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Carbonyl-Insertion Reactions of Square-Planar Complexes

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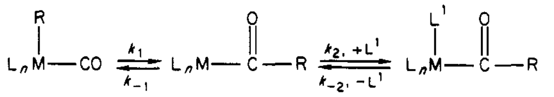
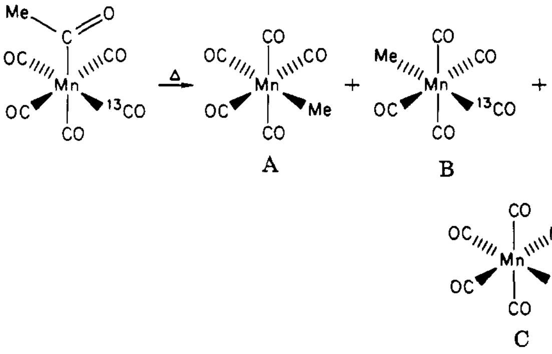
The term "insertion" is widely used in organometallic chemistry to describe a large class of reactions, yet it is a term that is frequently misleading. It is used to describe the process whereby an unsaturated moiety, which may or may not be coordinated to the metal initially, becomes bonded to the metal and to a saturated ligand (which was initially attached to the metal center). In the case of insertion of carbon monoxide into a metal–carbon bond, the process, which usually involves an incoming ligand, may be depicted as in eq 1. Although generally referred to as insertion reactions, most evidence suggests that they are, in fact, best regarded as organic group *migrations*; that is, the organic group migrates from the metal to the previously coordinated carbon monoxide.



$$L_nM(R)\text{—CO} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} L_nM\text{—C(=O)—R} \underset{k_{-2},\,-L^1}{\overset{k_2,\,+L^1}{\rightleftharpoons}} L_nM(L^1)\text{—C(=O)—R} \quad (1)$$

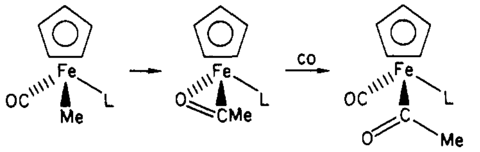
The first example of such a reaction to be studied in detail was the carbonylation of $CH_3Mn(CO)_5$.[1] Treatment of this compound with ^{13}CO yielded only $(CH_3CO)Mn(CO)_4(^{13}CO)$, indicating that it is only initially coordinated carbon monoxide that finds its way into the acyl group. In addition, the ^{13}CO molecule is cis to the acyl, where it has filled the site left vacant by the migrating group, which shows that a cis arrangement of the combining moieties is required. Thermal decarbonylation of this complex (eq 2) yields a 1:1:2 mixture of the products A–C, respectively: this is consistent only with migration of the methyl group, which, by the principle of microscopic reversibility, is established as the carbonylation reaction mechanism.



(2)

These features, namely, the combination of mutually cis ligands, alkyl-group migration to CO, and the intermediacy of a coordinatively unsaturated species, are generally accepted[2] and further support continues to be found.[3] Theoretical calculations are in agreement,[4] and recent studies provide kinetic evidence that a solvent molecule rapidly attacks the metal center as the organic group migrates,[5] such that the migrations are essentially solvent catalyzed (this could account for reports of different rate laws in different solvents[1,2]). They can also be promoted by organometallic cations,[6] aluminum halides,[7] and heterogeneous surfaces such as alumina[8] (coordination of a carbonyl oxygen to an electrophile is probably a common feature of these processes).

The evidence is not 100% in favor of migration pathways, however. Recently reported configurational changes at an iron complex indicate *insertion* of resident CO group into the Fe–C bond to be the critical step in this case at least (eq 3).[9] Several η^2-acyl complexes of the type proposed as intermediate are known.[10]



(3)

Square-planar complexes are of particular interest in the context of the carbonyl-insertion reaction, since they have potentially more reaction pathways available to them. They are commonly 16-electron species, so the

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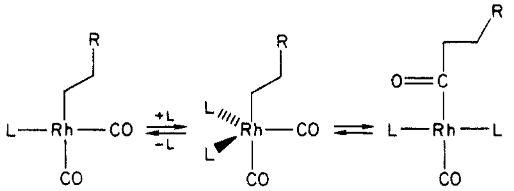
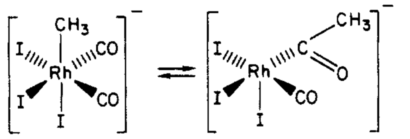
insertion/migration (we will use the term "insertion" from here on to indicate the result of the overall change; no mechanistic significance should be attached unless specifically stated) may proceed spontaneously in the square plane or an incoming nucleophile may promote the reaction by coordinating to produce an 18-electron intermediate. Interest in such systems is more than academic since the carbonyl-insertion step is central to many industrial, catalytic processes involving carbon monoxide.

The hydroformylation or oxo reaction, for example (that is, the reaction of an alkene with carbon monoxide and hydrogen to produce an aldehyde), which may be catalyzed by cobalt[11] or rhodium[12] complexes, apparently involves in each case carbonyl insertion from a five-coordinate, 18-electron species. In the rhodium system the carbonyl insertion step is believed to occur as in eq 4.



