Preparation and Properties of Monoalkylnickel(II) Complexes Having a Phenoxo, Benzenethiolato, Oximato, β-Diketonato, or Halo Ligand

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Thirteen complexes of a type NiR(Y)L_n (R=CH_3 (Me), C_2H_5 (Et); Y=OC_6H_5, *p*-cyanophenoxo, *p*-phenylphenoxo, 8-quinolinolato, OCOEt, OCOPh, acetophenone oximato, acetylacetonato, benzoylacetonato, Cl; L=triethylphosphine (PEt_3), 2,2′-bipyridine (bpy)) have been prepared by reactions of dialkylnickel(II) complexes NiR_2L_2 (**1**) with the corresponding active hydrogen compounds HY. Reactions of **1** with R′COY (Y=OC_6H_5, $OCOC_6H_5$, Cl) also afford the NiR(Y)L_n type complexes with formation of unsymmetrical ketones RCOR′. Reactions of **1** with alcohols lead to dehydrogenation of alcohols to afford aldehydes or ketones. The NiR(Y)L_n type complexes have been characterized by elemental analysis and spectroscopies (IR, NMR, visible). NMR spectra of *trans*-NiMe(OCOPh)$(PEt_3)_2$, NiMe(acetophenone oximato)(PEt_3) (**11**), NiMe(benzoylacetonato)(PEt_3) show temperature dependence, indicating occurrence of rapid dynamic reactions on NMR time scale in these complexes. The acetophenone oximato ligand in **11** is proposed to serve as an oxa-, aza-π-allylic ligand on the bases of IR and NMR spectroscopies. NiEt($OCOC_2H_5$)(bpy) (**8**), NiEt($OCOC_6H_5$)(bpy), and NiEt(Cl)(bpy) (**14**) undergo disproportionation reaction to give $NiEt_2$(bpy) and NiY_2(bpy) type complexes. Diethyl ketone is also produced during the disproportionation of **8**. Reactions of **14** with olefins having electron-withdrawing substituents afford $NiCl_2$(bpy) and Ni(olefin)$_2$(bpy).

Nickel complexes of a type NiR(Y)L_n, where R is an alkyl, alkenyl, or aryl group and Y is an anionic ligand such as Cl, OPh, or NR^1R^2, are often assumed as key intermediates in various Ni-catalyzed reactions such as isomerization of olefin and polymerization or oligomerization of olefins and dienes.[1–4] However, only a few papers[5–7] have reported on the isolation and chemical properties of the NiR(Y)L_n type complexes except for monoaryl(halo)nickel(II) complexes such as Ni(aryl)X$(PR_3)_2$[8,9] and Ni(aryl)X(bpy).[10]

In our preceding paper[11] we reported preparation of monoalkyl(amido)nickel(II) complexes, NiR(NR^1R^2)L_2, by reactions of dialkylnickel(II) complexes, NiR_2L_2, with corresponding N–H compounds. As an extention of the work we have carried out reactions of NiR_2L_2 with phenols, alcohols, benzenethiol, carboxylic acids, oximes, β-diketones, and hydrogen halides and isolated several new NiR(Y)L_n type complexes from the reaction mixtures. This paper deals with the preparation and chemical properties of the complexes. In some cases the NiR(Y)L_n type complexes can be prepared also by reactions of NiR_2L_2 with carbonyl compounds such as CH_3COCl, $CH_3COOC_6H_5$, and $(C_6H_5CO)_2O$, and the results are included in this paper.

Results and Discussion

Preparation of NiR(Y)L_n. *Reactions of NiR_2L_2 with Active Hydrogen Compounds HY*: Dialkylnickel(II) complexes, NiR_2L_2, react with equimolar amounts of active hydrogen compounds to give monoalkylnickel(II) complexes of the type NiR(Y)L_n:

$$\underset{1}{NiR_2L_2} + \underset{1}{HY} \longrightarrow \underset{\mathbf{2\text{—}14}}{NiR(Y)L_n} + RH \quad (1)$$

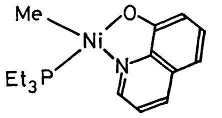
1a: $NiMe_2$(bpy)
1b: $NiEt_2$(bpy)
1c: $NiMe_2(PEt_3)_2$

