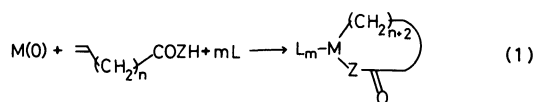# Preparation of Ni- or Pt-Containing Cyclic Esters by Oxidative Addition of Cyclic Carboxylic Anhydrides and Their Properties

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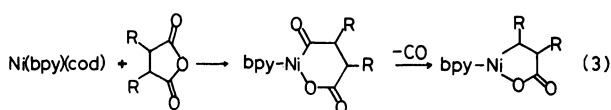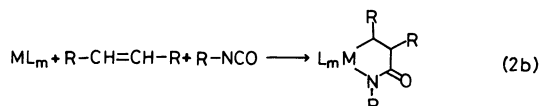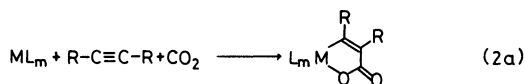
(Received March 21, 1984)

Metal containing cyclic ester complexes, $\overline{LNiCHR^1CHR^2COO}$ (L=1,2-bis(diphenylphosphino)ethane (dpe) or 2,2'-bipyridine (bpy); R^1, R^2=H or CH_3) and L_n $\overline{PtCOCH_2CH_2COO}$ (L=tricyclohexylphosphine (PCy_3) or dpe; n=1 or 2), have been prepared by oxidative addition of cyclic carboxylic anhydrides to zero-valent metal complexes. These complexes have been characterized by elemental analysis and spectroscopies (IR as well as ^1H-, $^{13}C\{^1H\}$-, and $^{31}P\{^1H\}$-NMR) and chemical reactivities. Rate of the oxidative addition of succinic anhydride to Ni(bpy)(cod) (cod=1,5-cyclooctadiene) is expressed by a second order rate equation, $R=k[Ni(bpy)(cod)][succinic anhydride]$, and temperature dependence of k gives the activation energy of $68\,kJ\,mol^{-1}$. The reaction of methylsuccinic anhydride with $Ni(cod)_2$ in the presence of tertiary phosphine or bpy affords two isomers, $\overline{L_nNiCH_2CH(CH_3)COO}$ and $\overline{L_nNiCH(CH_3)CH_2COO}$, corresponding to two modes of C-O bond cleavage in methylsuccinic anhydride promoted by Ni; dependence of the ratio between the two isomers on the kind of ligand added and reaction conditions has been examined.

Metallacycles are regarded as key intermediates in numerous metal-catalyzed reactions.[1] Especially, much attention has been paid to the role of the metallacycles in metathesis[2] and cycloaddition[3] of olefins and isolation of several metallacycles consisting of transition metal and hydrocarbons has been reported. However, there have been only few reports concerning with the metallacycles containing functional groups, which have potential value in synthetic chemistry. Our research group has reported preparation of metal-containing cyclic amide and ester type complexes by the reaction of zero-valent metal complexes with unsaturated amides and acids.[4,5a]

$$ M(0) + \underset{(CH_2)_n}{\overset{(CH_2)_n}{\diagdown}} COZH + mL \longrightarrow L_m\text{-}M \overset{(CH_2)_{n+2}}{\underset{Z}{\diagup}} \tag{1} $$

n=1,0 M= Ni , Pd ; Z = NH,O
m=1,2

Other research groups also, independently from our work described above, reported preparation of similar metallacycles through two different synthetic routes: (i) Cycloaddition of olefin or acetylene with carbon dioxide or isocyanate (Eq. 2)[6] and (ii) oxidative addition of cyclic carboxylic anhydrides.[7]

$$ ML_m + R\text{-}C\equiv C\text{-}R + CO_2 \longrightarrow L_m M \tag{2a} $$

$$ ML_m + R\text{-}CH=CH\text{-}R + R\text{-}NCO \longrightarrow L_m M \tag{2b} $$

$$ Ni(bpy)(cod) + \longrightarrow bpy\text{-}Ni \xrightarrow{-CO} bpy\text{-}Ni \tag{3} $$

bpy : 2,2'-bipyridine.   cod : 1,5-cyclooctadiene

However, as for the latter preparative method (Eq. 3) characterization of the complexes obtained is based only on their rough elemental analysis and IR spectra, and more unequivocal characterization of the com-

plexes by other instrumental analysis and chemical reactivities is required.

In order to develop the chemistry of the transition metal-containing cyclic ester type complexes and to establish the mechanism of the oxidative addition of cyclic carboxylic anhydrides to transition metal complexes, we have expanded this oxidative addition reaction by using other transition metal complexes as well as other cyclic carboxylic anhydrides and characterized the isolated complexes by elemental analysis, spectroscopy (IR and NMR), and chemical reactivities. Upon confirmation of the structures of these complexes, we examined kinetics of oxidative addition of cyclic carboxylic anhydrides to the Ni(0) complexes.