(4)

The carbonylation of methanol, whose catalysis by rhodium complexes has made possible the Monsanto acetic acid process, provides another example of an industrially important reaction that involves carbonyl insertion. The catalytic species here is believed to be the square-planar $[RhI_2(CO)_2]^-$ anion,[13] which undergoes oxidative addition of methyl iodide, carbonyl insertion, and then reductive elimination of acetyl iodide (which is subsequently hydrolyzed to acetic acid). The carbonyl-insertion step, which occurs at an octahedral, 18-electron rhodium(III) species, is shown in eq 5. The analogous iridium system involves two catalytic cycles, involving neutral and anionic complexes, both of which incorporate carbonyl insertion from $[IrI_2(CH_3)(CO)_3]$.[14] The former involves insertion to give an acetyl complex that is probably dimeric (eq 6), whereas the anionic route is promoted by iodide to give a monomeric acetyl species (eq 7). In each case, reductive elimination of acetyl iodide, which is hydrolyzed to acetic acid, follows.



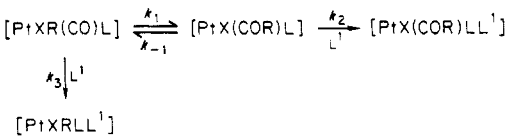
(5)

$$[IrI_2(CH_3)(CO)_3] \rightleftarrows [IrI_2(COCH_3)(CO)_2]_2 \quad (6)$$

$$[IrI_2(CH_3)(CO)_3] \underset{-I^-}{\overset{I^-}{\rightleftarrows}} [IrI_3(COCH_3)(CO)_2]^- \quad (7)$$

It is clear, then, that carbonyl-insertion reactions of square-planar complexes are of considerable importance, yet, in the above instance, little is known regarding the conditions that favor the insertion step. Our approach to this problem has been aimed primarily at platinum(II) complexes, which offer a number of advantages in terms of compound characterization and in mechanistic studies. The compounds are readily handled, the existence of a magnetic isotope with $I = {}^1/_2$ (^{195}Pt, 34% natural abundance) allows multinuclear magnetic resonance techniques to be used to advantage, and their reactions are generally clean and can be readily monitored. Moreover, platinum and palladium complexes themselves catalyze a number of carbonylation reactions.[15,16] For example, the conversion of aryl halides into esters is catalyzed by palladium,[17] where carbonylation of an intermediate arylpalladium(II) species is believed to be a crucial step (eq 8). The mechanism of this reaction has been the subject of a detailed kinetic study.[18]

Scheme I



$$[PdX(R)(PPh_3)_2] + CO \rightarrow [PdX(COR)(PPh_3)_2] \quad (8)$$

We will first consider reactions involving complexes with initially coordinated carbon monoxide. A knowledge of the transformations that occur in these can then be brought to bear effectively on the carbonylation mechanism for $[MXRL_2]$ and other complexes, which can involve a variety of reaction pathways.

Spontaneous Insertion at Square-Planar Carbonyl Complexes

The first evidence of spontaneous insertion at four-coordinate, square-planar platinum(II) complexes was provided by Mawby and co-workers.[19–21] Although insertion at [PtXR(CO)L] (L = tertiary phosphine or arsine) was found to be promoted by nucleophiles L^1, the reaction rate was independent of L^1 or solvent. Occasionally, carbonyl substitution was observed instead. Scheme I summarizes these findings. High concentrations of L^1, leading to a large $k_3[L^1]$, promote the substitution, a result in keeping with other reports.[22] More powerful nucleophiles L^1 (R_3P, rather than R_3As or N donors) also favor the k_3 step. Bulky resident ligands, L, favor insertion via k_1 and k_2, presumably a reflection of easier L^1 attack at a three-coordinate, or solvated, intermediate.

The presence of a $I = {}^1/_2$ nucleus for platinum makes it ideally suited to NMR studies of these reactions. In fact, we were able to prepare all three isomers of the complexes [PtXR(CO)L] and to identify them by their

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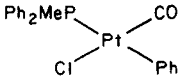
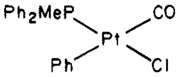
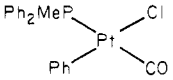
Table I
NMR Spectroscopic Data for [PtClPh(CO)(PMePh$_2$)]

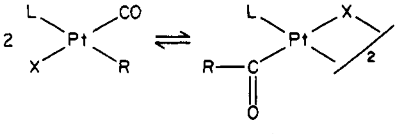
compd	δC[a]	^1J(Pt,C)[b]	^2J(P,C)[b]	δP[c]	^1J(Pt,P)[d]
 I	162.1	1947	8	6.8	1402
 II	177.4	906	6	−1.7	3920
 III	173.3	1427	158	5.7	3481

[a] For samples prepared with 90% ^{13}CO; chemical shifts are in ppm relative to Me$_4$Si, positive shifts representing deshielding. [b] Coupling constants are in hertz; the carbon atom is that of CO. [c] Chemical shifts are in ppm, relative to external H$_3$PO$_4$, positive shifts representing deshielding. [d] Coupling constants are in hertz.

