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ALKOXYCARBENE COMPLEXES OF NICKEL(II) *

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Summary

Alkynylnickel complexes *trans*-$C_6Cl_5Ni(PPhMe_2)_2C{\equiv}CR$ (IIIa, R = H; IIIb, R = Me; IIIc, R = Et; IIId, R = CH_2OH; IIIe, R = CH_2CH_2OH; IIIf, R = Ph; IIIg, R = C_6H_4OMe-*p*) have been prepared from *trans*-$[C_6Cl_5Ni(PPhMe_2)_2L]ClO_4$ and monosubstituted acetylenes in the presence of triethylamine, and their reactions with alcohols in the presence of perchloric acid were studied. Complexes IIIa and IIIe afforded alkoxycarbene complexes *trans*-$[C_6Cl_5Ni(PPhMe_2)_2\{C(OR')Me\}]ClO_4$ (IVa, R' = Me; IVb, R' = Et; IVc, R' = n-Pr) or *trans*-$[C_6Cl_5Ni(PPhMe_2)_2\{\overline{C(CH_2)_3O}\}]ClO_4$ (IVd), respectively, but IIIb either decomposed or afforded *trans*-$C_6Cl_5Ni(PPhMe_2)_2CH{=}C(OMe)Me$, depending on the amount of acid used. Treatment of IVa—IVd with amines resulted in deprotonation to give α-alkoxyvinyl complexes, *trans*-$C_6Cl_5Ni(PPhMe_2)_2C(OR'){=}CH_2$ (VIa—VIc) or *trans*-$C_6Cl_5Ni(PPhMe_2)_2\overline{C{=}CHCH_2CH_2O}$ (VId), the reaction being reversible. A ^1H NMR study indicated: (i) that the carbene methyl and the vinyl protons in IV or VI are D-exchangeable by MeOD without catalyst; (ii) that the basicity of VIa is comparable to those of amines; (iii) that the carbene complexes IVa—IVc have two isomers due to hindered rotation about the C(carbene)—O bond in solution, IVb existing in the *Z*-form in the solid state; (iv) that the rotational barriers ($\Delta G^{\neq}$) about the C(carbene)—O bond in IVb and the Ni—C(carbene) bond in IVd are 20 (or more) and 11.7 kcal/mol, respectively. These results are explained in term of double bond character of the carbene carbon and its surrounding atoms.

Introduction

Since the discovery of transition metal carbene complexes by Fischer and Maasböl [2], numerous investigations have been reported [3—7]. However, only

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* For a preliminary report of this work, see ref. 1.

a few carbene complexes of nickel have been isolated, in spite of their presumed importance as reaction intermediates in organic syntheses [3,4]. A nickel(0) complex, $\mathrm{Ni(CO)_3\{C(NEt_2)OEt\}}$, and its analogs have been reported [8], followed by the nickel(II) complexes, *trans*-$\mathrm{[NiCl(PPhEt_2)\{\overline{CN(Me)CH_2CH_2NMe}\}_2]BF_4}$ [9] and *trans*-$\mathrm{[NiCl(PPh_3)\{\overline{CN(Me)CH{=}C(Me)S}\}]BF_4}$ [10]. However, alkyl(alkoxy)carbenenickel complexes, which are thought to be more useful in organic syntheses [6,7], have not been known. Here we report reactions of several alkynylnickel(II) 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 [11,12]. It has been shown that the introduction of a $\mathrm{C_6Cl_5}$ group into nickel complexes enables the isolation of a variety of stable cationic complexes, *trans*-$\mathrm{[C_6Cl_5Ni(PR_3)_2L]ClO_4}$ (L = neutral ligand), as well as neutral complexes, *trans*-$\mathrm{C_6Cl_5Ni(PR_3)_2R'}$ ($\mathrm{R'}$ = organic group) [13—16]. The thermally and kinetically stable pentachlorophenyl—nickel bond [17,18] is expected to be inert during the preparative processes of the carbene complexes.