NiMe(OC_6H_5)(bpy)
2

NiMe(OC_6H_4-*p*-CN)(bpy)
3

NiEt(OC_6H_4-*p*-CN)(bpy)
4

trans-NiMe(OC_6H_4-*p*-C_6H_5)$(PEt_3)_2$
5



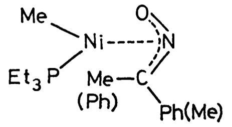
6

trans-NiMe(SC_6H_5)$(PEt_3)_2$
7

NiEt(OCOEt)(bpy)
8

NiEt(OCOPh)(bpy)
9

trans-NiMe(OCOPh)$(PEt_3)_2$
10



11

NiMe(acac)(PEt_3)
12

NiMe(benzoylacetonato)(PEt_3)
13

NiEt(Cl)(bpy)
14

Me=CH_3. Et=C_2H_5. Ph=C_6H_5. acac=2,4-pentanedionato (acetylacetonato). PEt_3=triethylphosphine. bpy=2,2′-bipyridine. benzoylacetonato=1-phenyl-1,3-butanedionato (bzac).

Table 1. Preparative conditions, yields, and analytical data of complexes **2**—**14**

Complex[a)]	Preparative conditions: NiR_2L_2 / mmol	Temp / °C	Solv. / (cm^3)	Time / h	Yield / %	Color[b)]	Mp[c)] / °C	Found (Calcd) (%): C	H	N	Ni	Cl
NiMe(OPh)(bpy) **2**	0.56	r.t.	THF (0.5)	24	87	p.	145 (dec)	63.0 (63.2)	5.1 (5.0)	8.2 (8.7)		
$NiMe(OC_6H_4CN)(bpy)$ **3**	1.4	r.t.	THF (7)	0.2	71	brown	137 (dec)	62.9 (62.1)	4.5 (4.3)	12.0 (12.1)		
$NiEt(OC_6H_4CN)(bpy)$ **4**	2.7	r.t.	THF (15)	0.2	62	p.	116 (dec)	63.4 (63.0)	4.5 (4.7)	11.2 (11.6)		
trans-$NiMe(OC_6H_4Ph)(PEt_3)_2$ **5**	2.4	r.t.	Ether (14)	0.2	78	yellow	109	62.3 (62.6)	9.0 (8.8)			
$NiMe(8\text{-quinolinolato})(PEt_3)$ **6**	3.0	r.t.	Ether (5)	0.5	76	red	74—75	56.8 (57.2)	7.4 (7.2)	4.0 (4.2)		
trans-$NiMe(SPh)(PEt_3)_2$ **7**	2.7	−20	Ether (10)	0.2	53	red	<r.t.		d)		14.1 (14.0)	
NiEt(OCOEt)(bpy) **8**	0.84	r.t.	THF (10)	0.2	62	red	110 (dec)	57.2 (56.8)	5.0 (5.7)	8.9 (8.8)		
NiEt(OCOPh)(bpy) **9**	1.5	r.t.	Toluene (25)	0.2	80	p.	130 (dec)	61.5 (62.5)	4.8 (5.0)	7.5 (7.7)		
trans-$NiMe(OCOPh)(PEt_3)_2$ **10**	0.59	r.t.	Ether (5)	0.1	85	yellow	76—77	55.2 (55.7)	8.1 (8.9)			
$NiMe(\text{acetophenone oximato})(PEt_3)$ **11**	1.9	0—15	Ether (5)	0.2	75	yellow	145 (dec)	55.0 (55.3)	8.4 (8.0)	3.6 (4.3)	Mw: 310[e)] (326)	
$NiMe(acac)(PEt_3)$ **12**	0.41	r.t.	Ether (1.5)	24	45	y.b.	<r.t.		d)		19.9 (20.2)	
$NiMe(bzac)(PEt_3)$ **13**	3.2	r.t.	Ether (15)	0.5	62	y.b.	63—64	57.7 (57.8)	7.9 (7.7)			
NiEt(Cl)(bpy) **14**	3.4	r.t.	THF-Ether (39)	0.1	36	p.	110 (dec)	51.2 (51.6)	4.5 (4.7)	9.9 (10.0)		12.2 (12.7)

a) bzac: benzoylacetonato. b) p.=purple. y.b.=yellowish brown. c) dec=decomposed. d) Microanalysis was not feasible due to the low melting point and high sensitivity to air. e) Cryoscopic in benzene.

TABLE 2. FORMATION OF KETONE OR ALDEHYDE BY REACTIONS OF DIALKYLNICKEL(II) COMPLEXES WITH ALCOHOLS[a)]

No.	NiR_2L_2	Alcohol	Product (mol/NiR_2L_2)
1	$NiMe_2$ (dpe)	$PhCH_2OH$	PhCHO (0.65), CH_4 (1.1)
2	$NiMe_2$ (dpe)	*i*-PrOH	Me_2CO (0.10), CH_4 (0.31)
3	$NiMe_2$ $(PEt_3)_2$	$PhCH_2OH$	PhCHO (0.79), CH_4 (1.2)
4	$NiMe_2$ $(PEt_3)_2$	*i*-PrOH	Me_2CO (1.0), CH_4 (2.0)
5	$NiMe_2$ $(PEt_3)_2$	$PhCH=CHCH_2OH$	PhCH=CHCHO (0.48), CH_4 (1.4), C_2H_6 (0.06)

a) Alcohol/dialkylnickel(II) complex=2. At room temperature.