^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra (Table I).[23] Isomer I was prepared exclusively by the action of organomercurials on *cis*-[PtX$_2$(CO)L]; it was readily identified by its low value of ^1J(Pt,P), which arises due to the mutually trans configuration of the tertiary phosphine and the high trans influence organic group. The trans influence of a ligand is a thermodynamic phenomenon that may be observed in the ground state of the molecule. It is the ability of that ligand to weaken the trans metal–ligand bond. The so-called "NMR trans influence" relates the magnitude of the one-bond metal–ligand coupling constant to the trans influence of the trans ligand; that is, the higher the trans influence of a ligand, the lower will be the one-bond coupling between the metal and the trans ligand. It is generally assumed[24] that the Fermi contact term dominates the one-bond coupling constant, so this is essentially a σ-bonding effect. A limited trans-influence series is as follows: alkyl, aryl > PR$_3$ > AsR$_3$ > CO > Cl$^-$.

Isomers II and III were made by treating [Pt$_2$(μ-X)$_2$R$_2$L$_2$] (which exists in solution as rapidly interchanging cis and trans isomers) with carbon monoxide. Isomer III is typified by a large ^2J(P,C) value, due to the trans disposition of the CO and PR$_3$ moieties, whereas isomer II exhibits a low value of ^1J(Pt,C) since the carbonyl ligand lies trans to the organic group.[25] Isomers II and III interconvert in solution via reversible CO loss, whereas III slowly converts to I by reversible elimination of L;[23] the latter process occurs so slowly that even in the most favorable case of L = PPh$_3$ decomposition proceeds at a similar rate.

Of these three isomers, only isomer I undergoes carbonyl insertion, which, in the absence of a nucleophile, yields the two isomers of the halide-bridged acyl or aroyl dimer (eq 9). There are very few examples of easily observed equilibria between carbonyl and acyl complexes,[1,2] and this system offered an ideal opportunity to observe the effects of all substituents on the carbonyl-insertion reaction at platinum. The reactions of the three isomers of [PtXR(CO)L] are summarized in Scheme II.



(9)

Scheme II

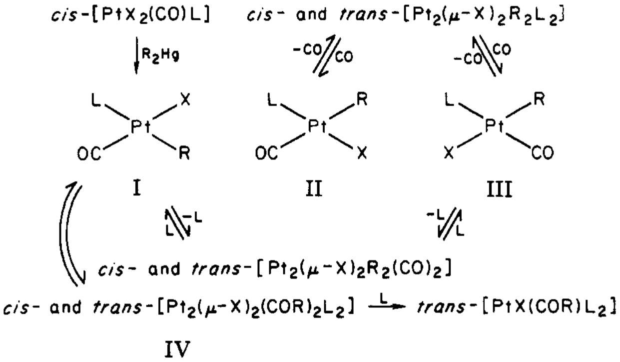


Table II
Equilibrium Constants for the Reaction 2[PtClPh(CO)L] ⇌ [Pt$_2$(μ-Cl)$_2$(COPh)$_2$L$_2$] in Chloroform Solution

L	K_c, L·mol^{-1}	L	K_c, L·mol^{-1}
PEt$_3$	690	PCy$_3$	8.0
PMe$_2$Ph	650	P(o-tol)$_3$[a]	~0
PMePh$_2$	160	AsMePh$_2$[a]	~0
PPh$_3$	31	AsPh$_3$[a]	~0

[a] The halide-bridged aroyl dimer could not be detected in solution by infrared or NMR spectroscopy.

The equilibrium between I and [Pt$_2$(μ-X)$_2$(COR)$_2$L$_2$], IV, is rapidly established and appears to be independent of solvent. As might be expected, IV is favored by strongly bridging halides, X = I > Br > Cl.[26] The effects of the neutral ligands, L, on the I/IV equilibria, however, are complex.[26] Insertion is promoted by L of high trans influence, a finding that is consistent with organic group migration to a cis carbonyl ligand being the mechanism involved (II has CO and R mutually trans, and thus unsuitable for insertion, while III has R trans to the low trans influence halides, which do not weaken the Pt–R bond, and thus insertion does not

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[23] Anderson, G. K.; Cross, R. J. *J. Chem. Soc., Dalton Trans.* **1979**, 1246.

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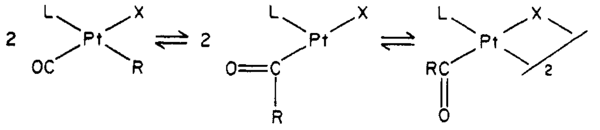
Table III
Thermodynamic Data for the Equilibrium
$2[PtClR(CO)(PMePh_2)] \rightleftharpoons [Pt_2(\mu\text{-}Cl)_2(COR)_2(PMePh_2)_2]$

R	K_c, L·mol$^{-1\,a}$	ΔH, kJ·mol^{-1}	ΔS, J·K^{-1}·mol^{-1}
p-$Me_2NC_6H_4$^{b}	∞		
p-$MeOC_6H_4$	2170	−60	−200
p-MeC_6H_4	360	−55	−190
m-MeC_6H_4	140	−56	−200
C_6H_5	100	−44	−170
m-$MeOC_6H_4$	70	−38	−150
p-ClC_6H_4	20	−45	−190
m-ClC_6H_4	3.3	−20	−120
p-$MeOCOC_6H_4$	3.3	−20	−120
p-NCC_6H_4^{c}	~0		
o-MeC_6H_4^{c}	~0		
o-$MeOC_6H_4$^{c}	~0		

[a] At 38 °C, see ref 30. [b] $[PtCl(C_6H_4NMe_2\text{-}p)(CO)(PMePh_2)]$ could not be detected spectroscopically. [c] The aroyl dimer could not be detected spectroscopically.

proceed). The equilibrium constants for reaction 9 for a series of neutral ligands, L, are given in Table II. These follow the order of trans influence for the smaller ligands,[27] but after a certain size the bulk of the ligand predominates, preventing R migration and overriding the electronic effect. Thus, for example, PCy_3 has a trans influence similar to PEt_3,[26,27] but the steric bulk of the former[27] inhibits R migration almost completely. This inhibition might arise in going from the four-coordinate species to a three-coordinate intermediate (eq 10), which could only be accounted for by a T-shaped rather than trigonal intermediate but could also be due to unfavorable steric interactions in the dimer.

