

# Oxidative Addition of Esters of Formic Acid and $\beta$ -Lactones to Ni(0)-Complexes Involving Cleavage of the C–O Bond

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**Synopsis.** Reactions of esters of formic acid,  $\text{HCOOR}$  ( $\text{R}=\text{C}_2\text{H}_5$ ,  $\text{CH}_2\text{C}_6\text{H}_5$ ), with Ni(0)-complexes (mixtures of bis(1,5-cyclooctadiene)nickel ( $\text{Ni}(\text{cod})_2$ ) and tertiary phosphines ( $\text{PR}'_3$ )) lead to decarbonylation of  $\text{HCOOR}$  to afford  $\text{Ni}(\text{CO})_n(\text{PR}'_3)_{4-n}$  and  $\text{ROH}$ . Vinyl formate gives a mixture of  $\text{CH}_3\text{CHO}$ ,  $\text{Ni}(\text{CO})_n(\text{PR}'_3)_{4-n}$ ,  $\text{C}_2\text{H}_4$ , and  $\text{CO}_2$  on interaction with the Ni(0)-complexes.  $\beta$ -Lactones liberate  $\text{CO}_2$  on treatment with the Ni(0)-complexes. Oxidative addition of the reactants to Ni involving cleavage of the C–O bond(s) accounts for the formation of the products.

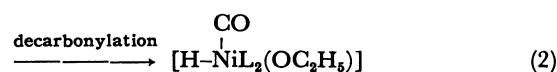
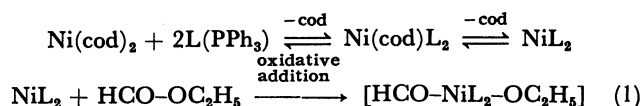
Oxidative addition of organic compounds to transition metals involving C–O bond cleavage is the subject of recent interest. In the previous papers we reported oxidative addition of aryl carboxylates,<sup>1)</sup> vinyl acetate,<sup>1a,2)</sup> allyl-O compounds<sup>2)</sup> to Ni(0)-complexes. We now report reactions of esters of formic acid,  $\beta$ -lactones, and related compounds with Ni(0)-complexes, where somewhat different types of C–O bond cleavage reactions occur.

## Results and Discussion

Table 1 shows products of reactions of formates and  $\beta$ -lactones with mixtures of bis(1,5-cyclooctadiene)-nickel,  $\text{Ni}(\text{cod})_2$  and tertiary phosphines,  $\text{PR}'_3$ .

**Ethyl and Benzyl Formates.** Although the reaction of  $\text{HCOOC}_2\text{H}_5$  with a mixture of  $\text{Ni}(\text{cod})_2$  and  $\text{PPh}_3$  at room temperature causes no C–O bond cleavage of the ester, the reaction at 60 °C causes C–O bond cleavage to afford  $\text{Ni}(\text{CO})(\text{PPh}_3)_3$  and  $\text{C}_2\text{H}_5\text{OH}$ . A similar decarbonylation reaction of methyl formate by Mo(0)-complexes to give  $\text{CH}_3\text{OH}$  has been reported.<sup>3)</sup>

The following reaction pathway involving the initial cleavage of  $\text{HCO-OC}_2\text{H}_5$  bond best accounts for the reaction products,



We have proposed a similar reaction mechanism involving cleavage of the  $\text{RCO-OC}_6\text{H}_5$  bond of phenyl carboxylates for the reaction of  $\text{RCOOC}_6\text{H}_5$  with Ni(0)-complexes.<sup>1)</sup> An alternative mechanism involving initial cleavage of the  $\text{H-COOC}_2\text{H}_5$  bond to give an  $\text{H-Ni-COOC}_2\text{H}_5$  intermediate and ensuing decarbonylation to give  $\text{H-Ni-OC}_2\text{H}_5$  is also conceivable, since the H–C bond in  $\text{HCOOC}_2\text{H}_5$  is considered to have a similar reactivity to that of the C–H bond of –CHO group in aldehydes which are known to oxidatively add to transition metals involving the C–H bond cleavage.<sup>4)</sup> This alternative mechanism, however, is less plausible, because alkoxycarbonylnickel(II) complexes,  $\text{Ni}(\text{X})(\text{COOR})\text{L}_n$ , are known to liberate  $\text{CO}_2$  on their degradation<sup>5)</sup> whereas the present reaction releases no  $\text{CO}_2$ .

