The 16 and 18 Electron Rule in Organometallic Chemistry and Homogeneous Catalysis

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1 Introduction

There has been a great increase in interest and activity in recent years in organometallic chemistry, especially in the area of homogeneous catalysis by transition-metal complexes. A number of publications have appeared dealing with particular organometallic reactions which occur in catalysis, such as oxidative addition,[1,2] insertion,[3] ligand exchange,[4] and reactions of complexes with Lewis acids.[5] A few authors have attempted to outline the principles of catalysis more generally.[6-8] There appears, however, to be no satisfactory scheme which relates the various reaction types or which permits mechanistic predictions.

In this review the various types of organometallic reactions involved in catalysis are organized in a systematic way, and some empirical rules are presented which may be used predictively to restrict the kinds of organometallic compounds which may exist under mild conditions and the types of reactions they may undergo.

The tendency of transition metals to form complexes in which the metal has an effective atomic number corresponding to the next higher inert gas has long been recognized.[9] There are, however, many exceptions, as illustrated by the following examples:

Compound	*NVE*
$TiCl_4$	8
$MeAuPPh_3$	14
$Co(CN)_5^{3-}$	17
$Ni(H_2O)_5^{2+}$	20

The number of valence electrons (NVE) consists of the valence electrons of the

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* Contribution No. 1821.

[1] J. P. Collman, *Accounts Chem. Res.*, 1968, **1**, 136; J. P. Collman and W. R. Roper, *Adv, Organometallic Chem.*, 1968, **7**, 53.

[2] J. Halpern, *Accounts Chem. Res.*, 1970, **3**, 386.

[3] R. F. Heck, *Adv. Chem. Ser.*, 1965, **49**, 181.

[4] C. H. Langford and H. B. Gray, 'Ligand Substitution Processes', Benjamin, New York. 1965.

[5] D. F. Shriver, *Accounts Chem. Res.*, 1970, **3**, 231.

[6] J. Halpern, *Discuss. Faraday Soc.*, 1968, **46**, 7.

[7] J. Halpern, *Adv. Chem. Ser.*, 1968, **70**, 1.

[8] R. Ugo, *Chimica e Industria*, 1969, **51**, 1319.

[9] N. V. Sidgwick, 'The Electronic Theory of Valency', O.U.P., London, 1929, p. 163.

metal and those electrons donated by or shared with the ligands, and would be 18 for an inert-gas configuration. If, however, one restricts attention to the diamagnetic organometallic complexes of Groups IVB—VIII, essentially all of the well-characterized compounds have 16 or 18 metal valence electrons.[10,11] This fact has not generally been adequately appreciated by organometallic chemists. In fact, the literature contains numerous examples of organometallic compounds which, as formulated, appeared to be exceptions to what can be called the 16 and 18 Electron Rule. Careful subsequent study has almost invariably shown that the original formulation was incorrect. The accessibility of 16 and 18 electron configurations also has important consequences for mechanisms of organometallic reactions, as outlined below.

Organometallic compounds, for the purposes of this discussion, are transition-metal complexes containing one or more ligands such as CO, N_2, CN^-, RNC, PR_3, $P(OR)_3$, olefin, acetylene, π-allyl, π-cyclopentadienyl, π-aryl, acyl, $-SiR_3$, -R, or -H. These 'soft'[12] or 'class *b*'[13] ligands are characterized by a high ligand-field strength and covalent bonding character and are the types typically found in homogeneous catalytic reactions such as hydrogenation, hydroformylation, hydrosilylation, and olefin isomerization and oligomerization.

The 16 and 18 Electron Rule.—Two postulates or rules for organometallic complexes and their reactions are proposed.

1. Diamagnetic organometallic complexes of transition metals may exist in a significant concentration at moderate temperatures only if the metal's valence shell contains 16 or 18 electrons. A significant concentration is one that may be detected spectroscopically *or kinetically* and may be in the gaseous, liquid, or solid state.
2. Organometallic reactions, including catalytic ones, proceed by elementary steps involving only intermediates with 16 or 18 metal valence electrons.

It is apparent that application of these rules requires that care be exercised in reaching conclusions on the NVE of a metal complex. Association or dissociation of the compound may occur. For example, $Ni[PPh_3]_4$ is substantially dissociated in solution into $Ni[PPh_3]_3$ and PPh_3.[14] π-Allyl palladium chloride is a 16 electron complex, with chloride ions bridging in a dimeric structure.[15] Polyfunctional ligands may co-ordinate at more than one site, and additional M—C and M—H bonds may form by reaction of a metal with C—H bonds of the ligands.[16]

When the complex is in solution, there is a potential ambiguity as to whether solvent is co-ordinated. The mere presence of solvent in the analysis of a crystalline solid is not good evidence for solvent co-ordination. One convenient criterion

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[10] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions', Wiley, New York, 1967, p. 526.

[11] G. E. Coates, M. L. H. Green, and K. Wade, 'Organometallic Compounds', Vol. 2, 'The Transition Elements', Methuen and Co., Ltd., London, 1968, p. 6.

[12] R. G. Pearson, *Science*, 1966, **151**, 172.

[13] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.*, 1958, **12**, 265.

[14] C. A. Tolman, W. C. Seidel, and D. H. Gerlach, *J. Amer. Chem. Soc.*, 1972, **94**, 2669.

[15] W. E. Oberhansli and L. F. Dahl, *J. Organometallic Chem.*, 1965, 3, 43.

[16] G. W. Parshall, *Accounts Chem. Res.*, 1970, 3, 139.

for solution studies is whether the electronic spectrum of the complex is substantially different in different solvents. Frequently a coloured complex will give dramatic colour changes when dissolved in a co-ordinating solvent. For example, $Ni[P(O\textit{o}\text{-tolyl})_3]_3$,[17] a red-orange solid, gives red-orange solutions in benzene, tetrahydrofuran, or methylene chloride, in which it remains three-co-ordinate, but gives a colourless solution in acetonitrile, from which the unstable adduct $MeCNNi[P(O\textit{o}\text{-tolyl})_3]_3$ has been isolated.[18]

2 Types of Organometallic Reactions

Reactions of ligands which do not directly involve the transition metal are excluded from this classification. Some examples of such reactions are methanolysis of $Ni(PF_3)_4$ to give $Ni(PF_3)_3[PF_{3-n}(OMe)_n]$, Friedel–Crafts acylation of ferrocene, and nucleophilic attack on a co-ordinated carbonyl by methoxide ion. Reactions which involve the transition metal directly can be broken down into five elementary reactions, each with a microscopic reverse. The classification is based upon the changes in number of metal valence electrons, formal oxidation state, and co-ordination number which accompany each reaction. The five elementary reactions are shown with examples in the Table. It will be seen that reactions 1 and 2 involve dissociation and association of ligands whereas 3—5 involve reactions between co-ordinated ligands. The latter can be classified according to the parity of the groups coupled, considering them to be uncharged. Thus coupling of two hydrogen atoms or two π-allyl groups (odd–odd coupling) is a reductive elimination. Coupling of an odd-electron fragment, such as a π-allyl, with an even one, such as ethylene, is an insertion. Even–even coupling, as between two π-bonded olefin molecules, is oxidative coupling.

