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REVIEW
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Carbonylation of Organometallic Compounds with Carbon Monoxide via Transmetallation*

Sakae Uemura, Kouichi Ohe, and Nobuyuki Sugita**

Representative examples of the carbonylation reactions of organometallic compounds of non-transition metals with carbon monoxide via transmetallation are summarized from synthetic viewpoint. Such non-transition metals as mercury, boron, thallium, silicon, tin, lead, and tellurium are found to be useful for this purpose, whereas transition metal salts such as palladium(II), rhodium(III), and rhodium(I) are employed stoicheiometrically or catalytically for transmetallation. These combined transmetallation/carbonylation reactions constitute a good method for the preparation of carboxylic acids, their esters, lactones, and ketones regio- and stereo-selectively under mild conditions; *i.e.*, generally with atmospheric pressure of CO and at room temperature.

1. INTRODUCTION

Insertion of carbon monoxide (CO) into a transition metal-carbon σ bond or, more realistically, a 1, 2 migration of the ligand alkyl or aryl group from the metal onto the carbon of a co-ordinated CO ligand is a very facile reaction and constitutes a key step in many industrially important processes such as transition metal catalyzed carbonylation of olefins and methanol. The products are normally carboxylic acids, their esters and amides, ketones, and aldehydes. On the other hand, the direct carbonylation of organometallic compounds of non-transition metals with CO itself is not a useful method for preparation of such compounds, because severe reaction conditions (*i.e.*, high temperature, long time, high pressure of CO *etc.*) are generally required and yet the yields are often poor. The addition of some transition metal salt to the reaction system, however, promotes this reaction profoundly and very mild reaction conditions (*i.e.*, room temperature and atmospheric pressure of CO) often suffice. In this case the reaction involves the transmetallation process to give organometallic species having a transition metal-carbon σ bond which is susceptible to CO as described above. Actually stoicheiometric amounts of palladium(II)


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salts are most commonly used, and in some instances the reaction proceeds even with catalytic amounts of them. Since organometallic compounds of non-transition metals are generally air stable and easily handled and many of them are prepared highly regio- and stereo-selectively, these combined transmetallation/carbonylation reactions, both being stereospecific, may constitute a good method for preparing various kinds of carbonyl compounds regio- and stereo-selectively. In addition to the synthetic utility the reactions are also important from the viewpoint of understanding the reaction mechanism, as the structure of the starting organometallic compounds are easily determined. In this review article we summarize representative examples of such reactions for each organometallic compound from synthetic viewpoint, though the kind of non-transition metal employed for this particular purpose is still limited. The chemistry on organomercury(II) compounds has been most studied. The carbonylations using metal carbonyls such as dicobalt octacarbonyl, nickel tetracarbonyl, and iron pentacarbonyl as reagents are not included here.

2. ORGANOMERCURY(II) COMPOUNDS

The first example of direct CO insertion to a carbon-mercury bond was reported by Davidson et al.[1] Thus, although the treatment of phenylmercury(II) acetate, hydroxide, and basic nitrate with CO (1–100 atm) in aqueous solution at 70–100°C resulted in the reduction of these compounds to diphenylmercury and/or mercury, the reaction of phenylmercury(II) basic nitrate with 300 atm of CO at 110°C in benzene afforded benzoic anhydride (66% yield), phenylmercury(II) benzoate, and mercury together with a small amount of benzoic acid (Scheme 1).[1,2] At low pressure of CO the yield of benzoic anhydride decreased. Similar reaction was also observed with

$$(PhHg)_2(OH, NO_3) \xrightarrow[\substack{benzene \\ 110°C}]{CO\ (300\ atm)} (PhCO)_2O + PhHgOCOPh + Hg + HNO_3$$
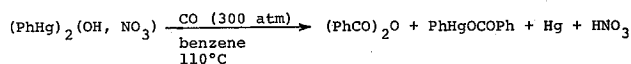
Scheme 1

phenylmercury(II) basic perchlorate and p-tolylmercury(II) basic nitrate, but the yields of the expected carboxylic acid or its derivatives were low despite severe reaction conditions.[2] The reaction scheme involving an in situ formation of unstable benzoyl-mercury species has been envisaged for these carbonylations (Scheme 2).

$$[\ PhHgCO^+ \longrightarrow PhCOHg^+ \underset{-Hg^°}{\longrightarrow} PhCO^+ \longrightarrow PhCO_2NO_2 \longrightarrow]$$
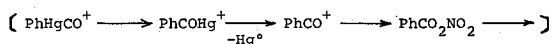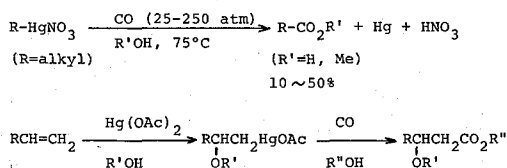
Scheme 2

The CO insertion also occurs to alkyl carbon-mercury bond to give the corresponding carboxylic aicd and ester in moderate yields under high pressure of CO and at high temperature (Scheme 3).[3,4]

Here, the so-called oxymercurials prepared by alkoxymercuration of olefins are certainly one of alkylmercury(II) compounds from which β-alkoxy carboxylic esters are produced (Scheme 3).[3,4]

$$\text{R–HgNO}_3 \xrightarrow[\text{R'OH, 75°C}]{\text{CO (25-250 atm)}} \text{R–CO}_2\text{R'} + \text{Hg} + \text{HNO}_3$$

(R=alkyl) (R'=H, Me)

10 ~ 50%

$$\text{RCH=CH}_2 \xrightarrow[\text{R'OH}]{\text{Hg(OAc)}_2} \underset{\underset{\text{OR'}}{|}}{\text{RCHCH}_2\text{HgOAc}} \xrightarrow[\text{R"OH}]{\text{CO}} \underset{\underset{\text{OR'}}{|}}{\text{RCHCH}_2\text{CO}_2\text{R"}}$$

