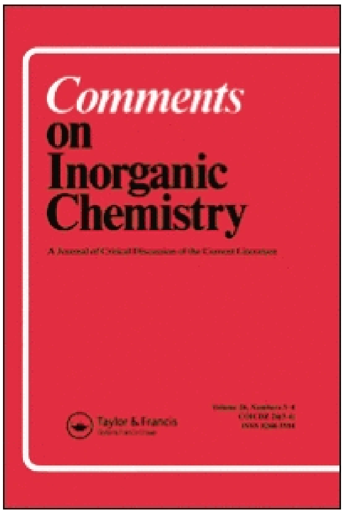

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Some Structure-Activity Relationships in Homogeneous Transition Metal Catalysts

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Some Structure–Activity Relationships in Homogeneous Transition Metal Catalysts

Mechanistic studies of homogeneous catalysts[1] have begun to give a fairly clear picture of the mechanism in a number of different systems. In the case of low valent organometallic catalysts, the metal often shuttles between two different oxidation states, and between 16- and 18-electron configurations.[2] Many catalysts have one or more labile ligands that dissociate to allow access for the substrate(s) involved in the reaction. We have been particularly interested for several years in studying complexes that have multiple labile ligands that can provide many sites for the substrate(s) to bind. This has led us to think in terms of the partitioning of the electron count of the catalytic intermediates between the part derived from the substrate(s) and from the permanently bound ligands. Since we can easily adjust the number of permanently bound ligands and the total electron count must not exceed[2] 18, this gives us a way of altering the number of sites available to the substrate(s). Such changes can have a profound effect on the outcome of the catalytic reaction. The purpose of this Comment is to rationalize the results of some transition metal catalyzed reactions on the basis of this partitioning scheme.

In order to explain these ideas, we will refer to Scheme 1. This shows a simplified version of one way in which Wilkinson's catalyst can hydrogenate olefins.[3] For our present purposes, it does not matter that the true mechanistic situation is somewhat more complicated in this particular case, because we are considering ways to think about mechanisms in general, and we use this merely as an example. The intermediates are written in Scheme 1 so that the substrate-derived

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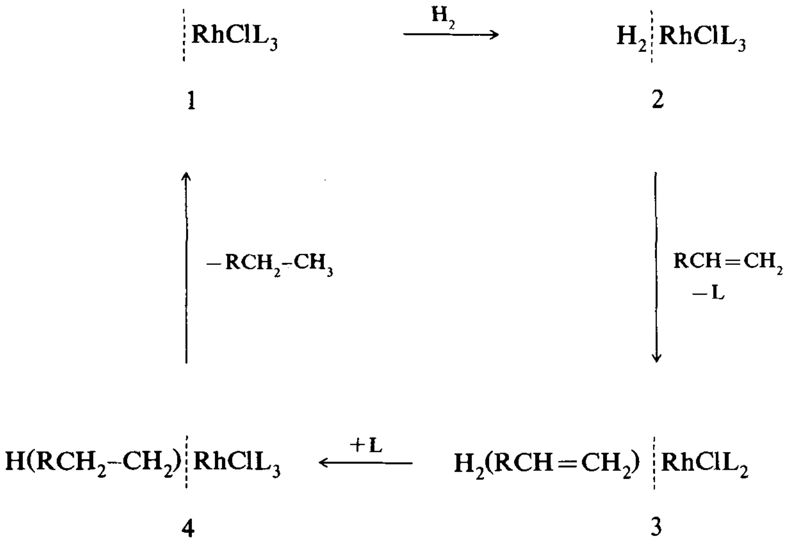
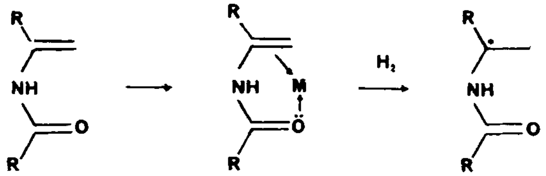


SCHEME 1 Simplified catalytic cycle for olefin hydrogenation with $[RhCl(PPh_3)_3]$.

