A theoretical vibrational analysis confirms the IR spectroscopic identification of the HSOH complex.

Matrix effects have not been taken into account in the present calculation, but they are expected to stabilize the complexes and shift slightly the infrared frequencies. The low temperature and the constraint of the matrix allowing only diffusion may inhibit the three-step mechanism and favor the process involving the complex [H_2SO].

Acknowledgment. J.L.W. acknowledges partial support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society. Appreciation is also extended to Professor S. D. Peyerimhoff for helpful discussions and hospitality during the latter stages of this work.

Preparation and Properties of Phosphine Complexes of Nickel-Containing Cyclic Amides and Esters

$[(PR_3)_n\overline{NiCH_2CH(R^1)COZ}\ (Z = NR^2, O)]$

Takakazu Yamamoto,* Kohji Igarashi, Sanshiro Komiya, and Akio Yamamoto*

Contribution from the Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan. *Received May 23, 1980*

Abstract: Reactions of α,β-unsaturated amides, $CH_2{=}C(R^1)CONHR^2$ (R^1 = H, CH_3; R^2 = H, CH_3, C_6H_5), with bis(1,5-cyclooctadiene)nickel, $Ni(cod)_2$, in the presence of tricyclohexylphosphine, $P(c\text{-}Hx)_3$, or ethyldi-*tert*-butylphosphine, $PEt(t\text{-}Bu)_2$, give nickel-containing cyclic amide complexes formulated as $(PR_3)\overline{NiCH_2CH(R^1)CON}R^2$. Reactions of $(P(c\text{-}Hx)_3)\overline{NiCH_2CH(CH_3)CON}H$ with triethylphosphine (PEt_3) and 1,2-bis(diphenylphosphino)ethane (dpe) afford corresponding ligand-exchanged products, $(PEt_3)\overline{NiCH_2CH(CH_3)CON}H$ and $(dpe)\overline{NiCH_2CH(CH_3)CON}H$. The nickel-containing cyclic amide structure was confirmed by IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopy as well as by chemical reactivities of the complexes. The complex with the PEt_3 ligand forms a trinuclear complex whereas the complex with dpe has a monomeric structure. A similar reaction of acrylic acid with $Ni(cod)_2$ in the presence of $P(c\text{-}Hx)_3$ affords a nickel-containing cyclic ester complex, $(P(c\text{-}Hx)_3)\overline{NiCH_2CH_2COO}$. Reactions of nickel-containing cyclic amide and ester complexes with carbon monoxide yield succinimides and succinic anhydrides, respectively. Addition of sterically less demanding and/or less basic phosphine ligands other than $P(c\text{-}Hx)_3$ and $PEt(t\text{-}Bu)_2$ in the reaction of α,β-unsaturated amides with $Ni(cod)_2$ leads to the formation of normal π-type complexes formulated as $Ni(PR_3)_m(\alpha,\beta\text{-unsaturated amide})_n$. Reactions of the π-type complexes with CO lead to simple ligand-exchange reactions to liberate the α,β-unsaturated amide with the formation of $Ni(PR_3)_m(CO)_{4-m}$. $Ni(P(c\text{-}Hx)_3)(\pi\text{-acrylamide})_2$ is converted into the nickel-containing cyclic amide complex, $(P(c\text{-}Hx)_3)\overline{NiCH_2CH_2CON}H$, on heating the π-type complex in THF. Occurrence of a reverse type of conversion from the nickel-containing cyclic amide complex to the π-type complex is postulated in thermolysis of the nickel-containing cyclic amide complex, which liberates α,β-unsaturated amide on the thermolysis. An intramolecular Michael reaction type shift of H from NH or COOH to the α-carbon of α,b-unsaturated amide or acid in an intermediate π-type complex is proposed as the reaction pathway to lead to the formation of the nickel-containing cyclic complex. Effects of basicity and bulkiness of tertiary phosphines on the formation of the nickel-containing cyclic complex are discussed on the basis of the proposed reaction pathway.

Introduction

Preparation of transition metallacyclic complexes and utilization of the complexes for synthetic reactions are the subject of recent interest.[1-5] However, most of the transition metallacyclic compounds reported are ones in which the ring consists of only the transition metal and carbons, and only a few reports have been given concerning the isolation of a metallacyclic complex in which the ring contains other elements such as N and O.[6] We previously reported in preliminary form the preparation of a nickel-containing cyclic amide complex by the reaction of bis(1,5-cyclooctadiene)nickel, $Ni(cod)_2$, with methacrylamide in the presence of tricyclohexylphosphine $P(c\text{-}Hx)_3$, and conversion of the complex into 2-methylsuccinimide by the reaction with CO (eq 1).[7] As the extension of the work we have carried out similar reactions

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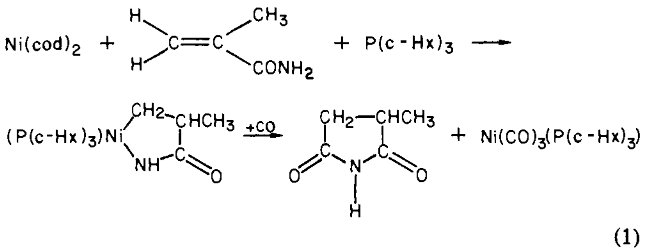
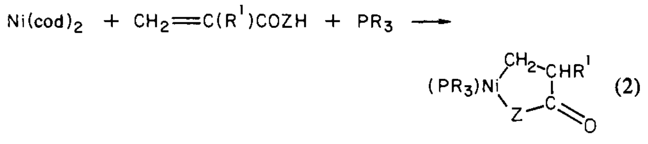


(1)

not only employing various α,β-unsaturated amides (acrylamide and N-substituted methacrylamides) and α,β-unsaturated acids (acrylic acid and methacrylic acid) but also employing various phosphines with a wide range of basicity and bulkiness to find out that (1) a wide range of the α,β-unsaturated amides and acids form analogous nickel-containing cyclic complexes by reactions with $Ni(cod)_2$ in high yields under mild conditions (see eq 2) when a highly stereodemanding phosphine with a high basicity is employed, whereas (2) when a less basic and/or less stereodemanding phosphine is employed, the reaction gives a usual π-type olefin complex.



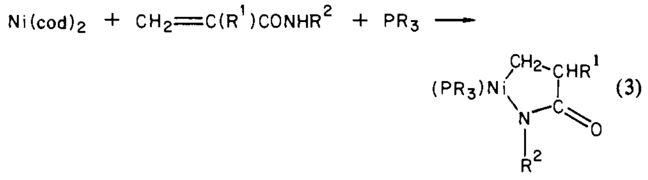
(2)

Z = NR², O

We now report the preparation of the two types of complexes, their IR and NMR data, and their chemical properties including the conversion of the nickel-containing cyclic imide and ester complexes into amides and carboxylic anhydrides by the reaction with carbon monoxide and interconversion between the two types of complexes, nickel-containing cyclic complex $\rightleftharpoons$ π-type complex.

Results and Discussion

Preparation of Nickel-Containing Cyclic Amide Complexes. Reaction of α,β-unsaturated amides with $Ni(cod)_2$ in the presence of tricyclohexylphosphine, $P(c\text{-}Hx)_3$, or ethyldi-*tert*-butylphosphine, $PEt(t\text{-}Bu)_2$, afford nickel-containing cyclic amide complexes (eq 3).



(3)

1

	PR_3	R^1	R^2
1a	$P(c\text{-}Hx)_3$	H	H
1b	$P(c\text{-}Hx)_3$	CH_3	H
1b-d_{33}	$P(c\text{-}Hx)_3$-d_{33}	CH_3	H
1b-d_2	$P(c\text{-}Hx)_3$	CH_3	D[a]
1c	$P(c\text{-}Hx)_3$	CH_3	CH_3
1d	$P(c\text{-}Hx)_3$	CH_3	C_6H_5
1e	$PEt(t\text{-}Bu)_2$	CH_3	H

[a] The methine H in the cycle is also deuteriated.