Experimental

General

The starting complexes, *trans*-$\mathrm{C_6Cl_5Ni(PPhMe_2)_2Cl}$ (I) and *trans*-$\mathrm{[C_6Cl_5Ni(PPhMe_2)_2L]ClO_4}$ (IIa, L = $\mathrm{OH_2}$; IIb, L = NCMe), were prepared as described previously [14,15]. Commercial grade alkynes and silver perchlorate were used without further purification. Infrared spectra were recorded on a Hitachi 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. Electronic spectra were recorded on a Hitachi Model 356 spectrophotometer. Melting points, analytical and spectral data were summarized in Tables 1—4.

Preparation of trans-$\mathrm{C_6Cl_5Ni(PPhMe_2)_2C{\equiv}CR}$ (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. 1 l) 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 (0.540 g, 89%).

Complex IIIc (R = Et). To a solution of IIb (0.725 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. 1 l) at room temperature. The mixture was treated as described above to give orange crystals of IIIc (0.590 g, 93%).

Complexes IIIb (R = Me), IIId (R = $\mathrm{CH_2OH}$), IIIe (R = $\mathrm{CH_2CH_2OH}$), IIIf (R = Ph), and IIIg (R = $\mathrm{C_6H_4OMe}$-p). A solution of silver perchlorate (0.207 g, 1 mmol) in 5 ml of acetone was added dropwise to a solution of I (0.620 g, 1 mmol) in 20 ml of acetone, and the silver chloride precipitate was filtered off. To the filtrate was added triethylamine (0.2 ml, 1.5 mmol) and an excess of gaseous propyne (ca. 1 l) at 0°C. The mixture was treated as described above to give orange crystals of IIIb (0.571 g, 91%). A similar reaction as above with a slight

TABLE 1

ANALYTICAL DATA FOR *trans*-$C_6Cl_5Ni(PPhMe_2)_2R$ (III, V, VI) AND *trans*-$[C_6Cl_5Ni(PPhMe_2)_2L]ClO_4$ (IV) [a]

Complexes		M.p. (°C)	Analysis found (calcd.) (%)		
No.	R or L		C	H	Cl
IIIa	$C{\equiv}CH$	126—128 [b]	47.11 (47.31)	3.71 (3.80)	29.33 (29.09)
IIIb	$C{\equiv}CMe$	134—135 [b]	47.80 (48.17)	3.95 (4.04)	
IIIc	$C{\equiv}CEt$	124—125 [b]	48.93 (48.99)	4.22 (4.27)	
IIId	$C{\equiv}CCH_2OH$	122—123 [b]	46.88 (46.97)	3.91 (3.93)	
IIIe	$C{\equiv}CCH_2CH_2OH$	138—139 [b]	47.94 (47.79)	4.23 (4.16)	
IIIf	$C{\equiv}CPh$	148—149	52.23 (52.57)	3.92 (3.97)	
IIIg	$C{\equiv}CC_6H_4OMe$-*p*	148—149	51.74 (52.04)	4.03 (4.09)	
IVa	C(OMe)Me	171—172 [b]	40.12 (40.48)	3.64 (3.80)	28.68 (28.67)
IVb	C(OEt)Me	158—159 [b]	40.99 (41.31)	3.83 (4.00)	
IVc	C(OPr-n)Me	145—147 [b]	41.83 (42.12)	4.20 (4.19)	
IVd	$\overline{C(CH_2)_3O}$	150—151 [b]	41.33 (41.42)	3.96 (3.74)	28.20 (28.22)
V	CH=C(OMe)Me	148—149 [b]	47.39 (47.65)	4.27 (4.46)	
VIa	$C(OMe)=CH_2$	118—119	46.72 (46.82)	4.29 (4.24)	27.44 (27.64)
VIb	$C(OEt)=CH_2$	118—119	47.43 (47.65)	4.25 (4.46)	
VIc	$C(OPr^n)=CH_2$	108—110	48.06 (48.44)	4.77 (4.67)	
VId	$\overline{C=CHCH_2CH_2O}$	125—126	47.72 (47.79)	4.09 (4.16)	27.03 (27.13)

[a] Cationic complexes IVa—IVd have molar conductance 59—66 ohm^{-1} cm^2 mol^{-1} at 10^{-4} *M* concentration in CH_2Cl_2. [b] Decomposition.

excess of propargyl alcohol or 3-butyn-1-ol at room temperature gave Id or Ie in a 75 or 68% yield, respectively. 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 If or Ig in 71 or 77% yield, respectively.

