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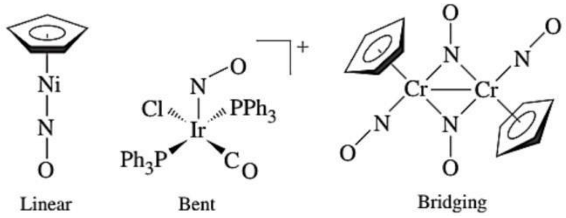
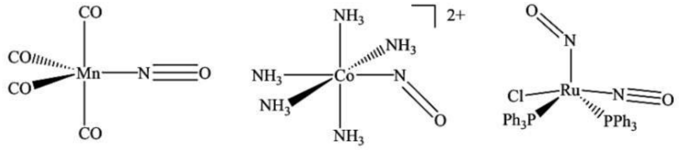
Nitrosyl (NO) complexes:

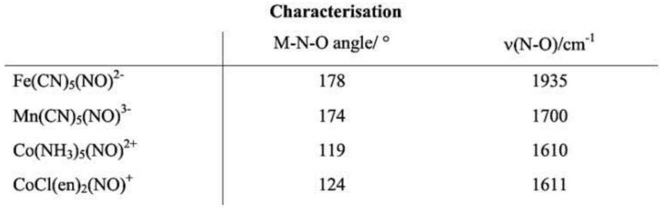
The NO (nitrosyl) ligand shares many similarities with CO. Like CO, it is a **σ-donor** and **π-acceptor** and can serve as a terminal or bridging ligand; useful information can be obtained about its compounds by analysis of its infrared spectra. Unlike CO, however, terminal NO has two common coordination modes, linear (like CO) and bent. Examples of NO complexes are in figure below.



* NO$^+$ is isoelectronic with CO; therefore, in its bonding to metals, linear NO is considered by electron counting scheme (ionic model) as NO$^+$, a 2-electron donor. By the (covalent model), linear NO is counted as a 3-electron donor (it has one more electron than the 2-electron donor CO). * The bent coordination mode of NO can be considered to arise formally from NO-, with the bent geometry suggesting *sp*^{2} hybridization at the nitrogen. By electron-counting scheme (ionic model), therefore, bent NO is considered the 2-electron donor NO$^-$, by the (covalent model), it is considered a 1-electron donor. * Useful information about the linear and bent bonding modes of NO is summarized in Figure below. Many complexes containing each mode are known, and examples are also known in which both linear and bent NO occur in the same complex. Although linear coordination usually gives rise to N-O stretching vibrations at a higher energy than the bent mode, there is enough overlap in the ranges of these bands that infrared

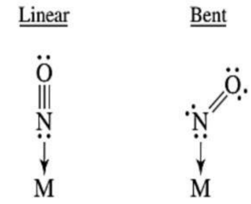
spectra alone may not be sufficient to distinguish between the two. Furthermore, the manner of packing in crystals may bend the M-N-O bond considerably from 180° in the linear coordination mode.





Characterisation

	M-N-O angle/ °	ν(N-O)/cm^{-1}
$Fe(CN)_5(NO)^{2-}$	178	1935
$Mn(CN)_5(NO)^{3-}$	174	1700
$Co(NH_3)_5(NO)^{2+}$	119	1610
$CoCl(en)_2(NO)^{+}$	124	1611

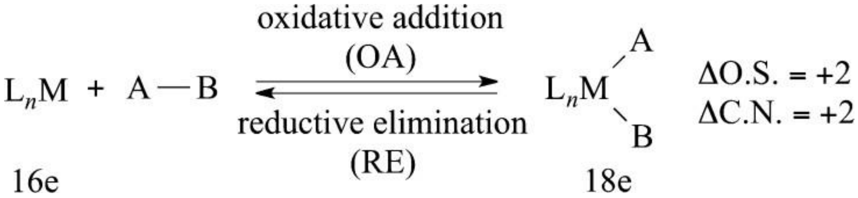


	Linear	Bent
M—N—O angle	165°–180°	119°–140°
ν (N-O) in neutral molecules	1610–1830 cm^{-1}	1520–1720 cm^{-1}
Electron donor count	2 (as NO^{+}) 3 (as neutral NO)	2 (as NO^{-}) 1 (as neutral NO)

Important types of reactions that play a key role in most catalytic cycles as well as in many synthetic pathways by the organometallic Compounds

1. **Oxidative addition and Reductive elimination**

A neutral ligands such as C_2H_4 or CO enter the coordination sphere by substitution. Now, how pairs of anionic ligands, A and B, do this by *oxidative addition* (OA) of A–B. In OA, A–B molecules such as H–H or CH_3–I add to a low valent metal, L*n*M, to produce L*n*M(A)(B). The equally important reverse reaction, *reductive elimination* (RE), leads to the release of A–B from L*n*M(A)(B). In the oxidative direction, the A−B bond breaks to form bonds from M to A and B. Since A and B are X-type ligands, the oxidation state, electron count, and coordination number all increase by two units during OA, the reverse taking place during RE. These changes in formal oxidation state (OS) justify the oxidative and reductive parts of the reaction names. In a catalytic cycle, a reactant often binds via OA and the product dissociates via RE.

