-1} for dissociation of the MMn bond. Approximate force constant calculations suggest, however, that the manganese-silicon bond has a higher force constant than that between manganese and germanium (53).

Positive and negative ions have been observed in the spectra of the bis (cyclopentadienyl) complexes of iron, cobalt, nickel and magnesium. The anion $C_5H_5^-$ is formed at low electron energies in all cases, the cross-section for capture of an electron increasing from iron and cobalt through magnesium to nickel. The transition metal complexes show compound negative ion resonances below 1 eV (54). In the high-pressure (around 0.01 Torr) mass spectrum of ferrocene, reactions

$$\begin{aligned} Fe^{+} + C_{10}H_{10}Fe &\rightarrow Fe + C_{10}H_{10}Fe^{+} \\ C_5H_5Fe^{+} + C_{10}H_{10}Fe &\rightarrow C_{15}H_{15}Fe_2^{+} \\ C_5H_5Fe^{+} + C_{10}H_{10}Fe &\rightarrow C_5H_5Fe + C_{10}H_{10}Fe^{+} \end{aligned}$$

has been observed and reaction rates inferred (55). Ion-molecule reactions are shown by $C_5H_5NiNO^+$ in the presence of donors; ions $C_5H_5NiL^+$ are observed and cyclohexene gives $C_5H_5NiC_6H_{12}^+$ (56).

The photoelectron (HeI) spectra of $(tsm)_4Cr$, $(tsm)_4Sn$, $(tsm)_4Pb$ and tsmCl, and of $(np)_4Cr$ (tsm = trimethylsilylmethyl, np = neopentyl) have been given. Bands at binding energies of 7.25 and 7.26 eV in $(tsm)_4Cr$ and $(np)_4Cr$ are attributed to the chromium d electrons, while a band between 8.4 and 8.7 eV, split by spin-orbit coupling in the lead compound, and absent in tsmCl, is attributed to the tsm-metal bonding electrons. Thus the carbon-metal σ-bond in $(tsm)_4Cr$ appears perfectly normal (57). The HeI, HeII and valence region X-ray photo-electron spectra of the Group VI hexacarbonyls have been assigned (58) using earlier MO calculations (59). Orbitals in order of increasing binding energy are 'metal' d-orbital, CO 1π and 5σ levels, CO 4σ, and at 35.5 eV CO 3σ (oxygen lone paid). This last is calculated to lie at 43 eV, but the ionisation energy is possibly lowered by large relaxation effects. The HeI spectra of H_3SiM and H_3GeM (M = $Mn(CO)_5$, $Re(CO)_5$, $Co(CO)_4$) have been reported, along with those of $Me_3SiMn(CO)_5$, $HRe(CO)_5$ and $HCo(CO)_4$. In no case are bands due to the electrons of the metal-metal σ-bond resolved. The binding energies of the d-electrons increases from methyl to germyl to silyl derivative, but this is as true for the b_2 level in octahedral complexes as for the a level, and the trend is therefore due to overall charge balance rather than to specific d - d back-bonding (60). The 9a, (σ Mn-X) electrons in pentacarbonylmanganese halides, and in cis-$Mn(CO)_4(CNMe)Br$, have been resolved and are located as predicted between 8e (mainly X pπ) and 7e (mainly d(xz yz)), with $2b_2$ d(xy), at higher binding energy. The relative attributions of 8e and 7e are confirmed by a spin orbit splitting of 0.30 eV in the first ionisation potential of $Mn(CO)_5I$, and a splitting of the third ionisation when CO is replaced by MeNC (61).

Core shifts have been reported from the XPE spectra of $Cr(CO)_6$, $Fe(CO)_5$, $H_3CMn(CO)_5$, $HMn(CO)_5$, $Mn(CO)_5X$ (X = Br, I, CF_3) $CH_3C_5H_4Mn(CO)_3$, and $Re(CO)_5Cl$, and compared with the results of calculations. The agreement is not good, suggesting that (if the calculations are adequate for this purpose) the core shifts are powerfully influenced by relaxation. The effects of changing the nature of X in $XMn(CO)_5$ are small, and less than calculated, and axial and equatorial carbonyl groups are not separately resolved (62).

The XPE spectra of metallocenes (the metals varying from vanadium to nickel) all show C 1s at lower binding energy than in free benzene. Multiplet splitting is observable in the metal 3s ionisation for the complexes of vanadium, chromium and manganese, and is explained in terms of spins partly but not entirely delocalised onto the rings (63). The Fe 2p binding energies increase along the series ferrocene, dibenzoylferrocene, $((C_5H_5FeC_5H_4)_2CH)^+BF_4^-$ (one signal only), $(C_5H_5)_2Fe^+BF_4^-$ (64). In the carbon 1s region each of the species $(C_6H_6)_2Cr$, $(C_6H_6)_2Cr^+$, $C_6H_6CrC_5H_5$, $(C_5H_5)(C_7H_7)Cr$ and $(C_5H_5)(C_7H_7)Cr^+$

gives only a single line, showing the real charges on the rings are the same within 1/3 electrons. Unlike the C 1s signal, the chromium core signals are sensitive to overall charge on the complex. The value found even in the neutral species corresponds to real positive charge on chromium, and the $(C_6H_6)(C_5H_5)Cr$ signal is in the same range as that of the other neutral species, despite the formal presence of Cr(I) (65). Shake-up satellites have been reported in the spectra of $(C_6H_6)_2Cr$, $C_6H_6Cr(CO)_3$ and $Cr(CO)_6$, and attempts made to identify the promotion processes involved by comparison with electronic spectra (66). The Sn 3d binding energies in complexes of type $(t\text{-}Bu)_2Sn(B)(m)$ ($m = Fe(CO)_4$, B = DMSO, pyridine; $m = Cr(CO)_5$, B = DMSO, pyridine, THF) are in the Sn(IV) region, consistent with a tin-transition metal ylid-like double bond; the tin Mossbauer spectrum is also consistent with this (67).

When methylene amino complexes, $C_5H_5Mo(CO)_2NCR_2$, are compared with the related aza-allene species $C_5H_5Mo(CO)_2(R_2CNCR_2)$, the latter show a higher binding energy for the nitrogen core electrons, while those on molybdenum are higher in the former series. Isomerism in the mode of aza-allene to metal bonding leads merely to unresolved broadening, but there is a good correlation overall between molybdenum core binding energy and CO frequency (68). In the complex $C_5H_5Mn(CO)_2N_2$, the nitrogen core binding energies are observed at 403.0 and 401.8, while that in $C_5H_5Mn(CO)_2NH_3$ is at 403.1, although free ammonia gives a lower value than does free dinitrogen. The difference between the two atoms of coordinated dinitrogen is almost twice that in the corresponding hydrazine complex. These facts can be understood if N_2 is a poorer net donor than NH_3, and if π-bonding (expressible as a contribution from such formulations as $C_5H_5Mn(CO)_2{=}N^+{=}N^-$) concentrates charge on the nitrogen atom further from the metal (69). In

$(Ph_3P)_2Ir(CO)Cl.TCNE$, the iridium binding energies place it in the Ir (III) rather than Ir(I) range. Addition of acetonitrile lowers the core binding energy at Ir, but does not alter the Mossbauer spectrum; this result can be understood if acetonitrile acts as a π-acceptor as well as a σ-donor (70). Ethylene, however, does not shift the nickel signal from the Ni(0) to Ni(II) region in $C_2H_4Ni(P(OC_6H_4CH_3)_3)_2$, despite the long carbon-carbon bond (71).

ELECTRONIC SPECTRA

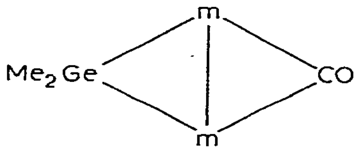
The electronic spectra of species of type $M(CO)_5$ and $M(CO)_5L$ (M = Cr, Mo, W) have been discussed using a simplified molecular orbital diagram, assigning the lowest energy observed band as d – d in origin, and making some rather far-fetched assumptions about the energies of the orbitals involved. However, the principal conclusion, that the frequency of the lowest observed band increases with π-acceptor character of L (72), is reasonable enough. The spectra have been examined of a number of species of type $(NN)Mo(CO)_4$, when (NN) is a bidentate ligand attached to molybdenum through two sp^2-hybridised nitrogens. When the two nitrogens are part of the same conjugated system of the free ligand, the $M(d) \rightarrow (NN)\ (\pi^*)$ charge transfer occurs in the visible region, but shifts to the ultra-violet if the conjugation is broken; thus coordination through metal does not of itself provide a conjugated pathway (73). The UV spectra of silver(I) complexes of benzene, toluene and xylene show bands at 260 and 230 nm. The former is essentially a forbidden transition of the aromatic ring, made allowed by coordination to metal, while the latter is a charge transfer band (74). Trends in the electronic spectra of species $C_5H_5Ni(PPh_3)X$ fit the accepted spectrochemical series for X, but ^{31}P nmr shifts fit no such simple pattern (75). Absorption and magnetic circular dichroism spectra of $(C_5H_5)_2Fe^+BF_4^-$ have been recorded at 290° and 9°K, and the esr spectrum at $20^{\circ}K$. The ground state is assigned as E''' (^2E_g) ($a_{1g}^2e_{2g}^3$), mixed with E'' (^2E_g) by a low-symmetry perturbation, and the assignment of the 16,200 cm^{-1} band as $L(e_{1u}) \rightarrow M(e_{2g})$ charge transfer is strongly confirmed (76). The visible spectrum of species $(C_8H_7R)_2U$ shifts to longer wavelength where R is electron-releasing, and is accordingly assigned as L → M charge transfer (77,78). The substituents have little effect, however, on the Mossbauer spectrum and magnetic properties (78).

PHOTOCHEMISTRY AND PHOTOLYSIS

The complex $C_5H_5MnC_7H_8$(C_7H_8 = cycloheptatriene), otherwise accessible only with difficulty, can be prepared photochemically from $C_5H_5Mn(CO)_3$ and C_7H_8 (79). A more surprising total decarbonylation is that of $Cr(CO)_6$ in pentane at room temperature, in the presence of excess NO, to give $Cr(NO)_4$ (80). Reactions between metal carbonyls and NO have also been investigated in argon matrices, as have the photochemistry of carbonyls and nitrosyls in matrices rich in CO. $Fe(CO)_2(NO)_2$ and its new analogue $Os(CO)_2(NO)_2$ have been prepared in this way, as have $Co(CO)_3NO$ and $Mn(CO)(NO)_3$. $Co(CO)_3NO$ is photoconverted to trigonal $Co(CO)_4$ in a CO matrix, while $Mn(CO)(NO)_3$ seems to give more than one product (81). $Co(CO)_4$ had earlier been prepared by CO matrix photolysis of $Co_2(CO)_8$ (82); the advantage of this technique is that it suppresses the simple loss of CO that is otherwise dominant. In an argon matrix, $Fe(CO)_5$ is photolysed to a species $Fe(CO)_4$. This process is readily photoreversed, even while an infrared spectrum is being run, by the red light from an unfiltered Nernst glower (83). The first observable process in the flash photolysis of $Cr(CO)_6$ in cyclohexane at room temperature is assigned as CO loss, and the absorption maximum of 503 nm for the new species confirms its formulation as $Cr(CO)_5$; this species is, however, rapidly destroyed by unidentified impurities (84). Vacuum UV photolysis of $Ni(CO)_4$, $Cr(CO)_6$ and probably $Fe(CO)_5$ in low temperature matrices gives charge separated species $M(CO)^-_{n-1}$ and CO^+ (85).

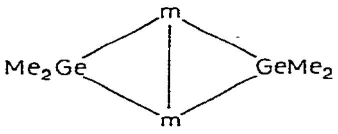
Photolysis of $Mo(CO)_5PCx_3$ (Cx = cyclohexyl) in hydrocarbon glass gives two species, assigned as $Mo(CO)_4(PCx_3)$ (cis-vacancy) and $Mo(CO)_4(PCx_3)$(trans-vacancy) on the basis of their ir spectra and analogy with $Mo(CO)_5$. The trans-vacancy isomer is slightly more thermally stable, but is photochemically converted to the cis isomer (86). Photolysis of the cyclobutadiene complex $C_4H_4Fe(CO)_3$ in an argon matrix gives only $C_4H_4Fe(CO)_2$ and CO as detectable fragments, with no loss of cyclobutadiene (87). This is hardly surprising; $Fe(CO)_3(P(4\text{-}C_6H_4CH_3)_3)_2$ and trans-$W(CO)_4(P(i\text{-}Pr)_3)_2$ both show CO loss but no phosphine ligand loss on irradiation in hydrocarbon glass, but photoinduced replacement of one phosphine by added CO in mobile solution at room temperature, and it may simply be that heavier fragments are being discarded but are unable to escape in a rigid matrix and recombine (88). There is infrared evidence for the formation of an ion pair $C_5H_5Ni^+ NO^-$ from the photolysis of C_5H_5NiNO in argon (89).

Photolysis of $Mn_2(CO)_{10}$ in tetrahydrofuran solution gives an esr signal, attributed to $Mn(CO)_5$ radicals (90). Photolysis of $Re_2(CO)_{10}$ in carbon tetrachloride gives $Re(CO)_5Cl$. The quantum yield and stoicheiometry indicates that the first step is formation of $Re(CO)_5$ radicals, which then abstract chlorine from solvent (91). The system $Mn_2(CO)_{10} - C_2F_4$ is an efficient photoinitiator of polymerisation; this property is attributed to the stability of σ-bonds between manganese and fluorocarbons, as in the suggested active species $(OC)_5Mn.CF_2CF_2^{\cdot}$ (92). Photolysis of vinylgermanium derivatives $Me_2Ge(C_2H_3)mCO$ did not lead to

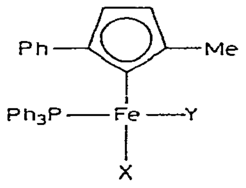


(III)

germa-allyl complexes, but to a range of other products, such as $Mn_2(CO)_{10}$ (mCO = $Mn(CO)_5$), III (m = $C_5H_5Fe(CO)$), and both $(C_5H_5Mo(CO)_3)_2$ and the novel species $(C_5H_5Mo(CO)_2)_2$ (mCO = $C_5H_5Mo(CO)_3$) (93). Photolysis of $Me_2Ge(mCO)_2$ gives species of type III for mCO = $C_5H_5Fe(CO)_2$, $Co(CO)_4$, but the compound $Me_2GeMn_2(CO)_9$ does not appear to be predominantly CO-bridged. Photolysis of species $Me_2GeCl.mCO$ (mCO = $Mn(CO)_5$, $Co(CO)_4$, $C_5H_5Cr(CO)_3$, $C_5H_5Mo(CO)_3$, $C_5H_5Fe(CO)_2$) proceeds with overall loss of CO and Cl to give the bis-germylene-bridged product IV (94). Photodecarbonylation of the acetyl complex Va gives, stereospecifically, the product Vb. Presumably this occurs via decarbonylation of the metal and methyl migration (95), since photodecarbonylation of $C_5H_5Fe(CO)_2{}^{13}COCH_3$ gives $C_5H_5Fe(CO)({}^{13}CO)CH_3$ (96). Photolysis of $C_5H_5Fe(CO)_2Cl$ in DMSO gives $(C_5H_5)_2Fe_2(CO)_4$; C_5H_6 and free chloride ion are also generated. Photolysis of $C_5H_5Mo(CO)_3Cl$, on the other hand, leads to $(C_5H_5Mo(CO)_2Cl)_2$ and the tungsten analogue behaves similarly (97). Loss of phosphine and phosphite ligands has also



(IV)

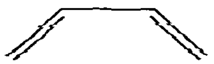


(V)

(a) X = CO ; Y = $COCH_3$
(b) X = CH_3; Y = CO

been demonstrated, since $C_5H_5Fe(CO)P(OPh)_3Br$ and $C_5H_5Mo(CO)_2LCl$ ($L = P(OPh)_3$, PPh_3, PCx_3) give $(C_5H_5)_2Fe_2(CO)_4$ and $(C_5H_5Mo(CO)_2Cl)_2$ respectively; $C_5H_5Fe(CO)PPh_3Br$, however, gives rise to $(C_5H_5Fe(CO)_2PPh_3)^+Br^-$ (98). Irradiation of ferrocene in carbon tetrachloride-ethanol mixtures in the presence of sodium acetate gives ethyl ferrocenecarboxylate, Fc. COOEt. The active species is presumably not that formed from ferrocene, since the product in the presence of azulene is ethyl 1-azulenecarboxylate (99).

Organocobalt(III) complexes of the type $(Co(III)(NH_3)_5 - org\ (\pi) \rightarrow Cu(I))$, in which the organic group is unsaturated and acts as a ligand to Cu(I), are unstable with respect to internal electron transfer, but the reaction is slow in the dark. However, irradiation either in the cobalt d-d or in the copper-ligand charge transfer region causes photoacceleration (100). Oxygen photoinsertion into the cobalt-carbon bands of alkylcobaloximes is accelerated by the coordination of a weakly basic ligand to the initial cobalt complex, or by organic groups which readily form free radicals (101). Light greatly enhances the activity of $RhH(CO)(PPh_3)_3$ and of $IrCl(CO)(PPh_3)_2$ as isomerisation catalysts towards 1-heptene but does not alter the final cis-trans ratio. A detailed electronic mechanism is proposed (102), but the reviewer would be reluctant to exclude activation by simple ligand loss. Relevant to this suggestion is the $Cr(CO)_6$ - photoassisted 1,4-hydrogenation of conjugated dienes. Competition experiments show the reaction to occur most readily for dienes that can adopt the S-cis conformation



(VI)

VI, and the process is a true photocatalysis, proceeding in the dark after photoinitiation (103).

MATRIX ISOLATION (See also Photochemistry and Photolysis, Vibrational Spectra).

The use of transition metal atoms in inorganic synthesis in matrices has been reviewed (104). Co-condensation of titanium atoms (or molybdenum atoms) and benzene gives species $(C_6H_6)_2M$ (M = Ti, Mo). The titanium compound is diamagnetic, gives a proton nmr singlet, and has an infrared spectrum related to that of the vanadium and chromium analogues (105). Co-condensation of arenes with chromium atoms may also be used to prepare normally inaccessible species $(\text{arene})_2Cr$ in which the arenes are chlorinated or fluorinated. Chromium atoms trimerise acetylene to benzene, isomerise 1-butene to a mixture of 2-butenes, react with cyclopentadiene to give $(C_5H_5)_2Cr$, and complex to butadiene and to propene (106). The same route has also been used to incorporate cumene and m-di-isopropylbenzene in bis(arene) chromium complexes. In the presence of PF_3, condensation of chromium or iron atoms with benzene gives species $C_6H_6Cr(PF_3)_3$ and $C_6H_6Fe(PF_3)_2$. Manganese atoms with NO and PF_3 give $Mn(NO)_3PF_3$ (note: exposure of metal atoms to NO is HAZARDOUS) (107). Deposition of palladium atoms in an excess of C_6F_5Br gives a polymeric material $(Br.Pd.C_6F_5)_n$ (108).

Co-condensation of neodymium or yttrium with carbon monoxide in argon gives rise to a range of carbonyl complexes. In the case of neodymium, analysis of the CO stretching bands of samples and the effects of annealing lends to the assignments of many bands to carbonyls of high symmetry, up to and including octahedral $Nd(CO)_6$ (109). The species PdCO, $Pd(CO)_2$ (linear), $Pd(CO)_3$ (trigonal planar) and $Pd(CO)_4$ (tetrahedral) have been characterised in inert gas matrices using $^{12}C^{16}O$ - $^{12}C^{18}O$ mixtures to place the assignments beyond doubt. The metal-carbon force constant in $Pd(CO)_4$ is estimated at 82 Nm^{-1} (for $Ni(CO)_4$, the corresponding value is 180 Nm^{-1}) (110). Similar results have been found for the Pt-$^{12}C^{16}O$ - $^{13}C^{16}O$ system either on its own or in an argon host. The CO force constant falls surprisingly slowly from $Pt(CO)_4$ to PtCO, compared with either the palladium or the nickel series (111). The co-deposition of Ni and CS in argon is said to give $Ni(CS)_4$, detected by its mass spectrum (112).

Co-condensation of nickel atoms, N_2, and CO gives a range of species $Ni(N_2)_m(CO)_{4-m}$ (m = 1 - 3). The ir spectra are interpreted, by comparison among each other and with those of species $Ni(CO)_x$, as showing that N_2 is at once a poorer σ-donor and a poorer π-acceptor than CO (113). Co-deposition of nickel with isotopically labelled N_2 leads to the observation of two lines corresponding to $Ni^{14}N^{15}N$ and $Ni^{15}N^{14}N$ in the N-N stretching region; this confirms that the dinitrogen is bound end-on, not side-on (114). Indeed, co-condensation gives all of the species $Ni(N_2)_x$ (x = 1 - 4) and $Pd(N_2)_y$ (y = 1 - 3). $Ni(N_2)_4$ is tetrahedral in argon, but the site symmetry seems to be lowered to C_2 in a dinitrogen matrix (115). Species PtN_2 and $Pt(N_2)_2$ have been prepared by similar techniques, together with other, less well characterised species. There is evidence that platinum atoms are more mobile in an argon matrix than are N_2 molecules (116).

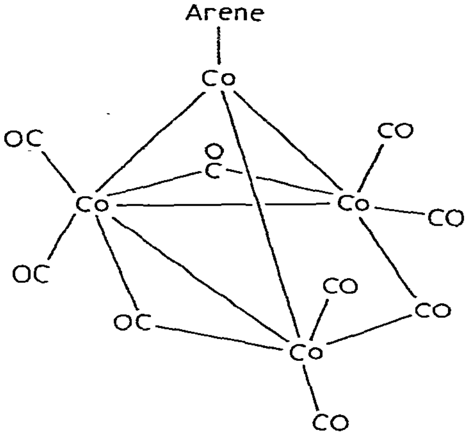
VIBRATIONAL SPECTRA

An index of vibrational spectra of inorganic and organometallic compounds has begun to appear (117).

The single crystal Raman spectrum of hexacarbonylmolybdenum has been analysed (118). The spectrum of $Fe(CO)_5$ in argon or in xenon shows extra bands, attributed to a local C_{2v} environment. Annealing reduces the intensity of these bands, probably by the formation of local pockets of hexagonal symmetry or by migration of $Fe(CO)_5$ to sites less distorted from D_{3h} (119). The spectrum of $Ni(CO)_4$ in argon has been studied under high resolution. The 422 cm^{-1} ir band shows structure corresponding to the isomer distribution of nickel, thus confirming the assignment of this band as principally a metal-carbon bond, while the NiCO band at 459 cm^{-1} is structureless (120). The ir and Raman spectra of $Co(CO)_3NO$ have been fully investigated using isotopically labelled CO and NO. A force field was fixed by constraining some interaction constants to take the same value as in $Ni(CO)_4$. Compared with $Ni(CO)_4$, the metal-carbon free constant is greater, as is the value of the MC,CO interaction constant, while the CO force constant is less. All these results indicate more metal-CO π-bonding in the cobalt compound. The MN,NO interaction constant is very small, a result that indicates competition between σ and π interaction effects (121).

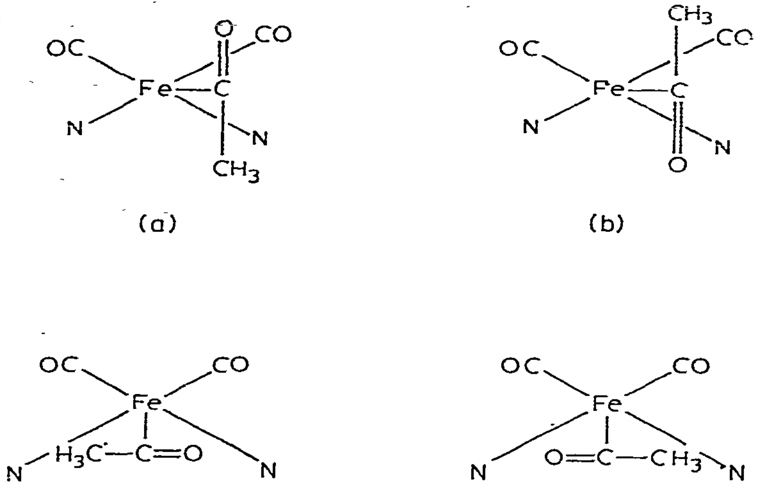
A full treatment has appeared (122) of the vibrational spectrum of $Mn(CO)_5Br$, slightly modifying earlier preliminary results (123). The energy factored carbonyl stretching field for octahedral species cis-$M(CO)_4L_2$ contains five parameters to be fixed from four frequencies. An iterative procedure has been described that apparently solves this impossible task, presumable by converging on one within the fairly small range of possible solutions, and a new recipe proposed for disentangling σ - and π-influences of ligand (124). Absolute intensities have been determined for all the ir-active bands of the Group VI hexacarbonyls, Dipole moment derivatives have been found, and interpreted in terms of a set of 'effective charges' on the various atoms; unfortunately, the results are ambiguous since the relative phases of the various oscillations are not known (125). The treatment has been further extended to $Ni(CO)_4$ and to $Co(CO)_4^-$. A moving charge dipole model places positive charge on carbon and negative charges on the metal in all these cases (126). The ir intensities of a range of complexes of the type <u>cis</u>-$W(CO)_4L_2$ have been measured, using analytic functions to deconvolute overlapping bands. The results are then further analysed in terms of the force field of ref. (124) ; the conclusion, which can only be as trustworthy as that analysis, is that orbital following in the M-L bonds is required to explain otherwise anomalously high intensities in the highest frequency band (127).

The spectra of the anions $((OC)_5Mn\text{-}M(CO)_5)^-$ (M = Cr, Mo, W) have been analysed in some detail but ignoring interactions across the metal-metal bond. The metal-metal force constant increases from $Mn\text{-}Cr^-$ to $Mn\text{-}W^-$ to Mn-Re. If the pseudo-diatomic approximation is to be used. this is best done by taking the M(CO)(axial) unit as the pseudo-atom (128). The carbonyl region spectra of $(OC)_5Mn\text{-}Co(CO)_4$ (129), (130) and $(OC)_5Re\text{-}Co(CO)_4$ (129) have been analysed, using the local symmetry approximation for each half of the molecule. For the former compound at least, it is necessary to go further and consider coupling of local a_1 and e modes on different $(MCO)_n$ fragments; in particular such coupling accounts for the existence of only one very strong ir-active E mode (130). The spectrum of $TcCo(CO)_9$ has been reported and assigned by analogy (131). The effect of isotopic labelling on the spectrum of $Co_3(CO)_4(SMe)_5$ has been investigated. It is found that bridge-terminal interactions are too small for labelling of one type of carbonyl to cause any detectable shift in the spectrum of the other (132). A range of species of type $(arene)Co_4(CO)_9$ (VII) have been prepared and their infrared spectra analysed. Since bridge-terminal coupling may safely be neglected, the observation of two ^{13}CO bands suffices to make the problem determinate. The three different kinds of interaction parameter linking CO groups on different



(VII)

metal atoms are all different and non-negligible (133). The binary combination regions of the spectra of species $Hg(Co(CO)_3L)_2$ are too rich for the selection rules of the D_{3d} molecular point-group, and it seems possible that a proportion of molecules are in a D_{3h} configuration (or indeed, the reviewer would suggest, an intermediate D_3 configuration) at any one time (134). The infrared spectrum of $(C_5H_5Mo(CO)_3)_2$ shows the existence of both trans and gauche forms, the latter being favoured by polar solvents. A more surprising finding is that in acetone at low temperatures the two different conformers give different nmr signals; the relatively high coalescence temperature (30°C) implies that barriers to rotation around crowded metal-metal bonds cannot be presumed negligible (135). The complex $(NNN)Fe(CO)_2.COCH_3$ (NNN = tri-1-pyrazolylborato) shows four terminal metal carbonyl and two acyl carbonyl bands; thus two of the possible isomers (VIII a, b, c) are present in solution, including presumably VIIIa which is the form found in the solid. Interconversion, however, appears fast since there is only one methyl proton nmr signal (136).