The reaction smoothly proceeds at room temperature to give the complexes in yields of 59–69%. The complexes **1b–e** can be obtained by the reaction over a wide range of the molar ratio of the α,β-unsaturated amides to $Ni(cod)_2$, but the formation of **1a** strongly depends on the molar ratio of acrylamide to $Ni(cod)_2$. When the acrylamide/$Ni(cod)_2$ ratio was 1, **1a** was the predominant product, whereas the π-type complex, $Ni(P(c\text{-}Hx)_3)(\pi\text{-acrylamide})_2$ (**3a**), was the main product when the ratio was 2. The formation of the π-type complex with two molecules of acrylamide is consistent with the high coordinating ability of acrylamide to Ni(0) complexes such as Ni(bpy) (bpy = 2,2′-bipyridine).[8] With other olefins with less coordinating ability such as ethyl methacrylate[9] and acrylaldehyde,[10] complexes of type $Ni(P(c\text{-}Hx)_3)$(olefin) have been isolated. Formation of the sterically packed complex of a type $Ni(P(c\text{-}Hx)_3)(olefin)_2$ in the presence of 2 mol of acrylamide/$Ni(cod)_2$ seems to prevent the formation of the nickel-containing cyclic amide complex, which is considered to be formed through a sterically nonpacked π-type complex such as $Ni(P(c\text{-}Hx)_3)$(olefin) (vide infra). Employment of less basic and/or less stereodemanding phosphines than $P(c\text{-}Hx)_3$ and $PEt(t\text{-}Bu)_2$ did not afford the nickel-containing cyclic complexes but gave the π-type complexes, **3**. Employment of crotonamide, a β-substituted acrylamide, in the reaction with the $Ni(cod)_2$–$P(c\text{-}Hx)_3$ mixture also afforded a similar nickel-containing cyclic amide type complex as judged from a sharp singlet amide band at 1572 cm^{-1} in the IR spectrum and formation of 3-methylsuccinimide by the reaction with CO. However, full characterization of the complex was not feasible due to difficulties in isolating the complex from the reaction mixture. Employment of cinnamamide, on the contrary, did not give the nickel-containing cyclic type complex, but it gave a usual π-type complex as judged from the infrared spectrum showing the amide I and amide II bands at 1662 and 1590 cm^{-1} which are observed charcteristically in the π-type complexes of α,β-unsaturated amides,[8] demonstrating the presence of some steric effects on the formation of the nickel-containing cycles.

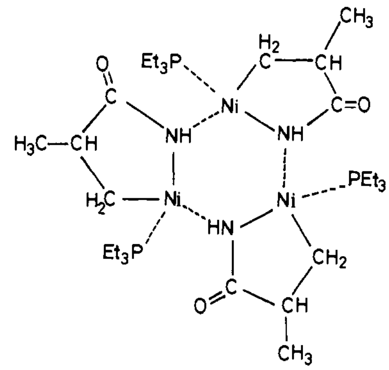
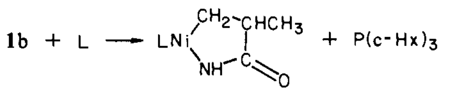


Figure 1. Postulated trinuclear structure for **1f**.

The $P(c\text{-}Hx)_3$ ligand in **1b** can be replaced by triethylphosphine, PEt_3, and 1,2-bis(diphenylphosphino)ethane, dpe, to give complexes **1f** and **1g** but not by PPh_3 (eq 4). Complexes **1f** and **1g** could not be obtained by the direct route starting from methacrylamide, $Ni(cod)_2$, and the ligand.



(4)

L = PEt_3 (**1f**), dpe (**1g**), $Ph_2CD_2CD_2PPh_2$, dpe-d_4, (**1g**-d_4)

Table I summarizes analytical data and physical properties of the nickel-containing cyclic amide complexes together with those of the other related complexes.

Physical Properties. The nickel-containing cyclic amide complexes are yellow or yellowish presumably due to the charge-transfer absorption band(s) characteristic of transition-metal phosphine complexes[11] in a near-ultraviolet region. Complexes **1a–e** have only poor solubilities in organic solvents suggesting a polynuclear structure, which is presumably formed through coordination of the amide group to nickel of other nickel-containing cyclic amide. The PEt_3-coordinated complex **1f** has high solubilities in organic solvents, and cryoscopic determination of the

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Table I. Analytical Data and Physical Properties of the Nickel-Containing Cyclic and π-Type Complexes

complex	color	mp, °C	dp,[b] °C	anal.[a] C	anal.[a] H	anal.[a] N	MW
$NiCH_2CH_2CONH(P(c\text{-}Hx)_3)$ (1a)	greenish yellow		211[c]	62.0 (61.5)	9.6 (9.4)	3.0 (3.4)	
$NiCH_2CH(CH_3)CONH(P(c\text{-}Hx)_3)$ (1b)	greenish yellow		239[c]	62.3 (62.3)	9.6 (9.4)	3.4 (3.3)	
$NiCH_2CH(CH_3)CONCH_3(P(c\text{-}Hx)_3)$ (1c)	yellow		159[c]	63.1 (63.0)	9.9 (9.7)	2.8 (3.2)	
$NiCH_2CH(CH_3)CONC_6H_5(P(c\text{-}Hx)_3)$ (1d)	reddish yellow		144[c]	67.2 (67.2)	9.0 (8.9)	2.8 (2.8)	
$NiCH_2CH(CH_3)CONH(PEt(t\text{-}Bu)_2)$ (1e)	yellow		191[c]	52.2 (52.9)	9.6 (9.5)	4.5 (4.4)	
$NiCH_2CH(CH_3)CONH(PEt_3)$ (1f)	yellow	96	160	45.4 (45.8)	8.7 (8.5)	5.2 (5.4)	810[d] (786)[e]
$NiCH_2CH(CH_3)CONH(dpe)$ (1g)	pale yellow	178	207	65.5 (66.4)	5.8 (5.8)	2.5 (2.6)	520[f] (542)
$NiCH_2CH_2COO(P(x\text{-}Hx)_3)$ (2)	yellow	125	198	60.5 (61.3)	9.1 (9.1)		
							α,β-unsaturated amide[g]/complex
$Ni(CH_2{=}CHCONH_2)_2(P(c\text{-}Hx)_3)$ (3a)	yellow	165	175	59.9 (59.2)	9.2 (9.1)	5.7 (5.8)	1.90
$Ni(CH_2{=}C(CH_3)CONH_2)(PPh_3)_2$ (3b)	yellow	110	165	71.4 (71.9)	5.8 (5.5)	1.9 (2.1)	0.91
$Ni(CH_2{=}C(CH_3)CONH_2)(PEt_3)_2$ (3c)	yellow	25	72		h		0.95
$Ni(CH_2{=}C(CH_3)CONH_2)_{0.5}(PBz_3)_2$ (3d)	yellow	142	166	67.8 (68.1)	6.3 (6.1)	1.4 (1.7)	0.50

[a] Calculated value in parentheses. [b] Decomposition point. [c] Decomposed before melting. [d] Cryoscopic in benzene. [e] Calculated as a trimer. [f] Vapor pressure osmometry. [g] α,β-Unsaturated amide liberated on the reaction with CO. [h] Microanalysis was not feasible due to the low melting point and high sensitivity of 3c toward air.

molecular weight suggests that **1f** has actually a trinuclear structure in benzene. As for the trinuclear complex, **1f**, we propose the following structure (Figure 1), which is consistent with NMR data of the complex as will be discussed below.

The cryoscopic molecular weight determination of **1b** also showed some association, but an accurate value for the degree of association was not obtainable due to the poor solubilities of the complex in organic solvents. Addition of dpe, a bidentate ligand, leads to breakage of the bridging Ni–N bond to give a mononuclear complex, **1g**, which has moderate solubilities in organic solvents.

IR Spectra. The IR spectra of the nickel-containing cyclic amide complexes are quite different from those of π-type complexes of α,β-unsaturated amides such as $Ni(acrylamide)_2(bpy)$[8] and $Ni(PR_3)_m(\alpha,\beta\text{-unsaturated amide})_n$ (vide infra), showing only one sharp strong band in a region of 1520–1600 cm^{-1}, the pattern being characteristic of cyclic amides.[12] As for **1a,b,e,f,g** the ν(N–H) band appears as a singlet around 3400 cm^{-1} in contrast to a doublet or triplet pattern of ν(N–H) of the π-type complexes. The ν(N–H) band was not observed for **1c** and **1d** derived from *N*-methyl- and *N*-phenylamides. Table II summarizes the IR and NMR data of the nickel-containing cyclic amide and related complexes.

