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Reactions of acyl(carbonyl)ruthenium(II) and acyl(carbonyl)iron(II) complexes with amines. Preparation of novel propionyl(carbamoyl)ruthenium(II) complexes *

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Abstract

Treatment of Ru(COEt)Cl(CO)(PPh$_3$)$_2$ (**1**) with secondary amines (R$_2$NH) under pressure of CO and/or ethylene gives propionyl-carbamoyl complexes Ru(COEt)(CONR$_2$)(CO)(PPh$_3$)$_2$ (NR$_2$ = NEt$_2$ (**4a**), N(CH$_2$)$_4$CH$_2$ (**4b**), NMe$_2$ (**4c**)) together with the ammonium salt R$_2$NH$_2$Cl. Complexes **4a**–c have been isolated as pale yellow crystals and characterized by means of NMR and IR spectroscopy and elemental analysis. Reactions of Fe(COMe)I(CO)$_2$(PMe$_3$)$_2$ and [Fe(COMe)(CO)$_3$(PMe$_3$)$_2$]BF$_4$ with nucleophiles (HNEt$_2$, LiNMe$_2$, EtOH (in conjunction with Et$_3$N) and NaOMe) give the corresponding acetamides and acetic acid esters.

Introduction

The recently developed double carbonylation reactions catalyzed by palladium and cobalt complexes provide convenient synthetic means for introducing two CO molecules into adjacent positions in organic compounds [1–3]. Detailed studies on the mechanism of the palladium-catalyzed reaction of aryl halides, secondary amines, and carbon monoxide to afford α-keto amides have revealed that the key step in the catalytic cycle involves nucleophilic attack of amine on a CO-coordinated aroylpalladium species (**A**) to give an aroyl(carbamoyl)palladium intermediate (**B**) which reductively eliminates α-keto amide [4,5].

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* Dedicated to Professor Akio Yamamoto on his retirement and in recognition of his contributions to organometallic chemistry.

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$$\underset{\mathbf{A}}{[\mathrm{ArCOPd(CO)L_2}]\mathrm{X}} \xrightarrow[-\,\mathrm{H_2NR_2X}]{+\,2\mathrm{HNR_2}} \underset{\mathbf{B}}{trans\text{-}\mathrm{ArCOPd(CONR_2)L_2}}$$

$$\xrightarrow{\text{isomerization}} \underset{\mathbf{C}}{cis\text{-}\mathrm{ArCOPd(CONR_2)L_2}} \xrightarrow{-\,\mathrm{PdL_2}} \mathrm{ArCOCONR_2} \qquad (1)$$

The aroyl(carbamoyl)palladium complex (**B**) was in fact isolated as a *trans* square planar complex of considerable thermal stability by using trimethylphosphine as a ligand of high coordination ability. The *trans* isomer undergoes *trans–cis* isomerization under certain conditions to give *cis*-aroyl-carbamoyl complex **C** which may release α-keto amide on reductive elimination [4g,h]. On the other hand, as a corresponding key complex to give amide as the by-product in the double carbonylation, *trans*-aryl(carbamoyl)palladium was also isolated by nucleophilic attack of a secondary amine on the CO ligand coordinated to an arylpalladium complex. Liberation of amide by reductive elimination of the aryl and carbamoyl ligands was also demonstrated [4h].

$$[\mathrm{ArPd(CO)L_2}]\mathrm{X} \xrightarrow[-\,\mathrm{H_2NR_2X}]{+\,2\mathrm{HNR_2}} trans\text{-}\mathrm{ArPd(CONR_2)L_2}$$

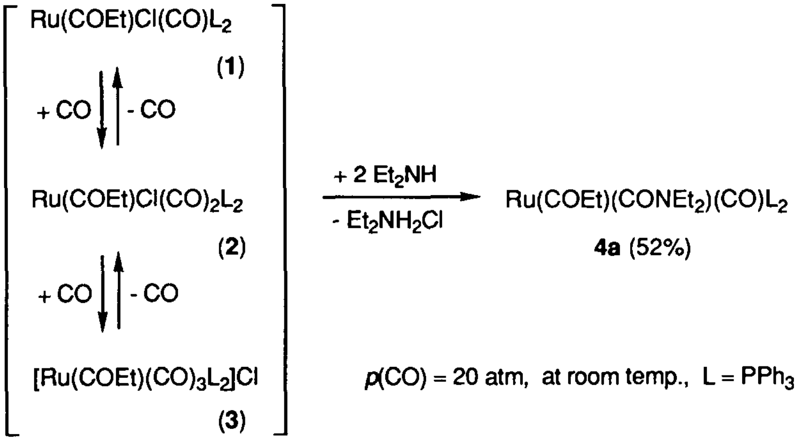
$$\xrightarrow{\text{isomerization}} cis\text{-}\mathrm{ArPd(CONR_2)L_2} \xrightarrow{-\,\mathrm{PdL_2}} \mathrm{ArCONR_2} \qquad (2)$$

Our search for a catalyst for the double carbonylation using transition metal complexes of other metals than palladium and cobalt has been so far unsuccessful. However, in view of the importance of establishing the mode of nucleophilic attack on transition metal bound acyl or CO ligand in potential development of novel carbonylation processes [6], we have examined the reactions of CO-coordinated transition metal acyl complexes with nucleophiles [7]. In this paper we describe that reaction of a CO-coordinated acylruthenium complex with secondary amines gives isolable acyl(carbamoyl)ruthenium complexes corresponding to the intermediate **B** or **C** in eq. (1). The isolated acyl(carbamoyl)ruthenium complexes differ in their behavior from the corresponding palladium analog **B** in that neither α-keto amide nor amide was released on thermolysis or protonolysis. For comparison, reactions of the corresponding CO-coordinated acyliron complexes with nucleophiles are also examined.

