

significantly different, implying that the negative charge on the cluster is more important than the nature of the X ligand. This in turn implies that the major effect of the X ligands is simply to supply the cluster with additional electron density.

In the halide-promoted catalytic reactions cited in the introduction, CO insertion into metal-alkyl bonds to give acyl complexes must be important reaction steps. The basis for the halide-promoted insertions in these reactions is likely the same as

for our methylene-to-ketene conversions since acyl ligands should be better electron acceptors than alkyl ligands. They thus better stabilize the extra electron density provided by the halide ligands, and the alkyl  $\rightleftharpoons$  acyl equilibrium is shifted to the right.

**Acknowledgment.** We thank the Department of Energy, Office of Basic Energy Sciences, for support of this work and the Englehard Corp. for a loan of osmium metal.

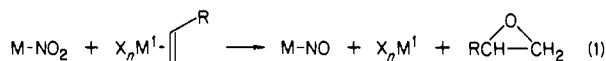
## Formation of Glycol Monoacetates in the Oxidation of Olefins Catalyzed by Metal Nitro Complexes: Mono- vs. Bimetallic System

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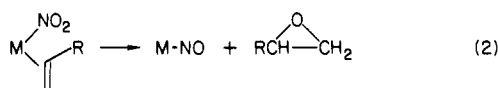
Contribution from the Allied Corporation, Corporate Research, Morristown, New Jersey 07960. Received April 16, 1984

**Abstract:** The oxidation of terminal olefins by bis(acetonitrile)chloronitropalladium(II) (**1**) in acetic acid leads to a mixture of glycol monoacetate isomers as the main products. Various amounts of ketones and unsaturated acetates are also formed. The rate of formation and the yield of glycol monoacetate decrease with increasing chain length. Cyclic olefins yield no glycol monoacetates. Replacement of acetic acid by stronger or sterically hindered carboxylic acids completely eliminates the formation of glycol monocarboxylates. Introduction of oxygen converts this stoichiometric reaction into a catalytic system. Our studies, including those carried out with complex **1** labeled with  $^{18}\text{O}$  in the nitro ligand, suggest that the glycol monoacetates and most of the ketones are the product of oxygen atom transfer from the nitro group, while the unsaturated acetates are the result of a Wacker-type reaction. In the glycol monoacetate, the  $^{18}\text{O}$  label is found exclusively in the acetate group. A mechanism which is in agreement with the above observations as well as a comparison of the above reaction with the oxidation of olefins by nitrate ions in the presence of palladium(II) salts is offered. The formation of glycol monoacetates in the monometallic system represented by complex **1** is to be compared with the results obtained in the bimetallic systems consisting of a combination of  $\text{py}(\text{TPP})\text{CoNO}_2$  and either  $(\text{CH}_3\text{CN})_2\text{PdCl}_2$  or  $\text{Pd}(\text{OAc})_2$ . In the latter systems, ketones or vinyl acetates are found as the predominant products. This fact underlines the difference between the mono- and bimetallic systems and strongly argues against alternative mechanisms involving nitro group transfer from cobalt to palladium before the olefin oxidation takes place. Additional evidence underlining the difference between these two systems is presented.

In the last 3 years, a novel approach has been developed for the specific oxidation of olefins.<sup>1-6</sup> The importance of this approach lies in the fact that it yields, for the first time, nonradical and nonperoxidic olefin epoxidation.<sup>2,4,6</sup> The principal step in this oxidation involves oxygen transfer from a nitro ligand to a coordinated olefin. Two basic systems have been discovered. The first published examples were of a bimetallic system (eq 1) in which the nitro ligand and the reacting olefin are bound to two different metal centers.<sup>1-4</sup> The second case is represented by a

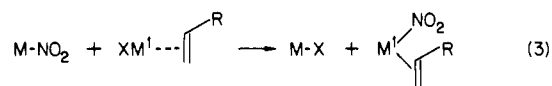


monometallic catalyst in which the nitro ligand and the reacting olefin are coordinated to the same metal (eq 2).<sup>4-6</sup> Only the



bimetallic system consisting of  $\text{L}(\text{TPP})\text{CoNO}_2$  and thallium(III) salts epoxidizes simple aliphatic olefins such as propylene and 1-octene to the corresponding epoxides as the main product.<sup>2</sup> With the monometallic system, only certain cyclic olefins and, to a lesser extent, isobutylene are converted to the corresponding epoxides.<sup>6c</sup>

Recently, it was suggested that the bi- and monometallic systems may react via an identical intermediate formed by migration of the nitro ligand from the cobalt nitro complex to the metal on which the olefin is activated (eq 3). Only then would



the olefin be oxidized.<sup>7</sup> Such a suggestion has far-reaching implications for the further development of these metal nitro-catalyzed oxidations. For this reason, a study was undertaken to examine this mechanistic possibility. The results of that study are presented herein and support the existence of both the mono- and bimetallic mechanisms for these reactions. Additional evidence against the suggested conversion of the bi- into the monometallic system comes from our work on oxidation of olefins by metal nitro complexes in protic solvents such as acetic acid. We have reported that, in acetic acid, the oxidation of ethylene by the bimetallic system ( $\text{L}(\text{TPP})\text{CoNO}_2 + \text{Pd}(\text{OAc})_2$ ) affords only vinyl acetate.<sup>1</sup> No oxygen transfer products have been detected. This reflects the fact that acetate ion effectively competes with the nitro ligand, which is expected to be an extremely weak

(1) Tovrog, B. S.; Mares, F.; Diamond, S. E. *J. Am. Chem. Soc.* **1980**, *102*, 6616-6618.

(2) Diamond, S. E.; Mares, F.; Szalkiewicz, A.; Muccigrosso, D. A.; Solar, J. P. *J. Am. Chem. Soc.* **1982**, *104*, 4266-4268.

(3) Muccigrosso, D. A.; Mares, F.; Diamond, S. E.; Solar, J. P. *Inorg. Chem.* **1983**, *22*, 960-965.

(4) Mares, F.; Diamond, S. E. In "Fundamental Research in Homogeneous Catalysis"; Graziani, M., Giorno, M., Eds.; Plenum Press: New York, 1983; Vol. 4.

(5) Andrews, M. A.; Kelly, K. P. *J. Am. Chem. Soc.* **1981**, *103*, 2894-2896.

(6) (a) Andrews, M. A.; Cheng, C.-W. F. *J. Am. Chem. Soc.* **1982**, *104*, 4268-4270. (b) Heumann, A.; Chavet, F.; Waegel, B. *Tetrahedron Lett.* **1982**, *23*, 2767-2768. (c) Andrews, M. A.; Chang, T. C.-T.; Cheng, C.-W. F.; Kelly, K. P. *Organometallics* **1984**, *3*, 1777-1785.

(7) Andrews, M. A.; Chang, T. C.-T.; Cheng, C.-W. F. *Organometallics* **1985**, *4*, 268-274.

**Table I.** Products of Propylene Oxidation in Acetic Acid<sup>a</sup>

run	complex (mmol)	LiOAc, mmol	O <sub>2</sub> , kPa	products % <sup>b</sup>			
				acetone	acetoxypropenes	propylene glycol monoacetates	total
1	<b>1</b> (0.38) <sup>c</sup>	0	0	38 (27)	30 (21)	75 (52)	143
2	<b>2</b> (0.13) <sup>c</sup>	0	0	0	63 (100)	0	63
3	<b>1</b> (0.38) <sup>d</sup>	0	345	352 (34)	157 (15)	522 (51)	1031
4	<b>2</b> (0.13) <sup>d</sup>	0	345	46 (9)	467 (91)	0	513
5	<b>1</b> (0.38) <sup>c</sup>	3.8	0	9	64 (47)	72 (53)	136
6	<b>1</b> (0.38) <sup>d</sup>	3.8	345	403 (19)	542 (26)	1132 (55)	2077

<sup>a</sup>All reactions were carried out in a mixture of propylene (~0.3 g) and acetic acid (5 mL) at 25 °C. <sup>b</sup>The yields are based on the number of millimoles of the complex. Selectivities are given in parentheses. <sup>c</sup>Determined after 2 h. <sup>d</sup>Determined after 18 h.

nucleophile. It can be argued that, in the monometallic system, the close proximity of the nitro ligand to the  $\pi$ -bonded olefin may either enable the nitro ligand to compete with an external nucleophile (e.g., acetate ion) or, if the external nucleophile attacks preferentially, allow oxygen transfer to favorably compete with  $\beta$ -hydride elimination. In either case, compounds other than vinylic acetates, the only product of the bimetallic system, should be formed. This work provides strong support for this working hypothesis and adds more support to our contention that a substantial difference exists between the mono- and bimetallic systems.

