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## BENZOYL(ACETYLACETONATO)NICKEL(II) COMPLEXES CONTAINING TERTIARY PHOSPHINE LIGANDS. THEIR SYNTHESIS, DYNAMIC BEHAVIOR IN SOLUTION, AND DECARBONYLATION

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### Summary

Carbon monoxide is readily inserted into the phenyl–nickel bond of  $\text{PhNi}(\text{acac})(\text{PR}_3)_n$  to give benzoylnickel complexes,  $\text{PhCONi}(\text{acac})\text{PR}_3$  ( $\text{R} = \text{Ph}, \text{Et}, \text{cyclo-C}_6\text{H}_{11}$ ), which were characterized by elemental analysis, IR and NMR spectroscopy, as well as chemical reactions. The reactions of the benzoylnickel complexes with methyl iodide and alcohols give acetophenone and corresponding benzoates, respectively, accompanied by some decomposition reactions. The solid benzoylnickel complexes when heated at elevated temperatures are decarbonylated and biphenyl, benzophenone and carbon monoxide are liberated. The dynamic behavior of the acac ligand in acetone solution was studied and the activation parameters for the acac exchange reactions were obtained. The decarbonylation reaction of the benzoyl complex  $\text{PhCONi}(\text{acac})\text{PPh}_3$  in acetone was studied by NMR, and found to be first order in the benzoylnickel complex.

### Introduction

Insertion of carbon monoxide into a transition metal–carbon  $\sigma$ -bond constitutes an essential elementary step in industrially important processes such as hydroformylation of olefins, carbonylation of methanol to acetic acid and probably in the Fischer–Tropsch process [1]. The reverse process, namely the decarbonylation of acyl and aroyl transition metal complexes to alkyl and aryl complexes, also is important in organic synthesis using transition metal complexes. In the metal-promoted decarbonylation of acyl or aroyl halides and of aldehydes, the extrusion of CO from an intermediate acyl or aroyl complex has been postulated to be an important step [2]. Although rather extensive discussions are often advanced in which the CO insertion and extrusion reactions are assumed, studies using isolated alkyl or acyl (aryl or aroyl) complexes are



TABLE 2

<sup>1</sup>H NMR SPECTRAL DATA OF THE BENZOYLNICKEL COMPLEXES <sup>a,b</sup>

Complex (solvent)	acac-CH <sub>3</sub>	acac-H	PhCONi		PR <sub>3</sub>
			<i>ortho</i>	<i>meta and para</i>	
I (benzene- <i>d</i> <sub>6</sub> )	1.58 (6, s) <sup>c</sup>	5.28 (1, s)	8.42–8.56 (2, m)	7.0–7.2 <sup>d</sup>	<i>o</i> -; 8.0–8.1 <i>m,p</i> -; 7.0–7.2 <sup>d</sup>
I (acetone- <i>d</i> <sub>6</sub> )	1.64 (6, s)	5.42 (1, s)	8.04–8.20 (2, m)	7.1–7.9 <sup>d</sup>	7.1–7.9 <sup>d</sup>
II (benzene- <i>d</i> <sub>6</sub> )	1.68 (6, s)	5.34 (1, s)	8.76–8.90 (2, m)	7.10–7.40 (m) <sup>e</sup>	0.60–1.52 (15, m)
II (acetone- <i>d</i> <sub>6</sub> )	1.76 (6, s)	5.44 (1, s)	8.30–8.50 (2, m)	7.42–7.60 (3, m)	0.96–1.68 (15, m)
II (dichloromethane- <i>d</i> <sub>2</sub> )	1.76 (6, s)	5.39 (s) <sup>e</sup>	8.28–8.48 (2, m)	7.34–7.52 (3, m)	0.96–1.60 (15, m)
III (benzene- <i>d</i> <sub>6</sub> )	1.66 (s) <sup>f</sup>	5.28 (1, s)	8.68–8.80 (2, m)	6.96–7.30 (m) <sup>e</sup>	1.90–2.24 (two blocks of m) <sup>f</sup>

<sup>a</sup> 100 MHz at 25°C, tetramethylsilane as internal standard; s, singlet; m, multiplet. <sup>b</sup> Chemical shifts are in  $\delta$  values (ppm). <sup>c</sup> The signals of the benzoylnickel complex and its decarbonylated product at  $\delta$  1.71(s) and 1.36(s) are integrated together. <sup>d</sup> The *meta* and *para* protons of PhCONi and PPh<sub>3</sub> were not distinguishable. <sup>e</sup> The relative peak intensity was not estimated because of the overlap with signals of the solvent impurity. <sup>f</sup> The signal of methyl protons of the acetylacetonato ligand is overlapped with those of PCy<sub>3</sub>. The overall relative peak intensity of this area was 39.

