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Reactions of Dialkylnickel(II) Complexes NiR_2L_2 with Alkyl (or Aryl) Halides, R′COY (Y=Cl, Br, OPh, OCOPh), and CS_2

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Reactions of $Ni(CH_3)_2(bpy)$ (**1**), $Ni(C_2H_5)_2(bpy)$ (**2**) (bpy=2,2′-bipyridine), *trans*-$Ni(CH_3)_2$(triethylphosphine)$_2$ (**3**), $Ni(CH_3)_2$(1,2-bis(diphenylphosphino)ethane) (**4**), and $Ni(CH_3)_2$(1,3-bis(diphenylphosphino)propane) (**5**) with alkyl or aryl halides, R′COY (Y=Cl, Br, OC_6H_5, $OCOC_6H_5$), and CS_2 have been investigated. The reactions of NiR_2L_2 with alkyl or aryl halides are classified into three types of reactions by their reaction products: Type A: $NiR_2L_2+R'X \rightarrow NiX(R')L_2+R\text{-}R$, Type B: $NiR_2L_2+R'X \rightarrow$ alkane (RH)+olefin (R′(−H)), and Type C: $NiR_2L_2+R'X \rightarrow NiR(X)L_2+R\text{-}R'$. Complexes **1** and **2** undergo mainly Type A reaction. Complex **3** gives Type A reaction product on treatment with C_6H_5Br, but it gives Type B reaction product on treatment with C_2H_5Br. On the other hand, **4** undergoes Type C reaction on interaction with C_6H_5Cl. The reactions with R′COY (Y=Cl, Br, OPh, OCOPh) are classified into two types of reactions by their reaction products: Type D: $NiR_2L_2+R'COY \rightarrow NiY(R)L_2+RCOR'$ and Type E: $NiR_2L_2+R'COY \rightarrow NiY(R')L_2+RCOR$. Complexes **1**—**3** undergo mainly Type D reaction, whereas complexes **4** and **5** mainly Type E reaction. The difference in the reaction route is discussed on the basis of presence or absence of vacant coordination site for attack by R′COY. The reaction of **4** with CS_2 affords $Ni(CS_2)$(1,2-bis(diphenylphosphino)ethane) with evolution of a reductive elimination product, ethane, whereas the reaction of **3** with CS_2 gives a 1:1 adduct of **3** and CS_2.

Although chemistry of organonickel complexes has been developed in the past two decades,[1] examples of isolated dialkylnickel(II) complexes[2—7] are still limited and chemical reactivities of the dialkylnickel complexes have been poorly understood in comparison with the chemical reactivities of much more stable dialkylplatinum(II) complexes. Our research group has been dealing with the dialkylnickel(II) complexes and has reported isolation and chemical reactivities of the dialkylnickel(II) complexes.[2,7—9] As an extension of the study on the dialkylnickel(II) complexes, we have examined chemical reactivities of the following dialkylnickel(II) complexes, NiR_2L_2, with organic halides and their analogues (R′X and R′COY) and CS_2. We now report the results of the reactions.

$NiMe_2(bpy)$ (**1**), $NiEt_2(bpy)$ (**2**), *trans*-$NiMe_2(PEt_3)_2$ (**3**), $NiMe_2(dpe)$ (**4**), $NiMe_2(dpp)$ (**5**). $Me=CH_3$, $Et=C_2H_5$. bpy=2,2′-Bipyridine. PEt_3=triethylphosphine. dpe=1,2-Bis(diphenylphosphino)ethane. dpp=1,3-Bis(diphenylphosphino)propane.

To clarify the process of the reaction of NiR_2L_2 with R′X is particularly important, since it often induces C–C coupling between R and R or R and R′ which is considered to be a crucial elemental step of Ni-catalyzed C–C coupling reactions between metal alkyls (*e.g.*, RMgX) and organic halides.[10]

Results and Discussion

Reactions with R′X. Table 1 shows results of the reactions of complexes **1**—**4** with R′X. It includes results of a previously reported reaction of **2** with C_6H_5Cl.[11] The reactions listed in Table 1 can be classified into the following three types of reactions according to their products,

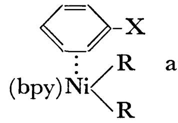
Type A: Formation of the reductive elimination product, R–R, and $NiX(R')L_2$.
$NiR_2L_2+R'X \rightarrow NiX(R')L_2+R\text{-}R$.
Type B: Hydrogen migration from R′ to R to release alkane, RH, and olefin, R′(−H).
$NiR_2L_2+R'X \rightarrow RH+R'(-H)$.
Type C: Cross coupling of R and R′ to form R–R′ and $NiR(X)L_2$.
$NiR_2L_2+R'X \rightarrow NiR(X)L_2+R\text{-}R'$.

Each type of reaction is discussed below.

