CATIONIC AND ALKYNYL COMPLEXES OF THE *trans*-(MESITYL)BIS(PHENYLDIMETHYLPHOSPHINE)NICKEL(II) MOIETY *

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Summary

A cationic complex, *trans*-[(mesityl)Ni(PPhMe$_2$)$_2$(NCMe)]ClO$_4$ (IIa), has been prepared from *trans*-(mesityl)Ni(PPhMe$_2$)$_2$Br and silver perchlorate in acetone/acetonitrile. IIa reacts with several neutral ligands to give *trans*-[(mesityl)-Ni(PPhMe$_2$)$_2$L]ClO$_4$ (L = 2-pic, 3-pic, 3,4-lut, 2,5-lut, methyl isonicotinate, *N*-ethyl imidazole, PPhMe$_2$, P(OMe)$_3$), with halide anions to give *trans*-(mesityl)-Ni(PPhMe$_2$)$_2$X (X = Cl, NNN), and with terminal alkynes in the presence of triethylamine to give *trans*-(mesityl)Ni(PPhMe$_2$)$_2$C≡CR (R = H, Me, CH$_2$CH$_2$OH, Ph, C$_6$H$_4$OMe-*p*). Some related alkynyl complexes *trans*-CCl$_2$=CClNi(PPhMe$_2$)$_2$-C≡CR (R = H, Me, Ph, C$_6$H$_4$OMe-*p*) and *trans*-{(*o*-MeO)$_2$C$_6$H$_3$}Ni(PPhMe$_2$)$_2$-C≡CR (R = H, Ph) also have been prepared from the corresponding *trans*-R'Ni-(PPhMe$_2$)$_2$Cl, silver perchlorate and HC≡CR in acetonitrile-triethylamine. *trans*-(Mesityl)Ni(PPhMe$_2$)$_2$C≡CH reacts with methanol in the presence of perchloric acid to give a cationic carbene complex, *trans*-[(mesityl)Ni(PPhMe$_2$)$_2$-{C(OMe)Me}]ClO$_4$.

Introduction

Among organometallic derivatives of divalent nickel, pentachlorophenyl-nickel(II) ccmplexes with a square-planar configuration are quite stable, and a variety of derivatives including cationic complexes of a type, *trans*-[RNi(PR'$_3$)$_2$L]$^+$ (R = C$_6$Cl$_5$), have recently been reported from this laboratory [1—6]. It is surprising that such cationic organonickel(II) complexes had received very little attention [7,8] except for R = C$_6$F$_5$ [9], although their presence in polar solvents had been postulated [10,11]. The substitution of chlo-

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* Dedicated to Professor Eugene G. Rochow on the occasion of his 70th birthday on October 4, 1979.

TABLE 1

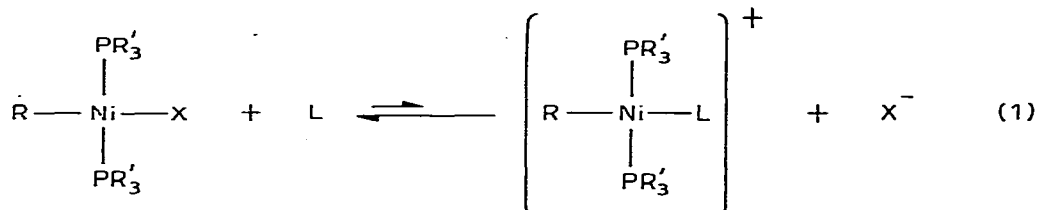ANALYTICAL AND PHYSICAL DATA FOR NEW ORGANONICKEL(II) COMPLEXES, trans-RNi(PPhMe$_2$)$_2$R' AND trans-[(mesityl)Ni(PPhMe$_2$)$_2$L]ClO$_4$

Complexes		M.p. (°C)[a]	Analyses (found (calcd.) (%))[b]			IR (cm^{-1})[b]	Conductivity[c] (ohm^{-1} cm^2 mol^{-1})
no.	R' or L		C	H	N		
R = mesityl							
Ib	Cl	174—175	61.67 (61.32)	6.79 (6.79)			
Ic	NNN	124—125	60.38 (60.51)	6.86 (6.70)	8.38 (8.47)	2070vs (NNN) 2058vs	
IIa	NCMe	140 [d]	54.14 (54.53)	6.19 (6.10)	2.04 (2.36)		186
IIb	2-pic	168—171 [d]	57.42 (57.57)	6.34 (6.23)	2.04 (2.17)		178
IIc	3-pic	145—147 [d]	57.33 (57.57)	6.44 (6.23)	2.07 (2.17)		179
IId	3,4-lut	131—140 [d]	57.88 (58.16)	6.50 (6.41)	2.16 (2.12)		176
IIe	3,5-lut	169—171 [d]	58.01 (58.16)	6.50 (6.41)	2.06 (2.12)		183
IIf	NC$_5$H$_4$COOMe-*p*	170—172 [d]	65.38 (55.64)	5.91 (5.84)	1.91 (2.03)	1733s (C=O)	168
IIg	NC$_3$H$_3$NEt	149—155 [d]	55.20 (55.45)	6.44 (6.36)	4.38 (4.31)		157
IIh	PPhMe$_2$	139—142 [d]	57.04 (57.30)	6.53 (6.41)			182
IIi	P(OMe)$_3$	126—127	49.42 (49.62)	6.43 (6.25)		1051vs (POC) 1011vs (POC)	184

