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## Crystal structures of a methylmethoxycarbene complex and the corresponding vinyl complex of nickel(II)

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### Abstract

The molecular structures of nickel complexes containing the simplest alkyl(alkoxy)carbene ligand or the corresponding vinyl ligand, *trans*-[Ni(C<sub>6</sub>Cl<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>{C(OMe)Me}]BF<sub>4</sub> or *trans*-[Ni(C<sub>6</sub>Cl<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>{C(OMe)=CH<sub>2</sub>}], respectively, have been determined by single-crystal X-ray diffraction. Crystals of the carbene complex are monoclinic, space group *P*2<sub>1</sub>/*n* with *Z* = 4 in a unit cell of dimensions *a* 13.382(7), *b* 11.173(5), *c* 16.599(6) Å, β 107.95(4)° at –100°C. Crystals of the vinyl complex are also monoclinic, space group *P*2<sub>1</sub>/*n* with *Z* = 4 in a unit cell of dimensions *a* 9.255(2), *b* 9.265(2), *c* 26.779(4) Å, β 95.06(2)° at 20°C. Structures were refined to *R* = 0.072 (4318 reflections) and *R* = 0.052 (3766 reflections) for the carbene and the vinyl complexes, respectively. The coordination geometry around the Ni atom is typically square-planar in each complex. The methylmethoxy carbene ligand is disordered even at –100°C in the crystal of the carbene complex. The Ni–C(carbene) bond (1.848 Å) is about 0.07 Å shorter than the corresponding Ni–C(vinyl) bond (1.916 Å). On the other hand, Ni–P bond lengths in the carbene complex (2.212 Å) are about 0.03 Å longer than those in the vinyl complex (2.178 Å). These facts indicate significantly the presence of π back-bonding in the Ni–C(carbene) bond in *trans*-[Ni(C<sub>6</sub>Cl<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>{C(OMe)Me}]BF<sub>4</sub>.

### Introduction

Since the first pioneering work of the tungsten and chromium complexes by Fischer and Maasboel [1], much attention has been given to transition metal–carbene

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complexes in the field of organometallic chemistry. Carbene complexes are not only important as reaction intermediates in organic chemistry but are also of interest in determining the nature of the bonding between the transition metal and electron-deficient carbon atoms [2].

In view of this, one of us (M.W.) has carried out the preparation and characterization of a series of alkylalkoxycarbene nickel(II) complexes of the type, *trans*-[NiRL<sub>2</sub>(carbene)]X (R = C<sub>6</sub>Cl<sub>5</sub> or C<sub>6</sub>H<sub>2</sub>Me<sub>3-2,4,6</sub>, L = PMe<sub>3</sub> or PMe<sub>2</sub>Ph, and X = ClO<sub>4</sub> or BF<sub>4</sub>) [3]. We have also carried out a series of X-ray diffraction studies of these complexes in order to obtain the precise structural information. We have already reported the structures of two nickel(II) complexes containing this type of carbene ligand, viz. *trans*-[Ni(C<sub>6</sub>Cl<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>(CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O)]BF<sub>4</sub> [4] and *trans*-[Ni(C<sub>6</sub>Cl<sub>5</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>{C(OMe)Me}]BF<sub>4</sub> [5]. In the case of the complex containing the simplest alkylalkoxycarbene ligand, however, we think that the direct comparison of this carbene complex with the corresponding vinyl(C(OMe)=CH<sub>2</sub>) complex, as done in the case of the former cyclic carbene complex, is indispensable in discussing the bonding nature of the metal-carbene bond.

Here, we describe the structures of both methylmethoxy carbene and corresponding vinyl complexes of nickel(II), *trans*-[Ni(C<sub>6</sub>Cl<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>{C(OMe)Me}]BF<sub>4</sub> and *trans*-[Ni(C<sub>6</sub>Cl<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>{C(OMe)=CH<sub>2</sub>}], which have the same ancillary ligands at positions *cis* or *trans* to the carbene or vinyl ligands. The structures have been determined on the basis of diffraction data collected at -100 °C for the carbene complex because of the observed disorder and at 20 °C for the vinyl complex.

