February, 1982] © 1982 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 55, 623—624 (1982) 623

Oxidative Addition of Esters of Formic Acid and β-Lactones to Ni(0)-Complexes Involving Cleavage of the C-O Bond

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(Received September 12, 1981)

Synopsis. Reactions of esters of formic acid, HCOOR ($R=C_2H_5$, $CH_2C_6H_5$), with Ni(0)-complexes (mixtures of bis(1,5-cyclooctadiene)nickel ($Ni(cod)_2$) and tertiary phosphines (PR'_3)) lead to decarbonylation of HCOOR to afford $(Ni(CO)_n(PR'_3)_{4-n}$ and ROH. Vinyl formate gives a mixture of CH_3CHO, $Ni(CO)_n(PR'_3)_{4-n}$, C_2H_4, and CO_2 on interaction with the Ni(0)-complexes. β-Lactones liberate 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,1) vinyl acetate,1a,2) allyl-O compounds2) to Ni(0)-complexes. We now report reactions of esters of formic acid, β-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 β-lactones with mixtures of bis(1,5-cyclooctadiene)-nickel, $Ni(cod)_2$ and tertiary phosphines, PR'_3.

Ethyl and Benzyl Formates. Although the reaction of $HCOOC_2H_5$ with a mixture of $Ni(cod)_2$ and 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 $Ni(CO)(PPh_3)_3$ and C_2H_5OH. A similar decarbonylation reaction of methyl formate by Mo(0)-complexes to give CH_3OH has been reported.3) The following reaction pathway involving the initial cleavage of $HCO–OC_2H_5$ bond best accounts for the reaction products,

$$Ni(cod)_2 + 2L(PPh_3) \xrightleftharpoons{-cod} Ni(cod)L_2 \xrightleftharpoons{-cod} NiL_2$$

$$NiL_2 + HCO–OC_2H_5 \xrightarrow{\text{oxidative addition}} [HCO–NiL_2–OC_2H_5] \quad (1)$$

$$\xrightarrow{\text{decarbonylation}} [H–\overset{\overset{\text{CO}}{|}}{Ni}L_2(OC_2H_5)] \quad (2)$$

$$\xrightarrow{-HOC_2H_5} Ni(CO)L_3. \quad (3)$$

We have proposed a similar reaction mechanism involving cleavage of the $RCO–OC_6H_5$ bond of phenyl carboxylates for the reaction of $RCOOC_6H_5$ with Ni(0)-complexes.1) An alternative mechanism involving initial cleavage of the $H–COOC_2H_5$ bond to give an $H–Ni–COOC_2H_5$ intermediate and ensuing decarbonylation to give $H–Ni–OC_2H_5$ is also conceivable, since the H–C bond in $HCOOC_2H_5$ 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.4) This alternative mechanism, however, is less plausible, because alkoxycarbonylnickel(II) complexes, $Ni(X)(COOR)L_n$, are known to liberate CO_2 on their degradation5) whereas the present reaction releases no CO_2.

When the nucleophilicity of Ni is enhanced by coordination of more basic PEt_3, the oxidative addition of $HCOOC_2H_5$ proceeds under milder conditions (Expt 2). In this case $Ni(CO)_2(PEt_3)_2$6) is formed

TABLE 1. REACTIONS OF FORMATES AND LACTONES WITH MIXTURES OF $Ni(cod)_2$ AND PHOSPHINE LIGANDS PR_3

Expt	Reactant mol/Ni	PR_3 mol/Ni	Solvent cm³/cm³ of reactant	Temp °C	Time h	Product a) mol%/Ni
1	$HCOOC_2H_5$ (38)	PPh_3 (2.0)	None	60	40	$Ni(CO)L_3$(60), C_2H_5OH(50), cod-isomers c)
2	$HCOOC_2H_5$ (38)	PEt_3 (2.0)	None	25	12	$Ni(CO)_2L_2$ b), C_2H_5OH(50)
3	$HCOOCH_2C_6H_5$ (4.0)	PPh_3 (3.0)	Eher (4)	65	4	$Ni(CO)L_3$(90), $C_6H_5CH_2OH$(93), C_6H_5CHO(tr), cod-isomers c)
4	$HCOOCH=CH_2$ (1.7)	PPh_3 (3.0)	Toluene (4)	26	24	CH_3CHO(15), $Ni(CO)L_3$(51), C_2H_4(2), CO_2(5), 1-butene(tr), butadiene(tr)
5	$HCOOCH=CH_2$ (2.0)	PCy_3 (2.0)	Toluene (28)	15	28	CH_3CHO(16), $Ni(CO)_2(PCy_3)_2$ b), CO_2(2), C_2H_4(2), 1-butene(4)
6	CH_2OCOCH_2 (120)	PPh_3 (2.0)	None	10	12	C_2H_4(45), CO_2 b), polyester, $Ni(CO)_2L_2$ b)
7	$CH_2=COCOCH_2$ (1.1)	PPh_3 (2.1)	Ether (7)	10	9	CO_2(42), polymer
8	$CH_2CH_2OCOCH_2$ (20)	PPh_3 (2.2)	None	65	48	No C–O bond cleavage proceeds

a) $L=PR_3$. 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 $Ni(CO)L_3$ type complex. The fact that the reaction proceeds more easily by using more basic PEt_3 indicates that the reaction proceeds through nucleophilic attack of the Ni(0) complex at the carbonyl carbon of HCOOR, similarly to the reactions of aryl carboxylates1) and allyl-O compounds2) with Ni(0)-complexes.