TABLE 3. PRODUCTS OF REACTIONS BETWEEN NiR_2L_2 AND R′COY[a)]

Run	NiR_2L_2	R′COY (R′COY/Ni)	Solvent	Product (mol%/NiR_2L_2)		
				$NiR(Y)L_n$	RCOR′	Others
1	**1b**	CH_3COCl (1)	Toluene	**14** (47)	$CH_3COC_2H_5$ (96)	
2	**1b**	C_2H_5COCl (1)	THF	**14** (68)	$(C_2H_5)_2CO$ (80)	
3	**1b**	CH_3COBr (1)	Toluene	**16** (35)	$CH_3COC_2H_5$ (76)	
4	**1c**	$CH_3COOC_6H_5$ (2)	Ether	**15** (60)	CH_3COCH_3 (56),	CH_4 (15), C_2H_6 (17)
5	**1c**	$(C_6H_5CO)_2O$ (1)	Ether	**10** (66)	$CH_3COC_6H_5$ (70)	

a) At room temperature. Reaction time: *ca.* 10 min for Runs 1—3, 1 d for Runs 4 and 5.

Preparation of $NiEt(OC_6H_5)(bpy)$ and $NiMe(OC_6H_5)$-(dpe) (dpe=1,2-bis(diphenylphosphino)ethane) by a similar method has been reported.[5,6)]

The reactions proceed more rapidly than the reactions of NiR_2L_2 with N–H compounds[11)] due to the higher acidity of the HY compounds than the N–H compounds. Addition of an excess HY afforded the same product as in the 1:1 reactions when the acidity of the HY was not so high (*e.g.*, phenols and benzenethiol), whereas addition of an excess of a highly acidic HY (carboxylic acids and HCl) led to a further reaction to give NiY_2L_2.

Table 1 shows preparative conditions, yield, melting points and analytical data of the complexes **2**—**14**. Coordination of two PEt_3 to Ni in the phenoxo complex **5** indicates that the phenoxo group bonds to Ni through oxygen serving as a monodentate ligand, although it sometimes coordinates to transition metal through the aromatic ring.[12)] The SC_6H_5 group in **7** also seems to coordinate to Ni through sulfur. The coordination of only one PEt_3 ligand to Ni in **6** and **11** suggests that the 8-quinolinolato and acetophenone oximato ligands serve as 3-electron ligands. As for the 8-quinolinolato ligand it is reasonable to assume intramolecular coordination of nitrogen to nickel to form a stable 5-membered chelate ring as observed in many such known complexes. As for the acetophenone oximato ligand we propose that it serves as an oxa-, aza-π-allylic ligand in the mononuclear (for Mw, see Table 1) complex **11**, whose IR and NMR data are consistent with the π-allylic coordinating mode of the acetophenone oximato ligand (*vide infra*). A THF solution of **14** shows only a minor electric conductivity indicating that the complex does not have an ionic structure. $NiMe(OC_6H_5)(PEt_3)_2$ **15** and NiEt-(Br)(bpy) **16** were also obtained by similar reactions as expressed by Eq. 1. However, isolation of analytically pure samples was not feasible due to instability in solutions (for **15**) or lack of a suitable solvent for recrystallization (for **16**).

In contrast to the reactions of phenols, reactions of alcohols with NiR_2L_2 do not give monoalkylnickel-(II) complexes but they lead to dehydrogenation of alcohols to yield aldehydes or ketones as shown in Table 2. The reaction most probably proceeds through abstraction of β-hydrogen by R group in an intermediate species formulated as $NiR(alkoxo)L_2$:

$$NiR_2L_2 + R^1R^2CHOH \xrightarrow{-RH} \left[L_2Ni\begin{matrix}OCHR^1R^2\\ R\end{matrix}\right] \underset{\mathbf{17}}{} \longrightarrow R^1R^2C{=}O + RH. \quad (2)$$

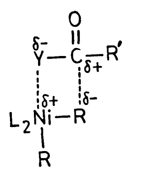
Among the reactions examined, treatment of **1c** with $i\text{-}C_3H_7OH$ (No. 4 in Table 2) gave quantitative yields of methane and acetone. The other reactions may follow the similar course but they were not pursued further.