NMR Spectra. **^{1}H NMR.** Figure 2 shows the ^{1}H NMR spectrum of the mononuclear complex **1g**. In the spectrum, signals of the two hydrogens attached to the α-carbon (H^a and H^c in a molecular formula depicted in Figure 2) appear at a fairly high field with the geminal coupling constant of 10.3 Hz.

The complicated spin–spin coupling patterns for H^a and H^c signals have been analyzed by ^{31}P-decoupling and triple resonance techniques, and the assignment is given in Figure 2b. The magnitudes of the geminal coupling constant, $J(H^a\text{–}H^c)$, and vicinal coupling constants, $J(H^a\text{–}H^d)$ and $J(H^c\text{–}H^d)$, are consistent with the nickel-containing cyclic amide structure.[13]

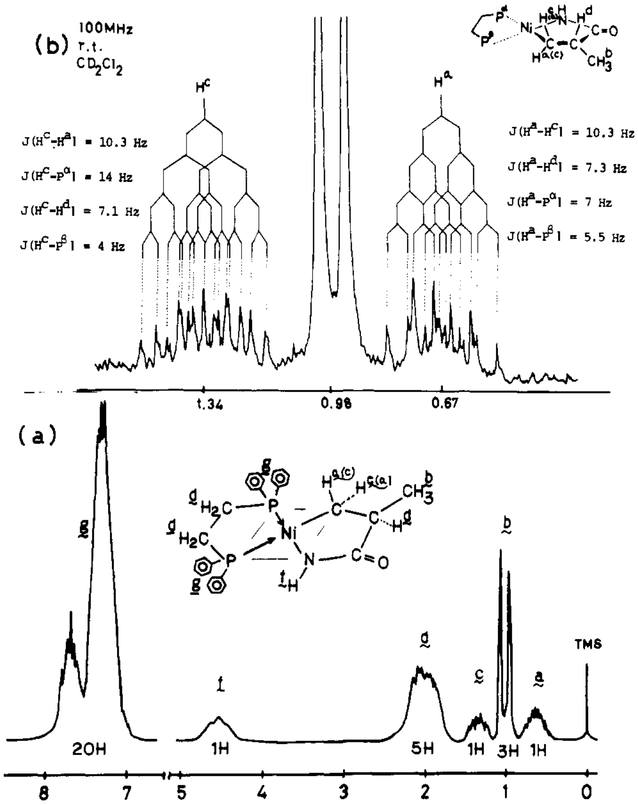

Figure 2. (a) ^{1}H NMR spectrum of **1g** in CD_2Cl_2 at 25 °C. (b) An expanded spectrum for the region of 0.5–1.5 ppm.

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Table II. IR and NMR Data of the Nickel-Containing Cyclic and π-Type Complexes

complex	ν(N–H) or ν(O–H), cm^{-1}	amide band(s) or ν(C=O), cm^{-1}	^{1}H NMR (δ)[a]	^{31}P{^{1}H}NMR,[a] ppm	^{13}C{^{1}H}NMR,[a] ppm
1a	ca. 3500 (w)	1572 (vs)			
1b	ca. 3400 (w)	1572 (vs)		ca. 32 (m)	
1b-d_{33}	ca. 3400 (w)	1572 (vs)	0.26 (2 H, m, $H^a + H^c$), 1.4–1.7 (3 H, m, H^b), 2.2–2.6 (1 H, m, H^d), 5.8–6.0 (1 H, br, NH)		
1c		1572 (vs)			
1d		1520 (vs)			
1e	ca. 3400 (w)	1572 (vs)			
1f	ca. 3400 (w)	1572 (vs)	0.25 (1 H, m, H^a), 0.9–1.9 (19 H, m, $H^b + H^c$ + P-*Et*), 2.43 (1 H, m, H^d), 5.87 (1 H, br, NH)	ca. 21 (m)	9.0 (C(γ), s), 11.0 (C(α), *J* = dd, 27.3, 5.9 Hz), 14.9 (P-C-C, d, *J* = 23.4 Hz), 23.2 (P-*C*, d, *J* = 25.4 Hz), 40.9 (C(β), m), 192.6 (C=O, d, *J* = 15.6 Hz)
1g	ca. 3400 (w)	1600 (vs)	0.67 (1 H, dddd, H^a),[b] 0.98 (3 H, d, H^b), 1.37 (1 H, dddd, H^c),[b] 2.1–2.4 (5 H, br, H^d + P-CH_2), 4.88 (1 H, br, NH), 7.4–7.7 (20 H, P-C_6H_5	46.66 (d, *J* = 2.9 Hz), 61.69 (d, *J* = 2.9 Hz)	21.9 (C(γ), dd, *J* = 4.8, 2.4 Hz), 25.3 (P-*C*, dd, *J* = 28.1 13.4 Hz), 29.5 (C(α), dd, *J* = 58.6 19.5 Hz), 29.8 (P-*C*, dd, *J* = 29.3 22.0 Hz), 41.3 (C(β), dd, *J* = 3.7 2.4 Hz), 195 (C=O, d, *J* = 13.2 Hz)
2		1570 (vs)			
3a	3450 (m), 3330 (m), 3170 (m)	1670 (s), 1605 (s)			
3b	3500 (m), 3400 (m), 3300 (m)	1645 (s), 1580 (s)	1.36 (3 H, d, *J* = 6 Hz, CH_3), 2.16 (1 H, m, =CH), 3.22 (1 H, m, =CH), 4.23 (2 H, br, NH_2), 6.9–7.3 (30 H, C_6H_5)	29.6 (d, *J* = 35, Hz), 35.6 (d, *J* = 35 Hz)	
3c	3400 (m), 3200 (m)	1640 (s), 1580 (s)	0.6–2.0 (33 H, m, CH_3, PEt_3), 5.04 (1 H, m, =CH), 5.46 (1 H, m, =CH)		
3e	3450 (m), 3350 (m)	1640 (s), 1580 (s)	2.16 (1.5 H, br, CH_3), 2.86 (6 H, s, P-CH_2), 5.47 (0.5 H, m, =CH), 6.18 (0.5 H, m, =CH), 7.2–7.6 (m, C_6H_5)		

[a] Downfield positive. ^{1}H and ^{13}C NMR from internal Me_4Si and ^{31}P NMR from exteral H_3PO_4. Solvent: toluene-d_8 for 1b-d_{33}, CD_2Cl_2 for 1f and 1g, C_6D_6 for 3b and 3c, and pyridine-d_5 for 3e.
[b] For the coupling pattern see Figure 2.

Table III. Products of the Reactions of 1a–g and 2 with CO

complex	imide, % yield	^{1}H NMR data of imide, δ	$NiL_n(CO)_{4-n}$	IR data of $NiL_n(CO)_{4-n}$ ν(C=O), cm^{-1}
1a	succinimide, 100		Ni(P(c-Hx)$_3$)(CO)$_3$	
1b	3-methylsuccinimide, 100	1.39 (3 H, d, *J* = 7 Hz, CH_3), 2.42 (1 H, dd, *J* = 21, 9 Hz, CH_2[a]), 3.02 (1 H, dd, *J* = 21, 9 Hz, CH_2[a]), 2.96 (1 H, m, methine), 8.47, *J* = 21, 9 Hz), (1 H, br, NH)	Ni(P(c-Hx)$_3$)(CO)$_3$	
1c	*N*-methyl-3-methylsuccinimide, 93	1.36 (3 H, d, *J* = 7 Hz, CH_3), 2.36 (1 H, dd, *J* = 21, 9 Hz, CH_2[a]), 2.93 (1 H, m, methine), 3.03 (3 H, s, N–CH_3)	Ni(P(c-Hx)$_3$)(CO)$_3$	
1d	*N*-phenyl-3-methylsuccinimide, 82	1.46 (3 H, d, *J* = 7 Hz, CH_3), 2.49 (1 H, dd, *J* = 22, 9 Hz, CH_2[a]), 3.10 (1 H, dd, *J* = 22, 9 Hz, CH_2[a]), 3.05 (1 H, m, methine), 7.3–7.6 (5 H, m, C_6H_5)	Ni(P(c-Hx)$_3$)(CO)$_3$	
1e	3-methylsuccinimide, 81		Ni(PEt(*t*-Bu)$_2$)(CO)$_3$	2055[b] 1980[b]
1f	3-methylsuccinimide, 100		Ni(PEt$_3$)(CO)$_3$	
1g	3-methylsuccinimide, 99		Ni(dpe)(CO)$_2$	

[a] It was not feasible to assign each signal to cis or trans H to CH_3. [b] In KBr disk.