(a) (b)

(c) (c')

(VIII)

^{13}CO and C ^{18}O modes of isotopically labelled $C_5H_5Mn(CO)_3$ and related species $C_5H_5Mn(CO)_2L$, have been reported. One notable case is that of $C_5H_5Mn(CO)_2CS$, in which the CO groups may be exchanged but the CS group remains attached (137). There is infrared evidence for the reversible formation of the species $Pt(CO)_3PPh_3$ and $Pd(CO)_3PPh_3$ from $Pt_3(CO)_3(PPh_3)_4$, $Pd_3(CO)_3(PPh_3)_3$ or $Pt(CO)_2(PPh_3)_2$ at room temperature in p-xylene under 350-550 atm. CO; but no evidence for the simple tetracarbonyls could be obtained (138). A further high-pressure equilibrium followed by the same technique is that between $(Rh(CO)_2X)_2$ + CO and $Rh(CO)_3X$ (139).

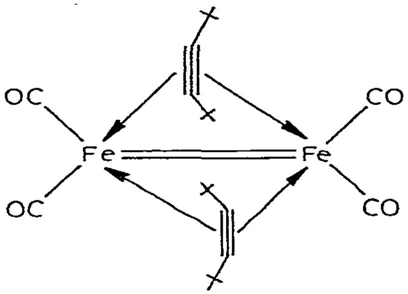
There is evidence, from the number of ν(CO) bands in solution, for conformational isomerism based on rotation round the metal-sulphur bond of species $C_5H_5Mn(CO)_2SR_2$; the ^{13}CO satellites of both conformers are observed and assigned (140). Rather more surprisingly, species of the type π-$C_3H_4XCo(CO)_2PR_3$ (R = OPh, OMe, Ph; X = H, 1-Me, 2-Me, 2-Cl) show anomalously rich carbonyl spectra, attributed to restricted rotation around the phosphorus-carbon or phosphorus-oxygen bonds (141); conformational isomerism around cobalt-ligand bonds does not explain the effects of change of phosphine on the spectra. The intensities of the CO stretching modes of the corresponding species π-$C_3H_4XCo(CO)_3$ have been measured, and used to estimate the CMC angles. These imply that the steric requirements of a π-allyl group are intermediate between those of NO (in $Co(CO)_3NO$) and butadiene (in $C_4H_6Fe(CO)_3$) (142).

Carbonyl infrared data for the phosphine sulphide and selenide complexes $(OC)_5M.SPPh_3$ and $(OC)_5M.SePPPh_3$ place these ligands in between amines and triphenyl-phosphine in net apparent acceptor character (143). The ligands CF_3PH_2 and $(CF_3)_2PH$ readily replace one or two CO groups from $Ni(CO)_4$, and one CO group from $Co(CO)_3NO$; ir data on the products show the ligands to resemble each other, and $P(CF_3)_3$, more closely than PH_3 (144). A most useful extension of the carbonyl frequency probe method is exemplified by the species $C_5H_5Fe(CO)_2CNMX_3$ (M = B, X = H, F, Cl, Br, Me; M = Al, Ga, X = Cl, Me). Here raising of the CO frequency (ν_2 was chosen) measures the electron pair acceptor strength of MX_3, giving the orders $BH_3 < BF_3 < BCl_3$, $BCl_3 > GaCl_3 > AlCl_3$, and $AlMe_3 > BMe_3 \sim GaMe_3$. It is noteworthy that BH_3 is a poorer acceptor than BF_3 but a far better acid, supporting the view that BF_3 requires a greater distortion energy (145). In species (arene)Cr-$(CO)_2$(Maleic anhydride), the CO stretching frequencies, and the stretching parameters derived from them, are higher than in (arene)$Cr(CO)_3$. Both metal and anhydride acyl CO frequency are lowered by electron-donating substituents on the arene (146).

Further studies, including Raman depolarisation studies, of the vibrational spectra of species $X_3MCo(CO)_4$ (X = Cl, Br, I; M = Si, Ge, Sn) lead (147) to the modification of earlier (148, 149) assignments. Infrared and oriented film low temperature Raman spectra of $C_3H_5Co(CO)_3$

give results in general agreement with earlier assignments (150), although some discrepancies occur below 700 cm^{-1} (151). The isoelectronic species $C_3H_5Fe(CO)_2NO$, and its perdeuteriated derivative, have been examined in liquid and solid phases, and the spectra assigned in the point-group C_s, using single crystal Raman spectra as an aid to assignment (152). The spectrum of $C_5H_5Mn(CO)_3$ has been re-examined (153), and the longstanding literature assignment (154) proved incorrect. There are too many bands for it to be said that the ring shows five-fold symmetry (in contrast to the spectra of $(C_5H_5)_2Ru$ and $(C_5H_5)_2Fe$, in which the selection rules for C_{5v} do apply). In particular, the e_2 bands become infrared-active and e_1 and e_2 both partly polarised in the Raman spectrum, as is possible in C_s, although the splitting of the 'doubly degenerate' bands is not in general resolved. The $Mn(CO)_3$ fragment can, however, be treated as if of effective C_{3v} symmetry, and the new assignments correlate well with those for the metal carbonyl fragment in $C_6H_6Cr(CO)_3$ (155). The spectrum of $C_5H_5W(CO)_3CH_3$ has been reported and assigned (156). The ν(CO) spectra have been examined of copper(I)-zeolite-carbon monoxide complexes. Coordinated CO absorbs at 2160 cm^{-1}, which shifts to 2080 on addition of ammonia. This is taken to indicate migration of Cu(I) from smaller cages into supercages on coordination of ammonia. In the presence of ethylenediamine, frequencies at 2090 and 1916 cm^{-1} occur and are attributed to terminal and bridging CO respectively (157).

The pre-resonance Raman spectra of azide complexes and of pentacarbonyls of type $W(CO)_5L$ have been studied. Pre-resonance enhancement is most marked in the M-N(azide) and M-C(carbonyl) regions (158). Resonance Raman spectroscopy leads to an assignment of the visible spectrum of the bridged acetylene complex $Fe_2(CO)_4(t\text{-}Bu_2C_2)_2$ (IX). The high iron-iron frequency of 284 cm^{-1} supports the formulation of the



(IX)

complex as containing an iron-iron double bond, but irradiating at 528 nm produces only pre-resonance enhancement of this frequency. True resonance is induced in the 531 cm^{-1} band, which is thought to be due to a metal-alkyne **stretch.** Thus the visible band is assigned as iron to alkyne charge transfer, and transitions involving the iron-iron bond are located at higher frequency (159).

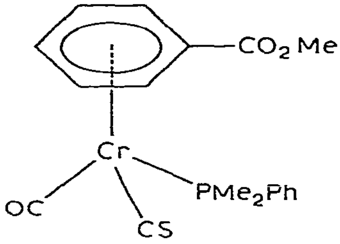
The spectra of species $C_5H_5TiX_3$, $(C_5H_5)_2MX_2$ (M=Ti, Zr, Hf) (X= Me, Hal) have been examined from 600 cm^{-1} to 50 cm^{-1}; the use of methyl complexes eliminates some problems due to band overlap. The metal-ring stretch in $C_5H_5TiCl_3$ is at 311 cm^{-1} and the 430 cm^{-1} band assigned to this mode by earlier workers (160) is in fact due to a degenerate ring tilt (161). Torsional frequency has been calculated as a function of barrier height for $(C_5H_5)_2Fe$ and $(C_6H_6)_2Cr$. Earlier estimates appear to be far too low for the accepted frequencies (162). In the infrared spectra of crystalline films of ferrocene, ruthenocene and osmocene, 'forbidden' bands occur and e_{1u}, e_{2u} modes show site group splitting. Factor group splitting is apparent in the low temperature spectrum of ferrocene, and appears more consistent with C_1 site symmetry than with C_2 (163). In an independent study, the librational modes of ferrocene and ferrocene-d_{10} were discussed, but assignment of this part of the low-temperature spectrum was regarded as not possible until the low temperature crystal structure is known (164). Assignments in other parts of the spectrum proved more tractable and accepted assignments were modified in some cases - in particular, the ring-metal-ring deformation was re-assigned from 166 to 179 cm^{-1} (165), a value confirmed in other recent work, in which Raman spectra of ruthenocene and ferrocene were compared down to 80K (166). The infrared and Raman spectra of species $(C_3H_5)_2Ni$, $(C_3H_5)_2Pd$, $(CH_2CMeCH_2)_2Ni$, $(C_3H_5)_3Rh$ and $(C_3H_5)_3Ir$ have been assigned, assuming effectively non-interacting ligands of C_s symmetry. The skeletal modes are assigned in C_{2v} for the complexes of type $(all)_2M$, and C_{3v} for the species $(all)_3M$ (167). The polarised infrared spectra of oriented films of C_5H_5NiNO and C_5D_5NiNO have been measured down to 100K. The solid state splitting indicates at least four molecules on C_s sites in a D_{2h} cell (168).

In complexes of type L_2Pd(maleic anhydride), where L is a phosphorus ligand, a more basic L causes the acyl CO frequency to shift to lower frequencies, but causes a downfield shift in the maleic anhydride proton signal (169). In complexes of the type trans-$PtCl(COR)(PPh_3)_2$, the platinum-chlorine frequency is in the range 254-272 cm^{-1}, showing the acyl group has a pronounced trans influence (170). From the vibrational spectra of the species $(C_5H_8PtCl_2)_2$, $(C_5H_8PtBr_2)_2$, and their palladium analogues (C_5H_8 = cyclopentene), it is concluded that platinum is acting as a better π-donor but a poorer σ-acceptor than palladium (171). Raman, infrared, and proton nmr spectra have been presented for a range of complexes of type $MeAuPR_3$ and Me_3AuPR_3. The vibrational spectra were analysed using the Urey-Bradley force field modified by the inclusion of some interaction constants. There is mixing of HCH and AuP modes. In $MeAuPMe_3$, there is a large negative interaction constant, i.e.

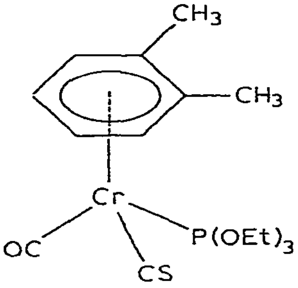
stretching the gold-phosphorus bond increases the equilibrium carbon-gold bondlength. In Me_3AuPMe_3, the two mutually *trans* methyl groups show a lower C-Au force constant than that for the group *trans* to phosphorus, and are linked by a positive interaction constant (172).

NMR SPECTRA: STATIC SYSTEMS

Nmr spectra of cyclopentadienyl compounds have been reviewed (173). The chiral complex $(C_5H_5)(C_9H_7)Ti(Cl)$ $SCHMe_2$ shows diastereotopic methyl proton resonances; indeed the conformation at titanium is stable enough for diastereomers to be separable by fractional crystallisation (174). Relatedly, proton nmr shows magnetic non-equivalence of phosphine methyl groups in (X), and of ring methyl groups in (XI) (175). Nmr spectroscopy shows that the acyls $C_5H_5Mo(PMe_2Ph)(CO)_2.COR$ exist exclusively as *trans* isomers, in contrast to the alkyl analogues which exist as a mixture of *cis* and *trans* isomers (176). Steric effects on ring orientation



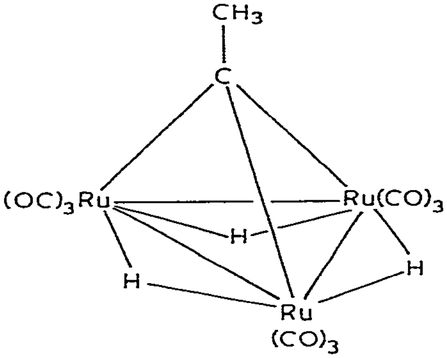
(X)



(XI)

have been studied in π-indenyl complexes of molybdenum and tungsten, using the magnetic anisotropy of the π-indenyl group as an aid to structural assignment (177). Previous reports (178) that in $C_5H_5W(CO)_3H$ the hydride ligand is effectively pseudo-axial are not supported by a closer analysis of the nematic phase proton nmr spectrum (179). The nematic phase spectrum of the cluster complex $H_3Ru_3(CO)_9CCH_3$ implies a structure (XII) in which the three hydrides are in a plane beneath the three metal atoms (180).

The proton nmr spectra of ferrocenylcarbonium ions suggest that the fulvene ligands are distorted from planarity (181) (compare (199), below). However, the long range proton couplings in the spectrum of tricarbonyliron dienes suggest a planar structure, consistent with the formulation (XIIIa); a large contribution from structures of type (XIIIb) would impose non-planarity on the σ-bonded ligand carbon atoms (182). In equilibrium studies on ferrocenylcyclohexanes substituted at position 4, nmr spectra are used to distinguish isomers. Chromatographic analysis then shows that the ferrocenyl substituent has about as much influence on conformational thermodynamics as does phenyl (183).

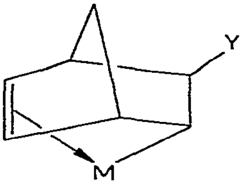


(XII)

(a) (b)

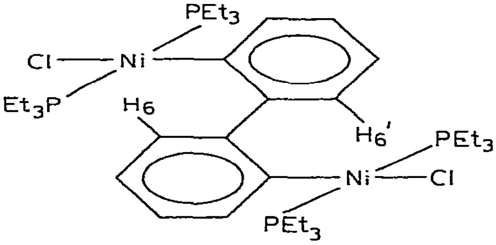
(XIII)

Norbornenyl complexes of type (XIV) have been investigated by proton and carbon-13 nmr spectroscopy. The results indicate distortion, relative to norbornenes, towards a homo-allylic system, with a high degree of carbon p character in the metal-carbon σ-bond (184). In the complex (XV), the proton signals of H(6), H(6') occur at $\tau = -2$, over 4 ppm downfield from the corresponding resonances in biphenyl; this effect is attributed to very short, formally non-bonding, hydrogen-nickel approaches (185). It has been shown for a range of cationic copper(I)-olefin complexes that chemical shifts on complexation are related to ligand denticity and coordination (186). 220 MHz nmr has been used to show nucleophilic addition of amines to olefins coordinated to platinum. Bonding occurs at the β-position, and the reaction is restricted to unhindered secondary amines of

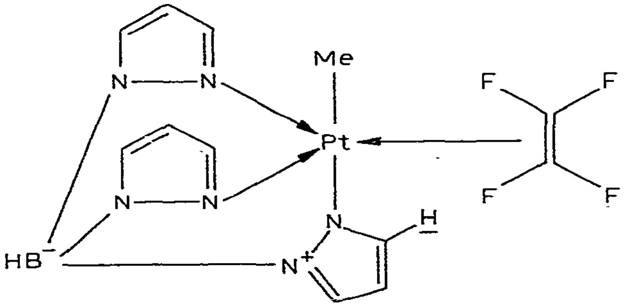


M = Pd (II), Pt (II)

(XIV)



(XV)

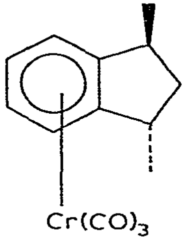


(XVI)

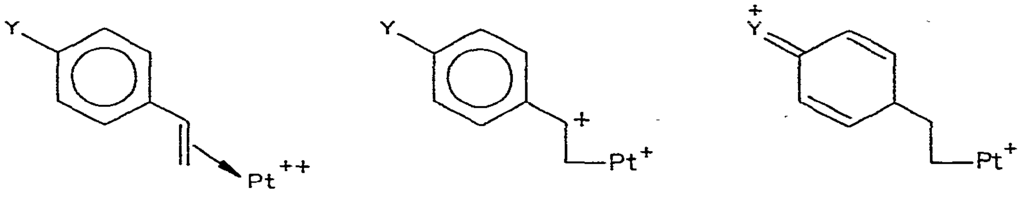
high basicity (187). The proton nmr spectra of π-allylpalladium complexes have been examined under improved resolution. It is found, for example, that the central hydrogen of $(Pd(C_3H_5)I)_2$ gives a signal split into fifteen components, which must be analysed as part of an $(AB)_2C$ system (188). The spectrum of cis-$Me_2Pt(PMe_3)_2$ is of type $(AR_3X_9)_2$, not $(AX_3)_2$ (189).

The platinum-fluorine and platinum-vinyl hydrogen coupling constants in complexes of the type $(trans\text{-}(PMe_2Ph)_2Pt(L).C(CF_3){:}CHOMe)^+$ (where L is a neutral ligand), and in the corresponding neutral species in which L has been replaced by an anionic ligand, correlate with the platinum-hydrogen coupling constants in the related methyls. These results may be explained if the variation in coupling constant is attributable in all these cases to changes in the degree of platinum 6s-character in the platinum-carbon bond (190). The hydrogen-fluorine coupling in complexes such as (XVI) is thought to take place by a through-space mechanism, and in (XVI) both methyl and H show 1:2:1 triplet structure due to coupling to two fluorine nuclei (191). Other claims for through-space coupling have proved less convincing. It had been argued (192) that the ring proton-ligand phosphorus coupling in complexes trans-$C_5H_5W(CO)_2PR_3X$ was of this type, since the ring carbon-ligand phosphorus coupling is near zero. However, the former coupling would always be positive, while the latter depends in magnitude and sign on the hybridisation at phosphorus; thus the low value of the latter does not in fact imply that through-bond interactions in such a system are negligible (193). It may be relevant that methyl proton to phosphorus coupling, in platinum(II) methyl complexes with phosphorus ligands, is positive when phosphorus and methyl are mutually cis but negative when they are trans, while the phosphorus to methyl carbon coupling is negative in all cases (194).

In $W(CO)_5PMe_2Ph$, and by implication in tungsten carbonyl phosphine complexes generally, the phosphorus-tungsten coupling constant is positive, consistent with dominance by the s-overlap term (195). The cmr (carbon-13 nmr) spectra of series of complexes of type $M(CO)_{6-n}L_n$ have been reported (M = Cr, Mo, W; $n = 1,2$). The chemical shift of CO depends on the donor capacity of L, and cis and trans groups can be distinguished. The phosphorus-carbon coupling varies with the nature of phosphine ligand in the same way as does the phosphorus-phosphorus coupling, and a common dependence on shared metal s-density is suggested. There is a general correlation between CO stretching constant and carbonyl carbon-13 chemical shift (196), confirmed by an independent study of the metal hexacarbonyls, species $W(CO)_{6-n}L_n$, and norbornadiene and arene Group VI metal carbonyl complexes; the correlation does not, however, extend to the rather different species



(XVII)



(a) (b) (c)

(XVIII)

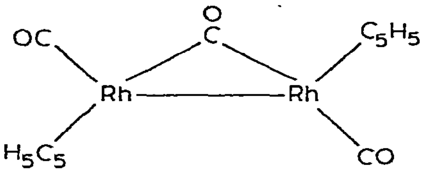
$C_5H_5W(CO)_3Me$ (197). The complex (XVII) shows a separate signal for each ring carbon atom, while the cmr spectrum of $C_3H_5Fe(CO)_3I$ gives evidence for two geometrical isomers, but $C_8H_8W(CO)_3$ is found to be fluxional (198). The cmr spectra of ferrocenylcarbonium ions $C_5H_5FeC_5H_4CHR^+$ (R = H, Me, Ph), and of their parent alcohols, have been examined, and it is concluded that the formal positive charge is delocalised over both rings (199) (compare (181) above). In *para*-substituted styrene complexes of platinum, the chemical shifts of C(1) and C(2) correlate with substituent σ_p^+, showing a significant contribution from structures (XVIII b,c) (200). The low field position of the carbene carbon signal in complexes $(OC)_5M{:}C(X)R$ (M = Cr, W; X = NH_2, OR; R = Me, Ph etc), and the strong interactions with X and with phenyl, are in accord with the view of carbene carbon as a 'stabilised carbonium ion'. Changing the solvent from chloroform to THF causes a 6-7 ppm upfield shift, attributed to donation from THF oxygen lone pair to carbene carbon. More electron-donating carbenes shift the *cis* CO group to lower field; the *trans* CO group is also affected but less markedly (201). The cmr spectra of carbene complexes of the type *cis* and *trans* $MX_2(PR_3)\overline{C.NR.CH_2.CH_2.NR}$ (M = Pd, Pt), of $Fe(CO)_4\overline{C.NR.CH_2CH_2NR}$, and of *cis*-$Cr(CO)_4(C(SMe)_2)_2$ have been reported. In the palladium and platinum complexes, the carbene carbon is deshielded as the *trans*-influence of the *trans* ligand increases (202). Rhodium-carbon coupling constants have been determined for a range of olefinic and cyclopentadienyl carbonyls. These constants are always smaller than those between rhodium and carbonyl or olefin carbon (203). The ^{13}C shielding and carbon-platinum coupling constants in complexes of type *trans*-$(MePt(AsMe_3)_2L)^+$, *trans*-$(MePt(PMe_3)_2L^+)$ have been discussed using the rehybridisation theory of nmr *trans*-influence (204). The changes in cmr spectrum of alkenes and arenes occurring on coordination to Ag(I) have been discussed (205). Cmr of coordinated CO showed the presence of three distinct types of Fe(II) in rabbits' blood; this is attributed to heterogeneity of blood proteins rather than to the existence of different sites on identical molecules (206).

From ^{19}F nmr shifts in a range of complexes, including trans-$(PMe_2Ph)_2Pt(SiPh_3)$(m- or p-C_6H_4F), it is concluded that $SiPh_3$ is a good σ-donor and also a good π-acceptor (207). The method has also been applied to a range of species of the type m- or p-$C_6H_4F.CH_2m$ (m = $C_5H_5Fe(CO)_2$, $Mn(CO)_5$, $Mn(CO)_4PPh_3$, $C_5H_5Mo(CO)_3$, $Co(CO)_3PPh_3$, $Co(III)(dmgH)_2L$, $Rh(III)(dmgH)_2L$) and to cis-$(p\text{-}C_6H_4F.CH_2)_2Pt(PEt_3)_2$. The transition metals in general appear to be good hyperconjugative donors, though Co(III) is least good and comparable to organic groups only (208). Species $Ir(C_6F_5)(CO)(PPh_3)_2XY$ (XY = eg Cl_2, Br_2, HCl, HBr), prepared by oxidative addition reactions, show five separate fluorine resonances, due apparently to restricted rotation of the C_6F_5 ring (209). The ^{55}Mn spectra have been obtained of a range of species of the type $X_3MMn(CO)_5$ (X = Cl, C_6F_5, C_6H_5; M = Ge, Sn, Pb). The large range of chemical shifts is attributed to an increase of σ-donor ability along the series $GeCl_3$, $SnCl_3$, $Sn(C_6F_5)_3$, $Si(C_6F_5)_3$, $PbPh_3$, $GePh_3$, $SiPh_3$. Line width is attributed to quadrupole splitting and is related to partial quadrupole splittings in Fe(II) Mossbauer spectroscopy. This implies a positive electric field gradient (210), in conflict with the results of calculations (211).

NMR SPECTRA: DYNAMIC SYSTEMS (see also refs. (135, 136) above)

The rearrangements of non-rigid tris-chelate complexes have been treated (212) according to the Longuet-Higgins group theory of non-rigid molecules (213). Rapid intramolecular rearrangements of 5-coordinate transition metal complexes have been reviewed (214). In the proton nmr spectra of solid ferrocene derivatives, line shapes provide evidence for ring reorientation motions (215).

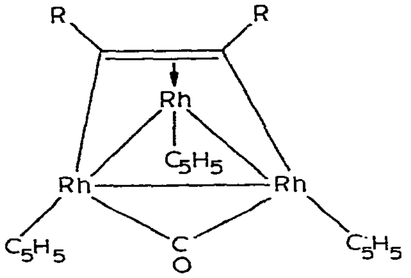
The species $C_7H_8Cr(CO)_3$ (C_7H_8 = cycloheptatriene) shows only one ^{13}CO signal at room temperature, but this splits in the expected 2:1 intensity ratio on cooling (216). In the cmr spectrum of $(C_5H_5)_2Rh_2(CO)_3$, known to have the structure XIX, the bridge and terminal CO signals have been unequivocally assigned at low temperature both by relative intensity data in the presence of the relaxation agent $Cr(acac)_3$, and by the splitting of the bridging CO signal into a triplet through coupling to two equivalent metal atoms; it is then possible to follow the interconversion of bridge and terminal CO between -60°C and 20°C (217).



(XIX)

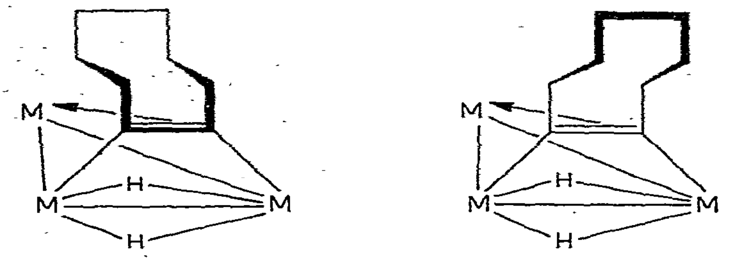
Cmr data have been presented for the isoelectronic species $(C_5H_5)_2Cr_2(NO)_4$, $(C_5H_5)_2Mn_2(CO)_2(NO)_2$, and $(C_5H_5)_2Fe_2(CO)_4$, and the crystal structure of the manganese complex reported. On average, this is centrosymmetric, with disorder of NO and CO over terminal and bridging sites. The trans-cis ratio, and the activation energies for cis-trans interconversion and for bridge-terminal interchange, fall from Cr to Mn to Fe (218). The proton and carbon nmr data for $(C_5H_5)_2Fe_2(CO)_4$, and for $(C_5H_5)_2Fe_2(CO)_2(CNMe)_2$, have been re-interpreted. All the data can be fitted to two assumptions, namely that bridges open and close only in pairs and that the rotational barriers in unbridged isomers are important. The idea of 1:1 bridge-terminal interchange is unnecessary, and incompatible with the data for $(C_5H_5)_2Fe_2(CO)_2(CNMe)_2$ (219). The idea of a significant rotational barrier is also invoked to explain results for $C_5H_5Mo(CO)_3 \cdot Mo(CO)_2(C_5H_5)(CNMe)$, which exists in solution as a mixture of non-bridged isomers and degenerate permutamers, all scrambled by unimolecular processes at room temperature. An important feature is rapid exchange of the isonitrile ligand between the two ends of the molecule, and doubly bridged species are suggested as intermediates. The solid, like $(C_5H_5)_2Mo_2(CO)_6$ itself, exists in the solid as the trans rotamer only (220).

The temperature variable cmr spectrum of $Rh_4(CO)_{12}$ has been studied in ^{13}CO-enriched samples. The structure in solution is the same as that in the solid, and collapse of the different signals towards the single peak of the high-temperature limit is uniform at all sites (221). The spectra of species $(C_5H_5)_3Rh_3(CO)(RCCR)$, shown to have the structure XX in the solid, show temperature dependence, averaging of (C_5H_5Rh) fragments occurring below room temperature for R = C_6H_5, but only above room temperature for R = C_6F_5 (222).



(XX)

The proton spectrum of $H_2Ru_3(CO)_9C_8H_{12}$ shows two distinct fluxional processes, one for interconversion of the hydrides and one for a conformational equilibrium in the ligand such as (XXIa ⇌ XXIb) (223).