Results and discussion

Reaction of acyl(carbonyl)ruthenium with secondary amines

The carbonyl(propionyl)ruthenium complex $\mathrm{Ru(COEt)Cl(CO)(PPh_3)_2}$ (**1**), which is prepared from $\mathrm{RuH(Cl)(CO)(PPh_3)_3}$ by treatment with CO and ethylene [8,9], was subjected to reactions with secondary amines ($\mathrm{R_2NH}$) under CO pressure to give carbamoyl-propionyl complexes $\mathrm{Ru(COEt)(CONR_2)(CO)(PPh_3)_2}$ (**4**). The



(3)

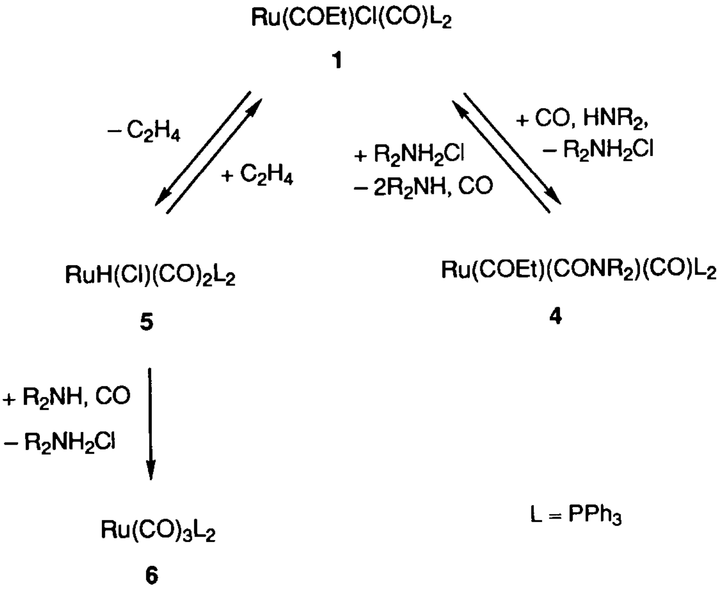
yield of **4** varied depending on the nature of the secondary amine employed and on the reaction conditions.

When complex **1** was treated with diethylamine (45 equiv./l) in acetone under CO pressure (20 atm) at room temperature, the initially heterogeneous reaction mixture quickly turned to a pale yellow solution and then a white precipitate was deposited from the solution. It has been reported that complex **1** in an acetone solution under CO pressure undergoes CO-coordination to give a dicarbonyl species (**2**) and subsequently a cationic tricarbonyl complex (**3**); the latter precipitates in the system under the reaction conditions (eq. (3)) [8].

Following the change described above, the color of the precipitate gradually turned to cream. After 40 h, the precipitate was collected by filtration and examined by IR spectroscopy, which showed the formation of propionyl-carbamoyl complex **4a** and Et_2NH_2Cl. Complex **4a** was isolated in 52% yield as pale yellow crystals by recrystallization from a benzene/hexane mixture after removal of the ammonium salt by washing the crude product with an acetone/water mixture.

When the reaction time was prolonged to 72 h, the same reaction system afforded a mixture of the propionyl-carbamoyl complex **4a** and $Ru(CO)_3(PPh_3)_2$ (**6**) [10] together with Et_2NH_2Cl. Neither amide nor α-keto amide (e.g., $EtCONEt_2$, $EtCOCONEt_2$, $HCONEt_2$, and $HCOCONEt_2$) was detected in the reaction solution, while formation of ethylene in the gas phase was qualitatively confirmed by GLC analysis. Complex **4a** was isolated in a low yield (28%) after recrystallization of the crude product from a CH_2Cl_2/acetone mixture. Preparation of **4a** could also be performed in THF instead of acetone as the solvent, whereas the reaction carried out in CH_2Cl_2 gave $Ru(CO)_3(PPh_3)_2$ (**6**), exclusively.

Reactions of **1** with piperidine and dimethylamine in place of diethylamine were examined similarly. Treatment of **1** with piperidine (37 equiv./l) under 10 atm of CO at room temperature for 6 h gave a pale yellow precipitate which predominantly consisted of $Ru(CO)_3(PPh_3)_2$ (**6**) and the ammonium salt $\overline{CH_2(CH_2)_4N}H_2Cl$ as confirmed by IR spectroscopy. Also noted in the reaction mixture was the presence of small amounts of $RuH(Cl)(CO)_2(PPh_3)_2$ (**5**) and $Ru(COEt)(CO)\{CO\overline{N(CH_2)_4CH_2}\}(PPh_3)_2$ (**4b**). In the case of dimethylamine, the reaction carried



