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Insertion of Carbon Monoxide into Nickel-Alkyl Bonds of Monoalkyl- and Dialkylnickel(II) Complexes, $NiR(Y)L_2$ and NiR_2L_2. Preparation of $Ni(COR)(Y)L_2$ from $NiR(Y)L_2$ and Selective Formation of Ketone, Diketone, and Aldehyde from NiR_2L_2

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Reactions of monoalkylnickel(II) complexes, $NiR(Y)L_2$ ($R=CH_3$, C_2H_5; Y=Cl, suc(succinimido), pht(phthalimido), OC_6H_4-*p*-CN; L=1/2 bpy (2,2′-bipyridine), PEt_3 (triethylphosphine)), with CO afford monoacylnickel(II) complexes, $Ni(COR)(Y)L_2$, which are characterized by elemental analysis and spectroscopies (IR and NMR). Reactions of the acylnickel(II) complexes with alcohols and aniline give the corresponding esters and amides, respectively. Exposure of $Ni(COR)(Y)L_2$ to dry air leads to oxidation of RCO to a RCOO ligand giving a complex formulated as $Ni(OCOR)(Y)L_2$. Reactions of dimethylnickel(II) complexes, $Ni(CH_3)_2L_2$ (L=1/2 bpy, PEt_3, 1/2 dpe (1,2-bis(diphenylphosphino)ethane, 1/2 dpp (1,3-bis(diphenylphosphino)propane), with carbon monoxide afford acetone and/or 2,3-butanedione in medium to high yields, the acetone/2,3-butanedione ratio varying with the ligand L, reaction temperature, and additives such as maleic anhydride and triphenylphosphine. Generally the acetone/2,3-butanedione ratio decreases with increase in thermal stabilities of $Ni(CH_3)_2L_2$. $Ni(C_2H_5)_2$(bpy) and $Ni(n\text{-}C_3H_7)_2$(bpy) give 3-pentanone and 4-heptanone, respectively, on treating them with CO, whereas $Ni(C_2H_5)_2$(dpe) produces C_2H_5CHO and C_2H_4.

Insertion of carbon monoxide into transition metal-carbon bond constitutes a crucial step in industrially important processes.[1] It is known that transition metal (Ni, Pd, *etc.*) compounds catalyze carbonylation of unsaturated compounds and organic halides in the presence of alcohols and amines to afford esters and amides, respectively,[1,2] and a mechanism involving nucleophilic attack of alcohol or amine to an acyl-transition metal intermediate is sometimes proposed for the reactions. However, in contrast to the well explored catalytic reactions, fundamental studies of the carbonylation process dealing with well characterized transition metal alkyl compounds are still limited[3] and chemical reactivities of acyltransition metal complexes prepared by the CO insertion reaction have not been well explored.

We have carried out reactions of isolated monoalkyl- and dialkylnickel(II) complexes, $NiR(Y)L_2$ and NiR_2L_2, with CO to find out that several isolable acylnickel(II) complexes are obtained in the reactions of the monoalkylnickel complexes with CO, whereas the reaction of NiR_2L_2 with CO gives ketone, diketone, and/or aldehyde. The paper deals with the results of the reactions of $NiR(Y)L_2$ and NiR_2L_2 with CO and chemical behavior of $Ni(COR)(Y)L_2$ with compounds such as alcohols and amines. A part of the results given in this paper has been reported in a communication form.[4]

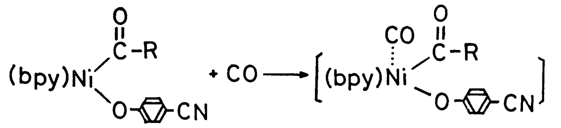
Results and Discussion

$$NiR(Y)L_2 + CO \longrightarrow Ni(COR)(Y)L_2 \qquad (1)$$

	R	Y	L
1	Et	Cl	1/2 bpy
2	Et	suc	1/2 bpy
3	Et	OC_6H_4-*p*-CN	1/2 bpy
4	Me	OC_6H_4-*p*-CN	1/2 bpy
5	Me	pht	PEt_3

$Me=CH_3$, $Et=C_2H_5$, suc=succinimido, pht=phthalimido, bpy=2,2′-bipyridine

I. Preparation of Acylnickel(II) Complexes. The following five acylnickel complexes can be prepared by reactions of the $NiR(Y)L_2$ type complexes[5] with CO. Although several acetylnickel(II) complexes have been prepared by several groups of researchers,[6,7] the propionylnickel complex has only one precedent.[7a] The acylnickel(II) complexes having the Cl, suc, or pht ligand can be prepared under a wide range of reaction conditions, whereas the complexes with the OC_6H_4-*p*-CN ligand can be prepared only by 1:1 reactions of $NiR(OC_6H_4$-*p*-CN)(bpy) with CO at low temperature (−78 °C). Carrying out the reaction of $NiR(OC_6H_4$-*p*-CN)(bpy) at −78 °C or above in the presence of excess CO leads to the formation of $RCOOC_6H_4$-*p*-CN and $Ni(CO)_2$(bpy), suggesting that coordination of CO to **3** and **4** enhances reductive coupling of the RCO and OC_6H_4-*p*-CN groups. In fact, **3** and **4** once isolated have considerably high stabilities in organic solvents even at room temperature, whereas addition of CO to the solution of **3** or **4** leads to rapid formation of $RCOOC_6H_4$-*p*-CN and $Ni(CO)_2$(bpy) almost quantitatively even at −78 °C,



$$\xrightarrow{+CO} RCOOC_6H_4\text{-}p\text{-}CN + Ni(CO)_2(bpy)\,. \qquad (2)$$

Complexes **1**, **2**, and **5** are stable in solutions and do not undergo the reductive coupling to produce RCOY even in the presence of excess CO, presumably due to high stabilities of the Ni–Cl, Ni–suc, and Ni–pht bonds.