## Experimental

### Crystal data and intensity data collection

The crystals of both carbene and vinyl complexes were prepared by methods previously reported [3b]. Crystal data are summarized in Table 1. The accurate

Table 1

Crystal data for the carbene and vinyl complexes, *trans*-[Ni(C<sub>6</sub>Cl<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>{C(OMe)Me}]BF<sub>4</sub> and *trans*-[Ni(C<sub>6</sub>Cl<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>{C(OMe)=CH<sub>2</sub>}]

	Carbene complex		Vinyl complex
Carbene/Vinyl	C(OMe)Me		C(OMe)=CH <sub>2</sub>
Formula	C <sub>15</sub> H <sub>24</sub> Cl <sub>5</sub> NiOP <sub>2</sub> ·BF <sub>4</sub>		C <sub>15</sub> H <sub>23</sub> Cl <sub>5</sub> NiOP <sub>2</sub>
<i>M.W.</i>	605.1		517.3
<i>F</i> (000)	548		1096
Crystal system	monoclinic		monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>		<i>P</i> 2 <sub>1</sub> / <i>n</i>
Temperature (°C)	-100	20	20
<i>a</i> (Å)	13.832(7)	13.904(3)	9.255(2)
<i>b</i> (Å)	11.173(5)	11.441(3)	9.265(2)
<i>c</i> (Å)	15.599(6)	16.637(4)	26.779(4)
<i>β</i> (°)	107.95(4)	108.29(2)	95.06(2)
<i>U</i> (Å <sup>3</sup> )	2440.6(18)	2512.9(10)	2287.3(6)
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.616	1.599	1.502
<i>Z</i>	4	4	4
<i>μ</i> (Mo- <i>K</i> <sub>α</sub> ) (cm <sup>-1</sup> )	15.0	14.6	15.6

Table 2

Conditions for the data collection and refinements

	Carbene complex	Vinyl complex
Crystal size (mm)	0.15 × 0.35 × 0.45	0.15 × 0.20 × 0.35
X-ray	Mo-K <sub>α</sub> , 40 kV, 200 mA Zr filter	Mo-K <sub>α</sub> , 40 kV, 30 mA graphite monochromator
Scan mode	θ-2θ	θ-2θ
Scan width in 2θ (°)	2.0 + 0.70 tan θ	1.8 + 0.70 tan θ
Scan speed in 2θ (° min <sup>-1</sup> )	8	4
Background intensity (sec)	4	5
2θ max (°)	54.0	54.0
Temperature (°C)	-100	20
No. of collected reflections	5839	5637
No. of independent reflections	5325	4991
R <sub>int</sub>	0.021	0.020
No. of  F <sub>o</sub>   > 3σ(F <sub>o</sub> ) reflections	4318	3766
Weighting parameters (See test)		
a	0.0800	0.0515
b	0.0040	0.0003
Final R value <sup>a</sup>	0.072	0.052
Final R <sub>w</sub> value <sup>b</sup>	0.102	0.061

$$^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b R_w = \left\{ \frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right\}^{1/2}.$$

unit-cell dimensions were determined by the least-squares fit of the 2θ values of 25 reflections. Intensity data were collected at 20 °C for both complexes on a Rigaku automated four-circle diffractometer. Data were also collected at -100 °C for the carbene complex (see below). Although a lower temperature was also tried for the data collection of the carbene complex, the crystal cracked below -100 °C. The low temperature was achieved by gas flow using liquid nitrogen. Data collection parameters are listed in Table 2. Four standard reflections measured at regular intervals to monitor the stability and orientation of the crystals showed no significant decay throughout the data collection of both complexes. Corrections for Lorentz and polarization effects were applied to the intensity data. No absorption corrections were carried out, which may have limited the accuracy of the present structure determination.

### Structure determination

Both structures were solved by the heavy atom method. All the non-hydrogen atoms were located on Fourier maps that were based on positions of the Ni and P atoms determined from the Patterson function.

### Structure refinement

The structures were refined by the block-diagonal least-squares procedure using the HBLS-V program [6] and by the full-matrix least-squares method in the X-ray system [7], the function minimized being  $\sum w(|F_o| - |F_c|)^2$ .

