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CARBON MONOXIDE INSERTION INTO TRANSITION METAL—CARBON SIGMA-BONDS

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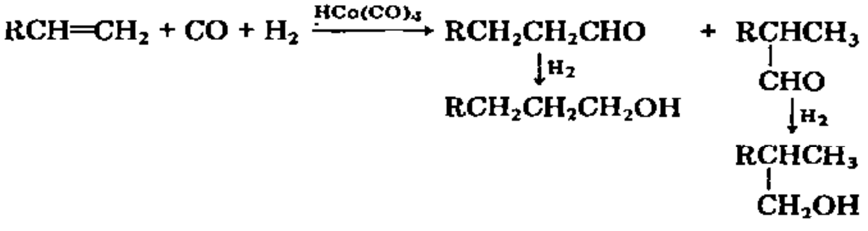
CONTENTS

A. INTRODUCTION

In the past twenty years increasing use has been made of transition metal complexes as catalysts for the combination reactions of various unsaturated species (e.g. CO, RNC, SO_2, SO_3, carbenes, olefins, acetylenes) with one another. Of paramount importance have been reactions incorporating carbon monoxide into unsaturated organic molecules derived from natural gas or petroleum. Particular examples of special interest include the well-known hydroformylation reaction [1] which converts olefins to aldehydes or alcohols;



$$RCH{=}CH_2 + CO + H_2 \xrightarrow{HCo(CO)_4} \begin{array}{c} RCH_2CH_2CHO \\ \downarrow H_2 \\ RCH_2CH_2CH_2OH \end{array} + \begin{array}{c} RCHCH_3 \\ | \\ CHO \\ \downarrow H_2 \\ RCHCH_3 \\ | \\ CH_2OH \end{array} \qquad (1)$$

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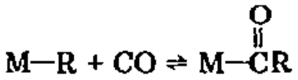
the Monsanto acetic acid synthesis [2] which converts methanol to acetic acid;

$$CH_3OH + CO \xrightarrow[H_2O]{Rh(CO)_2I_2^{\ominus}} CH_3CO_2H \qquad (2)$$

and the Reppe synthesis [3] affording acids (or esters) from olefins.

$$RCH{=}CH_2 + CO \xrightarrow[H_2O]{HNi(CO)_3I} RCH_2CH_2COOH \qquad (3)$$

These and other industrially important processes have served to generate considerable interest in isolable model compounds which bear on the scope and mechanism of carbonylation reactions. A common feature in these syntheses is thought to be the insertion of CO into the σ-bond formed between the transition metal catalyst and an alkyl group. Hence, numerous studies have been made on this reaction and its reverse namely, decarbonylation.



$$M{-}R + CO \rightleftharpoons M{-}\overset{\overset{\large O}{\|}}{C}R \qquad (4)$$

M represents a transition metal with its ancillary ligands which may include CO.

Two earlier reviews have treated carbon monoxide insertion reactions. Wojcicki's excellent article [4] discussed both mechanistic and synthetic aspects. Calderazzo's more recent paper [5] provides a very lucid treatment of advances in the field up to early 1976. This review focuses on new studies since that time and provides a more complete coverage of the literature from 1973 through mid-1979. It is intended to be complementary to the others.

B. GENERAL

As pointed out by Calderazzo [5] the current understanding of carbonylation reactions of alkyl manganese pentacarbonyls serves as a touchstone for studies of CO insertion. These results may be briefly summarized. (1) The inserted CO is one already bound to Mn. A 1,2 migration of the alkyl group onto a *cis*-CO is thought to occur leaving a vacant coordination position which can be occupied by incoming CO or other ligand L. (2) The insertion is highly stereospecific probably involving retention of configuration of the alkyl group. (3) Kinetic studies are consistent with the following mechanism.

$$RMn(CO)_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [RCOMn(CO)_4] \underset{k_{-2}(-L)}{\overset{k_2(+L)}{\rightleftharpoons}} RCOMn(CO)_4L \qquad (5)$$

where L may be CO or another two-electron donor.

Recent results of general interest will be discussed using the manganese reactions as a frame of reference. Following this, a survey of carbonylation reactions by periodic group will be presented.

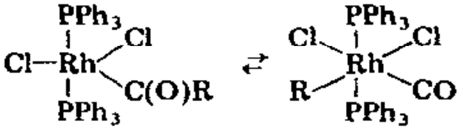
C. STEREOCHEMICAL STUDIES

Carbonylation of $M(CO)_2(CH_3)XL_2$ (M = Fe, Ru; L = PMe_3; X = Me, Cl, Br, I) with ^{13}CO gives a product in which ^{13}CO and acetyl occupy *cis* positions. Thus, a previously-coordinated CO is the inserted one for these Group VIII metals also [6].

Carbonyl insertion into $Me_3CHDCHDZrClCp_2$ (Cp = $(\eta^5\text{-}C_5H_5)$) was shown to proceed with retention of configuration about the carbon [7].

Work on pseudo tetrahedral complexes of the type $Cp^*Fe(CO)(PR'_3)C(O)R$ has revealed that photochemical decarbonylation proceeds stereospecifically at Fe [8,9] and occurs with inversion at the metal [10,11]. Recent experiments [12], however, indicate that the stereochemistry at Fe may be dependent not only on solvent but also on initial concentration of $CpFe(CO)(PPh_3)R$ (R = C_2H_5, i-C_4H_9) when carbonylation is effected at 1400 psi CO and 25°C. Carbonylation of *threo*-$Me_3CCHDCHDFe(CO)_2Cp$ with PPh_3 or $Me_3CN{\equiv}C$ affords the acyl with >95% retention of configuration at C [13]. More recently *threo*-$PhCHDCHDFe(CO)_2Cp$ has been found [14] to yield *threo*-$PhCHDCHDC(O)Fe(CO)(PPh_3)Cp$.

Treatment of *S*-(+)-α-deuteriophenylacetyl chloride with $Rh(PPh_3)_3Cl$ gave *S*-(+)-α-deuteriobenzyl chloride with only 20—27% retention of configuration [15]. On the other hand *S*-(+)-$Ph^*C(CF_3)HC(O)Cl$ gave a completely racemic product on treatment with the Rh complex [16]. Since the acyl complex could be isolated and was optically active and since the acyl and alkyl chlorides were stable under the experimental conditions, racemization must occur via non-stereospecificity in the alkyl migration



(6)

Kinetic studies [16] indicate the possibility of a tight radical pair in the migration step. Thus, several successive acyl ⇌ alkyl rearrangements preceding elimination of RCl with some loss of activity at each could account for the observations. In the case of $(C_6H_5)(CF_3)^*CH{=}R$ the optically active complex $RRh(PPh_3)_2(CO)Cl_2$ was prepared [16] by an independent route and found to yield the optically active alkyl chloride thus ruling out racemization in the elimination step.

Decarbonylation of *erythro*- and *threo*-2,3-diphenylbutanoyl chlorides with $Rh(PPh_3)_3Cl$ gives exclusively *trans*- and *cis*-methylstilbenes [17] respectively. This result is consistent with alkyl migration occurring with retention followed by a *cis* β elimination (and also with inversion, *trans* β elimination). Attempts to study the reaction further using $C_6D_5CD_2CH_2C(O)Cl$ [15] as well as *threo*-$PhCHDCHDC(O)Cl$ [17] were frustrated by the occurrence of H—D scrambling.

The five-coordinate complex *threo*-$PhCHDCHDC(O)Ir(PPh_3)_2Cl_2$ rearranges [18] to the isolable alkyl *threo*-$PhCHDCHDIr(CO)(PPh_3)_2Cl_2$ showing that alkyl migration proceeds with retention of configuration. On the other hand, secondary acyl halides give complexes containing primary alkyl groups on treatment with $Ir(N_2)(PPh_3)_2Cl$ [19]. A β-elimination was shown to be responsible.

D. KINETIC AND MECHANISTIC STUDIES

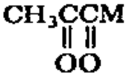
When the entering ligand L is present in large excess k_{obs} for carbonylation of alkyl manganese pentacarbonyls can be identified with k_1, the rate constant for alkyl migration. Recent studies [20] on the carbonylation of a series of substituted benzyl complexes p-$XC_6H_4CH_2Mn(CO)_5$ by isocyanides at 27° in THF give the following rate constants when L = n-C_4H_9NC [20,21].

	X = NO_2	Cl	H	CH_3
$k_1 \times 10^5$ (sec^{-1})	0	3.43 ± 0.30	5.32 ± 0.38	7.24 ± 0.11

The ordering of these rate constants is similar to that for the reverse migration in the series of substituted phenylacetyl derivatives of Ir, p-$XC_6H_4CH_2$-$C(O)Ir(PPh_3)_2Cl_2$ [22].

	X = NO_2	CH_3	CH_3O
$k_1 \times 10^4$ (sec^{-1})	3.9	8.35	9.2

If, as seems plausible, rates of migration in Mn and Ir series are influenced by the breaking of M—C and C(O)—C bonds, respectively, then the strengths of both kinds of bonds are affected similarly by the nature of X. However, the magnitude of the effect must be greater for Mn—C bonds since the migration of p-$NO_2C_6H_4CH_2$ onto CO does not occur at all. This view has recently been confirmed by work on the carbonylation of $RCH_2Mn(CO)_5$ where R = cyclohexyl, H, Ph, OCH_3, HOC(O) and on decarbonylation of the corresponding acyl complexes [23]. The kinetics of carbonylation of $RCH_2Fe(CO)_4^{\ominus}$ were also measured. A linear free energy relationship was established for carbonylation of both series with ρ^* the same within experimental error (—8.8 and —8.7 for Mn and Fe alkyls, respectively). Both carbonylation and decarbonylation were markedly retarded by electron-withdrawing R groups. Mn alkyls display a tenfold greater sensitivity to the nature of R in the carbonylation reaction than do Co alkyls [24].

In another study [25] it has been shown that acetyl migration is not an important pathway in the decarbonylation of manganese acetyl complexes.  $CH_3\underset{\overset{\|}{O}}{C}\underset{\overset{\|}{O}}{C}Mn(CO)_5$ was prepared and shown to lose CO 21 times more slowly than the acetyl. Hence it cannot be an intermediate in the acetyl reaction.

