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STUDIES ON
STABLE ORGANONICKEL COMPLEXES

1979
KEISUKE OGURO

Department of Petroleum Chemistry
Osaka University
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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 RNiL₂R', 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., C₆Cl₅ or CCl₂=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 alkynynickel(II) complexes is described. In chapter 3, preparation of alkoxyacabene complexes from the alkynynickel(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,

2) Cationic Carbonyl and Related Complexes of Pentachlorophenylnickel(II)
   M. Wada and K. Oguro,

3) Alkoxy carbene Complexes of Nickel(II)
   K. Oguro, M. Wada, and R. Okawara,

4) Organonickel(III) Complexes
   K. Oguro, M. Wada, and N. Sonoda,

5) Reactions of Some Diorganonickel(II) Complexes with N-bromosuccinimide
   K. Oguro, M. Wada, and N. Sonoda,
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.

\[
\begin{array}{cccc}
\text{R-Ni-L} & \text{ClO}_4^- + \text{HC≡CR'} & \text{Et}_3\text{N} & \text{R-Ni-C≡CR'} \\
\text{PPhMe}_2 & \text{PPhMe}_2 & \text{PPhMe}_2 & \text{PPhMe}_2
\end{array}
\]  (1)

\( (R = \text{C}_6\text{Cl}_5, \text{CCl}_2\text{=CCl}, (\text{o-MeO})_2\text{C}_6\text{H}_3; L = \text{OH}_2, \text{NCOME}, \text{solvent}, \text{none}; \)

\( R' = \text{H}, \text{alkyl}, \text{aryl} \)

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. \(^1\)H 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 \((R = \text{C}_6\text{H}_5)\) was prepared in the literature \([3]\) method.

Complex Ib \((R = \text{CCl}_2=\text{CCl})\). To a suspension of Ni\((\text{PPhMe}_2)_2\text{Cl}_2\) \((2.00 \text{ g, 5 mmol})\) in 20 ml of tetrachloroethylene/ethanol (1/1) was added dropwise a solution of \(\text{NaBH}_4\) \((0.4 \text{ g, 10 mmol})\) 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 \((1.88 \text{ g, 75%})\), which were purified by recrystallization from methanol/water. The product was identified by its melting point and IR and \(^1\)H NMR spectra \([4]\).

Complex Ic \((R = (\text{o-MeO})_2\text{C}_6\text{H}_3)\). To a solution of Ni\((\text{PPhMe}_2)_2\text{Cl}_2\) \((4.00 \text{ g, 10 mmol})\) in 80 ml of benzene was added dropwise a solution of 2,6-dimethoxyphenyllithium \([5]\) \((10 \text{ mmol})\) in ether \((20 \text{ ml})/\text{benzene (100 ml})\) 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 \((2.15 \text{ g, 43%})\), m.p. 116-117°C. \((\text{Found: C, 56.58; H, 6.13.} \quad \text{C}_{24}\text{H}_{31}\text{O}_2\text{P}_2\text{ClNi calcd.: C, 56.79; H, 6.16%}. \quad \text{\(^1\)H NMR (CDCl}_3\): \delta(\text{PCH}_3)\ 1.26t, 12H \left(\frac{2J_P}{2J_P + 4J_P} = 7.5 \text{ Hz}\right); \delta(\text{OCH}_3) \ 3.45s, 6H; \delta(\text{o-H})\ 5.94d, 2H \left(J_H = 8 \text{ Hz}\right); \delta(\text{p-H}) \ 6.75m, 1H; \delta(\text{C}_6\text{H}_5) \ 7.2-7.6m, 10H.)

Isolation of a cationic complex.

A solution of Ia \((0.310 \text{ g, 0.5 mmol})\) in 10 ml of dry benzene was added under nitrogen atmosphere to a solution of silver perchlorate \((0.113 \text{ g, 0.55 mmol})\), which had been dried over \(\text{P}_2\text{O}_5\), 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-[C₆Cl₅Ni(PPhMe₂)₂OH₂]ClO₄⁻ (IIa) (71% yield), m.p. 129-133°C. (Found: C, 37.79; H, 3.37; Cl, 30.15. C₂₂H₂₄O₅P₂Cl₆Ni 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 OH₂ at 3260m-broad and 1625vw-broad cm⁻¹ and bands due to ClO₄⁻ at 1143, 1100 and 1036 cm⁻¹. The ¹H NMR spectrum showed δ(PCH₃) 1.60t, 12H (²J_p + ⁴J_p = 8 Hz) and δ(OH₂) 2.69s-broad, 2H (5% CH₂Cl₂ solution), and δ(PCH₃) 1.62t and δ(OH₂) 1.91s (1% solution). The molar conductivities of 1.0 × 10⁻³, 10⁻⁴, 10⁻⁵, and 10⁻⁶ M solutions in CH₂Cl₂ at 25°C were 2.4, 6.8, 20.0, and 46.0 Ω⁻¹ cm² M⁻¹, respectively.

