

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.

(49) Leading references: (a) Lin, Z.; Le Marechal, J.-F.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* 1987, 109, 4127. (b) Jeske, G.; Lauke, H.; Mauermann, H.; Sweptson, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* 1985, 107, 8091. (c) Jordan, R. F.; Bajgur, C. S.; Willett, R.; Scott, B. *J. Am. Chem. Soc.* 1986, 108, 7410. (d) Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. J.; Lee, F. L. *J. Am. Chem. Soc.* 1985, 107, 7219. (e) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* 1985, 18, 51. (f) Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* 1984, 56, 1.

## Aspects of Intermediacy of Carbalkoxymetal Complexes in CO Reactions

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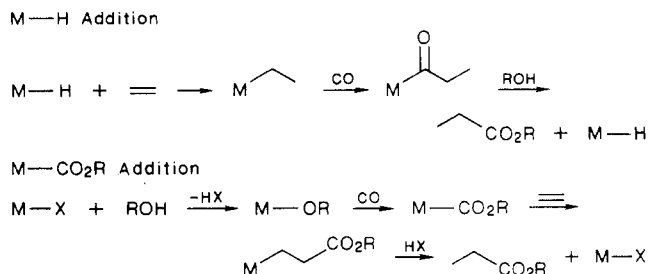
Carbonylation reactions rank among the most useful transformations homogeneously catalyzed by transition-metal complexes, forming the basis for industrial and laboratory processes currently in practice. Among these are a considerable number of reactions that lead to formation of carbalkoxy-containing 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	$M-CO_2R + R'OH \rightarrow RO_2C-M-CO_2R$
carbamates from amines	$M-CO_2R + R'NH_2 \rightarrow R'NHCO_2R$
methyl formate from CO/H <sub>2</sub>	$M-CO_2CH_3 + H_2 \rightarrow HCO_2CH_3$

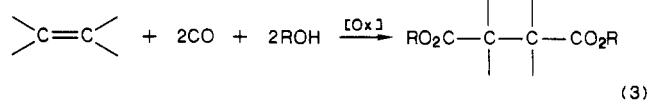
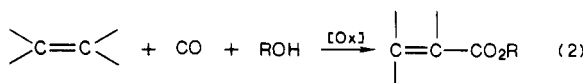
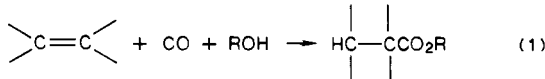
Scheme I



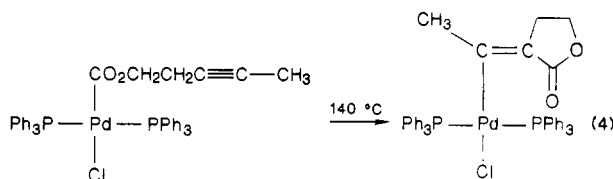
question of intermediacy of such species in those reactions is being addressed, emphasizing recent work from our laboratory.

## 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>

(1) For a review and recent papers on preparation and properties of carbomethoxymetal complexes, see: (a) Angelici, R. *J. Acc. Chem. Res.* 1972, 5, 335. (b) Minghetti, G.; Bonati, F.; Banditelli, G. *Synth. Inorg. Met.-Org. Chem.* 1973, 3, 415. (c) Vitagliano, A. *J. Organomet. Chem.* 1974, 81, 261. (d) Bellon, P. L.; Manassero, M.; Porta, F.; Sansoni, M. *J. Organomet. Chem.* 1974, 80, 139. (e) Michelin, R. A.; Napoli, M.; Ros, R. *J. Organomet. Chem.* 1979, 175, 239. (f) Zhir-Lebed, L. N.; Kuzmina, L. G.; Struohkov, Yu. T.; Temkin, O. N.; Golodov, A. N. *Koord. Khim.* 1978, 4, 1046. (g) Rivetti, F.; Romano, U. *J. Organomet. Chem.* 1978, 154, 323. (h) Behrens, H.; Ellermann, J.; Hohenberger, E. F. *Z. Naturforsch.* 1980, 35, 661. (i) Brown, D. A.; Glass, W. K.; Hussein, F. M. *J. Organomet. Chem.* 1980, 186, C58. (j) Gross, D. C.; Ford, P. C. *Inorg. Chem.* 1982, 21, 1702. (k) Thorn, D. L. *Organometallics* 1982, 1, 197. (l) Burk, P. L.; Van Engen, D.; Campo, K. S. *Organometallics* 1984, 3, 493. (m) Vasapollo, G.; Nobile, C. F.; Sacco, A. *J. Organomet. Chem.* 1985, 296, 435. (n) Tasi, M.; Pályi, G. *Organometallics* 1985, 4, 1523.