Accordingly, this paper consists of two parts. The first part describes the oxidation of olefins by bis(acetonitrile)chloronitropalladium(II) (**1**) in acetic acid. The second part summarizes our data which support the existence of both mono- and bimetallic mechanisms in metal nitro complex mediated oxidations.

## Results and Discussion

**Part I. Oxidation of Olefins.** The stoichiometric and catalytic oxidations of olefins utilizing bis(acetonitrile)chloronitropalladium(II) (**1**)<sup>5</sup> have been carried out in neat carboxylic acids or in nitromethane containing the desired carboxylic acids. All the solvents and carboxylic acids were carefully dried before use. In acetic acid, treatment of propylene with complex **1** at room temperature under anaerobic conditions affords a mixture of three groups of products (Table I, run 1). Acetone is the first product. The second group consists of a mixture of 1-, 2-, and 3-acetoxypropenes. The third, and most interesting group, consists of 1-acetoxy-2-hydroxypropane and 1-hydroxy-2-acetoxypropane formed in a ratio of approximately 1:1.5 (Table II). At the end of the reaction, the originally soluble nitro complex **1** is found to have been reduced to a mixture of [Pd(NO)Cl]<sub>n</sub>, PdCl<sub>2</sub>, and palladium black. In agreement with the literature,<sup>8</sup> we have shown that under exactly the same conditions, bis(acetonitrile)dichloropalladium(II) does not react with propylene. The weak tendency of palladium chloride to undergo Wacker-type chemistry in dry acetic acid is further underlined by our observation that the oxidation of propylene in acetic acid by py(TPP)CoNO<sub>2</sub> in the presence of (CH<sub>3</sub>CN)<sub>2</sub>PdCl<sub>2</sub> leads to acetone (90%) as the main product. However, palladium acetate (**2**) oxidizes propylene to a mixture of 1-, 2-, and 3-acetoxypropenes (Table I) with concomitant reduction of palladium(II) to palladium metal.<sup>9</sup> Comparison of these reactions suggests that, in the oxidation of propylene by complex **1**, the formation of the first and third groups of products involves participation of the nitro ligand, while the second group of products is the result of a Wacker-type<sup>9</sup> oxidation of the olefin.

When the oxidation of propylene is carried out in an oxygen atmosphere, a catalytic system results, since the palladium nitrosyl complex formed in the oxygen transfer step from complex **1** to propylene is recycled in situ by its reaction with molecular oxygen.<sup>5</sup>

(8) It has been reported previously that PdCl<sub>2</sub> does not oxidize olefins in dry acetic acid if no acetate salts are present in the reaction mixture, ref 9c, p 193.

(9) (a) Maitlis, P. M. "The Organic Chemistry of Palladium"; Academic Press: New York, 1971; Vol. 2, pp 93-105. (b) Sheldon, R. A.; Kochi, J. K. "Advances in Catalysis"; Eley, D. D., Pine, H., Weisz, P. B., Eds.; Academic Press: New York, 1976; pp 363-367. (c) Sheldon, R. A.; Kochi, J. K. "Metal-Catalyzed Oxidations of Organic Compounds"; Academic Press: New York, 1981; Chapter 7.

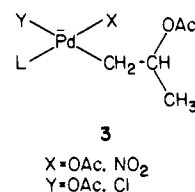
**Table II.** Isomer Distribution in the Products of Propylene Oxidation

run	acetoxypropenes		propylene glycol monoacetates		
	2-OAc	mix of 1-OAc + 3-OAc	1-OAc-2-OH	1-OH-2-OAc	1-OAc-3-OH
1	60	40	40	60	0
2	63	37	0	0	0
3	63	37	46	34	20
4	70	30	0	0	0
5	61	39	45	55	0
6	59	41	45	46	9

However, the total yield of the resulting products amounts to only approximately 10 turnovers of palladium. At the end of the reaction, the palladium is precipitated as [Pd(NO)Cl]<sub>n</sub> containing various amounts of PdCl<sub>2</sub> and palladium black. Again, in the catalytic system, if complex **1** is replaced by palladium acetate, no propylene glycol monoacetates are formed (Table I). Only vinylic acetates and a very small amount of acetone are formed. The formation of the latter compound is apparently due to either adventitious contamination of the reaction mixture by water or a palladium(II)-catalyzed reaction of acetoxypropene with acetic acid.<sup>9c</sup>

The relative amounts of the various products in the stoichiometric and catalytic oxidations are very similar (Table II) with the exception that, in the catalytic system, the mixture of propylene glycol monoacetates includes not only 1,2-isomers but also 1-acetoxy-3-hydroxypropane. This last compound is formed exclusively at the expense of 1-hydroxy-2-acetoxypropane (Table II, compare run 1 with 3 and 5 with 6). The fact that the product distribution is nearly identical in the stoichiometric and catalytic reactions suggests that the reaction mechanism is the same in both cases.

In all the reactions listed in Table I, the ratio of 2-acetoxypropene to the mixture of 1-acetoxy- and 3-acetoxypropenes remains roughly constant (Table II) regardless of whether complex **1** or palladium acetate is employed as the stoichiometric oxidant or catalyst. This fact suggests that the unsaturated acetates are derived from a  $\beta$ -hydride elimination of intermediate **3**, or its isomers. On the other hand, most of the acetone and all the



propylene glycol monoacetates should be the products of oxygen atom transfer from the ligand in complex **1**. This hypothesis is confirmed by the <sup>18</sup>O labeling studies discussed below.

The stoichiometric oxidation of ethylene by complex **1** in acetic acid yields a mixture of vinyl acetate, 1-hydroxy-2-acetoxyethane, and 1,2-diacetoxyethane (Table III). No acetaldehyde has been detected. Higher olefins also react (Table III); however, the reaction rate is slower and the yields are lower. In contrast, cyclic olefins such as cyclooctene and norbornene do not form glycol monoacetates. Instead, cyclooctene gives only an unsaturated

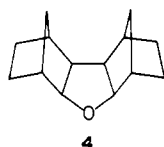
Table III. Oxidation of Olefins by Complex 1<sup>a</sup>

olefin	ketone, %	unsaturated, acetates, %	glycol monoacetates, %	other prod (%)
1-octene	21	16	33	octenol (18)
1-octene <sup>b</sup>	63	40	122	octenol (118)
ethylene <sup>c</sup>		20	50	1,2-diacetoxyethane (7)
cyclooctene	0	major	0	
norbornene	0	0	0	dimer

<sup>a</sup>Unless stated otherwise, the oxidations were run at 25 °C in 5 mL of acetic acid containing 1 g of olefin and 0.38 mmol of 1. The yields are based on the amount of 1. <sup>b</sup>Run under 345 kPa of O<sub>2</sub>. <sup>c</sup>The pressure of ethylene was 345 kPa.

acetate of unknown structure, and norbornene forms a high yield of an oxidized dimer with the proposed structure 4.<sup>3</sup>

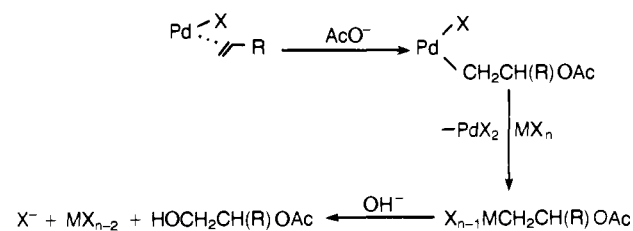
The first step in the formation of the desirable glycol monoacetates could be the attack of acetate anion on an olefin  $\pi$ -bonded to palladium(II). It was, therefore, logical to examine the effect of acetate ion concentration on the product distribution (Table I, runs 5 and 6). In both the stoichiometric and catalytic systems,



the addition of lithium acetate to the mixture of propylene and complex 1 in acetic acid increases the yield of the unsaturated acetate solely at the expense of acetone. However, the relative yield of the propylene glycol monoacetates remains constant (~50%, Table I). In the catalytic system, the presence of lithium acetate also increases the number of turnovers (20.8 vs. 10.3 in the absence of LiOAc, Table II, runs 3 and 6), but the formation of acetone is not suppressed completely, as is the case in the stoichiometric oxidation. The replacement of the acetic acid by a sterically hindered carboxylic acid, such as pivalic or 2,6-dimethylbenzoic acid, or by a more acidic acid yielding a less reactive carboxylate anion (e.g., benzoic acid), completely eliminates the formation of the propylene glycol monocarboxylates (Table IV). This also either eliminates or strongly suppresses the formation of the Wacker-type products. Even the addition of lithium pivaloate does not induce the appearance of 2-pivaloylpropene or propylene glycol pivaloates. Correspondingly, acetone becomes the main product. In these special cases, the reaction proceeds as if no external nucleophile was present.

