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# STUDIES ON
# STABLE ORGANONICKEL COMPLEXES

(安定な有機ニッケル錯体に関する研究)

1979

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CONTENTS

# CHAPTER 1

# INTRODUCTION

The role of organometallic compounds is significant as reaction intermediates in transition metal catalyzed organic syntheses. In order to understand the reaction steps of catalyst, we are interested in the reactions of isolable organometallic compounds. Although nickel is useful in catalysis in terms of its high activity and low price, reactions or properties of organonickel complexes have not been thoroughly studied owing to the instability of the complex.

In a study of reactions of coordinated organic group R' in complex $RNiL_2R'$, the other ligands (R or L) are desired to be inert enough to avoid complex side-reactions. In order to stabilize the complex, it is favorable to introduce the organic group R which has the following characters: i) absence of β-hydrogen; ii) high balkiness (e.g. ortho-substituted aryl group); iii) high electronegativity (e.g. $C_6Cl_5$ or $CCl_2$=CCl). In the present studies on reactions and properties of organonickel complexes, mainly pentachlorophenyl group has been used for the organic group R and dimethylphenylphosphine for the neutral ligand L. The phosphine coordinates strong to nickel and can offer structural information of the complex through its spectra.

In chapter 2, preparation of alkynylnickel(II) complexes is described. In chapter 3, preparation of alkoxycabene complexes from the alkynylnickel(II) complexes, and the chemical properties of the carbene complexes are described. In chapter 4, structure and bonding character of the carbene complexes are described. In chapter 5, reactions of organonickel(II) complexes with N-bromosuccinimide are described. The reactions resulted in formation of trivalent organonickel complexes or bromination of organic ligands.

The content of this thesis is mainly composed of the following papers.

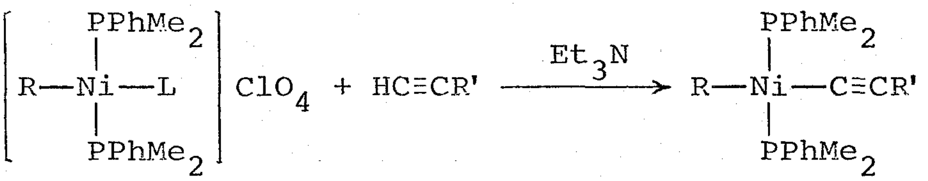
1) Cationic Carbene Complexes of Nickel(II)
K. Oguro, M. Wada, and R. Okawara,
J. Chem. Soc., Chem. Commun., (1975) 889.
2) Cationic Carbonyl and Related Complexes of Pentachlorophenylnickel(II)
M. Wada and K. Oguro,
Inorg. Chem., 15 (1976) 2346.
3) Alkoxycarbene Complexes of Nickel(II)
K. Oguro, M. Wada, and R. Okawara,
J. Organometal. Chem., 159 (1978) 417.
4) Organonickel(III) Complexes
K. Oguro, M. Wada, and N. Sonoda,
J. Organometal. Chem., in press.
5) Reactions of Some Diorganonickel(II) Complexes with N-bromosuccinimide
K. Oguro, M. Wada, and N. Sonoda,
J. Organometal. Chem., in press.

# CHAPTER 2

# PREPARATION OF ALKYNYLNICKEL(II) COMPLEXES

## 2-1. Introduction

Generally in the preparation of alkynylnickel(II) complexes, alkali metal salts of alkynes or alkynyl Grignard reagents have been employed [1,2]. However, alkynes containing an active proton cannot be used in these procedures. We have found a much easier and probably more general reaction (eq. 1) to prepare alkynylnickel(II) complexes.



$$\left[\begin{array}{c} \mathrm{PPhMe_2} \\ | \\ \mathrm{R{-}Ni{-}L} \\ | \\ \mathrm{PPhMe_2} \end{array}\right]\mathrm{ClO_4} + \mathrm{HC{\equiv}CR'} \xrightarrow{\mathrm{Et_3N}} \begin{array}{c} \mathrm{PPhMe_2} \\ | \\ \mathrm{R{-}Ni{-}C{\equiv}CR'} \\ | \\ \mathrm{PPhMe_2} \end{array} \qquad (1)$$

(R = $C_6Cl_5$, $CCl_2{=}CCl$, $(o\text{-}MeO)_2C_6H_3$; L = $OH_2$, NCMe, solvent, none; R' = H, alkyl, aryl)

## 2-2. Experimental

### General

Commercial grade alkynes and silver perchlorate were used without further purification. Infrared spectra were recorded on a Hitachi 215 or 225 spectrophotometer using Nujol mulls. $^1H$ NMR spectra were recorded on a Jeol Model JNM-PS-100 spectrometer operating at 100 MHz using tetramethylsilane as an internal standard. Melting points, analytical and spectral data were summarized in Table 1.

### Preparation of trans-RNi$(PPhMe_2)_2$Cl (Ia-Ic).

Complex Ia (R = $C_6Cl_5$) was prepared in the literature [3] method.

Complex Ib (R = $CCl_2$=CCl). To a suspension of Ni($PPhMe_2$)$_2Cl_2$ (2.00 g, 5 mmol) in 20 ml of tetrachloroethylene/ethanol (1/1) was added dropwise a solution of $NaBH_4$ (0.4 g, 10 mmol) in 30 ml of ethanol at ca. 50°C under nitrogen. The solvents were removed by heating under reduced pressure, and the residue was extracted with diethyl ether/water. The ethereal layer, on concentration, gave brown crystals of Ib (1.88 g, 75%), which were purified by recrystallization from methanol/water. The product was identified by its melting point and IR and $^1H$ NMR spectra [4].

Complex Ic (R = (o-MeO)$_2C_6H_3$). To a solution of Ni($PPhMe_2$)$_2Cl_2$ (4.00 g, 10 mmol) in 80 ml of benzene was added dropwise a solution of 2,6-dimethoxyphenyllithium [5] (10 mmol) in ether (20 ml)/benzene (100 ml) at ca. 5°C. The mixture was dried on a steam bath and the residual solid was recrystallized from hexane using a Soxhlet extractor to give Ic (2.15 g, 43%), m.p. 116-117°C. (Found: C, 56.58; H,6.13. $C_{24}H_{31}O_2P_2$-ClNi calcd.: C, 56.79; H, 6.16%). $^1H$ NMR ($CDCl_3$): $\delta(PCH_3)$ 1.26t, 12H ($^2\underline{J}_P + {}^4\underline{J}_P$ = 7.5 Hz); $\delta(OCH_3)$ 3.45s, 6H; δ(o-H) 5.94d, 2H ($J_H$ = 8 Hz); δ(p-H) 6.75m, 1H; $\delta(C_6H_5)$ 7.2-7.6m, 10H.

## Isolation of a cationic complex.

A solution of Ia (0.310 g, 0.5 mmol) in 10 ml of dry benzene was added under nitrogen atmosphere to a solution of silver perchlorate (0.113 g, 0.55 mmol), which had been dried over $P_2O_5$, in 20 ml of dry benzene. The silver chloride precipitate was removed by filtration to give an orange-brown solution. Addition of n-hexane did not cause any crystal formation and the solvents were removed under reduced pressure. The resultant sticky brown material was successfully crystallized from undried benzene/hexane or diethyl ether/hexane under air to give cationic aquonickel complex trans-$[C_6Cl_5Ni(PPhMe_2)_2OH_2]ClO_4^-$ (IIa) (71% yield), m.p. 129-133°C. (Found: C, 37.79; H, 3.37; Cl, 30.15. $C_{22}H_{24}O_5P_2Cl_6Ni$ calcd.: C, 37.65; H, 3.45; Cl, 30.31%). This complex was obtained more conveniently using moist acetone as the reaction solvent followed by recrystallization from diethyl ether/hexane. The IR spectrum showed bands due to $OH_2$ at 3260m-broad and 1625vw-broad $cm^{-1}$ and bands due to $ClO_4^-$ at 1143, 1100 and 1036 $cm^{-1}$. The $^1H$ NMR spectrum showed $\delta(PCH_3)$ 1.60t, 12H ($^2\underline{J}_P + {}^4\underline{J}_P$ = 8 Hz) and $\delta(OH_2)$ 2.69s-broad, 2H (5% $CH_2Cl_2$ solution), and $\delta(PCH_3)$ 1.62t and $\delta(OH_2)$ 1.91s (1% solution). The molar conductivities of $1.0 \times 10^{-3}$, $10^{-4}$, $10^{-5}$, and $10^{-6}$ M solutions in $CH_2Cl_2$ at 25°C were 2.4, 6.8, 20.0, and 46.0 $\Omega^{-1}cm^2M^{-1}$, respectively.

### Preparation of trans-$C_6Cl_5Ni(PPhMe_2)_2C{\equiv}CR'$ (IIIa-IIIg).

Complex IIIa (R' = H). To a solution of IIa (0.702 g, 1 mmol) in 20 ml of acetone was added triethylamine (0.2 ml, 1.5 mmol) and a large excess of gaseous acetylene (ca. 1l) at 0°C. The initial brown color of the solution changed to a light orange. The mixture was kept at 0°C for 2 h and then volatile materials were removed under reduced pressure. The residue was recrystallized from acetone/methanol to give orange crystals of IIIa (0.54 g, 89%).

Complex IIIc (R'= Et). To a solution of trans-[$C_6Cl_5$Ni-$(PPhMe_2)_2$NCMe]$ClO_4$ (IIb) [6] (0.715 g, 1 mmol) in 20 ml of acetone was added triethylamine (0.2 ml, 1.5 mmol) and a large excess of gaseous 1-butyne (ca. 1l) at room temperature. The mixture was treated as described above to give orange crystals of IIIc (0.59 g, 93%).