Scheme 3

In the presence of palladium(II) chloride, on the contrary, the CO insertion to aryl carbon-mercury bond has been revealed to proceed much easily under atmospheric CO pressure at 25°C to yield moderate yields of the corresponding carboxylic acid or its derivatives. Diaryl ketones and biaryls were produced in smaller quantities. The results have been explained by transmetallation giving arylpalladium(II) species which reacts with CO (Scheme 4).[5] Similar but independent work has shown that diaryl
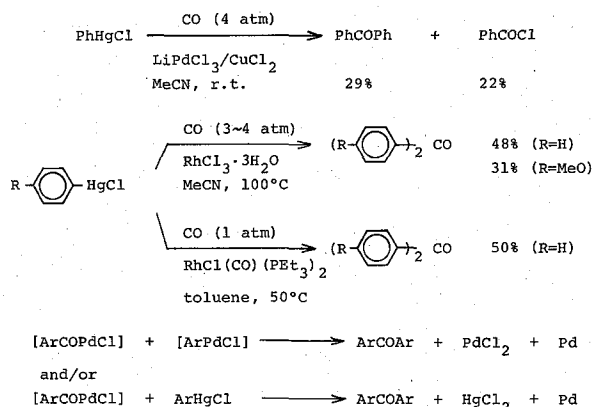
$$\text{Ph}_2\text{Hg} \xrightarrow[\substack{\text{PdCl}_2 \\ \text{MeCN}}]{\text{CO (1 atm)}} \text{PhCOCl}$$

42%
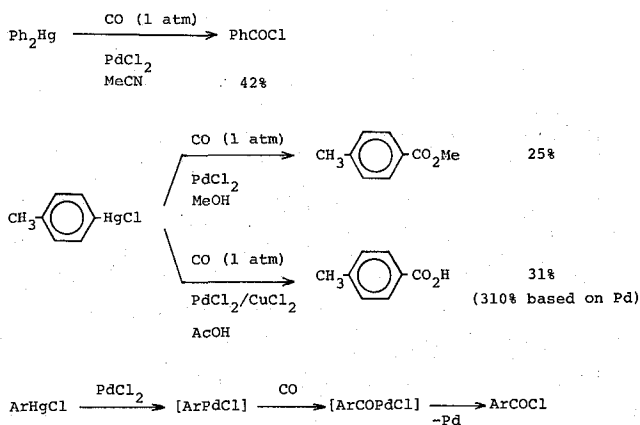
ketones were mainly produced in fair yields at slightly higher pressure of CO (3–4 atm) and by use of non-hydroxylic solvents such as acetonitrile and toluene.[6] Catalytic amounts of rhodium(III) chloride, rhodium(I) carbonyl complex, and lithium chloropalladate(II) were employed in these cases, rhodium salt being effective for the ketone formation (Scheme 5). The mechanism involving a reaction of an acyl-palladium (or rhodium) compound with an arylpalladium or arylmercury compound has been proposed for formation of diaryl ketones (Scheme 5).
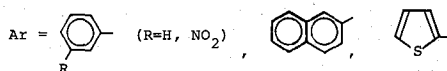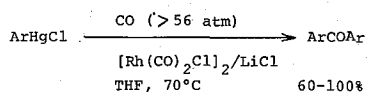
Improved yields of symmetrical diaryl ketones from arylmercury(II) compounds were obtained by using [Rh(CO)$_2$Cl]$_2$ as a catalyst under higher pressure of CO (70–107 atm) at 70°C in tetrahydrofuran (Scheme 6).[7] Here, organorhodium compound *via* transmetallation was presumed to be an intermediate. Similar work has been reported with *p*-substituted phenylmercury(II) chloride and diarylmercury(II) by using either PhPdI(PPh$_3$)$_2$ or [Rh(CO)$_2$Cl]$_2$ in hexamethylphosphoric amide as the solvent.[8]

Application of this transmetallation/carbonylation reaction to furyl-, thiophenyl-, and ferrocenyl-mercury(II) compounds by using stoicheiometric amount of lithium

$$PhHgCl \xrightarrow[\substack{LiPdCl_3/CuCl_2 \\ MeCN, \; r.t.}]{CO \; (4 \; atm)} PhCOPh \quad + \quad PhCOCl$$

$$29\% \qquad\qquad 22\%$$

R—⟨◯⟩—HgCl

$$\xrightarrow[\substack{RhCl_3 \cdot 3H_2O \\ MeCN, \; 100°C}]{CO \; (3\sim4 \; atm)} (R-⟨◯⟩)_2 CO \quad \begin{array}{l} 48\% \; (R=H) \\ 31\% \; (R=MeO) \end{array}$$

$$\xrightarrow[\substack{RhCl(CO)(PEt_3)_2 \\ toluene, \; 50°C}]{CO \; (1 \; atm)} (R-⟨◯⟩)_2 CO \quad 50\% \; (R=H)$$

$$[ArCOPdCl] \quad + \quad [ArPdCl] \longrightarrow ArCOAr \quad + \quad PdCl_2 \quad + \quad Pd$$

and/or

$$[ArCOPdCl] \quad + \quad ArHgCl \longrightarrow ArCOAr \quad + \quad HgCl_2 \quad + \quad Pd$$

Scheme 5

$$ArHgCl \xrightarrow[\substack{[Rh(CO)_2Cl]_2/LiCl \\ THF, \; 70°C}]{CO \; (>56 \; atm)} ArCOAr$$
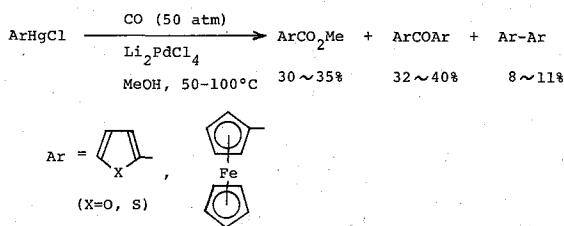
$$60-100\%$$

Ar = ⟨◯⟩— (R=H, NO₂), ⟨◯◯⟩—, ⟨S⟩—
     |
     R

Scheme 6

chloropalladate (II) under 50 atm of CO and at 50–100°C resulted in a formation of the corresponding carboxylic esters together with comparable amounts of the corresponding symmetrical ketones and a small amount of biaryl (Scheme 7).[9,10]

$$ArHgCl \xrightarrow[\substack{Li_2PdCl_4 \\ MeOH, \; 50-100°C}]{CO \; (50 \; atm)} ArCO_2Me \quad + \quad ArCOAr \quad + \quad Ar-Ar$$

$$30\sim35\% \qquad 32\sim40\% \qquad 8\sim11\%$$

Ar = ⟨S⟩—, ⟨◯⟩—Fe⟨◯⟩
 |
         X
(X=O, S)