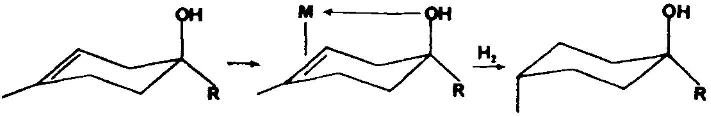
fragment which leads to products (SF) appears on the left while the metal and ligands, the catalyst-derived fragment (CF), appear to the right in each case; a dotted line shows this division explicitly. This particular mechanism shares a property common to many others: the SF at first increases in size as the reagents are assembled on the metal and then decreases as the products are formed, while the CF decreases and then increases correspondingly. If we consider how the SF[4] valence electron count varies during the cycle: **1**, 0; **2**, 2; **3**, 4; **4**, 2, then it is clear that the 4-electron H_2(ol) fragment in **3** is the most electronically demanding fragment (maximum SF or MSF). The MSF implies a limiting electron count of 14 for the corresponding CF, in this case the 14-electron fragment $RhClL_2$, which we shall call the MCF (minimal CF).

In order to show why this picture can be a useful one, we consider two important variants of hydrogenation, in each of which a further electronic demand is placed on the metal, because the corresponding MSFs have a larger electron count than for a simple hydrogenation. For both asymmetric[5] (Eq. (1)) and directed[6] hydrogenation (Eq. (2)) to be efficient, a group on the substrate olefin has to chelate to the metal during the reaction. In the asymmetric hydrogenation of acet-
It will be seen that this can only occur if the MCF has 12 electrons,

amido-substituted olefins, the C=O group binds to the metal, and in directed hydrogenation a —OH group on the substrate binds.



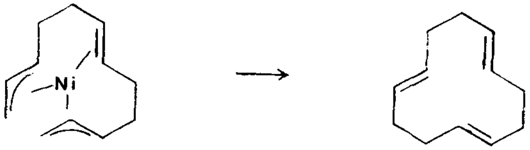
(1)



(2)

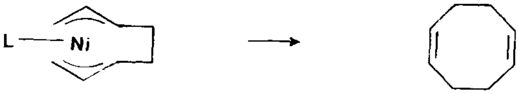
not 14, because the MSF is now (ol⌒L)H_2M (where (ol⌒L) is the olefin with its chelating group). This is the reason $RhClL_3$, with its 14-electron MCF $RhClL_2$, is incapable of efficient asymmetric or directed hydrogenations. The 12-electron catalysts $[M(cod)L_2]BF_4$ (M = Rh or Ir; cod = 1,5-cyclooctadiene) (MCF: ML_2^+) are the catalysts of choice both for asymmetric and for directed hydrogenation. The catalyst of lower MCF is in principle more versatile and may be able to catalyze any reaction up to the available limiting MSF electron count. Accordingly, $[M(cod)L_2]BF_4$ can catalyze classical hydrogenation (MSF: 4e) as well as the more demanding directed and asymmetric hydrogenations (MSF: 6e). These two classes of hydrogenation (MSF: 4e and MSF: 6e) might be termed facile and demanding reaction types, respectively.

The elegant work of Wilke[7] provides an example of the most electronically demanding catalytic mechanistic type of which we are aware. The 8-electron MSF **5** has been proposed for the cyclotrimerization of butadiene to **6** by the 10-electron MCDF "naked" Ni(0) (Eq. (3)). The addition of 1 mol of any of a variety of ligands L yields NiL, having a 12-electron MCF. This can only go as far as to dimerize butadiene to cyclooctadiene via the intermediate **7**, having a 6-electron MDF (Eq. (4)). Once again, a change in reaction type is observed in response to a change in the catalyst structure, and this change can be rationalized on the basis of SF/CF partitioning in the intermediates.