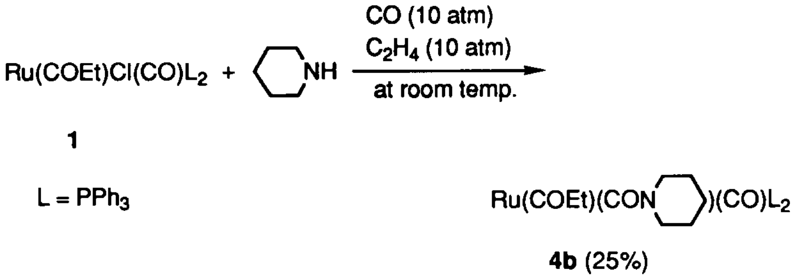
Scheme 1

out under similar conditions gave a mixture of $RuH(Cl)(CO)_2(PPh_3)_2$ (**5**), $Ru(CO)_3(PPh_3)_2$ (**6**), and the ammonium salt $Me_2NH_2BF_4$. This reaction also gave ethylene, while no trace of α-keto amide and amide was detected in the reaction system (GLC).

These results may be rationalized by reaction processes illustrated in Scheme 1 where carbonyl(propionyl)ruthenium complex **1** undergoes two types of reactions. Nucleophilic attack of amine on the carbonyl ligand, probably after CO-coordination to **1** giving the di- and tricarbonyl species (**2** and **3**, respectively), affords carbamoyl-propionyl complex **4**. As we confirmed recently for palladium analogs [4f], the conversion of ruthenium carbonyl into carbamoyl complex **4** may be reversible. Thus, the carbamoyl group in **4** may undergo protonation by the ammonium salt to reproduce carbonyl-propionyl complex **1** and amine.

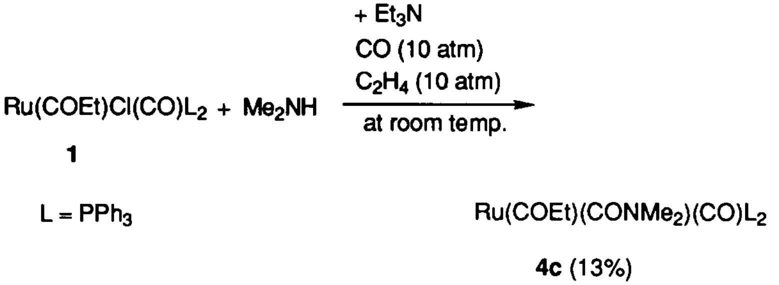
On the other hand, complex **1** undergoes decarbonylation to give an ethylruthenium species, which subsequently undergoes β-hydrogen elimination to afford hydridoruthenium chloride complex **5** and ethylene. Complex **5** thus formed may further interact with amine to give Ru(0) carbonyl complex **6** and the ammonium salt.

On assumption of the reaction processes in Scheme 1, we re-examined preparation of carbamoyl-propionyl complexes with piperidino and dimethylamino groups (**4b** and **4c**, respectively). First, the reaction of **1** and piperidine was examined under pressure of CO and ethylene (1 : 1 ratio, totally 20 atm), with the hope of deterring the formation of the hydridoruthenium complex **5** and ethylene by β-hydrogen elimination. Under the reaction conditions, the carbamoyl complex **4b** could be isolated in a low yield (25%).



(4)

The carbamoyl complex having dimethylamino group (**4c**) could be obtained in 13% yield by the reaction of **1** and dimethylamine in acetone containing triethylamine under pressure of CO and ethylene. In this case the presence of triethylamine was essential to obtain **4c**. Triethylamine as a good trapping agent of HCl may facilitate the equilibrium between **1** and **4** in Scheme 1 towards **4**, allowing us to isolate the carbamoyl complex **4c**.



(5)

*Characterization of carbamoyl(propionyl)ruthenium complexes **4a–c***

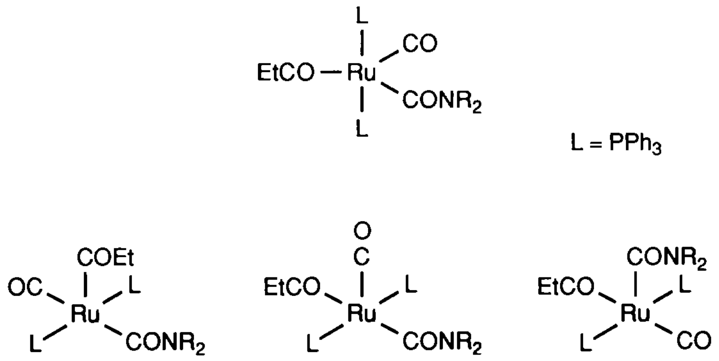
Complexes **4a–c** have been characterized by means of NMR and IR spectroscopy and elemental analysis. The characteristic NMR and IR data are listed in Table 1 together with those for the propionyl chloride complex **1**. The assignments for **4a–c** have been performed by using the ^{13}CO-labeled complex Ru(COEt)-(CONEt$_2$)(^{13}CO)(PPh$_3$)$_2$ (**4a**-^{13}CO) (see below) and by comparison with the IR and NMR data for benzoyl(carbamoyl)palladium and platinum analogs [4h].