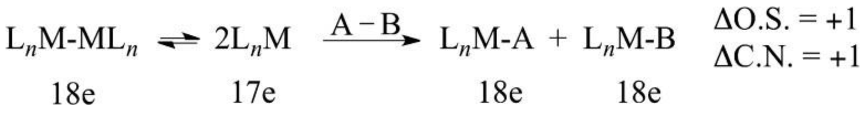


$$\underset{16e}{L_nM} + A{-}B \underset{\text{reductive elimination (RE)}}{\overset{\text{oxidative addition (OA)}}{\rightleftarrows}} \underset{18e}{L_nM\begin{smallmatrix}A\\B\end{smallmatrix}} \quad \begin{matrix}\Delta O.S. = +2\\ \Delta C.N. = +2\end{matrix}$$

Eq. 1

Oxidative additions go by a variety of mechanisms, but since the metal electron count increases by two, a vacant 2e site is always needed. We may start with a 16e complex, or a 2e site may be opened up by initial ligand loss from an 18e complex. The change in oxidation state means that to undergo in the above Eq1, a complex must have a stable OS two units more positive (and vice versa for RE). Reductive elimination, the reverse of oxidative addition, is most often seen in higher oxidation states because the formal OS of the metal drops by two units in RE. The reaction is particularly efficient for the group 10–11 d^8 metals, Ni(II), Pd(II), and Au(III), and Group 9-10 d^6 metals, Pt(IV), Pd(IV), Ir(III), and Rh(III).

First row metals typically prefer a one-unit change in oxidation state, electron count, and coordination number. Equation Eq 2 shows how *binuclear oxidative addition* conforms to this pattern. We start with a 17e complex or an M−M bonded 18e complex that can dissociate into 17e fragments. The metal must now have a stable OS more positive by one unit for OA. Table 4 shows common types of OAs by d^n configuration and position in the periodic table. Whatever the mechanism, two electrons from M transfer into the A−B σ*, while the A−B σ bonding pair donate to M. This cleaves the A−B bond and makes the new bonds to A and B. OA is favored in low oxidation states and is rare for M(III) and higher, except with powerful oxidants, such as Cl_2. OA is also favored where the A–B bond is weak relative to M–A and M–B. The opposite holds for RE, where a high OS metal and a product with a strong A–B bond are favorable for the reaction.

