

concentrations: *p*-dimethoxybenzene (0.43 M), Pd(O<sub>2</sub>CMe)<sub>2</sub> (0.09 M), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (1.1 M).

### Conclusion

It is clear from the preceding discussions that the reaction pathways favored by electrophilic metal complexes differ significantly from those involved in reactions of electron-rich metal compounds. However, more detailed mechanistic studies are required to fully understand the reactivity profile of electrophilic metal species and how it can be influenced by the proper choice of the metal and the ligands attached to it. Apart from their fundamental scientific importance, such studies are also useful from a practical standpoint. As the rich organic chemistry of Pd(II)<sup>46</sup> and Ln(III)<sup>47</sup> (to pick two very different metals as examples) clearly indicates, electrophilic metal ions are employed in many different facets of organic synthesis. In addition, since electrophilic metal ions are less sensitive to oxidizing agents than electron-rich metal centers, it should be easier to design catalytic systems employing the former

(46) Review: ref 5. Few specific recent examples: (a) Trost, B. M. *J. Organomet. Chem.* 1986, 300, 263. (b) Hegedus, L. S.; Mulhern, T. A.; Asada, H. *J. Am. Chem. Soc.* 1986, 108, 6224.

(47) Review: Natale, N. R. *Org. Prep. Proced. Int.* 1983, 15, 387. Few specific recent examples: Bednarski, M.; Danishefsky, S. *J. Am. Chem. Soc.* 1986, 108, 7060.

species to convert hydrocarbon raw materials to valuable oxidatively functionalized organic products. This is particularly relevant to the problem of catalytic oxidative functionalization of alkanes.

Finally, while we have restricted our discussions to one class of electrophilic metal complexes, work on other types of electrophilic early transition, lanthanide, and actinide compounds has shown that they play a critical role in such important reactions as C-H<sup>3</sup> and C-C<sup>48</sup> activation and polymerization of simple olefins.<sup>49</sup>

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(48) Leading reference: (a) Reference 3a. (b) Vol'pin, M. E.; Akhrem, I. S.; Reznichenko, S. V.; Grushin, V. V. *J. Organomet. Chem.* 1987, 334, 109. See also: Crabtree, R. H.; Dion, R. P. *J. Chem. Soc., Chem. Commun.* 1984, 1260.

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## Aspects of Intermediacy of Carbalkoxymetal Complexes in CO Reactions

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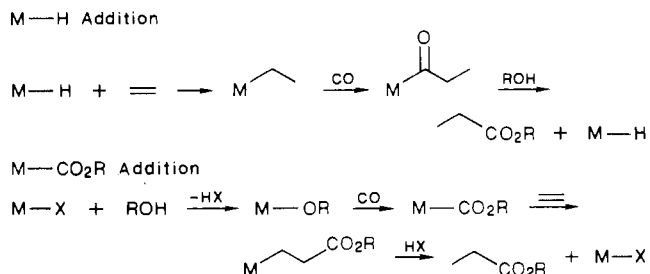
Carbonylation reactions rank among the most useful transformations homogeneously catalyzed by transition-metal complexes, forming the basis for industrial and laboratory processes currently in practice. Among these are a considerable number of reactions that lead to formation of carbalkoxy-containing organic molecules. These diverse reactions, some of which are summarized in Table I, may have as a unifying mechanistic theme the generation and controlled decomposition of a carbalkoxymetal intermediate, M-CO<sub>2</sub>R.<sup>1</sup>

In this Account, we describe mechanistic aspects of olefin carbalkoxylation, alkyl halide carbalkoxylation, carbalkoxylation of  $\pi$ -alkyl complexes, and CO hydrogenation. By utilizing model carbalkoxy complexes, the

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process	proposed key reaction
olefin carbalkoxylation	$M-CO_2R + \text{olefin} \rightarrow M-\text{CH}_2\text{CH}_2\text{CO}_2R$
RX carbonylation	$R'-M-CO_2R \rightarrow R'/CO_2R$
oxalates from alcohols	$RO_2C-M-CO_2R \rightarrow RO_2C-CO_2R$
carbonates from alcohols	$M-CO_2R + R'OH \rightarrow ROCO_2R'$
carbamates from amines	$M-CO_2R + R'NH_2 \rightarrow R'NHCO_2R$
methyl formate from CO/H <sub>2</sub>	$M-CO_2CH_3 + H_2 \rightarrow HCO_2CH_3$

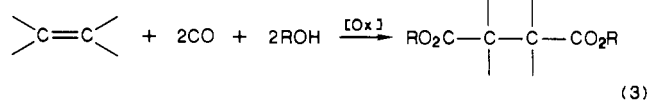
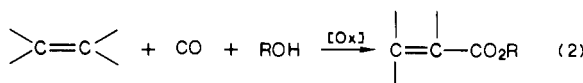
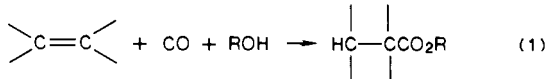
### Scheme I



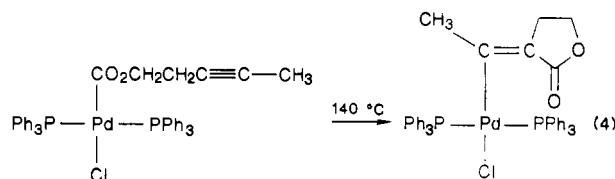
question of intermediacy of such species in those reactions is being addressed, emphasizing recent work from our laboratory.