Preparation of trans-$[C_6Cl_5Ni(PPhMe_2)_2\{C(OR)Me\}]ClO_4$ *(IVa—IVc)*

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.

TABLE 2

IR AND ^{1}H NMR DATA FOR ALKYNYL COMPLEXES *trans*-$C_6Cl_5Ni(PPhMe_2)_2C{\equiv}CR$ (III)

Complexes		IR [a] (cm^{-1})		^{1}H NMR [b] (ppm)	
No.	R.	$\nu(C{\equiv}C)$	ν(CH) or ν(OH)	$\delta(P{-}CH_3)$ [c]	δ(R) [d]
IIa	H	1947s	3280m	1.78t	2.40t
IIIb	Me	2011w		1.69t	1.88t
IIIc	Et	2100vw		1.70t	2.23q-t (CH_2), 1.01t (CH_3)
IIId	CH_2OH	2085s	3600s	1.68t	4.13d-t (CH_2), 1.04t (OH)
IIIe	CH_2CH_2OH	2090w	3480m	1.64t	2.39t-t (CCH_2), 3.37q (CH_2O), 1.50t (OH)
IIIf	Ph	2090s		1.73t	
IIIg	C_6H_4OMe-*p*	2085m		1.78t	6.73d and 7.06d (C_6H_4), 3.77s (OMe)

[a] In Nujol mulls. [b] In $CDCl_3$. [c] $^2J(P) + {}^4J(P)$ = 7.5—8.0 Hz. [d] $^4J(P)$ 3.8 Hz and $^5J(P)$ 2.5—3.0 Hz.

TABLE 3

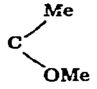
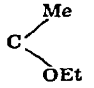
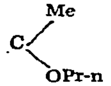
IR AND ^{1}H NMR SPECTRAL DATA FOR ALKOXYALKENYL COMPLEXES *trans*-$C_6Cl_5Ni(PPhMe_2)_2R$ (V, VI)

Complexes		IR [a] (cm^{-1})		^{1}H NMR [b]				
No.	R	$\nu(C{=}C)$	ν(COC)	$\delta(P{-}CH_3)$ [c] (ppm)	C=CH		Alkoxy protons	
					δ (ppm)	*J*(P) (Hz)	δ(O—CH) (ppm)	Others
V	CH=C(OMe)Me	1598s	1099vs	1.02t 1.10t	3.46t	4.7	3.27s	[d]
VIa	C(OMe)=CH_2	1578s	1132vs 1017s	1.48t	3.68d-t 4.26d-t	2.5 3.0	3.10s	
VIb	C(OEt)=CH_2	1558s	1150vs 1043s	1.47t	3.63d-t 4.19d-t	2.5 3.0	3.29q	0.93t
VIc	C(OPr-n)=CH_2	1579m	1152vs 1012s	1.47t	3.59d-t 4.19d-t	2.5 3.0	3.18t	0.84t [e]
VId	$\overline{C{=}CH(CH_2)_2O}$	1550s	1005s	1.45t	4.26qn [f]	2.5	3.64t	2.22m

[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] $\delta(CCH_3)$ 1.66t (*J*(P) 2.2 Hz). [e] $OCCH_2$ signals are obscured by P—CH_3 signals. [f] $^3J(H)$ 2.5 Hz.

TABLE 4

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

Complexes			$\delta(P—CH_3)$ [b] (ppm)	$\delta(C_{carb}—CH)$ [c] (ppm)	Alkoxy protons		
No.	L	Form			$\delta(O—CH)$ (ppm)	$^5J(P)$ (Hz)	Others
IVa		Z	1.55t, 1.65t	2.48t	4.64s		
		E	d	1.99t	3.96t	1.5	
IVb		Z	1.53t, 1.66t	2.54t	4.91q		1.29t
		E	1.53t	2.13t	3.99q-t	1.5	1.36t
IVc		Z	1.4—1.7 [e]	2.60t	4.64t		0.87t [f]
				2.12t	3.88t-br	1	1.00t [f]
IVd	$\overline{C(CH_2)_3O}$	E	1.56t	2.88t-t	4.64t-t	1.0	1.14qn

[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 $P—CH_3$ resonance of Z-isomer. [e] Not well resolved and overlapped with $OCCH_2$ resonance. [f] CCH_3 protons.

