# Preparation and Properties of Nickel–Phosphine Complexes Coordinated with α,β-Unsaturated Ester

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Reactions of bis(1,5-cyclooctadiene)nickel, $Ni(cod)_2$, with α,β-unsaturated esters in the presence of tertiary phosphine give a series of nickel–phosphine complexes formulated as Ni(tertiary phosphine)$_n$L (L=alkyl methacrylates, methyl acrylate, or methyl cinnamate; $n=2$ for $P(C_6H_5)_3$, $P(C_2H_5)(C_6H_5)_2$, $P(CH_3)_2(C_6H_5)$, $P(C_2H_5)_3$, $n=1$ for P(cyclo-$C_6H_{11})_3$). Elemental analyses, IR and NMR spectra, and chemical properties of the complexes confirm the molecular formula. The olefinic proton signals of methyl acrylate and alkyl methacrylates coordinated to nickel shift to upfield by 2.6—4.9 ppm from those of free olefins in the $^1$H-NMR spectra, indicating that the α,β-unsaturated esters coordinate to nickel through the double bond. The IR spectra show only small low frequency shifts of the $\nu$(C=O) bands of the α,β-unsaturated esters on complex formation. The reactions of Ni(P-$(C_6H_5)_3)_2$ (ethyl methacrylate) and Ni(P(cyclo-$C_6H_{11})_3$) (ethyl methacrylate) with vinyl acetate at room temperature cause the scission of the C–O bond in vinyl acetate to yield ethylene and nickel acetate.

Although a number of nickel–olefin complexes are known,[1] only a few reports have appeared on the isolation of nickel complexes coordinated with α,β-unsaturated esters.[2] No studies seem to have been carried out on the isolation of a series of α,β-unsaturated ester–nickel complexes with stabilizing ligands such as tertiary phosphines or on the effects of the stabilizing ligands on the properties of the isolated complexes. In the course of our study on the C–O bond activation of esters in contact with some zero-valent nickel complexes,[3] we found that the reactions of bis(1,5-cyclooctadiene)nickel $Ni(cod)_2$ with α,β-unsaturated esters in the presence of tertiary phosphine ligands serve as a convenient and versatile synthetic route to α,β-unsaturated ester–coordinated nickel complexes having various tertiary phosphine ligands, although the reactions of $Ni(cod)_2$ with other types of esters (alkenyl acetates, phenyl carboxylates, *etc.*) in the presence of tertiary phosphine ligands often lead to the scission of the C–O bonds in the esters.[3]

In this paper we report the isolation of α,β-unsaturated ester–nickel complexes having tertiary phosphine ligands from the reaction mixtures of $Ni(cod)_2$, α,β-unsaturated esters (methyl acrylate, alkyl methacrylate, and methyl cinnamate), and tertiary phosphine ligands and some chemical properties of the isolated complexes.

## Results and Discussion

Reactions of $Ni(cod)_2$ with methyl acrylate (mac), methyl methacrylate (mma), ethyl methacrylate (ema), and methyl cinnamate (mci) in the presence of tertiary phosphines at room temperature give orange or red nickel–phosphine complexes formulated as Ni(tertiary phosphine)$_n$(α,β-unsaturated ester) in high yields (62—92%):

$$Ni(cod)_2 + \text{tertiary phosphine} + CH(R_1)=C(R_2)COOR_3 \longrightarrow (PR_3)_nNi(\eta^2\text{-}CR_1H\text{-}CR_2COOR_3) \quad (1)$$

where $PR_3$ represents the tertiary phosphine ligand,

| | Tertiary phosphine | $R_1$ | $R_2$ | $R_3$ | $n$ |
|---|---|---|---|---|---|
| **1a** | $PPh_3$ | H | $CH_3$ | $C_2H_5$ | 2 |
| **1b** | $PEtPh_2$ | H | $CH_3$ | $C_2H_5$ | 2 |
| **1c** | $PMe_2Ph$ | H | $CH_3$ | $C_2H_5$ | 2 |
| **1d** | $PEt_3$ | H | $CH_3$ | $C_2H_5$ | 2 |
| **1e** | $PCy_3$ | H | $CH_3$ | $C_2H_5$ | 1 |
| **1f** | $PPh_3$ | H | $CH_3$ | $CH_3$ | 2 |
| **1g** | $PPh_3$ | H | H | $CH_3$ | 2 |
| **1h** | $PPh_3$ | $C_6H_5$ | H | $CH_3$ | 2 |

$PCy_3$: tricyclohexylphosphine.

