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Preparation and Properties of Monoalkylnickel(II) Complexes $NiR(NR^1R^2)L_2$ Having Imido, Imidazolato, or Methyl Phenylcarbamato-*N* Ligand

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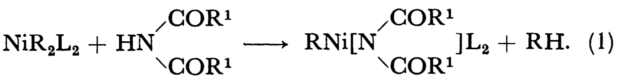
Reactions of dialkylnickel(II) complexes NiR_2L_2 **1** ($R=CH_3$, C_2H_5; $L=1/2$ bpy(2,2′-bipyridine), 1/2 dpe (1,2-bis(diphenylphosphino)ethane), PEt_3) with compounds having acidic N–H bonds (succinimide, phthalimide, diacetamide, pyromellitimide (1,2 : 4,5-benzenebis(dicarboximide)), imidazole) gave corresponding monoalkylnickel(II) complexes having Ni–N bond formulated as $NiR(NR^1R^2)L_2$. A reaction of $NiMe_2(PEt_3)_2$ with CH_3OH and phenyl isocyanate gives $NiMe(N(Ph)COOMe)(PEt_3)_2$. The IR, NMR, and visible spectroscopic studies of the complexes indicate that the electronegativity of Ni is enhanced by the replacement of one of the two R groups in **1** with the NR^1R^2 ligand. NMR spectra of complexes of a type $NiMe(NR^1R^2)(PEt_3)_2$ show that they have *trans*-configurations. Thermolyses of the monoalkylnickel(II) complexes start at temperatures higher by 80—100 °C than those of **1**, liberating RH, R–R, and olefin R(–H). Exposure of monoethylnickel(II) complexes to air releases ethylene as the main gaseous product. Reactions of the complexes of a type NiR(phthalimido)L_2 with R′X ($R'=C_6H_5$, $C_6H_5CH_2$) and C_6H_5COCl produce *N*-alkyl- or *N*-arylphthalimide and ketone C_6H_5COR, respectively.

Although a number of compounds having metal-nitrogen (M–N) covalent bonds have been prepared with various transition metals such as Ti, V, and Mo,[1,2] only a few reports[3–5] have appeared on the preparation of compounds having Ni–N covalent bonds. We previously reported in preliminary form the preparation and some chemical properties of monoalkylnickel(II) complexes with a succinimido or phthalimido ligand by reactions of dialkylnickel(II) complexes with the imides:[6]



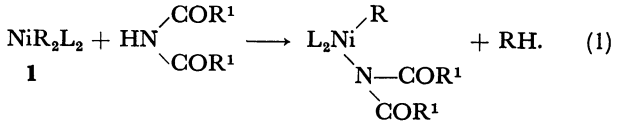
$$NiR_2L_2 + HN\begin{matrix}COR^1\\COR^1\end{matrix} \longrightarrow RNi[N\begin{matrix}COR^1\\COR^1\end{matrix}]L_2 + RH. \quad (1)$$

We have expanded the work by using other several active N–H compounds such as pyromellitimide (1,2 : 4,5-benzenebis(dicarboximide)) and imidazole to obtain the corresponding monoalkylnickel(II) complexes with the covalent Ni–N bond.

This paper deals with details of the preparation, characterization, spectroscopic data, and chemical properties of the monoalkylnickel(II) complexes with succinimido, phthalimido, or the other *N*-ligands. In connection with the preparation of the monoalkylnickel(II) complexes having the *N*-anionic ligands, we also report the preparation of a monoalkylnickel(II) complex with a methyl phenylcarbamato-*N* ligand by treating $NiMe_2(PEt_3)_2$ with CH_3OH and Ph-N=C=O.

Results and Discussion

Preparation of Complexes. Dialkylnickel(II) complexes, NiR_2L_2 ($R=CH_3$, C_2H_5; $L=1/2$ bpy (2,2′-bipyridine), PEt_3, 1/2 dpe (1,2-bis(diphenylphosphino)ethane)), react smoothly at room temperature with imides including succinimide ($pK_a=9.6$[7,8]), phthalimide ($pK_a=9.9$[8]), diacetamide, and pyromellitimide to give monoalkylnickel(II) complexes with covalent Ni–N bonds in medium to high yields (52—94%) with evolution of 1 mol of RH per NiR_2L_2:

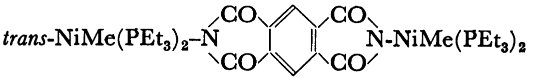


$$\underset{\mathbf{1}}{NiR_2L_2} + HN\begin{matrix}COR^1\\COR^1\end{matrix} \longrightarrow L_2Ni\begin{matrix}R\\N{-}COR^1\\COR^1\end{matrix} + RH. \quad (1)$$

2—11

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

NiMe(suc)(bpy) **2**
NiMe(pht)(bpy) **3**
NiEt(suc)(bpy) **4**
NiEt(pht)(bpy) **5**
trans-NiMe(suc)$(PEt_3)_2$ **6**
trans-NiMe(pht)$(PEt_3)_2$ **7**
NiMe(suc)(dpe) **8**
NiMe(pht)(dpe) **9**
trans-NiMe$[N(COCH_3)_2](PEt_3)_2$ **10**



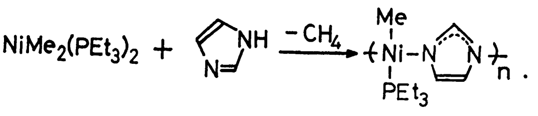
11

suc = Succinimido. pht = Phthalimido.
Me = Methyl. Et = Ethyl.