Preparation of trans-C₆Cl₅Ni(PPhMe₂)₂C=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. 11) 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-[\text{C}_6\text{Cl}_5\text{Ni-}(\text{PPhMe}_2)_2\text{NCMe}]\text{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. 11) at room temperature. The mixture was treated as described above to give orange crystals of IIIC (0.59 g, 93%).

Complexes IIId (R' = CH\text{$_2$OH}), IIIf (R' = CH\text{$_2$CH\text{$_2$OH}}), IIIf (R' = Ph), and IIIg (R' = C$_6$H$_4$OMe-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. 11) at 0°C. The mixture was treated as described above to give orange crystals of IIId (0.57 g, 91%). A similar reaction as above with a slight excess of propargyl alcohol or 3-butyn-1-ol at room temperature gave IIIf 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(\text{PPhMe}_2)_2C=CR' (IIIh–IIIm) (R = CC\text{$_2$}-CC\text{$_1$}, (o-MeO)$_2$C$_6$H$_3$).

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 = CCl₂=CCL, R' = H) (0.31 g, 63%). Complexes IIIi-IIIk (R = CCl₂=CCL, R' = Me, Ph, C₆H₄OMe-p) were prepared in a manner similar to above in 50-70% yield.

Complex IIIl or IIIm (R = (ο-MeO)₂C₆H₃, 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(PPhMe₂)₂Cl (Ia, R = C₆Cl₅; Ib, R = CCl₂=CCL; Ic, R = (ο-MeO)₂C₆H₃) 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 properties of IIa: i) the splitting of IR absorption of ClO₄⁻; ii) ¹H 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 containing labile ligand such as solvent acetone, acetonitrile or water react with terminal alkynes. When a base such as triethylamine is present, alkynyl-nickel complexes IIIa-IIIm are obtained, but IIIf or IIIg can be
TABLE 1-1 MELTING POINTS, ANALYTICAL AND IR DATA FOR trans-RNi(PPhMe2)2C=CR' (III)

<table>
<thead>
<tr>
<th>Complexes</th>
<th>M.p. (°C)</th>
<th>Analysis (%)</th>
<th>IR ν (cm⁻¹)</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>Found (calcd.)</td>
<td>v(C=)</td>
</tr>
<tr>
<td>No. R</td>
<td>R'</td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>IIIa C₆Cl₅</td>
<td>H</td>
<td>126-128(d)</td>
<td>47.11</td>
</tr>
<tr>
<td></td>
<td>(47.31)</td>
<td></td>
<td>(3.80)</td>
</tr>
<tr>
<td>IIIb</td>
<td>Me</td>
<td>134-135(d)</td>
<td>47.80</td>
</tr>
<tr>
<td></td>
<td>(48.17)</td>
<td></td>
<td>(4.14)</td>
</tr>
<tr>
<td>IIIc</td>
<td>Et</td>
<td>124-125(d)</td>
<td>48.93</td>
</tr>
<tr>
<td></td>
<td>(48.99)</td>
<td></td>
<td>(4.27)</td>
</tr>
<tr>
<td>IIId</td>
<td>CH₂OH</td>
<td>122-123(d)</td>
<td>46.88</td>
</tr>
<tr>
<td></td>
<td>(46.97)</td>
<td></td>
<td>(3.93)</td>
</tr>
<tr>
<td>IIIe</td>
<td>CH₂CH₂OH</td>
<td>138-139(d)</td>
<td>47.94</td>
</tr>
<tr>
<td></td>
<td>(47.79)</td>
<td></td>
<td>(4.16)</td>
</tr>
<tr>
<td>IIIf</td>
<td>Ph</td>
<td>148-149</td>
<td>52.23</td>
</tr>
<tr>
<td></td>
<td>(52.57)</td>
<td></td>
<td>(3.97)</td>
</tr>
<tr>
<td>IIIg</td>
<td>C₆H₄OMe-P</td>
<td>148-149</td>
<td>51.74</td>
</tr>
<tr>
<td></td>
<td>(52.04)</td>
<td></td>
<td>(4.09)</td>
</tr>
<tr>
<td>IIIh CCl₂=CCl</td>
<td>H</td>
<td>81-82(d)</td>
<td>49.19</td>
</tr>
<tr>
<td></td>
<td>(48.98)</td>
<td></td>
<td>(4.73)</td>
</tr>
<tr>
<td>IIIi</td>
<td>Me</td>
<td>108-110(d)</td>
<td>49.46</td>
</tr>
<tr>
<td></td>
<td>(50.00)</td>
<td></td>
<td>(5.00)</td>
</tr>
<tr>
<td>IIIj</td>
<td>Ph</td>
<td>98-99(d)</td>
<td>55.26</td>
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<td></td>
<td>(55.12)</td>
<td></td>
<td>(4.80)</td>
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<td>IIIk</td>
<td>C₆H₄OMe-P</td>
<td>129-131(d)</td>
<td>54.05</td>
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<td></td>
<td>(54.36)</td>
<td></td>
<td>(4.88)</td>
</tr>
<tr>
<td>III (o-MeO)₂C₆H₃</td>
<td>H</td>
<td>97(d)</td>
<td>63.18</td>
</tr>
<tr>
<td></td>
<td>(62.81)</td>
<td></td>
<td>(6.49)</td>
</tr>
<tr>
<td>IIIm</td>
<td>Ph</td>
<td>101-102(d)</td>
<td>67.18</td>
</tr>
<tr>
<td></td>
<td>(67.04)</td>
<td></td>
<td>(6.33)</td>
</tr>
<tr>
<td>Complexes No.</td>
<td>δ(PCH₃)</td>
<td>δ(C≡CH) or δ(C≡CCH)</td>
<td>J_潘 (Hz)</td>
</tr>
<tr>
<td>-------------</td>
<td>---------</td>
<td>----------------------</td>
<td>----------</td>
</tr>
<tr>
<td>IIIa</td>
<td>1.73t</td>
<td>2.34t</td>
<td>3.8</td>
</tr>
<tr>
<td>IIIb</td>
<td>1.69t</td>
<td>1.88t</td>
<td>3.0</td>
</tr>
<tr>
<td>IIIc</td>
<td>1.70t</td>
<td>2.23t-q</td>
<td>2.5</td>
</tr>
<tr>
<td>IIId</td>
<td>1.68t</td>
<td>4.13t-d</td>
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<td>IIIe</td>
<td>1.64t</td>
<td>2.39t-t</td>
<td>3.0</td>
</tr>
<tr>
<td>IIIf</td>
<td>1.73t</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IIIg</td>
<td>1.73t</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IIIh</td>
<td>1.65t, 1.72t</td>
<td>2.20t</td>
<td>3.5</td>
</tr>
<tr>
<td>IIIi</td>
<td>1.66t, 1.71t</td>
<td>1.77t</td>
<td>3.0</td>
</tr>
<tr>
<td>IIIj</td>
<td>1.69t, 1.75t</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IIIk</td>
<td>1.72t, 1.76t</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IIIl</td>
<td>1.36t</td>
<td>2.15t</td>
<td>3.5</td>
</tr>
<tr>
<td>IIIm</td>
<td>1.39t</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

