Reversible CO Insertion into an Ni–C Bond of Alkyl(acetylacetonato)(triphenylphosphine)nickel(II)

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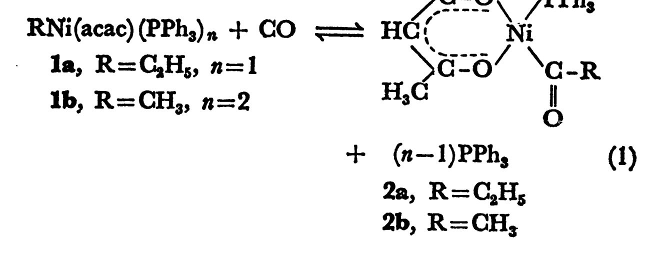
Reaction of alkyl(acetylacetonato)(triphenylphosphine)nickel(II), RNi(acac)$(PPh_3)n$ ($R=C_2H_5$, $n=1$ (**1a**); $R=CH_3$, $n=2$ (**1b**)) with carbon monoxide gives acyl(acetylacetonato)(triphenylphosphine)nickel(II) RCONi(acac)(PPh_3) ($R=C_2H_5$ (**2a**); $R=CH_3$ (**2b**)). Elemental analysis, IR and NMR spectra, and chemical properties of the acylnickel complexes support the structure. A variable temperature NMR spectroscopic study has revealed that the acac ligand in the acyl complexes exchanges rapidly in solution on NMR time scale. The acylnickel complexes **2a** and **2b** tend to decarbonylate at room temperature, the decarbonylation tendency of **2b** being greater than **2a**. They undergo further disproportionation according to the stoichiometry: $3RCONi(acac)(PPh_3) \rightarrow RCOR + Ni(CO)_2(PPh_3)_2 + Ni(acac)_2 + RNi(acac)(PPh_3)$. The mechanism involving the cross coupling of the acylnickel complex with the alkylnickel complex is proposed for the reaction on the basis of formation of $CH_3COC_2H_5$ on reaction of **2a** with **1b**.

Insertion of carbon monoxide into a transition metal-carbon bond to give an acyltransition metal complex and its reverse process, decarbonylation from an acyltransition metal complex to an alkyl complex, consitute crucial elementary steps in industrially important processes such as carbonylations of olefins[1] and methanol[2] and in synthetically important decarbonylation reactions.[3] However, studies of the carbonylation and decarbonylation processes dealing with well characterized complexes are relatively limited.[4] Particularly, the study with an acylnickel complex has received less attention because of its unstable nature,[5] and only recently the first stable acylnickel complex $CH_3CONiCl(PMe_3)_2$ has been isolated by Klein.[6]

We report here the preparation of new stable acylnickel complexes RCONi(acac)(PPh_3) from the corresponding alkylnickel complexes and describe their properties in solutions including facile decarbonylation and ketone formation.

Results and Discussion

*Preparation of Acyl(acetylacetonato)(triphenylphosphine)nickel **2a** and **2b**.* Bubbling of carbon monoxide through a toluene solution of ethyl(acetylacetonato)bis(triphenylphosphine)nickel(II)[7,8] (**1a**) below 0 °C gives its CO insertion product (**2a**). A similar reaction of methyl(acetylacetonato)bis(triphenylphosphine)nickel(II) (**1b**),[7] at 20 °C gives the corresponding acetylnickel complex (**2b**).



(1)

It is necessary to carry out the reaction at the low temperature for obtaining the propionyl complex **2a**, since **2a** is thermally unstable and the reaction at room temperature readily gives its decomposition products, $Ni(CO)_2(PPh_3)_2$ and diethyl ketone (*vide infra*).