Type A: The reaction of **1**, a homologue of **2**, with 2-chlorotoluene leads to the evolution of the reductive elimination product, ethane, which is accompanied by formation of NiCl(2-tolyl)(bpy), similarly to the reaction of **2** with chlorobenzene.[11] The results indicate that the Ni–R bonds in $NiR_2(bpy)$ is activated by interaction with haloarene to induce the reductive elimination of R–R,

$$NiR_2(bpy) + \text{chloroarene} \longrightarrow NiCl(aryl)(bpy) + R\text{-}R. \quad (1)$$

Since it is known that electron transfer from Ni in $NiR_2(bpy)$ to an electron accepting ligand causes activation or weakening of the Ni–R bonds,[2d,12] we assume that the elimination of R–R is promoted by the electron transfer from nickel to the coordinating chloroarene in reaction intermediates such as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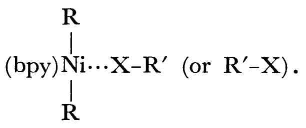
and


6′

$$(bpy)\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R}{|}}{Ni}}\cdots X\text{-}R' \text{ (or } R'\text{-}X).$$

In the intermediate **6**, the haloarene coordinates with nickel through the aromatic ring and an electron migration from Ni to π^* orbital(s) of chloroarene is assumed. On the other hand, in the intermediate **6′**, chloroarene (R′X) approaches to Ni through the electron-withdrawing halogen atom or positively charged R′ carbon bonded to X. When the reductive elimination takes place, the reaction is considered to be followed by a rapid oxidative addition of chloroarene

TABLE 1. REACTIONS OF NiR_2L_2 WITH R′X

No.	NiR_2L_2	R′X[a]	Temp °C	Time h	Product(%-yield/NiR_2L_2)						
					Complex	Gaseous product[b]					
						RH	R(-H)	R-R	R-R′	R′H	R′(-H)
1	**1**	2-Chlorotoluene	50	3	NiCl(2-tolyl)(bpy) (73)	sm	—	84	—	—	—
2	**2**	PhCl	r.t.	2	NiCl(Ph)(bpy)(0.5 PhCl) (60)[e]			Major[e]			
3	**2**	$(CH_3)_3CCl$	r.t.	72	$NiCl_2(bpy)$ (70)	2	1	64	0	4	50
4	**2**	$\{CH_2\text{-}CH(Cl)\}_n$	r.t.	1	$\{CH_2\text{-}CH(NiCl(bpy))\}_n$	sm	sm	70	—	—	—
5	**3**	PhBr	r.t.	24	$NiBr(Ph)(PEt_3)_2$ (36)	9	0	35	17	0	—
6	**3**	PrBr	r.t.	12	$NiBr_2(PEt_3)_2$ (71)	115	0	46	sm	35	127
7[c]	**3**	EtBr	r.t.	24	$NiBr_2(PEt_3)_2$ (66)	(53)	(98)	(117)		(53)	(98)
8	**4**	PhCl	r.t.	120	NiCl(Me)(dpe) (*ca.* 55)[f]	11	sm	14	50	0	—
9[d]	**4**	EtBr	35	48	$NiBr_2$(dpe) (48)	78	0	(70)	10	(70)	33

a) R′X=Excess. Ph=Phenyl. Pr=Propyl. b) sm=Small. c) In this reaction, R equals R′. Therefore total yields of RH and R′H, R(-H) and R′(-H), and R-R R-R′ are given in parentheses. d) In this case, both R-R and R′H represents ethane, whose amount is given in the parentheses. e) Data from Ref. 11. f) Based on weight of a solid recovered after the reaction and $^{31}P\{^1H\}$-NMR data of the solid (see Experimental).

TABLE 2. REACTIONS OF NiR_2L_2 WITH ACYL HALIDES AND ITS ANALOGUES

No.	NiR_2L_2	R′COX (R′COX/Ni)	Temp °C	Time h	Product(%-yield/NiR_2L_2)				
					Ni-complex	Ketone			Others[a]
						RCOR′	RCOR	RCOR′/RCOR	
1	**1**	C_6H_5COCl (3)	r.t.	24	b)	74	11	6.7	C_1(13), C_2(13)
2[c]	**2**	CH_3COCl (1)	r.t.	0.2	$NiCl(Et)L_2$ (47)	96	0	Large	
3[c]	**2**	CH_3COBr (1)	r.t.	0.2	$NiBr(Et)L_2$ (35)	76	0	Large	C_1(2), C_2(13), C_2'(9)
4	**2**	C_6H_5COCl (3)	r.t.	24	b)	70	0	Large	C_2'(4), C_4(23), C_6(15)
5	**2**	$(C_6H_5CO)_2O$ (3)	r.t.	24	$NiEt(OCOPh)L_2$, d)	36	0	Large	R′COR′(6), C_2(30), C_4(10)
6	**3**	C_2H_5COCl (2)	r.t.	24	$NiCl_2L_2$ (40)	66	sm	Large	R′COR′(6), C_1, d)
7	**3**	C_6H_5COCl (3)	0—15	24	b)	54	sm	Large	R′COR′(2), C_1(28), C_2(53), Toluene(2), C_6(8)
8[c]	**3**	$(C_6H_5CO)_2O$ (1)	r.t.	24	$NiMe(OCOPh)L_2$ (66)	70	0	Large	C_1(41)
9[e]	**3**	$C_6H_5COOC_6H_5$ (2)	r.t.	120	b)	21	12	1.75	C_1(14), C_2(39), Toluene(2), Ph-Ph(16)
10[e]	**4**	C_6H_5COCl (1)	r.t.	24	$NiCl(Ph)L_2$ (83)	sm	51	*ca.* 0	C_1(28), C_2(2)
11	**4**	C_2H_5COCl (2.6)	r.t.	24	$NiCl_2L_2$ (88)	0	21	0	C_1(51), C_2(8), C_2'(15)
12	**4**	$(C_6H_5CO)_2O$ (3)	r.t.	24	b)	1	34	0.03	PhCOPh(1), C_1(43), Ph-Ph(4)
13	**5**	C_6H_5COCl (3)	r.t.	24	b)	0	26	0	C_1(9), C_2(41)
14	**5**	$(C_6H_5CO)_2O$ (3)	r.t.	24	b)	0	46	0	C_1(40), C_2(5)