² J_潘 = 7.0-8.0 Hz. ³ J_潘 = 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].

2-4. References

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(PPh$_{Et_2}$)$_2$[CN(Me)CH$_2$CH$_2$NMe$_2$]$_2$BF$_4$ [8] and trans-[NiCl(PPh$_3$)[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 alkylnickel complexes, which were directed toward 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$_6$Cl$_5$Ni(PPhMe$_2$)$_2$]$_2$[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 \text{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\textsubscript{2}Cl\textsubscript{2}-methanol to give IVb (R= Et) (0.46 g, 60\%) or IVc (R= \text{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\textsubscript{2}Cl\textsubscript{2} to give [PhMe\textsubscript{2}(C\textsubscript{6}Cl\textsubscript{5})P]ClO\textsubscript{4} (0.030 g, 12\%). (Found: C, 34.55; H, 2.21. C\textsubscript{18}H\textsubscript{11}O\textsubscript{4}PCl\textsubscript{6} calcd.: C, 34.53; H, 2.28\%). \textsuperscript{1}H NMR (MeNO\textsubscript{2}): \(\delta\) (CH\textsubscript{3}) 2.88 (doublet, 6H, \(J_p = 14\) Hz), \(\delta\) (C\textsubscript{6}H\textsubscript{5}) 7.6-8.0 ppm (multiplet, 5H). From the above filtrate C\textsubscript{6}Cl\textsubscript{5}H (0.044 g, 36\%) and the complex I (0.118 g, 38\%) were obtained. The product C\textsubscript{6}Cl\textsubscript{5}H was identified from its melting point (85°C) and IR spectrum [12].

Preparation of trans-[C\textsubscript{6}Cl\textsubscript{5}Ni(PPhMe\textsubscript{2})\textsubscript{2}[C(CH\textsubscript{2})\textsubscript{3}O])ClO\textsubscript{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\textsubscript{2}Cl\textsubscript{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 $\text{trans-C}_6\text{Cl}_5\text{Ni}(\text{PPhMe}_2)_2\text{CH}=\text{C}(\text{OMe})\text{Me}$ (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-$\eta$-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-$\eta$ were collected by trap-to-trap distillation. $^1\text{H}$ 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 $\text{trans-C}_6\text{Cl}_5\text{Ni}(\text{PPhMe})_2\text{C}($OR$)=\text{CH}_2$ (VIa-c) ($R$ = Me, Et, or $\eta$-Pr) or $\text{trans-C}_6\text{Cl}_5\text{Ni}(\text{PPhMe}_2)_2\text{C}=\text{CHCH}_2\text{CH}_2\text{O}$ (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 $\text{trans-C}_6\text{Cl}_5\text{N}^+$($\text{PPhMe}_2)_2\text{R}$ (V, VI).