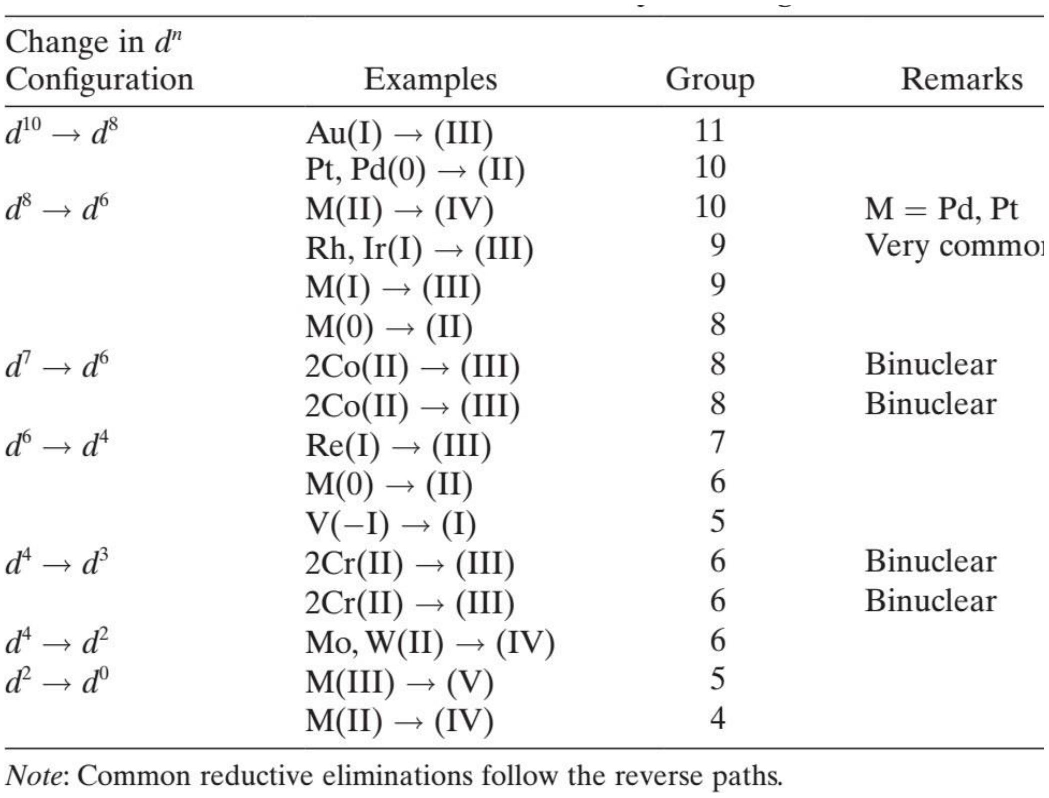


$$\underset{18e}{L_nM\text{-}ML_n} \rightleftharpoons \underset{17e}{2L_nM} \xrightarrow{A-B} \underset{18e}{L_nM\text{-}A} + \underset{18e}{L_nM\text{-}B} \qquad \begin{matrix}\Delta O.S. = +1\\ \Delta C.N. = +1\end{matrix}$$

Eq. 2

OA is also favored by strongly donor coligands, Ln, because these stabilize the oxidized LnM(A)(B) state. While the formal ΔOS for Eq. 1 is always +2, the real change in metal charge is less than this because A and B do not have full −1 charges in $L_nM(A)(B)$. The change in real charge depends mostly on the electronegativity of A and B, so that H2 < HCl < Cl_2 are increasingly oxidizing. This order comes from measuring the IR spectral change in ν(CO) on going from $IrCl(CO)L_2$ to $Ir(A)(B)Cl(CO)L_2$ (Table 5), where a high Δν(CO) during OA corresponds to a greater degree of oxidation by raising the positive charge on M and so reducing M–CO back bonding.

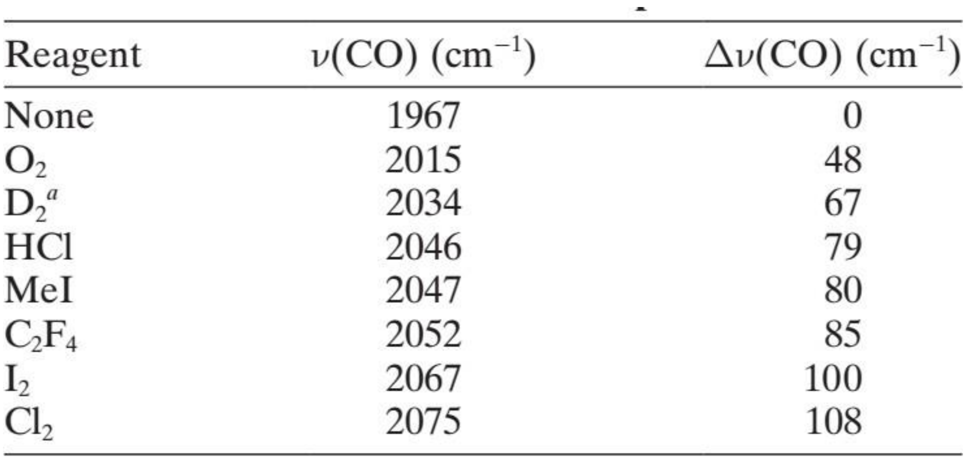
Table 4: Common Oxidative Addition by d^n Configuration



Change in d^n Configuration	Examples	Group	Remarks
$d^{10} \rightarrow d^8$	Au(I) → (III)	11	
	Pt, Pd(0) → (II)	10	
$d^8 \rightarrow d^6$	M(II) → (IV)	10	M = Pd, Pt
	Rh, Ir(I) → (III)	9	Very commo
	M(I) → (III)	9	
	M(0) → (II)	8	
$d^7 \rightarrow d^6$	2Co(II) → (III)	8	Binuclear
	2Co(II) → (III)	8	Binuclear
$d^6 \rightarrow d^4$	Re(I) → (III)	7	
	M(0) → (II)	6	
	V(−I) → (I)	5	
$d^4 \rightarrow d^3$	2Cr(II) → (III)	6	Binuclear
	2Cr(II) → (III)	6	Binuclear
$d^4 \rightarrow d^2$	Mo, W(II) → (IV)	6	
$d^2 \rightarrow d^0$	M(III) → (V)	5	
	M(II) → (IV)	4	

Note: Common reductive eliminations follow the reverse paths.

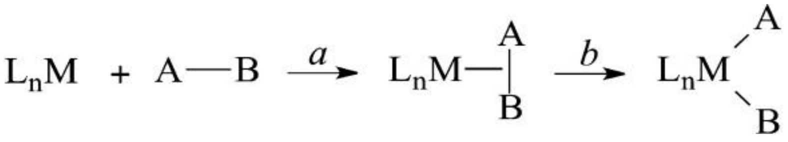
Table 5 : Carbonyl Straching frequencies in Oxidative Addition reaction with Vaska's complex



Reagent	ν(CO) (cm^{-1})	$\Delta\nu$(CO) (cm^{-1})
None	1967	0
O_2	2015	48
D_2[a]	2034	67
HCl	2046	79
MeI	2047	80
C_2F_4	2052	85
I_2	2067	100
Cl_2	2075	108