Some of the terms in the Table are used in a way which may be unfamiliar to the reader and warrant further discussion. The term 'Lewis base ligand' is used to include ligands such as CO which are not normally considered as bases, in addition to more usual ones such as phosphines, on the basis that they contribute two electrons to the metal's valence shell. Lewis acid ligands, such as H^+, BF_3, and SO_2, contribute no valence electrons.

In common parlance 'oxidative addition' is used to describe an over-all reaction in which the formal oxidation state of the metal and the co-ordination number increase by either one or two.[2] In this discussion only a concerted one-step reaction which increases both co-ordination number and oxidation state by two is termed an oxidative addition. The narrower definition is used in order to break reactions down into elementary steps and to distinguish between different types of mechanisms. An increase in co-ordination number by one as in

$$H^+ + Co(CO)_4^- \longrightarrow HCo(CO)_4 \qquad (1)$$

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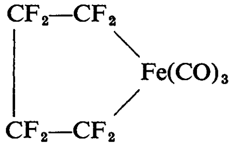
[17] L. W. Gosser and C. A. Tolman, *Inorg. Chem.*, 1970, **10**, 2350.
[18] C. A. Tolman, *Inorg. Chem.*, 1971, **7**, 1540.

Table *Elementary organometallic reactions*

Reaction	ΔNVE[a]	ΔOS[b]	ΔN[c]	*Example*	*Reverse Reaction*	ΔNVE	ΔOS	ΔN
1. Lewis acid ligand dissociation	0	0	−1	$CpRh(C_2H_4)_2SO_2 \rightleftharpoons SO_2 + CpRh(C_2H_4)_2$	Lewis acid association	0	0	+1
or	0	−2	−1	$HCo(CO)_4 \rightleftharpoons H^+ + CoCO_4^-$	or	0	+2	+1
2. Lewis base ligand dissociation	−2	0	−1	$NiL_4 \rightleftharpoons NiL_3 + L$	Lewis base association	+2	0	+1
3. Reductive elimination	−2	−2	−2	$H_2IrCl(CO)L_2 \rightleftharpoons H_2 + IrCl(CO)L_2$	Oxidative addition	+2	+2	+2
4. Insertion	−2	0	−1	$MeMn(CO)_5 \rightleftharpoons MeCOMn(CO)_4$	Deinsertion	+2	0	+1
5. Oxidative coupling	−2	+2	0	$(C_2F_4)_2Fe(CO)_3 \rightleftharpoons$ 	Reductive decoupling	+2	−2	0

[a] Change in the number of metal valence electrons; [b] Change in the formal oxidation state of the metal. The usual convention which regards hydrides, alkyls, π-allyls, and π-cyclopentadienyls as uninegative ions is used; [c] Change in co-ordination number.

is regarded as a Lewis acid ligand association reaction. A two-step reaction, as in

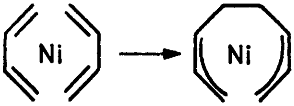
$$\mathrm{IrCl(CO)L_2 + CH_3I \longrightarrow [CH_3IrCl(CO)L_2]^+I^-} \qquad (2)$$

$$\mathrm{[CH_3IrCl(CO)L_2]^+I^- \longrightarrow CH_3IrCl(I)(CO)L_2} \qquad (3)$$

is regarded as a Lewis acid ligand association followed by a Lewis base ligand association.

Reaction of molecules such as O_2 or tetracyanoethylene with a transition metal can be regarded as an oxidative addition in which only part of a multiple bond is broken to form two new metal–ligand bonds, leaving the two ligands joined. With less electronegative olefins, such as C_2H_4 or C_2F_4, it may be more convenient to regard their co-ordination as a Lewis base addition rather than as an oxidative addition. The real extent of electron transfer must be determined by ESCA or some other means. The count of metal valence electrons in either case is the same.

The terms 'oxidative coupling' and 'reductive decoupling' are new. The former is used to denote reactions such as that shown in reaction (4), in which the formal oxidation state of the metal increases by two but the co-ordination number does not change.



(4)

3 Applications of the Rule to General Organometallic Reactions

The 16 and 18 Electron Rule severely restricts the types of reaction which a particular complex may undergo. Dissociation or association of Lewis acid ligands may occur with either 16- or 18-electron complexes. Lewis base ligand dissociation, reductive elimination, insertion, and oxidative coupling are restricted to 18-electron complexes. Lewis base ligand association, oxidative addition, deinsertion, and reductive decoupling reactions can occur only with 16-electron complexes. A number of examples from the literature will serve to illustrate these points.

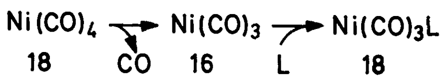
A. Lewis Acid Dissociation–Association.—That Lewis acids may react with either 16- or 18-electron complexes is shown by the formation of adducts of BF_3 with 16-electron $IrCl(CO)(PPh_3)_2$[19] or with 18-electron $HRe(\pi\text{-}C_5H_5)_2$.[20] Other

[19] R. N. Scott, D. F. Shriver, and L. Vaska, *J. Amer. Chem. Soc.*, 1968, **90**, 1079.

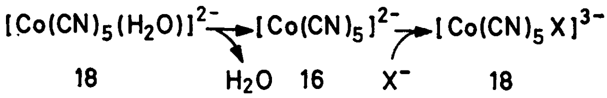
[20] M. P. Johnson and D. F. Shriver, *J. Amer. Chem. Soc.*, 1966, **88**, 301.

examples of reactions of 18-electron complexes with Lewis acids include formation of $[(\pi\text{-}C_5H_5)Rh(CO)PMePh_2Cl]^+$ from $(\pi\text{-}C_5H_5)Rh(CO)PMePh_2$ and Cl_2[21] and of $HNi[P(OEt)_3]_4^+$ from $Ni[P(OEt)_3]_4$ and H^+.[22]

B. Lewis Base Dissociation–Association.—Ligand-exchange reactions are the most thoroughly studied type of organometallic reaction. They generally proceed *via* Lewis base ligand dissociation as a first step for 18-electron complexes and *via* ligand association for 16-electron complexes. Examples include exchange of CO from $Ni(CO)_4$ by L = CO or PPh_3 in reaction (5),[23] displacement of H_2O from $[Co(CN)_5(H_2O)]^{2-}$ by $X^- = N_3^-$ or SCN^- in reaction (6),[24] and the reaction