		mp (°C)	C found (calc)	H found (calc)	IR
IIIa	C≡CH	115–117 [d]	67.34 (67.60)	7.15 (7.17)	3279w (CH); 1937s (C≡C); 2101w (C≡C) [e]
IIIb	C≡CMe	108–109 [d]	68.28 (68.18)	7.49 (7.36)	
IIIc	C≡CCH$_2$CH$_2$OH	113–114 [d]	66.66 (66.56)	7.55 (7.32)	3380m (OH); 2088w (C≡C); 2070m (C≡C)
IIId	C≡CPh	107–108	71.16 (71.38)	6.86 (6.90)	
IIIe	C≡CC$_6$H$_4$OMe-p	117–119	70.03 (69.77)	7.08 (6.89)	2080m (C≡C)
IV	C(OMe)Me	150–154 [d]	54.53 (54.98)	6.53 (6.43)	1320s (COC) 178
R = CCl$_2$=CCl					
IIIf	C≡CH	81–82 [d]	49.19 (48.98)	4.79 (4.73)	3278, (CH); 1952s (C≡C); 2111w (C≡C)
IIIg	C≡CMe	108–110 [d]	49.46 (50.00)	4.73 (5.00)	
IIIh	C≡CPh	98–99 [d]	55.26 (55.12)	4.85 (4.80)	2083s (C≡C)
IIIi	C≡CC$_6$H$_4$OMe-p	129–131 [d]	54.05 (54.36)	4.91 (4.88)	2090m (C≡C)
R = (o-MeO)$_2$C$_6$H$_3$					
IIIj	C≡CH	97 [d]	63.18 (62.81)	6.73 (6.49)	3253m (CH); 1944m (C≡C); 2078s (C≡C)
IIIk	C≡CPh	101–102 [d]	67.18 (67.04)	6.56 (6.33)	

[a] In an evacuated capillary. [b] In Nujol mulls; data for $\nu(ClO_4)$ are omitted. [c] 10^{-4} M Solution in acetone at 25°C. [d] Decomposition. [e] The reported $\nu(C≡C)$ frequency for *trans*-C$_6$Cl$_5$Ni(PPhMe$_2$)$_2$C≡CMe [4] should be read also as 2101 cm^{-1} instead of 2011 cm^{-1}.

ride anion in *trans*-(mesityl)Ni(PEt$_3$)$_2$Cl by a neutral ligand L such as pyridine has been known for many years [10], but the equilibrium (eq. 1) lies far to the
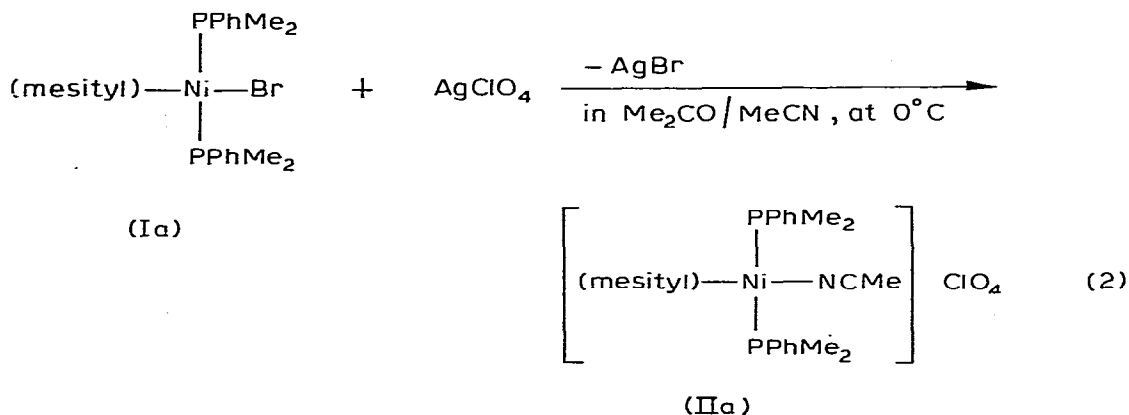
$$R\!-\!\!\!\underset{\underset{\textstyle PR'_3}{|}}{\overset{\overset{\textstyle PR'_3}{|}}{Ni}}\!\!\!-\!X \quad + \quad L \quad \rightleftharpoons \quad \left[R\!-\!\!\!\underset{\underset{\textstyle PR'_3}{|}}{\overset{\overset{\textstyle PR'_3}{|}}{Ni}}\!\!\!-\!L \right]^{+} \quad + \quad X^{-} \qquad (1)$$