Table 1

Characteristic IR and NMR data for Ru(COEt)(CONR$_2$)(CO)(PPh$_3$)$_2$ complexes [a]

Complex	IR (ν_{CO}) [b]			^{13}C{^{1}H} NMR [c]			^{31}P{^{1}H} NMR [i]
	COEt	CONR$_2$	CO	COEt	CONR$_2$	CO	
4a	1610s	1520s	1926vs	256.5 (t) [e]	208.7 (t) [h]	205.8 (t) [g]	33.0 (s)
4b	1610s	1520s	1931vs	256.1 (t) [e]	208.7 (t) [h]	205.7 (t) [g]	34.1 (s)
4c	1615s	1540s	1937vs	255.3 (t) [e]	208 7 (t) [h]	205.6 (t) [g]	34 7 (s)
1	1637s	–	1942vs 1918s	244 3 (t) [d]	–	204 5 (t) [f]	31 2 (s)

[a] All data are collected at room temperature ^{1}H NMR data are reported in the experimental section. [b] In CH$_2$Cl$_2$, wavenumbers in cm^{-1} [c] 125 MHz, in CD$_2$Cl$_2$ Chemical shifts are in δ referred to an internal SiMe$_4$ standard. Coupling constant (^2J(P–C) Hz): [d] 6, [e] 8, [f] 14, [g] 15, [h] 16 [i] 40 MHz, in CD$_2$Cl$_2$. Chemical shifts are in δ referred to an external 85% H$_3$PO$_4$ standard.



Scheme 2

Complexes **4a–c** exhibit a singlet signal in the $^{31}P\{^1H\}$ NMR spectra. In the $^{13}C\{^1H\}$ NMR spectra, the three carbonyl carbons in each complex appear as three sets of triplets due to the coupling with the two phosphorus nuclei. These coupling patterns and the relatively small $^2J(P\text{–}C)$ values for the carbonyl carbons suggest a trigonal-bipyramidal or square-pyramidal structures having the two triphenylphosphine ligands in mutually *trans* positions (Scheme 2).

Complexes **4a–c** exhibit three strong IR absorptions at about 1930, 1610, and 1520 cm^{-1}, assignable to $\nu(CO)$ bands of the terminal carbonyl, propionyl, and carbamoyl groups, respectively. Under a ^{13}CO atmosphere in a CH_2Cl_2 solution, the CO ligand in **4a** has been readily replaced by ^{13}CO molecule to give the ^{13}CO-labeled complex *trans*-$Ru(COPh)(CONEt_2)(^{13}CO)(PPh_3)_2$ (**4a**-^{13}CO) which shows the $\nu(^{13}CO)$ band at 1890 cm^{-1}. The wave numbers of ~ 1520 cm^{-1} for the carbamoyl groups are comparable to those for the *trans*-$M(COPh)(CONR_2)L_2$ complexes (M = Pd and Pt; $\nu(CO)_{carbamoyl} = 1515\text{–}1528\ cm^{-1}$) [4h]. The values of 1610 (**4a** and **4b**) and 1615 cm^{-1} (**4c**) for the propionyl groups are consistent with the η^1-acyl structure rather than the η^2 structure [11]. These values are slightly lower than the $\nu(CO)$ for the propionyl chloride complex **1** having a similar structure to **4a–c**. This drop in wave number is attributable to the replacement of the electron-attracting chloride group in **1** by the less electron-attracting carbamoyl groups in **4a–c**. Similar tendency has been observed in the analogous palladium and platinum systems [4h].

*Reactions of $Ru(COEt)(CONEt_2)(CO)(PPh_3)_2$ (**4a**)*

Thermolysis of **4a** in toluene at 100°C gave ethylene together with unidentified ruthenium carbonyl complexes. No trace of α-keto amide ($EtCOCONEt_2$, $HCOCONEt_2$) and amide ($EtCONEt_2$, $HCONEt_2$) has been detected in the system. Furthermore, no α-keto amide formation was observed when the thermolysis was carried out under CO pressure (10 atm). Treatment of **4a** with MeCOCl, on the other hand, afforded $MeCONEt_2$ in 48% yield.

Reactions of acetyl(carbonyl)iron complexes with nucleophiles

With expectation of observing chemical behavior similar to the CO-coordinated propionylruthenium complex **3**, we examined reactions of two types of acetyl(carbonyl)iron complexes, $Fe(COMe)I(CO)_2(PMe_3)_2$ (**7**) and [Fe(COMe)-

Table 2

Reactions of $Fe(COMe)I(CO)_2(PMe_3)_2$ (**7**) and $[Fe(COMe)(CO)_3(PMe_3)_2]BF_4$ (**8**) with nucleophiles [a]

Entry	Complex	Nucleophile (equiv./Fe)	Product (%/Fe)
1	**7**	$HNEt_2$ (50)	$MeCONEt_2$ (6)
2	**7**	$HNEt_2$ (50)	$MeCONEt_2$ (9)
3	**8**	$HNEt_2$ (8)	$MeCONEt_2$ (100)
4	**8**	$LiNMe_2$ (2)	$MeCONMe_2$ (100)
5	**8**	EtOH (10) + Et_3N (10)	MeCOOEt (32)
6	**8**	NaOMe (2)	MeCOOMe (37)

[a] The reactions were carried out at room temperature under a CO atmosphere $p(CO) = 60$ atm (entries 1–3 and 5), 1 atm (entries 4 and 6). Solvent CH_2Cl_2 (entries 1, 3, and 5), acetone (entry 2), THF (entries 4 and 6).

