Coordination Chemistry Reviews, 53 (1984) 227–259
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

REAGENT AND CATALYST INDUCED SUBSTITUTION REACTIONS OF METAL CARBONYL COMPLEXES

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(Received 28 April 1983)

CONTENTS

LIGAND ABBREVIATIONS

bipy	2,2′-bipyridyl
dppe	1,2-bis(diphenylphosphino)ethane
RNC	isonitrile
py	pyridine
pic	α-picoline

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0010-8545/84/$09.90

phen	1,10-phenanthroline
1,5-COD	1,5-cyclooctadiene
CHT	cycloheptatriene
NBD	norbornadiene
DAD	diazadiene
Me	methyl
Et	ethyl
Pr	propyl
Bu	butyl
Ph	phenyl
n, i, t	normal-, iso-, tertiary-
THF	tetrahydrofuran
COT	cyclooctatetraene

A. INTRODUCTION

The role of transition metal carbonyl complexes in the development of coordination chemistry [1], as a ready source of low oxidation state metals in synthetic organometallic chemistry [2], and as catalysts and reagents in organic synthesis and industrial processes [3,4], has ensured the prominence of metal carbonyl chemistry in the research literature of the last 90 years [5]. Further, the importance of the carbonyl substitution reaction has endured, and it is to be found as an important step in many synthetic and catalytic processes [3–5].

Despite this, a survey of the literature reveals that many apparently simple carbonyl substitution reactions remain difficult or impossible to accomplish by classical thermal and photochemical techniques. The numerous problems associated with the simple transformation (1) have, for instance, been re-emphasised in recent years by the general upsurge of interest in polynuclear metal carbonyl complexes and their derivatives [6]. The metal atom–carbon monoxide interaction has also come under renewed scrutiny within the context of catalysis, such as in the water gas shift reaction [7] and the Fischer–Tropsch process [8].

$$M(CO)_n + L \rightarrow M(CO)_{n-1}L + CO \qquad (1)$$

Traditionally, substitution reactions of metal carbonyl complexes have been carried out under thermal and/or photochemical conditions [9]. If certain desirable goals in a general carbonyl substitution reaction are recognised to be (a) mild reaction conditions, (b) multiple, stepwise replacement of CO ligands, (c) high product yields and (d) short reaction times, these conditions are not always met by classical procedures. In response, a number of methods have been devised that contribute to the improvement of certain metal carbonyl substitution reactions. A general survey of the literature has thus been undertaken with a view to delineating and evaluating the applications and limitations of these alternative methods. The survey which follows has been broadly subdivided into either *reagent promoted* or *catalysed* substitution reactions of metal carbonyl complexes.

The use of the term "reagent promoted substitution reaction" has been restricted to cases represented by reaction (2), thus excluding instances where reagents can achieve the *formal* substitution of a CO ligand via

$$M(CO)_nL_m + L' \xrightarrow{\text{reagent}} M(CO)_{n-1}L_mL' + CO \qquad (2)$$

chemical transformation of the carbon monoxide molecule, with concomitant inclusion of all or parts of that molecule in the substituent *. Specifically, the following reaction types will be excluded from discussion: (a) nucleophilic attack at CO by organolithium compounds [10] or Grignard reagents [11], resulting in metal carbene complexes; (b) nucleophilic attack at CO by amine to give carbomoyl complexes [12]; (c) nucleophilic attack at CO by hydride to give formyl complexes [13]; (d) nucleophilic attack at CO by hydroxide to yield hydroxycarbonyl complexes [14]; (e) reaction of coordinated CO with azide [15]; (f) ^{18}O exchange with aqueous base [16]; and (g) electrophilic attack by Lewis acids at carbonyl oxygen [17]. The possible intermediacy of formyl and hydroxycarbonyl complexes will, however, be considered briefly within the context of hydride facilitated and phase-transfer catalysed substitution reactions, respectively (vide infra). Also excluded from discussion will be certain solvent effects variously described as "catalytic" and "substitution assisting" [18], as well as the labilising effects of certain ligands contained in the metal coordination sphere [19].

The literature has been reviewed up to mid-1982, although certain pertinent papers that have been published since then are also included.

B. REAGENT PROMOTED SUBSTITUTION REACTIONS OF METAL CARBONYL COMPLEXES

(i) *Trimethylamine* N*-oxide induced reactions*

The use of trimethylamine *N*-oxide (Me_3NO) to induce CO ligand replacement reactions has proven to be a useful synthetic technique and is now a well established procedure in metal carbonyl chemistry. This section highlights the advantages and novel uses to which Me_3NO has been applied in metal carbonyl chemistry.

The earliest report of the reaction of an amine oxide with a transition

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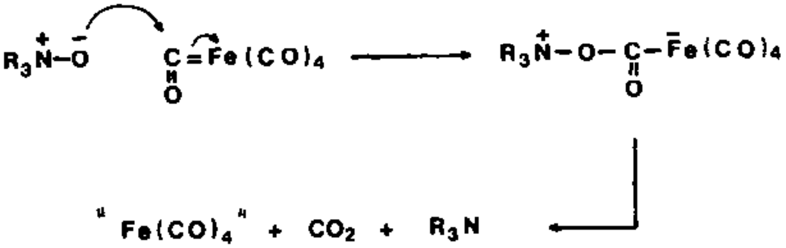
* The role of catalysts in the CO insertion reaction will, however, be mentioned.

metal carbonyl complex was made by Hieber and Lipp in 1959 [20]. They reported that pyridine *N*-oxide reacted with iron pentacarbonyl to yield pyridine and iron oxides. Subsequent work by Alper and Edward [21] established the generality of the reaction and showed that amine oxides (aromatic, aliphatic and heterocyclic) were reduced to the respective amines by reaction with $Fe(CO)_5$. In addition, other oxygenated nitrogen compounds (e.g. azoxybenzenes, nitrones, nitro and nitroso compounds, and nitrosamines) were also found to react with $Fe(CO)_5$ with subsequent deoxygenation. The mechanism proposed for the reaction involved nucleophilic attack of amine oxide at a carbonyl carbon atom (Scheme 1).



Scheme 1

The fate of the iron carbonyl fragment was not investigated, but the reaction was found ultimately to give oxides of iron.

In a related study [22] it was reported that the reduction of nitroaryls by $Fe_3(CO)_{12}$, in the presence of methanol, led to the formation of aromatic amines. A mechanism involving $HFe_3(CO)_{11}^-$ as the active reducing species was suggested and is equivalent to the mechanism proposed by Alper and Edward [21].

The reduction of amine oxides by iron carbonyls has been utilised by Shvo and Hazum [23] in novel olefin disengagement reactions. Amine oxides, and in particular trimethylamine *N*-oxide, were used to induce the mild oxidative disengagement of organic ligands L, from $LFe(CO)_n$ complexes.

$$LFe(CO)_n + R_3NO \rightarrow L + R_3N + CO_2 + \text{Fe oxides} \quad (3)$$

In a second publication [24] the authors made the significant observation that the formally reversed reaction is also of synthetic utility. Thus, iron carbonyl, in the presence of diene ligands L, and trimethylamine *N*-oxide, is rapidly converted under mild reaction conditions to the diene complex $LFe(CO)_3$, viz.

$$Fe(CO)_5 + L + Me_3NO \rightarrow LFe(CO)_3 + Me_3N + CO_2 + CO \quad (4)$$

The reaction was suggested to proceed via ligand attack at an $Fe(CO)_4$ unit generated from $Fe(CO)_5$ and trimethylamine *N*-oxide. In addition, the reaction was shown not to proceed via the intermediacy of $Fe_2(CO)_9$, nor in

TABLE 1

Products obtained from the reaction between metal carbonyls and ligands in the presence of Me_3NO as CO replacement reagent

Substrate	Ligand	Product(s)	Ref.
$Fe(CO)_5$	NMe_3	$Fe(CO)_4(NMe_3)$	25
	diene (e.g. COT)	$Fe(CO)_3(diene)$	24
$Fe(CO)_4(CNR)$	RNC	$Fe(CO)_3(CNR)_2$	48
$M(CO)_6$ (M = Cr, Mo, W)	L = NMe_3, py	$M(CO)_5L$,	29, 136
	MeCN, NBD	$M(CO)_4L_2$	
$Mo(CO)_6$	Bu^tNC	$Mo(CO)_{6-n}(CNBu^t)_n$ ($n = 1, 2$)	115
$(\eta^5\text{-}C_5H_5)Mo(CO)_3I$	PPh_3	$(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)I$	41
$(\eta^5\text{-}C_5H_4CH_3)Mn(CO)_3$	L = py, PPh_3, $\frac{1}{2}$NBD,	$(C_5H_4CH_3)Mn(CO)_2L$	29
$[(\eta^5\text{-}C_5H_5)Fe(CO)_3]PF_6$	L = PR_3	$[(\eta^5\text{-}C_5H_5)Fe(CO)_2L]PF_6$	46
$Ru(CO)_2X_2L_2$ [a]	py	$Ru(CO)(py)L_2X_2$	33, 56
$Ru(CO)(py)Cl_2L_2$ [b]	L^1 = phen, bipy	$Ru(L^1)L_2Cl_2$	33, 56
$Ru(CO)_2Cl_2L_2$ [b]	L^1 = phen, bipy	$[Ru(L_2)(L^1_2)]^+$	33, 56
$Mn_2(CO)_{10}$	L = CH_3CN, py, PPh_3, pic	$Mn_2(CO)_9L$	28, 55
	L = py, PPh_3	$Mn_2(CO)_8L_2$	28
$Re_2(CO)_{10}$	L = CH_3CN, py, PPh_3, pic	$Re_2(CO)_9L$	28
	L = H_2O, NMe_3	$Re_2(CO)_9L$	50
	L = CH_3CN, py, PPh_3	$Re_2(CO)_8L_2$	28, 55
$Os(CO)_4Me_2$	PPh_3	$Os(CO)_3(PPh_3)Me_2$	39
$Os_3(CO)_{12}$	MeCN	$Os_3(CO)_{11}(NCMe)$ [c]	35, 53
	pyrazidine	$Os_3(CO)_{10}(pyrazidine)$	47
	C_2H_4	$Os_3(CO)_{11}(C_2H_4)$	35
	MeCN	$Os_3(CO)_{10}(NCMe)_2$	35, 53
$Os_3(CO)_{10}(NO)_2$	NMe_3	$Os_3(CO)_9(NMe_3)(NO)_2$	52
$H_2Os_3(CO)_9S$	MeCN	$H_2Os_3(CO)_8(NCMe)S$	36
$M_3(CO)_{12}$ (M = Os, Ru)	$Ph_2PC{\equiv}CR$ [d]	$M_3(CO)_{11}(PPh_2C{\equiv}CR)$	51
$M_3(CO)_{11}(PPh_2C{\equiv}CR)$ [d]	–	$M_3(CO)_9(C{\equiv}CR)PPh_2$	49
$H_4Ru_4(CO)_{12}$	dppe	$H_4Ru_4(CO)_{10}(dppe)$	38