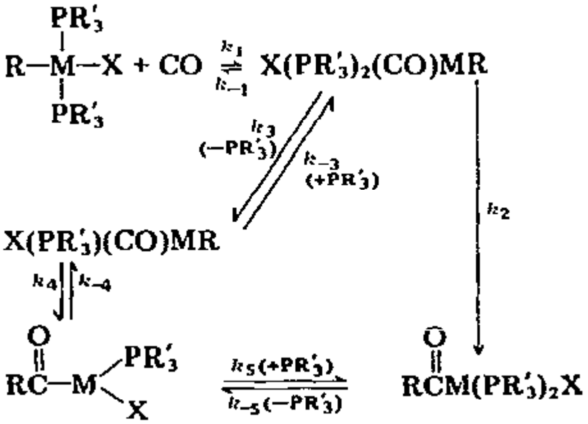
Photolysis of a hexane solution of $CpFe(CO)_2{}^{13}C(O)CH_3$ [26] gave $CpFe(CO)({}^{13}CO)CH_3$ with all the label retained in the decarbonylated species.

This shows that the CO lost is one terminally bound to the Fe and not the one "inserted" into the Fe—CH_3 bond paralleling the situation for Mn. If the photolysis is conducted in the presence of PPh_3, the products are $CpFe(CO)(PPh_3)^{13}C(O)CH_3$ and $CpFe(^{13}CO)(PPh_3)CH_3$. This is consistent with the production of an unsaturated intermediate which is captured by PPh_3 faster than the methyl group migrates. Again the behavior is like that of the Mn complexes.

Photolysis of $CpFe(CO)_2CH_3$ results in the production of an unsaturated intermediate $CpFe(CO)CH_3$ (probably in a solvent cage) which is then captured by ligands L in the order $PPh_3 > AsPh_3 > SbPh_3$ [27] to give $CpFe(CO)LCH_3$. Intermediacy of an acetyl species $CpFe(CO)LC(O)CH_3$ is excluded by the fact that the acetyl loses CO more slowly than does the methyl.

The kinetics of rearrangement from acyl to alkyl complexes have been examined for two series: $p\text{-}XC_6H_4C(O)Rh(PPh_3)_2Cl_2$ and $p\text{-}XC_6H_4CH_2C(O)Rh(PPh_3)_2Cl_2$ [28]. Electron-withdrawing groups enhance the rate of rearrangement of the benzoyl complexes but retard it for the phenylacetyl series. For both series, the magnitude of ρ was small enough to fall in the range for reactions involving radical intermediates. The effect of substituents on the rate of the acyl → alkyl conversion parallels that seen for $p\text{-}XC_6H_4CH_2C(O)Ir(PPh_3)_2Cl_2$ complexes. A study of the acyl → alkyl conversion in the series $CH_{3-n}F_nC(O)Ir[P(CH_3)Ph_2]_2Cl_2$ showed the rather surprising result that rates decrease in the order $CH_2F > CF_3 > CF_2H$ [29].

An extensive study [30] involving kinetic measurements on some sixty systems has elucidated the mechanism of carbonylation of $RMXL_2$ (R = alkyl; X = Cl, Br, I; L = phosphorus ligand; M = Ni, Pd, Pt) complexes. The following pathways were observed.



(7)

The existence of several steps and variations in their relative importance with the nature of the complex make overall k_{obs} as well as $\Delta S^{\neq}$ difficult to interpret.

$CH_3Pt(CO)(PPh_3)I$ reacts with ligands L = $AsPh_3$, $As(p\text{-}CH_3C_6H_4)_3$, $As(CH_3)$-

(o-$CH_3C_6H_4)_2$, $SbPh_3$ to afford $CH_3C(O)Pt(PPh_3)LI$. The kinetics of these reactions depend [31] neither on the solvent nor L. The rate-determining step seems to be alkyl migration to produce the unsaturated $PtC(O)CH_3(PPh_3)I$ which can then be attacked by L.

E. THERMODYNAMIC DATA

The paucity of thermodynamic data on carbonyl insertion reactions is currently being remedied. Available data are reported in Table 1 while equilibrium constants for some Rh systems appear in Table 2.

For the carbonylation reactions, standard enthalpies of carbonylation in solution are related to those in the solid state by eqn. (8) [32],

$$\Delta H_{\text{soln}} = \Delta H^0_{\text{solid}} + \Delta H_{\text{acyl}} - \Delta H_{\text{alkyl}} \tag{8}$$

where the last two terms refer to enthalpies of solvation of the acyl and alkyl species, respectively. The solvation terms are likely to be rather similar so that

$$\Delta H_{\text{soln}} \approx \Delta H^0_{\text{solid}} \tag{9}$$

In many cases, the heat of reaction is likely to bear a relationship to bond energy terms.

$$\begin{aligned}\Delta H^0_{\text{solid}} &= E(\text{M—R}) + E(\text{M—CO}) + E(\text{C}{\equiv}\text{O}) \\ &\quad - \{E(\text{C(O)—R}) + E(\text{M—C(O)R}) + E(\text{C}{=}\text{O})\}\end{aligned} \tag{10}$$

Making the assumption of constancy of energies for those bonds separated by two or more bonds from the R group for a given metal,

$$\Delta H_{\text{soln}} \approx \Delta H^0_{\text{solid}} \approx [E(\text{M—R}) - E(\text{C(O)—R})] + \text{constant} \tag{11}$$

The enthalpy may, if these assumptions are valid, be related to metal—alkyl and C(O)—R bond strengths.

A number of experimental observations may be rationalized on the basis of eqn. (11). In particular, the increasingly positive enthalpies of carbonylation for $CH_{3-n}F_nIr(PPh_3)_2(CO)Cl_2$ (n = 0—3) as fluorine is successively substituted for hydrogen may reflect the increase in Ir—R bond strength with increasingly electronegative R [34]. Similar trends seem to be operative in the Mn systems listed in Table 1. The same trend, considerably attenuated, may be discerned in the insertion reaction of p-$XC_6H_4CH_2Ir(CO)(PPh_3)_2Cl_2$. The nearly equal values of enthalpies of carbonylation for $Cp_2Hf(CH_3)_2$ and $Cp_2Hf(CH_2C_6H_5)_2$ are possible evidence that the bond energy term contributed by the η^2-acyl group [32] dominates (vide infra).

The equilibrium constants reported in Table 2 reveal a surprising lack of dependence on the nature of ancillary ligands as well as a rather random relationship to the nature of R group. The inability to observe the presence of ClC(O)Rh and $ClCH_2C(O)Rh$ species is quite likely related to the Rh—Cl and $RhCH_2Cl$ bond strengths [37].

TABLE 1

Thermodynamic data for CO insertions $MR + CO \rightleftharpoons M\overset{O}{\overset{\|}{C}}R$

Alkyl	Acyl	ΔH^0 (kJ mole^{-1})	ΔS^0 (J K^{-1} mole^{-1})	Ref.
$Cp_2Hf(CH_3)_2$	$Cp_2Hf(C(O)CH_3)CH_3$	−53.1 ± 7.9	−138 ± 23	32
$Cp_2Hf(CH_2C_6H_5)_2$	$Cp_2Hf(C(O)CH_2C_6H_5)(CH_2C_6H_5)$	−48.1 ± 0.87	−120 ± 2	33
$CH_3Mn(CO)_5$	$CH_3C(O)Mn(CO)_5$	−52.7	−126	32
$C_2H_5Mn(CO)_5$	$C_2H_5C(O)Mn(CO)_5$	−40.0	−64.8	32
n-$C_3H_7Mn(CO)_5$	n-$C_3H_7C(O)Mn(CO)_5$	−31.3	−37	32
$C_6H_5Mn(CO)_5$	$C_6H_5C(O)Mn(CO)_5$	−45.2	−115	32
$CH_3Rh(PPh_3)_2(CO)Cl_2$	$CH_3C(O)Rh(PPh_3)_2Cl_2$	+30 ± 2	+35 ± 2	33
$CF_3Ir(PPh_3)_2(CO)Cl_2$	$CF_3C(O)Ir(PPh_3)_2Cl_2$	+1470 ± 70 [a]		28
$CF_2HIr(PPh_3)_2(CO)Cl_2$	$CF_2HC(O)Ir(PPh_3)_2Cl_2$	+1200 ± 140 [a]		28
$CFH_2Ir(PPh_3)_2(CO)Cl_2$	$CFH_2C(O)Ir(PPh_3)_2Cl_2$	+800 ± 90 [a]		28
$CH_3Ir(PPh_3)_2(CO)Cl_2$	$CH_3C(O)Ir(PPh_3)_2Cl_2$	+470 ± 90 [a,b]		28
p-$NO_2C_6H_4CH_2Ir(PPh_3)_2(CO)Cl_2$	p-$NO_2C_6H_4CH_2C(O)Ir(PPh_3)_2Cl_2$	+280 ± 18 [a]		35
p-$CH_3C_6H_4CH_2Ir(PPh_3)_2(CO)Cl_2$	p-$CH_3C_6H_4CH_2C(O)Ir(PPh_3)_2Cl_2$	+245 ± 35 [a]		35
p-$CH_3OC_6H_4CH_2Ir(PPh_3)_2(CO)Cl_2$	p-$CH_3OC_6H_4CH_2C(O)Ir(PPh_3)_2Cl_2$	+230 ± 70 [a]		35
$C_6H_5Pt(PPh_3)_2Cl$	$C_6H_5C(O)Pt(PPh_3)_2Cl$	−593 ± 24 [a]		36
p-$ClC_6H_4Pt(PPh_3)_2Cl$	p-$ClC_6H_4C(O)Pt(PPh_3)_2Cl$	−525 ± 18 [a]		36
p-$CH_3C_6H_4Pt(PPh_3)_2Cl$	p-$CH_3C_6H_4C(O)Pt(PPh_3)_2Cl$	−350 ± 18 [a]		36
p-$NO_2C_6H_4Pt(PPh_3)_2Cl$	p-$NO_2C_6H_4C(O)Pt(PPh_3)_2Cl$	−315 ± 8 [a]		36

[a] Measured in the solid state by differential scanning calorimetry.