Addition of excess imides afforded the same products and further replacement of the R ligand in $NiR[N(COR^1)_2]L_2$ by the $-N(COR^1)_2$ ligand did not proceed. A reaction of **1c** with *N*-phenylbenzamide also led to liberation of 1 mol of CH_4 per **1c** with formation of a pale brown complex whose IR spectrum suggests the formation of a complex of a type $NiR(NR^1R^2)L_2$. However, isolation of the complex was not feasible.

The reaction expressed by Eq. 1 generally proceeds more rapidly with **1c** than with the other dialkylnickel(II) complexes with bidentate ligands (see Table 1). NMR spectroscopic studies of **1c** indicate that the PEt_3 ligand in **1c** rapidly exchanges with free PEt_3, partly liberated from **1c** into solution, presumably through a dissociative mechanism involving formation of a three coordinate intermediate. The formation of the three coordinate species in solution seems to account for the high reactivities of **1c** toward the imides.

Employment of compounds with less acidic N–H bonds such as benzimide (pK_a=13—14[8]), diphenylamine (pK_a=23[7]), and methyl phenylcarbamate did not lead to the formation of NiR(NR^{1}R^2)L$_2$, but addition of imidazole with a pK_a value of 14.5[8] leads to the formation of a polymeric monoalkylnickel(II) complex:



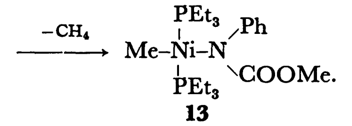
(2)

1c **12**

It is known that the N–H bond in imidazole ring has high reactivities toward metals such as Hg,[10] Cu,[3] and Ni[3] to form complexes of a type M(C$_3$H$_3$N$_2$)$_m$X$_n$, in spite of its weak acidity.

Although methyl phenylcarbamate did not react with NiR$_2$L$_2$ to give a complex with the –N(Ph)COOMe ligand, the complex with the –N(Ph)COOMe ligand can be prepared through a different reaction pathway:

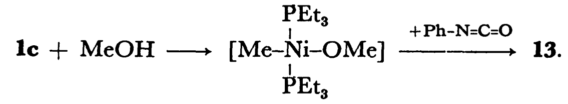
$\text{NiMe}_2(\text{PEt}_3)_2 + \text{MeOH} + \text{Ph–N=C=O}$
1c



$$\xrightarrow{-\text{CH}_4} \text{Me–}\overset{\text{PEt}_3}{\underset{\text{PEt}_3}{\text{Ni}}}\text{–N}\begin{matrix}\text{Ph}\\ \text{COOMe.}\end{matrix} \qquad (3)$$

13

The reaction most probably proceeds through insertion of phenyl isocyanate into a Ni–O bond in an intermediate species, NiMe(OCH$_3$)(PEt$_3$)$_2$:



$$\mathbf{1c} + \text{MeOH} \longrightarrow [\text{Me–}\overset{\text{PEt}_3}{\underset{\text{PEt}_3}{\text{Ni}}}\text{–OMe}] \xrightarrow{+\text{Ph–N=C=O}} \mathbf{13}. \qquad (4)$$

Several examples of insertion of isocyanates into metal-alkoxy bonds to form the M–N compounds are known.[11,12]

Table 1 shows preparative conditions, yields, melting points, and analytical data of the complexes **2**—**13**.

The bpy-coordinated complexes are reddish brown and PEt$_3$ or dpe-coordinated complexes are yellow or yellowish. The complexes with the bidentate neutral ligand (bpy, dpe) have moderate stabilities to air in solid, whereas those with the PEt$_3$ ligand are very sensitive to air even in the solid state. All of the complexes are very sensitive to air in solutions.

Characterization of the Complexes. IR, NMR, and visible spectroscopic data are summarized in Table 2.