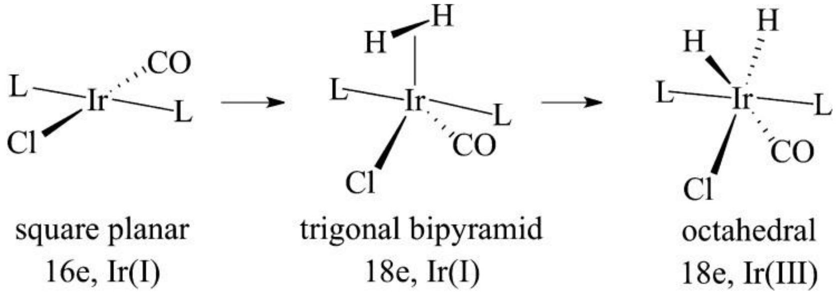
Concerted Addition

Concerted, three-center OA starts out as an associative substitution in which an incoming ligand, A–B, binds as a σ complex but then undergoes A–B bond breaking if back donation from the metal into the A–B σ* orbital is strong enough. This mechanism applies to nonpolar reagents, such as H_2, $R_3C–H$ or $R_3Si–H$ (Eq.3; A = H; B = H, C, or Si). The associative step *a* of Eq. 3 forms the σ complex; if this is stable, the reaction stops here. Otherwise, metal electrons are transferred to the A–B σ* in step *b*, the oxidative part of the reaction. The classic examples, from the Estonian-American chemist, Lauri vaska (1925–), involve OA to the 16e square planar d^8 species, $IrCl(CO)(PPh_3)_2$, known as *Vaska's complex*. The 18e d^6 octahedral dihydride of Eq. 4, has mutually cis hydrides; conversely, in an RE such as the loss of H_2 from a dihydride, the two H ligands need to become mutually cis. In OA of H_2 to vaska's complex, the initially *trans*-Cl–Ir–(CO) set of ligands folds back to become cis both in a proposed transient H_2 complex and in the final product (Eq. 4). As a powerful π acceptor, the CO prefers to be in the equatorial plane of the resulting TBP transient, following the same pattern we saw in A substitution. This tendency for a trans pair of very strong π-acceptor ligands on a strongly π donor metal to fold back can be so great that a d^8 ML_4, normally expected to be square planar, distorts toward TBP even in the absence of an fifth ligand as in following fig. (L = P(t-Bu)$_2$Me). Bending enhances the π donor power of the metal by raising the energy of the relevant *d* orbitals, as well as avoiding the CO ligands being mutually *trans*. In 18e complexes, a ligand may be lost to give the 2e site needed for OA, as occurs in initial CO loss from $[Ir(CO)_3L_2]^+$ in the OA of H_2 to give $[Ir(H)_2(CO)_2L_2]^+$.

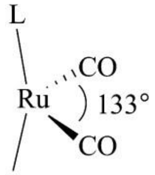


Eq. 3

M(0)/ 16e M(0)/ 18e M(II)/ 18e



Eq. 4



(L = P(t-Bu)$_2$Me)

σ - Bond Metathesis

Apparent OA/RE sequences can in fact go by a different route, σ-bond metathesis or σ-bond complex-assisted metathesis. These are most easily identified for d^0 early metal complexes, such as Cp_2ZrRCl or WMe_6, where OA is forbidden, since the product would have to be d^{-2} When a d^0 complex reacts with H_2 (Eq. 3.32), path a of Fig. X is therefore forbidden and path b or c must take over. Path b and *c* differ only in that *c* explicitly postulates an intermediate σ-complex. In d^2–d^{10} transition metals, both OA and σ-complex formation is usually permitted, but distinguishing between them is hard since both the products and the kinetics are identical. In a Rh(III) alkyl, path *a* is technically allowed, but Rh(V) is an unusual oxidation state, so paths *b* or *c* would be preferred. Pathway *a* is typical when OA occurs readily. In the same way, to avoid forbidden oxidation states, reaction of d^0 alkyls with acids cannot go via initial protonation at the metal (step *a* in Fig. Y) because as a d^0 system, the metal has no M($d\pi$) lone pairs. Instead, protonation of the M–R bond must take place. Formation of an alkane σ-complex would then lead to loss of alkane. For d^2–d^{10} metals, where all pathways are allowed, it is again hard to tell which is followed; pathway *a* is normally assumed to operate in the absence of specific evidence to the contrary.

