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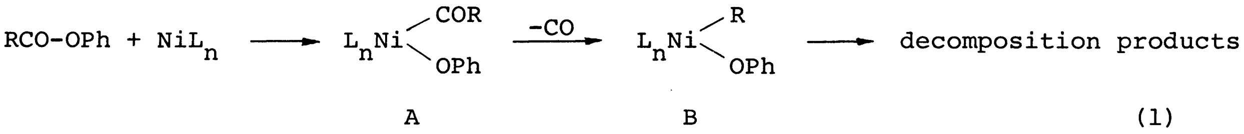
PREPARATION OF ACYL(p-CYANOPHENOXO)(2,2'-BIPYRIDINE)NICKEL AND REDUCTIVE ELIMINATION OF PHENYL ESTERS FROM ACYL(PHENOXO)NICKEL COMPLEXES

Teiji KOHARA, Sanshiro KOMIYA, Takakazu YAMAMOTO,*
and Akio YAMAMOTO*
Research Laboratory of Resources Utilization, Tokyo Institute
of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227

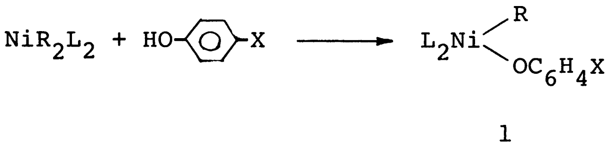
The reaction of NiR(O-p-C_6H_4CN)(bpy) (R = C_2H_5 (**1a**), CH_3 (**1b**)) with CO in a 1:1 ratio affords Ni(COR)(O-p-C_6H_4CN)(bpy) (R = C_2H_5 (**2a**), CH_3 (**2b**)). p-Cyanophenyl esters are reductively eliminated from **2** on treating the complexes with π-acids such as maleic anhydride and CO. Reactions of various alkyl(phenoxo)nickel complexes NiR(OC_6H_4X)L_2 with CO give $RCOOC_6H_4X$ in high yields.

A previous paper from this laboratory has shown that carboxylic esters can be selectively cleaved at CO-O bond as well as at COO-R bond under mild aprotic conditions by means of zero-valent nickel complexes.[1] The CO-O bond cleavage of phenyl carboxylates was postulated to proceed through an intermediate acylnickel phenoxide (A) which is decarbonylated to give alkylnickel phenoxide (B) to be followed by collapse of B:



$$\mathrm{RCO\text{-}OPh} + \mathrm{NiL}_n \longrightarrow \mathrm{L}_n\mathrm{Ni}\begin{matrix}\diagup \mathrm{COR}\\ \diagdown \mathrm{OPh}\end{matrix} \xrightarrow{-\mathrm{CO}} \mathrm{L}_n\mathrm{Ni}\begin{matrix}\diagup \mathrm{R}\\ \diagdown \mathrm{OPh}\end{matrix} \longrightarrow \text{decomposition products} \tag{1}$$

In the ester cleavage reactions the isolation and characterization of the postulated intermediates A and B were not feasible. We now report the stepwise preparation of the corresponding alkyl(phenoxo)nickel(II) **1** and acyl(phenoxo)nickel(II) **2** type complexes from dialkylnickel(II) complexes and demonstrate that the acyl(phenoxo)-nickel(II) type complex may be activated by π-acids to cause the reductive elimination of the phenyl carboxylates:



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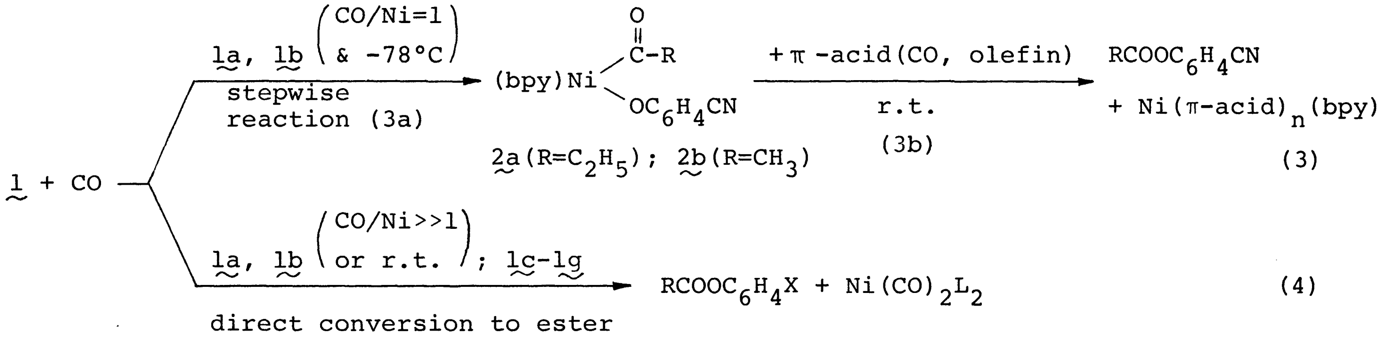
	R	X	L_2
1a	C_2H_5	p-CN	bpy
1b	CH_3	p-CN	bpy
1c	C_2H_5	H	bpy
1d	CH_3	H	bpy
1e	CH_3	H	dpe
1f	CH_3	H	$(PEt_3)_2$
1g	CH_3	p-C_6H_5	$(PEt_3)_2$