[a] X = Cl, Br, CH_3CO_2; L_2 = phen, bipy, $2PPh_3$. [b] L = phen, bipy. [c] This product readily reacted with a wide range of donor ligands L (L = CO, PPh_3, C_2H_4, RNC, C_5H_5N [35], NH_3 [34] or substituted pyridines [30], to give $Os_3(CO)_{11}L$ complexes. [d] R = ^iPr, Bu^t, Ph, M = Ru, Os.

a reaction solution containing trimethylamine rather than its oxide.

Recently, the complex $Fe(CO)_4(NMe_3)$ has been isolated as an intermediate in the reduction of trimethylamine *N*-oxide by iron pentacarbonyl [25,26]. Addition of $Fe(CO)_5$ in THF to a suspension of Me_3NO in THF ($-30°C$) gives, instantly, a red solution with evolution of CO_2. An orange-red compound was isolated and identified as $Fe(CO)_4(NMe_3)$, thus supporting earlier suggestions as to the mechanism of the reaction between $Fe(CO)_5$ and Me_3NO. Since these early reports on the reactions of Me_3NO with iron carbonyls, investigations have been extended to many other metal carbonyl complexes. These results are summarised in Table 1. Notable generalisations from the literature are:

(1) Me_3NO is an inexpensive, white crystalline hygroscopic material available commercially (e.g. Aldrich Chemical Co.) as the dihydrate, $Me_3NO \cdot 2\,H_2O$. It has been used as purchased, but if necessary it can also be dehydrated by either sublimation techniques or by use of a Dean–Stark apparatus (benzene or toluene as solvents). The reagent has been used in a variety of solvents including THF [27], acetonitrile [28], benzene [23], toluene [29], dichloromethane [30], chloroform [31], acetone [32], 2-methoxyethanol [33] and methanol [34]. (It is readily soluble in methanol.) In many instances a donor co-solvent, e.g. MeCN, is added [35]. The high volatility of trimethylamine produced in the reaction leads to its facile removal from reaction mixtures.

(2) Both substituted and unsubstituted metal carbonyl complexes will undergo CO replacement reactions.

(3) The reagent has been used extensively in metal carbonyl cluster substitution reactions. In particular, Lewis and co-workers [36], and Shapley and co-workers [37], have synthesised a wide variety of ligand substituted products starting from $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ (Table 1).

(4) The reaction conditions utilised are generally mild (25–70°C). This allows for the synthesis of products not normally accessible under more extreme thermal conditions. For instance, an isomer of $H_4Ru_4(CO)_{10}(dppe)$ [38a] can be synthesised from $H_4Ru_4(CO)_{12}$, dppe and Me_3NO (25°C) in which the bidentate ligand spans two different ruthenium atoms. In the unassisted thermal reaction an isomer in which the phosphorus ligand chelates one ruthenium atom is obtained [38b]. Similarly, the thermal reaction between $Os(CO)_4Me_2$ and PPh_3 yields $Os(CO)_4(PPh_3)$, whereas in the presence of Me_3NO (lower reaction temperature) $Os(CO)_3(PPh_3)Me_2$ is obtained [39].

(5) Koelle [29] has proposed that metal carbonyls with IR stretching frequency $\nu(CO) < 2000\ cm^{-1}$ will not react with Me_3NO. However, recent work by Black et al. [33] has shown that reaction of Me_3NO with, for instance, $RuCO(py)(bipy)Cl_2$ ($\nu(CO) \sim 1940\ cm^{-1}$) does indeed occur.

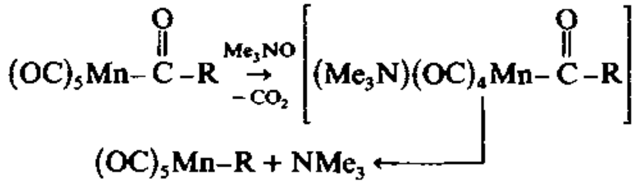
(6) On occasion greater than equivalent amounts of Me_3NO reagent are required to ensure complete conversion of the starting materials. This sometimes leads to product decomposition caused by product reaction with excess amine oxide reagent [29]. In the presence of strong donor ligands these side reactions can be minimised.

(7) The use of acetonitrile as a donor solvent in the reactions of $M(CO)_n$ and Me_3NO allows for the isolation, in many instances, of $M(CO)_{n-1}(NCMe)$ complexes. The MeCN ligand can then be displaced from the metal under mild reaction conditions. For instance, this route can be used in the synthesis of isotopically labelled complexes [40], normally inaccessible in high purity by conventional routes, e.g.

$$Mn_2(CO)_9(NCMe) + {}^{13}CO \rightarrow Mn_2(CO)_9({}^{13}CO) + MeCN \qquad (5)$$

Decarbonylation reactions

Further studies have included the use of trimethylamine *N*-oxide as a decarbonylation agent for the acylmanganese pentacarbonyl system [41] (Scheme 2),



Scheme 2

and more recently for the decarbonylation of $(\eta^5\text{-}C_5H_5)Ru(CO)_2(COC_{10}H_{13})$ to $(\eta^5\text{-}C_5H_5)Ru(CO)_2(C_{10}H_{13})$ [42]. It has also been established [41] that reactions of $PhMn(CO)_5$ and $(\eta^5\text{-}C_5H_5)M(CO)_3X$ (M = Mo, W; X = halide) with Me_3NO in the presence of phosphines and arsines give *cis*-$PhMn(CO)_4L$ and *cis*-$(\eta^5\text{-}C_5H_5)M(CO)_2LX$, respectively. Interestingly, it was also found that Me_3NO, or even Me_3N, promoted isomerisation of the complex $(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)I$. Thus, solutions of *cis*- or *trans*-$(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)I$ were rapidly isomerised to the thermodynamic isomeric mixture (50 : 50) by Me_3N. This process was suggested to occur via nucleophilic attack of base at the carbonyl carbon with subsequent labilisation of the *cis*-carbonyl ligand.

Cluster synthesis

The generality and ease of the trimethylamine *N*-oxide induced CO replacement reaction has resulted in its use in the synthesis of transition metal cluster complexes. Thus, oxidative decarbonylation by Me_3NO in the *absence* of added ligand, L (6), produces a highly reactive ("unsaturated")

$$M(CO)_n + Me_3NO \rightarrow M(CO)_{n-1}(NMe_3) + CO_2 \rightleftarrows M(CO)_{n-1} + NMe_3 \quad (6)$$

intermediate which could then interact, interalia, with its saturated precursor with concomitant metal–metal bond formation. In this manner, reaction of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ with Me_3NO [43] was found to give an efficient route to $[(\eta^5\text{-}C_5H_5)Rh(CO)]_3$, together with formation of $(\eta^5\text{-}C_5H_5)_2Rh_2(CO)_3$ and $(\eta^5\text{-}C_5H_5)_4Rh_4(CO)_2$. This method has also provided a novel route to a complex containing a metal–metal double bond. Thus, the reaction of $(\eta^5\text{-}C_5Me_5)Rh(CO)_2$ with Me_3NO yields the complex $[(\eta^5\text{-}C_5Me_5)Rh(CO)]_2$ [32].

Utilising the cluster building potential of the M–H bond, interaction of $Os_3(CO)_{11}(NCMe)$ (prepared from $Os_3(CO)_{12}$ and Me_3NO in acetonitrile) with excess $HRe(CO)_5$ gave the condensed species, $HReOs_3(CO)_{16}$ [44]. Variations in procedure gave the species $HReOs_3(CO)_{15}$ and $H_2Re_2Os_3(CO)_{19}$. In general, oxidative decarbonylation by Me_3NO, followed by metal hydride coupling has been shown to possess considerable potential in the synthesis of heterometallic cluster complexes [45].

Other related oxidising agents

Dimethylsulphoxide has been used to replace a CO group in $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^+$ by a phosphine ligand. However, Me_3NO was found to be a superior reagent [46]. Although, by analogy, the use of phosphine oxides (R_3PO) might have been expected to give a similar reaction to the amine oxides, this has not been found to be the case (vide infra).