Table 1 summarizes the analytical data of the isolated complexes. Complex **1a** was also obtained by the ligand exchange reaction of $Ni(cod)(PPh_3)_2$ with ema. When the cone angle $\theta$[4] of the phosphine ligand is large as in the case of tricyclohexylphosphine $PCy_3$ ($\theta=179°$) a complex with one phosphine ligand (**1e**) is obtained. Similar acrylonitrile–nickel[5] and acrylaldehyde–nickel[6] complexes with one $PCy_3$ ligand are known. On the contrary, in other cases when the cone angle of the phosphine ligand is smaller as given in Table 1, complexes with two phosphine ligands are obtained. Since triethylphosphine and tricyclohexylphosphine have similar basicities, the difference in the number of the coordinated ligands can be ascribed mainly to the steric rather than electronic effect. Attempts to prepare an ema–nickel complex by use of bidentate phosphine ligands, 1,2-bis(diphenylphosphino)ethane(dpe), gave only $Ni(dpe)_2$, no ema–coordinated dpe complex being isolated. Among the ema complexes with two phosphine ligands (**1a**—**1d**) the sensitivity of the complex to oxygen increases with the increase in the basicity of the phosphine ligand in the order **1a**<**1b**<**1c**<**1d**. Complex **1a** is moderately stable in air. However, complex **1d** is highly air-sensitive.

*NMR and IR Spectra of the Complexes.* Table 2 summarizes the IR and $^1$H-NMR data of the complexes. Figure 1 shows the $^1$H-NMR spectrum of complex **1a** in benzene at room temperature with and without $^{31}$P-decoupling. The signals of olefinic protons of ema shift on complex formation to the upfield region where the signals of olefinic protons in the usual

Table 1. Analytical data of Ni(tertiary phosphine)$_n$(α,β-unsaturated ester)

| Complex[a] | | Yield (%) | Color | Mp (°C) | Cone angle[b] (°) | Analytical data[c] C | H | Ni |
|---|---|---|---|---|---|---|---|---|
| $Ni(PPh_3)_2$ (ema) | **1a** | 90 | red | 141—143 | 145 | 72.5 (72.3) | 6.0 (5.8) | 8.4 (8.4) |
| $Ni(PEtPh_2)_2$ (ema) | **1b** | 67 | orange | 75— 80 | 141 | 68.1 (67.9) | 6.9 (6.7) | 9.3 (9.8) |
| $Ni(PMe_2Ph)_2$ (ema) | **1c** | 79 | orange | 46— 48 | 127 | 58.7 (58.8) | 7.5 (7.2) | 13.2 (13.1) |
| $Ni(PEt_3)_2$ (ema) | **1d** | 62 | orange | −15 | 132 | d) | | 21.6 (21.9) |
| $Ni(PCy_3)_2$ (ema) | **1e** | 75 | orange | 134—136 | 179 | 63.7 (63.6) | 10.1 (9.6) | |
| $Ni(PPh_3)_2$ (mma) | **1f** | 85 | red | 137—138 | 145 | 72.0 (72.1) | 5.7 (5.6) | 8.5 (8.6) |
| $Ni(PPh_3)_2$ (mac) | **1g** | 65 | red | 133—136 | 145 | 71.7 (71.8) | 5.5 (5.4) | 10.4 (10.5) |
| $Ni(PPh_3)_2$ (mci) | **1h** | 65 | red | 155—156 | 145 | 74.5 (74.1) | 5.5 (5.4) | |

a) $PPh_3=P(C_6H_5)_3$, $PEtPh_2=P(C_2H_5)(C_6H_5)_2$, $PMe_2Ph=P(CH_3)_2(C_6H_5)$, $PEt_3=P(C_2H_5)_3$, $PCy_3=P(\text{cyclo-}C_6H_{11})_3$, ema=ethyl methacrylate, mma=methyl methacrylate, mac=methyl acrylate, mci=methyl cinnamate. b) See Ref. 4. The cone angles of $PEtPh_2$ and $PMe_2Ph$ are not given in the reference but calculated by using the equation given in Ref. 4b). c) Calculated values are in parentheses. d) Microanalyses of C and H were not obtained due to the low melting point and high air-sensitivity of complex **1d**.

