

H), 3.50–3.80 (m, 1 H), 2.58 (s, 3 H), 1.40–2.10 (m, 6 H).

Anal. Calcd for $C_{16}H_{18}O$: m/e^+ 226.135758. Found: m/e^+ 226.135719.

2,2'-Bis(2-((methylamino)carbonyl)ethyl)-4,4',5,5'-tetramethoxybiphenyl (75): from *N*-methyl-3-(3,4-dimethoxyphenyl)propionamide (mp (acetone) 68–70 °C; NMR ($CDCl_3$) δ 6.73 (s, 3 H), 6.27 (br s, 1 H), 3.82 (s, 6 H), 2.91 (t, 2 H), 2.75 (d, 3 H), 2.47 (t, 2 H); IR ($CHCl_3$) 3450, 2935, 1662, 1595 (weak) cm^{-1}), 3 mmol scale, 1–2 s reaction time; R_f (5% methanol/chloroform) 0.27; yield, 6%; mp (acetone) 216–217 °C; IR ($CHCl_3$) 3450, 1650 cm^{-1} ; NMR ($CDCl_3$) δ 6.80 (s, 2 H), 6.60 (s, 2 H), 5.80–6.10 (br s, 2 H), 3.90 (s, 6 H), 3.82 (s, 6 H), 2.76 (s, 3 H), 2.73 (t, 4 H), 2.70 (s, 3 H), 2.30 (t, 4 H).

Anal. Calcd for $C_{24}H_{32}N_2O_6$: C, 64.85; H, 7.26; N, 6.30. Found: C, 64.69; H, 7.14; N, 6.12.

2,2'-Bis(2-cyanoethyl)-4,4',5,5'-tetramethoxybiphenyl (77): from 3-(3,4-dimethoxyphenyl)propionitrile (oil, prepared from the corresponding acrylonitrile by Mg/methanol reduction; NMR ($CDCl_3$) δ 6.73–6.85 (m,

3 H), 3.88 (s, 3 H), 3.85 (s, 3 H), 2.88 (t, 2 H), 2.58 (t, 2 H); IR (neat) 2250, 1595, 1517 cm^{-1}), 10 mmol scale, 20 s reaction time. The crude material was passed through a silica gel filtration column ($CHCl_3$) and then chromatographed (silica gel, 5% acetone/chloroform) to give the biaryl 77: R_f (5% acetone/chloroform) 0.46; yield, 34%; mp (acetone/hexane) 169–171 °C; IR ($CHCl_3$) 2935, 2250, 1607 cm^{-1} ; NMR ($CDCl_3$) δ 6.87 (s, 2 H), 6.72 (s, 2 H), 3.93 (s, 6 H), 3.85 (s, 6 H), 2.30–2.95 (m, 8 H).

Anal. Calcd for $C_{22}H_{24}N_2O_4$: C, 69.46; H, 6.36; N, 7.36. Found: C, 69.24; H, 6.54; N, 7.21.

3-(3,4-Dimethoxy-5-hydroxyphenyl)propionitrile (78) was obtained from the above preparation: R_f 0.38; mp (carbon tetrachloride) 116–118 °C dec; yield, 49%; IR ($CHCl_3$) 3515, 2935, 2250, 1600 cm^{-1} ; NMR ($CDCl_3$) δ 6.43 (d, 1 H, $J = 2$ Hz), 6.34 (d, 1 H, $J = 2$ Hz), 6.10 (br s, 1 H), 3.86 (s, 6 H), 2.45–2.95 (m, 4 H).

Anal. Calcd for $C_{11}H_{13}O_3N$: m/e^+ 207.089537. Found: m/e^+ 207.089492.

Interaction of Nickel(0) Complexes with Allyl Carboxylates, Allyl Ethers, Allylic Alcohols, and Vinyl Acetate. π -Complex Formation and Oxidative Addition to Nickel Involving Cleavage of the Alkenyl–Oxygen Bond

Takakazu Yamamoto,* Junichi Ishizu, and Akio Yamamoto

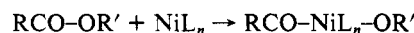
Contribution from the Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan. Received April 15, 1981

Abstract: Interaction of various allylic compounds with bis(1,5-cyclooctadiene)nickel, $Ni(cod)_2$, in the absence and presence of tertiary phosphines, causes cleavage of allyl–oxygen bonds. Allyl acetate reacts with $Ni(cod)_2$ to afford a mixture of $Ni(\eta^3-C_3H_5)_2$ and $Ni(OCOCH_3)_2$ presumably through an intermediate, allylnickel acetate, followed by its disproportionation. Similar reactions in the presence of tertiary phosphine ligands, PR_3 (triphenylphosphine (PPh_3), ethyldiphenylphosphine ($PEtPh_2$), tricyclohexylphosphine ($P-c-Hx_3$)), give $Ni(\eta^3-C_3H_5)(OCOCH_3)(PR_3)$ (1–3). Allyl formate can be catalytically converted into propylene and CO_2 at 25 °C by a $Ni(cod)_2-PPh_3$ mixture. A reaction of allyl phenyl ether with a mixture of $Ni(cod)_2$ and PPh_3 at 30 °C also leads to cleavage of the C–O bond to yield $Ni(\eta^3-C_3H_5)(OC_6H_5)(PPh_3)$ (4). Complexes 1–4 react with morpholine to produce *N*-allylmorpholine in 65–82% yields. On the other hand, similar reactions of diallyl ether with mixtures of $Ni(cod)_2$ and phosphine ligands do not cause C–O bond cleavage under mild conditions and yield complexes formulated as $Ni(\pi\text{-diallyl ether})(PR_3)$ ($PR_3 = PPh_3, P-c-Hx_3$) (5 and 6). Allylic alcohols $RCH=CHCH_2OH$ ($R = H, CH_3, C_6H_5$) are dismutated into $RCH=CHCH_3$, $RCH=CHCHO$, and H_2O on interaction with mixtures of $Ni(cod)_2$ and phosphines at 30–50 °C. The mixture of $Ni(cod)_2$ and PPh_3 serves as a catalyst for the allylation of morpholine by allyl alcohol. The C–O bond in vinyl acetate is also cleaved on interaction with $Ni(cod)_2$ alone or mixtures of $Ni(cod)_2$ and phosphines. Complexes 1–6 are characterized by elemental analysis and spectroscopy (IR and NMR). As for the mechanism of the C–O bond-cleavage reaction of allyl–oxygen compounds, one involving coordination of the allylic compound to Ni through the C=C double bond followed by a bond rearrangement involving C–O bond cleavage is proposed.

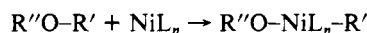
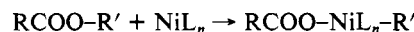
Oxidative addition of a substrate to a transition metal often constitutes a key elementary step in various catalytic reactions, and extensive studies were made on the oxidative addition of compounds such as alkyl halides and acyl halides to transition metals.¹

In comparison with oxidative addition reactions involving carbon–halogen bond cleavage those involving C–O bond cleavage of esters and ethers were much less explored.² In previous papers

we examined the C–O bond cleavage of aryl esters involving acyl–O scission promoted by Ni(0) complexes under mild conditions.^{3a,b}



We now report on other types of oxidative addition involving the allyl–O and vinyl–O bond cleavages of allyl carboxylates, vinyl acetate, allyl aryl ethers, and allylic alcohols.



$R = \text{alkyl or H, } R' = \text{allyl or vinyl group, } R'' = \text{aryl or H}$

The oxidative additions involving the allyl–carboxylate bond cleavage were recognized and utilized for organic synthesis^{1b,c,2b,h} and polymerization.^{2a} There are, however, very few examples

(1) For example: (a) Heck, R. F. "Organotransition Metal Chemistry"; Academic Press: New York, 1974. (b) Tsuji, J. "Organic Synthesis by Means of Transition Metal Complexes"; Springer-Verlag: West Berlin, 1977. (c) Trost, B. M. *Tetrahedron* 1977, 33, 2615. (d) Baker, R. *Chem. Rev.* 1973, 73, 487. (e) Olah, G. A.; Kreinenfuhr, P. *J. Org. Chem.* 1967, 32, 1614. (f) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980.

