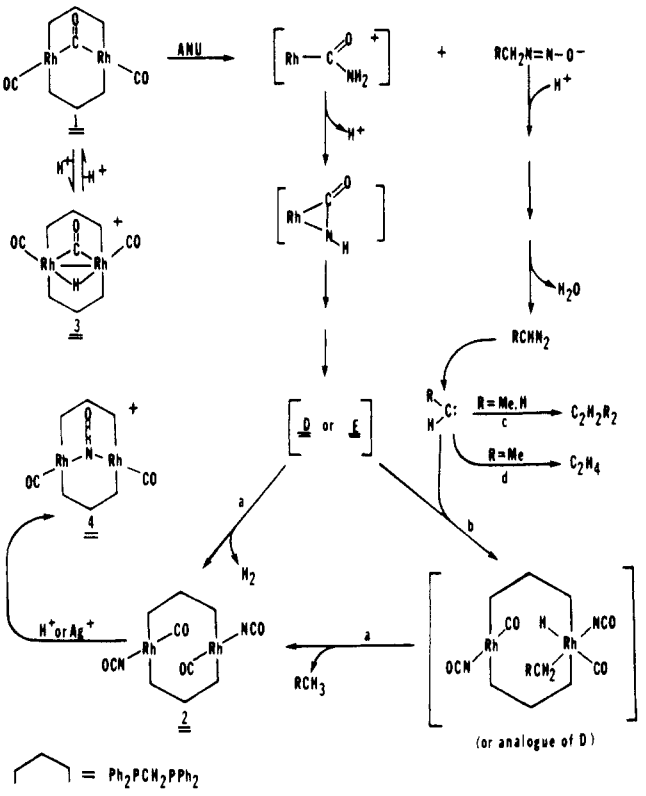
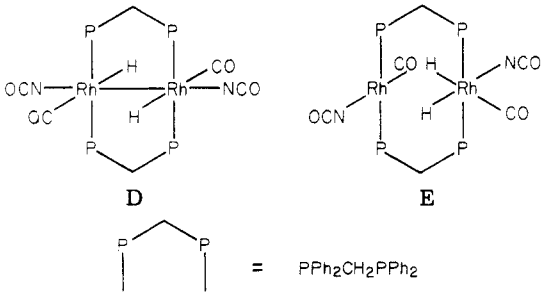
Scheme I



a,reductive elimination; b,carbene insertion; c,dimerization; d,internal rearrangement

followed by rearrangement. An alternative to eq 4 in which diazoic acid, R—N=N—OH, serves as the leaving group and formulations of A and B differ slightly from the formulations above cannot be ruled out at this time. However, the possibility of a direct reaction of complex 1 with preformed alkyl isocyanate, which is known to form in ANU decompositions,[12] was ruled out by a control experiment in which a benzene solution of 1 and MeNCO is heated at reflux and yields quantitative recovery of 1.

The production of H_2 follows a reductive elimination path. Since both 1 and 2 are binuclear and since 2 e^- are needed for H_2 formation, we propose that the species penultimate to H_2 generation has either structure D or E.



The former has metal–metal bonded Rh(II) centers and is analogous to binuclear oxidative addition products observed by Balch[13] while the latter has a Rh(I) Rh(III) structure similar to an iridium system reported by Pignolet and Wang.[14] The formation of methane is readily envisioned from D or E by CH_2 insertion into one of the Rh–H bonds followed by reductive elimination. Half of the hydrogens of the CH_4 product thus originate as the N-bound protons of the MNU substrate consistent with our labeling experiment.

The reaction chemistry thus shows that the binuclear complex 1 promotes ANU decomposition leading to the diisocyanate complex 2 and carbene formation. The hydride intermediate formed following promotion of ANU decomposition may then reductively eliminate H_2 or, if MNU is the substrate, undergo CH_2 insertion followed by reductive elimination. In the case of ENU, insertion of methylcarbene into the Rh–H bond and subsequent formation of ethane may be obviated by a relatively rapid 1,2-hydrogen atom shift in free CH_3CH forming ethylene which is observed in the product gases. The reaction chemistry thus described is summarized in the Scheme I. The factors influencing the relative ease of carbene insertion into the binuclear hydride formed, and the relative propensity of these systems to form isocyanate complexes vs. bridging carbene complexes are under continuing study.