## Olefin Carbalkoxylation

Transition-metal-catalyzed carbalkoxylation (eq 1) and oxidative carbalkoxylation (eq 2 and 3) of olefins



to esters<sup>2</sup> can in principle proceed by two main mechanisms, involving M-H or M-CO<sub>2</sub>R addition to the double bond, as proposed for the Pd-catalyzed reactions based on consideration of regioselectivity and stereochemistry of the products formed<sup>3,4</sup> (Scheme I). Supporting evidence for the feasibility of ester formation by addition of a carbalkoxy complex to an olefin included reaction of ClPd(PPh<sub>3</sub>)<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub> with olefins to yield small amounts of unsaturated esters<sup>5</sup> and carbalkoxylation of olefins with a combination of PdCl<sub>2</sub> and ClHgCO<sub>2</sub>CH<sub>3</sub>.<sup>6</sup> Intramolecular additions of carbomethoxypalladium complexes to double and triple bonds were demonstrated, the latter being a key step in Pd-catalyzed methylene lactone synthesis<sup>7</sup> (eq 4).



On the other hand, reaction of [Pt(CO<sub>2</sub>R)(PPh<sub>3</sub>)<sub>2</sub>(CO)]<sup>+</sup> with acetylenes led to products derived from decarbonylation rather than addition of the carbalkoxy ligand.<sup>8</sup>

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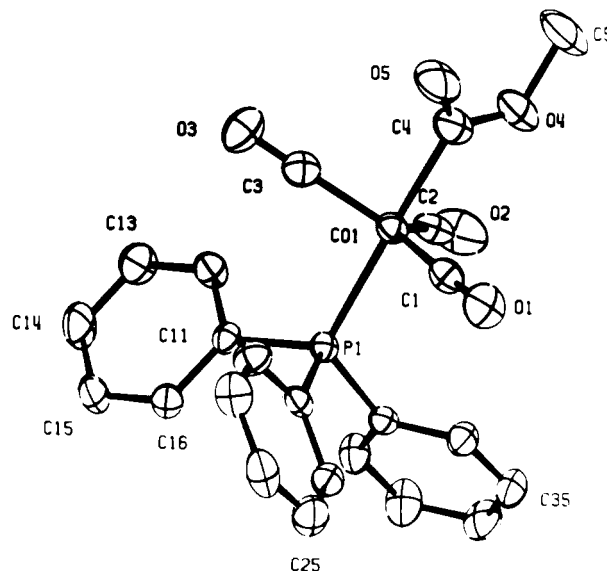
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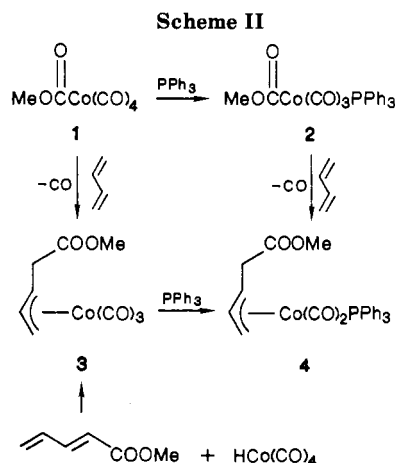
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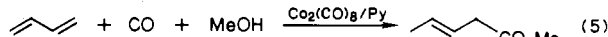
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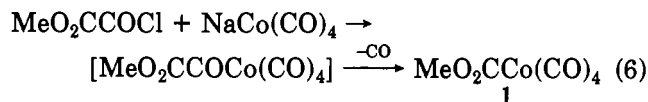
**Figure 1.** ORTEP drawing of a molecule of 2. Hydrogens have been left out for clarity. Selected bond lengths (Å) and angles (deg): Co-P, 2.232; Co-C(axial), 1.976; Co-C(equatorial), 1.786; P-C, 1.823; C=O(carbonyl), 1.138; C=O(carbomethoxy), 1.196; C-O(carbomethoxy), 1.342; CH<sub>3</sub>-O, 1.484; P<sub>1</sub>-Co-C<sub>4</sub>, 174.7; Co-C<sub>4</sub>-O<sub>4</sub>, 112.9; C<sub>4</sub>-O<sub>4</sub>-C<sub>5</sub>, 113.1.



We became interested in mechanistic aspects of olefin carbalkoxylation when studying the mechanism of the pyridine (Py)-promoted, Co<sub>2</sub>(CO)<sub>8</sub>-catalyzed carbomethoxylation of butadiene to methyl 3-pentenoate,<sup>9</sup> a potential commercial precursor to adipic acid for nylon-6,6 manufacture (eq 5).



To probe the plausibility of a route based on a carbomethoxycobalt complex we prepared 1 according to eq 6.<sup>10</sup>



The obvious route of reaction of Co(CO)<sub>4</sub><sup>-</sup> with ClCO<sub>2</sub>Me failed because of a lack of electrophilicity of the carbonyl in this acid chloride. Compound 1 is a volatile liquid that decomposes slowly at 25 °C (τ<sup>1/2</sup> ≈ 1 h) but can be converted into the more stable MeO-

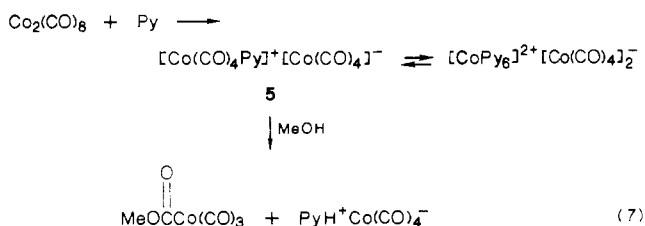
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(10) Milstein, D.; Huckaby, J. L. *J. Am. Chem. Soc.* 1982, 104, 6150.

