

## Reactions of $\text{PhCOPdX(PPh}_3)_2$ ( $\text{X} = \text{I, Cl}$ ) with alkylmetals under carbon monoxide; formation of $\alpha$ -diketones and $\alpha$ -hydroxyketones under stoichiometric and catalytic conditions

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### Abstract

The reactions of  $\text{PhCOPdX(PPh}_3)_2$  (Ia:  $\text{X} = \text{I}$ ; Ib:  $\text{X} = \text{Cl}$ ) with alkylmetals under carbon monoxide have been investigated. The reactivity of ethylmetals toward Ia was found to decrease in the order:  $\text{Et}_2\text{M}$  ( $\text{M} = \text{Zn, Cd, Hg}$ )  $\sim$   $\text{EtZnCl}$   $\sim$   $\text{EtCu}$   $>$   $\text{EtMgBr}$   $\sim$   $\text{EtMnI}$   $\sim$   $\text{Et}_3\text{Al}$   $>$   $\text{Et}_2\text{AlCl}$   $>$   $\text{Et}_3\text{B}$   $\sim$   $\text{Et}_4\text{Sn}$  (no reaction). In these reactions, the simple coupling product,  $\text{PhCOEt}$  (II) and/or the carbonylative coupling products IIIa–IIIc (IIIa:  $\text{PhCOCOEt}$ ; IIIb:  $\text{PhCEt(OH)COEt}$ ; IIIc:  $\text{PhCOCeEt}_2(\text{OH})$ ) were formed depending on the nature of the ethylmetal.  $\text{Et}_2\text{Hg}$  and  $\text{Et}_3\text{Al}$  gave exclusively II.  $\text{EtMgBr}$ ,  $\text{EtCu}$ , and  $\text{EtZnCl}$  gave both of II and III.  $\text{EtMnI}$  and  $\text{Et}_2\text{M}$  ( $\text{M} = \text{Zn, Cd}$ ) selectively gave III. The use of  $\text{Ar}_2\text{Zn}$  ( $\text{Ar} = \text{Ph, } p\text{-Tol}$ ) in place of  $\text{Et}_2\text{Zn}$  gave decreased yields of the carbonylative coupling products. The palladium complex Ib showed almost the same reactivity toward  $\text{Et}_2\text{Zn}$  as Ia. Further to this palladium-catalyzed carbonylation reactions of  $\text{PhCOCl}$  with alkylmetals were examined. The reaction with  $\text{Et}_2\text{Zn}$  catalyzed by  $\text{PdCl}_2(\text{PR}_3)_2$  ( $\text{R} = \text{Ph, } p\text{-FC}_6\text{H}_4$ ) afforded III (mainly IIIb and IIIc, about 200%/Pd). The combination of  $\text{Pd(PPh}_3)_4$  and  $\text{Et}_3\text{Al}$  more effectively afforded III (mainly acyloin-type reduced products, about 900%/Pd).

### Introduction

Palladium-catalyzed coupling of acyl halides with organometallic reagents of Sn, Zn, and Al has been one of the important methods for ketone synthesis [1–6]. In addition, some carbonylative coupling reactions of organic halides with organometallics under carbon monoxide pressure are also available now [7]. In these reactions an acylpalladium species is generally presumed to be formed as a key intermediate, but its reactivity toward organometallics, in particular under carbon monoxide, has

Table 1

Reactions of  $\text{PhCOPdI}(\text{PPh}_3)_2$  (Ia) with ethylmetals under carbon monoxide <sup>a</sup>