IR Spectra: The ν(C=O) bands of succinimide (1700 cm^{-1}), phthalimide (1755 cm^{-1}), diacetamide (1965 cm^{-1}), and pyromellitimide (1700 cm^{-1}) are shifted to lower frequencies by 50—130 cm^{-1} on complex formation, and the shift is accounted for by asumming electron migration from Ni to the imido ligands. The magnitudes of the shifts are comparable to those observed with Pd,[13] Pt,[13] and Cu[14] imido complexes which have

TABLE 1. PREPARATIVE CONDITIONS, YIELDS, AND ANALYTICAL DATA OF COMPLEXES **2**—**13**

Complex[a]	Preparative conditions				Yield %	Color[b]	Mp[c] °C	Found (Calcd) (%)					
	NiR$_2$L$_2$ mmol	Temp °C	Solv. ml	Time h				C	H	N	R/Ni[d]	Imi/Ni[d]	Mw
NiMe (suc)(bpy) **2**	0.37	r.t.	THF (2)	24	89	r.b.	190 (dec)	55.4 (55.4)	4.5 (4.6)	12.8 (12.8)			
NiMe (pht)(bpy) **3**	2.1	r.t.	THF (4)	24	87	r.b.	230 (dec)	60.1 (60.7)	3.8 (4.0)	11.0 (11.2)	0.93	0.99	
NiEt (suc)(bpy) **4**	1.3	r.t.	THF (4)	24	79	r.b.	175 (dec)	56.2 (56.2)	4.8 (5.0)	12.2 (12.3)	0.94	0.92	
NiEt (pht)(bpy) **5**	0.97	r.t.	THF (4)	24	87	r.b.	190 (dec)	60.7 (61.6)	4.2 (4.4)	10.4 (10.8)			
trans-NiMe(suc)-(PEt$_3$)$_2$ **6**	3.3	r.t.	Ether (6)	0.5	94	y.b.	76—77	49.3 (50.0)	9.7 (9.1)	3.5 (3.4)			352 (408)
trans-NiMe(pht) (PEt$_3$)$_2$ **7**	0.37	r.t.	Ether (2)	0.5	82	y.	158 (dec)	55.5 (55.3)	8.5 (8.2)	3.0 (3.1)	0.93	0.99	
NiMe(suc)(dpe) **8**	1.1	r.t.	THF (4)	24	79	y.	220 (dec)	65.2 (65.3)	5.5 (5.5)	2.6 (2.5)			
NiMe(pht)(dpe) **9**	1.0	r.t.	THF (4)	24	74	y.	200 (dec)	68.9 (68.0)	5.0 (5.1)	2.3 (2.3)			
trans-NiMe[N-(COMe)$_2$](PEt$_3$)$_2$ **10**	1.8	r.t.	Ether (5)	0.5	52	y.	67—68	—[e]	—[e]	—[e]			
trans, *trans*-Ni$_2$Me$_2$-(PEt$_3$)$_4$[C$_6$H$_2$(CO)$_4$-N$_2$] **11**	2.3	r.t.	Ether (10)	3	80	Orange	195 (dec)	51.1 (51.8)	8.4 (8.2)	3.5 (3.4)			
[NiMe(NC$_3$H$_3$N)-(PEt$_3$)]$_n$**12**	0.71	r.t.	Ether (5)	0.2	97	y.	175 (dec)	46.4 (46.4)	8.3 (8.2)	10.2 (10.8)	0.95		
NiMe(N(Ph)-COOMe)(PEt$_3$)$_2$ **13**	1.0	0 °C	Ether (3)	18	55	y.		55.0 (54.8)	9.1 (9.0)	3.0 (3.0)			

a) suc=succinimido. pht=phthalimido. b) r.b.=reddish brown. y.b.=yellowish brown. y.=yellow. c) dec=decomposed. d) Moles of RH and imide per Ni liberated on acidolysis of the complex. e) Micro analysis of **10** was not feasible since it is very sensitive to air, thus **10** was identified by NMR spectroscopy.

