Synthesis and Catalytic Activity of Water-Soluble Iridium-Sulfonated Triphenylphosphine Complex. Hydration of Nitriles

Chong Shik Chin,* Sang Yull Kim, Kwang-Suk Joo, Gyongshik Won, and Daesung Chong

Department of Chemistry, Sogang University, Mapoku, Seoul 121-742, Korea
Received January 15, 1999

Five coordinated water-soluble iridium(I) complex, $IrH(CO)(TPPTS)_3$ (**1**) (TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3 \cdot xH_2O$) has been prepared from the reaction of $IrCl_3 \cdot 3H_2O$ with TPPTS and HCHO in H_2O/EtOH solution. Complex **1** catalyzes the hydration of nitriles (RC ≡ N, R = CH_3, $ClCH_2$, $CH_3(CH_2)_4$, Ph) in aqueous solution to give the corresponding amides ($RCONH_2$) at 100 °C. The hydration of unsaturated nitriles (R'C ≡ N, R' = CH_3CH=CH, CH_3OCH=CH, *trans*-PhCH=CH, CH_2=$C(CH_3)$) takes place regioselectively on -C ≡ N group to give unsaturated amides ($R'CONH_2$) leaving the olefinic group intact. The yields of the amides seem to be depending on the electrophilicity of the carbon of nitrile: The more the electron withdrawing ability of the substituents on nitriles, the more amides are obtained. The hydration of dinitriles (NC-R-CN, R = $(CH_2)_4$, $(CH_2)_6$) with complex **1** initially gives mono-hydration products (NC-R-$CONH_2$) which are slowly hydrated further to give dihydration products (H_2NCO-R-$CONH_2$). The hydration of 1,4-dicyanobutane has been found to be somewhat faster than that of 1,6-dicyanohexane.

Introduction

Unsaturated amides are very useful compounds[1] since their polymers are used in various chemical industries such as paper and surfactant production,[2] waste water treatment and oil recovery.[3] Amides are in general prepared by hydration of nitriles in the presence of strong acid or base catalyst.[4] Under these conditions, amides are further hydrolyzed to give carboxylic acids,[5] and hydrolysis of other functional groups of unsaturated nitriles (*e.g.*, olefinic group) also takes place. Transition metal complexes have been successfully utilized as catalysts in order to obtain the catalytic hydration of nitriles in the absence of strong acid or base as well as the regioselective hydration of unsaturated nirtriles.[6] To the best of our knowledge, no report has been made for catalytic hydration of nitriles with a water-soluble metal complex although there are some advantages for using water-soluble metal complexes as catalysts for hydration in aqueous solutions.

We recently found that water-soluble complexes, $RhCl(CO)(TPPTS)_2$ and $IrCl(CO)(TPPTS)_2$ (TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3 \cdot xH_2O$) are efficient catalysts for the hydration of terminal alkynes to produce corresponding ketones[7] and polymerization of terminal alkynes to give stereoselective polymers of alkynes[8] in aqueous solutions. We now wish to report the catalytic hydration of nitriles to the corresponding amides by a five coordinated water-soluble Ir(I) complex, $IrH(CO)(TPPTS)_3$ (**1**). This report also includes a more convenient synthetic method for complex **1** than the method reported previously.[9]

Results and Discussion

Synthesis of Water-Soluble $IrH(CO)(TPPTS)_3$ (1) (TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3 \cdot xH_2O$). This complex was previously prepared by refluxing $IrH(CO)(PPh_3)_3$ in the presence of TPPTS in toluene/water biphasic solution for 5 days.[9] In the course of looking for the synthetic method of **1** with shorter reaction time and higher yield, we found that complex **1** can be prepared directly from the reaction of $IrCl_3 \cdot 3H_2O$, TPPTS and HCHO/NaOH in refluxing H_2O/EtOH for 20 hours (see eq 1 and Experimental). Complex **1** has been characterized by spectral data (^1H NMR, ^{31}P NMR and IR) which are in good agreement with those previously reported[9] (see Experimental).

$$IrCl_3 \cdot 3H_2O + 3TPPTS + HCHO/NaOH \xrightarrow[\text{reflux/20 h}]{H_2O/EtOH} \underset{\mathbf{1}}{IrH(CO)(TPPTS)_3} \quad (1)$$