| Entry | Ethylmetal<br>(EtM)             | Recovered<br>Ia <sup>b</sup> (%) | Yield <sup>c</sup> (%) |          |                                               |
|-------|---------------------------------|----------------------------------|------------------------|----------|-----------------------------------------------|
|       |                                 |                                  | PhCOEt                 | PhCOCOEt | PhCEt(OH)COEt<br>+ PhCOCeEt <sub>2</sub> (OH) |
| 1     | Et <sub>4</sub> Sn              | 99                               | 0                      | 0        | 0                                             |
| 2     | Et <sub>3</sub> B               | 99                               | 0                      | 0        | 0                                             |
| 3     | Et <sub>2</sub> AlCl            | 86                               | 1                      | 0        | 0                                             |
| 4     | Et <sub>3</sub> Al              | 82                               | 15                     | 0        | 0                                             |
| 5     | EtMnI <sup>d</sup>              | 70                               | trace                  | 3        | trace                                         |
| 6     | EtMgBr                          | 67                               | 8                      | 5        | trace                                         |
| 7     | EtCu <sup>d</sup>               | 0                                | 21                     | 12       | 17                                            |
| 8     | EtZnCl <sup>d</sup>             | 0                                | 56                     | 0        | 21                                            |
| 9     | Et <sub>2</sub> Zn              | 0                                | 9                      | 22       | 6 <sup>e</sup>                                |
| 10    | Et <sub>2</sub> Zn <sup>d</sup> | 0                                | 4                      | 7        | 68                                            |
| 11    | Et <sub>2</sub> Cd <sup>d</sup> | 0                                | 2                      | 8        | 71                                            |
| 12    | Et <sub>2</sub> Hg <sup>d</sup> | 0                                | 91                     | 0        | 0                                             |

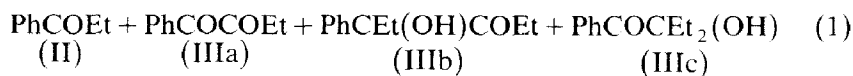
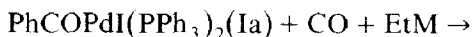
<sup>a</sup> Reaction conditions: Ia 0.05 mmol, ethylmetal 0.1 mmol, THF 2.5 ml (THF/hexane (v/v 24/1) 2.5 ml for entries 2, 3, 4, and 9; Et<sub>2</sub>O 2.5 ml for entry 5), CO 30 atm (at -50 °C), room temperature 2 h. <sup>b</sup> Estimated by IR. <sup>c</sup> Yield based on charged Ia. <sup>d</sup> The reaction was effected in the presence of 0.1 mmol MgBrI (entry 5 and 7), 0.1 mmol MgClBr (entry 8) or 0.2 mmol MgClBr (entries 10, 11, and 12) in situ generated during the preparation of the ethylmetal reagents. <sup>e</sup> PhCH(OH)COEt and PhCOCHEt(OH) were also formed (23%).

not been extensively investigated. We have already reported on the reactions of  $\text{PhCOPdX}(\text{PPh}_3)_2$  (X = I, ClO<sub>4</sub>) with alcohols under carbon monoxide in relation to the mechanism of palladium-catalyzed double carbonylations of aryl halides which yield  $\alpha$ -keto esters [8,9]. We have extended our study to the reactions of  $\text{PhCOPdX}(\text{PPh}_3)_2$  (Ia: X = I; Ib: X = Cl) with various alkylmetals under carbon monoxide, and have found that  $\alpha$ -diketones and further alkylated products ( $\alpha$ -hydroxy ketones) are formed in some cases. Attempts to effect the carbonylative coupling of PhCOCl with alkylmetals catalytically by palladium complexes are also described.

## Results and discussion

### Reactions of $\text{PhCOPdI}(\text{PPh}_3)_2$ (Ia) with ethylmetal reagents under carbon monoxide

To examine the influence of metals in alkylmetal reagents, Ia was allowed to react with various ethylmetals under carbon monoxide (35 atm) at room temperature (Table 1). The simple coupling product II, and carbonylative coupling products, PhCOCOEt (IIIa), PhCEt(OH)COEt (IIIb), and PhCOCeEt<sub>2</sub>(OH) (IIIc) were formed (eq. 1). In some cases benzaldehyde was also formed in small amounts

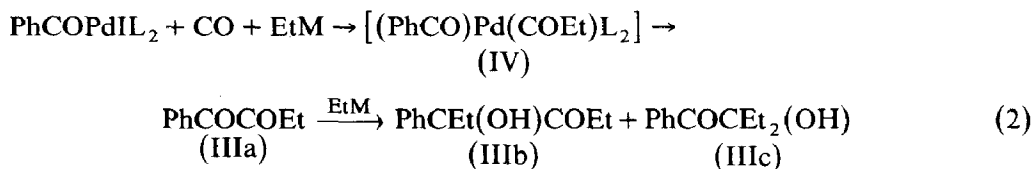


(EtM = ethylmetal)