a) $C_1=CH_4$. $C_2=C_2H_6$. $C_2'=C_2H_4$. $C_4=C_4H_{10}$. $C_6=C_6H_6$. $Ph=C_6H_5$. b) Isolation of complexes was not feasible. c) Reported previously.[8b] d) Formation of the complex was confirmed by IR or GLC, but its yield was not measured. e) Reactions were carried out twice, and average of the yields is given.

to Ni^0 species.

An alternative reaction mechanism involving oxidative addition of chloroarene to $NiR_2(bpy)$ to form a quadrivalent $Ni(R)_2(aryl)(Cl)(bpy)$ species and elimination of R–R from the intermediate is also conceivable. However, this mechanism is less plausible as judged from selective formation of R–R and no liberation of the cross coupling product, R–aryl, although formation of such a four valent nickel species as a reaction intermediate is assumed as for the Types B and C reactions (*vide infra*).

The reaction of **1** with 2-chlorotoluene requires a somewhat higher temperature than for a similar reaction of **2**,[11)] reflecting stronger Ni–R bonds in **1** than in **2**.[2d)]

When an alkyl halide, *t*-butyl chloride, was employed in the reaction with **2**, the reaction also led to liberation of R–R, butane, with formation of a reddish brown complex, which may be assignable to NiCl(*t*-butyl)(bpy). Attempts to isolate this complex failed due to its instabilities, and prolonged reaction caused formation of light green $NiCl_2(bpy)$ (proved by IR) and evolution of isobutene and a small amount of isobutane which are considered to be formed through the thermal decomposition of the *t*-butyl–Ni complex. When poly(vinyl chloride) is employed in the reaction with **2**, the chloro(alkyl)nickel complex produced, $\{CH_2\text{-}CH(NiCl(bpy))\}_n$ (see experimental), has some stabilities and can be used for further reaction with CO to afford an acylnickel group pending in poly(vinyl chloride),

$$\mathbf{2} + \{CH_2\text{-}CHCl\}_n \longrightarrow \{CH_2\text{-}CH(NiCl(bpy))\}_n + R\text{-}R \qquad (2)$$

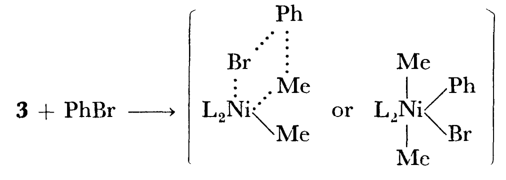
$$\{CH_2\text{-}CH(NiCl(bpy))\}_n + CO \longrightarrow \{CH_2\text{-}CH(CONiCl(bpy))\}_n. \qquad (3)$$

In the case of the activation of the Ni–Et bonds in **2** by the alkyl halides, formation of the intermediate complex of type **6** is not possible and the reaction is considered to proceed through formation of the intermediate of type **6′**.

Similar reductive elimination of R–R in the PEt_3-coordinated dimethylnickel complex **3** is also induced by the interaction with an haloarene, bromobenzene. The reductive elimination is again accompanied by the formation of an oxidative addition product, *trans*-

$$\mathbf{3} + PhBr \xrightarrow[\text{2) oxidative addition}]{\text{1) reductive elimination}} Me\text{-}Me + NiBr(Ph)(PEt_3)_2 \qquad (4)$$

$NiBr(Ph)(PEt_3)_2$, which was prepared by Morrell and Kochi[13)] through a different reaction pathway. The formation of a small amount of toluene in the reaction of **3** with PhBr suggests that the following cross coupling reaction (Type C reaction) partially occurs,



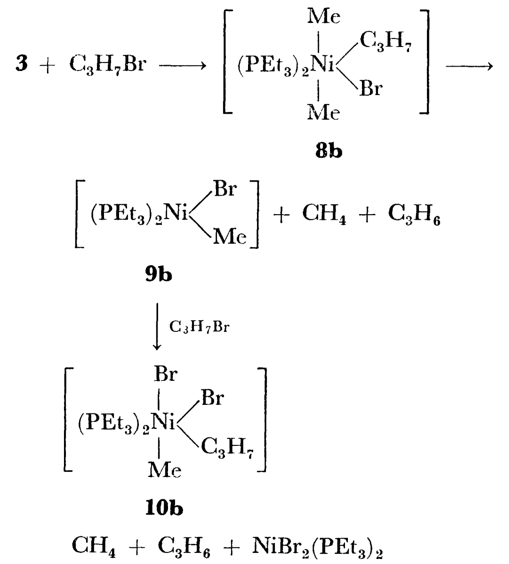
7a **8a**

$$\longrightarrow (NiBr(Me)(PEt_3)_2) + CH_3C_6H_5. \qquad (5)$$

9a

In the above reaction, formation of a bromo(methyl)-nickel complex **9a** is assumed. However, detection of **9a** was not feasible.