(IIb, L = 2-pic; IIc, L = 3-pic; IId, L = 3,4-lut; IIe, L = 3,5-lut; L = Methyl iso-nicotinate; IIg, L = *N*-ethyl imidazol; IIh, L = PPhMe$_2$; IIi, L = P(OMe)$_3$) side of the neutral complex, and the ionic species was not isolated. Removal of the chloride ligand in *trans*-(*o*-tolyl)Ni(PPhMe$_2$)$_2$Cl as silver chloride was complicated, since the precipitate of silver chloride was quickly reduced to metallic silver and no *o*-tolylnickel(II) species could be obtained from the system [12]. We report here the results of the work intended to isolate such cationic complexes of the *trans*-(mesityl)Ni(PPhMe$_2$)$_2$ moiety. Some reactions and spectroscopic properties of these complexes will be discussed and compared with those of the pentachlorophenylnickel(II) analogs.
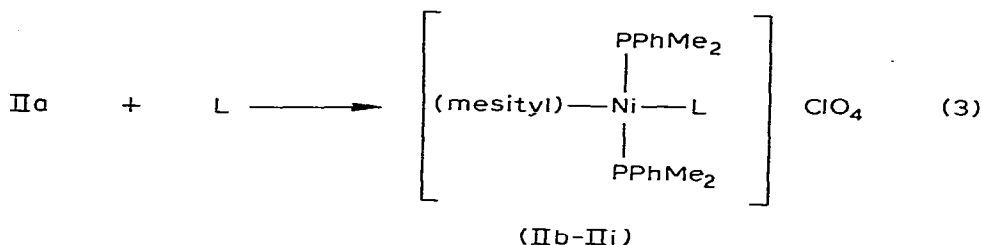
Results and discussion

Preparation and reactions

The analytical, physical and spectral data for the new organonickel(II) complexes prepared in the present work are summarized in Tables 1 and 2.

In a preliminary experiment the complex *trans*-(mesityl)Ni(PPhMe$_2$)$_2$Br (Ia) was treated with silver perchlorate in benzene solution by a procedure similar to that used for *trans*-C$_6$Cl$_5$Ni(PPhMe$_2$)$_2$Cl [1—3]. This experiment, however, resulted in the reduction of silver ion and in the decomposition of the mesityl-nickel(II) complex. It soon was found that the reduction of silver ion was suppressed considerably in acetone, and completely in cold acetone containing acetonitrile. From this solution the first cationic mesitylnickel(II) complex, *trans*-[(mesityl)Ni(PPhMe$_2$)$_2$(NCMe)]ClO$_4$ (IIa), could be isolated (eq. 2).

$$(mesityl)\!-\!\!\!\underset{\underset{\textstyle PPhMe_2}{|}}{\overset{\overset{\textstyle PPhMe_2}{|}}{Ni}}\!\!\!-\!Br \quad + \quad AgClO_4 \quad \xrightarrow[\text{in Me$_2$CO / MeCN , at 0°C}]{-\,AgBr}$$

(Ia)

$$\left[(mesityl)\!-\!\!\!\underset{\underset{\textstyle PPhMe_2}{|}}{\overset{\overset{\textstyle PPhMe_2}{|}}{Ni}}\!\!\!-\!NCMe \right] ClO_4 \qquad (2)$$

(IIa)

$$\text{IIa} \quad + \quad \text{L} \quad \longrightarrow \quad \left[\begin{array}{c} \text{PPhMe}_2 \\ | \\ \text{(mesityl)} - \text{Ni} - \text{L} \\ | \\ \text{PPhMe}_2 \end{array} \right] \text{ClO}_4 \quad (3)$$
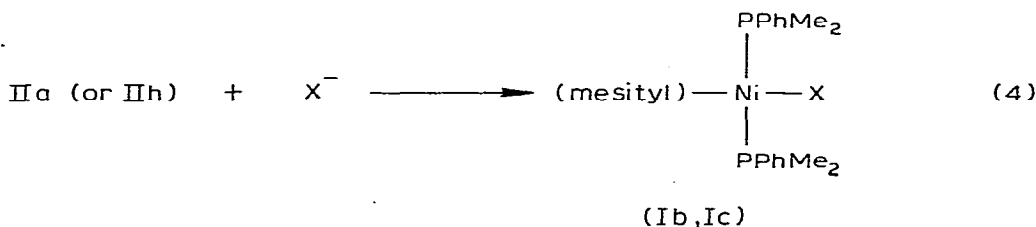
(IIb-IIi)