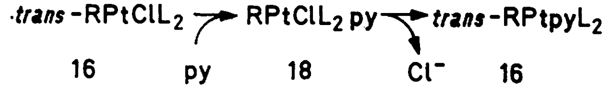


$$\underset{18}{Ni(CO)_4} \xrightarrow[CO]{} \underset{16}{Ni(CO)_3} \xrightarrow[L]{} \underset{18}{Ni(CO)_3L} \qquad (5)$$



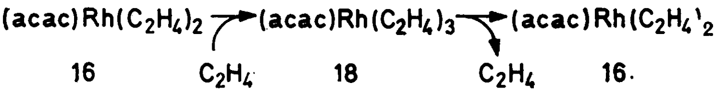
$$\underset{18}{[Co(CN)_5(H_2O)]^{2-}} \xrightarrow[H_2O]{} \underset{16}{[Co(CN)_5]^{2-}} \xrightarrow[X^-]{} \underset{18}{[Co(CN)_5X]^{3-}} \qquad (6)$$

of pyridine with *trans*-$RPtCl(PEt_3)_2$ complexes in reaction (7).[25] In these reactions the number beneath each complex indicates the NVE.



$$\underset{16}{trans\text{-}RPtClL_2} \xrightarrow[py]{} \underset{18}{RPtClL_2py} \xrightarrow[Cl^-]{} \underset{16}{trans\text{-}RPtpyL_2} \qquad (7)$$

The initially puzzling observations by Cramer[26] that $(acac)Rh(C_2H_4)_2$ exchanges ethylene rapidly on an n.m.r. time scale, whereas $(\pi\text{-}C_5H_5)Rh(C_2H_4)_2$ is very inert to exchange are readily explained. The acetylacetonate complex can exchange *via* the associative mechanism shown in reaction (8). For the 18-electron $(\pi\text{-}C_5H_5)Rh(C_2H_4)_2$ the associative pathway is blocked. The 16-electron (C_2H_4)-



$$\underset{16}{(acac)Rh(C_2H_4)_2} \xrightarrow[C_2H_4]{} \underset{18}{(acac)Rh(C_2H_4)_3} \xrightarrow[C_2H_4]{} \underset{16}{(acac)Rh(C_2H_4)_2} \qquad (8)$$

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[21] A. J. Oliver and W. A. G. Graham, *Inorg. Chem.*, 1970, **9**, 243.

[22] W. C. Drinkard, D. R. Eaton, J. P. Jesson, and R. V. Lindsey, jun., *Inorg. Chem.*, 1970, **9**, 392.

[23] J. P. Day, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1968, **90**, 6927.

[24] A. Haim and W. K. Wilmarth, *Inorg. Chem.*, 1962, **1**, 573.

[25] F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.*, 1961, 2207.

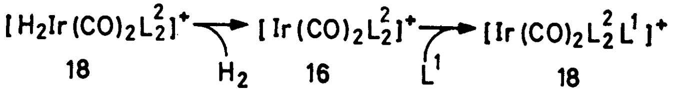
[26] R. Cramer, *J. Amer. Chem. Soc.*, 1967, **89**, 4621.

$Ni[P(Oo\text{-tolyl})_3]_2$ exchanges ethylene very rapidly but can be recovered unchanged after prolonged exposure of a solution to vacuum.[27] Again, the 16-electron complex can associate a two-electron ligand but does not dissociate.

C. Reductive Elimination–Oxidative Addition.—The kinetics of reaction (9),

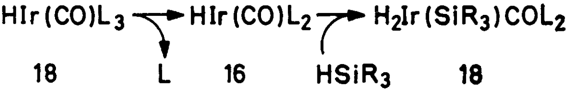
$$[H_2Ir(CO)_2L^2_2]^+ + L^1 = H_2 + [Ir(CO)_2L^2_2L^1]^+ \qquad (9)$$

involving reductive elimination of H_2, have been studied.[28] The rate of the reaction is independent of the concentration and nature of L^1 [L^1 = CO, $P(OMe)_3$, $P(OPh)_3$, or $PMePh_2$] as required for rate-determining loss of H_2 in the mechanism shown in reaction (10). The 16-electron intermediate was actually isolated for $L^2 = P(C_6H_{11})_3$.



$$[H_2Ir(CO)_2L^2_2]^+ \xrightarrow{-H_2} [Ir(CO)_2L^2_2]^+ \xrightarrow{+L^1} [Ir(CO)_2L^2_2L^1]^+ \qquad (10)$$
$$18 \qquad\qquad 16 \qquad\qquad 18$$

Oxidative addition of H_2 to the 16-electron complex $IrCl(CO)(PPh_3)_2$ is first-order in both H_2 and Ir complex,[29] as required for a concerted reaction. Reaction of the 18-electron complex $HIr(CO)(PPh_3)_3$ with $HSi(OEt)_3$, as expected, does not occur in a single step.[30] The mechanism found is shown in reaction (11) (L = PPh_3, R = OEt).



$$HIr(CO)L_3 \xrightarrow{-L} HIr(CO)L_2 \xrightarrow{+HSiR_3} H_2Ir(SiR_3)COL_2 \qquad (11)$$
$$18 \qquad\qquad 16 \qquad\qquad 18$$

The need to dissociate a ligand from an 18-electron complex before oxidative addition can occur is also shown in the reactions of H_2 or HCl with $EtCOM(CO)_2(PPh_3)_2$. High concentrations of CO inhibit the formation of aldehyde.[31]

Pearson has recently shown that optically active $MeCHBrCO_2Et$ reacts with $Mn(CO)_5^-$ with inversion of configuration.[32] The 18-electron complex cannot undergo an oxidative addition without first losing a CO ligand. Since CO dissociation from $Mn(CO)_5^-$ is extremely slow,[33] the reaction is forced to proceed in a way which does not increase the NVE of Mn. The S_N2 Walden inversion which occurs at the asymmetric carbon can be regarded as a special case of Lewis

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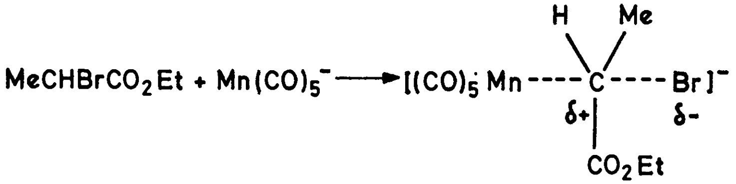
[27] W. C. Seidel and C. A. Tolman, *Inorg. Chem.*, 1970, **9**, 2354.
[28] M. J. Mays, R. N. F. Simpson, and F. P. Stefanini, *J. Chem. Soc.* (*A*), 1970, 3000.
[29] P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, 1966, **88**, 3511.
[30] J. F. Harrod and C. A. Smith, *Canad. J. Chem.*, 1970, **48**, 870.
[31] G. Yagupsky, C. K. Brown, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1970, 1392.
[32] R. W. Johnson and R. G. Pearson, *Chem. Comm.*, 1970, 986.
[33] W. Hieber and K. Wollmann, *Chem. Ber.*, 1962, **95**, 1552, found no exchange with ^{14}CO in 20 h at 40 °C.

acid ligand association, the bromine leaving with the electron pair it had shared with carbon (reaction 12).