(I–III) are rather insensitive to air and thermally stable in the solid state. In their IR spectra the  $\nu(\text{C}=\text{O})$  band is observed between 1620 and 1640  $\text{cm}^{-1}$ , which is slightly lower than  $\nu(\text{C}=\text{O})$  of the acetylnickel (1680  $\text{cm}^{-1}$ ) and of the propionynickel (1665  $\text{cm}^{-1}$ ) in RCONi(acac)PPh<sub>3</sub> [6] and close to  $\nu(\text{C}=\text{O})$  of PhCONiX(PEt<sub>3</sub>)<sub>2</sub> (1650–1610  $\text{cm}^{-1}$ , X = halogen) [3] and PhCONiCl(PPh<sub>3</sub>)<sub>2</sub> (1620  $\text{cm}^{-1}$ ) [9]. <sup>1</sup>H-NMR data listed in Table 2 also support the characterization of complexes I–III. They will be discussed in more detail later in this report.

#### Thermolysis of the benzoylnickel complexes

Although the benzoylnickel complexes are thermally stable in the solid state, decomposing in the range 100–110°C, they are more labile in solution and susceptible to loss of CO with reversion to the respective phenylnickel complexes. When the solid samples were pyrolyzed, they decomposed with liberation of carbon monoxide, but gas chromatographic analysis of the pyrolysis products revealed that considerable amounts of biphenyl, benzophenone and benzene were formed, as shown in Table 3. Although the total amount of CO groups in the products was far less than one mol per nickel when pyrolyzed in the solid state in vacuum (0.34 and 0.30 mol per one mol of complex pyrolyzed for complexes I and II, respectively), phenyl groups were recovered almost quantitatively in the form of benzene, biphenyl and benzophenone (1.1 and 0.9 mol, respectively, for I and II). The rest of the CO groups may be trapped with the Ni(PR<sub>3</sub>)<sub>2</sub> moiety to give Ni(CO)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>. In fact, examination of the IR spectrum of the pyrolysis residue of PhCONi(acac)PCy<sub>3</sub> (III, Cy = cyclohexyl group) revealed that it consisted of a mixture of PhNi(acac)PCy<sub>3</sub> and Ni(CO)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub>. Thus decarbonylation, decomposition and disproportionation processes appear

TABLE 3  
PYROLYSIS OF BENZOYLNICKEL COMPLEXES

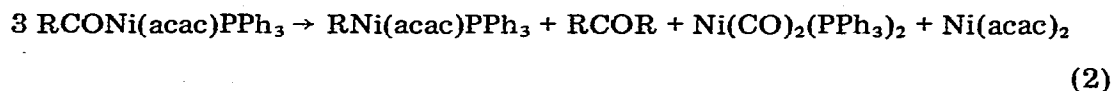
Complex	Solvent or atmosphere	Temperature (°C)	Time (min)	Evolved products (mol/mol of complex)			
				Carbon monoxide	Ph-H	Ph-Ph	PhCOPh
I	Solid in vacuo	170	5	0.25	trace	0.48	0.09
II	Solid in vacuo	170	10	0.19	0.08	0.28	0.11
II	Solid in carbon monoxide	170	30	<sup>a</sup>	0.17	0.02	0.09
I	Toluene	93	60	0.09	0.03	0.25	0.20 <sup>b</sup>
I	Pyridine	96	120	trace	0.25	0.15	trace
II	Pyridine	96	180	0.18	0.19	0.27	0.05
I	Acetone <sup>c</sup>	55	190	trace	trace	trace	0.21

<sup>a</sup> Not measured because of the existence of a large amount of unreacted carbon monoxide initially present.

<sup>b</sup> Besides the products shown in the Table, 0.03 (mol/mol of complex) of PhCOCOPh was produced.

<sup>c</sup> The pyrolysis in acetone did not go to completion and starting PhCONi(acac)PPh<sub>3</sub> and decarbonylated PhNi(acac)PPh<sub>3</sub> remained undecomposed in the system (See experimental).

to be occurring. A similar process has been reported to take place in the case of acylnickel complexes in solution [6].



The decarbonylation of the benzoylnickel complexes appears to have occurred on heating and the phenylnickel complex thus produced may have reacted either with the remaining benzoylnickel complex to give benzophenone or with another molecule of the phenylnickel complex via disproportionation, eventually giving biphenyl and Ni(acac)<sub>2</sub>, or decomposing by hydrogen abstraction to give benzene. Table 3 shows that the formation of biphenyl on pyrolysis of II was significantly suppressed and that benzene was the principal product when II was pyrolyzed in an atmosphere of carbon monoxide. This result suggests that the presence of CO affected the decomposition pathway of the benzoylnickel complex considerably.