Reactions of NiR_2L_2 with Organic Acyl Compounds R′COY: The monoalkylnickel(II) complexes, NiR-(Y)L_2, can be prepared also by reactions of NiR_2L_2 with organic acyl compounds with simultaneous formation of unsymmetrical ketone.

$$NiR_2L_2 + R'COY \longrightarrow NiR(Y)L_n + RCOR' \quad (3)$$

R′COY: phenyl carboxylate ($Y=OC_6H_5$)
carboxylic anhydride ($Y=OCOR'$)
acyl chloride ($Y=Cl$)

The results suggest a four-centered mechanism,

$NiR_2L_2 + R'COY \longrightarrow$ 

$\longrightarrow NiR(Y)L_2 + RCOR'$. (4)

TABLE 4. SPECTRAL DATA OF COMPLEXES **2**—**14**

Complex	IR[a)] $\tilde{\nu}$/cm^{-1}	Conditions	^{1}H-NMR δ/ppm[b)] Ni-R	Ni-Y	L	^{31}P{^{1}H}-NMR/ppm[c)]	Visible λ/nm
2	1585 1480 1295	d)	0.10(3H, s)	6.48(1H, t, 6 Hz, *p*-Ph) 6.9—7.6(6H, m, *o*, *m*-Ph + bpy)	7.7(4H, m) 8.5(2H, m)		508(THF)
3	2190 1500 1330	d)	0.06(3H, s)	7.2—7.6(6H, m) 7.8—8.0(4H, m) 8.2(2H, m)	} OC$_6$H$_4$CN + bpy		490(THF)
4	1585 1500 1335	d)	0.58(3H, t, 7 Hz, CH$_3$) 1.00(2H, q, 7 Hz, CH$_2$)	7.1—7.6(6H, m) 7.7—8.1(4H, m) 8.3(1H, m) 8.5(1H, m)	} OC$_6$H$_4$CN + bpy		503(THF)
5	1580 1480 1325	e)	−1.04(3H, t, 10 Hz)	7.0—7.8(9H, m)	1.04(qui, 7 Hz) 1.2(m) } 30H[i)]	32.3 s	
6	1495 1460 1320	e)	−0.46(3H, s)	6.63(1H, dd, 8 Hz and 5 Hz) 6.72(1H, d, 7 Hz) 7.15(1H, d, 7 Hz) 7.39(1H, t, 7 Hz) 7.60(1H, d, 8 Hz) 8.10(1H, d, 5 Hz)	0.9—1.7(15 H, m)	45.5 s	
		f)	−0.68(3H, s)	6.68(1H, d, 8 Hz) 6.96(1H, d, 8 Hz) 7.40(1H, t, 8 Hz) 7.60(1H, dd, 8 Hz and 5 Hz) 8.4(2H, m)	1.3(9H, m) 1.7(6H, m)		
7	2960 2930 1465	e)	−0.42(3H, t, 9 Hz)	7.1(3H, m, *m*, *p*-Ph) 8.18(2H, d, *o*-Ph)	1.00(18H, qui, 7 Hz) 1.50(12H, m)	44.4 s	
8	1560* 1435 1395			j)			
9	1610* 1360 760	d)	0.60(3H, t, 7 Hz, CH$_3$) 1.10(2H, q, 7 Hz, CH$_2$)	7.4—8.4(13H, Ph + bpy)			522(THF) 535 (Toluene)
10	1605* 1350 720	e)	−0.92(3H, s)	7.2(3H, m, *m*, *p*-Ph) 8.45(2H, m, *o*-Ph)	1.10(t, 6 Hz) 1.38(q, 6 Hz) } 30H[i)]	32.5 s	
		f)	−1.16(3H, t, 10 Hz)	7.42(3H, m, *m*, *p*-Ph) 7.90(2H, m, *o*-Ph)	1.22(qui, 7 Hz) 1.5(m) } 30H[i)]		
11	1030 965 750	g)	−1.04(1.2H, d, 6 Hz) 0.00(1.8H, d, 6 Hz)	2.2(1.2H, s, CH$_3$) 2.3(1.8H, s, CH$_3$)	0.8—2.0(15H, m)		
		h)	−0.6(3H, br)	2.26(3H, s, CH$_3$)	1.0—2.0(15H, m)		
12	k)	e)	−0.20(3H, d, 6 Hz)	1.68(3H, s, CH$_3$) 1.88(3H, s, CH$_3$) 5.37(1H, s, CH)	0.9—1.5(15H, m)		
13	1565* 1510 1390	e)	−0.10(3H, s)	1.89(3H, s, CH$_3$) 6.10(1H, s, CH) 7.2—7.9(5H, m, Ph)	1.1—1.3(15H, m)	46.3 s	
		f)	−0.69(1.5H, d, 6 Hz) −0.65(1.5H, d, 6 Hz)	1.88(1.5H, s, CH$_3$) 1.99(1.5H, s, CH$_3$) 6.24(0.5H, s, CH) 6.28(0.5H, s, CH) 7.5—8.0(5H, m, Ph)	1.0—1.8(15H, m)		
14	2840 1450 760	d)	0.60(3H, t, 7 Hz, CH$_3$) 1.10(2H, q, 7 Hz, CH$_2$)		7.48(2H, br) 7.90(4H, br) 8.48(1H, br) 9.10(1H, br)		533(THF) 555 (Toluene)