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 ppm (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 complex I (0.118 g, 38%) were obtained. The former was identified from its melting point (85°C) and IR spectrum [19].

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%). Complex IVd can also be obtained from a reaction of IIIe with an equivalent of 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) under similar conditions 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 of perchloric acid under similar conditions 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. The ^{1}H NMR spectrum of the distillate showed the resonances due to propyne (δ 1.76 doublet and 2.16 ppm quartet, J 3 Hz), methanol (δ 3.31 ppm singlet), and water (δ 2.92 ppm broad singlet).

Deprotonation of the carbene complexes IVa—IVd

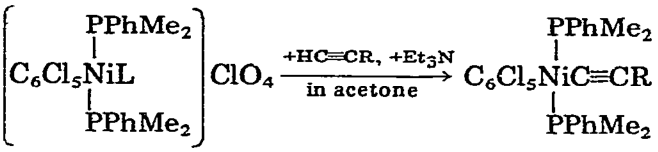
To a suspension of IVa—IVd (0.5 mmol) in 2 ml of acetone was added triethylamine (0.6 mmol) to give a clear solution. An addition of 5 ml of methanol gave yellow crystals of *trans*-$C_6Cl_5Ni(PPhMe)_2C(OR)=CH_2$ (VIa—VIc) (R = Me, Et, or n-Pr) or *trans*-$C_6Cl_5Ni(PPhMe_2)_2\overline{C=CHCH_2CH_2O}$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

Protonation of VIa—VId was carried out in ethereal solution. An addition of 60% perchloric acid gave light yellow crystals of IVa—IVd, respectively, in 90—100% yields.

Results and discussion

Preparation of the alkynyl complexes

Generally in the preparation of alkynylnickel(II) complexes, alkali metal salts of alkynes or alkynyl Grignard reagents have been employed [20,21]. 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 complexes III.



$$\left[\begin{array}{c} PPhMe_2 \\ | \\ C_6Cl_5NiL \\ | \\ PPhMe_2 \end{array}\right]ClO_4 \xrightarrow[\text{in acetone}]{+HC\equiv CR,\ +Et_3N} \begin{array}{c} PPhMe_2 \\ | \\ C_6Cl_5NiC\equiv CR \\ | \\ PPhMe_2 \end{array} \qquad (1)$$

(IIa—IIc) (IIIa—IIIg)

(IIa, L = OH_2; IIb, L = NCMe; IIc, L = solvent or none *; IIIa, R = H; IIIb, R = Me; IIIc, R = Et; IIId, R = CH_2OH; IIIe, R = CH_2CH_2OH; IIIf, R = Ph; IIIg, R = C_6H_4OMe-*p*)

The reaction can be performed even in a moist solvent in air. The arylethynyl complexes IIIf, IIIg could be obtained even in the absence of the amine. Several attempts to isolate, or detect spectroscopically, a cationic π-alkynenickel(II) complex which is the probable intermediate of this reaction have failed, although some analogous platinum(II) complexes are known [11].

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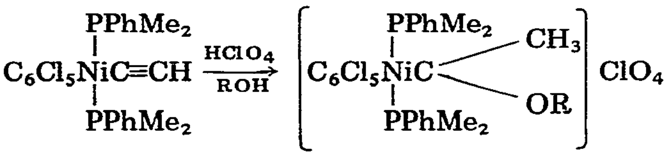
* The perchloratonickel IIc (L = none) of methyl(diphenyl)phosphine analog is isolable [15].

Reaction of the alkynyl complexes with alcohols in the presence of perchloric acid

The ethynyl complex IIIa reacted with alcohols in the presence of perchloric acid to give stable cationic carbene complexes, as shown in eq. 2. Examination of the product ratio from a reaction performed in mixed alcohol solution showed

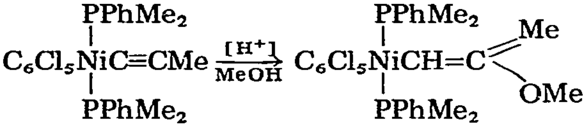


$$C_6Cl_5Ni(PPhMe_2)_2C{\equiv}CH \xrightarrow[ROH]{HClO_4} [C_6Cl_5Ni(PPhMe_2)_2C(CH_3)(OR)]ClO_4 \qquad (2)$$