The structure of the carbene complex was at first refined using the data collected at 20 °C. After several cycles of the anisotropic refinement with the convergence of an R value to 0.10, a significantly large peak corresponding to 2–3 electrons was

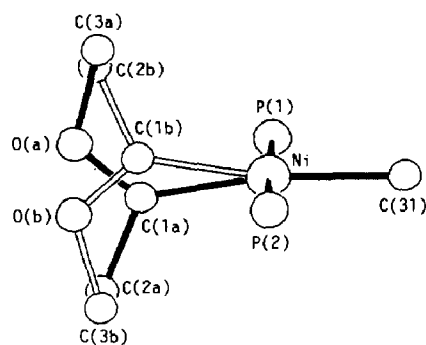


Fig. 1. A refined model for the disordered structure of the carbene ligand in *trans*-[Ni(C<sub>6</sub>Cl<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>{C(OMe)Me}]BF<sub>4</sub>. The major and minor components are labeled as a and b, respectively.

found to remain near the C(1) and O atoms of the carbene ligand on the difference Fourier map. This fact as well as the relatively high *R* value led us to collect the intensity data at a low temperature. However, the same peak remained even on the difference Fourier map based on the data at  $-100^{\circ}\text{C}$  in spite of the fact that the *R* value (0.08) was smaller than that at  $20^{\circ}\text{C}$ . The peak was located on the plane formed by the C(1), C(2), O and C(3) atoms of the carbene ligand and at distances of about 1.0, 1.3 and 1.0 Å from the C(1), C(2) and O atoms, respectively. In addition to this remaining peak, the observed bond distances in the carbene ligand were unusual; for example, the C(1)–C(2) 1.67 and C(1)–O 1.19 Å. At this stage, we took a disordered structure of the carbene ligand into consideration, in which two conformational isomers about the Ni–C(1) bond with a conformational angle of about  $180^{\circ}$  exist as depicted in Fig. 1 (the final, refined structure). A similar disordered model for the methylmethoxy carbene ligand has been reported in the case of [Pt(Me)(PMe<sub>2</sub>Ph)<sub>2</sub>{C(OMe)Me}]PF<sub>6</sub> [8]. This disordered model constructed on the basis of the geometrical parameters of [Ni(C<sub>6</sub>Cl<sub>5</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>{C(OMe)Me}]BF<sub>4</sub> [5] (referred to as the PMe<sub>2</sub>Ph carbene complex) was refined as two rigid groups by use of the group refinement procedure in the X-ray System [7]. The occupancy parameters for the disordered carbene ligand were estimated from the peak heights of electron densities of the oxygen atom as 2/3 and 1/3 for the major and minor components (labeled a and b), respectively.

On the difference Fourier maps after the anisotropic refinement of both complexes, electron densities which could be assigned for the hydrogen atoms except for those of the carbene ligand were found at essentially the same positions as those calculated from stereochemical considerations. These H atoms were included in the structure factor calculation in the carbene complex, whereas they were refined isotropically in the vinyl complex. The weighting scheme used was  $w = (\sigma_{\text{cs}}^2 + a |F_{\text{o}}| + b |F_{\text{o}}|^2)^{-1}$ , where  $\sigma_{\text{cs}}$  is the standard deviation obtained from the counting statistics, and *a* and *b* are constants adjusted during the refinement cycles. Table 2 also summarizes the conditions for the course of refinements including the final *R* and *R<sub>w</sub>* values. The atomic scattering factors were taken from International Tables for X-ray Crystallography [9].

The group parameters of the carbene complex are presented in Table 3. The final atomic positional parameters for the carbene and vinyl complexes together with the

Table 3

Positional and rotational parameters of the rigid groups of the disordered carbene ligand in *trans*-[Ni(C<sub>6</sub>Cl<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>(C(OMe)Me)]BF<sub>4</sub>

The center of gravity of the group,  $x_{cg}$ ,  $y_{cg}$  and  $z_{cg}$  (fractional coordinates), and the group orientation angles,  $\theta$ ,  $\phi$ ,  $\psi$  (°)

Carbene <sup>a</sup>	$x_{cg}$	$y_{cg}$	$z_{cg}$	$\theta$	$\phi$	$\psi$	Occupancy
a	0.5374(6)	0.1111(8)	0.1190(4)	21.9(14)	6.9(14)	-22.4(13)	2/3
b	0.5203(11)	0.1073(15)	0.1104(7)	21.8(26)	23.8(33)	-40.0(37)	1/3

<sup>a</sup> The major and minor components of the disordered carbene ligands as a and b, respectively.