a) Strongest three peakes are given. The peak with * mark is assigned to ν(C=O). b) s=singlet, d=doublet, t=triplet, q=quartet, qui=quintet, m=multiplet, br=broad. c) From external H_3PO_4 (downfield positive). Measured at r.t. in C_6D_6. d) In CD_2Cl_2 at r.t. e) In C_6D_6 at r.t. f) In acetone-d_6 at −60 °C. g) In pyridine-d_5 at r.t. ^{1}H-NMR spectrum of **11** in acetone-d_6 at r.t. shows almost the same pattern as that in pyridine-d_5. h) In pyridine-d_5 at 86 °C. i) Two signals are overlapped with each other. j) Good spectrum was not obtained due to instability of the complex in solutions (see text). k) IR spectrum was not taken due to the low melting point and high sensitivity of **12** to air.

Preparation of the $NiR(Y)L_n$ type complex by the method expressed by Eq. 3 has no precedent.

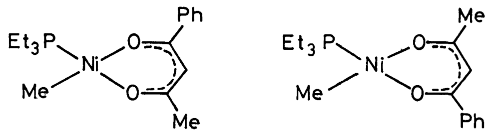
Characterization of the Complexes by Means of Spectroscopy. IR, NMR, and visible spectroscopic data are summarized in Table 4.

IR Spectra: All of the IR spectra of the complexes are consistent with the formulation of the complexes given in Table 1, showing bands due to R, Y, and L ligands. IR spectra of the bpy-coordinated compounds show δ(C–H) bands of bpy at 750—780 cm^{-1}, and those of the PEt_3-coordinated complexes do strong ν(C–H) bands of the PEt_3 ligand in a region of 2850—3000 cm^{-1}. IR spectra of the phenoxo type complexes **2**—**6** shows strong ν(C–O) at about 1300 cm^{-1} characteristic of transition metal phenoxides. ν(C≡N) bands of **3** and **4** are observed at about 2200 cm^{-1}.

The benzoato complexes **9** and **10** give rise to ν(C=O) bands in a region where the ν(C=O) bands of unidentate carboxylato complexes appear.[13] The ν(C=O) band of the propionato complex **8** appears at a somewhat lower frequency, suggesting the presence of some interaction between Ni and the carbonyl oxygen of the propionato ligand. The benzoylacetonato complex **13** shows ν(C=O) band at 1565 cm^{-1}, indicating the formation of an *O,O'*-bonded six-membered chelate ring.[13] The IR spectrum of the oximato complex shows no ν(O–H) band, excluding the possibility that the oxime bonds to nickel as a neutral base through nitrogen[14] or as a chelating ligand through *ortho*-metalated carbon of the aromatic ring and nitrogen.[15]

NMR Spectra: In ^{1}H-NMR spectra of the methylnickel complexes **2**, **3**, **5**—**7**, and **10**—**13** the CH_3 signals are observed at normal regions where CH_3 signals of methylnickel(II) complexes are expected.[1,11] Similarly to ^{1}H-NMR spectra of the monoethyl(amido)nickel complexes the ^{1}H-NMR spectra of **4**, **9**, and **14** show CH_2 signals of the ethyl ligand at lower field than CH_3 signals, indicating the electronegativity of nickel is increased through replacement of one of the Et ligands of **1b** by the electron-withdrawing Y ligand.[11]