Catalytic Hydration of Nitriles. Nitriles readily undergo hydration to give corresponding amides in the presence of **1** at 100 °C under N_2 in aqueous solution (eq 2). The water-insoluble iridium analog $IrH(CO)(PPh_3)_3$ shows no catalytic activity for the hydration of nitriles in $CHCl_3/H_2O$ solution under reflux condition. The hydration of nitriles does not occur in the presence of TPPTS and/or *conc.* H_2SO_4 only (*i.e.*, in the absence of **1**). In the presence of NaOH, it occurs very slowly with no regioselectivity in cases of unsaturated nitriles.

$$RC{\equiv}N \xrightarrow[H_2O,\ 100\,^oC]{IrH(CO)(TPPTS)_3} RCONH_2 \quad (2)$$

The hydration of chloroacetonitrile ($ClCH_2CN$) is found to be faster than that of other nitriles such as CH_3CN and $CH_3(CH_2)_4CN$ (see Table 1). This may be understood in terms of the enhancement of the electrophilicity of the nitrile carbon by the substituent.[6c,10] The electron withdrawing effect of the substituents increases in the order of $CH_3(CH_2)_4$ < CH_3 < CH_2Cl, which predicts easier nucleophlic attack by

Table 1. Hydration of Nitriles (3.0 mmol) in the Presence of IrH(CO)(TPPTS)$_3$, **1** (0.05 mmol) in Aqueous Solution at 100 °C for 4 h under N_2

nitrile	product	yield (%)[d]
CH_3CN	CH_3CONH_2	38
$CH_3(CH_2)_4CN$	$CH_3(CH_2)_4CONH_2$	35
C_6H_5CN	$C_6H_5CONH_2$	54[e]
$ClCH_2CN$	$ClCH_2CONH_2$	73
$CH_3CH=CHCN$ (65:35)[a]	$CH_3CH=CHCONH_2$ (31:69)[a]	65
$CH_3OCH=CHCN$ (37:63)[a]	$CH_3OCH=CHCONH_2$ (22:78)[a]	31
$CH_3CH_2OCH=CHCN$ (37:63)[a]	$CH_3CH_2OCH=CHCONH_2$ (25:75)[a]	29
trans-$C_6H_5CH=CHCN$	*trans*-$C_6H_5CH=CHCONH_2$	96
$CH_2=C(CH_3)CN$	$CH_2=C(CH_3)CONH_2$	54
$HCC(CH_2)_3CN$	alkyne oligomers[c]	nd[f]
$NC(CH_2)_4CN$	$NC(CH_2)_4CONH_2$	47
	$H_2NCO(CH_2)_4CONH_2$	53
$NC(CH_2)_6CN$	$NC(CH_2)_6CONH_2$	48
	$H_2NCO(CH_2)_6CONH_2$	25
NCCH=CHCN	no reaction	0
NC-C_6H_4-CN	no reaction	0
$NC(CH_2)_4CONH_2$[b]	$H_2NCO(CH_2)_4CONH_2$	89[e]
$NC(CH_2)_6CONH_2$[b]	$H_2NCO(CH_2)_6CONH_2$	81[e]

[a]The ratio of the isomers; *cis*:*trans*. [b]1.5 mmol of the substrate was used (nitrile/Ir = 30). [c]Identified by GC/mass. [d]Measured by ^{1}H NMR (D_2O, 25 °C, 300 MHz). [e]Weight % after isolation. [f]Not determined.

H_2O on the carbon of $ClCH_2$***C***N than that of other nitriles. The same effect has been also observed for the rate of hydration of unsaturated nitriles. Higher rate of hydration is observed for $C_6H_5CH=CHCN$ than for $CH_3CH=CHCN$ and $CH_2=C(CH_3)CN$ (see Table 1). That relatively lower hydration rates are measured for $CH_3OCH=CHCN$ and $C_2H_5OCH=CHCN$ may be explained by the resonance structure **B** (see eq 3) which decreases the electrophilicity of the carbon of the nitriles.

$$\underset{\mathbf{A}}{RO-CH=CH-CN} \leftrightarrow \underset{\mathbf{B}}{R\overset{+}{O}=CH-\overset{-}{C}H-CN} \qquad (3)$$

It is surprising to find that complex **1** shows no catalytic activity for the hydration of unsaturated nitriles such as $CH_2=CHCN$, $CH_2=CHCH(CH_3)CN$, $CH_2=CClCN$, $BrCH=C(CH_3)CN$ and $CH_2=CHCH_2CN$ for which no plausible explanation has been found thus far.