(< 2%). The product distribution and the reaction rate (consumption of Ia) varied significantly depending on the ethylmetal used. Thus, the ethyl derivatives of Sn, B,

Al, Mn, and Mg did not show high reactivity under the present conditions. On the other hand, the reaction with  $\text{Et}_2\text{Hg}$  was rapid, but selective formation of propiophenone resulted. Of the ethylmetals examined, only those of Cu, Zn, and Cd gave carbonylative coupling products, III, in appreciable amounts. In particular, the reaction with  $\text{Et}_2\text{Zn}$  or  $\text{Et}_2\text{Cd}$  in the presence of a magnesium salt \* was most selective to the carbonylative coupling, though the main product was not IIIa, but IIIb and IIIc. Addition of the magnesium salt promotes the addition of  $\text{Et}_2\text{Zn}$  to ketones as was previously suggested [10].

On the basis of studies previously published [11–16], the formation of III is presumably rationalized by the reaction sequence which involves (benzoyl)(propionyl)palladium species (IV) and its reductive elimination, as outlined in eq. 2.



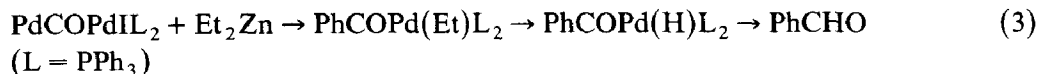
(L =  $\text{PPh}_3$ , EtM = ethylmetal)

After reaction IR spectrum of each mixture showed absorption bands at 1849, 1868, 1894, and  $2024\text{ cm}^{-1}$ . The absorption at  $1849\text{ cm}^{-1}$  is presumably due to the bridging carbonyl of  $\text{Pd}_3(\text{CO})_3(\text{PPh}_3)_3$  [17]. The assignment of the other bands is ambiguous, but these are also thought to arise from mono- or poly-nuclear carbonylpalladium(0) species. Accordingly, when benzoyl chloride was added, these bands disappeared and a new band ascribable to  $\text{PhCOPdCl}(\text{PPh}_3)_2$  (Ib) appeared at  $1646\text{ cm}^{-1}$ . These observations suggest the possibility to effect the carbonylative coupling of benzoyl chloride with organometallic reagents using palladium complexes as catalysts (vide infra).

*Reactions of  $\text{PhCOPdX}(\text{PPh}_3)_2$  ( $X = \text{I}, \text{Cl}$ ) with diorganozinc reagents and the effects of the reaction conditions*

Since  $\text{Et}_2\text{Zn}$  afforded good yields of the carbonylative coupling products III, factors which may have affected the reaction of diorganozincs were examined. The results are summarized in Table 2.

In the reaction of Ia with  $\text{Et}_2\text{Zn}$ , a decrease in the carbon monoxide pressure from 30 to 10 atm did not cause much difference. But the content of benzaldehyde increased with further decrease in CO pressure, and under nitrogen, benzaldehyde was predominantly formed. Its formation is presumably due to the reaction of Ia with  $\text{Et}_2\text{Zn}$  to give an (ethyl)(benzoyl)palladium intermediate, that undergoes  $\beta$ -hydride abstraction, with subsequent reductive elimination of benzaldehyde from the resulting (hydrido)(benzoyl)palladium species as outlined in eq. 3.



In a previous paper on the mechanism of the double carbonylation, we examined the reaction of Ia with alcohols in the presence of triethylamine, and reported that

\* The magnesium salt was generated in situ during the preparation of the ethylmetal reagents using  $\text{EtMgBr}$  and zinc or cadmium chloride salts. Use of salt-free  $\text{Et}_2\text{Zn}$  in the presence of added  $\text{MgBr}_2$  gave the same result.

