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PREPARATION OF ACYL(CARBOXYLATO)NICKEL AND -PALLADIUM COMPLEXES $M(COR)(OCOR')L_2$ (M = Ni, Pd) AND REVERSIBLE REDUCTIVE ELIMINATION OF CARBOXYLIC ANHYDRIDES, RCOOCOR'

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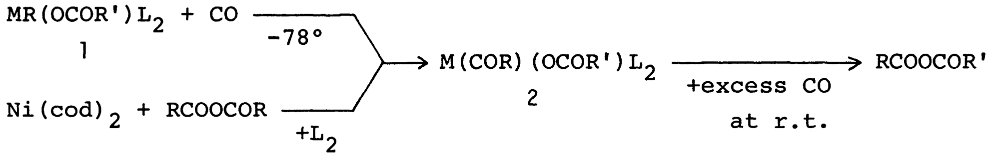
Acyl(carboxylato)nickel(II) and -palladium(II) complexes, $M(COR)(OCOR')L_2$ 2 are prepared by 1 : 1 reactions of $MR(OCOR')L_2$ 1 with CO at -78°, whereas similar reactions in the presence of excess CO at room temperature afford the reductive elimination products, RCOOCOR'. Acid anhydrides add oxidatively to an Ni(0)-complex to afford a complex of the type 2.

Carbonylations of organic compounds using transition metals are of great importance in various organic syntheses. Insertion of carbon monoxide into a metal-carbon bond has been recognized as a most important step in these reactions.[1,2] Previously we reported CO insertion into Ni-R bonds of $NiR(phenoxo)L_2$-type complexes to afford $Ni(COR)(phenoxo)L_2$ and reductive elimination of phenyl carboxylates from the $Ni(COR)(phenoxo)L_2$-type complexes.[3,4] We now report preparation of a new class of acylnickel(II) and -palladium(II) complexes having carboxylato ligands, $M(COR)(OCOR')L_2$ 2 (M = Ni, Pd) by the reaction of $MR(OCOR')L_2$ 1 with CO and reductive elimination of RCOOCOR' from the complexes. As for nickel complexes reversibility of the reductive elimination of RCOOCOR' is also demonstrated,



$$\left.\begin{array}{l} \underset{1}{MR(OCOR')L_2} + CO \xrightarrow{-78^\circ} \\ Ni(cod)_2 + RCOOCOR \xrightarrow[+L_2]{} \end{array}\right\rangle \longrightarrow \underset{2}{M(COR)(OCOR')L_2} \xrightarrow[\text{at r.t.}]{\text{+excess CO}} RCOOCOR' \qquad (1)$$

2a ; $Ni(COMe)(OCOPh)(PEt_3)_2$
2b ; $Ni(COMe)(OCOMe)(PEt_3)_2$
2c ; Ni(COEt)(OCOPh)(bpy)
2d ; $Pd(COMe)(OCOPh)(PEt_3)_2$

Interaction of an equimolar amount of carboxylic acid with dialkyl-nickel or -palladium complexes smoothly affords alkyl(carboxylato)nickel or -palladium complexes 1 in high yield with evolution of one mole of alkane similarly to our previous paper.[3,5] Alkyl(carboxylato)metal complexes 1 were characterized by IR and NMR spectroscopies, elemental analysis, and chemical reactions.[13] ^1H- and $^{31}P\{^1H\}$-NMR spectra of 1a, 1d, and 1e having PEt_3 ligands show triplets for the M-$\underline{Me}$ group and singlets for $\underline{P}Et_3$ respectively, suggesting *trans* geometry around the central metal.

$$MR_2L_2 + R'COOH \longrightarrow L_2MR(OCOR') + RH \tag{2}$$

1a: $NiMe(OCOPh)(PEt_3)_2$, 1b: $NiMe(OCOMe)(PEt_3)_2$,
1c: $NiEt(OCOPh)(bpy)$, 1d: $PdMe(OCOPh)(PEt_3)_2$,
1e: $PdMe(OCOMe)(PEt_3)_2$