Although the acylnickel complexes are unstable in solution, they are stable in the solid state once it is isolated. The IR spectrum of **2a** shows a ν(C=O) band of the nickel-bonded acyl group at 1665 and that of **2b** at 1680 cm^{-1} which may be compared with the ν(C=O) bands of acylplatinum, palladium and nickel complexes in the region of 1610 to 1675 cm^{-1}.[6,9] The IR bands due to the acetylacetonato and triphenylphosphine ligands in **2a** and **2b** are similar to those of the starting alkylnickel complexes **1a** and **1b**.

*NMR Spectrum and Chemical Properties of **2a**.* The NMR spectrum of **2a** in toluene-d_8 at 20 °C (Fig. 1A) shows a triplet at δ 0.70 (3H, CH_3 of the propionyl group), a quartet at δ 2.85 (2H, CH_2 of the propionyl

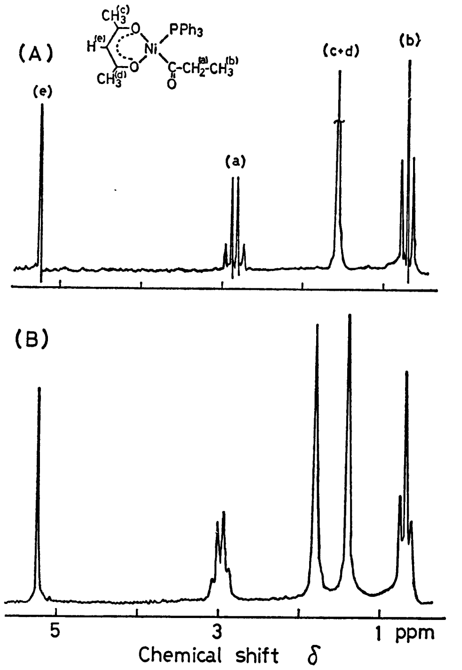
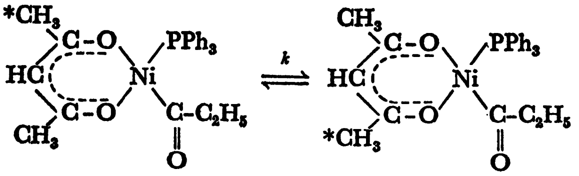


Fig. 1. NMR spectra of $C_2H_5CONi(acac)(PPh_3)$ in toluene-d_8 at (A) 20 °C and (B) −40 °C.

Table 1. The rate constants of the acac interchange in **2a** in toluene-d_8

Temp (°C)	Rate constant (s^{-1})
−40	7±2
−30	16±2
−20	70
−10	140
0	500

group), a singlet at δ 1.56 (6H, two CH_3 groups of acac) and a singlet at δ 5.25 (1H, CH of acac). Although the two CH_3 groups of the acac ligand in **2a** give a sharp singlet peak at room temperature, the singlet peak becomes broad on cooling the toluene-d_8 solution of **2a** and then separates on further cooling into two peaks indicating a rapid exchange of the acac ligand in the square planar nickel complex at room temperature on NMR time scale. Figure 1B shows the NMR spectrum of **2a** at −40°C, where the exchange is very slow. The rate constants of the exchange of the acac ligand calculated from the temperature variation of the NMR spectrum are tabulated in Table 1.



(2)

The rate constant of the acac exchange is expressed as,

$$k = 2.5 \times 10^{13} \exp(-13400/RT) \tag{3}$$

In the parent ethylnickel complexes **1a**, on the other hand, the exchange of the acac ligand is much slower in benzene, toluene, acetone and tetrahydrofuran. The methyl protons of the acac ligand in **1a** are observed as magnetically non-equivalent signals at room temperature which coalesce at elevated temperatures (~—70 °C). The higher exchange rate of the acac ligand in the propionylnickel complex may be due to the electron-withdrawing effect of the acyl group bonded to nickel.