Scheme 7

A patent work has claimed that by using a catalytic amount of palladium(II) chloride bis(triphenylphosphine) complex better yields of the corresponding aromatic carboxylic esters were obtained under slightly higher CO pressure (4–9 atm) and at higher temperature (70–110°C) in an alcohol (Scheme 8)[11].

$$ArHgX \xrightarrow[\substack{PdCl_2(PPh_3)_2 \\ ROH}]{CO \; (4-9 \; atm)} ArCO_2R$$

$$10\sim99\%$$
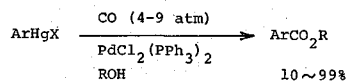
Scheme 8

Alkylmercury(II) compounds such as oxymercurials of cyclohexene and norbornadiene also suffered CO insertion to a carbon-mercury bond under atmospheric

pressure of CO when a stoicheiometric amount of lithium chloropalladate(II) is present. Although the yields of carbomethoxylated products were low to moderate (7–44%), the reaction was found to proceed with predominant retention of configuration at carbon (Scheme 9).[12] Since the carbomethoxylation of alkylpalladium compounds
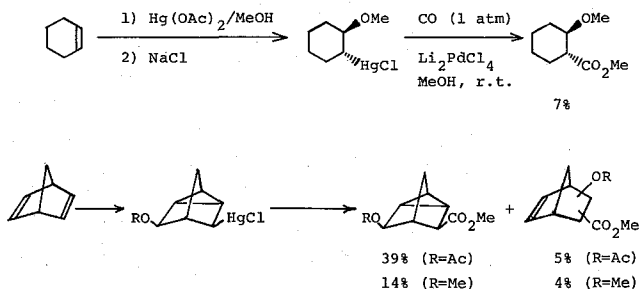
Scheme 9

is known to occur with complete retention of configuration at carbon,[13] the above results show that the exchange of palladium for mercury occurs with predominant retention of configuration. This fact is consistent with a four-centre bimolecular electrophilic exchange of palladium for mercury or an oxidative addition of oxymercurials to a palladium(II) species with retention of configuration at carbon (Scheme 10).[12]
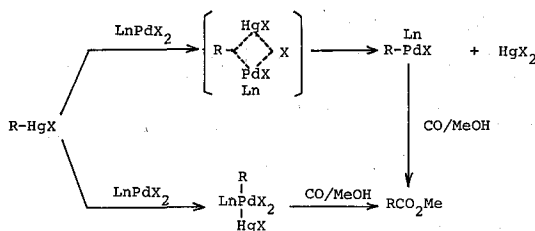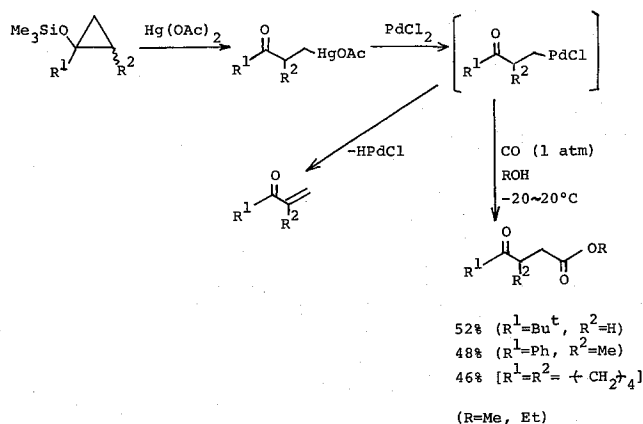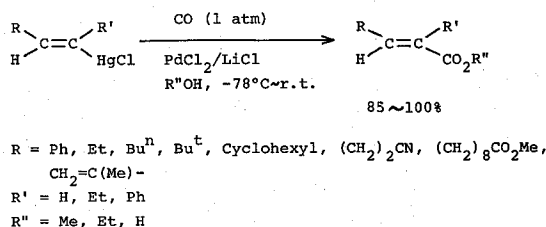

Scheme 10

β-Acetoxymercuri ketones prepared by the reaction of siloxy-cyclopropanes with mercury(II) acetate were converted to γ-ketoesters in moderate yields by treatment with a flow of CO in the presence of a stoicheiometric amount of palladium(II) chloride (Scheme 11).[14] In the absence of CO a dehydropalladation occurred to afford good yields of α-methylene ketones.[14]

Vinylmercury(II) compounds react much readily than aryl- and alkyl-mercury (II) compounds with atomospheric pressure of CO in the presence of stoicheiometric amounts of palladium(II) chloride and lithium chloride in an alcohol to afford α, β-unsaturated carboxylic esters almost quantitatively (Scheme 12).[15] The lower reaction temperature ($-78\sim0°C$) was generally employed for this reaction. Similarly, the corresponding acids were obtained by employing 1–5% aqueous tetrahydrofuran as the solvent. The mercury-palladium exchange and carbonylation reactions proceeded highly stereospecifically with retention of configuration at the vinylic carbon. Similar carbonylation of *trans-β*-chlorovinylmercury(II) chloride with CO (1.8~
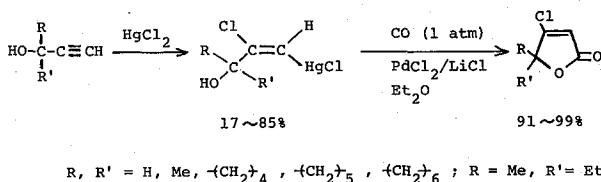
$$52\% \ (R^1=Bu^t, \ R^2=H)$$
$$48\% \ (R^1=Ph, \ R^2=Me)$$
$$46\% \ [R^1=R^2=\ -(CH_2)_4]$$

(R=Me, Et)