Table 2. IR and NMR data of the α,β-unsaturated ester–nickel complexes

| Complex | | ν(C=O)[a] ($cm^{-1}$) | Δν[b] ($cm^{-1}$) | NMR signals of the α,β-unsaturated ester ligand[c] (δ, ppm from TMS) $-CH_2$(COOR) | H-C=(*cis*) | H-C=(*trans*) | H-C=(α) | α-$CH_3$ | $CH_3$(COOR) |
|---|---|---|---|---|---|---|---|---|---|
| $Ni(PPh_3)_2$(ema) | **1a** | 1685 | 43 | 3.87(m) | 3.21(m) | 2.28(m) | | 1.69 (d, 6 Hz) | 1.05 (t, 7 Hz) |
| $Ni(PEtPh)_2$(ema) | **1b** | 1664 | 64 | 4.02 (q, 7 Hz) | 2.90(m) | 2.15(m)[d] | | 1.87 (d, 6 Hz) | 1.07 (t, 7 Hz) |
| $Ni(PMe_2Ph)_2$(ema) | **1c** | 1662 | 66 | 4.10 (q, 7 Hz) | 2.80(br) | 2.20(br) | | 1.97(s) | 1.12 (t, 7 Hz) |
| $Ni(PEt_3)_2$(ema) | **1d** | 1672[e] | 56 | 4.10(m) | 2.31(m) | 1.71(m) | | 1.73 (d, 6 Hz) | 1.11 (t, 8 Hz)[d] |
| Ni(PCy$_3$)(ema) | **1e** | 1707 | 21 | 4.06 (q, 7 Hz) | 3.34(m) | 2.70(m) | | 1.87 (d, 4 Hz) | 1.12 (t, 7 Hz)[d] |
| $Ni(PPh_3)_2$(mma) | **1f** | 1688 | 44 | | 1.24(m) | 0.92(m) | | 1.66 (d, 6 Hz) | 3.28(s) |
| $Ni(PPh_3)_2$(mac) | **1g** | 1675 | 64 | | 3.00(m) | 2.10(m) | 3.50(m) | | 3.06(s) |
| $Ni(PPh_3)_2$(mci) | **1h** | 1681 | 43 | | 4.46(m) | | 3.72(m) | | 3.25(s) |

a) In KBr disk except for **1d**. b) $\nu(C{=}O)_{free}-\nu(C{=}O)_{complex}$. c) In $C_6D_6$ at room temperature; s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet; br=broad; *cis*- and *trans*-CH are referred to the ester groups. The tertiary phosphine signals are omitted from the table. d) This signal is partly overlapped with the tertiary phosphine signals. e) In benzene.

π-type transition metal–olefin complexes are observed.[1] Without $^{31}P$-decoupling the two olefinic protons of ema in **1a** give rise to complex multiplet signals due to the geminal coupling and the coupling with one or two $^{31}P$'s (Fig. 1a). The $^{31}P$-decoupled $^1H$-NMR spectrum of **1a** gives an AB quartet pattern typical of the geminal olefinic protons coupled with each other (Fig. 1b). The α-$CH_3$ protons are coupled with one of the $^{31}P$ nuclei of the two $PPh_3$ ligands. The existence of the coupling between $^{31}P$ of $PPh_3$ ligand and $^1H$'s of ema indicates that these ligands are bonded to nickel on NMR time scale.

The appearance of $PPh_3$ signal as a sharp quartet in $^{31}P\{H\}$-NMR spectrum of **1a** (Fig. 2a) reveals that two $PPh_3$ ligands occupy magnetically non-equivalent positions to each other in the square planar complex, there being neither rapid dissociation of ligands nor rotation of the ema ligand around the Ni–ema bond axis.

