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The Reactions of Carbon Monoxide and Phenols  
Promoted by Palladium Complexes

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Summary

The reaction of phenols with carbon monoxide at atmospheric pressure and room temperature in the presence of palladium chloride and a tertiary amine produces diaryl carbonates and aryl salicylates. Only diaryl carbonates are produced when palladium carbonyl chloride is substituted for palladium chloride. Reaction pathways are proposed.

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Introduction

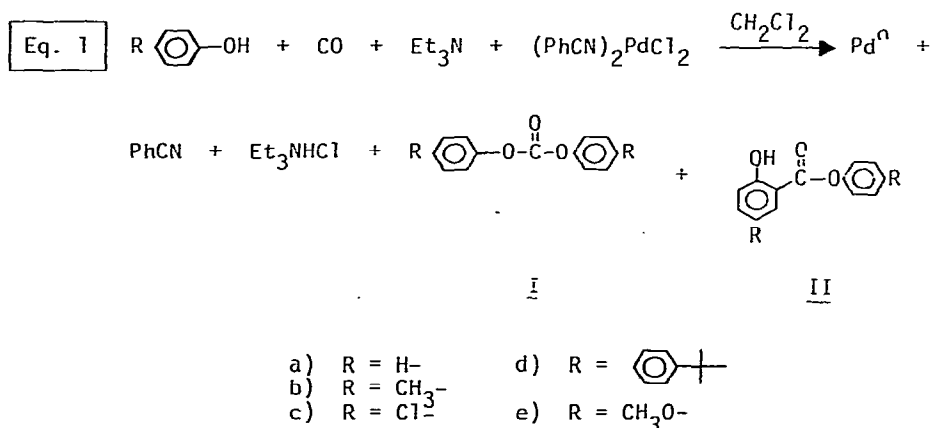
The formation of dialkyl carbonates from the reaction of alcohols and carbon monoxide has been reported to be promoted by transition metal and post transition metal compounds.<sup>1-7</sup> Diaryl carbonates have not been synthesized from phenols in analogous reactions. Evidently the lower basicities of phenols and the ease of phenol oxidation has lead to a variety of side reactions instead of carbonates.

Recently, it was reported that diphenyl carbonate was found in moderate yield from phenol and carbon monoxide in the presence of a base and a stoichiometric quantity of a Group VIIIB metal salt.<sup>8</sup>

As part of a general investigation of the carbonylation of phenols, we have studied the interaction of phenols with carbon monoxide and palladium salts under ambient conditions. The results are described below.

### Results and Discussion

Bubbling carbon monoxide through a methylene chloride solution of a phenol, a tertiary amine, and bis(benzonitrile) palladium (II) chloride resulted in the immediate deposition of metallic palladium and a mixture of carbonate I and salicylate II, Equation 1.



Para substituted phenols reacted under these conditions to produce carbonates in moderate yields and, in most cases, salicylates, Table 1. Only para-chlorophenol among the phenols tested failed to produce a salicylate.

Table 1  
Reactions of Phenols and CO in the Presence of (PhCN)<sub>2</sub>PdCl<sub>2</sub>

Substituent	% Yield <u>I</u> <sup>a</sup>	% Yield <u>II</u> <sup>b</sup>
a	49	49
b	44	55
c	67	0
d	58	32
e	32	17

<sup>a</sup>Yield based on Pd as per Scheme 2

<sup>b</sup>Yield based on Pd as per Scheme 1

Control experiments indicated that I and II did not interconvert under the reaction conditions, although I is converted to II at elevated temper-

atures.<sup>9</sup> Reactions carried out in benzene, THF, chlorobenzene, methylene chloride, or hexane as solvent resulted in similar mixtures of I and II. Employment of tertiary amines such as triethylamine, diisopropylethylamine, or 1,2,2,6,6-pentamethylpiperidine, amines which differ greatly in their ability to complex palladium, resulted in similar mixtures of products although the structurally more hindered amines invariably resulted in cleaner reaction mixtures. Finally, palladium (II) nitrate, palladium (II) acetate, bis-(benzonitrile)palladium (II) chloride, and palladium (II) chloride were equally effective palladium sources and gave similar product mixtures.

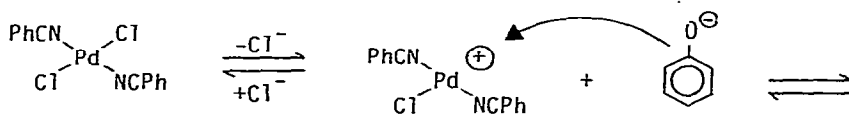
However, varying the time interval between introduction of carbon monoxide and addition of the tertiary amine had a dramatic effect on the ratio of Ia to IIa. When the amine was added first, subsequent introduction of carbon monoxide resulted in high specificity for phenyl salicylate. On the other hand, introduction of carbon monoxide first followed by the amine after one hour resulted in high specificity for carbonate. The results are summarized in Table 2.