$(CO)_3(PMe_3)_2]BF_4$ (**8**) [12], which have similar structures to the ruthenium complexes **2** and **3** in eq. (3), respectively. In contrast to the ruthenium analogs, the iron complexes did not form acyl-carbamoyl complexes on reaction with diethylamine under CO pressure but selectively gave acetamide as the single carbonylation product (Table 2). Treatment of **8** with EtOH and Et_3N or with NaOMe gave the single carbonylation product, ethyl or methyl acetate, respectively.

Summary

The carbonyl(propionyl)ruthenium complex **1** in solution under CO pressure was found to undergo nucleophilic attack of secondary amines on the coordinated CO ligand to give isolable acyl(carbamoyl)ruthenium complexes **4** in a parallel behavior with the previously reported acyl(carbonyl)palladium complexes [4g,h]. However, the isolated acyl(carbamoyl)ruthenium complexes differ in their behavior from the palladium analogs in their inactivity to release α-keto amide. The exact reason for the different behavior is not clear. A possible explanation for the reluctance of reductive elimination from the acyl(carbamoyl)ruthenium complex is that the acyl and the carbamoyl ligands are situated at unfavorable sites for a concerted reductive elimination to occur. In a theoretical treatment of reductive elimination of two organic groups from a five-coordinated nickel complex, it has been discussed that (i) the organic ligands both situated at equatorial positions in a trigonal-bipyramidal complex are symmetrically forbidden to undergo the reductive elimination process, and (ii) kinetic barriers for pseudorotation to bring the concerned organic ligands to axial and equatorial sites are very high [13]. A similar argument might be advanced in the present case but we would rather defer from advancing the discussion further until more bis-acyl type complexes are prepared and their behavior examined.

Experimental

All manipulations were carried out under an atmosphere of argon, nitrogen or carbon monoxide or *in vacuo*. ^1H, ^{13}C and ^{31}P NMR spectra were measured on JEOL FX-100, GX-270 and GX-500 spectrometers by Dr. Y. Nakamura, Ms. R. Ito, and Ms. A. Kajiwara in our laboratory. ^1H and ^{13}C signals are referred to

Me_4Si as an internal standard and ^{31}P NMR signals to 85% H_3PO_4 as an external reference. IR spectra were recorded on a JASCO IR-810 spectrometer. Elemental analysis was carried out by Dr. M. Tanaka and Mr. T. Saito of our laboratory by using a Yanagimoto CHN autocorder type MT-2. Solvents and amines were dried in the usual manner, distilled, and stored under an argon atmosphere. Carbon monoxide was used as purchased (Nippon Sanso) without further purification. ^{13}CO (99% isotopic purity) was purchased from CEA.

$Ru(COEt)Cl(CO)(PPh_3)_2$ (**1**) [8,9] and $Fe(COMe)I(CO)_2(PMe_3)_2$ (**7**) [12] were prepared according to the literature methods and characterized by means of NMR and IR spectroscopy.

Preparation of $Ru(COEt)(CONEt_2)(CO)(PPh_3)_2$ *(**4a**)*

To a glass pressure bottle containing $Ru(COEt)Cl(CO)(PPh_3)_2$ (0.32 g, 0.42 mmol) were added acetone (10 mL) and diethylamine (2 mL, 19 mmol). CO gas (20 atm) was introduced, and the pale yellow heterogeneous mixture was stirred for 40 h at room temperature. After purging the CO gas, the cream-colored precipitate was collected by filtration. The IR spectrum (KBr) of the precipitate shows the presence of **4a** and Et_2NH_2Cl [$\nu(NH) = 2405$ and 2505 cm^{-1}]. The crude product was washed with an acetone/water mixture (1 : 1; 1 mL × 3) and then with dry acetone (1 mL), and dried under vacuum. The resulting solid was recrystallized from a benzene/hexane mixed solvent to give pale yellow crystals of **4a** (0.19 g, 52%). ^1H NMR (CD_2Cl_2) δ −0.01 (t, $J = 7.3$ Hz, 3H, $COCH_2CH_3$), 0.27 and 0.49 (br, 3H each, $N(CH_2CH_3)_2$), 2.30 (q, $J = 7.3$ Hz, 2H, $COCH_2$), 2.33 and 2.61 (br, 2H each, $N(CH_2CH_3)_2$), 7.3–7.5 (m, Ph) ppm. Anal. Found: C, 67.23; H, 5.65; N, 1.80. $C_{45}H_{45}NO_3P_2Ru$ calc.: C, 66.72; H, 5.55; N, 1.73%.

A similar reaction was carried out for 72 h at room temperature under CO pressure (20 atm) using $Ru(COEt)(CO)Cl(PPh_3)_2$ (2.0 g, 2.7 mmol), diethylamine (10 mL, 97 mmol), and acetone (60 mL) as the solvent. The IR spectrum (KBr) of the resulting solid shows the formation of **4a**, Et_2NH_2Cl, and $Ru(CO)_3(PPh_3)_2$ [$\nu(CO) = 1900$ cm^{-1} (lit. 1895 cm^{-1} [10])]. The crude product was washed with acetone (5 mL × 2), an acetone/water mixture (1 : 1, 5 mL × 1), and then with dry acetone (5 mL), and dried under vacuum (0.73 g). This product contained **4a** and $Ru(CO)_3(PPh_3)_2$ as confirmed by IR spectroscopy. The Ru^0 carbonyl complex was removed by recrystallization from a CH_2Cl_2/acetone mixture to give pale yellow crystals of **4a** (0.64 g, 28%).