The $CH_2$ protons of $OC_2H_5$ group of ema in **1a** give rise to a complex pattern (probably a double quartet) in the $^1H$-NMR spectrum. The pattern is not simplified by the $^{31}P$-decoupling, indicating that the two protons in the $OCH_2$ group are magnetically non-equivalent. The non-equivalence of the two protons most probably arises from the prevention of free rotation about the O–$CH_2$ bond axis due to steric hindrance.

The IR spectrum of **1a** shows a shift of ν(C=O) band

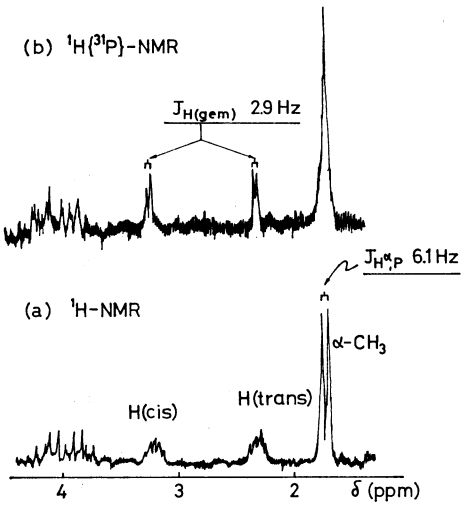



Fig. 1. (a) $^1H$-NMR spectrum of complex **1a**, (b) $^{31}P$-decoupled $^1H$-NMR spectrum of **1a**; in benzene-$d_6$ at room temperature. *cis*-H and *trans*-H are referred to the ester group.

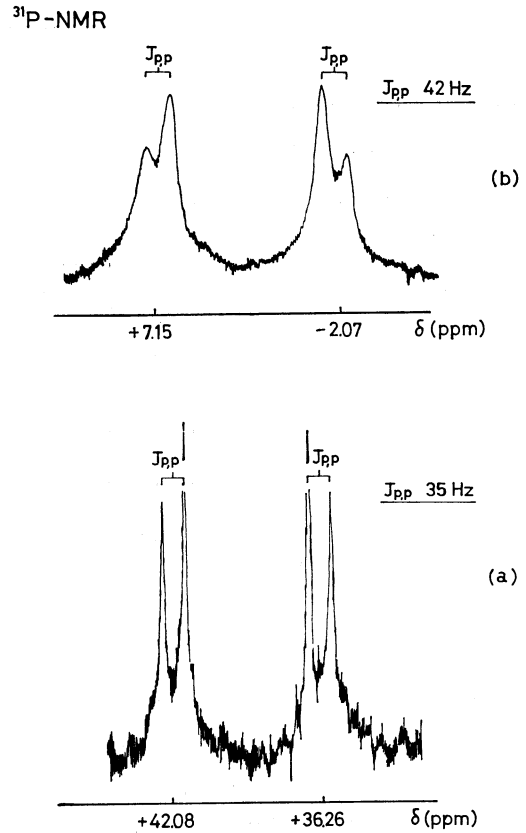


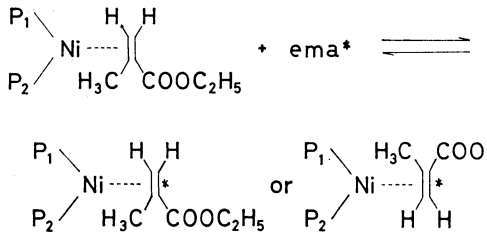

Fig. 2. $^{31}P$-NMR spectra of (a) **1a** and (b) **1c** in toluene at room temperature. $\delta$ value is referred to external $PPh_3$ (downfield positive).

of ema to a lower frequency by 43 $cm^{-1}$, suggesting that there is no direct end-on type interaction between the C=O group and the nickel atom. When a carbonyl group of an ester has direct end-on type interaction with a metal, the $\nu$(C=O) band usually shifts to lower frequency by more than 100 $cm^{-1}$.[7]

These NMR and IR data indicate that the ema ligand in **1a** is coordinated to nickel predominantly through the C=C double bond. It has recently been established by X-ray structural analysis that methyl acrylate (mac) in solid Ni(2,2′-bipyridine)$(mac)_2$ is coordinated to nickel through the C=C double bond the carbonyl group not participating in the direct bonding.[8] In this complex the $\nu$(C=O) of mac shifts to lower frequency by 50 $cm^{-1}$ on coordination.[2a]