Table 2

Reactions of  $\text{PhCOPdX(PPh}_3)_2$  (Ia:  $\text{X} = \text{I}$ ; Ib:  $\text{X} = \text{Cl}$ ) with  $\text{R}_2\text{Zn}$  ( $\text{R} = \text{Et, Ph, } p\text{-Tol}$ ) under carbon monoxide <sup>a</sup>

| Entry | Pd complex | R             | P(CO)<br>(atm) | Additive<br>(mmol)      | Yield <sup>b</sup> (%) |                 |         |                                           |
|-------|------------|---------------|----------------|-------------------------|------------------------|-----------------|---------|-------------------------------------------|
|       |            |               |                |                         | PhCHO                  | PhCOR           | PhCOCOR | PhCR(OH)COR +<br>PhCOCR <sub>2</sub> (OH) |
| 10    | Ia         | Et            | 30             | —                       | trace                  | 4               | 7       | 68                                        |
| 13    | Ia         | Et            | 10             | —                       | 3                      | 5               | 11      | 62                                        |
| 14    | Ia         | Et            | 1              | —                       | 21                     | 6               | 16      | 24                                        |
| 15    | Ia         | Et            | 0 <sup>c</sup> | —                       | 63                     | 8               | 0       | 0                                         |
| 16    | Ia         | Et            | 30             | $\text{PPh}_3$ (0.4)    | 2                      | 5               | 5       | 81                                        |
| 17    | Ia         | Et            | 30             | $\text{P(OMe)}_3$ (0.2) | 0                      | 1               | 14      | 66                                        |
| 18    | Ia         | Ph            | 30             | —                       | 0                      | 58              | 40      | trace                                     |
| 19    | Ia         | <i>p</i> -Tol | 30             | —                       | 0                      | 54 <sup>d</sup> | 31      | trace                                     |
| 20    | Ib         | Et            | 30             | —                       | 3                      | 9               | 8       | 61                                        |

<sup>a</sup> Reaction conditions were the same as those for entry 10; see footnotes to Table 1. <sup>b</sup> Yield based on carbonyl of Ia or Ib. <sup>c</sup> Carried out under nitrogen. <sup>d</sup> (*p*-Tol)<sub>2</sub>CO was also formed (0.005 mmol).

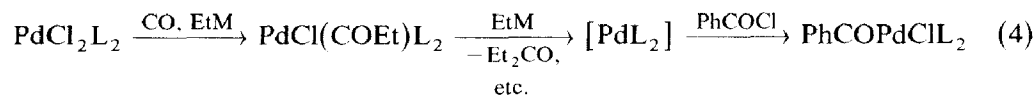
the addition of extra  $\text{PPh}_3$  enhanced the selectivity to the carbonylated products, e.g.  $\alpha$ -keto esters (vs. simple esters) at the expense of the reaction rate [9]. However, in the present reaction, the favorable effect by the extra  $\text{PPh}_3$  for the formation of III was only marginal. On the other hand, the addition of  $\text{P(OMe)}_3$  seemed to suppress the formation of II and doubled the relative amount of IIIa, though there is no clear reason for this.

When  $\text{Et}_2\text{Zn}$  was replaced with  $\text{Ph}_2\text{Zn}$  or  $(p\text{-Tol})_2\text{Zn}$  in the reaction with Ia, a large amount of the simple coupling product (ketone) was formed, and the amounts of carbonylative coupling products decreased. In addition,  $\alpha$ -diketones were almost the sole carbonylative coupling product, along with traces of arylated products. This is probably due to the weak nucleophilicity of the diarylzinc reagents.

In the reaction of  $\text{PhCOPdX(PPh}_3)_2$  with methanol in the presence of triethylamine, the product distribution ( $\text{PhCOCOOME}$  vs.  $\text{PhCOOME}$ ), has been found to depend significantly on the identity of X (Cl, I) [18]. However, in the present reaction, Ib gave nearly the same distribution as Ia.