(2) (a) Dawans, F.; Marechal, J. C.; Teyssie, P. *J. Organomet. Chem.* 1970, 21, 259. (b) Chiusoli, C. P. *Proc. Int. Congr. Pure Appl. Chem.*, 23rd 1971, 6, 196. (c) Ittel, S. D.; Tolman, C. A.; English, A. D.; Jesson, J. P. *J. Am. Chem. Soc.* 1978, 100, 7577. (d) Tatsumi, T.; Tominaga, H.; Hidai, M.; Uchida, Y. *Chem. Lett.* 1977, 37. (e) Chiusoli, C. P.; Salerno, G.; Dallatomasina, F. *J. Chem. Soc., Chem. Commun.* 1977, 793. (f) Catellani, M.; Chiusoli, G. P.; Salerno, G.; Dallatomasina, F. *J. Organomet. Chem.* 1978, 146, C19. (g) Dawans, F.; Teyssie, P. *J. Polym. Sci., Part B* 1969, 7, 111. (h) Kurosawa, H. *J. Chem. Soc., Dalton Trans.* 1979, 939.

(3) (a) Ishizu, J.; Yamamoto, T.; Yamamoto, A. *Chem. Lett.* 1976, 1091. (b) Yamamoto, T.; Ishizu, J.; Kohara, T.; Komiya, S.; Yamamoto, A. *J. Am. Chem. Soc.* 1980, 102, 3758. (c) Yamamoto, T.; Ishizu, J.; Yamamoto, A. *Chem. Lett.* 1979, 991. (d) *Ibid.* 1979, 1385. (e) Ishizu, J.; Yamamoto, T.; Yamamoto, A. "Proceedings of the 25th Symposium on Organometallic Chemistry"; Osaka, Japan 1978; No. 208.

Table I. Products of Reactions of Allyl-Oxygen and Vinyl-Oxygen Compounds with Mixtures of Ni(cod)₂ and Ligands

expt	reactant ^a (mol/Ni)	ligand ^b (mol/Ni)	solvent ^c (mL/mL of reactant)	temp, °C	time, h	products ^d (% yield/Ni(cod) ₂)
1	CH ₂ =CHCH ₂ OCOCH ₃ (1.0)	none	ether (10)	10	2	Ni(η ³ -C ₃ H ₅) ₂ , ^e Ni(OCOCH ₃) ₂ (69)
2	CH ₂ =CHCH ₂ OCOCH ₃ (3.1)	PPh ₃ (2.0)	none	rt	12	Ni(η ³ -C ₃ H ₅)(OCOCH ₃)(PPh ₃), 1 (71)
3	CH ₂ =CHCH ₂ OCOCH ₃ (3.0)	PEtPh ₂ (1.5)	ether (4.0)	rt	48	Ni(η ³ -C ₃ H ₅)(OCOCH ₃)(PEtPh ₂), 2 (50)
4	CH ₂ =CHCH ₂ OCOCH ₃ (1.8)	P-c-Hx ₃ (1.5)	ether (1.0)	-5	48	Ni(η ³ -C ₃ H ₅)(OCOCH ₃)(P-c-Hx ₃), 3 (60)
5 ^f	CH ₂ =CHCH ₂ OCOCH ₃ (ex)	Ni(ema)(PPh ₃) ₂	none	-25	24	Ni(η ³ -C ₃ H ₅)(OCOCH ₃)(PPh ₃), ^e 1
6 ^f	CH ₂ =CHCH ₂ OCOCH ₃	Ni(ema)(P-c-Hx ₃)	none	rt	24	Ni(η ³ -C ₃ H ₅)(OCOCH ₃)(P-c-Hx ₃), 3 (90)
7	CH ₂ =CHCH ₂ OCOH (8.5)	PPh ₃ (2.1)	toluene (2.0)	25	26	C ₃ H ₆ (785), CO ₂ (234), NiCO ₂ complex ^e
8	CH ₂ =CHCH ₂ OC ₆ H ₅ (4.2)	PPh ₃ (1.1)	THF (2.5)	30	4	Ni(η ³ -C ₃ H ₅)(OC ₆ H ₅)(PPh ₃), 4 (81)
9	(CH ₂ =CHCH ₂ -) ₂ O (3.0)	PPh ₃ (1.0)	ether (0.8)	rt	12	Ni(π-diallyl ether)(PPh ₃), 5 (60)
10	(CH ₂ =CHCH ₂ -) ₂ O (3.0)	P-c-Hx ₃ (1.5)	ether (1.0)	-25	12	Ni(π-diallyl ether)(P-c-Hx ₃), 6 (66)
11	CH ₂ =CHCH ₂ OCH ₃ (7.7)	PPh ₃ (2.0)	toluene (2.6)	rt	48	Ni(cod)(PPh ₃) ₂ ^e
12	CH ₂ =CHCH ₂ OH (3.8)	PPh ₃ (2.2)	THF (4.9)	30	48	Ni(CH ₂ =CHCHO)(PPh ₃) ₂ (93), C ₃ H ₆ (97), H ₂ O (92)
13	CH ₂ =CHCH ₂ OH (ex)	P-c-Hx ₃ (1.0)	none	30	48	C ₃ H ₆ (51), H ₂ O, ^e polymer of CH ₂ =CHCHO
14	CH ₂ =CHCH ₂ OH (ex)	PMe ₂ Ph (2.0)	none	30	48	C ₃ H ₆ (93), H ₂ O, ^e polymer of CH ₂ =CHCHO
15	CH ₂ =CHCH ₂ OH (ex)	bpy (1.0)	THF (1.6)	30	7	C ₃ H ₆ (400), polymer of CH ₂ =CHCHO
16	CH ₂ =CHCH ₂ OH (ex)	none	none	30	11	C ₃ H ₆ (10), Ni metal
17	CH ₃ CH=CHCH ₂ OH (8.7)	PPh ₃ (2.1)	THF (4.0)	30	48	Ni(CH ₃ CH=CHCHO)(PPh ₃) ₂ (51), <i>t</i> -C ₄ H ₈ (44), <i>c</i> -C ₄ H ₈ (15), 1-C ₄ H ₈ (3), H ₂ O (51)
18	C ₆ H ₅ CH=CHCH ₂ OH (3.8)	PPh ₃ (2.2)	THF (2.1)	30	48	Ni(C ₆ H ₅ CH=CHCHO)(PPh ₃) ₂ , 7 (30), C ₆ H ₅ CH=CHCH ₃ (53), C ₆ H ₅ CH=CH ₂ (9), C ₆ H ₅ CH=CHCHO (tr), H ₂ O ^e
19	CH ₂ =CHCH ₂ OH (3.6) + CH ₃ CH=CHCH ₂ OH (3.6)	PPh ₃ (2.0)	THF (2.9)	50	6	C ₃ H ₆ (90), <i>t</i> -C ₄ H ₈ (0.1), a mixture of Ni-CH ₂ =CHCHO and -CH ₃ CH=CHCHO complexes ^e
20	CH ₂ =CHCH ₂ OH (4.5) + C ₆ H ₅ CH=CHCH ₂ OH (4.5)	PPh ₃ (2.0)	THF (2.6)	50	6	C ₆ H ₅ CH=CHCH ₃ (38), C ₆ H ₅ CH=CH ₂ (57), C ₃ H ₆ (24), Ni-CH ₂ =CHCHO and -C ₆ H ₅ CH=CHCHO complexes ^e
21	CH ₂ =CHOCOCH ₃ (ex)	none	none	40	96	Ni(OCOCH ₃) ₂ (18), C ₂ H ₄ (14), cod ^e
22	CH ₂ =CHOCOCH ₃ (ex)	PPh ₃	none	47	5	Ni(OCOCH ₃) ₂ , ^e C ₂ H ₄ (6), cod ^e
23 ^f	CH ₂ =CHOCOCH ₃ (ex)	Ni(PPh ₃) ₄	none	25	2	Ni(OCOCH ₃) ₂ (42), C ₂ H ₄ (26), cod (1), vinyl cyclohexene-4 (12)
24	CH ₂ =CHOCOCH ₃ (ex)	bpy (1.0)	none	25	12	Ni(OCOCH ₃) ₂ (bpy) _n , ^e C ₂ H ₄ (16)
25	CH ₂ =CHOCOCH ₃ (ex)	dpe	none	60	12	Ni(dpe) ₂ , ^e cod ^e