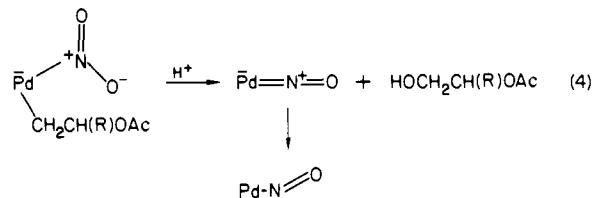
**<sup>18</sup>O Labeling Studies.** The stoichiometric oxidation of propylene by complex 1 containing <sup>18</sup>O in the nitro ligand has been carried out in acetic acid under exactly the same conditions as with the unlabeled complex 1. As expected, only acetone and the isomeric propylene glycol monoacetates were found to contain labeled oxygen. The unsaturated acetates, 1-, 2-, and 3-acetoxypropenes, did not contain any label. The most important observation is that the <sup>18</sup>O label is located exclusively in the acetoxy group of the glycol monoacetates and that the hydroxy group contains only <sup>16</sup>O. This statement is supported by careful examination of both chemical ionization (CI) and electron impact (EI) mass spectral data. The CI spectra reveal that the <sup>18</sup>O concentration in the protonated parent ion (M + 1) and the ion obtained by water elimination (M + 1 - 18) is the same within the experimental error. This assignment is further strengthened by comparison of the mass spectra with that obtained from an authentic sample of 1-acetoxy-2-hydroxypropane specifically labeled in the acetoxy group. The ratio of the fragments at *m/e* 43 and 45 as measured by EI suggests that most of the <sup>18</sup>O label is located in the carboxyl oxygen of the acetate group. It is also important to note that the <sup>18</sup>O content in the acetoxy group is quite high despite the fact that the oxidation was carried out in a huge excess of acetic acid (molar ratio of complex 1 to acetic acid = 220). Thus, the transfer of <sup>18</sup>O from the nitro group of complex 1 to the product cannot be

Scheme I. Mechanism of Olefin Oxidation in the Presence of High-Valent Metal Oxidants



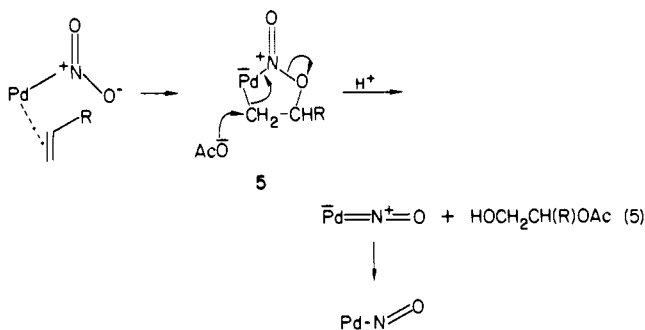
preceded by an indiscriminate scrambling with the solvent.

**Reaction Mechanism.** The formation of glycol mono- and diacetates in the palladium-promoted or -catalyzed oxidations of ethylene and propylene has been observed previously.<sup>9</sup> This reaction requires the presence of an excess of an oxidant such as copper(II), thallium(III), lead(IV), or nitrate ion.<sup>9,10</sup> The role of the nitrate ion has not been explained in the literature. In the case of copper(II) and, possibly, the other higher valent metals, a mechanism summarized in Scheme I has been proposed.<sup>9c</sup> The key steps are the transfer of the acetoxyethyl group from palladium to the higher valent metal followed by the oxidation of this group to the product with the concomitant reduction of the oxidant. If the nitro ligand of complex 1 plays the role of the oxidant or if the participation of the nitro ligand in the redox reaction proceeds via a concerted mechanism (eq 4), then the <sup>18</sup>O label would either



be lost by exchange with solvent or transferred into the hydroxy group, respectively. Both of these possibilities contradict the experimental data.

A similar disagreement with the experimental results is encountered if it is assumed that the first step in the olefin oxidation by complex 1 is the formation of the metallacycle 5 (eq 5), which



has been demonstrated in aprotic media.<sup>5-7</sup> The metallacycle could then undergo acetolysis as shown below (eq 5). Again, the label would be transferred to the hydroxy group.

Another theoretical possibility is the formation of an epoxide followed by its acetolysis to glycol monoacetate. This is a plausible pathway since certain olefins, in which  $\beta$ -hydride elimination is inhibited, have been shown to form appreciable amounts of epoxides when oxidized by complex 1 in aprotic media.<sup>6</sup> However, even in this case, the <sup>18</sup>O label should be found in the hydroxy group. Furthermore, epoxides added to the reaction mixture were found to be stable.

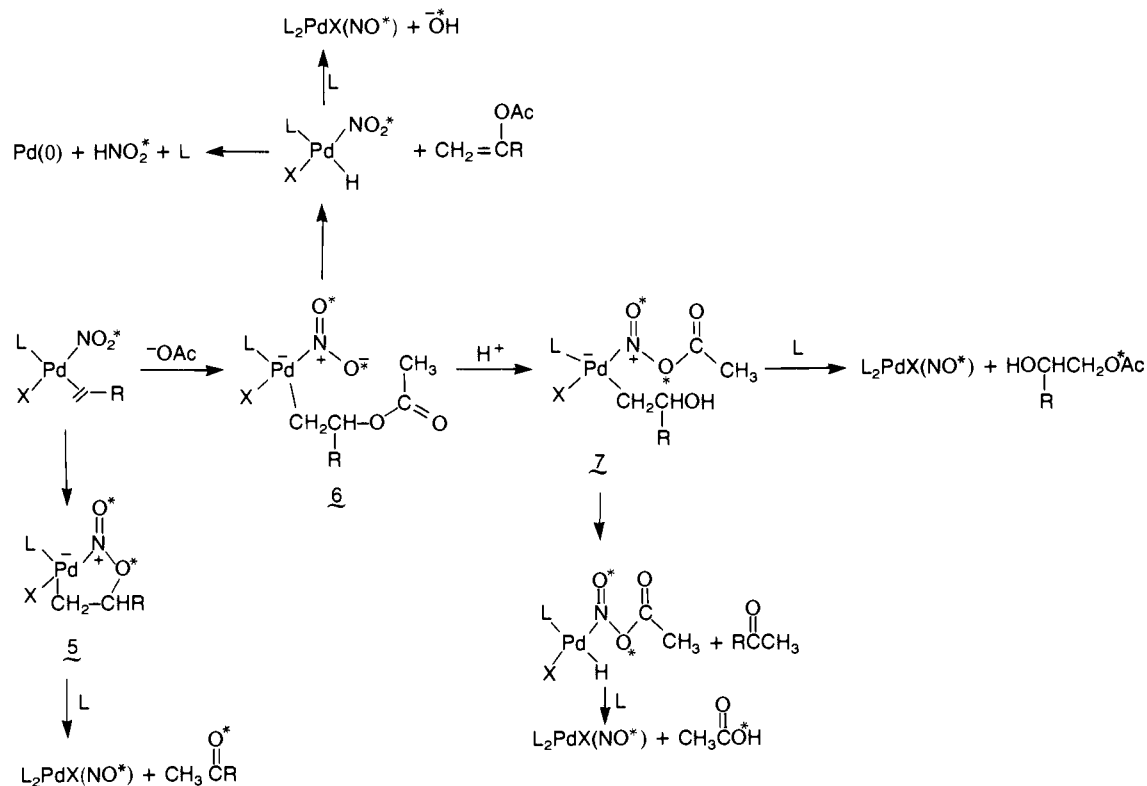
A mechanism which agrees with all the data accumulated at this time is summarized in Scheme II. The formation of acetone

(10) (a) Tamura, M.; Yasui, T. *J. Chem. Soc., Chem. Commun.* **1968**, 1209-1210. (b) Henry, P. M. *J. Org. Chem.* **1974**, *39*, 3871-3874. (c) Volkonskii, M. G.; Libbrolovov, J. A.; Ermakov Yu. I. *Kinet. Katal.* **1977**, *18*, 790-791. (d) *Ibid.* **1979**, *20*, 362-366. (e) *Ibid.* **1983**, *24*, 578-585.

**Table IV.** Oxidation of Propylene in the Presence of Carboxylic Acids<sup>a</sup>

acid (g)	solvent (mL)	temp, °C	time, h	acetone, %	other products
pivalic acid (5)	neat	40	2	38	
pivalic acid (5)	neat	40	2	237 <sup>b</sup>	
pivalic acid (5)	neat	40	2	35 <sup>c</sup>	
2,6-dimethylbenzoic acid (1)	CH <sub>3</sub> NO <sub>2</sub> (5)	25	18	25	propenyl dimethylbenzoate
benzoic acid (1)	CH <sub>3</sub> NO <sub>2</sub> (5)	25	18	44	propenyl benzoate
benzoic acid (1)	CH <sub>3</sub> NO <sub>2</sub> (5)	25	18	1250 <sup>b</sup>	acetol benzoate, propene oxide (~1%)

<sup>a</sup>All reactions utilized 0.38 mmol of **1**. <sup>b</sup>Carried out under 345 kPa of O<sub>2</sub>. <sup>c</sup>Lithium pivaloate (3.8 mmol) was added.