(2)



The establishment of the reversibility of the reaction, i.e., oxidative addition of carboxylic esters to Ni(0) and their reductive elimination from Ni(II) complexes, indicates the potential applicability of the metal-promoted reactions to organic syntheses in combination with other substrates.

The complexes of type **1** were readily prepared by the reaction of the corresponding dialkylnickel complex and the corresponding phenol in similar manners to those reported by Wilke and Herrman[2a)] and Green and Smith.[2b)] In every case analytically pure alkyl(phenoxo)nickel complexes were obtained in high yields.

When 407 mg (1.12 mmol) of $Ni(C_2H_5)(O\text{-}p\text{-}C_6H_4CN)(bpy)$ **1a** in tetrahydrofuran (7 ml) was treated with an equimolar amount of CO at -78°C, a gradual absorption of CO took place and the reaction was completed in 4 h. A deep reddish purple precipitate was obtained by adding excess hexane to the reaction solution. Recrystallization of the precipitate from THF-hexane gave deep reddish purple crystals of $Ni(COC_2H_5)(O\text{-}p\text{-}C_6H_4CN)(bpy)$ **2a** (yield = 78 %); mp(decomp.) 120°C; Anal. Found: Ni, 14.7. Calcd.: Ni, 15.0; IR(KBr): 1650 cm^{-1} ($\nu_{C=O}$); ^1H NMR (acetone-d_6, r.t.): δ: 0.99 ppm (3H, t, J=8Hz, CH_3), 3.04 ppm (2H, q, J=8Hz, CH_2), 7.4 ppm - 8.6 ppm (12H, bpy and OC_6H_4CN). An acetyl analog $Ni(COCH_3)(O\text{-}p\text{-}C_6H_4CN)(bpy)$ **2b** was also obtained in a similar manner as deep reddish purple crystals (yield = 89 %); Anal. Found: Ni, 15.1. Calcd.: Ni, 15.6; IR(KBr): 1650 cm^{-1} ($\nu_{C=O}$): ^1H NMR (acetone-d_6, r.t.): δ : 2.42 ppm (3H, s, CH_3), 7.2 ppm - 8.6 ppm (12H, bpy and OC_6H_4CN). The acylnickel complexes are highly sensitive to air and their microanalyses of C, H, and N were not feasible.

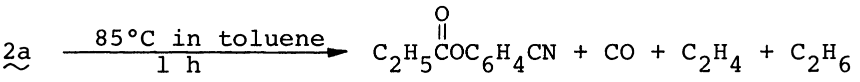
In contrast to the 1:1 reactions at -78°C between $NiR(OC_6H_4CN)(bpy)$ and CO, treatment of **1a** with an excess of CO under an atmospheric pressure at the same temperature gave p-cyanophenyl propionate in good yield (0.74 mol/Ni) as confirmed by gas chromatography. Addition of excess hexane to the resulted red solution at -78°C gave $Ni(CO)_2(bpy)$[3)] (0.67 mol/Ni, isolated yield) as confirmed from its IR spectrum ($\nu_{C=O}$ = 1970, 1890 cm^{-1}, KBr).

Carring out the reaction at higher temperature (r.t.) gave $C_2H_5COOC_6H_4CN$ and $Ni(CO)_2(bpy)$, regardless of the ratio of CO to **1a**. When **1a** was treated with an equimolar CO at room temperature, $C_2H_5COOC_6H_4CN$ (ca. 1/3 mol/Ni) and $Ni(CO)_2(bpy)$ were obtained with a small amount of **2a**. About 2/3 of **1a** remained intact after the completion of the reaction. The reaction of **1a** and excess CO at room temperature gave $C_2H_5COOC_6H_4CN$ (0.79 mol/Ni) and $Ni(CO)_2(bpy)$ (isolated yield = 0.42 mol/Ni) in good yield.