<table>
<thead>
<tr>
<th>Complexes</th>
<th>$\nu$(C=C)</th>
<th>$\nu$(COC)</th>
<th>$\delta$(P-CH$_3$)</th>
<th>$\delta$(C=CH)</th>
<th>$\delta$(O-CH)</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>R</td>
<td>IR$^a$, cm$^{-1}$</td>
<td>$\nu$(C=CH)</td>
<td>$\delta$</td>
<td>$J_P$, Hz</td>
<td>$\delta$(O-CH)</td>
</tr>
<tr>
<td>V</td>
<td>-CH=C(OMe)Me</td>
<td>1598 s 1099 vs</td>
<td>1.02 t 1.10 t</td>
<td>3.46 t</td>
<td>4.7</td>
<td>3.27 s</td>
</tr>
<tr>
<td>VIa</td>
<td>-C(OMe)=CH$_2$</td>
<td>1578 s 1132 vs 1017 s</td>
<td>1.48 t</td>
<td>3.68 d-t 4.26 d-t</td>
<td>2.5</td>
<td>3.10 s</td>
</tr>
<tr>
<td>VIb</td>
<td>-C(OEt)=CH$_2$</td>
<td>1558 s 1150 vs 1043 s</td>
<td>1.47 t</td>
<td>3.63 d-t 4.19 d-t</td>
<td>2.5</td>
<td>3.29 q 0.93 t</td>
</tr>
<tr>
<td>VIc</td>
<td>-C(OPr$^n$)=CH$_2$</td>
<td>1579 m 1152 vs 1012 s</td>
<td>1.47 t</td>
<td>3.59 d-t 4.19 d-t</td>
<td>2.5</td>
<td>3.18 t 0.84 t$^e$</td>
</tr>
<tr>
<td>VIId</td>
<td>-C=CHCH$_2$CH$_2$O</td>
<td>1550 s 1005 s</td>
<td>1.45 t</td>
<td>4.26 qn$^f$</td>
<td>2.5</td>
<td>3.64 t 2.22 m</td>
</tr>
</tbody>
</table>

$^a$ In Nujol mulls. $^b$ Chemical shifts (ppm) measured for CH$_2$Cl$_2$ or CD$_2$Cl$_2$ solution except for V (C$_6$H$_6$). $^c$ $2J_P + 4J_P = 8.0-8.5$ 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$_6$Cl$_5$Ni(PhMe$_2$)$_2$L]ClO$_4$.

<table>
<thead>
<tr>
<th>No.</th>
<th>L</th>
<th>Form</th>
<th>P-CH$_3$</th>
<th>C$_{\text{carb}}$-CH$_2$</th>
<th>Alkoxy protons</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\delta$</td>
<td>$\delta$</td>
<td>$\delta$(O-CH)</td>
<td>$^J_P$, Hz</td>
</tr>
<tr>
<td>IVa</td>
<td>:C</td>
<td>Me</td>
<td>Z</td>
<td>1.55 t, 1.65 t</td>
<td>2.48 t</td>
<td>4.64 s</td>
</tr>
<tr>
<td></td>
<td>:C</td>
<td>OMe</td>
<td>E</td>
<td>d</td>
<td>1.99 t</td>
<td>3.96 t</td>
</tr>
<tr>
<td>IVb</td>
<td>:C</td>
<td>Me</td>
<td>Z</td>
<td>1.53 t, 1.66 t</td>
<td>2.54 t</td>
<td>4.91 q</td>
</tr>
<tr>
<td></td>
<td>:C</td>
<td>OEt</td>
<td>E</td>
<td>1.53 t</td>
<td>2.13 t</td>
<td>3.99 q-t</td>
</tr>
<tr>
<td>IVc</td>
<td>:C</td>
<td>Me</td>
<td>Z</td>
<td>1.4-1.7$^e$</td>
<td>2.60 t</td>
<td>4.64 t</td>
</tr>
<tr>
<td></td>
<td>:C</td>
<td>OPr$^n$</td>
<td>E</td>
<td>2.12 t</td>
<td>3.88 t-br</td>
<td>1.0</td>
</tr>
<tr>
<td>IVd</td>
<td>:C</td>
<td></td>
<td>E</td>
<td>1.56 t</td>
<td>2.88 t-t</td>
<td>4.64 t-t</td>
</tr>
</tbody>
</table>

$^a$ Chemical shifts in ppm, in CH$_2$Cl$_2$ or CD$_2$Cl$_2$ 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-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 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).