The reductive coupling is considered to proceed through a concerted mecahnism involving simultaneous loosening of the Ni–COR and Ni–Y bonds and overlapping of bonding orbitals of the COR and Y groups. When there is a difference in bond energies

TABLE 1. IR, NMR, AND VISIBLE SPECTROSCOPIC DATA OF $Ni(COR)(Y)L_2$

Complex	IR[a] $\tilde{\nu}/cm^{-1}$	^{1}H-NMR δ/ppm[b]			^{31}P-NMR[b] δ/ppm	$^{13}C\{^1H\}$-NMR[b] δ/ppm	λ_{max}[c] nm
		COR[d]	Y	L			
Ni(COEt)(Cl)(bpy) **1**	2950 1655* 1595 1440 880 765	1.14(CH_3) 3.19(CH_2)		7.3(2H, m) 7.9(5H, m) 8.7(1H, d, 5 Hz)			503
Ni(COEt)(suc)(bpy) **2**	1620* 1445 1345 1220 770	0.98(CH_3) 3.11(CH_2)	2.60(s, CH_2)	7.1—8.2			480
$Ni(COEt)(OC_6H_4$-*p*-CN)(bpy) **3**	2200 1650* 1580 1320 1145 770	0.99(CH_3) 3.04(CH_2)	7.2—8.6 (Y + L)				482
$Ni(COMe)(OC_6H_4$-*p*-CN)(bpy) **4**	2190 1645* 1580 1330 1155 765	2.42(CH_3)	7.2—8.6 (Y + L)				488
Ni(COMe)(pht)-$(PEt_3)_2$ **5**	2960 1650* 1600 1300 1120 760 535	2.65(CH_3)	7.03(2H, dd, 5 Hz and 7 Hz) 7.72(2H, dd, 5 Hz and 7 Hz)	0.98(18H, qui, 7 Hz, CH_3) 1.3(12H, m, CH_2)	32.5 (s) (in C_6D_6)	7.84(s, PCH_2-$\underline{C}H_3$) 13.46(s, P-$\underline{C}H_2$) 32.47(t, 8 Hz, $CO\underline{C}H_3$) 121.16, 132.22, 138.10 aromatic ring of pht 180.51(d, 16 Hz, $-N(CO)_2$) 258.31(t, 22 Hz, COMe)	

a) In KBr. The band with an asterisk is assigned to ν(C=O) of the RCO ligand. b) s=singlet, d=doublet, dd=double doublet, qui=quintet, m=multiplet. Chemical shifts of ^{31}P- and $^{13}C\{^1H\}$-NMR spectra are referred to external PEt_3 and internal TMS, respectively (downfield positive). Solvents for ^{1}H-NMR: CD_2Cl_2 for **1** and **2**, acetone-d_6 for **3** and **4**, and C_6D_6 for **5**. The solvent for $^{13}C\{^1H\}$-NMR: THF-d_8. c) Measured in THF. d) The CH_3 and CH_2 groups of COEt give rise to a triplet and a quartet, respectively, with the *J* value of 7—8 Hz.

between the Ni–COR and Ni–Y bonds, however, the ease of reductive elimination may be critically dependent on the ease of activation of the stronger bond, Ni–Y in this case. If the Ni–Y bond is too stable, the complex may be decomposed by other route than reductive elimination.

Reactions of $NiMe(OC_6H_5)(bpy)$,[5] $NiEt(OC_6H_5)(bpy)$,[8] and $NiMe(OC_6H_4$-*p*-$C_6H_5)(PEt_3)_2$[5] with an equimolar amount of CO at −78 °C gave nickel carbonyl complexes, $Ni(CO)_2L_2$, and the corresponding esters, $CH_3COOC_6H_5$, $C_2H_5COOC_6H_5$, and $CH_3COOC_6H_4$-*p*-C_6H_5, respectively, but the acylnickel(II) complexes were not obtained in these reactions. The Ni–OC_6H_5 and Ni–OC_6H_4-*p*-C_6H_5 bonds in these complexes are expected to have lower stabilities than the Ni–OC_6H_4-*p*-CN bonds in $NiR(OC_6H_4$-*p*-CN)(bpy) since an OR group generally binds to metals more strongly when the electron-withdrawing ability of the OR group increases. This effect may account for the successful isolation of the *p*-cyanophenoxo(acyl)nickel complexes **3** and **4** and failure of isolation of the supposed intermediates Ni(acyl)$(OC_6H_5)L_2$ and Ni(acyl)$(OC_6H_4$-*p*-$C_6H_5)L_2$ which may reductively eliminate esters even in the absence of excess CO and at −78 °C.

The isolated acylnickel(II) complexes **1**—**5** have relatively high thermal stabilities but are sensitive to air to give carboxylatonickel(II) complexes (*vide infra*).

IR, NMR, and Visible Spectroscopic Data. Table 1 summarizes spectroscopic data of the complexes. IR spectra of the acylnickel(II) complexes show ν(C=O) bands at about 1650 cm^{-1} which may be compared with the ν(C=O) bands of reported acylnickel(II) comlexes observed in the region of 1680 to 1625 cm^{-1}.[6,7]

In the ^{1}H-NMR spectrum, the CH_3 signal of the Et ligands in the ethyl complexes $NiEt(Y)L_2$[5] is only slightly shifted by the CO insertion into the Ni–Et bond, whereas the CH_2 signals of the Et ligand is considerably shifted to lower field. The acetyl complexes, **4** and **5**, give rise to signals of $COCH_3$ in a region where the signal of $COCH_3$ of acetyltransition metal complexes is usually observed.[1,3,6,7] The complexes are stable in solutions and signals of decarbonylated complexes ($NiR(Y)L_2$) are not observed at room temperature.