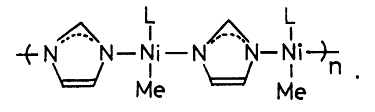
TABLE 2. SPECTRAL DATA OF COMPLEXES **2**—**13**

Complex	IR$^{a)}$ $\tilde{\nu}$/cm^{-1}	^{1}H-NMR δ/ppm$^{b)}$			^{31}P{^{1}H}-NMR$^{c)}$ δ/ppm	Visible λ/nm
		Ni–R	Ni–NR^{1}R^2	L		
2	1630* 1235 765	−0.08 (3H, s)	2.64 (4H, s)	7.4 (2H, m) 7.8—8.2 (5H, m) 8.36(1H, d, 6 Hz)		498 (THF) 479 (CH_2Cl_2)
3	1655* 1600 725	0.00 (3H, s)	7.2—8.4 (12H) (Overlapped to each other)			
4	1620* 1610* 1230	0.61(3H, t, 7 Hz, CH_3) 0.90(2H, q, 7 Hz, CH_2)	2.64(4H, s)	7.4 (2H, m) 7.9 (5H, m) 8.35 (1H, d, 6 Hz)		512 (THF) 530 (Toluene) 495 (CH_2Cl_2)
5	1620* 1350 1230	0.63(3H, t, 6 Hz, CH_3) 0.96(2H, q, 6 Hz, CH_2)	7.2—8.4 (12H) (Overlapped to each other)			492 (CH_2Cl_2)
6	1650* 1300 725	−0.74(3H, t, 10 Hz, CH_3)	2.24(4H, s)	0.9—1.5(30H, m)		
7	1620* 1340 1220	−0.30 (3H, t, 10 Hz, CH_3)	7.04 (2H, m) 7.73 (2H, m)	0.8—1.6(30H, m)	36.1	
8	1610* 1350 1240	−0.03 (3H, dd, 7 Hz and 5 Hz)	2.17 (4H, s)	2.12(4H, d, 17 Hz, CH_2) 7.5 (12H, *m,p*-CH_5) 7.8 (8H, m)		
9	1650* 1375 1305	0.06 (3H, dd, 7 Hz and 5 Hz)	7.2—8.2 (24H) (Overlapped to each other)	2.14 (4H, d, 17 Hz, CH_2)		
10	1640* 1600* 1305	−0.78 (3H, s)	2.57 (6H, s)	0.8—1.1 (30H, m)		
		−1.06 (3H, t, 10 Hz)$^{d)}$	2.42 (6H, s)	1.0—1.6 (30H, m)$^{d)}$		
11	1645* 1380 1295	−0.88 (3H, t, 10 Hz)	7.50 (1H, s)	e)		
12	1080 1035 740	Not measurable due to poor solubilities in solvents.				
13	1650* 1330 760	−0.88 (3H, t, 9 Hz)	3.80 (3H, s, CH_3) 6.98 (1H, t, 8 Hz, *p*-C_6H_5) 7.43 (2H, t, 8 Hz, *m*-C_6H_5) 9.12 (2H, d, 8 Hz, *o*-C_6H_5)	0.92 (qui, 7 Hz) 1.24 (m) 30H	31.3	

a) Strongest three peaks are given. The absorption peaks with an asterisk are assigned to ν(C=O). b) Measured at r.t. s=singlet, d=doublet, t=triplet, q=quartet, qui=quintet. Solvent: CD_2Cl_2 for **2**, **3**, **4**, **5**, **8**, and **9**; C_6D_6 for **6**, **7**, **10**, and **13**; THF-d_8 for **11**. c) From external H_3PO_4 (downfield positive). d) In acetone-d_6 at −60 °C. e) Signals of the PEt_3 ligand are overlapped with signals of impurities of THF-d_8.

covalent M–N bonds. The covalency of the Ni–N bonds in **2**—**9** is supported by negligible electric conductivities (Λ=0.17−0.80 S cm^2) of CH_2Cl_2 solutions of the complexes. The possibility that one of the two N–H bonds in pyromellitimide remains intact is excluded not only on the basis of the analytical data given in Table 1 but also by the absence of ν(N–H) bands in the IR spectrum.

The IR spectrum of **12** resembles those of polymeric Hg(II)[10] and Tl(III)[15] complexes with the imidazolato ligand, showing bands characteristic of the imidazole ring at 1480 and 1080 cm^{-1} and no band associated with an NH group. The insolubility of **12** in common organic solvents suggests a polymeric structure which has been proposed for the Hg(II) and Tl(III) complexes:



Coordination of only one PEt_3 ligand to Ni in **12** is consistent with the polymeric structure.

The IR spectrum of **13** shows a similar pattern to that of methyl phenylcarbamate except for the N–H region, showing ν(C=O) and ν(C–O) bands at 1650 and 1330 cm^{-1}, respectively, and no ν(N–H) band. The IR data together with NMR data given in Table 1 support the formation of **13**.

NMR Spectra: Patterns of ^{1}H-NMR spectra of complexes **2**—**11** and **13** are consistent with the formulation of the complexes as given in Table 1. The CH_3 signals of **2**, **3**, **6**—**11**, and **13** appear at normal positions where $\mathrm{CH_3}$ signals of methylnickel(II) complexes appear.[4,16,17] ^{1}H-NMR spectra of **4** and **5** show $\mathrm{CH_2}$ signals of the ethyl ligand at lower field than $\mathrm{CH_3}$ signals, in contrast to the NMR spectrum of $\mathrm{NiEt_2(bpy)}$ **1b** which shows the $\mathrm{CH_2}$ signal (δ 0.8 ppm) at higher field than the $\mathrm{CH_3}$ signal (δ 1.1 ppm).[17] Since it is known[18] that the chemical shift difference between the $\mathrm{CH_2}$ and $\mathrm{CH_3}$ signals ($\Delta = \delta_{\mathrm{CH_2}} - \delta_{\mathrm{CH_3}}$) increases linearly with the increase in the electronegativity of the atom to which the ethyl group is attached, the appearance of the $\mathrm{CH_2}$ signal at the lower magnetic field can be taken as an indication of an increase in electronegativity of nickel through replacement of the Et ligand of **1b** by the electron-withdrawing imido ligand.