When **2a** was allowed to stand in solution for 1 week at room temperature, it underwent disproportionation reaction to give $C_2H_5COC_2H_5$ (24 mol % per **2a**), **1a**, $Ni(CO)_2(PPh_3)_2$ and $Ni(acac)_2$. Figure 2 shows the NMR spectrum of the solution of **2a** observed after the disproportionation reaction. Each of peaks with an arrow (a,c,e, and g) is due to **1a**.[7] The ethyl group of **1a** gives rise to a singlet peak as previously reported.[7] The amount of **1a** formed is about 30 mol % per **2a**. The triplet and quartet peaks in Fig. 2 (b, d) are assigned to the methyl and methylene groups of $C_2H_5COC_2H_5$ by comparison of the spectrum with that of the authentic sample. Formation of $Ni(CO)_2(PPh_3)_2$ and $Ni(acac)_2$ was confirmed by elemental analyses and IR spectra of the complexes isolated from the reaction mixture. Heating the reaction solution further for 6 hr at 70 °C caused a slight increase in the amount of $C_2H_5COC_2H_5$ (29 mol % per **2a**) with a partial thermal decomposition of **1a** to give ethane (7 mol % per **2a**) and ethylene (23 mol % per **2a**).

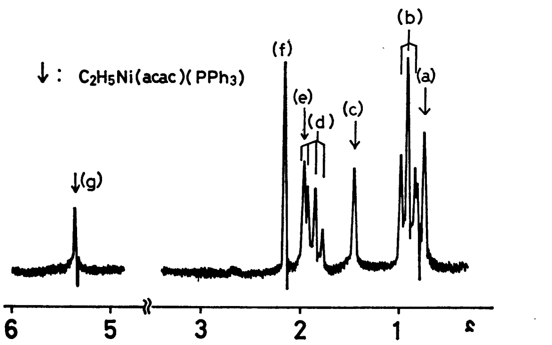


Fig. 2. NMR spetrum of the disproportionation products of **2a** in benzene. A peak (f) at δ 2.10 is due to toluene contained in C_6H_6. For assignment of the peaks (a~g) see the text.

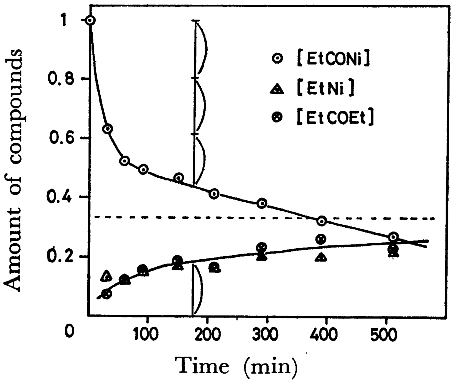


Fig. 3. Time curves for disappearance of **2a** and formation of **1a** and diethylketone during the disproportionation of **2a**. Units of the amounts of the compounds are arbitrary (calculated from areas in the NMR spectrum).

The decrease of **2a** and the accompanying increases of $C_2H_5COC_2H_5$ and **1a** with time were followed by the NMR spectroscopy. Figure 3 shows the time curves of the amounts of **2a**, $C_2H_5COC_2H_5$ and **1a**. It is seen in Fig. 3 that the amount of **1a** produced is equal to that of $C_2H_5COC_2H_5$ produced within experimental error and 1 mol equivalent of $C_2H_5COC_2H_5$ is formed with the consumption of 3 mol of **2a**. These facts suggest that the following reaction is taking place in the solution.

$$3Ni(COC_2H_5)(acac)(PPh_3)$$
$$\rightarrow C_2H_5COC_2H_5 + NiC_2H_5(acac)(PPh_3)$$
$$\mathbf{2a} \qquad\qquad \mathbf{1a}$$
$$+ Ni(CO)_2(PPh_3)_2 + Ni(acac)_2 \tag{4}$$

A detailed kinetic analysis of the reaction has been unsuccessful due to the complexity of the reaction process. However, the following disproportionation mechanism seems to be most probable. (1) The first step of the reaction is the decarbonylation of **2a** to give **1a**.