\[
\begin{align*}
\text{C}_6\text{Cl}_5\text{Ni}-\text{C}≡\text{CH} & \xrightarrow{\text{ROH}} \left\{ \begin{array}{c}
\text{IIIa} \\
\text{IVa-c}
\end{array} \right. \\
\text{C}_6\text{Cl}_5\text{Ni}-\text{C}≡\text{Me} & \xrightarrow{[\text{H}^+]} \text{MeOH} \rightarrow \text{C}_6\text{Cl}_5\text{Ni}-\text{CH}≡\text{C} & \xrightarrow{\text{V}} \text{C}_6\text{Cl}_5\text{Ni}-\text{OH}_2 \\
\text{V} & \xrightarrow{\text{HClO}_4} \left\{ \begin{array}{c}
\text{C}_6\text{Cl}_5\text{Ni}-\text{OH}_2 \\
\text{IIa}
\end{array} \right. \text{ClO}_4^- + \text{MeC}≡\text{CH} + \text{MeOH} (4)
\end{align*}
\]
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-$[C_{6}Cl_{5}Ni\{PPhMe_{2}\}2\{C(NRR')Me\}]ClO_4$, but a neutral $d$-methoxyvinyl complex VIa derived by deprotonation at the $d$ carbon atom of the carbene ligand as shown in

*$^\text{trans-Pt(tolyl-p)}\{C(OMe)=CHMe\}\{PPhMe_{2}\}2$ has been reported by Chisholm et al. $^1$H NMR: $\delta$(CHMe) = 1.23 doublet, $J$(HCCH$_3$) = 5 Hz [14].
<table>
<thead>
<tr>
<th>Complexes</th>
<th>M.p. (°C)</th>
<th>Found (calcd.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%C</td>
<td>%H</td>
</tr>
<tr>
<td>IVa C(OMe)Me</td>
<td>171-172(d)</td>
<td>40.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(40.48)</td>
</tr>
<tr>
<td>IVb C(OEt)Me</td>
<td>158-159(d)</td>
<td>40.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(41.31)</td>
</tr>
<tr>
<td>IVc C(OPr)Me</td>
<td>145-147(d)</td>
<td>41.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(42.12)</td>
</tr>
<tr>
<td>IVd C(CH₂)₃O</td>
<td>150-151(d)</td>
<td>41.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(41.42)</td>
</tr>
<tr>
<td>V CH=C(OMe)Me</td>
<td>148-149(d)</td>
<td>47.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(47.65)</td>
</tr>
<tr>
<td>VIa C(OMe)=CH₂</td>
<td>118-119</td>
<td>46.72</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(46.82)</td>
</tr>
<tr>
<td>VIb C(OEt)=CH₂</td>
<td>118-119</td>
<td>47.43</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(47.65)</td>
</tr>
<tr>
<td>VIc C(OPr)=CH₂</td>
<td>108-110</td>
<td>48.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(48.44)</td>
</tr>
<tr>
<td>VIId C=CHCH₂CH₂O</td>
<td>125-126</td>
<td>47.72</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(47.79)</td>
</tr>
</tbody>
</table>

*a Cationic complexes IVa-IVd have molar conductance 59-66 Ω⁻¹cm²mol⁻¹ at 10⁻⁴ M concentration in CH₂Cl₂.*
eq. 5. The other alkoxy carbene complexes IVb-d also gave

\[
\begin{align*}
\text{IVA} & \xrightarrow{\text{+ amines} + \text{HClO}_4} \text{C}_6\text{Cl}_5\text{Ni} - \text{CH}_2 \text{OMe} \\
\rightarrow & \text{VIa}
\end{align*}
\]

corresponding \(\delta\)-alkoxy vinyl 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\(_3\)OD 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 \(pK_a\) 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](PPhMe2)2]PF6 (X= Cl or CF3) [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.

3-4. References

(1973) 202, and ref. therein.


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 alkoxy carbene 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-CH₃ 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:
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 rotating 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 evidence for this conclusion include i) the decrease of the isomer ratio (Z/E) as the alkoxy group lengthens (Table 5), ii) the free rotation

* An analogous $^1$H NMR spectrum of a mixture of two isomers has been observed for a cationic imidate complex, $\text{trans-}[\text{C}_6\text{Cl}_5\text{Ni(PPhMe}_2)_2\{\text{NH}=\text{C(OMe)Ph}\}]\text{ClO}_4$; see ref. 5.
TABLE 5

ISOMER RATIO \( \frac{Z}{E} \) OF \( \text{trans-}[C_6\text{Cl}_5\text{Ni}(\text{PPhMe}_2)_2\{\text{C(OR)Me}\}]\text{ClO}_4 \) (IVa-c) IN VARIOUS SOLVENTS

<table>
<thead>
<tr>
<th>Complexes</th>
<th>CDCl(_3)</th>
<th>CH(_2\text{Cl}_2)</th>
<th>C(_6\text{H}_5\text{NO}_2)</th>
<th>(CD(_3))(_2\text{CO})</th>
</tr>
</thead>
<tbody>
<tr>
<td>IVa Me</td>
<td>---(^a)</td>
<td>5</td>
<td>10</td>
<td>&gt;10</td>
</tr>
<tr>
<td>IVb Et</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>IVc Pr(^n)</td>
<td>0.9</td>
<td>1.5</td>
<td>2.5</td>
<td>3</td>
</tr>
</tbody>
</table>