When the nucleophilicity of Ni is enhanced by coordination of more basic  $\text{PEt}_3$ , the oxidative addition of  $\text{HCOOC}_2\text{H}_5$  proceeds under milder conditions (Expt 2). In this case  $\text{Ni}(\text{CO})_2(\text{PEt}_3)_2$ <sup>6)</sup> is formed

TABLE 1. REACTIONS OF FORMATES AND LACTONES WITH MIXTURES OF  $\text{Ni}(\text{cod})_2$  AND PHOSPHINE LIGANDS  $\text{PR}_3$ 

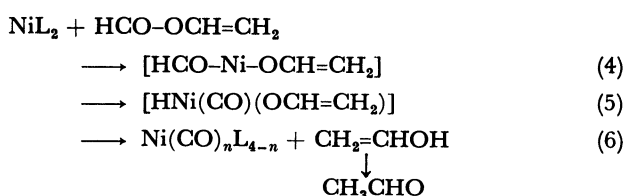
| Expt | Reactant<br>mol/Ni                          | $\text{PR}_3$<br>mol/Ni | Solvent<br>$\text{cm}^3/\text{cm}^3$ of<br>reactant | Temp<br>°C | Time<br>h | Product <sup>a)</sup><br>mol%/Ni  |
|------|---|-------------------------|---|------------|-----------|---|
| 1    | $\text{HCOOC}_2\text{H}_5$ (38)             | $\text{PPh}_3$ (2.0)    | None  | 60         | 40        | $\{\text{Ni}(\text{CO})\text{L}_3(60), \text{C}_2\text{H}_5\text{OH}(50),$<br>$\text{cod-isomers}^c\}$  |
| 2    | $\text{HCOOC}_2\text{H}_5$ (38)             | $\text{PEt}_3$ (2.0)    | None  | 25         | 12        | $\text{Ni}(\text{CO})_2\text{L}_2^b, \text{C}_2\text{H}_5\text{OH}(50)$   |
| 3    | $\text{HCOOCH}_2\text{C}_6\text{H}_5$ (4.0) | $\text{PPh}_3$ (3.0)    | Ether (4)   | 65         | 4         | $\{\text{Ni}(\text{CO})\text{L}_3(90), \text{C}_6\text{H}_5\text{CH}_2\text{OH}(93),$<br>$\text{C}_6\text{H}_5\text{CHO}(\text{tr}), \text{cod-isomers}^c\}$                    |
| 4    | $\text{HCOOCH}=\text{CH}_2$ (1.7)           | $\text{PPh}_3$ (3.0)    | Toluene (4)   | 26         | 24        | $\{\text{CH}_3\text{CHO}(15), \text{Ni}(\text{CO})\text{L}_3(51),$<br>$\text{C}_2\text{H}_4(2), \text{CO}_2(5), 1\text{-butene}(\text{tr}),$<br>$\text{butadiene}(\text{tr})\}$ |
| 5    | $\text{HCOOCH}=\text{CH}_2$ (2.0)           | $\text{PCy}_3$ (2.0)    | Toluene (28)  | 15         | 28        | $\{\text{CH}_3\text{CHO}(16), \text{Ni}(\text{CO})_2(\text{PCy}_3)_2^b,$<br>$\text{CO}_2(2), \text{C}_2\text{H}_4(2), 1\text{-butene}(4)\}$                                     |
| 6    | $\text{CH}_2\text{OCOCH}_2$ (120)           | $\text{PPh}_3$ (2.0)    | None  | 10         | 12        | $\{\text{C}_2\text{H}_4(45), \text{CO}_2^b, \text{polyester},$<br>$\text{Ni}(\text{CO})_2\text{L}_2^b\}$  |
| 7    | $\text{CH}_2=\text{COCOCH}_2$ (1.1)         | $\text{PPh}_3$ (2.1)    | Ether (7)   | 10         | 9         | $\text{CO}_2(42), \text{polymer}$   |
| 8    | $\text{CH}_2\text{CH}_2\text{OCOCH}_2$ (20) | $\text{PPh}_3$ (2.2)    | None  | 65         | 48        | No C–O bond cleavage proceeds   |