Isolation of 2 When an equimolar amount of CO was introduced into a THF solution of 1a at -78°, slow absorption of CO took place and the reaction was completed in ca. 1 h. After removal of solvent *in vacuo*, recrystallization of the residual solid gave yellow crystals of $Ni(COMe)(OCOPh)(PEt_3)_2$ 2a. IR spectrum of 2a showed a strong absorption band at 1650 cm^{-1} assignable to ν(C=O) of the nickel-acyl group. ^1H-NMR of 2a shows no signal of Ni-$\underline{Me}$, but a singlet of Ni-CO$\underline{Me}$ at 2.48 ppm. $^{31}P\{^1H\}$-NMR of 2a showed only one singlet, suggesting its *trans* geometry. Similar reactions of 1b and 1c with equimolar amounts of CO at -78° gave the acyl nickel complexes 2b and 2c. Spectral data of the acyl complexes are summarized in Table 1. IR spectra of all the acyl complexes showed ν(C=O) bands at ca. 1650 cm^{-1} and ^1H-NMR showed new signals assignable to the acyl group. These acyl complexes are stable at room temperature under nitrogen.

Palladium analog 1d also reacted with CO to give a palladium acyl complex 2d, but in this case the reaction required an excess amount of CO and higher reaction temperature (r.t.). 1e gave reductively eliminated product MeCOOCOMe (*vide infra*) on interaction with CO, and no acyl complex was obtained.

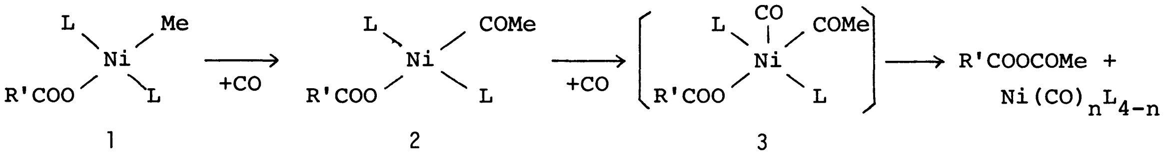
Table 1 Spectroscopic Data of Acyl(carboxylato) Complexes

Complex	^1H-NMR (ppm from TMS)			$^{31}P\{^1H\}$-NMR	IR(cm^{-1})
	M-CO$\underline{R}$	M-$O_2C\underline{R}'$	L	(ppm from ext. PPh_3)	ν(C=O)
2a[a]	2.48(3H,s)	7.4(3H,m) 7.9(2H,m)	0.5-1.6(30H,m)	21.9(s)	1650[c]
2b[a]	2.36(3H,s)	1.64(3H,s)	0.5-1.6(30H,m)	21.8(s)	1640[d]
2c[b]	1.09(3H,t, J(H-H)=7Hz) 3.10(2H,q,7)	7.4-8.0(13H,m)			1660[c]
2d[a]	2.37(3H,t, J(P-H)=1Hz)	7.3(3H,m) 8(2H,m)	1.09(18H,qui, J(P-H)=8Hz) 1.7(12H,m)	23.1(s)	1670[d]

Abbriviation, s; singlet, t; triplet, q; quartet, qui; quintet, m; multiplet.
a) in acetone-d_6, b) in CD_2Cl_2, c) KBr, d) KRS-5.

Formation of RCOOCOR' In contrast to the 1 : 1 reactions between the alkyl(carboxylato)nickel complexes with CO at -78°, reaction of 1a - 1c with excess CO at room temperature gave acid anhydride in high yields, the results being shown in Table

2. A mixture of RCOOCOR', RCOOCOR and R'COOCOR' was obtained in the reactions of 1a or 1c with excess CO. Unsymmetrical acid anhydride RCOOCOR' itself is known to disproportionate easily into RCOOCOR and R'COOCOR'.$^{6)}$ Formation of acid anhydride in the present reaction is considered to proceed through the insertion of CO into Ni-alkyl bond giving an acyl(carboxylato)nickel intermediate followed by C-O bond formation (reductive elimination) between the acyl and carboxylato ligands promoted by the coordination of CO to Ni. In fact the isolated acyl intermediate complexes 2 react with excess CO to afford acid anhydride quantitatively as shown in Table 2. The reductive elimination of acid anhydride promoted by CO is similar to those of ester and R-R from nickel acyl(phenoxo) complexes and dialkylnickel complexes, respectively, by the interaction with π-acids such as olefins and CO.$^{3,4,7)}$ *Trans* to *cis* isomerization of acyl(carboxylato)nickel intermediate 2 or configurational rearrangement of the 5-coordinated intermediate 3 prior to the reductive elimination of acid anhydride may be required in order to cause a smooth reductive elimination.$^{8,9)}$



(4)