**Scheme II.** Proposed Mechanism of Olefin Oxidation by Palladium Nitro Complexes in Acetic Acid

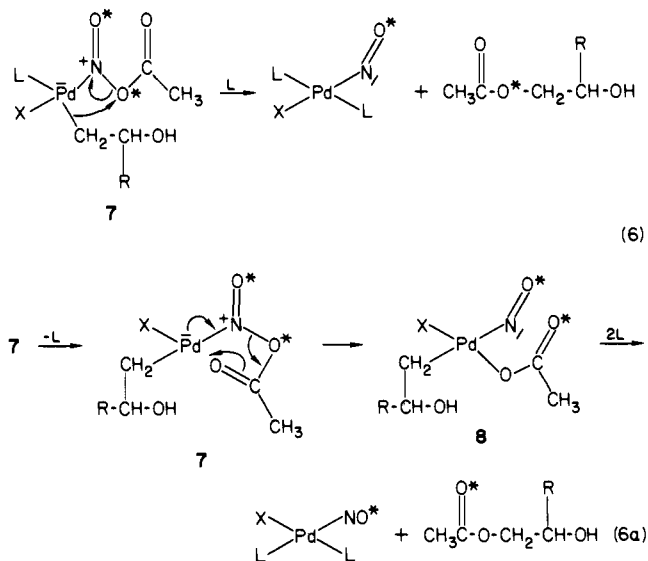
requires that the internal nucleophile (the nitro ligand) competes with the external nucleophile (the acetate ion). Correspondingly, an increase in the concentration of acetate ion, by the addition of lithium acetate, decreases or completely eliminates acetone formation. Alternatively, if the external nucleophile is weak, e.g., benzoic acid, or bulky, and therefore unable to attack the coordinated olefin, such as in the case of pivalic and 2,6-dimethylbenzoic acids, acetone is the main product. The intermediate complex **6**, which is presumed to be present in any Wacker-type oxidation and is formed by the attack of acetate ion on the coordinated olefin, may decompose by either of two competing pathways. The first one is the well-known  $\beta$ -hydride elimination route which leads to the observed acetoxypropene isomers.<sup>9c</sup> The second possibility is formation of the glycol monoacetates via intermediate **7**. This ensures that the hydroxy group of the product will not contain any <sup>18</sup>O label.

The  $\beta$ -hydride elimination from intermediates **6** or **7** does not necessarily produce palladium metal since the nitro ligand in **6** or its acetyl derivative in **7** may undergo redox reactions, leading to a nitrosylpalladium(II) complex. Alternatively, the HNO<sub>2</sub> formed after the  $\beta$ -hydride elimination from **6** may oxidize the palladium(0) (Scheme II).

The acetyl transfer in the conversion of intermediate **6** to **7** requires the addition of a proton. Addition of lithium acetate to the reaction mixture decreases the proton concentration. Thus, the proposed mechanism suggests that, upon addition of lithium acetate, the expected rate of enhancement in formation of intermediate **6** may be balanced by the rate decrease in the acyl transfer leading to intermediate **7**. Our data show that addition of lithium acetate increases the formation of unsaturated acetates

solely at the expense of acetone, while the content of glycol monoacetates in the products remains constant.

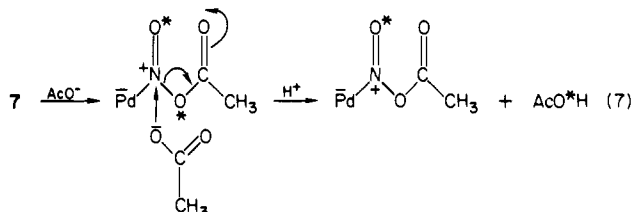
The decomposition of intermediate **7** to propylene glycol monoacetate may proceed directly via an electrophilic attack of the acetoxy oxygen on the carbon adjacent to palladium (eq 6).



Alternatively, transfer of the acetate group from the ligand in intermediate **7** to palladium may first lead to intermediate **8** which

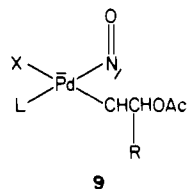
would undergo reductive elimination to glycol monoacetate (eq 6a). The fact that a substantial amount of the  $^{18}\text{O}$  label has been found in the carbonyl function of the glycol monoacetates would favor the pathway shown in eq 6a.

The content of  $^{18}\text{O}$  in either acetone ( $35.5 \pm 2.0\%$  of  $^{18}\text{O}$ ) or the glycol monoacetate isomers ( $39.2 \pm 0.4\%$  and  $37.9 \pm 1.3\%$  of  $^{18}\text{O}$ ) is lower than in the nitro complex **1** ( $51 \pm 2\%$ ). The lower  $^{18}\text{O}$  content in acetone is also in agreement with the pathway summarized in Scheme II since  $\beta$ -hydride elimination from intermediate **7** should lead to unlabeled acetone. The labeled acetone can be formed only via metallacycle **5** (Scheme II) as shown previously.<sup>5,6c,11</sup> The lower than expected  $^{18}\text{O}$  content in the glycol monoacetates would suggest that some exchange of the acetate ion with the solvent (acetic acid) takes place before the acetyl group is incorporated into the product. This may be accomplished by an attack of acetate ion on the nitroacyl ligand in **7** (eq 7) or



on the central metal in **8**. The high content of  $^{18}\text{O}$  in the glycol monoacetates ( $\sim 75\%$  of the theoretical value) suggests that the decomposition of the intermediate **7** is a concerted process which does not involve the formation of free radicals or carbonium ions by cleavage of the Pd-C bond.

The 1-acetoxy-3-hydroxypropane observed in the catalytic system cannot be obtained directly from either of the isomeric forms of complex **7**. The formation of this isomer requires the occurrence of a 1,2-hydride shift which could take place in intermediate **6**, **7** (Scheme II), or **9** (below). However, the observation that the 1,3-isomer is formed only during the catalytic and not the stoichiometric oxidation suggests that the 1,2-hydride shift takes place in intermediate **9**. In this case, the 1,2-hydride

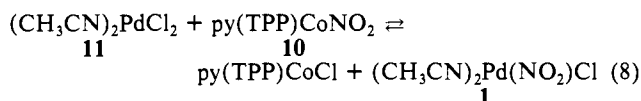


shift can take place before the nitrosyl ligand is reoxidized by molecular oxygen to the nitro ligand. Only after the regeneration of the nitro ligand can the oxidation of the Pd-C bond leading to the glycol acetate take place.

The oxidation of olefins catalyzed by complex **1** in acetic acid appears to be very similar to the well-known palladium(II)-catalyzed oxidation of olefins by nitrate ion in the same medium. Recently, Ermakov and co-workers observed that, during the induction period in this reaction, lower nitrogen oxides are formed.<sup>10d</sup> They postulated that these can react with the palladium(II) to form nitro complexes, analogous to **1**, which would carry out the oxidation of olefins to the observed product. This hypothesis could be tested by introduction of nitrate ion enriched by  $^{18}\text{O}$ . If the proposed analogy exists, then the resulting glycol monoacetate should be labeled exclusively or predominantly in the acetoxy group.

**Part II. Experimental Support for the Bimetallic System.** Recently, an alternate mechanism for the oxidation of olefins catalyzed by the bimetallic system in aprotic media has been proposed.<sup>7</sup> In this case, a mixture of (pyridine)(tetraphenylporphyrinato)nitrocobalt(III) (**10**) and bis(acetonitrile)dichloropalladium(II) (**11**) would react by transferring the nitro ligand

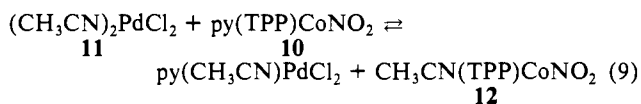
from complex **10** to **11** (eq 8). This would then lead to the



formation of complex **1** which would serve as the oxidant. The observations that the chloride in (pyridine)(tetraphenylporphyrinato)chlorocobalt(III) can be replaced by the nitro ligand from complex **1** and, in addition, that the oxidation of *cis*- and *trans*-cyclooctene in the bimetallic system is not strictly stereoselective have been used as possible evidence for this proposal.<sup>6c,7</sup>

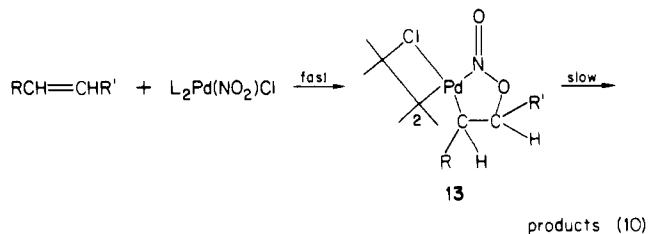
There are, however, very strong spectroscopic, kinetic, and other data which point to an enormous difference between these two systems and support the existence of a bimetallic mechanism. These points are summarized below.