(IIb, L = 2-pic; IIc, L = 3-pic; IId, L = 3,4-lut; IIe, L = 3,5-lut; IIf, L - Methyl isonicotinate; IIg, L = N-ethyl imidazol; IIh, L = PPhMe$_2$; IIi, L = P(OMe)$_3$)
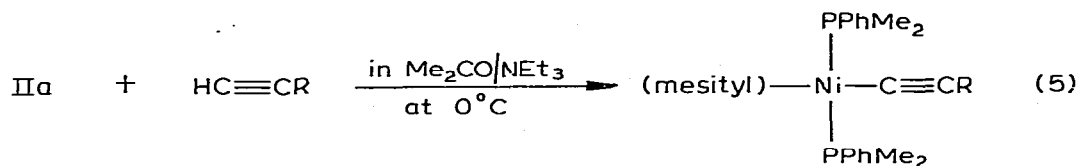
IIa is thermally less stable than the pentachlorophenylnickel(II) analog [2], decomposing in vacuo at ca. 140°C to dark brown material, and is slightly air sensitive, decomposing at 100°C in 4 h to a sticky yellow-brown material. In ethanol it decomposed at lower temperatures, giving a turbid brown solution in vacuo at 100°C or a turbid light yellow-green solution in air at 70°C. Although we had difficulties in the separation of these decomposition products, Almemark and Åkermark [13] have recently reported the anodic oxidation of *trans*-(mesityl)$_2$Ni(PEt$_3$)$_2$ to give polymeric material via a cationic mesitylnickel(II) species.

The acetonitrile ligand in IIa is readily substituted by some neutral ligands L to give the corresponding cationic complexes *trans*-[(mesityl)Ni(PPhMe$_2$)$_2$L]-ClO$_4$ (IIb—IIi) (eq. 3). In contrast to IIa, these complexes are stable in air, as is evident from the IR spectra of samples heated at 100°C. They are soluble in dichloromethane, acetone and hot alcohols, and insoluble in diethyl ether, n-hexane and water. Some are soluble in benzene. The acetone solutions of IIa—IIi showed the high conductivities anticipated for 1/1 electrolytes [14] (Table 1). Attempts to prepare a cationic carbonyl complex were unsuccessful. IIe was recovered from neat 3,5-lutidine solution at 100°C, although the pentachlorophenylnickel(II) analog reacted to give *cis*-[C$_6$Cl$_5$Ni(PPhMe$_2$)-(3,5-lut)$_2$]ClO$_4$ [1].

The acetonitrile ligand in IIa is also substituted readily by halide anions (Cl, NNN) to give the corresponding neutral complexes, *trans*-(mesityl)Ni-(PPhMe$_2$)$_2$X (Ib, Ic) (eq. 4), which had not been obtained previously from Ia [15]. It was further found that even the phenyldimethylphosphine ligand *trans* to mesity group in IIh was substituted readily by chloride, but the remaining two phosphines were substitutionally inert. A positive charge and the strong *trans* effect of the mesityl group might be expected to enhance the substitution. Reactions of IIa with acetate anion resulted in failure.

Reactions of terminal alkynes with IIa were performed via analogous methods to that used for pentachlorophenylnickel(II) complexes [5] (eq. 5). The
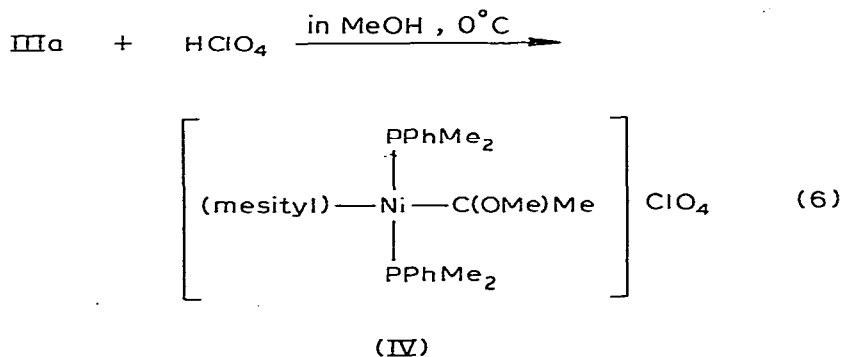
$$\text{IIa (or IIh)} \quad + \quad \text{X}^- \quad \longrightarrow \quad \begin{array}{c} \text{PPhMe}_2 \\ | \\ \text{(mesityl)} - \text{Ni} - \text{X} \\ | \\ \text{PPhMe}_2 \end{array} \quad (4)$$