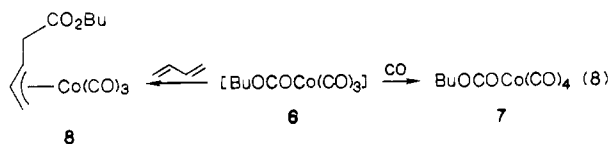
$\text{CoCo}(\text{CO})_3\text{PPh}_3$  (**2**), whose structure was determined crystallographically (Figure 1). Other routes to carbalkoxycobalt tetracarbonyl complexes have been recently reported.<sup>1m</sup> Compound **1** adds smoothly to butadiene at 25 °C to give the  $\pi$ -allylic complex **3**. Reaction of **3** with  $\text{PPh}_3$  yields **4**, which can be obtained directly by the much slower addition of **2** to butadiene. The structure of **3** can be confirmed by its independent preparation by addition of  $\text{HCo}(\text{CO})_4$  to methyl 2,4-pentadienoate (Scheme II).

These experiments directly demonstrate addition of a well-characterized carbalkoxy complex to an olefin. Carbomethoxypalladium complexes generated in situ by reaction of  $\text{ClHgCO}_2\text{Me}$  with  $\text{LiPdCl}_3$  also add to dienes, although in low yield.<sup>11</sup> In agreement with the catalytic reaction (5), **3** and **4** react rapidly with  $\text{HCo}(\text{CO})_4$  or  $\text{PyH}^+\text{Co}(\text{CO})_4^-$  [free  $\text{HCo}(\text{CO})_4$  is unlikely to be present in significant amounts in the basic reaction medium] to yield methyl 3-pentenoate. Thus, a mechanism based on *synergistic* catalysis by  $\text{MeOCO-Co}(\text{CO})_4$  and  $\text{HCo}(\text{CO})_4$ , in which the former adds to butadiene and the latter is involved in the product-forming step, seems plausible. How would a carbomethoxy complex be formed? We have proposed methanolysis of the ion pair **5**, the intermediacy of which has been invoked in the pyridine-promoted disproportionation of  $\text{Co}_2(\text{CO})_8$ <sup>12</sup> (eq 7). An analogous



reaction of  $[\text{Co}(\text{CO})_3(\text{PPh}_3)_2]^+$  is known<sup>13</sup> and reaction of  $\text{Co}_2(\text{CO})_8$  with alkoxides to yield carbalkoxycobalt complexes was reported recently.<sup>1m</sup>

Note that an *unsaturated* carbalkoxy complex is formed here. To demonstrate that addition of such a complex to butadiene is preferred over that of  $\text{PyH}^+\text{Co}(\text{CO})_4^-$ , the carbobutoxy complex **6** was generated at -40 °C from  $\text{NaCo}(\text{CO})_4$  and *n*-BuOCl. Under CO, the saturated complex **7** is formed, whereas in the presence of butadiene, instantaneous addition to form **8** takes place (eq 8). Addition of  $\text{PyH}^+\text{Co}(\text{CO})_4^-$  to butadiene

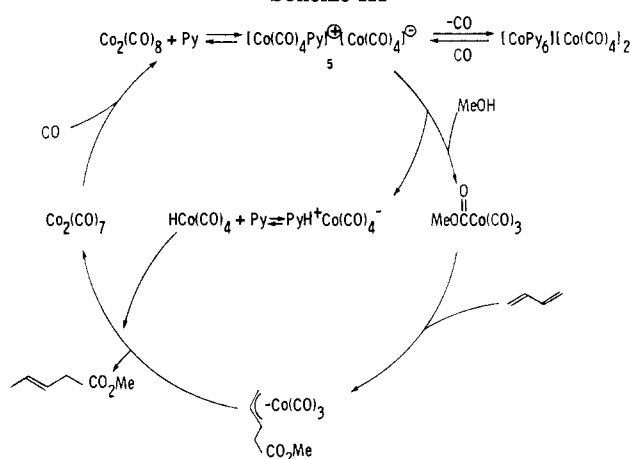


is incomplete even after 2 h at 25 °C. As expected, the rate of addition of carbalkoxy complexes to butadiene follows the trend  $[\text{BuOCOC}(\text{CO})_3] > \text{MeOCOC}(\text{CO})_4 \sim \text{BuOCOC}(\text{CO})_4 > \text{MeOCOC}(\text{CO})_3\text{PPh}_3$ , suggesting that in this process generation of a coordinatively unsaturated complex by ligand dissociation is rate determining.<sup>10</sup>

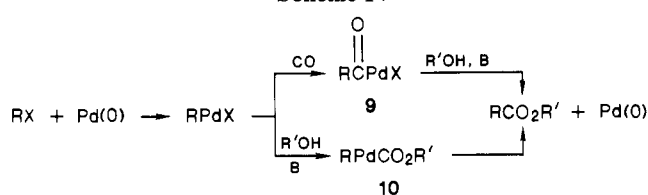
On the basis of the above observations a plausible comprehensive mechanism for reaction 5 is presented in Scheme III.

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 (13) Heiber, W.; Duchatsch, H. *Chem. Ber.* **1965**, *98*, 1744.