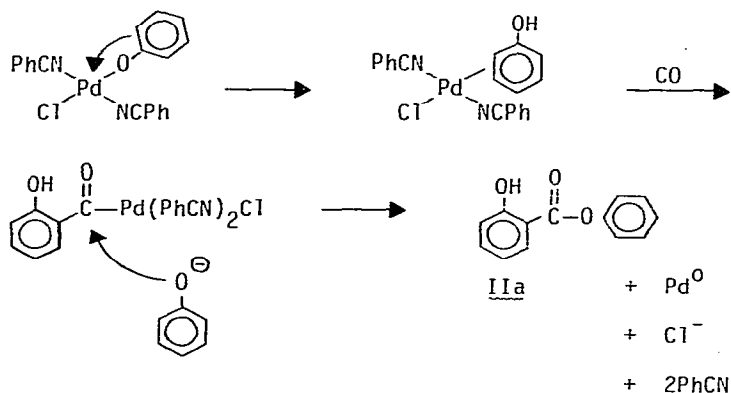
Table 2  
Effect of Pretreatment of  $(\text{PhCN})_2\text{PdCl}_2$  with CO

	Molar Ratio <u>Ia</u> / <u>IIa</u>
$\text{R}_3\text{N}$ added first	0.05
$\text{R}_3\text{N}$ added after 5 minutes	0.25
$\text{R}_3\text{N}$ added after 20 minutes	5.0
$\text{R}_3\text{N}$ added after 1 hour	>50

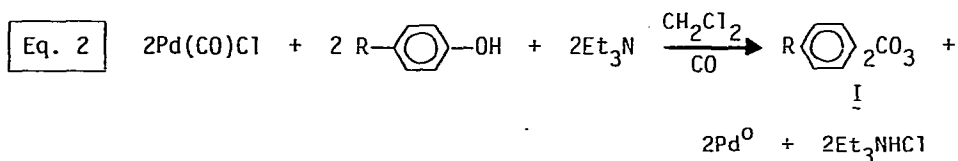
The following reaction scheme, or a similar one, could account for the salicylate products. Scheme 1 is a combination of two well-known reactions of palladium, palladation<sup>10</sup> and carbon monoxide "insertion."<sup>11</sup>

Scheme 1





Carbonate may not be formed from the palladium (II) halide, but rather from a preformed palladium carbonyl species resulting from the interaction of the palladium halide with carbon monoxide. The reaction of bis(benzonitrile) palladium (II) chloride with carbon monoxide in wet chloroform has been reported to produce a yellow powder of the composition  $\text{Pd}(\text{CO})\text{Cl}$ .<sup>12</sup> Subsequent reaction with chloride ion has been shown to generate the  $[\text{Pd}_2(\text{CO})_2\text{Cl}_4]^-$  ion.<sup>13</sup> Either of these species may be generated in the course of the reaction and could be the precursor to the observed carbonates. Both palladium compounds were prepared and allowed to react with phenols, Equation 2. In all cases, salicylates were not detected and carbonates were formed in high yields, Table 3.

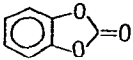
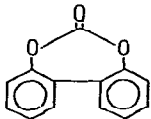


- |                          |                           |
|--------------------------|---------------------------|
| a) R = H-                | d) R =                    |
| b) R = CH <sub>3</sub> - | e) R = CH <sub>3</sub> O- |
| c) R = Cl-               |                           |

This new reaction of a palladium (I) species to form carbonates, formally a two electron change, is quite unusual, possibly involving two metal centers in the transformation. Surprisingly, although the stoichiometry of the

Table 3

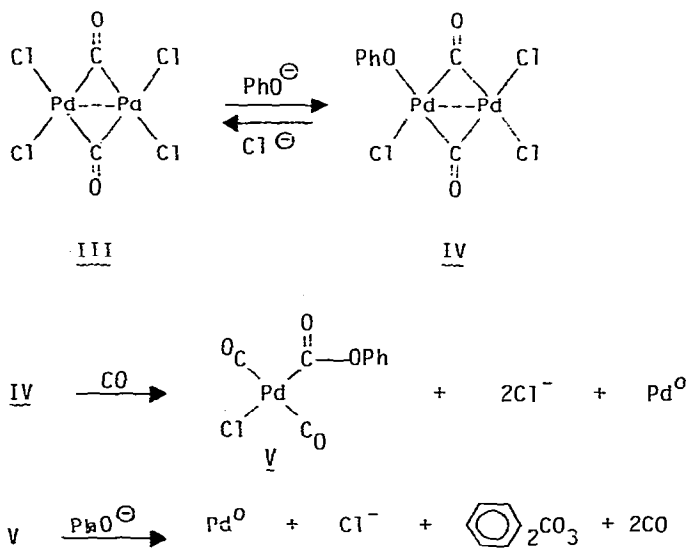
## Reactions of Phenols with Pd(CO)Cl

<u>Product</u>	<u>% Yield</u>
Ia	99
Ib	95
Ic	35
Id	90
Ie	45
	90
	75
$(\text{o-CH}_3\text{C}_6\text{H}_4)_2\text{CO}_3$	35