In the decomposition of the benzoylnickel complexes in solution the rate and decomposition pathway are strongly affected by the nature of the solvent. The decomposition rate of I is much faster in toluene or pyridine than in acetone, and considerable amounts of benzene, biphenyl and benzophenone were produced, whereas a relatively clean decarbonylation which yielded PhNi(acac)PR<sub>3</sub> took place slowly in acetone. The more detailed study on the decarbonylation of the benzoyl complexes by means of <sup>1</sup>H NMR spectroscopy will be mentioned later.

#### Reaction of benzoylnickel complexes with alcohol

Information concerning the reaction of alcohol with acyl-transition metal complex is important in understanding the mechanism of the oxo process of the ester formation from an olefin, carbon monoxide and alcohol. Thus the alcoholysis products of the benzoylnickel complexes with methanol, ethanol and phenol were examined. The benzoylnickel complexes were found not to be highly

TABLE 4  
REACTION PRODUCTS OF BENZOYLNICKEL COMPLEXES  $\text{PhCONi}(\text{acac})\text{PR}_3$  WITH ALCOHOLS ( $\text{R}'\text{OH}$ )<sup>a</sup>

Complex	R'OH (solvent)	Products (mol/mol of complex)			
		PhCOOR'	Ph-H	Ph-Ph	PhCOPh
I	MeOH	0.15	0.27	— <sup>d</sup>	— <sup>d, b</sup>
II	MeOH	0.02	0.18	— <sup>d</sup>	— <sup>d</sup>
III	MeOH	0.10	0.19	— <sup>d</sup>	— <sup>d, b</sup>
I	EtOH	0.16	0.26	0.00	0.00 <sup>b</sup>
II	EtOH	0.01	0.11	0.08	0.00 <sup>c</sup>
I	PtOH (ether)	0.06	0.13	0.05	0.15 <sup>b</sup>
II	PhOH (ether)	0.03	0.06	0.12	0.00 <sup>c</sup>

<sup>a</sup> Reaction was carried out at room temperature for 2 days. <sup>b</sup> Besides the products shown in the Table, phenyl complex  $\text{PhNi}(\text{acac})\text{PR}_3$  and  $(\text{CO})_2\text{Ni}(\text{PR}_3)_2$  were produced. <sup>c</sup> About 60% of benzoyl complex was recovered and  $(\text{CO})_2\text{Ni}(\text{PR}_3)_2$  was not detected in the reaction mixture. <sup>d</sup> Not measured.

reactive toward alcohols. Sixty percent of the benzoylnickel complex II was recovered unchanged in the reactions of II with ethanol or phenol at room temperature for 2 days and yields of esters were low. The reactions were further complicated by occurrence of decarbonylation to give benzene, biphenyl and benzophenone, as Table 4 shows.

#### Reaction of the benzoylnickel complexes with methyl iodide

The reaction of the benzoylnickel complexes I—III with methyl iodide at room temperature afforded benzil together with acetophenone and benzophenone (Table 5). These results can be compared with the reaction of the parent phenyl complexes,  $\text{PhNi}(\text{acac})\text{PR}_3$ , with methyl iodide, in which toluene and biphenyl were the products [10]. In comparison with the results of the alcoholysis of benzoylnickel complexes, in which the yields of esters were low (vide supra), fairly high yields of acetophenone and the production of benzil in the reactions of methyl iodide with the benzoylnickel complexes were noted. In line with this observation, the yields of biphenyl and benzene were significantly lower than in the alcoholysis reactions. Methyl iodide may first add oxidatively to the

TABLE 5  
REACTION OF BENZOYLNICKEL COMPLEXES WITH METHYL IODIDE<sup>a, b</sup>

Complex	Products (mol/mol of complex)			
	PhCOCH <sub>3</sub>	PhCOPh	PhCOCOPh	Ph-Ph
I	0.43	0.15	0.05	0.01
II	0.15	0.22	0.09	0.02
III	0.23	0.19	0.08	0.01

<sup>a</sup> Reactions were carried out at room temperature for 1 day. <sup>b</sup> Me-acac and MeCO-acac were often produced besides above products.

benzoylnickel complex to give a quadrivalent active intermediate  $\text{PhCONi}(\text{CH}_3)\text{-I}(\text{acac})(\text{PR}_3)$  which is hexacoordinate and lacks the vacant site which is necessary for the decarbonylation to proceed. Thus, the decarbonylation might be prevented as compared with the case of alcoholysis and the decomposition of a quadrivalent intermediate may give acetophenone and benzil in relatively high yields. Similar chemistry has been reported for the benzoylhalogen complex,  $\text{PhCONiCl}_2$ , where L is a bulky phosphite ligand such as tris(bornyl)phosphite. The ease of its decarbonylation was discussed in terms of the steric requirements whether the room for coordination of carbonyl exists or not [5].