## Scheme III



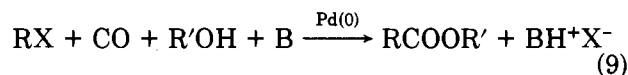
## Scheme IV



It is interesting to note that the catalytic cycle involves CO only in the final step—the low-pressure regeneration of  $\text{Co}_2(\text{CO})_8$  from  $\text{Co}_2(\text{CO})_7$ . We believe that the CO pressure requirements of the process are a result of the need to retard the facile oxidative decarbonylation process of the ion pair **5**. The reversibility of this process was recently demonstrated.<sup>14</sup>

## Carbalkoxylation of Organic Halides

A mechanistic outline for the synthetically important Pd-catalyzed carbalkoxylation of organic halides to esters<sup>15</sup> (eq 9) is presented in Scheme IV.



B = base (usually a tertiary amine)

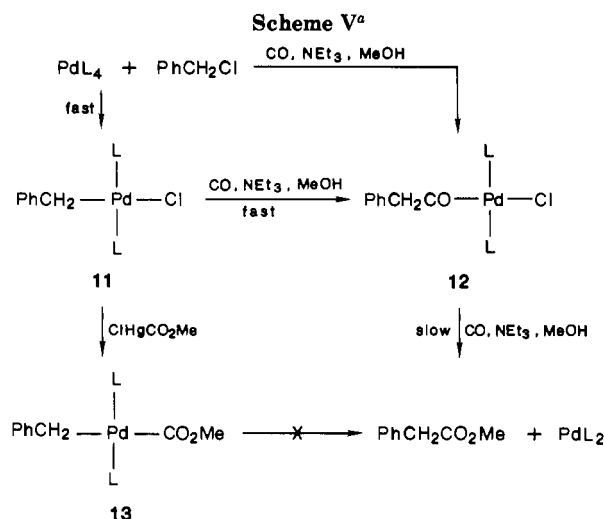
In principle, two main mechanisms are possible, both involving oxidative addition of the organic halide to  $\text{Pd}(0)$  as the first step. In the first, CO insertion into the Pd-C bond takes place to yield an acylpalladium complex **9**, which yields the ester upon base-assisted alcoholysis, whereas in the second, a carbalkoxy intermediate **10** is generated, either by CO insertion into the M-O bond or by nucleophilic attack on coordinated CO, and the product ester is formed by reductive elimination. CO insertion into  $\text{Pd-C}$  to form acylpalladium complexes in *inert solvents*<sup>15,16</sup> and their alcoholysis<sup>15,17</sup>

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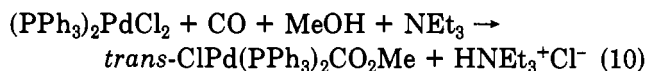
(16) (a) Kudo, K.; Sato, M.; Uchida, Y. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2823. (b) Garrou, P. E.; Heck, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 4115. (c) Sugita, M.; Minkiewicz, J. V.; Heck, R. F. *Inorg. Chem.* **1978**, *17*, 2809. (d) Stille, J. K.; Lau, K. S. Y. *J. Am. Chem. Soc.* **1976**, *98*, 5841.

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<sup>a</sup>L = PMe<sub>3</sub>. All steps are essentially irreversible.

are known, and so is formation of a carbalkoxy-palladium complex under conditions similar to those employed in the carbomethoxylation of organic halides<sup>18</sup> (eq 10).



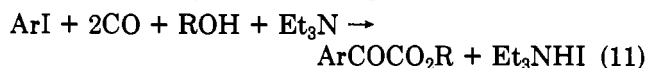
In order to gain information on the nature of the product-forming step, we wanted to render it rate determining and observe it directly. In other work, we kinetically stabilized Rh and Ir complexes toward dissociative elimination processes by use of the small, basic PMe<sub>3</sub> ligand.<sup>19</sup> Since C–C bond formation by reductive elimination from Pd(II) is preceded by phosphine dissociation<sup>20</sup> and since nucleophilic attack on an acylpalladium complex would be retarded by an increase in the electron density on the metal, we hoped that use of PMe<sub>3</sub> instead of PPh<sub>3</sub> would result in stabilization of the acylpalladium or carbomethoxypalladium complexes and allow for direct observation of the product-forming step. This was indeed the case,<sup>21</sup> as outlined in Scheme V.

Treatment of 11 with CO in NEt<sub>3</sub>–MeOH at 25 °C resulted in formation of 12 with no 13. Heating this solution at 80 °C resulted in quantitative formation of PhCH<sub>2</sub>CO<sub>2</sub>Me. The CO insertion into Pd–C is irreversible, since partial decomposition of 12 under <sup>13</sup>CO resulted in no incorporation of <sup>13</sup>CO into the recovered complex or the product ester. Complex 12 can be obtained directly from Pd(PMe<sub>3</sub>)<sub>4</sub>, benzyl chloride, and CO in methanol–NEt<sub>3</sub> at 25 °C, again with no trace of a carbomethoxy complex. Complex 13 can be prepared separately by treatment of 11 with ClHgCO<sub>2</sub>Me. It is thermally stable and does not undergo reductive elimination of PhCH<sub>2</sub>CO<sub>2</sub>Me upon heating at 80 °C. All these experiments taken together unambiguously demonstrate that the rate-determining product-forming step involves methanolysis of 12 and not reductive elimi-

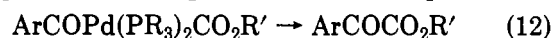
nation of a carbalkoxy complex (Scheme IV). In fact, 12 is the only Pd complex observed by <sup>31</sup>P NMR under actual catalysis conditions. Similar results are obtained when iodobenzene is used instead of benzyl chloride, indicating that the acylpalladium mechanism for alkoxycarbonylation is probably quite general. In fact, a recent study<sup>22</sup> of carbalkoxylation of aryl iodides catalyzed by PdPPh<sub>3</sub> complexes reaches a similar conclusion and provides further insight into the product-forming step, according to which the ester is formed by reductive elimination of a PhCOPd(OR)(PPh<sub>3</sub>) intermediate, rather than by direct nucleophilic attack on the acyl ligand.