$^{13}C\{^1H\}$-NMR spectrum of **5** shows a triplet (*J*=

Table 2. Reactivities of acylnickel complexes

No.	Complex	Reactant a) mol/complex	Solvent	Temp °C	Time h	Products (mol%/complex)
I. Thermolysis						
1	**1**		none	200	5	CO(27), C_2H_4(17), C_2H_6(7), EtCOEt(6)
2	**1**		toluene	80	3	CO(27), C_2H_4(13), C_2H_6(4), EtCOEt(13)
3	**2**		none	200	5	CO(31), C_2H_4(34), C_2H_6(19), EtCOEt(2)
4	**3**		toluene	80—90	1	CO(17), C_2H_4(12), C_2H_6(4), EtCOOC$_6$H$_4$-*p*-CN(12)
5	**4**		toluene	80—85	1	CO(43), CH_4(4),MeCOOC$_6$H$_4$-*p*-CN(3)
6	**5**		*p*-xylene	90	2	CO(10), MeCOMe(12)
II. Reactions with alcohols or aniline						
7	**1**	MeOH(ex)	none	50—60	2	EtCOOMe(14)
8b)	**1**	MeOH(ex)	none	r.t.	8	EtCOOMe(92)
9b)	**1**	*i*-PrOH(ex)	none	r.t.	24	EtCOO-*i*-Pr(72)
10b)	**2**	MeOH(ex)	none	r.t.	9	EtCOOMe(82)
11b)	**2**	EtOH(ex)	none	r.t.	1	EtCOOEt(73)
12b)	**2**	*n*-PrOH(ex)	none	r.t.	1	EtCOO-*n*-Pr(76)
13b)	**2**	*i*-PrOH(ex)	none	r.t.	1	EtCOO-*i*-Pr(78)
14	**3**	MeOH(ex)	none	r.t.	24	EtCOOMe(30)
15	**1**	PhNH$_2$(ex)	none	r.t.	48	EtCOONHPh(41)
16b)	**1**	PhNH$_2$(ex)	none	r.t.	24	EtCOONHPh(40)
17	**2**	PhNH$_2$(ex)	none	r.t.	24	EtCOONHPh(53), succinimide(56)
18	**4**	PhNH$_2$(ex)	none	r.t.	1	MeCOONHPh(45)
III. Reactions with O_2 c)						
19	**1**	O_2(1)	none	r.t.	48	EtCOOH(63), NiCl$_2$(bpy)(100)
20	**1**	O_2(1.2)	benzene	r.t.	48	EtCOOH(82)
21	**2**	O_2(ex)	none	r.t.	15	EtCOOH(56), succinimide(45)
22	**2**	O_2(1.1)	benzene	r.t.	24	EtCOOH(75), succinimide(56)
23	**4**	O_2(1.3)	benzene	r.t.	24	MeCOOH(100)
IV. Reactions with π-acids						
24	**3**	MAH(3.8)	THF	r.t.	24	EtCOOC$_6$H$_4$-*p*-CN(62), Ni(MAH)$_2$(bpy)(90)
25	**3**	EMA(ex)	none	r.t.	6	EtCOOC$_6$H$_4$-*p*-CN(31)
26	**5**	MAH(ex)	THF	r.t.	4	MeCOOC$_6$H$_4$-*p*-CN(70), Ni(MAH)$_2$(bpy)(77)
27	**3**	CO(ex)	THF	r.t.	1	EtCOOC$_6$H$_4$-*p*-CN(79), Ni(CO)$_2$(bpy)(42)
V. Reactions with NiR$_2$(bpy)						
28d)	**5**	NiMe$_2$(bpy) (1.0)	C_6D_6	40	72	MeCOMe(33), NiMe(pht)(PEt$_3$)$_2$(100), Ni(CO)$_2$(bpy)e)
29	**5**	NiEt$_2$(bpy) (1.0)	C_6D_6	40	24	EtCOEt(12), MeCOEt(2), NiMe(pht)(PEt$_3$)$_2$e) Ni(CO)$_2$(bpy)e)

a) ex=excess, Me=CH_3, Et=C_2H_5, Ph=C_6H_5, Pr=C_3H_7, MAH=maleic anhydride, EMA=ethyl methacrylate. b) The reaction was carried out under an atmosphere of CO. c) Dry air (not pure O_2) was added. The last column shows compounds recovered after treating the produced complex with dry HCl. d) Followed by NMR. e) Formation of the complex was confirmed by IR but the amount not measured.

22 Hz) at 258.31 ppm assignable to the CO carbon of the COCH$_3$ ligand, the triplet pattern indicating that **5** has a *trans* configuration. The *trans* configuration is consistent with an observation of an only one sharp singlet in ^{31}P-NMR spectrum of **5**.

Visible spectra of the bpy-coordinated complexes, **1**—**4**, in THF show Ni→bpy CT-band ($\varepsilon \fallingdotseq 3\times10^3$) at 480—503 nm, the λ_{max} values being shifted to shorter wave length by 20—30 nm from the starting NiR(Y)(bpy) type complexes.5) The shift suggests that the electronegativity of Ni is increased by replacing the R ligand with the COR ligand.9)

Chemical Reactivities of Ni(COR)(Y)L$_2$. Products of thermolysis and reactions of NiR(Y)L$_2$ with various compounds are summarized in Table 2.