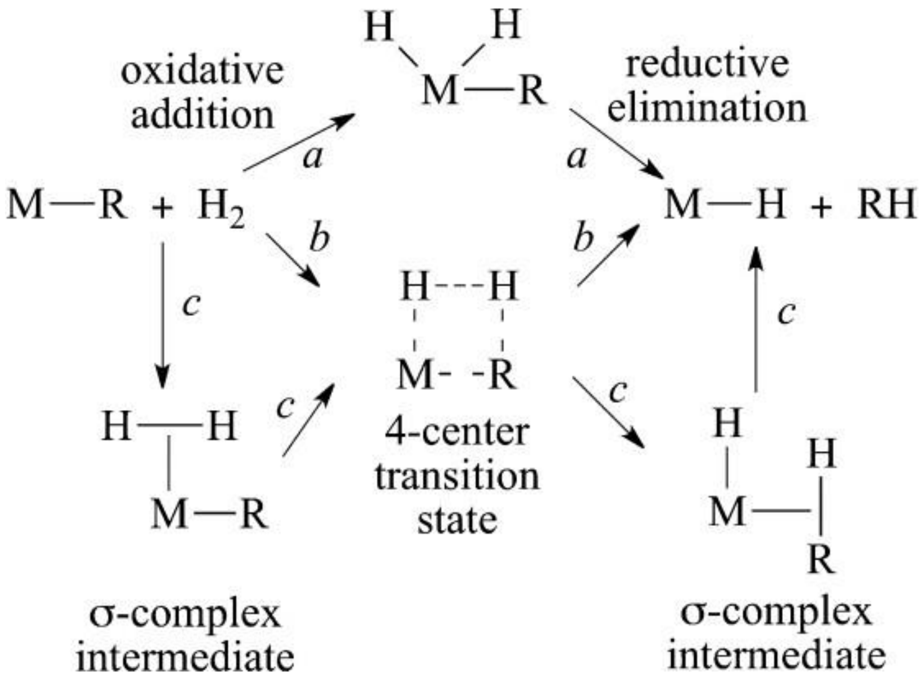


Fig. X: Sigma bond metathesis (paths *b* and *c*) and OA/RE (path *a*) are hard to distinguish for d^2–d^{10} complexes, but for d^0 cases, only sigma bond metathesis is allowed because OA would produce a forbidden oxidation state.

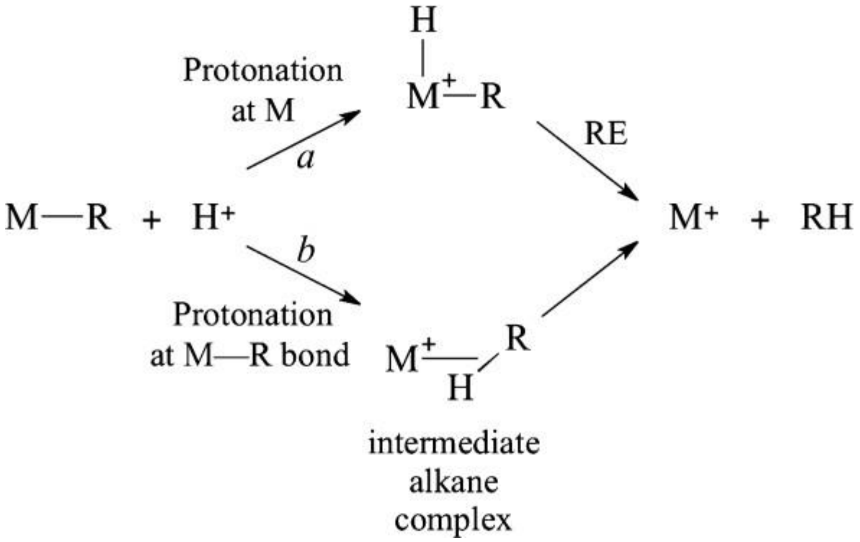


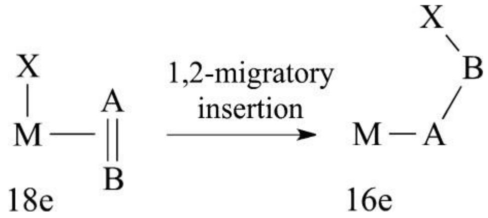
Fig. Y: Protonation has similar limitations. Protonation at the metal (path *a*) and at the M–R bond (path *b*) are hard to distinguish for d^2–d^{10} complexes, but for d^0 cases, only path *a* is allowed because protonation at the metal would produce a forbidden oxidation state.

Insertion and Elemination Reactions:

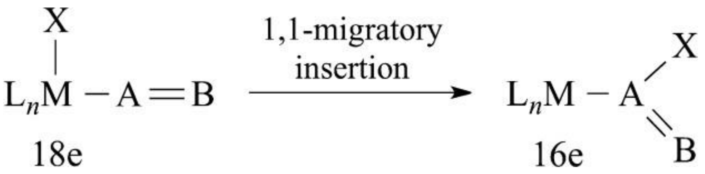
Oxidative addition and substitution allow us to introduce a variety of 1e and 2e ligands into the coordination sphere of a metal. With insertion, and its reverse, elimination, we can combine and transform these ligands, ultimately to expel these transformed ligands to give useful products, often in the context of a catalytic cycle. In this way, organometallic catalysis can convert organic reagents into organic products with regeneration of the metal species for subsequent reaction cycles.