Acknowledgment. We wish to thank the National Science Foundation (Grant CHE 80-11974) for support of this work. We also wish to acknowledge helpful discussions with Professors J. A. Kampmeier and W. D. Jones and the Johnson Matthey Co., Inc., for a generous loan of precious metal salts.

Registry No. 1, 74507-92-9; 2, 77010-18-5; 3, 74507-93-0; 4, 81616-70-8; MNU, 684-93-5; ENU, 759-73-9.

(12) Irie, H.; Kishimoto, T.; Vyeo, S. *J. Chem. Soc. C* **1969**, 1645.
(13) Balch, A.; Labadie, J. W.; Delker, G. *Inorg. Chem.* **1979**, *18*, 1224. Balch, A. *J. Am. Chem. Soc.* **1976**, *98*, 8049.
(14) Pignolet, L.; Wang, H. H. "Abstracts of Papers", 180th National Meeting of the American Chemical Society, Las Vegas, NV; American Chemical Society, Washington, DC, 1980; Paper No. 168. Wang, H. H. Ph.D. Thesis, University of Minnesota, 1981.

Mild, Low-Pressure Carbonylation of (π-Allyl)palladium Complexes†

David Milstein
Central Research and Development Department
Experimental Station, E. I. du Pont de Nemours & Company
Wilmington, Delaware 19898

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Summary: In the presence of carboxylic acid anions, the normally difficult carbonylation of (π-allyl)palladium complexes can be achieved quantitatively at low pressure and temperature, thereby providing a new low-pressure route to β,γ-unsaturated esters from olefins. A (π-allyl)carbalkoxypalladium complex is proposed to be a key intermediate in this reaction.

Organic synthesis via (π-allyl)palladium complexes has attracted much attention in recent years.[1,2] Pd(II) salts provide activation of the allylic position of an olefin, thus forming the basis for a variety of allylic alkylation reactions.[2] Carbonylation of (π-allyl)palladium complexes, although still a useful reaction, has found much less application in organic synthesis since it requires high CO pressure, high temperature, is very slow, and results in modest yields of carbonylation products.[3,4] Difficulties

† Contribution No. 3001.
(1) (a) Tsuji, J. "Organic Synthesis with Palladium Compounds"; Springer Verlag: New York, 1980. (b) Chiusoli, G. P.; Cassar, L. In "Organic Synthesis Via Metal Carbonyls", Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Part II, p 297.
(2) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385.
(3) (a) Long, R.; Whitfield, G. H.; *J. Chem. Soc.* **1964**, 1852. (b) Tsuji, J.; Kiji, J.; Morikawa, M.; *Tetrahedron Lett.* **1963**, 1811. (c) Tsuji, J.; Imamura, S.; Kiji, J. *J. Am. Chem. Soc.* **1964**, *86*, 4491. (d) Brews, S.; Hughes, P. R. *J. Chem. Soc., Chem. Commun.* **1965**, 157.

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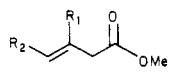
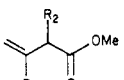
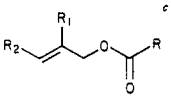
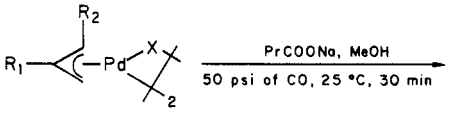
Table I. Carbomethoxylation of (π-Allyl)palladium Complexes According to Eq 1[a]

			yield,[b] %		
					 [c]
R_1	R_2	X			
H	H	Cl	68		18
H	H	OAc	72		15
CH_3	H	Cl	95		4
CH_3	H	OAc	91		6
H	CH_3	Cl	85	4	6
H	CH_3	OAc	92	1	3

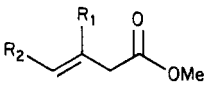
[a] The reactions were carried out by using 1 mmol of the palladium complex and 10 mmol of sodium butyrate in 30 mL of methanol under initial CO pressure of 50 psi until CO absorption was complete. [b] By GLC based on Pd. Structures confirmed by GC/MS. [c] R = $CH_3(CH_2)_2$ for X = Cl and R = CH_3 for X = OAc.

are usually encountered in carbonylation of other (π-allyl)metal complexes as well as a result of the high stability of the allylic system in the π form. A method for effecting low-pressure, mild carbonylation of (π-allyl)palladium complexes would clearly be of interest, both synthetically and mechanistically.