Complexes IIIb (R' = Me), IIId (R' = $CH_2OH$), IIIe (R' = $CH_2CH_2OH$), IIIf (R' = Ph), and IIIg (R' = $C_6H_4OMe$-p). A solution of silver perchlorate (0.207 g, 1 mmol) in 5 ml of acetone was added dropwise to a solution of Ia (0.620 g, 1 mmol) in 20 ml of acetone, and the silver perchlorate precipitate was filtered off. To the filtrate was added triethylamine (0.2 ml, 1.5 mmol) and an excess of gaseous propyne (ca. 1l) at 0°C. The mixture was treated as described above to give orange crystals of IIIb (0.57 g, 91%). A simlar reaction as above with a slight excess of propargyl alcohol or 3-butyn-1-ol at room temperature gave IIId or IIIe in a 75 or 68% yield, respectively. Complex IIId or IIIe was recrystallized from cyclohexane/hexane. A similar reaction as above with phenylacetylene or p-methoxyphenylacetylene, but in the absence of triethylamine, gave a light yellow solution, which was concentrated to ca. 1/3 volume, and an addition of an equal volume of methanol gave IIIf or IIIg in 71 or 77% yield, respectively.

Preparation of trans-RNi$(PPhMe_2)_2$C≡CR' (IIIh-IIIm) (R = $CCl_2$=CCl, $(o\text{-}MeO)_2C_6H_3$).

To a solution of Ib (0.50 g, 1 mmol) in 20 ml of acetonitrile was added dropwise a solution of silver perchlorate

(0.207 g, 1 mmol) in 10 ml of acetonitrile, and the silver chloride precipitate was filtered off. To the filtrate was added triethylamine (0.2 ml, 1.5 mmol) and 50 ml of acetylene gas at 0°C. The mixture was kept at 0°C for 2 h and then volatile materials were removed under reduced pressure. the residue was recrystallized from methanol to give orange crystals of IIIh (R = $CCl_2$=CCl, R' = H) (0.31 g, 63%). Complex IIIi-IIIk (R = $CCl_2$=CCl, R' = Me, Ph, $C_6H_4$OMe-p) were prepared in a manner similar to above in 50-70% yield.

Complex IIIl or IIIm (R = (o-MeO)$_2C_6H_3$, R = H, Ph) was prepared from Ic in a manner similar to above in 50-60% yield.

## 2-3. Results and discussion

The chloride ligand in trans-RNi($PPhMe_2$)$_2$Cl (Ia, R = $C_6Cl_5$; Ib, R = $CCl_2$=CCl; Ic, R = (o-MeO)$_2C_6H_3$) is labile and the complexes react readily with silver perchlorate resulting in the precipitation of silver chloride. The resulted complexes are assumed to be solvent-(acetone or acetonitrile) or water-coordinated cationic species. The cationic pentachlorophenyl-(aquo)nickel complex IIa is isolable. The propaties of IIa: i) the spriting of IR absorption of $ClO_4^-$ ; ii) $^1$H NMR spectra which changes on concentration; iii) the low conductivity values; suggest the presence of interaction which is probably hydrogen bondings between aquo ligand and perchlorate anion.

The cationic complexes cotaining labile ligand such as solvent acetone, acetonitrile or water react with terminal alkynes. When a base such as triethylamine is present, alkynylnickel complexes IIIa-IIIm are obtained, but IIIf or IIIg can be

TABLE 1-1 MELTING POINTS, ANALYTICAL AND IR DATA FOR trans-RNi$(PPhMe_2)_2C{\equiv}CR'$ (III)

| Complexes | | | M.p. | Analysis (%) Found (calcd.) | | IR ($cm^{-1}$) | |
|---|---|---|---|---|---|---|---|
| No. | R | R' | (°C) | C | H | ν(C≡C) | ν(CH) or ν(OH) |
| IIIa | $C_6Cl_5$ | H | 126-128(d) | 47.11<br>(47.31) | 3.71<br>(3.80) | 1947s | 3280m |
| IIIb | | Me | 134-135(d) | 47.80<br>(48.17) | 3.95<br>(4.14) | 2100w | |
| IIIc | | Et | 124-125(d) | 48.93<br>(48.99) | 4.22<br>(4.27) | 2100vw | |
| IIId | | $CH_2OH$ | 122-123(d) | 46.88<br>(46.97) | 3.91<br>(3.93) | 2085s | 3600s |
| IIIe | | $CH_2CH_2OH$ | 138-139(d) | 47.94<br>(47.79) | 4.23<br>(4.16) | 2090w | 3480m |
| IIIf | | Ph | 148-149 | 52.23<br>(52.57) | 3.92<br>(3.97) | 2090s | |
| IIIg | | $C_6H_4OMe$-p | 148-149 | 51.74<br>(52.04) | 4.03<br>(4.09) | 2085m | |
| IIIh | $CCl_2{=}CCl$ | H | 81 - 82(d) | 49.19<br>(48.98) | 4.79<br>(4.73) | 1960s | 3270m |
| IIIi | | Me | 108-110(d) | 49.46<br>(50.00) | 4.73<br>(5.00) | 2115w | |
| IIIj | | Ph | 98 - 99(d) | 55.26<br>(55.12) | 4.85<br>(4.80) | 2090s | |
| IIIk | | $C_6H_4OMe$-p | 129-131(d) | 54.05<br>(54.36) | 4.91<br>(4.88) | 2100m | |
| IIIl | (o-MeO)$_2C_6H_3$ | H | 97(d) | 63.18<br>(62.81) | 6.73<br>(6.49) | 1950s | 3260m |
| IIIm | | Ph | 101-102(d) | 67.18<br>(67.04) | 6.56<br>(6.33) | 2090vs | |

TABLE 1-2 $^1$H NMR SPECTRAL DATA FOR trans-RNi(PPhMe$_2$)$_2$C≡CR' (III)[a]

| Complexes No. | δ(PCH$_3$)[b] | δ(C≡CH) or δ(C≡CCH) | $\underline{J}_P$ (Hz) | Other resonances[c] |
|---|---|---|---|---|
| IIIa | 1.73t | 2.34t | 3.8 | |
| IIIb | 1.69t | 1.88t | 3.0 | |
| IIIc | 1.70t | 2.23t-q | 2.5 | 1.01t (CMe) |
| IIId | 1.68t | 4.13t-d | 2.5 | 1.04t (OH) |
| IIIe | 1.64t | 2.39t-t | 3.0 | 3.37q (CH$_2$O), 1.50t (OH) |
| IIIf | 1.73t | | | |
| IIIg | 1.73t | | | 6.73d and 7.06d (C$_6$H$_4$), 3.77s (OMe) |
| IIIh | 1.65t, 1.72t | 2.20t | 3.5 | |
| IIIi | 1.66t, 1.71t | 1.77t | 3.0 | |
| IIIj | 1.69t, 1.75t | | | |
| IIIk | 1.72t, 1.76t | | | 6.67d and 6.89d (C$_6$H$_4$), 3.73s (OMe) |
| IIIl | 1.36t | 2.15t | 3.5 | 6.84t-br (p-H), 6.14d (m-H), 3.51s (OMe) |
| IIIm | 1.39t | | | 6.86m (p-H), 6.17d (m-H), 3.52s (OMe) |

[a] IIIh, IIIj, IIIl and IIIm in CH$_2$Cl$_2$, others in CDCl$_3$. [b] $^2\underline{J}_P + {}^4\underline{J}_P$ = 7.0-8.0 Hz.

[c] $^3\underline{J}_{HH}$ = 6.0-9.0 Hz.

obtained even in the absence of the amine. The reaction can be performed even in a moist solvent in air. Several attempts to isolate, or detect spectroscopically, a cationic π-alkyne-nickel(II) complex which is the probable intermediate of this reaction have failed, although some analogous platinam(II) complexes are known [7].

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# CHAPTER 3

# PREPARATION AND CHEMICAL PROPERTIES OF CARBENE COMPLEXES OF NICKEL(II)

## 3-1. Introduction

Since the discovery of transition metal carbene complexes by Fischer and Maasböl [1], numerous investigations have been reported [2-6]. However, only a few carbene complexes of nickel have been isolated, in spite of their presumed importance as reaction intermediates in organic syntheses [2,3]. A nickel(0) complex, $Ni(CO)_3\{C(NEt_2)OEt\}$, and its analogs have been reported [7], followed by the nickel(II) complexes, *trans*-$[NiCl(PPhEt_2)\{\overline{CN(Me)CH_2CH_2N}Me\}_2]BF_4$ [8] and *trans*-$[NiCl(PPh_3)\{\overline{CN(Me)CH{=}C(Me)S}\}]BF_4$ [9]. However, alkyl(alkoxy)carbenenickel complexes, which are thought to be more useful in organic syntheses [5,6], have not been known. Here we report reactions of several alkynylnickel complexes, which were directed toword the preparation of alkyl(alkoxy)carbenenickel(II) complexes by a method analogous to that used by Chisholm and Clark for platinum(II) complexes [10,11].

## 3-2. Experimental

### Preparation of trans-$[C_6Cl_5Ni(PPhMe_2)_2\{C(OR)Me\}]ClO_4$ (IVa-c).

A mixture of IIIa (3.05 g, 5 mmol) and 60% aqueous perchloric acid (0.6 ml, 5.5 mmol) in 30 ml of benzene-methanol (2:1) was kept at room temperature under nitrogen atmosphere to give light yellow crystals of IVa (R= Me) (3.12 g, 84%).

A mixture of IIIa (1 mmol) and the perchloric acid (1 mmol) in 3 ml of ethanol or *n*-propanol was stirred under nitrogen for 12 h at room temperature. The resulting light yellow precipitate was washed with ether and recrystallized from ethanol or $CH_2Cl_2$-methanol to give IVb (R= Et) (0.46 g, 60%) or IVc (R= *n*-Pr) (0.41 g, 54%).