Oxidative addition of acyclic carboxylic anhydrides to Ni(0) and Pd(0) complexes has been already reported from our research group,[5c] and some of the data described in this paper have been reported in communication form.[5b]
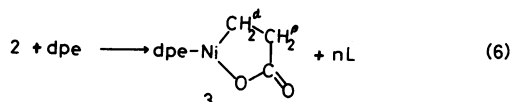
Results and Discussion

Oxidative Addition of Cyclic Carboxylic Anhydride to Zero-valent Nickel Complexes.   Succinic Anhydride: The reaction of Ni(0) with succinic anhydride in the presence of appropriate ligands such as bpy and PCy_3 gives five membered nickel-containing cyclic esters, **2**.

$$ Ni(cod)_2 + nL + \longrightarrow L_n\text{-}Ni \xrightarrow{-CO} L_n\text{-}Ni \tag{4} $$

1	2
1a : bpy	2a : bpy
1b : PR₃	2b : PR₃
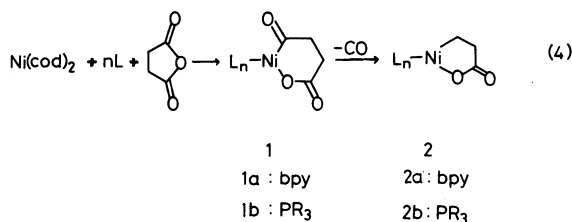
Complex **2** is considered to be formed through oxidative addition of succinic anhydride to Ni giving six-membered 2-oxo-nickel-containing cyclic ester **1** first followed by its decarbonylation. Carbon monoxide thus released is trapped by Ni(0) complexes to afford $Ni(CO)_2L_n$, (see Experimental); therefore stoichiometry of the formation of **2** seems to be expressed by the following equation,

$$3Ni(cod)_2 + (2n+n')L + \text{succinic anhydride}$$

$$\longrightarrow 2\ 2 + Ni(CO)_2L_{n'} \quad (5)$$
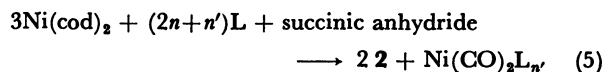
Uhlig and his coworkers reported the isolation of **1a**,[7b] however our attempts to isolate the intermediate complex **1a** have not been successful. High sensitivity to air and/or low solubility of **2** prevented its full characterization, and thus **2** has been converted into a stable and soluble dpe complex by ligand exchange reaction,

$$2 + \text{dpe} \longrightarrow \text{dpe-Ni}\overset{\displaystyle CH_2^{\alpha} \diagdown CH_2^{\beta}}{\underset{O\diagdown C\diagdown O}{}} + nL \quad (6)$$

3

dpe : 1,2 -bis(diphenylphosphino)ethane

Use of dpe-d_4, $Ph_2PCD_2CD_2PPh_2$, affords **3**-d_4. In our previous work we observed that Ni-containing cyclic ester type complexes having dpe ligand have high stability and solubility in solvents,[4] and dpe has much higher coordinating ability than bpy and monodentate phosphine toward divalent organonickel complexes.[8] Attempts to prepare **3** directly according to Eq. 4 was not successful presumably due to formation of inert $Ni(dpe)_2$.

Table 1 summarizes the analytical data, yields, and color of **3** and related complexes. Figure 1 shows the ^{1}H-NMR spectrum of **3**. Its NMR data, together with those of other related complexes are summarized in Table 2. The coupling patterns of H^{α} and H^{β} have been analyzed by homodecouplings. Magnitudes of the

TABLE 1. ANALYTICAL DATA OF NICKEL AND PLATINUM-CONTAINING CYCLIC ESTERS

Complex	Analysis[a]			Color	Mp $\theta_m/°C$	Yield/%[c]
	C	H	Ni			
3	66.0 (65.8)	5.3 (5.3)		yellow	300(decomp.)	33
4[b]			19.5 (19.5)	red	155—180 (decomp.)	60
5	66.7 (66.2)	5.7 (5.5)		yellow	175—180 (decomp.)	43
8	65.7 (66.2)	5.9 (5.5)		yellow	260(mp) 265(decomp.)	57
9	46.3 (45.9)	6.7 (6.4)		white	170—175	34
10	56.1 (56.2)	8.2 (8.7)		white	170—175 (decomp.)	37
11	52.0 (51.9)	4.5 (4.4)		yellow	132—135 (decomp.)	45