Scheme 11

$$85\sim100\%$$

R = Ph, Et, Bu^n, Bu^t, Cyclohexyl, $(CH_2)_2CN$, $(CH_2)_8CO_2Me$,
    $CH_2=C(Me)-$
R' = H, Et, Ph
R" = Me, Et, H

Scheme 12

$$17\sim85\% \qquad\qquad 91\sim99\%$$

R, R' = H, Me, $-(CH_2)_4$, $-(CH_2)_5$, $-(CH_2)_6$; R = Me, R'= Et
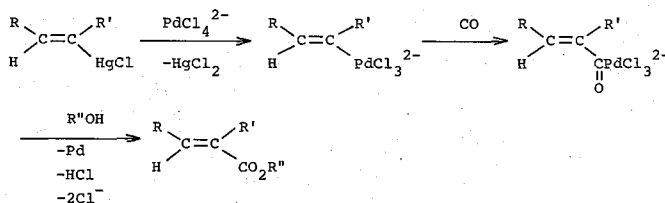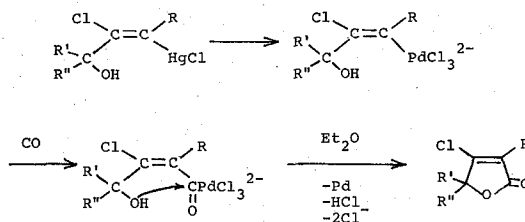
Scheme 13

2.2 atm) in the presence of palladium(II) chloride and its kinetic study have also been reported.[16] Carbonylation of *trans*-β-chlorovinylmercury(II) chlorides derived from propargylic alcohols and mercury(II) chloride in diethyl ether provides the corresponding β-chloro-$\Delta^{\alpha,\beta}$-butenolides almost quantitatively (Scheme 13).[15,17,18] The reaction can be carried out catalytically with respect to palladium(II) chloride or palladium on carbon if a stoicheiometric amount of anhydrous copper(II) chloride or iron(III) chloride was added as a re-oxidant.

   These reactions proceeded undoubtedly *via* an initial mercury-palladium exchange reaction, CO insertion into the resultant carbon-palladium bond of vinylpalladium(II) species and subsequent solvolysis to give the product acids, esters, or butenolides and palladium metal (Schemes 14 and 15).

   As an extention of the work a novel route to furans has been developed, though the reaction seems to have a limited scope. Thus, vinylmercurials obtained by *syn*-addition

Scheme 14

Scheme 15

of mercury(II) chloride to 4-hydroxy-2-alkyn-1-ones react with atmospheric pressure of CO in the presence of lithium chloropalladate(II) at lower temperature to afford 3-furyl carbonyl compounds.[19] The reaction may proceed through furylmercurials and the products depended on the solvent employed (Scheme 16). The ketone may be formed by the reaction between the starting organomercury(II) compound and the resulting organopalladium(II) species as proposed in the case of diaryl ketone formation (Scheme 17, cf. Sheme 5).
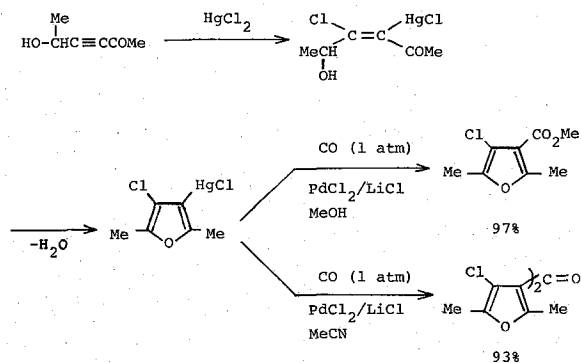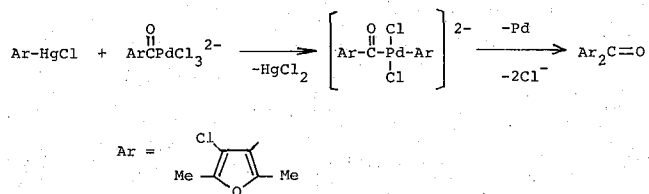
Scheme 16

Scheme 17

In connection to this reaction, it is worthwhile to note that vinylmercury(II) chlorides readily reacted with rhodium(I) and rhodium(III) catalysts and CO to give excellent yields of the corresponding divinyl ketones. The best reaction conditions are 0.5 mol% $[Rh(CO)_2Cl]_2$ and 2 equivalents of lithium chloride under 1 atm of CO at room temperature (Scheme 18).[7] Various rhodium catalysts such as $Rh(CO)$-

Scheme 18

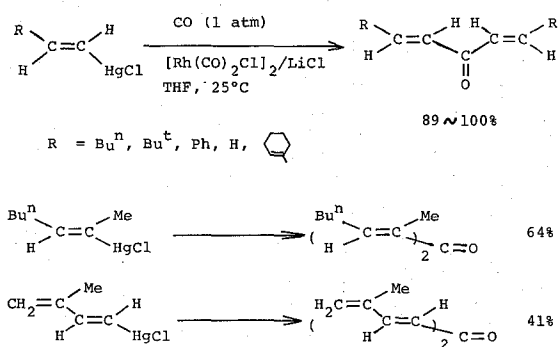$Cl(PPh_3)_2$, $RhCl(PPh_3)_3$, $[Rh(CH_2=CH_2)Cl]_2$, $RhCl_3 \cdot 3H_2O$, and $[Rh(nor-bornadiene)Cl]_2$ are effective, but palladium(II) salt showed a very low activity. In all cases, the stereochemistry of the vinylmercurial is preserved in the resulting divinyl ketone as exemplified in Scheme 18. Vinylmercurials derived from terminal alkynes produce nearly quantitative yields of divinyl ketones after 24 h, while diminished yields are observed with vinylmercurials derived from internal alkynes or enynes even with longer reaction times. The proposed reaction mechanism is as follows: (1) oxidative addition of the vinylmercurial to a rhodium(I) species or transmetallation between mercury and rhodium, (2) insertion of CO to form an acyl-rhodium derivative, (3) transmetallation of this species by another vinylmercurial, and (4) reductive elimination of the divinyl ketone to generate the rhodium(I) catalyst (Scheme 19).[7]
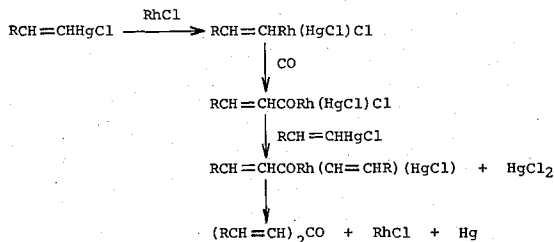
Scheme 19