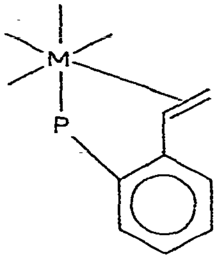


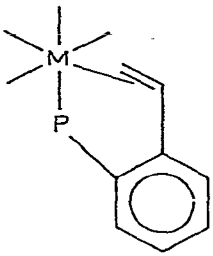
$M = Ru(CO)_3$, $Os(CO)_3$

(a) (b)

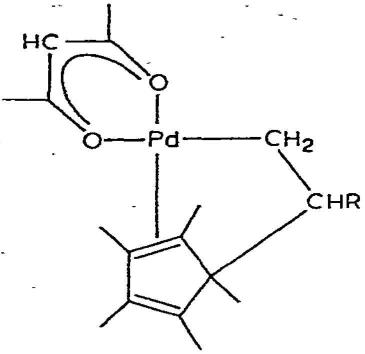
(XXI)

Fluxionality in metal phosphine hydrides has attracted attenion. Thus the species $ReH_3(dppe)_2$ and $ReH_3(dpae)_2$ (dppe is $Ph_2PCH_2CH_2PPh_2$; dpae is $Ph_2AsCH_2CH_2AsPh_2$) show low temperature hydride spectra fitting AB_2X_4 and AB_2 patterns respectively. This is consistent with two of the hydrides being in mirror-imaged positions while the third is unique. In $ReH_3(dppe)(PPh_3)_2$ the hydride signal is a triplet of triplets; thus three equivalent hydride nuclei are coupled to two distinct pairs of phosphorus atoms (224). The 8-coordinate species $ReH_5(PPh_2Et)_3$ and $ReH_5(AsPh_2Et)_3$ have also been investigated. In the arsine complex, the low temperature limit consists of four lines with intensity ratio 1:2:1:1; thus only two of the hydrides are equivalent. If we label the system as $H^aH^b{}_2H^cH^d$ (moving upfield), then between -100^oC and 30^oC one can distinguish merging of H^b and H^d, merging H^a and H^c, and finally general merging (225). Stereochemical non-rigidity has been examined in iron and ruthenium phosphine hydrides of the types H_2ML_3CO and H_2ML_4. Hydride migration is describable as a jump between faces of an ML_4 near-tetrahedron. The barriers to this process appear insensitive to the steric or electronic effects of L but are higher for ruthenium than for iron (226). The unsaturated phosphine and arsine chelates

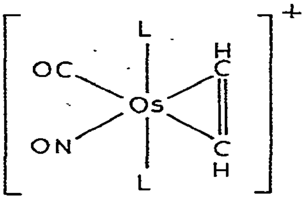

(a)


(b)

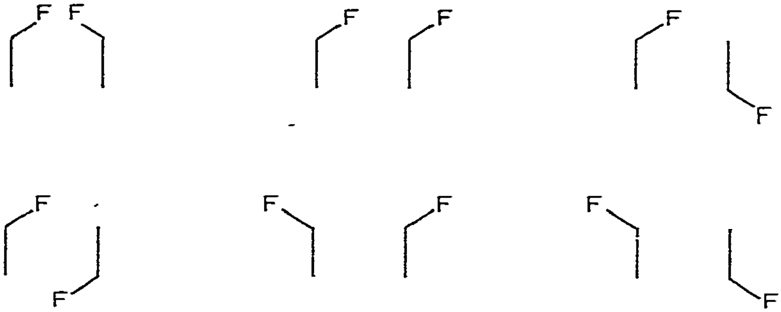
$(o\text{-}C_6H_4(EPh_2).C_2H_3)M(CO)_4$ (E = P, As; M = Mo, W) exist in two isomeric forms, presumably XXIIa and XXIIb, but the solution nmr spectrum shows only a time-averaged signal at room temperature (227). The compounds XXIII show a slightly different kind of time-averaging, in which the palladium atom confers an average plane of symmetry by moving from one double bond of the ring to the other (228). Fluxionality due to rotation of an acetylenic ligand has been reported for complexes of type (XXIV) (229), while rotation of the vinyl fluoride ligands in $C_5H_5Rh(CH_2{:}CHF)_2$ gives rise to all six isomers (XXV); rotation is less facile than in $C_5H_5Rh(C_2H_4)_2$, but is fast enough to cause time-averaging above room temperature (230). Spin-lattice relaxation in the protons of solid $ClIr(C_2H_4)_4$ between 77K and room temperature is largely due to interactions on different ligands, and is ascribed to a relatively facile 180^0 rotation of coordinated ethylene around its bond to metal (231). Dimerisation and ligand interchange have been studied by proton nmr in the complex $C_3H_5Pt(hfac)$ (hfac = $CF_3CO.CH.COCF_3$). The signal from the non-equivalent protons in the dimer is temperature dependent, and the phenomenon is attributed to the interchange of degenerate isomers XXVI(a),(b) (232). $((CH)_8)_2Ti$, known to contain h^8 and h^4 cyclooctadiene rings, shows fluxional intramolecular interchange of ligands (233). The material XXVII,



(XXIII)



(XXIV)

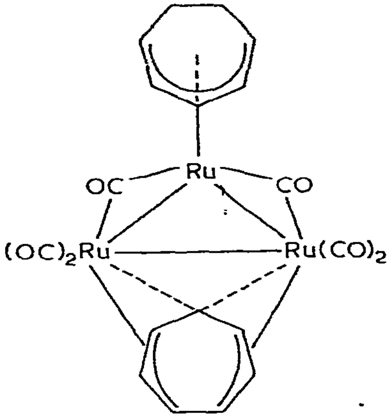


(XXV)

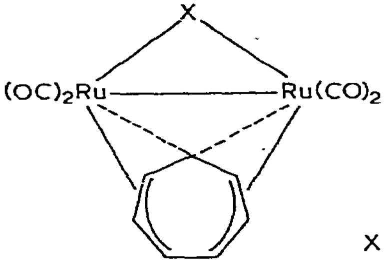
(a) (b)

(XXVI)

prepared by reaction of cycloheptatriene with $Ru_3(CO)_{12}$, contains a fluxional C_7H_7 group, mobile to –100°C, and the same is true of

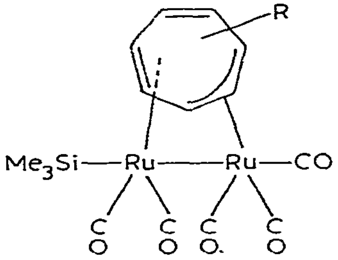


(XXVII)



X = Cl, I

(XXVIII)



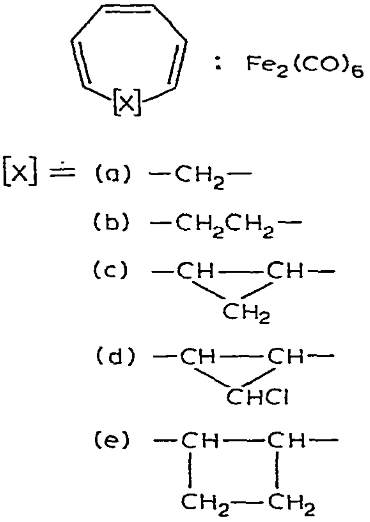
(a) R = H

(b) R = C_6H_5

(c) R = CH_3

(d) R = C_6F_5

(XXIX)

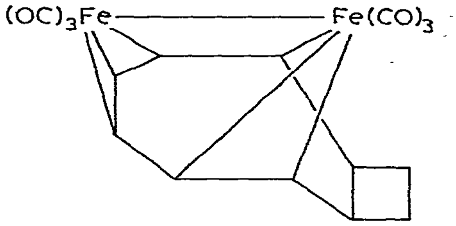


(XXX)

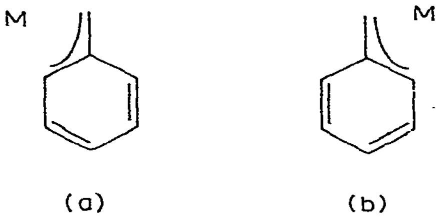
the materials XXVIII, formed from XXVII by reaction with iodine, CCl_4 or CBr_4 (234). There is reason to think that such behaviour in complexes of bridging C_7H_7 may be widespread. Reaction of $(Ru(CO)_4SiMe_3)_2$ with substituted cycloheptatrienes gives species

XXIX. In XXIX(a), derived from cycloheptatriene itself, the organic ring is mobile down to -90°C, while in the phenyl derivative XXIXb, the spectrum between -90°C and +60°C is highly temperature-dependent (235). The cmr (ring and carbonyl) spectra of the five $Fe_2(CO)_6$(triene) complexes XXX(a)-(e) have been examined. In all cases the organic ligand appears to possess a mirror plane at high temperature; this may be real, or due to time-averaging. The carbonyl ligands give two distinct signals for XXX(a),(c), but one signal only for the others. This indicates fluxional behaviour of the carbonyls, which may contribute to time-averaging in the organic ligand. In the species XXX(b),(e), at least two separate processes are involved, and these may represent separate fluxional behavious of ring and CO groups (236). The low temperature limiting spectrum of XXX(e) is consistent with the instantaneous structure XXXI, found crystallographically in the solid (237).

Cobalt phosphite methyls $CH_3Co(P(OR)_3)_4$ do not show low-temperature limiting spectra even at -160°C, but $Hg(Co(P(OMe)_3)_4)_2$ is fluxional, showing $AB_3 \rightleftharpoons A_4$ behaviour in the ^{31}P spectrum. $Co_2(P(OMe)_3)_8$ is more sterically encumbered, and is rigid up to 100°C. The π-allyls $C_3H_5Co(P(OMe)_3)_3$ and $(CH_3.CH.CH.CH_2)Co(P(OMe)_3)_3$ do not show syn-anti scrambling within the π-allyl ligands, but do show high temperature equivalence of the phosphorus atoms with low temperature limiting spectra freezing out between -90°C and -130°C to AB_2 and ABC patterns; the suggested mechanism is rotation of the allyl ligand. The π-benzyl complexes show equivalence of the two _ortho_ (and of the two _meta_) carbon atoms even at -130°, indicating that the exchange XXXII(a) $\rightleftharpoons$ (b) is fast (238). In $CH_3Co(PF_3)_4$, the methyl proton signal is a quintet, indicating



(XXXI)



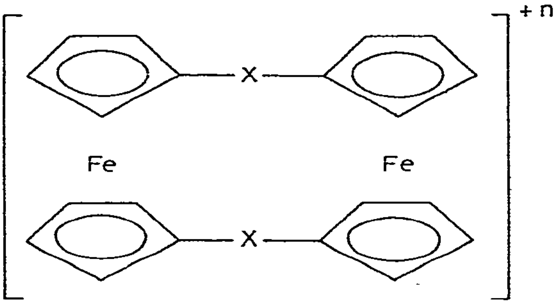
(XXXII)

scrambling of all the PF_3 ligands, while the fluorine signal is a doublet of quartets, as required for an $(A_3X)_4$ system with small AA' or XX' coupling. Incidentally, the methyl proton signal at τ8.9 indicates a low degree of polarity in the carbon-cobalt bond (239). The complexes $C_5H_5M(CO)L_2X$ (M = Mo, W; L = phosphine ligand) show temperature-variable nmr spectra; possible processes are (a) restricted rotation around metal-ligand bonds or (b) cis-trans isomerisation at the metal. The latter explanation is preferred because of effects on ring (as well as ligand) proton signals, but difficulties then remain in explaining the influence of ligand size on rate of averaging (240). Comparison of diastereotopic behaviour in systems Ph_3P-CH_2- and $Ph_3PNi(C_5H_5)-CH_2-$ suggest that in the latter, as in the former, the non-equivalence of the methylene protons is due to incipient chirality, caused by propeller-like packing of the aromatic rings attached to phosphorus (241).

In the species $(C_5H_5)_2UR$, an allyl group R is monohapto but fluxional, while an isopropyl group R shows restricted rotation around the U–R bond. The nmr spectrum of the R group shows large contact shifts, with negative spin density on the carbon atom bonded to metal (242). The spectra of the complexes $(acac)Ni(PPh_3)_2Me$ and $(acac)Ni(PPh_3)Et$ (acac = acetylacetonato) are strongly dependent on solvent. At room temperature in both complexes, the acac methyl groups are non-equivalent in benzene but equivalent in pyridine: this equivalence is frozen out in the ethyl complex below −36°C. The ethyl group of this complex gives rise to a single proton signal in benzene,acetone, THF or toluene down to −100°C, suggesting very rapid, reversible β-elimination; this process is suppressed by such strongly donating solvents as pyridine or triethylamine, in which the ethyl group gives rise to a normal A_2X_3 pattern (243).

ESR AND MAGNETIC STUDIES

The paramagnetism of solid vanadium hexacarbonyl has been studied from 4.2 to 300 K. Above 66 K, the molecules are octahedral but the $^2T_{2g}$ ground state is strongly coupled to the nuclear motions. Below 66 K, an axial distortion appears, as does magnetic pair exchange (244). The esr spectra in dilute glasses have been obtained for a range of complexes of the type $(C_5H_5)_2VX_2$ and $(C_5H_5)_2NbX_2$ (X = Cl, SCN, OCN, CN). In most cases the odd electron is in a non-bonding $d(z^2)$ orbital with some $d(x^2-y^2)$ character, but in the cyanide complexes there is delocalisation into ligand atom p-orbitals (245). The esr and nmr spectra of $(C_5H_5)Cr(C_6H_6)$ and $((C_5H_5)Cr(C_7H_7))^+$ have been examined; the results are similar to those for the isoelectronic species $(Cr(C_6H_6)_2)^{+}$ (246). The diamagnetic complex $(C_5H_5)Cr(C_7H_7)$ can be reduced in dimethoxyethane to the corresponding radical anion, the esr spectrum of which suggests that the odd electron is occupying a ligand π^*-orbital (247). However, the esr spectra of radical anions generated in this solvent from $(C_6H_6-C_5H_4)Mn(CO)_3$ and its methylated derivatives indicate considerable spin density at the metal (248). Radical anions can also be generated by reduction of the cluster compounds $RCCo_3(CO)_9$; in this case the extra electron is delocalised over the three equivalent cobalt atoms (249). Esr has been used to investigate the effect of Co gamma-irradiation on the complex $(C_6H_8)Fe(CO)_2PPh_3$ (C_6H_8 = cyclohexadiene) under various conditions. Either in 2-methyltetrahydrofuran glass (in which irradiation generates solvated electrons) or on its own, the complex gives rise to a radical anion, in which the extra electron seems to be in an iron d-orbital. Irradiation in butyl chloride followed by annealing gives a different product, formed by addition of a butyl radical to the diene (250).



(XXXIII)

The biferrocenylene dication (XXXIII; n = 2, X = nothing) has been reported as diamagnetic with two different anions by two different groups of workers (251, 252); however salts of the diferrocenylmethane dication show intermolecular but no intramolecular exchange (252).

MÖSSBAUER SPECTRA (see also (67) above)

Mössbauer spectroscopy has been widely used in the investigation of exchange phenomena in oxidised or partly oxidised species containing two ferrocenyl or ferrocenylene fragments. For example, $(PhCOC_5H_4)_2Fe$ and the diferrocenylmethane monocation (as fluoroborate) give very similar spectra, showing the iron atoms to be equivalent on the relevant time scale in the latter compound; this is in accord with ESCA results cited, but should be contrasted with magnetic data (252) for the dication and also with results (below) for the biferrocenium monocation. $(C_5H_5)_2FeBF_4$ gives a spectrum similar to that of other ferrocenium salts, although earlier workers had reported it as anomalous (253). The biferrocenylene monocation (as picrate) gives rise to only one, split, Mössbauer signal, showing again that the iron atoms are equivalent; this is in accord with the magnetic moment, which unlike that in the ferrocenium cation shows quenching of the orbital contribution (254). Equivalence in the biferrocenylene cation (this time as tri-iodide) has been confirmed; but the biferrocenium monocation gives two separate signals, implying an exchange rate less than $10^{-1}s^{-1}$. Consideration of the electronic (near ir) spectrum leads to an over-estimate of the exchange rate, and possible reasons for this are discussed (255). The large quadrupole splitting in the spectrum of the biferrocenylene dication has been ascribed to Fe-Fe interaction. The temperature dependence of the spectra of the ferrocenophane monocations (XXXIII,

$n = 1$, $X = CH_2$, CHMe) is unusual. At 300K (X = CHMe) there are distinct Fe(II) and Fe(III) signals, while at 4.2K there are three signals the third of which is ascribed to an averaged-valence species. For $X = CH_2$, the averaged valence species is in evidence even at 300K (256).

The room temperature Mossbauer spectra have been obtained of seven complexes $LFe(CO)_4$ and fifteen complexes $L_2Fe(CO)_3$. The s-electron density of the nucleus increases with π-acceptor character of L, a result explained by synergic enhancement of σ-donor power (257). In substituted iron carbonyls, the magnitude and sign of the electric field gradient at the iron nucleus are markedly affected by substituents, such as bis(diphenylphosphino)ethane, that destroy the 3-fold symmetry, but Mossbauer spectroscopy is not helpful in giving further stereochemical details (258). The ^{57}Fe spectra of the tetracarbonyliron dihalides have been re-examined, giving results differing from those of earlier work, and the ^{129}I spectrum of the di-iodide has also been analysed (259). Partial quadrupole splittings have been derived from data on series of compounds of the type $Fe(CO)_2L_2X_2$; it turns out to be necessary to postulate that the pqs of CO is sensitive to the molecular environment (260).

The ^{119}Sn spectra of series of compounds of the type $R_aX_bSn(Co(CO)_4)_n$ have been discussed. The pqs of $Co(CO)_4$ indicates it to be a poorer donor than either $Mn(CO)_5$ or $C_5H_5Fe(CO)_2$ (261). The high isomer shift of iridium in $(Ph_3P)_3Ir(CO)H$, as compared with $(Ph_3P)_3Ir(CO)CN$, is attributed to the high σ-donor power of ligand hydride (70).

Ion cyclotron resonance has been used to study reactions between neutral metal carbonyls and anionic fragments. Binuclear species produced in this way include $Cr_2(CO)_6^-$ (from $Cr(CO)_3^-$ and $Cr(CO)_6$) $Cr_2(CO)_8^-$ (from $Cr(CO)_4^-$ and $Cr(CO)_6$), $Fe_2(CO)_6^-$ (from $Fe(CO)_4^-$ and $Fe(CO)_6$) and $Ni_2(CO)_6^-$(from $Ni(CO)_3^-$ and $Ni(CO)_4$) (262). Nuclear quadrupole resonance studies on X in species $X_3SnMn(CO)_5$ (X = Cl, Br, I) have been performed both at room temperature and at 77K. The chloride and bromide appear to have similar crystal structures while the iodide shows non-equivalence of iodine atoms. The degree of ionic character in the Sn–Cl bond in species $XSnCl_3$ indicates that $Mn(CO)_5$ as X is a more electron releasing group than Cl, $Co(CO)_4$, or even, more surprisingly, n-butyl (263). The microwave spectrum of $C_4H_4Fe(CO)_3$ indicates it to be a symmetric top, with rotational constants in accord with the molecular dimensions found by electron diffraction (264). The electrical conductivity of aryl ethynyl copper(I) compounds is vastly enhanced by light, especially in the presence of dry air, which is thought to trap electrons and leave mobile holes behind (265). β-decay of $^{99}Mo(CO)_6$ gives the $^{99m}Tc(CO)_5$ radical, which reacts with $Mn(CO)_5I$ to give $ITc(CO)_5$ (266).

Polarographic oxidation experiments on bridged biferrocenes add to the information obtained from the Mossbauer and ESCA studies already mentioned. Biferrocene itself, biferrocenylene, and diferrocenylmethane all undergo two quasi-reversible one-electron oxidation steps, while biferrocenes with longer bridges show a single irreversible 2-electron step (252). In the one-electron oxidation of a range of species of type

$M(CO)_{6-n}L_n$, $E_{\frac{1}{2}}$ closely follows the apparent net donor-acceptor balance for each ligand. This is taken to be an indirect effect, since calculations do not show the metal d-electrons to be intensely delocalised even over such substituents as trimethylphosphine or CMe(OMe) (267). One electron and two electron oxidation has been studied in a range of tricarbonylchromium derivatives of substituted benzenes. The half wave potential depends on the number and nature of the substituents but not on positional isomerism, and correlates well both with $E_{\frac{1}{2}}$ for the free ligands and with the ionisation potentials both of ligands and of their complexes (268). Oxidative voltammetry has been carried out on a range of complexes of type $(C_5H_5m)_2(SR)_2$ (m = MoNO, FeCO, Co, Ni). One oxidation step is detected in all cases, a second step being detected for the iron and nickel complexes (269). Complexes of the type $((C_5H_5)_2VS_2CNR_2)^+$ show two reduction waves at a dropping mercury electrode. The first of these is fully reversible and is assigned to the placing of an electron in a non-bonding d-orbital on vanadium. The reduced species loses an $S_2CNR_2^-$ anion, in the presence of which mercury is oxidised to Hg(I), giving an $\overrightarrow{E}C\overleftarrow{E}C$ process (270):

$$((C_5H_5)_2V(IV)S_2CNR_2)^+ + e^- \rightarrow (C_5H_5)_2V(III)S_2CNR_2 \qquad E$$

$$(C_5H_5)_2V(III)S_2CNR_2 \rightarrow ((C_5H_5)_2V(III))^+ + S_2CNR_2^- \qquad C_1$$

$$S_2CNR_2^- + Hg \rightarrow Hg(I)S_2CNR_2 + e^- \qquad E$$

$$2Hg(I)S_2CNR_2 \rightarrow Hg(II)(S_2CNR_2)_2 + Hg \qquad C_2$$

The ferrocenylcarbonium ions $(C_5H_5)FeC_5H_4CRR'^+$, generated in acid from their parent alcohols, are reduced at the dropping mercury electrode. Controlled potential electrolysis establishes the mechanism as electrodimerisation of free radicals generated in an initial one-electron process (271). Diferrocenylmercury shows an anodic wave for oxidation to a monocation. Ferrocenylmercuric chloride shows two reduction waves; the first corresponds to the formation of ferrocenylmercury(I) with loss of chloride, while the second gives ferrocene and free mercury. Cymantrylmercuric chloride shows similar behaviour, as indeed do organomercuric chlorides in general (272). Mono- and disubstituted cobalticenium salts undergo two successive one-electron reduction steps, in accord with a sequence

$$(RC_5H_4)_2Co^+ \rightarrow (RC_5H_4)_2Co \rightarrow (RC_5H_4)_2Co^{-1}$$

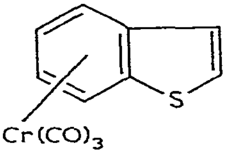
In acid, catalytic polarographic currents are observed; this is as expected if the anion is first protonated to a species $(RC_5H_4)_2CoH$. This species could then react with excess protons to give dihydrogen and regenerate the original cation (273).

Vapour pressures and triple points have been measured for the species $(C_5H_5)_3Ln$ (Ln = La-Gd) (274). A calorimetric study of the reaction of dicobalt octacarbonyl with bromine in carbon tetrachloride gives a heat of formation of solid $Co_2(CO)_8$ of -299 kcal mol^{-1}, and an estimated average metal—CO dissociation energy of 33 kcal mol^{-1}, intermediate between the accepted values for $Fe(CO)_5$ and $Ni(CO)_4$ (275). High temperature microcalorimetric studies have been carried out for the thermal decomposition, and for the reaction with iodine, of dibenzenechromium and a range of arenechromium tricarbonyls. Hexamethylbenzene is attached to the $Cr(CO)_3$ fragment with greater binding energy than is benzene (276). Relatedly, studies of competition equilibria show than an electron-releasing group Y in a potential ligand Y $C_6H_4(p).CH{=}CH_2$ increases complexation with palladium(II); the importance of ligand p (π) metal donation is thus reaffirmed (277). Similarly, complexation between silver(I) and species $XCH_2C \equiv CH$ in water-ethanol mixtures is apparently facilitated by electron-releasing groups X (278). The thermodynamics of alkene complexation to rhodium(I) in methylene chloride have been studied. The order of displacement energies for dienes is the same as that found for Pd(II), and the replacement of two monoenes by a diene is strongly exothermic (279). The use of methylene chloride is important in minimising solvation effects; thus the order of heats of complexation of various ligands to hexafluoroacetylacetonatosilver(I) in CH_2Cl_2 is

Ph_3P > cyclo-octene > 1,5-cyclooctadiene > cyclohexene > cycloheptene > cyclopentene

which is totally different from the order in better solvents.(280)

DTA/TGA studies of the thermolysis of species $(arene_2Cr)I$ indicate that in air an intermediate areneCrI is converted to Cr_2O_3, while in vacuo this same intermediate disproportionates endothermically without weight loss to CrI_2 and $(arene)_2Cr$; the latter is converted eventually to chromium metal (281). The dipole moments of substituted benzene and thiophene tricarbonylchromium complexes depend on the substituents. In general, thiophene complexes have moments 0.95D higher than their benzene analogues, a difference attributed to a high S–Cr bond moment. Dipole moment comparisons show that benzo(b)thiophene tricarbonylchromium has the structure (XXXIV) (282). Dipole moment studies on complexes $Ph_3SnFe(CO)_2(NO)L$ (L=CO, PPh_3, $AsPh_3$, $P(OPh)_3$) and $(LFe(CO)_2(NO))_2Hg$(L = $P(OPh)_3$ show L to occupy an equatorial position in the coordination trigonal



(XXXIV)

bipyramid, in marked contrast to what is known about species $Ph_3SnCo(CO)_3L$ (283).

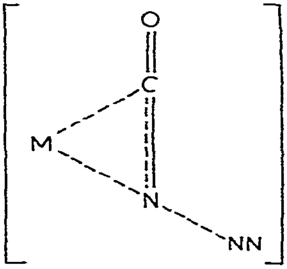
The usefulness of high speed liquid-liquid partition chromatography has been demonstrated in the separation of tricarbonyliron complexes of dienes and dienones (284).

KINETICS AND MECHANISM (See also Catalysis)

The replacement of amines from complexes $Mo(CO)_5$(amine) by phosphines in hexane obeys a two-part law. The first part is dissociation with competitive recombination. The second is kinetically second order but with very little dependence of parameters on the nature of the incoming ligand, and is suppressed in more coordinating solvents; it is attributed to a dissociative interchange in which occlusion of substrate and entering group in the same solvent cage precedes or accompanies amine loss (285). Similarly, replacement of amine in species cis $Mo(CO)_4(PPh_3)$(amine) is first order in substrate, and independent of the concentration of the entering ligand L at low L concentrations. Competition reactions give, for rate of attack on the intermediate $Mo(CO)_4PPh_3$, an order

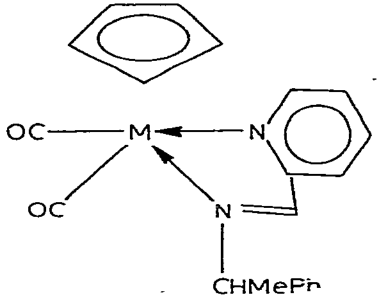
$P(OCH_2)CHCH_3 > SbPh_3 >$ piperidine $> PBu_3^n > AsPh_3 > CO$

However, even addition of CO must be rapid compared with isomerisation of the intermediate, since use of ^{13}CO leads exclusively to formation of the cis-substituted product (286). Kinetic parameters have been obtained for the reaction of $(OC)_5Cr{:}C(OMe)Ph$ with species $H\text{-}ER_3$ (E = Ge, Sn, Pb) in pyridine to give $(OC)_5CrNC_5H_5$ and $HC(OMe)PhER_3$. Again there are both first and second order components, but the first order component has a negative entropy of activation, indicating that the transition state does not involve rupture of the Cr–C bond (287). Carbenes from chromium carbonyl complexes may also be trapped by electron-demanding alkenes, giving cyclopropanes. Complexes $L^{*}Cr(CO)_4C(OMe)Ph$ (where L^{*} is optically active) give rise to optically active cyclopropanes, demonstrating that the carbene, at the moment of attack on olefin, is still coordinated (288). The displacement of dipyridyl from $W(CO)_4$dipy by phosphites shows complicated kinetics, interpreted in terms of three pathways; reversible dissociation of one nitrogen, dissociative loss of CO, and association (289). The effects of pressure on the rates of carbonyl substitution imply positive volumes of activation for the first order reactions of $Ni(CO)_4$ with $P(OEt)_3$, and of $Cr(CO)_6$ or $Mo(CO)_6$ with PPh_3, negative volumes for the reaction of $W(CO)_6$ with PPh_3 (which is second order), and a near-zero change for the second-order reaction between $Cr(CO)_6$ and the azide anion. This last result lends to the postulation of a transition state, such as XXXV, in which both bond-making and bond-loosening have occurred (290).