In special cases where CO insertion into M–C is difficult, carbomethoxy complexes may be involved. A case in point is carbomethoxylation of (π-allyl)palladium complexes described below. Another relevant reaction is the recently reported ECH<sub>2</sub>Co(CO)<sub>4</sub> (E = electron-withdrawing group) catalyzed carbomethoxylation of aryl halides, where ECH<sub>2</sub>Co(CO)<sub>3</sub>CO<sub>2</sub>Me<sup>–</sup> is formed, probably because of the low migratory aptitude of the ECH<sub>2</sub> group. The nature of the step that yields the aryl carboxylic ester is unclear in this case and may involve either CO insertion into the Co–Ar bond or reductive elimination.<sup>23</sup>

By use of bulky phosphine ligands, secondary alcohols, and higher CO pressure, it is possible to direct the Pd-catalyzed carbalkoxylation of aryl iodides toward “double carbonylation”<sup>22,25</sup> (eq 11).



The product-forming step in this reaction is thought to be reductive elimination of an acyl carbalkoxy complex (eq 12). An analogous mechanism is operative in



carbonylation of organic halides to α-keto amides.<sup>24</sup> Because of the low migratory aptitude of the acyl ligand, this route is preferred over generation of an intermediate of the type RCOCOM.

### Carbomethoxylation of (π-Allyl)palladium Complexes

Our mechanistic studies of butadiene carbomethoxylation,<sup>10</sup> which involves π-allyl intermediates, have led us to explore low-pressure routes for carbonylation of such complexes. Carbonylation of (π-allyl)metal complexes is generally difficult due to the low tendency of the π-allyl ligand to undergo the migratory insertion process, which is likely to require intermediacy of the σ-allyl form. (π-Allyl)palladium complexes, for example, were reported to undergo carbonylation only under forcing conditions.<sup>25</sup> Since such complexes are readily available from the corresponding olefins,<sup>27</sup> we thought

(22) Ozawa, F.; Kawasaki, N.; Okamoto, H.; Yamamoto, T.; Yamamoto, A. *Organometallics* 1987, 6, 1640.

(23) Foà, M.; Francalanci, F.; Beucini, E.; Gardano, A. *J. Organomet. Chem.* 1985, 285, 293.

(24) (a) Ozawa, F.; Soyama, H.; Yamamoto, T.; Yamamoto, A. *Tetrahedron Lett.* 1982, 23, 3383. (b) Kobayashi, T.; Tanaka, M. *J. Organomet. Chem.* 1982, 233, C64. (c) Chen, J. T.; Sen, A. *J. Am. Chem. Soc.* 1984, 106, 1506. (d) Ozawa, F.; Soyama, H.; Yanagihara, H.; Aoyama, I.; Takino, H.; Izawa, K.; Yamamoto, T.; Yamamoto, A. *J. Am. Chem. Soc.* 1985, 107, 3235.

(25) (a) Ozawa, F.; Kawasaki, N.; Yamamoto, T.; Yamamoto, A. *Chem. Lett.* 1985, 567. (b) Tanaka, M.; Kobayashi, T.; Sakakura, T.; Itatani, H.; Danno, K.; Zushi, K. *J. Mol. Catal.* 1985, 32, 115. (c) Tanaka, M.; Kobayashi, T.; Sakakura, T. *J. Chem. Soc., Chem. Commun.* 1985, 537.

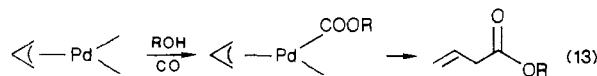
(18) Hidai, M.; Kokura, M.; Uchida, Y. *J. Organomet. Chem.* 1973, 52, 431.

(19) (a) Milstein, D.; Calabrese, J. C. *J. Am. Chem. Soc.* 1982, 104, 3773. (b) Milstein, D. *J. Am. Chem. Soc.* 1982, 104, 5227. (c) Milstein, D. *Acc. Chem. Res.* 1984, 17, 221.

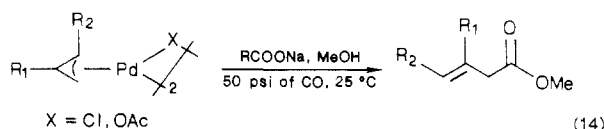
(20) (a) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* 1980, 102, 4933. (b) Ozawa, F.; Ito, T.; Nakamura, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* 1981, 54, 1868. (c) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* 1981, 54, 1957.

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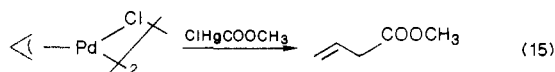
that a method for their low-pressure carbonylation could be of synthetic, as well as mechanistic, interest. Our strategy was to alleviate the problematic CO insertion into Pd-allyl by generation of a carbomethoxy complex that could then lead to ester formation by reductive elimination (eq 13).



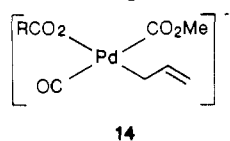
Since carboxylate anions were thought to promote formation of carbalkoxypalladium complexes,<sup>3b</sup> we tried carbomethoxylation in their presence and found that indeed a low-pressure process is possible<sup>28</sup> (eq 14).