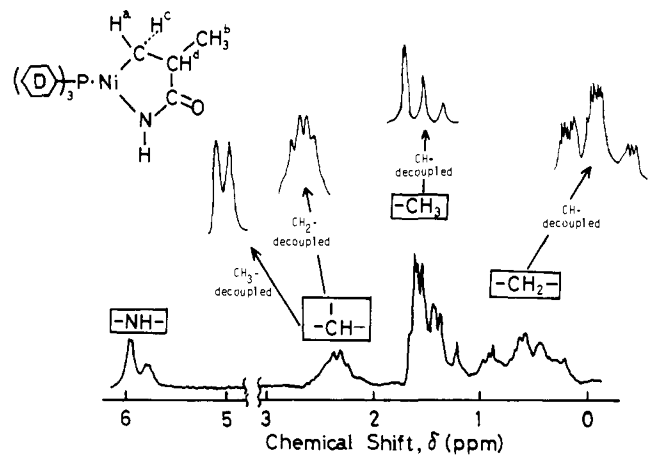


Figure 3. ^{1}H NMR spectrum of **1b-*d*$_{33}$** in toluene-d_8 at 25 °C.

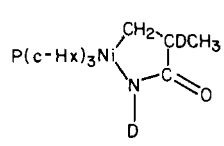
The methine proton in the cyclic structure gives rise to a signal at a somewhat higher field than the ones in usual organic amides, whereas the CH_3 proton gives rise to a doublet at an ordinary position. The signal of the N–H proton appears as a broad triplet at a somewhat higher field than that of the N–H proton in organic amides, suggesting some diamagnetic shielding by nickel.

The assignment of the signals in ^{1}H NMR spectra of **1b–*d*$_{33}$** and **1f** is essentially the same as that of **1g**, although the H^a, H^b, H^c, and H^d signals showed very complex patterns due to not only the couplings with the other protons and ^{31}P but also the trinuclear structure as depicted in Figure 1.

In the ^{1}H NMR spectrum of **1b-*d*$_{33}$** (Figure 3) the N–H signal is split into two peaks and the H^d-decoupled signal of H^b into three peaks with different peak areas. These splittings may be due to the presence of some stereoisomers. If **1b** has a trinuclear structure as depicted in Figure 1, there may exist some stereoisomers due to the chiral center in each monomer unit. It is also possible that boat and chair forms exist concerning the central six-membered ring, giving rise to further complication of the spectra.

By employing methacrylamide-*N,N*-d_2 as the starting material in eq 3, one obtains **1b-*d*$_2$**, whose ^{1}H NMR spectrum shows disappearance of the signals of H^d and N–H, demonstrating not only that the assignments are reasonable but also that H^d comes from NH$_2$ of methacrylamide (eq 5).

$$Ni(cod)_2 + P(c\text{-}Hx)_3 + H_2C{=}C(CH_3)COND_2 \longrightarrow$$



(5)

1b-*d*$_2$

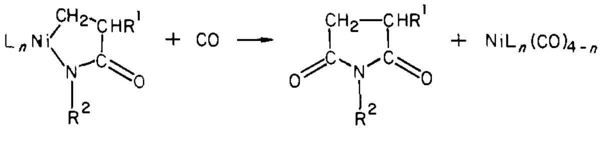
^{31}P NMR. The ^{31}P{^{1}H} NMR spectrum of **1g** in CD$_2$Cl$_2$ at room temperature shows two doublets with the same peak areas at 61.69 and 46.66 ppm downfield from external H$_3$PO$_4$, the pattern being reasonable for the square-planar structure and indicating that the phosphine ligand is tightly bonded to nickel on NMR time scale. The doublet at 46.66 ppm is sharp enough (half width = 1.2 Hz), but the one at 61.69 ppm is somewhat broadened (half width = 2.6 Hz), implying that the latter doublet is due to phosphorus located at the trans position to nitrogen which makes the doublet broad due to its spin and quadrupole.

The ^{31}P{^{1}H} NMR spectra of **1b** and **1f** showed a multiplet presumably composed of several sets of singlet(s), doublet(s), triplets(s), etc.[14] The results may be explained by assuming the trinuclear structure in which the presence of several magnetically nonequivalent ^{31}P nuclei is possible due to the chirality in each monomer unit.

^{13}C NMR. Figure 4 shows the ^{13}C{^{1}H} NMR spectrum of **1g**. The signals of the CH$_2$ carbons of the dpe ligand (C(v) and C(w) in Figure 4) were assigned unequivocally by comparing the ^{13}C{^{1}H} NMR spectrum of **1g** with that of **1g-*d*$_4$**. In the latter spectrum the signals of the dpe CH$_2$ carbons virtually disappeared due to the lack of NOE. As for the two CH$_2$ carbons of dpe, it was not determined which CH$_2$ group (C(v) or C(w) in Figure 4) gives rise to the signal at a higher magnetic field.

The signals of CH$_3$ (C(γ)), CH$_2$ (C(α)), CH (C(β)), and C=O carbons of the nickel-containing cyclic ring were assigned on the basis of their chemical shifts and the magnitudes of the ^{13}C–^{31}P coupling constants. It is noteworthy that the magnitude of the coupling constant between ^{31}P and ^{13}C(α) is larger than that of ^{31}P and ^{13}C which is adjacent to ^{31}P in the diphosphine ligand. The ^{13}C{^{1}H} NMR spectrum of **1f** shows essentially the same pattern for carbons in the nickel-containing cyclic amide. The C(α) adjacent to Ni in **1f** gives rise to a double doublet due to couplings with ^{31}P in the same monomer unit in the postulated trinuclear complex and with ^{31}P in one of the other two monomer units.

Reaction with Carbon Monoxide. The nickel-containing cyclic amide complexes smoothly react with carbon monoxide at room temperature to give succinimides in almost quantitative yields (eq 6). Table III summarizes the results of the reactions. IR and/or NMR data are also included for several products for which the data have not been reported. The formation of succinimides can be most reasonably explained by assuming a reaction pathway involving initial insertion of CO into the Ni–C bond and ensuing reductive elimination of the imide. It is known that CO is inserted into Ni-C bonds of alkyl(imido)nickel(II) complexes to yield acyl(imido)nickel(II) complexes[15] and that metallacyclic compounds give cyclic ketones on reaction with CO.[1c,2b] The reaction of **1b-*d*$_2$** with CO gives 3-methylsuccinimide-*1,3*-d_2.

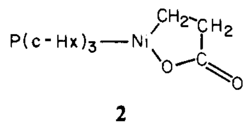


(6)

The Co$_2$(CO)$_8$-catalyzed preparation of succinimides from α,β-unsaturated amides and CO under severe conditions has been reported[16] and the results obtained here suggest the formation of an intermediate cobaltacyclic amide under these catalytic conditions.

Preparation, Characterization, and Properties of Nickel-Containing Cyclic Ester Complexes. Similar to the reaction of α,β-unsaturated amides with Ni(cod)$_2$, the reaction of acrylic acid with Ni(cod)$_2$ in the presence of P(c-Hx)$_3$ affords a yellow nickel-containing cyclic compound, **2**, at 5 °C, **2** having moderate stabilities to air (eq 7). The product of the reaction of acrylic acid with the Ni(cod)$_2$–P(c-Hx)$_3$ mixture, however, depends on

$$Ni(cod)_2 + CH_2{=}CHCOOH + P(c\text{-}Hx)_3 \xrightarrow{5\ ^\circ C}$$



(7)

2

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(13) (a) Jackman, L. M.; Sternhell, S. "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry"; Pergamon Press: Oxford, 1969. (b) Lemieux, R. U.; Lown, W. J. *Can. J. Chem.* **1964**, *42*, 893.

(14) The ^{31}P{^{1}H} NMR spectrum of **1b** in benzene seemingly shows 7 peaks in which at least one triplet (31.53 ppm downfield from H$_3$PO$_4$, J = 29.3 Hz) seems to be included. The ^{31}P{^{1}H} NMR spectrum of **1f** seemingly shows 9 peaks in which at least one triplet (21.48 ppm, J = 12.2 Hz) seems to be included.

(15) Kohara, T.; Komiya, S.; Yamamoto, T.; Yamamoto, A. *Chem. Lett.* **1979**, 1513.