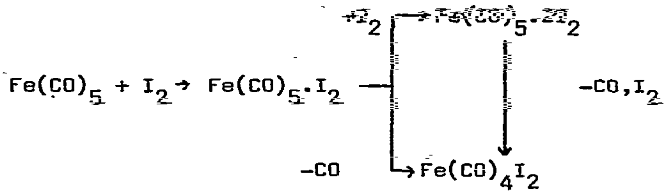
(XXXV)

Reactions of the metal hexacarbonyls and of species $W(CO)_5L$ with methyl lithium have been studied by the stopped flow method, using ether as solvent. The reactions are first order in substrate and of order 1/4 in methyl lithium, indicating pre-equilibrium between CH_3Li and $(CH_3Li)_4$, and subsequent attack by monomer on substrate. The rates are in the sequence W > Mo > Cr for the hexacarbonyls and L = $P(OPh)_3$ > L = $AsPh_3$ > L = PPh_3 for species $W(CO)_5L$. This is in marked contrast to the order Mo > W; Cr ~ 0 for S_N2 attack by phosphine ligands, and it is suggested that phosphines and methyl lithium initially attack at different sites. The dependence of the rates in the substituted tungsten carbonyls on the nature of the substituent is low, suggesting yet a different kind of initial association (291,292). Attack by amines on cations $M(CO)_4L_2^+$ (M = Mn, Re), to give complexes of type $M(CO)_3L_2 \cdot CONHR$, is second order in amine and first order in substrate, indicating a base-catalysed associative mechanism (293). The reactions of dipy$W(CO)_4$ with stannic chloride, organotin(IV) chlorides and germanium tetraiodide indicate that two successive reversible additions of oxidant to carbonyl complex occur, and are followed by other rapid steps (294). The epimerisation of the complexes XXXVI occurs by a first order process and is faster for the tungsten than for the molybdenum complex. The mechanism is



(XXXVI)

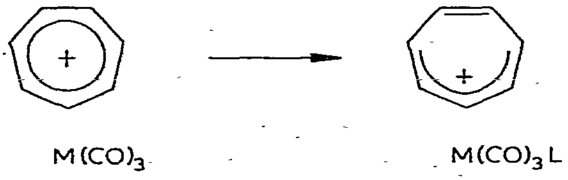
thought to be an intramolecular pseudorotation (295). The reaction between iron pentacarbonyl and iodine has been interpreted (296) in terms of a scheme



$Fe(CO)_5.I_2$ is provisionally identified with the known (297) species of this formula. Reaction of phosphine and related ligands with species $Fe_2(CO)_6$(S–org–S) is second order. The corresponding reactions of $Fe_2(CO)_6(SR)_2$ are complicated by syn–anti interconversion processes, but each of these isomers reacts with phosphine by a (presumably similar) second order mechanism. Steric effects can be understood if the entering phosphine enters the coordination shell of iron <u>cis</u> to the bridging sulphur; the reviewer notes that this is consistent with breaking of the bridge by an S_N2 edge displacement process at the metal (298). The reaction of $(C_5H_5Ni)_2(CO)_2$ with alkynes has been further examined. There are two mechanisms, one dissociative while the other is bimolecular associative; the rate of this latter process is greater with more electron–withdrawing alkynes (299).

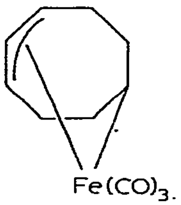
The reactions of $(Mn(CO)_4P(OPh)_3)_2$ and of $(Re(CO)_4PPh_3)_2$ with triphenylphosphite are of order 0.5 in the metal complexes, and the products show esr and ir spectra characteristic of monomeric $M(CO)_3L_2$. The rates are independent of the concentration of phosphite, and it is suggested that the slow step is loss of CO from species $M(CO)_4L$ in equilibrium with the parent dimers. Relatedly, the oxidation of dimanganese decacarbonyl is of order 1 at low concentrations of complex, but 0.5 at higher concentrations; this suggests that either dissociation of dimer to monomer, or reaction of monomer (in equilibrium with dimer) can be rate–determining, depending on conditions (300). There is an interesting correlation between the rates of reactions of this type, the estimated metal-metal force constant, and the frequency of the $M{-}M\sigma \rightarrow M{-}M\sigma^*$ band (301). The reactions of $Ru_3(CO)_{12}$ with phosphorus and arsenic donors are second order, and the rates are very highly dependent on the nature of the incoming ligand, indicating a high degree of bond-making in the transition state (302). The first product detectable is $Ru_3(CO)_9L_3$, suggesting fast-moving CO bridges in intermediate species. The behaviour of $Ru_3(CO)_{10}(NO)_2$ provides an interesting contrast. The final product is $Ru_3(CO)_8(NO)_2L_2$, with an intermediate (presumably $Ru_3(CO)_9(NO)_2L$) being detected spectroscopically. The primary substitution is dissociative and the two steps are comparable in rate (303).

The displacement of cyclo-octene from $C_5H_5Mn(CO)(CS)(C_8H_{14})$ by triphenylphosphine is first order in substrate, zero order in phosphine, and has a high positive entropy of activation; thus the process is dissociative. The alkene is more labile than in $(C_5H_5)Mn(CO)_2(C_8H_{14})$ (304). Displacement of tropylium from $C_7H_7M(CO)_3{}^+BF_4{}^-$ (M = Cr,Mo,W) by acetonitrile in, for example, 1,2-dichloroethane, is associative, in accord with the mechanism of Scheme 1 (305). The deuteration has been studied of substituted cyclopentadienylmanganese and benzenechromium carbonyls by deuterioacids. It appears that, while replacement of CO by phosphine increases the rate of proton (deuteron) uptake (presumably at

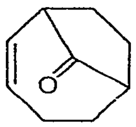


Scheme 1

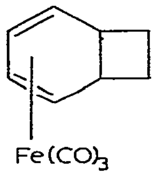
the metal), it is a separate process of hydrogen migration to ring followed by ring proton loss that controls exchange (306). Ring substituents generally lower the rate of reaction between chlorobenzene chromium tricarbonyl and thiocyanate. Complexation increases the dissociative nature of the reaction (307). The complex XXXVII reacts with phosphines by two separate mechanisms. A dissociative pathway leads to replacement of CO by phosphine, while association gives the ketone XXXVIII and $Fe(CO)_3L_2$ (308). The electrocyclic ring closure of cyclooctatriene iron tricarbonyl to XXXIX is first order and proceeds at 102°C to over 99% completion; contrast the uncomplexed species, in which cyclooctatriene is thermodynamically favoured over the bicyclic isomer (309). The reaction of methylenecyclopropanes XL(a) with $Fe_2(CO)_9$ is completely disrotatory, giving products XL(b); it is suggested on this evidence that thermal ring opening of the free ligands would be conrotatory (310).



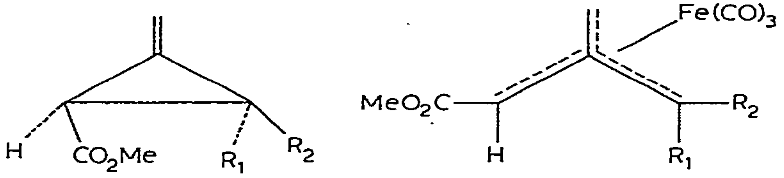
(XXXVII)



(XXXVIII)



(XXXIX)

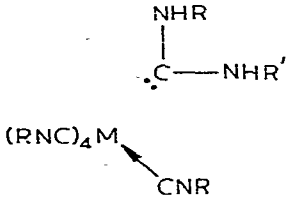


(a) (b)

(XL)

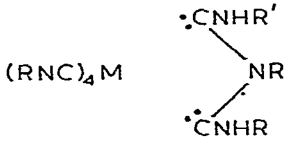
The oxidation of bis(arene)chromium or molybdenum complexes by oxygen is not slowed down by free radical reaction inhibitors, is catalysed by water although water is not essential, and is accompanied by oxidation of ligands (e.g. conversion of ethylbenzene to acetophenone) (311). The oxidation of optically active 1-methyl, 2-ethylcyclobutadiene iron tricarbonyl in the presence of dimethylmaleate leads to the formation of the expected bicyclic Diels-Alder product as a racemic mixture; this loss of chirality implies that the diene adds to the alkene only after having been released from the complex (312).

The addition of CD_3NH_2 to $((CH_3NC)_6Ru)^{++}$ to give the carbene $((CH_3NC)_5RuC(NHCH_3)(NHCD_3))^{++}$ is an example of a known reaction; heating leads to exchange between the CD_3 group of the carbene and the isonitrile. The suggested mechanism is a series of interchanges of type XLI(a) $\rightleftharpoons$ XLII(a). In the iron complexes XLII(b) scrambling is even more facile, and a similar process involving intermediates XLI(b) is invoked (313). The reaction of complexes $PtX(R)L_2$ (L = phosphine ligand) with isonitriles to give the insertion product $PtX(-C(R):NR')L_2$ proceeds via a 1:1 adduct, presumably a 5-coordinate Pt(II) complex (314). Evidence has been presented that a complex



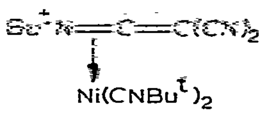
(a) M = Ru
(b) M = Fe

(XLI)

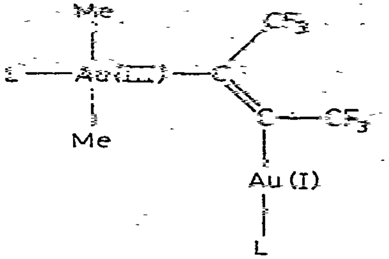


(a) M = Ru
(b) M = Fe

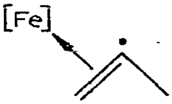
(XLII)



(XLIII)



(XLIV)



(XLV)

$Ni(N_2C(CN)_2)(CNBu^t)_3$ is an important intermediate in the reaction of dicyano-diazomethane with $Ni(CNBu^t{}_3)_4$ to give the keteneimine complex XLIII, the structure of which has been determined crystallographically. It is possible that the role of nickel is to generate and stabilise singlet dicyanocarbene, since free dicyanodiazomethane does not show stereospecificity in its addition to alkenes, and reacts in a totally different manner, not involving nitrogen loss, with free tert-butylisonitirle (315).

Halide promotes the reaction
$RCOCl + C_2H_2 + Ni(CO)_4 + H_2O \rightarrow R\text{-}\overline{C{:}CH.CH_2\text{-}CO.O} + NiClOH + 3CO$ and it is suggested (316) that a key step in the process is
$RCOCl + Ni(CO)_3X^- \rightarrow R.CO.Ni(CO)_2Cl + CO + X^-$. The addition of species L_4Ni ($L = PEt_3$, PPh_3) to <u>cis</u> or <u>trans</u> bromostyrene gives products $PhCH{:}CH.NiL_2Br$ with retention of configuration; configuration is also retained in the deuterioacidolysis or carboxymethanolysis products $PhCH{:}CHD$ and $PhCH{:}CH{:}COOMe$. Thermolysis gives bistyryl, again on the whole with retention (317). The addition of trifluoroacetic acid

to $Pd(dppe)(CF_3C{\equiv}CCF_3)$, giving $Pd(-O-COCF_3)(-C(CF_3){:}CHCF_3)$ is second order. For the corresponding triphenylphosphine complex, the kinetics are more complex; there is a dissociative pathway, and the phosphines in the product are mutually trans (318). Activation energies have been determined for the reactions

$$L_2\overline{Pt - CFXC}F_2 \rightarrow L_2Pt(X).CF{:}CF_2$$

($L = PPh_3$; X = Cl, Br). For the corresponding reactions of cis and trans CFCl:CFCl complexes, stereochemistry at carbon is retained, suggesting a mechanism (such as migration of halide within a tight ion pair) that allows formation of Pt-X and rupture of one Pt-CFX bond to be synchronous (319). The addition of methylgold(I) phosphine complexes to hexafluorobut-2-yne gives a material $(CH_3AuL)_2C_4F_6$, which decomposes to give either $LAuC(CF_3){:}C(CF_3)AuL$ and ethane, or cis-$LAuC(CF_3){:}C(CF_3)CH_3$ and CH_3AuL; the intermediate has been shown (320) to have the structure XLIV, so that the two decomposition pathways correspond to two different reductive elimination processes at the Au(III) centre.

The nature of the metallation of coordinated azobenzene has been studied by product analysis using as a probe a meta fluorine substituent (which is ortho or para to the possible substitution sites). Palladation is electrophilic, occurring mainly in the unsubstituted ring, while such metallation as does occur in the substituted ring takes place para to fluorine. Reaction of methylpentacarbonylmanganese, however, gives metallation of the carbon ortho to fluorine, and thus most activated towards nucleophiles by the inductive mechanism (321). The reaction of $IrCl(CO)(PPh_3)_2$ with species $YC_6H_4S(a)S(b)-C_6H_3(NO_2)_2$ is first order in each component and is insensitive to the nature of Y; thus we seem to have nucleophilic attack of Ir(I) on S(b) in all cases (322). The rate of attack by $Ir(Hal)(CO)L_2$ on methyl iodide increases with increasing basicity of L; it also falls with increasing atomic number of the halogen while the CO stretching frequency increases. This halogen dependence is the reverse of that found for the addition of dioxygen or dihydrogen, and it is suggested that the difference is in accord with a difference in mechanism; the attack on methyl iodide being nucleophilic (backside) attack at carbon rather than frontal oxidative insertion (323).

A theoretical treatment has been attempted of the reaction of the $Co(CN)_5^{3-}$ radical with alkyl halides. The most facile pathway found involves approach of the CX bond at an angle, rather than directly along an axis, towards the vacant metal site, and in the transition state the C–X bond is weakened by overlap with the filled d(xz) orbital (324). The reaction of $IrCl(CO)(PMe_3)_2$ with PhCHF.CH(COOEt)Br proceeds to give the same product mixture whatever the stereochemistry of the starting material, and $CH_3CHBrCOOEt$ reacts with $IrCl(CO)(PMePh_2)_2$ with loss of activity, in contrast to earlier (325) findings. Galvanoxyl inhibits. $Pt(PPh_3)_2C_2H_4$ also reacts with ethyl a-bromopropionate, destroying its optical activity, and it thus seems that reaction of a-bromoesters with low-valent transition metal complexes is quite generally a free radical process (326). Such a process could plausibly be regarded as halogen atom abstraction, and indeed a range of radicals R can be trapped as their tert-butylnitrosyl adducts in the reaction of RX with zerovalent platinum species, which in the absence of this radical trap gives finally the 'oxidation addition' products $L_2Pt(X)R$ (327). Free radicals have also been invoked in Pt-R bond cleavage, in the room temperature dark reaction of $(bipy)PtR_2$

with diethyl fumarate and tert-butylnitrosyl to give radicals $RCH(CO_2Et)CH(CO_2Et)N(O)Bu^t$ (328).

CIDNP experiments show that the $FeCl_2$ -catalysed reaction of Grignards with alkyl halides involves alkyl radical production, presumably by halogen transfer to Fe(II), but that the decomposition of the organo-iron species proceeds by non-free-radical processes (329). Bound radicals (XLV) have been suggested as intermediates in the reduction of vinyl halides and acetates to vinyl hydrides by pentacarbonyliron; the reaction proceeds most smoothly in a hydrogen atom donor solvent or in the presence of a hydrogen atom reducing agent ($Bu^n{}_3SnH$), and reaction in dry dibutyl ether followed by workup with D_2O gives no incorporation of deuterium (330).

The nmr evidence for rapid β-elimination equilibria in $(acac)Ni(PPh_3)Et$ has been discussed above; it is also relevant that in the presence of excess pyridine this complex decomposes to give $(acac)_2Ni(py)_2$, $(Ph_3P)_2NiC_2H_4$ and C_2H_6 (243). Reversible β-migration, leading to a 1-2 shift, is presumably also responsible for the quantitative first order rearrangement of $Bu^tMe_2AuPPh_3$ to the isobutyl species. The reaction is inhibited by excess phosphine, and a dissociative pre-equilibrium would appear plausible (331).

The reactions of $(C_5H_5)_2MoD_2$ with dimethyl fumarate and dimethylmaleate have been studied. The first step is cis-addition of a metal-deuterium bond across the double bond of the alkenes followed by reductive elimination of deuterium and a carbon to give stereospecifically dideuterated species $MeO_2C.CHD.CHD.CO_2Me$. Kinetic studies of these processes were complicated by the preformation of charge transfer complexes (332). The stereochemistry has also been studied of an interesting new process, oxidative carboxyethanolysis of groups attached to metal in the presence of

Cu(II). Thus reaction of cis(or trans) (phenylsulphonyl), 4-methylcyclohexane with the Fp^- (i.e. $(C_5H_5)Fe(CO)_2^-$) ion gives trans (or cis) metallo-4-methylcyclohexane; the inversion is as expected and is confirmed by the nmr of model compounds. These species react with copper(II) in ethanol to give carboxyethyl, 4-methylcyclohexane with retention. It is suggested that the first step is 1-electron oxidation of $C_5H_5Fe(CO)_2R$ to a radical cation. This process will increase the electrophilicity of coordinated CO and thus lead to an alkyl shift giving $C_5H_5Fe(CO).COR^+$ (with retention at R) followed by ethanolysis to RCOOEt (333). Reactions of species $(C_5H_5)Fe(CO)_2R$ with liquid SO_2 have been followed using changes in ν(CO) over the range $-70^\circ C$ to $-23^\circ C$. Rates decrease with increasing Taft σ^* of R and with ν(CO), except where steric effects distort. The suggested mechanism is electrophilic attack by SO_2 at R to give a tight ion pair $Fp^+SO_2R^-$, which rearranges in turn to O-sulphinate and finally S-sulphinate. The associative mechanism is in accord with the observed negative entropy of activation (334). Retention at iron in this process has been elegantly established by circular dichroism correlation studies on the reaction of $C_5H_5Fe(CO)(PPh_3)CH_2COOC_{10}H_{19}$ ($OC_{10}H_{19}$ = (-)mentholate), converted by SO_2 to $C_5H_5Fe(CO)(PPh_3)SO_2CH_2COOC_{10}H_{19}$. The mentholate serves to make possible the separation of starting material epimers, but does not affect the CD spectrum since the spectra of these epimers are mirror-images, and SO_2 insertion fails to reverse the CD spectrum (335). The mechanism of oxygen insertion into the cobalt-carbon bond of an alkyl (pyridine)cobaloxime is clearly quite different, since optical activity at C(α) is thereby destroyed (336). Metal-carbon bonds including those in species $TiCH_3Cl_3$, NiR_2(bipy),

$CrEtCl_2(py)_3$, FeR_2 (bipy)$_2$ and $CH_3Cu(PPh_3)_3$ are activated towards cleavage by aluminium trialkyls. In the case of the nickel complexes, it has been shown that the rate of cleavage is proportional to aluminium trialkyl concentration at low concentration, but excess aluminium trialkyl inhibits. These results are explained by competition between dimerisation of the aluminium alkyl and formation of a labile nickel-aluminium complex (337).

The pyrolysis of trimethylsilylmethyl copper(I), which is approximately tetrameric, gives tetramethylsilane and other products, consistent with a free radical mechanism (338), but examples of the importance of β-elimination and concerted elimination processes in the thermolysis of transition metal-carbon bonds continue to accumulate. The thermolysis of species $(C_5H_5)_3UR$ takes place with hydrogen abstraction from a cyclopentadienyl group to give RH, the configuration at C(α) of R being retained (242). Decomposition of $CH_3TiCl_3.2THF$ in d_8-toluene does indeed give CH_3D, but this very likely arises through specific abstraction from coordinated toluene. In ether-alkene mixtures, CH_3D is formed when the ether is labelled but deuterium is not abstracted from labelled alkene; thus we are dealing with a concerted reaction of the $CH_3TiO(R_D)_2$ system rather than with a free radical process. In pure $(C_2D_5)_2O$ solution, the main product is methane, CH_3D not being produced even by light, which does, however accelerate the reaction; it is suggested that the reaction is autocatalytic and binuclear (339). The reduction of activated halides RX (R = e.g. benzyl) by VCl_2Py_4 or vanodocene gives RR not RH; it is suggested that V(II) acts as an efficient trap for R radicals generated by halide abstraction from RX, or else that the reaction between V(II) and RX is an oxidative insertion, but in any case a VR bond is clearly formed and its cleavage is not a free radical process (340).

Reaction between Li_3MoPh_6 and $MoCl_3.3THF$ gives benzyne, trapped by addition to benzene (341). Thermolysis or photolysis of pyridylcobaloxime alkyls RCHR'. CHR. $Co(Dmg)_2(py)$ gives both the expected products of β-elimination, RR':CHR and $HCo(DMG)_2(py)$ (342). The reality of a reverse process, and of Co(III) π-complex formation postulated (343) to explain catalysis of rearrangements by vitamin B_{12}, has been confirmed by the conversion of $CH_2:CHOEt$ to $(Co(III))CH_2CH(OEt)_2$ or $(Co(III))CH_2CHO$ by cobalamin(III) bromide in ethanol or water, and of $CH_2:CH.OC_2H_4OH$ to $Co(III)CH_2\overline{CH.O.C_2H_4.O}$ by hydroxocobalamin in water (344). Labelling and kinetic experiments show that thermolysis of $(PhMe_2P)_2PtIMe_3$ gives $(PhMe_2P)_2PtIMe$ and ethane by a first order, intramolecular process, whose activation energy is less than the mean platinum-methyl dissociation energy (345). The thermal stability of Pt(II) dialkyls is greater when the C-Pt-C system forms part of a 5- or 6-membered ring; this effect is attributed to the unfavourable geometry for β-elimination, which nevertheless appears from product analysis to be the favoured pathway. Secondary derivatives are no less stable than primary, and the decomposition of the $Pt(II)(CH_2)_5$ ring is accelerated by added triphenylphosphine (346). Biaryls but not arenes are major products from the air oxidation of copper(I) aryls and similar results are found with lithium organocopper 'ate' complexes; thus we are dealing with concerted or near-concerted eliminations rather than with free radical processes, even, presumably, in Cu(II)-Ar bonds (347). The cleavage of ethyl-silver bonds, formed in silver triflate-catalysed decomposition of tetraethyllead, can take place by more than one mechanism. In acetic acid, the main products are ethane and silver acetate, but there is some formation of metallic silver.

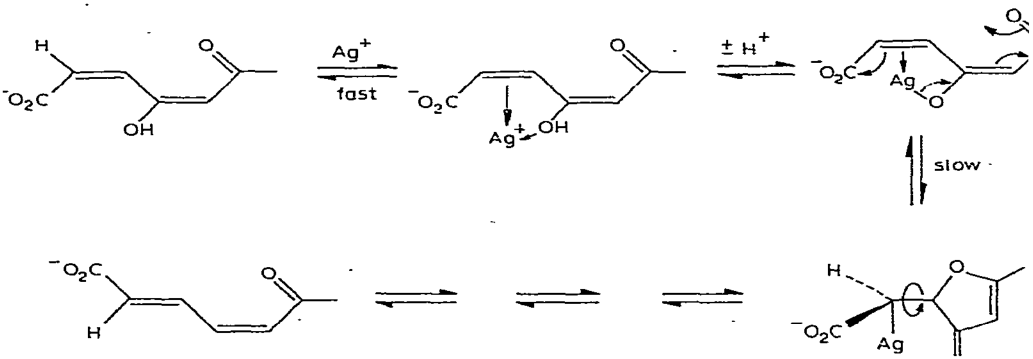
In THF butane is formed by an oxygen-insensitive concentration-dependent process, presumably bi- or polynuclear. There is some production of ethane, inhibited by oxygen, while ethylene production is unaffected, and it is suggested that the reaction has some free radical component (348). The decomposition of trans $EtMe_2AuPh_3$ in decalin gives propane, while that of the cis isomer gives a mixture of propane and ethane, thus the reductive elimination is cis. Added phosphine retards the reaction; thus elimination is in this case faster from a phosphine-free intermediate, but within this 3-coordinate intermediate the initial stereochemistry is maintained (349). The reductive elimination of ethane from species $((CH_3)_2AuL_2)^+$ is facilitated by steric crowding, i.e. by bulkier ligands L (350). The decomposition of $MeAuPPh_3$ in decalin gives ethane by a first order process retarded by triphenylphosphine; a probable slow step is loss of triphenylphosphine from the complex followed either by reversal or by a dinuclear elimination involving both complexed and phosphine-free gold methyl. The ethyl complex gives predominantly butane, but the isopropyl and tert-butyl complexes gave mainly the disproportionation products RH, R − H (351). The reaction between cobaloxime(III) alkyls and hydrated chromium (II), to give in acid the cobaltous ion, penta-aquochromium(III) alkyl, and free dimethylglyoxime, is first order in both reagents. The reaction, which is slowed down by substitution at C(α), appears to be either a true S_H2 radical transfer, or a carbanion ion transfer with linked electron transfer (352). The mechanisms of methyl group transfer between cobalt ions in various environments have been considered in terms of electrophilic, nucleophilic or radical attack on the cobalt-carbon bond. The methyl donor power of a cobalt complex depends on the other ligands in the same way as does the Co(II)-Co(III) couple. Trends in equilibria of the types

$$\text{Chel-Co(III)Me} + \text{Chel-Co(III)} \rightleftharpoons \text{Chel-Co(III)} + \text{Chel-Co(III)Me}$$

$$\text{Chel-Co(III)Me} + \text{Chel-Co(I)} \rightleftharpoons \text{Chel-Co(I)} + \text{Chel-Co(III)Me}$$

are opposed, consistent with the expectation that the former process, formal methyl anion transfer, is reductive, while the latter, formal methyl cation transfer, is oxidative (353).

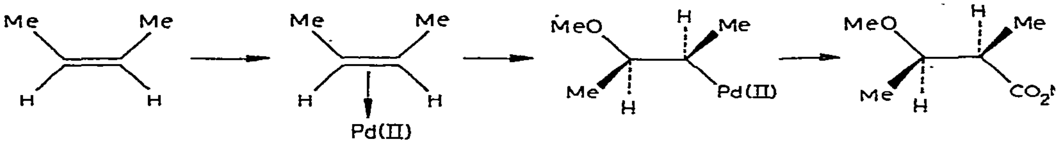
The formation of silver-carbon σ-bonds is thought to be implicated in the silver-catalysed isomerisation of a range of double-bonded species capable of enolisation (Scheme 2) (354).