In insertion reaction, a π-bound 2e ligand, A=B, inserts into an M–X bond to give M–(AB)–X, where AB has formed a new bond with both M and X. There are two main types of insertion, either 1,1 (Eq. 5) or 1,2 (Eq. 6). In 1,1 insertion, M and X end up bound to the same atom of AB, but in the 1,2 type, M and X end up on adjacent atoms of AB. The type of insertion in any given case depends on the nature of A=B. For example, CO gives only 1,1 insertion where both M and X end up bound to CO carbon. On the other hand, ethylene gives only 1,2 insertion, where the product, MCH2CH2X, has M and X on adjacent atoms of the ligand.

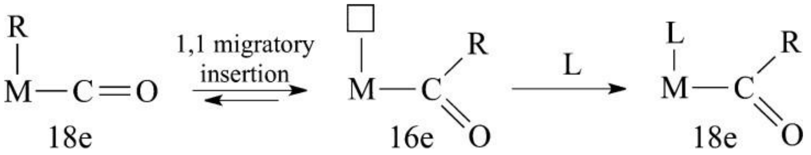
In general, η^1 ligands give 1,1 insertion, and η^2 ligands give 1,2 insertion. SO_2 is the only common ligand that can give both types of insertion and accordingly, SO_2 can either be an η^1 (S) or η^2 (S,O) ligand.



Eq. 5



Eq. 6



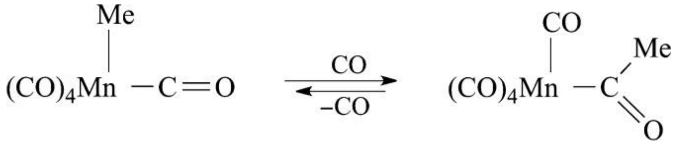
Eq. 7

Both the 1e and 2e ligands normally need to coordinate to the metal before insertion. This means that a 3e set of ligands in the intermediate converts to a 1e ligand in the insertion product, so that a 2e vacant site (□) is generated (Eq. 6). Binding of an external 2e ligand can trap the insertion product (Eq. 7). Conversely, the elimination requires a 2e vacant site, so that an 18e complex cannot undergo the reaction unless a ligand first dissociates. The insertion also requires a cis arrangement of the 1e and 2e ligands, while the elimination generates a cis arrangement of these ligands. The formal oxidation state does not change during the reaction.

In one useful picture of insertion, the X ligand migrates with its M–X bonding electrons (e.g., as H− or Me−) to attack the π* orbital of the A=B ligand. In this intramolecular nucleophilic attack on A=B, the migrating group, R, retains its stereochemistry. This picture also justifies the term "migratory insertion," often applied to these reactions, in that the X migrates to the A=B group. A component of M–(A=B) bonding is back donation, in which an M dπ electron pair is partially transferred to the A=B π*; in an insertion, an M–X bonding electron pair is fully transferred to the A=B π*.

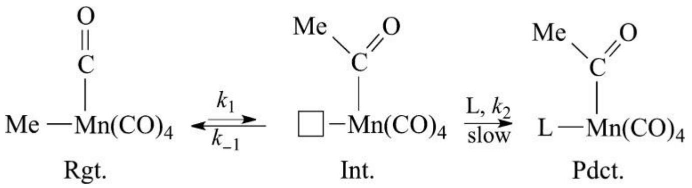
CO insertion:

CO shows a strong tendency to insert into metal–alkyl bonds to give metal acyls, a reaction that has been carefully studied for a number of systems. Although the details may differ, most follow the pattern set by the best-known case:



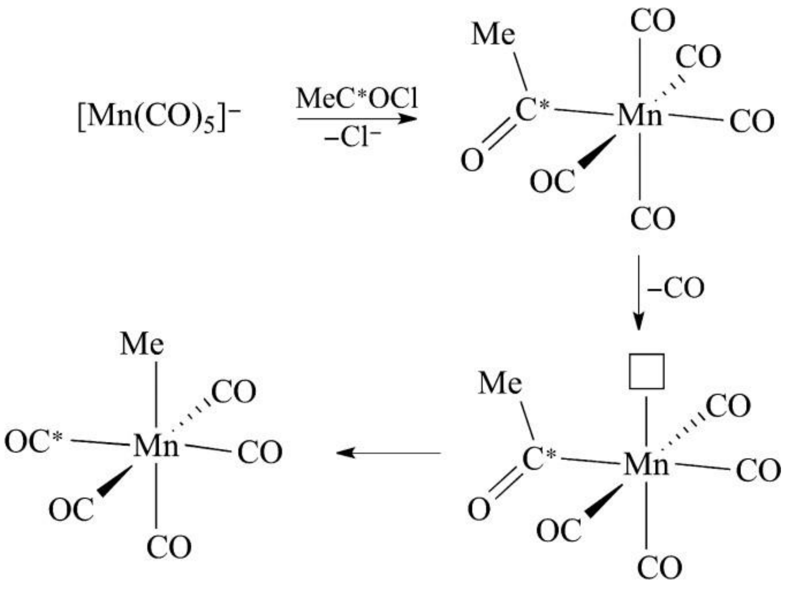
Eq. 8

The usual mechanism of migratory insertion is shown in Eq. 9. The alkyl group in the reagent (Rgt) undergoes a migration to the CO to give an acyl intermediate (Int.) that is trapped by added ligand, l, to give the final product (Pdct)