A similar reaction of IIIa (0.305 g, 0.5 mmol) in benzene-isopropanol (2:1) gave after 4 days a white precipitate, which was washed with $CH_2Cl_2$ to give $[PhMe_2(C_6Cl_5)P]ClO_4$ (0.030 g, 12%). (Found: C, 34.55; H, 2.21. $C_{18}H_{11}O_4PCl_6$ calcd.: C, 34.53; H, 2.28%). $^1H$ NMR ($MeNO_2$): $\delta(CH_3)$ 2.88 (doublet, 6H, $J_P$= 14 Hz), $\delta(C_6H_5)$ 7.6–8.0 ppm (multiplet, 5H). From the above filtrate $C_6Cl_5H$ (0.044 g, 36%) and the complex I (0.118 g, 38%) were obtained. The product $C_6Cl_5H$ was identified from its melting point (85°C) and IR spectrum [12].

### Preparation of trans-$[C_6Cl_5Ni(PPhMe_2)_2\{\overline{C(CH_2)_3O}\}]ClO_4$ (IVd).

A solution of I (1.24 g, 2 mmol) in 20 ml of benzene was added dropwise to a solution of silver perchlorate (0.41 g, 2 mmol) in 40 ml of benzene. The resulting silver chloride precipitate was filtered off. To the filtrate was added 3-butyn-1-ol (0.4 ml, 5 mmol), and the mixture was stirred under nitrogen atmosphere for 2 days at room temperature. The resulting precipitate was recrystallized from $CH_2Cl_2$-methanol to give light yellow crystals of IVd (0.89 g, 58%). The complex IVd can also be obtained from a reaction of IIIe with an equivalent perchloric acid in benzene (yield 28%).

### Reaction of IIIb with methanol in the presence of perchloric acid.

A mixture of IIIb (0.312 g, 0.5 mmol) and 60% perchloric acid (0.006 ml, 0.05 mmol) in 3 ml of benzene-methanol (2:1) was kept at room temperature for 15 h under nitrogen, and the volatile materials were removed under reduced pressure. The residual solid was recrystallized from ether-methanol to give orange crystals of trans-$C_6Cl_5Ni(PPhMe_2)_2CH{=}C(OMe)Me$ (V) (0.23 g, 70%).

A reaction of IIIb (0.5 mmol) with the perchloric acid (0.055 ml, 0.5 mmol) in a condition similar to above gave brown crystals of the aquo complex IIa (0.25 g, 71%) after recrystallization from benzene-*n*-hexane.

A reaction of V with an equivalent perchloric acid in a condition similar to above also gave IIa (yield 56%). Identification of the volatile products was carried out independently. The volatile materials in a reaction mixture of V and the perchloric acid in acetone-$d_6$ were collected by trap-to-trap distillation. $^1H$ NMR spectrum of the distillate showed the resonances due to propyne ($\delta$ 1.76 doublet and 2.16 ppm quartet, *J*= 3 Hz), methanol ($\delta$ 3.31 ppm singlet), and water ($\delta$ 2.92 ppm broad singlet).

Deprotonation of the carbene complexes IVa-d.

To a suspension of IVa-d (0.5 mmol) in 2 ml of acetone was added triethylamine (0.6 mmol) to give a clear solution. An addition of 5 ml of methanol gave yellow crystals of trans-$C_6Cl_5Ni(PPhMe)_2C(OR){=}CH_2$ (VIa-c) (R= Me, Et, or *n*-Pr) or trans-$C_6Cl_5Ni(PPhMe_2)_2\overline{C{=}CHCH_2CH_2O}$ (VId), respectively, in 80-90% yields.

Protonation of VIa-d was carried out in etherial solution. An addition of 60% perchloric acid gave light yellow crystals of IVa-d, respectively, in 90-100% yields.

TABLE 4

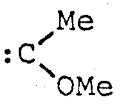
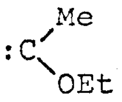
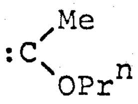
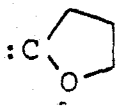
IR AND $^1$H NMR SPECTRAL DATA FOR ALKOXYALKENYL COMPLEXES *trans*-$C_6Cl_5Ni(PPhMe_2)_2R$ (V,VI).

| Complexes | | IR[a], cm$^{-1}$ | | $^1$H NMR[b] | | | | |
|---|---|---|---|---|---|---|---|---|
| No. | R | $\nu$(C=C) | $\nu$(COC) | P-$CH_3$[c] | C=CH | | Alkoxy protons | |
| | | | | $\delta$ | $\delta$ | $J_P$, Hz | $\delta$(O-CH) | Others |
| V | -CH=C(OMe)Me | 1598 s | 1099 vs | 1.02 t<br>1.10 t | 3.46 t | 4.7 | 3.27 s | |
| VIa | -C(OMe)=$CH_2$ | 1578 s | 1132 vs<br>1017 s | 1.48 t | 3.68 d-t<br>4.26 d-t | 2.5<br>3.0 | 3.10 s | |
| VIb | -C(OEt)=$CH_2$ | 1558 s | 1150 vs<br>1043 s | 1.47 t | 3.63 d-t<br>4.19 d-t | 2.5<br>3.0 | 3.29 q | 0.93 t |
| VIc | -C(OPr$^n$)=$CH_2$ | 1579 m | 1152 vs<br>1012 s | 1.47 t | 3.59 d-t<br>4.19 d-t | 2.5<br>3.0 | 3.18 t | 0.84 t[e] |
| VId | $-\overline{\mathrm{C{=}CHCH_2CH_2O}}$ | 1550 s | 1005 s | 1.45 t | 4.26 qn[f] | 2.5 | 3.64 t | 2.22 m |

[a] In Nujol mulls. [b] Chemical shifts (ppm) measured for $CH_2Cl_2$ or $CD_2Cl_2$ solution except for V ($C_6H_6$). [c] ${}^2J_P + {}^4J_P$= 8.0-8.5 Hz. [d] $\delta(CCH_3)$ 1.66 t ($J_P$= 2.2 Hz). [e] $OCCH_2$ signals are obscured by P-$CH_3$ signals. [f] ${}^3J_H$= 2.5 Hz.

TABLE 3

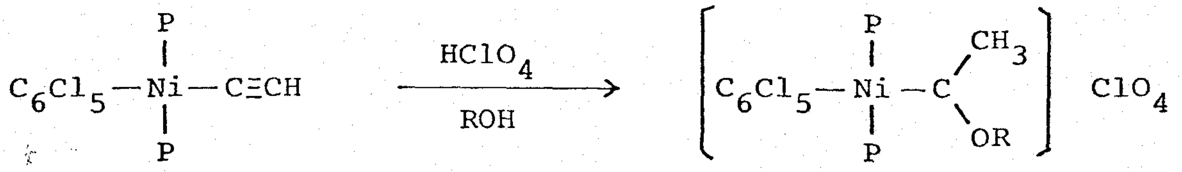
$^1$H NMR DATA[a] FOR CARBENE COMPLEXES *trans*-[$C_6Cl_5Ni(PPhMe_2)_2L]ClO_4$.

| Complexes | | | $P\text{-}CH_3$[b] | $C_{carb}\text{-}CH$[c] | Alkoxy protons | | |
|---|---|---|---|---|---|---|---|
| No. | L | Form | $\delta$ | $\delta$ | $\delta$(O-CH) | $^5J_P$, Hz | Others |
| IVa |  $:C(Me)(OMe)$ | *Z* | 1.55 t, 1.65 t | 2.48 t | 4.64 s | | |
| | | *E* | d | 1.99 t | 3.96 t | 1.5 | |
| IVb |  $:C(Me)(OEt)$ | *Z* | 1.53 t, 1.66 t | 2.54 t | 4.91 q | | 1.29 t |
| | | *E* | 1.53 t | 2.13 t | 3.99 q-t | 1.5 | 1.36 t |
| IVc |  $:C(Me)(OPr^n)$ | *Z* | 1.4-1.7[e] | 2.60 t | 4.64 t | | 0.87 t[f] |
| | | *E* | | 2.12 t | 3.88 t-br | 1 | 1.00 t[f] |
| IVd |  | *E* | 1.56 t | 2.88 t-t | 4.64 t-t | 1.0 | 1.14 qn |

[a] Chemical shifts in ppm, in $CH_2Cl_2$ or $CD_2Cl_2$ at 23°C. [b] $^2J_P + {}^4J_P$ = 8.0-8.5 Hz. [c] $^4J_P$ = 2.0-2.5 Hz. [d] Obscured by $P\text{-}CH_3$ resonance of *Z*-isomer. [e] Not well resolved and overlapped with $OCCH_2$ resonance. [f] $CCH_3$ protons.