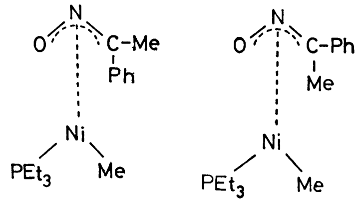
Coupling patterns of the Ni–CH_3 signals of $NiMe(Y)(PEt_3)_n$ also reflect the increase in the electronegativity of nickel through the replacement of one of the two Me ligands of **1c**, whose ^{1}H-NMR shows no coupling between ^{31}P of PEt_3 and ^{1}H of CH_3 even at −60 °C due to a rapid exchange reaction between the coordinated PEt_3 and free PEt_3 in solution partly liberated from **1c**. Similarly to the ^{1}H-NMR spectra of the complexes of the type $NiMe(amido)(PEt_3)_2$,[11] the ^{1}H-NMR spectra of **5**, **7**, **11**, and **12** at room temperature clearly show the coupling between ^{1}H of the CH_3 ligand and ^{31}P of the PEt_3 ligand, indicating that the Ni–PEt_3 bonding becomes stronger due to the increase in the electronegativity of Ni through the replacement of the Et ligand by the Y ligand. In contrast to the ^{1}H-NMR spectra of **5**, **7**, **11**, and **12**, the ^{1}H-NMR spectra of **6**, **10**, and **13** do not show the ^{1}H–^{31}P coupling at room temperature. In the case of **6** the weak bonding between Ni and PEt_3 is attributable to an increase in the basicity of Ni through the intramolecular coordination of N of the 8-quinolinolato ligand. The CPK molecular model shows steric repulsion between the OCOPh ligand and PEt_3 ligands in **10**, accounting for the rapid dissociation of PEt_3 from **10** on NMR time scale. In the case of the benzoylacetonato complex **13**, however, the molecular model shows no special steric repulsion between the Ph group of the bzac ligand and PEt_3, and therefore the difference in the dynamic behavior of the PEt_3 ligand between **12** and **13** at room temperature seems to be attributable to a difference in an electronic effect between the acac and bzac ligands. In cases of **10** and **13** the rapid exchange of the PEt_3 ligand is frozen on lowering the temperature to −60 °C where the NMR spectra show the ^{31}P–^{1}H coupling. The NMR spectrum of **13** at −60 °C reveals that **13** is composed of a 1:1 mixture of the following isomers



13a **13b**

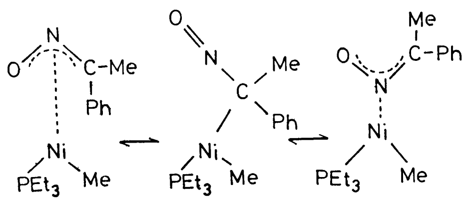
at the temperature. The exchange of the PEt_3 ligand in **6** is not frozen even at −60 °C.

The ^{1}H-NMR spectrum of **11** at room temperature shows two sets of signals with a peak area ratio of 1.2:1.8, suggesting that there exist the following two stereoisomers in the solution,[16] The fairly large dif-



Z-form *E*-form

ference in chemical shifts of the Ni–CH_3 signal between the two steroisomers may be due to a large difference in the anisotropic magnetic effect of the phenyl ring of the oxa, aza-π-allyl ligand. On raising temperature to 86 °C, the ^{1}H-NMR spectrum shows averaged somewhat broad signals, demonstrating occurrence of a rapid exchange reaction between the two stereoisomers. Such a dynamic exchange reaction is often observed for nickel π-allyl complexes[1,17] and the following exchange process involving formation of an 1-nitrosoalkylnickel intermediate is suggested for the present complex,



(5)

Z-form *E*-form

Visible Spectra: Similarly to visible spectra of NiR(imido)(bpy) type complexes,[11] those of **2**, **3**, **4**, **9**, and **14** show Ni→bpy CT bands at about 500 nm ($\varepsilon=3\times10^3$), which are shifted to shorter wavelength by about 150 nm from the position of Ni→bpy CT bands of $NiR_2(bpy)$,[18] demonstrating that the highest occupied level of Ni is lowered by the replacement of the R ligand by the Y ligand.

Chemical Properties. *Thermolysis, Acidolysis, and Degradation in Air*: Although complexes **2**—**14** have higher thermal stabilities than the original dialkylnickel complexes, their thermal stabilities are not so high as the $NiR(NR^1R^2)L_n$ type complexes[11] presumably due to lower stability of the Ni–Y bond than the Ni–NR^1R^2 bond against the thermolysis. The ethyl complex evolves a *ca.* 1:1 mixture of C_2H_4 and C_2H_6 on the thermolysis, and the methyl complex does a mixture of CH_4 and C_2H_6, the CH_4/C_2H_6 ratio varying from *ca.* 2.0 to 0.5 depending on the complex. Acidolysis of $NiR(Y)L_n$ by HCl gives RH and HY ($Y=OC_6H_5$, OCOR) with formation of $NiCl_2L_n$. The complexes with bpy have moderate stabilities to air in solid, whereas those with PEt_3 are very sensitive to air even in the solid state. All of the complexes are very sensitive to air in solutions. On exposure of an ethereal solution of **14** to air C_2H_4 (0.2 mol/Ni) was evolved exclusively as a gaseous product, suggesting β-hydrogen elimination promoted by oxygen.