(Ib,Ic)

$$\text{IIa} \quad + \quad \text{HC}{\equiv}\text{CR} \quad \xrightarrow[\text{at 0°C}]{\text{in Me}_2\text{CO/NEt}_3} \quad \text{(mesityl)}{-}\underset{\underset{\text{PPhMe}_2}{|}}{\overset{\overset{\text{PPhMe}_2}{|}}{\text{Ni}}}{-}\text{C}{\equiv}\text{CR} \qquad (5)$$

(IIIa - IIIe)

(Ib, X = Cl; Ic, X = NNN; IIIa, R = H; IIIb, R = Me;
IIIc, R = CH₂CH₂OH; IIId, R = Ph; IIIe, R = C₆H₄OMe-p)

expected alkynyl complexes *trans*-(mesityl)Ni(PPhMe₂)₂C≡CR (IIIa—IIIe) were obtained as yellow to orange crystals. Complexes IIIa—IIIc are thermally less stable than the aromatic alkynyl complexes IIId and IIIe; they all melt at ca. 110°C, the former with immediate decomposition.

Few alkynylnickel complexes of this type have been known [7,8] except for *trans*-CCl₂=CClNi(PEt₃)₂C≡CPh [16], and it was reported [17] that treatment of *trans*-(1-naphthyl)Ni(PPhEt₂)₂Br with NaC≡CPh in liquid ammonia afforded *trans*-(PhC≡C)₂Ni(PPhEt₂)₂. A new method using a CuX catalyst has not been applied to these nickel(II) complexes [18]. Our reaction could be extended further to the preparation of four alkynyl(trichlorovinyl)nickel(II) complexes, *trans*-CCl₂=CClNi(PPhMe₂)₂C≡CR (IIIf—IIIi), and two alkynyl(di-o-methoxy-phenyl)nickel(II) complexes, *trans*-{(o-MeO)₂C₆H₃}Ni(PPhMe₂)₂C≡CR (IIIj, IIIk) (IIIf and IIIj, R = H; IIIg, R = Me; IIIh and IIIk, R = Ph; IIIi, R = C₆H₄OMe-p). In these preparations the intermediate cationic acetonitrile complexes were prepared in situ in acetonitrile.

Reactions of these alkynylnickel(II) complexes with alcohols in the presence of acid are under investigation. Such a reaction is known for alkynylplatinum(II) complexes to give cationic alkoxycarbene complexes [19], but more varied behavior have been observed with alkynyl(pentachlorophenyl)nickel(II) complexes [5]. At the present stage, it has been found that IIIa reacted in methanol at 0°C in the presence of perchloric acid to give a cationic methyl-(methoxy)carbene complex, *trans*-[(mesityl)Ni(PPhMe₂)₂{C(OMe)Me}]ClO₄ (IV) (eq. 6). The complex IV in solution is quite stable even in air.

$$\text{IIIa} \quad + \quad \text{HClO}_4 \quad \xrightarrow{\text{in MeOH , 0°C}}$$

$$\left[\text{(mesityl)}{-}\underset{\underset{\text{PPhMe}_2}{|}}{\overset{\overset{\text{PPhMe}_2}{|}}{\text{Ni}}}{-}\text{C(OMe)Me} \right] \text{ClO}_4 \qquad (6)$$

(IV)

^1H NMR spectra

The ^1H NMR spectra (Table 2) in the region of phosphine methyl protons establish the configuration of the complexes which were prepared in this work. A single 1 : 2 : 1 triplet pattern observed for Ib, Ic and IIa is typical of a *trans* square-planar configuration [15]. The double 1 : 2 : 1 triplet pattern observed for IIb is indicative that this complex has a *trans* configuration with the 2-picoline ligand oriented perpendicularly to the nickel(II) coordination plane [15]. Such a double triplet pattern due to lack of a free rotation about the nickel(II)—pyridine bond is observed for all the three complexes containing an

TABLE 2

^1H NMR SPECTRAL DATA FOR NEW ORGANONICKEL(II) COMPLEXES, *trans*-RNi(PPhMe$_2$)$_2$R, AND *trans*-[(mesityl)Ni(PPhMe$_2$)$_2$L]ClO$_4$ [a]