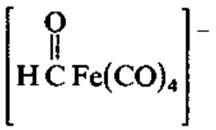
(ii) Hydride facilitation

Chatt et al. [57] have reported that the substitution of the carbon monoxide ligand in the Group 6 metal hexacarbonyls by tertiary alkyl or aryl phosphines, arsines or stibines, and also certain tertiary amines, is promoted by sodium borohydride in ethanol. Reagent quantities of metal hydride were found to reduce the volatility of the metal carbonyl and also to promote the substitution of predominantly two, and up to three, CO groups. Substitution apparently occurs in a stepwise manner, although significant amounts of intermediate products were not detected. In general, reaction times were short and yields moderate to good. In the absence of borohydride, little reaction was detected.

Although no mechanism was proposed, attack by hydride ion was presumed to occur either at carbonyl carbon, or directly into the coordination shell of the metal. The latter would appear to be unlikely, especially in the case of $Cr(CO)_6$, although recent suggestions [58] draw attention to the phosphine cleavage reactions of the anion, $\mu\text{-}H[Cr(CO)_5]_2^-$ (producing

$Cr(CO)_4L_2$, exclusively), as well as the possible intermediacy of a tetrahydroborato complex such as $[^-H_3B{-}H{-}Cr(CO)_5^-]$ [58].

Sodium borohydride, as well as lithium aluminium hydride, has been found to have moderate control over, and to promote the substitution of, iron pentacarbonyl by Group 5 donor ligands [59]. The participation of the formyl complex

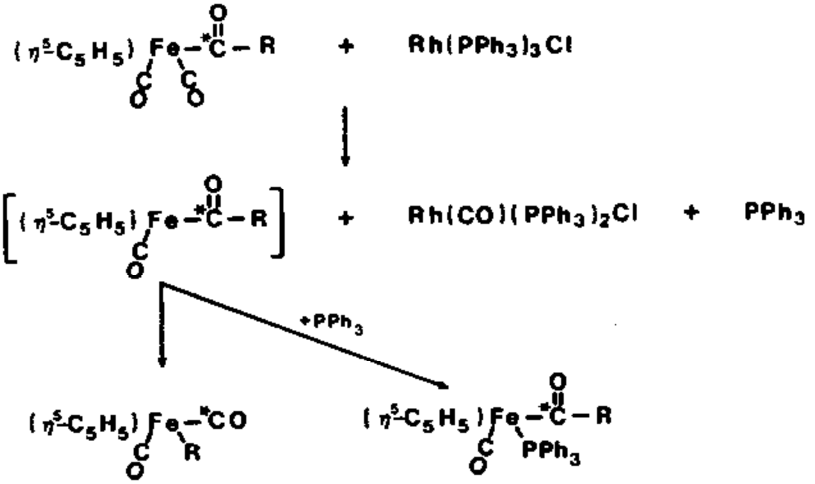


$$\left[H\overset{O}{\overset{\|}{C}}Fe(CO)_4\right]^-$$

was suggested by IR spectroscopy.

(iii) Abstraction of coordinated carbon monoxide by Group 8 metal complexes

$Rh(PPh_3)_3Cl$ has been found to abstract CO from organic acyl halides and aldehydes to give alkyl halides, olefins and alkanes [60]. Similarly, transition metal carbonyl complexes containing the acyl group have been chemically decarbonylated by Wilkinson's catalyst to give the corresponding alkyl complex and $Rh(CO)(PPh_3)_2Cl$ as the rhodium-containing product [61,62]. The mechanism [61] has been established, by ^{13}C labelling experiments, to proceed via abstraction of a terminal carbon monoxide ligand followed by alkyl migration (Scheme 3). Alexander [63] has further suggested nucleophilic attack on coordinated CO by $Rh(PPh_3)_2Cl$ (formed from



Scheme 3

$Rh(PPh_3)_3Cl$ by phosphine dissociation).

Further studies [64] have indicated that chemical decarbonylation may also be achieved by the complexes $Ir(PPh_3)_3Cl$ and $Ru(PPh_3)_3Cl_2$, whereas $Ir(PPh_3)_2(N_2)Cl$, $Pt(PPh_3)_4$ and $Pt(PPh_3)_3$ failed to show any decarbonylation activity. Decarbonylation reactions involving $M(PPh_3)_3Cl$ (M = Rh, Ir) and $Ru(PPh_3)_3Cl_2$ were not found to be catalytic.

The use of Wilkinson's catalyst, as well as other Rh(I) complexes, as CO abstraction reagents in organometallic chemistry has been extended by Varshavsky and co-workers [65], and includes the mild synthesis from $Fe(CO)_5$ and $Mo(CO)_6$, of $Fe(CO)_4(PPh_3)$, $Fe(CO)_3(PPh_3)_2$, (diene)-$Fe(CO)_3$ (diene = 1,3-butadiene, isoprene), $Mo(CO)_4(PPh_3)_2$, and (arene)-$Mo(CO)_3$ (arene = benzene, toluene, mesitylene).

Although complete CO removal from the metal carbonyl substrates was suspected to be a minor pathway (and indeed shown to be possible with $Ni(CO)_4$, $Fe(CO)_5$, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ in hexamethylphosphoramide solution using $[Rh(C_8H_{14})_2Cl]_2$), the fragments $M(CO)_3$ (M = Fe, Mo) were found, in general, to be relatively inert to further reaction. Thus, the preparation of (diene)$Fe(CO)_3$ complexes from $Fe(CO)_5$ and $Rh(diene)_2Cl$, and (arene)$Mo(CO)_3$ from $Mo(CO)_6$, and a complex formulated as being $Rh(PPh_3)(C_2H_4)Cl$, in benzene, toluene or mesitylene, was possible.

The addition of PPh_3 to $Fe(CO)_5$ and $Rh(PPh_3)_3Cl$ markedly decreased the rate of consumption of $Fe(CO)_5$, but still gave $Fe(CO)_3(PPh_3)_2$ in high yield. The authors interpreted this phenomenon in terms of the dissociation product $Rh(PPh_3)_2Cl$ being more active in CO abstraction than its precursor

$$Rh(PPh_3)_3Cl \rightleftharpoons Rh(PPh_3)_2Cl + PPh_3 \qquad (7)$$

[65]. As in earlier studies, these reactions were found to be non-catalytic. More recently, it has been reported [66] that the coordinatively unsaturated complex, $(\eta^5\text{-}C_5H_5)CoMe_2$, abstracted a CO ligand from iron pentacarbonyl to give $Fe(CO)_4$ which in the presence of PPh_3 could be trapped as $Fe(CO)_4(PPh_3)$. In general, the technique of using Group 8 metal complexes for CO removal from a metal carbonyl substrate suffers from a number of drawbacks. These include: (a) the use of expensive Group 8 metals; and (b) the difficulty experienced in the subsequent removal of the CO ligand from the metal reagent.

(iv) Electrochemically induced substitution reactions of metal carbonyl complexes

The use of electrodes as reagents and catalysts in organic and inorganic chemistry is well established [67]. In recent years a considerable amount of interest has been shown in the application of electrochemical reactions and techniques to organometallic and metal carbonyl complexes. For instance, the electrochemical oxidation of neutral 18-electron metal carbonyl complexes gives labile 17-electron radical cations [68], e.g. chromium hexacarbonyl is cleanly oxidised to $\mathrm{Cr(CO)}_6^{\dot{+}}$ which decays via nucleophilic attack of solvent or loss of carbon monoxide. In contrast, $\mathrm{Mo(CO)}_6$, $\mathrm{W(CO)}_6$, and $\mathrm{Fe(CO)}_5$ undergo irreversible oxidations where the initial intermediate, viz. $\mathrm{M(CO)}_n^{\dot{+}}$, is highly susceptible to nucleophilic attack.

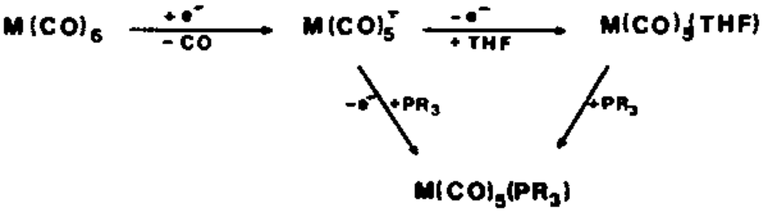
Electrochemical reduction of $\mathrm{M(CO)}_6$ [68c] ($\mathrm{M} = \mathrm{Cr, Mo, W}$) has also been observed to occur via a one-electron process, to give, probably (or at least initially), the radical anion $\mathrm{M(CO)}_6^{\dot{+}}$. $[\mathrm{M_2(CO)_{10}}]^{2-}$ was found to be the final electrolysis product,

$$2\mathrm{M(CO)}_6 + 2\mathrm{e}^- \rightarrow [\mathrm{M_2(CO)_{10}}]^{2-} + 2\mathrm{CO} \qquad (8)$$

and the overall electrode process was suggested to involve either $\mathrm{M(CO)}_6^{\dot{-}}$ or $\mathrm{M(CO)}_5^{\dot{-}}$ as quasi-stable intermediates.

$$\mathrm{M(CO)}_6 + \mathrm{e}^- \rightarrow \mathrm{M(CO)}_6^{\dot{-}} \overset{-\mathrm{CO}}{\rightarrow} \mathrm{M(CO)}_5^{\dot{-}} \rightarrow \tfrac{1}{2}[\mathrm{M_2(CO)_{10}}]^{2-} \qquad (9)$$

It is only recently, however, that the electrochemically induced synthesis of metal carbonyl derivatives, based on the expected and observed reactivity of 17-electron radical cations and 19-electron radical anions has been exploited [64]. Thus, Grobe and co-workers have achieved, via electro-reduction, the substitution of the Group 6 metal hexacarbonyls [70a] by solvent molecules (e.g. THF, pyridine), and also by phosphine ligands (e.g. $\mathrm{PMe_3}$, $\mathrm{PPh_3}$). Good yields of the complexes $\mathrm{M(CO)}_{6-n}\mathrm{L}_n$ ($n = 1$–3) were achieved by one-electron reduction of the metal carbonyl complex $\mathrm{M(CO)}_6$ in the presence of the appropriate donor ligand (Scheme 4).