a) Calculated value in parentheses. b) Microanalysis was not feasible due to its high sensitivity to air. c) Mol of isolated complex per mol of the starting metal complex.
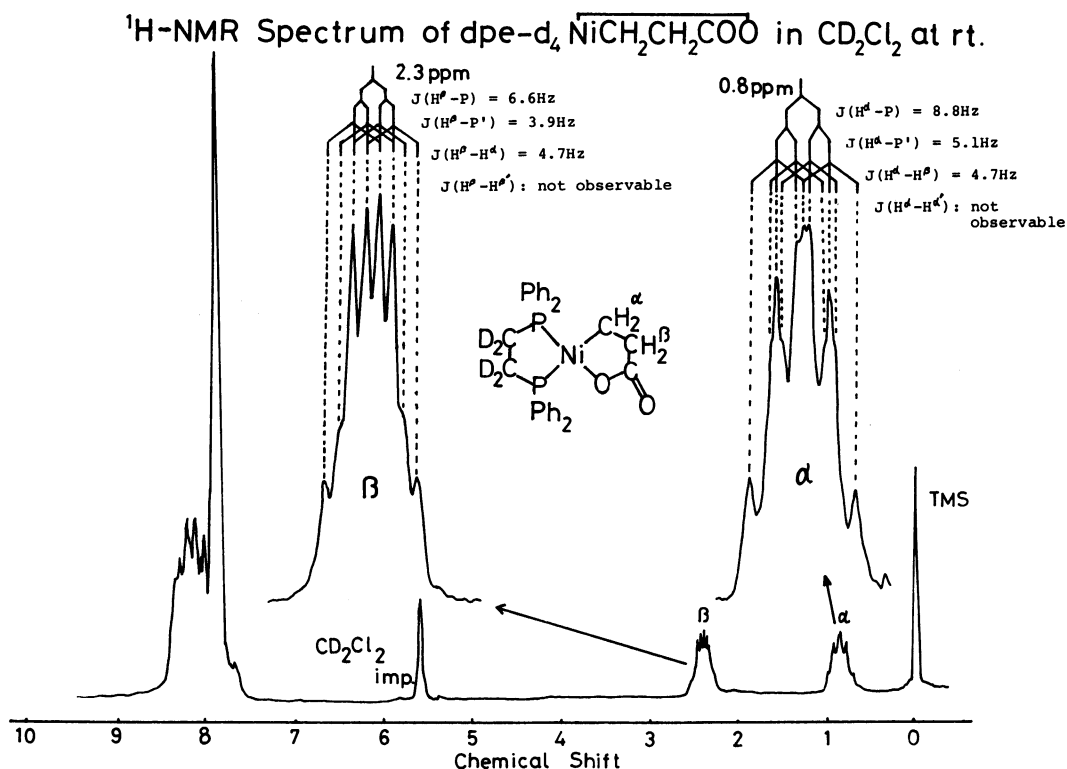
^{1}H-NMR Spectrum of dpe-d_4 $\overline{NiCH_2CH_2COO}$ in CD_2Cl_2 at rt.

2.3 ppm
$J(H^{\beta}-P) = 6.6Hz$
$J(H^{\beta}-P') = 3.9Hz$
$J(H^{\beta}-H^{\alpha}) = 4.7Hz$
$J(H^{\beta}-H^{\beta'})$: not observable

0.8 ppm
$J(H^{\alpha}-P) = 8.8Hz$
$J(H^{\alpha}-P') = 5.1Hz$
$J(H^{\alpha}-H^{\beta}) = 4.7Hz$
$J(H^{\alpha}-H^{\alpha'})$: not observable

Fig. 1. ^{1}H-NMR spectrum of **3**-d_4 in CD_2Cl_2.

TABLE 2. IR AND NMR DATA OF NICKEL AND PLATINUM-CONTAINING CYCLIC ESTERS

Complex	IR^a) $\nu_{(C=O)}$/cm⁻¹	¹H-NMR (δ)/ppm^b) Condition		¹³C{¹H}-NMR/ppm^b)	³¹P{¹H}-NMR ppm^c)
3	1635 vs	d	0.8 (2H, ddt, 8.8Hz, 5.1Hz, 4.7Hz, CH_2^α), 2.3 (2H, ddt, 6.6Hz, 3.9Hz, 4.7Hz, CH_2^β), 7.5—7.9 (20H, m, Ph)	18.6 (dd, 60.1Hz, 23.5Hz, CH₂), 22.6 (dd, 29.3Hz, 11.7 Hz, CH₂ of dpe), 28.4 (dd, 30.8Hz, 22.0Hz, CH₂ of dpe, 37.9 (s, CH₂), 129—133 (m, Ph), 190.8 (d, 6.1Hz, C̲O)	41.2(s) 64.9(s)
4	1620 vs 1360 s	d	0.8 (2H, br, CH_2^α), 1.3 (2H, br CH_2^β), 2.2 (2H, br, CH_2^γ), 7.8—9.0 (8H, m, bpy)		
		e	1.2 (2H, br, CH_2^α), 1.6 (2H, br, CH_2^β), 2.6 (2H, br, CH_2^γ)		
5	1640 vs	d	0.4—0.9 (1H, m, CH₂), 1.0 (3H, d, 6.8Hz, CH₃), 2.0—2.6 (1H, m, CH₂), 2.3—2.6 (1H, br, CH), 7.2—7.6 (20H, m, Ph)	21.7 (dd, 10.3Hz, 2.9Hz, C̲H₃), 25.1 (dd, 29.3Hz, 11.7Hz, C̲H₂ of dpe), 29.3 (dd, 58.6Hz, 21.98 Hz, C̲H₂), 30.0 (dd, 29.3 Hz, 20.5Hz, C̲H₂ of dpe), 42.5 (s, C̲H), 129—133 (m, Ph), 191.2 (s, C̲O),	40.9 (d, 1.95Hz), 65.1 (d, 1.95Hz),
8	1640 vs	d	0.52 (3H, t, 7Hz, CH₃) 1.4 (1H, m, CH), 1.7 (1H, ddd, 16Hz, 13Hz, 6Hz, CH₂), 2.9 (1H, dd, 16Hz, 6Hz, CH₂), 7.2—7.6 (20H, m, Ph)	19.3 (d, 3.5Hz, C̲H₃), 22.3 (dd, 27.8Hz, 4.7Hz, C̲H₂ of dpe), 27.4 (dd, 18.7 Hz, 56.4Hz, C̲H), 34.2 (dd, 27.6Hz, 17.3Hz, C̲H₂ of dpe) 46.5(d, 2.3Hz, C̲H₂), 127.6—131.2 (m, Ph), 201.0 (d, 5.0Hz, C̲O)	63.5 (d, 9.8Hz), 42.1 (d, 9.8Hz),
9	1560 vs 1650 m				
10	1610 vs 1640 sh				
11	1630 vs	d	2.2 (2H, td, 6.1Hz, 2.4Hz, CH_2^α), 2.9 (2H, t, 6.1Hz, CH_2^β), 7.5—7.9 (20H, m, Ph)	36.0—42.7 (m, CH₂ of dpe), 46.6 (t, 8.5Hz, $C̲H_2^\alpha$), 50.95 (d, 36.6Hz, $C̲H_2^\beta$), 127.1—134.0 (m, Ph), 205.6 (d, 3.7Hz, C̲OO), 204.3 (s, C̲O)	38.3 (d, 4.4Hz, with satellites J(Pt−P)= 1430.2Hz), 43.5 (d, 4.4Hz, with satellites J(Pt−P)= 3510.9Hz)