The interaction of equimolar amounts of complexes **10** and **11** was carefully examined by using FTIR at room temperature in 1,2-dichloroethane. The same solvent was employed in the previous studies of olefin oxidation by the bimetallic system. This study has established that a relatively fast exchange between the pyridine ligand in complex **10** and the acetonitrile ligands in complex **11** takes place (eq 9). The half-life of this reaction is



about 2 min. The equilibrium is fully established in 10 min. At equilibrium, the concentration of complex **12** reaches about 30% of the original amount of **10**. This reaction can be followed by recording the decrease in the intensity of the peaks at 800 and 820  $\text{cm}^{-1}$ , characteristic of the nitro ligand in complex **10** and its pyridine-free analogue, and by appearance of a peak at 812  $\text{cm}^{-1}$  assigned to **12**. During this reaction, the ratio of the band intensities at 800 and 820  $\text{cm}^{-1}$  remains constant. Even after 1 h, no evidence for the formation of complex **1** has been observed. Complex **1** also absorbs at 820  $\text{cm}^{-1}$ . However, computer simulation and a blank experiment have demonstrated that as little as 3% of complex **1** can be detected. It is, therefore, necessary to conclude that if equilibrium **8** is established, it lies heavily (97% or more) on the side of the cobalt nitro complex **10**.

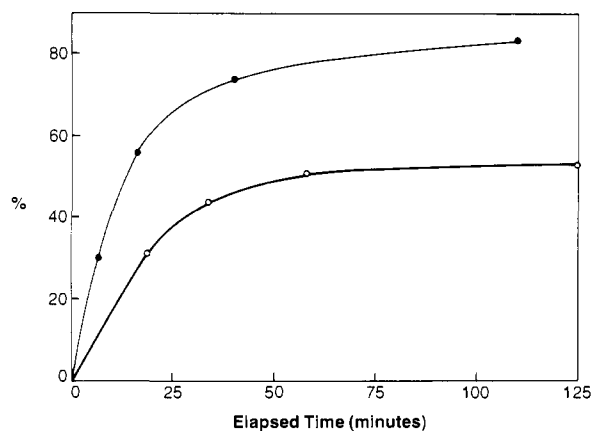
Next, the rates of olefin oxidation in both the bimetallic and monometallic systems have been examined under the same conditions used for the above FTIR studies. Ethylene and norbornene have been chosen as the substrates since they represent two extremes in the choice of olefins. In the oxidation of norbornene by complex **1**, the formation of metallacycle **13** is relatively fast and nearly quantitative. The decomposition is the slow, rate-determining step (eq 10).<sup>6c,11</sup> In the case of ethylene, the for-



mation of metallacycle **13** is again rapid, but its content is limited to about 30% of the amount of **1**. However, the metallacycle decomposition, although still the rate-determining step, is much faster than in the case of norbornene.<sup>6c,11</sup>

The equilibrium concentration of the metallacycle strongly depends on the concentration of olefin and complex **1**. On the basis of the FTIR studies, the concentration of **1**, if ever present in the bimetallic system, cannot at any time be higher than 3% of the amount of **1** relative to the monometallic system. If, indeed, the bimetallic system is converted into its monometallic analogue, then the rate of oxidation of ethylene would always be slower in the bimetallic system and the rate of norbornene oxidation in the

(11) Andrews, M. A.; Chang, T. C.-T.; Cheng, C.-W. F.; Emge, T. J.; Kelly, K. P.; Koetzle, T. F. *J. Am. Chem. Soc.* **1984**, *106*, 5913-5920.



**Figure 1.** Conversion of ethylene in bimetallic (●) and monometallic (○) systems. The yield is based on the amount of metal nitro complex present.

bimetallic system could at best only approach the rate in the monometallic system.

In sharp disagreement with this expectation is the fact that the rates of norbornene and ethylene oxidation in the bimetallic system are faster than those in the monometallic system. Thus, oxidation of norbornene to *exo*-epoxynorbornene by complex **1** at room temperature requires 80 h.<sup>6c</sup> Even though this rate is reported to be substantially enhanced by the presence of cobalt(III) complexes such as py(TPP)CoCl, it still takes more than 1 h.<sup>7</sup> In the bimetallic system, the maximum yield of *exo*-epoxynorbornene (74%) is obtained in 10 min.<sup>3</sup> The dimer **4** is the second major product. In the case of ethylene, the experimental data (Figure 1) again demonstrate that not only the rate of oxidation but also the yield of acetaldehyde is higher in the bimetallic than in the monometallic system.

The oxidation of olefins by metal complexes in acetic acid further underlines the difference between the mono- and bimetallic systems. If the proposed conversion of the bimetallic system does take place, then the products of the olefin oxidation in acetic acid should be the same in both systems. Again, the experimental results do not support this expectation. The stoichiometric and catalytic oxidation of ethylene in the bimetallic system give either predominantly acetone or exclusively vinyl acetate,<sup>1</sup> depending on the cocatalyst. However, glycol monoacetate is the main product in the monometallic system under otherwise analogous conditions.

Finally, the epoxidation of olefins by **10** in the presence of thallium(III) salts<sup>2</sup> is another strong indication of the existence of a bimetallic system.

## Experimental Section

**Materials.** Solvents and other chemicals were commercial grade unless otherwise stated. Acetone and nitromethane were dried over calcium sulfate and molecular sieves. Glacial acetic acid was first treated with boron triacetate and then distilled.<sup>12</sup> Commercially available 1,2-epoxyoctene was purified by distillation, bp 100 °C/95 torr. Sodium metal was employed for drying 1-octene.

1-Acetoxy-2-hydroxypropane was prepared by treating dry acetic acid (5.15 g, 0.086 mol) with propylene oxide (10 g, 0.172 mol) and a catalytic amount of triethylamine (265 mg, 2.6 mmol) at 45 °C. After 48 h, a mixture of propylene glycol monoacetates, containing predominantly 1-acetoxy-2-hydroxypropane, was produced. The product was purified by distillation at 95 °C/20 torr; the structure was confirmed by NMR spectroscopy.

1-Acetoxy-2-hydroxyoctane was prepared by treatment of the corresponding epoxide (22.0 g, 0.172 mol) with acetic acid (16.7 g, 0.27 mol) in the presence of triethylamine (265 mg). After 72 h at 45 °C, the mixture was neutralized with aqueous sodium bicarbonate. The product was extracted with ether and isolated by standard methods, bp 94 °C/2 torr; the NMR spectrum is in agreement with the proposed structure.

Bis(acetonitrile)chloronitropalladium(II) was prepared according to a literature procedure.<sup>3</sup>

Anhydrous lithium acetate and lithium pivaloate were prepared by the reaction of 1 equiv of *n*-butyllithium with the dried acids. The volatiles were evaporated under vacuum.

**Analytical.** The reaction mixtures were analyzed on a Hewlett-Packard 5880 gas chromatograph equipped with a flame ionization detector. Separations were performed on a 6-ft glass column packed with 5% OV-225 on Chromosorb GHP by employing triethylene glycol dimethyl ether (triglyme) as an internal standard. GC-MS data were recorded on a Finnigan 3300 instrument, and GC-IR analyses were carried out on a Nicolet 170SX instrument.

**Procedures.** The oxidations of olefins by complex **1** were carried out in a standard manner. Below are several illustrative examples of the procedures employed in this study.

**Oxidation of Propylene by Complex 1 in Acetic Acid.** A thick-walled glass tube equipped with a magnetic stirring bar and a Teflon stopcock was charged with 105.7 mg (0.39 mmol) of **1** and 49.6 mg of triglyme. After the mixture was degassed on a vacuum line, acetic acid (5 mL) and liquid propylene (0.5 mL) were condensed into the tube. The mixture was warmed to room temperature and stirred for 2 h. During this time, the initially orange solution turned nearly colorless with the concurrent precipitation of a dark solid. The apparatus was vented, the slurry filtered, and the filtrate analyzed as described above. The products (% yields) in order of elution were: acetone (30%), 2-acetoxypropene (18%), a mixture (12%) of 1-acetoxy- and 3-acetoxypropene, and a mixture (75%) of 1-acetoxy-2-hydroxypropane and 1-hydroxy-2-acetoxypropane. The yields are based on the palladium nitro complex. The precipitate contains 0.99% carbon, 0.06% hydrogen, 4.83% nitrogen, 20.69% chlorine, and 63.35% palladium. The IR spectra exhibit bands at 1755 and 1715, cm<sup>-1</sup> typical for [Pd(NO)Cl]<sub>n</sub>.<sup>5,13</sup> On the basis of the IR and elemental analysis, the solid appears to be a mixture of palladium metal, PdCl<sub>2</sub>, and [Pd(NO)Cl]<sub>n</sub>. In a similar reaction utilizing (CH<sub>3</sub>CN)<sub>2</sub>PdCl<sub>2</sub>, no products were observed. Only 2-acetoxypropene (40%) and a mixture of 1- and 3-acetoxypropenes were produced in the presence of palladium(II) acetate.