Thermolysis: Although the acylnickel(II) complexes have fairly high thermal stabilities, they undergo decarbonylation reaction at 100—150 °C in solid to liberate CO and a mixture of C_2H_4 and C_2H_6 from the propionyl complexes or CH_4 from the acetyl complex (Nos. 1—6 in Table 2). Formation of ester in the thermolysis of **3** and **4** indicates occurrence of the reductive coupling of the RCO and OC$_6$H$_4$-*p*-CN groups at the elevated temperature. Thermolyses of **1**, **2**, and **5** which have stronger Ni–Y bonds, on the other hand, do not give the reductive coupling product RCOY even at the elevated temperature, but they afford ketone RCOR presumably through a coupling reaction between Ni(COR)(Y)L$_2$ and NiR(Y)L$_n$ formed in the thermolysis. The thermolysis of Ni(COR)-

TABLE 3. REACTIONS OF NiR_2L_2 WITH CO[a)]

No.	Complex	Dp[b)] °C	Additive (mol/Ni)	Solvent	Temp °C	Time h	Products (% yield/Ni) RCOCOR	RCOR	RCHO	R(-H)
I. Reactions at −78 °C (effects of R and L).										
1	**6** (R=Me, L_2=bpy)	160	none	Et_2O	−78	24	89	0	0	0
2	**6**		none	THF	−78	24	76	0	0	0
3	**7** (R=Me, L_2=dpe)	140	none	Et_2O	−78	12	76	4	0	0
4	**7**		none	toluene	−78	6.5	48	25	0	0
5	**8** (R=Me, L_2=dpp)	95	none	THF	−78	24	21	75	0	0
6	**8**		none	Et_2O	−78	24	44	47	0	0
7	**9** (R=Me, L_2=2PEt_3)	40	none	Et_2O	−78	0.2	0	98	0	0
8	**10** (R=Et, L_2=bpy)	105	none	THF	−78	0.1	0	100	0	0
9	**11** (R=*n*-C_3H_7, L_2=bpy)	50	none	THF	−78	0.1	0	100	0	0
10	**12** (R=Et, L_2=dpe)	50	none	THF	−78	6.5	0	0	38	c)
11	**12**		none	Et_2O	−78	24	0	0	15	c)
II. Reactions at temperatures higher than −78 °C (effect of temperature).										
12	**6**		none	Et_2O	−45	5	89	0	0	0
13	**6**		none	Et_2O	−17	24	68	8	0	0
14	**6**		none	Et_2O	1	7	42	39	0	0
15	**6**		none	Et_2O	13	3	0	90	0	0
16	**7**		none	Et_2O	r.t.	48	0	73	0	0
17	**7**		none	toluene	r.t.	8	3	83	0	0
18	**8**		none	THF	r.t.	2	0	80	0	0
19	**9**		none	Et_2O	r.t.	1.5	0	93	0	0
20	**10**		none	THF	r.t.	0.1	0	90	0	0
21	**11**		none	acetone	r.t.	0.1	0	79	0	0
22	**12**		none	THF	−40	3.5	0	0	58	c)
23	**12**		none	THF	r.t.	24	0	2	24	59
24	**12**		none	toluene	r.t.	3	0	0	29	41
III. Reactions in the presence of additives.										
									(Remarks)	
25	**6**		bpy(5.3)	THF	r.t.	0.1	0	100	no effect	
26	**6**		dpe(excess)	THF	−78	1.5	50	5	ligand exchange	
27	**6**		MAH(3.2)	THF	−78	24	2	37	RCOR increases	
28	**7**		MAH(3.3)	THF	−78	1	27	73	RCOR increases	
29	**9**		PEt_3(3.2)	Et_2O	r.t.	1.5	0	98	no effect	

a) Reactions are carried out in the presence of excess (more than 3 mol/Ni) CO. b) Decomposition temperature of the complex (see Refs. 9, 12, and 13). c) Evolution of C_2H_4 was confirmed by GLC, but measurement of its amount was not feasible due to high solubility of C_2H_4 in the solvent at the temperature.

$$\begin{tikzcd} Ni(COR)(Y)L_2 \arrow[r, shift left] & NiR(Y)L_2 + CO \arrow[l, shift left] \arrow[d, "+Ni(COR)(Y)L_2"] \\ & RCOR \end{tikzcd} \qquad (3)$$

$(Y)L_2$ proceeds at lower temperature in solutions.

Reactions with Alcohols and Aniline: $Ni(COR)(Y)L_2$ reacts with alcohols and aniline to afford esters and amides, respectively,

$$Ni(COR)(Y)L_2 + R'OH \longrightarrow RCOOR', \qquad (4)$$

$$Ni(COR)(Y)L_2 + C_6H_5NH_2 \longrightarrow RCOONHC_6H_5. \qquad (5)$$

Carrying out the reaction with R'OH in the absence of excess CO gives RCOOR' only in a low yield presumably due to a partial decarbonylation of $Ni(COR)(Y)L_2$ in the presence of R'OH, and the yield increases considerably when the reaction is carried out in the presence of excess CO. In the reaction with aniline,

$$\begin{tikzcd} Ni(COR)(Y)L_2 \arrow[r, shift left] & NiR(Y)L_2 + CO \arrow[l, shift left] \\ RCOOR' & \end{tikzcd} \qquad (6)$$

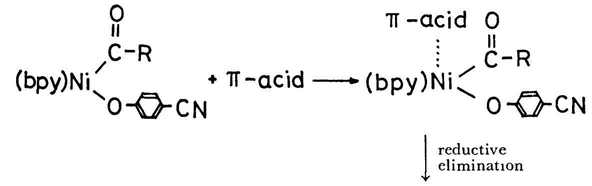
on the contrary, the yield of amide is virtually independent of the presence or absence of excess CO. These reactions which may be regarded as nucleophilic attack of alcohol or amine on the acyl ligand are relevant to the transition metal-catalyzed synthesis of esters or amides from organic halide, CO, and alcohols or amines.[1,2)]

Oxidation of the RCO Ligand: $Ni(COR)(Y)L_2$ absorbs O_2 (about 0.5 mol/Ni) in dry air. Acidolysis of the paramagnetic product by dry HCl gives RCOOH in 56—100% yield, indicating that oxidation of the acyl to a carboxylato ligand takes place on exposure of $Ni(COR)(Y)L_2$ to dry air,

$$Ni(COR)(Y)L_2 + O_2 \longrightarrow [Ni(OCOR)(Y)L_n] \Big\downarrow{\scriptstyle +HCl} \; RCOOH \qquad (7)$$

Isolation of $Ni(OCOR)(Y)L_n$ was not feasible due to the lack of suitable solvents for recrystallization, but IR spectrum of a complex formed by the reaction of **2** with dry air is identical to that of a product formed by an 1:1 reaction of NiEt(suc)(bpy) with C_2H_5COOH, supporting the occurrence of the reaction expressed by Eq. 7.