a) Measured in KBr disk, vs=very strong, s=strong, sh=shoulder, b) From internal TMS, s=singlet, d= doublet, t=triplet, m=multiplet, br=broad. c) From external PPh₃ (downfield positive). d) In CD₂Cl₂ at room temperature. e) In pyridine-d₅ at room temperature.

coupling constants between protons as well as proton and ³¹P are reasonable for the metallacyclic structure shown above. Figure 1 shows magnetic equivalence of the two Hᵅ's and Hᵝ's due to planarity of Ni-containing 5-membered ring or rapid steric interconversion of 5-membered ring. Figure 2 shows the ¹³C{¹H}-NMR spectrum of 3. The signals of the CH₂ carbons of dpe ligand are assigned unequivocally by comparing the ¹³C{¹H}-NMR spectrum of 3 with that of 3-d_4. The other signals are assigned on the basis of their chemi-

cal shifts and magnitudes of the ¹³C– ³¹P coupling constants. The appearance of the Hᵅ and C̲Hᵅ₂ signals at considerably high magnetic fields in the ¹H- and ¹³C{¹H}-NMR spectra, respectively, indicates the presence of the CH₂ group directly bonded to nickel. IR spectrum of the complex 3 shows a strong $\nu_{(C=O)}$ band at 1640 cm⁻¹.

The reaction of complex 3 with CO gives succinic anhydride and nickel carbonyl complex. The result not only supports the structure shown above but also

¹³C{¹H}-NMR Spectrum of dpe N̄iCH₂CH₂CŌŌ in CD₂Cl₂ at rt.
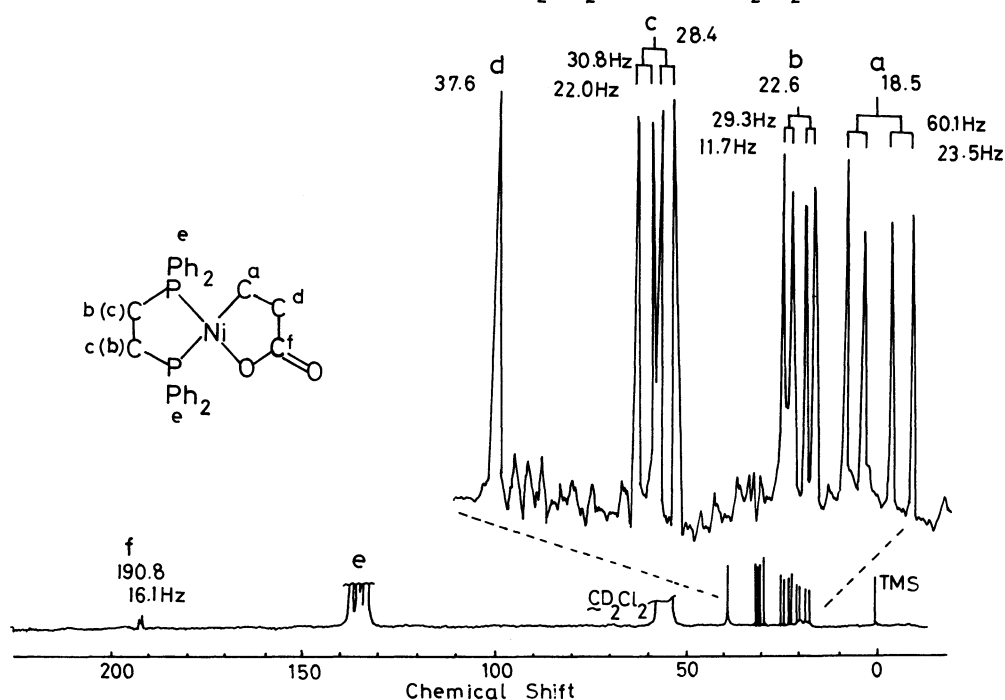
Fig. 2.   ¹³C{¹H}-NMR spectrum of 3 in CD₂Cl₂.

reveals reversibility of the decarbonylation reaction and the oxidative addition.