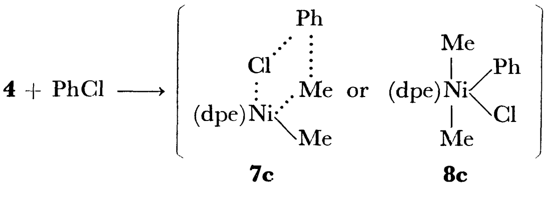
Type B: When propyl bromide is employed in the reaction with **3**, a similar inductive effect of the alkyl bromide on the reductive elimination of R–R, ethane, was observed. However, in this case, methane and propylene became the major gaseous products, suggesting that occurrence of hydrogen migration from the propyl group to the methyl group on a Ni^{IV} species formed by oxidative addition of propyl bromide to **3**.



Scheme 1.

The formation of C_3H_8 in this reaction indicates that certain hydrogen abstraction reaction by the C_3H_7 group in the intermediate species takes place. Although the number of isolated Ni^{IV} complexes is not large,[14)]var ious Pt^{IV} complexes including alkylplatinum(IV) complexes are known[15)] and the results of the reaction of **3** with propyl bromide is most straightforwardly explained by assuming the Ni^{IV} intermediate as shown in Scheme 1. The agreement of the amount of CH_4 evolved with that of C_3H_6 supports the mechanism shown above.

Type C: In the case of the reaction of **4** with PhCl, a cross coupling reaction such as expressed by Eq. 5 constitutes the main reaction route, and a complex of type **9**, NiCl(Me)(dpe) (**9c**), is formed as the main nickel product.



7c **8c**

$$\longrightarrow NiCl(Me)(dpe) + CH_3C_6H_5 \qquad (6)$$

The partial formation of ethane and NiPh(Cl)(dpe) (proved by acidolysis) indicates that the reductive elimination of Me–Me in **8c** or the reductive elimination induced by PhCl as discussed for the reactions of **1** and **2** with aryl halides also takes place (see Experimental),

$$\mathbf{4} + \mathrm{PhCl} \xrightarrow{\text{minor route}} [\mathbf{6}, \mathbf{6'}, \text{ or } \mathbf{8c}] \longrightarrow \mathrm{Me\text{-}Me} + \mathrm{NiCl(Ph)(dpe)}. \qquad (7)$$

In contrast to the reaction of **4** with PhCl, that with an alkyl halide, ethyl bromide (No. 9), affords the cross coupling product, propane, in only a small yield, and the reaction causes evolution of other gaseous products which are produced through the Type A (ethane) and Type B (methane and ethylene) reaction routes.

The results shown above indicate that subtle differences in the structures of the dialkylnickel complex and R'X cause a considerable change in the reaction route. It may be noted that the intermediate formed in the reaction of a diphosphine-coordinated dialkylnickel complex with alkyl halide having β-hydrogen has a trend to undergo the hydrogen shift reaction (or β-elimination reaction) from R' to R, and this may be related to the fact that the C–C coupling catalyzed by nickel–phosphine complexes does not give good results when alkyl halides are used as the reactants.[10)]

Reactions with R'COY. Table 2 shows results of the reactions of the dialkylnickel(II) complexes with acyl halides and their analogues, R'COY. It includes some previously reported results[8b)] of the reactions of $\mathrm{NiR_2L_2}$ with R'COY. The reaction listed in Table 2 can be classified into the following two types of reactions according to the product distribution:

Type D: Formation of asymmetric ketone, RCOR', and $\mathrm{NiX(R)L_2}$.

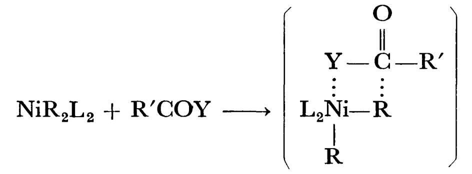
$$\mathrm{NiR_2L_2 + R'COY \rightarrow NiY(R)L_2 + RCOR'}$$

Type E: Formation of symmetric ketone RCOR, accompanied by formation of $\mathrm{NiX(R')L_2}$.

$$\mathrm{NiR_2L_2 + R'COY \rightarrow NiY(R')L_2 + RCOR.}$$

Each type of the reaction is discussed below.

Type D: Complexes **1**—**3** undergo Type D reaction on treatment with R'COY or its analog (Nos. 1—9 in Table 2). The formation of these products is explained by assuming the following four-center mechanism.



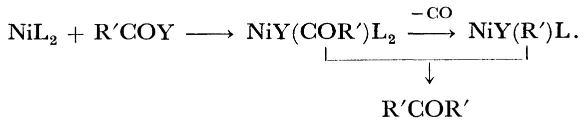
11

$$\longrightarrow \mathrm{NiY(R)L_2 + RCOR'} \qquad (8)$$

Scheme 2.