In addition to the products listed in Table 5, the formation of (acetyl)acetylacetone (3-acetyl-2,4-pentanedione) and (methyl)acetylacetone (3-methyl-2,4-pentanedione) was observed in the reaction of methyl iodide with complex II (see Experimental). The formation of (acetyl)acetylacetone suggests occurrence of a series of processes involving CO extrusion from the benzoylnickel complex, followed by the CO insertion into the previously assumed hexa-coordinated methylnickel intermediate to give an acetylnickel acetylacetonate complex which on reductive elimination would give (acetyl)acetylacetone.

#### *Dynamic behavior of acetylacetonato ligand of $\text{PhCONi}(\text{acac})\text{PR}_3$ in acetone solution*

We have previously studied in detail the exchange reaction of the acac ligand in  $\text{C}_2\text{H}_5\text{Ni}(\text{acac})\text{PPh}_3$  [11] and  $\text{Pd}(\text{acac})(\gamma\text{-acac})\text{py}$  [12] ( $\gamma\text{-acac}$  stands for the acetylacetonato ligand coordinated to the metal through its central carbon ( $\gamma$ -) atom). The present benzoylnickel complexes also exhibit similar exchange reactions of the acac ligand and the dynamic behavior was studied by variable temperature  $^1\text{H}$  NMR spectroscopy. The signal of the methyl protons of the acac ligand which appears as a singlet above room temperature (Table 2), splits into a doublet on cooling the solution below room temperature. This indicates that two acac-methyl groups, which are unequivalent in the ground state due to the difference of *trans* ligands, become equivalent by rapid exchange at the elevated temperature. The rate constants of the exchange of the acac ligand at various temperatures were calculated for complex I and II from the line widths of the acac methyl proton signals using Gutowsky's equation [13], and are summarized in Table 6 together with appropriate activation parameters. As the decarbonylation reaction of complex I occurs at elevated temperature in

TABLE 6

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR acac EXCHANGE REACTIONS OF  $\text{PhCONi}(\text{acac})\text{PR}_3$  IN ACETONE SOLUTION

Complex	$\text{PhCONi}(\text{acac})\text{PPh}_3$ (I)	$\text{PhCONi}(\text{acac})\text{PEt}_3$ (II)
Rate constants, $k$ ( $\text{sec}^{-1}$ )	$\left\{ \begin{array}{l} 208 (20^\circ\text{C}) \\ 495 (30^\circ\text{C}) \\ 986 (39^\circ\text{C}) \end{array} \right.$	$\left\{ \begin{array}{l} 19 (20^\circ\text{C}) \\ 208 (30^\circ\text{C}) \\ 1433 (40^\circ\text{C}) \\ 4032 (48^\circ\text{C}) \end{array} \right.$
$\Delta H^\ddagger$ (kcal $\text{mol}^{-1}$ )	14.3	35.4
$\Delta S^\ddagger_{298\text{K}}$ (cal $\text{deg}^{-1}$ $\text{mol}^{-1}$ )	1.0	68.5
$\Delta G^\ddagger_{298\text{K}}$ (kcal $\text{mol}^{-1}$ )	14.0	15.0

acetone solution (vide infra), care was paid to minimize the extent of heating the solution so as not to cause extensive decarbonylation. In the case of  $\text{PhCONi}(\text{acac})\text{PCy}_3$  (III) the overlap of the acac-methyl signals with the methylene proton signals of the phosphine ligand in the  $^1\text{H}$  NMR spectrum prevented studies of the line shape analysis of the acac exchange process.

Although there have been a large number of kinetic studies on the exchange of acac ligand in six coordinate octahedral complexes [14], little has been reported on such a process in a square planar, four-coordinate complex [6,11,12,15]. It is noted in Table 6 that, in spite of fairly large differences in the values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  between complexes I and II, similar  $\Delta G^\ddagger$  values are obtained for both complexes, suggesting the presence of a kind of compensation effects, and the mechanism of chelated acac-methyl exchange involving a rupture of one of two  $\text{M}-\text{O}$  bonds [12] may be applicable to the present two benzoylnickel systems. The larger value of  $\Delta H^\ddagger$  for II than for I may be related to the higher electron-donating ability of the triethylphosphine ligand vs. triphenylphosphine. The propionyl complex analogous to I ( $\text{EtCONi}(\text{acac})\text{PPh}_3$ ) has been reported to have an activation energy of 13.4 kcal/mol for the acac ligand exchange process in toluene- $d_8$  solution [6]. This is slightly smaller than the value for I ( $E_a$  14.6 kcal/mol).