\(^a\) Not measured due to the poor solubility.
of the cyclic carbene ligand in IVd, iii) the observation of \( \frac{J}{J_p} \) 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 \(^1\)H NMR spectra. The rate from Z- to E-isomers followed first order kinetics with the rate constant of \((7.1 \pm 0.4) \times 10^{-5} \text{ sec}^{-1}\) at \(-16^\circ\text{C}\), 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 \(^1\)H 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-CH\(_3\) resonances was \(-34^\circ\text{C}\), and the rotational \(\Delta G^\ddagger_{239}\) value of 11.7 kcal/mol could be calculated.

The spectra of d-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$_2$Cl$_2$ at -16°C.
Fig. 2. P-CH₃ region of ¹H NMR spectra of trans-[C₆Cl₅Ni(PPhMe₂)₂{C(OEt)Me}]ClO₄ (IVb):
(a) in CDCl₃, isomer ratio (Z/E)= 1; (b) in (CD₃)₂CO, isomer ratio= 5.
Fig. 3. Temperature dependence of $^1$H NMR spectrum of trans-$[\text{C}_6\text{Cl}_5\text{Ni(PPMe}_2_2\}_2\{\text{C(CH}_2_3\text{O})\}]\text{ClO}_4$ (IVd) in $\text{CH}_2\text{Cl}_2$. 
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 VIIb, but in the spectrum of cyclic alkoxyvinyl complex VIId the P-CH$_3$ resonance started to coalesce only at ca. -80°C (Tc < -100°C). It is tentatively suggested, therefore, that the restricted rotation 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 strictly almost equivalent with the alkoxyvinyl group in VIId which showed a low barrier to rotation about the Ni-C(vinyl) bond. The presence of Ni-C(carbene)

\[
\begin{align*}
\text{Ni} = C & \quad \text{Ni} = C \\
\text{OR} & \quad \text{OR} \\
+ \text{CH}_3 & \quad + \text{CH}_3 \\
\text{A} & \quad \text{B} \\
\text{C} & \quad \text{D}
\end{align*}
\]

π-bonding is also evident from electronic spectra. The carbene complexes IVa-d showed a d$_{xy}$-$d_{x^2-y^2}$ 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)
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 $d$-alkoxyvinyl complexes VIa-c. The rotational barriers in IVa,b are significantly higher than that reported for Cr(CO)$_5\{C(OMe)Me\}$ ($E_a = 12.4 \pm 1.0$ kcal/mol) by Kreiter and Fischer [7]. The high acidity of the carbene-methyl, or $\alpha$-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 $\pi$-base to contribute in resonance form A.

4-4. References

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(PPh₃)₂I₂ (R = CF₃ or C₃F₇) [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 NH₄Br. The solution was refluxed for 10 min, and addition of water gave brown crystals of trans-CCl₂=CClNi(PPhMe₂)₂Br, in quantitative yield, mp 134-135°C. (Found: C, 39.78; H, 4.18. C₁₈H₂₂P₂Cl₃BrNi calcd.: C, 39.65; H, 4.07%). ¹H NMR (CH₂Cl₂): δ(CH₃) 1.62t and 1.69t, 12H (2J_p + 4J_p = 7.5 Hz); δ(C₆H₅) 7.35-7.86m, 10H.

An ethereal suspension (30 ml) of 2,6-dimethoxyphenyl-lithium [8] (22 mmol) was cooled with an ice-bath under nitrogen, and Ni(PPhMe₂)₂Cl₂ (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 recrystal-
lized from acetone/methanol to give crystals of trans-Ni-
$\{C_6H_3(OMe-o)\_2\}_2(PPhMe_2)_2$ (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 ($^2J_p + ^4J_p = 7$ Hz) 12H; $\delta$(OMe) 3.63s 12H; $\delta$(m-H)
6.07d ($^3J_H = 8$ 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$_2$)$_2$C$_6$H$_3$(OMe-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
$\nu$(CH) 1700vs cm$^{-1}$. $^1H$ NMR (CDCl$_3$): $\delta$(PMe) 1.37t ($^2J_p + ^4J_p = 7.5$ Hz) 12H;
$\delta$(OMe) 3.25s 3H and 3.35s 3H; $\delta$(m-H) 5.91d ($^3J_H = 8$ 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$_2$)$_2$Br (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$_2$)$_2$Br$_2$ (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$_6$Cl$_5$Ni(PPhMe$_2$)$_2$Br reacted with N-bromosuccinimide
in similar manner to give C$_6$Cl$_5$Ni(PPhMe$_2$)$_2$Br$_2$ 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$_2$Cl$_2$): $\lambda_{\text{max}}(\epsilon)$ 1060 (33), 840 (28),
466 (8400), 350 (7900), 318 (11400) nm. Magnetic susceptibility (powder, 289°K): $\mu_{\text{eff}} = 2.05\ \mu_B$. EPR ($\text{CH}_2\text{Cl}_2$, 77°K): $g = 2.20$ (broad singlet).