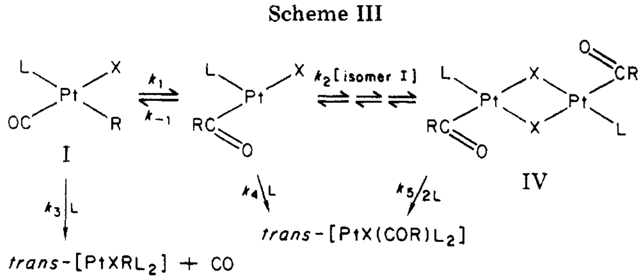


(10)

Equilibrium 9 is also dramatically affected by the nature of the organic group. The tendency toward R migration diminishes along the series R = Et > Ph > Me > CH_2Ph, C≡CMe, C≡CPh, CCl=CCl_2, C_5H_5 (for the last series of R groups, no dimer formation could be detected.[23,28,29] This is not readily explained, but similar orders prevail for other metals.[1,2] A systematic study using substituted aryls[30] showed that electron-donating substituents in meta or para positions thermodynamically promoted the migrations, whereas electron-withdrawing groups inhibited them (Table III). This suggests that the aroyl carbonyl in IV is more electron withdrawing than the PtX(CO)L fragment in I. The correlation is with Hammett σ values rather than Taft σ_I or σ_R parameters. Ortho-substituted aryls do not fit the series, and no insertion was observed. Presumably this again is a reflection of steric hindrance.

A preliminary kinetic investigation of equilibrium 9 in chloroform revealed a second-order reaction at infinite dilution but first-order kinetics at high concentration.[31] This is compatible with I spontaneously forming a T-shaped intermediate that reacts with more I, leading, eventually, to IV. The reverse reaction, formation of I from IV, always exhibits first-order kinetics. Scheme III summarizes the principal steps. The coordinatively unsaturated T-shaped intermediates have not been detected under any conditions, and k_{-1} is presumably large. Thus, the reverse of CO insertion, namely, decarbonylation, is generally brought about by achieving such unsaturation; for example, this may be by halide removal (eq 11).[32] Such a decarbonylation

Scheme III



$$trans\text{-}[PtCl(COR)(PPh_3)_2] \xrightarrow[-AgCl]{Ag^+} trans\text{-}[PtR(CO)(PPh_3)_2]^+ \quad (11)$$

process must be accompanied by a number of isomerization steps, since the organic group migration step itself must proceed to give a cis arrangement of R and CO, and several routes are available for these.[33]

The effects of free ligand on the equilibria 9 are interesting: except when the equilibrium constant approaches zero, rapid reaction to produce *trans*-$[PtX(COR)L_2]$ results. Also, in a number of cases (R = CH_2Ph, L = $PMePh_2$;[23] R = Ph, L = $AsMePh_2$ or $AsPh_3$[26]) when no spontaneous insertion is observed, slow addition of L results in insertion, although rapid addition causes CO displacement (eq 12), a situation

$$[PtXR(CO)L] + L \begin{array}{l} \xrightarrow{slow} trans\text{-}[PtX(COR)L_2] \\ \xrightarrow[fast]{} trans\text{-}[PtXRL_2] \end{array} \quad (12)$$

consistent with Schemes I and III. No insertion resulted, however, from even slow addition of $PMePh_2$ to $[PtClR(CO)(PMePh_2)]$ (isomer I) with R = p-NCC_6H_4, o-$MeOC_6H_4$,[30] CCl=CCl_2,[28] or C_5H_5,[29] reflecting even more negligible equilibrium constants (or slower forward steps) for eq 9.

Addition of free ligand to a II/III equilibrium mixture always results in CO loss. When the addition is performed at low temperature, a mixture of *trans*-$[PtR(CO)L_2]X$ and *trans*-$[PtXRL_2]$ is initially obtained,[34] a consequence of the trans-directing ability of L, but when the mixture is warmed, quantitative conversion to the latter species is achieved. Here we are considering the trans effect of L, namely, its ability to cause substitution at the site trans to L.[35] This is a kinetic rather than thermodynamic, phenomenon. In this case the trans-directing ability of L is such that II is converted quantitatively into *trans*-$[PtR(CO)L_2]X$, while III yields *trans*-$[PtXRL_2]$, at low temperature.

The situation is somewhat different, however, for analogous palladium(II) systems. The complexes $[Pd_2(\mu\text{-}X)_2R_2L_2]$ react rapidly with CO at ambient

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temperature to produce $[Pd_2(\mu\text{-}X)_2(COR)_2L_2]$[36] rather than the palladium analogues of II and III. Addition of L then yields *trans*-$[PdX(COR)L_2]$ quantitatively, and no CO loss is observed.