(16) (a) Falbe, J.; Korte, F. *Chem. Ber.* **1962**, *95*, 2680. (b) Heck, R. F. "Organotransition Metal Chemistry"; Academic Press: New York, 1974. (c) Falbe, J. "Carbon Monoxide in Organic Synthesis"; Springer-Verlag: West Berlin, 1970. (d) Tsuji, J. "Organic Synthesis by Means of Transition Metal Complexes"; Springer-Verlag: West Berlin, 1975.

(17) Weiss, E.; Stark, K.; Lancaster, J. E.; Murdoch, H. D. *Helv. Chim. Acta* 1963, *46*, 288.

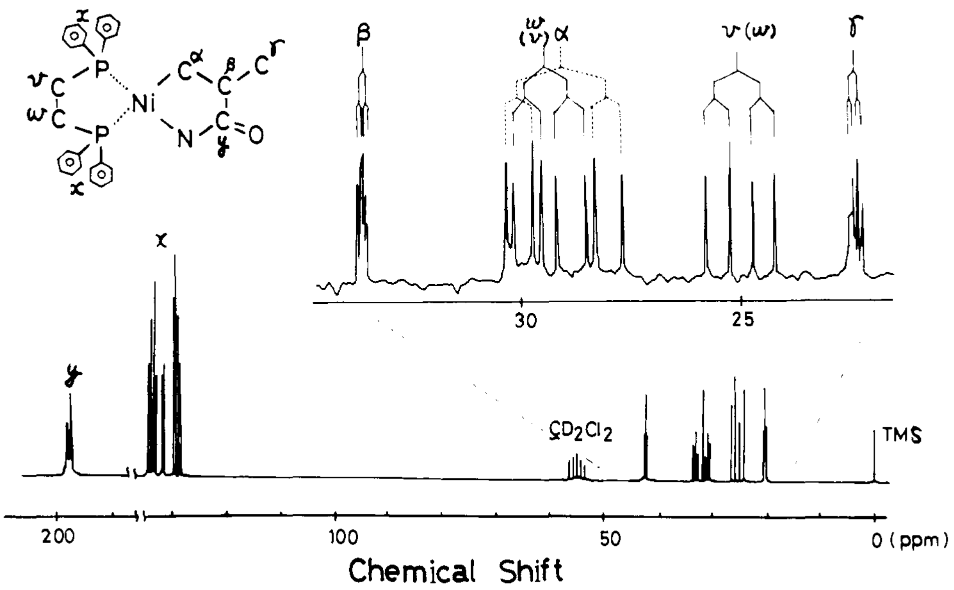

Figure 4. $^{13}C\{^1H\}$ NMR spectrum of **1g** in CD_2Cl_2 at 25 °C.

the reaction temperature; carrying out the reaction at -10 to 0 °C affords a ca. 1:1 mixture of **2** and a π-type complex, whereas carrying out the reaction above 20 °C led to the polymerization of acrylic acid. Physical properties and analytical data of **2** are given in Table I. Employment of methacrylic acid in the reaction with the $Ni(cod)_2$–$P(c\text{-}Hx)_3$ mixture also afforded a similar nickel-containing cyclic ester type complex as judged from its IR spectrum (ν(C=O) at 1565 cm^{-1}) and formation of 3-methylsuccinic anhydride on its reaction with CO. However, full characterization of the complex was not feasible due to the difficulties in isolating an analytically pure compound from the reaction mixture.

The IR spectrum of **2** shows a sharp strong ν(C=O) band at 1570 cm^{-1} but no ν(O–H) band which is observed in IR spectra of π-acrylic acid complexes.[17] Complex **2** is scarcely soluble in organic solvents and not amenable to a structural study by means of NMR spectroscopy. Complex **2** smoothly reacts with CO at room temperature to give succinic anhydride in 64% yield, supporting the nickel-containing cyclic ester structure. The reaction is proposed to proceed through a similar reaction pathway proposed for the reaction of nickel-containing cyclic amide complexes with CO.

Preparation, Characterization, and Properties of π-Type Complexes. Addition of a less basic and/or less stereodemanding phosphine ligand than $P(c\text{-}Hx)_3$ and $PEt(t\text{-}Bu)_2$ in the reaction of α,β-unsaturated amide with $Ni(cod)_2$ did not lead to the formation of the nickel-containing cyclic amide complex, but the reaction gave usual π-type complexes over a wide range of preparative conditions (eq 8).

$$Ni(cod)_2 + CH_2{=}C(R^1)CONH_2 + PR_3 \rightarrow Ni(PR_3)_m(CH_2{=}C(R^1)CONH_2)_n \quad (8)$$

	PR_3	m	R^1	n
3a	$P(c\text{-}Hx)_3$	1	H	2
3b	$PPh_3{}^a$	2	CH_3	1
3c	$PEt_3{}^b$	2	CH_3	1
3d[c]	$PBz_3{}^d$	1	CH_3	1/2

[a] PPh_3 = triphenylphosphine. [b] PEt_3 = triethylphosphine. [c] 3d is supposed to have a binuclear structure. [d] PBz_3 = tribenzylphosphine.

In contrast to the sharp singlet absorption band in the amide region (ν(C=O) + δ(N–H)) in the IR spectrum of the nickel-containing cyclic complexes **1a–g**, the IR spectra of the π-type complexes show two absorption bands in the amide region, amide I and amide II, which are shifted by 0–35 cm^{-1} from the original frequencies on coordination. The appearance of the two absorption bands in the amide region can be employed as a simple convenient criterion of the formation of the π-type complex.

The ^1H NMR spectrum of **3b** shows the signal of the N–H proton at δ 4.23 with a relative peak area of 2 H, excluding the possibility of the formation of the nickel-containing cyclic amide type complex. In the ^1H NMR spectrum of **3b**, the signals of the olefinic protons of methacrylamide shift on complex formation with $Ni(PPh_3)_2$ to the upfield region where the signals of olefinic protons in usual π-type transition metal–olefin complexes are observed.[10b,18] In addition to the signals due to methacrylamide coordinated to Ni, the ^1H NMR spectrum of **3b** shows small signals due to free methacrylamide, indicating partial dissociation of methacrylamide from **3b** in benzene. Both sets of signals are sharp enough, excluding the possibility of rapid exchange between the coordinating methacrylamide and free methacrylamide on NMR time scale. The ^1H NMR spectra of **3c** and **3d** are also consistent with the structures. It is noteworthy that **1f** can be prepared as a stable compound by the ligand-exchange reaction between **1b** and PEt_3, whereas the direct reaction of methacrylamide with $Ni(cod)_2$ in the presence of PEt_3 gives the π-type complex **3c**.

Reactions of the π-type complexes with CO lead to a simple ligand-exchange reaction to liberate α,β-unsaturated amide almost quantitatively (Table I) with formation of $Ni(PR_3)_m(CO)_{4-m}$. $Ni(cod)_2$–dimethylphenylphosphine (PMe_2Ph)–methacrylamide and $Ni(cod)_2$–$P(c\text{-}Hx)_3$–cinnamamide systems also afforded similar π-type complexes as judged from appearance of amide I and amide II bands in the IR spectra of the products as well as from liberation of the corresponding amide on reactions with CO. However, isolation of analytically pure complexes from the systems was not feasible.

In contrast to the reaction of acrylic acid with the $Ni(cod)_2$–$P(c\text{-}Hx)_3$ mixture at 5 °C leading to the formation of **2**, carrying out the same reaction at -10 °C leads to the formation of a ca. 1:1 mixture of **2** and a π-type complex probably formulated as $Ni(P(c\text{-}Hx)_3)(CH_2{=}CHCOOH)$. The mixture is very air-sensitive and burns up on exposure to air. The IR spectrum of the mixture shows a broad ν(O–H) band in a region of 3500–2500 cm^{-1} and a ν(C=O) band at 1660 cm^{-1} besides the ν(C=O) band of **2**. When a THF solution of the mixture stood at 10 °C, most of the π-type complex was converted into **2** as proved by the IR spectrum of the product.

Interconversion between the Nickel-Containing Cyclic Complexes and the π-Type Complexes. Heating the π-type complex **3a** in

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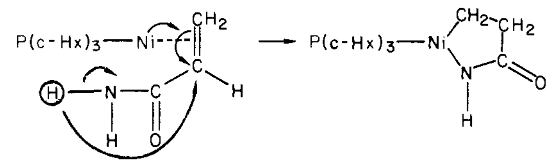
[18] Herberhold, M. "Metal π-Complexes"; Elsevier: Amsterdam, 1972; Vol. II.