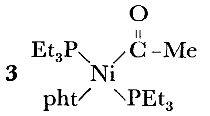
*π-Acid Induced Reductive Elimination of Ester from **3** and **4***: As described above, reductive elimination of $RCOOC_6H_4$-*p*-CN from $Ni(COR)(OC_6H_4$-*p*-CN)(bpy) is enhanced by addition of CO, which is regarded as a typical π-acid. Addition of other π-acids such as maleic anhydride (MAH) and ethyl methacrylate (EMA) also enhances the reductive elimination (No. 24—26). The Ni–COR and/or $Ni–OC_6H_4$-*p*-CN bond seems to be activated by coordination of the π-acid to cause the reductive elimination,



$RCOOC_6H_4$-*p*-CN + Ni(π-acid)(bpy). (8)

Similar enhancement of reductive elimination of R–R from $NiR_2(bpy)$ by coordination of π-acid to Ni has been reported.[9)] A stronger π-acid, MAH, affords the ester in a higher yield than a weaker π-acid, EMA. The reaction (8) can be regarded as a reverse process of oxidative addition of ester to a Ni(0) complex.[10)] Addition of MAH does not induce such a reductive elimination of RCOY from complexes **1**, **2**, and **5** having stronger Ni–Y bonds.

Reactions with Ni(0)- and Dialkylnickel(II) Complexes: Addition of $Ni(PPh_3)_4$ (PPh_3=triphenylphosphine) to a solution of **4** leads to formation of a mixture of NiMe(OC_6H_4-*p*-CN)(bpy) and $Ni(CO)(PPh_3)_3$. The reaction is considered to proceed through partial decarbonylation of **4** and trapping of CO by $Ni(PPh_3)_4$. A similar decarbonylation of an acetylnickel(II) complex enhanced by Ni(0) complexes has been observed.[6a)] The acylnickel(II) complexes are also decarbonylated on treatment with dialkylnickel(II) complexes. For example, a reaction of **5** with $NiMe_2(bpy)$ **6** (1:1) at 40 °C (No. 28) gives acetone (33%, determined by ^1H-NMR), the decarbonylated product NiMe(pht)$(PEt_3)_2$ (100%), $Ni(CO)_2(bpy)$,[11)] and intact **6** (67%), suggesting CO partly liberated from **5** is trapped by **6** to release acetone and $Ni(CO)_2(bpy)$ according to the following stoichiometry,



$$3\,\underset{\mathbf{5}}{Ni(COMe)(pht)(PEt_3)_2} + \underset{\mathbf{6}}{NiMe_2(bpy)} \longrightarrow MeCOMe + 3NiMe(pht)(PEt_3)_2 + Ni(CO)_2(bpy). \qquad (9)$$

When $NiEt_2(bpy)$ is added to a solution of **5**, a cross coupling reaction to give MeCOEt takes place (No. 29) besides the simple CO trapping reaction by $NiEt_2(bpy)$ to give EtCOEt. The results suggest the occurrence of intermolecular alkyl or acyl transfer reactions.

II. Reactions of NiR_2L_2 with CO. In contrast to the reactions of monoalkylnickel(II) complexes with CO, reactions of dialkylnickel(II) NiR_2L_2 with CO did not afford any isolable acylnickel complexes, but they produced carbonylated compounds of the alkyl ligands, ketone, diketone, and/or aldehyde:

$$NiR_2L_2 + CO \longrightarrow RCOR,\ RCOCOR,\ \text{and/or}\ RCHO. \qquad (10)$$

6 $NiMe_2(bpy)$
7 $NiMe_2(dpe)$
8 $NiMe_2(dpp)$
9 $NiMe_2(PEt_3)_2$
10 $NiEt_2(bpy)$
11 Ni(*n*-$C_3H_7)_2$(bpy)
12 $NiEt_2(dpe)$

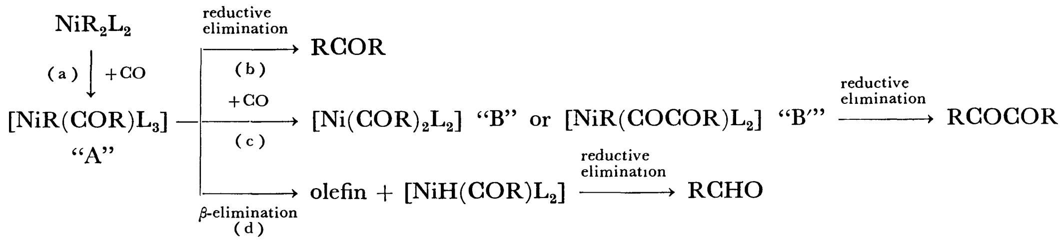
dpe = 1,2-bis(diphenylphosphino)ethane
dpp = 1,3-bis(diphenylphosphino)propane

Table 3 summarizes results of the reactions. It is seen in Table 3 that the product of the reaction (10) varies with changes in the R and L ligands and reaction conditions. Following is details of effects of the ligands and reaction conditions on the product.