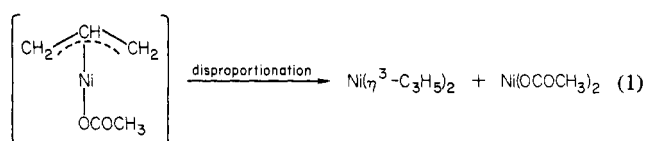
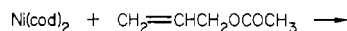
^a ex = excess (10–20 mol/Ni(cod)₂). ^b Me = CH₃, Et = C₂H₅, Ph = C₆H₅, c-Hx = cyclo-C₆H₁₁, and ema = ethyl methacrylate coordinated to Ni. ^c Ether = diethyl ether. ^d Yields of the Ni complexes given in this table represent values after recrystallization. ^e Formation of a considerable amount of the compound was confirmed by chemical reactivities of the compound, spectroscopies (IR and NMR), and/or gas chromatography, but yields of the compounds were not measured. ^f The Ni complex shown in the third column was employed instead of the mixture of Ni(cod)₂ and ligand.

which unequivocally characterized the oxidative addition products. We have characterized the oxidative addition products of these allylic compounds and established further that the isolated allylnickel complexes smoothly react with bases such as morpholine to give allylated products. The simple reactions of allyl acetate and aryl allyl ethers with Ni(cod)₂ and tertiary phosphines reported here provide a new route to the preparation of allylnickel complexes. Part of the results were briefly reported previously in communication form.^{3c-e}

Results and Discussion

Table I summarizes the products of the reactions of allyl acetate, allyl formate, allyl ethers, allylic alcohols, and vinyl acetate with bis(1,5-cyclooctadiene)nickel, Ni(cod)₂, in the absence or presence of ligands.

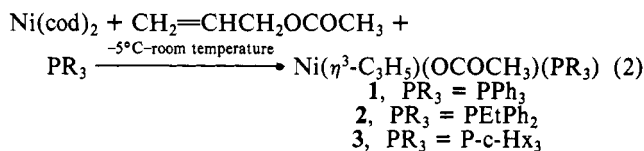
Allyl Acetate. A 1:1 reaction between Ni(cod)₂ and allyl acetate at 10 °C produces Ni(η³-C₃H₅)₂⁴ and Ni(OCOCH₃)₂. The reaction probably proceeds through the oxidative addition of allyl acetate to Ni to form a (η³-allyl)(acetato)nickel intermediate⁵ which further disproportionates as shown in eq 1. The supposed



(4) Wilke, G.; Bogdanovic, B. *Angew. Chem.* **1961**, 73, 756.

(5) It was reported that the reaction of Ni(cod)₂ with allyl acetate gave Ni(η³-C₃H₅)(OCOCH₃)₂.^{2a,8} However, our attempts to isolate the complex were not successful, and only the disproportionation products Ni(η³-C₃H₅)₂ and Ni(OCOCH₃)₂ were obtained.

intermediate (η³-allyl)(acetato)nickel can be trapped by adding stabilizing ligands such as triphenylphosphine, PPh₃, and tricyclohexylphosphine, P-c-Hx₃ (experiments 2–4 in Table I) to yield the new (η³-allyl)nickel complexes 1–3. Table II summarizes



IR and NMR data of complexes isolated in the present work. Variable-temperature ¹H NMR spectra of 1–3 reveal the fluxional motion of the η³-allyl ligand at higher temperatures. At low temperatures (–60 °C or below) the ¹H NMR spectra show an ABCDX spin pattern for the allyl ligand, but when the temperature is raised, dynamic exchanges between the methylene protons of the allyl ligand occur and an A₂M₂X pattern (for 1 at 25 °C and 3 at 0 °C) or A₄X pattern (for 2 at 25 °C and 3 at 40 °C) is observed. Such dynamic exchanges between the methylene protons are considered to proceed through a rapid σ–π conversion of the allyl ligand and rotation of the CH=CH₂ group around the C–C bond in the σ-allyl ligand.⁶

The oxidative addition of allyl acetate to Ni takes place also in reactions with Ni(0)-olefin π complexes such as Ni(PR₃)₂(ema) (ema = ethyl methacrylate)⁷ to give readily the corresponding (η³-allyl)nickel(II) complexes (experiments 5 and 6).

(6) (a) Vrieze, K. "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Jackman, L. M., Cotton, F. A., Eds., Academic Press: New York, 1975. (b) Warin, R.; Julemont, M.; Teyssie, Ph. *J. Organomet. Chem.* **1980**, 185, 413.

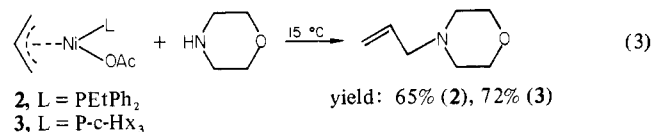
(7) (a) Ishizu, J.; Yamamoto, T.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1978**, 51, 2646. (b) Yamamoto, T.; Ishizu, J.; Komiya, S.; Nakamura, Y.; Yamamoto, A. *J. Organomet. Chem.* **1979**, 171, 103.

Table II. IR and NMR Data of Complexes 1-7

com- plex	IR, ^a cm ⁻¹	solvent	temp, °C	¹ H NMR, ^b δ (ppm)			¹³ C{ ¹ H} and ³¹ P{ ¹ H} NMR ^e
				allyl group	phosphine	others	
1	3060	CD ₂ Cl ₂	25	2.58 (2 H, br)	7.0-7.8 (15 H, m)	1.53 (3 H, s, OCOCH ₃)	
	1580*			3.18 (2 H, br)			
	1435			5.68 (1 H, qui, 10 Hz)			
	1092		-80	1.3 (1 H, br) ^c	7.0-7.8 (15 H, m)	1.40 (3 H, s, OCOCH ₃) ^c	
	740			2.4 (1 H, br)			
	690			3.3 (1 H, br)			
2	1610*	toluene- <i>d</i> ₈	25	4.0 (1 H, br)			
	1385			5.7 (1 H, br)			
	1330			2.6 (4 H, br)	1.0 (3 H, br, CH ₃)	2.1 (3 H, br, OCOCH ₃) ^c	
	1105			5.2 (1 H, que, 11 Hz)			
	740				2.1 (2 H, br, CH ₂) ^c		
					7.0-7.4 (6 H, <i>m</i> - and <i>p</i> -C ₆ H ₅)		
3	2920	toluene- <i>d</i> ₈	40	2.72 (4 H, d, 11 Hz)	7.5-7.8 (4 H, <i>o</i> -C ₆ H ₅)	1.96 (3 H, s, OCOCH ₃) ^c	
	2850			5.26 (1 H, qui, 11 Hz)	1.0-2.1 (33 H) ^c		
	1615*						
	1360						
	1310		-60 ^f	2.4 (1 H) ^c	1.0-2.1 ^c (33 H)	1.96 (3 H, s, OCOCH ₃) ^c	
	1000			3.34 (1 H, dd, 14 Hz and 4 Hz)			
4	1590	CD ₂ Cl ₂	-69	4.06 (1 H, br)			
	1490			5.5 (1 H, br)	ca. 7.4 (15 H, m)	6.09 (2 H, d, 7 Hz, <i>o</i> -OC ₆ H ₅)	
	1435			1.64 (1 H, br)		6.37 (1 H, m, <i>p</i> -OC ₆ H ₅)	
	1310			2.20 (1 H, br)			
	1300			3.31 (1 H, br)		6.94 (2 H, t, 7 Hz, <i>m</i> -OC ₆ H ₅)	
	1470			4.09 (1 H, br)			
5 ^d	1470	C ₆ D ₆	25 ^g	5.70 (1 H, br)	7.0-7.6 (15 H, m)		50.1 (s, C ₁), 70.7 (s, C ₃), 72.1 (d, <i>J</i> (³¹ P- ¹³ C ₂) = 7 Hz), 127-137 (PPh ₃) ^h
	1430			2.30 (2 H, d, H _A)			
	1380			2.52 (2 H, t, H _B)			
	1180			2.61 (2 H, dd, H _B)			
	1095			3.76 (2 H, dddd, H _C)			
	2895			4.83 (2 H, dd, H _D)			
6 ^d	2895	C ₆ D ₆	25	2.08-2.36 (2 H, H _A) ^c	0.8-2.1 (33 H) ^c		41.2 (s) ⁱ
	2805						
	1450			2.36-2.64 (4 H, H _B + H _C) ^c			
	1180			3.60 (2 H, dddd, H _C)			
	1070			4.97 (2 H, dd, 12.5 Hz and 3.5 Hz, H _D)			
				olefinic ligand	phosphine		
7	1620*	CD ₂ Cl ₂	25	4.0 (1 H, m, =CHCHO)	7.0-7.8 (20 H, m, PC ₆ H ₅ + =CC ₆ H ₅)		
	1440						
	1090			6.76 (1 H, m, C ₆ H ₅ CH=)			
	740			9.16 (1 H, d, 4 Hz, CHO)			
	690						
	505						