Intramolecular solvomercuration of a number of ortho substituted arylacetylenes with mercury(II) acetate in acetic acid readily afforded benzofuran, benzothiophene, isocoumarin, and chromone organomercury(II) chlorides, the resulting vinyl carbon-mercury bond suffers CO insertion very easily. This route has provided a new ap-

proach to the coumarin and coumestan ring systems if suitable alkynes were chosen (Scheme 20).[20]
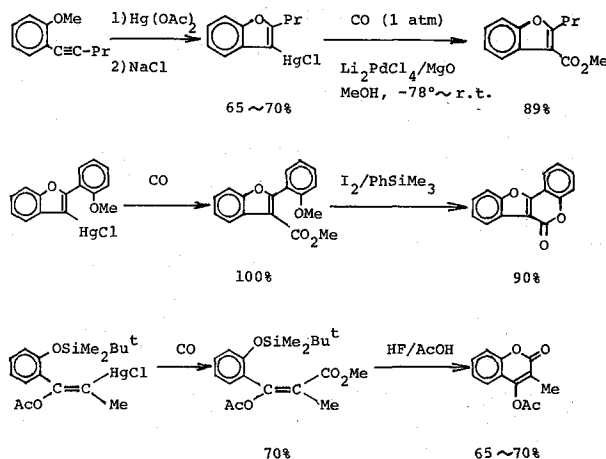
Scheme 20

The examples known for CO insertion to an alkynyl carbon-mercury bond *via* transmetallation are limited to the reaction of bis(phenylethynyl)mercury and bis-(ethylethynyl)mercury with CO (20 atm) in an alcohol at 25°C in the presence of stoicheiometric amounts of palladium(II) chloride and lithium chloride (Scheme 21).[21] Maleate ester was mainly obtained together with small amounts of fumaric ester and the expected acetylenic ester. The reaction has been explained to proceed by the following steps: mercury-palladium exchange, CO insertion to the carbon-palladium bond, alcoholysis giving HPdCl and acetylenic ester, the fast re-addition of eliminated HPdCl to the acetylenic ester, second CO insertion to the re-formed carbon-palladium bond leading to maleate and fumarate ester as shown in Scheme 21.
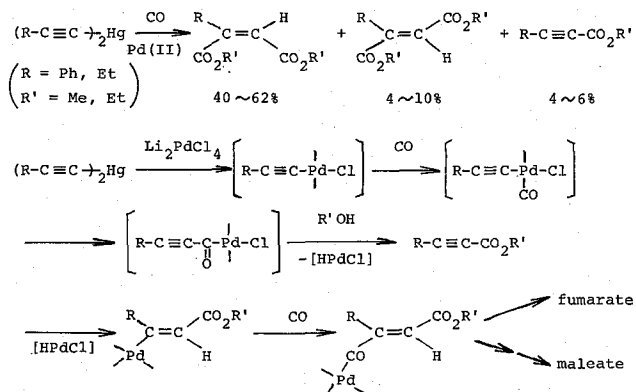
Scheme 21

3. ORGANOTHALLIUM(III) COMPOUNDS

Phenylthallium(III) compounds such as $PhTl(OH)NO_3$, $PhTlCl_2$, and $PhTl$-$(OCOPr^i)_2$ have been known to react with CO in benzene or methanol to give benzoic acid or its methyl ester, but the reaction requires high temperature ($\sim 120°C$), high pressures (~ 220 atm), and long reaction time (~ 18 h) (Scheme 22).[22] Under similar severe reaction conditions a small amount ($\sim 3\%$) of methyl benzoate was obtained from a mixture of benzene, thallium(III) nitrate, and methanol.[23]

$$PhTl(OH)NO_3 \xrightarrow[\text{MeOH, }100°C]{\text{CO(210 atm)}} PhCO_2Me + TlNO_3 + H_2O$$
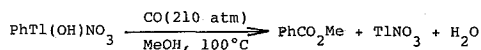
Scheme 22

In the presence of palladium(II) salt, however, the reaction proceeded very smoothly with much lower CO pressure and at room temperature to afford such carboxylic acid derivatives (Scheme 23).[24-26] The thallium-palladium transmetallation is a key step of the reaction and CO insertion occurs to the carbon-palladium

$$ArTlX_2 \xrightarrow[\substack{\text{cat. } PdX_2 \\ \text{ROH, r.t.}}]{\text{CO(1 atm)}} ArCO_2R + TlX + HX$$

Scheme 23

bond of the produced arylpalladium(II) species before it couples to biaryls (Scheme 24). As can be seen from Scheme 24, catalytic amounts of palladium salt are required for this reaction and no additional re-oxidant for palladium cycle is needed.
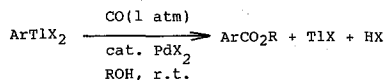
$$ArTlX_2 + PdX_2 \longrightarrow ArPdX + TlX_3$$
$$ArPdX + CO \longrightarrow ArCOX + Pd$$
$$ArCOX + ROH \longrightarrow ArCO_2R + HX$$
$$Pd + TlX_3 \longrightarrow PdX_2 + TlX$$
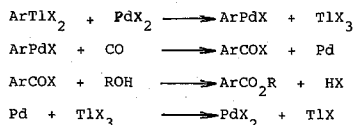
Scheme 24