#### *Attempted synthesis of $\alpha$ -diketone derivatives via catalytic carbonylative coupling of PhCOCl with ethylmetals*

The palladium complexes such as  $\text{PdCl}_2(\text{PR}_3)_2$  when treated with carbon monoxide, ethylmetals, and  $\text{PhCOCl}$ , are expected to be transformed into  $\text{PhCOPdCl(PR}_3)_2$  via the reaction given (eq. 4). In addition, we have learned that the complexes Ia and Ib react with  $\text{Et}_2\text{Zn}$  and carbon monoxide to yield



( $\text{L} = \text{PR}_3$ ;  $\text{EtM} = \text{ethylmetal}$ )

the carbonylative coupling products ( $\alpha$ -diketone derivatives) and palladium(0) species. The latter was readily converted back to Ib when treated with  $\text{PhCOCl}$ . These considerations and results combined led us to examine the catalytic synthesis

Table 3

Reactions of  $\text{PhCOCl}$  with  $\text{R}_2\text{Zn}$  ( $\text{R} = \text{Et}, \text{Ph}, p\text{-Tol}$ ) under carbon monoxide in the presence of palladium complexes <sup>a</sup>

| Entry | R             | Pd complex                                             | Yield <sup>b</sup> (%) |                       |             |                                        |
|-------|---------------|--------------------------------------------------------|------------------------|-----------------------|-------------|----------------------------------------|
|       |               |                                                        | PhCHO                  | PhCOR                 | PhCOCOR     | PhCR(OH)COR + PhCOCR <sub>2</sub> (OH) |
| 21    | Et            | $\text{PdCl}_2(\text{PCy}_3)_2$ <sup>c</sup>           | 27 (3)                 | 753 (75)              | < 5 (< 0.5) | 6 (1)                                  |
| 22    | Et            | $\text{PdCl}_2(\text{PMe}_3)_2$                        | 0 (0)                  | 993 (99)              | 0 (0)       | 0 (0)                                  |
| 23    | Et            | $\text{PdCl}_2(\text{PhCN})_2$                         | 0 (0)                  | 28 (3) <sup>e</sup>   | 0 (0)       | 0 (0)                                  |
| 24    | Et            | $\text{PdCl}_2(\text{PPh}_3)_2$                        | 74 (7)                 | 232 (23)              | 24 (2)      | 171 (17)                               |
| 25    | Et            | $\text{PdCl}_2[\text{P}(p\text{-FC}_6\text{H}_4)_3]_2$ | 77 (8)                 | 145 (15)              | 11 (1)      | 196 (20)                               |
| 26    | Et            | $\text{PdCl}_2(\text{dppb})$ <sup>d</sup>              | 17 (2)                 | 511 (51)              | 6 (1)       | 72 (7)                                 |
| 27    | Ph            | $\text{PdCl}_2(\text{PPh}_3)_2$                        | 0 (0)                  | 732 (73)              | 56 (6)      | < 5 (< 0.5)                            |
| 28    | <i>p</i> -Tol | $\text{PdCl}_2(\text{PPh}_3)_2$                        | 0 (0)                  | 479 (48) <sup>f</sup> | 15 (2)      | < 5 (< 0.5)                            |

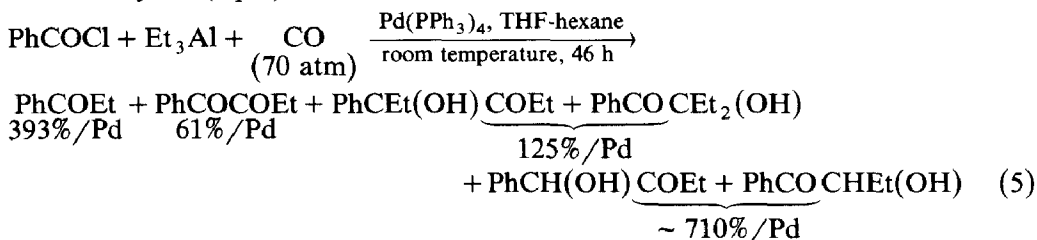
<sup>a</sup> Reaction conditions:  $\text{PhCOCl}$  0.5 mmol,  $\text{R}_2\text{Zn}$  1 mmol,  $\text{MgClBr}$  2 mmol, Pd complex 0.05 mmol, THF 20 ml, CO 30 atm, room temperature 16 h. <sup>b</sup> Yield based on the Pd complex. Figures in parentheses are yields based on charged  $\text{PhCOCl}$ . <sup>c</sup> Dichlorobis(tricyclohexylphosphine)palladium.