^a In KBr disks. The band with an asterisk is assigned to ν(C=O). ^b s = singlet; d = doublet; t = triplet; qui = quintet; m = multiplet; br = broad. ^c Overlapped with each other. ^d ¹H{³¹P} NMR data are given. ^e Ppm from internal Me₄Si for ¹³C{¹H} NMR and from external PPh₃ for ³¹P{¹H} NMR. ^f One of the CH₂ protons in the π-allyl ligand is hidden under the peak of P-c-Hx₃. ^g For coupling constants, see Figure 1. ^h ³¹C{¹H} NMR (C₆D₆, 25 °C). ⁱ ³¹P{¹H} NMR (C₆D₆, 25 °C).

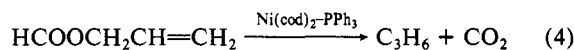
The η³-allyl ligand in the complexes, similar to that in the (η³-allyl)palladium complexes,⁸ is captured by nucleophiles such as morpholine to yield allylated compounds, e.g., eq 3. In the



reaction of 3, liberation of acetic acid (ca. 40%) accompanies the allylation reaction. Employment of diethylamine as the nucleophile in the reaction with 3 gives a lower yield of the allylated compound allyldiethylamine (14% (3)) under similar conditions as shown in reaction 3. Transition-metal-catalyzed allylation of nucleophiles by allyl acetate or allyl phenyl ether has been reported.^{1c,9a-d} The

reaction has been proposed to proceed through a mechanism involving oxidative addition of the allyl compounds to transition metal and ensuing attack on the η³-allyl transition-metal intermediate by the nucleophile. Occurrence of reaction 3 supports the proposed mechanism.

Allyl Formate. The Ni(cod)₂-PPh₃ mixture catalyzes degradation of allyl formate into C₃H₆ and CO₂ at 25 °C (experiment 7).

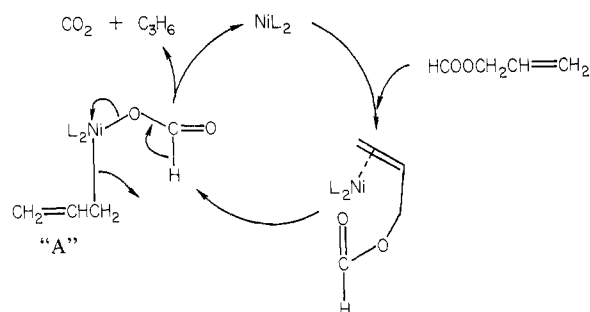


The reaction is considered to proceed through oxidative addition

(8) Stakem, F. G.; Heck, R. F. *J. Org. Chem.* **1980**, *45*, 3584.

(9) (a) Onoue, H.; Moritani, I.; Murahashi, S. *Tetrahedron Lett.* **1973**, 121. (b) Takahashi, K.; Miyake, A.; Hata, G. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 230. (c) Tsuji, J.; Takahashi, H. *Tetrahedron Lett.* **1965**, 4387. (d) Tsuji, J. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1897. (e) Tsuji, J.; Yamakawa, T. *Tetrahedron Lett.* **1979**, 613.

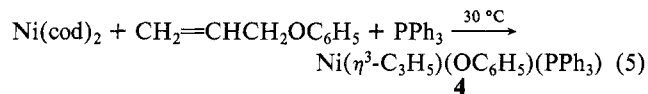
of allyl formate to Ni similar to that of allyl acetate with ensuing decarbonylation of the formate ligand.



In this reaction, in contrast to that of allyl acetate, NiL_2 serves as a catalyst and the degradation of allyl formate proceeds quantitatively as judged from the amount of C_3H_6 evolved, though the amount of CO_2 is considerably smaller than the calculated value. A part of the CO_2 is trapped by the Ni complex, and acidolysis of the solid residue which remains after the reaction releases a considerable amount of CO_2 . The catalytic decarboxylation of the allyl formate by the Ni(0) complex is related to the catalytic reductive decarboxylation promoted by palladium complexes proceeding through a supposed intermediate, allylmethyl formate, as utilized in organic synthesis by Tsuji.^{9c}

Concerning the decarboxylation from the allyl(formato)nickel(II) intermediate "A", it has been reported¹⁰ that the methyl(formato)nickel(II) complex undergoes a similar decarboxylation to liberate CH_4 and CO_2 . An alternative mechanism involving initial cleavage of the $\text{H}-\text{COOCH}_2\text{CH}=\text{CH}_2$ bond and ensuing decarboxylation reaction of the hydrido(allyloxy)carbonylnickel complex is also conceivable since the $\text{H}-\text{C}$ bond in formates is considered to have reactivity similar to that of the $\text{C}-\text{H}$ bond of the formyl group in aldehyde and the oxidative addition of aldehydes to transition-metal is known.^{1b,11} However, such a mechanism is less plausible because ethyl formate does not react with a mixture of $\text{Ni}(\text{cod})_2$ and PPh_3 at room temperature. At a higher temperature (60 °C) the reaction of ethyl formate with the $\text{Ni}(\text{cod})_2-\text{PPh}_3$ mixture affords a decarbonylation product ($(\text{Ni}(\text{CO})(\text{PPh}_3)_2/\text{Ni}(\text{cod})_2 = 60\%)$ and $\text{C}_2\text{H}_5\text{OH}$ (50%)), suggesting the occurrence of formyl-O bond cleavage followed by decarbonylation of the formyl group.

Allyl Ethers. The allyl-O bond of allyl phenyl ether is also cleaved in the reaction with $\text{Ni}(\text{cod})_2$ under mild conditions. The reaction provides a new, convenient route for the preparation of the (η^3 -allyl)(phenoxy)nickel(II) complex **4** (experiment 8)



Preparation of **4** from $[\text{Ni}(\eta^3\text{-C}_3\text{H}_5)\text{Br}]_2$, $\text{C}_6\text{H}_5\text{ONa}$, and PPh_3 has been reported in dissertation form by Bönemann.¹² The variable-temperature ^1H NMR spectrum of **4** also shows the fluxional motion of the allyl ligand at room temperature or above. Eisch and Im carried out similar reactions between allyl phenyl ether and $\text{Ni}(\text{cod})_2$ or $\text{Ni}(\text{PPh}_3)_4$.¹³ They added HCl to the reaction product without isolating it and obtained 80–100% of phenol and propylene per Ni. We assume that they also obtained a compound similar to **4** in their reaction. Wayaku and his co-workers reported cleavage of the $\text{C}-\text{O}$ bond of allyl ethers by rhodium compounds at higher temperature without isolating the resulting rhodium complexes.¹⁴

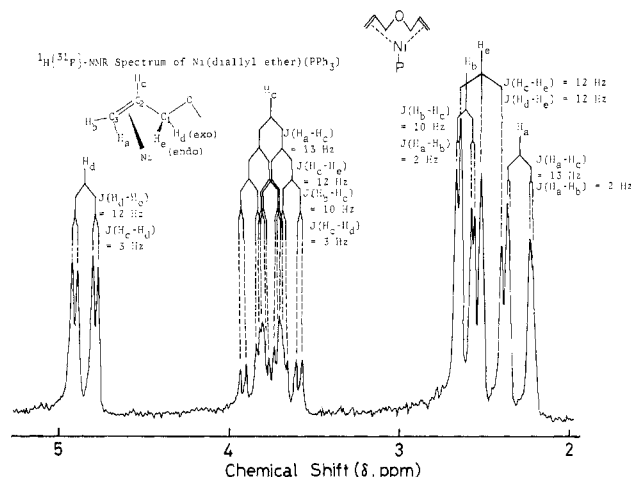
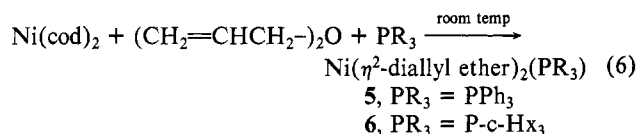


Figure 1. $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of **5** in benzene- d_6 at room temperature (region of the allylic protons).