As described above the $\mathrm{PEt_3}$ ligand of $\mathrm{NiMe_2(PEt_3)_2}$ **1c** rapidly exchanges at room temperature with free $\mathrm{PEt_3}$ in solutions partly liberated from **1c** and therefore the ^{31}P–^{1}H coupling is not observable for the Ni–$\mathrm{CH_3}$ signal of **1c**, whereas the Ni–$\mathrm{CH_3}$ signals of **6**, **7**, **11**, and **13** clearly show the ^{31}P–^{1}H coupling, indicating that the $\mathrm{PEt_3}$ ligand in the complexes is bonded to Ni on NMR time scale. The difference in the dynamic behavior between **1c** and complexes of the type $\mathrm{NiR(NR^1R^2)(PEt_3)_2}$ is accounted for by the increase in the electronegativity of nickel through the replacement of the Me ligand by the $\mathrm{NR^1R^2}$ ligand, since electron-donating ligands such as $\mathrm{PEt_3}$ are expected to bond to the central atom more strongly when the electronegativity of the central atom increases. Triplet patterns of the Ni–$\mathrm{CH_3}$ signals in the $\mathrm{NiR(NR^1R^2)L_2}$-type complexes indicate not only that the complexes have a trans configuration but also that the complexes have monomeric structures, since if the complexes have multi-nuclear structures, the coupling patterns will become more complex. For **6** the monomeric structure has been established by cryoscopic measurement of the molecular weight (Table 1).

The methylene protons of the succinimido ligand in *cis*-complexes **2**, **4**, and **8** appear as a sharp singlet, indicating that the four hydrogens in the succinimido ligand are magnetically equivalent either due to rapid rotation of the imido ligand around the Ni–N bond or due to accidental coincidence of chemical shifts. The $\mathrm{CH_2}$-signal of **4** appears as a sharp singlet even at −30 °C.

Each of ^{31}P{^{1}H}-NMR spectra of **7** and **13** shows only one sharp signal and this also supports that the two $\mathrm{PEt_3}$ ligands bonds tightly to Ni occupying the trans position to each other.

Visible Spectra: Solutions of the monoalkylnickel(II) complexes with the bpy ligand have very strong ($\varepsilon \fallingdotseq 3\times10^3$) adsorption bands at about 500 nm, which are assignable to Ni→bpy CT-bands. The dialkyl complexes **1a** and **1b**, show the Ni→bpy CT-bands of lowest transition energy at about 650 nm. The blue shift of the CT-band from 650 nm to 500 nm on the replacement of the Et ligand by the imido ligand is associated with the lowering of the highest occupied level of Ni due to the electron-withdrawing imido ligand.[21]

Chemical Properties. Thermolysis, Acidolysis, and Degradation in Air: Complexes $\mathrm{NiR(NR^1R^2)L_2}$ have remarkably high thermal stabilities as shown in Table 1. Their thermolyses start at temperatures by 80—100 °C higher than those of the starting dialkylnickel(II) complexes $\mathrm{NiR_2L_2}$.[17a,19,20] For example, **3** begins to decompose at 230 °C, the temperature being one of the highest decomposition temperatures among dialkyl- and monoalkylnickel(II) complexes reported to date.[4] Even if the alkyl group has β-hydrogens as in **4** and **5**, the complexes is thermally stable up to 175 and 190 °C, respectively.

In cases of Ni–bpy complexes the starting dimethyl- and diethylnickel(II) complexes decomposes mainly through unimolecular reductive elimination process,[21]

$$\mathrm{NiR_2(bpy)} \longrightarrow \mathrm{R\text{-}R}. \qquad \mathrm{R = Me,\ Et} \tag{5}$$

The marked enhancement of the thermal stability by the replacement of one of the ethyl ligands by the imido ligand may be attributed to the lack of the low energy intramolecular reductive elimination pathway with NiR(imido)(bpy). Thermolyses of **2** and **3** give $\mathrm{C_2H_6}$ as the main product (Table 3), suggesting a bimolecular process in the thermolyses. Thermolyses of **4** and **5** afford disproportionation products, $\mathrm{C_2H_4}$ and $\mathrm{C_2H_6}$, which are considered to be formed through a β-elimination process,

$$\begin{tikzcd} \mathrm{NiEt(imido)(bpy)} \arrow[r] & \underset{[\mathbf{14}]}{[\mathrm{NiH(imido)(bpy)}]} \arrow[d, "+\ \mathrm{NiEt(imido)(bpy)}"] & + \mathrm{C_2H_4}. \quad (6) \\ & \mathrm{C_2H_6} & \end{tikzcd}$$

Mechanisms involving coupling between metal hydrides and metal alkyls have been proposed for thermolyses of a few transition alkylmetals.[22] Evolution of $\mathrm{CH_4}$ and $\mathrm{C_2H_4}$ as main products together with some ethane (Table 3) in the thermolysis of a mixture of **2** and **4** (*ca.* 1 : 1) supports the β-elimination mechanism shown above and suggests further that the hydride intermediate [**14**] reacts with the methyl **2** and the ethyl complex **4** to form methane and ethane. In thermolysis of com-

$$\begin{tikzcd} & \mathrm{CH_4} \\ {[\mathbf{14}]} \arrow[ur, "\mathbf{2}"] \arrow[dr, "\mathbf{4}"'] & & (7) \\ & \mathrm{C_2H_6} \end{tikzcd}$$