(IIIa) (IVa—IVc)

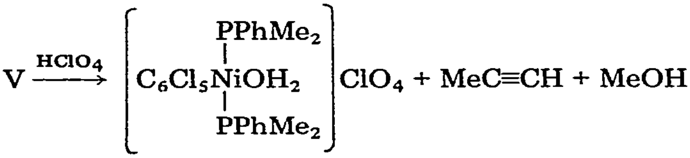
(IVa, R = Me; IVb, R = Et; IVc, R = n-Pr)

that the reactivity of the alcohol decreased in the order: methanol > ethanol > n-propanol; isopropanol was unreactive. The propenyl 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. Complex V reacted with perchloric acid to give IIa, propyne and methanol, but not methyl propenyl ether (eq. 4).



$$C_6Cl_5Ni(PPhMe_2)_2C{\equiv}CMe \xrightarrow[MeOH]{[H^+]} C_6Cl_5Ni(PPhMe_2)_2CH{=}C(Me)(OMe) \qquad (3)$$

(IIIb) (V)



$$V \xrightarrow{HClO_4} [C_6Cl_5Ni(PPhMe_2)_2OH_2]ClO_4 + MeC{\equiv}CH + MeOH \qquad (4)$$

(IIa)

Complexes IIIc and IIId also decomposed in the presence of methanol and one equivalent of the acid to give IIa, and gave unidentified noncrystalline materials in the presence of a catalytic amount of the acid. 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 and IIIg were recovered almost quantitatively from a solution of methanol/benzene containing perchloric acid.

The ^1H NMR spectrum of V showed resonances for only one kind of methoxypropenyl group, though it could not be determined whether the structure of the *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 $J(HCCH_3)$ *. The difference in

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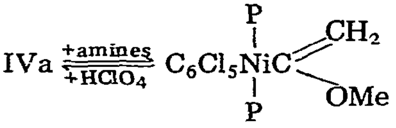
* *trans*-Pt(tolyl-*p*){C(OMe)=CHMe}(PPhMe$_2$)$_2$ has been reported by Chisholm et al. ^1H NMR: δ(CHMe) 1.23 ppm doublet, $J(HCCH_3)$ 5 Hz [22].

the reactivities of IIIa and IIb is astonishing in relation to analogous platinum chemistry [22]. It can be explained, however, if we assume that the relative stabilizing ability of the intermediate carbenium cation A—C$^+$=CH—B is in the order, A = Pt > CH$_3$ > Ni > H = B. This order must be related to that of π-basicity.

Reactions of the carbene complexes

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 [6], as well as of platinum(II) [23]. The reaction of 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 rather a neutral α-methoxyvinyl complex VIa derived by deprotonation at the α-carbon atom of the carbene ligand as shown in eq. 5. The other alkoxycarbene complexes IVb—IVd also gave corresponding α-alkoxyvinyl complexes VIb—VId by the



$$\mathrm{IVa} \underset{+\mathrm{HClO_4}}{\overset{+\mathrm{amines}}{\rightleftharpoons}} \mathrm{C_6Cl_5}\overset{\mathrm{P}}{\underset{\mathrm{P}}{\mathrm{Ni}}}\mathrm{C}{\begin{smallmatrix}\nearrow \mathrm{CH_2}\\ \searrow \mathrm{OMe}\end{smallmatrix}} \qquad (5)$$

(VIa)

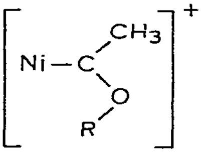
reaction with triethylamine, the vinyl complexes reacting with perchloric acid to give the original carbene complexes.

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—IVd also showed an easy H—D exchange. The vinyl complexes VIa—VId 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 triethanolamine 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_b values for these two amines in water being 7.8 and 7.4, respectively [24]. An analogous H—D exchange has been reported by Kreiter [25] for $Cr(CO)_5\{C(OMe)Me\}$ catalysed by sodium methoxide, as well as deprotonation with butyllithium by Casey and Anderson [26]. 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$_3$) [22].

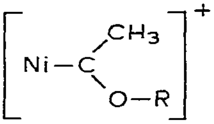
Reaction of mercaptans with alkoxycarbene complexes is known to give thioalkoxycarbene complexes [6], but IVa was recovered from a solution containing an excess of mercaptan.