The hydration of a mixture of *cis*- and *trans*-$CH_3CH=CHCN$ has been investigated in order to obtain more information on the effects of the olefinic group of the unsaturated nitriles. At the early stage of the catalysis, the *trans* isomer (*trans*-$CH_3CH=CHCN$) seems to undergoes the hydration faster than does the *cis*-isomer (*cis*-$CH_3CH=CHCN$) (see Table 2). At the later stage, the isomerization of the hydration product (*cis*-$CH_3CH=CHCONH_2$ to *trans*-$CH_3CH=CHCONH_2$) is clearly observed (see Table 2), which suggests significant interactions between the olefinic group of unsaturated amides and the catalyst **1**. These interactions have been also observed in the reaction of $CH_2=CHCH_2CN$ with catalyst **1**: The hydration product was not detected in the reaction of $CH_2=CHCH_2CN$ with **1** in aqueous solution at 100 °C for 4 h while a significant amount of the isomerization-hydration product, $CH_3CH=CHCONH_2$ has been observed after 24 h during which time neither $CH_2=CHCH_2CONH_2$ nor $CH_3CH=CHCN$ has been detected. This may be understood in terms of slow isomerization of $CH_2=CHCH_2CN$ (to $CH_3CH=CHCN$) followed by fast hydration of the nitrile group to give $CH_3CH=CHCONH_2$ or slow hydration of $CH_2=CHCH_2CN$ (to give $CH_2=CHCH_2CONH_2$) followed by fast isomerization to give $CH_3CH=CHCONH_2$. It may be mentioned here that the isomerization of $CH_2=CHCH_2OH$ is fast enough to observe a simple enol, $CH_3CH=CHOH$ in the presence of another water-soluble iridium(I) complex, [Ir(1,5-cyclooctadiene)(TPPTS)$_2$]Cl in aqueous solution at 25 °C.[11]

Table 2. Hydration of $CH_3CH=CHCN$ (3.0 mmol) in the Presence of IrH(CO)(TPPTS)$_3$, **1** (0.05 mmol) in Aqueous Solution at 100 °C under N_2

reaction time (h)	unreacted $CH_3CH=CHCN$ (%)[a]		$CH_3CH=CHCONH_2$ (%)[a]		yield (%)[b]
	cis	*trans*	*cis*	*trans*	
0	65	35	0	0	0
2	38	9	23	30	53
4	27	8	20	45	65
6	7	2	45	46	91
8	7	2	42	49	91
10	7	2	33	58	91

[a]Determined by ^{1}H NMR ($CDCl_3$, 25 °C, 300 MHz). [b]Detemined by ^{1}H NMR (D_2O, 25 °C, 300 MHz).

Reaction of an acetylenic nitrile $HC\equiv C(CH_2)_3CN$ with complex **1** in aqueous solution gives no hydration product but oligomers which are characterized by mass (m/e = 186, 279) and IR ($\nu_{C\equiv N}$, 2248 cm^{-1}) spectra. It has been found in a separate experiment that complex **1** is also catalytically active for the oligomerization of styrene in aqueous solution at 100 °C.[12]

Complex **1** also catalyzes the hydration of dinitriles such as $NC(CH_2)_4CN$ and $NC(CH_2)_6CN$ to give mono- and di-hydration products, respectively at 100 °C while no hydration products have been detected from the reactions of NCCH=CHCN and *p*-NC-C_6H_4-CN (1,4-dicyanobenzene) (see Table 1). It seems possible to isolate significant amounts of mono-hydration products, $NC(CH_2)_4CONH_2$ (*ca.* 37%) and $NC(CH_2)_6CONH_2$ (*ca.* 24%) from the reaction mixtures (see Table 3). It is noticed that the first hydration is much faster for $NC(CH_2)_4CN$ than for $NC(CH_2)_6CN$ while the electrophilicity of the nitrile carbon (-***C***N) of both dinitriles may not be much different from each other. The difference in hydration rates may come from the fact that $NC(CH_2)_4CN$ could readily chelate on metal through M-N bonds while it may cause a strain for $NC(CH_2)_6CN$ to make chelate on metal.