**Catalytic Oxidation of Propylene by Complex 1 in Acetic Acid.** A glass liner equipped with a magnetic stirring bar was charged with 96.9 mg (0.36 mmol) of complex **1**, 47.7 mg of triglyme, and 5 mL of acetic acid. The liner was inserted into a high-pressure stainless steel reactor and the apparatus assembled. The mixture was cooled in liquid nitrogen, the reactor evacuated, and 1 mL of liquid propylene transferred into the assembled system. The reactor was pressurized with 50 psi oxygen and warmed to room temperature, after which it was allowed to stir for 18 h at 25 °C. The apparatus was then vented. The solution was filtered to remove a dark precipitate, consisting of [Pd(NO)Cl]<sub>n</sub>, PdCl<sub>2</sub>, and palladium metal, and the filtrate was analyzed by gas chromatography. The following products (% yields) were observed and are listed in the order of elution: acetone (352%), a mixture of isomeric acetoxypropenes (157%), and a mixture of propylene glycol monoacetates (522%). Three isomers were found in the mixture of propylene glycol monoacetates. In a similar reaction with Pd(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> substituted for complex **1**, only acetone (46%), 2-acetoxypropene (331%), and a mixture of 1- and 3-acetoxypropene (136%) were found. All of the yields are based on the amount of the palladium complex, and the products were confirmed by GC/MS analysis.

**Oxidation of Propylene by Complex 1 in Pivalic Acid.** A thick-walled glass tube fitted with a Teflon stopcock and a magnetic stirring bar was charged with 102.5 mg (0.38 mmol) of complex **1** and 400 mg (3.7 mmol) of lithium pivalate in a drybox. Pivalic acid (5 mL) and triglyme (44.6 mg) were subsequently added. After the mixture was degassed on a vacuum line, 1 mL of liquid propylene was condensed into the tube and the resulting mixture heated to 40 °C for 2 h. During this time, palladium metal, PdCl<sub>2</sub>, and [Pd(Cl)NO]<sub>n</sub> coprecipitated as a dark solid. After the solid was vented, 5 mL of nitromethane was added, the reaction filtered, and the filtrate analyzed by gas chromatography. Acetone (35% yield based on palladium) was the only product observed. This result was confirmed by GC/MS analysis.

**Oxidation of Ethylene by Complex 1 in Acetic Acid.** A Fisher-Porter tube was charged with 102.6 mg (0.38 mmol) of complex **1**, 48.8 mg of triglyme, and 5 mL of acetic acid. The mixture was degassed and pressurized with 40 psi ethylene. After warming to room temperature, the reaction mixture was stirred for 4 h, during which time the palladium-containing solids precipitated from the solution. The apparatus was vented, the solution filtered, and the filtrate analyzed by gas chromatography. The following products were observed and are listed in the order of elution: vinyl acetate (20%), ethylene glycol monoacetate (50%), and ethylene glycol diacetate (7%).

**Oxidation of 1-Octene by Complex 1 in Acetic Acid.** Bis(acetonitrile)chloronitropalladium(II) (102.4 mg, 0.38 mmol) and triglyme

(12) Jolly, W. L. "The Synthesis and Characterization of Inorganic Compounds"; Prentice-Hall: Englewood Cliffs, NJ, 1970; p 116.

(13) Smidt, J.; Jira, R. *Chem. Ber.* 1960, 93, 162-165.

(51.5 mg) were added to a reaction tube, and the mixture was degassed. Acetic acid (5 mL) and 1-octene (1 mL) were condensed into the reaction vessel, and the mixture was warmed to room temperature and stirred for 18 h. The progress of the reaction was followed by the formation of a dark precipitate. The slurry was filtered and the filtrate analyzed by GC and GC/MS. Four major products were observed; however, only two were unambiguously identified, 2-octanone (21%) and a mixture of 1,2-octylene glycol monoacetate (33%). The identifications were based upon retention times and the molecular weights of the parent ion (128 and 188, respectively). The other two products are believed to be octenol and octylene acetate. These identifications are based upon GC/MS analysis. For octenol, a small molecular ion at  $m/e$  129 was observed with a major fragment at  $m/e$  111 corresponding to the  $(M - H_2O)^+$  ion in the chemical ionization (CI) spectrum. In the electron ionization (EI) spectra, ions were observed at  $m/e$  128, 95, 85, 81, 72, 68, 55, and 43. These data closely resembled those of authentic samples of 2-octen-1-ol and 1-octen-3-ol. In the CI analysis of octylene acetate, a protonated molecular ion is observed at  $m/e$  171 and a fragment ion at  $m/e$  111 corresponding to  $[M + H - CH_3CO_2H]^+$ . The spectrum closely resembles those of other unsaturated acetates. Unfortunately, all of the possible isomers were not available and therefore unambiguous determination of the products was not possible.

**Oxidation of Norbornene by Complex 1 in Acetic Acid.** Norbornene was oxidized by complex 1 in a manner similar to that previously described for 1-octene. Analysis of the reaction mixture by gas chromatography revealed a single product (neither norcamphor nor *exo*-2,3-epoxynorbornane). A molecular weight of 204 was determined by GC/MS analysis, suggesting the formation of a dimer containing one oxygen atom with a possible structure 4. Further evidence for this structure was obtained by GC/IR analysis which yielded a spectrum containing major features at 2920, 1100, and 1060  $cm^{-1}$ . No evidence for unsaturation was found. The peaks at 1100 and 1060  $cm^{-1}$  are consistent with C–O–C stretches found in substituted five-membered cyclic ethers.<sup>14</sup> The same "dimer" was formed in oxidation of norbornene by a mixture of py(TPP)CoNO<sub>2</sub> and (CH<sub>3</sub>CN)<sub>2</sub>PdCl<sub>2</sub>.<sup>3</sup>

**Oxidation of Cyclooctene by Complex 1 in Acetic Acid.** Cyclooctene was treated with complex 1 in a manner similar to that described for 1-octene. Analysis of the reaction mixture revealed two products; neither was cyclooctene oxide nor cyclooctanone. GC/MS analysis gave similar CI spectra with a base peak at  $m/e$  109 and a fragment ion at  $m/e$  67 for both products. In the EI mass spectra, both compounds again displayed a similar pattern. The spectrum for the most intense peak exhibited a small molecular ion at  $m/e$  168 and another ion at  $m/e$  109 corresponding to  $(M - O_2CCH_3)^+$ . These data are consistent with the presence of a cyclooctenyl acetate. In the IR spectrum of this compound, bands at 3020, 2920, and 1720  $cm^{-1}$  were found. These features are consistent with an unsaturated species containing an ester moiety. However, the position of acetate substitution could not be ascertained.

**Oxidation of Propylene by py(TPP)CoNO<sub>2</sub> and (CH<sub>3</sub>CN)<sub>2</sub>PdCl<sub>2</sub> in Acetic Acid.** A thick-walled glass tube equipped with a magnetic stirring bar and a Teflon stopcock was charged with 172 mg (0.66 mmol) of (CH<sub>3</sub>CN)<sub>2</sub>PdCl<sub>2</sub>, 248 mg (0.34 mmol) of py(TPP)CoNO<sub>2</sub>, and 50.9 mg of triglyme. After the mixture was degassed on a vacuum line, acetic acid (5 mL) and liquid propylene (0.5 mL) were condensed into the tube. The mixture was stirred 18 h at 60 °C and filtered and the filtrate analyzed by GC. The oxidation products in order of elution were acetone (90%), 2-acetoxypropenes (3%), and a mixture (14%) of 1-acetoxy-2-hydroxypropane and 1-hydroxy-2-acetoxypropane. The yields are based on the amount of palladium nitro complex used.

**Preparation of <sup>18</sup>O-Labeled 1.** The <sup>18</sup>O-labeled nitro palladium complex was prepared according to a literature procedure.<sup>5</sup> The <sup>18</sup>O content was determined to be 51 ± 2% from the absorbances at 803, 822, and 840  $cm^{-1}$  (KCl pellet) assigned the N<sup>18</sup>O<sub>2</sub>, N<sup>18</sup>O<sup>16</sup>O, and N<sup>16</sup>O<sub>2</sub> ligands, respectively. The content of <sup>18</sup>O in 1 must be determined at the time when it is used for the olefin oxidation since the <sup>18</sup>O content decreases with time when in contact with air or moisture.