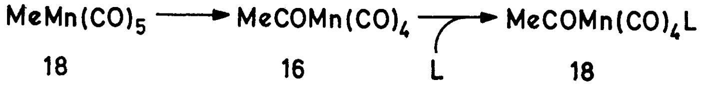


$$\mathrm{MeCHBrCO_2Et + Mn(CO)_5^- \longrightarrow [(CO)_5Mn\text{----}\overset{H\quad Me}{\underset{\delta+\,|\,CO_2Et}{C}}\text{----}\underset{\delta-}{Br}]^-}$$

(12)

On the other hand, reaction of $IrCl(CO)(PMePh_2)_2$ with $MeCHBrCO_2Et$ is reported to proceed with retention.[34] A concerted oxidative addition with retention of configuration is possible for the Ir complex because it has 16 valence electrons. Lewis acid association with inversion is also possible.

D. Insertion–Deinsertion.—The insertion of CO in the reaction of 18-electron $MeMn(CO)_5$ with L = PPh_3 or $P(OPh)_3$ involves CO insertion as a first step, followed by reaction of the 16-electron intermediate with L, as shown in reaction (13).[35] Insertion followed by ligand association is also consistent with the

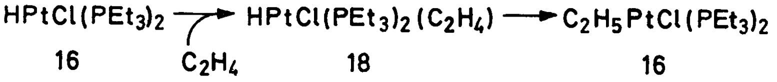


$$\underset{18}{\mathrm{MeMn(CO)_5}} \longrightarrow \underset{16}{\mathrm{MeCOMn(CO)_4}} \xrightarrow[\mathrm{L}]{} \underset{18}{\mathrm{MeCOMn(CO)_4L}}$$

(13)

result that treatment of $MeMn(CO)_5$ with ^{14}CO gives an acyl with a non-labelled CO;[36] some elegant experiments with ^{13}CO have demonstrated that the methyl group moves.[37]

Another type of insertion reaction is illustrated by reaction (14).[38] The existence of a hydrido-olefin intermediate has been supported by deuterium-labelling experiments.[39]



$$\underset{16}{\mathrm{HPtCl(PEt_3)_2}} \xrightarrow[\mathrm{C_2H_4}]{} \underset{18}{\mathrm{HPtCl(PEt_3)_2(C_2H_4)}} \longrightarrow \underset{16}{\mathrm{C_2H_5PtCl(PEt_3)_2}}$$

(14)

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[34] R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, 1970, **92**, 5519.

[35] R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, 1964, **86**, 3994.

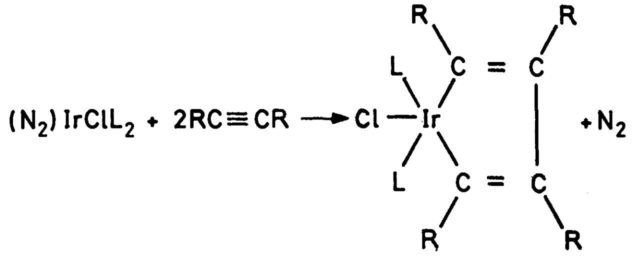
[36] T. H. Coffield, J. Kozikowski, and R. D. Closson, *J. Org. Chem.*, 1957, **22**, 598; 'Internat. Conf. on Co-ord. Chem., London, 1959', The Chemical Society, London (Special Publication No. 13), 1959, p. 126.

[37] K. Noack and F. Calderazzo, *J. Organometallic Chem.*, 1967, **10**, 101.

[38] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1962, 5075.

[39] J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc.* (*A*), 1968, 190.

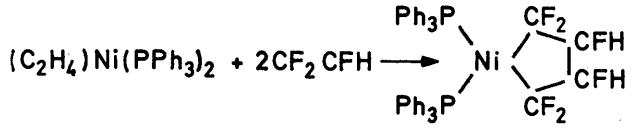
E. Oxidative Coupling–Reductive Decoupling.—An example of oxidative coupling is given by reaction (15),[40] where R = CO_2Me and L = PPh_3. The reaction



(15)

probably proceeds *via* oxidative coupling of the acetylenes in an $(RC_2R)IrClL_2$ intermediate.

Another example is given in reaction (16).[41] The details of the reaction are not



(16)

known; however, it probably proceeds by oxidative coupling of the olefins in $(C_2F_3H)_2Ni(PPh_3)_2$. There is a precedent for $(olefin)_2NiL_2$ complexes in $(CH_2{=}CHCN)_2Ni(PPh_3)_2$.[42]

4 Applications of the Rule to Homogeneous Catalytic Reactions

Homogeneous catalytic reactions proceed by the same elementary steps (see the Table) as general organometallic reactions. The unique feature of a catalytic system is that a series of steps is connected in a cyclic way, to form a loop. Mechanisms of some well-studied catalytic processes will now be described in detail.

A. Hydroformylation of Olefins by $HCo(CO)_4$.[43]—The hydroformylation of a terminal olefin is shown in Figure 1. The electron configurations and co-ordination numbers in the d^nN notation[44] are shown by each complex. The mechanism is basically that of Heck and Breslow,[45] but modified to show explicitly the

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[40] J. P. Collman, J. W. Kang, W. F. Little, and M. F. Sullivan, *Inorg. Chem.*, 1968, **7**, 1298.

[41] J. Ashley-Smith, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 3019.

[42] G. N. Schrauzer, *J. Amer. Chem. Soc.*, 1960, **82**, 1008.

[43] For a review see A. J. Chalk and J. F. Harrod, *Adv. Organometallic Chem.*, 1968, **6**, 119.

[44] d^n gives the number of *d* electrons for a particular oxidation state while *N* is the co-ordination number.

[45] R. F. Heck and D. S. Breslow, *J. Amer. Chem. Soc.*, 1961, **83**, 4023.

oxidative addition of hydrogen and reductive elimination of aldehyde. The first step of the reaction, starting with $HCo(CO)_4$, is Lewis base ligand dissociation from the 18-electron complex to give $HCo(CO)_3$. The reactions[45] proceeding clockwise around the loop are then: (2) olefin (Lewis base) association to give an 18-electron hydrido-olefin complex; (3) insertion of olefin to give a 16-electron alkyl; (4) association of CO to give an 18-electron alkyl; (5) insertion of CO to give a 16-electron acyl; (6) oxidative addition by H_2 to give an 18-electron acyl cobalt dihydride; and (7) reductive elimination of aldehyde product with regeneration of $HCo(CO)_3$. Step (8) connects the loop reversibly to a species not on the loop. Inhibition of hydroformylation by high CO pressure is due to reduction in the concentrations of loop species by step (8) and the reverse of (1).