High regioselectivity is observed—CO is inserted only into the least substituted terminal Pd-C bond. In the absence of sodium butyrate, decomposition takes place with no carbonylation. The rate roughly parallels the  $pK_a$  ( $\text{H}_2\text{O}$ ) of the carboxylate salt, the same as observed in the Pd-catalyzed olefin carbalkoxylation to diesters, where intermediacy of a carbomethoxypalladium has been invoked. Other bases are much less effective and lead to products of nucleophilic attack on the allylic ligand. The unique effect of carboxylate anions, together with the observation<sup>29</sup> of reaction 15, suggests

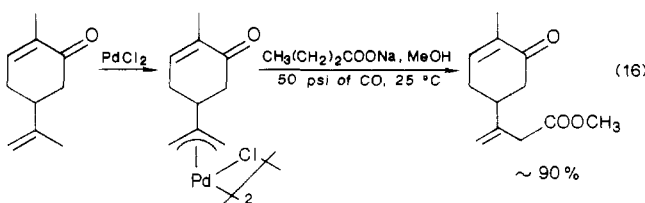


the intermediacy of a carbomethoxypalladium complex. To account for the requirement of excess carboxylate salts (a ratio of  $\text{PrCO}_2\text{Na}/\text{Pd} = 5$  is optimal), a  $\sigma$ -allylic complex such as 14 seems plausible.



The carbomethoxy ligand in 14 may be formed by insertion of CO into a Pd-OCOR bond followed by alcoholysis of the anhydrido ligand or through direct base-catalyzed attack of methanol on coordinated CO.

The synthetic utility of low-pressure carbonylation of ( $\pi$ -allyl)palladium complexes is exemplified in the selective, high-yield carbomethoxylation of (+)-carvone to (+)-carbomethoxycarvone<sup>28</sup> (eq 16).



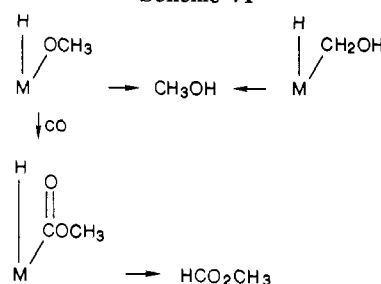
(26) (a) Tsuji, J.; Kiji, J.; Morikawa, M. *Tetrahedron Lett.* 1963, 1811. (b) Long, R.; Whitfield, G. H. *J. Chem. Soc.* 1964, 1852. (c) Tsuji, J.; Imamura, S.; Kiji, J. *J. Am. Chem. Soc.* 1964, 86, 4491. (d) Tsuji, J.; Kiji, J.; Imamura, S.; Morikawa, M. *J. Am. Chem. Soc.* 1964, 86, 4350. (e) Brews, S.; Hughes, P. R. *J. Chem. Soc., Chem. Commun.* 1965, 157.

(27) Trost, B. M.; Strege, P. E.; Weber, L.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* 1978, 100, 3407.

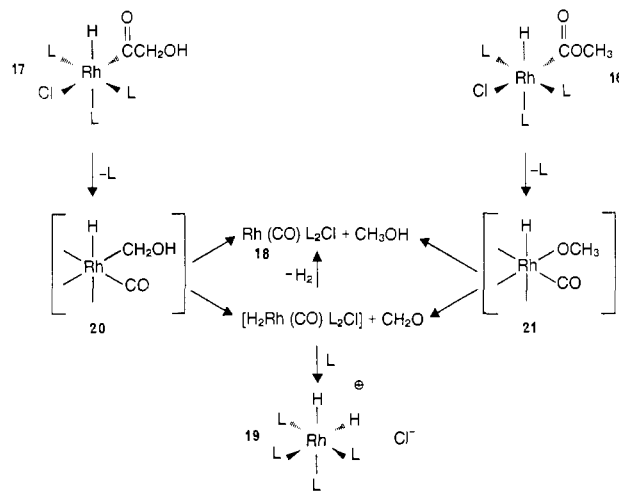
(28) Milstein, D. *Organometallics* 1982, 1, 888.

(29) Saegusa, T.; Tsuda, T.; Nishijima, K. *Tetrahedron Lett.* 1967, 4255.

## Scheme VI



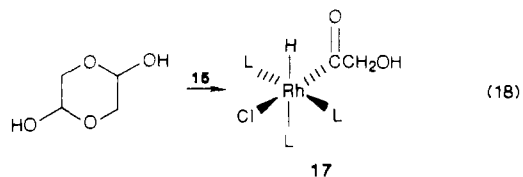
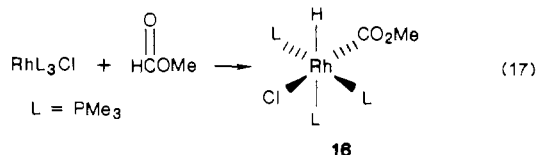
## Scheme VII



## Models for CO Hydrogenation

The product-forming step in hydrogenation of CO to methanol, elimination of methanol from a metal complex, may proceed by C-H reductive elimination of a hydrido hydroxymethyl complex or by O-H reductive elimination of a hydrido methoxy intermediate.<sup>30</sup> Carbonylation of the methoxy complex followed by hydrido-carbomethoxy reductive elimination may lead to methyl formate (Scheme VI).