Table 3. Hydration of Dinitriles (3.0 mmol) in the Presence of $IrH(CO)(TPPTS)_3$, **1** (0.05 mmol) in Aqueous Solution at 100 °C under N_2

substrate	reaction time (h)	unreacted dinitrile (%)[a]	mono-hydration product (%)[b]	di-hydration product (%)[b]
$NC(CH_2)_4CN$	0.5	63	37	0
	1	35	54	11
	4	0	47	53
	12	0	8	92
	24	0	0	100
$NC(CH_2)_6CN$	1	76	24	0
	2	41	41	18
	4	26	48	25
	24	0	0	100

[a]Determined by GC. [b]Weight % after isolation.

Metal Complex(es) During Catalysis. In order to obtain information on metal complexes during the catalytic cycle, metal complexes have been isolated from the catalytically active reaction mixtures. The isolated complex(es), **C** from the reaction of **1** with $CH_3CH=CHCN$ after 4 h under the catalytic conditions gives more spectral information than any other solids isolated from reaction mixtures of **1** with other nitriles.

Infrared and ^{13}C NMR spectra of the complex **C** show that it contains moieties of Ir-C≡O and $-CONH_2$ by showing strong absorptions at 1993 (Ir-C≡O) and 1633 ($-CONH_2$) cm^{-1} and signals at 187 (Ir-C≡O) and 172 ($-CONH_2$) ppm, respectively. ^{31}P NMR data for **C** suggest the dissociation of TPPTS and oxidation of TPPTS during the catalysis: ^{31}P NMR spectrum shows four signals at -5.13, -0.36 (d, J = 62 Hz), 1.75 (d, J = 62 Hz) and 35.3 ppm. The signals at -5.13 and 35.3 ppm are due to free TPPTS and TPPTS-oxide ($O=P(m\text{-}C_6H_4SO_3Na)_3 \cdot xH_2O$), respectively. The two doublets at -0.36 and 1.75 ppm seem due to the TPPTS remained in the coordination sphere. Complex **C** is also obtained in the reaction of complex **1** with excess $CH_3CH=CHCONH_2$ in aqueous solution at 100 °C. Reaction of **C** with excess TPPTS under CO (100 psi) in aqueous solution at 70 °C gives complex **1** and $CH_3CH=CHCONH_2$. Stirring aqueous solution of **C** at room temperature produces $CH_3CH=CHCONH_2$ and unidentifed iridium complex(es). Complex (es) **C** could be a mixture of more than one iridium complex and is currently under investigation for further characterization.

Experimental Section

General Information. The NMR spectra were measured on a Varian Gemini 300 MHz for ^1H, 75.4 MHz for ^{13}C and 121.3 MHz for ^{31}P. Electronic absorption and infrared spectra were obtained by Shimadzu UV-240 and Shimadzu IR-440 and/or Nicolet 205 spectrophotometers. Gas chromatographs and mass spectra were obtained by Varian 3700 and Hewlett Packard HP5890A at Organic Chemistry Research Center, Sogang University.

All chemicals were purchased reagent grade from Aldrich and used without further purification. TPPTS was prepared by the literature method.[7]