The aromatic thallation with thallium(III) trifluoroacetate in trifluoroacetic acid is generally rapid and its orientation can be controlled by the reaction temperature and time (kinetic *vs.* thermodynamic control) and the kind of substituent (chelation *etc.*).[27,28] Since transmetallation followed by CO insertion occurs at the position where thallium was attached previously, the aromatic thallation and subsequent palladium-catalyzed carbonylation (at room temperature for 24 h under 1 atm of CO) constitute a new and facile route of introduction of CO into aromatic nuclei with all the orientation control potential inherent in the initial thallation process. Thus, the method was applied for preparation of a wide variety of aromatic esters (Scheme 25), aromatic lactones such as phthalides and 3, 4-dihydroisocoumarins, aromatic anhydrides, and aromatic phthalimides (Scheme 26), the reaction being highly regio- and stereo-specific.[25,26] Here, thallation of normal mono-substituted aromatic compounds occurs with a

very high p-selectivity, while o-substitution predominates when oxygen or nitrogen atom is present at a suitable position of the substituent due to intramolecular delivery of the thallium electrophile by the oxygen or nitrogen.[29]

$$R-\langle\text{ }\rangle \xrightarrow[CF_3CO_2H]{Tl(OCOCF_3)_3} R-\langle\text{ }\rangle-Tl(OCOCF_3)_2 \xrightarrow[10\%PdCl_2/LiCl/ \atop MgO, MeOH, r.t.]{CO (1 atm)} R-\langle\text{ }\rangle-CO_2Me$$

55% (R=H)
42% (R=F)
62% (R=MeO)
80% (R=Bu^t)

Scheme 25

33% (X=H)
89% (X=MeO)
95% (X=OH)
45% (X=Cl)

Z=OCOCF$_3$

51% (X=H)
58% (X=MeO)

77%

88%

44% (Y=OH, Z=O)
83% (Y=NH$_2$, Z=NH)

63%
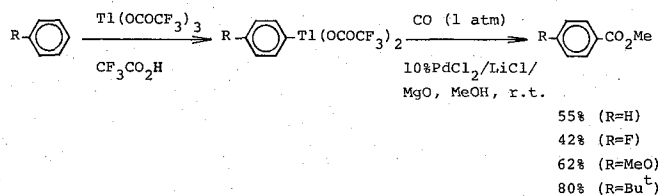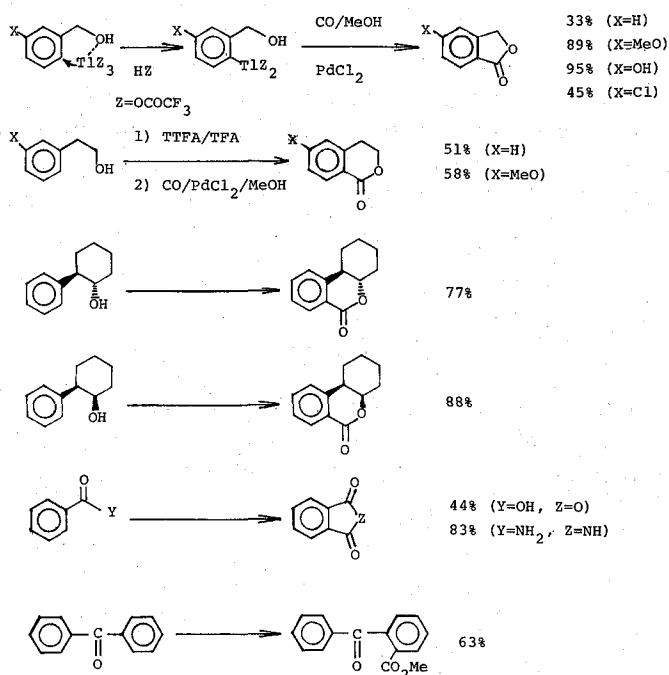
Scheme 26

4. ORGANOBORON(III) COMPOUNDS

It was first shown in 1962 that trialkylboranes react with CO under very severe conditions (at $500\sim900$ atm, at $50\sim150°C$) to give excellent yields of organoboron intermediates such as trialkylcarbonylboronic anhydrides $[(R_3CBO)_3]$ which can be oxidized to trialkylcarbinols (Scheme 27).[30] It has been noted at the same time that the reactions proceeded even by passing a stream of CO, but the conversion was low. Brown *et al.* have later found, however, that these carbonylation reactions

$$R_3B \xrightarrow{CO(500\sim900atm)} (R_3CBO)_3 \xrightarrow[NaOH]{H_2O_2} R_3C-OH$$
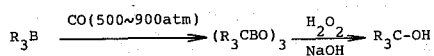
Scheme 27

actually proceeded smoothly in a glass flask at atmospheric pressure of CO at 100~ 125°C in glyme to produce various organoboron intermediates from which a wide variety of alcohols, ketones, and aldehydes has been prepared.[31,32]

There seem to be no reports on the application of the above carbonylations to vinylic compounds. It was rather recently reported,[33] however, that transmetallation method can be well applied to these boron compounds. Thus, 1-alkenylboranes prepared by hydroboration of alkynes smoothly reacted with CO (1 atm) in the presence of an equimolar amounts of palladium(II) chloride and sodium acetate in methanol to give the corresponding α, β-unsaturated carboxylic esters with retention of configuration in good yields (Scheme 28). The reaction can be carried out catalytically with respect to palladium(II) chloride when p-benzoquinone is added as a re-oxidant.

92% (R= Bu^n, R'= H)
93% (R= $C_6H_{13}^n$, R'= H)
95% (R= R'= Et)
87% (R= Bu^n, R'= Me_3Si)
70% (R= Ph, R'= H)
66% (R= $HC\equiv C-(CH_2)_4-$, R'= H)