<sup>d</sup> Dichloro[1,4-bis(diphenylphosphino)butane]palladium. <sup>e</sup>  $\text{PhCO}_2(\text{CH}_2)_4\text{Cl}$  was also formed (22%/PhCOCl). <sup>f</sup> (*p*-Tol)<sub>2</sub>CO was also formed (0.12 mmol).

of  $\alpha$ -diketone derivatives using  $\text{PdCl}_2(\text{PR}_3)_2$  as the catalyst. The results are summarized in Table 3.

The outcome of the catalyzed reactions of  $\text{PhCOCl}$  with  $\text{Et}_2\text{Zn}$  under carbon monoxide was significantly dependent on the nature of phosphine ligand of the catalyst. Complexes of strongly-bound phosphines such as  $\text{P}(\text{cyclo-C}_6\text{H}_{11})_3$ ,  $\text{PMe}_3$ , and  $\text{dppb}$  were better catalysts for simple coupling (formation of ketone), but not for the carbonylative coupling. The phosphine-free complex,  $\text{PdCl}_2(\text{PhCN})_2$ , showed no activity for carbonylative coupling.  $\text{PPh}_3$  and  $\text{P}(p\text{-FC}_6\text{H}_4)_3$ , the coordination of which to palladium is not too strong or too weak, were found to be the best ligands in terms of the selectivity, and the  $\alpha$ -diketone derivatives were formed in about 200%/Pd combined yield. The  $\text{PPh}_3$  complex, when used in the reaction with  $\text{Ph}_2\text{Zn}$  or (*p*-Tol)<sub>2</sub>Zn, promoted simple coupling, but not carbonylative coupling.

Although the formation of  $\alpha$ -diketone derivatives from  $\text{PhCOCl}$ ,  $\text{Et}_2\text{Zn}$ , and carbon monoxide proceeded catalytically with respect to palladium, the efficiency was not satisfactory. Hence, we further examined the carbonylative coupling using other ethylmetal reagents. As a result, it turned out that the reaction with  $\text{Et}_3\text{Al}$  in the presence of  $\text{Pd}(\text{PPh}_3)_4$  afforded the  $\alpha$ -diketone derivatives in about 900%/Pd combined yield (eq. 5) \*.



\* The acyloin-type reduced products were readily converted into the  $\alpha$ -diketone when oxidized with  $\text{Cu}(\text{OAc})_2$ ; see Experimental.

Complex Ib is probably involved in the catalysis. However, the analogous complex Ia did not undergo the carbonylative coupling when treated with  $\text{Et}_3\text{Al}$  under carbon monoxide (Table 1). These somewhat puzzling results may have arisen from the difference in conditions; the catalytic reaction was run using 0.4 M  $\text{Et}_3\text{Al}$  in THF/hexane (v/v 3/2) under 70 atm of carbon monoxide while the stoichiometric reaction was carried out using 0.04 M  $\text{Et}_3\text{Al}$  in THF/hexane (v/v 24/1) under 30 atm of carbon monoxide. The concentration of  $\text{Et}_3\text{Al}$  and the degree of its complexation with the various solvents are known to affect the monomer–dimer equilibrium [19]. An increase in the carbon monoxide pressure promotes the coordination of carbon monoxide to the palladium center. Accordingly, it is possible that the use of different conditions (variation of the concentration, the solvent, and the pressure) caused the change in reactivity of  $\text{Et}_3\text{Al}$  and the palladium complex.

Although the catalytic efficiency is low, and the mechanistic details have not been elucidated, the results reported herein should open up the field of the carbonylative coupling of acid halides with carbon nucleophiles.

## Experimental

Infrared spectra were recorded on a Jasco A-302 spectrometer. Mass spectral determinations were made by use of a Shimadzu QP-1000 GC-MS spectrometer (70 eV).

Solvents and organic halides were dried by standard methods and distilled under nitrogen or in vacuo.  $\text{Et}_4\text{Sn}$  was prepared by a published procedure [20]. Hexane solutions (1 M) of  $\text{Et}_3\text{B}$ ,  $\text{Et}_2\text{AlCl}$ ,  $\text{Et}_3\text{Al}$ , and salt-free  $\text{Et}_2\text{Zn}$  were used as purchased. Other alkylmetals were prepared by the reaction of Grignard reagents with suitable inorganic salts in THF and were used without removal of the magnesium salts.  $\text{PhCOPdI}(\text{PPh}_3)_2$  [21] and  $\text{PhCOPdCl}(\text{PPh}_3)_2$  [22] were prepared as reported.