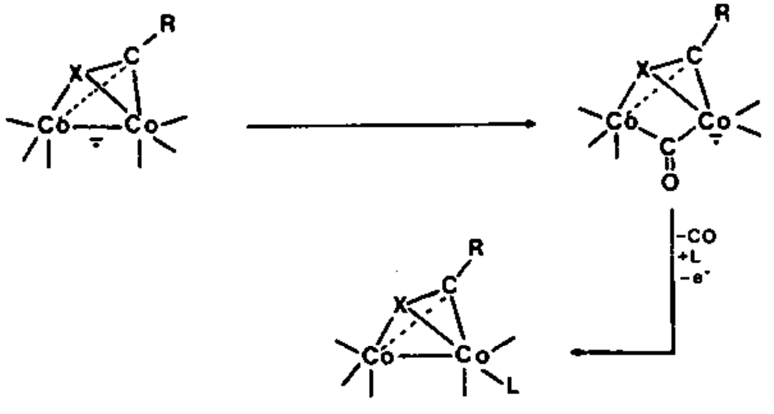


Scheme 4

Although the authors suggest dissociative CO loss on reduction of $\mathrm{M(CO)}_6$, nucleophilic attack by solvent or other donor ligand on the radical anion $\mathrm{M(CO)}_6^{\dot{-}}$ is also conceivable.

An attempted extension [70b] to the synthesis of the di- and tri-substituted products, $M(CO)_4(PR_3)(PR'_3)$ and $M(CO)_3(PR_3)(PR'_3)_2$, from $M(CO)_5(PR_3)$ and PR'_3, failed due to the simultaneous replacement of both CO and PR_3, which resulted in product mixtures of the type $M(CO)_4L_2$ and $M(CO)_3L_3$ ($L = PR_3, PR'_3$).

However, electrochemical displacement of CO from substituted metal carbonyl complexes can be specific. For instance, electrochemical oxidation of $(DAD)Mo(CO)_4$ (DAD = diazadiene) in the presence of acetonitrile results in CO displacement *only* and formation of $(DAD)Mo(CO)_3(NCMe)$ [71]. The reactivity of radical anionic species is further substantiated by a recent report [72a] that the substituted alkylidyne cluster $YCCo_3(CO)_8L$ (Y = Ph, Cl; L = Group 5 donor ligand) is produced on electrochemical reduction of $YCCo_3(CO)_9$ in the presence of L. Similarly, cyclic voltamograms of $PhCCo_3(CO)_8(PPh_3)$ under one atmosphere of CO show complete substitution of CO for PPh_3. Thus, electrolytic one-electron reduction produces a radical anion which is then suggested to react rapidly with ligand L (Scheme 5). Reoxidation to the substitution product occurs either at the electrode or by the parent compound, the latter reaction leading to a catalytic substitution process (see Section C(iii)). Similar observations have been made for the reduction of $(R_2C_2)Co_2(CO)_6$ (R = Ph, Bu^t, etc.) in the presence of ligands PPh_3, $P(Bu^n)_3$ and $P(OMe)_3$ [72b].



X = RC, $Co(CO)_3$

Scheme 5

Electro-reduction of $Fe(CO)_5$ is, in a similar manner, believed to produce the radical anion $Fe(CO)_5^{\cdot-}$ that may react rapidly with a ligand L (Scheme 6), or react in a major competing radical dimerisation reaction to produce ultimately $Fe_2(CO)_8^{2-}$ [72a,73].

$$Fe(CO)_5^{\cdot-} + L \rightarrow Fe(CO)_4L^{\cdot-} + CO \rightarrow Fe(CO)_4L$$
$$\qquad\qquad\qquad\qquad \rightarrow \text{oxidant}$$

Scheme 6

(v) Other reagents

n-Butylphosphine oxide (Bu^n_3PO) has been used for the assisted replacement of CO on metal carbonyl complexes by ^{13}CO [74,75]. No CO_2 was evolved in the reaction and little is understood about the reaction mechanism. Experimental difficulties in separation of solvent and phosphine oxide from the labelled metal carbonyls (e.g. $Cr(^{13}CO)_6$) limit the method's general applicability.

The chemical generation of metal carbonyl radicals which subsequently react with donor ligands in a non-catalytic reaction has been reported. Thus, the generation of $Mn(CO)_5^{\cdot}$ from $NaMn(CO)_5$ and $C_7H_7^+Br^-$ in the presence of PPh_3 yields $Mn_2(CO)_8(PPh_3)_2$ [76]. Similarly, the reaction of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]Na$ and $C_7H_7^+BF_4^-$ in the presence of RNC ($R = Bu^t$, $C_6H_3Me_2$-2,6) gave $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_{4-n}(CNR)_n]$ ($n = 1, 2$) complexes [77]. Mild conditions are used and yields are moderate to excellent in both of the above reactions.

C. CATALYSED SUBSTITUTION REACTIONS OF METAL CARBONYL COMPLEXES

(i) Introduction

In recent years the use of catalysts to induce CO substitution in metal carbonyl complexes has been explored in some detail. However, by comparison, catalytic rather than reagent induced metal carbonyl substitution reactions are still rare.

Catalytic carbon monoxide exchange was first studied by Webb and Mitchel [78] in 1959. In an exhaustive study of various metals and metal oxides as potential catalysts, the authors determined the order of decreasing activity $Pt > Ni >> Fe_3O_4 > Cu > Fe > Al_2O_3 > Fe_2O_3$ for the exchange of ^{14}CO with $Fe(CO)_5$ at 0°C. The suggested mechanisms for the catalytic reaction were based on: (a) an associative process

$$Fe(CO)_5 + \text{catalyst} \rightleftharpoons Fe(CO)_5\,\text{catalyst} \qquad (10)$$

or (b) a dissociative replacement reaction

$$Fe(CO)_5 + \text{catalyst} \rightleftharpoons Fe(CO)_4\text{catalyst} + CO \qquad (11)$$

The authors, in noting the general electron acceptor properties of the catalysts, supported an associative mechanism (viz. (a)).

Basolo et al. [79] reported that exchange of ^{14}CO with $Fe(CO)_5$ was catalysed by trifluoroacetic acid in 1,2-dichloroethane, although these results were only partially substantiated in a more recent ^{13}CO and $C^{18}O$ infrared spectroscopic study [80]. In contrast, however, palladium metal (10% supported on alumina or activated carbon) was found to give rapid exchange and complete scrambling in a heptane solution of a 1 : 1 mixture of natural $Fe(CO)_5$ and $Fe(C^{18}O)_5$ [80]. Similarly, a statistical distribution was rapidly reached by the shaking of a heptane solution of natural $Fe(CO)_5$ with suspended palladium catalyst in an atmosphere of ^{13}CO or $C^{18}O$ [80]. (The substitution of coordinated carbon monoxide by ^{13}CO in the preparation of ^{13}CO-enriched metal carbonyl complexes in the presence of palladium on carbon has also been reported by other workers recently [47,81].)

Within the last decade various other methods to induce, catalytically, CO substitution on metal carbonyl complexes have been discovered. These methods generally involve the generation of odd-electron metal carbonyl species by electrochemical, photochemical, or chemical techniques, i.e. radical species which show enhanced ligand lability relative to their diamagnetic precursors [82,83]. These techniques are described in Sections C(ii)–(vi). Also included in this section is the use of phase-transfer catalysis (Section C(vii)) in the CO substitution reaction.

(ii) Photo-induced radical catalysis

Recent work, mainly by Brown and co-workers, has established the importance of the radical chain pathway in the substitution reactions of metal carbonyl complexes [84]. In addition, photo-induced radical catalysts have been found that not only greatly increase reaction rates and product yields, but also affect the product distribution in such processes. For instance, the complex $HRe(CO)_5$, shown to be inert towards substitution via CO dissociation or hydride migration, has been found to react readily with donor ligands L ($L = P(Bu^n)_3$, PPh_3) in a radical chain process [84]. The formation of the products, $HRe(CO)_3L_2$, via such a process is shown in Scheme 7 [85].

$$R^{\cdot} + HRe(CO)_5 \rightarrow RH + Re(CO)_5^{\cdot} \tag{a}$$

$$Re(CO)_5^{\cdot} \rightleftharpoons Re(CO)_4^{\cdot} + CO \tag{b}$$

$$Re(CO)_4^{\cdot} + L \rightleftharpoons Re(CO)_4L^{\cdot} \tag{c}$$

$$Re(CO)_4L^{\cdot} \rightleftharpoons Re(CO)_3L^{\cdot} + CO \tag{d}$$

$$Re(CO)_3L^{\cdot} + L \rightleftharpoons Re(CO)_3L_2^{\cdot} \tag{e}$$

$$\mathrm{Re(CO)_4L^{\cdot} + HRe(CO)_5 \rightarrow Re(CO)_5^{\cdot} + HRe(CO)_4L} \tag{f}$$

$$\mathrm{Re(CO)_3L_2^{\cdot} + HRe(CO)_5 \rightarrow Re(CO)_5^{\cdot} + HRe(CO)_3L_2} \tag{g}$$

$$\mathrm{Re(CO)_3L_2^{\cdot} + HRe(CO)_4L \rightarrow Re(CO)_4L^{\cdot} + HRe(CO)_3L_2} \tag{h}$$

$$\mathrm{Re(CO)_{5-\mathit{n}}L_{\mathit{n}}^{\cdot} + Re(CO)_{5-\mathit{m}}L_{\mathit{m}}^{\cdot} \rightarrow Re_2(CO)_{10-\mathit{n}-\mathit{m}}L_{\mathit{n}+\mathit{m}}} \tag{i}$$

Scheme 7

Generally, adventitious radicals (e.g. derived from peroxides) have been proposed as the initiators R, with chain propagation occurring in steps (f)–(h), and termination in step (i). It was suggested, as shown in steps (b)–(e), that a facile substitution of the radical $Re(CO)_5^{\cdot}$ (or $Re(CO)_4L^{\cdot}$) occurs, probably in a dissociative manner [76,85].

$Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ have both been found to be photocatalysts for the reactions of $HRe(CO)_5$ with phosphorous donor ligands. Thus, catalytic amounts (1–10 mole percent) of either $Re_2(CO)_{10}$ or $Mn_2(CO)_{10}$ under photochemical conditions generate the radical $M(CO)_5^{\cdot}$ [9,86] which was then postulated to take the role of initiator $R^{\cdot}$, in the substitution reaction.

Support for the mechanistic steps proposed was obtained from a study of the $Mn(CO)_5^{\cdot}$ radical [76]. Thus, generation of $Mn(CO)_5^{\cdot}$ from $Mn(CO)_5^-$ and a chemical one-electron oxidant (e.g. $C_3Ph_3^+BF_4^-$), in the presence of PPh_3, gave rapid formation of the expected $Mn_2(CO)_8(PPh_3)_2$, together with only small quantities of $Mn_2(CO)_{10}$ and $Mn_2(CO)_9(PPh_3)$.

The substitution of $(\eta^5\text{-}C_5H_5)W(CO)_3H$ by $P(Bu^n)_3$, has also been studied by Brown and co-workers [87]:

$$(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{W(CO)_3H + L \rightarrow} (\eta^5\text{-}\mathrm{C_5H_5})\mathrm{W(CO)_2(L)H + CO} \tag{12}$$
$$(\mathrm{L = PR_3})$$

Addition of catalytic amounts (< 10 mole percent) of the dimeric species $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (M = Mo, W), followed hy irradiation, again resulted in rapid substitution of $(\eta^5\text{-}C_5H_5)W(CO)_3H$ by $P(Bu^n)_3$. In a similar chain mechanism to that proposed for $HRe(CO)_5$, adventitious radicals or the photochemically generated $(\eta^5\text{-}C_5H_5)M(CO)_3^{\cdot}$ radicals were suggested as initiators. Product formation followed via rapid substitution on the radical $(\eta^5\text{-}C_5H_5)W(CO)_3^{\cdot}$ by L.

Similar photo-induced catalysis of metal carbonyl substitution reactions has been observed in a number of other systems. These are the substitution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)$ [88] and $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-allyl})$ [89] by phosphine ligands catalysed by the dimer $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, and the substitution of $(\eta^5\text{-}C_5H_5)Mo(CO)_3X$ [90] (X = Br, I) by PPh_3, catalysed by $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$. Also, the substitution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ [91] and $(\eta^5\text{-}C_5H_5)Mo(CO)_3I$ [92] by isonitriles, catalysed by $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ or $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ has been observed (see Section C(v)). In all of these processes, radical chain mechanisms have been proposed, in accordance with the scheme outlined for $HRe(CO)_5$.

Although there is unanimity on the increased labilisation of CO in 17-electron metal carbonyl radicals relative to their 18-electron counterparts, controversy still surrounds the nature of the CO replacement reaction. Evidence has been presented for a dissociation of CO from $M(CO)_n^{\cdot}$ species to give $M(CO)_{n-1}^{\cdot}$, which then reacts with a substituting ligand L to give $M(CO)_{n-1}L^{\cdot}$ (cf. Scheme 7) [76,85]. However, recent results on the photochemical reactions of $Re_2(CO)_{10}$ give unambiguous evidence for an associative radical substitution pathway [93] viz.

$$Re_2(CO)_{10} \overset{h\nu}{\rightleftharpoons} 2Re(CO)_5^{\cdot} \tag{a}$$

$$Re(CO)_5^{\cdot} + L \rightarrow Re(CO)_5L^{\cdot} \tag{b}$$

$$Re(CO)_5L^{\cdot} \rightarrow Re(CO)_4L^{\cdot} + CO \text{ etc.} \tag{c}$$

Scheme 8

More recent results by Brown and co-workers also suggest that the associative pathway may be the preferred reaction sequence for certain substitution reactions of $Mn_2(CO)_{10}$ [94]. This pathway has been given further credence by the kinetic results obtained from the reaction of $V(CO)_6$ and $PR_3^{\cdot}$; an associative pathway was observed [95].

Finally, mention should be made of a report by Wrighton and co-workers [96] in which ligand labilisation is brought about by a photochemically induced change in oxidation state of the central metal atom. (It is to be noted that in an earlier publication Hepp and Wrighton [97] indicated that a one-electron oxidation of a photogenerated radical was a viable chemical reaction.) It was found that the reaction between $Re(CO)_3(phen)(NCMe)^+$ and L (L = py, PPh_3) could be catalysed by 436 nm irradiation (quantum yield > > 1). The reaction was expected to occur via an electron-transfer process, viz.

$$[Re(CO)_3(phen)(NCMe)]^+ \xrightarrow{h\nu} [Re(CO)_3(phen)(NCMe)]^{+*} \tag{a}$$

$$[Re(CO)_3(phen)(NCMe)]^{+*} + PPh_3 \rightarrow [Re(CO)_3(phen)(NCMe)]^0 + PPh_3^{+} \tag{b}$$

$$[Re(CO)_3(phen)(NCMe)]^0 + L \rightarrow [Re(CO)_3(phen)L]^0 + MeCN \tag{c}$$

$$[Re(CO)_3(phen)L]^0 + PPh_3^{+} \rightarrow [Re(CO)_3(phen)L]^+ + PPh_3 \tag{d}$$

Scheme 9

The same sequence could also be achieved electrochemically (cf. Section

B(iv)). Although the above reaction sequence does not involve CO labilisation, in principle this reaction type should also be feasible by this technique.

(iii) Electrocatalysis

In an earlier section (B(iv)) the use of electrochemical techniques to induce CO labilisation on metal carbonyl complexes was discussed. In this section the extension of the technique to generate a catalytic CO displacement cycle is described. As has been observed previously [96], a change in the oxidation state of a metal complex can bring about ligand lability. Indeed, induced electron shifts or intra-molecular interactions could also bring about the same effect [98]. Whether a catalytic cycle follows the above effect will depend on a variety of factors, best discussed in terms of a typical reaction (Scheme 10).

$$\mathrm{M(CO)}_n + \mathrm{e}^- \xrightarrow{E_1^0} \mathrm{M(CO)}_n^{\cdot -} \qquad \text{(a)}$$

$$\mathrm{M(CO)}_n^{\cdot -} + \mathrm{L} \xrightarrow{k_b} \mathrm{M(CO)}_{n-1}\mathrm{L}^{\cdot -}\mathrm{i} + \mathrm{CO} \qquad \text{(b)}$$

$$\mathrm{M(CO)}_{n-1}\mathrm{L}^{\cdot -} \xrightarrow{E_2^0} \mathrm{M(CO)}_{n-1}\mathrm{L} + \mathrm{e}^- \qquad \text{(c)}$$

$$\mathrm{M(CO)}_{n-1}\mathrm{L}^{\cdot -} + \mathrm{M(CO)}_n \rightarrow \mathrm{M(CO)}_{n-1}\mathrm{L} + \mathrm{M(CO)}_n^{\cdot -} \qquad \text{(d)}$$

Scheme 10

An analysis of the above type of reaction scheme, termed an $\vec{\mathrm{E}}\mathrm{C}\overleftarrow{\mathrm{E}}$ mechanism, has been given by Feldberg and Jeftic [99]. In the above scheme a radical anion is generated electrochemically, (step (a)). This radical anion can react with a ligand L in an associative or dissociative manner, (b). Two possibilities then exist depending on the reaction conditions: (1) either the substituted radical anion undergoes electron loss, for example via interaction with the anode to yield the product in a non-catalytic sequence ($E_2^0 > E_1^0$), (c); or (2) an electron transfer to the substrate can occur (d). This latter reaction would result in the regeneration of $\mathrm{M(CO)}_n^{\cdot -}$ which can then re-enter the reaction cycle, thus bringing about an overall catalytic transformation. Notable features of the reactions are:

(1) for catalysis to occur as described in Scheme 10, i.e. for the formation of a radical anion, $E_1^0 > E_2^0$;

(2) it should only be necessary to "trigger" the reaction sequence with a small concentration of $\mathrm{M(CO)}_n^{\cdot -}$. The number of Faradays required per mole of product formed should hence be theoretically less than unity;

(3) Vlček [100], from analysis of the reaction scheme, has concluded that the rate of reaction (b) relative to the rate of diffusion and/or rate of change

of the electrode potential is a significant factor in determining the reaction pathway. Thus, when reaction (b) tends to zero (i.e. $k_b \rightarrow 0$), only formation of $M(CO)_n^{-}$ is observed (using cyclic voltammetry or dc polarography). When reaction (b) is rapid ($k_b \rightarrow \infty$) the reaction resembles a simple D/C redox couple. Further, if coulometric conditions are used (i.e. constant potential electrolysis conditions) then electrochemical catalysis is obtained even when not observed under the polarography or cyclic voltammetry conditions;

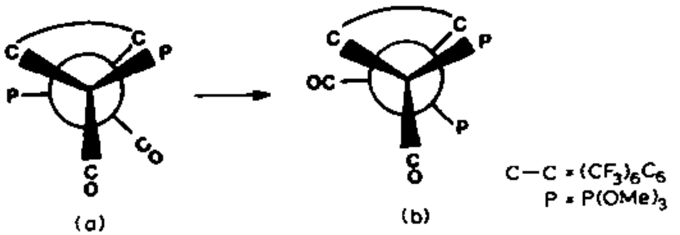
(4) catalytic cycles involving the generation of radical cations can also be demonstrated [101]; and

(5) in the catalytic cycle described in Scheme 10 it is possible to generate the $M(CO)_n^{-}$ radical via non-electrochemical means. Indeed, this has been achieved using photochemical irradiation [96] and chemical means [102].