(7)
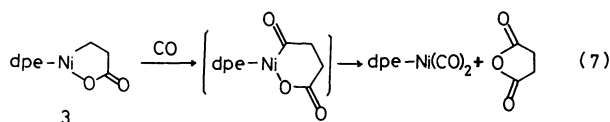
Results of reaction of metal-containing cyclic complexes with CO are summarized in Table 3.

Glutaric Anhydride: Reaction of glutaric anhydride with Ni(bpy)(cod) in THF gives a new six-membered ring complex, **4**.

(8)
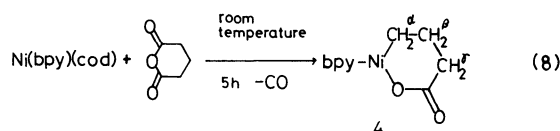
CO released is trapped as Ni(bpy)(CO)₂ similarly to the case of reaction with succinic anhydride. Complex **4** is very air sensitive but has a moderate solubility in organic solvents. ¹H-NMR spectrum of **4** shows three groups of signals of the methylene groups of **4** with the same intensity at 0.8, 1.3, and 2.2 ppm in CD₂Cl₂. The NMR signals are somewhat broadened possibly by a paramagnetic character of **4**, contamination with paramagnetic decomposition product(s) of **4** or rapid conformational change of the six-membered ring of **4**. Reaction of **4** with CO affords glutaric anhydride in 29% yield. On treatment with maleic anhydride in CH₂Cl₂ **4** gives a β-elimination product, 3-butenoic acid, in quantitative yield. These observations support the above six-membered structure of **4**.

Thermal decomposition of complex **4** in solid state or in a CH₂Ph₂ solution above 160 °C releases CO₂ and propylene in 20—30% yield, demonstrating occurrence

TABLE 3.   REACTION OF METAL- CONTAINING CYCLIC ESTERS WITH CO

Complex	Products (% yield per the complex)
3	Succinic anhydride (55) dpeNi(CO)₂[a]
4	Glutaric anhydride (29) bpyNi(CO)₂[a]
8	Methylsuccinic anhydride (96) dpeNi(CO)₂[a]
9	Succinic anhydride (13) Pt-(CO) complex[a]
11	No reaction

a) Identified by IR.

of the following bond cleavage in six-membered ring or ring contracted five-membered ring.
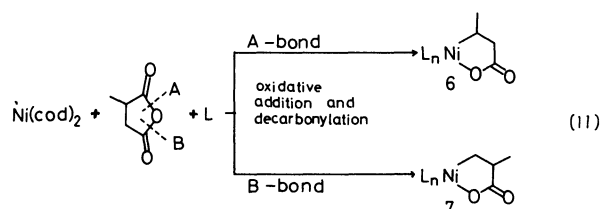

(9)
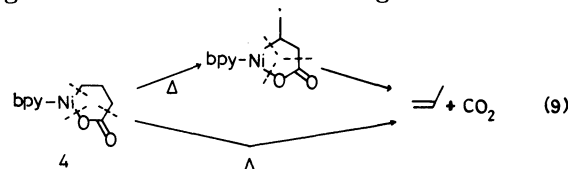
Addition of dpe to the solution of complex **4** gives a five-membered complex **5** in a high yield, demonstrating that complex **4′** has been completely isomerized to the five membered complex **5** under the experimental conditions.[5a]
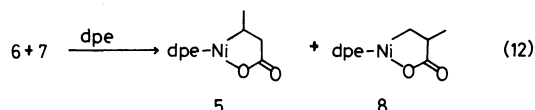

(10)
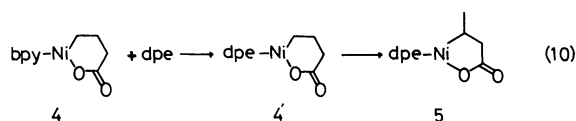
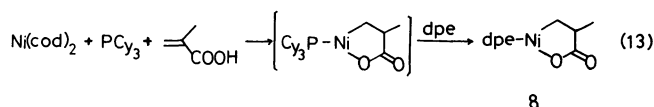Factors controlling the ring contraction will be reported elsewhere.

Methylsuccinic Anhydride: Oxidative addition of methylsuccinic anhydride to Ni(bpy)(cod) gives two isomeric complexes, **6** and **7**, corresponding to two modes (A or B) of the oxidative addition.

$Ni(cod)_2$ + [structure with A-bond and B-bond labels] + L → oxidative addition and decarbonylation → L_nNi **6** / L_nNi **7**   (11)

The ratio of **6** to **7** was determined by measuring intensity of $^{31}P\{^1H\}$-NMR signals of complexes **5** and **8** after ligand exchange reaction with dpe. The **6/7** ratio varies depending on the ligand employed and the reaction temperature. The results are given in Table 4.

6 + 7 $\xrightarrow{\text{dpe}}$ dpe-Ni [structure] **5** + dpe-Ni [structure] **8**   (12)

Complex **8** was independently prepared according to the following reaction.