(2) (a) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980; p 82. (b) Pino, P.; Piacenti, F.; Bianchi, M. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; p 233. (c) Mullen, A. In *New Synthesis with Carbon Monoxide*; Falbe, J., Ed.; Springer-Verlag: New York, 1980; p 243. (d) Stille, J. K.; James, D. E. In *The Chemistry of Double Bonded Functional Groups*; Patai, S., Ed.; Wiley: New York, 1977; p 1099. (e) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: New York, 1980; p 81.

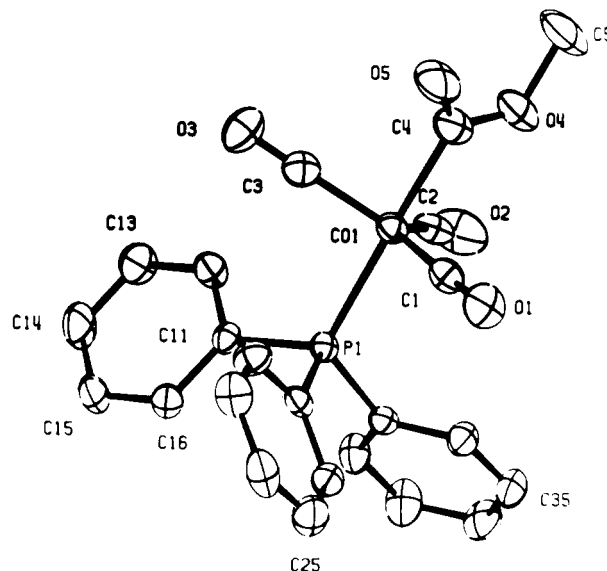
(3) Pd-CO<sub>2</sub>R mechanism: (a) James, D. E.; Hines, L. F.; Stille, J. K. *J. Am. Chem. Soc.* 1982, 98, 1806. (b) James, D. E.; Stille, J. K. *Ibid.* 1976, 98, 1810. (c) Fenton, D. M. *J. Org. Chem.* 1973, 38, 3192. (d) Heck, R. F. *J. Am. Chem. Soc.* 1972, 94, 2712. (e) Zhir-Lebed, L. N.; Mekhyrakova, N. G.; Temkin, O. N.; Flid, R. M. *Kinet. Katal.* 1974, 15, 537.

(4) Pd-H mechanism: (a) Knifton, J. *J. Org. Chem.* 1976, 41, 793. (b) Knifton, J. *Ibid.* 1976, 41, 2885. (c) Bard, R.; Del Pra, A.; Piazzesi, A. M. *Inorg. Chim. Acta* 1979, 35, L345.

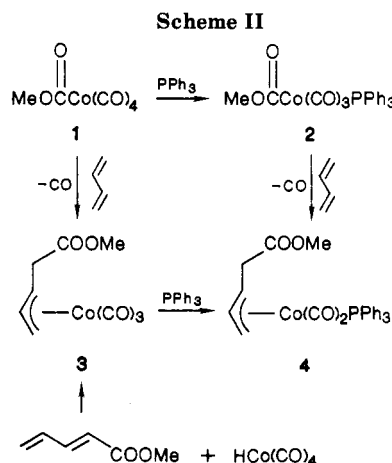
(5) Otsuka, S.; Nakamura, A.; Yoshida, T.; Naruto, M.; Ataka, K. *J. Am. Chem. Soc.* 1973, 95, 3180.