$$Ni(COC_2H_5)(acac)(PPh_3)$$
$$\rightarrow Ni(C_2H_5)(acac)(PPh_3) + CO \tag{5}$$

(2) The second step is the formation of $C_2H_5COC_2H_5$,

$Ni(acac)_2$ and $Ni(PPh_3)_2$ from **2a** and **1a** presumably *via* a binuclear interaction between **2a** and **1a**.

$$Ni(COC_2H_5)(acac)(PPh_3) + Ni(C_2H_5)(acac)(PPh_3) \rightarrow C_2H_5COC_2H_5 + Ni(acac)_2 + Ni(PPh_3)_2 \qquad (6)$$

$Ni(PPh_3)_2$ produced will immediately accept carbon monoxide liberated from **2a** by equation 5, thus completing Eq. 4.

In order to test the assumption that the ketone is formed by interaction of the acylnickel complex with alkylnickel complex the reaction of the propionyl complex **2a** with the ethyl complex **1a** in a 1 : 1 molar ratio was examined. The amount of $C_2H_5COC_2H_5$ produced increased to 47 mol % per **2a** compared with 24 mol % produced in the absence of **2a**. The reaction was accompanied by the evolution of ethane (22 mol % per **2a**) and ethylene (22 mol % per **2a**) which may be formed from an intermediate unstable ethylnickel complex produced in the process of the disproportionation reaction.

Assumption of coupling of the acylnickel complex with the alkyl complex was further supported by formation of $CH_3COC_2H_5$ in the reaction of the propionyl complex **2a** with the methyl complex **1b**. The reaction was accompanied by formation of $C_2H_5COC_2H_5$ probably produced by coupling of the propionyl group in **2a** with the ethyl complex **1a** generated by decarbonylation of **2a**. Some methane, ethylene and ethane were also formed, which may be produced by decomposition of unstable intermediate methyl and ethynickel complexes generated during the disproportionation process as in the reaction of **2a** with **1a**.

In relation to Eq. 6 a somewhat analogous disproportionation of $NiC_2H_5(acac)(PPh_3)$ in pyridine producing $Ni(acac)_2$, $Ni(C_2H_4)(PPh_3)_2$ and ethane according to a second-order reaction kinetics has been observed.7)

*NMR Spectrum and Chemical Properties of **2b**.* Although **2b** is stable in the solid state and the IR spectrum of **2b** in the solid state indicates that the compound is not contaminated with **1b**, the NMR spectrum of **2b** (Fig. 4) shows not only the peaks assignable to **2a** (δ 2.23 (3H, CH_3 of CH_3CO), δ 1.60 (6H, CH_3 of acac), δ 5.26 (1H, CH of acac)) but also peaks of **1b**7) (shown with an arrow) which is formed by the decarbonylation of **2b**. This fact suggests that **2b** readily liberates CO in solution reverting itself to **1b** in a greater decarbonylation tendency than **2a** and that **1b** and **2b** are in equilibrium in the solution. The presence of equilibrium in solution accounts for the experimental fact that **2b** was isolable from solution only under an atmosphere of CO. Attempts to isolate **2b** under an atmosphere of nitrogen were unsuccessful and **1b** was recovered from the solution.

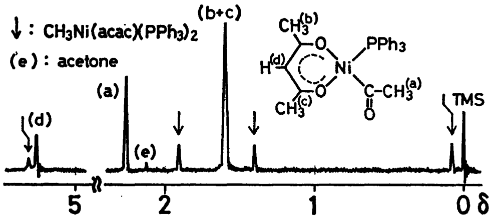


Fig. 4. NMR spectrum of $CH_3CONi(acac)(PPh_3)$ in benzene at 25 °C. The assignment of each signal (a—d) is indicated on the spectrum with reference to the formula of **2b**. Each of peaks with an arrow is due to $CH_3Ni(acac)(PPh_3)$.7) Formation of a small amount of acetone by the disproportionation of **2b** is seen (peak e).