Decomposition of Ni(III) complexes.

A solution of $\text{CCL}_2=\text{CCLNi(PPhMe}_2\text{)}_2\text{Br}_2$ (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 $\text{trans-CCL}_2=\text{CCLNi(PPhMe}_2\text{)}_2\text{Br}$ (0.175 g, 64%).

Similar treatment of $\text{C}_6\text{Cl}_5\text{Ni(PPhMe}_2\text{)}_2\text{Br}_2$ gave $\text{trans-C}_6\text{Cl}_5\text{Ni(PPhMe}_2\text{)}_2\text{Br}$, in 82% yield.

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

To a solution of $\text{trans-Ni C}_6\text{H}_3(\text{OMe}-\text{o})_2\text{2(PPhMe}_2\text{)}_2$ (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-CCl₂=CClNi(PPhMe₂)₂Br with N-bromo-succinimide in acetone affords a pentacoordinated organo-nickel(III) complex CCl₂=CClNi(PPhMe₂)₂Br₂, as shown in the following scheme:

\[
\begin{array}{c}
\text{L} \\
\text{R} \quad \text{Ni} \quad \text{Br} \\
\text{L}
\end{array}
\rightarrow
\begin{array}{c}
\text{L} \\
\text{R} \quad \text{Ni} \\
\text{Br} \\
\text{L}
\end{array}
\]

\[L = \text{PPhMe}_2, \quad R = \text{CCl}_2=\text{CCl} \quad \text{or} \quad \text{C}_6\text{H}_{14}\]

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 (\(\mu_{\text{eff}} = 1.74 \mu_B\) at 291 °K), which is consistent with the presence of low-spin d⁷ nickel(III), (v) the electronic spectrum of its dichloromethane solution exhibiting absorptions at 1050 (\(\varepsilon = 50\)), 840 (shoulder), 700 (\(\varepsilon = 180\)), 493 (\(\varepsilon = 6400\)); 425 (\(\varepsilon = 6000\)), 368 (\(\varepsilon = 8300\)) and 320 (\(\varepsilon = 8100\)) nm, an analogous spectrum having been reported for Ni(VPP)Br₃ [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 ($\lambda_{\text{max}} = 587$ 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$_2$)$_2$Br.

A pentachlorophenyl analog, trans-C$_6$Cl$_5$Ni(PPhMe$_2$)$_2$Br, also afforded a paramagnetic complex, C$_6$Cl$_5$Ni(PPhMe$_2$)$_2$Br$_2$, 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.

<table>
<thead>
<tr>
<th>X'</th>
<th>OMe</th>
<th>L</th>
<th>OMe</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>OMe</td>
<td>L</td>
<td>OMe</td>
<td>X'</td>
</tr>
</tbody>
</table>

VIIIa : $X = X' = \text{H}$.
IXa : $X = \text{H}$, $X' = \text{Br}$.
IXb : $X = X' = \text{Br}$

$L = \text{PPhMe}_2$.

Complex VIIIa was brominated stepwise and selectively at the meta positions of the C$_6$H$_3$(OMe-ο)$_2$ 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 is sterically less hindered than that in VIIIa.

\[
\begin{align*}
\text{[Ni]-C\equiv CH} & \quad \xrightarrow{\text{NBS}} \quad \text{[Ni]-C=Br} \\
\text{[Ni]-C\equiv CMe} & \quad \xrightarrow{\text{NBS}} \quad \text{[Ni]-CBr=C(Suc)Me} \quad \text{or} \quad \text{[Ni]-C(Suc)=CBrMe} \\
\text{[Ni]-C(OMe)=CH} & \quad \xrightarrow{2 \text{NBS}} \quad \text{[Ni]-C(OMe)=CBr}_2 \\
& \quad \xrightarrow{\text{NCS}} \quad \text{[Ni]-C(OMe)=CHCl} \\
\text{[Ni]} & = \text{trans-C}_6\text{Cl}_5\text{Ni(PPHMe}_2)_2, \quad \text{Suc} = \text{NC(O)CH}_2\text{CH}_2\text{CO}.
\end{align*}
\]

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 \( \text{N-chlorosuccinimide} \) gave an \( \text{E/Z} \) mixture of monochloro-substituted complexes (VIIIib). 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(PPMe$_2$)$_2$ Complexes