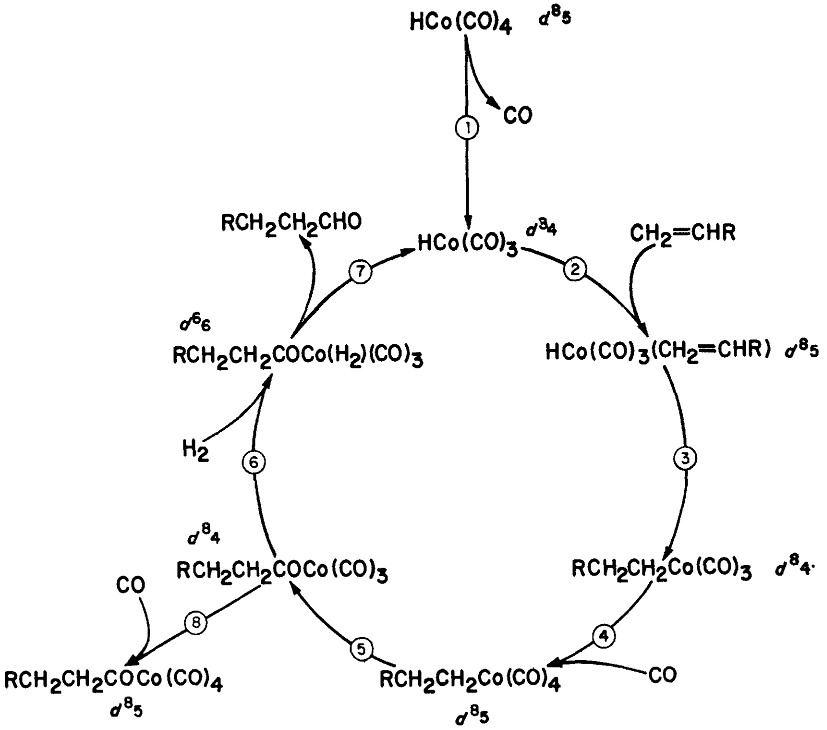

Figure 1 *Hydroformylation of a terminal olefin by* $HCo(CO)_4$

Figure 1 has been simplified in that it does not show formation of internal aldehydes, hydrogenation of aldehydes to alcohols and of olefins to alkanes, or olefin isomerization, which also occur in the system.

B. Hydrogenation of Olefins with $RhCl(PPh_3)_3$.—Application of the 16 and 18 Electron Rule to olefin hydrogenation with Wilkinson's catalyst[45] is shown in

Figure 2. Two loops arise from the possibility of co-ordinating hydrogen and olefin in either order. Step (1) represents oxidative addition of hydrogen to the square-planar 16-electron complex to give an 18-electron dihydride. Step (2), Lewis base dissociation, is followed by olefin co-ordination in step (3). Insertion in step (4) gives an unstable hydrido-alkyl with NVE = 16. Phosphine association in step (5) gives an 18-electron hydrido-alkyl which produces alkane by reductive elimination, regenerating $RhCl(PPh_3)_3$. Wilkinson's isolation of $(C_2H_4)RhClL_2$ and observation that the ethylene complex is not readily hydrogenated[46] suggest that step (9) is very slow, so that the bulk of the reaction goes *via* the loop which contains steps (1)—(6). The inhibition of hydrogenation on addition of triphenylphosphine to the system can be understood in terms of its suppression of ligand dissociation in step (2). The mechanism in Figure 2 is somewhat different from the one originally proposed, which included phosphine ligand dissociation as the first step in the reaction and simultaneous addition of both hydrogens to the double bond. The phosphine-dissociation step was based on a low value for the molecular weight of $RhCl(PPh_3)_3$. Molecular weight determinations[47] under scrupulously oxygen-free conditions indicated that the

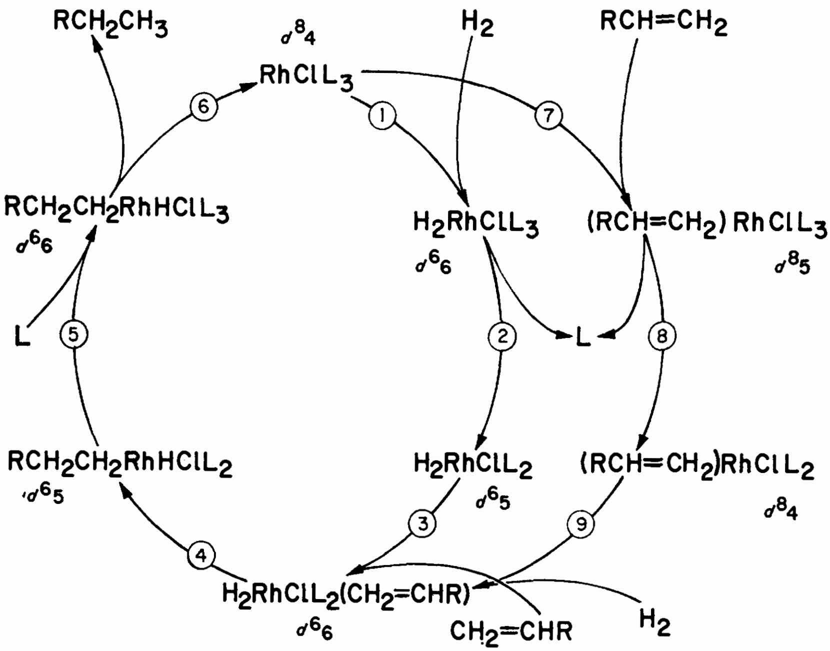

Figure 2 *Hydrogenation of a terminal olefin by* $RhCl(PPh_3)_3$

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[46] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1711.

[47] D. D. Lehman, D. F. Shriver, and I. Wharf, *Chem. Comm.*, 1970, 1486.

complex does not dissociate to any great extent. This conclusion was also supported by n.m.r. studies.[48] Studies[49] employing a combination of spectrophotometry and ^{31}P and ^{1}H n.m.r., indicate that $RhCl(PPh_3)_3$ dissociates only to a very small extent to give a dimer and that its reaction with H_2 gives $H_2RhCl(PPh_3)_3$,[50] rather than $H_2RhCl(PPh_3)_2S$ (S = solvent) as originally proposed.[46] Dissociation to $H_2RhCl(PPh_3)_2$ is slight, but does provide a mechanism for ligand exchange.

