CHEMISTRY LETTERS, pp. 695-698, 1982.

PREPARATION OF SEVERAL NEW Ni- OR Pd-CONTAINING CYCLIC AMIDE AND ESTERS, $(PR_3)_n\overline{NiCH_2CH_2CH_2COZ}$ (Z = NH, O) AND $PCy_3\overline{PdCH_2CH_2CH_2COO}$, AND RING CONTRACTION OF THE SIX-MEMBERED Ni-CONTAINING CYCLIC ESTER TO ITS FIVE-MEMBERED ISOMER

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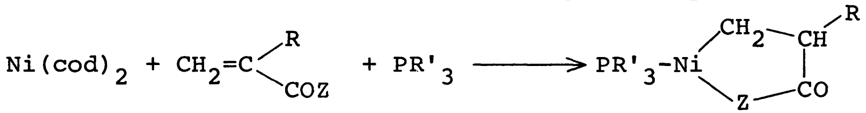
New metallacyclic amide and esters ($PCy_3\overline{NiCH_2CH_2CH_2CONH}$, $(PR_3)_n\overline{NiCH_2CH_2CH_2COO}$, $PCy_3\overline{PdCH_2CH_2CH_2COO}$) have been prepared by reactions of zero-valent nickel and palladium complexes with unsaturated amide and acid. The 6-membered Ni-containing cyclic ester undergoes a ring contraction reaction to a 5-membered isomer.

A previous study in our group revealed that reactions of $Ni(cod)_2$ (cod = 1,5-cyclooctadiene) with α,β-unsaturated amides and acids (e.g., methacrylamide and acrylic acid) in the presence of bulky and basic phosphines afford Ni-containing 5-membered cyclic amides and esters, respectively.[1)]

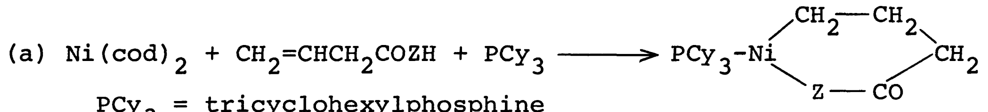


(1)

Z = O, NR"

The 5-membered Ni complexes easily react with carbon monoxide to afford carbonylated cyclic compounds (carboxylic anhydrides and imides), and the complexes are regarded as model compounds of possible intermediates formed during ring closure carbonylation reaction of α,β-unsaturated amides and acids catalyzed by cobalt carbonyls.[2)]

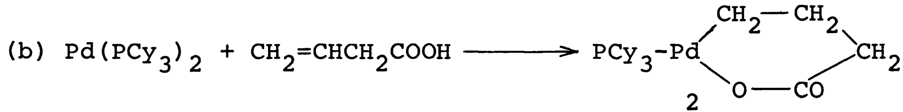
We now report that the metallacycle formation reaction is not restricted to the combination shown in Eq. 1, but (a) reactions using β,γ-unsaturated amide or acid as well as (b) reactions using a Pd(0)-complex, $Pd(PCy_3)_2$, also afford similar metal-containing cyclic amide and esters,



(2)

PCy_3 = tricyclohexylphosphine

1a (Z = O), 1b (Z = NH)



(3)

2

The PCy_3 ligand in 1a can be replaced by 1,2-bis(diphenylphosphino)ethane, dpe, to give complex 1c.

$$\mathbf{1a} + \text{dpe} \longrightarrow \underset{\mathbf{1c}}{(\text{dpe})\overline{\text{NiCH}_2\text{CH}_2\text{CH}_2\text{COO}}} + \text{PCy}_3 \qquad (4)$$

The 6-membered metallacycle complexes **1a** and **1c** are easily isomerized to their 5-membered isomers, $(\text{PR}_3)_m\overline{\text{NiCH(CH}_3)\text{CH}_2\text{COO}}$ **3**, in solvents.

Preparation and Properties of The Nickel Complexes.

A homogeneous solution of THF (7.7 cm^3) containing $Ni(cod)_2$ (211 mg, 0.77 mmol), PCy_3 (215 mg, 0.77 mmol), and 3-butenoic acid (0.066 cm^3, 0.77 mmol) was stirred at room temperature for 1 day to obtain a yellow precipitate, which was washed repeatedly by ether and hexane and dried in vacuum to yield 106 mg (32%) of **1a**. Complex **1b** was prepared analogously (yield = 28%). Analytical data of **1a**, **1b**, and other related complexes are given in Table 1.