Synthesis of $IrH(CO)(TPPTS)_3$ (1). A reaction mixture of $IrCl_3 \cdot 3H_2O$ (0.2 mmol, 70 mg) and TPPTS (0.6 mmol, 374 mg) in H_2O (4 mL) and EtOH (10 mL) was refluxed for 1 h before NaOH (114 mg) in H_2O (2 mL) and HCHO (4 mL, 37% H_2O) were added to the yellow solution. The reaction mixture was refluxed for further 19 h and cooled down to room temperature. Addition of EtOH (80 mL) to the reaction mixture resulted in precipitation of the yellow product of **1**, which was filtered and washed with EtOH (60 mL) and Et_2O (20 mL). This crude product was recrystallized using H_2O (1 mL) and EtOH (30 mL). The yield was 0.38 g (0.18 mmol, 90 %). ^1H NMR (D_2O, 25 °C): δ -10.6 (q, 1H, $J_{H\text{-}P}$ = 21.3 Hz, Ir-*H*, lit.[9] -10.6). ^{31}P NMR (D_2O, 25 °C): δ 18.6 (s, 3P, Ir-*P*, lit.[9] 19.2). IR (KBr, cm^{-1}) 2084 ($\nu_{Ir\text{-}H}$, lit.[9] 2128), 1935 (ν_{CO}, lit.[9] 1927). Electronic absorption (H_2O, 25 °C): λ_{max} (nm) 322.

Catalytic Hydration of Nitriles. All catalytic reactions were carried out practically in the same manner as described below. A reaction mixture of $IrH(CO)(TPPTS)_3$ (**1**) (0.1 g, 0.05 mmol) and a nitrile (3.00 mmol) in H_2O (5 mL) was stirred for 4 h at 100 °C under N_2 and cooled down to room temperature before the solvent and unreacted nitrile were removed by vacuum distillation to obtain yellowish residue. Amide was extracted from the residue twice with acetone (30, 20 mL) that was removed by vacuum distillation. The white solid (amide) was characterized by ^1H NMR ($CDCl_3$, 25 °C), infrared (KBr) and GC/mass spectra.

Only mass spectral (MS) data are given for those amides (CH_3CONH_2, $CH_3(CH_2)_4CONH_2$, $C_6H_5CONH_2$, $ClCH_2CONH_2$, *trans*-$C_6H_5CH=CHCONH_2$, and $CH_2=CH(CH_3)CONH_2$) whose ^1H NMR data are available in "*The Aldrich Library of ^{13}C and ^1H NMR spectra*", 1st ed., Aldrich Chem. Co., 1993 (edited by Pouchant).

CH_3CONH_2: MS: 59 ($(M)^+$). $CH_3(CH_2)_4CONH_2$: MS: 116 ($(M+1)^+$). $C_6H_5CONH_2$: MS: 121 ($(M)^+$). $ClCH_2CONH_2$: MS: 93 ($(M)^+$). *cis*-$CH_3CH=CHCONH_2$: ^1H NMR: δ 2.1 (dd, 3H, $J_{H\text{-}H}$ = 7.2 Hz and $J_{H\text{-}H}$ = 1.8 Hz, CH_3), 5.7 (br, 2H, NH_2), 5.8 (dd, 1H, $J_{H\text{-}H}$ = 11.4 Hz and $J_{H\text{-}H}$ = 1.8 Hz, *CH*CO), 6.1-6.2 (m, 1H, CH_3CH). IR: 1617 (s, $\rho_{N\text{-}H}$), 1678 (s, $\nu_{C=O}$), 3201, 3394 (m, $\rho_{N\text{-}H}$). MS: 85 ($(M)^+$). *trans*-$CH_3CH=CHCONH_2$: ^1H NMR: δ 1.9 (dd, 3H, $J_{H\text{-}H}$ = 6.9 Hz and $J_{H\text{-}H}$ = 1.8 Hz, CH_3), 5.5 (br, 2H, NH_2), 5.9 (dd, 1H, $J_{H\text{-}H}$ = 15.6 Hz and $J_{H\text{-}H}$ = 1.8 Hz, *CH*CO), 6.8-6.9 (m, 1H, CH_3CH). IR: 1617 (s, $\nu_{N\text{-}H}$), 1678 (s, $\nu_{C=O}$), 3201, 3394 (m, $\nu_{N\text{-}H}$). MS: 85 ($(M)^+$). *cis*-$CH_3OCH=CHCONH_2$: ^1H NMR: δ 3.9 (s, 3H, CH_3O), 4.9 (d, 1H, $J_{H\text{-}H}$ = 10.9 Hz, *CH*CO), 5.4 (br, 2H, NH_2), 6.5 (d, 1H, $J_{H\text{-}H}$ = 10.9 Hz, OC*H*). MS: 101 ($(M)^+$). *trans*-$CH_3OCH=CHCONH_2$: ^1H NMR: δ 3.7 (s, 3H, CH_3O), 5.2 (d, 1H, $J_{H\text{-}H}$ = 21.8 Hz, *CH*CO), 5.4 (br, 2H, NH_2), 7.6 (d, 1H, $J_{H\text{-}H}$ = 21.8 Hz, OC*H*). MS: 101 ($(M)^+$). *cis*-$C_2H_5OCH=CHCONH_2$: ^1H NMR: δ 1.4 (t, 3H, $J_{H\text{-}H}$ = 6.9 Hz, CH_3C), 4.0 (q, 2H, $J_{H\text{-}H}$ = 6.9 Hz, CH_2O), 5.0 (d, 1H, $J_{H\text{-}H}$ = 6.9 Hz, *CH*CO), 5.4 (br, 2H, NH_2), 6.5 (d, 1H, $J_{H\text{-}H}$ = 6.9 Hz, OC*H*). MS: 115 ($(M)^+$). *trans*-$C_2H_5OCH=CHCONH_2$: ^1H NMR: δ 1.3 (t, 3H, $J_{H\text{-}H}$ = 6.9 Hz, CH_3C), 3.9 (q, 2H, $J_{H\text{-}H}$ = 6.9 Hz, CH_2O), 5.2 (d, 1H, $J_{H\text{-}H}$ = 12.0 Hz,