Employment of $HCOOCH_2C_6H_5$ also leads to a similar type of bond cleavage in the reaction with the mixture of $Ni(cod)_2$ and PPh_3 affording $Ni(CO)(PPh_3)_3$ and $C_6H_5CH_2OH$ (Expt 3).

Vinyl Formate. Vinyl formate undergoes a similar type of bond cleavage to give $Ni(CO)_n(PR'_3)_{4-n}$ and CH_3CHO, a tautomer of vinyl alcohol, in the reaction with the mixture of $Ni(cod)_2$ and PR'_3 (PR'_3=PPh_3 and tricyclohexylphosphine (PCy_3)) at room temperature.

$$\begin{aligned}&NiL_2 + HCO\text{-}OCH{=}CH_2\\ &\longrightarrow [HCO\text{-}Ni\text{-}OCH{=}CH_2] && (4)\\ &\longrightarrow [HNi(CO)(OCH{=}CH_2)] && (5)\\ &\longrightarrow Ni(CO)_nL_{4-n} + \underset{\displaystyle CH_3CHO}{\underset{\downarrow}{CH_2{=}CHOH}} && (6)\end{aligned}$$

However, in this case the ester undergoes, besides the C–O bond cleavage described above, another type of bond cleavage between HCOO– and $-CH{=}CH_2$ groups to liberate CO_2 and C_2H_4,

$$\begin{aligned}&NiL_2 + HCOO\text{-}CH{=}CH_2\\ &\longrightarrow [HCOO\text{-}NiL_2\text{-}CH{=}CH_2] && (7)\\ &\xrightarrow{-CO_2} [H\text{-}NiL_2\text{-}CH{=}CH_2] && (8)\\ &\longrightarrow CH_2{=}CH_2 + NiL_2. && (9)\end{aligned}$$

This type of bond cleavage has been observed for reactions of Ni(0)-complexes with alkenyl acetates.2)

β-Lactones. 2-Oxetanone liberates C_2H_4 and CO_2 on interaction with a mixture of $Ni(cod)_2$ and PPh_3, indicating both the $O\text{-}CH_2$ and $CO\text{-}CH_2$ bonds in the lactone are cleaved in the reaction. Oxidative addition of 2-oxetanone involving cleavage of the $O\text{-}CH_2$ or $CO\text{-}CH_2$ bond to form a nickel-containing cyclic compound (*e.g.*, $L_2\overline{Ni\text{-}OCOCH_2C}H_2$) and bond rearrangement in the supposed cyclic intermediate account for the evolution of C_2H_4 and CO_2. A part of 2-oxetanone is converted into polyester, $\{CH_2CH_2COO\}_n$.

A reaction of 4-methylene-2-oxetanone with the $Ni(cod)_2/PPh_3$ mixture also causes cleavage of the C–O bond in the four-membered ring to liberate 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,7) and occurrence of such reactions accounts for the absence of propadiene in the liquid phase. Dihydro-2(3*H*)-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 deoxygenated nitrogen or argon or under vacuum. $Ni(cod)_2$ 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.8) 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^3, 38 mmol) was added to a Schelnk tube containing $Ni(cod)_2$ (0.27 g, 0.98 mmol) and PPh_3 (0.25 g, 2.0 mmol) at −50 °C. The reaction mixture was stirred at 60 °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 $Ni(CO)(PPh_3)_3$, showing a sharp $\nu(C{=}O)$ band at 1926 cm^{-1}.9)

Expt 3: Benzyl formate (0.50 cm^3, 4.0 mmol) was added to a Schlenk tube containing $Ni(cod)_2$ (0.25 g, 0.91 mmol), PPh_3 (0.72 g, 2.7 mmol), and diethyl ether (2 cm^3) at room temperature. The mixture was stirred at 65 °C for 4 h to obtain a pale brown homogeneous solution, which was cooled down to −30 °C to yield a yellow solid of $Ni(CO)(PPh_3)_3$ (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, $\{CH_2CH_2COO\}_n$ (1750 cm^{-1} (ν(C=O)), 1350 cm^{-1} (ν(C–O)), 1170 cm^{-1}. 1010 cm^{-1}).10)

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