**Oxidation of Propylene by (CH<sub>3</sub>CN)<sub>2</sub>Pd(Cl)N<sup>18</sup>O<sub>2</sub> in Acetic Acid.** A reactor was charged with 50.7 mg of (CH<sub>3</sub>CN)<sub>2</sub>Pd(Cl)N<sup>18</sup>O<sub>2</sub> of unknown <sup>18</sup>O content and 51.7 mg of triglyme. The mixture was degassed, and acetic acid (2 mL) and propylene (0.3 mL) were added. After the reaction and workup in a manner previously described, the filtrate was analyzed by GC/MS. Three groups of products were confirmed: acetone, the acetoxypropenes, and the propylene glycol monoacetates. The CI mass spectra show no incorporation of <sup>18</sup>O in either of the three acetoxypropane isomers. In the CI spectrum of acetone, a pair of ions at  $m/e$  59 and 61 corresponding to  $(M + H)^+$  was observed. In the EI spectrum, the molecular ions of both the unlabeled and labeled species

were present at  $m/e$  58 and 60, respectively. Another ion pair was also seen at  $m/e$  43 and 45, corresponding to the loss of methyl from the molecular ions. From the intensity ratios of these ion pairs, incorporation of <sup>18</sup>O was estimated to be 58 ± 2%.

For the propylene glycol monoacetates, the CI spectrum exhibited a pair of protonated molecular ions at  $m/e$  119 and 121. These, in addition to other ion pairs at  $m/e$  101 and 103 ( $M + H^+ - 18$ ) and  $m/e$  61 and 63 ( $M + H^+ - 60$ ), represent conclusive evidence for incorporation of <sup>18</sup>O into the propylene glycol monoacetate. In the EI spectrum, the molecular ions were not observed. The following ion pairs were present:  $m/e$  101 and 103 ( $M - OH$ )<sup>+</sup>,  $m/e$  87 and 89 ( $M - CH_3O$ )<sup>+</sup>,  $m/e$  74 and 76 ( $M - 44$ )<sup>+</sup>, and  $m/e$  43 and 45 ( $CH_3CO$ )<sup>+</sup>.

The intensity ratios of the ion pairs for one run are described in detail. Two GC fractions corresponding to two glycol monoacetate isomers have been taken, and the <sup>18</sup>O concentration has been determined: (a) from CI spectra using peaks at  $m/e$  119/121 (<sup>18</sup>O = 56.6 and 56.2%),  $m/e$  101/103 (<sup>18</sup>O = 52.4% and 54.0%), and  $m/e$  89/91 (<sup>18</sup>O = 53.7 and 56.1%); (b) from EI spectra using peaks at  $m/e$  87/89 (<sup>18</sup>O = 54.5 and 56.4%) and  $m/e$  74/76 (<sup>18</sup>O = 55.8 and 55.0%). In this specific case, the peaks at  $m/e$  101/103 were clearly observable but too small for quantitative determination of the <sup>18</sup>O content. The peak at  $m/e$  58 ( $M^+ -$  acetic acid) shows no analogue at  $m/e$  60 for the <sup>18</sup>O-labeled fragment. The maximum error in the analysis of the <sup>18</sup>O content is ±2%. The use of the GC/MS method for the analysis of the reaction products in acetic acid as the solvent resulted in the appearance of a small but definite background of acetic acid in most of the GC fractions. For this reason, the peaks at  $m/e$  43/45 in the EI spectra and at  $m/e$  61/63 in the CI spectra could be used only for qualitative but not quantitative determination of the <sup>18</sup>O content. Furthermore the EI spectra even for the unlabeled glycol monoacetates always shows peaks at  $m/e$  43 and 45. Nevertheless, the enormous change in the ratio of these peaks for labeled vs. unlabeled glycol monoacetates allows us to conclude that most of the <sup>18</sup>O label must reside in the carboxyl function of the acetate esters.

In a similar run in which complex 1 contained 51 ± 2% <sup>18</sup>O, the content of <sup>18</sup>O in the acetone was found to be 35.5 ± 2.0%. The <sup>18</sup>O content in ions produced from the glycol monoacetate isomers was determined from CI spectra (average of three to five measurements):  $m/e$  119/121, 39.2 ± 0.4% and 37.9 ± 1.3%;  $m/e$  101/103, 37.9 ± 1.5% and 38.0 ± 1.5%;  $m/e$  89/91, 37.6 ± 1.2% and 35.2 ± 2.0%. In the EI spectra, the ion  $m/e$  58 shows no counterpart at  $m/e$  60. Ions at  $m/e$  43/45 suggest appreciable content of <sup>18</sup>O.

**Preparation of <sup>18</sup>O-Labeled Propylene Glycol Monoacetate.** An authentic sample of 1-acetoxy-2-hydroxypropane labeled in the acetate moiety was prepared by reacting 100  $\mu$ L of 1-acetoxy-2-hydroxypropane with 1 mL of H<sub>2</sub><sup>18</sup>O containing 100  $\mu$ L of glacial acetic acid at room temperature for maximum 72 h. Samples were withdrawn at various time intervals and analyzed by GC/MS. As an example, the CI spectrum of one sample showed the following ions and their <sup>18</sup>O content:  $m/e$  119/121 (<sup>18</sup>O = 26.5%),  $m/e$  101/103 (<sup>18</sup>O = 24.6%), and  $m/e$  89/91 (<sup>18</sup>O = 24.3%). Also observed were the ions at  $m/e$  61 and 63 corresponding to the protonated acetic acid and its <sup>18</sup>O-labeled analogue. Another sample was analyzed by the EI method. The following ions and their <sup>18</sup>O content were observed:  $m/e$  87/89 (<sup>18</sup>O = 18.9%) and  $m/e$  74/76 (<sup>18</sup>O = 18.0%). The ions at  $m/e$  101/103 were too small for the <sup>18</sup>O content determination. Also observed were the ions at  $m/e$  43 and 45, indicating <sup>18</sup>O incorporation into the carbonyl function of the acetate group. The ion peak at  $m/e$  58 obtained by loss of acetic acid from the parent ion had no <sup>18</sup>O-labeled analogue at  $m/e$  60.

**Attempt to Detect Nitro Ligand Transfer from (Pyridine)(tetraphenylporphyrinato)nitrocobalt(III) to Bis(acetonitrile)dichloropalladium(II).** Standard solutions were prepared of bis(acetonitrile)dichloropalladium(II) (0.00779 M), (pyridine)(tetraphenylporphyrinato)nitrocobalt(III) (0.00763 M), and of complex 1 (0.0206 M) in 1,2-dichloroethane. The spectra of the standard solutions were then recorded on a Nicolet 170 SX FTIR instrument using a liquid sodium chloride cell of a path length = 0.187 mm. Computer subtraction of the 1,2-dichloroethane spectrum from the standard solution spectra showed two characteristic bands at 800 and 820  $cm^{-1}$  assigned to the nitro ligand of (pyridine)(tetraphenylporphyrinato)nitrocobalt(III) and its pyridine-free analogue.<sup>14</sup> The complex 1 exhibited one characteristic peak at 820  $cm^{-1}$ . The standard solutions of the cobalt nitro complex 11 and of the bis(acetonitrile)dichloropalladium(II) were mixed in a 1:1 ratio, and the mixture was scanned every 50 s. Only one new band at 812  $cm^{-1}$  gradually grew in, while bands at 800 and 820  $cm^{-1}$  gradually decreased in intensity. The intensity ratio of these two last peaks remained constant even after 1 h. The band at 812  $cm^{-1}$  has been assigned to (acetonitrile)tetraphenylporphyrinato)nitrocobalt(III).<sup>15</sup> The half-life of this

(14) Colthub, N. B.; Duly, L. H.; Wiberley, S. E. "Introduction to Infrared and Raman Spectroscopy"; Academic Press: New York, 1975; p 315.

(15) The same band is observed on dissolution of (pyridine)(tetraphenylporphyrinato)nitrocobalt(III) in acetonitrile; see also ref 7.

reaction is approximately 2 min at room temperature. The equilibrium is fully established in approximately 10 min. No formation of complex **1** has been detected. Computer simulation and addition of the standard solution of complex **1** to the above reaction mixture suggest that more than 3% conversion of complex **10** to complex **1** would be detectable.

**Comparison of the Rate of Ethylene Oxidation in Mono- and Bimetallic Systems. A. Monometallic System.** A Fisher-Porter tube was charged with complex **1** (89 mg, 0.33 mmol), evacuated, and pressurized (345 kPa) with ethylene. A degassed solution of *n*-undecane (4.53 mg, internal standard) in 1,2-dichloroethane (10 mL) was added with the aid of air-tight syringe. The reaction mixture was stirred at room temperature, the ethylene pressure was kept constant at 345 kPa, and samples were withdrawn at appropriate time intervals by using an air-tight syringe. The formation of acetaldehyde was monitored by GC using a 6 ft glass column packed with Poropack PS (Figure 1).