Complexe no.	Solvent	P-Me [b] δ (ppm)	o-Me δ (ppm)	p-Me δ (ppm)	m-H δ (ppm)	R' or L δ (ppm) [J(Hz)]
Ib	CDCl$_3$	1.22t	2.45s	2.12s	6.40s	
Ic	CDCl$_3$	1.22t	2.41s	2.12s	6.41s	
IIa	CDCl$_3$	1.31t	2.53s	2.17s	6.54s	2.00s (CMe)
IIb	CDCl$_3$	1.04t 1.33t	2.70s 2.88s	2.24s	6.68s	2.29s (2-Me); 8.87 d[6] (6-H)
IIc	CDCl$_3$	1.09t 1.35t	2.85s 2.92s	2.25s	6.71s	1.96s (3-Me); 7.65s (2-H); 8.33d[5] (6-H)
IId	CDCl$_3$	1.07t 1.31t	2.82s 2.88s	2.21s	6.68s	1.87s and 2.16s (3- and 4-Me); 7.51s (2-H); 8.16d[5] (6-H)
IIe	CDCl$_3$	1.16t	2.89s	2.24s	6.69s	2.05s (3,5-Me); 7.70s (2,6-H)
IIf	CDCl$_3$	1.23t	2.88s	2.24s	6.69s	3.93s (OMe); 8.53d[6] (2,6-H)
IIg	CDCl$_3$	1.13t	2.29s	2.22s	6.62s	3.86q[7.5] (NCH$_2$); 1.25t[7.5] (CMe)
IIh	CDCl$_3$	1.10t	2.75s	2.20s	6.68s	0.88d[7] (PMe)
IIi	CDCl$_3$	1.30t	2.50s	2.19s	6.64s	3.34d[11] (OMe)
IIIa	CH$_2$Cl$_2$	1.31t	2.21s	2.13s	6.46s	2.31t[3.5] (CH)
IIIb	CDCl$_3$	1.32t	2.14s	2.13s	6.40s	1.91t[3] (CMe)
IIIc	CDCl$_3$	1.30t	2.25s	2.15s	6.45s	2.44tt[6] [3] (CCH$_2$); 3.38dt[6] [6] (CH$_2$O); 1.71t[6] (OH)
IIId	CDCl$_3$	1.37t	2.19s	2.16s	6.45s	
IIIe	CDCl$_3$	1.37t	2.19s	2.15s	6.44s	3.75s (OMe); 6.70d and 7.07d[8] (C$_6$H$_4$)
IIIf	CH$_2$Cl$_2$	1.65t 1.72t				2.20t[4.5] (CH)
IIIg	CDCl$_3$	1.66t 1.71t				1.77t[3] (CMe)
IIIh	CH$_2$Cl$_2$	1.69t 1.75t				
IIIi	CDCl$_3$	1.72t 1.76t				3.73s (OMe); 6.67d and 6.89d[8] (C$_6$H$_4$)
IIIj	CH$_2$Cl$_2$	1.36t	3.51s (o-OMe)		6.14d [c]	2.15t[3.5] (CH)
IIIk	CH$_2$Cl$_2$	1.39t	3.52s (o-OMe)		6.17d [c]	
IV	CDCl$_3$	1.35t 1.44t	2.32s 2.52s	2.22s	6.67s	2.33t[2] (CMe); 4.59s (OMe)

[a] Data for some aromatic protons are omitted. [b] J_P = 7—8 Hz. [c] $J_{H(para)}$ = 8 Hz.

unsymmetrically substituted pyridine ligand, IIb—IId, irrespective of the position of the substituent. Consistent with this result is the magnetic nonequivalence of the two *ortho*-methyl groups in their mesityl group. Due to the symmetry of the pyridine ligand in IIe and IIf, it is not possible to elucidate the orientation of the ligand, although we believe that there also is no free rotation of these ligands on the ^{1}H NMR time scale. On the other hand, the observation of single triplet pattern for the phosphine methyl protons in the spectrum of IIg is probably due to rapid free rotation about the nickel(II)—ethyl imidazole bond, since the mesityl *ortho*-methyl protons are also magnetically equivalent. These results are important in relation to the understanding of the so-called "*ortho*-effect" of arylnickel(II) complexes [20], and are in good agreement with those found for *trans*-$C_6Cl_5Ni(PPhMe_2)_2R$ (R = aryl group) [20]. In both cases the rotation about the nickel(II)—L or nickel(II)—R bonds is hindered for six-membered-ring ligands (L, R), but is free for five-membered-ring ligands (L, R). Observations of the analogous double triplet pattern for IIIf—IIIi are due to the perpendicular orientation of the trichlorovinyl group [21]. The mesityl *meta* proton resonance seems to be useful for distinguishing between the cationic and the neutral complexes; the resonances were observed in the region above or below δ 6.50 ppm, respectively.