Complex **4** reacts with CO at room temperature to yield allyl phenyl ether (39% (**4**)) and Ni-CO complexes, indicating that the oxidative addition of allyl phenyl ether to Ni is a reversible process. A similar promotion effect in reductive elimination of acyl-aryloxy and acyl-carboxylato groups from nickel complexes, $\text{Ni}(\text{COR})(\text{OAr})\text{L}_2^{3b}$ and $\text{Ni}(\text{COR})(\text{O}_2\text{CR}')\text{L}_2$,¹⁵ by carbon monoxide has been observed.

The nucleophilic attack on the allyl ligand in **4** by amines also occurred, giving *N*-allylmorpholine in a 82% yield on treatment of **4** with morpholine at 15 °C.

These oxidative addition reactions of the allylic compounds to nickel (eq 1, 2, 4, 5) are believed to proceed through the initial coordination of the allylic compounds to nickel through the $\text{C}=\text{C}$ double bond. Due to the rapid $\text{C}-\text{O}$ bond cleavage reaction of the allylic compounds promoted by Ni(0) complexes, the isolation of such an η^2 -type intermediate adduct between the allylic compounds described above and nickel is not feasible. Reactions of diallyl ether with Ni(0) complexes, on the other hand, afford bis η^2 -type complexes **5** and **6** and no $\text{C}-\text{O}$ bond cleavage took place



under mild conditions (experiments 9 and 10). Although the Rh and Pt complexes of diallyl ether are known,¹⁶ Ni complex of diallyl ether has no precedent. Figure 1 shows the $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of **5**, which shows an ABCDE spin pattern, indicating that the two allyl groups in **5** are chemically equivalent to each other. The complicated spin-spin coupling patterns for the allylic protons of **5** have been analyzed with the aid of homodecoupling techniques, and the assignment is given in Figure 1.

On coordination to Ni, the two protons attached to the carbon adjacent to the oxygen ($\text{O}-\text{CH}_2$) in diallyl ether become magnetically nonequivalent, giving rise to two resonances at δ 2.52 and 4.83 due to hindrance of free rotation around the $\text{O}-\text{CH}_2$ and $\text{OCH}_2-\text{CH}=\text{CH}_2$ bonds of the diallyl ether on complexation to nickel. We assign the resonances at δ 2.52 and 4.83 to the endo H and exo H (endo and exo refer to Ni), respectively, since the endo H will receive greater diamagnetic shielding by the electrons of the Ni. Values of the H_c-H_d (exo H) and H_c-H_e (endo H) coupling constants (see Figure 1) are reasonable for the $\text{H}_c-\text{C}-\text{C}-\text{H}_d$ and $\text{H}_c-\text{C}-\text{C}-\text{H}_e$ dihedral angles (ca. 70° and 170°, respectively) measured by using a CPK molecular model

(10) Klein, H.-F.; Karsh, H. H. *Chem. Ber.* **1973**, *10*, 1433.

(11) (a) Suggs, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 640. (b) Trost, M. B.; Preckel, M. *Ibid.* **1973**, *95*, 7862. (c) Dawson, D. J.; Ireland, R. F. *Tetrahedron Lett.* **1968**, 1899. (d) Tsuji, J.; Ohno, K. *Synthesis* **1967**, *1*, 157.

(12) H. Bönemann, Ph.D. Dissertation, Technische Hochschule, Aachen 1967.

(13) Eisch, J. J.; Im, K. R. *J. Organomet. Chem.* **1977**, *139*, C45.

(14) Wayaku, M.; Kaneda, K.; Imanaka, T.; Teranishi, S. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1957.

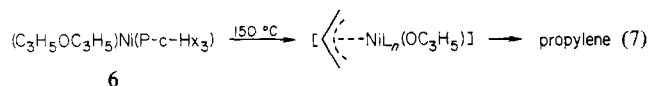
(15) Komiya, S.; Yamamoto, A.; Yamamoto, T. *Chem. Lett.* **1981**, 193.

(16) (a) Grigg, R.; Kongkathip, B.; King, T. J. *J. Chem. Soc., Dalton Trans.* **1978**, 333. (b) Jones, R. *J. Chem. Soc. A* **1969**, 2477.

of **5**. Although separation of the signals of the two O—CH₂ protons in olefins on coordination to the transition metal was observed for Pt(π -diallyl ether)Cl₂^{16b} and Ni(ema)(PR₃)₂,⁷ such a great separation of the signals of the two protons ($\delta(\text{H}_\text{A}) - \delta(\text{H}_\text{B}) = 2.31$ ppm) has no precedent to our knowledge. The averaged chemical shift of the endo and exo protons, $\frac{1}{2}(\delta(\text{H}_\text{A}) + \delta(\text{H}_\text{B})) = 3.68$ ppm, is shifted to a higher magnetic field by 0.25 ppm from that of the O—CH₂ protons in free diallyl ether. The signals of olefinic protons are shifted upfield by a larger amount (2.11–2.98 ppm) due to complex formation.

The ¹³C{¹H} NMR spectrum of **5** indicates that the signal of the C₁ carbon adjacent to oxygen is scarcely shifted on coordination to Ni, whereas the signals of the olefinic C₂ and C₃ carbons are shifted upfield by 63.2–66.1 ppm in accordance with the bis η^2 -type coordination mode. Liberation of a quantitative amount of diallyl ether on iodolysis of **5** renders additional support for the bis η^2 -type complexation. The ¹H NMR spectrum of the P-c-Hx₃-coordinated complex **6** is also consistent with the coordination mode of diallyl ether to Ni.

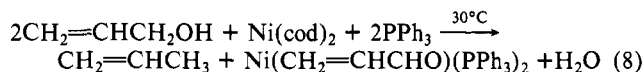
As described above the allyl—O bond of diallyl ether is not cleaved in the reactions with Ni(0) complexes under mild conditions, but such an inert allyl—O bond is cleaved when **6** is heated in benzene at 150 °C (in a sealed tube). The thermolysis affords propylene (ca. 0.5 mol/**6**), which is believed to be produced through allyl—O bond cleavage. The source of hydrogen which gives propylene from the η^3 -C₃H₅ ligand was not clarified.



Similar thermolysis of **5** does not lead to the C—O bond cleavage, but it causes liberation of diallyl ether and formation of a mirror of nickel. It has been reported that platinum hydrides cleave the C—O bond of diallyl ether.¹⁷ However, in this case the C—O bond cleavage is believed to proceed not through the oxidative addition of the ether to Pt but through insertion of the C=C double bond into the Pt—H bond.

Reactions of allyl alkyl ethers such as allyl methyl ether (experiment 11) and allyl isopropyl ether with mixtures of Ni(cod)₂—PR₃ led neither to the C—O bond cleavage nor to the π -complex formation, and Ni(cod)(PR₃)₂¹⁸ was recovered from the reaction mixture.