OC*H*), 5.4 (br, 2H, NH_2), 7.5 (d, 1H, $J_{H\text{-}H}$ = 12.0 Hz, C*H*CO). MS: 115 ((M)$^+$). *trans*-C_6H_5CH=CHCONH$_2$: MS: 147 ((M)$^+$). CH_2= CH(CH_3)CONH$_2$: MS: 85 ((M)$^+$).

Catalytic Hydration of Dinitriles. All catalytic reactions with dinitriles were carried out in the same manner as described below. A reaction mixture of IrH(CO)(TPPTS)$_3$ (**1**) (0.1 g, 0.05 mmol) and a dinitrile (3.00 mmol) in H_2O (5 mL) was refluxed for 4 h, and cooled down to room temperature under N_2 before the solvent was removed by vacuum distillation. Unreacted dinitrile and mono-hydration product (NC-R-CONH$_2$) were extracted from the residue twice with acetone (30, 20 mL), which was reduced to 2 mL by vacuum distillation. Addition of *n*-hexane (50 mL) resulted in precipitation of white mono-hydration product which was obtained by filtration, washed with *n*-hexane (50 mL), and dried under vacuum. The residue (mixture of unknown iridium complex and di-hydration product, H_2NCO-R-CONH$_2$) was washed three times with H_2O (20 mL) to obtain the water-insoluble white di-hydration product. The products, mono- and di-hydration products were characterized by ^{1}H NMR ($CDCl_3$, 25 °C), infrared (KBr) and GC/mass spectra. NC(CH_2)$_4$CONH$_2$: ^{1}H NMR: δ 1.7-1.8 (m, 4H, (CH_2)$_2$), 2.3 (t, 2H, $J_{H\text{-}H}$ = 6.3 Hz, CH_2CN), 2.4 (t, 2H, $J_{H\text{-}H}$ = 6.9 Hz, CH_2CO), 5.7 (br, 2H, NH_2)). ^{13}C NMR ($CDCl_3$, 25 °C): δ 23.1, 30.9, 31.2, 41.1, 128.6 (*C*N), 186.2 (*C*=O). IR: 1622 (m, $\rho_{N\text{-}H}$), 1683 (s, $\nu_{C=O}$), 2248 (m, $\nu_{C\equiv N}$), 3216, 3420 (s, $\rho_{N\text{-}H}$). MS: 127 ((M+1)$^+$). $NH_2CO(CH_2)_4CONH_2$: IR: 1653 (s, $\nu_{C=O}$), 3180, 3379 (s, $\nu_{N\text{-}H}$). MS: 144 ((M)$^+$). NC(CH_2)$_6$-CONH$_2$: ^{1}H NMR: δ 1.3-1.5 (m, 4H, (CH_2)$_2$), 1.6-1.7 (m, 4H, (CH_2)$_2$), 2.2 (t, 2H, $J_{H\text{-}H}$ = 7.2 Hz, CH_2CN), 2.3 (t, 2H, $J_{H\text{-}H}$ = 6.9 Hz, CH_2CO), 5.5 (br, 2H, NH_2). ^{13}C NMR: δ 14.6, 22.7, 23.2, 25.7, 25.9, 33.3, 120.5 (*C*N), 178.6 (*C*=O). IR: 1648 (s, $\nu_{C=O}$), 2243 (m, $\nu_{C\equiv N}$), 3196, 3389 (s, $\nu_{N\text{-}H}$). MS: 155 ((M+1)$^+$). $NH_2CO(CH_2)_6CONH_2$: IR: 1648 (s, $\nu_{C=O}$), 3185, 3379 (s, $\nu_{N\text{-}H}$). MS 173 ((M+1)$^+$).