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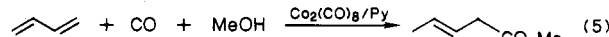
(7) Samsel, E. G.; Norton, J. R. *J. Am. Chem. Soc.* 1984, 106, 5505.



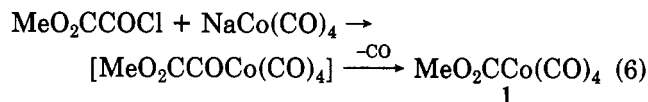
**Figure 1.** ORTEP drawing of a molecule of 2. Hydrogens have been left out for clarity. Selected bond lengths (Å) and angles (deg): Co-P, 2.232; Co-C(axial), 1.976; Co-C(equatorial), 1.786; P-C, 1.823; C=O(carbonyl), 1.138; C=O(carbomethoxy), 1.196; C-O(carbomethoxy), 1.342; CH<sub>3</sub>-O, 1.484;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



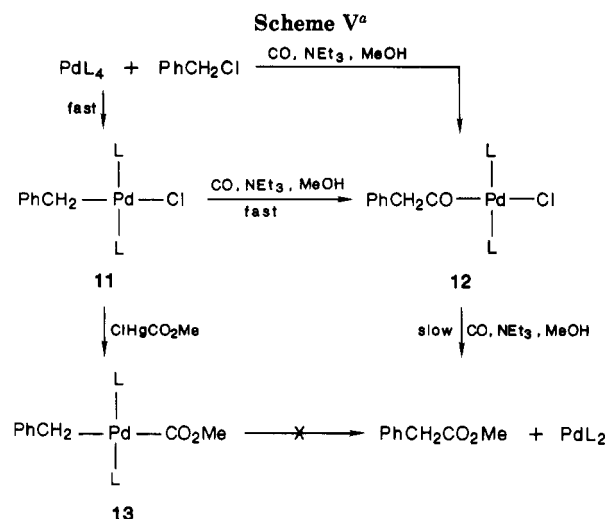
The obvious route of reaction of Co(CO)<sub>4</sub><sup>-</sup> with ClCO<sub>2</sub>Me failed because of a lack of electrophilicity of the carbonyl in this acid chloride. Compound 1 is a volatile liquid that decomposes slowly at 25 °C (τ<sup>1/2</sup> ≈ 1 h) but can be converted into the more stable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

(8) Clark, H. C.; Werner, K. V. *Chem. Ber.* 1977, 110, 667.

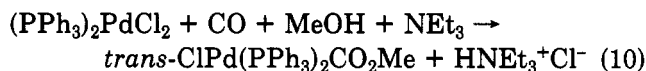
(9) Inyanitov, N. S.; Rudkovskii, D. M. *Zh. Prikl. Khim.* 1966, 39, 2335. (b) Matsuda, A. *Bull. Chem. Soc. Jpn.* 1973, 46, 524.

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





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).



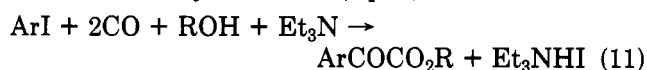
In order to gain information on the nature of the product-forming step, we wanted to render it rate determining and observe it directly. In other work, we kinetically stabilized Rh and Ir complexes toward dissociative elimination processes by use of the small, basic PMe<sub>3</sub> ligand.<sup>19</sup> 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-

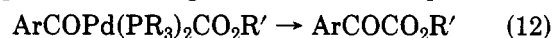
nation of a carbalkoxy complex (Scheme IV). In fact, 12 is the only Pd complex observed by <sup>31</sup>P NMR under actual catalysis conditions. Similar results are obtained when iodobenzene is used instead of benzyl chloride, indicating that the acylpalladium mechanism for alkoxycarbonylation is probably 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.

(21) Milstein, D. *J. Chem. Soc., Chem. Commun.* 1986, 817.





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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**Registry No.** CO, 630-08-0.