Spontaneous insertions at square-planar complexes appear to operate with isocyanide ligands (isoelectronic with CO) also. Treatment of *cis*-$[PdCl_2(CNPh)(PPh_3)]$ with Ph_2Hg or other heavy metal phenylating agents leads to insertion products analogous to IV (eq 13).[37]

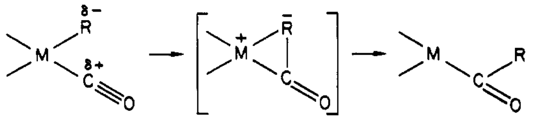
$$2\,cis\text{-}[PdCl_2(CNPh)(PPh_3)] \xrightarrow[-2PhHgCl]{2Ph_2Hg} [Pd_2(\mu\text{-}Cl)_2\{C(Ph){=}NPh\}_2(PPh_3)_2] \quad (13)$$

It is thus most probable that this reaction also proceeds through an analogue of I. Similar products result from the addition of diorganomercurials to *cis*-$[PdCl_2(CNR)_2]$ (eq 14),[38-40] although double insertions arise when the

$$2\,cis\text{-}[PdCl_2(CNR)_2] \xrightarrow[-2R^1HgCl]{2R^1{}_2Hg} [Pd_2(\mu\text{-}Cl)_2\{C(R^1){=}NR\}_2(CNR)_2] \xrightarrow{4L} 2\,trans\text{-}[PdCl\{C(CR^1{=}NR)NR\}L_2] \quad (14)$$

products are subsequently treated with tertiary phosphines. The second step of eq 14 is independent of the nature of L, once again suggesting a spontaneous migration, but is dependent on the nature of R, the reaction being faster for R = p-$MeOC_6H_4$ than for R = c-C_6H_{11}.[40] Related reactions at platinum are considerably slower, indicating both a slower substitution by R_2Hg and a slower migration/insertion.[41]

The overall picture of the spontaneous insertion process at square-planar complexes, therefore, is one of R migration to adjacent CO (or CNR^1) to produce a reactive three-coordinate intermediate (eq 15). The



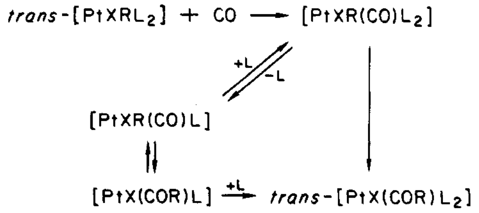
(15)

process is enhanced if the M–R bond is weakened (due to the trans influence of the trans ligand), if R carries a partial negative charge on the carbon bonded to the metal (via other ligands[42] or due to electron-releasing substituents) and if the carbon atom of the CO (or CNR^1) ligand carries a partial positive charge. The promotional effect of cations[6,7] may be due to this.

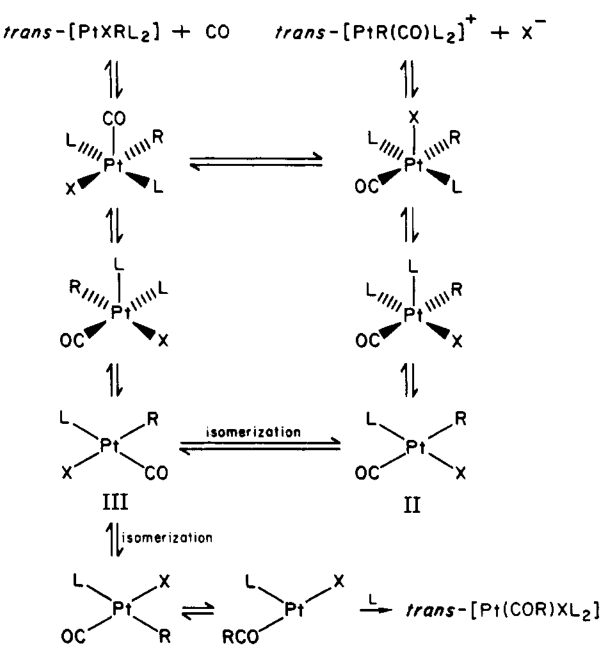
Carbonylation of $[MXRL_2]$ Complexes

Early reports of CO insertions into metal–carbon bonds in complexes of the type $[MXRL_2]$ (M = Ni, Pd, Pt; L = tertiary phosphine) tended to assume that they took place from five-coordinate species, since it was obviously necessary for CO to enter the coordination sphere of the metal.[43,44] Detailed studies by Garrou and Heck, however, provided the first clues that the true situation is, in fact, considerably more complex.[18] Direct insertions from five-coordinate adducts of CO and $[MXRL_2]$ were found to occur, but another, often dominant, route was via L displacement to yield four-coordinate species $[MXR(CO)L]$ (Scheme IV). It was reasonable to assume that for the platinum complexes, at least, the four-coordinate intermediate must correspond to isomer I, with R trans to L.[23] Further investigation showed that II and III were, in fact, produced.[34] Since these do not undergo insertion, isomerization must also be involved; moreover, it became apparent that ionic species are also featured. Scheme V summarizes these relationships. The geometry changes presumably take place via pseudorotation and trigonal-bipyramidal intermediates. Such rearrangements at five-coordinate nickel(II), palladium(II), and platinum(II) complexes are becoming more widely recognized.[33,45] Generally the four-coordinate route is favored by less basic triarylphosphines, which are more readily displaced from platinum by CO. After elimination they can be trapped by sulfur as Ar_3PS.[34] With more basic phosphines, direct insertion from five-coordinate species predominates.