Disproportionation: On standing a THF solution of **14** at room temperature the color gradually changes from purple to deep green with eventual formation of a light green precipitate of $NiCl_2(bpy)$, indicating that a disproportionation reaction proceeds in the solution,

$$\underset{\text{purple}}{2\,\mathrm{NiEt(Cl)(bpy)}} \longrightarrow \mathrm{NiCl_2(bpy)} + \underset{\text{deep green}}{\mathbf{1b}}. \qquad (6)$$

The disproportionation reaction is greatly accelerated by adding π-acids such as acrylonitrile and maleic anhydride, although in these cases the products are $NiCl_2(bpy)$, butane, ethane, ethylene, and $Ni(\pi\text{-acid})_n$-(bpy) ($n=1$ or 2), since **1b** once formed reacts with the π-acid to afford $Ni(\pi\text{-acid})_n(bpy)$ with evolution of a gas mainly composed of butane.[18] The carboxylato complexes **8** and **9** also undergo similar disproportionation reactions to give $Ni(carboxylato)_2(bpy)$ and **1b**. In the case of **8** formation of diethyl ketone (*ca.* 50%/Ni) takes place besides the disproportionation reaction, the result suggesting occurrence of a coupling reaction between the COR group in the OCOR ligand and the Et ligand.[19]

Reactions with Other Reagents: Complex **10** reacts with excess EtBr to afford PhCOOEt (0.73 mol/Ni). Acetylene is trimerized to benzene by **13** and aldehydes (CH_3CHO, C_2H_5CHO) are dimerized by **2** or **3**. A reaction between **14** and i-C_3H_7ONa affords acetone (0.72 mol/Ni) with evolution of C_2H_6. Acetone seems to be formed through a metathesis reaction between the two reactants to produce an intermediate ethyl(propoxo)nickel species **18** and β-hydrogen elimination from **18**.

$$\mathbf{14} + i\text{-}C_3H_7ONa \xrightarrow{-NaCl} \underset{\mathbf{18}}{\left[(bpy)Ni\begin{smallmatrix}C_2H_5\\ OC_3H_7\end{smallmatrix}\right]} \longrightarrow \text{acetone} + C_2H_6 \qquad (7)$$

Experimental

General, Materials, Analysis, and Spectroscopic Measurements. Reactions, analysis, and spectroscopic measurements were carried out as reported in the preceding paper.[11] Complexes **1a**—**1c** were prepared according to literature.[18,20]

Preparation of Complexes. *Phenoxo and Benzenethiolato Complexes 2—7 and 15 (cf. Table 1)*: THF (0.5 cm³) containing 53 mg (0.57 mmol) of phenol was added to 140 mg (0.57 mmol) of **1a** and the mixture was stirred for 24 h at room temperature to obtain a purple solution. Hexane (10 cm³) was added to the solution to obtain a purple solid, which was recrystallized from acetone to yield 160 mg (89%) of **2**. The other phenoxo and benzenethiolato complexes were prepared in similar ways under conditions shown in Table 1 (phenol:**1**=1:1). Solvents for recrystallization were actone for **3** and **4** and diethyl ether for **5**—**7**. A reaction between **1c** (150 mg, 0.47 mmol) and phenol (45 mg, 0.47 mmol) at room temperature in 1.4 cm³ of benzene afforded **15**, whose NMR shows a Ni-CH_3 signal at δ −1.08 (3H, t, 8.5 Hz) and PEt_3 signals around δ 1 ppm (30H, m). However, isolation of the complex failed.

Carboxylato Complexes 8—10: Propionic acid (0.062 cm³, 0.84 mmol) was added to a THF (10 cm³) solution of **1b** (230 mg, 0.84 mmol) at −78 °C. The mixture was warmed to room temperature and stirring the solution at the temperature for 20 min gave 0.75 mmol of C_2H_6 and a deep red solution, which was condensed to 2 cm³ to obtain a dark red solid of **8** (170 mg, 62%). Longer reaction time led to the disproportionation reaction (see text) and the complex obtained was not recrystallized due to the instabilities of **8** in solutions.