The isolation of NiY(Et)(bpy) in Nos. 2 and 3 indicates that NiY(Et)(bpy) is less reactive toward R'COY than **2**. The isolation of $\mathrm{NiMe(OCOPh)(PEt_3)_2}$ in No. 8 also indicates the isolated complex is not reactive toward $\mathrm{(C_6H_5CO)_2O}$. When an excess of $\mathrm{C_2H_5COCl}$ is added, complex **3** is transformed to *trans*-$\mathrm{NiCl_2(PEt_3)_2}$, suggesting that $\mathrm{NiCl(Me)(PEt_3)_2}$ initially formed reacts further with $\mathrm{C_2H_5COCl}$.

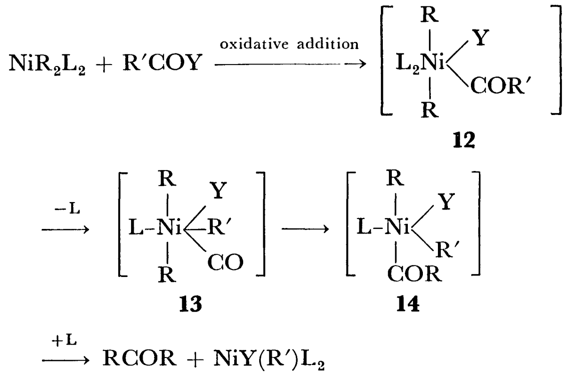
In most cases, the formation of RCOR' and $\mathrm{NiY(R)L_2}$ is accompanied by evolution of alkanes (RH and R–R) and alkene (ethylene from **2**), indicating that activation of the Ni–R bond on interaction with R'COY takes place. The formation of RCOR in Nos. 1 and 9 suggests that Type E reaction occurs partly. R'COR' obtained in Nos. 5—7 seems to be formed through oxidative addition of R'COY to Ni^0 complex(es) which is formed in the reaction system, *e.g.*,



$$\mathrm{NiL_2 + R'COY \longrightarrow NiY(COR')L_2 \xrightarrow{-CO} NiY(R')L} \qquad \downarrow \ \mathrm{R'COR'}$$

Type E: The diphosphine-coordinated dialkylnickel(II) complexes, **4** and **5**, undergo Type E reaction to afford RCOR. In the case of the reaction of **4** with PhCOCl (No. 10), the complex of the type $\mathrm{NiY(R')L_2}$ is isolable. $\mathrm{NiCl_2(dpe)}$ obtained in No. 11 is considered to be formed by a reaction of initially formed NiCl(Et)(dpe) with $\mathrm{C_2H_5COCl}$.

The formation of RCOR clearly indicates migration of CO from R'COCl to $\mathrm{NiR_2L_2}$. As for the process to produce RCOR, we consider the following two mechanisms.

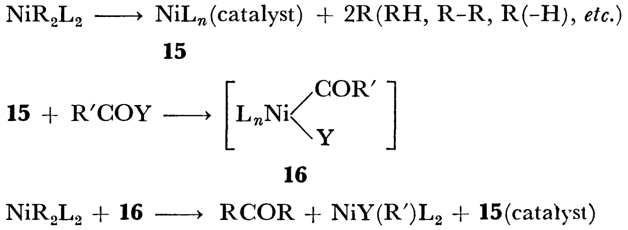


12

13 **14**

$$\xrightarrow{+L} \mathrm{RCOR + NiY(R')L_2}$$

Scheme 3.



$$\mathrm{NiR_2L_2 \longrightarrow NiL_{\mathit{n}}(catalyst) + 2R(RH, R\text{-}R, R(\text{-}H), \mathit{etc.})}$$

15

$$\mathbf{15} + \mathrm{R'COY} \longrightarrow \left[\mathrm{L_{\mathit{n}}Ni}\begin{matrix}\mathrm{COR'}\\ \mathrm{Y}\end{matrix}\right]$$

16

$$\mathrm{NiR_2L_2} + \mathbf{16} \longrightarrow \mathrm{RCOR + NiY(R')L_2} + \mathbf{15}\mathrm{(catalyst)}$$

Scheme 4.

Scheme 3 involves oxidative addition of R'COX to $\mathrm{NiR_2L_2}$ to form a Ni$^{\mathrm{IV}}$ species **12**, decarbonylation from the R'CO– ligand in **12**, insertion of the CO ligand into the Ni–R bond, and reductive elimination of RCOR from the four-valent nickel intermediate. Ruddick and Shaw showed that pyrolysis of $\mathrm{PtCl(Me)_2(COMe)(PMe_2Ph)_2}$ gave acetone and *trans*-$\mathrm{PtCl(Me)(PMe_2Ph)_2}$ as the sole products.[16a)]

In Scheme 4, we assume initial formation of Ni^0 complex, $\mathrm{NiL_{\mathit{n}}}$, by thermal decomposition of $\mathrm{NiR_2L_2}$. The Ni^0 species thus formed is assumed to react with

R′COY to give the oxidative addition product **16**, which further reacts with NiR_2L_2 to yield RCOR with resumption of NiL_n, which thus serves as a catalyst to carry the decarbonylative CO transfer agent. Oxidative addition of RCOX to Ni^0 complexes is well known,[17)] and we previously reported[18)] formation of RCOR and the $NiY(R')L_2$ type complex by reactions of an acylnickel(II) complex, *trans*-Ni(COMe)(phthalimido)$(PEt_3)_2$ (Y=phthalimido), with $NiR_2(bpy)$ (R=Me, Et).