[b] Extrapolated from data on fluorinated species. Acetyl complex not isolable.

TABLE 2

Equilibrium constants for CO insertions $MR + CO \rightleftharpoons M\underset{\substack{\| \\ O}}{C}R$ at 298 K in $CDCl_3$

Alkyl	Acyl	$K_{eq.}$	Ref.
$HRh(CO)(PPh_3)_2Cl_2$	$HC(O)Rh(PPh_3)_2Cl_2$ [a]	<0.025	32
$CH_3Rh(CO)(PPh_3)_2Cl_2$	$CH_3C(O)Rh(PPh_3)_2Cl_2$	3.45 ± 0.23	37
$CH_3Rh(CO)[P(C_6H_4F)_3]_2Cl_2$	$CH_3C(O)Rh[P(C_6H_4F)_3]_2Cl_2$	2.86 ± 0.10	37
$CH_3Rh(CO)[P(C_6H_4CH_3)_3]_2Cl_2$	$CH_3C(O)Rh[P(C_6H_4CH_3)_3]_2Cl_2$	2.63 ± 0.07	37
$ClCH_2Rh(CO)(PPh_3)_2Cl_2$	$ClCH_2C(O)Rh(PPh_3)_2Cl_2$ [a]	<0.025	37
$C_2H_5Rh(CO)(PPh_3)_2Cl_2$	$C_2H_5C(O)Rh(PPh_3)_2Cl_2$	>50	33
$C_6H_5CH_2Rh(CO)(PPh_3)_2Cl_2$	$C_6H_5CH_2C(O)Rh(PPh_3)_2Cl_2$	>50	33
p-$ClC_6H_4CH_2Rh(CO)(PPh_3)_2Cl_2$	p-$ClC_6H_4CH_2C(O)Rh(PPh_3)_2Cl_2$	0.073	37
$C_6H_5Rh(CO)(PPh_3)_2Cl_2$	$C_6H_5C(O)Rh(PPh_3)_2Cl_2$	<0.05	37
$Rh(CO)(PPh_3)_2Cl_3$	$ClC(O)Rh(PPh_3)_2Cl_2$ [a]	<0.025	33

[a] Not observed in solution.

Related to these considerations is the recent observation [38] that treatment of $CF_3Mn(CO)_5$ with 333 atm CO at temperatures up to 200°C gave no $CF_3C(O)Mn(CO)_5$ presumably owing to the high Mn—CF_3 bond strength. Also, no $CH_3C(O)Re(CO)_5$ could be detected on subjecting $CH_3Re(CO)_5$ to CO at a pressure 320 atm with temperatures up to 140°. The acyl compound has been independently prepared and is stable. The CH_3—Rh bond energy has been measured [39] as ~200 kJ mole^{-1} as compared to ~110 kJ mole^{-1} for the CH_3—Mn bond energy.

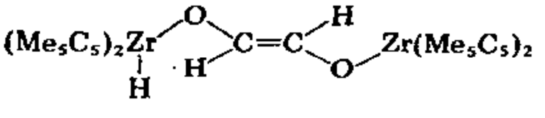
F. SOME OTHER RESULTS OF GENERAL INTEREST

A problem related to CO insertion into M—C bonds is insertion of CO into metal hydride bonds to afford a formyl complex, a putative intermediate in Fischer—Tropsch chemistry. The first such complex was prepared by the reaction of formic acetic anhydride with $Fe(CO)_4^{2\ominus}$ to give $Fe(CO)_4CHO^{\ominus}$ [40]. The neutral complex CpRe(CO)(NO)CHO has recently been prepared by two groups [41,42] by the action of a hydridic reagent on $CpRe(CO)_2(NO)^{\oplus}$. The failure to prepare formyl complexes via a hydride migration route has been attributed [23] to the very electron-withdrawing nature of H ($\sigma^* = 0.5$) which makes the reaction undetectably slow.

Other results indicate the possibility of a hydride migration path. For example, treatment of $Mn(CO)_5^{\ominus}$ with formic acetic anhydride leads not to the expected $Mn(CO)_4CHO$ but instead to a mixture of $HMn(CO)_5$ and $Mn_2(CO)_{10}$ [43]. A possible route to these products would be a transfer of a formyl group to give the unstable $HC(O)Mn(CO)_5$ which decarbonylates with loss of terminal CO and hydride migration to give $\overset{*}{H}Mn(CO)_5$ which then decomposes to $Mn_2(CO)_{10}$. Use of labeled $H^*C(O)OC(O)CH_3$ in this reaction leads to $Mn_2(CO)_{10}$ containing 60—80% of the original label consistent with the hydride migration mechanism [44]. Another reaction possibly proceeding via migration is shown in eqn. (12) [45].

$$Fe(CO)_3(P(OPh)_3)\overset{\overset{\displaystyle O}{\|}}{C}H^{\ominus} \xrightarrow[\text{reflux}]{\text{THF}} Fe(CO)_4H^{\ominus} + P(OPh)_3 \tag{12}$$

The conversion of $(\eta^5\text{-}Me_5C_5)_2Zr(H)_2(CO)$ to I above −50°C may also involve hydride migration [46].



I

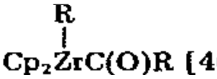
Moreover, treatment of $Os(PPh_3)_2(CO)(CS)Cl(H)$ with CO gives the thioformyl $Os(PPh_3)_2(CO)_2(\underset{\underset{\displaystyle S}{\|}}{C}H)Cl$ [47].

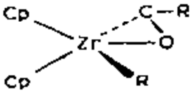
A theoretical treatment of the alkyl migration has recently appeared [48].

Finally, the first example of carbonylation of organoactinides has been observed [49].

G. SURVEY OF REACTIONS

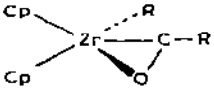
(i) Titanium triad

The first example of carbonyl insertion into Group IV metal alkyls has been recently reported. $Cp_2Ti(R)Cl$ can be carbonylated in heptane or toluene at room temperature and atmospheric pressure to give $CpTiC(O)RCl$ when R is CH_3, CH_2CH_3 or $CH_2C_6H_5$ [50]. Likewise, Cp_2ZrR_2 where R is CH_3 or $CH_2C_6H_5$, inserted a CO into one of the metal alkyl bonds to give  $Cp_2\overset{\overset{R}{|}}{Zr}C(O)R$ [46]. The crystal structure of this complex (II) shows the acyl moiety acting as a three-electron donor with the absence of any CO stretching frequency in the $1600-2000$ cm^{-1} range; instead $\nu_{C=O}$ becomes ~1500 cm^{-1}. This is the first example of an acyl ligand acting as a three-electron donor to a metal although a similar structure has been proposed for an acyl derivative of ruthenium [51]. The crystal structure of $Cp_2TiC(O)(CH_3)I$ [52] also shows the presence of an η^2-acyl. However, in this and other Ti acyl derivatives $\nu_{C=O}$ is around 1600 cm^{-1}.



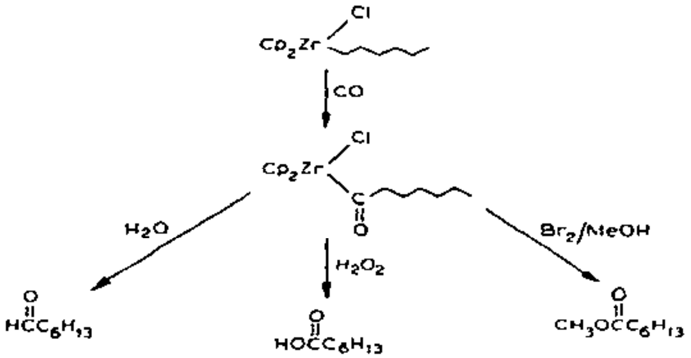
II

Carbonylation of Cp_2ZrR_2 (R = Ph, *p*-tolyl) should lead to isomer III as well as II [53]. This isomer has now been prepared. On warming above −78°C, it rearranges to II intramolecularly and irreversibly.



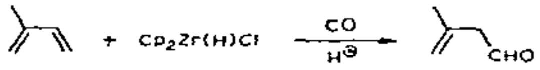
III

The utilization of $Cp_2Zr(H)Cl$ as a hydroformylation reagent has been recently investigated. Reaction of the zirconium hydride with 1-hexene as well as with *cis*- or *trans*-3-hexene results in one product only, $Cp_2Zr(C_6H_{13})Cl$ which readily inserts CO [54] (see eqn. (13)). Hydrozirconation was found to be different from most hydroformylation reactions in that the metal attaches itself at the least hindered carbon atom in the alkyl chain as evidenced by reaction (14) [55]. $Cp_2Zr(R)H$ compounds react with CO to



(13)

give the products of reductive elimination, RH, induced by CO as well as the products of CO reduction,



(14)

RCH_2OH, arising from a Zr acyl [56]. The pentamethylcyclopentadienyl analogues undergo rapid insertion into the Zr—C bond and subsequent reductive elimination to RCHO.

(ii) Vanadium triad

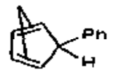
There has been one example of a CO insertion into a vanadium—alkyl bond to give the acyl when R is CH_3 or $CH_2C_6H_5$ [57].

$$\mathrm{Cp_2VR + 2\,CO \rightarrow Cp_2V(CO)C(O)R} \qquad (15)$$

Again, low values of $\nu_{C=O}$ are indicative of an η^2-acyl giving an $18e^-$ species. However, when R is Ph, the reaction takes a different course in that migration of the aryl group to the cyclopentadienyl ring occurs.

$$\mathrm{Cp_2VC_6H_5 + CO \rightarrow Cp_2V(CO)C_6H_5 \xrightarrow{CO} Cp_2V(CO)C(O)C_6H_5}$$

$$\xrightarrow{25^\circ\mathrm{C}} \mathrm{Cp(\eta^5\text{-}C\ H_5C_5H_4)V(CO) + CO + \tfrac{1}{2}\,H_2} \qquad (16)$$



Recently the reaction of $[V(CO)_4L_2]$ (L_2 = diphos, arphos) with H_2 and triphenylcyclopropenium bromide has been reported [58] to give $(Ph_3C_3H_2)$-$C(O)V(CO)_3L_2$.