Table 1. Preparation and Characterization of Ni- or Pd-Containing Cyclic Ester and Amide.

Complex	Analysis a)			mp (°C)	Yield (%)	IR(cm^{-1}) b) ν(C=O) or amide band	Product of Reaction with CO
	C	H	N				
1a	61.9	9.5		155-160	32	1580	glutaric anhydride 22%
	(62.2)	(9.2)		(dec.)			$NiPCy_3(CO)_3$
1b	61.9	9.7	3.1	210-215	28	1560	glutarimide 66%
	(62.3)	(9.4)	(3.3)	(dec.)			$NiPCy_3(CO)_3$
1c	66.5	5.7		110-115	57	1600	glutaric anhydride 41%
	(66.2)	(5.5)		(dec.)			3-methyl succinic anhydride 8%
2	55.4	8.7		180-185	24	1580	glutaric anhydride 10%, c)
	(55.9)	(8.3)		(dec.)			
3	66.7	5.7		175-180	65	1640	3-methyl succinic anhydride 100%
	(66.2)	(5.5)		(dec.)			

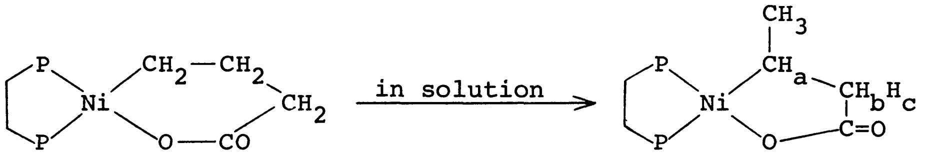
a) Calculated value in the parentheses.

b) IR spectra of **1a**, **1c**, **2**, and **3** showed no ν(O-H) band.

c) Reaction in the presence of 2,2'-bipyridine (see the text).

Complexes **1a** and **1b** are sparingly soluble in organic solvents,3) preventing characterization by NMR. However, IR spectra of **1a** and **1b** showing only sharp ν(C=O) and amide band characteristic of the nickel-containing cyclic esters and amides1) at 1580 cm^{-1} and 1560 cm^{-1}, respectively, as well as production of corresponding cyclic carbonylated products (glutaric anhydride (yield = 22%) and glutarimide (66%)) by reactions of **1a** and **1b** with CO (cf. Table) support the formation of the 6-membered Ni-containing cyclic ester and amide.

Complex **1a** decomposes in pure CS_2, but when dissolved in CS_2 which contains dpe (1 mol/**1a**) at room temperature a smooth ligand exchange reaction proceeds to give a yellow precipitate of a dpe-containing complex **1c** (yield = 57%) after 5 min without apparent decomposition of the complex. In methanol, CH_2Cl_2, pyridine, chlorobenzene, and methoxybenzene **1c** is rapidly isomerized to the 5-membered ring complex, **3**, which shows a completely different IR spectrum (for ν(C=O), see Table 1) and reactivity with CO from that of **1c**,



1c 3 (5)

By using dpe-d_4 ($Ph_2PCD_2CD_2PPh_2$) we prepared 3-d_4 and analyzed the NMR spectra of the complex. 3-d_4: ^{1}H-NMR(CD_2Cl_2,δ): 0.52 (3H, t, $J^3(^1H-^1H)=J^4(^1H-^{31}P)$=7 Hz, CH_3), 1.4 (1H, m, H_a), 1.70 (1H, ddd, 16, 13, and 6 Hz, H_b), 2.90 (1H, dd, 16 and 6 Hz, H_c). $^1H\{^{31}P\}$-NMR data are consistent with the assignment. $^{13}C\{^1H\}$-NMR(CD_2Cl_2, ppm from TMS): 19.3 (d, 3.5 Hz, $\underline{C}H_3$), 22.3 (dd, 27.8 and 4.7 Hz, dpe-CH_2), 27.4 (dd, 56.4 and 18. 7 Hz, $\underline{C}H_a$), 34.2 (dd, 27.6 and 17.3 Hz, dpe-$\underline{C}H_2$), 46.5 (d, 2.3 Hz, $\underline{C}H_bH_c$), 200.98 (s, $\underline{C}$=O). Occurrence of the facile ring contraction indicates that the 5-membered ring is considerably more stable than the 6-membered ring as usually observed in chelate compounds. A mechanism involving β-hydride elimination and readdition accounts for the isomerization reaction. Occurrence of ring contraction reactions from metallacyclopentane to metallacyclobutane has been proposed for Pt$^{4)}$ and Ta$^{5)}$ complexes to account for the thermolysis products of these complexes, but isolation of the ring-contracted complex has no precedent.