a)  $\text{L}=\text{PR}_3$ . tr=Trace. b) Formation of the compound was confirmed by IR, GLC, and/or NMR, but the amount was not measured. c) Cod isomers: 1,3-cyclooctadiene, 1,4-cyclooctadiene, bicyclooctene-1, and bicyclooctene-2.

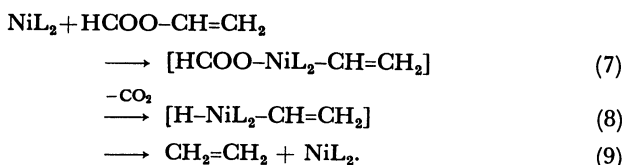
instead of the  $\text{Ni}(\text{CO})\text{L}_3$  type complex. The fact that the reaction proceeds more easily by using more basic  $\text{PEt}_3$  indicates that the reaction proceeds through nucleophilic attack of the  $\text{Ni}(0)$  complex at the carbonyl carbon of  $\text{HCOOR}$ , similarly to the reactions of aryl carboxylates<sup>1)</sup> and allyl-O compounds<sup>2)</sup> with  $\text{Ni}(0)$ -complexes.

Employment of  $\text{HCOOCH}_2\text{C}_6\text{H}_5$  also leads to a similar type of bond cleavage in the reaction with the mixture of  $\text{Ni}(\text{cod})_2$  and  $\text{PPh}_3$  affording  $\text{Ni}(\text{CO})(\text{PPh}_3)_3$  and  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$  (Expt 3).

**Vinyl Formate.** Vinyl formate undergoes a similar type of bond cleavage to give  $\text{Ni}(\text{CO})_n(\text{PR}'_3)_{4-n}$  and  $\text{CH}_3\text{CHO}$ , a tautomer of vinyl alcohol, in the reaction with the mixture of  $\text{Ni}(\text{cod})_2$  and  $\text{PR}'_3$  ( $\text{PR}'_3 = \text{PPh}_3$  and tricyclohexylphosphine ( $\text{PCy}_3$ )) at room temperature.



However, in this case the ester undergoes, besides the C-O bond cleavage described above, another type of bond cleavage between  $\text{HCOO}-$  and  $-\text{CH}=\text{CH}_2$  groups to liberate  $\text{CO}_2$  and  $\text{C}_2\text{H}_4$ ,



This type of bond cleavage has been observed for reactions of  $\text{Ni}(0)$ -complexes with alkenyl acetates.<sup>2)</sup>

**$\beta$ -Lactones.** 2-Oxetanone liberates  $\text{C}_2\text{H}_4$  and  $\text{CO}_2$  on interaction with a mixture of  $\text{Ni}(\text{cod})_2$  and  $\text{PPh}_3$ , indicating both the  $\text{O}-\text{CH}_2$  and  $\text{CO}-\text{CH}_2$  bonds in the lactone are cleaved in the reaction. Oxidative addition of 2-oxetanone involving cleavage of the  $\text{O}-\text{CH}_2$  or  $\text{CO}-\text{CH}_2$  bond to form a nickel-containing cyclic compound (e.g.,  $\text{L}_2\text{Ni}-\text{OCOCH}_2\text{CH}_2$ ) and bond rearrangement in the supposed cyclic intermediate account for the evolution of  $\text{C}_2\text{H}_4$  and  $\text{CO}_2$ . A part of 2-oxetanone is converted into polyester,  $(\text{CH}_2\text{CH}_2\text{COO})_n$ .