Stepwise rather than simultaneous addition of hydrogens during olefin hydrogenation is indicated by deuteriation[51] and olefin isomerization studies.[52]

It should be noted that both formation of $RhCl(PPh_3)_2$ and simultaneous addition of hydrogens to the olefin are prohibited by the 16 and 18 Electron Rule. $RhCl(PPh_3)_3$ is already a 16-electron complex and would drop to 14 if a PPh_3 were lost. Simultaneous addition of both hydrogens to an olefin would decrease the NVE by 4, and is not allowed since ΔNVE can only be 0 or ± 2.

C. Olefin Isomerization by $Ni[P(OEt)_3]_4$ and H_2SO_4.—An example of a catalytic system involving a Lewis acid is the isomerization of butenes catalysed by $Ni[P(OEt)_3]_4$ and H_2SO_4,[53] shown in Figure 3. In this case, two steps are required before the metal enters the loop: (1) Lewis acid association with 18-electron NiL_4 and (2) Lewis base ligand dissociation to give 16-electron $HNiL_3^+$. The reader can readily follow through the steps in the loop. Figure 3 is oversimplified in that side-reactions of catalyst decomposition and $P(OEt)_3$ dealkylation which occur in the system are not shown.

D. Orthodeuteriation of Triarylphosphines.—A catalytic reaction which involves oxidative addition of a transition metal by a C—H bond is the *ortho*-deuteriation of triaryl phosphine. Triphenylphosphine is converted catalytically under D_2 into tri-(2,6-dideuteriophenyl)phosphine by $HRuCl(PPh_3)_3,C_6H_5CH_3$.[54] The complex $HRuCl[P(OPh)_3]_4$ also exchanges H for D on the *ortho*-positions of the ligand phenyl rings, but is a very poor catalyst for the catalytic formation of tri-(2,6-dideuteriophenyl) phosphite; addition of $P(OPh)_3$ to a solution of $HRuCl[P(OPh)_3]_4$ under D_2 prevents deuteriation even of the original phosphite ligands. The result can be readily understood in terms of the 16 and 18 Electron Rule. $HRuCl(PPh_3)_3$ is a 16-electron complex and oxidative addition by an *ortho*-C—H bond can readily proceed. The 18-electron complex $HRuCl[P(OPh)_3]_4$ must dissociate a ligand, in an equilibrium suppressed by added ligand, before oxidative addition can occur.

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[48] D. R. Eaton and S. R. Suart, *J. Amer. Chem. Soc.*, 1968, **90,** 4170.
[49] J. P. Jesson, P. Meakin, and C. A. Tolman, *J. Amer. Chem. Soc.*, 1972, **94,** 3240.
[50] A. Sacco, R. Ugo, and A. Moles, *J. Chem. Soc. (A)*, 1966, 1670.
[51] A. S. Hussey and Y. Takeuchi, *J. Amer. Chem. Soc.*, 1969, **91,** 672.
[52] J. P. Candlin and A. R. Oldham, *Discuss. Faraday Soc.*, 1968, **46,** 60.
[53] C. A. Tolman, *J. Amer. Chem. Soc.*, 1972, **94,** 2994.
[54] G. W. Parshall, W. H. Knoth, and R. A. Schunn, *J. Amer. Chem. Soc.*, 1969, **91,** 4990.

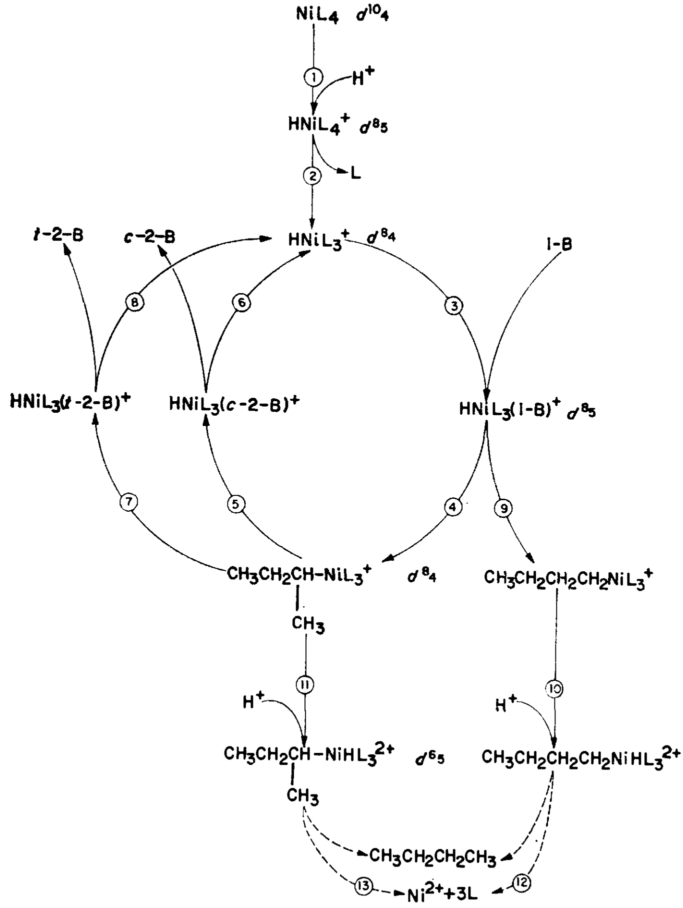

Figure 3 *Isomerization of butenes by* $Ni[P(OEt)_3]_4$ *and* H_2SO_4. 1-B, c-2-B, *and* t-2-B *represent but*-1-*ene*, cis-*but*-2-*ene*, and trans-*but*-2-*ene*. *From Ref.* 53

5 Apparent Exceptions to the Rule

A. Possible Alternative Explanations.—Some compounds appear at first sight to react in an exceptional way. The 18-electron complexes $Co(NO)(CO)_3$,[55] and $(\pi\text{-}C_5H_5)Rh(CO)_2$[56] undergo $S_{N}2$ reactions with phosphines to give $Co(NO)(CO)_2L$, and $(\pi\text{-}C_5H_5)Rh(CO)L$. Their anomalous behaviour can be explained in terms of an electron rearrangement to make available an empty bonding orbital.[57] This rearrangement can be thought of as an intramolecular conversion

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[55] E. M. Thorsteinson and F. Basolo, *J. Amer. Chem. Soc.*, 1966, **88**, 3929.

[56] H. G. Schuster-Woldan and F. Basolo, *J. Amer. Chem. Soc.*, 1966, **88**, 1657.

[57] Ref. 10, p. 571.

of the 18-electron complex into a 16-electron complex. Collman[58] has recently reported i.r. evidence which suggests that several $CoCl_2(NO)L_2$ complexes actually exist in solution as an equilibrium mixture of 16-electron [NO^- ligand] and 18-electron [NO^+ ligand] forms.