## 3-3. Results and discussion

The ethynyl complex IIIa reacted with alcohols in the presence of perchloric acid to give the stable cationic carbene complexes, as shown in eq. 2. Examination of the

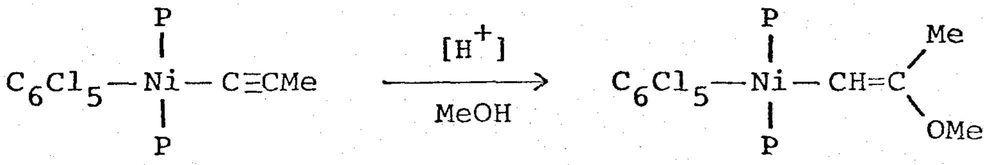


$$C_6Cl_5-\overset{P}{\underset{P}{Ni}}-C\equiv CH \xrightarrow[ROH]{HClO_4} \left[C_6Cl_5-\overset{P}{\underset{P}{Ni}}-C\begin{smallmatrix}CH_3\\ OR\end{smallmatrix}\right]ClO_4 \quad (2)$$

IIIa IVa-c

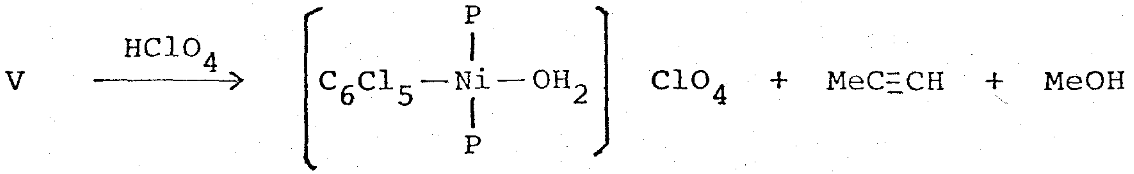
(R= a, Me; b, Et; c, n-Pr)

product ratio from a reaction performed in mixed alcohol solution showed that the reactivity of alcohol decreased in the order: methanol > ethanol > n-propanol; isopropanol was unreactive. The propynyl complex IIIb, on the other hand, decomposed in the presence of methanol and 1 equivalent of perchloric acid to give the cationic aquo complex IIa. When only a catalytic amount of the acid was used, a vinyl complex V (see eq. 3) was obtained. The complex V reacted with perchloric acid to give IIa, propyne and methanol, but not ethyl propenyl ether (eq. 4).



$$C_6Cl_5-\overset{P}{\underset{P}{Ni}}-C\equiv CMe \xrightarrow[MeOH]{[H^+]} C_6Cl_5-\overset{P}{\underset{P}{Ni}}-CH=C\begin{smallmatrix}Me\\ OMe\end{smallmatrix} \quad (3)$$

IIIb V



$$V \xrightarrow{HClO_4} \left[C_6Cl_5-\overset{P}{\underset{P}{Ni}}-OH_2\right]ClO_4 + MeC\equiv CH + MeOH \quad (4)$$

IIa

The complexes IIIc,d also decomposed in the presence of methanol and 1 equivalent of the acid to give IIa, and gave in the presence of a catalytic amount of the acid unidentified noncystalline materials. The 4-hydroxy-1-butynyl complex IIIe, however, reacted with perchloric acid to give a cyclic carbene complex IVd. This complex also could be prepared by the direct reaction of I with silver perchlorate and 3-butyn-1-ol. The arylethynyl complexes IIIf,g were recovered almost quantitatively from a solution of methanol-benzene containing perchloric acid.

$^1$H NMR spectrum of V showed resonances for only one kind of methoxypropenyl group, though it could not be determined whether the structure is E- or Z-form about the C=C bond in Ni-CH=C(OMe)Me. The structure Ni-C(OMe)=CHMe is precluded due to the lack of $J(HCCH_3)$*.

Reaction of primary and/or secondary amines with alkyl-(alkoxy)carbene complexes is well-known to give aminocarbene complexes of the group VI metal carbonyls [5], as well as of platinum(II) [13]. The reaction of the complex IVa with methylamine or dimethylamine, however, did not give the expected aminocarbene complex trans-$[C_6Cl_5Ni(PPhMe_2)_2\{C(NRR')Me\}]ClO_4$, but a neutral $\alpha$-methoxyvinyl complex VIa derived by deprotonation at the $\alpha$ carbon atom of the carbene ligand as shown in

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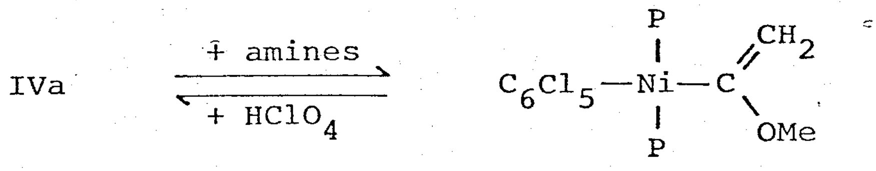
*trans-Pt(tolyl-p)$\{C(OMe)=CHMe\}(PPhMe_2)_2$ has been reported by Chisholm et al. $^1$H NMR: $\delta$(CHMe)= 1.23 doublet, $J(HCCH_3)$= 5 Hz [14].

TABLE 2 trans-$[C_6Cl_5Ni(PPhMe_2)_2L]ClO_4$ (IV)[a]
and trans-$C_6Cl_5Ni(PPhMe_2)_2R$ (V, VI)

| Complexes | | M.p. | Found (calcd.) | | |
|---|---|---|---|---|---|
| No. | L or R | (°C) | %C | %H | %Cl |
| IVa | C(OMe)Me | 171-172(d) | 40.12 | 3.64 | 28.68 |
| | | | (40.48) | (3.80) | (28.67) |
| IVb | C(OEt)Me | 158-159(d) | 40.99 | 3.83 | |
| | | | (41.31) | (4.00) | |
| IVc | $C(OPr^n)Me$ | 145-147(d) | 41.83 | 4.20 | |
| | | | (42.12) | (4.19) | |
| IVd | $\overline{C(CH_2)_3O}$ | 150-151(d) | 41.33 | 3.96 | 28.20 |
| | | | (41.42) | (3.47) | (28.22) |
| V | CH=C(OMe)Me | 148-149(d) | 47.39 | 4.27 | |
| | | | (47.65) | (4.46) | |
| VIa | $C(OMe)=CH_2$ | 118-119 | 46.72 | 4.29 | 27.44 |
| | | | (46.82) | (4.24) | (27.64) |
| VIb | $C(OEt)=CH_2$ | 118-119 | 47.43 | 4.25 | |
| | | | (47.65) | (4.46) | |
| VIc | $C(OPr^n)=CH_2$ | 108-110 | 48.06 | 4.77 | |
| | | | (48.44) | (4.67) | |
| VId | $\overline{C=CHCH_2CH_2O}$ | 125-126 | 47.72 | 4.09 | 27.03 |
| | | | (47.79) | (4.16) | (27.13) |

[a] Cationic complexes IVa-IVd have molar conductance 59-66 $\Omega^{-1}cm^2mol^{-1}$ at $10^{-4}$ M concentration in $CH_2Cl_2$.

eq. 5. The other alkoxycarbene complexes IVb-d also gave



$$\mathrm{IVa}\ \underset{+\ \mathrm{HClO_4}}{\overset{+\ \text{amines}}{\rightleftharpoons}}\ \mathrm{C_6Cl_5{-}\overset{\displaystyle P}{\underset{\displaystyle P}{Ni}}{-}C({=}CH_2)OMe} \qquad (5)$$

VIa

corresponding α-alkoxyvinyl complexes VIb-d by the reaction with triethylamine, the vinyl complexes reacting with perchloric acid to give the original carbene complexes.

The high acidity of the carbene complexes is also evident from the observation in the $^1$H NMR spectrum that the C(carbene)-$CH_3$ resonances of IVa readily disappeared on addition of an excess of $CH_3OD$ to the dichloromethane solution, due possibly to H-D exchange. The exchange rate, however, must be slower than the NMR time scale, because the C(carbene)-$CH_3$ signals of IVa in dichloromethane-methanol (8:1, v/v) remained sharp with the couplings to the phosphorus nuclei. The other carbene complexes IVb-d also showed an easy H-D exchange. The vinyl complexes VIa-d also showed analogous H-D exchange. The basicity of VIa (or the acidity of IVa) was estimated by measurement of the $^1$H NMR spectra of the solution containing IVa and a suitable reference base; 2 equivalents of triethanol amine gave a 10:90 ratio of IVa:VIa, and 5 equivalents of 2,4,6-trimethylpyridine gave a 55:45 ratio of IVa:VIa in dichloromethane. Thus, the basicity of VIa is between that of triethanolamine and that of 2,4,6-trimethylpyridine in dichloromethane, the $p\underline{K}_b$ values for these two amines in water being 7.8 and 7.4, respectively [15]. An analogous H-D exchange has been reported by Kreiter [16] for $Cr(CO)_5\{C(OMe)Me\}$ catalised by sodium methoxide, as well as deprotonation with butyllithium by Casey and Anderson [17]. A closely related study has recently been reported by Chisholm et al. for trans-$[PtX\{C(OMe)Me\}(PPhMe_2)_2]PF_6$ (X= Cl or $CF_3$) [14].

Reaction of mercaptans with alkoxycarbene complexes is known to give thioalkoxycarbene complexes [5], but IVa was recovered from a solution containing an excess of mercaptan.

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# CHAPTER 4

# STRUCTURE AND BONDING CHARACTER OF CARBENE COMPLEXES

## 4-1. Introduction

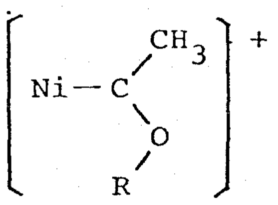
A number of spectroscopic and X-ray crystallographic studies on structure of transition metal carbene complexes or metal-carbene bonding have been reported with a various conclusions: back π-bonding is strong or weak [1-3]. Here we report the structure of nickel alkoxycarbene complexes in solution and the bonding character of the carbene ligands.

## 4-2. Experimental

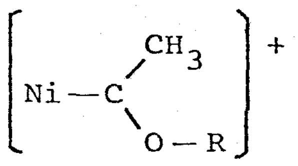
Electronic spectra were recorded on a Hitachi Model 356 spectrophotometer. $^1H$ NMR spectral data are showed in Table 3 and 4 in Chapter 3.