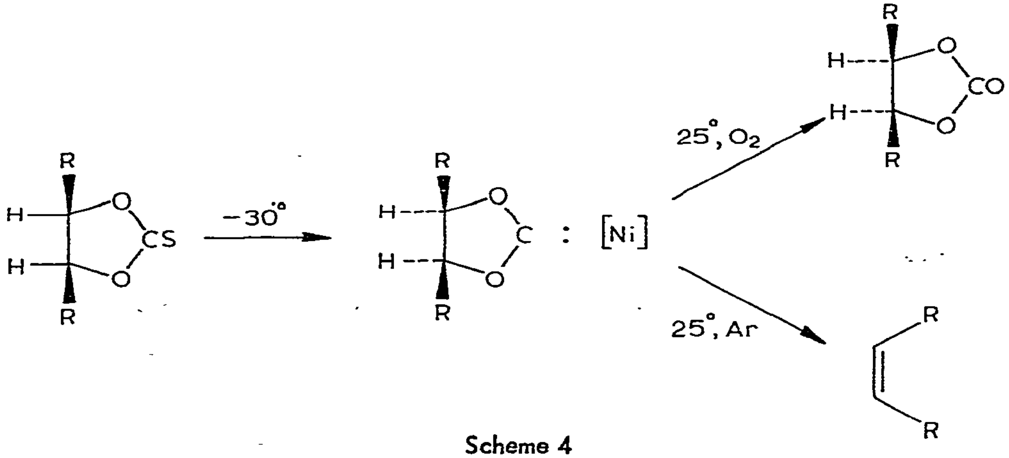
Scheme 2

Studies continue on the silver(I)-catalysed isomerisation of tricycloheptanes to bicycloheptenes, cycloheptadienes or methylenecyclohexenes. The course of reaction is markedly influenced by substituents, which seem to determine which of the strained bonds is attacked by the silver ion, and steric congestion and steric accessibility both play a part in determining the reaction pathways (355). Carbenoid intermediates, postulated in rhodium(I) - catalysed rearrangements of bicyclobutanes, have been trapped by addition to methyl acrylate. The complexed carbene is a nucleophile rather than an electrophile, being more efficiently trapped by more electronegative alkenes; this indicates extensive back-donation from metal to carbene carbon (356).

Methoxypalladation of trans-but-2-ene, followed by carbonylation and methanolysis, is stereospecific. Using the knowledge (357) that carbonylation of a palladium-carbon σ-bond takes place with retention at carbon it is possible to construct Scheme 3 for the processes involved, and it follows (358) that the initial methoxypalladation is initially trans, contrary to what had commonly been supposed. The reaction of diphenylmercury with $NBDPdCl_2$ (NBD = norbornadiene) gives XLVI, the structure of which has been established crystallographically. However, this endo- addition is not truly anomalous, since the corresponding reaction of $NBDPtCl_2$ gives NBDPtClPh(and eventually $NBDPtPh_2$), so

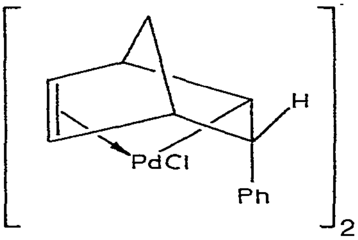


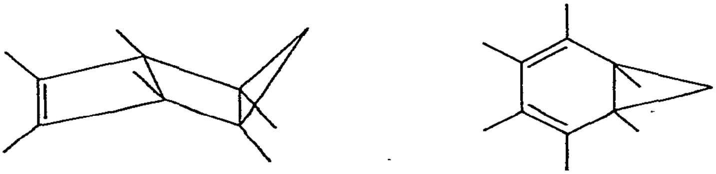
Scheme 3



Scheme 4

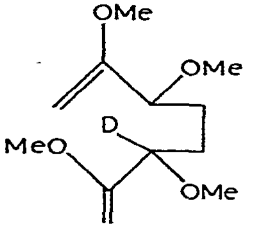
that the observed product could arise from the insertion of one part of the diene into a pre-formed Pd-Ph bond (359). The rearrangement of XLVII(a) to XLVII(b), catalysed by $(Rh(CO)_2Cl)_2$, gives in addition the carbene abstraction product C_6Me_6; the carbene can be trapped by cyclohexene. Cycloheptatrienes also show carbene elimination, and 1,6-dimethyloxepine undergoes elimination of an oxygen atom (fate unknown) to give o-xylene (360). These results clearly support the suggestion of carbene elimination in rhodium(I) - catalysed rearrangements of strained polycyclic systems. Carbene complexes are also implicated in the conversion of thiocarbonates to alkenes by $(COD)_2Ni$ (COD = 1,5-cyclooctadiene). The reaction is highly stereospecific, and if carried out in the presence of oxygen gives the carbonate, in accord with Scheme 4 (361).

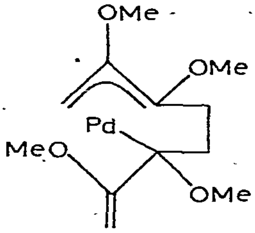



(a) (b)

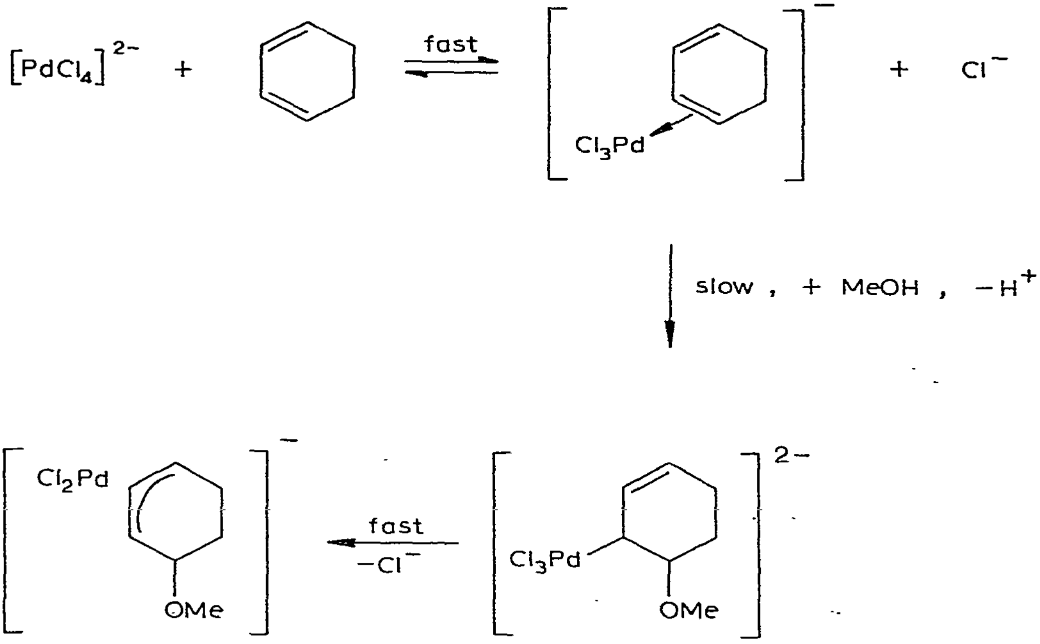
(XLVII)

The dimerisation of 2,3-dimethoxybutadiene by


(XLVIII)


(XLIX)

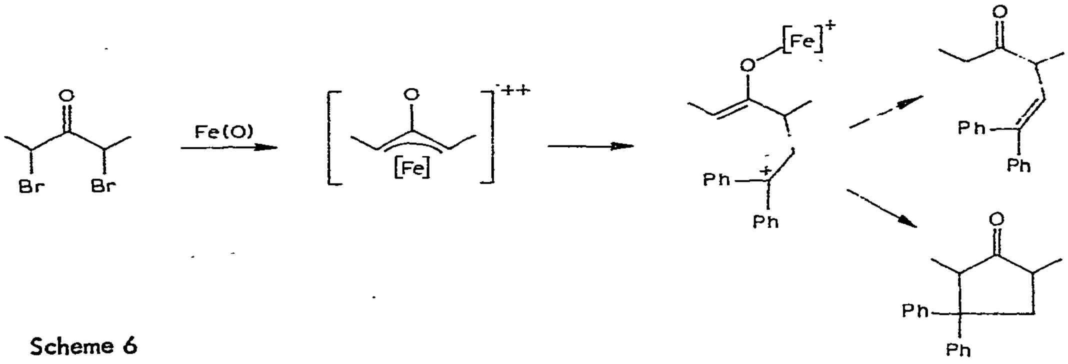
palladium(II) acetylacetonate in the presence of triphenylphosphine, with CH_3OD as solvent, gives XLVIII and isomers. This result suggests the intermediacy of such species as XLIX, and confirms the importance of protonolysis by solvent in the formation of acyclic dimers (362). The allylic complexes $CH_2CHCMe_2M(PF_3)_3$ (M = Co, Rh) isomerise on heating to anti- and syn- $CH_2CMeCHMeM(PF_3)_3$ respectively. The suggested mechanism involves the formation of h^4-2-methylbutadiene.$M(PF_3)_3H$ as intermediate (363). The kinetics have been studied of the known methoxypalladation of cyclohexadiene by tetrachloropalladate(II) in methanol and the results understood in terms of Scheme 5 (364). The reaction of h^5-cyclopentadienyl, h^3-allylnickel with triethylphosphite to give the metal tetrakis-phosphite complex obeys a third order rate law, while the corresponding palladium complex reacts with triphenylphosphite according to second order kinetics. The proposed mechanism involves addition of successive molecules of phosphite, presumably with reduction in the degree of attachment of the organic ligands and their final reductive elimination. The kinetics then indicate that for the palladium case the first phosphite addition is rate-determining, while in the nickel case it is reversible and the second addition of phosphite controls the rate (365).



Scheme 5

In support of this mechanism, low temperature nmr spectroscopy shows species of the type $h^5(C_5H_5)h^1(C_3H_5)PdL$, as well as the coupling product of the allyl and cyclopentadienyl groups, which subsequently isomerises (366).

Labelling experiments show that double bond migration induced by platinum(II) hydrides proceeds by a series of reversible anti-Markownikov additions; thus $CH_2{:}CH.CH_2OR$ is converted to $CH_2{:}CD.CH_2OR$ and to $CH_3CHDCHO$ (367). The mechanism of the $Fe_2(CO)_9$- induced coupling of α,α'- dibromoketones to alkenes has been further discussed. The process takes place with retention of olefin configuration, but this is not necessarily proof of concertedness, and the isolation of the open chain species $C_2H_5CO.CHMe.CH{:}CPh_2$ from the coupling of α,α' -dibromodiethylketone with 1,1-diphenylacetylene is consistent with Scheme 6 (368). The concept of 'a' unique mechanism for a



Scheme 6

process is of course misleading, and further confirmation of this comes from the reaction of tris(triphenylphosphine) platinum with but-2-yne to give $(Ph_3P)_2Pt(alkyne)$. This reaction occurs both by a dissociative pathway (via $Pt(PPh_3)_2$) and an associative route (via $Pt(PPh_3)_3$ alkyne) (369).

CHEMICAL RESULTS OF GENERAL INTEREST

Carbyne complexes have been prepared, in which the grouping CR acts as a three-electron donor. The crystal structure of $IW(CO)_4(CPh)$ shows a tungsten-carbyne carbon bond shorter by 26 pm than the tungsten-carbonyl carbon bonds (370). A new technique in the synthesis of organometallic complexes is reversed osmosis in which, for example, a semi-permeable membrane allows loss of a reversibly dissociated ligand. Thus $RuH_2(PPh_3)_4$ under nitrogen in a cell with membrane permeable to triphenylphosphine gives under nitrogen the known species $RuH_2(N_2)(PPh_3)_3$, and the new species $(Ph_3P)_2Ru(Cl)Cl_3Ru(N_2)(PPh_3)_2$ and $RuH(N_2)(N_3Ph_2)(PPh_3)_2$ may be similarly prepared from $RuCl_2(PPh_3)_4$ and $RuH(N_3Ph_2)(PPh_3)_3$ respectively. The extensions to the coordination of weakly held carbon ligands, and to the formation of metal-carbon σ-bonds by oxidative addition, are obvious (371).

The protonation of organometal carbonyl complexes has been studied quantitatively by ir; the order of increasing basicity is, for given L,

$C_5H_5Mn(CO)_2L < C_5H_5V(CO)_3L < C_6H_6Cr(CO)_2L < C_5H_5Re(CO)_2L$
$\lesssim C_5H_5Nb(CO)_3L$

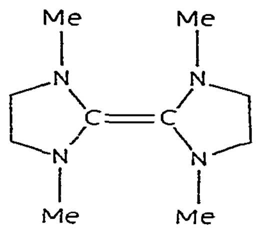
(372). CH_3SO_3F and $(CH_3)_3O^+$ can donate a methyl cation to low-valent metals in the same way as acids can donate a proton; the reaction has been demonstrated for $((Ph_2PCH_2)_3PPh)RhCl$, $Pt(PPh_3)_3$, $Ir(PPh_3)_2(CO)Cl$ and $Mo(phen)(PBu_3)_2(CO)_2$ (phen = o-phenanthroline) (373, 374). Of course, the carbonyl ligand provides a donor site independent of the metal, and has been shown by ir to function in this way in the species $Co_2(CO)_8AlBr_3$, $(C_5H_5)_2Fe_2(CO)_4(BF_3)_n$ and $(C_5H_5Fe(CO))_4(BX_3)_n$ (n = 1, 2; X = F, Cl, Br) (375). The same appears to be true on ir evidence for a whole range of species of type $(m(CO)_n)_2Mg(py)_4$ ($m(CO)_n = Co(CO)_4$, $C_5H_5Fe(CO)_2$, $Mn(CO)_5$; py = pyridine) and on X-ray evidence for the species ($m(CO)_n = C_5H_5W(CO)_3$); thus the earlier suggestion (376) that species of this kind were 'metal Grignards' with a transition metal bonded to magnesium must be revised. The reagents are nonetheless useful as a source of nucleophilic metal carbonyl anions in non-polar media; thus $(Mn(CO)_5)_2Mg(py)_4$ in toluene, unlike the $(Mn(CO)_5)^-$ ion itself in THF, reacts with triphenylsilyl chloride to give $(OC)_5MnSiPh_3$ (377). A rare example of a CO ligand linearly bridging two transition metal ions is provided by $(C_5H_5Mo(CO)_3)_2Mn(py)_4$, prepared by the reaction of $(C_5H_5Mo(CO)_3)_2Hg$ in THF with manganese metal followed by recrystallisation from pyridine (378). However, yttrium, lanthanide, and manganese 'metal Grignards', with no low-frequency CO stretching modes and where appropriate with suitable f-f spectra, have been claimed; $Mn(CO)_5Br$, $C_3H_5Fe(CO)_3I$,

$(C_5H_5Mo(CO)_3)_2$ and $C_5H_5Cr(CO)_3HgCl$ were used as starting materials (379).

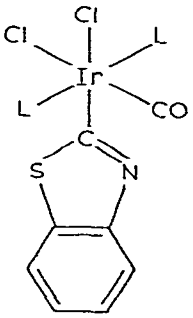
Isonitriles react with dicobalt octacarbonyl to give both ionic products $((RNC)_5Co)^+(Co(CO)_4)^-$ and covalent, CO-bridged species $(RNC)_xCo_2(CO)_{8-x}$ $(x = 1-3)$. Cyclopentadienyliron dicarbonyl dimer gives only covalent substitution products; these exist in solution as mixtures of <u>cisoid</u> and <u>transoid</u> and of CO- and RNC-bridged isomers, with bridging isonitrile less in evidence for bulkier R (380). Nitric oxide in chloroform has been investigated as an oxidising agent for carbonyl complexes; $Mo(CO)_2(dppe)_2$ undergoes a 1-electron oxidation in chloroform, while $(C_5H_5)_2Fe_2(CO)_4$ is converted to the $(C_5H_5Fe(CO)_3)^+$ cation. Relatedly $Mn(CO)_3(P(OPh)_3)_2Br$ reacts with NO in the presence of air (i.e. with NO_2) to give a simple cation by one-electron loss; but if air is excluded the product is $Mn(NO)_2(P(OPh)_3)_2Br$ (381).

The electron-rich alkene shown in fig. L, which we shall write as $(R_2C{:}CR_2)$, acts as a source of the $R_2C{:}$ carbene ligand. It is comparable with triphenylphosphine in reactivity, and able to displace CO, alkene, phosphine or halide. Species prepared include cis-$Cr(CO)_4(CR_2)_2$, $Fe(CO)_4CR_2$, $(Ir(CO)(CR_2)(PPh_3)_2)^+BF_4^-$, $(Ir(CO)(CR_2)_3)^+BF_4^-$, $(Au(CR_2)_2)^+BF_4^-$, $(NiCl(CR_2)_3)^+BF_4^-$, <u>trans</u>-$(PdCl(CR_2)(PEt_3)_2)^+BF_4^-$, $(Pt(H)(CR_2)_3)^+BF_4^-$ and $(PtCl(\sigma\text{-}C_3H_5)(CR_2)_2PPh_3)^+Cl^-$ (382). Oxidative addition of 2-chlorobenzthiazole to $IrCl(CO)(PMePh)_2$ gives LI, which is reversibly protonated to the carbene complex LII; 2-chloro-4-methylthiazole and 2-chlorobenzoxazole behave similarly, and $Pt(PhCH{:}CHPh)(PEt_3)_2$ undergoes similar oxidative additions (383).

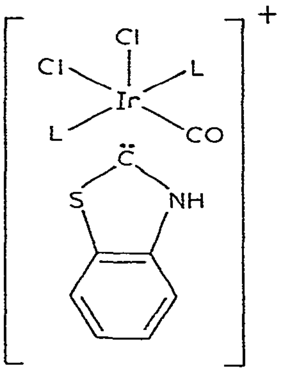
A range of monocyclic diynes, such as 1,7-cyclododecadiyne, react with $(C_5H_5)_2Ni_2(CO)_2$ and with $Co_2(CO)_8$ to give products



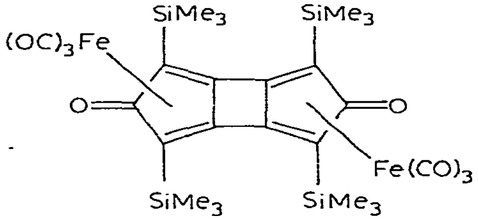
(L)



(LI)



(LII)



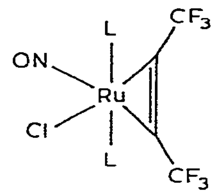
(LIII)

(diyne)(NiC_5H_5)$_2$, (diyne)(NiC_5H_5)$_4$ and (diyne) ($Co_2(CO)_6$)$_2$; in all these cases, the diyne is acting as a source of one or two bridging alkyne groups (384). The acetylene $Me_3SiCCSiMe_3$ forms complexes of the type (alkyne) $Fe(CO)_4$, (alkyne)$Co_2(CO)_6$ and (alkyne)$Mn(CO)_2C_5H_5$; the diacetylene $Me_3SiC_4SiMe_3$ gives some related derivatives, but reacts with $Fe_3(CO)_{12}$ to give LIII (385).

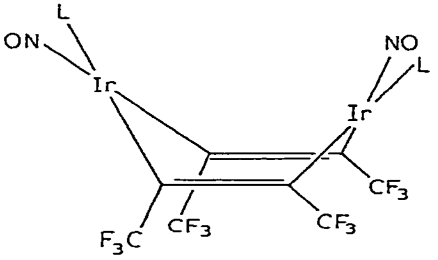
Reaction of tsm or np lithium or Grignard derivatives (tsm = trimethylsilylmethyl; np = neopentyl) with metal halides gives products $((tsm)_2M)_2(CSiMe_3)_2$ (M = Nb, Ta), np_4M (np = Ti, Zr), np_3TaCl_2 and Mo_2np_6; the products formed from VCl_4 or $VOCl_3$ are less clearly characterised (386). Species of type mCH_2Cl (m = $C_5H_5Mo(CO)_3$, $C_5H_5W(CO)_3$, $C_5H_5Fe(CO)_2$) have been prepared by nucleophilic attack on $ClCH_2I$ by m^-; they are not, however, suitable intermediates for the preparation of species mCH_2m, since nucleophilic attack would displace m^- from C in preference to displacing Cl^- from C (387).

The oxidation of species Ar.m(CO) by ceric ion in methanol ($m(CO) = C_5H_5Mo(CO)_3$, $C_5H_5W(CO)_3$, $C_5H_5Fe(CO)_2$) gives products ArCOOMe, probably by Ar-migration in intermediates $(Ar.m(CO))^+$, followed by solvent attack on $(Ar.CO.m)^+$ (388). The 2-alkynyls $mCH_2C{:}CR$ ($m = Mn(CO)_5$, $C_5H_5Fe(CO)_2$, $C_5H_5Mo(CO)_3$) react with sulphur trioxide (or, better, its dioxan adduct) to give products $m\text{-}\overline{C{:}CR.SO_2.O\text{-}C}H_2$ (389). The closely related reaction with chlorosulphonyl isocyanate, $ClSO_2NCO$, gives $m\text{-}\overline{C{:}CR.CO.N(SO_2Cl).C}H_2$, while for $m = C_5H_5Fe(CO)_2$ 2-alkenyls have been used, to give a product in which the ring is saturated (390). The acyl groups in $C_5H_5Mo(CO)_3.COR$ and $C_5H_5Fe(CO)_2.COR$ lose carbon monoxide to $Rh(PPh_3)_3Cl$, to give a mixture of products $C_5H_5M(CO)_{n-1}(PPh_3).COR$ and $C_5H_5M(CO)_nR$. The probable mechanism is loss of carbonyl CO, followed either by triphenylphosphine capture or by alkyl migration to the vacant site (391). The tricyanomethanide grouping has been introduced into a range of complexes by the use of tricyanomethane or its isomer $(NC)_2C{:}C{:}NH$, both of which react with $Pt(PPh_3)_4$ to give $(Ph_3P)_2Pt(H).C(CN)_3$. Species $(Ph_3P)_2PtX_2$ and their palladium analogues react with tricyanomethane to give products $(Ph_3P)_2M(X).C(CN)_3$. $(Ph_3P)_2Rh(CO)X$ and the iridium analogue give $(Ph_3P)_2M(CO).C(CN)_3$, but $Mn(CO)_5Br$ and $Re(CO)_5Cl$ give products $(M(CO)_3(NC)C(CN)_2)_n$, which react with triphenylphosphine to give $M(CO)_3(PPh_3)_2.N{:}C{:}C(CN)_2$ (392).

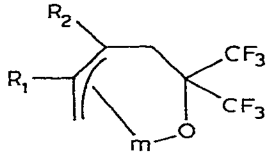
$RCl(NO)L_2$ ($L = PPh_3$, $PMePh_2$, PMe_2Ph) and $Ir(PPh_3)_3NO$ react with tetrafluoroethylene to give the isoelectronic products $RuCl(NO)L_2(C_2F_4)$ and $Ir(NO)(PPh_3)_2(C_2F_4)$. Hexafluorobut-2-yne reacts similarly with the ruthenium compounds givino products LIV, but the iridium complex gives the dimeric species LV (393).



(LIV)



(LV)



(a) m = $Fe(CO)_3$; $R_1 = R_2 =$ Me

(b) m = $(C_5H_5)Rh$; R_1 = Me ; R_2 = H

(c) m = $(C_5H_5)Rh$; R_1 = H ; R_2 = Me

(d) m = $(HO{\cdot}C(CF_3)_2 \cdot C_5H_4)$ Rh ; $R_1 = R_2 =$ Me

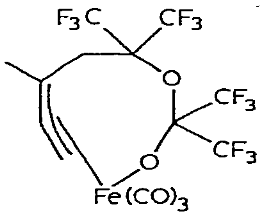
(LVI)

Coordinated hexafluorobut-2-yne undergoes reactions

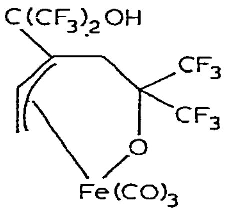
$$m(CF_3.C{:}C.CF_3) + HX \rightarrow m(X).C(CF_3){:}CHCF_3$$

(m = $(Ph_3P)_2Pt$, $(Ph_3P)_2RhCl$, $(Ph_3P)_2Ir(CO)Cl$; HX = CF_3COOH or HCl; Cl-HgCl reacts similarly to Cl-H towards the platinum complex) but the rather differently bonded species $CH_3CNW(C_4F_6)_3$ does not show the reaction (394). Hexafluoroacetone inserts into a metal-carbon bond of 2,3-dimethylbutadieneiron tricarbonyl to give LVI(a), and reacts similarly with the related species (isoprene) $Rh(C_5H_5)$ to give the isomers LVI(b,c). However, with (isoprene)$Fe(CO)_3$ the 2:1 adduct LVII was isolated, which isomerised on heating to LVIII, and with $(CH_2{:}CMe.CMe{:}CH_2)Rh(C_5H_5)$, attack on the ring and on the diene-metal bond both occur to give LVI(d) (395).

The oxidative addition of hexachlorodisilane to $Pt(PPh_3)_4$ giving



(LVII)



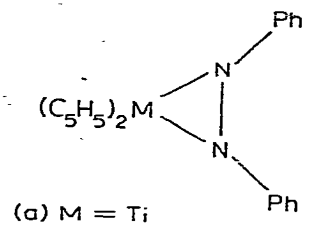
(LVIII)

$(Ph_3P)_2Pt(SiCl_3)_2$, has been confirmed; but the alleged (396) dehalogenation of this species by triphenylphosphine to a silene complex is more probably hydrolysis to $(Ph_3P)_2\overline{PtSiCl_2.O.SiCl}_2$ or a related species. Si_2Cl_6 reacts with $(C_5H_5Mo(CO)_3)_2$ to give $C_5H_5Mo(CO)_3SiCl_3$, and with $IrCl(CO)(PPh_3)_2$ to give $IrCl(CO)(PPh_3)_2(SiCl_3)_2$. Reaction with $Fe(CO)_5$ gives eventually $(Fe(CO)_4)_2(SiCl_2)_2$ (397).

The de-amination of Me_3SnNMe_2 by metal hydrides has been used to prepare species $(C_5H_5)_2Ta(H)_2SnMe_3$, $(C_5H_5)_2Mo(H)SnMe_3$ and $(C_5H_5)_2W(H)SnMe_3$; these latter are oxidised by alkyl halides to products $(C_5H_5)_2M(X)SnMe_3$ (398). A more surprising route to trimethylstannyl derivatives is the reaction between $(Me_3Sn)_3N$ or $(Me_3Sn)_2O$ and a range of dimeric metal carbonyls to give products $mSnMe_3$ ($m = C_5H_5Mo(CO)_3$, $C_5H_5Fe(CO)_2$, $C_5H_5Ni(CO)$, $Mn(CO)_5$, $Co(CO_4)$)with, it would seem, generation of N_2 or O_2 (399).

Trialkyltin phenylacetylides show a range of reaction types with metal complexes; there are examples of metathesis (with $RhCl(CO)(PPh_3)_2$ to give $Rh(C:CPh)(CO)(PPh_3)_2$ and R_3SnCl), oxidative addition (with $Ir(C:CPh)(CO)L_2$ to give $Ir(C:CPh)_2(SnMe_3)(CO)L_2$; with $Pt(PPh_3)_3$ to give $Pt(C:CPh)(SnMe_3)(PPh_3)_2$) and oxidative cleavage (with $(C_5H_5Mo(CO)_3)_2$ to give $C_5H_5Mo(CO)_3SnMe_3$) (400). Allyl trimethyltin is a novel reagent for the preparation of π-allyls from metal carbonyl halides rather than for the preparation of metal-tin bonds; π-allyls have been prepared in this way of many organometallic groupings including $Mn(CO)_4$, $Re(CO)_4$, $Fe(CO)_3I$, $C_5H_5Mo(CO)_2$, $C_5H_5Ru(CO)$ and $C_3H_5Ru(CO)_2$. The reaction may be used to give complexes of the π-indenyl and other substituted π-allyl ligands, while dimeric species such as $Mn_2(CO)_{10}$, $Co_2(CO)_8$ react to give a mixture of π-allyl complex and metal-tin compound (401).