One possible way to alleviate the problematic CO insertion into a Pd–C bond of the allyl ligand is to generate a carbalkoxy ligand attached to palladium which could then lead to formation of the carbalkoxylated product through reductive elimination. Since carboxylic acid anions are thought to uniquely promote formation of carbalkoxypalladium intermediates,[5] we reasoned that low-pressure carbonylation of (π-allyl)palladium complexes in the presence of these anions may be possible. Indeed, carbonylation of chloro- and acetato-bridged complexes can be accomplished at low CO pressure at 25 °C provided that a carboxylic acid salt is present (eq 1). Previously,



X = Cl, OAc

 (1)

1400–2800 psi of CO at 50–75 °C for 5 h were required to affect carbonylation of chloro-bridged (π-allyl)palladium complexes in modest yields,[3] whereas only formation of allylic acetates with no carbonylation is reported for reaction of the acetato-bridged complexes with CO.[6] The carbonylation reaction in the presence of carboxylate salts is accompanied by formation of small amounts of coupling products of the allyl ligand with the carboxylate anion for X = Cl, whereas when X = OAc, coupling of the acetato and allyl ligands to give allylic acetates takes place to a small extent. Some typical results are presented in Table I.

The following procedure for the preparation of methyl 3-methyl-3-butenoate is representative. A solution containing 1 g (2.54 mmol) of 2-methallylpalladium chloro dimer and 2.79 g (25.4 mmol) of sodium butyrate in 80 mL of methanol was stirred under 50 psi of CO at room temperature. Pd metal precipitated after 20 s, and CO absorption took place during 20 min, after which the CO was vented and the solution was filtered and analyzed by GC/MS to show formation of 94% of methyl 3-methyl-3-butenoate and 4% of 2-methyl-2-propenyl *n*-butyrate. The solvent was removed by distillation to give 510 mg (88% yield based on Pd) of methyl 3-methyl-3-butenoate: IR ν 3080 (C=CH_2), 1745 (C=O), 1650 cm^{-1} (C=C); NMR (CD_2Cl_2) δ 1.75 (s, 3 H, CH_3C=C), 3.03 (s, 2 H, CH_2C=C), 3.65 (s, 3 H, OCH_3), 4.86 (d, 2 H, C=CH_2); MS, *m/e* 114 (M^+).

In absence of sodium butyrate, decomposition of the chloro-bridged complexes takes place without formation of carbonylation products. Some carbonylation, however, does take place in the case of acetato-bridged complexes, but it is relatively slow and accompanied by substantial amounts of allylic acetates as a result of ligand coupling. It is noteworthy that only this coupling reaction, with no carbonylation at all, was observed upon reaction of acetato-bridged complexes with CO in nonalcoholic solvents and in the absence of carboxylate salts.[6] Thus, carbonylation in the presence of carboxylate anions is much faster than the facile intramolecular migration of the acetate from palladium to carbon. High regioselectivity is observed in which insertion of CO occurs at the least substituted terminal allylic carbon, as reported also in high-pressure carbonylations of chloro-bridged palladium complexes.[3,4]