(iii) Chromium triad

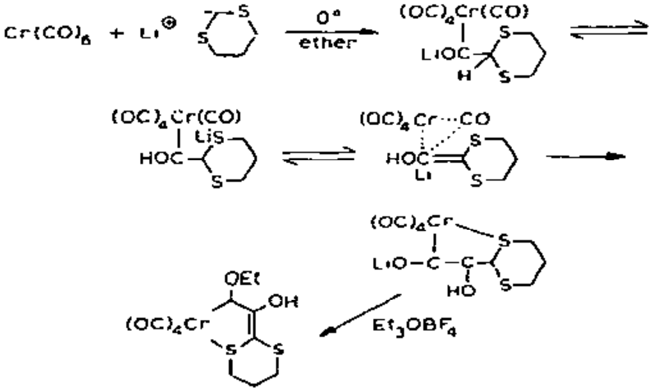
The first well-defined example of CO insertion into a chromium alkyl bond has been reported in the reaction of the metal alkyl with various phosphines in acetonitrile at room temperature [59].

$$\mathrm{CpCr(CO)_3CH_3 + L \rightarrow \textit{trans}\text{-}CpCr(CO)_2(L)\overset{\overset{\displaystyle O}{\|}}{C}CH_3} \qquad (17)$$

$L = PPh_3$, $P(p\text{-}C_6H_4OCH_3)_3$, $PPhMe_2$

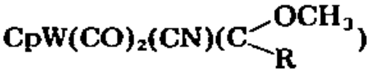
A photochemical reaction of the methyl compound with PPh_3 has been reported [60] to give a 6% yield of *cis*- + *trans*-$CpCr(CO)_2(PPh_3)C(O)CH_3$.

A carbonyl insertion occurs in reaction (18) sequence affording a novel carbene product [61].



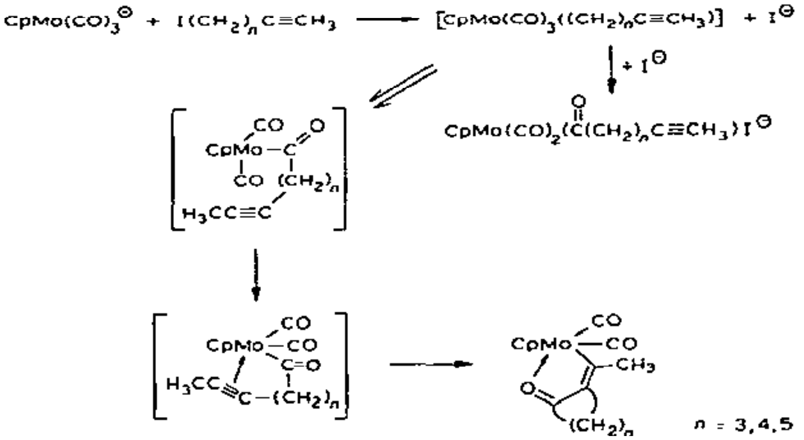
(18)

The low temperature reaction of $CpMo(CO)_3CH_3$ with $L = SbPh_3$ and $AsPh_3$ gives $CpMo(CO)_2LC(O)CH_3$ [62] correcting an earlier report of no reaction. At higher temperatures L is lost from the acyls while photochemical treatment preferentially cleaves a Mo—CO bond. Complexes of the formula $CpMo(CO)_2(L)C(O)CH_3$ (L = phosphine) decarbonylate readily upon heating to give $CpMo(CO)_2(L)CH_3$. This reaction was found to be solvent independent but markedly dependent on the steric bulk of L with sigma donor/pi acceptor effects playing only a minor role. Temperature dependence studies suggest that dissociation of a terminal CO is the rate-limiting step [63]. Noteworthy is the observation that the thermal decarbonylation of $CpMo(CO)_3C(O)C_6H_5$ generates $[(\eta^5\text{-}PhC_5H_4)Mo(CO)_3]_2$ with migration of the aryl group to the cyclopentadienyl ring. The authors suggested a radical pathway [64].

Cyanide ion also induces methyl migration resulting in *cis*-$K[CpMo(CO)_2(CN)C(O)R]$ for $R = CH_2C_6H_5$, C_2H_5 and $CH_2CH_2CH_2CN$ [65]. With analogous tungsten alkyls similar acyl products are obtained which give a mixture of $\mathrm{CpW(CO)_2(CNCH_3)C(O)R}$ and  $\mathrm{CpW(CO)_2(CN)(C{<}^{OCH_3}_{R})}$ on reaction with $\mathrm{Me_3O^{\oplus}BF_4^{\ominus}}$ [66].

$\mathrm{Me_4N^{\oplus}GeCl_3^{\ominus}}$ reacts with $\mathrm{CpMo(CO)_3CH_3}$ to produce *trans*-$\mathrm{Me_4N^{\oplus}[CpMo(CO)_2(GeCl_3)C(O)CH_3]^{\ominus}}$ [67].

$\mathrm{CpMo(CO)_3^{\ominus}}$ was recently found to react with alkynyl iodides, eqn. (19) [68].



(19)

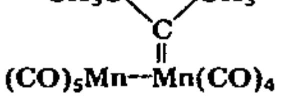
Similar products can be obtained with W under UV irradiation.

Cationic $\mathrm{Cp_2Mo(CO)(CH_3)^{\oplus}}$ undergoes carbonylation with $\mathrm{PMe_2Ph}$ giving $\mathrm{Cp_2Mo(PMe_2Ph)C(O)CH_3^{\oplus}}$ [69].

$\mathrm{Me_4N^{\oplus}[W(CO)_4C(O)CH_3]^{\ominus}}$ is photochemically decarbonylated. Conversion of the methyl product to an acetyl species can be brought about by $\mathrm{PPh_3}$ or by CO. The phenylacetyl and benzoyl species behave similarly [70].

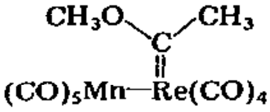
(iv) Manganese triad

Carbonyl insertion into manganese-substituted benzyl bonds is accomplished by isocyanides. This reaction occurs instead of direct insertion to give iminoacyl complexes [71]. Anionic reagents also produce insertion. Reaction of $\mathrm{CH_3Mn(CO)_5}$ with $\mathrm{Br^{\ominus}}$ or $\mathrm{I^{\ominus}}$ forms the anionic manganese complexes $\mathrm{[Mn(CO)_4C(O)CH_3X]^{\ominus}}$. The acyl oxygen in this complex can be protonated to generate the corresponding carbene $\mathrm{Mn(CO)_4(C(OH)CH_3)X}$ [54]. Similar behavior occurs with $\mathrm{CH_3Mn(CO)_5}$ or $\mathrm{C_6H_5Mn(CO)_5}$ and $\mathrm{GeCl_3^{\ominus}}$ [72]. When $\mathrm{NaMn(CO)_5}$ is allowed to react with $\mathrm{CH_3Mn(CO)_5}$ the acyl species $\mathrm{(CO)_5Mn{-}Mn(CO)_4C(O)CH_3^{\ominus}}$ is the product. This anion can be alkylated to give the carbene complex IV.



IV

Surprisingly, the analogous set of reactions between $Re(CO)_5^{\ominus}$ and $CH_3Mn(CO)_5$ affords V on alkylation.



$$(CO)_5Mn{-}\overset{\overset{CH_3O\diagdown\ \diagup CH_3}{C}}{\overset{\|}{Re}}(CO)_4$$

V

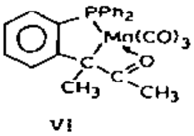
In V the carbene has migrated onto Re [73].

A series of bidentate P and As ligands (L—L) was observed to react with $CH_3Mn(CO)_5$ in a stepwise fashion [74] to give acetyl complexes. These could be thermally decarbonylated >80° to *fac* isomers of $CH_3Mn(CO)_3(L{-}L)$. The very sterically hindered ligand $Ph_2PC(CH_3)_2PPh_2$, however, gave only the *mer* isomer. Ligands with intermediate steric requirement gave a mixture of *fac* and *mer* isomers. Other workers failed to observe the decarbonylation of $C_6H_5CH_2C(O)Mn(CO)_3(Ph_2PCH_2CH_2PPh_2)$ at 90° in vacuo [75].

The bis(acyl) complex *cis*-$Mn(CO)_4(COCH_3)(COC_6H_5)^{\ominus}$ was obtained by treating $C_6H_5COMn(CO)_5$ with MeLi at $-78°C$ [76,77]. On heating a sample of the labeled tetramethylammonium salt of $Mn(CO)_4(COCH_3)(^{13}COC_6H_5)^{\ominus}$, acetophenone with natural abundance of ^{13}C was obtained. This experiment shows the preferential migration of the phenyl group. The authors proposed that the decomposition proceeds through a decarbonylated intermediate. Thermal treatment of the analogous Re complex produced a 97 : 3 mixture of the acyl alkyl *cis*-$Re(CO)_4(C_6H_5)(COCH_3)^{\ominus}$: *cis*-$Re(CO)_4(CH_3)(COC_6H_5)^{\ominus}$ reflecting thermodynamic control of the reaction [78]. This mixture also yields acetophenone on thermal decomposition and makes plausible the earlier postulation of a decarbonylated intermediate in the Mn case.

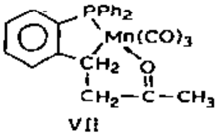
Heating a mixture of $Mn(CO)_5C(O)CH_2C_6H_5$ with $P(OPh)_3$ results in the decarbonylation of the manganese complex to give $Mn(CO)_4(P(OPh)_3)$-$CH_2C_6H_5$. Upon further heating, this complex lost a molecule of toluene generating the internally metallated $\overline{Mn(CO)_3(P(OPh)_3)P(OPh)_2OC_6H_4}$ [75].