5 6

(3)



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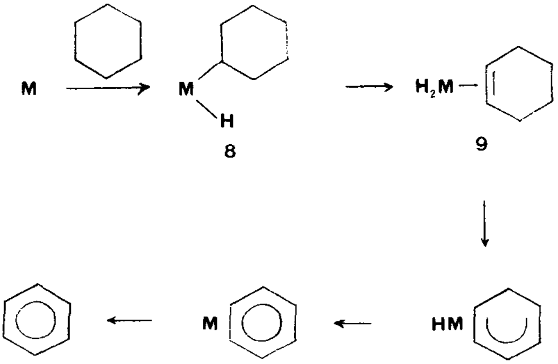
(4)

Similar arguments hold for alkane activation (Eq. (5))



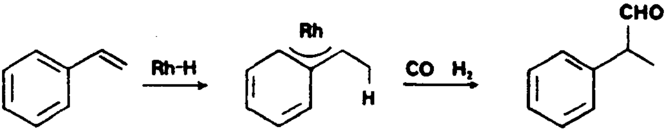
8 9 10 11

(5)

Here the proposed 16e MCF of Bergman *et al.*[8] ($\mathrm{Cp^*IrL}$ from $\mathrm{Cp^*IrLH_2}$ [$\mathrm{Cp^*} = \mathrm{C_5Me_5}$]) stoichiometrically dehydrogenates cyclohexane to give *8*. A number of systems go on to catalytically dehydrogenate alkanes to the corresponding alkenes. These have 14-electron rather than 16-electron MCFs. $\mathrm{ReH_7(PPh_3)_2}$ [9] is a typical catalyst for which $\mathrm{ReH_3L_2}$ has been proposed as MCF. Both $\mathrm{[IrH_2(Me_2CO)(PPh_3)_3]^+}$ and $\mathrm{IrH_2(OCOCF_3)(PPh_3)_2}$ are also catalysts[10c] for which $\mathrm{IrL_3^+}$ and $\mathrm{IrXL_2}$ have been proposed (X = $\mathrm{OCOCF_3}$, which can act as a 1-electron donor when it is monodentate). $\mathrm{[IrH_2(Me_2CO)_2(PPh_3)_2]^+}$ [10a] permits an even greater degree of dehydrogenation to give **10**, **11** and free arene. The 12-electron MCF IrL_2^+ is probably involved in the formation of **10**, but IrL^+ may be implicated in the conversion of **10** to **11** and free arene.

Unlike the case of hydrogenation, where the catalyst of lowest MCF could effect both facile and demanding types of hydrogenation, here each type seems to have its own characteristic reaction type.

In a recent paper,[10d] we suggested that the selectivity for branched aldehydes in styrene hydroformylation with rhodium catalysts is due to the formation of an η^3-benzyl intermediate. Tolman independently made a similar suggestion in the case of hydrocyanation.



(6)

It is significant that the ratio of branched to linear products is strongly dependent on the PPh_3/Rh ratio, n. The branched/linear ratio begins to fall[10e] only above $n \approx 1.8$, probably because excess phosphine competes with the arene C=C bond for the metal. If the 5-electron MSF $M(\eta^3\text{-benzyl})(CO)$ is proposed for the "directed" hydroformylation, a 13-electron "$Rh(PPh_3)_2$" MCF would be appropriate, and explain the product ratio change above $n \approx 1.8$ as $Rh(PPh_3)_3$ becomes important as the MCF. Hydrosilation[11] with H_2PtCl_6 also shows anomalous isomer ratios that may well be due to directing effects analogous to the case of Eq. (6). Styrene and $EtOCH{=}CH_2$ give branched products, but addition of certain ligands suppresses the branched product in favor of the linear.[11b] If $M(\eta^3\text{-benzyl})(SiR_3)$ is proposed as the MFLP (4-electrons), then $PtCl_2$ (12-electrons) is plausible as the MCF in the absence of added ligand.