We were interested in probing the feasibility of these processes and, in particular, in getting an idea which is a more likely process for methanol generation. In previous studies<sup>31</sup> we found that kinetically stabilized cis hydrido acyl complexes are formed by oxidative addition of aldehydes to  $\text{Rh}(\text{PMe}_3)_3\text{Cl}$  (15). Methyl formate yields the stable complex 16 (eq 17).



(30) See, for example: (a) Dombek, B. D. *ACS Symp. Ser.* 1981, No. 152, 213. (b) Fahey, D. R. *J. Am. Chem. Soc.* 1981, 103, 136. (c) Feder, H. M.; Rathke, J. W.; Chen, J. M.; Curtiss, L. A. *ACS Symp. Ser.* 1981, No. 152, 19. (d) Keim, W. *Catalysis in C<sub>1</sub> Chemistry*; D. Reidel: Dordrecht, The Netherlands, 1983; p 89.

(31) Milstein, D. *Organometallics* 1982, 1, 1549. (b) Milstein, D. *J. Chem. Soc., Chem. Commun.* 1982, 1357.

For comparison, the hydroxyacetyl complex 17 was prepared<sup>32</sup> by oxidative addition of glycoaldehyde dimer (eq 18).

When 0.1 M solutions of 16 and 17 in dioxane are heated at 70 °C, they undergo complete decomposition, leading to formation of the same products but in very different amounts. Formaldehyde is the major organic product obtained from 17 (87%) in addition to methanol (13%), Rh(CO)(PMe<sub>3</sub>)<sub>2</sub>Cl (18) (61%), and H<sub>2</sub>Rh(PMe<sub>3</sub>)<sub>4</sub><sup>+</sup>Cl<sup>-</sup> (19) (39%), whereas 16 yields methanol (93%), formaldehyde (7%), 18 (96%), and 19 (4%). A mechanistic interpretation of these results is shown in Scheme VII.<sup>33</sup>

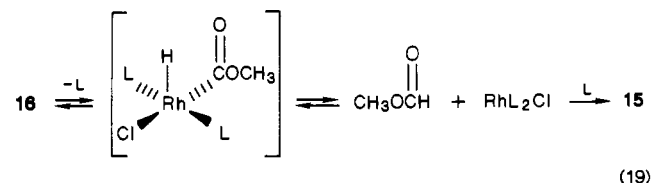
Both 16 and 17 undergo PMe<sub>3</sub> dissociation followed by deinsertion leading to intermediate hydroxymethyl hydride 20 and methoxy hydride 21, which undergo competing reductive elimination leading to methanol and 18 and β-hydride elimination to formaldehyde and H<sub>2</sub>Rh(CO)(PMe<sub>3</sub>)<sub>2</sub>Cl. The latter, which was not observed, reacts with PMe<sub>3</sub> to yield 19, but it can also reductively eliminate hydrogen to form 18. Indeed, when treated with CO, 19 immediately eliminates hydrogen. Both the reductive elimination and β-elimination processes are irreversible—18 does not react with methanol nor 19 with formaldehyde (in the presence or absence of CO). In support of this scheme, disappearance of 16 and 17 follows first-order kinetics and, significantly, almost the same rate constants are observed (at 70 °C  $k(\text{obsd}) = 4.85 \times 10^{-4}$  and  $4.47 \times 10^{-4}$  s<sup>-1</sup> for 16 and 17, respectively).<sup>33</sup> This is most likely a result of both processes having the same rate-determining step. Various elimination modes of octahedral *cis*-acylrhodium hydride-PMe<sub>3</sub> complexes<sup>19c,32</sup> as well as reductive elimination from *cis*-alkylrhodium hydride-PMe<sub>3</sub> complexes<sup>19b,c</sup> proceed via an unsaturated five-coordinate intermediate formed by a rate-determining PMe<sub>3</sub> dissociation from the position *trans* to the hydride. This is also most likely the case for the hydroxyacetyl complex 17 and thus also for 16. This conclusion, coupled with the observation that no incorporation of deuterium into 16 is seen at the 50% decomposition level of 16 in the presence of CD<sub>3</sub>OD, excludes a mechanism for methanol formation from 16 by deprotonation involving methoxide anion generated from the carbomethoxy ligand. It is noteworthy that this indicates, by microscopic reversibility, a concerted migratory mechanism for CO insertion into Rh-OCH<sub>3</sub>, in agreement with results obtained for Pt(dppe)-(OCH<sub>3</sub>)CH<sub>3</sub>.<sup>34</sup> An ionic mechanism was proposed, however, for carbonylation of Ir(PPh<sub>3</sub>)<sub>2</sub>(CO)(OR).<sup>35</sup>

We conclude that in our system methanol formation via an alkoxy hydride intermediate is preferred over methanol elimination from a hydroxymethyl hydride complex, which favors β-hydride elimination to yield formaldehyde. This conclusion is relevant also to the mechanism of formaldehyde hydroformylation<sup>36</sup> and aldehyde hydrogenation,<sup>37,38</sup> favoring alcohol formation

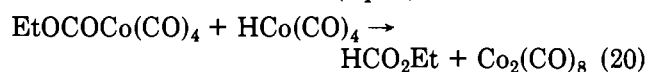
by O-H rather than C-H reductive elimination.

Since thermodynamic considerations<sup>33</sup> indicate that reductive elimination of methanol is the preferred process, the prevalence of β-elimination for 17 is probably kinetic in nature.

Interestingly, if 16 is decomposed under high vacuum, collecting the volatile products as formed, significant amounts of methyl formate and Rh(PMe<sub>3</sub>)<sub>3</sub>Cl are formed<sup>39</sup> as a result of a competing, reversible reductive elimination process of 16 (eq 19).