An interesting addition product results from the reaction of $CH_3Mn(CO)_5$ with (*o*-vinylphenyl)diphenylphosphine affording $Mn(CO)_4(phos)C(O)CH_3$. This complex can then add $Mn{-}C(O)CH_3$ across the vinyl double bond to give both VI and VII as determined by crystal structure analysis [79]. The



VI

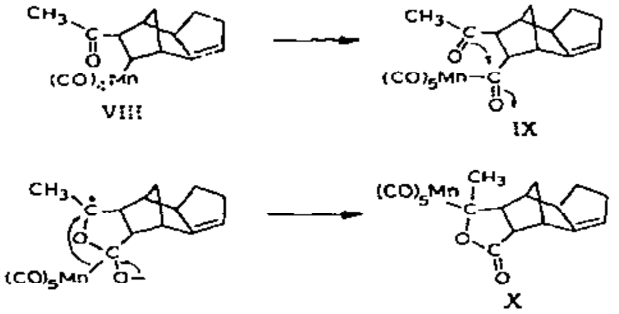
(acetyl to 1 position followed by hydrogen migration)



VII

(acetyl to 2 position)

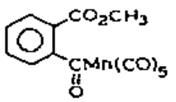
$Mn{-}C(O)CH_3$ bond in $CH_3C(O)Mn(CO)_5$ also adds across a double bond in dicyclopentadiene to give VIII. This product can easily carbonylate forming IX which then undergoes a ring closure to give the lactone X [80].



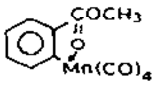
(20)

The ease of formation of metal complexes such as XI was investigated in the thermal decarbonylation of XII to give XIII. The authors suggested that

XI



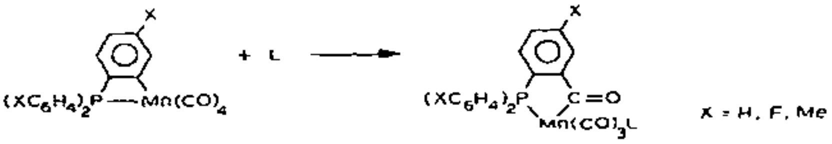
XII



XIII

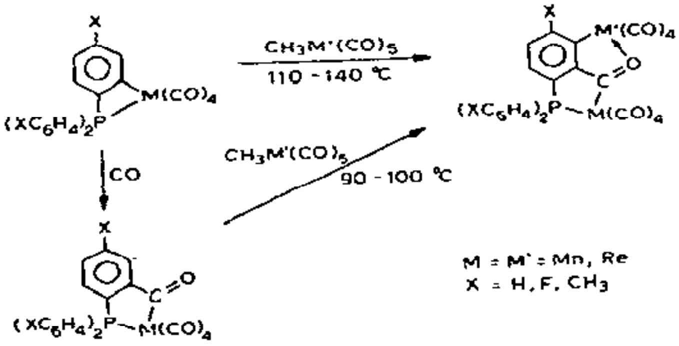
formation of a conformationally preferred chelate due to the position of the double bond, and not electronic stabilization, was the basis for its stability [81,82].

Carbonyl insertion was found to occur on treatment of *o*-metallated Mn species with L = CO or PPh_3 [83], (eqn. (21)).

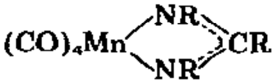


(21)

Carbonylation was also observed with products of secondary metallation [84], (eqn. (22)).

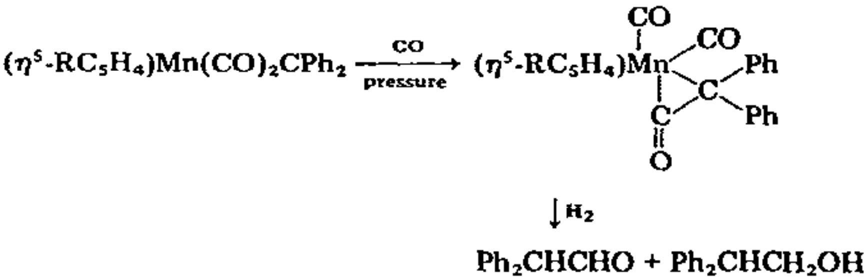


(22)

The thermal or photolytic decarbonylation of $(CO)_4\overline{MnCNR{-}CR'{=}N}R$, where the carbamoyl can be viewed as being isoelectronic with an acyl group, has resulted in  $(CO)_4Mn\langle{}^{NR}_{NR}\rangle CR'$. This product would not insert CO to reform the starting material under 2000 psi CO, 125°C for 48 h [85].

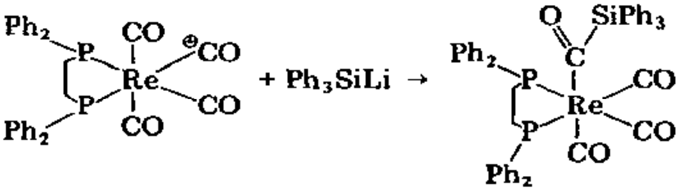
Treatment of an 85 : 15 mixture of *cis* : *trans* σ-crotyl manganese pentacarbonyl with $[Ir(diphos)_2]Cl$ results in decarbonylation giving an 85 : 15 mixture of *syn* : *anti* $(\eta^3\text{-}C_4H_7)Mn(CO)_4$ showing that geometry at the double bond is maintained in the $\sigma \rightarrow \pi$ rearrangement [86].

Photochemical decarbonylation of $(\eta^6\text{-}(CH_3)_nC_6H_{6-n})Mn(CO)_2C(O)R$ ($n = 0, 3, 5, 6$; $R = CH_3$, Ph) has been reported [87]. An interesting insertion of CO into a Mn—carbene bond was recently discovered [88], (eqn. (23)).



(23)

Although it is not the product of CO insertion, the first silyl acyl has recently been prepared, eqn. (24) [89].



(24)

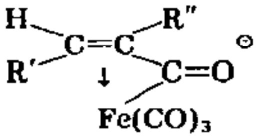
The C=O stretch appears at 1490 cm⁻¹.

(v) Iron triad

The reaction of alkyl halides with $Na_2Fe(CO)_4$, Collman's reagent, leads to the formation of $R_2Fe(CO)_4$. A carbonyl insertion to give $RC(O)Fe(R)(CO)_3(S)$ followed by reductive elimination was thought to be responsible for the appearance of the dialkyl ketone and $Fe(CO)_3(S)$ where S may be a solvent molecule or a ligand [90].

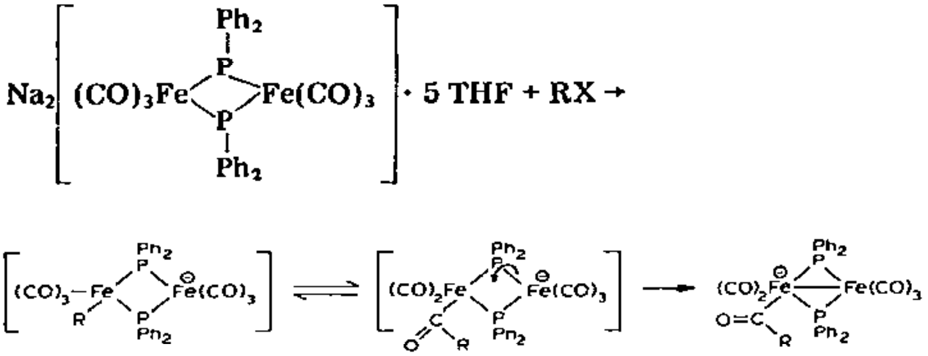
A kinetic study of alkyl migration in $RFe(CO)_4^{\ominus}$ [91] shows acceleration by small cations. A 1000-fold increase in rate occurs on substituting $Li^{\oplus}$ for $PPN^{\oplus}$. Second order kinetics are observed with CO and phosphines.

Acetylenes react with $HFe(CO)_4^{\ominus}$ to afford the insertion product XIV [92].



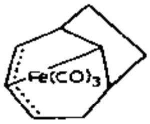
XIV

An especially interesting example of a metal-assisted CO insertion in a dinuclear complex has been reported recently [93], (eqn. (25)), where the two species in equilibrium are postulated intermediates [93].

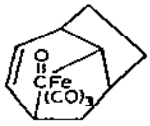


(25)

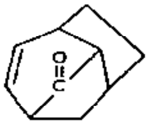
A transannular carbonylation was noted when XV was treated with CO. The product was identified as XVI which can undergo reductive elimination of the iron affording XVII. The nature of the iron product formed with XVII was not described [94].



XV



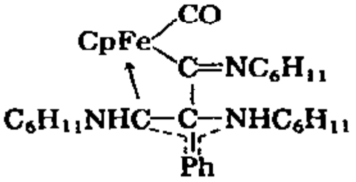
XVI



XVII

The reaction of $CpFe(CO)_2R$ with various ligands L to give $CpFe(CO)(L)$-$C(O)R$ was thought to involve a coordinatively unsaturated solvated or unsolvated sigma or pi acyl species, $CpFe(CO)C(O)R$. A solvated intermediate has now been observed in the reaction of $CpFe(CO)_2$ R where R can be C_6H_{11} or $CH_2C_6H_{11}$ with various ligands in DMSO. However a kinetic study of the reaction showed no specific acceleration in DMSO as compared to other solvents where no intermediates could be observed. Also no specific correlation of rate with solvent-donor properties was observed thereby suggesting a two-step reaction mechanism involving formation of a coordinatively unsaturated iron intermediate which can react with ligand L. In DMSO, however, the solvated intermediate has a sufficient lifetime to be observed [95].

Cyclohexyl isocyanide was found to cause CO insertion in its reaction with $CpFe(CO)_2CH_3$ to give $CpFe(CO)(CNC_6H_{11})C(O)CH_3$. However, with $CpFe(CO)_2CH_2C_6H_5$ cyclohexyl isocyanide gave multiple insertions into the metal—alkyl bond resulting in the formation of the carbene XVIII [96,97].



XVIII

When the compounds $CpFe(CNR')(CO)R$ ($R = C_6H_5CH_2$, $p\text{-}ClC_6H_4CH_2$, $p\text{-}ClC_6H_4$; $R' = C_6H_{11}$, $C_6H_5CH_2$) were allowed to react with CO preferential insertion of isocyanide took place to give the iminoacyls $CpFe(CO)_2C({=}NR')\text{-}R$ [98]. Ultraviolet irradiation of $CpFe(CO)(CNC_6H_{11})C(O)CH_3$ results in preferential loss of CNC_6H_{11} [99]. Although $SbPh_3$ and $AsPh_3$ do not react with $CpFe(CO)_2CH_3$ under thermal conditions, photolysis is reported [100] to yield the corresponding acyl compounds. This behavior is in contrast to that of Mo species [62].