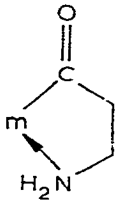
There has been considerable interest in complexes of nitrogen ligands. Sodium dicyanomethanide reacts with Group VIII chlorides to give species of type m.N:C:CH(CN), as well as the anticipated complexes $m.C(H)(CN)_2$ (402). Several complexes of the diazonium group have been prepared, in some at least of which it is acting as a 3-electron donor. Thus benzenediazonium tetrafluoroborate reacts with $Fe(CO)_3(PPh_3)_2$ to give a product $PhNNFe(CO)_2(PPh_3)_2{}^+BF_4{}^-$, in which (403) the PhNN grouping shows a CNN angle of 120°, the NNFe grouping is linear, and the phosphines occupy the axial sites in trigonal bipyramidal coordination around iron. Related species, formed by reaction of diazonium salt with a carbonyl or similar anion, followed by triphenylphosphine, are $ArN_2Fe(CO)(NO)PPh_3$ and $ArN_2Co(CO)_2PPh_3$. Reaction took place with $V(CO)_6{}^-$, $Mn(CO)_5{}^-$, $C_5H_5Fe(CO)_2{}^-$, $Ph_3SnFe(CO)_4{}^-$ and $C_5H_5Ni(CO)^-$, but the products could not be isolated (404). A complex formulated as LIX(a) is formed by the reaction between dicyclopentadienyltitanium dicarbonyl and azobenzene; this is hydrolysed to hydrazobenzene. Vanadocene adds azobenzene to give a species with one unpaired spin, formulated as LIX(b); in both cases the ease with which azobenzene can be displaced rules out ortho-metallated structures (405). While tetracarbonylcobalt hydride is known (406) to react with ethylene oxide to give $(OC)_4Co\text{-}CH_2CH_2OH$, in the reaction of aziridine with



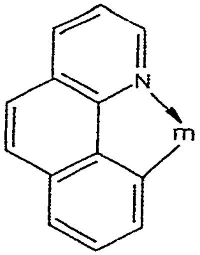
(a) M = Ti

(b) M = V

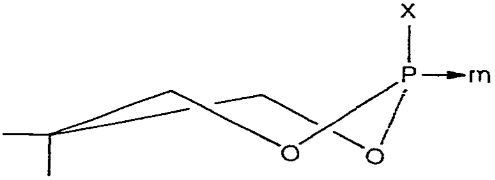
(LIX)



(LX)



(LXI)



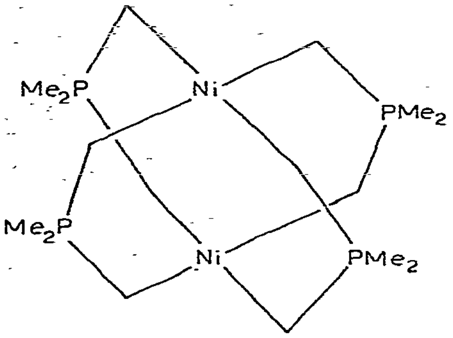
(LXII)

metal carbonyl hydrides Hm(CO) (m = $Mn(CO)_4$, $Mn(CO)_3PPh_3$, $C_5H_5Mo(CO)_2$, $C_5H_5W(CO)_2$) the presumed intermediate $m(CO).CH_2CH_2NH_2$ rearranges to give products of type LX (407). Benzo-h-quinoline (BqH) is readily metallated to give products of type MBq (LXI); thus $BqMn(CO)_4$ and $BqRe(CO)_4$ are prepared from the pentacarbonyl metal methyls, the carbonyls $M_3(CO)_{12}$ (M = Ru, Os) give products $M(CO)_2\ (Bq)_2$, and $(Rh(CO)_2Cl)_2$ gives $Bq_2Rh(III)(Cl)_2Rh(I)(CO)_2$ (408). New 'sandwich' complexes of the poly-1-pyrazolylmethane family include $(C_6H_6Ru(Pz_3CH))^{++}$, $(Ph_4C_4Co(Pz_3CH))^{+}$, and $(C_5Me_5Rh(Pz_3CH))^{++}$ (409). The mono- and dicyanocyclopentadienyl derivatives of tricarbonylmanganese and tricarbonylrhenium are analogous to the cyclopentadienyl derivatives, but species $(Me_4N)(M\ (C_5H_3(CN)_2)_3(CO)_6)$ can be prepared in which the dicyanocyclopentadienyl group bridges through nitrogens, and more extensively cyanidated rings give rise to N-bonded polymers only (410).

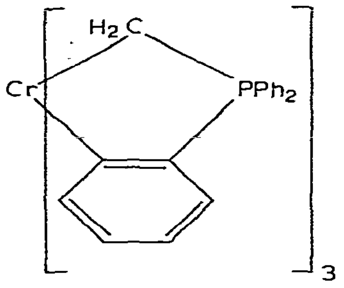
In complexes of type LXII (m = $Cr(CO)_5$, $W(CO)_5$, $Fe(CO)_4$, $Ni(CO)_3$), even when Y is fairly bulky group (cases Y = Cl, OMe, SPh, Ph, Me, NMe_2 have been studied) the ligand ring appears in all cases, from the size of the nmr coupling constants, to adopt a chair conformation with m equatorial (411). P_2H_4 gives complexes $P_2H_4(Cr(CO)_5)_2$ and $P_2H_4(Mn(C_5H_5)(CO)_2)_2$, both far less reactive than the free ligand (412). The photochemical reactions of 7,8-$B_9H_{10}CHP^-$ and the 7,9-isomer with $Fe(CO)_5$ or $Mn_2(CO)_{10}$ lead to complexes in which the phosphaborane has replaced one CO and is apparently functioning merely as a phosphine ligand (413). Trimethylphosphine ylid reacts with $(Me_3P)_2NiCl_2$ in pentane to give $(Me_3P)Ni(Cl).(CH_2.PMe_3)_2^+$, but in THF the product is LXIII (414), while in a closely related reaction the THF complex of triphenylchromium reacts with triphenylphosphine ylid to give LXIV (415).

The photochemical reactions of metal carbonyls or cyclopentadienylmetal carbonyls with the disulphides $(CF_3)_2S_2$ and $(C_6F_5)_2S_2$ give species $Mn(CO)_5SR$ and $C_5H_5Ni(CO)SR$, which readily dimerise with loss of CO, and $((C_5H_5)Fe(CO)SCF_3)_2$ as a mixture of isomers, while the hexacarbonyls of molybdenum and tungsten give the metal-metal bonded, bridged species $(M(CO)_4SR)_2$ (416). The species $(Mn(CO)_4SR)_2$ react with hexafluorobut-2-yne to give LXV, formally analogous to LXVI which is formed by reaction between hexafluorobut-2-yne and $C_5H_5Co(PF_3)_2$. In both LXV and LXVI, it has been established that the ring is attached to the metal through carbon only, the hetero atom being bent away from the C_4 plane (417).

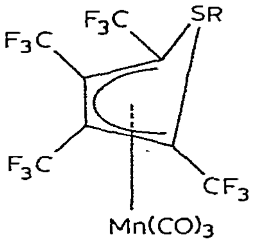
The trihalides of arsenic antimony and bismuth react with



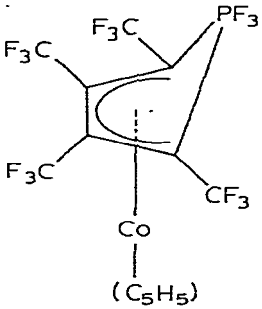
(LXIII)



(LXIV)

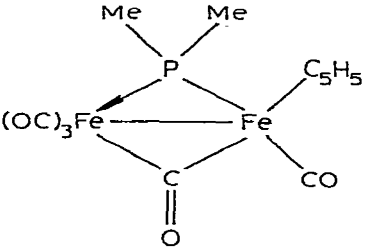


(LXV)

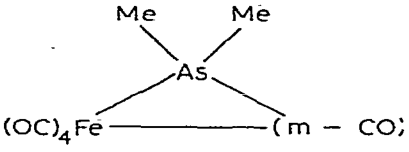


(LXVI)

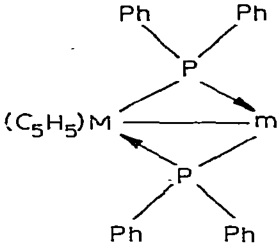
metal carbonyl anions to give a range of species of type X_2MM', and also such surprising products as $(X_2M(Fe(CO)_2C_5H_5)_2)^+$ (X = Cl, Br; M = As, Sb), $(Sb(Fe(CO)_2(NO)PPh_3)_4)^+$ and $(Sb(Co\ (CO)_3PPh_3)_4)^+$ (418). The species $(OC)_4FePMe_2Cl$ and $(OC)_3NiPMe_2Cl$ have been prepared by phosphine replacement of CO and react with $C_5H_5Fe(CO)_2^-$ to give the expected products of type $MPMe_2{-}M'$. The iron-iron complex loses CO photochemically to give LXVII(419), the structure of which has been confirmed crystallographically (420). Use of $Mn(CO)_5^-$ on $(OC)_4FePMe_2Cl$ did not lead to isolation of novel Fe–P–Mn bridged species, but $(OC)_5Cr{-}AsMe_2Cl$ reacts with $Mn(CO)_5^-$ and also other species ($C_5H_5Mo(CO)_3^-$, $Re(CO)_5^-$, $Co(CO)_4^-$, $C_5H_5Fe(CO)_2^-$) to



(LXVII)



(LXVIII)



(a) $M = Co$, $m = Fe(CO)_3$
(b) $M = Rh$, $m = Fe(CO)_3$
(c) $M = Rh$, $m = Co(C_5H_5)$
(d) $M = Rh$, $m = Rh(C_5H_5)$

(LXIX)

give products $(OC)_5CrAsMe_2{-}m$ (421), which are photochemically decarbonylated to give products LXVIII (422). A slightly different route to phosphide bridged dinuclear complexes is provided by diphenylphosphine complexes. Thus bis(diphenylphosphine) iron tricarbonyl reacts with $C_5H_5Co(CO)I_2$ to give LXIX (a), while $C_5H_5M(PPh_2H)I_2$ (M = Co, Rh) react with $I_2Fe(CO)_4$ to give LXIX (a,b). $C_5H_5Rh(PPh_2H)I_2$ reacts with $C_5H_5Co(CO)_2I_2$ to give LXIX(c), or with itself to give LXIX(d); this last reaction is shared by the cobalt and iridium analogues (423).Germanium- and tin-bridged species may be prepared by reaction sequences

$$m.Sn.Cl \rightarrow m.SnH \xrightarrow{m'2} m.Sn.m'$$

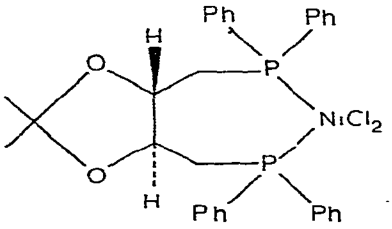
Materials so prepared include $((OC)_5Mn)_2Sn(Co(CO)_4)_2$, $(OC)_5MnSn(Ph)_2Fe(CO)_2C_5H_5$, $(OC)_5Mn.GePh_2.Co(CO)_4$, and by reaction of $(OC)_5MnGePh_2H$ with $Fe_2(CO)_9$, $(OC)_5Mn{-}GePh_2.Fe(CO)_4.GePh_2Mn(CO)_5$ (424).

CATALYSIS

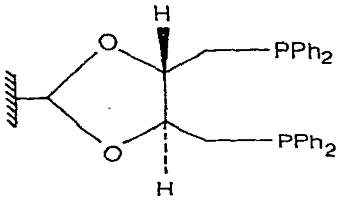
Professor Karl Ziegler has been commemorated in a series of important reviews dedicated to areas of catalysis: the 'nickel effect' in aluminium alkyl catalysis of ethylene polymerisation (425), asymmetric synthesis using homogeneous transition metal catalysts (426), allyl cobalt systems (427), and cyclo-oligomerisation using transition metal catalysts (428). Elsewhere, hydrogenation has been reviewed twice (429,430), and other review topics include catalytic olefin and CO insertion (431), transition metal-carbon compounds as catalysts for vinyl and diene polymerisation (432), addition reactions of butadiene catalysed by palladium complexes (433), and palladium(II)-catalysed isomerisation and exchange reactions in general (434).

The optically active nickel complex LXX has been used to couple stereospecifically tertiary Grignards RR'CHMgBr (used as racemic mixtures) and vinyl chloride (435). In a coming together of two growth areas of catalysis research, asymmetric polymer of type LXXI has been prepared; this polymer takes up rhodium to give an insoluble material capable of catalysing asymmetric hydrogenation and hydrosilation reactions (436).

$(C_5H_5)_2MoH_2$ is a specific catalyst for 1,2-, not total or 1,4-, hydrogenation of 1,3-dienes; the proposed mechanism is



(LXX)



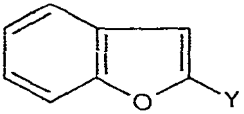
(LXXI)

1,2-addition of $H{-}Mo(C_5H_5)_2H$, followed by elimination of molybdenocene, which will add to H_2. Specificity is presumably associated with the impossibility of the diene acting as a 4-electron donor to molybdenocene. The tungsten compound is inactive as are chromocene and $(C_5H_5)_2ReH$ (437). Manganese carbonyl is a hydrogenation catalyst; it is also a hydroformylation catalyst converting cyclohexene to $C_6H_{11}CH_2OH$ or even $C_6H_{11}CH_2O.CO.H$, depending on temperature (438). $(C_6H_6)RuCl_2$ in DMF is a catalyst for the hydrogenation of alkenes and it is suggested that the active species is a benzeneruthenium hydride (439). $IrH_3(CO)PPh_3$ is a homogeneous catalyst for the hydrogenation of ethylene in DMF. The rate is proportionate to the concentrations of catalyst and ethylene. Hydrogen and triphenylphosphine inhibit; this inhibition cannot be explained solely in terms of displacement of dissociation equilibria, and is attributed at least in part to competition between the hydrogenation of complexed ethylene, and its displacement (440). Cinnamic acids are hydrogenated or deuterated by the complex $(Co(CN)_5)^{3-}$, and it is concluded from detailed studies of the processes involved that in <u>cis</u>-cinnamic acids, the first hydrogen atom transfer takes place to the α-carbon, while in the <u>trans</u> isomers it is to the β-carbon (441).

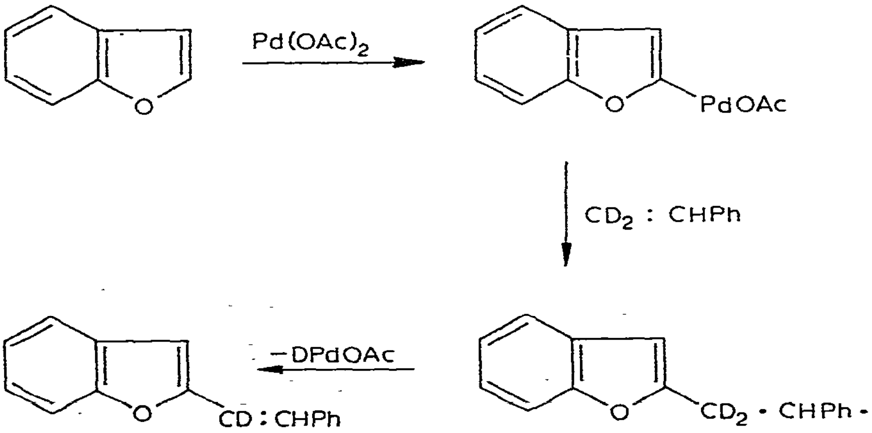
Ir(III) (introduced as chloride complex) is a homogenous catalyst for hydrogen exchange between aromatic hydrocarbons and D_2 at 130°C. Exchange is preferentially into the ring, rather than into the methyl group, of toluene, but with longer chain alkylbenzenes the terminal methyl group takes part in exchange. It is suggested that in the toluene case excessive stability reduces the catalytic activity of a π-benzyl intermediate (442).

It had been suggested (443) that some kind of charge transfer between metal and alkane was responsible for the Pt(II)-catalysed exchange of hydrogen between hydrocarbons and D_2O, but attempts to find evidence for such charge transfer have been unsuccessful (444). The isomerisation of 1,6-cyclodecadienes by rhodium complexes in ethanol has been described and it is suggested, from analysis of side-products, that the solvent is acting as a hydride source (445).

Palladium aryls are suggested intermediates in the Pd(II)-catalysed oxidative coupling of arenes, in the presence of O_2, to biaryls and other products (446). Species ArPdCl convert benzo(b)furan (LXXII, Y = H) into the 2-aryl derivative (Y = Ar). If deuterated starting material (Y = D) is used, deuterium is absent from the product, showing that no hydrogen shift occurs, while palladium acetate couples benzo(b)furan with

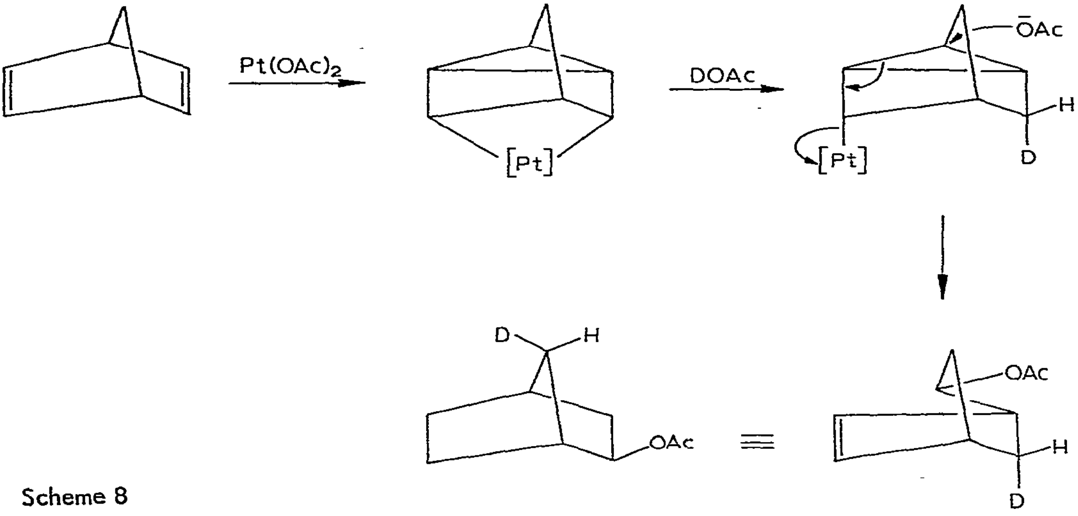


(LXXII)



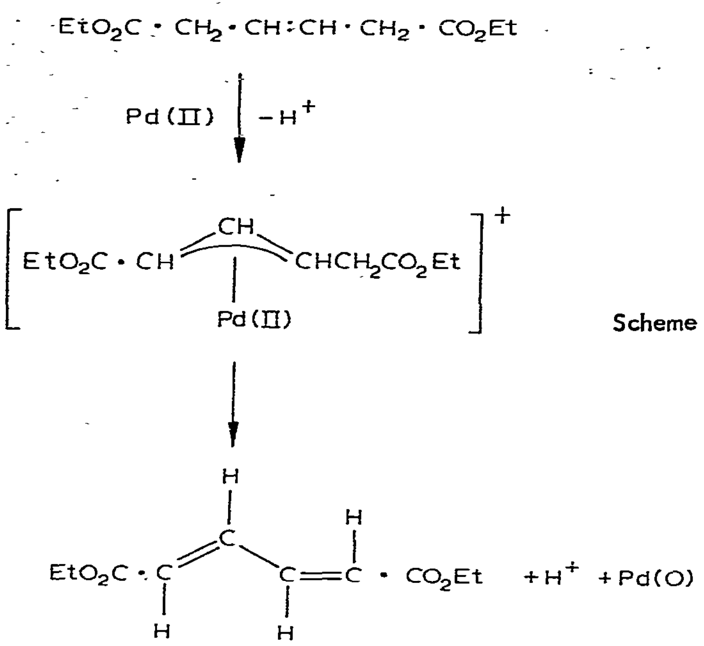
Scheme 7

styrene; labelling experiments indicate the sequence of events of Scheme 7 (447). The addition of acetic acid to norbornadiene is catalysed by bis(triphenylphosphine) palladium(II) acetate, but the reaction is far from straightforward. Addition of CH_3COOD gives an isomer quite different from that naively expected, and a reaction sequence such as Scheme 8, in which the organic skeleton rearranges, must be involved. Palladium(II) catalyses the acetolysis of dihaloethylenes and their subsequent isomerisation to 1,1- diacetates. The suggested mechanism is addition of Pd(II)-acetate, followed by elimination of Pd(II) halide (449). 3-Hexenedioate is converted by Pd(II) to <u>trans, trans</u> -2, 4-hexadienedioate, a process that can be rendered catalytic by using Cu(II) and air. The proposed mechanism (Scheme 9) is palladation of the allylic carbon, followed by formal palladium hydride loss (450).



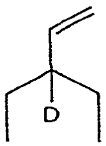
Scheme 8

The $Fe_3(CO)_{12}$-catalysed isomerisation of LXXIII to LXXIV is accompanied by positional scrambling of the deuterium label

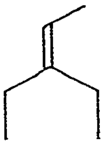


Scheme 9

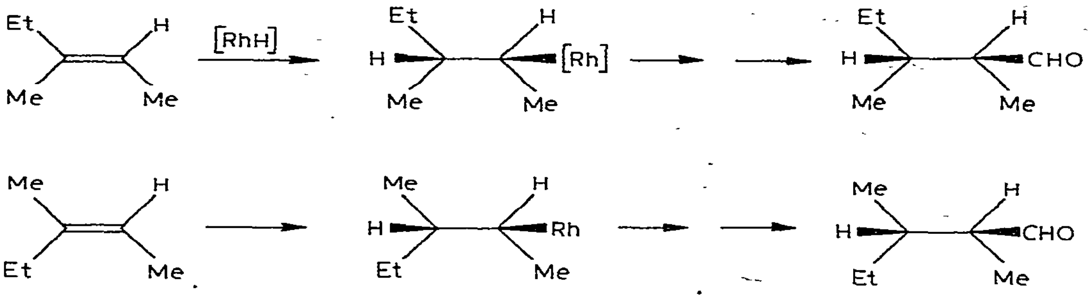
over all three terminal methyl groups, and positional scrambling has also occurred in non-isomerised starting material. There is, however, no exchange of material with isoprene. It follows that deuterium scrambling occurs by an intramolecular mechanism, and that isomerisation and its reversal are faster than release of the alkene from the iron complex within which H-(or D-) migration occurs (451). Reversible additions and eliminations of metal hydride are also important in a re-examination (452) of a purported (453) instance of metal insertion into an alkane carbon-hydrogen bond. It had already been established that



(LXXIII)



(LXXIV)



Scheme 10

attack on the methyl group occurs to a small extent in the cobalt carbonyl catalysed hydroformylation of 3-methyl-1-hexene. It is now shown that such hydroformylation is accompanied also by a shift of a deuterium label from C(3) to C(2). This can only occur by a hydride addition elimination process. Direct insertion would have left the position of the label unchanged while an allylic intermediate would have caused the label to shift to C(1) (452). Hydroformylation of 3-methylhexene-2 catalysed by $RhH(CO)(PPh_3)_3$ proceeds stereospecifically according to Scheme 10, indicating an initial cis addition of Rh-H across the double bond. A small amount of 'wrong' epimer is shown, by the occurrence of two deuterium atoms in the product when D_2 is used instead of H_2, to have arisen from isomerisation products (454). Hydroformylation of olefins using $RhCl(CO)(PPh_3)_2$ is accelerated by cyclohexenyl hydroperoxides which convert the rhodium complex into far more active $RhCl(CO)_2PPh_3$ (455).

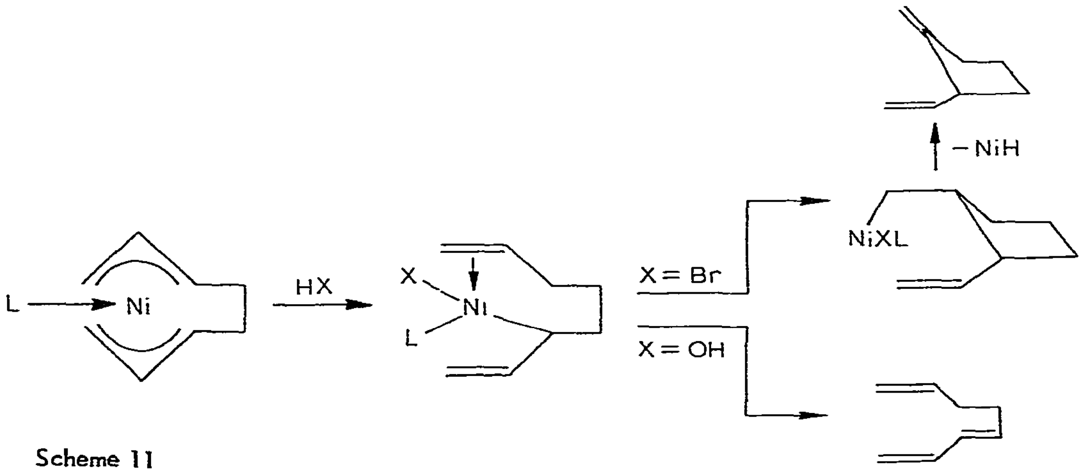
Nickel phosphine complexes can in favourable cases catalyse the conversion of aryl halides to nitriles; oxidative insertion is followed by halide-cyanide metathesis, and reductive elimination follows (456).

$$NiL_4 + ArX \rightarrow L_2Ni(X)Ar + 2L$$
$$L_2Ni(X)R + CN^- \rightarrow L_2Ni(CN)R + X^-$$
$$L_2Ni(CN)R + 2L \rightarrow L_4Ni + ArCN$$

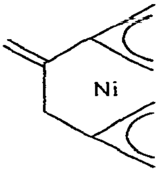
The nickel-catalysed cross-coupling of Grignard reagents into halo-olefins is stereospecific, but both cis and trans 1,2-dihaloethenes commonly give the cis-olefin (457).
It has been concluded from studies of product distribution that the active olefin dimerisation catalyst in $(Ph_3P)_2Ni(Br)(Aryl)$ systems is a nickel hydride. The system shows strong preference for ethylene over propylene, and co-dimerises ethylene and propylene, apparently by a process (458).

Ni–H + alkene → NiR; NiR + alkene → NiR' → Ni–H + alkene'

The nickel complex catalysed dimerisation of butadiene is modified by alkoxide or by hydrohalic acid according to Scheme 11 to give 1,3,7-octatriene or 2-methylenevinylcyclopentane respectively (459). The reactions of allenes with amines or species with active methylene groupings are catalysed by Ni(0) to give among other products, those derived from addition of



Scheme 11



(LXXV)

N-H or C-H across the trimerised allene fragment of the known complex LXXV (460). Ni(0) complexes catalyse the coupling of allyl halides to alkenes in the presence of CO to give a range of products, including cyclic ketones with 5-membered rings formed by CO insertion (461). Such CO insertion had been suggested earlier as a catalytically important step but had not been observed (462); it has now been demonstrated by the reaction of CO with species trans-$(Me_3P)_2Ni(X)CH_3$ to give the corresponding acyls. These acyls are decarbonylated by species of type NiL_4, which are themselves converted to $NiL_3(CO)$, and had thus (463) escaped detection in earlier work. π-allylnickel acetate is a very efficient homogeneous catalyst for the 1-4 polymerisation of butadiene, and monomer-dimer equilibrium had been postulated. This suggestion derives support from the observation, by proton and carbon-13 nmr, of such an equilibrium, in the complex 2,6-heptadienylpalladium(II) acetate. The monomer contains a pentahapto organic ligand, while the dimer contains a trihapto ligand with carboxylate bridges (464). The linear dimerisation of butadiene in the presence of palladium(II) and free acid gives 1,7-octadiene (465). Rhodium(III) in methanol catalyses the codimerisation of styrene with alkenes, especially ethylene. The suggested mechanism is addition of a rhodium hydride to styrene, to give $Rh\text{-}CHPh.CH_3$, followed by alkene insertion in the metal-carbon bond, and rhodium hydride elimination, to give 3-phenyl 1-butene (466).