reaction would suggest that an excess of carbon monoxide groups were already present as ligands bound to the palladium, external carbon monoxide was found to promote the reaction. However, C<sup>13</sup> labeling of the bound carbonyl groups in III, has shown that external carbon monoxide did not end up in the products even though scrambling is fairly rapid. Finally, the reaction rate was retarded by an excess of chloride ion. With large amounts of added chloride ion, reaction times were increased from minutes to hours. A possible reaction scheme is suggested below.

Evidently in structures III and/or IV<sup>14</sup> the carbon monoxide ligand is activated toward nucleophilic attack by phenoxide. The transformation of IV to V involves an internal redox reaction promoted by carbon monoxide. Recently, structures analogous to V have been postulated as intermediates in dialkyl carbonate<sup>15, 16</sup> and oxalate<sup>17</sup> formation. An analogous phosphine complex has been isolated.<sup>18</sup>

Scheme 2



Currently we are extending this study to determine the scope and limitations of carbon monoxide activation by palladium (I) carbonyl complexes.

### Experimental

#### General

Phenol (Mallinckrodt), para-cumylphenol (Aldrich), para-methoxyphenol (Eastman), catechol (Baker) and 2,2'-biphenol (Aldrich) were used as received. Para-chlorophenol (Aldrich), para-cresol (Eastman), and ortho-cresol (Aldrich) were distilled prior to use. Triethylamine (Eastman) and N-ethyl-diisopropyl-amine (Aldrich) were used as received. 1,2,2,6,6-pentamethylpiperidine was prepared by the literature route.<sup>19</sup> Tetra-butylammonium chloride was dried in vacuo at 100°C for 48 hours before use. Bis(benzonitrile)palladium chloride (Strem), palladium acetate (Engelhard), palladium nitrate (Fisher), palladium chloride (Fisher) were used as received. Palladium carbonyl chloride,<sup>12</sup> and bis(tetrabutyl ammonium)

dicarbonyl tetrachlorodipalladite (I)<sup>13</sup> were prepared by the literature routes. All of the products were separable by gc techniques (10' x 2 mm 3% OV-17 on Gas Chrom Q) or by liquid chromatography. Products were characterized by ir, nmr, ms, and elemental analysis. Only typical examples of each reaction type are given below.

#### Carbonylation of Phenol with (PhCN)<sub>2</sub>PdCl<sub>2</sub>

A 25 ml three neck flask equipped with a stir bar, a subsurface carbon monoxide inlet tube, and an exit tube ("Standard Reaction Vessel") was charged with 1.50 g (4.0 mmol) of (PhCN)<sub>2</sub>PdCl<sub>2</sub>, 0.77 g (8.0 mmol) of phenol, and 10 ml of methylene chloride. The mixture was stirred, then slowly flushed with carbon monoxide. To this was added 1.5 g (11.6 mmol) of *i*-Pr<sub>2</sub>NEt. Immediately the solution turned black and a precipitate of palladium metal formed. After stirring at room temperature for 3 hours, the mixture was filtered. The precipitate was washed with methylene chloride, then dried in a stream of air, to yield 0.43 g (101%) of palladium metal. The filtrate was analyzed by gc and the identity of the materials determined by gc-ms. An internal yield analysis indicated the presence of 0.45 g (53%) of phenyl salicylate and 0.23 g (52%) of diphenyl carbonate. The materials were separated by liquid chromatography and their identities confirmed by ir, nmr, and ms.

#### Carbonylation of Phenol with Pd(CO)Cl

The "Standard Reaction Vessel" was charged with 0.54 g (3.2 mmol) of Pd(CO)Cl, 0.30 g (3.2 mmol) of phenol and 10 ml of methylene chloride. The mixture was saturated with carbon monoxide, then 1.00 g (6.4 mmol) of 1,2,2,6,6-pentamethylpiperidine was added. Immediately the mixture turned black and 0.33 g (97%) of metallic palladium was isolated. GC analysis of the reaction mixture showed the presence of 0.34 g (99%) of diphenyl carbonate as the only product. Extraction of the reaction mixture with aqueous acid followed by solvent removal resulted in a pale oil which was recrystallized from cyclohexane to yield white needles of diphenyl carbonate 0.27 g (82%) mp 79-80°. Lit. 78-80.5.

Acknowledgments

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