## 4-3 . Results and discussion

The spectra of carbene complexes are time-dependent, in general. Representative spectra are shown in Fig. 1. A very fresh solution of IVb in dichloromethane exhibited two 1:2:1 triplets of equal intensity for the P-$CH_3$ protons. This observation is indicative that the complex has a trans-bis-phosphine configuration [4] with the carbene ligand fixed perpendicularly to the nickel coordination plane. The time-dependence of the spectra can be explained in term of isomerization of the carbene ligand between Z- and E-forms, as shown below:



(*Z*)



(*E*)

At the equilibrium the spectrum shows two triplets for the C(carbene)-$CH_3$ protons and two quartets for the O-$CH_2$ protons with a relative intensity of 2:1, respectively (Table 3 and 5). A detailed measurement showed that the weaker quartet protons were magnetically coupled with the two tertiary phosphines to give a quartet of 1:2:1 triplets. The relative ratio of isomers varied with the solvent used (Table 5). The spectra in the P-$CH_3$ proton resonance region exhibit complicated features at the equilibrium. The spectra of IVb in several solvents (Figs. 1 and 2), however, can be analysed as an overlap of two 1:2:1 triplets of equal intensity (the major isomer) and a single 1:2:1 triplet (the minor isomer). Thus, the minor isomer is expected to have a trans configuration with the carbene ligand freely rotaing around the nickel-carbene bond*. From a steric point of view, relative to phosphine ligands, the major isomer can be assigned to a *Z*-isomer and the minor to an *E*-isomer. The supporting evidences for this conclusion include i) the decrease of the isomer ratio (*Z*/*E*) as the alkoxy group lengthens (Table 5), ii) the free rotation

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* An analogous $^1H$ NMR spectrum of a mixture of two isomers has been observed for a cationic imidate complex, *trans*-$[C_6Cl_5Ni(PPhMe_2)_2\{NH{=}C(OMe)Ph\}]ClO_4$; see ref. 5.

TABLE 5

ISOMER RATIO (Z/E) OF trans-[$C_6Cl_5Ni(PPhMe_2)_2\{C(OR)Me\}]ClO_4$ (IVa-c) IN VARIOUS SOLVENTS

| Complexes<br>No. | <br>R | $CDCl_3$ | $CH_2Cl_2$ | $C_6H_5NO_2$ | $(CD_3)_2CO$ |
|---|---|---|---|---|---|
| IVa | Me | ---[a] | 5 | 10 | > 10 |
| IVb | Et | 1 | 2 | 3 | 5 |
| IVc | $Pr^n$ | 0.9 | 1.5 | 2.5 | 3 |

[a] Not measured due to the poor solubility.

of the cyclic carbene ligand in IVd, iii) the observation of $^5\underline{J}_P$ for the $OCH_2$ resonance of IVa-c(E-isomers), as well as IVd, and iv) the observation of $OCH_2$ resonance of the Z-isomers at lower magnetic field than that of the E-isomers, probably due to the paramagnetic anisotropy of the nickel(II) atom [5,6].

An isomerization rate was measured for IVb with $^1H$ NMR spectra. The rate from Z- to E-isomers followed first order kinetics with the rate constant of $(7.1 \pm 0.4) \times 10^{-5}$ $sec^{-1}$ at -16°C, giving the rotational barrier ($\Delta G^{\ddagger}_{257}$) of 20 kcal/mol, as calculated for the direct rotation about C(carbene)-OR bond. Since IVb is very acidic, an alternate isomerization route involving deprotonation, rapid rotation in the neutral VIb species, and reprotonation also can be considered. If this latter route operates the rotational barrier about C(carbene)-OR bond must be still higher than 20 kcal/mol. The rotational barrier for IVa could be estimated to be higher than 18 kcal/mol from the observation of the two isomer resonances even at 80°C in nitrobenzene (above 80°C it decomposed).

The $^1H$ NMR spectra of cyclic carbene complex IVd are temperature dependent (Fig. 3), and the observation can be explained in term of the rotation about the Ni-C(carbene) bond. The coalescence temperature of the $P\text{-}CH_3$ resonances was -34°C, and the rotational $\Delta G^{\ddagger}_{239}$ value of 11.7 kcal/mol could be calculated.

The spectra of $\alpha$-alkoxyvinyl complexes VIa-c at ambient temperature showed only one kind of alkoxy proton resonance

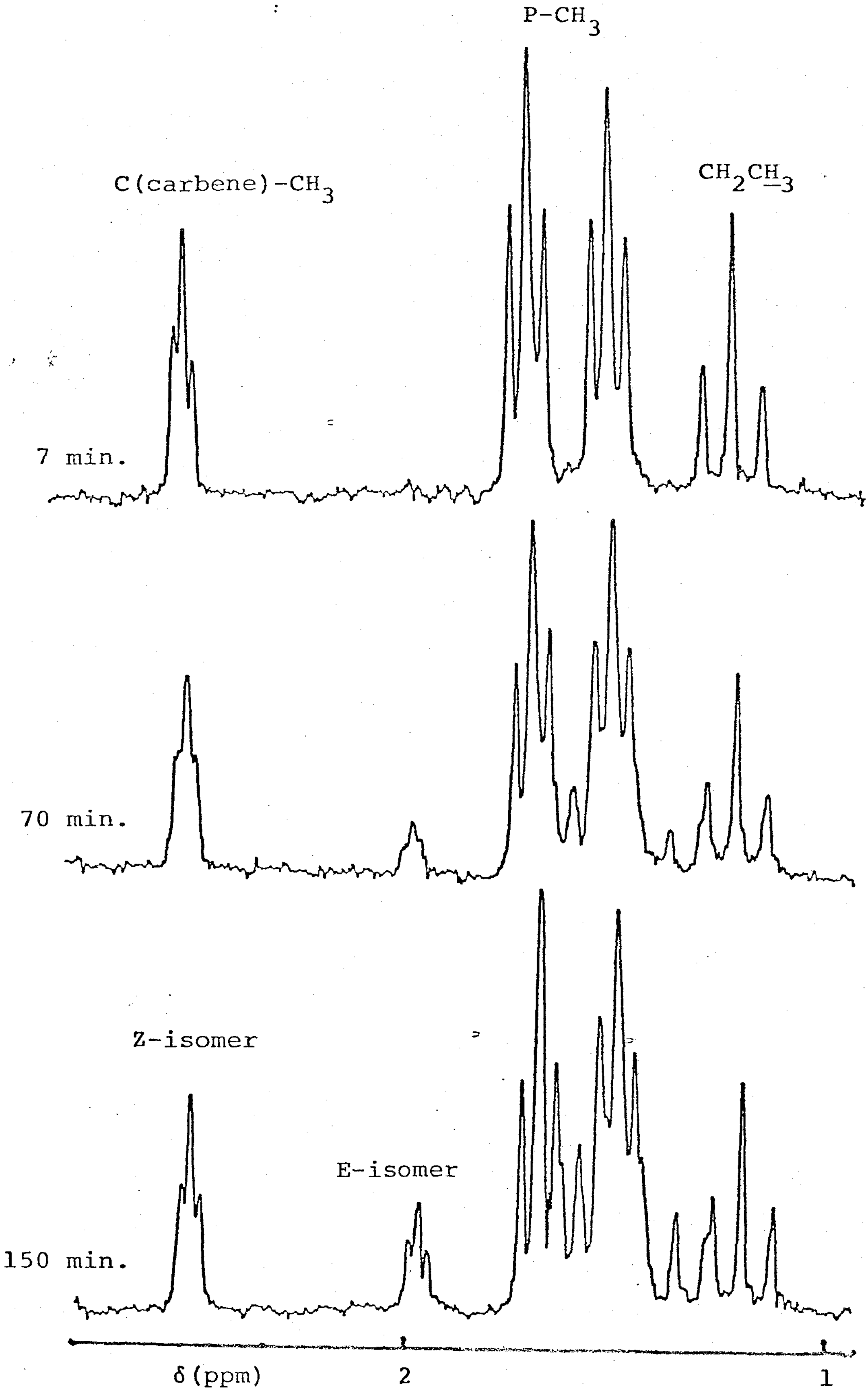


Fig. 1. Time dependence of $^1$H NMR spectrum of trans-[$C_6Cl_5Ni(PPhMe_2)_2\{C(OEt)Me\}]ClO_4$ (IVb) in $CH_2Cl_2$ at -16°C.

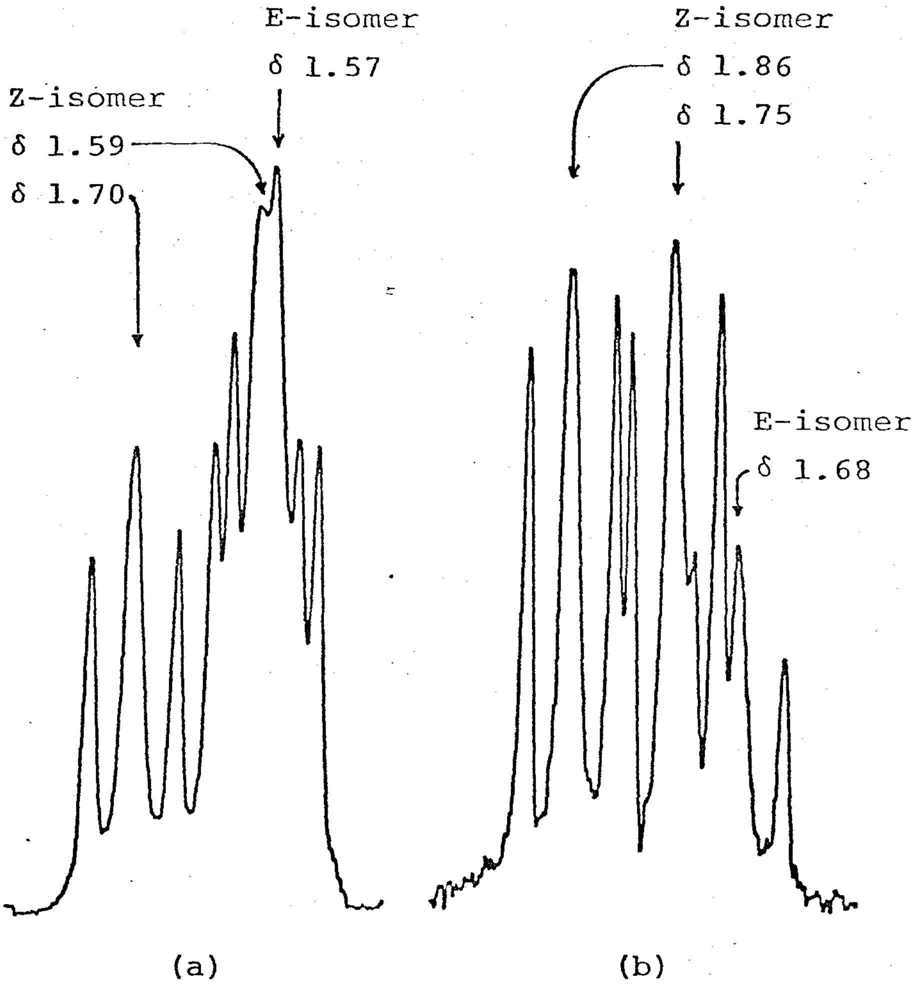


Fig. 2. P-$CH_3$ region of $^1H$ NMR spectra of <u>trans</u>-[$C_6Cl_5Ni(PPhMe_2)_2\{C(OEt)Me\}]ClO_4$ (IVb): (a) in $CDCl_3$, isomer ratio (Z/E)= 1; (b) in $(CD_3)_2CO$, isomer ratio= 5.