$Ni(cod)_2$ + PCy_3 + [structure COOH] → [Cy_3P-Ni structure] $\xrightarrow{\text{dpe}}$ dpe-Ni [structure] **8**   (13)

PCy_3 : tricyclohexylphosphine

The new complex **8** is characterized by elemental analysis, IR- and NMR (^1H-, $^{13}C\{^1H\}$-, and $^{31}P\{^1H\}$-) spectroscopy, and chemical reactivities. Coupling patterns observed in ^1H- and $^{31}P\{^1H\}$-NMR spectra are similar to those observed in ^1H- and $^{31}P\{^1H\}$-NMR spectra of the previously reported nickel-containing cyclic amides complex $(dpe-\overline{NiCH_2CH(CH_3)CONH})$ prepared from methacrylamide.[4] The NMR data are included in Table 2. Reaction of complex **8** with CO gives methylsuccinic anhydride in a quantitative yield as shown in Table 3. Table 4 summarizes effect of ligand added and reaction conditions on the distribution of products, **6** and **7**, which are formed by cleavage of A- and B-bonds, respectively. Examination of Table 4 clearly indicates that the oxidative addition involving the B-bond cleavage proceeds preferentially to the oxidative addition with the A-bond cleavage. This seems to be attributable to steric influence of the methyl substituent rather than electronic influence of the methyl substituent. When bpy or 4,4'-dimethyl-2,2'-bipyridine is used as ligand, the ratio of **7** against **6** increases with lowering of the reaction temperature, indicating that activation energy for the oxidative addition of the B-bond is smaller than that of the A-Bond.

Kinetics of the Oxidative Addition: Oxidative addition of succinic anhydride to Ni(bpy)(cod) is followed by observing change of visible spectrum which shows clear isosbestic points. The reaction obeys first order kinetics concerning the concentration of Ni(bpy)(cod) as shown in Fig. 3.

$$-\frac{d[Ni(bpy)(cod)]}{dt} = k'[Ni(bpy)(cod)].$$ (14)

The dependence of the pseudo-first-order rate constant k' on the concentration of succinic anhydride is shown in Fig. 4, which demonstrates that k' is proportional

TABLE 4. EFFECT OF ADDITIVE LIGAND ON THE REGIOSERECTIVITY OF C–O BOND CLEAVAGE OF METHYLSUCCINIC ANHYDRIDE

Ligand(L)	L/Ni	Temp/°C	6(%)	7(%)
bpy	1	30	45	55
bpy	1	20	44	56
bpy	1	10	36	64
bpy	1	0	28	72
$Me_2bpy^{a)}$	1	20	29	71
$Me_2bpy^{a)}$	1	10	24	76
$Me_2bpy^{a)}$	1	0	25	75
PCy_3	1	20	36	64
PCy_3	1	10	42	58
PCy_3	1	0	44	56
PEt_3	4	20	25	75
PEt_3	4	10	27	73
PEt_3	4	0	18	82
$P(n-Bu)_3$	4	10	21	79
PEt_2Ph	2	10	28	72

a) 4, 4'-dimethyl-2,2'-bipyridine.
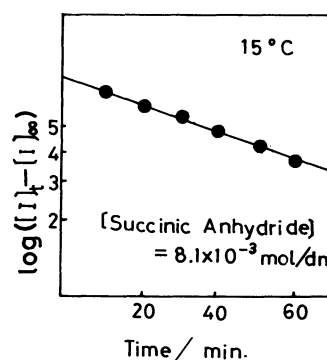
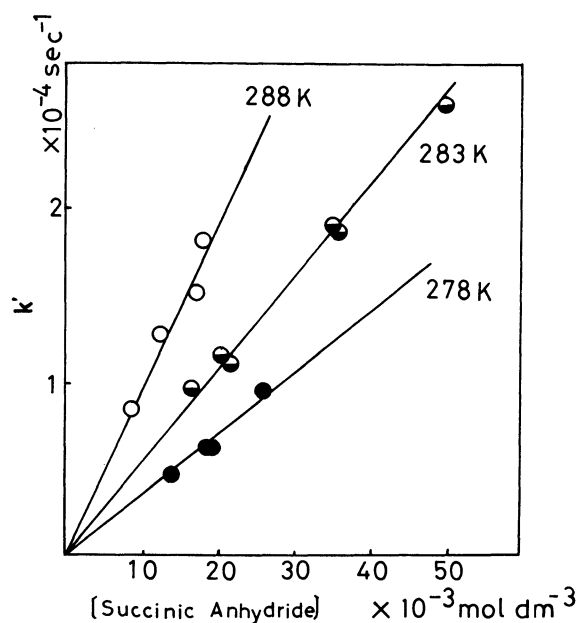Fig. 3. First-order plot for the reaction of Ni(bpy)-(cod) with succinic anhydride.

Fig. 4. Dependence of k' on concentration of succinic anhydride.

to [succinic anhydride]. Thus, the rate of reaction is expressed by second-order rate equation,

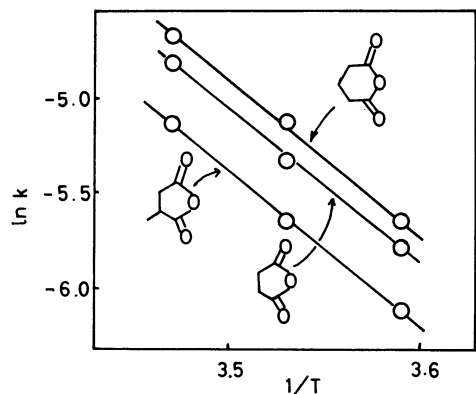$$-\frac{d[Ni(bpy)(cod)]}{dt} = k[Ni(bpy)(cod)][\text{succinic anhydride}],$$

(15)

Fig. 5. Arrhenius plot of the rate constant.