Eq. 9

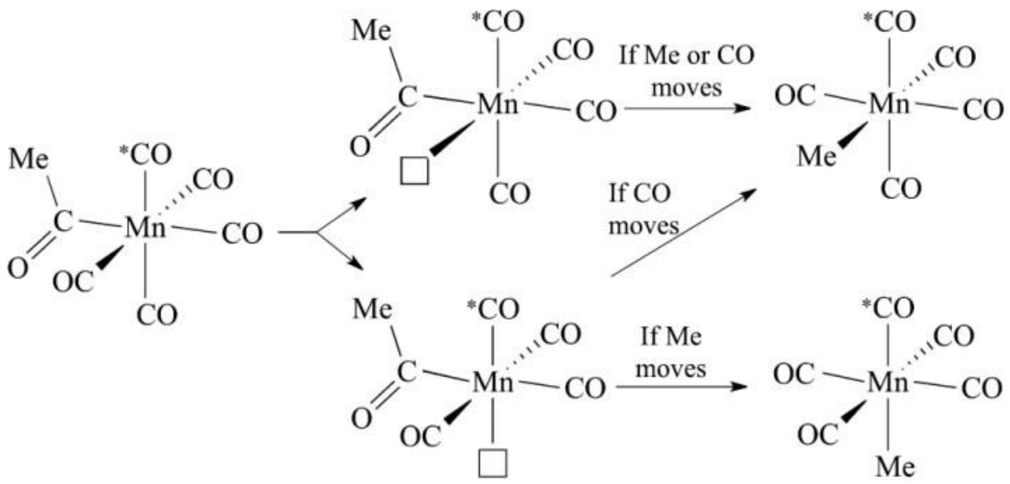
When the incoming ligand in Eq. 9 is ^{13}CO, the product contains only one labeled CO, cis to the newly formed acetyl. This suggests that the acetyl group is initially formed cis to a vacant site in the intermediate. The labeled CO can be located in the product by NMR and IR spectroscopy. In an example of a useful general strategy, we can learn about any forward process by looking at the reverse reaction—here, α elimination of CO from $Me^{13}COMn(CO)_5$ (Eq. 10; C* = ^{13}C). We can easily label the acyl carbon with ^{13}C by reaction of $[Mn(CO)_5]^-$ with $Me^{13}COCl$ and find that after α elimination of CO, the label ends up in a CO cis to the methyl in the product.



Eq. 10

By microscopic reversibility, the forward and reverse reactions of a thermal process must follow the same path. In this case, if the labeled CO ends up cis to Me in the elimination direction, the CO to which a methyl group migrates in the insertion direction must also be cis to methyl. We are fortunate in seeing the kinetic products of these reactions. If a subsequent scrambling of the COs had been fast, we could have deduced nothing.

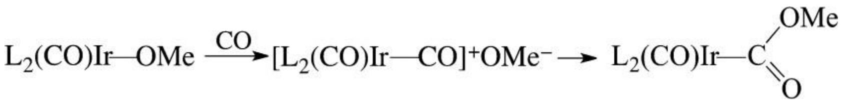
We now know that Me and CO must be mutually cis to insert, but we do not yet know if Me migrates to the CO site or vice versa. It is also possible to use reversibility arguments to show that it is Me, not CO, that moves. To do this, we look at CO elimination in *cis*-(MeCO)Mn$(CO)_4(^{13}CO)$, in which the labeled CO is cis to the acetyl. If the acetyl CO migrates during the elimination, then the methyl in the product will stay where it is and so remain cis to the label. If the methyl migrates, then it will end up both cis and trans to the label, as is in fact observed (Eq. 11)



Eq. 11

This implies that the methyl also migrates in the insertion direction. The *cis*-(MeCO)Mn$(CO)_4(^{13}CO)$ required for this experiment can be prepared by the photolytic method. This migration of Me not CO is one feature of migratory insertion that does not reliably carry over to other systems, where the product acyl is occasionally found at the site originally occupied by the alkyl. Consistent with this mechanism, any stereochemistry at the alkyl carbon is retained both on insertion and on elimination.