In contrast to the non-rigid character of the acac ligand in the benzoyl complexes, the phosphine ligands in I and II proved to be non-dissociative under the same conditions. This was evidenced by the  $^{31}\text{P}$  NMR spectra of the acetone solutions of complexes I and II, in which a single sharp signal of the coordinated phosphine nucleus remained unchanged without any indication of the broadening for the temperature range of  $-40$  to  $+40^\circ\text{C}$  (for complex I) and  $-20$  to  $+50^\circ\text{C}$  (for II).

#### *The kinetic studies of the decarbonylation of $\text{PhCONi}(\text{acac})\text{PPh}_3$ in acetone solution*

The examination of the  $^1\text{H}$  NMR spectra of the benzoylnickel complexes revealed that complexes II and III containing  $\text{PEt}_3$  and  $\text{PCy}_3$  ligands are fairly stable in acetone solution. Complex II especially was found to be quite stable and it remained unchanged even after it had been heated at  $55^\circ\text{C}$  for 1 h. The basic ligands such as  $\text{PEt}_3$  and  $\text{PCy}_3$  seem to stabilize the benzoylnickel complexes. A similar observation has been reported in the case of the acetylpladium-(II) complexes,  $\text{MeCOPdCl}(\text{PR}_3)_2$  [16]. On the other hand, the  $^1\text{H}$ -NMR spectrum of  $\text{PhCONi}(\text{acac})\text{PPh}_3$  (I) in acetone solution changed gradually on standing even at room temperature. In addition to the singlet due to the acac-methyl protons of I at  $\delta$  1.64 ppm (Table 2), two singlets at  $\delta$  1.79 and 1.40 ppm, assignable to the acac-methyl protons in  $\text{PhNi}(\text{acac})\text{PPh}_3$  [10], appeared and grew with time at the expense of the original singlet. This indicates that the decarbonylation of the  $\text{PPh}_3$ -coordinated benzoyl complex to phenyl complex is taking place in the acetone solution.

The rate of decomposition of benzoyl complex I in acetone can be measured by following the rate of decrease in the relative intensities of the  $^1\text{H}$  NMR signal due to  $\text{PhCONi}(\text{acac})\text{PPh}_3$  (I). The reaction obeyed the first order kinetics until over 94% of the starting benzoyl complex was decomposed after 206 min at  $50^\circ\text{C}$ , as judged by observing the disappearance of the signal at  $\delta$  1.64 ppm

TABLE 7

RATE CONSTANTS OF DECARBONYLATION REACTION OF  $\text{PhCONi}(\text{acac})\text{PPh}_3$  IN ACETONE SOLUTION AND KINETIC PARAMETERS

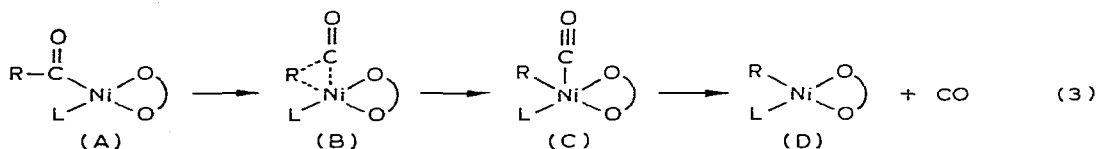
Rate constants, $k$ ( $\text{sec}^{-1}$ )	$\left\{ \begin{array}{l} 0.96 \times 10^{-2} (45^\circ\text{C}) \\ 1.39 \times 10^{-2} (50^\circ\text{C}) \\ 2.01 \times 10^{-2} (55^\circ\text{C}) \\ 3.13 \times 10^{-2} (60^\circ\text{C}) \end{array} \right.$
$\Delta H^\ddagger$ ( $\text{kcal mol}^{-1}$ )	15.5
$\Delta S^\ddagger_{298\text{K}}$ ( $\text{cal deg}^{-1} \text{mol}^{-1}$ )	-19.2
$\Delta G^\ddagger_{298\text{K}}$ ( $\text{kcal mol}^{-1}$ )	21.2