All the reaction products were identified by the comparison of GC retention times with those of authentic samples and/or by the analysis of the MS fragmentation patterns of the product. The amount of product in each case was estimated by GC using internal standards.

The spectral data of  $\text{PhCEt}(\text{OH})\text{COEt}$ , which was prepared by the reaction of  $\text{PhCOCOEt}$  with  $\text{Et}_2\text{Zn}$ , are as follows;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 1.88 (t,  $J$  7.2 Hz,  $\text{CH}_3$ ), 1.93 (t,  $J$  7.2 Hz,  $\text{CH}_3$ ), 2.21 (q,  $J$  7.2 Hz,  $\text{CH}_2$ ), 2.39 (q,  $J$  7.2 Hz,  $\text{CH}_2$ ), 4.54 (s, OH), 7.24–7.64 (m,  $\text{C}_6\text{H}_5$ ) ppm; IR (neat): 1706 ( $\text{C}=\text{O}$ ), 3490 (OH)  $\text{cm}^{-1}$ ; MS  $m/e$  (intensity): 57 (100), 135 (65).

*Reactions of  $\text{PhCOPdX}(\text{PPh}_3)_2$  (Ia:  $X = \text{I}$ ; Ib:  $X = \text{Cl}$ ) with alkylmetals under carbon monoxide (Tables 1 and 2)*

A typical procedure is as follows; to complex Ia (0.05 mmol) placed in an autoclave equipped with a glass insert, was added under nitrogen THF (2 ml) and CO at a pressure of 20 atm was introduced. After the autoclave had been cooled at  $-50^\circ\text{C}$ , the carbon monoxide was discharged. A THF solution of  $\text{Et}_2\text{Zn}$  (0.2 M, 0.5 ml) containing  $\text{MgClBr}$  (about 0.2 mmol) was added under a stream of CO and 30 atm of CO was introduced. The cooling bath was removed, and the mixture was stirred at room temperature for 2 h. After CO had been discharged, the reaction mixture was acidified with saturated aqueous solution of  $\text{NH}_4\text{Cl}$  (3 ml) and the

products were extracted with ether (30 ml). The ether layer was concentrated, and the products were analyzed by GC-MS and GC, which revealed the formation of PhCOEt (4%), PhCOCOEt (7%), and PhCET(OH)COEt + PhCOCOEt<sub>2</sub>(OH) (68%, about 6/1 mixture) with a trace amount of PhCHO.

*Reactions of PhCOCl with R<sub>2</sub>Zn (R = Et, Ph, p-Tol) under carbon monoxide in the presence of palladium complexes (Table 3)*

The procedure is similar to that described above. To a palladium catalyst (0.05 mmol) placed in an autoclave, THF (17 ml) and PhCOCl (0.5 mmol) was added at room temperature under nitrogen. After a THF solution of Et<sub>2</sub>Zn (0.33 M, 3 ml) was added at -50 °C, the mixture was stirred at room temperature for 16 h.

*Reaction of PhCOCl with Et<sub>3</sub>Al under carbon monoxide in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub>*

To Pd(PPh<sub>3</sub>)<sub>4</sub> (0.05 mmol) placed in an autoclave equipped with a glass insert, THF (3 ml), PhCOCl (1.76 mmol), and a hexane solution of Et<sub>3</sub>Al (1 M, 2 ml) were added under nitrogen at room temperature. Carbon monoxide (70 atm) was introduced, and the mixture was stirred for 46 h. After the usual work-up, the products were analyzed by GC-MS and GC, which revealed the formation of the compounds shown in eq. 5. Then, the reaction mixture was dissolved in 70% AcOH (3 ml), and Cu(OAc)<sub>2</sub> (1 mmol) was added. The resulting mixture was stirred at 100 °C for about 1 h. After further work-up, the products were analyzed to reveal almost quantitative transformation of the acyloin-type reduced products into PhCOCOEt (758%/Pd, 22%/PhCOCl).

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