84%
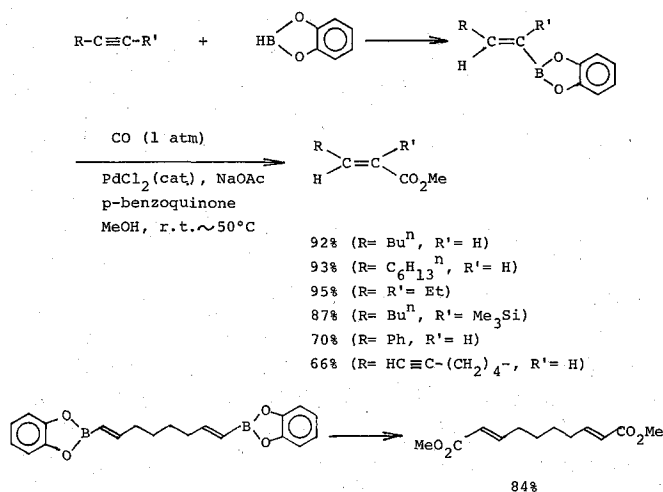
Scheme 28

This reaction provides a method of regio- and stereo-selective *anti*-Markownikoff hydrocarboxylation of alkynes *via* hydroboration as shown in Scheme 28. Phenylboric acid also reacted with CO under similar conditions to give methyl benzoate (Scheme 29). The reaction may proceed most probably *via* boron-palladium transmetallation affording alkenylpalladium species where CO insertion into vinylic carbon-palladium bond occurs. Experimental results indicated that transmetallation occurred with retention of configuration as observed in the cases of alkenylmercury(II) compounds and alkenyl silicates. Similar reaction occurred with 1-alkenyldisiamylboranes as well when two siamyl groups [$Me_2CHCH(Me)-$] are oxidized with trimethylamine oxide before the carbomethoxylation.[33]
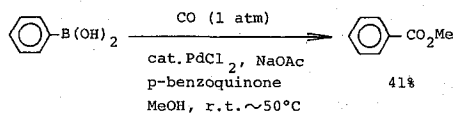
Scheme 29

5. ORGANOSILICON(IV) COMPOUNDS

There are no reports on direct carbonylation of general organosilicon compounds with CO. The first and successful carbonylation of some organosilicon compounds has used palladium(II) salt, the reaction most probably involving silicon-palladium transmetallation.[34,35] Thus, alkenylpentafluorosilicates readily reacted with atmospheric pressure of CO in the presence of stoicheiometric amounts of palladium salts and sodium acetate in methanol at 25°C to afford α, β-unsaturated carboxylic esters in high yields (Scheme 30). Alkenylpentafluorosilicates are available by

$$R-C\equiv C-R' \; + \; HSiCl_3 \xrightarrow{H_2PtCl_6} \; \underset{H}{\overset{R}{>}}C=C\underset{SiCl_3}{\overset{R'}{<}}$$

$$\xrightarrow[H_2O]{KF} \; K_2\left[\underset{H}{\overset{R}{>}}C=C\underset{SiF_5}{\overset{R'}{<}}\right] \xrightarrow[\substack{PdCl_2/NaOAc \\ MeOH,\ r.t.}]{CO\ (1\ atm)} \; \underset{H}{\overset{R}{>}}C=C\underset{CO_2Me}{\overset{R'}{<}}$$

91% (R= $C_6H_{13}^n$, R'= H)
90% (R= Bu^t, R'= H)
76% (R= Ph, R'= H)
61% (R= $MeOCH_2$, R'= H)
88% (R=R'= Bu^n)
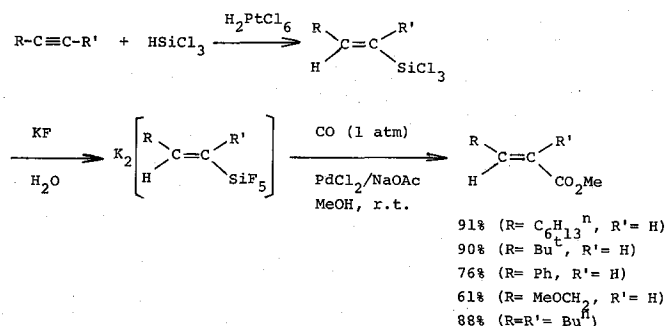
Scheme 30

hydrosilylation of alkynes followed by treatment with potassium fluoride. Here, palladium(II) chloride and bromide exhibited higher activities than the acetate and no carbonylation occurred with palladium(II) chloride bis(triphenylphosphine) complex. The reaction proceeded highly stereoselectively with both the terminal and internal alkenylsilicates. On the other hand, phenyl- and alkyl-silicates gave only trace amounts of carboxylation products.

Recently, α-silylalkyllithiums or α-lithioalkylsilanes were shown to react with CO under very mild conditions to afford good yields of acylsilanes or their enol silyl ethers
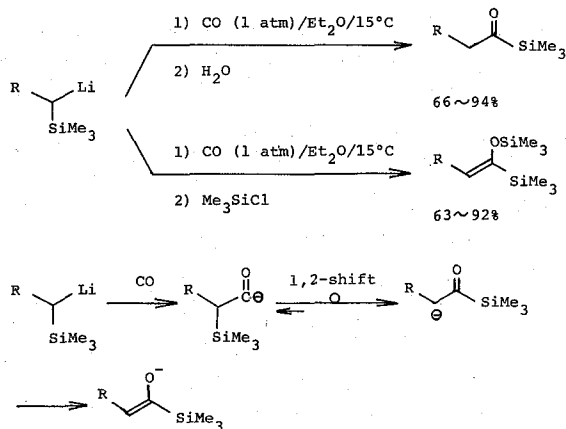
Scheme 31

by quenching the reaction mixture with water or chlorotrimethylsilane, respectively (Scheme 31).[36] The reaction involves 1, 2-silicon shift after CO insertion to anionic carbon-lithium bond, resulting in an introduction of CO into carbon-silicon bond eventually. The reaction proceeds as well with α-silylallylsilanes (Scheme 32).[37] Similar CO insertion is also known for the compounds having thorium or zirconium in place of lithium.[38]

$$
\begin{array}{c}
\text{1) n-BuLi/THF/TMEDA} \\
\hline
\text{2) CO (1 atm), 15°C} \\
\text{3) Me}_3\text{SiCl}
\end{array}
$$

79% (E/Z=95/5)