Oxidation of the metal promotes ligand migration reactions perhaps via polarization of coordinated CO [101,102] (eqn. (26)).

$$CpFe(CO)_2R + CuCl_2 \xrightarrow[CO]{R'OH} RCOOR' + CuCl \tag{26}$$

$R = CH_2C_6H_{11}$, C_6H_{11}, $CH_2CH_2C_6H_5$

Chemical decarbonylation of Fe complexes has also received attention. By treatment of $CpFe(CO)_2C(O)C_6H_4C(O)H$ with $Rh(PPh_3)_3Cl$ it was shown [103] that a terminally bonded CO is abstracted in preference to the aldehyde CO at ambient temperature. The product $CpFe(CO)(PPh_3)C(O)C_6H_4C\text{-}(O)H$ results from attack on the unsaturated intermediate by PPh_3 released from $Rh(PPh_3)_3Cl$.

Three series of Fe complexes were studied [103] in their reactions with $Rh(PPh_3)_3Cl$.

I. $CpFe(CO)_2X$ ($X = C(O)CF_3$, $C(O)C_6H_5$, $C(O)CH_3$, C_6H_5, CH_3, NCS, SO_2CH_3, CN, F, Cl, Br, I)
II. $CpFe(CO)LC(O)CH_3$ ($L = CO$, $P(OPh)_3$, $P(On\text{-}C_4H_9)_3$, PPh_3, $P(n\text{-}C_4H_9)_3$, $CNCH_3$, CNPh)
III. $CpFe(CO)_2L^{\oplus}PF_6^{\ominus}$ ($L = CO$, CS, $CNCH_3$, PPh_3)
$CpFe(CO)(CNCH_3)_2^{\oplus}PF_6^{\ominus}$
$CpFe(CNCH_3)_3^{\oplus}PF_6^{\ominus}$

Results on Series I indicate that CO abstraction is directly related to the electron-withdrawing ability of X as measured by ν_{CO} and σ_I. Of the compounds in Series II, only the dicarbonyl loses CO. This presumably reflects the poorer π-acidity of other L compared to CO.

Since attachment to a positive Fe center seemed to enhance decarbonylation, the cationic series III was examined. No abstraction was observed with $CpFe(CO)_2(PPh_3)^{\oplus}$, $CpFe(CO)(CNCH_3)_2^{\oplus}$ or $CpFe(CNCH_3)_3^{\oplus}$. Interestingly, $CNCH_3$ which is isoelectronic with CO, was never abstracted even though $Rh(PPh_3)_2(CNCH_3)Cl$ is a known compound. With $CpFe(CO)_2(CS)^{\oplus}$, CS is found to be preferentially abstracted. These results are consistent with a picture involving attack of a Rh species on the ligand with the lowest energy unfilled orbital.

A kinetic study of the reaction in benzene between $Rh(PPh_3)_3Cl$ and $CpFe(CO)_2C(O)CH_3$ was undertaken. The observations were consistent with the following mechanism (in eqn. (27)).

$$Rh(PPh_3)_3Cl \overset{K_{eq}}{\rightleftharpoons} Rh(PPh_3)_2Cl + PPh_3$$

$$Rh(PPh_3)_2Cl + CpFe(CO)_2C(O)CH_3 \xrightarrow{\text{slow}} Rh(PPh_3)_2(CO)Cl + CpFe(CO)C(O)CH_3$$

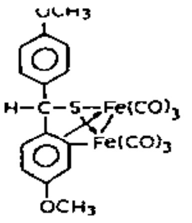
$$CpFe(CO)C(O)CH_3 \xrightarrow{\text{fast}} CpFe(CO)_2CH_3$$

$$CpFe(CO)C(O)CH_3 + PPh_3 \xrightarrow{\text{fast}} CpFe(CO)(PPh_3)C(O)CH_3 \qquad (27)$$

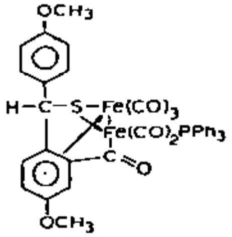
The results described above suggested that other transition metal complexes might serve to abstract CO and other small molecules from organometallic species thus possibly generating new products. Requisite properties of such transition metal complexes would seem to include ability to dissociate a ligand to give an unsaturated species as well as high electron density on the metal to promote "nucleophilic" (or LUMOphilic) attack.

Several complexes were tested for activity as decarbonylating agents using $CpFe(CO)_2C(O)CH_3$ as a substrate. $Ir(PPh_3)_3Cl$ and $Ru(PPh_3)_3Cl_2$ were found active in CO abstraction while (surprisingly) $Ir(PPh_3)_3(N_2)Cl$, $Pt(PPh_3)_3$ and $Pt(PPh_3)_4$ showed no activity [104].

Reaction of XIX with PPh_3 gives CO insertion leading to XX [105].

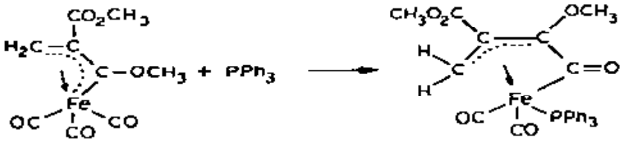


XIX



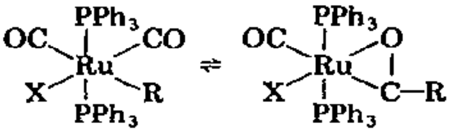
XX

Japanese workers have reported the insertion of CO into a vinyl—carbene—Fe bond [106] (eqn. (28)).



(28)

Two examples of CO insertion into Ru—alkyl bonds have been reported [107,108]. In one of these [108] an equilibrium is set up between an octahedral alkyl and an acyl.



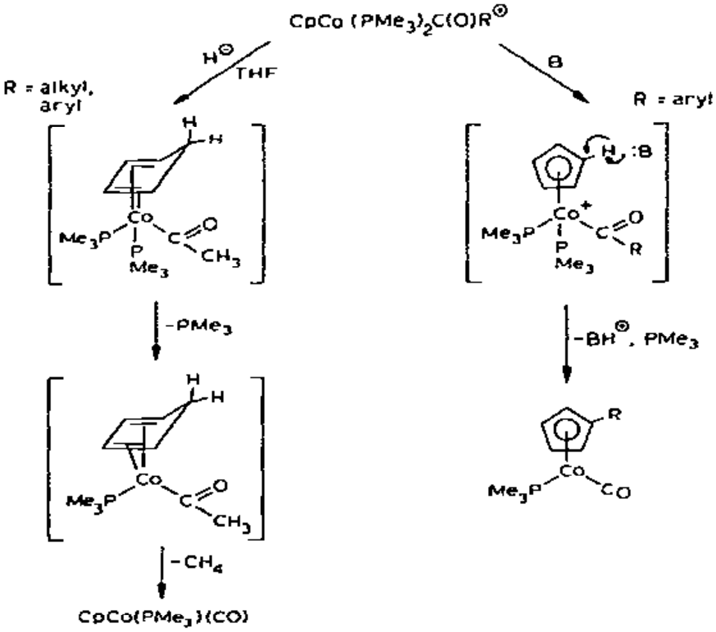
(29)

On heating, $RuRCl(CO)(PPh_3)_2(CNR)$ (R = *p*-tolyl) affords an η^2-iminoacyl complex displaying a preference for isocyanide over CO insertion [109] as seen in Fe complexes [98].

Similarly $OsRX(CO)(PPh_3)_2(CS)$ and $OsRX(CNR)(PPh_3)_2(CS)$ (R = *p*-tolyl; X = Cl, Br, I, O_2CCF_3) afford η^2-thioacyl complexes demonstrating a preference for insertion of CS over either CO or CNR [110].

(vi) Cobalt triad

Since alkyl cobalt tetracarbonyl complexes possess such low stability, the corresponding phosphine complex was investigated for carbonyl insertion. Thus $CH_3Co(PMe_3)_4$ was treated with carbon monoxide which results in the



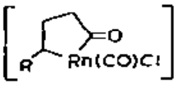
(30)

formation of two products, $CH_3C(O)Co(CO)_2(PMe_3)_2$ and $[Co(CO)_2(PMe_3)_2]_2$ [111]. Note that the reaction of $RCo(CO)_4$ with various phosphines or phosphites gave [112] only the mono-substituted product $RC(O)Co(CO)_3(L)$. $CH_3Co[N(CH_2CH_2PPh_2)_3]^{\oplus}$ affords the acetyl when allowed to react with CO. The benzyl compound, however, undergoes reduction to give $(CO)Co[N(CH_2CH_2PPh_2)_3]$ [113].

Migration reactions which do not result in CO loss occur with $CpCo(PMe_3)_2C(O)R^{\oplus}$ (R = alkyl or aryl) [114] on treatment with NaH (eqn. (30)). The base B arises from impurities in commercial NaH. A similar mechanism involving CO instead of PMe_3 elimination and remigration prevails when $CpCo(PMe_3)_2C(O)CH_3^{\oplus}$ is treated with NaOH giving $CpCo(PMe_3)_2CH_3^{\oplus}$.

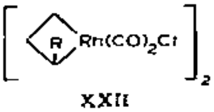
Even though, as mentioned above, carbonylation products involving the Co tetracarbonyl group are not stable enough to isolate, phase transfer catalysis of the carbonylation of substituted benzyl chlorides by $Co(CO)_4^{\ominus}$ gives as products pyruvic acid derivatives when the substituent group is very electron-withdrawing [115]. These could be the result of double carbonyl insertion which would be surprising in view of the results on Mn and Fe insertion [23].