[19] Henderson, W. A.; Buckler, S. A. *J. Am. Chem. Soc.* **1960**, *82*, 5794.

[20] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

Scheme I



THF under reflux causes the conversion of **3a** to **1a** with liberation of 1 mol of acrylamide (eq 9). Since the direct reaction of a 1:1:1

$$\mathbf{3a} \xrightarrow[\text{6 h}]{\text{THF, reflux}} \mathbf{1a} + \mathrm{CH_2{=}CHCONH_2} \qquad (9)$$

$$\text{yield} = 70\%$$

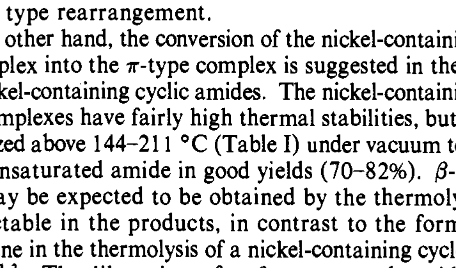
mixture of $Ni(cod)_2$, $P(c\text{-}Hx)_3$, and acrylamide affords **1a** as described in eq 3, the conversion of **3a** to **1a** most probably proceeds through dissociation of one of the acrylamide ligands in **3a** to form $Ni(P(c\text{-}Hx)_3)(\pi\text{-acrylamide})$ and ensuing intramolecular Michael reaction type rearrangement of the intermediate π-type complex into **1a** (Scheme I). The conversion of the π-acrylic acid complex into **2** is also supposed to proceed through a similar type rearrangement.

On the other hand, the conversion of the nickel-containing cyclic type complex into the π-type complex is suggested in thermolysis of the nickel-containing cyclic amides. The nickel-containing cyclic amide complexes have fairly high thermal stabilities, but they are thermolyzed above 144–211 °C (Table I) under vacuum to liberate the α,β-unsaturated amide in good yields (70–82%). β-Lactams which may be expected to be obtained by the thermolysis were not detectable in the products, in contrast to the formation of cyclobutane in the thermolysis of a nickel-containing cyclopentane complex.[1,3] The liberation of α,β-unsaturated amide in the thermolysis of the nickel-containing cyclic amide complex seems to proceed through a reverse type bond rearrangement of the one depicted in Scheme I at high temperature with ensuing dissociation of the α,β-unsaturated amide ligand.

These results indicate that the π-type complex and the nickel-containing cyclic amide complex can interconvert.

Factors Controlling the Formation of the Nickel-Containing Cyclic Complexes. As described above employment of a phosphine having a high basicity and a large cone angle is required to yield the nickel-containing cyclic amide complex.

Effect of the Basicity of Phosphine. On the basis of ^1H and ^{13}C NMR studies[9] as well as structural analysis by X-ray crystallography[21] of $Ni(PR_3)_2$(ethyl methacrylate), we have proposed the mixing of the following canonical structures I and II in the



I II

ground state and that the degree of the contribution of II increases with increase in the basicity of PR_3. A similar resonance is also conceivable with the π-type nickel–α,β-unsaturated amide complex, and if the formation of the nickel-containing cyclic amide complex proceeds through the bond rearrangement depicted in Scheme I, which is triggered by the intramolecular Michael reaction type shift of proton to the β-carbon, the increase in the basicity of phosphine ligand is expected to enhance the formation of the nickel-containing cyclic amide complex. This view accounts for the difference in the products between the reaction in the presence of $P(c\text{-}Hx)_3$ ($pK_a = 9.05$,[19] cone angle (θ) = 170°[20]) or $PEt(t\text{-}Bu)_2$ ($pK_a = 9.52$, $\theta = 170°$) and that in the presence of PBz_3 ($pK_a = 5.31$, $\theta = 165°$).

Effect of the Bulkiness of Phosphine. The CPK molecular model shows that the nickel-containing cyclic structure demands larger space around nickel than the π-type structure. This may seem to be a contradiction with the fact that addition of a highly stereodemanding phosphine ligand is required for the nickel-containing cyclic amide complex to be produced. However, the following observations concerning π-type nickel–olefin complexes reveal that the π-olefin ligand has larger space around nickel when highly stereodemanding phosphine such as $P(c\text{-}Hx)_3$ is employed. (i) Employment of a highly stereodemanding phosphine produces nickel–olefin complexes with one phosphine ligand such as $Ni(P(c\text{-}Hx)_3)$(ethyl methacrylate)[9] and $Ni(P(c\text{-}Hx)_3)$(acrylaldehyde)[10] even in the reaction using excess phosphine. (ii) Employment of less stereodemanding phosphine such as PEt_3 ($pK_a = 8.65$, $\theta = 132°$), on the contrary, produces nickel complexes with two phosphine ligands coordinated such as $Ni(PEt_3)_2$(ethyl methacrylate)[9] and $Ni(PEt_3)_2(CH_2{=}CH_2)$.[22] In the present $Ni(cod)_2$–PEt_3–methacrylamide system addition of 1 mol of $PEt_3/Ni(cod)_2$ did not lead to the formation of nickel complex with one PEt_3 ligand ($Ni(PEt_3)$(methacrylamide)), but it gave a 1:1 mixture of $Ni(PEt_3)_2$(methacrylamide) and intact $Ni(cod)_2$, indicating that $Ni(PEt_3)$(methacrylamide) is not a stable species.

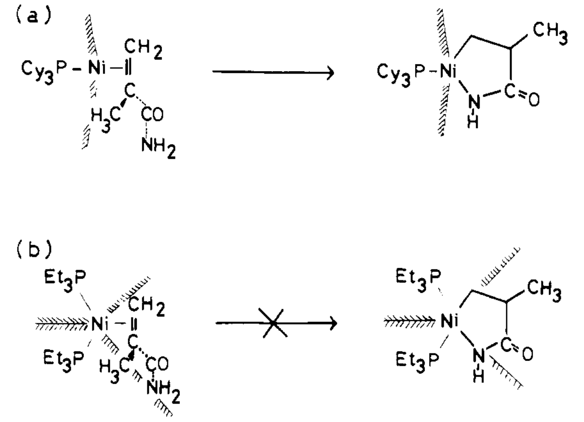


Figure 5. Circumstances around the methacrylamide ligand in the π-type complex: (a) for phosphine = $P(c\text{-}Hx)_3$; (b) for phosphine = PEt_3. In (a) Cy_3P is $P(c\text{-}Hx)_3$.

Figure 5 depicts the circumstances around the methacrylamide ligand in the π-type complex formed in the $Ni(cod)_2$–PR_3–methacrylamide system on the basis of the observations described above. It is seen that the bond rearrangement as assumed in Scheme I cannot proceed for steric reasons when PEt_3 is employed as the ligand.

The observations concerning the $Ni(cod)_2$–$P(c\text{-}Hx)_3$–acrylamide system also support the view that the steric freedom around the α,β-unsaturated amide ligand is essential. Since acrylamide is a smaller molecule than methacrylamide and has a stronger coordinating ability to Ni(0) complexes,[8] two molecules of acrylamide can coordinate to $Ni(P(c\text{-}Hx)_3)$ to form $Ni(P(c\text{-}Hx)_3)(\text{acrylamide})_2$, which will not be able to rearrange to the nickel-containing cyclic amide complex due to the sterically packed structure. However, liberation of one acrylamide lignd will give the remaining coordinating acrylamide ligand steric freedom and the rearrangement will proceed.

The present view implies that kinetic factors rather than thermodynamic factors control the conversion of the π-type complex into the nickel-containing cyclic complex. This is actually demonstrated by the fact that **1f** once produced is stable enough although **1f** could not be obtained by the direct reaction of methacrylamide with $Ni(cod)_2$ in the presence of PEt_3.

An alternative reaction pathway to the formation of the nickel-containing cyclic complexes is the one involving an oxidative addition of the N—H bond of α,β-unsaturated amide and ensuing insertion of the C=C double bond into the Ni—C bond. This also seems to be plausible since oxidative addition of the N—H bond to transition-metal complexes is known.[23] However, we

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[21] Komiya, S.; Ishizu, J.; Yamamoto, A.; Yamamoto, T.; Takenaka, A.; Sasada Y. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1283.

[22] Wilke, G.; Hermann, G. *Angew. Chem.* **1962**, *74*, 693.