Preparation of $Ru(COEt)(CO\overline{N(CH_2)_4C}H_2)(CO)(PPh_3)_2$ *(**4b**)*

To a glass pressure bottle containing $Ru(COEt)Cl(CO)(PPh_3)_2$ (0.20 g, 0.27 mmol) were added acetone (2 mL) and piperidine (100 μL, 1.0 mmol). Ethylene (10 atm) and CO gas (10 atm) (20 atm in total) were introduced to the system, and the pale yellow heterogeneous mixture was stirred for 5.5 h at room temperature. After purging the gas, the pale yellow precipitate was collected by filtration, washed with an acetone/water mixture (1 : 1; 1 mL × 3) and then with dry acetone (1 ml), and dried under vacuum. The crude product was recrystallized from a benzene/hexane mixture to give pale yellow crystals of **4b** (0.050 g, 24%). This crystalline product contains one equivalent per **4b** of H_2O. ^1H NMR (CD_2Cl_2) δ 0.03 (t, $J = 7.3$ Hz, 3H, $COCH_2CH_3$), 2.34 (q, $J = 7.3$ Hz, 2H, $COCH_2$), 0.82, 1.11 and 2.52 (br; 4H, 2H and 4H, respectively; piperidino ring protons), 7.3–7.6 (m, Ph). Anal. Found: C, 65.36; H, 5.42; N, 1.30. $C_{46}H_{45}NO_3P_2Ru \cdot H_2O$ calc.: C, 65.70; H, 5.63; N, 1.67%.

Reaction of 1 and piperidine in the absence of ethylene

The complex $Ru(COEt)Cl(CO)(PPh_3)_2$ (0.20 g, 0.27 mmol) was placed in a glass pressure bottle, and THF (2 mL) and piperidine (1 mL, 10 mmol) were added. CO gas (10 atm) was introduced, and the pale yellow heterogeneous mixture was stirred for 17 h at room temperature. GLC analysis of the gas phase revealed the formation of ethylene (column: Porapack Q, 1 m). After purging the gas, the volatile material was collected by trap-to-trap distillation and analyzed by GLC (column: PEG-20M, 1 m) and GC-mass spectrometry. No formation of amide and α-keto amide has been confirmed. The pale yellow solid (0.26 g) remained after the trap-to-trap distillation was examined by IR spectroscopy (KBr). The spectrum exhibited a strong broad peak due to ν(CO) band of $Ru(CO)_3(PPh_3)_2$ at 1895 cm^{-1}. Also observed were the ν(CO) bands of $RuH(Cl)(CO)_2(PPh_3)_2$ (**5**) [2025 and 1973 cm^{-1} (lit. 2037 and 1978 cm^{-1} [9])] in medium intensity and weak peaks due to the ν(CO) bands of **4b**.

Preparation of $Ru(COEt)(CONMe_2)(CO)(PPh_3)_2$ (4c)

To a glass pressure bottle containing $Ru(COEt)Cl(CO)(PPh_3)_2$ (0.26 g, 0.35 mmol) were added acetone (2 mL), an acetone solution of Me_2NH (80% in volume, 60 μL) and Et_3N (100 μL, 0.72 mmol). Ethylene (10 atm) and CO gas (10 atm) (20 atm in total) were introduced to the system, and the pale yellow heterogeneous mixture was stirred for 14 h at room temperature. After purging the gas, the pale yellow precipitate was collected by filtration, washed with an acetone/water mixture (1:1, 1 mL × 3) and then with dry acetone (1 ml), and dried under vacuum. The crude product was recrystallized from a benzene/hexane mixture to give pale yellow crystals of **4c** (0.035 g, 13%). ^1H NMR (CD_2Cl_2) δ 0.10 (t, $J = 7.3$ Hz, 3H, $COCH_2CH_3$), 2.40 (q, $J = 7.3$ Hz, 2H, $COCH_2$), 1.97 (br, 6H, NMe_2), 7.3–7.6 (m, Ph). Anal. Found: C, 65.77; H, 5.62; N, 1.65. $C_{43}H_{41}NO_3P_2Ru$ calc.: C, 65.98; H, 5.28; N, 1.79%.

Reactions of $Ru(COEt)(CONEt_2)(CO)(PPh_3)_2$ (4a)

Thermolysis. Complex **4a** (0.088 g, 0.11 mmol) was placed in a Schlenk tube and dissolved in toluene (3 mL) at room temperature. The system was evacuated and heated at 100°C for 20 h under vacuum. GLC analysis (column: Porapack Q, 1 m) of the gas phase showed formation of ethylene. No formation of amide and α-keto amide (e.g., $EtCOCONEt_2$, $EtCONEt_2$, and $HCONEt_2$) in the reaction solution has been confirmed by means of GLC (column: PEG-20M, 1 m). Evaporation of the reaction solution by pumping gave a pale yellow solid (0.076 g), which exhibited ν(CO) absorptions at 2024, 1973, 1926, and 1895 cm^{-1} in its IR spectrum (KBr).