Various carboxylic acid salts are effective; reactivity as measured by the rate of CO absorption follows the trend sodium butyrate > sodium propionate > sodium acetate > sodium palmitate ≫ sodium oxalate, which roughly parallels the order of pK_a (H_2O) of these bases. A similar pattern was observed in the palladium-catalyzed olefin carbonylation reaction to diesters in which a (carbomethoxy)palladium complex is proposed to be the active catalytic species.[5] Other bases such as amines and alkoxides are ineffective for carbonylation and lead to products of nucleophilic attack on the allyl moiety. Only low yields of carbonylation products are obtained when nonnucleophilic bases such as CaO, Na_2CO_3, and 2,6-lutidine are employed instead of carboxylate salts. The yield of the carbonylation products is optimal at PrCOONa/Pd = 5. At higher base concentration, considerable amounts of allyl butyrates are formed, undoubtedly as a result of competing nucleophilic attack of the butyrate anion on the (π-allyl)palladium complex. Triphenylphosphine has an inhibiting effect on the carbonylation reaction. At a ratio of Pd/PPh_3 = 1, the rate of CO uptake under the standard reaction conditions using sodium butyrate and (π-methallyl)palladium chloride dimer is 11 times slower than that of the corresponding reaction in absence of triphenylphosphine and leads to formation of 41% of methyl 3-methyl-3-butenoate and 47% of 2-methallyl *n*-butyrate. The large increase in the amount of the latter can be attributed both to blocking of the CO coordination site and to higher susceptibility of the phosphine-substituted complex to nucleophilic attack.[2] Nevertheless, the marked influence of carboxylate anions is observed here also—in absence of sodium butyrate not even traces of carbonylation products are formed. This suggests that the role of those anions in promoting the carbonylation of the bridged complexes is not associated with the bridge-splitting step.

Since (π-allyl)palladium complexes are readily available in good yields from the corresponding olefins, regio- and chemoselectively,[7] a mild, high-yield carbonylation of these

(4) Tsuji, J.; Kiji, J.; Imamura, S.; Morikawa, M. *J. Am. Chem. Soc.* **1964**, *86*, 4350.
(5) James, D. E.; Stille, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 1810.
(6) (a) Takahashi, A. Y.; Tsukiyama, K.; Sakai, S.; Ishii, Y. *Tetrahedron Lett.* **1970**, 1913. (b) Bäckvall, J. E.; Nordberg, R. E.; Björkman, E. E.; Moberg, C. *J. Chem. Soc., Chem. Commun.* **1980**, 943.
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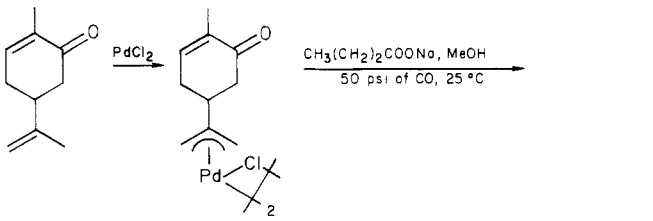
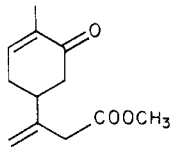
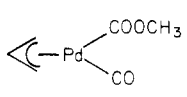
complexes offers considerable synthetic utility. This is demonstrated in the selective carbomethoxylation of (+)-carvone to (+)-carbomethoxycarvone (1).[8]



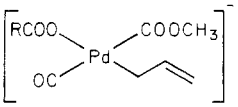


1, 90%

Mechanistically, we believe that the reaction involves generation of a (carbomethoxy)(π-allyl)palladium complex, **2**, which can be formed by insertion of CO into a Pd–O



2



3

bond[10] followed by alcoholysis of the anhydrido ligand or through direct base-catalyzed nucleophilic attack of methanol on a coordinated CO.[11] In addition to the unique effect of carboxylate anions in promoting formation of (carbomethoxy)palladium species where other bases fail,[5] formation of such an intermediate in our system is supported by the observation that (π-allyl)palladium chloride dimer reacts with (carbomethoxy)mercuric chloride to afford methyl 3-butenoate.[9] To account for the requirement of excess carboxylate salts, a σ-allylic intermediate such as complex **3** seems plausible. Clearly, more work is needed in order to define the mechanism of this reaction. Attempts to isolate complexes of the type **2** by carbonylation of 1,3-substituted (π-allyl)palladium complexes are now in progress. Also planned are extension of our studies to other allylic metal systems as well as catalytic reactions. So far we have demonstrated the feasibility of the latter by low-pressure and -temperature carbomethoxylation of allyl chloride in the presence of sodium butyrate using (π-methallyl)palladium chloride dimer as a catalyst.[12]

Acknowledgment. I am grateful to Professors J. K. Kochi and B. M. Trost for helpful discussions and to Mr. M. A. Cushing, Jr., for excellent technical assistance.