^{1}H NMR spectra of the carbene complexes and α-alkoxyvinyl complexes

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 [27] with the carbene ligand fixed perpendicularly to the nickel coordination plane. The time-dependence of the spectra can be explained in terms of isomerization of the carbene ligand between *Z*- and *E*-forms:



(Z)



(E)

At 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 4 and 5). 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 (Fig. 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 as a *Z*-isomer and the minor as an *E*-isomer. The supporting evidence for this conclusion includes (i) the decrease of the isomer ratio (*Z*/*E*) as the alkoxy group lengthens (Table 5), (ii) the free rotation of the cyclic carbene ligand in IVd, (iii) the observation of ^5J(P) for the OCH_2 resonance of IVa—IVc (*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 [14,28].

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 $(7.1 \pm 0.4) \times 10^{-5}$ sec^{-1} at —16°C, giving the rotational barrier ($\Delta G^{\neq}_{257}$) 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 the 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).

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* An analogous ^{1}H NMR spectrum of a mixture of two isomers has been observed for a cationic imidate complex, *trans*-$[C_6Cl_5Ni(PPhMe_2)_2\{NH{=}C(OMe)Ph\}]ClO_4$ [14].

TABLE 5

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

Complexes		$CDCl_3$	CH_2Cl_2	$C_6H_5NO_2$	$(CD_3)_2CO$
No.	R				
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.

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

The spectra of α-alkoxyvinyl complexes VIa—VIc at ambient temperature

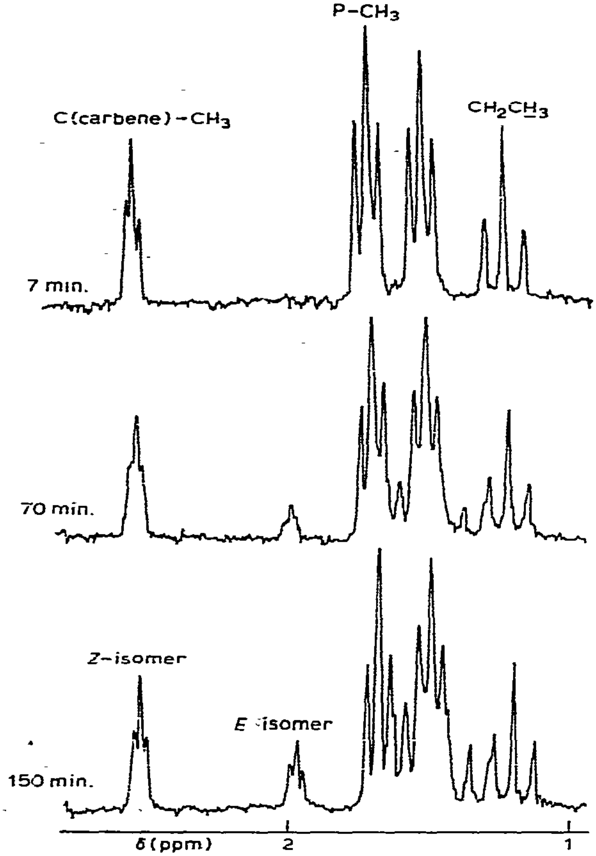


Fig. 1. Time dependence of ^1H NMR spectrum of *trans*-$[C_6Cl_5Ni(PPhMe_2)_2\{C(OEt)Me\}]ClO_4$ (IVb) in CH_2Cl_2 at −16°C.

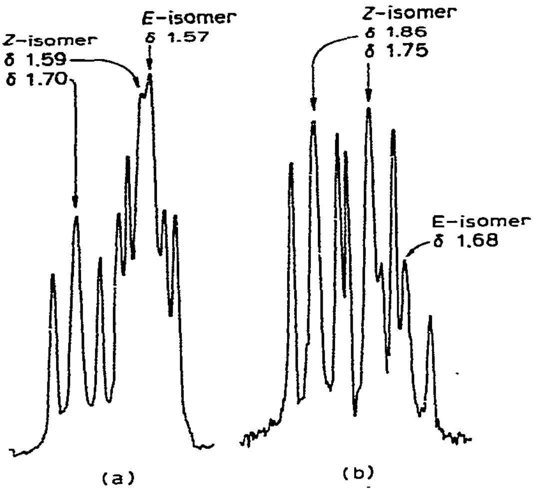


Fig. 2. P—CH_3 region of ^1H NMR spectra of *trans*-[$C_6Cl_5Ni(PPhMe_2)_2$ {C(OEt)Me}]ClO_4 (IVb): (a) in $CDCl_3$, isomer ratio (*Z*/*E*) = 1; (b) in $(CD_3)_2CO$, isomer ratio (*Z*/*E*) = 5.