Table 3. Products of thermolysis of NiR(imido)(bpy)[a)]

Complex	Gaseous products (mol/Ni) $\mathrm{CH_4}$	$\mathrm{C_2H_6}$	$\mathrm{C_2H_4}$	ΣR/Ni[b)]
R=Methyl				
2	0.19	0.35	—	0.89
3	0.09	0.39	Trace	0.87
R=Ethyl				
4	—	0.40	0.53	0.93
5	—	0.24	0.36	0.60
2 (0.16 mmol) + **4** (0.19 mmol)	0.11 mmol	0.07 mmol	0.14 mmol	

a) At 220—230 °C, in solid in a vacuum. b) $\Sigma\mathrm{R} = \mathrm{CH_4} + 2(\mathrm{C_2H_6} + \mathrm{C_2H_4})$ for methyl complexes, $= \mathrm{C_2H_6} + \mathrm{C_2H_4}$ for ethyl complexes.

TABLE 4. PRODUCTS OF THE REACTIONS OF $NiR(imido)L_2$ WITH ORGANIC HALIDES ($R'X$ AND $R'COX$)$^{a)}$

No	Complex	Organic halide	Temp °C	Time h	Products (%-yield/Ni)		
					R'-Imide	R-R'	Others
1	**3**	$C_6H_5CH_2Br^{b)}$	100	1	83	74	
2	**4**	$C_6H_5CH_2Br^{b)}$	50—60	6	51	51	C_2H_4 (6)
3	**6**	$C_6H_5CH_2Br^{b)}$	30	0.8	29	66	Bibenzyl (26)
4	**7**	$C_6H_5Br^{b)}$	120	1	95	30	
					RCOR'		
6	**7**	$C_6H_5COCl^{c)}$	r.t.	12	71		

a) 0.2—0.4 mmol of the complex was used. b) In *N*,*N*-dimethylacetamide (1 ml). c) In THF (0.5 ml).

plexes containing the PEt_3 ligand, the amount of C_2H_4 evolved sometimes exceeded 1 mol/Ni. The evolution of excess C_2H_4 seems to be due to thermal degradation of the PEt_3 ligand on Ni. Evolution of more than 1 mol of C_2H_4 per Ni was observed also in the thermolysis of complexes with the dpe ligand.

As described above complexes **2**—**13** do not react with excess HNR^1R^2, although a complex having a composition of $Ni(phthalimido)_2(bpy)$ is known.[5] The poor reactivities of the monoalkylnickel complexes seem to be attributable to decrease in nucleophilicity of nickel or the Ni-bound alkyl group by bonding of the electron-withdrawing NR^1R^2 ligand. Treatment of the monoalkylnickel(II) complexes with stronger acids such as CH_3COOH, HCl, and H_2SO_4, however, leads to acidolysis of the Ni–R bond to liberate RH quantitatively (Table 1). Imides are also released from complexes of a type $NiR(imido)L_2$ on the acidolysis by dry HCl.

Complexes **2**—**13** are decomposed on exposure to air as described above. In cases of the ethylnickel complexes, **4** and **5**, they generate C_2H_4 as the main gaseous product on exposure to dry air,

$$\text{e.g., } \mathbf{4}(\text{solid}) + \text{dry air} \longrightarrow C_2H_4(40\%/\text{Ni}) + C_2H_6(\text{trace}). \quad (8)$$

The fact suggests that β-hydrogen elimination process is promoted by interaction of the complex with dioxygen or by direct interaction of β-hydrogens with oxygen. IR spectrum of the residue shows strong ν(O–H) absorption band, implying the presence of an Ni–OH or Ni–OOH bond in the residual substance.

Reactions with Organic Halides: Reactions of complexes $NiR(imido)L_2$ with alkyl or aryl halides R'X give *N*-alkyl or -aryl imides with formation of alkanes R–R' (Table 4). Relative reactivities of Ni–N and Ni–R bonds toward R'X varies with the complex and R'X employed. For example, the Ni–CH_3 bond in **6** reacts smoothly with $C_6H_5CH_2Br$ to liberate ethylbenzene in a 66% yield, whereas only 29% of the imido ligand is alkylated. An opposite trend is observed for the reaction of **7** with C_6H_5Br, whereas both the Ni–C and Ni–N bonds in **3** are reactive toward $C_6H_5CH_2Br$. Occurrence of the reaction of **7** with C_6H_5Br to liberate *N*-phenyl phthalimide stands in contrast to the known poor reactivity of potassium phthalimide against aryl halides in Gabriel synthesis of amines, and the reaction may be applied to prepare arylamines from phthalimide and aryl halides. A reaction of **7** with C_6H_5COCl affords ketone $CH_3COC_6H_5$ in 71% yield, accompanied by decarbonylation from C_6H_5COCl to afford benzene and biphenyl. A similar reaction of **9** also affords the same ketone with a lower yield (18%/Ni).