A whole range of catalytic reactions and even of stoichiometric processes can be assigned MSFs and MCFs (Table I). Suitability of the MCF is clearly a necessary but not sufficient condition for catalytic activity in any given metal complex.

As always, a distinction should be drawn between the catalyst precursor for a given catalytic system and the active catalyst itself. For example $[Rh(cod)(PPh_3)_2]BF_4/NEt_3/PPh_3$ [10d] gives a hydroformylation catalyst with properties that are almost indistinguishable

TABLE I

MSFLP and MCF values for various proposed mechanisms in homogeneous catalysis

Reaction[a]	Proposed Intermediates	MSF[a] *e*-Count	MCF *e*-Count	MCF Example	FOD[b]	Ref.
Diene Cyclotrimerization	**5**[c]	8	10	Ni	2	7
Diene Cyclodimerization	**7**[c]	6	12	NiL	2	7
Directed Hydrogenation	$\mathrm{MH_2(ol{\frown}L)}$[d]	6	12	$\mathrm{IrL_2^+}$	2	6
Asymmetric Hydrogenation	$\mathrm{MH_2(ol{\frown}L)}$[d]	6	12	$\mathrm{RhL_2^+}$	2	5
Olefin Hydroformylation	MH(CO)(ol)	5	13	$\mathrm{RhL_2}$	2	12
Olefin Hydrogenation	$\mathrm{MH_2(ol)}$	4	14	$\mathrm{RhClL_2}$	2	3
Olefin Hydrosilation	$\mathrm{MH(SiR_3)(ol)}$	4	12[e]	$\mathrm{PtCl_2}$	2	11
Methanol Carbonylation	MMe(I)CO	4	14	$\mathrm{Rh(CO)I_2}$	2	18
Alkyne Trimerization	$\mathrm{M(RC{\equiv}CR)_2}$	4	14	CpCo	2	19
Water Gas Shift	MH(CO)	3	13[e]	$\mathrm{PtL_2^+}$	2	20
Wacker Process	$\mathrm{M(C_2H_4)}$	2	14	$\mathrm{PtCl_2(H_2O)}$	2	21
Oxygen Carrier	$\mathrm{M(O_2)}$	2	16	$\mathrm{IrCl(CO)L_2}$	2	22
Vitamin B_{12}	$\mathrm{M{-}CR_3}$ [f]	1	17	Co(corrin)L	1	23
Water-Splitting	$M(e^-)$	1	17	$\mathrm{Ru(bpy)_3^{2+}}$	1	14

[a] Not all examples of these reactions will have the same MSF *e*-count; this will depend on the particular mechanism adopted in each specific case.

[b] The change in formal oxidation state during the cycle.

[c] Shown in the text.

[d] L are 2-electron donor groups on the substrate (see text).

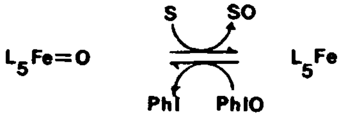
[e] Pt(II) often has a 16-electron configuration (Ref. 2). The H_2O is not included in the FLP because it is not incorporated into the product.

[f] This assumes Co–C bond homolysis leads to products; other mechanisms are possible.

from those of the catalyst derived from $RhHCO(PPh_3)_3$.[12] A simple way of expressing this identify is in terms of the identity of the MCFs in each case: $Rh(PPh_3)_2$.[12b]

Also listed in Table I are the maximum changes in formal oxidation state during the processes. This is a less useful criterion for characterizing the mechanism, partly because of ambiguity[2c] in the assignments, and partly because the value is so often 2.