An insertion that appears to be migratory can in fact go by an entirely different route (Eq. 12). Since MeO− is a good π donor bound to a d^6 π-donor metal, the MeO− group easily dissociates to give an ion pair with a 2e vacancy at the metal. The free CO present then binds to this 2e site and is strongly activated toward nucleophilic attack at the CO carbon owing to the positive charge on the metal. The product is the interesting metalloester shown in Eq. 12.



$$L_2(CO)Ir{-}OMe \xrightarrow{CO} [L_2(CO)Ir{-}CO]^+OMe^- \longrightarrow L_2(CO)Ir{-}C(=O)OMe$$

Eq.12

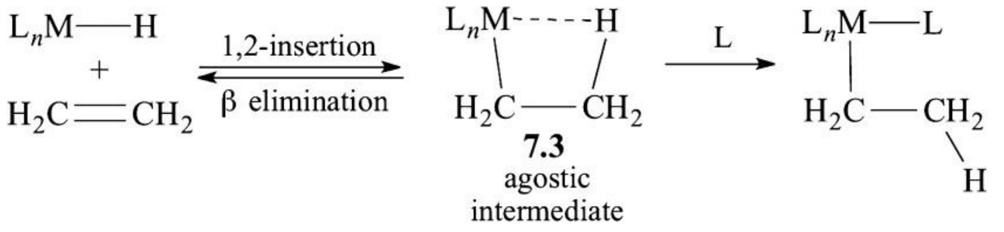
Genuine migratory insertions into M–O bonds are also possible. For *trans*-[Pt(Me)(OMe)(dppe)], CO inserts into the Pt–OMe bond, while for [Ni(Me)(*O*-*p*-C_6H_4CN)(bipy)], CO inserts into Ni–Me. For nickel, the M–Me bond is significantly stronger than M–OMe, but migratory insertion with M–Me is marginally preferred owing to the weaker C–O bond of the aryloxycarbonyl. For platinum, M–Me and M–OMe bonds are equally strong, so the stronger methoxycarbonyl C–O bond favors reaction with the M–OMe bond.

Double Insertion?

Given that the methyl group migrates to the CO, why stop there? Why does the resulting acyl group not migrate to another CO to give an MeCOCO ligand? To see why, we can treat $[Mn(CO)_5]^-$ with MeCOCOCl to give $[MeCOCOMn(CO)_5]$, which easily and irreversibly eliminates CO to give $MeCOMn(CO)_5$. This means that the double-insertion product does not form because it is thermodynamically unstable with respect to $MeCOMn(CO)_5$ + CO. The –CHO and CF_3CO– groups also eliminate CO irreversibly to give M–H and M–CF_3 complexes, implying that these insertions cannot occur thermally. Thermodynamics drives these eliminations because the M–COMe, M–H, and M–CF_3 bonds are all distinctly stronger than the M–CH3 bond that is formed in CO elimination from the acetyl. In contrast to CO, isonitriles can undergo repeated migratory insertion to give $R(CNR)_mM$ polymers, with m as high as 100. The instability of $R(CO)_mM$ is associated with having successive δ+ carbonyl carbons mutually adjacent; =NR being less electronegative than =O, the problem is less severe for RNC than for CO.

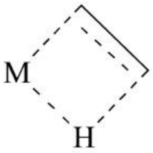
Alkene Insertion :

The insertion of coordinated alkenes into M–H bonds leads to metal alkyls and constitutes a key step in a variety of catalytic reactions. For example, the commercially important alkene polymerization reaction involves repeated alkene insertion into the growing polymer chain. As η^2-ligands, alkenes give 1,2 insertion in the reverse of the familiar β elimination (Eq. 13). Some insertions give agostic (**7.3**) rather than classical alkyls, and species of type **7.3** probably lie on the pathway for insertion into M–H bonds. The position of equilibrium depends not only on whether an incoming ligand, L in Eq. 13, is available to trap the alkyl, but also very strongly on the alkene and the insertion thermodynamics. For simple alkenes, such as ethylene (Eq. 12), the equilibrium tends to lie to the left and the alkyl prefers β elimination, but for alkenes such as C_2F_4, which form strong M–R bonds, insertion is preferred and the product alkyl $L_nMCF_2CF_2H$ does not β-eliminate.

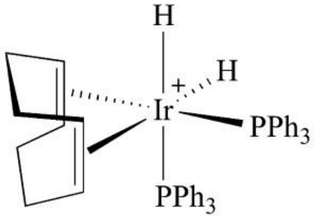


Eq. 13.

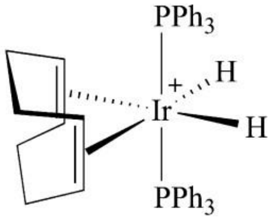
The transition state for insertion, **7.4**, resembles **7.3** in having an essentially coplanar M–C–C–H arrangement, and this implies that both insertion and elimination also require the M–C–C–H system to become coplanar. We can stabilize alkyls against β elimination by having a noncoplanar M–C–C–H system. The same principles apply to stabilizing alkene hydride complexes. Compound **7.5** undergoes insertion at least 40 times more rapidly than **7.6**, although the alkene and M–H groups are cis in both cases, only in **7.6** is there a noncoplanar M–C–C–H arrangement.



7.4



7.5



7.6