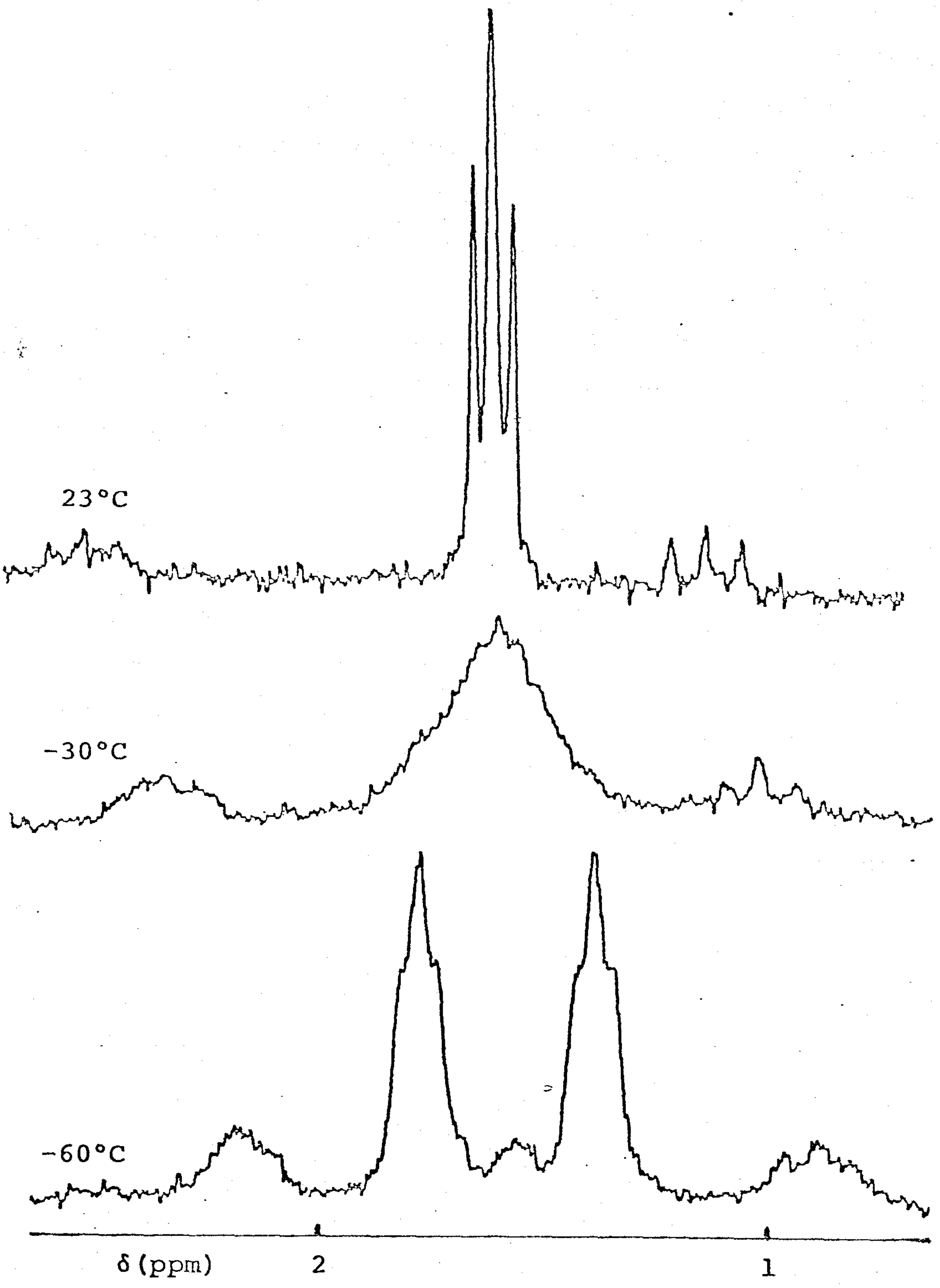
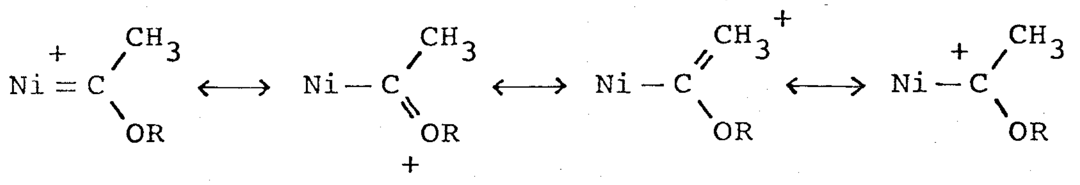


Fig. 3. Temperature dependence of $^1H$ NMR spectrum of trans-$[C_6Cl_5Ni(PPhMe_2)_2\{\overline{C(CH_2)_3O}\}]ClO_4$ (IVd) in $CH_2Cl_2$.

and a single triplet resonance of the P-$CH_3$ protons, probably due to the presence of the free rotation about the C(vinyl)-O and Ni-C(vinyl) bonds. The P-$CH_3$ triplet of VIa coalesced to a broad singlet at -24°C and sharpened to two triplets separated by 0.20 ppm at -60 °C, while the $OCH_3$ proton resonance remained a singlet. An analogous spectral change was observed for VIb, but in the spectrum of cyclic alkoxyvinyl complex VId the P-$CH_3$ resonance started to coalesce only at ca. -80°C ($T_C < -100$°C). It is tentatively suggested, therefore, that the restricted rotaion about the Ni-C(vinyl) bond in VIa,b at low temperature is caused by the steric hindrance between the alkoxy group and the bulky phosphine ligands.

The barrier to rotation about the Ni-C(carbene) bond in IVd suggests the presence of Ni-C(carbene) π-bonding (resonance form A). The steric effect on the rotation must be small, because the carbene ligand in IVd is strically almost equivalent with the alkoxyvinyl group in VId which showed a low barrier to rotation about the Ni-C(vinyl) bond. The presence of Ni-C(carbene)



A B C D

π-bonding is also evident from electronic spectra. The carbene complexes IVa-d showed a $\underline{d_{xy}}-\underline{d_{x^2-y^2}}$ band at 332-335 nm (shoulder character) and VIa-d showed the band at 373-385 nm (shoulder character). The energy difference (ca. 10 kcal/mol) between the d-d band of the carbene complexes and that of the α-alkoxyvinyl complexes is attributable to the Ni-C(carbene) π-bonding energy.

The high barrier to rotation about the C(carbene)-O bond, or the presence of the isomers in IVa-c suggests the presence of double bond character in the bond (resonance form B), rather than any steric hindrance in view of the result for α-alkoxyvinyl complexes VIa-c. The rotational barriers in IVa,b are significantly higher than that reported for $Cr(CO)_5\{C(OMe)Me\}$ ($E_a$= 12.4 ± 1.0 kcal/mol) by Kreiter and Fischer [7]. The high acidity of the carbene-methyl, or -methylene, group in IVa-d is attributable to the presence of the hyperconjugation (resonance form C) or the carbenium ion character (resonance form D) of the carbene ligand. The larger contributions of resonance forms B and C in our nickel complexes than in $Cr(CO)_5\{C(OMe)Me\}$ indicate that the nickel moiety is weaker as a π-base to contribute in resonance form A.

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# CHAPTER 5

# REACTIONS OF ORGANONICKEL(II) COMPLEXES WITH N-BROMOSUCCINIMIDE; PREPARATION OF ORGANONICKEL(III) COMPLEXES

## 5-1. Introduction

Organonickel(III) complexes appear to be intermediates in the reductive elimination process of diorganonickel(II) complexes [1-3]. Although some nickel(III) complexes have been reported [4-6], few organonickel(III) complexes have hitherto been known, except for $RNi(PPh_3)_2I_2$ ($R = CF_3$ or $C_3F_7$) [7]. We here report the reactions of organonickel(II) complexes with N-bromosuccinimide. The reactions resulted in the formation of organonickel (III) complexes or the bromination of organic ligands.

## 5-2. Experimental

Preparation of Starting Materials.

The chloride complex Ib was dissolved in methanol containing $NH_4Br$. The solution was refluxed for 10 min, and addition of water gave brown crystals of trans-$CCl_2{=}CClNi(PPhMe_2)_2Br$, in quantitative yield, mp 134-135°C. (Found: C, 39.78; H, 4.18. $C_{18}H_{22}P_2Cl_3BrNi$ calcd.: C, 39.65; H, 4.07%). $^1H$ NMR ($CH_2Cl_2$): $\delta(CH_3)$ 1.62t and 1.69t, 12H ($^2\underline{J}_P + {}^4\underline{J}_P$ = 7.5 Hz); $\delta(C_6H_5)$ 7.35-7.86m, 10H.