Since this is a reversible process, if HCO<sub>2</sub>Me is not removed as formed, only products of the overall irreversible migratory process are observed. Reaction 17, which demonstrates the feasibility of formate generation by intramolecular reductive elimination, is analogous to our findings of aldehyde reductive elimination.<sup>19c,32a</sup> Formation of methyl formate by hydrogenation of Ru<sub>3</sub>(CO)<sub>10</sub>(CO<sub>2</sub>CH<sub>3</sub>)<sup>-</sup> may also involve such a process.<sup>40</sup> Carbalkoxy complexes are proposed as intermediates in synthesis gas reactions, which generate formate esters.<sup>41</sup> Formates can be formed also by intramolecular elimination<sup>43</sup> (eq 20).



The rate-determining step of this reaction involves generation of the unsaturated intermediate EtOCO-Co(CO)<sub>3</sub>.<sup>41</sup> The relatively small difference in rate of reactions of this complex with HCo(CO)<sub>4</sub> vs H<sub>2</sub> implies that both *inter*- and intramolecular generation of formate esters may be possible.<sup>42,43</sup>

### Concluding Remarks

It is clear that carbalkoxy complexes may be plausible intermediates in carbonylation reactions involving alcohols as reactants or products. Utilizing appropriate carbalkoxymetal compounds, it is possible to model key steps in catalytic carbonylation cycles and gain relevant mechanistic insight. A likely mechanism for cobalt-catalyzed carbomethoxylation of butadiene involves both Co-CO<sub>2</sub>CH<sub>3</sub> and Co-H complexes synergistically, the first complex adding to the olefin, whereas the hydrido complex is involved in the product-forming step. Pd-catalyzed carbalkoxylation of organic halides to esters does not normally involve a carbalkoxy complex,

(38) Reduction of benzaldehydes with CO and water is thought, on the basis of electronic effects, to involve Rh-OR intermediacy rather than Rh-CHROH, and it is suggested that this is true also for methanol synthesis: Thompson, W. J.; Laine, R. M. *ACS Symp. Ser.* 1981, No. 152, 133.

(39) Milstein, D., unpublished results.

(40) Taube, D. J.; Roklicki, A.; Anston, M.; Ford, P. C. *Inorg. Chem.* 1987, 26, 526.

(41) (a) Sternberg, H. W.; Wender, I. *Spec. Publ.—Chem. Soc.* 1959, 13, 35. (b) Markó, L. *Proc. Chem. Soc. London* 1962, 67. (c) Martin, J. T.; Barid, M. C. *Organometallics* 1983, 2, 1073. (d) Wood, C. D.; Garrou, P. E. *Organometallics* 1984, 3, 170.

(42) (a) Ungváry, F.; Markó, L. *Organometallics* 1983, 2, 1608. (b) Hoff, C. D.; Ungváry, F.; King, R. B.; Markó, L. *J. Am. Chem. Soc.* 1985, 107, 666.

(43) It is thought that cleavage of MeCOC(CO)<sub>3</sub>L to C<sub>2</sub> products in methanol homologation involves attack by H<sub>2</sub> rather than cleavage by a hydride: Martin, J. T.; Baird, M. C. *Organometallics* 1983, 2, 1073.

(32) Milstein, D.; Fultz, W. C.; Calabrese, J. C. *J. Am. Chem. Soc.* 1986, 108, 1336.

(33) Milstein, D. *J. Am. Chem. Soc.* 1986, 108, 3525.

(34) Bryndza, H. E. *Organometallics* 1985, 4, 1686.

(35) Rees, M. W.; Churchill, M. R.; Fettingner, J. C.; Atwood, J. D. *Organometallics* 1985, 4, 2179.

(36) Chan, A. S. C.; Carroll, W. E.; Willis, W. E. *J. Mol. Catal.* 1983, 19, 377 and references therein.

(37) Sanchez-Delgado, R. A.; Andriollo, A.; DeOchoa, D. L.; Suarez, T.; Valencia, N. *J. Organomet. Chem.* 1981, 209, 77 and references therein.

with the exception of the double-carbonylation reaction and reactions involving ( $\pi$ -allyl)palladium complexes. Utilizing a rhodium carbomethoxy complex, the feasibility of intramolecular H-CO<sub>2</sub>R reductive elimination was demonstrated. By comparison of the elimination modes of this complex with those of its hydroxyacetyl isomer, it was possible to conclude that formation of methanol by migratory deinsertion proceeds preferably by C-O rather than C-H bond formation, indicating a plausible product-forming step in CO hydrogenation.

It may be useful to consider circumstances that may favor intermediacy of carbalkoxymetal complexes:

(a) A basic reaction medium may promote generation of a carbalkoxy ligand by alkoxide attack at coordinated CO or attack at the metal (followed by CO insertion).

(b) Lower concentration of acidic metal hydrides [such as HCo(CO)<sub>4</sub>] in a basic reaction medium may enhance the competitive addition of carbalkoxy com-

plexes to unsaturated molecules.

(c) Difficult migration of CO to M-R [e.g., when R =  $\pi$ -allyl, RCO, or ECH<sub>2</sub> (E = electron-withdrawing group)] may result in carbonylation via generation of a carbalkoxy ligand followed by reductive elimination. A basic reaction medium may be beneficial in such cases.

(d) Carboxylate salts may promote carbonylation of ( $\pi$ -allyl)metal complexes, not only by providing a basic medium but also by promotion of the reductive elimination process via a  $\sigma$ -allyl intermediate.

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