Since the isolated acylnickel complex 2a is stable in solid state and even in solution at room temperature in the absence of excess CO as revealed by ^1H NMR, these results indicate that the coordination of excess CO to the acyl(p-cyanophenoxo)-nickel complex induces the reductive coupling of acyl and p-cyanophenoxo groups on the acyl(p-cyanophenoxo)nickel complex. At room temperature, CO seems to react preferentially with the produced acylnickel complex 2a to afford $C_2H_5COOC_6H_4CN$ and $Ni(CO)_2(bpy)$, and when only an equimolar amount of CO per 1a was introduced, about 2/3 of 1a remained intact due to the consumption of CO according to the stoichiometry of reaction 4.

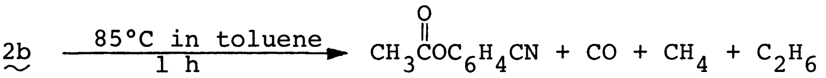
The reductive elimination of ester from the isolated acyl(p-cyanophenoxo)nickel complexes was promoted also by the interaction of various π-acids such as maleic anhydride (MAH) and ethyl methacrylate (Reaction 3b). When 2a and 2b were treated with excess MAH in THF at room temperature for 1 day, p-cyanophenyl esters C_2H_5COO-C_6H_4CN (0.62 mol/Ni) and $CH_3COOC_6H_4CN$ (0.70 mol/Ni) and $Ni(MAH)_2(bpy)$4) (0.90 - 0.77 mol/Ni) were obtained in high yields, indicating that the Ni-COR and $Ni-OC_6H_4CN$ bonds of 2 are activated by the coordination of MAH to cause the reductive elimination of the ester. Addition of a somewhat weaker π-acid, ethyl methacrylate, also causes the reductive elimination with lower yield. A similar effect of an olefin having an electron-withdrawing group for the reductive elimination of R-R from $NiR_2(bpy)$ has been observed4) and MAH was found to be the most effective olefins for the reductive elimination.

In contrast to the clean reductive elimination promoted by MAH, the thermolysis of 2 gives a mixture of products formed by both decarbonylation and reductive elimination:



$$\mathbf{2a} \xrightarrow[\text{1 h}]{\text{85°C in toluene}} C_2H_5\overset{\overset{O}{\|}}{C}OC_6H_4CN + CO + C_2H_4 + C_2H_6 \qquad (5)$$

0.12 0.17 0.12 0.04 (mol/Ni)



$$\mathbf{2b} \xrightarrow[\text{1 h}]{\text{85°C in toluene}} CH_3\overset{\overset{O}{\|}}{C}OC_6H_4CN + CO + CH_4 + C_2H_6 \qquad (6)$$

0.03 0.43 tr tr

Decarbonylation from acetylnickel complex 2b seems to proceed more easily than propionyl analog 2a, a similar trend having been observed with $Ni(COR)(acac)PPh_3$5).

Other alkyl(phenoxo)nickel complexes 1c-1g with various combinations of the alkyl, phenoxo, and basic ligands smoothly gave the corresponding phenyl esters in quantitative yields on treatment with CO (reaction 4), but attempts to isolate the intermediate acyl(phenoxo)nickel type complexes failed except for the cyanophenoxo complexes.

Yields of $RCOOC_6H_4X$ and $Ni(CO)_2L_2$ in reaction (4)

Complex	1a	1c	1d	1e	1f	1g
$RCOOC_6H_4X$ (mol%/Ni)	79	70	100	93	90	88
$Ni(CO)_2L_2$ (mol%/Ni) (isolated yield)	42	-	21	23	-	-

-: formation of $Ni(CO)_2L_2$ was confirmed by IR but the amount was not measured.

Even when the reaction was carried out at -78°C and only an equimolar amount of CO was introduced to avoid the acceleration effect of excess CO on the reductive elimination, only the final products, esters and $Ni(CO)_2L_2$, were formed, indicating that the reductive elimination of esters from acyl(phenoxo)nickel intermediates formed in the reaction of 1c-1g with CO proceeds more easily than that from acyl(p-cyanophenoxo)nickel complexes 2. The successful isolation of 2 may be due to the high stability of the $Ni-OC_6H_4CN$ bond, which prevents the reductive elimination of the esters at -78°C.

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