$$\mathrm{Ni(COMe)Y(PEt_3)_2 + NiR_2(bpy)} \longrightarrow \mathrm{RCOR + NiMeY(PEt_3)_2}$$
$$\mathrm{Y = phthalimido}$$

At the moment, we have no strong evidence to prove or disprove the mechanisms. However, the decarbonylation reaction from the coordinatively saturated **12** to **13** seems to require partial or full dissociation of the bidentate diphosphine ligand. Therefore, if we take into account the previously observed fact[9)] that the diphosphine ligands have much higher coordinating abilities toward nickel complexes than PEt_3 and bpy, the present observation that Type E reaction does not proceed with the dialkylnickel(II) complexes having the weakly coordinating PEt_3 or bpy ligand but with the complexes having the strongly coordinating dpe or dpp ligand seems not compatible with the mechanism shown in Scheme 3. Moreover, if the reaction proceeds by Scheme 3, the reaction would give RCOR′ besides RCOR.

If we assume Schemes 2 and 4, the variation of the products depending on the nature of the dialkylnickel(II) may be explained by the presence or absence of an open coordination site in the dialkylnickel complexes for interaction with R′COY to form the active intermediate **11**. Complexes **1** and **2** having the flat bpy ligand possess an open vacant site for R′COX at their apical positions as can be seen on the CPK molecular model, and **3** has a trend to liberate the PEt_3 ligand as shown by variable temperature NMR spectroscopy[7)] which shows a rapid exchange between the coordinating PEt_3 ligand and free PEt_3 in solutions even at low temperatures (*e.g.*, −60 °C). Under these circumstances, R′COY has an access to coordinate to Ni in **1**—**3**, and thus can undergo Type D reaction. On the other hand, the bulky and strongly coordinating diphosphine ligands in **4** and **5** block the coordination site in the nickel dialkyls. Therefore, the production of the unsymmetrical ketone RCOR′ in the reactions of **4** and **5** with R′COY is hindered, and complexes **4** and **5** take a different reaction course as shown in Scheme 4.

Reaction with CS_2. The reductive elimination of R–R from **4** is induced by interaction with CS_2, and the Ni(0) complex thus formed takes up one molecular of CS_2 per the nickel complex,

$$\mathbf{4} + \mathrm{CS_2} \longrightarrow \underset{69\%}{\mathrm{Me\text{-}Me}} + \underset{\mathbf{17}(84\%)}{\mathrm{Ni(CS_2)(dpe)}}. \tag{9}$$

Baird and Wilkinson reported formation of a similar CS_2 adduct of $Ni(PPh_3)_2$ by a reaction of $Ni(PPh_3)_4$ with CS_2.[19)] An absorption band at 1190 cm^{-1} in an IR spectrum (KBr) of **17** is comparable with reported ν(C=S) vibrations of $Ni(CS_2)(PPh_3)_2$ (1196, 1117 cm^{-1} in CS_2),[19)] $Pd(CS_2)(PPh_3)_2$ (1193 cm^{-1} in CS_2),[19)] and $Pd(CS_2)$(dpe) (1178, 1167, 1152 cm^{-1}).[20)] The CS_2 in **17** is strongly coordinated with Ni, and it is not replaced even by CO at 1 atm. The reaction of **3** with CS_2, on the contrary, does not lead to the reductive elimination of R–R, but it gives a 1:1 adduct of **3** and CS_2 as shown by elemental analysis of the adduct. IR spectrum of the adduct shows new bands at 1430, 1270, and 605 cm^{-1}, suggesting a different mode of the coordination of CS_2 to Ni from that in **17**.

Experimental

Manipulation, Material, and Analysis. Manipulation of complexes and reactions were carried out under atmosphere of N_2 or Ar or under vacuum. Complexes **1**—**5** were prepared according to literature.[2,7)] Solvents were dried over Na, distilled under N_2, and stored under N_2. Microanalysis of C, H, N, and S was performed by Mr. T. Saito of our research laboratory. The amount of gas produced was measured with a Toepler pump and the gas collected was analyzed by GLC using a Shimadzu GC-3BT gas chromatograph. IR and NMR spectra were recorded on a Hitachi Model 295 infrared spectrometer and a JEOL JNM-PS-100 spectrometer, respectively.

Reaction with R′X (cf. Table 1). *No. 1*: 2-Chlorotoluene (3 cm^3) was added to a tube containing 360 mg (1.5 mmol) of deep green **1** at −78 °C. After the tube was evacuated, the mixture was warmed to 50 °C and stirred for 3 h at the temperature. Evolution of 1.23 mmol of C_2H_6 (84% per **1**) and a small amount of CH_4 was observed. The reddish brown precipitate formed was filtered off and crystallized from acetone (yield=250 mg, 73%). The reddish brown complex was characterized as NiCl(2-tolyl)(bpy) by comparing its IR spectrum with that of an authentic sample prepared according to literature.[11b)]