due to I. At this stage, however, conversion of I into  $\text{PhNi}(\text{acac})\text{PPh}_3$  was estimated to be 50%. The difference corresponding to 44% of  $\text{PhCONi}(\text{acac})\text{PPh}_3$  is believed to have been consumed by secondary reactions without affecting the first order kinetics concerning the disappearance of I. Possibly  $\text{PhNi}(\text{acac})\text{PPh}_3$  may be consumed by reacting with I in the presence of liberated CO producing benzophenone,  $\text{Ni}(\text{acac})_2$  and  $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$ . In fact 0.21 mol of benzophenone, corresponding to 0.42 mol of the nickel complex and accounting for the most of the missing 0.44 mol of I was found in the solution as determined by GLC and the formation of  $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$  was confirmed by examining the IR spectrum of the residual solid obtained by evaporating the solvent after completion of the reaction. In the previously reported decarbonylation of the propionylnickel complex  $\text{EtCONi}(\text{acac})\text{PPh}_3$ , the decomposition reaction was found to take place according to eq. 2 obeying neither first nor second order kinetics [6]. In the present system on the other hand, the fact that the reaction obeys first order kinetics over a wide range suggests that the CO extrusion is the rate determining step and that the secondary reactions do not affect the kinetic pattern. The first order rate constants thus obtained at various temperatures and kinetic parameters are shown in Table 7.

Kinetic studies of the insertion of carbon monoxide into the carbon-metal  $\sigma$ -bond have been reported for some other alkyl-transition metal complexes [17] such as  $\text{CH}_3\text{Mn}(\text{CO})_5$  [18],  $\text{CH}_3\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2$  [19],  $\text{CH}_3\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3$  [19], and  $\text{C}_2\text{H}_5\text{PtCl}(\text{CO})(\text{L})$  [20]. On the other hand, reports of kinetic studies of the decarbonylation reaction of acyl or aroyl complexes have been few in number [21,22]. The fairly large negative value of  $\Delta S^\ddagger$  ( $-19.2 \text{ cal deg}^{-1} \text{ mol}^{-1}$ ) in the present system stands in contrast to the result obtained with  $(\text{PhCO})\text{Mn}(\text{CO})_5$  in which a positive value of  $\Delta S^\ddagger$  ( $22 \pm 3 \text{ cal deg}^{-1} \text{ mol}^{-1}$ ) was reported [22]. The decarbonylation reaction induced by ligand (CO) dissociation was assumed for the latter system. No evidence was obtained concerning the dissociation of phosphine ligand in the decarbonylation process of I as judged from the absence of line broadening in the  $^{31}\text{P}$  NMR spectrum of the system in which the decarbonylation reaction is taking place. Furthermore, the fluxional character of the acac ligand (vide supra) was proved not to affect the decarbonylation, because similarly facile exchange of acac ligands was observed at room temperature for all three complexes I, II, and III, whereas a moderately rapid decarbonylation was observed only for complex I at the same temperature. The mechanism of the decarbonylation reaction of the present benzoylnickel complexes may be one which passes through the transition state of three-centered benzoyl-



nickel bonding (B in the following scheme). Restriction of free rotation of the



benzoyl group around the Ni—C bond at the transition state B may account for the negative  $\Delta S^\ddagger$  value for this decarbonylation reaction.

A negative value of  $\Delta S^\ddagger$  ( $-8 \text{ cal deg}^{-1} \text{ mol}^{-1}$ ) has been reported for the intramolecular carbonyl insertion reaction of  $\text{C}_2\text{H}_5\text{PtCl}(\text{CO})\text{L}$  [20].

## Experimental

### General

All reactions and manipulations were carried out under dry, oxygen-free nitrogen or in vacuo using Schlenk-type flasks. Filtrations were carried out using siphons with sintered-glass disks under positive pressure of nitrogen.

Carbon monoxide was dried by passing the gas through columns containing  $\text{CaCl}_2$ . Solvents such as diethyl ether, hexane and toluene were purified and dried by distillation over sodium wire and stored under nitrogen. Methanol and ethanol were dried by distilling over Drierite and stored under nitrogen. Phenyl-(acetylacetonato)(tertiary phosphine)nickel(II),  $\text{PhNi}(\text{acac})(\text{PR}_3)_n$  ( $n = 1$ ,  $\text{R} = \text{Ph}$  and cyclo- $\text{C}_6\text{H}_{11}$ ;  $n = 2$ ,  $\text{R} = \text{Et}$ ), were prepared according to the method reported previously [8,10].

The carbon/hydrogen microanalyses were performed by Mr. T. Saito of our Laboratory by using a Yanagimoto CHN Autocorder Type MT-2. Infrared spectra were recorded on a Hitachi model 295 spectrometer using KBr disks prepared under inert atmosphere. NMR spectra were measured in vacuo on a JNM-PS-100 spectrometer by Mr. Y. Nakamura of our laboratory.