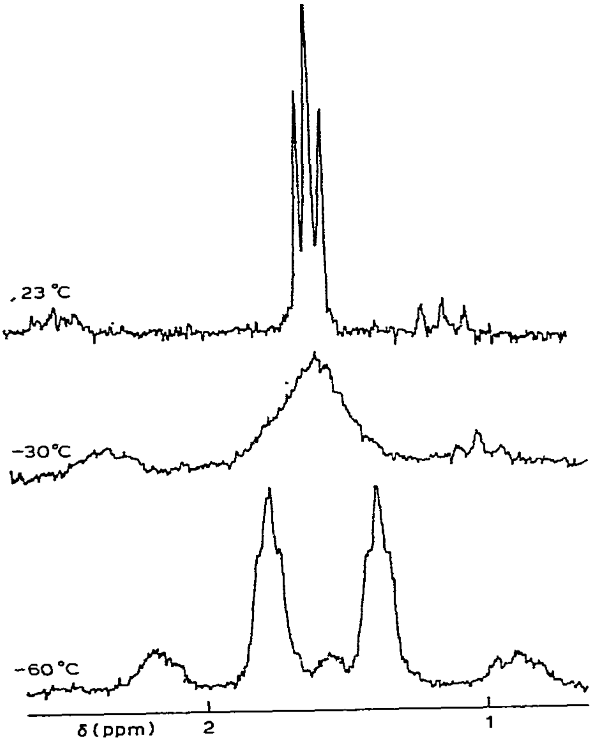
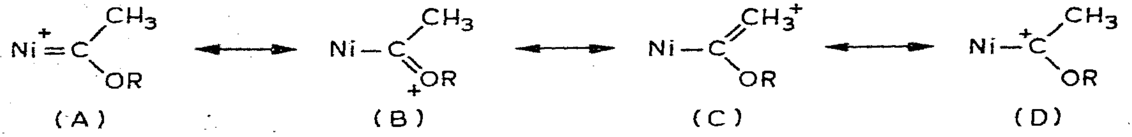


Fig. 3. Temperature dependence of ^1H NMR spectrum of *trans*-[$C_6Cl_5Ni(PPhMe_2)_2$ {$\overline{C(CH_2)_3O}$}]ClO_4 (IVd) in CH_2Cl_2.

showed only one kind of alkoxy proton resonance 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 the 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 rotation about the Ni—C(vinyl) bond in VIa and VIb at low temperature is caused by steric hindrance between the alkoxy group and the bulky phosphine ligands.

Bonding character of the carbene ligands

A number of spectroscopic and X-ray crystallographic studies on metal—carbene complexes have been reported with a variety of conclusions: back π-bonding is strong or weak [4,5,29]. In our carbene complexes, the barrier to rotation about the Ni—C(acrbene) 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 sterically almost equivalent to the alkoxyvinyl group in VId which showed a low barrier to rotation about the Ni—C(vinyl) bond. The presence of Ni—C(carbene) π-bonding is also evident from the electronic spectra. The carbene complexes IVa—IVd showed a $d_{xy} - d_{x^2-y^2}$ band * at 332—335 nm (shoulder character) and VIa—VId 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—IVc suggests double bond character in the bond (resonance form B), rather than any steric hindrance in view of the result for α-alkoxyvinyl complexes VIa—VIc. The rotational barriers in IVa and IVb 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 [30]. The high acidity of the carbene-methyl or -methylene group in IVa—IVd 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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* Electronic spectra for a variety of complexes of types *trans*-$C_6Cl_5Ni(PPhMe_2)_2X$ and *trans*-$[C_6Cl_5Ni(PPhMe_2)_2L]ClO_4$ have been reported, recently [15,16,31,32].

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