Three different species $(ac)_2Os_3(CO)_8$, $(ac)_3Os_3(CO)_7$, and$(ac)_3Os_3(CO)_6$,have been isolated from the reaction mixture during the catalytic cyclisation of alkynes at $Os_3(CO)_{12}$. The last of these gives a benzene readily and is thought to contain three alkynes already linked (467). $(Ph_3P)_3Pd$ is a catalyst for the formation of anthraquinone derivatives from p-benzophenone and mono olefins. Some of the benzoquinone functions as a hydrogen abstractor, and the mono-olefin is converted to a diene which then adds to a further benzoquinone molecule (468). Copper(I) triflate, CF_3SO_3Cu, catalyses the cyclopropanation of alkenes by azo-derivatives N_2CHR. The reaction is first order in catalyst and inhibited by excess olefin, and it is presumed that reaction occurs by way of an intermediate in which both the olefin and the azo-species are bonded to copper (469). Copper(I) complexes in concentrated sulphuric acid catalyse the conversion of C_n alcohols to C_{n+1} carboxylic acids, and a species $(Cu(CO)_3)^+$ has been postulated as an intermediate (470), while the molybdenum tricarbonyl complexes of arenes have been examined as Friedel-Crafts catalysts (471). The cobalt cluster compounds $Co_3(CO)_9CY$ are free radical polymerisation initiators (472).

REFERENCES

1. F. Calderazzo, Pure Appl. Chem., 33 (1973) 453.
2. G.N. Schrauzer, Pure Appl. Chem., 33 (1973) 545.
3. M.E. Vol'pin and I.S Kolomnikov, Pure Appl. Chem., 33 (1973), 567.
4. J. Organometal. Chem., 61 (1973) C65.

5. Inorganic Syntheses XIII (1972).

6. Inorganic Syntheses XIV (1973).

7. S.J. Ashcroft and G. Beech, Inorganic Thermodynamics, Van Nostrand – Reinhold, London, 1973, chapter 5.

8. R.E. Dessy and L.A. Bates, Accounts Chem. Res., 5 (1972) 415.

9. D.R. Wiles, Adv. Organometal. Chem., 11 (1973) 207.

10. F.R. Hartley, Chem. Rev., 73 (1973) 163.

11. J.P. McCue, Coord. Chem. Rev., 10 (1973) 265.

12. A.D. Allen, R.O. Harris, B.R. Loescher, J.R. Stevens and R.N. Whiteley, Chem. Rev., 73 (1973) 11.

13. J.S. Valentine, Chem. Rev., 73 (1973) 235.

14. J.G. Verkade, Coord. Chem. Rev., 9 (1972) 1.

15. R.J. Clark and M.A. Busch, Accounts Chem. Res., 6 (1973) 246.

16. C.S. Cundy, B.M. Kingston and M.F Lappert, Adv. Organometal Chem., 11 (1973) 253.

17. (a) D.J. Cardin, B. Çetinkaya and M.F. Lappert, Chem. Rev., 72 (1972) 545.

    (b) D.J. Cardin, B. Cetinkaya, M.J. Doyle and M.F. Lappert, Chem. Soc. Rev., 2 (1973) 99.

18. F.A. Cotton and C.M. Lukehart, Prog. Inorg. Chem., 16 (1973) 487.

19. P.M. Treichel, Adv. Organometal. Chem., 11 (1973) 21.

20. H. Köhler, Z. Chem., 13 (1973) 401.

21. I.I. Kritskaya, Russian Chem. Rev., 41 (1972) 1027.

22. D.I. Hall, J.H. Ling and R.S. Nyholm, Structure and Bonding, 15 (1973) 3.

23. J.M. Pratt and P.J. Craig, Adv. Organometal Chem., 11 (1973) 332.

24. D. Dodd and M.D. Johnson, J. Organometal Chem., 52 (1973) 1.

25. B.R. Penfold and B.H. Robinson, Accounts Chem. Res., 6 (1973) 73.

26. D.O. Cowan, C. LeVanda, J. Park and F. Kaufman, Accounts Chem. Res., 6 (1973) 1.

27. E.V. Leonova and N.S. Kochetkova, Russian Chem. Rev., 42 (1973) 278.

28. M.H. Chisholm and H.C. Clark, Accounts Chem. Res., 6 (1973) 202.

29. A. Wojcicki, Adv. Organometal Chem., 11 (1973) 88.

30. R. Jira and W. Freiesleben, Organometallic Reactions, 3 (1972) 1.

31. A. Efraty, J. Organometal Chem., 57 (1973) 1.

32. C.W Bird, J. Organometal Chem., 47 (1973) 281.

33. G.H. Posner, Organic Reactions, 19 (1972) 1.

34. M.F. Semmelhack, Organic Reactions, 19 (1972) 115.

35. A.N. Nesmeyanov, M.I. Rybinskaya, L.V. Rybin and V.S.Kaganovich, J. Organometal Chem., 47 (1973) 1.

36. F. Pietra, Chem. Rev., 73 (1973) 293.

37. P.S. Braterman and R.J. Cross, Chem. Soc. Rev., 2 (1973) 271.

38. M.I. Bruce, Adv. Organometal. Chem., 11 (1973) 448.

39. N.J. Fitzpatrick and N.J. Mathews, J. Organometal. Chem., 61 (1973) C45.

40. D.A. Brown, H.L. Clarke and N.J. Fitzpatrick, J. Organometal. Chem., 47 (1973) C11.

41. P.J. Hauser, R.S Evans and A.F. Schreiner, Theor.Chimica Acta, 32 (1973) 87.

42. S. Sasaki, Theor.Chimica Acta, 30 (1973) 159.

43. J. Demuynck and A. Veillard, Theor.Chimica Acta, 28 (1973) 241.

44. M.-M. Rohmer and A. Veillard, J.C.S. Chem. Commun.,(1973) 250.

45. A. Trautwein and F.E. Harris, Theor.Chimica Acta, 30 (1973) 45.

46. K.D. Warren, J. Phys. Chem.,77 (1973) 1681.

47. A.N. Nesmeyanov, Yu. S. Nekrasov, V.F. Sizoi, O.V. Nogina, V.A. Dubovitsky and Ye. I. Sirotkina, J. Organometal. Chem., 61. (1973) 225.

48. H. Sakurai and J. Hayashi, J. Organometal.Chem., 63 (1973) C10.

49. J.E. Alsop and R. Davis, J.C.S. Dalton (1973) 1686.

50. J. Müller, G.E Herberich and H. Müller, J. Organometal. Chem., 55 (1973) 165.

51. J.R. Gilbert, W.P. Leach and J.R. Miller, J. Organometal. Chem., 49 (1973) 219.

52. F.E. Saalfeld, M.V. McDowell, J.J. DeCorpo, A.D. Berry and A.G. MacDiarmid, Inorg. Chem., 12 (1973) 48.

53. R.A. Burnham and S.R. Stobart, J.C.S. Dalton, (1973) 1269.

54. G.M. Begun and R.N. Compton, J. Chem. Phys., 58 (1973) 2271.

55. S.M. Schildcrout, J. Amer. Chem. Soc., 95 (1973) 3846.

56. J. Müller and W. Goll, Chem. Ber., 106 (1973) 1129.

57. S. Evans, J.C. Green and S.E. Jackson, J.C.S. Faraday II, 69 (1973) 191.

58. B.R. Higginson, D R. Lloyd, P. Burroughs, D.M. Gibson and A.F. Orchard, J.C.S. Faraday II, 69 (1973) 1659.

59. I.H. Hillier and V.R. Saunders, Mol. Phys., 22 (1971) 1025.

60. S. Cradock, E A.V. Ebsworth and A. Robertson, J.C.S. Dalton (1973) 22.

61. D.L. Lichtenberger, A.C. Sarapu and R.F. Fenske, Inorg. Chem., 12 (1973) 702.

62. J.A Connor, M.B. Hall, I.R. Hillier, W.N.E. Meredith, M. Barber and Q. Herd, J.C.S. Faraday (II), 69 (1973) 1677.

63. M. Barber, J.A. Connor, L.M.R. Derrick, M.B. Hall and I.H. Hillier, J.C.S. Faraday (II), 69 (1973) 559.

64. R. Gleiter, R. Seeger, H. Binder, E. Fluck and M. Cais, Angew. Chem. Internat. Edn., 11 (1972) 1028.

65. H. Binder and Ch. Elschenbroich, Angew. Chem. Internat. Edn., 12 (1973) 659.

66. S. Pignataro, A. Foffani and G. Distefano, Chem. Phys., Letters, 20 (1973) 350.

67. G.W. Grynkewich, B.Y.K. Ho, T.J. Marks, D.L. Tomaja and J.J. Zuckerman, Inorg. Chem., 12 (1973) 2522.

68. D. Briggs, D.T. Clark, H.R. Keable and M. Kilner, J.C.S. Dalton, (1973) 2143.

69. H. Binder and D. Sellmann, Angew. Chem. Internat. Edn., 12 (1973) 1017.

70. F. Holsboer, W. Beck and H.D. Bartunik, Chem. Phys. Letters, 18 (1973) 217.

71. C.A. Tolman, W.M. Riggs, W.J. Linn, C.M. King and R.C. Wendt, Inorg. Chem.,12 (1973) 2770.

72. F A. Cotton, W.T. Edwards, F.C. Rauch, M.A. Graham, R.N. Perutz and J.J. Turner, J. Coord. Chem., 2 (1973) 247.

73. D. Walther and R. Hallpap, Z. Chem., 13 (1973) 387.

74. B. Reichman and L. Eliezer, J. Chem. Phys., 59 (1973) 5219.

75. J. Thomson and M.C. Baird, Can. J. Chem., 51 (1973) 1179.

76. M.D. Rowe and A.J. McCaffery, J. Chem. Phys., 59 (1973) 3786.

77. A. Streitweiser, Jr., and C.A. Harmon, Inorg. Chem., 12 (1973) 1102.

78. D G. Karraker, Inorg. Chem., 12 (1973) 1105.

79. P.L. Pauson and J.A. Segal, J. Organometal. Chem., 63 (1973) C13.

80. B.I. Swanson and S.K. Satija, J.C.S. Chem. Commun.,(1973) 40.

81. O. Crichton, M. Poliakoff, A.J. Rest and J.J. Turner, J.C.S. Dalton, (1973) 1321.

82. A.J. Rest, cited in (81).

83. M. Poliakoff and J.J. Turner, J.C.S. Dalton, (1973) 1351.

84. J.M. Kelly, H. Hermann and E. Koerner von Gustorf, J.C.S. Chem. Commun.,(1973) 105.

85. J.K. Burdett, J.C.S. Chem. Commun., (1973) 763.

86. J.D. Black and P.S. Braterman, J. Organometal. Chem., 63 (1973) C19.

87. O.L. Chapman, J. Pacansky and P.W. Wojtkowski, J.C.S. Chem. Commun., (1973) 681.

88. J.D. Black, M.J. Boylan, P.S. Braterman and W.J. Wallace, J. Organometal. Chem., 63 (1973) C21.

89. O. Crichton and A.J. Rest, J.C.S. Chem. Commun.,(1973) 407.

90. S.A Hallock and A. Wojcicki, J. Organometal.Chem.,54 (1973) C27.

91. M. Wrighton and D. Bredesen, J. Organometal.Chem., 50 (1973) C35.

92. C.H. Bamford and S. U. Mullik, J.C.S. Faraday I, 69 (1973) 1127.

93. R.C. Job and M.D. Curtis, Inorg. Chem., 12 (1973) 2510.

94. R.C. Job and M.D. Curtis, Inorg. Chem., 12 (1973) 2514.

95. T.G. Attig, P. Reich-Rohrwig and A. Wojcicki, J. Organometal. Chem., 51 (1973) C21.

96. J.J. Alexander, private communication, cited in (95).

97. L.H. Ali, A. Cox and T.J. Kemp, J.C.S. Dalton, (1973) 1475.

98. D.M. Allen, A. Cox, T.J. Kemp and L.H. Ali, J.C.S. Dalton, (1973) 1899.

99. T. Ishigami, T. Akiyama, H. Watanabe, T. Kato and A. Sugimori, J.C.S. Chem. Commun., (1973) 871.

100. J.K. Hurst and R.H. Lane, J. Amer. Chem. Soc., 95 (1973) 1703.

101. C. Giannotti and B. Septe, J. Organometal. Chem., 52 (1973) C36.

102. W. Strohmeier, J. Organometal. Chem., 60 (1973) C60.

103. M. Wrighton and M.A. Schroeder, J. Amer. Chem. Soc., 95 (1973) 5764.

104. G.A. Ozin and A. Vander Voet, Accounts Chem. Res., 6 (1973) 313.

105. F.W.S Benfield, M.L.H. Green, J.S. Ogden and D. Young, J.C.S. Chem. Commun., (1973) 866.

106. P.S. Skell, D.L. Williams-Smith and M.J. McGlinchey, J. Amer. Chem. Soc., 95 (1973) 3337.

107. R. Middleton, J.R. Hull, S.R. Simpson, C.H. Tomlinson and P.L. Timms, J.C.S. Dalton, (1973) 120.

108. K.J. Klabunde and J.Y.F. Low, J. Organometal. Chem., 51 (1973) C33.

109. J.L. Slater, T.C. DeVore and V. Calder, Inorg. Chem., 12 (1973) 1918.

110. J.H. Darling and J.S. Ogden, J.C.S. Dalton, (1973) 1079.

111. E.P. Kündig, D. McIntosh, M. Moskovits and G.A. Ozin, J. Amer. Chem. Soc., 95 (1973) 7234.

112. L.W. Yarbrough II, G.V. Calder and J.G. Verkade, J.C.S Chem. Commun., (1973) 705.

113. E.P. Kündig, M. Moskovits and G.A. Ozin, Can. J. Chem., 51 (1973) 2737.

114. M. Moskovits and G.A. Ozin, J. Chem. Phys., 58 (1973) 1251.

115. H. Huber, E.P. Kündig, M. Moskovits and G A. Ozin, J. Amer. Chem. Soc.,95 (1973) 332.

116. D.W. Green, J. Thomas and D M. Gruen, J. Chem. Phys., 58 (1973) 5453.

117. N.N. Greenwood, E.J.F. Ross and B.P. Straughan, Index of Vibrational Spectra of Inorganic and Organometallic Compounds, Butterworths, London, Vol. I, 1972.

118. D.M. Adams, W.S. Fernando and M.A. Hooper, J.C.S. Dalton, (1973) 2264.

119. B.I. Swanson, L.H. Jones and R.R. Ryan, J. Mol. Spectrosc., 45 (1973) 324.

120. A.D. Cormier, J.D. Brown and K. Nakamoto, Inorg. Chem., 12 (1973) 3011.

121. L.H. Jones, R.S. McDowell and B.I. Swanson, J. Chem. Phys., 58 (1973) 3757.

122. D.K. Ottesen, H.B. Gray, L.H. Jones and M. Goldblatt, Inorg. Chem., 12 (1973) 1051.

123. L H. Jones, Inorg. Chem., 7 (1968) 1681.

124. R.T. Jernigan, R.A. Brown and G.R. Dobson, J. Coord. Chem.,2 (1972) 47.

125. S. Kh. Samvelyan, V.T. Aleksanyan and B.V. Lokshin, J. Mol. Spectrosc., 48 (1973) 47.

126. S. Kh. Samvelyan, B.V. Lokshin and V.T. Aleksanyan, J. Mol. Spectrosc., 48 (1973) 566.

127. C.L. Hyde and D.J. Darensbourg, Inorg. Chem.,12 (1973) 1075.

128. J.R. Johnson, R.J. Ziegler and W.M. Risen, Jr., Inorg. Chem., 12 (1973) 2349.

129. W.T. Wozniak and R.K. Sheline, J. Inorg.Nucl. Chem., 35 (1973) 1199.

130. G. Sbrignadello, G. Bor and L. Maresca, J. Organometal. Chem., 46 (1972) 345.

131. G. Sbrignadello, G. Tomat, L. Magon and G. Bor, Inorg. Nucl. Chem. Letters, 9 (1973) 1073.

132. G. Bor, G. Sbrignadello and G. Natile, J. Organometal. Chem., 56 (1973) 357.

133. G. Bor, G. Sbrignadello and F. Marcati, J. Organometal. Cham., 46 (1972) 357.

134. D. de Montauzon and R. Poilblanc, J. Organometal.Chem., 54 (1973) 291.

135. R.D. Adams and F.A. Cotton, Inorg. Chim. Acta, 7 (1973) 153.

136. F.A. Cotton, B.A. Frenz and A. Shaver, Inorg. Chim. Acta, 7 (1973) 161.

137. I.S. Butler and A.E. Fenster, J. Organometal.Chem., 51 (1973) 307.

138. R. Whyman, J. Organometal.Chem., 63 (1973) 467.

139. D.E. Morris and H.B. Tinker, J. Organometal. Chem., 49 (1973) C53.

140. I.S. Butler and T. Sawai, Inorg. Chem., 12 (1973) 1994.

141. H.L. Clarke and N.J. Fitzpatrick, Inorg. Nucl. Chem. Letters, 9 (1973) 75.

142. H.L. Clarke and N.J. Fitzpatrick, Inorg. Nucl. Chem. Letters, 9 (1973) 81.

143. P.M. Boorman, S.A. Clow, D. Potts and H. Wieser, Inorg. Nucl. Chem. Letters, 9 (1973) 941.

144. I.H. Sabherwal and A.B. Burg, Inorg. Chem., 12 (1973) 697.

145. J.S. Kristoff and D.F. Shriver, Inorg. Chem., 12 (1973) 1788.

146. M. Herberhold and C.R. Jablonski, Inorg. Chim. Acta, 7 (1973) 241.

147. G.C. v.d. Berg, A. Oskam and K. Vrieze, J. Organometal. Chem., 57 (1973) 329.

148. K.L. Watters, J.N. Brittain and W.M. Risen, Jr., Inorg. Chem., 8 (1969) 1347.

149. K.L. Watters, W.M. Butler and W.M. Risen, Jr., Inorg. Chem., 10 (1971) 1970.

150. D.C. Andrews and G. Davidson, J.C.S. Dalton, (1972) 1381.

151. G. Paliani, S.M. Murgia, G. Cardaci and R. Cataliotti, J. Organometal. Chem., 63 (1973) 407.

152. G. Paliani, A. Poletti, G. Cardaci, S.M. Murgia and R. Cataliotti, J. Organometal. Chem., 60 (1973) 157.

153. D.M. Adams and A. Squire, J. Organometal. Chem., 63 (1973) 381.

154. I.J. Hyams, R.T. Bailey and E.R. Lippincott, Spectrochim. Acta, 23A (1967) 273.

155. D.M. Adams and A. Squire, J. Chem. Soc. (A), (1970) 814.

156. G. Davidson and E.M. Riley, J. Organometal. Chem., 51 (1973) 297.

157. Y.-Y. Huang, J. Amer. Chem. Soc., 95 (1973) 6636.

158. C.-J. Oetker and W. Beck, Spectrochim. Acta, 29A (1973) 1975.

159. G.J. Kubas and T.G. Spiro, Inorg. Chem.,12 (1973) 1797.

160. O.S. Roshchupkina, V.A. Dubovitskii and Yu.G. Borodko, Zh. Strukt. Khim., 12 (1971) 1007.

161. E. Samuel, R. Ferner and M. Bigorgne, Inorg. Chem., 12 (1973) 881.

162. J. Laane, J. Coord. Chem., 1 (1971) 75.

163. Ya.-M.Kimel'fel'd, E.M. Smirnova and V.T. Aleksanyan, J. Mol. Structure, 19 (1973) 329.

164. I.J. Hyams, Chem. Phys. Letters, 18 (1973) 399.

165. I.J. Hyams, Spectrochim. Acta, 29A (1973) 839.

166. J.S. Bodenheimer and W. Low, Spectrochim. Acta, 29A (1973) 1733.

167. D.C. Andrews and G. Davidson, J. Organometal. Chem.,55 (1973) 383.

168. A. Poletti, R. Cataliotti and G. Paliani, Spectrochim. Acta, 29A (1973) 277.

169. H. Minematsu, Y. Nonaka, S. Takahashi and N. Hagihara, J. Organometal. Chem., 59 (1973) 395.

170. S.P. Dent, C. Eaborn, A. Pidcock and B. Ratcliff, J. Organometal. Chem., 46 (1972) C68.

171. D.W. Wertz, D.F. Bocian and M.J. Hazouri, Spectrochim. Acta, 29A (1973) 1439.

172. C.F. Shaw and R.S. Tobias, Inorg. Chem., 12 (1973) 965.

173. N.M. Sergeyev Prog. NMR Spectrosc., 9 (1973) 71.

174. H. Brunner and H.-D. Schindler, J. Organometal. Chem., 55 (1973)C71.

175. G. Jaouen, A. Meyer and G. Simmoneaux, Tetrahedron Letters, (1973) 5163.

176. P.J. Craig and J. Edwards, J. Organometal. Chem., 46 (1972) 335.

177. J.W. Faller, C.-C. Chen, M.J. Mattina and A. Jakubowski, J. Organometal. Chem., 32 (1973) 361.

178. M.C. McIvor, J. Organometal. Chem., 27 (1971) C59.

179. D. Bailey, A.D. Buckingham, M.C. McIvor and A.J. Rest, J. Organometal. Chem., 61 (1973) 311.

180. A.D. Buckingham, J.P. Yesinowski, A.J. Canty and A.J. Rest, J. Amer. Chem. Soc., 95 (1973) 2732.

181. T.D. Turbitt and W.E. Watts, J. Organometal. Chem., 49 (1973) C30.

182. P. Crews, J. Amer. Chem. Soc., 95 (1973) 636.

183. H. Falk, H. Lehner and K. Schlögl, J. Organometal. Chem., 95 (1973) 191.

184. R. P. Hughes and J. Powell, J. Organometal. Chem., 60 (1973) 427.

185. D.R. Fahey, J. Organometal. Chem., 57 (1973) 385.

186. R.G. Salomon and J.K. Kochi, J. Amer. Chem. Soc., 95 (1973) 1889.

187. D. Hollings, M. Green and D.V. Claridge, J. Organometal. Chem., 54 (1973) 399.

188. B.E. Mann, R. Pietropaolo and B.L. Shaw, J.C.S. Dalton, (1973) 2390.

189. R.J. Goodfellow, M.J. Hardy and B.F. Taylor, J.C.S. Dalton, (1973) 2450.

190. T.G. Appleton, M.H. Chisholm, H.C. Clark and L.E. Manzer, Can. J. Chem., 51 (1973) 2243.

191. H.C. Clark and L.E. Manzer, J.C.S. Chem. Commun., (1973) 870.

192. T.A. George and C.D. Turnipseed, Inorg. Chem., 12 (1973) 394.

193. J.D. Kennedy, W. McFarlane and D.S. Rycroft, Inorg. Chem., 12 (1973) 2742.

194. M.A. Bennett, R. Bramley and I.B. Tomkins, J.C.S. Dalton, (1973) 166.

195. W. McFarlane and D.S. Rycroft, J.C.S. Chem. Commun., (1973) 336.

196. P.S. Braterman, D.W. Milne, E.W. Randall and E. Rosenberg, J.C.S. Dalton, (1973) 1827.

197. B.E. Mann, J.C.S. Dalton, (1973) 2012.

198. E.W. Randall, E. Rosenberg and L. Milone, J.C.S. Dalton, (1973) 1672.

199. G.H. Williams, D.D. Traficante and D. Seyferth, J. Organometal. Chem., 60 (1973) C53.

200. D.G. Cooper, G.K. Hamer, J. Powell and W.F. Reynolds, J.C.S. Chem. Commun., (1973) 449.

201. G.M. Bodner, S.B. Kahl, K. Bork, B.N. Storhoff, J.E. Wuller and L.J. Todd, Inorg. Chem., 12 (1973) 1071.

202. D.J. Cardin, B. Çetinkaya, E. Çetinkaya, M.F. Lappert, E.W. Randall and E. Rosenberg, J.C.S. Dalton, (1973) 1982.

203 D.E. Axelson, C.E. Holloway and A.J. Oliver, Inorg. Nucl. Chem. Letters, 9 (1973) 885.

204. M.H. Chisholm, H.C. Clark, L.E. Manzer, J.B. Stothers and J.E.H. Ward, J. Amer. Chem. Soc., 95 (1973) 8574.

205. J.P.C.M. van Dongen and C.D.M. Beverwijk, J. Organometal. Chem., 51 (1973) C36.

206. N.A. Matwiyoff, P.J. Vergamini, T.E. Needham, C.T. Gregg, J.A. Volpe and W.S. Caughey, J. Amer. Chem. Soc., 95 (1973) 4429.

207. C. Eaborn, M.R. Harrison, P.N. Kapoor and D.R.M. Walton, J. Organometal. Chem., 63 (1973) 99.

208. C.W. Fong and M.D. Johnson, J.C.S. Perkin II, (1973) 986.

209. R.L. Bennett, M.I. Bruce and R.J. Goodfellow, J. Fluorine Chem., 2 (1973) 447.

210. G.M. Bancroft, H.C. Clark, R.G. Kidd, A.T. Rake and H.G. Spinney, Inorg. Chem., 12 (1973) 728.

211. R.F. Fenske and R.L. De Kock, Inorg. Chem., 9 (1970) 1053.

212. S.S. Eaton and G.R. Eaton, J. Amer. Chem. Soc., 95 (1973) 1825.

213. H.C. Longuet-Higgins, Mol. Physics, 6 (1963) 445.

214. J.R. Shapley and J.A. Osborn, Accounts Chem. Res., 6 (1973) 305.

215. M.K. Makova, E.V. Leonova, Yu.S. Karimov and N.S. Kochetkova, J. Organometal. Chem., 55 (1973) 185.

216. C.G. Kreiter and M. Lang, J. Organometal. Chem., 55 (1973) C27.

217. J. Evans, B.F.G. Johnson, J. Lewis and J.R. Norton, J.C.S. Chem. Commun., (1973) 79.

218. R.M. Kirchner, T.J. Marks, J.S. Kristoff and J.A. Ibers, J. Amer. Chem. Soc., 95 (1973) 6602.

219. R.D. Adams and F.A. Cotton, J. Amer. Chem. Soc., 95 (1973) 6589.

220. R.D. Adams, M. Brice and F.A. Cotton, J. Amer. Chem. Soc., 95 (1973) 6594.

221. J. Evans, B.F.G. Johnson, J. Lewis, J.R. Norton and F.A.Cotton, J.C.S. Chem. Commun.,(1973) 807.

222. T. Yamamoto, A.R. Garber, G.M. Bodner and L.J. Todd, J. Organometal. Chem., 56 (1973) C23.

223. A.J. Canty, A.J.P. Domingos, B.F.G. Johnson and J. Lewis, J.C.S. Dalton, (1973) 2056.

224. A.P. Ginsberg and M.E. Tully, J. Amer. Chem. Soc., 95 (1973) 4749.

225. A.P. Ginsberg, S.C. Abrahams and P.B. Jamieson, J. Amer. Chem. Soc., 95 (1973) 4751.

226. P. Meakin, E.L. Muetterties and J.P. Jesson, J. Amer. Chem. Soc., 95 (1973) 75.

227. M.A. Bennett and I.B. Tomkins, J. Organometal. Chem., 51 (1973) 289.

228. T. Hosokawa, C. Calvo, H.B. Lee and P.M. Maitlis, J. Amer. Chem. Soc., 95 (1973) 4914.

229. J. Ashley-Smith, B.F.G. Johnson and J.A. Segal, J. Organometal. Chem., 49 (1973) C38.

230. R. Cramer and G.S. Reddy, Inorg. Chem., 12 (1973) 346.

231. K. Van Putte and A. van der Ent, Inorg. Chim. Acta, 7 (1973) 497.

232. R.P. Hughes and J. Powell, J. Organometal. Chem., 55 (1973) C45.

233. J. Schwartz and J.E. Sadler, J.C.S. Chem. Commun., (1973) 172.

234. R. Bau, J.C. Burt, S.A.R. Knox, R.M. Laine, R.P. Phillips and F.G.A. Stone, J.C.S. Chem. Commun., (1973) 726.

235. A. Brookes, J. Howard, S.A.R. Knox, V. Riera, F.G.A. Stone and P. Woodward, J.C.S. Chem. Commun., (1973) 727.

236. G. Deganello, J. Organometal. Chem., 59 (1973) 329.

237. F.A. Cotton, R.A. Frenz, G. Deganello and A. Shaver, J. Organometal. Chem., 50 (1973) 227.

238. E.L. Muetterties and F.J. Hirsekorn, J. Amer. Chem. Soc., 95 (1973) 5419.

239. Th. Kruck, G. Sylvester and I.-P. Kunau, Z. Anorg. Allg. Chem., 396 (1973) 165.

240. G. Wright and R.J. Mawby, J. Organometal. Chem., 51 (1973) 281.

241. J.M. Brown and K. Mertis, J. Organometal. Chem., 47 (1973) C5.

242. T.J. Marks, A.M. Seyam and J.R. Kolb, J. Amer. Chem. Soc., 95 (1973) 5529.

243. A. Yamamoto, T. Yamamoto, T. Saruyama and Y. Nakamura, J. Amer. Chem. Soc., 95 (1973) 4073.

244. J.C. Bernier and O. Kahn, Chem. Phys. Letters, 19 (1973) 414.

245. C.P. Stewart and A.L. Porte, J.C.S. Dalton, (1973) 722.

246. Ch. Elschenbroich and F. Gerson, J. Organometal. Chem., 49 (1973) 445.

247. Ch. Elschenbroich, F. Gerson and F. Stohler, J. Amer. Chem. Soc., 95 (1973) 6956.

248. N.G. Gogan, C.-K. Chu and G.W. Gray, J. Organometal. Chem., 59 (1973) 323.

249. T.W. Matheson, B.M. Peake, B.H. Robinson, J. Simpson, and D.J. Watson, J.C.S. Chem. Commun., (1973) 894.

250. D.P. Sanderson and M.C.R. Symons, Inorg. Chem., 12 (1973) 1932.

251. U.T. Mueller-Westerhoff and P. Eilbracht, Tetrahedron Letters, (1973) 1855.

252. W.H. Morrison, Jr., S. Krogsrud and D.N. Hendrickson, Inorg. Chem., 12 (1973) 1998.

253. E. Fluck and F. Hausser, Z. Anorg. Allg. Chem., 396 (1973) 257.

254. D.O. Cowan, C. LeVanda, R.L. Collins, G.A. Candela, U.T. Mueller-Westerhoff, and P. Eilbracht, J.C.S. Chem. Commun., (1973) 329.