Gases evolved in the reactions were measured and collected by means of a Toepler pump and analyzed using either gas chromatography or mass spectrometry. The liquid organic products formed in the various reactions of the benzoyl complexes were analyzed quantitatively by gas chromatography using ethylbenzene as an internal reference unless otherwise stated. Gas chromatographic analysis was performed on a Shimadzu Type GC-3B or GC-6A gas chromatograph using SDC-550 or PEG-20M columns and hydrogen or helium as a carrier gas.

### Preparation of $\text{PhCONi}(\text{acac})\text{PCy}_3$

Into a cooled (below  $0^\circ\text{C}$ ) mixture of  $\text{PhNi}(\text{acac})\text{PCy}_3$  (1.14 g, 2.79 mmol) and hexane (25 ml), carbon monoxide was bubbled for 30 min. The initially pale yellow suspension changed to a red solution then finally to an orange suspension. The orange precipitate formed was filtered, washed with hexane at  $0^\circ\text{C}$  and dried under vacuum at room temperature. The  $\text{PhCONi}(\text{acac})\text{PCy}_3$  thus obtained weighed 1.32 g (yield 87%). Analytical data and physical properties are listed in Table 1.

### *Preparation of PhCONi(acac)PPh<sub>3</sub>*

A mixture of PhNi(acac)PPh<sub>3</sub> (0.74 g, 1.49 mmol), toluene (10 ml) and hexane (15 ml) was cooled to  $-10^{\circ}\text{C}$ . On bubbling carbon monoxide through the lemon yellow suspension for 10 min, the color of the suspension changed to deep yellow. After further bubbling of carbon monoxide for 30 min., a deep yellow precipitate was filtered and washed with hexane. It was dried under vacuum at room temperature. The PhCONi(acac)PPh<sub>3</sub> thus obtained weighed 0.72 g (yield 92%). Analytical and physical data are listed in Table 1.

### *Preparation of PhCONi(acac)PEt<sub>3</sub>*

To the cooled (below  $0^{\circ}\text{C}$ ) red solution of PhNi(acac)(PEt<sub>3</sub>)<sub>2</sub> (0.63 g, 1.34 mmol) in toluene (10 ml), CO gas was bubbled for 60 min. To the resulting deep red solution was added 15 ml of hexane to afford a pale orange solution. After it has been kept for one day at  $-30^{\circ}\text{C}$ , orange plates crystallized. These were filtered, washed with hexane and dried in vacuo. The PhCONi(acac)PEt<sub>3</sub> thus obtained weighed 0.46 g (yield 90%) and was recrystallized from acetone. Analytical and physical data of this compound are listed in Table 1.

### *Pyrolysis of PhCONi(acac)PR<sub>3</sub> under vacuum*

PhCONi(acac)PPh<sub>3</sub> (0.0908 g, 0.173 mmol) was heated under vacuum at  $196^{\circ}\text{C}$  for 9 min. The complex melted at the first stage to give a red oil and then gradually turned to a black oil. After cooling to room temperature, the volume of the evolved gas was measured (0.95 ml, 0.0424 mmol). Mass spectral analysis revealed that the gas was exclusively CO. Diethyl ether (5 ml) and ethylbenzene (10  $\mu\text{l}$ , as an internal standard) were admitted to this flask and the amounts of pyrolysis products such as biphenyl (0.082 mmol) and benzene (0.016 mmol) were measured by GLC (Table 3).

Pyrolysis of PhCONi(acac)PEt<sub>3</sub> was carried out similarly under vacuum at  $170^{\circ}\text{C}$  using 0.153 g (0.402 mmol) of the complex.

### *Pyrolysis of PhCONi(acac)PR<sub>3</sub> in pyridine*

Pyridine (1 ml) was added to PhCONi(acac)PPh<sub>3</sub> (0.0922 g, 0.176 mmol) in a Schlenk flask at  $-20^{\circ}$ . After being degassed by the freeze-thaw method, the Schlenk flask was put into the oil bath at  $96^{\circ}\text{C}$  and shaken. The initial red solution turned to a black solution after 60 min. After having been shaken for 120 min at  $96^{\circ}\text{C}$ , the liquid pyrolysis products were analyzed by means of GLC (Table 3).

Pyrolysis of PhCONi(acac)PEt<sub>3</sub> in pyridine was carried out similarly using 0.172 g of complex.