It should be mentioned that the use of electrodes as catalysts is not restricted to transition metal substitution reactions. This technique has been used successfully in organic substitution reactions [103], and the concept of electron-transfer chain catalysis is well documented in non-transition metal chemistry [82,83,104].

The technique of electrocatalysis has, to date, only been applied to very few examples in metal carbonyl chemistry. However, the synthetic utility can be recognised from these limited cases discussed below.

$Fe_3S_2(CO)_8(C_3H_2S_2)$ reacts in a stepwise manner with $P(OMe)_3$ under controlled potential electrolysis to give $Fe_3S_2(CO)_{8-n}(C_3H_2S_2)[P(OMe)_3]_n$ ($n = 1$–3) in greater than 59% yield at each step [105]. This is to be compared with the non-catalysed reaction in which product mixtures are obtained. Using the same electrochemical technique as above it was shown recently that the catalysed reactions between $(CF_3)_6C_6Co_2(CO)_4$ and $P(OMe)_3$ readily gave $(CF_3)_6C_6Co_2(CO)_{4-n}[P(OMe)_3]_n$ ($n = 1, 2$) [106]. Further, reduction of the disubstituted derivative results in its catalytic conversion into another disubstituted isomer, i.e. (a) → (b),



Scheme 11

Recent papers by Kochi and co-workers [101,107] have indicated the potential of using electrochemically generated radical cations in catalytic reactions. Although the reactions involved substitution of MeCN and not CO groups, for example (13), the principles described are applicable to CO

$$(\eta^5\text{-}C_5H_4Me)Mn(CO)_2(NCMe) + PPh_3 \rightarrow (\eta^5\text{-}C_5H_4Me)Mn(CO)_2(PPh_3) + MeCN \qquad (13)$$

displacement from transition metal carbonyl complexes. Similar comments apply to the catalysed substitution reaction (14) [96].

$$[Re(CO)_3(phen)(NCMe)]^+ + PPh_3 \rightarrow [Re(CO)_3(phen)(PPh_3)]^+ + MeCN \qquad (14)$$

A novel use of the electrochemical techniques described above has been in the CO insertion reaction [100,108,109]. Typically, formation of a metal carbonyl radical anion leads to increased reactivity towards ligand substitution, *but CO incorporation* into the molecule, rather than CO loss is also a viable pathway, e.g.

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2Me + PPh_3 \rightarrow (\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COMe) \qquad (15)$$

The reaction is catalytic and provides a high yield synthesis of the CO insertion product.

(iv) Organic reagents as catalysts

The major development in this field has been the recognition that radical anions can be generated by chemical as opposed to electrochemical techniques [102]. In particular, the use of sodium diphenylketyl in tetrahydrofuran as a reducing agent has led to the synthesis of a wide range of substituted metal carbonyl cluster compounds [102,110,111]. Important features of this approach are:

(1) reaction conditions are generally mild (typically room temperature);

(2) the reducing agent is readily synthesised and can be easily handled under inert atmosphere conditions;

(3) reactions tend to be characterised by stepwise and specific CO replacement, for example,

$$Ru_3(CO)_{12} + L \xrightarrow{\text{catalyst}} Ru_3(CO)_{11}L + CO \qquad (16)$$

($L = PPh_3$, Bu^tNC, etc.). In the above reaction, yields are generally greater than 80%; the thermal reaction leads to the trisubstituted derivative [102]; and

(4) the following requirements with respect to completing a catalytic reaction cycle have been found to be necessary [102]: (a) the cluster carbonyl anion must have a significant lifetime relative to competing fragmentation reactions; (b) the ligand L must be less π-acidic than CO; and (c) the ligand L must not be reduced by $Ph_2CO^{\cdot-}$.

TABLE 2

Products obtained from the reaction between metal carbonyls and ligands (L) in the presence of $Ph_2CO^{\cdot-}$ as catalyst

Substrate	Ligand	Product	Ref.
$Fe_3(CO)_{12}$	L = RNC, PR_3, $P(OR)_3$	$Fe_3(CO)_{11}L$	102
$Ru_3(CO)_{12}$	L = RNC, PR_3, etc.	$Ru_3(CO)_{12-n}L_n$ ($n = 1$–3)	102
$H_4Ru_4(CO)_{12}$	L = RNC, PR_3, $P(OR)_3$	$Ru_3(CO)_{12-n}L_n$ ($n = 1$–3)	102
$Os_3(CO)_{12}$	L = RNC, PPh_3	$Os_3(CO)_{12-n}L_n$ ($n = 1$–3)	102
$Co_3(CCl)(CO)_9$	L = Bu^tNC, diphos	$Co_3(CCl)(CO)_8(CNBu^t)$ $Co_3(CCl)(CO)_7(diphos)$	102
$Rh_6(CO)_{16}$	L = Bu^tNC	$Rh_6(CO)_{12}(CNBu^t)_4$	
$Ru_3(CO)_{11}(CNBu^t)$	L = CO, Bu^tNC, PR_3	$Ru_3(CO)_{11}L$, $Ru_3(CO)_{10}(CNBu^t)L$	110
$Ru_3(CO)_{12}$	diphos	$Ru_3(CO)_{11}(diphos)$ $Ru_3(CO)_{12-n}(diphos)_n$ ($n = 1, 2$) $[Ru_3(CO)_{11}]_2(diphos)$	111

The mechanism is similar to that given in Scheme 10. In this instance the $M(CO)_n^{\cdot-}$ radical is generated by electron transfer from $Ph_2CO^{\cdot-}$, rather than electrochemically. Some examples of synthetic utility have been selected from the literature and are given in Table 2.

Prior to the use of $Ph_2CO^{\cdot-}$ as catalyst, as reported by Bruce and co-workers [102], there have been a number of other reports which could possibly involve similar catalytic cycles.

Butts and Shriver [112] have reported that the substitution of iron pentacarbonyl by ligands L [L = PPh_3, $P(OPh)_3$, $P(OMe)_3$]

$$Fe(CO)_5 + L \rightarrow Fe(CO)_4L + CO \qquad (17)$$

is catalysed by a catalyst generated by the in situ reaction of a small amount of $Fe(CO)_5$ and sodium diphenylketyl. (However, catalysis was also demonstrated with $Fe(CO)_5$ and L in the presence of added catalytic quantities of $[Fe_2(CO)_8]^{2-}$, $[Fe_3(CO)_{11}]^{2-}$, or $[Fe_4(CO)_{13}]^{2-}$.) The authors suggested that reaction may occur via the activation of iron pentacarbonyl by coordinatively unsaturated iron carbonyl radicals or radical anions.

Hoffman and Brown [87] have reported that the reaction of $(\eta^5\text{-}C_5H_5)W(CO)_3H$ and $P(Bu^n)_3$ to give $(\eta^5\text{-}C_5H_5)W(CO)_2[P(^nBu)_3]H$ is catalysed by small amounts (< 20 mole percent) of galvinoxyl, nitrosodurene or benzoyl peroxide in the absence of light. However, no further details were given.

(v) Transition metal catalysts

Prior to 1979 the only reported use of transition metals to induce catalytic CO displacement from metal carbonyl complexes was in ^{14}CO and ^{13}CO incorporation studies [47,78,80,81]. The extension to substitution by other ligands had not been considered. Since then a wide range of catalysts have been found which can be used to bring about CO replacement by ligands such as isonitriles and phosphines. The reaction mechanism(s) have generally not been determined, but are expected to involve labilisation of CO ligands by a change in oxidation state of the metal carbonyl substrate or by metal carbonyl radical formation. Consequently, this section will discuss results in terms of an arbitrary breakdown into catalyst types. (It is conceivable that different mechanisms operate within a catalyst type.)

(1) Transition metal salts (e.g. $CoCl_2$, $NiCl_2$)

$CoCl_2$ has been found to be an effective catalyst for the substitution of CO on $Fe(CO)_5$ by isonitriles to yield a range of complexes of the type $Fe(CO)_{5-n}(CNR)_n$ ($n = 1$–5) [113]. Reaction conditions are mild (80°C) and reaction times generally short. As expected, multiple replacement of CO by isonitrile (RNC) is more facile when R is an aryl rather than an alkyl group [114]. Mechanistic studies have revealed that CO is evolved in the reaction, that the reaction is unaffected by light or radical initiators and that it can be carried out in a wide range of solvents. Many other transition metal salts have been found which will also catalyse the standard reaction

$$Fe(CO)_4(CNBu^t) + Bu^tNC \rightarrow Fe(CO)_3(CNBu^t)_2 + CO \qquad (18)$$

These include NiX_2 ($X = Cl$, Br, I, NO_3, acetate, ClO_4), CoX_2 ($X = Br$, I, NO_3, acetate, PF_6, $\frac{1}{2}SO_4$), $RhCl_3 \cdot xH_2O$, PdX_2 ($X = Cl$, Br), and $IrCl_3 \cdot xH_2O$ [113,115]. Although many metal salts have been found that do not catalyse the reaction, e.g. CoF_2, $NiSO_4$, $NiCO_3$, CuBr, $CuBr_2$ and $CrCl_3 \cdot 6\,H_2O$, no statement about catalyst prediction can yet be made.