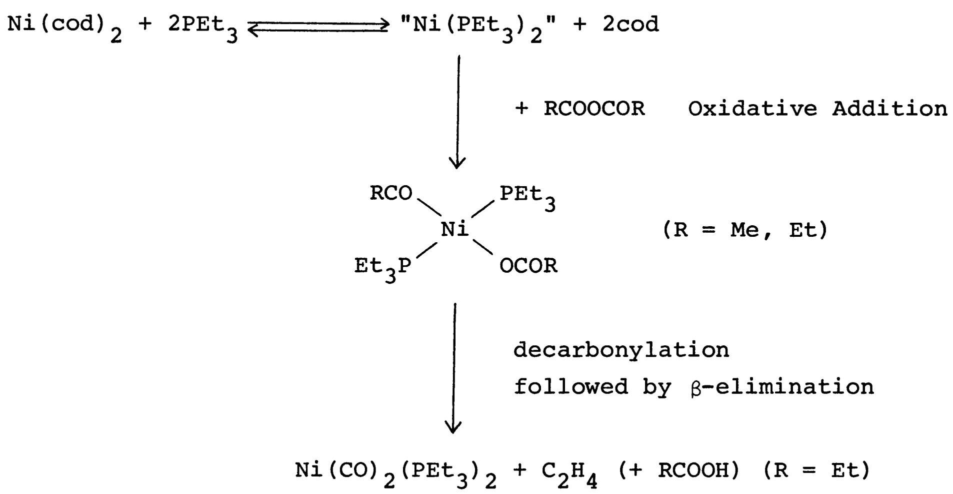
Table 2 Formation of RCOOCOR' by the Reaction of 1 and 2 with CO$^{a)}$

Complex	Product(s) (yield, mole/M)$^{b)}$
1a	$CH_3COOCOPh(0.50)$, $CH_3COOCOCH_3(0.25)$, PhCOOCOPh(0.25)
1b	$CH_3COOCOMe(0.97)$
1c	EtCOOCOPh(0.36), EtCOOCOEt(0.25), PhCOOCOPh(0.25)
1e	$MeCOOCOCH_3(0.90)$
2a	MeCOOCOPh(0.50), MeCOOCOMe(0.25), PhCOOCOPh(0.25)
2b	MeCOOCOMe(1.00)

a) Reaction conditions: CO/M>>1, solvent = THF, Temp. = r.t. Reaction time = 1 day.

b) estimated by ^1H NMR.

Oxidative Addition of RCOOCOR On the other hand, C-O bond cleavage of acid anhydride by low valent nickel complex is demonstrated. Excess of acetic anhydride reacted with a $Ni(cod)_2$-PEt_3 (1:2) mixture in THF at room temperature to give a yellow solution. Removal of the volatile matters *in vacuo* gave a yellow oil whose IR and ^1H-NMR spectra were identical with those of 2b. A weak signal assignable to $Ni\underline{Me}(OCOMe)(PEt_3)_2$ was also detected in the ^1H NMR, suggesting the occurrence of partial decarbonylation from Ni-acyl group. Propionic anhydride gave a similar acyl complex with carboxylato ligand under similar conditions, but slow decarbonylation took place to afford $Ni(CO)_n(PEt_3)_{4-n}$ with evolution of ethylene in 2 days at room temperature. The reaction is considered to proceed *via* oxidative addition of acid anhydride to Ni similarly to our previous report on the oxidative addition of esters to the Ni(0) complexes.$^{10,11)}$



(5)

CO insertion into the C-O bond of allyl ester to give acid anhydride in the presence of Pd has been previously reported by Tsuji et al.[12)] The present results suggest that the reported reaction proceeds *via* oxidative addition of allyl ester to Pd giving type 1 complex, followed by insertion of CO into Pd-C bond and reductive elimination of acid anhydride. This example may indicate a great potentiality of further applications of the metal-promoted oxidative cleavage of C-O bonds to various organic syntheses.

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13) Satisfactory values of elemental analyses for 1 were obtained. ^{1}H-NMR(ppm from TMS in acetone-d$_6$): 1a, -1.22(3H, t, 9Hz); 1b, -1.22(3H, s); 1c, 0.60(3H, t, 7Hz) and 1.10(2H, q, 7Hz); 1d, 0.07(3H, t, 6Hz); 1e, -0.08(3H, t, 6Hz) for M-R. ^{31}P{^{1}H}-NMR(ppm from ext. PPh$_3$ in acetone-d$_6$): 1a, 26.0(s); 1b, 26.3(s); 1d, 28.4(s).

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