It was reported previously that the carbene complexes, *trans*-[(C_6Cl_5Ni-($PPhMe_2)_2${C(OR)Me}]ClO_4$, have two isomers due to hindered rotation about the C(carbene)—O bond in solution [5], as shown below:

Z-form   *E*-form
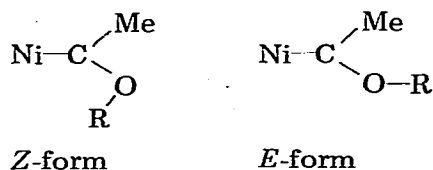
The ^{1}H NMR spectra of IV, however, showed the presence of only one isomer, the carbene ligand of which is fixed perpendicularly to the nickel(II) coordination plane. The spectral pattern and the chemical shift values are in accord with those of the *Z*-form. This result is unexpected, provided the relative stabilities of the two isomers were determined solely by steric hindrance, since the *ortho* substituents (CH_3) of mesityl group have a larger van der Waals radius (2.0 Å) than those (Cl, 1.80 Å) of pentachlorophenyl group. A detailed investigation of the chemical and physical properties of IV will be reported later.

Experimental

^{1}H NMR spectra were determined on a JEOL Model JNM-PS-100 spectrometer operating at 100 MHz using tetramethylsilane as internal standard. Infrared spectra were recorded on a Hitachi 225 spectrophotometer using Nujol mulls. The starting complexes, *trans*-(mesityl)Ni(PPhMe$_2$)$_2$Br (Ia) [15] and *trans*-CCl_2-$CClNi(PPhMe_2)_2Cl$ [22], were prepared by published methods.

trans-{(o-MeO)$_2$C$_6$H$_3$}Ni(PPhMe$_2$)$_2$Cl

A solution of 2,6-dimethoxyphenyllithium [23] (10 mmol) in ether (20 ml)/

benzene (100 ml) was added dropwise to a solution of $Ni(PPhMe_2)_2Cl_2$ (4.0 g, 10 mmol) in 80 ml of benzene at ca. 5°C under nitrogen. The mixture was heated to reflux for a short period, and the solvent was removed under reduced pressure. The residual solid was recrystallized from hexane using a Soxhlet extractor to give brown crystals of trans-{(o-MeO)$_2$C$_6$H$_3$} Ni(PPhMe$_2$)$_2$Cl (2.15 g, 43%), m.p. 116—117°C. (Found: C, 56.58; H, 6.13. $C_{24}H_{31}O_2P_2ClNi$ calcd.: C, 56.79; H, 6.16%.) ^{1}H NMR (CDCl$_3$): δ (PCH$_3$) 1.26t (J_P = 7.5 Hz); δ (OCH$_3$) 3.45s; δ (m-H) 5.94d (J_H = 8 Hz); δ (p-H) 6.75m; δ (C$_6$H$_5$) 7.2—7.6m.

trans-[(mesityl)Ni(PPhMe$_2$)$_2$(NCMe)]ClO$_4$ (IIa)

Complex Ia (5.35 g, 10 mmol) was dissolved in 150 ml of acetone containing 3 ml of acetonitrile. A solution of silver perchlorate (2.07 g, 10 mmol) in 50 ml of acetone was added to the above solution at 0°C. The silver bromide precipitate was removed by filtration to give an orange brown filtrate. The solvent was removed under reduced pressure. The residual yellow solid was recrystallized from ethanol under a nitrogen atmosphere without heating above 30°C to give yellow crystals of IIa (4.35 g, 73%). IIa was stored either in vacuo or at a temperature below 0°C.

trans-[(mesityl)Ni(PPhMe$_2$)$_2$(2-pic)]ClO$_4$ (IIb)

To a solution of IIa, prepared in situ as above from Ia (1 mmol) in acetone/acetonitrile, was added 0.2 ml (an excess) of 2-picoline at 0°C. The mixture was stirred at room temperature for several minutes, and the solvent was removed under reduced pressure. The residue was recrystallized from methanol to give IIb (0.499 g, 77%).

trans-[(mesityl)Ni(PPhMe$_2$)$_2$(L)]ClO$_4$ (IIc—IIi)

These complexes were prepared in 50—90% yield in manners similar to IIb, using IIa prepared in situ and a neutral ligand L (a slight excess).

trans-(mesityl)Ni(PPhMe$_2$)$_2$Cl (Ib)

To a solution of IIh (0.692 g, 1 mmol) in 20 ml of acetone was added NH$_4$Cl (0.080 g, 1.5 mmol) dissolved in 3 ml of water. The mixture was kept in a refrigerator overnight to give crystals of Ib (0.398 g, 81%). Complexes IIa and IIe could be used in place of IIh.

trans-(mesityl)Ni(PPhMe$_2$)$_2$NNN (Ic)