Allylic Alcohols. A reaction of allyl alcohol with a mixture of Ni(cod)₂ and PPh₃ at 30 °C causes the dismutation of allyl alcohol to afford C₃H₆, Ni(CH₂=CHCHO)(PPh₃)₂, and water in about 1:1:1 ratio; yields of the products based on Ni(cod)₂ are almost quantitative (experiment 12).^{3c}



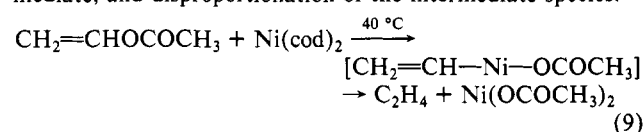
Reactions in the presence of P-c-Hx₃ and PMe₂Ph give similar results, although in these cases the polymerization of a part of acrylaldehyde takes place (experiments 13, 14). In contrast to the reactions in the presence of phosphine ligands, the reaction in the presence of 2,2'-bipyridine (bpy) gives more than 1 mol of C₃H₆/Ni(cod)₂ (experiment 15). The difference in the yield between reactions in the presence of PPh₃ and bpy may be attributed to differences in the stability of the Ni-acrylaldehyde complexes and in the catalytic activities of the complexes for the polymerization of acrylaldehyde. Ni(CH₂=CHCHO)(PPh₃)₂ is believed to be so stable that it does not catalyze further the dismutation of allyl alcohol, whereas acrylaldehyde formed by the dismutation of allyl alcohol by the Ni(cod)₂—bpy system is polymerized easily and is displaced from nickel to leave intact Ni(bpy) which further catalyzes the dismutation. It is known that a mixture of pyridine and water^{19a,b} and organoiron complexes

with bpy ligands^{19c} initiate the polymerization of acrylaldehyde. The dismutation of allyl alcohol also proceeds to some extent with Ni(cod)₂ alone. In this case, however, the reaction is accompanied by formation of metallic nickel (experiment 16). The catalytic degradation of allyl alcohol to propylene, acrylaldehyde, and water has a precedent in which RuCl₃·3H₂O was used.²⁰

The reaction of CH₃CH=CHCH₂OH yields an equilibrated mixture of *trans*-C₄H₈, *cis*-C₄H₈, and 1-C₄H₈ together with Ni(CH₃CH=CHCHO)(PPh₃)₂ and H₂O. C₆H₅CH=CH₂OH is also dismutated to C₆H₅CH=CHCH₃ and C₆H₅CH=CHCHO on interaction with Ni(cod)₂ in the presence of PPh₃, and a part of C₆H₅CH=CHCHO further undergoes a decarbonylation reaction to give C₆H₅CH=CH₂ and Ni(CO)(PPh₃)₃.

A 1:1 mixture of CH₃CH=CHCH₂OH and CH₂=CHCH₂OH gives C₃H₆ in a much higher yield than that of butenes (experiment 19), whereas a 1:1 mixture of C₆H₅CH=CHCH₂OH and CH₂=CHCH₂OH gives C₃H₆ in a lower yield than that of C₆H₅CH=CHCH₃ (experiment 20). These results reveal that the reactivity of allylic alcohols increases with an increase in the electron-withdrawing ability of the RCH=CHCH₂ group (CH₃CH=CHCH₂ < CH₂=CHCH₂ < C₆H₅CH=CHCH₂). Reactions of saturated alcohols and propargyl alcohol with mixtures of Ni(cod)₂ and phosphine ligands gave Ni(cod)(PR₃)₂. No C—O bond cleavage was observed.

Vinyl Acetate. A reaction of vinyl acetate with Ni(cod)₂ affords C₂H₄ and Ni(OCOCH₃)₂ in about a 1:1 ratio (experiment 21). The reaction most probably proceeds through oxidative addition of vinyl acetate to Ni, giving a vinyl(acetato)nickel(II) intermediate, and disproportionation of the intermediate species.



In this reaction the source of hydrogen which yields ethylene was not identified yet.

Similar reactions of vinyl acetate with Ni(cod)₂ in the presence of ligands such as PPh₃ and bpy give similar results (experiments 22 and 24). IR spectra of the residues recovered from these systems show the formation of (acetato)nickel(II) complexes coordinated with PPh₃ and bpy, respectively, but repeated washing of the residues with solvents gave Ni(OCOCH₃)₂, indicating that the ligands do not have strong affinities toward Ni(OCOCH₃)₂. On the other hand, when 1,2-bis(diphenylphosphino)ethane (dpe), which has stronger coordinating ability to Ni than monodentate phosphine and bpy,²¹ is employed, the reaction gives Ni(dpe)₂²² and no C—O bond cleavage occurred (experiment 25).

A reaction of Ni(PPh₃)₄ with vinyl acetate affords 4-vinylcyclohexene and cod besides Ni(OCOCH₃)₂ and C₂H₄ (experiment 23). 4-Vinylcyclohexene and cod are considered to be formed through Ni-catalyzed dimerization of butadiene^{22a} which is formed through a bimolecular coupling reaction of the vinyl groups in an intermediate species produced on oxidative addition of vinyl acetate to Ni(0). The cleavage of the vinyl—O bond of vinyl acetate also proceeds when the ester is treated with the (π -olefin)nickel complexes, Ni(ema)(PR₃)₂,⁷ at ambient temperature to afford C₂H₄ and Ni(OCOCH₃)₂. The C—O bond of vinyl acetate is known to be cleaved on interaction with transition metal hydrides to afford transition-metal acetates and C₂H₄.²³ However, in these cases the reaction is believed to proceed in a manner different from that of the present systems, i.e., through insertion of C=C double

(19) (a) Yamashita, N.; Sumitomo, H.; Maeshima, T. *Kogyo Kagaku Zasshi* **1968**, *71*, 1723. (b) Yamashita, N.; Yoshihara, M.; Maeshima, T. *J. Polym. Sci., Part B* **1972**, *10*, 643. (c) Yamamoto, T.; Yamamoto, A.; Ikeda, S. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1111.

(20) Nicholson, J. K.; Shaw, B. L. *Proc. Chem. Soc.* **1963**, 282.

(21) Kohara, T.; Yamamoto, T.; Yamamoto, A. *J. Organomet. Chem.* **1980**, *192*, 254.

(22) (a) Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: New York, 1974; Vol. 1; 1975; Vol. 2. (b) Behrens, H.; Müller, A. Z. *Anorg. Allg. Chem.* **1965**, *341*, 124. (c) Bogdanovic, B.; Bönnemann, H.; Wilke, G. *Angew. Chem.* **1966**, *78*, 591.

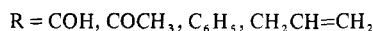
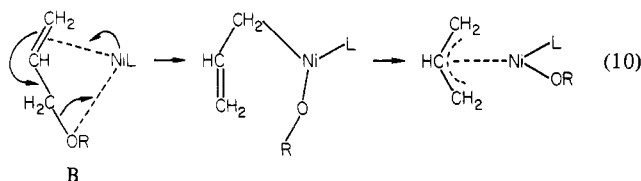
(23) Komiya, S.; Yamamoto, A. *J. Organomet. Chem.* **1970**, *87*, 333.

(17) Clark, H. C.; Kurosawa, H. *Inorg. Chem.* **1973**, *12*, 357.

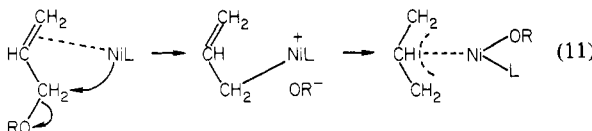
(18) (a) Wilke, G.; Müller, E. W.; Kröner, M. *Angew. Chem.* **1961**, *73*, 33. (b) Imaizumi, F.; Ikeda, H.; Hirayanagi, S.; Mori, K. *J. Chem. Soc. Jpn.* **1975**, 2205.

bond into the transition metal—hydride bond followed by β abstraction of the OCOCH_3 group by the metal.

Reaction Mechanism of the Allyl—Oxygen Bond Cleavage. For the C—O bond in allyl acetate and allyl ethers to be cleaved, it is reasonable to assume the prior coordination of the allyl group to nickel through the double bond. In fact the interaction of nickel with the allyl groups of diallyl ether through the double bonds is supported on the basis of NMR spectra of the diallyl ether complexes **5** and **6**. For the allylic compounds to cause the C—O bond cleavage on complexation with nickel, two alternative routes are conceivable. One is a process involving the rearrangement of the bonds in a postulated intermediate "B" where the allylic



compound is coordinated to nickel through the double bond and an other coordination site such as the ether oxygen and the carbonyl group. The cleavage of the allyl—O bond with concomitant formation of the *cis*-allylNi(OR)L complex followed by σ — π rearrangement of the allyl group would give the resultant (η^3 -allyl)nickel complexes. The other route is the trans-type process which may be regarded as the reverse process of the $\text{S}_{\text{N}}2$ -type trans attack of the π -allyl group coordinated to nickel by a nucleophile.



The two pathways are indistinguishable in the present case. It is noted, however, that the presence of a good leaving group in the allylic compounds provides a driving force for facile C—O bond cleavage as shown by the smooth reactions of allyl carboxylates and allyl phenyl ethers having OCOR and OPh groups with Ni(0) complexes with the C—O bond scission under mild conditions. The diallyl ether having a poorer leaving group or a weaker electron-withdrawing group²⁴ is oxidatively cleaved only under more forcing conditions provided that the more electron-releasing phosphine P-c-Hx₃ was used in place of PPh_3 .