Isolation of Metal Complexes. Catalysis was stopped by quenching the catalytically active reaction mixture to room temperature under N_2. Yellowish solid was obtained by removing the unreacted nitrile and H_2O by vacuum distillation, washed with acetone, and dried under vacuum.

Acknowledgment. This paper was financially supported by NON DIRECTED RESEARCH FUND, Korea Research Foundation, 1996.

References

1. (a) Matsuda, F. *Chemtech* **1977**, *7*, 306. (b) Gaset, A.; Constant, G.; Kalck, P.; Villain, G. *J. Mol. Catal.* **1980**, *7*, 355. (c) Hayashi, H.; Nishi, H.; Watanabe, Y.; Okazaki, T. *J. Catal.* **1981**, *69*, 44.
2. Casey, J. M. *Pulp and Paper*, 3rd ed.; Wiley-Interscience: New York, 1981; Vol. 3, p 1449.
3. Casey, J. M. *Pulp and Paper*, 3rd ed.; Wiley-Interscience: New York, 1981; Vol. 2, p 1269.
4. (a) Compagnon, P. L.; Miocque, M. *Ann. Chim.* **1970**, *5*, 11. (b) Hegedus, K. S.; Nade, L. G. *Compendium or Organic Synthetic Methods*; Wiely: New York, 1977. (c) March. J. *Advanced Organic Chemistry*, 4th ed.; Wiley-Interscience: New York, 1992; p 887, and references cited therein.
5. March. J. *Advanced Organic Chemistry*, 4th ed.; Wiley-Interscience: New York, 1992; p 383, and references cited therein
6. (a) Jensen, C. M.; Trogler, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 723, and references cited therein. (b) Ravindranathan, M.; Kalyanam, N.; Sivaram, S. *J. Org. Chem.* **1982**, *47*, 4812, and references cited therein. (c) Kaminskaia, N. V.; Kosti, N. M. *J. Chem. Soc., Dalton Trans.* **1996**, 3677.
7. Chin, C. S.; Chang, W.-T.; Yang, S.; Joo, K.-S. *Bull. Korean Chem. Soc.* **1997**, *18*, 324.
8. Joo, K.-S.; Kim, S. Y.; Chin, C. S. *Bull. Korean Chem. Soc.* **1997**, *18*, 1296.
9. Herrman, W. A.; Kellner, J.; Riepl, H. *J. Organomet. Chem.* **1990**, *389*, 103.
10. (a) Wilgus, C. P.; Downing, S.; Molitor, E.; Bains, S.; Pagni, R. M.; Kabalka, G. W. *Tetrahedron Lett.* **1995**, *36*, 3469. (b) Wiberg, K. B. *J. Am. Chem. Soc.* **1955**, *77*, 2519.
11. Unpublished results. For enol detection, see (a) Chin, C. S.; Park, J. *Chem. Commun.* **1987**, 1214. (b) Chin, C. S.; Lee, S. Y.; Park, J.; Kim, S. *J. Am. Chem. Soc.* **1988**, *110*, 8244.
12. Unpublished results.