The reaction of 3 with CO at room temperature proceeded smoothly in all solvents at room temperature to afford 3-methyl succinic anhydride almost quantitatively in 1 h (Table 1), whereas the reaction of a suspension of 1c with CO in hexane at room temperature proceeded very slowly to give glutaric anhydride (28%/1c) and 3-methyl succinic anhydride (5%/1c) after 24 h. Their yields rose to 41% and 8%, respectively, after 48 h.

3 + CO ⟶ 3-methyl succinic anhydride (6)

1c + CO ⟶ glutaric anhydride (7)

The formation of 3-methyl succinic anhydride in the reaction of 1c with CO seems to be due to partial isomerization of 1c to 3 during the reaction with CO, since 1c employed for the reaction was not contaminated with 3 as judged from its IR spectrum. It has been reported that the CO insertion into Ti-C bond of 6-membered titanocycle is much slower than that in the Ti-C bond of 5-membered titanocycle.$^{6)}$ The reaction of CO with 1c-d_1, prepared by using CH_2=$CHCH_2COOD$, gave [4-^{2}H]glutaric anhydride, supporting the metallacycle structure.

In contrast to the facile ligand exchange reaction with 1a, 1b did not undergo the ligand exchange reaction.

Preparation and Properties of The Pd-Complex 2.

A reaction of $Pd(PCy_3)_2$ with 3-butenoic acid yielded the 6-membered complex, 2, as shown in Eq. 3. The close resemblance of its IR spectrum to that of the Ni analog supports the proposed structure. Complex 2 was not soluble in solvents tested. The PCy_3 ligand of 2 was also replaced by dpe in CS_2 to yield a soluble complex whose IR spectrum was almost superimposable on that of 1c, but detailed examination of the structure by NMR was not feasible due to the instability of the complex in solution. The reaction of 2 with CO in the presence of 2,2'-bipyridine (bpy) afforded glutaric anhydride (10%/2), although the reaction of 2 with CO in the absence of bpy did not give glutaric anhydride. P. Diversi and his coworkers reported a similar difference in the reactivities of bpy- and phosphine-*coordinated palladacyclopentanes with CO; a bpy-coordinated palladacyclopentane* afforded cyclopentanone in the reaction with CO whereas a phosphine-coordinated complex did not afford the carbonylated compound.[7)] Palladium complexes generally have lower reactivities against CO than nickel complexes.

In contrast to the facile formation of Ni-containing cyclic amides in the reactions of Ni(0)-complexes with α,β- or β,γ-unsaturated amides, similar reactions using $Pd(PCy_3)_2$ did not afford the corresponding Pd-containing cyclic amides.

Reactions of $Pt(cod)_2$ with unsaturated acids and amides in the presence of phosphine ligands did not afford Pt-containing esters and amides. They usually gave Pt hydride and π-type complexes, respectively.

References

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3) The Ni- or Pd-containing cyclic amides and esters have a trend to form an oligo- or polymeric structure through the intermolecular coordination of Ni or Pd to amide or ester group of another unit; for $PEt_3\text{-}\overline{NiCH_2CH(CH_3)CONH}$ formation of a tetrameric cyclic cluster has been established by X-ray crystallography (Y. Kushi et al., private communication). The oligo- or polymeric complexes are usually sparingly soluble in solvents and come out from the reaction mixture as almost analytically pure compounds. The intermolecular coordinating bond can be cleaved by addition of excess ligand or bidentate ligands such as dpe (see text) to form soluble complexes.
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(Received March 23, 1982)