Similar second-order rate equations are also obtained for other cyclic carboxylic anhydrides. From the Arrhenius plot of k against $1/T$, the activation energy for the oxidative addition of cyclic carboxylic anhydride to Ni(bpy)(cod) is estimated as shown in Table 5. The ΔH^{*} values obtained for the present oxidative addition of cyclic carboxylic anhydrides are considerably smaller than the ΔH^{*} value (88 kJ mol^{-1})[8] obtained for the oxidative addition of phenyl propionate to Ni(0) complex, indicating that the oxidative addition of cyclic carboxylic anhydride to Ni(0) is an energetically easier process than the oxidative addition of ester to Ni(0).

Oxidative Addition to Zero-valent Platinum.   A reaction of Pt(cod)$_2$ with a mixture of PCy$_3$ (1 mol/ Pt(cod)$_2$) and succinicanhydride (1 mol/Pt(cod)$_2$) in THF at room temperature affords a white insoluble complex, which is considered to have the following platinum-containing cyclic structure as judged from its IR spectrum and analytical data (Table 1). When 2 mol of PCy$_3$ per mol of Pt(cod)$_2$ is added, the reaction affords a similar platinum cyclic complex 10 having two PCy$_3$ ligands.

(16)

9

(17)

10
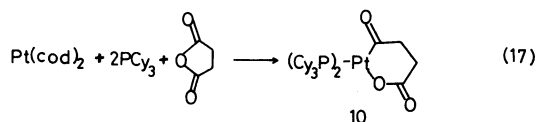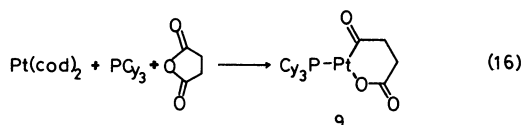
Low solubility of these complexes presumably due to its polymeric structure prevented analyzing their structures by NMR spectroscopy. However, a ligand exchange reaction with dpe in CS$_2$ gives a soluble dpe-coordinated complex 11.


(18)

11
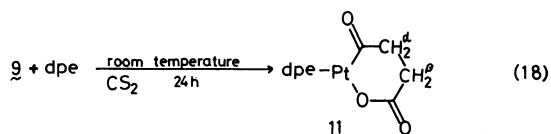
By using dpe-d_4, 11-d_4 is prepared.

IR spectrum of complex 9 shows two strong bands at 1650 cm^{-1} and 1560 cm^{-1} assignable to $\nu_{(C=O)}$ of the acyl group and $\nu_{(C=O)}$ of the carboxylato group. These two

TABLE 5. ACTIVATION PARAMETERS FOR OXIDATIVE ADDITION OF CYCLIC CARBOXYLIC ANHYDRIDES TO ZERO-VALENT NICKEL [a]

Substrate	ΔE_a^{*} kJ mol^{-1}	ΔS_{283}^{*} J deg^{-1}mol^{-1}	ΔH_{283}^{*} kJ mol^{-1}	ΔG_{283}^{*} kJ mol^{-1}
Succinic anhydride	67.7	−48.5	65.2	79.0
Methyl-succinic anhydride	69.4	−45.1	66.9	71.9
Glutaric anhydride	67.7	−46.8	65.2	78.6

a) Ni(bpy)(cod).

peaks overlap in IR spectra of 10 and 11. NMR data of 11 are included in Table 2, and consistent with the above structure. Appearance of the peak of the acyl carbon at 240.3 ppm in ^{13}C{^{1}H}-NMR spectrum as well as the appearance of all H and $\underline{C}H_2$ signals at relatively low magnetic fields in the ^{1}H- and ^{13}C{^{1}H}-NMR spectra, respectively, indicates that the decarbonylation has not taken place, in contrast to the analogous nickel complex 1 which undergoes the ready decarbonylation. Reaction of 11 with Br$_2$ affords the reductive elimination product, succinic anhydride, in 27% yield.

(19)

11
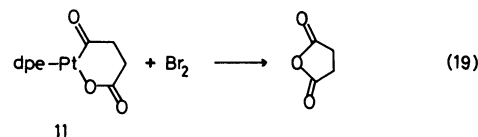
These observations support the non-decarbonylated 2-oxo-platinum-containing cyclic structure shown above.

When other ligands (bpy, PPh$_3$, P(CH$_2$Ph)$_3$, PMePh$_2$, dpe) are added to the mixture of Pt(cod)$_2$ and succinic anhydride, oxidative addition did not take place even at elevated temperatures. Blake and his coworkers[7] reported oxidative addition of perfluorinated succinic anhydride to Pt(PPh$_3$)$_2$(C$_2$H$_4$).

In contrast to the Ni(0) and Pt(0) complexes, Pd(0) complexes (Pd(PCy$_3$)$_2$ and bis(1,5-diphenyl-1,4-pentadien-3-one) palladium (0))[9] did not show any apparent change on interaction with the cyclic carboxylic anhydrides at room temperature. A coordinatively unsaturated Rh(I) complex, RhCl(PPh$_3$)$_3$, showed no apparent change on the interaction with the cyclic carboxylic anhydrides, either.