Effects of R and L: Reactions of dimethylnickel complexes **6**—**9** with CO give 2,3-butanedione and acetone and the ratio of the two products varies with the nature of L and the reaction temperature. At −78 °C the fraction of the diketone increases in an increasing order of a thermal stability of $NiMe_2L_2$, **9**<**8**<**7**<**6**.[9,12,13)]

Among the complexes of a type $NiR_2(bpy)$ examined, only the methyl complex which has the higher thermal stability than the ethyl and propyl homologs gives diketone at −78 °C, and less stable complexes **10** and **11** afford ketones exclusively at −78 °C. These results suggest that the ketone/diketone ratio at −78 °C may be related to the thermal stability of NiR_2L_2 (or the strength of the Ni–R bond). The reaction of **12** with CO gives a different type of product, propanal, with evolution of ethylene.

Effect of Temperature: On raising the reaction temperature, the fraction of acetone formed in the reaction of **6** with CO increases and at 13 °C or above acetone becomes a sole liquid product. Similar increases in the proportion of acetone on raising the reaction temperature to room temperature are observed in the reactions of diphosphine-containing complexes **7** and **8** with CO. Complexes **9**, **10**, and **11** which give ketones as the sole liquid products at −78



Scheme 1.

°C afford the same products at room temperature.

Effect of Additive: Addition of maleic anhydride increases the fraction of acetone formed in the reactions of **6** and **7** with CO at −78 °C presumably due to the activating effect of the alkyl and/or acyl ligands by coordination of the π-acid. Addition of bpy and PEt_3 in the reactions of the dimethyl complexes **6** and **9** with CO, respectively, seems to affect neither the product nor the rate of the reaction.

Other Factors: Table 3 shows results of the reactions carried out in the presence of excess CO (more than 3 mol/Ni) which left no intact NiR_2L_2. When the reaction is carried out in the presence of a less amount of CO, however, the yield of the product decreases. For example, reactions of **9** in the presence of 1.0 and 2.0 mol of CO per **9** at −78 °C afford acetone in 21 and 68% yields, respectively. Since $Ni(CO)_2(PEt_3)_2$ is isolated from the reaction mixture, the stoichiometry of the reaction of **9** with CO can be written as follows,

$$NiMe_2(PEt_3)_2 + 3CO \longrightarrow MeCOMe + Ni(CO)_2(PEt_3)_2 \qquad (11)$$

and the yields obtained in the presence of 1.0 and 2.0 mol of CO per **9** roughly agree with the stoichiometry. $Ni(CO)_2(dpe)$[14] (isolated yield=76%), $Ni(CO)_2(dpp)$[14] (81%), and $Ni(CO)_2(bpy)$[11] (50%) are obtained in the reaction Nos. 3, 5, and 20 (see Table 3), respectively.

Although detailed examination has not been made concerning rates of the reactions, among the phosphine-coordinated complexes the monodentate PEt_3-coordinated complex **9** seems to react with CO at a faster reaction rate than the bidentate phosphine coordinated complexes **7** and **8**.

Among the complexes of the type $NiR_2(bpy)$, the dimethyl complex **6** reacts with CO most slowly. At −78 °C the reaction of **6** with CO requires more than 10 h to be completed, whereas the reactions of **10** and **11** with CO are completed in few minutes even at the temperature. A competitive reaction between the dimethyl and diethyl complexes, **6** and **10**, (1:1) in the presence of 1 mol of CO per Ni (**6**+**10**) at room temperature produces 3-pentanone (30%/**10**) exclusively and all of **6** remains intact, indicating **10** reacts with CO much faster than **6**. The difference in the rate may be related to the difference in relative strength of the Ni–C bond of the complex and/or to the difference in relative affinity of the complex to CO. It is known that the $Ni–CH_3$ bond in **6** is stronger than the $Ni–C_2H_5$ and $Ni–C_3H_7$ bonds in **10** and **11** and that **6** has a weaker affinity toward π-acids than **10** and **11** due to its weaker Lewis basicity.[9]

Reaction Scheme and Factors Controlling the Distribution of Products. These results of the reactions of NiR_2L_2 with CO can be reasonably explained by a scheme involving formation of a monoalkyl(acyl)nickel(II) complex "A" as the key reaction intermediate (Scheme 1). In the reaction scheme CO inserts into one of the Ni–R bonds of NiR_2L_2 (step (a)) to form an intermediate monoalkyl(acyl)nickel(II) complex "A". The intermediate "A" undergoes reductive elimination to give ketone (step (b)). Further CO-insertion reaction may give a diacylnickel(II) complex "B" or alkyl(pyruvoyl)nickel(II) complex "B′" from which diketone is produced (step (c)). When the ethyl group is employed, β-elimination reaction from "A" may produce olefin (R(–H)) and aldehyde. Formation of acetone from isolated platinum (IV) complexes having both methyl and acetyl groups have been reported.[15] In the case of the reaction of **6** with CO, the intermediacy of "A" is supported by production of 2-butanone on carrying out the reaction in the presence of C_2H_5Br. Attempts to isolate NiMe(COMe)(bpy), however, have not been successful presumably due to instability of the complex.

As described above, $CH_3COC_2H_5$ is produced in the reaction of **6** with CO at −78 °C in the presence of C_2H_5Br, whereas no $CH_3COCOC_2H_5$ was detected in the product. This suggests that 2,3-butanedione is produced through the intermediate diacyl species "B" rather than "B′". However, at present it is not possible to exclude the possibility for the intermediacy of the doubly CO-inserted species, since a transition metal complex having a CH_3COCO ligand is known[16] and evidence for the double CO-insertion has been obtained for carbonylation of a dimethylpalladium complex.[17]

According to Scheme 1, the distribution of the products is determined by relative rates of the elemental reactions (b)—(d), and the results described above indicate that the relative rates depend on the R and L ligands, reaction temperature, and additives in following ways.