Reactions of NiR(imido)(bpy) with dihalomethanes afford RCH_2CH_2R, RCH_2R, RCH_3, and olefin R(–H)=CH_2 (*e.g.*, propylene from ethyl complexes) besides normal degradation products (R–R, RH, and R(–H)).[23] The formation of the unusual products can be accounted for by assuming insertion of CH_2 carbene formed from CH_2X_2 into the Ni–R bonds.

Reactions with Unsaturated Compounds: Complexes of the type $NiR(imido)L_2$ (**2**, **4**, **7**, **8**) initiate polymerization of acrylonitrile to yield polyacrylonitrile in high yields (>70%). Attempts to yield a copolymer from butadiene and acrylonitrile were not successful and only homopolymers of acrylonitrile were obtained. Methyl methacrylate is polymerized by **4** to give syndiotactic poly(methyl methacrylate) (Bovey's σ value[24]=0.17) in a 35% yield. Vinyl monomers with less electron-withdrawing substituents such as styrene and vinyl acetate were not polymerized by NiR(imido)L_2. The trend is similar to the polymerization of vinyl monomers initiated by isolated transition metal alkyls and hydrides.[25] Acetylene was trimerized by **7** to benzene and propionaldehyde was dimerized to EtCH=CMeCHO by **2**.

Experimental

General and Materials. All reactions were carried out under nitrogen or argon or in vacuum by using Schlenk type tubes. Complexes **1a**—**1d** were prepared according to literature.[17,19,21] The compounds with N–H bonds were used as purchased from Tokyo Kasei Co. Ltd. Solvents were dried over Na wires or CaH_2, distilled under N_2, and stored under an atmosphere of N_2.

Analyses and Spectroscopic Measurements. Microanalysis of C, H, and N was performed by Mr. T. Saito in our laboratory with a Yanagimoto CHN Autocorder Type MT-2. The melting point was measured in a sealed glass capillary. Amounts of gases evolved during reactions or thremolysis were measured with a Toepler pump and analyzed by GLC using a Shimadzu GC-3BT gas chromatograph. Identification and quantitative analysis of organic compounds were carried out by NMR spectroscopy and GLC.

IR and NMR spectra were recorded on a Hitachi Model 295 infrared spectrophotometer and a JEOL JNM-PS-100 spectrometer, respectively. Visible spectra were obtained by using a Hitachi Model 200-20 spectrophotometer. Electric conductivities of the CH_2Cl_2 solutions of complexes were measured by a Toa Model CM-5B conduct meter.

Preparation of Complexes. *NiMe(suc)(bpy)* **2** *and NiMe(pht)(bpy)* **3**: THF (2 cm^3) was added to a mixture of **1a** (91 mg, 0.37 mmol) and succinimide (38 mg, 0.38 mmol). Stirring the solution for 1 d at room temperature gave a reddish brown precipitate, which was recrystallized from CH_2Cl_2–hexane to give 109 mg (89%) of **2**. Evolution of CH_4 (0.94 mol/Ni) was observed during the reaction.

A similar reaction of **1a** (500 mg, 2.1 mmol) with phthalimide (300 mg, 2.1 mmol) in THF (4 cm^3) and recrystallization from CH_2Cl_2–hexane yielded 670 mg (87%) of **3**.

NiEt(suc)(bpy) **4** *and Other Complexes with suc or pht Ligand* **5**–**9**: THF (4 cm^3) was added to a mixture of **1b** (350 mg, 1.3 mmol) and succinimide (130 mg, 1.3 mmol). Stirring the solution at room temperature for 1 d gave a reddish brown precipitate with evolution of C_2H_6 (0.92 mol/Ni). The reddish brown precipitate was recrystallized from CH_2Cl_2–hexane to yield 344 mg (79%) of **4**.

The other complexes were prepared in similar manners under conditions listed in Table 1. Solvents for recrystallization were diethyl ether for **6** and **7** and a mixture of CH_2Cl_2 and hexane for **5**, **8**, and **9**.

trans-*NiMe(diacetamido)(PEt$_3$)$_2$* **10**: Diethyl ether (5 cm^3) was added to a mixture of **1c** (580 mg, 1.8 mmol)and diacetamide (180 mg, 1.8 mmol) at −10 °C. On warming the solution to room temperature, a smooth reaction occurred with vigorous evolution of CH_4. A red solution was obtained after 30 min and cooling the solution to Dry Ice temperature gave 520 mg of yellow crystals. Recrystallization from diethyl ether gave 270 mg (52%) of **10**.

trans, trans-*Ni$_2$Me$_2$(pyromellitimido)(PEt$_3$)$_2$* **11**: Diethyl ether (10 cm^3) was added to a mixture of **1c** (740 mg, 2.3 mmol) and pyromellitic diimide (240 mg, 1.2 mmol) at −20 °C and then the mixture was warmed to room temperature. Stirring the mixture for 3 h at room temperature afforded a yellow precipitate, which was collected by filtration and recrystallized from THF to yield 760 mg (80%) of **11**.