The $^1H$-NMR spectrum of **1d** is similar to that of **1a**, showing coupling of olefinic and $\alpha$-$CH_3$ protons with $^{31}P$ of $PEt_3$ and non-equivalence of the two protons in the $OCH_2$ group. The $^1H$-NMR spectrum of **1b** is also similar to that of **1a** showing the coupling of $^{31}P$ of $PEtPh_2$ with olefinic and $\alpha$-$CH_3$ $^1H$'s of ema, but in this spectrum the $OCH_2$ signal appears as a simple quartet indicating that free rotation around the O–$CH_2$ bond occurs.

In contrast to **1a**, **1b**, and **1d**, the $^1H$-NMR spectrum of **1c** shows that the $\alpha$-$CH_3$ protons of ema are not coupled with $^{31}P$ of $PMe_2Ph$ and the signals of the olefinic protons of ema are somewhat broadened at room temperature. The $^{31}P$-NMR spectrum of **1c** also shows broadening of the AB quartet (Fig. 2b). On cooling a toluene solution of **1c** to −70 °C the coupling between $\alpha$-$CH_3$ protons and $^{31}P$ of $PMe_2Ph$ becomes observable in the $^1H$-NMR spectrum and the AB quartet in the $^{31}P$-NMR spectrum becomes sharp. These results indicate that coordinated ema in **1c** is rapidly exchanged at room temperature with a trace amount of free ema liberated from the complex:




Peaks assignable to free ema are not observable in the $^1H$-NMR of **1c** both at room temperature and at −70 °C presumably because of minor dissociation of ema from the complex.

In the Ni–ema complexes having two phosphine ligands there is a tendency that the upfield shift of the olefinic protons of ema on coordination increases with increase in the basicity of the phosphine ligand. The trend is more obvious with *cis*-olefinic proton than with *trans*-olefinic proton. Figure 3 shows plots of the chemical shifts of the olefinic protons against the $pK_a$ value of the conjugate acid of the phosphine ligand. The relation shown indicates that the coordination of a basic phosphine ligand enhances the migration of electrons from nickel to ema to increases the shielding of the olefinic protons. The shift of $\nu$(C=O) to lower frequency also supports this view. When the IR spectrum is taken in a KBr disc the coordination of a more basic phosphine ($PEtPh_2$($pK_a$[9])=4.9) or $PMe_2Ph$($pK_a$[9])=6.2)) to nickel causes a larger shift of $\nu$(C=O) than the coordination of the less basic phosphine ($PPh_3$-($pK_a$[9])=3.0)), suggesting that the coordination of a more basic phosphine causes a greater Ni→ema back-

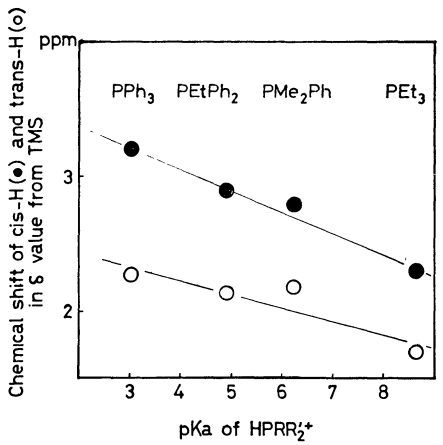



Fig. 3. Polts of the chemical shifts of *cis*-H(●) and *trans*-H(○) of Ni(ema)(tretiary phosphine)$_2$ against the p$K_a$[9] value of conjugate acids of the tertiary phosphines.

donation decreasing the bond order of the C=O group.

The olefinic protons of mma, mac, and mci are also shifted upfield in the $^1$H-NMR spectra on complex formation, the coupling between $^{31}$P of $PPh_3$ and α-$CH_3$ protons of mma being observable in the $^1$H-NMR spectrum of **1f**.