(i) Effect of R and L: The relative rate of the reaction (b) at −78 °C to that of the reaction (c) increases when the thermal stability of the starting dialkylnickel(II) complex NiR_2L_2 decreases. If the strength of either or both of the Ni–R and Ni–COR bonds in "A" is controlled by the nature of the R and L ligands in a similar way to that of the Ni–R bonds in NiR_2L_2, these results indicate that the reductive elimination of RCOR from "A" takes place prior

to the further attack of CO at "A" (step (c) in Scheme 1) when the Ni–R and/or Ni–COR bond is weak. On the contrary, when the bonds are stronger, the intermediate "A" can wait for the further attack of CO to form "B" or "B′" and diketone is formed in this case.

(ii) Effect of Temperature: When the reaction temperature is raised, the Ni–R and Ni–COR bonds in "A" will be activated to cause the reductive elimination and the proportion of ketone will thus increase.

(iii) Effect of Additive: The effect of MAH to increase the proportion of ketone may be related to the MAH-induced reductive elimination of $RCOOC_6H_4$-*p*-CN from **3** and **4**. Namely, coordination of MAH to "A" may lead to activation of the Ni–R and Ni–COR bonds as in the case of **3** and **4**, and therefore the fraction of ketone will increase on the addition of MAH. An alternative explanation of the effect of MAH is that MAH coordinates to "A" to block the coordination site to prevent the further attack of CO at "A". We consider that the former explanation is more reasonable since the effect of MAH on the reductive elimination of esters and R–R from the acyl(phenoxo)-type complexes and NiR_2(bpy) (R=Me, Et),[9] respectively, is so pronounced.

*(iv) Difference between **10** and **12***: The difference in the products of the reaction of **10** with CO and that of **12** with CO may be related to the difference of thermolysis between **10** and **12**; the former gives mainly the coupling product C_4H_{10} on the thermolysis,[9] whereas the latter exclusively affords the disproportionation products, C_2H_6 and C_2H_4,[12] indicating that the β-elimination in **12** proceeds more easily than that in **10**. If coordination of dpe to Ni having ethyl ligand(s) makes the abstraction of the β-hydrogen in the Et ligand by Ni easier, the formation of C_2H_5CHO and C_2H_4 through the path (d) in Scheme 1 can be reasonably explained. Lower yield of C_2H_5CHO than that of C_2H_4 seems to be due to partial polymerization of C_2H_5CHO catalyzed by Ni complexes.[18]

Conclusion and Scope

Carbon monoxide inserts into Ni–R bonds of monoalkyl- and dialkylnickel(II) complexes, NiR(Y)L_2 and NiR_2L_2, to give complexes of a type Ni(COR)(X)L_n (X=R, Cl, phenoxo, imido). When the X ligand has a moderate or strong bonding ability to Ni as in Cl, OC_6H_4-*p*-CN, and imido ligands, the acylnickel(II) complex can be isolated. On the contrary, when X has only a weak bonding ability as R, OC_6H_5, and OC_6H_4-*p*-C_6H_5, the reductive elimination of RCOX takes place under the reaction conditions and the acylnickel(II) complex could not be isolated. In the case of NiR(COR)L_n, other types of reactions, namely, further insertion of CO to form "B" (or "B′") and β-elimination of C_2H_5CHO and C_2H_4, can also take place depending on nature of the R and L ligands and the reaction conditions. The acylnickel(II) complexes having a moderately strong bonding ligand, OC_6H_4-*p*-CN, are activated by coordination of π-acids (CO, MAH, EMA) to cause the reductive elimination of $RCOOC_6H_4$-*p*-CN. Such a reductive elimination, however, is not induced on adding the π-acids to complexes having stronger Ni–X bonds such as Ni–Cl and Ni–imido. The isolated acylnickel(II) complexes afford esters, amides, and carboxylato complexes in the reactions with alcohols, aniline, and O_2, respectively.

These results obtained in this work may be useful in planning carbonylation of organic compounds by CO. The formation of ketone from NiR_2L_2 has been actually applied to nickel-catalyzed synthesis of ketone from RMgX, RX, and CO.[4a]

Experimental

General. Manipulation of nickel complexes was carried out under deoxygenated nitrogen or argon or in a vacuum. IR spectra were taken on a Hitachi Model 295 spectrometer using KBr discs under nitrogen. NMR spectra were taken by using a Japan Electron Optics Lab. JNM-PS-100 spectrometer. Microanalysis of C, H, and N was performed by T. Saito in our laboratory with a Yanagimoto CHN Autocorder Type MT-2. High sensitivities of the nickel complexes to air should be taken into account concerning the microanalysis. Nickel contents of the complexes were measured by volumetric titration after acidolysis of the complexes. Gases evolved were analyzed with a Hitachi RMU 5B mass-spectrometer and a Shimadzu GC-5B gas chromatograph, their volumes being measured with a Toepler pump. Liquid products were analyzed with a Shimadzu GC-5B gas chromatograph.

Material. The monoalkyl-[5] and dialkylnickel(II)[9,12,13] complexes were prepared as described in literature. Solvents were dried over Na wires or CaH_2, distilled under N_2, and stored under N_2. CO gas was dried by bubbling through concd H_2SO_4.