A reaction of 4-methylene-2-oxetanone with the  $\text{Ni}(\text{cod})_2/\text{PPh}_3$  mixture also causes cleavage of the C-O bond in the four-membered ring to liberate  $\text{CO}_2$ , although propadiene which is expected to be formed as the product of the C-O bond cleavage was not obtained. It is known that Ni complexes catalyze polymerization and oligomerization of propadiene,<sup>7)</sup> and occurrence of such reactions accounts for the absence of propadiene in the liquid phase. Dihydro-2(3H)-furanone having stable 5-membered ring does not undergo the C-O bond cleavage.

### Experimental

**General Procedures and Materials.** Manipulation of complexes and the reactions were carried out under deoxygen-

ated nitrogen or argon or under vacuum.  $\text{Ni}(\text{cod})_2$  was purchased from Merck Co., Ltd., and recrystallized. Formates and lactones were purified by repeated distillation until their gas chromatogram show no significant peaks of contaminants. Tertiary phosphine ligands were used as purchased or synthesized by the methods given in the literature.<sup>8)</sup> Solvents were dried by usual procedures, distilled, and stored under argon or nitrogen.

**Spectral Measurement and Analysis.** IR spectra were taken on a Hitachi Model 295 spectrometer using KBr disks under nitrogen. The analysis of gaseous and liquid products was carried out with a Shimadzu GC-3BT or GC-6A gas chromatograph.

**Reactions of Formates and Lactones (cf. Table 1).** **Expt 1:** Ethyl formate (3 cm<sup>3</sup>, 38 mmol) was added to a Schlenk tube containing  $\text{Ni}(\text{cod})_2$  (0.27 g, 0.98 mmol) and  $\text{PPh}_3$  (0.25 g, 2.0 mmol) at  $-50^\circ\text{C}$ . The reaction mixture was stirred at  $60^\circ\text{C}$  for 40 h to obtain a brown solution. GLC analysis of the solution showed formation of 0.49 mmol of ethanol. Removing volatile material under vacuum yielded 0.63 g of a light yellow solid whose IR spectrum is almost identical with that of  $\text{Ni}(\text{CO})(\text{PPh}_3)_3$ , showing a sharp  $\nu(\text{C}=\text{O})$  band at  $1926\text{ cm}^{-1}$ .<sup>9)</sup>

**Expt 3:** Benzyl formate (0.50 cm<sup>3</sup>, 4.0 mmol) was added to a Schlenk tube containing  $\text{Ni}(\text{cod})_2$  (0.25 g, 0.91 mmol),  $\text{PPh}_3$  (0.72 g, 2.7 mmol), and diethyl ether (2 cm<sup>3</sup>) at room temperature. The mixture was stirred at  $65^\circ\text{C}$  for 4 h to obtain a pale brown homogeneous solution, which was cooled down to  $-30^\circ\text{C}$  to yield a yellow solid of  $\text{Ni}(\text{CO})(\text{PPh}_3)_3$  (0.72 g, 90%). GLC analysis of the solution showed formation of 0.84 mmol of benzyl alcohol.

The other reactions listed in Table 1 were carried out analogously. IR spectrum of the viscous polymer obtained in expt. 6 showed absorption bands characteristic of the polyester,  $(\text{CH}_2\text{CH}_2\text{COO})_n$  ( $1750\text{ cm}^{-1}$  ( $\nu(\text{C}=\text{O})$ ),  $1350\text{ cm}^{-1}$  ( $\nu(\text{C}-\text{O})$ ),  $1170\text{ cm}^{-1}$ ,  $1010\text{ cm}^{-1}$ ).<sup>10)</sup>

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