No. 3: $(CH_3)_3CCl$ (3 cm^3) was added by trap-to-trap distillation to a tube containing 176 mg (0.64 mmol) of deep green **2** by using a vacuum line. When the green solution was stirred at room temperature, a smooth reaction proceeded to give a brown solution and a precipitate. At this point, evolution of butane was checked by GLC. Further stirring of the reaction mixture at room temperature for 3 d gave a greenish gray precipitate. Analysis of the gas phase showed evolution of gases shown in Table 1. The gaseous and liquid materials in the reaction system was removed by evaporation under vacuum and the gray precipitate was identified as $NiCl_2$ (bpy) from its IR spectrum.[2d)]

No. 4:[21)] When **2** (230 mg, 0.86 mmol) was added into a THF solution (20 cm^3) of poly(vinyl chloride) (M.W.=103000, 1.0 g, 16 mmol), the deep green homogeneous solution initially obtained rapidly changed to a deep red color with evolution of butane (0.60 mmol). The nickelated poly(vinyl chloride) was recovered by adding hexane, washed with hexane repeatedly, and dried under vacuum. The visible spectrum of the nickelated poly(vinyl chloride) showed a strong band assignable to a CT band at 535 nm ($\varepsilon = 2\times 10^3$), the λ_{max} and ε values being the same as that of a low molecular weight analogue of the polymer–nickel adduct, NiEt(Cl)(bpy)[8b)] ($\lambda_{max} = 533$ nm, $\varepsilon = 2\times 10^3$). The reaction of the nickelated poly(vinyl chloride) with carbon monoxide was carried out as follows. Carbon monoxide (atmospheric pressure) was introduced into a vessel containing a THF solution of the nickelated poly(vinyl chloride). After stirring the solution for 20 min, the polymer was recovered by adding hexane to the THF solution and dried under vacuum. The infrared spectrum of the product of the reaction with carbon monoxide showed a ν(C=O) band at 1640 cm^{-1}. The infrared spectrum of a low molecular weight analogue of $\{CH_2\text{-}CH(CONiCl(bpy))\}_n$, Ni(COEt)Cl(bpy),[18] shows the ν(C=O) band at 1660 cm^{-1}. The carbonylated complex, $\{CH_2\text{-}CH(CONiCl(bpy))\}_n$ reacts with methanol to give a $\{CH_2\text{-}CHCOOCH_3\}_n$ monomer unit introduced into poly (vinyl chloride) as proved by IR (ν(C=O)=1730 cm^{-1}). This also supports the formation of $\{CH_2\text{-}CH(CONiCl(bpy))\}_n$.

No. 5: Bromobenzene (82×10^{-3} cm^3, 0.78 mmol) was added into a diethyl ether (2 cm^3) solution of **3** (120 mg, 0.36 mmol) at −50 °C. After evacuation of the reaction vessel, the reaction mixture was stirred at room temperature for 1 d. GLC analysis showed formation of gaseous and liquid products shown in Table 1. A yellow precipitate obtained by adding hexane to the reaction mixture was collected by filtration and dried under vacuum to yield 57 mg (36%) of a yellow solid, which was characterized as *trans*-NiBr(Ph)(PEt$_3$)$_2$ by comparing its IR and NMR spectra with those of an authentic sample prepared according to literature.[13]

No. 6: Propyl bromide (0.10 cm^3, 1.1 mmol) was added into a toluene (1 cm^3) solution of **3** (120 mg, 0.37 mmol). The reaction mixture was stirred at room temperature for 12 h. GLC analysis showed the formation of the gaseous and liquid products shown in Table 1. After removing toluene under vacuum, the complex formed was crystallized from a mixture of diethyl ether and hexane to yield reddish purple crystals (120 mg, 0.26 mmol, 71%), which were characterized as *trans*-NiBr$_2$(PEt$_3$)$_2$ from its IR spectrum and elemental analysis. The reactions of **3** and **4** with EtBr (Nos. 7 and 9) were carried out analogously.

No. 8: A mixture of **4** (380 mg, 0.79 mmol) and chlorobenzene (6 cm^3) was stirred at room temperature for 5 d. Analysis of the gaseous and liquid products by GLC showed evolution of 0.90 mmol of CH$_4$, 0.11 mmol of C$_2$H$_6$, and 0.39 mmol of toluene. Addition of hexane to the reaction mixture gave a brownish yellow precipitate. The precipitate was dissolved in THF and a yellow solid (260 mg) was recovered by addition of hexane to the THF solution. ^{1}H and ^{31}P {^{1}H}-NMR spectra showed that it contained NiMe(Cl)dpe as a chief component and NiCl$_2$(dpe) and NiPh(Cl)-dpe (*cf.* No. 10 in Table 2, *vide infra*) as minor. The ratios between these three complexes were determined as 79:7:14 from the area ratios of their peaks in ^{31}P {^{1}H}-NMR spectrum. Attempts to separate these compounds have not been successful. Acidolysis of 46 mg of this yellow solid gave 0.08 mmol of CH$_4$ and 0.01 mmol of C$_6$H$_6$ in accord with its ^{31}P {^{1}H}-NMR data. An authentic sample of NiMe(Cl)-dpe was prepared separately from a 1:1 reaction of **4** with HCl according to the procedure shown below.