Other significant findings include the observation that the mechanism does not involve a bridging mechanism between catalyst and substrate which involves either halide or RNC. Although no evidence for an electron-transfer process was found, the known ability of cobalt(II) to undergo facile oxidation and reduction would suggest this as a possible mechanism [116].

The reaction has also been extended to other substrates and ligands. Thus, the reaction of $Mo(CO)_6$ with isonitriles to give $Mo(CO)_{6-n}(CNR)_n$ ($n = 1$–4) [117], or with RNH_2 to give $Mo(CO)_5(RNH_2)$ [117]; the reaction of $Fe(CO)_5$ with PR_3 to give $Fe(CO)_4(PR_3)$ [118], and the reaction of $Fe(CO)_4$(olefin) with RNC to give $Fe(CO)_{4-n}(CNR)_n$(olefin) ($n = 1$–3) [115], have all been studied. Although initially it was suggested that $CoCl_2$

could also be used to catalyse CO replacement in metal carbonyl clusters [113a], more recent work [119] has suggested that the effect of $CoCl_2$ is to catalyse substitution reactions of the cluster fragments rather than the cluster. $CoCl_2$ actually inhibits CO substitution reactions of metal carbonyl dimers [77].

Finally, it has been reported by Chauvin and Commereuc [120] that $TiCl_4$, when mixed in the dark with $(CO)_5W{=}C(OEt)C_4H_9$, brings about the slow evolution of one equivalent of carbon monoxide. The authors went on to show that subsequent thermal or photochemical activation produces an extremely efficient cyclopentene metathesis catalyst system. (The stable compound $(CO)_5W{=}C(OEt)C_4H_9$ alone does not display catalytic activity.) The role of $TiCl_4$ is not understood, but it appears to promote carbonyl displacement.

(2) Transition metal complexes

The initial discovery that $[Ru(CHT)Cl_2]_n$ and $[Ru(NBD)Cl_2]_n$ catalysed the reaction between $Fe(CO)_5$ and Bu^tNC eventually led to the discovery of alternative and more readily available transition metal catalysts [115]. The limited applicability of the above catalysts is shown by their inability to bring about multiple CO substitution on $Fe(CO)_5$. Similar findings were also made for $Ru(PPh_3)_3Cl_2$ [121a]. Unexpectedly, $Rh(PPh_3)_3Cl$ (as well as $Rh(PPh_3)_3Br$ and $Ir(CO)(PPh_3)_2Cl$) was found to be an excellent catalyst for a variety of metal carbonyl substitution reactions [121] (Table 3). It is to be noted that $Rh(PPh_3)_3Cl$ was used as a *catalyst*, in contrast to other reports on metal carbonyl substitution reactions in which it was used as a *reagent* (see Section B(iii)).

(3) Transition metals and metal oxides

In 1959 it was discovered that iron pentacarbonyl reacted with ^{14}CO, in the presence of platinum and other metals and metal oxides, to give $Fe(^{14}CO)_5$ [78]. Similar enrichment studies with ^{13}CO in the presence of palladium catalysts have also been reported [80,81]. More recently, however, a study of the use of metals, metal oxides, and supported metals as catalysts has shown that CO substitution of metal carbonyl complexes with ligands other than ^{13}CO or ^{14}CO can be achieved [122]. Palladium metal, palladium dispersed on a variety of supports and supported platinum were found to be highly efficient catalysts for the model reaction, (18). Numerous metal oxides were also used, but only PtO_2 and PdO showed catalysis. Thus, CuO, Cu_2O, Ag_2O, TiO_2, V_2O_5, MoO_3, WO_3, ZnO, CdO, and MnO_2 did not catalyse the reaction [115]. Thus, it is apparent that at present this phenomenom is associated with Group 8 metals.

The technique of using palladium oxide and supported palladium cata-

TABLE 3

Products obtained from the reaction between metal carbonyls and ligands (L) in the presence of transition metals as catalysts [a]

Substrate	Ligand	Product	Catalyst	Ref.
$Fe(CO)_5$	RNC	$Fe(CO)_{5-n}(CNR)_n$ $(n = 1\text{–}5)$	CoX_2, NiX_2	113, 121
			$Rh(PPh_3)_3Cl$, $Ru(PPh_3)_3Cl_2$	122
	L = PPh_3, $P(OR)_3$	$Fe(CO)_4L$ $Fe(CO)_3L_2$	$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ $CoCl_2$	118, 128
	^{13}CO	$Fe(^{13}CO)_5$	Pd/C	80
$Fe(CO)_4(olefin)$	RNC	$Fe(CO)_{4-n}(CNR)(olefin)$ $(n = 1\text{–}3)$	$Rh(CO)(PPh_3)_2Cl$, $CoCl_2$.	115, 121
$M(CO)_6$ (M = Cr, Mo, W)	RNC	$M(CO)_{6-n}(CNR)_n$ $(n = 1\text{–}6)$	$CoCl_2$, $NiCl_2$, Pd/C, PdO	117,123
$(\eta^5\text{-}C_5H_5)Mo(CO)_3I$	RNC	$(\eta^5\text{-}C_5H_5)Mo(CO)_{3-n}(CNR)_nI$ $(n = 1\text{–}3)$	$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$	92
	PPh_3.	$(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)I$	$[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$	92
$(\eta^5\text{-}C_5H_5)Fe(CO)_2I$	RNC	$(\eta^5\text{-}C_5H_5)Fe(CO)_{2-n}(CNR)_nI$	$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$	91
	PR_3	$(\eta^5\text{-}C_5H_5)Fe(CO)(PR_3)I$	$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$	91
$(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(COMe)$	CO	$(\eta^5\text{-}C_5H_5)Fe(CO)_2(COMe)$	$(\eta^5\text{-}C_5H_5)V(CO)_3H^-$	135
$Mn_2(CO)_{10}$	RNC	$Mn_2(CO)_{10-n}(CNR)_n$ $(n = 1\text{–}4)$	Pd/C, PdO	122, 124
$Os_3(CO)_{12}$	RNC	$Os_3(CO)_{12-n}(CNR)_n$ $(n = 1\text{–}4)$	Pd/C, PdO	122
$Ir_4(CO)_{12}$	RNC	$Ir_4(CO)_{12-n}(CNR)_n$ $(n = 1\text{–}7)$	Pd/C	122
$Re_2(CO)_{10}$	RNC	$Re_2(CO)_{10-n}(CNR)_n$ $(n = 1\text{–}4)$	PdO	125
	PR_3	$Re_2(CO)_{10-n}(PR_3)_n$ $(n = 1\text{–}2)$	Pd/C	122
$(arene)Cr(CO)_3$	RNC	$(arene)Cr(CO)_2(CNR)$	$PdO\text{-}[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$	133, 134
$(\eta^5\text{-}C_5H_5)Mn(CO)_3$	RNC	$(\eta^5\text{-}C_5H_5)Mn(CO)_2(CNR)$	PdO	126, 133
$(\eta^5\text{-}C_5H_5)V(CO)_4$	RNC	$(\eta^5\text{-}C_5H_5)V(CO)_3(CNR)$	PdO	125
	PR_3	$(\eta^5\text{-}C_5H_5)V(CO)_3(PPh_3)$	$(\eta^5\text{-}C_5H_5)V(CO)_3H^-$	135

[a] This table does not include all possible reactant and catalyst combinations that have been reported in the literature.

lysts has been used successfully on a number of other systems:

(a) $Mo(CO)_6 + RNC \rightarrow Mo(CO)_{6-n}(CNR)_n$ ($n = 1$–6) [123] (19)

(b) $Mn_2(CO)_{10} + RNC \rightarrow Mn_2(CO)_{10-n}(CNR)_n$ ($n = 1$–4) [124] (20)

(c) $Re_2(CO)_{10} + RNC \rightarrow Re_2(CO)_{10-n}(CNR)_n$ ($n = 1$–4) [125] (21)

(d) $(\eta^5\text{-}C_5H_5)Mn(CO)_3 + RNC \rightarrow (\eta^5\text{-}C_5H_5)Mn(CO)_2(CNR)$ [126] (22)

The reaction has also been extended to substitution reactions of $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ [122], as well as the substitution of CO on $Re_2(CO)_{10}$ by phosphines [122]. The mechanism for the reaction is presently not understood, but is assumed to involve catalytic electron transfer between catalyst and substrate [122]. Labelling studies with $Mn_2(^{13}CO)_{10}$ and $Mn_2(^{12}CO)_{10}$ in the reaction

$$Mn_2(CO)_{10} + Bu^tNC \overset{Pd/C}{\rightarrow} Mn_2(CO)_9(CNBu^t) + CO \qquad (23)$$

have, however, established that CO dissociation from the *metal dimer* is consistent with the experimental results obtained from mass spectral analysis of the reaction product [127]. This rules out a process involving $Mn(CO)_5^{\cdot}$ radicals formed by interaction of $Mn_2(CO)_{10}$ and palladium on carbon.

(4) *Transition metal complexes containing a metal–metal bond*

The well known phenomena of the light-induced formation of radicals from metal carbonyl dimers has already been discussed (Section C(ii)). In this section the use of the dimers in *thermal* substitution reactions is considered.

Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ with isonitrile in the presence of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ as catalyst (80°C) readily leads to the products $(\eta^5\text{-}C_5H_5)Fe(CO)_{2-n}(CNR)_nI$ ($n = 1, 2$) [91]. In the absence of catalyst, reactions are slow. At this temperature crossover experiments using catalyst–substrate combinations such as $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3(CNR)]$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$, or $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and $(\eta^5\text{-}C_5H_4Me)Fe(CO)_2I$, were performed. The results indicated that a chain-transfer process was operating, with the reaction dependent on the formation and reactivity of the $(\eta^5\text{-}C_5H_5)Fe(CO)_2^{\cdot}$ radical [91] (Scheme 12):

$$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2 \overset{\Delta}{\rightleftarrows} 2(\eta^5\text{-}C_5H_5)Fe(CO)_2^{\cdot} \qquad (a)$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2^{\cdot} + L \rightarrow (\eta^5\text{-}C_5H_5)Fe(CO)L^{\cdot} \qquad (b)$$

$$(\eta^5\text{-}C_5H_5)Fe(CO)L^{\cdot} + (\eta^5\text{-}C_5H_5)Fe(CO)_2I$$
$$\rightarrow (\eta^5\text{-}C_5H_5)Fe(CO)LI + (\eta^5\text{-}C_5H_5)Fe(CO)_2^{\cdot} \text{ etc.} \qquad (c)$$

Scheme 12

This mechanism is totally consistent with the mechanism proposed by Brown [84] and others for the photochemically catalysed reactions using metal dimers as catalysts. However, reactions carried out at 40°C indicated that another mechanism was operating at this lower temperature. The data were consistent with an electron-transfer process. One possible mechanism is shown in Scheme 13.

$$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2 \xrightarrow{\Delta} A \tag{a}$$

$$A + (\eta^5\text{-}C_5H_5)Fe(CO)_2I \rightarrow A\text{–}[(\eta^5\text{-}C_5H_5)Fe(CO)_2I] \tag{b}$$

$$A\text{–}[(\eta^5\text{-}C_5H_5)Fe(CO)_2I] + L \rightarrow A\text{–}[(\eta^5\text{-}C_5H_5)Fe(CO)(L)I] + CO \tag{c}$$

$$A\text{–}[(\eta^5\text{-}C_5H_5)Fe(CO)(L)I] \rightarrow A + (\eta^5\text{-}C_5H_5)Fe(CO)LI \tag{d}$$

(A = activated iron dimer, $L = RNC$)

Scheme 13

Consideration of the experimental data suggested that: (a) the dimer should catalyse ligand substitution on substrates that do not contain the $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ unit; and (b) that the interaction between substrate and catalyst should lead to general ligand activation of the substrate. These features of the reaction were subsequently borne out by the catalysed reactions shown below [128,91].

$$Fe(CO)_5 + PR_3 \rightarrow Fe(CO)_4(PR_3) + CO \tag{24}$$

$$(\eta^5\text{-}C_5H_5)Fe(CNR)_2I + RNC \rightarrow (\eta^5\text{-}C_5H_5)Fe(CNR)_3^+\,I^- \tag{25}$$

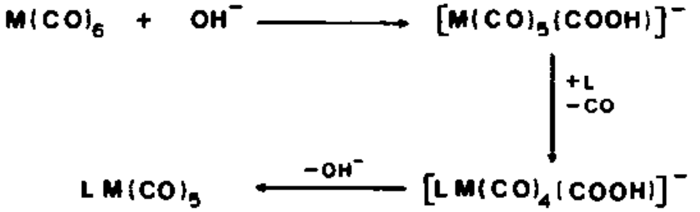
The substitution of $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$ by phosphines in the presence of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ has also been achieved [91]. Similarly, the reaction between $(\eta^5\text{-}C_5H_5)M(CO)_3I$ and RNC to give $(\eta^5\text{-}C_5H_5)M(CO)_{3-n}(CNR)_nI$ ($n = 1$–3; M = Mo, W) using catalysts such as $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ and $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2$ has been accomplished [92].

(vi) Phase-transfer catalysis

The use of phase-transfer catalysis in organometallic chemistry (including organometallic synthesis) has recently been reviewed [129]. A number of publications pertinent to carbonyl substitution reactions will, however, be briefly considered here.

Shaw and co-workers [130] have made use of phase-transfer catalysis in the substitution reactions of the Group 6 metal hexacarbonyls. Thus, $M(CO)_6$ (M = Cr, Mo, W) was found, under phase-transfer conditions, to be readily substituted by Group 5 donor ligands L ($L = PPh_3$, $AsPh_3$, diphos, bipy, etc.) to give predominantly the $M(CO)_5L$ product in moderate to excellent yield [130a]. Substitution by RNC, ($R = Bu^t$, 3-$CH_3C_6H_4$) has also been achieved and gives products of the type $M(CO)_5L$ and *cis*-$M(CO)_4L_2$ in varying yields, and usually as mixtures [130b].

It has been proposed by Hui and Shaw [130a] that the substitution reaction proceeds by initial nucleophilic attack of hydroxide anion at a carbonyl carbon atom of $M(CO)_6$ to give an anionic hydroxycarbonyl complex (Scheme 14). The COOH moiety was considered to be a labilising ligand, leading to carbonyl substitution followed by hydroxide loss to give the substituted product $M(CO)_5L$.



Scheme 14

Brown and Bellus have proposed that the hydroxycarbonyl ligand in such reactions is specifically to be considered a *cis*-labilising ligand [131].

Studies by Darensbourg and co-workers [132] on the mechanism of the phase-transfer catalysed phosphine substitution of CO on the Group 6 metal hexacarbonyls, using as labels ^{13}CO and $H_2{}^{18}O$, do not unequivocally indicate a specific mechanism for the process. The results, however, imply possible participation of the incoming phosphine ligand in the CO labilisation process. This would seem to suggest that the actual mechanism is more complex than simple labilisation by the COOH ligand as postulated by Shaw [130a] and Brown [131].

(vii) General

Some further examples of the use of transition metals (and their supports) in the catalysis of metal carbonyl substitution reactions are listed below.

(1) The use of physically *mixed* transition metal catalysts to effect CO replacement in reaction (17) has been carried out. Whereas metal carbonyl clusters such as $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2]_2$, $Re_2(CO)_{10}$ and $Os_3(CO)_{12}$, and supported metals such as $Pd/CaCO_3$, when used in reaction (18) (at 25°C) show no catalysis, combinations of the metal carbonyl and supported metal used together show catalytic action [133]. This technique has been used to catalytically synthesise (arene)$Cr(CO)_2(CNR)$ complexes [134], e.g.

$$(\eta^6\text{-}C_6H_6)Cr(CO)_3 + Bu^tNC \rightarrow (\eta^6\text{-}C_6H_6)Cr(CO)_2(CNBu^t) \qquad (26)$$

$$(\text{catalyst} = [(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2/PdO)$$

(2) Investigations into the use of supported metals as catalysts for reaction (18) revealed that some of the catalyst *supports* showed catalytic properties, e.g. certain activated carbons [122]. This effect could be due to trace impurities found in the supports.

(3) Zeolites containing exchanged metals, e.g. Ru and Ni, have been found to catalyse reaction (18) [122].

(4) A rhodium complex attached to a polymer support has been used as a transition metal CO substitution catalyst [121a].

(5) $(\eta^5\text{-}C_5H_5)V(CO)_3H^-$ has been used as a catalyst to bring about the reaction [135]

$$(\eta^5\text{-}C_5H_5)V(CO)_4 + PR_3 \xrightarrow{\text{catalyst}} (\eta^5\text{-}C_5H_5)V(CO)_3(PR_3) + CO \qquad (27)$$

A chain mechanism involving the chain carrier $(\eta^5\text{-}C_5H_5)V(CO)_4^{\overline{\cdot}}$ was proposed to account for the experimental data.

(6) The reaction

$$Fe(CO)_5 + PR_3 \rightarrow Fe(CO)_4(PR_3) + CO \qquad (28)$$

is catalysed by iron carbonyl species [112]. This reaction almost certainly involves radical ion iron carbonyl complexes as chain carriers in the catalytic cycle.

D. CONCLUSION

It is apparent from the above literature review that the recent developments in the use of reagents and catalysts to induce CO labilisation in metal carbonyl complexes have allowed for the synthesis of a wide range of previously inaccessible complexes. It has also been shown that in many instances the reaction mechanisms involve the generation of odd-electron metal carbonyl complexes produced either by metal–metal bond cleavage or by a one-electron redox change on the substrate. These odd-electron metal carbonyl complexes show enhanced ligand lability relative to their even-electron precursors, and the phenomenon is analogous to the well known induced-ligand lability as found for instance in Co^{2+}/Co^{3+} and Cr^{2+}/Cr^{3+} chemistry.

The ability to achieve either radical formation or a redox change on the metal carbonyl substrate is not in itself sufficient to generate a catalytic cycle, but techniques (electrochemical, photochemical and chemical) are now available to complete the catalytic cycle.

The extension of the above concepts to (a) substitution reactions of metals containing ligands other than CO [91,107] and (b) other fundamental organometallic reaction types, e.g. oxidative addition reactions and insertion reactions [100,109], appear logical and the exploitation of this chemistry can be predicted to occur in the near future.

ACKNOWLEDGEMENTS

Financial support from the University of the Witwatersrand and the Council for Scientific and Industrial Research is gratefully acknowledged.

NOTE ADDED IN PROOF

Pertinent papers have appeared in the literature since this paper was submitted [137–153].

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