[23] (a) Roundhill, D. M. *J. Chem. Soc., Chem. Commun.* **1969**, 567. (b) *Inorg. Chem.* **1970**, *9*, 254.

rather prefer the reaction pathway involving the intramolecular Michael reaction type rearrangement in the π-type complex to the alternative one since 1,5-cyclooctadiene, which is easily converted into its isomers when it is treated with reaction systems generating the Ni—H species,[24] was not isomerized in the course of the present reactions.

Conclusions and Scope

Reactions of α,β-unsaturated amides and acids with $Ni(cod)_2$ in the presence of highly stereodemanding phosphine ligands with a high basicity lead to the formation of the nickel-containing cyclic amide and ester complexes, respectively. The reaction seems to proceed through the bond rearrangement in the usual π-type complex. The conversion of the complexes into succinimides and succinic anhydrides suggests a possibility to develop a nickel-catalyzed process to form the organic compounds from α,β-unsaturated amides or acids and CO under mild conditions. If unsaturated molecules such as acetylenes and olefins can be inserted into the Ni–C or Ni–N(Ni–O) bond in the nickel-containing cyclic complex, development of a new process to produce lactams or lactones from α,β-unsaturated amides or acids and the unsaturated reactants may become possible.

Experimental Section

Material and General Procedures. PPh_3 and PEt_3 were used as purchased. $P(c\text{-}Hx)_3$,[25] PBz_3,[26] dpe,[27] and $PEt(t\text{-}Bu)_2$[28] were synthesized by the methods given in literature. $P(c\text{-}Hx)_3\text{-}d_{33}$ was prepared by the reaction of PCl_3 with cyclohexylmagnesium-d_{11} bromide derived from bromocyclohexane-d_{11} which was synthesized by the reaction of cyclohexane-d_{12} with Br_2–HgO.[29] dpe-d_4 was prepared by using dibromoethane-d_4 purchased from Merck Co., Ltd. Acrylamide, methacrylamide, crotonamide, cinnamamide, acrylic acid, and methacrylic acid were purchased from Tokyo Kasei Co., Ltd., and purified by distillation or recrystallization. *N*-Methylmethacryalmide was prepared according to a method given in literature.[30] *N*-Phenylmethacrylamide was synthesized by adding a benzene solution of methacryl chloride (27 g) to a mixture of aniline (24 g) and an aqueous solution (50 mL) of NaOH (43 g) at 0 °C. Recrystallization from ethyl acetate gave analytically pure *N*-methylmethacrylamide (yield = 67%). Methacrylamide-*N*,*N*-d_2 was prepared by repeated H–D exchange of methacrylamide-d_0 with D_2O at 55 °C. $Ni(cod)_2$ was purchased from Merck Co., Ltd., and recrystallized before use. Preparation and recrystallization of the complexes were carried out under deoxygenated nitrogen or argon. Solvents were dried by the usual methods, distilled under N_2, and stored under N_2.

Preparation of Nickel-Containing Cyclic Amide Complexes. 1a. A THF (10 mL) solution of a mixture of $Ni(cod)_2$ (1.1 g, 4.1 mmol), $P(c\text{-}Hx)_3$ (1.1 g, 4.0 mmol), and acrylamide (0.30 g, 4.2 mmol) was stirred for 2 h to obtain greenish yellow powder suspended in a deep greenish yellow solution. The reaction mixture was allowed to stand at −40 °C for 1 day, and a greenish yellow precipitate was separated by filtration. Washing the precipitate with CH_2Cl_2 gave **1a** (1.2 g, yield = 69%).

1b–e. $Ni(cod)_2$ (0.57 g, 2.1 mmol), $P(c\text{-}Hx)_3$ (0.58 g, 2.1 mmol), and methacrylamide (0.35 g, 4.0 mmol) were dissolved in 7 mL of THF, and the solution was stirred for 6 h to obtain a greenish yellow precipitate. After the precipitate was washed by diethyl ether, it was dissolved in hot toluene (60 °C). Cooling the solution to room temperature gave greenish yellow crystals of **1b** (0.58 g, yield = 65%). Preparations of **1c**, **1d**, and **1e** were carried out in similar manners to that of **1b** and yields were 59%, 63%, and 60%, respectively.

1f. PEt_3 (4.5 mL, 31 mmol) was added to a toluene (25 mL) solution of **1b** (0.54 g, 1.3 mmol). After the mixture was stirred for 12 h, the homogeneous solution obtained was cooled to −78 °C to precipitate $P(c\text{-}Hx)_3$. After $P(c\text{-}Hx)_3$ was separated by filtration, the remaining solution was condensed to about 8 mL by evaporation and the condensed solution was cooled to −78 °C to yield a yellow precipitate. Recrystallization from a mixture of benzene and hexane gave 0.22 g (yield = 64%) of **1f**. The reaction of methacrylamide with $Ni(cod)_2$ in the presence of PEt_3 afforded the π-type complex, but **1f** was not obtained by the reaction.

1g. 1,2-Bis(diphenylphosphino)ethane, dpe (0.60 g, 1.5 mmol), was added to a toluene (30 mL) solution of **1b** (0.63 g, 1.5 mmol), and the mixture was stirred for 12 h to yield a pale yellow precipitate, which was separated by filtration. Recrystallization from CH_2Cl_2–hexane gave 0.74 g (yield = 91%) of **1g**. The reaction of methacrylamide with $Ni(cod)_2$ in the presence of dpe did not give **1g**, but the reaction gave a complex having cod and dpe ligands (presumably Ni(cod)(dpe) as judged by its IR spectrum).

Reaction of Crotonamide with $Ni(cod)_2$ in the Presence of $P(c\text{-}Hx)_3$. $Ni(cod)_2$ (1.4 g, 5.3 mmol), $P(c\text{-}Hx)_3$ (1.6 g, 5.6 mmol), and crotonamide (0.46 g, 5.4 mmol) were dissolved in 15 mL of methyl alcohol. The solution was stirred for 4 days at room temperature to yield an orange precipitate, which was separated by filtration and washed by hexane and diethyl ether. The IR spectrum showed not only a strong band at 1572 cm^{-1} characteristic of the nickel-containing cyclic amide type complex but also a weak band at 1650 cm^{-1} assignable to the amide I band of the π-type complex (the amide II band seems to be hidden in the strong band at 1572 cm^{-1}), suggesting contamination of $(P(c\text{-}Hx)_3)NiCH(CH_3)CH_2CONH$ with a π-type complex. Formation of 3-methylsuccinimide by the reaction of the product with CO as the major product also supports the formation of the nickel-containing cyclic amide complex, but isolation of the complex was not feasible due to lack of suitable solvent for recrystallization. A similar product was obtained by the same reaction in ethyl alcohol. However, the reaction did not proceed in organic solvents other than alcohols, probably due to insolubility of crotonamide in the solvents.

Preparation of 2. Acrylic acid (0.22 mL, 3.2 mmol) was added to a THF (8 mL) solution containing $Ni(cod)_2$ (0.78 g, 2.8 mmol) and $P(c\text{-}Hx)_3$ (0.81 g, 2.9 mmol) at 5 °C. Stirring of the solution for 12 h gave a yellow precipitate of **2**, which was purified by washing with diethyl ether repeatedly; yield = 0.43 g (35%). The product of the reaction was sensitive to temperature. Carrying out the same reaction at 20 °C led to polymerization of acrylic acid, and the reaction at −10 to 0 °C afforded a yellow precipitate whose IR spectrum showed not only the absorption bands of **2** (ν(C=O) at 1570 cm^{-1}) but also absorption bands characteristic of π-type complexes of acrylic acid[17] at 3500–2500 (ν(O—H)) and 1660 cm^{-1} (ν(C=O)). No reaction proceeded below −40 °C, and $Ni(cod)_2$ was recovered.

Preparation of π-type Complexes of α,β-Unsaturated Amides. 3a. $Ni(cod)_2$ (0.62 g, 2.3 mmol), $P(c\text{-}Hx)_3$ (1.0 g, 3.6 mmol), and acrylamide (0.48 g, 6.8 mmol) were dissolved in THF, and the solution was stirred for 3 h to obtain a yellow precipitate. Washing by THF and diethyl ether gave **3a** (1.0 g, 91%).