An ethereal suspension (30 ml) of 2,6-dimethoxyphenyllithium [8] (22 mmol) was cooled with an ice-bath under nitrogen, and $Ni(PPhMe_2)_2Cl_2$ (4.00 g, 10 mmol) was added with stirring. The mixture was stirred for 1 h at room temperature to give a yellow precipitate. Methanol (30 ml) was added at 0°C, and the precipitate was filtered and recrystallized from acetone/methanol to give crystals of trans-Ni-$\{C_6H_3(OMe\text{-}\underline{o})_2\}_2(PPhMe_2)_2$ (4.72 g, 79%), m.p. 153°C (dec). (Found: C, 63.26; H, 6.88. $C_{32}H_{40}O_4P_2Ni$ calcd.: C, 63.08; H, 6.62%). IR: $\nu$(COC) 1225vs and 1100vs $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$(PMe) 1.07t ($^2\underline{J}_P + {}^4\underline{J}_P$ = 7 Hz) 12H; $\delta$(OMe) 3.63s 12H; $\delta$(m-H) 6.07d ($\underline{J}_H$ = 8 Hz) 4H; $\delta$(p-H and PPh) 6.7-7.1m 12H.

Similar treatment of Ib with 2,6-dimethoxyphenyllithium in ether/benzene (1/1) gave trans-$CCl_2{=}CClNi(PPhMe_2)_2C_6H_3(OMe\text{-}\underline{o})_2$ (60%), m.p. 124-125°C. (Found: C, 51.59; H, 5.24. $C_{26}H_{31}O_2P_2Cl_3Ni$ calcd.: C, 51.83; H, 5.19%). IR: $\nu$(COC) 1225vs and 1100vs $cm^{-1}$. $^1H$ NMR ($CDCl_3$): $\delta$(PMe) 1.37t ($^2\underline{J}_P + {}^4\underline{J}_P$ = 7.5 Hz) 12H; $\delta$(OMe) 3.25s 3H and 3.35s 3H; $\delta$(m-H) 5.91d ($\underline{J}_H$ = 8 Hz) 2H; $\delta$(p-H) 6.75m 1H; $\delta$(PPh) 7.15s and 7.17s 10H.

## Isolation of Ni(III) Complexes.

To a solution of trans-$CCl_2{=}CClNi(PPhMe_2)_2Br$ (0.55 g, 1 mmol) in 5 ml of acetone was added N-bromosuccinimide (0.18 g, 1 mmol) in 3 ml of acetone to give a dark red solution. Addition of methanol (5 ml) gave dark red crystals of $CCl_2{=}CClNi(PPhMe_2)_2Br_2$ (0.44 g, 53%), mp 112-113°C (dec). (Found: C, 34.89; H, 3.68; Br, 26.0. $C_{18}H_{22}P_2Cl_3Br_2Ni$ calcd.: C, 34.58; H, 3.55; Br, 25.6%).

trans-$C_6Cl_5Ni(PPhMe_2)_2Br$ reacted with N-bromosuccinimide in similar manner to give $C_6Cl_5Ni(PPhMe_2)_2Br_2$ in a yield of 57%, mp 133-136°C (dec). (Found: C, 36.08; H, 2.77; Br, 21.0. $C_{22}H_{22}P_2Cl_5Br_2Ni$ calcd.: C, 35.35; H, 2.98; Br, 21.5%). Electronic spectrum ($CH_2Cl_2$): $\lambda_{max}(\varepsilon)$ 1060 (33), 840 (28), 466 (8400), 350 (7900), 318 (11400) nm. Magnetic susceptibility (powder, 289°K): $\mu_{eff} = 2.05\ \mu_B$. EPR ($CH_2Cl_2$, 77°K): *g* = 2.20 (broad singlet).

### Decomposition of Ni(III) complexes.

A solution of $CCl_2{=}CClNi(PPhMe_2)_2Br_2$ (0.313 g, 0.5 mmol) in 2 ml of benzene was refluxed for 10 min under nitrogen. The color of solution turned to deep green. An addition of methanol (1 ml) gave an orange solution which was concentrated to dryness. The residual solid was recrystallized from methanol to give *trans*-$CCl_2{=}CClNi(PPhMe_2)_2Br$ (0.175 g, 64%).

Similar treatment of $C_6Cl_5Ni(PPhMe_2)_2Br_2$ gave *trans*-$C_6Cl_5Ni(PPhMe_2)_2Br$, in 82% yield.

### Reactions of diorganonickel(II) complexes with N-bromosuccinimide.

To a solution of trans-Ni $C_6H_3(OMe\text{-}\underline{o})_2$ $_2(PPhMe_2)_2$ (0.608 g, 1 mmol) in 50 ml of acetone was added dropwise during about 5 min a solution of *N*-bromosuccinimide (0.358 g, 2 mmol) in 20 ml of acetone at room temperature. The solvent was removed under reduced pressure, and the residual solid was recrystallized from acetone/methanol to give IXa (0.56 g, 74%). Use of 4 mmol of NBS dissolved in 40 ml of acetone in the above reaction afforded IXb (0.62 g, 67%).

Complex VIIIb, IIIa or VIa reacted in analogous manner with 2, 1 or 2 equivalents of NBS in acetone to give X (77%), XI (69%) or XIIIa (75%), respectively.

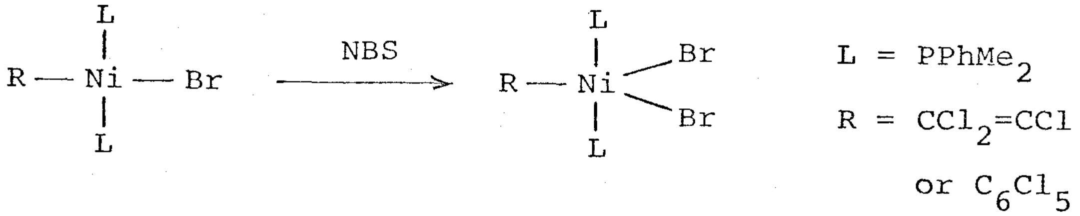
Similar treatment of VIa with 1 equivalent of *N*-chlorosuccinimide at 0°C gave XIIIb (65%).

A mixture of IIIb (0.312 g, 0.5 mmol) and NBS (0.089 g, 0.5 mmol) in 25 ml of acetone was kept at room temperature overnight. Similar work-up as above gave XII (0.27 g, 67%).

The analytical and spectral data are summarized in Table 6.

## 5-3. Results and discussion

Treatment of trans-$CCl_2$=CClNi$(PPhMe_2)_2$Br with N-bromosuccinimide in acetone affords a pentacoordinated organonickel(III) complex $CCl_2$=CClNi$(PPhMe_2)_2Br_2$, as shown in the following scheme:

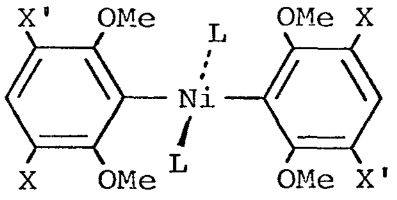


The Ni(III) complex is stable in the solid state. Evidence for this complex formation includes (i) the elemental analyses, (ii) the presence of two ionic bromide ligands, (iii) its nonelectrolyte character in freshly prepared $10^{-3}$M dichloromethane, (iv) the magnetic susceptibility ($\mu_{eff}$ = 1.74 $\mu_B$ at 291 °K), which is consistent with the presence of low-spin $d^7$ nickel(III), (v) the electronic spectrum of its dichloromethane solution exhibiting absorptions at 1050 (ε 50), 840 (shoulder), 700 (ε 180), 493 (ε 6400), 425 (ε 6000), 368 (ε 8300) and 320 (ε 8100) nm, an analogous spectrum having been reported for Ni(VPP)$Br_3$ [2], and (vi) the EPR spectrum of a dichloromethane solution at room temperature which shows a single broad signal. The observed g value (2.19) falls in the range expected for Ni(III) species rather than for any nickel(II)-stabilized radical ligand [3].

The dark red solution of the complex in nonpolar solvents is sensitive toward heat or daylight to give a diamagnetic green solution ($\lambda_{max}$ = 587 nm). No evidence of nickel-carbon bond cleavage is obtained at present, but addition of alcohols or water to the green solution resulted in the formation of stating Ni(II) complex trans-$CCl_2=CClNi(PPhMe_2)_2Br$.

A pentachlorophenyl analog, trans-$C_6Cl_5Ni(PPhMe_2)_2Br$, also afforded a paramagnetic complex, $C_6Cl_5Ni(PPhMe_2)_2Br_2$, which showed analogous spectral, physical and chemical properties.

Then, we intended to extend the above reaction to several diorganonickel(II) complexes. Unexpectedly, the reaction resulted in the facile formation of a variety of novel bromo-organonickel(II) complexes. The reaction were performed in acetone at room temperature without any catalyst.

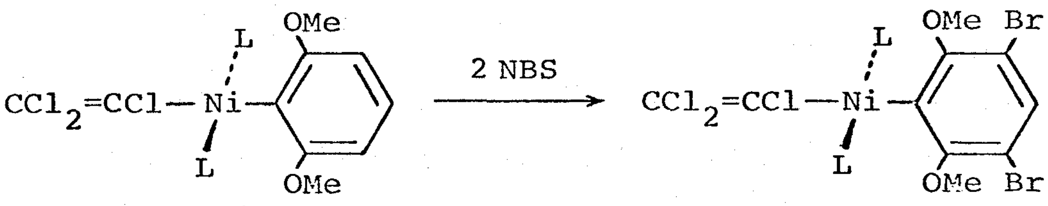


VIIIa : X = X' = H.