Experimental

General, Materials, Analysis, and Spectroscopic Measurement. Reactions were carried out under N$_2$ or Ar as reported in papers from our research group.[4] Pt(cod)$_2$ was prepared according to the literature.[11] Commercially available Ni(cod)$_2$ was recrystallized from hot toluene. Microanalysis of C and H was performed by Mr. Saito of our laboratory with Yanagimoto CHN Autocorder MT-2. Ni content of 4 was determined by titration method.[12] IR spectra were recorded on a Hitachi Model 295 spectrometer, ^{1}H-NMR spectra on a JEOL Model JNM-PS-100 spectrometer, and ^{13}C- and ^{31}P-NMR spectra on JEOL Model JNM-PFT-PS-100 Fourier transform spectrometer. GLC analysis of organic products was performed with Shimadzu GC-3BT gas chromatograph.

Preparation of Complexes.   2: Complex 2a was pre-

pared according to literature.[7] From the reaction system we obtained $Ni(CO)_2(bpy)$ (confirmed by IR^{13}) besides 2a. Other complexes of type 2 were prepared analogously by using monodentate tertiary phosphines, but isolation of the complexes was not feasible and the crude complexes were used in further reaction with dpe (see text).

3: A THF ($10\,cm^3$) solution containing 340 mg (1.2 mmol) of $Ni(cod)_2$, 190 mg (1.2 mmol) of bpy, and 120 mg (1.2 mmol) of succinic anhydride was stirred for 3 h at 25 °C to obtain a red precipitate from the homogeneous solution. The precipitate was separated by filtration and washed with hexane repeatedly, and then dissolved in CH_2Cl_2 ($10\,cm^3$) containing 490 mg (1.2 mmol) of dpe at room temperature. The solution was filtered, and the filtrate was dried under reduced pressure. The residual solid was washed with THF repeatedly and dried under vacuum to obtain yellow 3. yield=221 mg (33%).

4: A THF solution ($40\,cm^3$) containing 3.0 g (11 mmol) of $Ni(cod)_2$, 1.7 g (11 mmol) of bpy, and 1.3 g (11 mmol) of glutaric anhydride was stirred for 6 h at 25 °C to obtain a red precipitate. The complex was filtered, washed with hexane repeatedly and dried to yield 2.0 g (60%) of a red complex 4.

5: A CH_2Cl_2 solution ($40\,cm^3$) containing 53 mg (0.18 mmol) of complex 4 and 70 mg (0.18 mmol) of dpe was stirred at room temperature. After change of color from red to yellow, the solution was filtered. The filtrate was dried under reduced pressure to obtain a yellow solid, which was washed with Et_2O repeatedly and dried to yield 41 mg (43%) of 5.

8: A THF solution ($5\,cm^3$) containing 510 mg (1.9 mmol) of $Ni(cod)_2$ and 520 mg (1.9 mmol) of PCy_3 and $0.16\,cm^3$ (1.9 mmol) of methacrylic acid was stirred for 24 h at 0 °C. Then, 740 mg (1.9 mmol) of dpe was added to the solution to obtain a yellow precipitate, which was separated by filtration, washed with THF and hexane repeatedly, and dried under vacuum to yield 580 mg (57%) of 8.

9 and 10: A THF ($4\,cm^3$) solution containing 170 mg (0.4 mmol) of $Pt(cod)_2$ and 41 mg (0.4 mmol) of PCy_3 was stirred for 1 h at room temperature to obtain a white precipitate, which was separated by filtration, washed with hexane repeatedly, and dried under vacuum to obtain 81 mg (31%) of 9. Complex 10 was prepared analogously using 2 mol of PCy_3 per mol of $Pt(cod)_2$ (yield=37%).

11: A CS_2 ($10\,cm^3$) solution containing 440 mg (0.80 mmol) of 9 and 320 mg (0.80 mmol) of dpe was stirred for 24 h. CS_2 was removed by evaporation and the residue was washed with benzene repeatedly. Extraction with acetone ($10\,cm^3$), and removing acetone by evaporation gave a white solid from which 11 was extracted by CH_2Cl_2. This extract was dried to obtain a white residue which was washed with hexane and dried to yield 245 mg (46%) of 11.

Reaction of Methylsuccinic Anhydride: A Schlenk tube containing a THF solution of $Ni(cod)_2$ (0.1 mol/cm^3) and methylsuccinic anhydride (0.1 mmol/cm^3) was placed in a thermostated water bath. Ligand (see text) was added to the solution to start the reaction. After 1 h, dpe was added to the solution and solvent was removed under reduced pressure. The residue was washed with hexane to remove dpe–$Ni(CO)_2$ and free ligands.

Reaction of the Complex with CO: A $20\,cm^3$-Schlenk tube

containing a CH_2Cl_2 (3—4 cm^3) solution of the complex (0.1—0.2 g) was evacuated and 1 atm of CO was introduced. The products were analyzed by GLC, GC-mass, and IR.

Kinetics: Dry THF was introduced into a quartz Schlenk tube connected to a UV cell by trap to trap distillation. 1,5-Cyclooctadiene was added to stabilize $Ni(bpy)(cod)$. Then, THF solutions containing cyclic carboxylic anhydride and $Ni(bpy)(cod)$ were added to the reaction vessel, and the change of visible spectrum with time was measured.

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