*Reactions of the Complexes.* The α,β-unsaturated esters are readily liberated from the complex on addition of excess amounts of tertiary phosphines or pyridine:

$$\mathbf{1a} + PPh_3 \text{ (excess)} \xrightarrow{\text{r.t.}} \text{ema (100\%)} + Ni(PPh_3)_4. \quad (2)$$

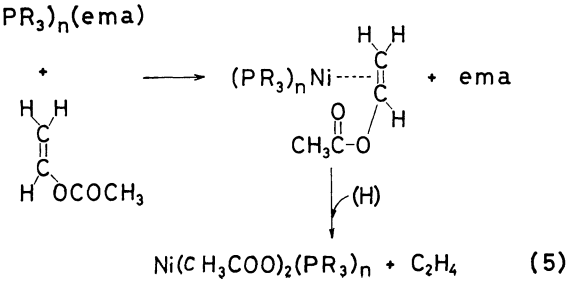
The α,β-unsaturated esters in the complexes are hydrogenated by dry HCl in diethyl ether to yield the corresponding saturated esters (*e.g.*, ethyl isobutyrate from ema).

Reactions of the α,β-unsaturated ester–nickel complexes with vinyl acetate give no nickel-vinyl acetate adduct expected as a product of a simple ligand exchange reaction. However, they lead to the scission of the C–O bond in vinyl acetate to yield ethylene and nickel acetate in high yields (Eq. 3), a result similar to our findings on the C–O bond activation of vinyl acetate by $RuH_2(PPh_3)_4$[10] and by bis(1,5-cyclooctadiene)nickel Ni(cod)$_2$ in the presence of phosphine ligands (Eq. 4):[3]

$$\mathbf{1} + CH_2{=}CHOCOCH_3 \longrightarrow Ni(CH_3COO)_2(PR_3)_n + CH_2{=}CH_2, \quad (3)$$

$$Ni(cod)_2 + CH_2{=}CHOCOCH_3 + PR_3 \longrightarrow Ni(CH_3COO)_2(PR_3)_n + CH_2{=}CH_2. \quad (4)$$

Reaction 3 presumably proceeds through the olefin exchange reaction and the activation of the C–O bond of vinyl acetate on the nickel atom:




Ease of the cleavage of the C–O bond in vinyl acetate promoted by **1** depends on the coordinated phosphine ligand. Thus, the $PCy_3$-coordinated complex **1e** promotes cleavage of the C–O bond even at 10 °C, whereas the $PPh_3$-coordinated complex **1a** causes it only at 50 °C or above. A similar effect of the coordinated phosphine ligand on the activation of the C–O bond in phenyl carboxylate by Ni has been found.[3] The sources of hydrogen to yield ethylene from the vinyl moiety (Eq. 5) have not been clarified yet.

The interaction of some transition metal complexes with olefic esters such as alkyl methacrylates and vinyl acetate causes the activation of the olefinic C–H bond to form σ-alkenyl-transition metal complexes.[11] However, no C–H bond activation of such a type has been observed for the nickel complexes we prepared.

## Experimental

*General Procedures and Materials.* Preparation and recrystallization of complexes **1a**—**1h** were carried out under deoxygenated nitrogen or argon. Melting points were determined in sealed tubes in a vacuum. Bis(1,5-cyclooctadiene)nickel, Ni(cod)$_2$ was purchased from Merck Co., Ltd. and recrystallized. α,β-Unsaturated esters were purified by distillation. Tertiary phosphine ligands were used as purchased or synthesized by the methods given in literature.[12] Solvents were dried by the usual procedures, distilled, and stored under argon or nitrogen. Yields and melting points of the complexes are given in Table 1.

*Preparation of α,β-Unsaturated Ester–Nickel Complexes.* *Ni(PPh$_3$)$_2$(ema)* ***1a***: ema (0.55 g, 4.8 mmol) was added to a mixture of Ni(cod)$_2$ (0.92 g, 3.4 mmol) and $PPh_3$ (1.76 g, 6.8 mmol) dispersed in 2 ml of hexane. Stirring of the mixture for 5 h at room temperature afforded an orange solution, which was condensed to give a light orange precipitate. The precipitate was collected by filtration and recrystallized from diethyl ether–hexane at −30 °C.