IXa : X = H, X' = Br.

IXb : X = X' = Br

L = $PPhMe_2$.



VIIIb X

Complex VIIIa was brominated stepwise and selectively at the meta positions of the $C_6H_3(OMe\text{-}\underline{o})_2$ groups to give either IXa or IXb depending on the amount of NBS employed. Reaction of VIIIa or IXb with an excess of NBS gave a green solution, but we have found no evidence for nickel(III) complex formation. Addition of alcohol or water to the green solution resulted in the recovery of IXb. Analogous bromination was observed with VIIIb, in which the nickel atom isastericaly less hindered than that in VIIIa.

$$\underset{\text{IIIa}}{[\mathrm{Ni}]\text{-}\mathrm{C{\equiv}CH}} \xrightarrow{\mathrm{NBS}} \underset{\text{XI}}{[\mathrm{Ni}]\text{-}\mathrm{C{\equiv}CBr}}$$

$$\underset{\text{IIIb}}{[\mathrm{Ni}]\text{-}\mathrm{C{\equiv}CMe}} \xrightarrow{\mathrm{NBS}} \underset{\text{XII}}{[\mathrm{Ni}]\text{-}\mathrm{CBr{=}C(Suc)Me} \quad \text{or} \quad [\mathrm{Ni}]\text{-}\mathrm{C(Suc){=}CBrMe}}$$

$$\underset{\text{VIa}}{[\mathrm{Ni}]\text{-}\mathrm{C(OMe){=}CH_2}} \xrightarrow{2\ \mathrm{NBS}} \underset{\text{XIIIa}}{[\mathrm{Ni}]\text{-}\mathrm{C(OMe){=}CBr_2}}$$

$$\underset{\text{VIa}}{[\mathrm{Ni}]\text{-}\mathrm{C(OMe){=}CH_2}} \xrightarrow{\mathrm{NCS}} \underset{\text{XIIIb}}{[\mathrm{Ni}]\text{-}\mathrm{C(OMe){=}CHCl}}$$

[Ni] = trans-$C_6Cl_5Ni(PPhMe_2)_2$, Suc = $\overline{\mathrm{NC(O)CH_2CH_2CO}}$.

The alkynyl proton in IIIa and the alkenyl protons in VIa were substituted quite easily, giving XI and XIIIa, respectively.* Although a monobromo(methoxy)vinyl complex could not be isolated from the reaction of VIa and NBS, a reaction with 1 equivalent of N-chlorosuccinimide gave an E/Z mixture of monochloro-substituted complexes (VIIIb). Such examples of alkynyl- or alkenyl-hydrogen substitution by halogen are, to our knowledge, quite limited in the chemistry of these halogenating agents [9-11]. The reaction of IIIb, on the other hand, was rather slow, and a product (XII) containing a succinimido group was isolated. Although the structure or geometry of the bromo(succinimide)-propenyl group in XII has not been determined, the product contained only a single isomer. The detailed mechanisms of

TABLE 6

ANALYTICAL AND SPECTRAL DATA FOR *trans*-R(R')Ni(PPhMe$_2$)$_2$

| Complexes No. | M.p. °C | Analyses, found (calcd.) | | | | IR Data (Nujol) cm$^{-1}$ | $^1$H NMR Data (CDCl$_3$) δ, ppm [*J*, Hz] |
|---|---|---|---|---|---|---|---|
| | | %C | %H | %N | %Cl+Br | | |
| IXa | 161[b] | 50.27<br>(50.10) | 4.90<br>(4.99) | | 20.82<br>(20.83) | 1220vs, 1080vs (νCOC) | 1.02t [7] 6H and 1.25t [7] 6H (PMe); 3.42s 6H and 4.20s 6H (OMe); 5.91d [8] 2H (*m*-H); 7.02d-t [1.3][c] (*p*-H); 6.6-7.2m 12H[d] (PPh) |
| IXb | 181[b] | 41.40<br>(41.56) | 3.71<br>(3.92) | | 34.60<br>(34.56) | 1205vs, 1060s (νCOC) | 1.23t [7] 12H (PMe); 3.68s 12H (OMe); 7.35t [1.3][c] 2H (*p*-H); 6.6-7.2m 10H (PPh) |
| X | 110-111 | 40.97<br>(41.07) | 3.74<br>(3.84) | | 34.81<br>(35.01) | 1205vs, 1060s (νCOC) | 1.40t [7.5] 6H and 1.55t [7.5] 6H (PMe); 4.06s 3H and 4.35s 3H (OMe); 7.2-7.3m 11H (*p*-H and PPh) |
| XI | 110[b] | 41.60<br>(41.88) | 3.08<br>(3.22) | | 37.58<br>(37.37) | 2050w (νC≡C) | 1.64t [8] 12H (PMe); 7.2-7.6m 10H (PPh) |
| XII | 202[b] | 43.20<br>(43.47) | 3.47<br>(3.65) | 1.62<br>(1.75) | 32.85<br>(32.09) | 1715vs (νC=O) | 1.63t [8] 6H and 1.76t [8] 6H (PMe); 1.98t [2.5][e] 3H (CMe); 2.73s 4H (CH$_2$CH$_2$); 7.1-7.3m 10H (PPh) |
| XIIIa | 161[b] | 37.48<br>(37.57) | 3.19<br>(3.15) | | 42.49<br>(42.18) | 1515m (νC=C)[f]<br>1115s (νCOC) | 1.53t [7.5] 6H and 1.65t [7.5] 6H (PMe); 3.93s 3H (OMe); 7.0-7.3m 10H (PPh) |
| XIIIb | 127[b] | 44.26<br>(44.43) | 3.82<br>(3.88) | | | 1520w (νC=C)[f]<br>1095s (νCOC) | 1.49t [8], 1.64t [8] and 1.35-1.7m-broad total 12H (PMe); 3.10s 1.9H and 3.59s 1.1H (OMe); 4.26t [3.0][g] 0.35H and 5.47t [4.0][g] 0.65H (CH); 7.1-7.4m 10H (PPh) |

[b] Decomposition. [c] $^6J_P$ value. [d] Total intensity of *p*-H and PPh proton signals. [e] $^5J_P$ value. [f] Tentative assignment. [g] $^4J_P$ value.

these reactions are unknown at present, although the reactions can be readily explained in terms of a radical process [12], or an ionic process [13]. Another possibility is an autocatalyzed radical process, with the nickel(II) complex forming a pentacoordinated diorganonickel(III) bromide intermediate.

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# CHAPTER 6

## SUMMARY

Cationic complexes, trans-$[RNi(PPhMe_2)_2L]ClO_4$ ($R = C_6Cl_5$, $CCl_2{=}CCl$ or $(o\text{-}MeO)_2C_6H_3$; L = labile neutral ligand such as NCMe), which have been prepared from trans-$RNi(PPhMe_2)_2Cl$ and silver perchlorate, react with terminal alkynes, $HC{\equiv}CR'$ (R' = H, alkyl or aryl), in the presence of triethylamine to give alkynylnickel(II) complexes, trans-$RNi(PPhMe_2)_2C{\equiv}CR'$.

Reactions of the alkynylnickel(II) complexes with alcohols in the presence of perchloric acid were investigated. The ethynylnickel Complex, trans-$C_6Cl_5Ni(PPhMe_2)_2C{\equiv}CH$, gave cationic alkoxycarbene complexes, trans-$[C_6Cl_5Ni(PPhMe_2)_2\{C(OR'')Me\}]ClO_4$ (R" = Me, Et or $Pr^n$), as well as trans-$C_6Cl_5Ni(PPhMe_2)_2C{\equiv}CCH_2CH_2OH$ afforded trans-$[C_6Cl_5Ni(PPhMe_2)_2\{\overline{C(CH_2)_3O}\}]ClO_4$, but the propynylnickel complex, trans-$C_6Cl_5Ni(PPhMe_2)_2C{\equiv}CMe$, either decomposed or afforded trans-$C_6Cl_5Ni(PPhMe_2)_2CH{=}C(OMe)Me$, depending on the amount of the acid used. Treatment of the carbene complexes with amines resulted in deprotonation to give α-alkoxyvinyl complexes trans-$C_6Cl_5Ni(PPhMe_2)_2C(OR''){=}CH_2$ or trans-$C_6Cl_5Ni(PPhMe_2)_2\overline{C{=}CHCH_2CH_2O}$, the reaction being reversible. The carbene methyl or the vinyl protons in the carbene complexes or the α-alkoxyvinyl complexes are D-exchangeable by MeOD without catalyst and the basicity of the α-alkoxyvinyl complex is comparable to those of amines.

The structure and bonding character of the carbene complexes have been investigated by $^1H$ NMR spectroscopy. The carbene complexes have two isomers due to hindered rotation about the

C(carbene)-O bond in solution, and the ethoxycarbene complex exists in the *Z*-form in the solid state. The rotational barriers ($\Delta G^{\ddagger}$) about the C(carbene)-O bond in the ethoxycarbene complex and the Ni-C(carbene) bond in the cyclic carbene complex are 20 (or more) and 11.7 kcal/mol, respectively. These rotational barriers are explained in terms of some double bond character of the carbene carbon and the oxygen or nickel atom.

The reaction of *trans*-RNi$(PPhMe_2)_2$Br (R = $C_6Cl_5$ or $CCl_2=CCl$) with *N*-bromosuccinimide afforded paramagnetic organonickel(III) complexes, RNi$(PPhMe_2)_2Br_2$. Thermolysis or photolysis of the organonickel(III) complex followed by treatment with methanol gave the mother organonickel(II) monobromide complex. On the other hand, the reactions of some diorganonickel(II) complexes with NBS resulted in facile bromine for hydrogen substitution in aromatic, alkynyl or alkenyl substituents, or in the addition of NBS to C≡C bond.

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