**B. Bimetallic System.** The procedure was analogous to that described above with the exception that the Fisher-Porter tube was charged with  $(\text{CH}_3\text{CN})_2\text{PdCl}_2$  (209 mg, 0.81 mmol) and  $\text{py}(\text{TPP})\text{CoNO}_2$  (248 mg,

0.31 mmol). The results are summarized in Figure 1.

**Acknowledgment.** We thank H. Njugana and D. Hindenlang for GC-MS and MS analysis and J. S. Szobota for FTIR spectra. In addition, we acknowledge many helpful suggestions from M. A. Andrews.

**Registry No.** **1**, 77933-52-9; **1-<sup>18</sup>O**, 96292-59-0; **1-<sup>18</sup>O<sub>2</sub>**, 96292-60-3; **4**, 96259-56-2; **10**, 75778-52-8; **11**, 14592-56-4;  $\text{CH}_3\text{CH}=\text{CH}_2$ , 115-07-1;  $\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}_2$ , 111-66-0;  $\text{CH}_2=\text{CH}_2$ , 74-85-1;  $\text{CH}_3\text{CO}_2\text{H}$ , 64-19-7;  $\text{Me}_2\text{CO}$ , 67-64-1;  $\text{CH}_3\text{C}(\text{OAc})=\text{CH}_2$ , 108-22-5;  $\text{CH}_3\text{CH}=\text{C}-\text{HOAc}$ , 3249-50-1;  $\text{CH}_2(\text{OAc})\text{CH}=\text{CH}_2$ , 591-87-7;  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OAc}$ , 627-69-0;  $\text{CH}_3\text{CH}(\text{OAc})\text{CH}_2\text{OH}$ , 6214-01-3;  $\text{AcO}(\text{CH}_2)_3\text{OH}$ , 36678-05-4; *t*-Bu-CO<sub>2</sub>H, 75-98-9;  $\text{CH}_2=\text{CHOAc}$ , 108-05-4;  $\text{CH}_2(\text{O}-\text{H})\text{CH}_2\text{OAc}$ , 542-59-6;  $\text{AcOCH}_2\text{CH}_2\text{OAc}$ , 111-55-7;  $\text{CH}_3(\text{CH}_2)_5\text{COC}-\text{H}_3$ , 111-13-7; cyclooctene, 931-88-4; norbornene, 498-66-8; 1,2-octylene glycol monoacetate, 57852-35-4; cyclooctenyl acetate, 96259-55-1.

## Metal-Promoted Fusion and Linkage of $\text{B}_5\text{H}_8^-$ , $1-\text{XB}_5\text{H}_7^-$ (X = D, CH<sub>3</sub>), $\text{B}_{10}\text{H}_{13}^-$ , and $(\eta^5-\text{C}_5\text{H}_5)\text{CoB}_4\text{H}_7^-$ . Facile Routes to $\text{B}_{10}\text{H}_{14}$ and $(\eta^5-\text{C}_5\text{H}_5)_2\text{Co}_2\text{B}_8\text{H}_{10}$ Isomers<sup>1</sup>

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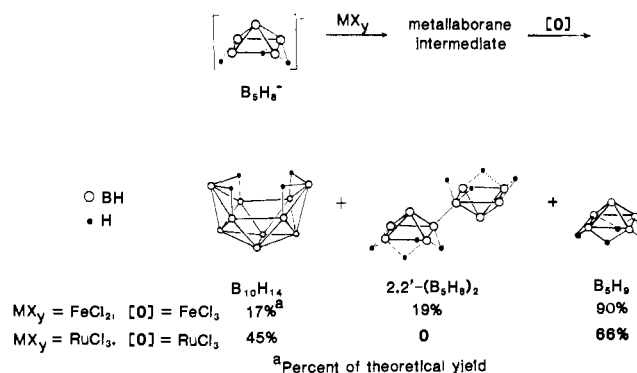
Contribution from the Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901. Received December 5, 1984

**Abstract:** This study examined the conversions, via oxidative fusion or coupling, of  $\text{B}_5\text{H}_8^-$  to  $\text{B}_{10}\text{H}_{14}$  and  $2,2'-(\text{B}_5\text{H}_8)_2$  in the presence of  $\text{FeCl}_2/\text{FeCl}_3$ , of  $\text{B}_5\text{H}_8^-$  to  $\text{B}_{10}\text{H}_{14}$  alone in the presence of  $\text{RuCl}_3$ , and of  $1-\text{XB}_5\text{H}_7^-$  (X = D and CH<sub>3</sub>) to  $2,4-\text{B}_{10}\text{H}_{12}\text{D}_2$  and  $2,2-(1-\text{CH}_3\text{B}_5\text{H}_7)_2$  with  $\text{RuCl}_3$  or  $\text{FeCl}_2/\text{FeCl}_3$ . The  $\text{B}_{10}\text{H}_{13}^-$  ion was shown to form *n*- and *i*- $\text{B}_{18}\text{H}_{22}$  on treatment with  $\text{RuCl}_3$  in THF and subsequent exposure to air. The  $\text{RuCl}_3$ -promoted fusions of the square-pyramidal cobaltaboranes  $2-(\eta^5-\text{C}_5\text{H}_5)\text{CoB}_4\text{H}_7^-$  and  $1-(\eta^5-\text{C}_5\text{H}_5)\text{CoB}_4\text{H}_7^-$  (both analogues of  $\text{B}_5\text{H}_8^-$ ) to give *nido*-( $\eta^5-\text{C}_5\text{H}_5$ )<sub>2</sub> $\text{Co}_2\text{B}_8\text{H}_{12}$  isomers were also studied. The 2-isomer yields primarily 5,8- 1,5-, and 1,7-( $\eta^5-\text{C}_5\text{H}_5$ )<sub>2</sub> $\text{Co}_2\text{B}_8\text{H}_{12}$ , while the 1-isomer affords only 2,4-( $\eta^5-\text{C}_5\text{H}_5$ )<sub>2</sub> $\text{Co}_2\text{B}_8\text{H}_{12}$ . All these observations support a fusion mechanism in which two square-pyramidal substrate molecules, facilitated by coordination to a common metal ion, are initially joined at their basal edges and then complete the fusion process to give a nido 10-vertex cage in which the original apex (1-vertex) atoms become the 2,4-vertexes in the product. The new compounds were characterized via infrared, <sup>11</sup>B and <sup>1</sup>H NMR, mass spectra, and in some cases by two-dimensional (2D) <sup>11</sup>B homonuclear NMR.

The application of transition metals as agents in synthesis, especially of organic compounds, has found wide acceptance and constitutes a tool of major importance in preparative chemistry.<sup>2</sup> A principal attribute of transition-metal ions is their ability, through coordination to substrates of interest, to facilitate processes that would otherwise be unfavorable. Moreover, metal-mediated reactions are often highly stereospecific, increasing still further their value in synthetic chemistry.

In the inorganic field, there are fewer examples of transition-metal ions as preparative agents per se; however, the boron hydride/carborane family, which like hydrocarbon chemistry features covalently bonded hydrogenated networks, seems particularly suited to such applications.<sup>3</sup> Our entry into this realm dates from the fortuitous discovery of the metal-induced fusion of  $\text{R}_2\text{C}_2\text{B}_4\text{H}_4^{2-}$  carborane ligands (R = alkyl) to give  $\text{R}_4\text{C}_4\text{B}_8\text{H}_8$  species.<sup>4</sup> In the

Scheme I



(1) Based in part on: Ph.D. Dissertation, Brewer, C. T. University of Virginia, 1984.

(2) Davies, S. G. "Organotransition Metal Chemistry: Applications to Organic Synthesis"; Pergamon Press: Oxford, 1982.

(3) A recent example of metal-induced coupling of boranes is the conversion of  $\text{B}_5\text{H}_8^-$  to  $1,2'-(\text{B}_5\text{H}_8)_2$  over  $\text{PdBr}_2$ : Corcoran, E. W. Jr.; Sneddon, L. G. *Inorg. Chem.* **1983**, *22*, 182.

(4) (a) Maxwell, W. M.; Miller, V. R.; Grimes, R. N. *J. Am. Chem. Soc.* **1974**, *96*, 7116. (b) *Inorg. Chem.* **1976**, *15*, 1343.

decade since our first report,<sup>4a</sup> we have observed similar fusion reactions with other carboranes and with metallacarboranes<sup>5</sup> and have elucidated some details of the conversion of  $(\text{R}_2\text{C}_2\text{B}_4\text{H}_4)_2\text{FeH}_2$  to  $\text{R}_4\text{C}_4\text{B}_8\text{H}_8$ .<sup>6</sup> The likelihood that metal-

(5) For recent reviews, see: (a) Grimes, R. N. *Acc. Chem. Res.* **1983**, *16*, 22. (b) *Adv. Inorg. Chem. Radiochem.* **1983**, *26*, 55.