When the reaction of CO with **1b** in toluene was carried out at room temperature in a closed system, 0.7 mol equivalent of CO was absorbed per mol of **1b** but the complex recovered from the solution turned out to be **1b**.

As in the propionyl complex **2a**, the NMR spectrum of the acetyl complex **2b** shows that the acac ligand exchanges rapidly at room temperature in benzene as indicated by appearance of the methyl signal of the acac ligand as a sharp singlet which splits on lowering the temperature. An accurate value of the rate constant of the acac exchange in **2b** could not be obtained, since the split peaks of CH_3(acac) group in **2b** were overlapped with the CH_3(acac) peaks of **1b** at the low temperatures. Roughly estimated values for the rate constants were of the same magnitude as those obtained for **2a**. When the benzene solution of **2b** was allowed to stand at room temperature for 1 week, **2b** underwent the disproportionation reaction to give CH_3COCH_3 (20 mol % per **2b**), $Ni(CO)_2(PPh_3)_2$, **1b** and $Ni(acac)_2$. The products of the disproportionation reaction suggest that a similar reaction expressed by Eq. 4 takes place with **2b**.

It is known that some acyltransition metal complexes give biacyls.4e,5,11) However, no biacyl has been detected in the disproportionation of **2a** and **2b**.

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Experimental

Materials. $C_2H_5Ni(acac)(PPh_3)$, **1a**, and $CH_3Ni(acac)(PPh_3)_2$, **1b**, were prepared as described in our previous paper.7) Solvents were dehydrated, purified and stored under nitrogen.

*Preparation of $C_2H_5CONi(acac)(PPh_3)$ **2a**.* Dehydrated carbon monoxide was bubbled into a toluene solution (6 ml) of **1a** (0.98 g, 2.2 mmol) for an hour at −20 °C. Hexane (25 ml) was added to the red solution under an atmosphere of CO at −78 °C and the orange crystals which separated were collected by filtration to yield 0.91 g (85%) of **2a**. Found: C, 65.4; H, 6.1%. Calcd for $C_{26}H_{27}NiO_3P$: C, 65.6; H, 5.8%. IR(KBr): 1665 cm⁻¹ (C=O), 595 cm⁻¹ (tentatively assigned to Ni-C). NMR(benzene, 25 °C): δ: 0.77 (3H, CH_3 of propionyl, t, J=7 Hz), 2.92 (2H, CH_2 of propionyl, q, J=7 Hz), 1.60 (6H, CH_3 of acac, s), 5.38 (1H, CH of acac, s).

The same product was obtained in a closed system by the reaction of **1a** (0.43 g, 0.96 mmol) with carbon monoxide (*ca.* 60 ml, 2.5 mmol) in toluene (10 ml) at 0 °C for 1 hr; yield=70%. However, bubbling of CO into a toluene solution of **1a** at room temperature for 3 hr did not give **2a** but yellow crystals and $C_2H_5COC_2H_5$. The yellow crystals were identified as $Ni(CO)_2(PPh_3)_2$ by the IR spectrum (2000 and 1935 cm⁻¹, ν(CO))5) and elemental analysis. Found: C, 71.8; H, 4.8%. Calcd for $C_{38}H_{30}NiO_2P_2$: C, 71.4;

H, 4.7%.

Preparation of $CH_3CONi(acac)(PPh_3)$ ***2b.*** Dehydrated carbon monoxide was bubbled into a toluene (50 ml) solution of **1b** (1.7 g, 2.4 mmol) for an hour at 20 °C. Hexane (50 ml) was added slowly to the red solution under an atmosphere of CO at −78 °C and the orange crystals which separated were collected by filtration to give 0.98 g (55%) of **2b**. Found: C, 65.3; H, 5.4%. Calcd. for $C_{25}H_{25}NiO_3P$: C, 64.9; H, 5.4%. IR(KBr): 1680 cm^{-1} (C=O), 580 cm^{-1} (tentatively assigned to Ni–C). Since an absorption peak of **1b** at 605 cm^{-1} (tentatively assigned to Ni–C) was not observed in the IR spectrum, the product is considered not contaminated with **1b**. Prolonged bubbling of CO into the toluene solution of **1b** resulted in the formation of $Ni(CO)_2(PPh_3)_2$ (confirmed by IR and elemental analysis) and acetone, but **2b** was not obtained.