Toluene (5 cm³) containing 180 mg (1.5 mmol) of benzoic acid was added to a toluene (20 cm³) solution of **1b** (400 mg, 1.5 mmol) and the mixture was stirred at room temperature. The color of the solution instantly changed from deep green to purple. Hexane (10 cm³) was added to the solution immediately after changing of the color to obtain a purple solid (430 mg, 80%). The disproportionation of **9** is not so fast as that of **8** and a sample for analysis could be obtained by recrystallization from acetone. Complex **10** was prepared analogously and crystallized from ether.

Acetophenone Oximato Complex 11: Diethyl ether (5 cm³) was added to a mixture of **1c** (600 mg, 1.9 mmol) and acetophenone oxime (250 mg, 1.9 mmol) at −10 °C. Stirring the mixture for 10 min at room temperature led to formation of a yellow precipitate, which was recrystallized from THF to yield 450 mg (75%) of **11**.

β-Diketonato Complexes 12 and 13: Acetylacetone (0.042 cm³, 0.41 mmol) was added to an ethereal solution of **1c** (130 mg, 0.41 mmol) and the mixture was stirred at room temperature for 24 h to obtain a brown solution. Cooling the solution to −78 °C gave yellowish brown crystals of **12** (74 mg, 45%). Complex **13** was prepared analogously.

Chloro Complex 14: Diethyl ether (19 cm³) containing 3.4 mmol of dry HCl was added to a THF (20 cm³) solution of **1b** (940 mg, 3.4 mmol). Color of the solution changed instantly from deep green to dark purple and then excess hexane was added to the solution to yield a dark purple precipitate, which was recrystallized from THF–hexane to yield 350 mg (36%) of **14**.

Reactions of Dialkylnickel(II) Complexes with R′COY (cf. Table 3). Propionyl chloride (0.46 cm³, 5.3 mmol) was added to a THF (60 cm³) solution of **1b** (1.4 g, 5.2 mmol). The color of the solution instantly changed from deep green to dark purple. Addition of hexane (50 cm³) gave a yellow precipitate (1.0 g, 68%) whose IR spectrum was identical to that of **14**. GLC analysis of the solution revealed formation of 4.2 mmol (80%) of diethyl ketone. A similar reaction between **1b** (200 mg, 0.74 mmol) and acetyl bromide (0.059 cm^3, 0.74 mmol) in toluene (10 cm^3) gave a purple powder of **16** (220 mg, 90%) with formation of ethyl methyl ketone (76%). IR spectrum of the purple powder showed almost a similar absorption pattern to that of **14** and the analytical data (Found: C, 42.1; H, 3.0; N, 8.2; Br, 24.6%. Calcd for: C, 44.5; H, 4.0; N, 8.7; Br, 24.7%) roughly agreed with the composition of NiEt(Br)(bpy). The reaction of dialkylnickel(II) complexes with $CH_3COOC_6H_5$ and $(C_6H_5CO)_2O$ were carried out analogously.

Reactions of Dialkylnickel(II) Complexes with Alcohol (cf. Table 2). Benzyl alcohol (0.073 cm^3, 0.71 mmol) was added to an ethereal (1 cm^3) solution of **1c** (110 mg, 0.35 mmol). Although no apparent change was observed after stirring the mixture for 12 h, GLC analysis and measurement of the amount of gas evolved with a Toepler pump showed formation of 0.40 mmol of CH_4 and 0.28 mmol of benzaldehyde. The other reactions listed in Table 2 were carried out analogously.

Disproportionation Reaction. A mixture of acrylonitrile (1.0 cm^3) and THF (1.5 cm^3) was added to **14** (140 mg, 0.51 mmol) to obtain a deep reddish purple homogeneous solution. A light green solid started to precipitate after stirring the mixture for 40 min at room temperature. After 1.5 h GLC analysis of the gas phase indicated evolution of 0.11 mmol of C_2H_4 and 0.03 mmol of n-C_4H_{10}.[21] On adding 20 ml of THF to the reaction mixture, the solid precipitated (54 mg, 37%) was separated by filtration and characterized as $NiCl_2$(bpy) by its IR spectrum.[18] The filtrate was condensed to 2 ml and then 20 ml of hexane was added to obtain 26 mg (19%) of a precipitate whose IR spectrum coincides with that of Ni(acrylonitrile)(bpy).[18]

Benzene (4 cm^3) was added to 140 mg (0.44 mmol) of **8** and the mixture was stirred for 20 h at 70 °C. GLC analysis of the solution showed formation of 0.20 mmol of diethyl ketone. A light yellow solid precipitated was $Ni(OCOC_2H_5)_2$(bpy) as proved by its IR spectrum.

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