There is another class of homogeneous catalyst that has not yet been mentioned. These do not require the substrate to coordinate to the metal at all. For example, many metalloenzymes and metal complexes can act as electron carriers which transfer electrons by outer sphere processes.[13] The example shown in Table I is $Ru(bpy)_3^{2+}$ which has been widely used in investigations on photolytic water splitting.[14] The very interesting work[15] on olefin epoxidation and alkane activation via high valent oxo-species provides another example of a class of catalyst in which the organic substrate does not need to bind directly. The system only becomes catalytic if the oxo group is regenerated. This can be accomplished directly by O-atom transfer from a donor such as PhIO [15] or OCl^-.[16] In the natural system, the mechanism of regeneration of the oxo group does not seem to have been fully established.

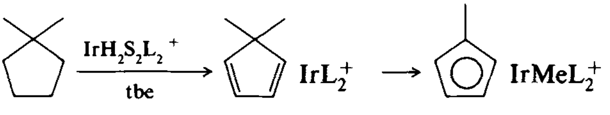


(7)

(L_5 = porphyrin and axial ligand; S = substrate)

The MSF count is 2 for this reaction, but the MCF is 15 not 16 because this high valent system does not obey the 18-electron rule.

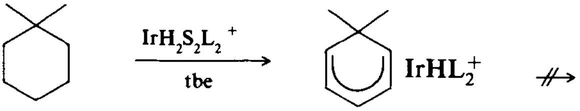
Recently we have described the first example of a reaction sequence for an unstrained alkane in which a C–C bond is broken[17] (Eq. (8)). This illustrates that the SF/CF partitioning can be useful in stoichiometric reactions as well. C–C bonds are hard to break, and this only occurs in **12** after several dehydrogenation steps have strongly activated the system.



(8)

12

(S = Me_2CO; L = PAr_3; tbe = *t*-BuCH=CH_2)

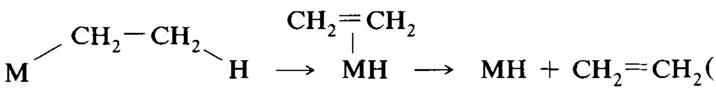


(9)

13

Only if the activated system has a 16-electron count will the C–C bond break. This difference is seen in Eq. (8) where the reaction occurs and the intermediate is 16-electron by comparison to Eq. (9) where the C–C cleavage fails to occur even under very vigorous conditions and the "intermediate" **13** is 18-electron; this is presumably for kinetic rather than thermodynamic reasons.

Elementary catalytic steps can also be described in a similar way. Some such steps lead to an increase in the SF electron count, some leave it unchanged, and some decrease it. In general, the first group of processes are the most demanding because a ligand will probably have to dissociate from the metal in order for that step to occur. A typical example is β-elimination (Eq. (10))



$$M{-}CH_2{-}CH_2{-}H \longrightarrow \overset{CH_2=CH_2}{\overset{|}{MH}} \longrightarrow MH + CH_2{=}CH_2 \quad (10)$$

In this reaction, the 1-electron alkyl undergoes β-abstraction to give a 3-electron $M(CH_2{=}CH_2)H$ species. The olefin is often subsequently lost by dissociation. Experimentally, ethyl complexes are usually only stable if they are coordinatively saturated and possess nondissociating ligands. On the other hand, elementary steps that either leave the SF *e*-count unchanged or decrease it are undemanding in the sense that no ligand dissociation needs to occur. If the step is thermodynamically favored, the kinetics are often fast. A typical example is the facile reductive elimination of alkane from an alkyl hydride complex. There are also examples of undemanding steps (in the sense that the SF decreases) which are not generally fast. The elimination of ethane from a dimethyl complex is likely to be thermodynamically favored,[24] but large numbers of complexes containing two or more methyl groups are known.[25] Here a significant kinetic barrier must be operating that is not connected with the electron count of the metal. This barrier may be steric in origin or may reflect the difficulty of simultaneously rehybridizing and distorting two methyl groups. To take the corresponding bond-breaking reactions, alkane C–H bond breaking[8,10] does not seem to have a large *kinetic* barrier associated with it, once a vacant site at the metal has been formed in some way. On the other hand, alkane C–C bond breaking has never been observed in such situations and the reaction does seem to have an intrinsic kinetic barrier. That is probably the reason why the first examples of alkene C–C bond breaking[16] have involved a 2-step process (Eq. (8)). C–C bond making and breaking therefore fail to fit the pattern described above. In general we expect predictions based on the change of SF electron count not to apply where there are special kinetic considerations not connected with SF changes. A second possible reason for failure of an undemanding reaction to occur is the thermodynamic instability of the products with respect to the starting materials. An example is the existence of large numbers of metal polyhydride complexes.[26] Loss of H_2 leads to a decrease in SF, yet many polyhydrides are remarkably stable. This is probably due to the exceptionally high M–H bond dissociation energies[24] (ca. 60 kcal mol^{-1}) compared with the bond dissociation energy for the product, H_2 (103 kcal mol^{-1}), especially for second and third row transition metals. First row polyhydrides are indeed much more labile and far fewer examples are known.