Reaction of **2a** *with Methyl Iodide.* CH_3I (1.33 g, 9.3 mmol) was added to a flask containing 0.145 g (0.30 mmol) of **2a** by a trap-to-trap distillation in vacuum. The mixture was allowed to stand for 1.5 days at room temperature. $CH_3COC_2H_5$ (0.130 mmol), ethylene (0.062 mmol), methane (0.018 mmol) and a trace amount of C_2H_6 were obtained from the reaction mixture. When the reaction time was shorter (4 hr), a smaller amount of $CH_3COC_2H_5$ (20 mmol % per **2a**) was formed.

Disproportionation Reaction of **2a** *and* **2b**. On allowing **2a** (0.42 g, 0.87 mmol) to stand in benzene for 1 week at room temperature, the color of the solution changed from red to yellow. The gas-chromatographic analysis of the solution indicated the formation of $C_2H_5COC_2H_5$ (0.20 mmol. Trace amounts of C_2H_6 and C_2H_4 were detected. Heating the obtained solution at 70 °C for 6 hr caused an increase in the amount of $C_2H_5COC_2H_5$ (0.25 mmol) with a thermal decomposition of **1a** to give ethane and ethylene.

On adding hexane to the reaction mixture a mixture of a yellow precipitate and a green precipitate was obtained. IR spectrum of the mixture indicated that it was a mixture of $Ni(CO)_2(PPh_3)_2$[5] and $Ni(acac)_2$. $Ni(CO)_2(PPh_3)_2$ was isolated by recrystallization from hexane. Similar results were obtained from the disproportionation of **2b**.

Reaction of **2a** (0.15 g, 0.32 mmol) with **1a** (0.13 g, 0.29 mmol) was carried out in benzene (1.5 ml). After allowing the mixture to stand at room temperature for 3 days 0.13 mmol of $C_2H_5COC_2H_5$, 0.07 mmol of ethane and 0.07 mmol of ethylene were obtained. Heating the reaction mixture further at 70 °C for 5 hr caused an increase in the amount of $C_2H_5COC_2H_5$ (0.15 mmol, 47 mol % per **2a**).

Reaction of **2a** (0.14 g, 0.29 mmol) with **1b** (0.23 g, 0.33 mmol) was carried out in benzene-d_6 (1.70 g) at 50 °C. After 5 hr 0.08 mmol of $CH_3COC_2H_5$, 0.09 mmol of $C_2H_5COC_2H_5$, 0.07 mmol of CH_4, 0.13 mmol of ethylene and 0.04 mmol of ethane were obtained. When the molar ratio of **1b** to **2a** was smaller (1 : 1.8), the molar ratio of $CH_3COC_2H_5$ to $C_2H_5COC_2H_5$ decreased to 1 : 2.5.

Spectral Measurements and Analysis. The IR spectra were obtained by using Hitachi Model EPI-G3 spectrometer. NMR spectra were measured by Mr. Y. Nakamura of our laboratory with a Japan Electron Optics Laboratory PS-100 spectrometer. Solvent and TMS were added by a trap-to-trap distillation in vacuum into an NMR tube containing **2a** or **2b** and the NMR tube was sealed. Chemical shifts are referred to internal TMS (down field positive).

The microanalysis of carbon and hydrogen was performed by Mr. T. Saito of our laboratory with a Yanagimoto CHN Autocorder Type Mr-2. The amounts of gases and ketones formed by the reactions of **2a** and **2b** were measured by gas chromatography with Shimadzu GC-3B gas chromatograph.

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