Scheme 32

6. ORGANOTIN(IV) COMPOUNDS

Tetraphenyltin reacted with CO in acetic acid in the presence of a stoicheiometric amount of palladium(II) chloride to afford benzoic acid as in the case of tetraphenyllead (Scheme 33).[5] By use of a catalytic amount of rhodium(III) chloride tetra-

$$
\text{Ph}_4\text{Sn}
\begin{array}{c}
\text{CO (1 atm)} \\
\xrightarrow{\hspace{2cm}} \text{PhCO}_2\text{H} \\
\text{PdCl}_2 \\
\text{AcOH, 25°C} \quad 25\% \\
\\
\text{CO (4 atm)} \\
\xrightarrow{\hspace{2cm}} \text{PhCOPh} \\
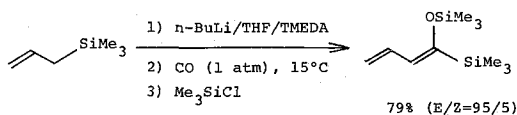\text{RhCl}_3 \cdot 3\text{H}_2\text{O} \\
\text{MeCN, 100°C} \quad 7\%
\end{array}
$$

Scheme 33
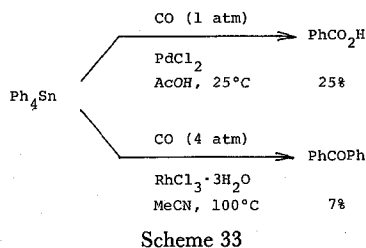
phenyltin afforded only benzophenone in low yield.[6] Although palladium-catalyzed cross-coupling of various organic halides with organotin compounds in the presence of CO has been developed for the synthesis of unsymmetrical ketones, the reaction seems to be out of the scope of this review as this has been explained by the mechanism involving oxidative addition of organic halides to palladium followed by CO insertion to carbon-palladium bond to produce acylpalladium(II) species which react with tin compound via transmetallation.[39, 40]

7. ORGANOLEAD(IV) COMPOUNDS

Phenyllead(IV) triacetate reacted with CO in methanol under very severe conditions (220 atm CO, 100°C, 18 h) to give methyl benzoate and benzoic acid.[22] In the presence of palladium(II) salt the reaction proceeded much smoothly. Thus, tetraphenyllead reacted with 1 atm of CO in acetic acid at 25°C to afford benzoic acid (34%) if a stoicheiometric amount of palladium(II) chloride to the lead compound was added (Scheme 34).[5] The reaction seems to proceed via lead-palladium transmetallation, but the details are not known at all. When rhodium(III) chloride was used as a catalyst tetraphenyllead gave only benzophenone in 9% yield.[6] No further studies seem to have appeared so far.

$$PhPb(OAc)_3 \xrightarrow[\text{MeOH, 100°C}]{\text{CO(220 atm)}} PhCO_2H + PhCO_2Me$$
$$35\% \quad 19\%$$

$$Ph_4Pb$$
$$\xrightarrow[\substack{\text{PdCl}_2 \\ \text{AcOH, 25°C}}]{\text{CO(1 atm)}} \begin{array}{c} PhCO_2H \\ 34\% \end{array}$$

$$\xrightarrow[\substack{\text{RhCl}_3 \cdot 3H_2O \\ \text{MeCN, 100°C}}]{\text{CO(4 atm)}} \begin{array}{c} PhCOPh \\ 9\% \end{array}$$

Scheme 34

8. ORGANOTELLURIUM(II) AND (IV) COMPOUNDS

Organotellurium(II) and (IV) compounds such as (Z)-phenyl styryl telluride, hexyl phenyl telluride, diphenyltellurium dichloride, and bis(4-methoxyphenyl)-tellurium dichloride did not react at all with 100 atm of CO at 100°C.[41] However, in the presence of palladium(II) chloride or lithium chloropalladate(II) they reacted smoothly with CO in acetonitrile, THF, or N, N-dimethylformamide as the solvent to give the corresponding carboxylic acid. Thus, treatment of (Z)-phenyl styryl telluride with atmospheric pressure of CO and at room temperature for 1.5 h in the presence of stoicheiometric amount of lithium chloropalladate(II) afforded cis- and trans-cinnamic acid in high yields (trans rich) together with benzoic acid (Scheme 35).[41]

$$PhC\equiv CH \xrightarrow{[PhTeH]} \underset{H}{\overset{Ph}{>}}C=C\underset{H}{\overset{TePh}{<}} \xrightarrow[\substack{\text{PdCl}_2/\text{LiCl} \\ \text{MeCN, r.t.}}]{\text{CO (1 atm)}} \xrightarrow[\substack{\text{2) CH}_2\text{N}_2}]{1) H_3O^+}$$

$$\underset{H}{\overset{Ph}{>}}C=C\underset{H}{\overset{CO_2Me}{<}} + \underset{H}{\overset{Ph}{>}}C=C\underset{CO_2Me}{\overset{H}{<}} + PhCO_2Me$$

$$28\sim32\% \qquad 52\sim55\% \qquad 8\sim10\%$$

Scheme 35

Acids were identified as their methyl esters. Interestingly, when the reaction was carried out at a higher pressure of CO, the cis-isomer became the major product irrespective of the reaction time and the presure (5~50 atm). For example, at 5, 20, and 50 atm of CO the product yields of cis- and trans-isomer were 34 and 21%, 46 and 22%, and 69 and 16%, respectively, the yield of benzoic acid being slightly lower and nearly constant (4–7%). It was revealed in the reactions under 1 atm of CO that the product ratio of cis- and trans-isomer depended profoundly on the kind of palladium(II) salt, trans- and cis-isomer being obtained almost selectively by using palladium(II) chloride and acetate, respectively.[42]

Similar treatment of diphenyltellurium dichloride and bis(4-methoxyphenyl)-tellurium dichloride with CO afforded the corresponding carboxylic acids together with biaryls, at higher pressure of CO resulting in an increase in the yield of carboxylic acid by suppressing the biaryl formation (Scheme 36).

It has been proposed that the reaction may proceed via the migration of R moiety

Scheme 36

from tellurium to palladium (transmetallation) in complexes such as $(R_2Te)_2PdCl_2$ and/or $[(R_2Te)PdCl_2]_2$ to give a reactive organopalladium species followed by CO insertion to carbon-palladium bond and hydrolysis.

The reaction could not be applied to the corresponding organo-sulfur and -selenium compounds under similar conditions, but it was recently clarified that small amounts of cinnamic acids and benzoic acid were formed from the reaction of (Z)-phenyl styryl selenide with 1 atm of CO when palladium(II) acetate was employed.[42]

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