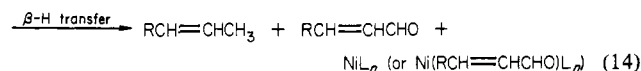
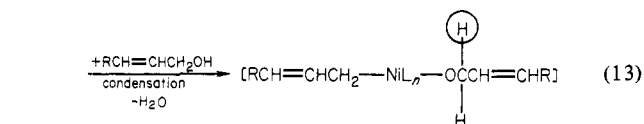
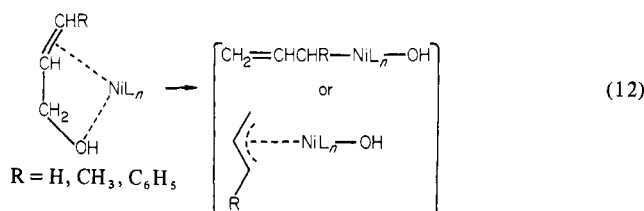
In these oxidative additions as well as those of aryl carboxylates with Ni(0) complexes,^{3b} the coordination of more basic ligands seems to facilitate the cleavage of the C—O bond.

The dismutation of allyl alcohols can be explained by a similar oxidative addition involving C—O bond cleavage followed by a dehydrative condensation reaction between the allyl alcohol and the nickel hydroxide formed by the oxidative addition (Scheme I). Formation of an (η^3 -allyl)nickel(II)-type intermediate from allylic alcohols and nickel compounds was proposed by Felkin and co-workers to explain the products of Ni-catalyzed coupling reactions between allylic alcohols and Grignard reagents proceeding through a somewhat different mechanism from the present case.^{25a,b} Hartley and Jones gave visible spectroscopic evidence for the formation of $[(\eta^3\text{-C}_3\text{H}_5)_2\text{PdCl}]_2$ from allyl alcohol and Na_2PdCl_4 in glacial acetic acid.^{25c}

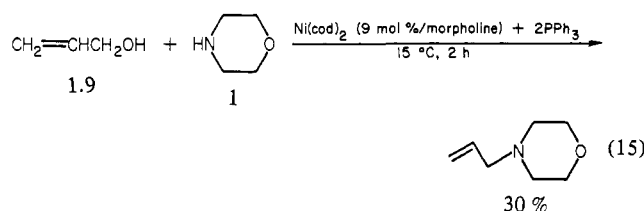
The intermediacy of the allylnickel(II) species in Scheme I is

(24) A direct comparison of the electron-withdrawing abilities of the OR groups is not possible since Hammett's σ values of some OR groups are not reported. We believe, however, that the electron-withdrawing abilities of OCOCH_3 and OC_6H_5 are larger than those of $\text{OCH}_2\text{CH}=\text{CH}_2$ and OC_2H_5 , since the pK_a values of *p*- $\text{CH}_3\text{COC}_6\text{H}_4\text{COOH}$ (3.70) and *p*- $\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{COOH}$ (4.20) are smaller than those of *p*- $\text{CH}_2=\text{CHCH}_2\text{C}_6\text{H}_4\text{COOH}$ (4.31; Bauer, G. M.; Darany, G.; Argentan, H. *J. Res. Natl. Bur. Stand., Sect. A* **1967**, 71A, 379) and *p*- $\text{C}_2\text{H}_5\text{C}_6\text{H}_4\text{COOH}$ (4.35). The electron-withdrawing abilities of COCH_3 and C_6H_5 groups are thus considered larger than those of $\text{CH}_2\text{CH}=\text{CH}_2$ and C_2H_5 groups.

Scheme I



supported by trapping the allyl ligand by morpholine. The Ni(cod)₂-PPh₃ mixture was found to catalyze allylation of morpholine.



The allylation reaction does not proceed in the absence of the nickel catalyst. Allylation of amines by allyl alcohol in the presence of other transition-metal compounds was reported.²⁶

Experimental Section

General Procedures and Materials. Manipulation of complexes and the reactions were carried out under deoxygenated nitrogen or argon or under vacuum. Ni(cod)₂ was purchased from Merck Co., Ltd., and recrystallized. Esters, ethers, and alcohols were purified by repeated distillation until their gas chromatograms show no significant peaks of contaminants. Tertiary phosphine ligands and bpy were used as purchased or synthesized by the methods given in the literature.²⁷ Solvents were dried by usual procedures, distilled, and stored under argon or nitrogen.

Reactions of Allyl—Oxygen and Vinyl—Oxygen Compounds with Nickel(0) Complexes (Refer to Table I). **Reactions of Allyl Acetate (Experiments 1–6).** (1) A mixture of allyl acetate (0.3 mL, 3.3 mmol) and diethyl ether (3 mL) was added to a Schlenk tube containing 900 mg (3.3 mmol) of Ni(cod)₂ at -78°C , and the mixture was stirred at 10°C . After the reaction mixture was stirred for 2 h, it was cooled to -78°C and diethyl ether was evaporated at the temperature by using a vacuum line. After complete removal of diethyl ether by evaporation, the Schlenk tube was warmed up to 0°C and the volatile material was collected by trap-to-trap distillation. The volatile material was found to be Ni($\eta^3\text{-C}_3\text{H}_5$)₂ by NMR spectroscopy. The IR spectrum of the yellow solid (380 mg) remaining in the Schlenk tube shows no peaks assignable to Ni(cod)₂ but $\nu(\text{C}=\text{O})_{\text{asym}}$ and $\nu(\text{C}=\text{O})_{\text{sym}}$ bands characteristic of metal acetates at 1576 and 1423 cm^{-1} , respectively. The yellow solid was characterized as Ni(OCOCH₃)₂ as follows. (a) Addition of hexane into a pyridine solution of the yellow solid gave blue-green prisms of Ni(OCOCH₃)₂(py). Anal. Calcd for C₉H₁₁NNiO₄: C, 42.2; H, 4.3; N, 5.5. Found: C, 42.9; H, 4.4; N, 6.1. IR (KBr, cm^{-1}): $\nu(\text{C}=\text{O})_{\text{asym}}$ 1620. (b) A reaction of

(25) (a) Chuit, C.; Felkin, H.; Frajerman, C.; Roussi, G.; Cwierzewski, C. *J. Organomet. Chem.* **1977**, 127, 371. (b) Buckwalter, B. L.; Bunfitt, I. R.; Felkin, H.; Joly-Goudket, M.; Naemura, K.; Salomon, M. F.; Wenkert, E.; Wovkulich, P. M. *J. Am. Chem. Soc.* **1978**, 100, 6445. (c) Hartley, F. R.; Jones, S. R. *J. Organomet. Chem.* **1974**, 66, 465.

(26) (a) Furukawa, J.; Kiji, J.; Yamamoto, K.; Tojo, T. *Tetrahedron* **1973**, 3149. (b) Murahashi, S.; Shimamura, T.; Moritani, I. *J. Chem. Soc., Chem. Commun.* **1974**, 931.

(27) (a) Goetz, H.; Domin, S. *Justus Liebigs Ann. Chem.* **1967**, 704, 1. (b) Kosolapoff, G. M.; Maier, L. "Organic Phosphorus Compounds"; Wiley: New York, 1972; Vol. 1, p 156.

the yellow solid with $\text{C}_2\text{H}_5\text{Br}$ gave $\text{CH}_3\text{COOC}_2\text{H}_5$ quantitatively.

(2) Allyl acetate (1.0 mL, 9.3 mmol) was added to a vessel containing $\text{Ni}(\text{cod})_2$ (820 mg, 3.0 mmol) and PPh_3 (1.5 g, 6.0 mmol). The mixture was stirred at room temperature for 12 h to obtain a brown precipitate, which was separated by filtration. The brown precipitate was recrystallized from THF–diethyl ether to yield deep red prisms of **1** (900 mg, 71%), mp 125–128 °C dec. Anal. Calcd for $\text{C}_{23}\text{H}_{23}\text{NiO}_2\text{P}$: C, 65.6; H, 5.5. Found: C, 65.3; H, 5.6. The same complex was obtained by the reaction of $\text{Ni}(\text{ema})(\text{PPh}_3)_2$ with allyl acetate at –25 °C (experiment 5).