Angelici and Graham[59] have reported a two-term rate law for the reaction of 18-electron $Mo(CO)_6$ with phosphines such as PBu_3:

$$k_{obs} = k_1 + k_2[L]$$

The S_N2 path may involve a 20-electron intermediate or, as the authors mention, could involve attack by the phosphine on co-ordinated CO.

An *X*-ray crystal structure determination on $PtI_2(diars)_2$ (diars = *o*-phenylenebisdimethylarsine) shows that the Pt^{II} is six-co-ordinate in the crystal, with equal bond distances from Pt to each of the I atoms.[60] The bond lengths are, however, exceptionally long, 3.50 Å. Though the compound appears to be a 20-electron complex, there is an alternative bonding description, first proposed by Rundle[61] for the analogous I_3^-, which preserves the noble-gas configuration for the central atom. In nitromethane the platinum complex dissociates to give the 18-electron $[PtI(diars)_2]^+$.[60]

X-Ray crystal structures of tetrabenzylzirconium[62] and tetrabenzyltitanium,[63] apparently 8-electron complexes, have been reported. Both show anomalously small M—C—C bond angles at the methylene carbons, suggesting participation of ring electrons in the bonding. Definitive evidence for participation of ring electrons in bonding in a benzyl complex has been found in the structure of $(h^3\text{-}4\text{-}MeC_6H_4CH_2)(h^5\text{-}C_5H_5)Mo(CO)_3$.[64]

B. Original Formulation shown to be Incorrect.—There are a number of cases in the organometallic literature where complexes formulated as having other than 16 or 18 metal valence electrons were proposed, but where subsequent work has shown that the original formulation was in error. The absence of dissociation of Wilkinson's hydrogenation catalyst to $RhCl(PPh_3)_2$ has already been mentioned. The apparent 14-electron complexes $Ni(PPh_3)_2$[65] and Ni[P(O*o*-tolyl)$_3$]$_2$[66] were later shown to be the 16-electron complexes $(C_2H_4)Ni(PPh_3)_2$[67] and (C_2H_4)Ni[P(O*o*-tolyl)$_3$]$_2$.[27]

A 20-electron complex $Ni(CN)_6^{4-}$ was proposed on the basis of equilibrium studies on $Na_2Ni(CN)_4$ containing various concentrations of added NaCN.[68]

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[58] J. P. Collman, P. Farnham, and G. Dolcetti, *J. Amer. Chem. Soc.*, 1971, **93**, 1788.

[59] R. J. Angelici and J. K. Graham, *J. Amer. Chem. Soc.*, 1966, **88**, 3568.

[60] N. C. Stephenson, *J. Inorg. Nuclear Chem.*, 1962, **24**, 791.

[61] R. E. Rundle, *Rec. Chem. Progr.*, 1962, **23**, 195.

[62] G. R. Davies, J. A. J. Jarvis, B. T. Kilbourn, and A. J. P. Pioli, *Chem. Comm.*, 1971, 677.

[63] I. W. Bassi, G. Allegra, R. Scordamaglia, and G. Chioccola, *J. Amer. Chem. Soc.*, 1971, **93**, 3787.

[64] F. A. Cotton and M. D. La Prade, *J. Amer. Chem. Soc.*, 1968, **90**, 5418.

[65] G. Wilke, E. W. Muller, and M. Kroner, *Angew. Chem.*, 1961, **73**, 33.

[66] M. A. McCall and H. W. Coover, B.P. 1 146 074/1969.

[67] G. Wilke and G. Herrmann, *Angew. Chem. Internat. Edn.*, 1962, **1**, 549.

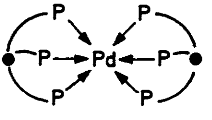
[68] R. A. Penneman, R. Bain, G. Gilbert, L. H. Jones, R. S. Nyholm, and G. K. N. Reddy, *J. Chem. Soc.*, 1963, 2266.

Later studies showed that the results were consistent with the presence of $Ni(CN)_4^{2-}$ and $Ni(CN)_5^{3-}$, 16- and 18-electron complexes, respectively, and that there was no evidence for the formation of 20-electron $Ni(CN)_6^{4-}$ even in 4M-NaCN.[69] An *X*-ray crystal-structure determination has shown that the compound originally formulated as $Mo(CH_2SiMe_3)_4$,[70] a 10-electron complex, is actually a cluster compound with a very short Mo—Mo bond distance.[71]

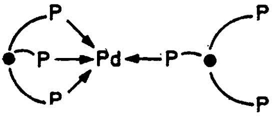
The 14-electron complex $Pt(PPh_3)_2$ has been proposed as an intermediate in oxidative addition reactions[2] of $Pt(PPh_3)_3$ and $(C_2H_4)Pt(PPh_3)_2$,[72] and in substitution reactions[73] of (alkyne)$Pt(PPh_3)_2$. The compound was first suggested on the basis of low molecular weights for $Pt(PPh_3)_3$ and $Pt(PPh_3)_4$.[74] The preparation of a yellow material said to be the 'probably monomeric species $Pt(PPh_3)_2$' has recently been reported.[75]

Recent careful physical studies have been made on the platinum(0)–triaryl phosphine–ethylene system which include a combination of molecular weight determinations, spectrophotometry, and ^1H and ^{31}P n.m.r.[76] These studies have shown that $Pt(PPh_3)_3$ and $(C_2H_4)Pt(PPh_3)_2$ do not dissociate to a detectable extent. Furthermore the behaviour of lineshapes in the n.m.r. spectra on adding C_2H_4 and/or PPh_3 to solutions of $(C_2H_4)Pt(PPh_3)_2$ or $Pt(PPh_3)_3$ requires the associative mechanisms for exchange of ethylene or phosphine expected for these 16-electron complexes.

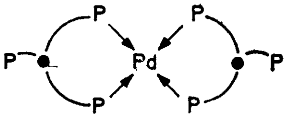
C. Predictions Based on the Rule.—The compound $Pd[MeC(CH_2PPh_2)_3]_2$ has been prepared in two crystalline forms.[77] The α-isomer was said to be a six-co-ordinate 22-electron complex (1), on the basis of a zero dipole moment, whereas the β-isomer with a dipole moment of 2.25 D was said to be (2). On the basis of the 16 and 18 Electron Rule it would be predicted that the α-isomer is (3). The true co-ordination number of the complexes could readily be established by ^{31}P n.m.r.



(1)



(2)



(3)

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[69] J. S. Coleman, H. Petersen, jun., and R. A. Penneman, *Inorg. Chem.*, 1965, **4**, 135.

[70] G. Yagupsky, W. Mowat, A. Shortland, and G. Wilkinson, *Chem. Comm.*, 1970, 1369.

[71] F. Huq, W. Mowat, A. Shortland, A. C. Skapski, and G. Wilkinson, *Chem. Comm.*, 1971, 1079.