Reaction with MeCOCl. Complex **4a** (0.0491 g, 0.061 mmol) was placed in a Schlenk tube and acetone (2 mL) was added. Acetyl chloride (8.7 μL, 0.122 mmol) was added by means of a syringe and the mixture was stirred at room temperature for 20 h. Formation of ethylene in the gas phase has been confirmed by means of GLC. The volatile material was collected by trap-to-trap distillation and examined by GLC using MeCOPh as an internal standard to reveal the formation of

$MeCONEt_2$ (48%/**4a**). The IR spectrum (KBr) of the pale yellow solid (0.043 g) remained after the trap-to-trap distillation exhibited strong absorptions due to the ν(CO) bands of $RuH(Cl)(CO)_2(PPh_3)_2$ (**5**) [2025 and 1973 cm^{-1} (lit. 2037 and 1978 cm^{-1} [9])].

Preparation of $[Fe(COMe)(CO)_3(PMe_3)_2]BF_4$ *(8)*

This complex was prepared by a procedure similar to $[Fe(COMe)(CO)_3(PMe_3)_2]BPh_4$ [12c]. The complex $FeMeI(CO)_2(PMe_3)_2$ (0.130 g, 0.319 mmol) was dissolved in dichloromethane (2 mL) under an argon atmosphere. After bubbling CO gas into the resulting orange solution for 3 min, an acetone solution (3 mL) of $AgBF_4$ (0.0624 g, 0.319 mmol), was added dropwise. The system was stirred for 13 h at room temperature under CO atmosphere, and the resulting white precipitate of AgI was removed by filtration to give a pale yellow solution. This solution was concentrated to dryness under reduced pressure to give a white solid of $[FeMe(CO)_3(PMe_3)_2]BF_4$ (0.126 g, 100%). IR (KBr) 2014vs cm^{-1}. ^1H NMR (CD_2Cl_2) δ 0.08 (t, $J = 7$ Hz, 3H, FeMe), 1.77 (t, $J = 9$ Hz, 18H, PMe) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 10.6 (s) ppm.

A test tube containing a dichloromethane solution (2 mL) of $[FeMe(CO)_3(PMe_3)_2]BF_4$ (0.246 g, 0.624 mmol) was placed in a 100-mL stainless-steel pressure bottle, and 60 atm of CO gas was introduced. The system was magnetically stirred for 30 min. After purging the CO gas, the resulting pale yellow solution was concentrated to dryness under reduced pressure to give a white precipitate of $[Fe(COMe)(CO)_3(PMe_3)_2]BF_4$ (0.263 g, 100%). IR (KBr) 2100 s, 2052 vs, 2014 vs, 1973 s, 1627 s cm^{-1}. ^1H NMR (CD_2Cl_2) δ 2.61 (s, 3H, COMe) 1.78 (t (br), 18H, PMe) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 13.6 (s) ppm. Anal. Found: C, 31.51; H, 5.44. $C_{11}H_{21}BF_4O_4P_2Fe$ calc.: C, 31.32; H, 5.02%.

Reactions of acetyliron complexes

The following procedure is representative. A test tube containing a CH_2Cl_2 solution (2 mL) of $[Fe(COMe)(CO)_3(PMe_3)_2]BF_4$ (0.245 g, 0.581 mmol), and Et_2NH (0.5 mL, 4.8 mmol) was placed in a 100-mL stainless-steel pressure bottle, and 60 atm of CO gas was introduced. The system was magnetically stirred at room temperature for 14 h. After purging the gas, the resulting solution was examined by GLC using MeCOPh as an internal standard and by GC-mass spectrometry to reveal the formation of $MeCONEt_2$ (100%/Fe).

The reactions of acetyliron complexes (**7** and **8**) with nucleophiles ($HNEt_2$, $LiNMe_2$, $EtOH + Et_3N$, and NaOMe) were similarly examined. The reaction conditions and the organic products are listed in Table 2.

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References

1 (a) T Kobayashi and M Tanaka, J Organomet Chem, 233 (1982) C64, (b) M. Tanaka, T. Kobayashi, T Sakakura, H Itatani, S Danno and K Zushi, J Mol Catal, 32 (1985) 115; (c) M

Tanaka, T Kobayashi and T Sakakura, J. Chem. Soc., Chem. Commun., (1985) 837; (d) H Yamashita, T. Kobayashi, T. Sakakura and M. Tanaka, J. Mol. Catal., 40 (1987) 333; (e) T Kobayashi, T. Sakakura and M. Tanaka, Tetrahedron Lett., 28 (1987) 2721, (f) M. Tanaka, Yuki Gosei Kagaku Kyokaishi (J Syn Org. Chem. Jpn.), 45 (1987) 716, and references cited therein; (g) B. Morin, A. Hirschauer, F. Hugues, D. Commereuc and Y. Chauvin, J. Mol Catal., 34 (1986) 317, (h) S. Murahashi, Y. Mitsue and K. Ike, J. Chem Soc, Chem Commun, (1987) 125.