*Ni(PEtPh$_2$)$_2$(ema)* ***1b***: $PEtPh_2$ (0.95 g, 5.8 mmol) was added to a mixture of Ni(cod)$_2$ (0.80 g, 2.9 mmol) and ema (1.0 g, 8.0 mmol) dispersed in 3 ml of diethyl ether. Stirring of the solution for 6 h at 10 °C gave an orange solution which was condensed to give an orange oil. The oil was dissolved in a mixture of ether and hexane and standing of the solution at −30 °C for 2 days yielded orange crystals.

*Ni(PMe$_2$Ph)$_2$(ema)* ***1c***: $PMe_2Ph$ (0.74 g, 5.4 mmol) was added to a mixture of Ni(cod)$_2$ (0.74 g, 2.7 mmol) and ema (0.46 g, 4.0 mmol) dispersed in 2 ml of diethyl ether. Stirring of the mixture at 10 °C for 6 h gave a homogeneous red solution. This was condensed to afford a black oil, which was crystallized from diethyl ether–hexane.

*Ni(PEt$_3$)$_2$(ema)* ***1d***: $PEt_3$ (0.46 g, 3.9 mmol) was added to a mixture of Ni(cod)$_2$ (0.54 g, 2.0 mmol) and ema (1 g, 0.88 mmol) dispersed in 3 ml of diethyl ether. After stirring the mixture at 10 °C overnight the orange solution obtained was condensed to give an orange oil. The oil was crystallized from hexane at −78 °C. The orange crystals obtained were washed several times with ether at −78 °C and dried in a vacuum.

*Ni(PCy$_3$)(ema)* ***1e***: ema (2.7 g, 24 mmol) was added to a mixture of Ni(cod)$_2$ (0.73 g, 2.7 mmol) and $PCy_3$ (1.9 g, 6.8 mmol) dispersed in a mixture of 2 ml of hexane. Stirring of the mixture for 1 h at −15—10 °C gave a homogeneous solution. After further stirring for 5 h at room temperature the yellow precipitate formed was collected by filtration and

recrystallized from tetrahydrofuran or toluene at −20 °C.

*Ni(PPh$_3$)$_2$(mma)* **1f**: mma (0.47 g, 4.7 mmol) was added to a mixture of Ni(cod)$_2$ (0.56 g, 2.0 mmol) and PPh$_3$ (1.1 g, 4.2 mmol) dispersed in a mixture of 2 ml of diethyl ether and 1 ml of hexane. The mixture was stirred at 0 °C for 6 h to give a homogeneous solution. This was cooled to −30 °C to yield a yellow precipitate, which was collected by filtration and recrystallized from toluene containing mma. When the solvent contained no excess mma, no analytically pure compound was obtained.

*Ni(PPh$_3$)$_2$(mac)* **1g**: mac (0.90 g, 10.6 mmol) was added to a mixture of Ni(cod)$_2$ (0.50 g, 1.8 mmol) and PPh$_3$ (0.96 g, 3.7 mmol) dispersed in 3 ml of diethyl ether. The solution was stirred at room temperature for 8 h to give a homogeneous orange solution, which was condensed to give an orange oil. The oil was dissolved in a mixture of tetrahydrofuran and hexane. Cooling of the solution to −20 °C gave red crystals.

*Ni(PPh$_3$)$_2$(mci)* **1h**: A toluene (2 ml) solution containing mci (0.68 g, 4.2 mmol), Ni(cod)$_2$ (1.13 g, 4.1 mmol), and PPh$_3$ (2.2 g, 8.4 mmol) was stirred at room temperature for 6 h to give a red precipitate, which was collected by filtration, washed with diethyl ether, and recrystallized from acetone.

*Spectral Measurements and Analysis.* IR spectra were recorded on a Hitachi Model 295 infrared spectrophotometer, $^1$H-NMR spectra on a Japan Electron Optics Laboratory (JEOL) Mode JNM-PS-100 spectrometer, and $^{31}$P-NMR spectra on a JEOL Model JNM-PFT-PS-100 Fourier transform spectrometer. PPh$_3$ was used as an external standard. Microanalyses of C and H were performed by Mr. T. Saito in our laboratory with a Yanagimoto CHN Autocorder Type MT-2. Macroanalyses of nickel were carried out by volumetric titration.[13] The analyses of gaseous and liquid products obtained by the reactions of complexes were carried out with a Shimadzu GC-3BT gas chromatograph.

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