In the absence of special considerations of this sort, we would generally expect the "slow step" (turnover limiting step[27]) of a catalytic reaction to be demanding, rather than the opposite. This seems to be true in some cases but not others. For $RhCl(PPh_3)_3$,[8] the complex itself, or under high H_2 pressures,[28] the dihydride $RhH_2Cl(PPh_3)_3$ builds up in solution. This follows our expectation because both H_2 addition to the Rh(I) complex and olefin addition to the dihydride both have SF values of $+2e$. On the other hand, for catalysts[29] of

TABLE II

Some common elementary processes with the corresponding SF values

Process	ΔSF
MEt → $M(CH_2{=}CH_2)H$	+2
RR′ + M → M(R)(R′)[a]	+2
$M(CH_2{=}CH_2)_2$ → $M(C_4H_8)$[b]	+2
M + C_2H_4 → $M(C_2H_4)$	+2
M + CO → M(CO)	+2
$M(C_3H_6)$[b] → $M({=}CH_2)(CH_2{=}CH_2)$	+2
$M(CH{=}CH_2)$ + H^+ → $M({=}CH{-}CH_3)^+$	0
M + H^+ → MH^+	0
R^- + $M(C_3H_5)^+$ → $(RCH_2CH{=}CH_2)M$[c]	0
R^- + $M(CO)^+$ → M(COR)	0
$MH(CH_2{=}CH_2)$ → MEt	−2
M(R)(R′)[a] → M + RR′	−2
$M(C_4H_8)$[b] → $M(CH_2{=}CH_2)_2$	−2
$M(C_2H_4)$ → M + C_2H_4	−2
M(CO) → M + CO	−2
$M({=}CH_2)(CH_2{=}CH_2)$ → $M(C_3H_6)$[b]	−2

[a] RR′ = H_2, R–H, or R–R. R = alkyl or aryl.

[b] $M(C_4H_8)$ and $M(C_3H_6)$ are metalacyclopentanes and butanes, respectively.

[c] Assuming nucleophilic attack takes place directly on the ligand, not *via* the metal.

the $Ir(cod)L_2^+/CH_2Cl_2/H_2$/olefin type (cod = 1,5-cyclooctadiene), $IrH_2(olefin)_2L_2^+$ builds up, in spite of the fact that the next step, olefin insertion, has a ΔSF of $-2e$. Presumably, the insertion occurs but is readily reversible, because these catalysts also rapidly isomerize olefins.

Table II lists some of the most common reaction steps in organometallic chemistry with their ΔSF values in each case.

CONCLUSION

We have illustrated how the electron count of the MCF can influence the type of catalytic chemistry observed. The more demanding reactions require a lower MCF, so the addition of ligands can suppress these processes in favor of more facile ones. Similarly, the electron count changes associated with single reaction steps determines whether dissociative steps are required for the step to proceed. We have also shown how other kinetic and thermodynamic factors can override the expectations based on these ideas in certain cases.

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