Preparation of the Acylnickel Complexes. *Propionyl(chloro)-(2,2′-bipyridine)nickel(II)* ***1***: A reaction vessel (60 cm^3) containing a THF (10 cm^3) solution of NiEt(Cl)(bpy) (420 mg, 1.5 mmol) was evacuated and then CO (50 cm^3, 1 atm) was introduced into the vessel. Stirring the solution for 10 min at room temperature gave a reddish brown solution, into which 40 cm^3 of hexane was added to obtain 440 mg of a reddish brown solid. The reddish brown solid was recrystallized from THF–hexane to yield brown crystals of **1** (220 mg, 48%); mp 130 °C (dec). Found: C, 51.2; H, 4.2; N, 9.1; Cl, 11.2%. Calcd for $C_{13}H_{13}ClN_2NiO$: C, 50.8; N, 4.3; N, 9.1; Cl, 11.5%.

Propionyl(succinimido)(2,2′-bipyridine)nickel(II) ***2***: A reaction vessel (60 cm^3) containing a CH_2Cl_2 (10 cm^3) solution of NiEt(suc)(bpy) (630 mg, 1.8 mmol) was evacuated and CO (50 cm^3, 1 atm) was introduced into the vessel. Stirring the solution for 30 min at room temperature gave a red solution and a small amount of a precipitate. The solution was separated by filtration and hexane was added to the filtrate to obtain a dark brown precipitate, which was recrystallized from THF–hexane to yield a reddish brown microcrystals of **2** (450 mg, 73%); mp 150 °C (dec). Found: C, 54.1; H, 4.9; N, 10.0%. Calcd for $C_{17}H_{17}N_3NiO_3$: C, 55.2; H, 4.6; N, 11.2%.

*Propionyl(*p*-cyanophenoxo)(2,2′-bipyridine)nickel(II)* ***3***: A reaction vessel containing a THF (7 cm^3) solution of NiEt(OC_6H_4-*p*-CN)(bpy) (420 mg, 1.2 mmol) was connected to a vacuum line and the vessel was evacuated. After cooling the solution to −78 °C, CO gas (1.2 mmol) whose amount was measured by a manometer was introduced and the solution was stirred for 3 h at −78 °C to obtain a reddish purple homogeneous solution. An excess amount of hexane was added to the solution to yield 430 mg (94%) of reddish purple crystals of **3**. A sample for the microanalysis was obtained by recrystallization from acetone–hexane; mp 120 °C (dec). Found: C, 60.8; H, 3.9; N, 11.1; Ni, 14.7%. Calcd for $C_{20}H_{17}N_3NiO_2$: C, 61.6; H, 4.4; N, 10.8; Ni, 15.1.

Acetyl(p-cyanophenoxo)(2,2′-bipyridine)nickel(II) **4**: A vessel containing a THF (20 cm³) solution of $NiMe(OC_6H_4\text{-}p\text{-}CN)(bpy)$ (1.0 g, 2.8 mmol) was connected to a vacuum line and the vessel was evacuated. After cooling the solution to −78 °C, a measured amount of CO (2.8 mmol) was introduced into the vessel and the solution was stirred at −78 °C for 5 h. Hexane (excess) was added to the solution to obtain a brown powder, which was recrystallized from acetone to yield reddish brown crystals of **4** (380 mg, 36%); mp 140 °C (dec). Found: C, 59.5; H, 4.1; N, 10.5; Ni, 15.6. Calcd for $C_{19}H_{15}N_3NiO_3$: C, 60.7; H, 4.0; N, 11.2; Ni, 15.6%.

Acetyl(phthalimido)bis(triethylphosphine)nickel(II) **5**: A vessel containing an ethereal solution (20 cm³) of $NiMe(pht)(PEt_3)_2$ was evacuated and then CO (100 cm³, 1 atm) was introduced into the vessel. Stirring the solution for 10 min at room temperature gave a yellow solution and a small amount of a precipitate. The yellow solution was separated by filtration and cooling the solution to −78 °C gave yellow crystals of **5** (470 mg, 83%); mp 100 °C (dec). Found: C, 54.0; H, 7.8; N, 2.9; Ni, 12.4%. Calcd for $C_{22}H_{37}NNiO_3P_2$: C, 54.6; H, 7.7; N, 2.9; Ni, 12.1%.

Reactions of NiR_2L_2 with CO (cf. Table 3). No. 1: Carbon monoxide (3.2 mmol) was introduced at −78 °C into an evacuated vessel containing 130 mg (0.53 mmol) of **6** in 6.5 ml of diethyl ether. The dimethylnickel(II) complex was partly soluble in diethyl ether at −78 °C and the solution was colored deep green (color of **6**) at the initial stage of the reaction. On stirring the mixture at −78 °C, the color of the solution gradually turned to red. After 1 d, a homogeneous red solution was obtained and GLC analysis of the solution indicated formation of 0.48 mmol of 2,3-butanedione. Drying up the solution in vacuum at −78 °C gave almost pure bpy, whereas drying up the solution after warming the solution to room temperature gave a mixture of bpy and $Ni(CO)_2(bpy)$,[11] indicating that there exists an equilibrium, $Ni(CO)_4 + bpy \rightleftarrows Ni(CO)_2(bpy) + 2CO$, and the equilibrium lies to the left at −78 °C.

Other Reactions of NiR_2L_2 with CO: Other reactions listed in Table 3, except for reactions in the presence of MAH, were carried out in similar ways to the reaction of **6** at −78 °C. Reactions of $NiR_2(bpy)$ with CO at room temperature gave $Ni(CO)_2(bpy)$ in high yields. Nickel carbonyl complexes, $Ni(CO)_2(bpy)$,[11] $Ni(CO)_2(PEt_3)_2$,[14] $Ni(CO)_2(dpe)$,[14] and $Ni(CO)_2(dpp)$[14] were identified by their IR spectra. Reactions in the presence of MAH require the following special attention to prevent NiR_2L_2 to decompose before the reaction with CO since MAH strongly activates the Ni–R bond of NiR_2L_2. A solution of NiR_2L_2 in THF was solidified by cooling to −196 °C and then MAH was added to the reaction system. CO was added immediately after the solution melted on raising temperature.

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