To a THF (25 cm^3) solution of **4** (500 mg, 1.0 mmol), a THF (5 cm^3) solution of dry HCl (0.95 mmol) was added dropwise at −50 °C. After stirring for 30 min at this temperature, the solvent was reduced to 10 cm^3 by evaporation. The yellow solid thus obtained was filtered, washed with hexane, and dried under vacuum. Recrystallization from THF-diethyl ether (1:1) gave orange yellow crystals of NiMe(Cl)dpe (160 mg). Found: C, 64.2; H, 5.3; Cl, 7.5%. Calcd for C$_{27}$H$_{27}$ClNiP$_2$: C, 63.9; H, 5.4; Cl, 7.0%. ^{1}H-NMR(*N,N*-dimethylformamide-d$_7$): δ=0.1 (3H, multiplet, CH$_3$-Ni), 1.9—2.8 (4H, multiplet, CH$_2$-P), and 7.3—8.1 (20H, multiplet, C$_6$H$_5$-P). ^{31}P {^{1}H}-NMR(CH$_2$Cl$_2$): 67.7 (d, J_{P-P}=8 Hz) and 43.7 (d, J=8 Hz) ppm from external PPh$_3$.

Reaction with R′COY (cf. Table 2). *No. 1*: When a mixture of **1** (110 mg, 0.42 mmol) and PhCOCl (0.16 cm^3, 1.4 mmol) in THF (1.5 cm^3) was stirred at room temperature, the color of the solution changed instantly from deep green to purple. The color of the solution, then, turned to brown gradually with formation of a brown precipitate. The GLC analysis after 1 d showed formation of ketones and other products shown in Table 2. Reactions Nos. 2 and 3 were carried out analogously as reported in our previous paper.[8b)] Reactions Nos. 4—9 were also carried out analogously. The nickel complexes obtained in Nos. 5 and 8 were characterized by comparing their IR spectra with authentic samples.[8b)]

No. 10: Toluene (5 cm^3) and PhCOCl (0.15 cm^3) were added into a reaction vessel containing 0.30 g of **4** at −196 °C. After evacuation of the vessel, the reaction mixture was stirred at room temperature for 1 d. GLC analysis of the gas and liquid phase indicated the formation of the gaseous and liquid products shown in Table 2. The yellow precipitate formed during the reaction was collected by filtration and crystallized from a mixture of THF and diethyl ether. The nickel complex thus isolated was identified as NiCl(Ph)dpe from its elemental analysis and IR and NMR spectra. The same complex was prepared by a ligand exchange reaction of known NiCl(Ph)(PPh$_3$)$_2$[22] with dpe. Found: C, 67.2; H, 5.1; Cl, 6.2. Calcd for C$_{32}$H$_{29}$ClNiP$_2$: C, 67.5; H, 5.1; Cl, 6.2. IR(KBr, cm^{-1}): 1560s, 1460vs, 320 m. ^{1}H NMR: δ=1.6—2.8 (4H, multiplet, CH$_2$-P), 6.6 (3H, *o*, *m*- or *m*, *p*-H of Ni-C$_6$H$_5$), 6.9—8.2 (22H, multiplet, C$_6$H$_5$-P and *o*- or *m*-H of Ni-C$_6$H$_5$). ^{31}P {^{1}H}-NMR-(CH$_2$Cl$_2$): 60.3 (d, J_{P-P}=20 Hz) and 43.4 (d, J=20 Hz) ppm from external PPh$_3$. Reactions Nos. 11—14 were carried out analogously. NiCl$_2$(dpe) obtained in No. 11 was characterized by comparing its IR spectrum with that of an authentic sample.[23]

Reaction with CS$_2$. Toluene (6 cm^3) and CS$_2$ (0.10 cm^3, 1.7 mmol) were added into a vessel containing **4** (0.28 g, 0.58 mmol) at −196 °C. After evacuation of the vessel, the reaction mixture was stirred at room temperature. After 1 h, formation of a green precipitate was observed. Analysis of the gas phase by gas chromatography indicated formation of 0.40 mmol (69%) of ethane and a small amount of CH$_4$. The green precipitate was collected by filtration, washed repeatedly with diethyl ether, and dried under vacuum to yield 260 mg of Ni(CS$_2$)(dpe). Found: C, 61.6; H, 4.7; S, 12.2. Calcd: C, 60.8; H, 4.5; S, 12.0. The complex was soluble in CH$_2$Cl$_2$, but it decomposes in the solvent as judged from IR spectra of a solid recovered from the CH$_2$Cl$_2$ solution. Ni(CS$_2$)(dpe) was sparingly soluble in other solvents, and recrystallization has not been succesful.

The reaction of **3** with CS$_2$ was carried out analogously by using 0.19 g (0.60 mmol) of **3** and 0.078 cm^3 (1.30 mmol) of CS$_2$ at −25 °C for 2 d (solvent=2 cm^3 of diethyl ether). The pale brown precipitate was collected by filtration at −30 °C, washed with diethyl ether at −30 °C, and dried under vacuum to yield 220 mg (85%) of a nickel complex having an approximate composition of NiMe$_2$(PEt$_3$)$_2$(CS$_2$). Found: C, 43.9; H, 9.4; S, 16.2%. Calcd: C, 44.9; H, 9.0; S, 16.0%. Acidolysis of NiMe$_2$(PEt$_3$)$_2$(CS$_2$) gave methane quantitatively.

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