2 (a) F. Ozawa, T. Soyama, T. Yamamoto and A. Yamamoto, Tetrahedron Lett, 23 (1982) 3383; (b) F Ozawa, H Yanagihara and A. Yamamoto, J. Org. Chem., 51 (1986) 415, (c) A. Yamamoto, T. Yamamoto and F Ozawa, Pure Appl Chem., 57 (1985) 1799; (d) T Son, H. Yanagihara, F Ozawa and A Yamamoto, Bull Chem Soc Jpn, 61 (1988) 1251, (e) F. Ozawa, M. Nakano, I Aoyama, T Yamamoto and A Yamamoto, J Chem. Soc, Chem. Commun., (1986) 382; (f) F Ozawa, I. Yamagami, M. Nakano, F. Fujisawa and A. Yamamoto, Chem Lett., (1989) 125, (g) F. Ozawa, N Kawasaki, T. Yamamoto and A Yamamoto, ibid, (1985) 567; (h) F Ozawa, N Kawasaki, H. Okamoto, T. Yamamoto and A Yamamoto, Organometallics, 6 (1987) 1640; (i) A. Yamamoto, F Ozawa, K Osakada, L Huang, T-I. Son, N Kawasaki and M-K. Doh, Pure Appl Chem, 63 (1991) 687

3 (a) H Alper, Adv. Organomet. Chem., 19 (1981) 183; (b) M. Foa and F Francalanci, J. Mol Catal., 41 (1987) 89, and references cited therein; (c) H des Abbayes and A. Bulop, J Chem Soc., Chem Commun., (1978) 1090; (d) F Francalanci, E Bencin, A Gardano, M. Vincent and M. Foa, J Organomet Chem, 310 (1986) C27, (e) K. Itoh, M. Miura and M Nomura, Bull Chem. Soc Jpn, 61 (1988) 4151, (f) K Kashimura, K. Kudo, S Mori and N Sugita, Chem Lett, (1986) 299 and 483, (g) H Alper, H. Arzoumanian, J. Petrignani and M. Saldana-Maldonado, J Chem. Soc, Chem. Commun., (1985) 340; (h) J.Y Lee and J W Wolfman, Jpn. Kokai Tokkyo Koho, (1984) JP 60-500445; (i) J.Y. Lee and T J Walter, U S Patent 1984, 4473706; (j) B Fell and H. Chrobaczek, Chem. Ztg., 108 (1984) 291; (k) J I. Kim and C M Ryu, Bull. Korean Chem Soc, 8 (1987) 246, (l) H Alper, A. Eisenstat and N. Satyanarayana, J Am Chem Soc, 112 (1990) 7060.

4 (a) F. Ozawa, H Soyama, H Yanagihara, I Aoyama, H Takino, K Izawa, T. Yamamoto and A Yamamoto, J Am. Chem Soc., 107 (1985) 3235, (b) F. Ozawa and A. Yamamoto, Chem Lett., (1982) 865; (c) F. Ozawa, T Sugimoto, Y Yuasa, M Santra, T Yamamoto and A. Yamamoto, Organometallics, 3 (1984) 683, (d) F. Ozawa, T Sugimoto, T. Yamamoto and A Yamamoto, ibid, 3 (1984) 692, (e) F. Ozawa, L. Huang and A. Yamamoto, J Organomet. Chem., 334 (1987) C9, (f) L. Huang, F. Ozawa, K. Osakada and A Yamamoto, Organometallics, 8 (1989) 2065; (g) L. Huang, F. Ozawa, K Osakada and A Yamamoto, J Organomet. Chem, 383 (1990) 587, (h) L Huang, F. Ozawa and A Yamamoto, Organometallics, 9 (1990) 2603 and 2612

5 (a) A. Sen, J.-T. Chen, W.M Vetter and R.R. Whittle, J Am. Chem Soc, 109 (1987) 148, (b) J.-T. Chen and A. Sen, ibid., 106 (1984) 1506; (c) T-M Huang, J.-T Chen, G-H Lee and Y Wang, Organometallics, 10 (1991) 175; (d) J-T Chen, T-M Huang, M.-C. Cheng and Y. Wang, ibid, 9 (1990) 539.

6 (a) R.J Angelici, Acc. Chem Res, 5 (1972) 335, (b) P C Ford and A Rokicki, Adv. Organomet Chem., 28 (1987) 139, and references cited therein; (c) ref 5a, (d) C.M. Lukehart, G.P. Torrence and J.V. Zeile, Inorg Chem, 15 (1976) 2393; (e) V Galamb and G. Palyi, Organometallics, 6 (1987) 861, (f) M. Tasi and G Palyi, ibid, 4 (1985) 1523, (g) F. Francalanci, A. Gardano, L Abis and M. Foa, J Organomet. Chem., 251 (1983) C5; (h) C P Casey and C A. Bunnell, J. Am. Chem. Soc, 98 (1976) 436, (i) C M Lukehart, Acc. Chem. Res., 14 (1981) 109.

7 N. Kawasaki, K Masuzoe, F. Ozawa and A Yamamoto, J Organomet. Chem., 361 (1989) C37.

8 K.R. Grundy and J Jenkins, J. Organomet. Chem., 265 (1984) 77.

9 S. Cenini, A Mantovani, A. Fusi and M Keubler, M Gazz. Chim. Ital, 105 (1975) 255

10 J P Collman and W P. Roper, J. Am Chem Soc, 87 (1965) 4008.

11 W.R Roper, G.E. Taylor, J.M. Waters and L.J Wright, J. Organomet. Chem., 182 (1979) C46.

12 (a) S C Wright and M C Baird, J Am Chem. Soc., 107 (1985) 6899; (b) G. Reichenback, D Cardaci and G Bellachioma, J Chem Soc., Dalton Trans, (1982) 847; (c) M. Pankowski and M Bigorgne, J Organomet Chem., 251 (1983) 333

13 K. Tatsumi, A Nakamura, S. Komiya, A. Yamamoto and T Yamamoto, J. Am Chem. Soc., 106 (1984) 8181.