3b. $Ni(cod)_2$ (0.62 g, 2.3 mmol), PPh_3 (1.2 g, 4.5 mmol), and methacrylamide (0.38 g, 4.5 mmol) were dissolved in 8 mL of THF, and the solution was stirred for 20 min. After a small amount of hexane was added, the solution was cooled to −78 °C to obtain yellow needles. Recrystallization from hot toluene afforded **3b** (1.2 g, 82%).

3c and 3d. They were prepared in similar manners to **3a** and **3b**, and the yields were 40% and 63%, respectively. Complex **3d** was recovered by recrystallization from THF containing excess methacrylamide, excluding a possibility that **3d** is a mixture of $Ni(PBz_3)$(π-methacrylamide) and $Ni(PBz_3)$.

Other π-Type Complexes. The reaction of methacrylamide (0.60 g, 7.0 mmol) with $Ni(cod)_2$ (0.92 g, 3.3 mmol) in the presence of PMe_2Ph (0.48 g, 3.3 mmol) in 7.5 mL of THF at room temperature afforded a very air-sensitive greenish yellow product with an approximate composition of $Ni(PMe_2Ph)_2$(methacrylamide) as the major product. Anal. Calcd: C, 52.4; H, 6.9; N, 7.6. Found: C, 49.8; H, 6.6; N, 7.0. The IR spectrum showed amide I and amide II bands at 1670 and 1600 cm^{-1}, respectively, indicating the formation of the π-type complex. The reaction of cinnamamide (0.68 g, 4.6 mmol) with $Ni(cod)_2$ (0.84 g, 3.1 mmol) in the presence of $P(c\text{-}Hx)_3$ (0.92 g, 3.2 mmol) in 10 mL of THF at room temperature afforded 0.83 g of a red product with an approximate composition of $Ni(P(c\text{-}Hx)_3)$(cinnamamide). Anal. Calcd: C, 66.7; H, 8.7; N, 2.9. Found: C, 65.8; H, 8.1; N, 3.8. The IR spectrum showed amide I and amide II bands at 1660 and 1570 cm^{-1}, respectively, indicating the formation of the π-type complex.

Analysis and Measurements of IR and NMR Spectra. Microanalyses of C, H, and N were performed by Mr. T. Saito in our laboratory with a Yanagimoto CHN autocorder Type MT-2. The analyses of products obtained in the reactions of complexes with CO and thermolyses were carried out with a Shimadzu GC-3BT gas chromatograph. Derivatives of succinimides produced by the reaction with CO were purified by recrystallization and characterized by IR and NMR spectroscopies (Table III). Relative sensitivities of the derivatives of succinimide in the GLC analysis were obtained by using the purified samples. IR spectra

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were recorded on a Hitachi Model 295 infrared spectrophotometer, ^1H NMR spectra on a Japan Electron Optics Laboratory (JEOL) Model JNM-PS-100 spectrometer, and ^{31}P and ^{13}C NMR spectra on a JEOL Model JNM-PFT-PS-100 Fourier transform spectrometer.

Melting Point and Decomposition Point. They were measured under vacuum. No color change was observed at the melting point, whereas the complex generally turned black with emergence of bubbles at the decomposition point.

Reactions of the Complexes with CO. The gas in a Schlenk type flask containing 41 mg (0.10 mmol) of **1a** dispersed in 3 mL of diethyl ether was evacuated, and then CO was introduced into the flask. Stirring of the mixture for 3 h gave a white precipitate, which was separated by filtration and found to be $Ni(P(c\text{-}Hx)_3)(CO)_3$ from its IR spectrum.[9b,31] α-Pyrrolidone (7.5 μL, 0.098 mmol) was added to the solution as an internal standard, and the amount of succinimide formed by the reaction was determined on the basis of a relative peak area of succinimide to that of α-pyrrolidone in the gas chromatogram and a relative sensitivity of succinimide to that of α-pyrrolidone. The reactions of other complexes with CO were carried out in similar manners.

Thermolysis of Nickel-Containing Cyclic Amide Complexes. A Schlenk type flask containing 45 mg (0.11 mmol) of **1b** was connected to a vacuum line, and the gas in the flask was evacuated. The flask was immersed in an oil bath, which was heated to 230 °C. The color of the complex turned black at the temperature, and sublimination of a white solid was observed. After 1 h the flask was cooled to room temperature, and the GLC analysis of the sublimed product indicated the liberation of 0.069 mmol (63%) of methacrylamide. Thermolysis of **1g** (41 mg, 0.076 mmol) at 230 °C for 1 h gave methacrylamide (0.062 mmol, 82%). The thermolyses of other complexes were carried out in similar manners.

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Characterization of Reactions of Hydrogen with Coordinated Sulfido Ligands

M. Rakowski DuBois,* M. C. VanDerveer, D. L. DuBois, R. C. Haltiwanger, and W. K. Miller

Contribution from the Department of Chemistry, University of Colorado,
Boulder, Colorado 80309

Abstract: Complexes of the formula $[(CH_3)_nC_5H_{5-n}Mo(S)SH]_2$, where $n = 0$, 1, and 5, have been prepared by the reaction of hydrogen with several different cyclopentadienylmolybdenum derivatives containing sulfido ligands. These include the insoluble polymeric products $[Me_nCpMoS_x]_y$, resulting from the reaction of elemental sulfur with $[Me_nCpMo(CO)_3]_2$. Excess sulfur in these species is converted to hydrogen sulfide during the course of the reaction with hydrogen. The hydrosulfido complexes have been characterized by spectral methods, and several reactions of these complexes have been studied. The complex $[MeCpMo(S)SH]_2$ catalyzes HD exchange between H_2 and D_2 as well as between H_2 and D_2O. The reduction of elemental sulfur to hydrogen sulfide by H_2 is catalyzed by the SH complexes under mild homogeneous conditions. Ethylene and acetylene react with the complexes to displace hydrogen from the SH ligands and form derivatives with bridging dithiolate ligands. Alkyl- and arylthiols react with the SH complexes to form H_2S and derivatives of the formula $[Me_nCpMo(S)SR]_2$ where R = CH_3, C_2H_5, $i\text{-}C_3H_7$, and C_6H_5. Spectral data suggest that these complexes have the same gross structures as the SH compounds. A single crystal of the derivative with $n = 1$ and R = CH_3 has been characterized by an X-ray diffraction study. The compound crystallizes in the space group $P2_1/c$ with the cell dimensions $a = 7.794$ (3) Å, $b = 14.184$ (7) Å, $c = 7.805$ (2) Å, and $\beta = 100.03$ (3)°. All four sulfur atoms in the complex occupy positions bridging the two metal ions. The *S*-methyl groups are oriented on trans sulfur atoms so as to form a centrosymmetric isomer. The relationship between the chemistry of these new complexes and aspects of proposed mechanisms of the hydrodesulfurization catalysts are discussed.

introduction

The hydrodesulfurization reaction, which involves the hydrogenolysis of organosulfur compounds, e.g., reactions 1-3, is an

$$RSH + H_2 \rightarrow RH + H_2S \qquad (1)$$

$$RSR + 2H_2 \rightarrow 2RH + H_2S \qquad (2)$$

$$RSSR + 3H_2 \rightarrow 2RH + 2H_2S \qquad (3)$$

important catalytic process in the purification of petroleum products.[1,2] The heterogeneous systems which catalyze these reactions most often contain sulfided molybdenum and cobalt species supported on alumina. The surface composition of the catalysts[3-9] and the sites which participate in catalytic activity[3,9-13] have been the subjects of extensive studies. It is generally agreed that a molybdenum sulfide surface is the catalytic site for the hydrogenolysis reaction.[9-13] On the basis of kinetic and other studies, several workers have proposed mechanisms for the hydrogenolysis of thiophene which involve two types of sites on the sulfided catalyst surface.[10-13] One site is a coordination vacancy on the molybdenum ion which permits interaction of the organosulfur compound with the metal. The second type of sites are the surface sulfide ligands which are proposed to react with molecular hydrogen to form hydrosulfido ligands. The hydrogenolysis reaction involving carbon-sulfur bond rupture and hydrogen atom transfer is proposed to occur between the species adsorbed on these sites.

Despite the mechanistic proposals for the hydrodesulfurization catalysts described above, the reaction of molecular hydrogen with coordinated sulfido ligands in discrete metal complexes to form SH ligands or H_2S has not been observed previously. Known hydrosulfido complexes have most often been prepared by metathesis reactions with HS^- salts or with H_2S.[14-23] Hydrolysis

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