[72] Dissociation constants for dissociation of $Pt(PPh_3)_3$ and $(C_2H_4)Pt(PPh_3)_2$ were reported by J. P. Birk, J. Halpern, and A. L. Pickard, *Inorg. Chem.*, 1968, **7**, 2672.

[73] A. D. Allen and C. D. Cook, *Canad. J. Chem.*, 1964, **42**, 1063.

[74] L. Malatesta and C. Cariello, *J. Chem. Soc.*, 1958, 2323.

[75] R. Ugo, G. La Monica, F. Cariati, S. Cenini, and F. Conti, *Inorg. Chim. Acta*, 1970, **4**, 390.

[76] C. A. Tolman, W. C. Seidel, and D. H. Gerlach, *J. Amer. Chem. Soc.*, 1972, **94**, 2669.

[77] J. Chatt, F. A. Hart, and H. R. Watson, *J. Chem. Soc.*, 1962, 2537.

Bis(trityl)nickel,[78] an apparent 12-electron complex, probably has a bis(π-allyl) structure in which each trityl group donates three electrons.[79]

Nickelocene is a paramagnetic complex in which the metal appears to have 20 valence electrons. Molecular orbital calculations, assuming a symmetric ferrocene-like structure (D_{5d}), show that the last two electrons should occupy a strongly anti-bonding doubly degenerate e_{1g} orbital.[80] This is consistent both with the instability of nickelocene compared with ferrocene and with the observed paramagnetism of the nickel complex. However, it can be predicted that the stable configuration of the compound is $({}^5h\text{-}C_5H_5)({}^3h\text{-}C_5H_5)Ni$, in which one of the rings is displaced off-centre. Easy accessibility of a number of equivalent configurations with a small activation energy between them should give a rapid fluxional behaviour, consistent with the results of recent electron-diffraction measurements on nickelocene vapour.[81]

Vaska[82] has reported H—D exchange of $HIrCl_2(PPh_3)_3$ and $HRuCl(CO)(PPh_3)_3$ with D_2 and suggested that the reactions go *via* eight-co-ordinate intermediates (20-electron complexes) formed in the direct oxidative addition of D_2 to the above complexes. Vaska has even attributed a special catalytic activity to this type of high co-ordination number (and high NVE) complex.[83] A prediction that added CO and PPh_3 will inhibit the rate of the exchange reaction, indicating that a Lewis base ligand is lost prior to oxidative addition by D_2, is nicely supported by the recent work of Burnett and Morrison[84] which shows that added PPh_3 inhibits the rate of reaction of H_2 with $HIr(CO)(PPh_3)_3$ to give $H_3Ir(CO)(PPh_3)_2$.

In homogeneous catalytic reactions it is to be expected that no reaction steps will be found in which the NVE of the metal in the complex changes by more than two. Thus *concerted* addition of two hydrogens to an olefinic double bond, coupling of two olefins to form a cyclobutane, and [2 + 2] valence isomerism of polycyclic hydrocarbons to cyclic dienes are excluded on the bases that $\Delta\text{NVE} = \pm 4$ in these reactions. The requirement that $\Delta\text{NVE} = 0, \pm 2$ adds severe restraints to those proposed by Mango and Schachtschneider based on orbital symmetry considerations.[85] There is considerable experimental evidence that catalysis of these reactions by Group VIII metal complexes is stepwise. For example, evidence has been presented to show that valence isomerization of cubane by $[Rh(diene)Cl]_2$ catalysts proceeds *via* a non-concerted oxidative addition mechanism.[86]

The products formed by cyclodimerization of penta-1,3-diene are consistent

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[78] G. Wilke and H. Schott, *Angew. Chem. Internat. Edn.*, 1966, **5**, 583.

[79] This suggestion has also been made by R. B. King in 'Annual Surveys of Organometallic Chemistry', Vol. 3, ed. D. Seyferth and R. B. King, Elsevier, Amsterdam, 1967, p. 403.

[80] J. H. Schachtschneider, R. Prins, and P. Ros, *Inorg. Chim. Acta*, 1967, **1**, 462.

[81] L. Hedberg and K. Hedberg, *J. Chem. Phys.*, 1970, **53**, 1228.

[82] L. Vaska, *Proc. 8th Internat. Conf. Co-ord. Chem. Vienna*, 1964, 99.

[83] L. Vaska, *Inorg. Nuclear Chem. Letters*, 1965, **1**, 89.

[84] M. G. Burnett and R. J. Morrison, *J. Chem. Soc. (A)*, 1971, 2325.

[85] F. D. Mango and J. Schachtschneider, *J. Amer. Chem. Soc.*, 1971, **93**, 1123.

[86] L. Cassar, P. E. Eaton, and J. Halpern, *J. Amer. Chem. Soc.*, 1970, **92**, 3515.

with a stepwise rather than a concerted reaction.[87] Heimbach[88] has also stressed the stepwise nature of reactions of this type, whose concerted reactions are forbidden in the absence of catalysts by the Woodward-Hoffmann rules.[89]

6 Conclusion

The 16 and 18 Electron Rule in organometallic chemistry is consistent with such a large body of experimental evidence, including studies on reaction mechanisms, that anyone proposing an exceptional compound or reaction path must bear the burden of proof. The Rule is, however, empirical at this point, and may be subject to exceptions in some cases, especially near the beginning and end of the transition series.[60,63] Nyholm[90] has discussed the relationship between transition metal, oxidation state, co-ordination number, and ligand type and has nicely correlated a great deal of data with atomic properties such as ionization potentials and electron promotion energies. More quantitative theoretical studies and further experience are now required to define the limits of applicability of the Rule.

The basic premise of this review is that 16- and 18-electron configurations are readily accessible to diamagnetic organometallic transition-metal complexes. Species with other configurations or reactions by other paths will generally be so energetically unfavourable by comparison that they are negligible.

If this review acts as a goad to the research of others, if only to challenge its generality, it will have served its purpose well.

I am indebted to R. Cramer, J. P. Jesson, G. W. Parshall, L. J. Guggenberger, and R. S. Nyholm for helpful discussions, and to G. Wilkinson and P. Heimbach for communication of results prior to publication.

Note Added in Proof: The application of the 16 and 18 Electron Rule to catalysis by transition-metal hydride complexes has recently been discussed by C. A. Tolman, 'Transition Metal Hydrides', ed. E. L. Muetterties, Marcel Dekker, Inc., New York, 1971, Ch. 6.

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[87] P. Heimbach and H. Hey, *Angew. Chem. Internat. Edn.*, 1970, **9**, 528.

[88] P. Heimbach, *Aspects of Homogeneous Catalysis*, in press.

[89] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781.

[90] R. S. Nyholm, *Proc. Chem. Soc.*, 1961, 273; 'Proc. 3rd Internat. Conf. on Catalysis', North Holland, Amsterdam, 1965, p. 25.