Although examples of carbonylation reactions employing rhodium are more numerous than those employing cobalt, the work is also more synthetic in nature. Thus $[Rh(CO)_2Cl]_2$ reacted with cyclopropylalkanes to give



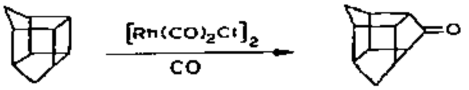
XXI

suggesting the formation of



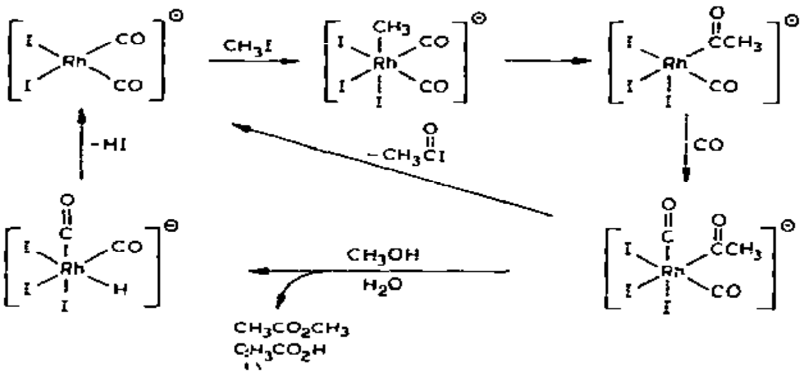
XXII

followed by carbonyl insertion [116]. $[Rh(CO)_2Cl]_2$ was also employed [117] in carbonylating 1,3-bishomocubane to trishomocubanone (eqn. (31)).



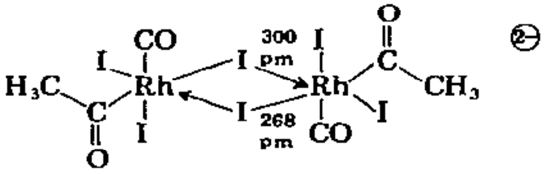
(31)

The mechanism of Monsanto's acetic acid synthesis from methanol, HI and $Rh(CO)_2I_2^{\ominus}$ was recently published. Once again the important step involves carbonyl insertion into a rhodium—methyl bond [2].



(32)

The crystal structure of $(\text{CH}_3)_4\text{N}^{\oplus}[\text{Rh}(\text{C(O)CH}_3)(\text{CO})\text{I}_2]^{\ominus}$ XXIII shows that two molecules are weakly bonded by bridging I [118]

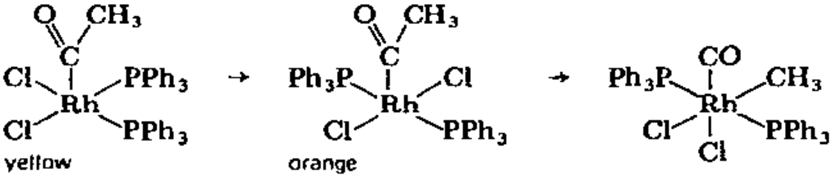


XXIII

Insertion of CO occurs on treatment of $\text{Rh(CO)(PPh}_3\text{)(mnt)}^{\ominus}$ (mnt = maleonitriledithiolate) with alkyl halides [119]. The $[\text{RhI(COC}_3\text{H}_7\text{)(PPh}_3\text{)(mnt)}]^{\ominus}$ anion adopts a square pyramidal structure with the acyl at the apex. Heating these anions results in alkyl migration from CO onto coordinated S.

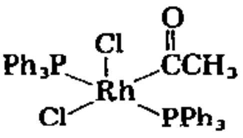
Alkyl halides react with dimeric $[(\text{PR}_3)(\text{CO})\text{RhCl}]_2$ ($\text{R}_3 = (\text{CH}_3)_3$, $(\text{CH}_3)_2\text{C}_6\text{H}_5$, $(\text{OMe})_3$) giving alkyl Rh^{III} species which are in equilibrium with acyl species when the halide is $\text{I}^{\ominus}$ [120]. With CO the phosphines are substituted to give $[\text{Rh(COCH}_3\text{)(CO)ClI}]_2$. Another dimeric species $[(\text{PhMe}_2\text{P})_2\text{Rh(COCH}_3\text{)Br}]_2^{2\oplus}$ with μ-$\text{Br}^{\ominus}$ results from treatment of $\text{CH}_3\text{Rh(CO)[PMe}_2\text{Ph]}_2\text{Br}_2$ with one equivalent of AgPF_6. The bridge can be cleaved by bipy to give a six-coordinate species [121].

^{31}P and ^{1}H NMR have been employed [37] to elucidate the structures of acyl species resulting when acyl halides are added oxidatively to $\text{Rh(PPh}_3\text{)}_3\text{Cl}$. Two acyls and one alkyl were unambiguously detected (eqn. (33)).



(33)

A third acyl isomer XXIV was proposed



XXIV

on the basis of a shoulder in the infrared and because such an isomer could account for the retention of only 1/3 of the ^{36}Cl by Rh in decarbonylation effected by $\text{Rh(PPh}_3\text{)}_3{}^{36}\text{Cl}$ [15].

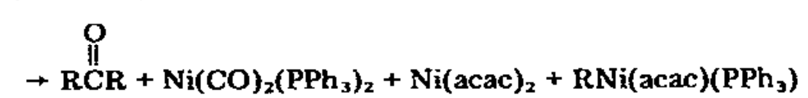
The use of rhodium complexes for decarbonylation of organic compounds has continued to draw interest. The heretofore unisolated intermediate from oxidative addition of an aldehyde to $Rh(PPh_3)_3Cl$ has been characterized recently [122]. This same Rh compound was employed to abstract CO from secondary amides [123], acyl phosphines [124] and mono carboxylic [123] acids to give nitriles, alkyl phosphines and carbinols. Ketones containing an acetylenic linkage can be decarbonylated [125] as well as α- and β-diketones [126] at elevated temperature. However, at room temperature the reaction with β-diketones resulted in the formation of a chelated Rh species which was inactive in decarbonylation. Likewise, the reaction of alcohols, RCH_2OH, with $Rh(PPh_3)_3Cl$ in the presence of an olefin results in the decarbonylation of the alcohol forming the alkane, RH, along with the accompanying reduction of the olefin [127].

The complexes $M(NO)(PPh_3)_3$ (M = Co, Rh, Ir) undergo oxidative addition of benzoyl chloride. Reductive elimination to give C_6H_5NO and $RhCl(CO)(PPh_3)_2$ [128] occurs for M = Rh. When M = Co the products are C_6H_5Cl and $Co(NO)(CO)(PPh_3)_2$.

A recent review [129] examines the mechanistic pathways for carbonylation of methanol by Rh and Ir complexes.

(vii) Nickel triad

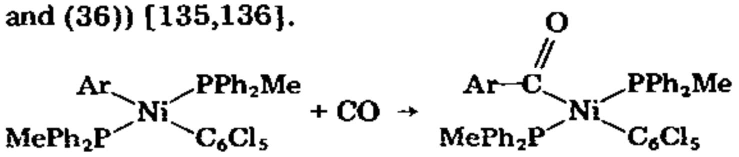
Several examples of carbonyl insertion into a nickel—alkyl bond have been described. Treatment of $(PMe_3)_2Ni(CH_3)X$ or $(PMe_3)Ni(CH_3)(acac)$ with CO results in the formation of $(PMe_3)_2Ni(COCH_3)X$ and $(PMe_3)_3Ni(COCH_3)(acac)$, respectively. However, addition of a protic acid to either product results in immediate evolution of carbon monoxide and methane with no evidence of acetaldehyde formation [130]. The crystal structure of $Ni(PMe_3)_2ClC(O)CH_3$ shows, as expected, a *trans* disposition of phosphines [131]. When $Ni(PMe_3)_2ClXC(O)CH_3$ (X = Cl, Br, I) are treated with $Ni(PMe_3)_4$ decarbonylation occurs giving a mixture of $Ni(PMe_3)_2MeX$ and $Ni(PMe_3)_3(CO)$ [132]. This observation explains why decarbonylation products are observed with oxidative addition of acyl halides to Ni(O) complexes. Likewise the reaction of $RNi(acac)(PPh_3)$ where R can be Me or Et with carbon monoxide affords $(RCO)Ni(acac)(PPh_3)$ which then decomposes to ketones according to the stoichiometry (eqn. (34)).



$$3(RCO)Ni(acac)(PPh_3) \rightarrow R\overset{\overset{O}{\|}}{C}R + Ni(CO)_2(PPh_3)_2 + Ni(acac)_2 + RNi(acac)(PPh_3) \qquad (34)$$

The mechanism of this decomposition is thought to involve cross coupling of an acyl nickel with an alkyl nickel based on the formation of $CH_3C(O)CH_2CH_3$ from the reaction of $(EtCO)Ni(acac)(PPh_3)$ with $MeNi(acac)(PPh_3)_2$ [133]. Treatment of $[NiRL][BPh_4]$ ($R = CH_3, C_2H_5, CH_2C_6H_5$; $L = N(CH_2CH_2AsPh_2)_3, N(CH_2CH_2PPh_2)_3$) with CO affords acyl products [134].

Insertion into a nickel aryl bond was also recently reported (eqns. (35) and (36)) [135,136].


(35)

Ar = p-$Me_2NC_6H_4$, p-$CH_3OC_6H_4$, p-$CH_3C_6H_4$

$$Ni(PPh_3)_4 + C_6H_5Cl \xrightarrow[CH_3OH]{Et_3N,\ CO} C_6H_5C(O)Ni(PPh_3)_2Cl \qquad (36)$$

The carbonylation in eqn. (36) also occurs with the Pd complex.

Other insertions into Ni—aryl bonds have been observed (eqns. (37) and (38)) [137,138].

$$Ni(PEt_3)_2Cl(Ar) + CO \rightarrow Ni(PEt_3)_2ClC(O)Ar \qquad (37)$$

Ar = Ph, m-ClC_6H_4, o-ClC_6H_4

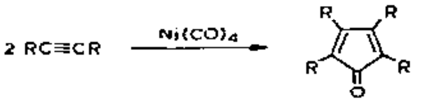
$$Ni(PR_3)_n(acac)Ph + CO \xrightleftharpoons[<0^\circ C]{\text{hexane or toluene}} Ni(PR_3)_n(acac)C(O)Ph \qquad (38)$$

$n = 1$: R = Ph, C_6H_{11}; $n = 2$: R = Et.