### *Pyrolysis of PhCONi(acac)PPh<sub>3</sub> in acetone*

Acetone (3 ml) was added to PhCONi(acac)PPh<sub>3</sub> (0.109 g, 0.207 mmol) in a Schlenk flask at  $-20^{\circ}\text{C}$ . After being degassed by the freeze-thaw method, the system was shaken at  $55^{\circ}\text{C}$ . The initial red solution turned to yellow after 60 min. After having been shaken for 190 min, the pyrolysis products in the solution were determined by GLC. Benzene (0.015 mmol), biphenyl (0.049 mmol) and benzophenone (0.043 mmol) were detected. In this case, however, a considerable amount of the decarbonylated complex PhNi(acac)PPh<sub>3</sub> remained in the system.

and biphenyl detected above might have come from the pyrolysis of the phenyl complex in the GLC injection room. Therefore the system was treated with HCl gas to convert  $\text{PhNi}(\text{acac})\text{PPh}_3$  into benzene prior to the GLC analysis. This procedure afforded only a trace amount of biphenyl indicating the net amount of biphenyl produced through pyrolysis in acetone solution at  $55^\circ\text{C}$  to be negligibly small.

#### *Pyrolysis of $\text{PhCONi}(\text{acac})\text{PEt}_3$ under 1 atm of CO gas*

The flask containing  $\text{PhCONi}(\text{acac})\text{PEt}_3$  (0.145 g, 0.380 mmol) was pumped out and CO gas was introduced into the flask up to atmospheric pressure (ca. 32 ml, 1.43 mmol). On heating the system at  $170^\circ\text{C}$ , the orange benzoyl complex melted to give a red oil and then turned to a black oil in 30 sec. After standing for 30 min at  $170^\circ\text{C}$ , the system was cooled to room temperature and diethyl ether (5 ml) was added to the system. The amounts of products were measured by GLC (Table 3).

#### *Reactions of $\text{PhCONi}(\text{acac})\text{PR}_3$ with alcohols*

Methanol was slowly added to  $\text{PhCONi}(\text{acac})\text{PPh}_3$  (0.105 g, 0.200 mmol) at  $-30^\circ\text{C}$ . After the mixture had stood at room temperature for 2 days, the initial orange suspension turned to a lemon yellow suspension. Reaction products such as benzene (0.060 mmol) and methyl benzoate (0.054 mmol) were analyzed by GLC. The lemon yellow precipitate then was filtered and characterized as a mixture of  $\text{PhNi}(\text{acac})\text{PPh}_3$  and  $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$  on the basis of its IR spectrum ( $\nu(\text{C}=\text{O})$ , 1930 and  $1990\text{ cm}^{-1}$ ).

The reactions of  $\text{PhCONi}(\text{acac})\text{PR}_3$  (R = Ph, Et, cyclo- $\text{C}_6\text{H}_{11}$ ) with ethyl and methyl alcohols were carried out similarly. The reactions with phenol were carried out similarly in diethyl ether solution. In the reactions of  $\text{PhCONi}(\text{acac})\text{-PEt}_3$  with ethanol and phenol, a considerable amount (ca. 60%) of unreacted  $\text{PhCONi}(\text{acac})\text{PEt}_3$  was recovered from the reaction mixture (Table 4).

#### *Reactions of $\text{PhCONi}(\text{acac})\text{PR}_3$ with methyl iodide*

To a flask containing  $\text{PhCONi}(\text{acac})\text{PPh}_3$  (0.148 g, 0.864 mmol), methyl iodide (2 ml) was added by vacuum distillation from  $\text{CaH}_2$ . The initial red solution turned to a red suspension on stirring for one day at room temperature. The amounts of organic products were measured by GLC (Table 5).

Similarly carried out were the reactions of  $\text{PhCONi}(\text{acac})\text{PR}_3$  (R = Et, cyclo- $\text{C}_6\text{H}_{11}$ ) with methyl iodide. In the case of  $\text{PhCONi}(\text{acac})\text{PEt}_3$ , formation of (acetyl)acetylacetone and (methyl)acetylacetone, in addition to the products listed in Table 5, were observed as judged by processive gas chromatography-mass spectrometry; mass spectrum (15 eV),  $m/e$  (relative intensity): 142(33), 127(4), 114(10), 99 (21), 86(50), 74(65), 71(52), 59(100).

#### **Kinetic studies**

The kinetic studies of decarbonylation reaction of  $\text{PhCONi}(\text{acac})\text{PPh}_3$  in acetone solution were effected by following the time dependent decrease of the methyl proton signals of the acac ligand in  $^1\text{H}$  NMR spectra taken at various temperatures. Each NMR sample was prepared so as to possess the similar con-

centration. The signals due to solvent impurities (non-deuteriated acetone) was used as an internal standard to estimate the relative intensities.

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