[NiMe(imidozolato)(PEt$_3$)]$_n$ **12**: Diethyl ether (5 cm^3) was added to a mixture of **1c** (230 mg, 0.71 mmol) and imidazole (49 mg, 0.72 mmol). Stirring the solution at room temperature caused precipitation of a yellow solid with evolution of CH_4. The precipitate was washed thoroughly with diethyl ether, THF, and toluene to yield 170 mg (93%) of **12**. The complex was insoluble in diethyl ether, benzene, toluene, THF, ethyl alcohol, acetone, and *N*,*N*-dimethylformamide.

*NiMe(methyl phenylcarbamato-*N*)(PEt$_3$)$_2$* **13**: A diethyl ether (3 cm^3) solution of **1c** (330 mg, 1.0 mmol) was solidified by cooling to −196 °C and then phenyl isocyanate (0.11 cm^3, 1.0 mmol) and methyl alcohol (0.041 cm^3, 1.0 mmol) were added by microsyringe at −196 °C. The mixture was warmed to 0 °C and the solution was stirred for 18 h at the temperature to give a homogeneous yellow solution. Evolution of CH_4 (0.86 mmol) during the reaction was observed. Cooling the yellow solution to −78 °C afforded yellow crystals, which were separated by filtration and recrystallized from diethyl ether to yield 260 mg (55%) of **13**.

Thermolysis, Acidolysis, and Degradation in Air. A Schlenk type tube containing 44 mg (0.13 mmol) of **2** was connected to a vacuum line and evacuated. The tube was immersed in an oil bath and the temperature of the oil bath was raised to 210 °C. After 2 h, evolution of 0.025 mmol (0.19/Ni) of CH_4 and 0.048 mmol (0.35/Ni) of C_2H_6 was observed. Thermolyses of other complexes were carried out in similar manners.

A Schlenk type tube containing a diethyl ether (0.5 cm^3) solution of **3** (30 mg, 0.080 mmol) was connected to a vacuum line and evacuated. Dry HCl (excess) was introduced to the vessel and the mixture was stirred for 1 d at room temperature to obtained 0.074 mmol of CH_4 and 0.080 mmol of phthalimide. Acidolyses of other complexes were carried similarly.

A Schlenk type tube (25 cm^3) containing **4** (120 mg, 0.35 mmol) was evacuated, and then dry air (1 atm) was introduced. After 11 h a brown powder (120 mg) was obtained with evolution of 0.14 mmol of C_2H_4. IR spectrum of the brown powder showed strong ν(O–H) and ν(C=O) bands at 3400 and 1590 cm^{-1}, respectively. Elemental analysis of the brown powder roughly agrees with a composition of Ni(OOH)–(succinimido)(bpy) (Found: C, 46.7; H, 3.9; N, 11.2%. Calcd: C, 48.6; H, 3.8; N, 12.1%). A reaction of **4** with dry air in diethyl ether and those of **5** in solid and in solution afforded similar results.

Reactions with Organic Halides. Benzyl bromide (0.063 cm^3, 0.53 mmol) was added to a *N*,*N*-dimethylacetamide solution of **3** (79 mg, 0.21 mmol). Stirring the solution at 100 °C for 1 h gave a green precipitate with formation of *N*-benzylphthalimide (0.17 mmol, 83%/Ni). Reactions of the Ni–phthalimido complexes with benzyl bromide or bromobenzene were carried out similarly under conditions listed in Table 4.

Benzoyl chloride (0.059 cm^3. 0.51 mmol) was added to a THF (0.5 cm^3) solution of **7** (46 mg, 0.10 mmol). Stirring the solution for 12 h at room temperature produced 0.071 mmol of acetophenone, 0.031 mmol of benzene, and 0.008 mmol of of biphenyl.

Reactions with Unsaturated Compounds. Acrylonitrile (3.3 g) was added to a vessel containing **2** (33 mg) by trap-to-trap distillation in a vacuum. Almost all of acrylonitrile was polymerized on standing the mixture for 40 min at room temperature. After 2 h the polymer was dissolved in *N*,*N*-dimethylformamide and precipitated by pouring the solution into HCl–methyl alcohol to yield 2.5 g (74%) of polyacrylonitrile. Other polymerizations were carried out similarly.

Acetylene (500 cm^3, 1 atm) was introduced into a vessel containing a THF (1 cm^3) solution of **7** (24 mg, 0.052 mmol). Stirring the solution for 30 min at room temperature gave a black precipitate. After 2 d formation of benzene (0.72 mmol) was observed.

Propionaldehyde (3.0 g, 51 mmol) was added to a vessel containing **2** (76 mg, 0.23 mmol). Stirring the solution for 12 h at room temperature gave a viscous pale green solution, in which 0.65 g (6.6 mmol) of $EtCH{=}C(CH_3)CHO$ was contained as determined by GLC.

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