Carbon monoxide insertion into a nickel—carbon bond has been postulated as one of the steps in several carbonylation reactions catalyzed by nickel. Thus the double insertion of acetylene followed by carbonylation would explain the formation of vinyl acrylic acid esters in the reaction of $Ni(CO)_3X^\ominus$ with acetylene (eqn. (39)) [139].

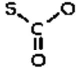
$$2\ HC{\equiv}CH + CO \xrightarrow[ROH]{Ni(CO)_3X^\ominus} CH_2{=}CHCH{=}CHCO_2R \qquad (39)$$

Likewise the stoichiometric reaction of dialkyl or diaryl acetylenes with tetracarbonyl nickel generates the tetrasubstituted cyclopentenones (eqn. (40)) [140].



(40)

and treatment of $Ni(SCH_2CH_2OH)_2$ in pyridine with four equivalents of carbon monoxide which results in the formation of XXV,

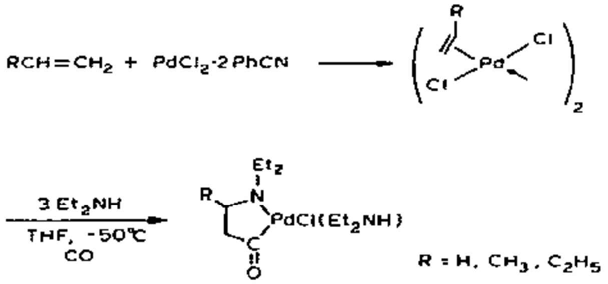


XXV

$HSCH_2CH_2OH$ and $Ni(Co)_3Py$ would seem to involve carbonyl insertion into a nickel—sulfur bond [141].

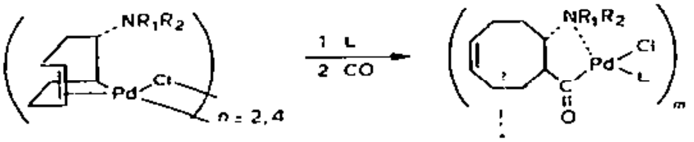
Treatment of NiBr(Ph)(dpb), (dpb = 1,4-bis(diphenylphosphino)butane) with CO afforded PhC(O)Br and $Ni(CO)_2(dpb)$. The authors suggested that carbon monoxide insertion into the nickel—phenyl bond followed by reductive elimination of PhC(O)Br was responsible for its formation [142].

Several examples of carbonyl insertions employing various palladium complexes exist. Again most of the work is synthetic in nature. For example, treatment of $Pd(PPh_3)_3(CO)$ with various alkyl halides produced the corresponding $Pd(PPh_3)_2(COR)X$ for R = CH_3, C_6H_5, $C_6H_5CH_2$, $CH_2{=}CHCH_2$, $CH_2{=}CH$ [143]. Pd acyl complexes can also be isolated from the reaction (41) [144].



(41)

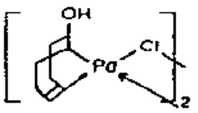
A similar reaction gives oligomers resulting from CO insertion (eqn. (42)) [145].



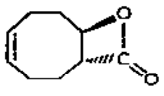
(42)

$n = 2$, $R_1 = R_2 = H$ $m = 2$, L = py
$n = 4$, $R_1 = H$, $R_2 = CH_2C_6H_5$ $m = 2$, L = PPh_3
$n = 2$, $R_1 = R_2 = N(CO)_2C_6H_4$ $m = 1$, L = py

Likewise the reaction of $PdCl_2(PPh_3)_2$ with C_6H_5I and CH_3OH under 200 psi CO and 60°C lead to the formation of $PhCO_2CH_3$ and $(PPh_3)_2PdX(CO_2CH_3)$ [146]. And the reaction of XXVI with CO resulted in the formation of XXVII [147].

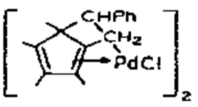


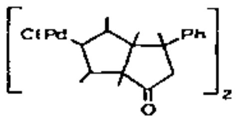
XXVI

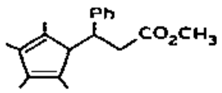


XXVII

The competition between sigma and pi bonded alkyls in carbonylation reactions was investigated [148,149]. Thus, the reaction of XXVIII with CO was shown to involve either insertion of a coordinated double bond affording XXIX, or in the presence of methoxide, nucleophilic attack at the acyl carbon to give XXX.


XXVIII


XXIX


XXX

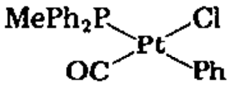
The effect of steric interactions in the chelate ring in $Pd(Ph_2P(CH_2)_n$-$PPh_2)Cl_2$ on the carbonylation of styrene in EtOH was investigated. For $n = 1$, 6 and 10 steric crowding leads to a decreasing participation of the monophosphine complex in carbonylation as would be expected [150].

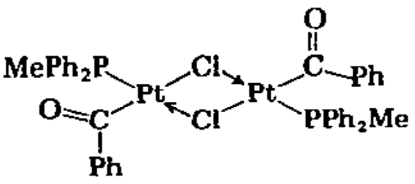
Carbonyl insertion has also been proposed for the carbonylation of olefins by Pd(II) complexes in alcohol [151,152] as well as the carbonylation of organomercurials, RCH=CHHgCl, by $PdCl_4^{2-}$ [153].

Although not really within the scope of this review, an interesting insertion of CO into a Pd—Pd bond has lately been observed [154].

Pt(Me)I(CO)(L) reacted with another ligand L to effect either CO insertion giving $Pt(COMe)I(L)_2$ or substitution affording $Pt(Me)I(L)_2$ when L = PPh_3, $PPh_2(o\text{-}MeC_6H_4)$, $PPh(o\text{-}MeC_6H_4)_2$, $AsPh_3$, $As(p\text{-}MeC_6H_4)_3$ or $AsMe(o\text{-}MeC_6H_4)_2$ [155]. The rate controlling step in this reaction was found to be independent of both ligand and solvent and was thought to involve formation of Pt(COMe)I(L). A balance of steric and electronic effects would determine whether substitution or insertion would occur.

Complex XXXI has been found [156] to be in equilibrium with the dimer XXXII in solution, the equilibrium lying farthest to the right in the order 95% > Ph > Me >> CH_2Ph (0%).

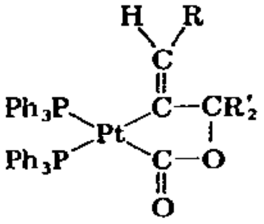

XXXI


XXXII

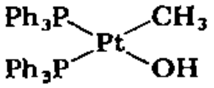
The other isomers of XXXI do not insert CO in this way suggesting that species similar to XXXI are the reactive intermediates in the scheme of Garrou and Heck [30].

Carbonylation of *trans*-$Pt(PPh_3)_2I(R)$ proceeds according to the mechanism of ref. 30. Rates of CO migration are in the order $p\text{-}CH_3O_2CC_6H_4 < p\text{-}ClC_6H_4 < C_6H_5 < p\text{-}CH_3OC_6H_4 < p\text{-}CH_3C_6H_4 > o\text{-}CH_3OC_6H_4$. The rates for the dissociative path are not very sensitive to the nature of R [157]. In the carbonylation of the few Pd complexes studied, the rates for stoichiometric carbonylations were found to be unrelated to those of the Pd-catalyzed benzoxycarbonylation of aryl iodides implying that CO migration is not rate-determining in the catalytic process [157].

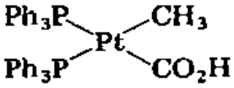
Several reactions involving Pt compounds are worth noting. A novel carbonylation/cyclization was reported to occur when Pt(RC≡CCR$'_2$OH)-(PPh$_3$)$_2$ was treated with carbon monoxide forming XXXIII [158]. Also a note has appeared showing CO insertion in the platinum—hydroxy bond of XXXIV to give the carboxylic acid, XXV [159].



XXXIII



XXXIV

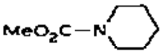


XXV

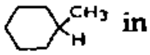
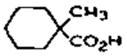
The conversion of PtCl(COR)(PPh$_3$)$_2$ to an alkyl has been effected by employing AgPF$_6$ to abstract the chloride. The resulting Pt(COR)(PPh$_3$)$_2^{\oplus}$ has a vacant coordination site so that alkyl migration can occur forming PtR(CO)-(PPh$_3$)$_2^{\oplus}$. However in a highly coordinating solvent such as acetonitrile, this intermediate can be captured as Pt(COR)(PPh$_3$)$_2$(CH$_3$CN)$^{\oplus}$ [160].

A reversible carbonylation/decarbonylation reaction has been reported for *trans*-PtCl(CH$_2$C$_6$H$_4$CN)L$_2$ when L = PPh$_3$, AsPh$_3$ [161]. Also a note should be made of the thermal decarbonylation of *trans*-PtCl(COR)(PPh$_3$)$_2$ when R is CH=CHC$_6$H$_5$ [162].

(viii) Copper triad

Interest in copper carbonyl chemistry has lead to several noteworthy reactions. Carbonylation of Cu(OMe)$_2$ initially resulted in the formation of MeOCuCO$_2$Me. This complex can then decompose to give Me$_2$CO$_3$ or react with piperidine to give  [163]. Kinetics of this reaction showed the mechanism in eqn. (43) to be plausible for X = OMe or Cl [164].

$$
\begin{aligned}
&\mathrm{Cu(OMe)X + CO \rightarrow Cu(CO)X} \\
&\mathrm{Cu(OMe)X + Cu(CO)X \rightleftharpoons Cu(OMe)X \cdot Cu(CO)X} \qquad (43) \\
&\mathrm{Cu(OMe)X \cdot Cu(CO)X \rightarrow Cu(CO_2Me)X + CuX} \\
&\mathrm{Cu(CO_2Me)X + Cu(OMe)X \xrightarrow{fast} Me_2CO_3 + CuX}
\end{aligned}
$$

Copper(I) tricarbonyls have been employed in several carbonylation reactions at room temperature and atmospheric pressure. Thus, saturated hydrocarbons e.g.  in the presence of H$_2$SO$_4$ and 1-hexene have been carbonylated by Cu(CO)$_3^+$ to give  and *t*-heptanoic acids [165]. Likewise alcohols have been converted to tertiary carboxylic acids [166].

ACKNOWLEDGEMENT

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