<table>
<thead>
<tr>
<th>Complexes</th>
<th>N.p.</th>
<th>Analyses, found (calcd.)</th>
<th>IR Data (Nujol)</th>
<th>$^1$H NMR Data (CDCl$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No.</td>
<td>°C</td>
<td>%C</td>
<td>%H</td>
<td>%N</td>
</tr>
<tr>
<td>IXa</td>
<td>161$^b$</td>
<td>50.27</td>
<td>4.90</td>
<td>20.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(41.56)</td>
<td>(3.92)</td>
<td>(34.60)</td>
</tr>
<tr>
<td>IXb</td>
<td>181$^b$</td>
<td>41.40</td>
<td>3.71</td>
<td>34.60</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(41.56)</td>
<td>(3.92)</td>
<td>(34.60)</td>
</tr>
<tr>
<td>X</td>
<td>110-111</td>
<td>40.97</td>
<td>3.74</td>
<td>34.81</td>
</tr>
<tr>
<td>XI</td>
<td>110$^b$</td>
<td>41.60</td>
<td>3.08</td>
<td>37.58</td>
</tr>
<tr>
<td>XII</td>
<td>202$^b$</td>
<td>43.20</td>
<td>3.47</td>
<td>1.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(45.47)</td>
<td>(3.65)</td>
<td>(1.75)</td>
</tr>
<tr>
<td>XIIIa</td>
<td>161$^b$</td>
<td>37.48</td>
<td>3.19</td>
<td>42.49</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(37.57)</td>
<td>(3.15)</td>
<td>(42.18)</td>
</tr>
<tr>
<td>XIIIb</td>
<td>127$^b$</td>
<td>44.26</td>
<td>3.82</td>
<td>1095s (vCOC)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(44.45)</td>
<td>(3.88)</td>
<td>(42.18)</td>
</tr>
</tbody>
</table>

$^b$ Decomposition. $^c$ $^6J_p$ value. $^d$ Total intensity of P-H and PPh proton signals. $^e$ $^5J_p$ value. $^f$ Tentative assignment. $^G$ 4-Jp 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.

5-4. References

Cationic complexes, \( \text{trans-[RNi(PPhMe_2)_2L]ClO}_4 \) (\( R = \text{C}_6\text{Cl}_5\), \( \text{C}_2\text{Cl}_2=\text{CCl} \) or (\( o-\text{MeO}\))\( _2\text{C}_6\text{H}_3; L = \) labile neutral ligand such as NCMe), which have been prepared from \( \text{trans-RNi(PPhMe_2)_2Cl} \) and silver perchlorate, react with terminal alkynes, \( \text{HC} \equiv \text{CR'} \) (\( R' = \text{H, alkyl or aryl} \)), in the presence of triethylamine to give alkynylnickel(II) complexes, \( \text{trans-RNi(PPhMe_2)_2C} \equiv \text{CR'} \).

Reactions of the alkynylnickel(II) complexes with alcohols in the presence of perchloric acid were investigated. The ethynylnickel Complex, \( \text{trans-C}_6\text{Cl}_5\text{Ni(PPhMe}_2)_2\text{C} \equiv \text{CH} \), gave cationic alkoxy carbene complexes, \( \text{trans-[C}_6\text{Cl}_5\text{Ni(PPhMe}_2)_2\{\text{C(OR')}\text{Me}\}]\text{ClO}_4 \) (\( R' = \text{Me, Et or Pr}^n \)), as well as \( \text{trans-C}_6\text{Cl}_5\text{Ni(PPhMe}_2)_2\text{C} \equiv \text{CCH}_2\text{CH}_2\text{OH} \) afforded \( \text{trans-[C}_6\text{Cl}_5\text{Ni(PPhMe}_2)_2\{\text{C(CH}_3)_2\text{OH}\}]\text{ClO}_4 \), but the propynyl nickel complex, \( \text{trans-C}_6\text{Cl}_5\text{Ni(PPhMe}_2)_2\text{C} \equiv \text{CMe} \), either decomposed or afforded \( \text{trans-C}_6\text{Cl}_5\text{Ni(PPhMe}_2)_2\text{CH} \equiv \text{C(OMe)Me} \), depending on the amount of the acid used. Treatment of the carbene complexes with amines resulted in deprotonation to give \( \alpha \)-alkoxyvinyl complexes \( \text{trans-C}_6\text{Cl}_5\text{Ni(PPhMe}_2)_2\text{C(OR')} = \text{CH}_2 \) or \( \text{trans-C}_6\text{Cl}_5\text{Ni-(PPhMe}_2)_2\text{C} \equiv \text{CHCH}_2\text{CH}_2\text{O} \), the reaction being reversible. The carbene methyl or the vinyl protons in the carbene complexes or the \( \alpha \)-alkoxyvinyl complexes are D-exchangeable by MeOD without catalyst and the basicity of the \( \alpha \)-alkoxyvinyl complex is comparable to those of amines.

The structure and bonding character of the carbene complexes have been investigated by \( ^1\text{H NMR spectroscopy} \). 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(PPhMe₂)₂Br (R = C₆Cl₅ or CCl₂=CCl) with N-bromosuccinimide afforded paramagnetic organonickel(III) complexes, RNi(PPhMe₂)₂Br₂. 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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