(3) Reactions of allyl acetate and $\text{Ni}(\text{cod})_2$ in the presence of $\text{P}(\text{EtPh})_2$ and P-c-Hx_3 were carried out analogously under conditions given in Table I, and complexes **2** and **3** were isolated. Solvents for the recrystallizations of **2** and **3** were mixtures of allyl acetate and hexane and of allyl acetate and toluene, respectively. **2**: mp 54–56 °C. Anal. Calcd for $\text{C}_{19}\text{H}_{23}\text{NiO}_2\text{P}$: C, 58.9; H, 6.1. Found: C, 59.5; H, 6.1. **3**: mp 75–79 °C. Anal. Calcd for $\text{C}_{23}\text{H}_{44}\text{NiO}_2\text{P}$: C, 62.9; H, 9.4. Found: C, 63.4; H, 10.3.

Reaction of Allyl Phenyl Ether (Experiment 8). Allyl phenyl ether (0.80 mL, 5.6 mmol) and THF (2.0 mL) were added to a vessel containing $\text{Ni}(\text{cod})_2$ (370 mg, 1.4 mmol) and PPh_3 (390 mg, 1.5 mmol). The mixture was stirred at 30 °C for 4 h to obtain a deep red homogeneous solution. When left standing overnight at –70 °C, the solution gave brownish orange crystals of **4** (500 mg, 81%), which were characterized by comparing its IR and NMR spectra with those of an authentic sample prepared by Bönnemann's method.¹²

Reactions of Diallyl Ether (Experiments 9 and 10). Diallyl ether (0.60 mL, 6.0 mmol) and diethyl ether (0.5 mL) were added to a vessel containing $\text{Ni}(\text{cod})_2$ (560 mg, 2.0 mmol) and PPh_3 (530 mg, 2.0 mmol). The mixture was stirred for 12 h at room temperature to obtain a yellow homogeneous solution. When left standing at –5 °C for 2 days the solution gave yellow prisms, which were washed repeatedly with diethyl ether and dried under vacuum to yield 630 mg of **5** (75%), mp 125–127 °C dec. Anal. Calcd for $\text{C}_{24}\text{H}_{25}\text{NiOP}$: C, 68.8; H, 6.0. Found: C, 68.4; H, 6.1.

Diallyl ether (0.50 mL, 5 mmol) and diethyl ether (0.5 mL) were added to a vessel containing $\text{Ni}(\text{cod})_2$ (460 mg, 1.7 mmol) and P-c-Hx_3 (790 mg, 2.5 mmol). The mixture was stirred at room temperature for 12 h to obtain a yellow homogeneous solution. When left standing at –25 °C for 2 days the solution gave crystals, which were separated by filtration and recrystallized from diethyl ether to yield white crystals of **6** (490 mg, 66%), mp 174–177 °C dec. Anal. Calcd for $\text{C}_{24}\text{H}_{43}\text{NiOP}$: C, 65.9; H, 9.9. Found: C, 65.2; H, 10.2.

Reactions of Allyl Alkyl Ethers (Experiment 11). Allyl methyl ether (1.0 mL, 13 mmol) and toluene (2.6 mL, 32 mmol) were added (1.0 mL, 13 mmol) to a vessel containing $\text{Ni}(\text{cod})_2$ (470 mg, 1.7 mmol) and PPh_3 (900 mg, 3.4 mmol). Stirring the solution for 2 days at room temperature

gave a dark brown solution, from which the solvent was removed by evaporation under vacuum. The remaining yellow solid was characterized as $\text{Ni}(\text{cod})(\text{PPh}_3)_2$ by its IR spectrum. Reactions of allyl ether and allyl isopropyl ether with the mixture of $\text{Ni}(\text{cod})_2$ and PPh_3 proceed similarly, and the occurrence of neither the C–O bond cleavage nor the π -complex formation reaction was observed.

Reactions of Allylic Alcohols (Experiments 12–20). Allyl alcohol (0.40 mL, 5.9 mmol) and THF (2.0 mL) were added into a vessel containing $\text{Ni}(\text{cod})_2$ (430 mg, 1.56 mmol) and PPh_3 (984 mg, 3.75 mmol). The mixture was stirred for 2 days at 30 °C to obtain a red solution and an orange precipitate. Evolution of 1.52 mmol of C_3H_6 and formation of 1.44 mmol of H_2O during the reaction were observed (Toepler pump and GLC). After the reaction mixture was cooled to –78 °C, the orange precipitate was separated by filtration, washed with hexane, recrystallized from toluene–hexane, and dried under vacuum to yield 942 mg (1.47 mmol, 93%) of orange crystals, which were identified as $\text{Ni}(\text{CH}_2=\text{CHCHO})(\text{PPh}_3)_2$ by comparing its IR and NMR spectra with those of an authentic sample.^{22a,28} The other reactions of allylic alcohols were carried out analogously. $\text{Ni}(\text{CH}_3\text{CH}=\text{CHCHO})(\text{PPh}_3)_2$ and $\text{Ni}(\text{C}_6\text{H}_5\text{CH}=\text{CHCHO})(\text{PPh}_3)_2$ were characterized by IR and NMR spectroscopies.^{22a,28}

Reactions of (η^3 -Allyl)nickel Complexes with Nucleophiles. Morpholine (0.30 mL, 2.4 mmol) was added to a vessel containing 110 mg (0.25 mmol) of **3** and the homogeneous solution thus obtained was stirred for 15 h at 15 °C. GLC analysis of the solution indicated formation of 0.18 mmol (72%) of *N*-allylmorpholine. The reaction of **3** with HNEt_2 and reactions of other (η^3 -allyl)palladium complexes with morpholine were carried out analogously in near nucleophile at 15–20 °C.

Allylation of Morpholine by Allyl Alcohol. Allyl alcohol (0.5 mL, 7.3 mmol) and morpholine (0.5 mL, 3.9 mmol) were added into a vessel containing 100 mg (0.36 mmol) of $\text{Ni}(\text{cod})_2$ and 200 mg (0.76 mmol) of PPh_3 . The homogeneous solution was stirred at 15 °C for 15 h to yield 1.2 mmol of *N*-allylmorpholine.

Spectral Measurement and Analysis. IR spectra were taken on a Hitachi Model 295 spectrometer by using KBr disks under nitrogen. ^1H NMR spectra were recorded on a Japan Electron Optics Laboratory (JEOL) Model JNM-PS-100 spectrometer and ^{13}C - and ^{31}P -NMR spectra on a JEOL Model JNM-PET-PS-100 Fourier transform spectrometer. Microanalysis of C, H, and N was performed by Mr. T. Saito of our laboratory with a Yanagimoto CHN Autocorder Type MT-2. The analyses of gaseous and liquid products were carried out with a Shimadzu GC-3BT or GC-6A gas chromatograph.

(28) (a) van der Linde, R.; Bogdanovic, B. "Proceedings of the 4th International Conference on Organometallic Chemistry", 1969; U8. (b) Fritz, H. P.; Schrauzer, G. N. *Chem. Ber.* 1961, 94, 650.

Crystal Structures of Repeating Peptides of Elastin. 2. *N*-(*tert*-Butoxycarbonyl)-L-valyl-L-prolylglycylglycine Benzyl Ester

Hiroshi Ayato, Isao Tanaka, and Tamaichi Ashida*

Contribution from the Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464, Japan. Received April 27, 1981.
Revised Manuscript Received July 6, 1981

Abstract: The crystal structure of Boc-Val-Pro-Gly-Gly-OBzl, one of the repeating peptides in elastin, has been determined by the X-ray method. The peptide crystallizes as an ethyl acetate solvate in the monoclinic space group $C2$ with $a = 36.485$ (5), $b = 9.210$ (2), $c = 10.215$ (1) Å, $\beta = 93.52$ (1)°, and $Z = 4$. The final R index is 0.078 for 3039 reflections with $2\theta \leq 128^\circ$. The basic conformation of the peptide is a type II β turn with Pro-Gly at the corner, as is compatible with the model proposed for Boc-Val-Pro-Gly-Gly-OMe in solution. This folded structure makes a sharp contrast with the extended one of Boc-Val-Pro-Gly-Val-Gly-OH, another repeating pentapeptide in elastin.

Tropoelastin, the precursor protein of elastin, has been shown to contain three kinds of short-range repetitions of amino acid

sequences, a tetrapeptide Val-Pro-Gly-Gly, a pentapeptide Val-Pro-Gly-Val-Gly, and a hexapeptide Val-Ala-Pro-Gly-Val-Gly.^{1,2}