Scheme IV



Scheme V



Ease of carbonylation of the complexes *trans*-$[MXRL_2]$ increases along the series M = Pt < Ni < Pd,[18] although the nickel case is complicated by the formation of zerovalent metal species. Ligand displacements from nickel or palladium occur more readily than from platinum, and the ease with which *trans*-$[PdX(COR)L_2]$ is produced from $[Pd_2(\mu\text{-}X)_2R_2L_2]$ by

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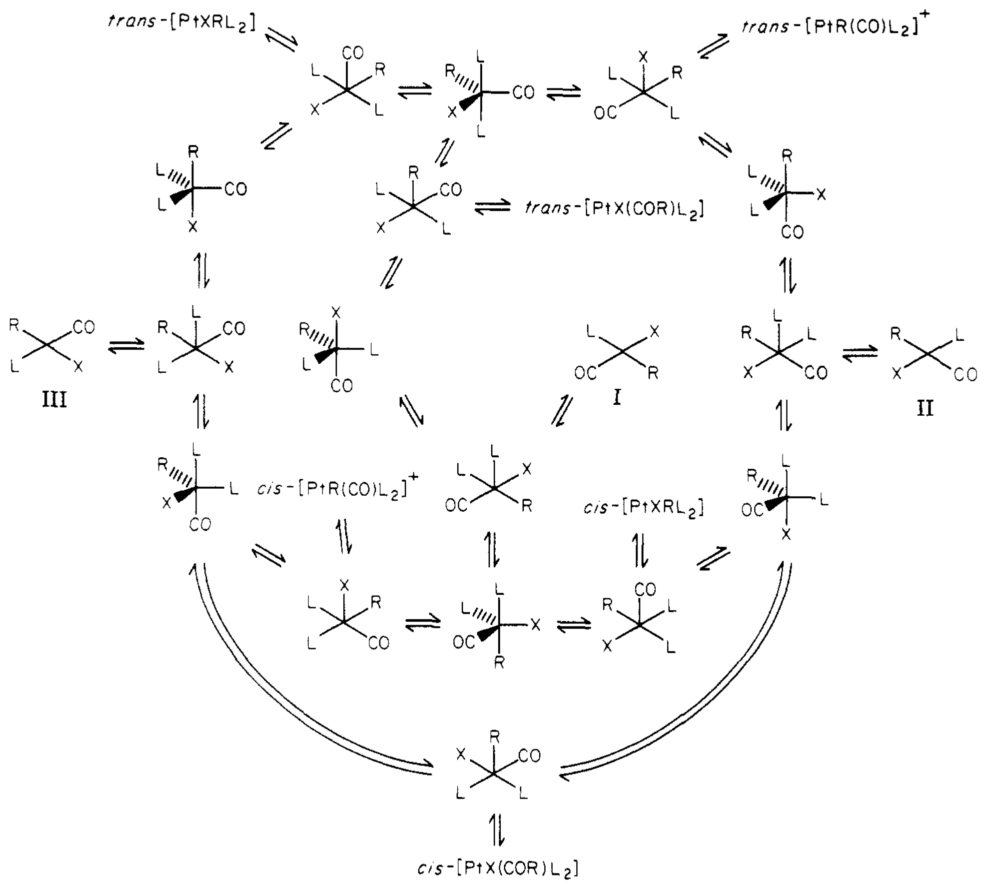
Scheme VI



carbonylation and L addition[36] suggests that these steps may well be involved in the reaction of *trans*-[$PdXRL_2$] with carbon monoxide. In the case of platinum, the isomerizations of four-coordinate species are probably the slowest steps. Thus, a combination of the ease of ligand displacement and the rate of isomerization of [MXR(CO)L] is likely to account for the differences in reactivity between the palladium and platinum complexes toward carbonylation. The rates of carbonylation of a series of related metal complexes are given in Table IV.

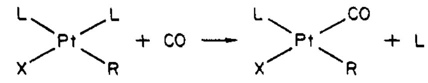
Electronic effects at aryl groups have a similar effect on the insertion process from five-coordinate species as they do on the four-coordinate route, electron-donating substituents promoting the migration step.[18,30,46] The magnitude of this effect is dependent on the neutral tertiary phosphine ligands also, however (Table V). Thus, it is clear that all the ligands exert an effect on this five-coordinate, 18-electron route, too.