255. W.H. Morrison, Jr., and D.N. Hendrickson, J. Chem. Phys., 59 (1973) 380.

256. W.H. Morrison, Jr., and D.N. Hendrickson, Chem. Phys. Letters, 22 (1973) 119.

257. W.E. Carroll, F.A. Deeney, J.A. Delaney and F.J. Lalor, J.C.S. Dalton, (1973) 718.

258. M.G. Clark, W.R. Cullen, R.E.B. Garrod, A.G. Maddock and J.R. Sams, Inorg. Chem.. 12 (1973) 1045.

259. P. Vasudev and C.H.W. Jones, Can. J. Chem., 51 (1973) 405.

260. G.M. Bancroft and E.T. Libbey, J.C.S. Dalton, (1973) 2103.

261. G.M. Bancroft and K.D. Butler, J.C.S. Dalton, (1973) 1694.

262. R.C. Dunbar, J.F. Ennever and J.P. Fackler, Jr., Inorg. Chem., 1 (1973) 2734.

263. Y. Kume, D. Nakamura, M. Kubo and S. Onaka, J. Mag. Res., 10 (1973) 58.

264. E.A.C. Lucken, R. Pozzi and K.R. Ramaprasad, J. Mol. Structure, 1 (1973) 377.

265. Y. Okamoto and S.K. Kundu, J. Phys. Chem., 77 (1973) 2677.

266. I.G. de Jong and D.R. Wiles, Inorg. Chem., 12 (1973) 2519.

267. M.K. Lloyd, J.A. McClaverty, D.G. Orchard, J.A. Connor, M.B. Hall, I.H. Hillier, E.M. Jones and G.K. McEwen, J.C.S. Dalton, (1973) 1743.

268. M.K. Lloyd, J.A. McCleverty, J.A. Connor and E.M. Jones, J.C.S. Dalton, (1973) 1768.

269. P.D. Frisch, M.K. Lloyd, J.A. McCleverty and D. Seddon, J.C.S. Dalton, (1973) 2268.

270. A.M. Bond, A.T. Casey and J.R. Thackeray, Inorg. Chem., 12 (1973) 887.

271. J. Tirouflet, E. Laviron, C. Moïse and Y. Mugnier, J. Organometal. Chem., 50 (1973) 241.

272. L.I. Denisovich and S.P. Gubin, J. Organometal. Chem., 57 (1973) 87, 109.

273. N. El Murr, R. Dabard and E. Laviron, J. Organometal. Chem., 47 (1973) C13.

274. G.K. Borisov, S.G. Krasnova and G. G. Devyatykh, Russian J. Inorg. Chem., 18 (1973) 346.

275. A. Cartner, B. Robinson and P.J. Gardner, J.C.S. Chem. Commun., (1973) 317.

276. J.A. Connor, H.A. Skinner and Y. Virmani, J.C.S. Faraday I, 69 (1973) 1218.

277. E.M. Ban, R.P. Hughes and J. Powell, J.C.S. Chem. Commun., (1973) 591.

278. T.G. Sukhova, O.N. Temkin, L.I. Kulashova and R.M. Flid, Russian J. Inorg. Chem., 18 (1973) 172.

279. W. Partenheimer and E.F. Hoy, J. Amer. Chem. Soc., 95 (1973) 2840.

280. W. Partenheimer and E.H. Johnson, Inorg. Chem., 12 (1973) 1274.

281. B.V. Strizhkov, A.P. Martynenko and B.V. Lokshin, Russian J. Inorg. Chem., 18 (1973) 75.

282. H. Lumbroso, C. Segard and B. Roques, J. Organometal. Chem., 61 (1973) 249.

283. S. Sorriso, G. Distefano and A. Foffani, J. Organometal. Chem., 47 (1973) 139.

284. R.E. Graf and C.P. Lillya, J. Organometal. Chem., 47 (1973) 413.

285. W.D. Covey and T.L. Brown, Inorg. Chem., 12 (1973) 2820.

286. C.L. Hyde and D.J. Darensbourg, Inorg. Chem., 12 (1973) 1286.

287. J.A. Connor, J.P. Day and R.M. Turner, J.C.S. Chem. Commun., (1973) 578.

288. M.D. Cooke and E.O. Fischer, J. Organometal. Chem., 56 (1973) 279.

289. M. N. Memering and G.R. Dobson, Inorg. Chem., 12 (1973) 2490.

290. K.R. Brower and T.-S. Chen, Inorg. Chem., 12 (1973) 2198.

291. J.R. Paxson and G.R. Dobson, J. Coord. Chem., 1 (1972) 321.

292. G.R. Dobson and J.R. Paxson, J. Amer. Chem. Soc., 95 (1973) 5925.

293. R.J. Angelici and R.W. Brink, Inorg. Chem., 12 (1973) 1067.

294. M.N. Memering, A. Moradi-Araghi and G.R. Dobson, J. Coord. Chem., 2 (1973) 271.

295. H. Brunner and W.A. Herrmann, Chem. Ber., 106 (1973) 632.

296. G.R. Dobson, R.T. Jernigan and P.-T. Chang, J. Organometal. Chem., 54 (1973) C33.

297. M.F. Farona and G.R. Camp, Inorg. Chim. Acta, 3 (1969) 395.

298. P.C. Ellgen and J.N. Gerlach, Angew. Chem., 12 (1973) 2526.

299. P.L. Stanghellini, R. Rossetti, O. Gambino and G. Cetini, Inorg. Chim. Acta, 7 (1973) 445.

300. J.P. Fawcett, A.J. Poë and M.V. Twigg, J. Organometal. Chem., 51 (1973) C17.

301. J.P. Fawcett, A.J. Poë and M.V. Twigg, J.C.S. Chem. Commun., (1973) 267.

302. A.J. Poë and M.V. Twigg, J. Organometal. Chem., 50 (1973) C39.

303. J.R. Norton and J.P. Collman, Inorg. Chem., 12 (1973) 476.

304. I.S. Butler and A.E. Fenster, Inorg. Chim. Acta., 7 (1973) 79.

305. K.M. Al-Kathumi and L.A.P. Kane-Maguire, J.C.S. Dalton, (1973) 1683.

306. V.N. Setkina, N.K. Baranetskaya, A.G. Ginsburg, V.I. Zdanovich, M.N. Nefedova and D.N. Kursakov, J. Organometal. Chem., 61 (1973) 287.

307. A. Ceccon and S. Sartori, J. Organometal Chem., 50 (1973) 161.

308. B.F.G. Johnson, J. Lewis and M.V. Twigg, J. Organometal. Chem., 52 (1973) C31.

309. M. Brookhart, N.M. Lippman and E.J. Reardon, Jr., J. Organometal. Chem., 54 (1973) 247.

310. I.S. Krull, J. Organometal. Chem., 57 (1973) 363.

311. V.M. Fomin, Yu. A. Alexandrov and V.A. Umilin, J. Organometal. Chem., 61 (1973) 267.

312. E.K.G. Schmidt, Angew. Chem., Internat. Edn., 17 (1973) 777.

313. D.J. Doonan and A.L. Balch, J. Amer. Chem., Soc., 95 (1973) 4769.

314. P.M. Treichel, K.P. Wagner and R.W. Hess, Inorg. Chem., 12 (1973) 1471.

315. D.J. Yarrow, J.A. Ibers, Y. Tatsuno and S. Otsuka, J. Amer. Chem. Soc., 95 (1972) 8590.

316. M. Foà and L. Cassar, Gazz. Chim. Ital., 103 (1973) 805.

317. L. Cassar and A. Giarrusso, Gazz. Chim. Ital., 103 (1973) 793.

318. J. Burgess, R.D.W. Kemmitt and G.W. Littlecott, J. Organometal. Chem., 56 (1973) 405.

319. M. Green and G.J. Parker, J.C.S. Dalton, (1973) 2099.

320. J.A. J. Jarvis, A. Johnson and R.J. Puddephatt, J.C.S. Chem. Commun., (1973) 373.

321. M.I. Bruce, B.L. Goodall and F.G.A. Stone, J.C.S. Chem. Commun., (1973) 558.

322. C.T. Lam and C.V. Senoff, Can. J. Chem., 51 (1973) 3790.

323. M. Kubota, G.W. Kiefer, R.M. Ishikawa and K.E. Bencala, Inorg. Chim. Acta., 7 (1973) 195.

324. K. Ohkubo, H. Kanaeda and T. Tsuchihashi, Bull.Chem. Soc. Japan, 46 (1973) 3095.

325. R.G. Pearson and W.R Muir, J. Amer. Chem. Soc., 92 (1970) 5519.

326. J.A. Labinger, A.V. Kramer and J.A. Osborn, J. Amer. Chem., Soc., 95 (1973) 7908.

327. M.F. Lappert and P.W. Lednor, J.C.S. Chem. Commun., (1973) 948.

328. N.G. Hargreaves, R.J. Puddephatt, L.H. Sutcliffe and P.J. Thompson, J.C.S. Chem. Commun., (1973) 861.

329. R.B. Allen, R.G. Lawler and H.R. Ward, J. Amer. Chem. Soc., 95 (1973) 1692.

330. S.J. Nelson, G. Detre and M. Tanabe, Tetrahedron Letters, (1973) 447.

331. A. Tamaki and J.K. Kochi, J.C.S. Chem. Commun.,(1973) 423.

332. A. Nakamura and S. Otsuka, J. Amer. Chem. Soc., 95 (1973) 7262.

333. K.M. Nicholas and M. Rosenblum, J. Amer. Chem. Soc., 95 (1973) 4449.

334. J.E. Jacobson and A. Wojcicki, J. Amer. Chem. Soc., 95 (1973) 6962.

335. T.C. Flood and D.L. Miles, J. Amer. Chem. Soc., 95 (1973) 6460.

336. F.R. Jensen and R.C. Kiskis, J. Organometal. Chem., 49 (1973) C46.

337. T. Yamamoto and A. Yamamoto, J. Organometal. Chem., 57 (1973) 127.

338. M.F. Lappert and R. Pearce, J.C.S. Chem. Commun., (1973) 24.

339. J.D. McCowan, Can. J. Chem., 91 (1973) 1083.

340. T.A. Cooper, J. Amer. Chem. Soc., 95 (1973) 4158.

341. B. Heyn and H. Still, Z. Chem., 13 (1973) 191.

342. K.N.V. Duong, A.Ahond, C. Merienne and A. Gaudemer, J. Organometal. Chem., 55 (1973) 375.

343. R.B. Silverman, D. Dolphin and B.M. Babior, J. Amer. Chem. Soc., 94 (1972) 4028.

344. R.B. Silverman and D. Dolphin, J. Amer. Chem. Soc., 95 (1973) 1686.

345. M.P. Brown, R.J. Puddephatt and C.E.E. Upton, J. Organometal. Chem. 49 (1973) C61.

346. J.X. McDermott, J.F. White and G.M.Whitesides, J. Amer. Chem. Soc., 95 (1973) 4451.

347. A. Camus and N. Marsich, J. Organometal. Chem., 46 (1972) 385.

348. M.A. Clinton and J.K. Kochi, J. Organometal. Chem., 61 (1973) 433.

349. A. Tamaki, S.A. Magennis and J.K. Kochi, J. Amer. Chem. Soc., 95 (1973) 6487.

350. C.F. Shaw, III, J.W. Lundeen and R.S. Tobias, J. Organometal. Chem., 51 (1973) 365.

351. A. Tamaki and J.K. Kochi, J. Organometal. Chem., 61 (1973) 441.

352. J.H. Espenson and J.S. Shveima, J. Amer. Chem. Soc., 95 (1973) 4468.

353. G. Mestroni, C. Cocevar and G. Costa, Gazz. Chim. Ital., 103 (1973) 273.

354. R.A. Johnson and S. Selzer, J. Amer. Chem. Soc., 95 (1973) 5700.

355. G. Zon and L.A. Paquette, J. Amer. Chem. Soc., 95 (1973) 4456.

356. P.G. Gassman and R. R. Reitz, J. Organometal. Chem., 52 (1973) C51.

357. L.F. Hines and J.K. Stille, J. Amer. Chem. Soc., 94 (1972) 485.

358. J.K. Stille, D. E. James and L.F. Hines, J. Amer. Chem. Soc., 95 (1973) 5062.

359. A. Segnitz, P.M. Bailey and P.M. Maitlis, J.C.S. Chem. Commun., (1973) 698.

360. H.C. Volger, H. Hogeveen and C.F. Roobeek, Rec. Trav. Chim. Pays-Bas, 92 (1973) 1223.

361. M.F. Semmelhack and R.D. Stauffer, Tetrahedron Letters, (1973) 2667.

362. J. Beger, C. Duschek and H. Reichel, Z. Chem., 13 (1973) 101.

363. M.A. Cairns, J.F. Nixon and B. Wilkins, J.C.S. Chem. Commun., (1973) 86.

364. R. Pietropaolo, E. Rotondo, F. Faraone and D. Pietropaolo, J. Organometal. Chem., 60 (1973)197.

365. V. Harder and H. Werner, Helv. Chim. Acta, 56 (1973) 549.

366. G. Parker and H. Werner, Helv. Chim. Acta, 56 (1973) 2819.

367. H.C. Clark and H. Kurosawa, Inorg. Chem., 12 (1973) 1566.

368. R. Noyori, K. Yokoyama and Y. Hayakawa, J. Amer. Chem. Soc., 95 (1973) 2722.

369. J. Halpern and T.A. Weil, J.C.S. Chem. Commun., (1973) 631.

370. E.O. Fischer, G. Kreis, C.G. Kreiter, J. Müller, G. Huttner and H. Lorenz, Angew. Chem. Internat. Edn., 12 (1973) 564.

371. L.W. Gosser, W.H. Knoth and G.W. Parshall, J. Amer. Chem. Soc., 95 (1973) 3436.

372. B.V. Lokshin, A.A. Pasinsky, N.E. Kolobova, K.N. Anisimov and Yu. V. Makarov, J. Organometal. Chem., 55 (1973) 315.

373. J.L. Peterson, T.E. Nappier, Jr., and D.W. Meek, J. Amer. Chem. Soc., 95 (1973) 8195.

374. D. Strope and D.F. Shriver, J. Amer. Chem. Soc., 95 (1973) 8197.

375. J.S. Kristoff, N.J. Nelson and D.F. Shriver, J. Organometal. Chem., 49 (1973) C82.

376. G.B.McVicker and R.S. Matyas, J.C.S. Chem. Commun., (1972) 972.

377. S.W. Ulmer, P.M. Skarstad, J.M. Burlitch and R.E. Hughes, J. Amer. Chem. Soc., 95 (1973) 4469.

378. T. Blackmore and J.M. Burlitch, J.C.S. Chem. Commun., (1973) 405.

379. A.E. Crease and P. Legzdins, J.C.S. Chem. Commun., (1973) 775.

380. M.J. Boylan, J. Bellerby, J. Newman and A.R. Manning, J. Organometal. Chem., 47 (1973) C33.

381. R.H. Reimann and E. Singleton, J. Organometal Chem., 57 (1973) C75.

382. B. Çetinkaya, P. Dixneuf and M.F. Lappert, J.C.S. Chem. Commun., (1973) 206.

383. P.J. Fraser, W.R. Roper and F.G.A. Stone, J. Organometal. Chem., 50 (1973) C54.

384. R.B. King, I. Haiduc and A.Efraty, J. Organometal. Chem., 47 (1973) 145.

385. K.H. Pannell and G.M. Crawford, J. Coord. Chem., 2 (1973) 251.

386. W. Mowat and G. Wilkinson, J.C.S. Dalton, (1973) 1120.

387. R.B. King and D.M. Braitch, J. Organometal. Chem., 54 (1973) 9.

388. S.N. Anderson, C.W. Fong and M.D. Johnson, J.C.S. Chem. Commun., (1973) 163.

389. D.W. Lichtenberg and A. Wojcicki, Inorg. Chim. Acta, 7 (1973) 311

390. T. Yamamoto and A. Wojcicki, Inorg. Chem., 12 (1973) 1779.

391. J.J. Alexander and A. Wojcicki, Inorg. Chem., 12 (1973) 74.

392. W. Beck, K. Schorpp, C. Oetker, R. Schlodder and H.S. Smedal, Chem. Ber., 106 (1973) 2144.

393. J. Clemens, M. Green and F.G.A. Stone, J.C.S. Dalton, (1973) 375.

394. R.D.W. Kemmitt, B.Y. Kimura and G.W. Littlecott, J.C.S. Dalton, (1973) 636.

395. M. Green and B. Lewis, J.C.S. Chem. Commun, (1973) 114.

396. G. Schmid and H.-J. Balk, Chem. Ber., 103 (1970) 2240.

397. F. Glockling and R.E. Houston, J. Organometal. Chem., 50 (1973) C31.

398. D.H. Harris, S.A. Keppie and M.F. Lappert, J.C.S. Dalton, (1973) 1653.

399. E.W. Abel and M.O. Dunster, J. Organometal. Chem., 49 (1973) 435.

400. B. Cetinkaya, M.F. Lappert, J. McMeeking and D.E. Palmer, J.C.S. Dalton, (1973) 1202.

401. E.W. Abel and S. Moorhouse, J.C.S. Dalton, (1973) 1706.

402. W.H. Baddley and P. Choudhury, J. Organometal. Chem., 60 (1973) C74.

403. J.A.Ibers, quoted in (404).

404. W.E. Carroll and F.J. Lalor, J. Organometal. Chem., 54 (1973) C37.

405. G. Fachinetti, G. Fochi & C. Floriani, J. Organometal. Chem., 57 (1973) C51.

406. R.F. Heck, J. Amer. Chem. Soc., 85 (1963) 1460.

407. W. Beck, W. Danzer and R. Höfer, Angew. Chem. Internat. Edn., 12 (1973) 77.

408 M.I. Bruce, B.L. Goodall and F.G.A. Stone, J. Organometal Chem., 60 (1973) 343.

409. D.J. O'Sullivan and F.J. Lalor, J. Organometal. Chem., 57 (1973) C58.

410. R.E.Christopher and L.M. Venanzi, Inorg. Chim. Acta, 7 (1973) 219, 489.

411. C.M. Bartisch and C.S. Kraihanzel, Inorg. Chem., 12 (1973) 391.

412. D. Sellmann, Angew. Chem., 12 (1973) 1020.

413. D.C. Beer and L.J. Todd, J. Organometal. Chem., 55 (1973) 363.

414. H.H. Karsch and H. Schmidbaur, Angew. Chem. Internat. Edn., 12 (1973) 853.

415. E. Kurras, U. Rosenthal, H. Mennenga and G. Oehme, Angew. Chem. Internat. Edn., 12 (1973) 854.

416. J.L. Davidson and D.W.S. Sharp, J.C.S. Dalton, 1957 (1973).

417. M.J. Barrow, J.L. Davidson, W. Harrison, D.W.A. Sharp, G.A. Sim and F.B. Wilson, J C.S. Chem. Commun., (1973) 583.

418. W.R. Cullen, D.J. Patmore and J.R. Sams, Inorg. Chem., 12 (1973) 867.

419. W. Ehrl and H. Vahrenkamp, J. Organometal. Chem., 63 (1973) 389.

420. H. Vahrenkamp, J. Organometal Chem., 63 (1973) 399.

421. W. Ehrl and H. Vahrenkamp, Chem. Ber., 106 (1973) 2550.

422. W. Ehrl and H. Vahrenkamp, Chem. Ber., 106 (1973) 2563.

423. K. Yasufuku and H. Yamazaki, Bull. Chem. Soc. Japan, 46 (1973) 1502.

424. J.P. Collman, J.K. Hoyano and D.W. Murphy, J. Amer. Chem. Soc., 95 (1973) 3424.

425. K. Fischer, K. Jonas, P. Misbach, R. Stabba and G. Wilke, Angew. Chem. Internat. Edn., 12 (1973) 943.

426. B. Bogdanović, Angew. Chem. Internat. Edn., 12 (1973) 954.

427. H. Bönnemann, Angew. Chem. Internat. Edn., 12 (1973) 964.

428. P. Heimbach, Angew. Chem. Internat. Edn., 12 (1973) 975.

429. R.E. Harmon, S.K. Gupta and D.J. Brown, Chem. Rev., 73 (1973) 21.

430. F.J. McQuillin, Prog. Org. Chem., 8 (1973) 314.

431. G.P. Chiusoli, Accounts Chem. Res., 6 (1973) 422.

432. D.G.H. Ballard, Advan. Catalysis, 23 (1973) 263.

433. J. Tsuji, Accounts. Chem. Res., 6 (1973) 8.

434. P.M. Henry, Accounts Chem. Res., 6 (1973) 16.

435. G. Consiglio and G. Botteghi, Helv. Chim. Acta, 56 (1973) 460.

436. W. Dumont, J.-C. Paulin, T. P. Dang and H.B. Kagan, J. Amer. Chem. Soc., 95 (1973) 8295.

437. A. Nakamura and S. Otsuka, Tetrahedron Letters, (1973) 4529.

438. T.A. Weil, S. Metlin and I. Wender, J. Organometal. Chem., 49 (1973) 227.

439. A.G. Hinze, Rec. Trav. Chim. Pays-Bas, 92 (1973) 342.

440. M.G. Burnett and R.J. Morrison, J.C.S Dalton, (1973) 632.

441. J. Basters, C.J. Groenenboom, H. van Bekkum and L.L. van Reijen, Rec. Trav. Chim. Pays-Bas, 92 (1973) 219.

442. J.L. Garnett, M.A. Long, A.B. McLaren and K.B. Peterson, J.C.S. Chem. Commun., (1973) 749.

443. R.J. Hodges, D.E. Webster and P.B. Wells, J. Chem. Soc. (A), (1971) 3230.

444. G.W. Littlecott and F.J.McQuillin, Tetrahedron Letters, (1973) 5003.

445. D.L. Schmitt and H.B. Jonassen, J. Organometal. Chem., 49 (1972) 469.

446. H. Yoshimoto and H.Itatani, Bull. Chem. Soc. Japan, 46 (1973) 2490.

447. A. Kasahara, T. Izumi, M. Yodono, R. Saito, T. Takeda and T. Sugawara, Bull. Chem. Soc. Japan, 46 (1973) 1220.

448. E.F. Magoon and L.H. Slaugh, J. Organometal. Chem., 55 (1973) 409.

449. M. Yamaji, Y. Fujiwara, R. Asano and S. Teranishi, Bull. Chem. Soc. Japan, 46 (1973) 90.

450. T. Susuki and J. Tsuji, Bull. Chem. Soc. Japan, 46 (1973) 655.

451. C.P. Casey and C.R. Cyr, J. Amer. Chem. Soc. 95 (1973) 2248.

452. C.P. Casey and C.R. Cyr, J. Amer. Chem. Soc., 95 (1973) 2240.

453. F. Piacenti, S. Pucci, M. Bianchi and P. Pino, J. Amer. Chem., Soc., 90 (1968) 6847.

454. A. Stefani, G. Consiglio, C. Botteghi and P. Pino, J. Amer. Chem. Soc., 95 (1973) 6504.

455. H.B. Tinker and D.E. Morris, J. Organometal. Chem.,52 (1973) C55.

456. L. Cassar, J. Organometal. Chem., 54 (1973) C57.

457. K. Tamao, M. Zembayashi, Y. Kiso and M. Kumada, J. Organometal. Chem., 55 (1973) C91.

458. K. Maruya, T. Mizoroki and A. Ozaki, Bull. Chem. Soc. Japan, 46 (1973) 993.

459. J. Kiji, K. Yamamoto, S. Mitani, S. Yoshikawa and J. Furukawa, Bull. Chem. Soc. Japan, 46 (1973) 1791.

460. R. Baker and A.H. Cook, J.C.S. Chem. Commun, (1973) 472.

461. G.P. Chiusoli, G. Cometti and V. Bellotti, Gazz. Chem. Ital., 103 (1973) 569.

462. D.R. Fahey, Organometal. Chem. Res., 7 (1972) 245, esp. p. 270.

463. H.-F. Klein, Angew. Chem. Internat. Edn., 12 (1973) 402.

464. R.P. Hughes, T. Jack and J. Powell, J. Organometal. Chem., 63 (1973) 451, and references therein.

465. P. Roffia, G. Gregorio, F. Conti, G.F. Pregaglia and R. Ugo, J. Organometal. Chem., 55 (1973) 405.

466. H. Umezaki, Y. Fujiwara, K. Sawara and S. Teranishi, Bull. Chem. Soc. Japan, 46 (1973) 2230.

467. G.A. Vaglio, O. Gambino, R.P. Ferrari and G. Cetini, Inorg. Chim. Acta, 7 (1973) 193.

468. P. Roffia, F. Conti, G. Gregorio, G.F. Pregaglia and R. Ugo, J. Organometal. Chem., 56 (1973) 391.

469. R.G Salomon and J.K. Kochi, J. Amer. Chem. Soc., 95 (1973) 3300.

470. Y. Souma and H. Sano, Bull. Chem. Soc. Japan, 46 (1973) 3237.

471. J.F. White and M.F. Farona, J. Organometal. Chem., 63 (1973) 329.

472. G. Palyi, F. Baumgartner, and I. Czájlik, J. Organometal. Chem., 49 (1973) C85.