(8) Spectral Data: IR (neat) 1670 cm^{-1} (C=O), 1735 (OC=O); NMR ($CDCl_3$) δ 1.78 (s, 3 H, CH_3), 2.43 (m, 5 H, CH_2CHCH_2), 3.10 (s, 2 H, CH_2COO), 3.67 (s, 3 H, $COOCH_3$), 5.00 (s, 2 H, $C=CH_2$), 6.70 (m, 1 H, C=CH); $[\alpha]_D$(hexane) +29.0 ± 1.5°. Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.22; H, 7.75. Found: C, 69.36; H, 7.94.

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

(10) Formation of a (carbomethoxy)palladium complex by CO insertion into a Pd–OAc bond in methanol has been observed: Rivetti, F.; Romano, U. *J. Organomet. Chem.* **1978**, *154*, 323.

(11) For an example of such a process with palladium, see: Hidai, M.; Kokura, M.; Uchida, Y. *J. Organomet. Chem.* **1973**, *52*, 431.

(12) 1400 psi of CO at 120 °C for 40 h are required for Pd-catalyzed carbonylation of allylchloride to ethyl 3-butenoate in absence of carboxylate salts: see ref 4.

Book Reviews

Transition Metal Chemistry. Current Problems of General, Biological and Catalytical Relevance. Edited by A. Müller and E. Diemann. Verlag Chemie, Weinheim. 1981. 338 pages. $55.00.

This book brings the lectures presented at a workshop held July 14–17, 1980, at the University of Bielefeld in Germany which was devoted to a discussion of some currently important areas of transition-metal chemistry. The workshop was of limited international scope: nine of the lectures were by German, five by British, and four by US chemists. According to the preface, the book provides "state-of-the-art reviews for some of the most exciting topics: new synthetic methods, metal-to-metal bonds, polynuclear compounds, unusual ligands, bioinorganic chemistry, and homogeneous catalysis". Unfortunately, these reviews are not of the state-of-the-art type in the sense of giving a balanced overview of the topics which they cover. Rather they are the more easily prepared (but less useful) accounts of research from the laboratories of the respective speakers. Nevertheless, there are, within this limitation, some excellent reviews in this book.

The specific topics covered within the general categories listed above are the following: transition-metal photochemistry (J. J. Turner); syntheses via metal atoms (P. L. Timms); synthesis of metal cluster complexes (H. Vahrenkamp); metal–metal multiple bonds in transition group 5 (F. A. Cotton); interactions of metal complexes with Lewis acids (D. Coucouvanis); polynuclear oxometallates (B. Krebs); coordination chemistry of alkylidenephosphoranes and phosphine–boranes (H. Schmidbaur); methylene and methylidyne complexes (W. A. Hermann); boron heterocycles as ligands (W. Siebert); zinc biochemistry (B. L. Vallee); transition metals in human biology and medicine (D. R. Williams); chemistry related to biological fixation of nitrogen (J. Chatt); transition-metal complexes with simple sulfur-containing ligands (A. Müller and E. Diemann); Mössbauer studies in bioinorganic chemistry (A. X. Trautwein and E. Bill); asymmetric synthesis (H. Brunner); optically active electron-rich olefins and their complexes (M. F. Lappert); metallocarborane catalysts (M. F. Hawthorne); palladium and platinum complexes (W. Beck). Which of these reviews will appeal to a particular reader will depend on his own interests in transition-metal chemistry. At least ten will be of interest to the organometallic chemist.

All manuscripts are photoreproduced typescripts. In spite of the lack of uniformity in appearance this brings, the book is well produced, with excellent figures and an attractive appearance. It should find its way to the shelves of all chemistry libraries.

Dietmar Seyferth, *Massachusetts Institute of Technology*

Metal-Catalyzed Oxidations of Organic Compounds. By Roger A. Sheldon and Jay K. Kochi. Academic Press, New York. 1981. xix + 424 pp. $56.00.

This book stands apart from the literature in the field of oxidation chemistry. Its uniqueness stems from the attempt of the authors to develop and present a general mechanistic approach for all types of oxidation reactions independently of their homogeneous, heterogeneous, or enzymatic nature. These three areas have been traditionally treated as separate disciplines with no relevance to each other. The writing style is good, and a fast