There are several five-coordinate species with R cis to CO, all capable in principle of insertion/migration. With ready interconversions between them, the problem of elucidating which one(s) may be responsible is not trivial. A study of the role of $SnCl_3^-$ as anion in these systems offers some insight, however.[45] When X = $SnCl_3$, ready formation of the ionic complex *trans*-[$PtPh(CO)L_2$]$SnCl_3$ occurs as kinetic product (Scheme V). Although reattack of $SnCl_3^-$ *can* release L(PPh_3), this is not a significant contribution to insertion in this case. Instead, reattack to produce the five-coordinate species [$Pt(SnCl_3)Ph(CO)L_2$] leads to insertion and production of the thermodynamic product *trans*-[$Pt(SnCl_3)(COPh)L_2$]. Figure 1 depicts the relative energies of these systems.[45] The choice of a transition state with apical Ph for the migration step seems logical: it is accessible by one pseudorotation from its known precursors, ligands in apical positions are prone to loss and, therefore, probably to migration, and the high activation energy[45] presumably reflects the lack of an ionic or ion-pair contribution to this configuration. This geometry is also in keeping with theoretical predictions.[4]

Table IV
Rate of Carbonylation of *trans*-[$MBrPh(PPh_3)_2$][a,b]

M	$10^4 k_{obsd}$, (2.3 °C), s^{-1}	k_{obsd}(rel)
Pt	0.19	1
Pd	35	184
Ni	22	115

[a] Data taken from ref 18. [b] Measured under 1 atm of CO in tetrachloroethane solution.



(16)

A few further relationships may be added to the overall picture of CO insertions from four- and five-coordinate complexes. Treatment of *cis*-[$PtXRL_2$] with CO leads readily to its isomerization but at low temperatures, and in the presence of a scavenger for L, [PtXR(CO)L] (isomer I) is produced reversibly (eq 16).[41] Scheme VI shows the complete set of relationships between all the reaction routes. Though few of the five-coordinate species have been detected, examples have been reported for nearly all of the transitions

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Table V
Rate Constants for the Carbonylation of *trans*-[PtIRL$_2$] in the Presence of Excess L (under 1 atm of CO)[a]

L	R	T, °C	10^2[L], M	10^2-[PtIRL$_2$], M	10^4-k_{obsd}, s^{-1}
PPh$_3$	p-MeC$_6$H$_4$	30	2.90	0.714	1.04
PPh$_3$	p-MeOC$_6$H$_4$	30	7.05	1.05	0.917
PPh$_3$	C$_6$H$_5$	30	5.23	0.683	0.392
PPh$_3$	p-ClC$_6$H$_4$	52	4.19	0.533	0.359
PPh$_3$	p-MeOCOC$_6$H$_4$	52	7.90	0.860	0.145
P(p-tol)$_3$	p-MeC$_6$H$_4$	43.6	3.85	1.13	8.3
P(p-tol)$_3$	p-MeOC$_6$H$_4$	43.6	6.83	0.90	12.2
P(p-tol)$_3$	C$_6$H$_5$	43.6	4.6	0.80	7.2
P(p-tol)$_3$	p-ClC$_6$H$_4$	43.6	3.7	0.82	6.59

[a] Data taken from ref 18 and 46.

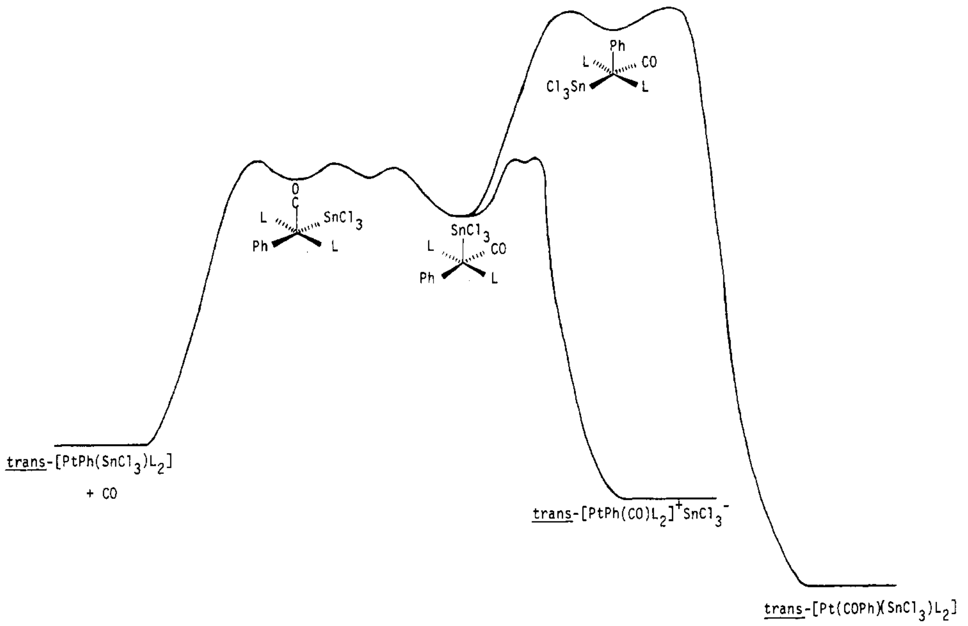


Figure 1.