To a solution of IIa, prepared in situ as above from Ia (1 mmol) in acetone/acetonitrile, was added sodium azide (0.10 g, 1.5 mmol) dissolved in 3 ml of water. Solvents were removed under a reduced pressure, and the residual solid was recrystallized from n-hexane to give fine needle crystals of Ic (0.293 g, 59%).

trans-(mesityl)Ni(PPhMe$_2$)$_2$C≡CH (IIIa)

To a solution of IIa (2.974 g, 5 mmol) in 100 ml of acetone at 0°C under nitrogen was added triethylamine (1 ml) and a large excess of gaseous acetylene (ca. 1 l). The mixture was kept at 0°C overnight to give a yellow precipitate. On

warming to room temperature this formed a yellow solution with a small amount of brown precipitate. The latter was filtered using cylindrical filtering paper under a nitrogen atmosphere. Methanol (50 ml) was added to the filtrate, and the solution was concentrated under reduced pressure to ca. 1/3 volume. The solution was kept in a refrigerator to give crystals of IIIa (1.813 g, 76%).

trans-(mesityl)Ni(PPhMe$_2$)$_2$C≡CMe (IIIb)

Complex IIIb could be prepared similarly from IIa and methylacetylene in 38% yield.

trans-(mesityl)Ni(PPhMe$_2$)$_2$C≡CCH$_2$CH$_2$OH (IIIc)

To a solution of IIa, prepared in situ from Ia (5 mmol) in acetone/acetonitrile as above, was added HC≡CCH$_2$CH$_2$OH (1 ml) and triethylamine (1 ml) at 0°C under a nitrogen atmosphere. The mixture was stirred at 0°C for 2 h, and then was concentrated under reduced pressure to ca. 1/3 volume to give a yellow precipitate. The latter was filtered and recrystallized from ethanol to give IIIc (0.878 g, 34%).

trans-(mesityl)Ni(PPhMe$_2$)$_2$C≡CPh (IIId)

To a solution of IIa, prepared in situ from Ia (3 mmol) in acetone/acetonitrile as above, was added phenylacetylene (0.6 ml) and triethylamine (0.6 ml) at 0°C under nitrogen atmosphere. The mixture was kept at 0°C overnight. After filtration of a small amount of brown solid, 45 ml of methanol was added. The solution was concentrated under reduced pressure to ca. 1/3 volume, and was kept in a refrigerator to give crystals of IIId (1.208 g, 73%). The analytical sample was obtained by recrystallization from methanol.

trans-(mesityl)Ni(PPhMe$_2$)$_2$C≡CC$_6$H$_4$OMe-p (IIIe)

This complex was prepared in 67% yield in a manner similar to IIId by the reaction of IIa, prepared in situ from Ia (3 mmol) in acetone/acetonitrile, and HC≡CC$_6$H$_4$OMe-p (0.6 ml) in the presence of triethylamine (0.6 ml).

trans-CCl$_2$=CClNi(PPhMe$_2$)$_2$C≡CH (IIIf)

To a solution of trans-CCl$_2$=CClNi(PPhMe$_2$)$_2$Cl (0.50 g, 1 mmol) in 20 ml of acetonitrile at 0°C 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. To filtrate, at 0°C under nitrogen, was added triethylamine (0.2 ml) and gaseous acetylene (ca. 100 ml). The mixture was kept at the temperature for 2 h, and then volatile materials were removed under reduced pressure. The residue was recrystallized from methanol to give crystals of IIIg (0.310 g, 63%).

trans-CCl$_2$=CClNi(PPhMe$_2$)$_2$C≡CR (IIIg—IIIi)

These complexes were prepared in 50—70% yield in a manner similar to IIIf, using the corresponding HC≡CR.

trans-{(o-MeO)$_2$C$_6$H$_3$}Ni(PPhMe$_2$)$_2$C≡CR (IIIj, IIIk)

These complexes were prepared in 50—60% yield in a manner similar to IIIf using trans-{(o-MeO)$_2$C$_6$H$_3$}Ni(PPhMe$_2$)$_2$Cl and the corresponding HC≡CR in acetonitrile.

trans-[(mesityl)Ni(PPhMe₂)₂{C(OMe)Me}]ClO₄ (IV)

To a suspension of IIIa (0.478 g, 1 mmol) in 5 ml of methanol at 0°C was added with stirring 0.12 ml (1.1 mmol) of 60% aqueous perchloric acid dissolved in 2 ml of methanol under a nitrogen atmosphere. The crystals of IIIa dissolved in a few minutes, and then a new microcrystalline solid appeared. The mixture was stirred at 0°C for 0.5 h. The precipitate was filtered and recrystallized from methanol to give IV (0.238 g, 39%).

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