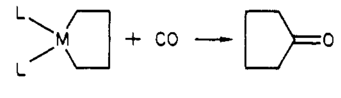
between the four-coordinate species (an exception is the final insertion to *cis*-[PtX(COR)L$_2$]). The square-pyramidal and trigonal-bipyramidal intermediates are closely related in energies.[33]

Elegant work by Stille and co-workers has shown that CO insertion into Pd–C bonds proceeds with retention of configuration at carbon.[47] The details of the mechanism involved were not elucidated: the presence of excess CO meant that it was difficult to determine whether four- or five-coordinate species were active. The carbonylation steps are very rapid, however, and carbonylation has been used to trap intermediates from slower reactions to check the stereochemistry at carbon before it is lost by subsequent reactions.[48]

The easier reactions at nickel and palladium, compared to platinum, have led to reports of carbonyl insertions from a wider variety of compound types. They include cyclopentadienyls,[49] allyls,[50] acetylacetonates,[51] dithiocarbamates,[52] and pentahaloaryls.[53]

Carbonylation of Multidentate Ligand Complexes

While the complexes *trans*-[PtXRL$_2$] (L = monodentate phosphine) readily react with CO to produce the corresponding acyl or aroyl species, analogous treatment of [PtXRL$_2$] (L$_2$ = bidentate phosphine) has no effect.[54] Similarly, the complexes [M{CH$_2$(CH$_2$)$_2$CH$_2$}L$_2$] (M = Ni[55] or Pd[56]) react readily with CO to produce cyclopentanone (eq 17) when L = PPh$_3$ but not when L$_2$ = dppe. These observations may be



(17)

due to the geometrical constraints placed on any five-

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coordinate intermediate by the chelating ligand or to a more difficult phosphine displacement, again because of the chelate effect.

In the case of diorganoplatinum complexes, reaction with CO causes displacement of one tertiary phosphine from $[PtR_2L_2]$ (L = PPh_3 or $PMePh_2$)[54] but no insertion, whereas no reaction occurs at all where L_2 = bidentate phosphine. With isocyanides, $[PtR_2L_2]$ complexes undergo insertion on prolonged heating, but again the initial reaction is phosphine displacement (eq 18).[57] Insertion is favored by the more basic phos-

$$[PtR_2L_2] + CNR^1 \rightleftharpoons [PtR_2(CNR^1)L] + L \xrightarrow{\Delta} [PtR\{C(R)=NR^1\}L_2] \quad (18)$$

phines, PEt_3 and PMe_2Ph, whereas phosphine displacement is more extensive for L = PPh_3 and $PMePh_2$.

Complexes of less strongly bonding chelating ligands in certain cases do undergo carbonylation, however. Thus, [PtXR(cod)] complexes react with CO to yield [PtX(COR)(cod)],[58] whereas only displacement of 1,5-cyclooctadiene by CO occurs for $[PtR_2(cod)]$. Addition of tertiary phosphine to solutions of the resulting $[PtR_2(CO)_2]$, however, did not induce insertion but, rather, resulted in displacement of carbon monoxide. The trigonal-bipyramidal complexes $[NiR(np_3)]BPh_4$ (np_3 = $(Ph_2PCH_2CH_2)_3N$)[59] undergo insertion of CO, where it is supposed that reversible cleavage of the relatively weak Ni–N bond occurs on CO coordination. In the above cases the relative ease of cleavage of the metal–olefin and metal–nitrogen bonds is doubtless a major contributor to their reactivity.

Conclusions

It is apparent that a great deal is now understood about the mechanisms of carbonyl insertion at square-planar complexes. Spontaneous insertion of carbon monoxide occurs, provided certain conditions are met: these include a cis arrangement of CO and the organic group and a ligand trans to R of sufficiently high trans influence to weaken the M–R bond. These are consistent with R migration being the reaction mechanism. In addition, the insertion step is favored by a partial negative charge on R and a partial positive charge on CO. The migration will rapidly reverse unless an incoming ligand is available to stabilize the initially formed three-coordinate species. This may be a bridging halide or an added species such as tertiary phosphine.

Carbonylation of $[MXRL_2]$ complexes proceeds by two routes, one of which involves L dissociation from the initially formed five-coordinate intermediate, $[MXR(CO)L_2]$. The reactions are faster for palladium than for platinum and occur most readily for triarylphosphine complexes, both observations being expected in the context of a mechanism involving displacement of tertiary phosphine. Thus, the dissociative pathway (usually the major route when L = triarylphosphine) involves isomerization of, and spontaneous CO insertion from, a square-planar complex, [MXR(CO)L]. The necessity for L dissociation is underlined by the inability of organoplatinum complexes containing bidentate phosphine ligands to undergo carbonylation. The five-coordinate route dominates the process in a few cases, including that involving the catalytically important $SnCl_3$ group as "nonparticipating" anion. These, too, probably proceed by R migration, but here from a species with R at the apex of a square-pyramidal configuration.

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Pressure Effects on the Dynamic Structure of Liquids

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In recent years there has been significant progress toward a better understanding of the liquid state on the basis of theoretical and experimental work. Particularly, studies in which pressure was used as an experimental variable have contributed in a major way to our knowledge of liquids. In view of my own expertise the following discussion is limited to NMR and laser Raman scattering studies of liquids at high pressure.[1-5]

It is well-known that NMR relaxation experiments provide detailed information about molecular motions and interactions in liquids, including reorientational correlation times, angular momentum correlation times, and diffusion coefficients. Laser Raman scattering experiments are restricted usually to simpler liquids but provide, on the other hand, more detailed information about a specific dynamic process in a liquid. From the analysis of Raman bandshapes using well-developed procedures, we can actually obtain the detailed time dependence of a correlation function.

The main goal of this Account is to show that pressure is an essential experimental variable in all studies that attempt to improve our basic understanding of the liquid state. The use of high pressure to investigate the

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