$B_{eq}$  values [10] are listed in Tables 4 and 5, respectively. Tables of anisotropic temperature factors, atomic parameters for hydrogen atoms, and observed and calculated structure factors (Tables S1–S6) are available from the authors.

Table 4

Final atomic coordinates and  $B_{eq}$  values for the carbene complex, *trans*-[Ni(C<sub>6</sub>Cl<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>(C(OMe)Me)]BF<sub>4</sub>

Atom	$x$	$y$	$z$	$B_{eq}$ (Å <sup>2</sup> )
Ni	0.49128(6)	0.18100(6)	0.23550(5)	1.7
C(1a)	0.4991	0.1152	0.1355	2.4
C(2a)	0.4044	0.0606	0.0708	3.0
O(a)	0.5738	0.1101	0.1081	3.7
C(3a)	0.6724	0.1584	0.1616	8.0
C(1b)	0.5435	0.1321	0.1481	2.4
C(2b)	0.6552	0.1531	0.1528	3.0
O(b)	0.4955	0.0856	0.0786	3.7
C(3b)	0.3864	0.0585	0.0622	8.0
P(1)	0.53680(13)	0.00855(13)	0.30214(10)	2.4
C(11)	0.6643(6)	-0.0401(7)	0.3125(5)	3.8
C(12)	0.4547(6)	-0.1161(6)	0.2523(5)	3.5
C(13)	0.5333(9)	-0.0009(7)	0.4102(5)	5.2
P(2)	0.44934(11)	0.35695(13)	0.17377(9)	1.9
C(21)	0.5205(6)	0.4067(7)	0.1041(4)	3.2
C(22)	0.3163(5)	0.3632(7)	0.1084(5)	3.4
C(23)	0.4601(6)	0.4848(6)	0.2426(5)	3.1
C(31)	0.4588(4)	0.2395(5)	0.3338(4)	1.7
C(32)	0.5328(4)	0.2918(5)	0.4021(4)	1.7
C(33)	0.5141(4)	0.3253(5)	0.4768(4)	1.8
C(34)	0.4171(5)	0.3076(5)	0.4842(4)	1.8
C(35)	0.3413(4)	0.2570(5)	0.4177(4)	1.8
C(36)	0.3645(4)	0.2234(5)	0.3449(4)	1.7
Cl(32)	0.65401(10)	0.30849(14)	0.39358(9)	2.4
Cl(33)	0.60948(11)	0.38489(14)	0.56024(9)	2.5
Cl(34)	0.39179(12)	0.34969(14)	0.57559(9)	2.6
Cl(35)	0.22198(11)	0.23183(14)	0.42727(10)	2.6
Cl(36)	0.27025(11)	0.15246(15)	0.26367(10)	2.8
B	0.9009(6)	0.2263(7)	0.3724(5)	2.7
F(1)	0.8668(4)	0.3436(4)	0.3723(3)	4.6
F(2)	1.0053(3)	0.2214(5)	0.4113(3)	4.4
F(3)	0.8781(4)	0.1867(5)	0.2909(3)	4.4
F(4)	0.8541(3)	0.1560(4)	0.4182(3)	4.0

Table 5

Final atomic coordinates and  $B_{\text{eq}}$  values for the vinyl complex, *trans*-[Ni(C<sub>6</sub>Cl<sub>5</sub>(PMe<sub>3</sub>)<sub>2</sub>(C(OMe)=CH<sub>2</sub>)]

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}$ (Å <sup>2</sup> )
Ni	0.29856(6)	0.32665(6)	0.387037(20)	2.6
C(1)	0.1904(5)	0.2058(5)	0.42825(16)	3.1
C(2)	0.2019(7)	0.2042(7)	0.47828(18)	4.6
C(3)	0.0065(7)	0.0223(7)	0.42650(22)	5.6
O	0.0940(4)	0.1176(4)	0.40020(12)	3.7
P(1)	0.45616(14)	0.15206(15)	0.38713(6)	3.9
C(11)	0.3838(8)	-0.0275(7)	0.3798(4)	8.3
C(12)	0.5740(8)	0.1412(9)	0.4452(3)	7.6
C(13)	0.5895(9)	0.1564(9)	0.3414(4)	8.9
P(2)	0.12351(15)	0.48346(14)	0.38825(6)	3.9
C(21)	-0.0588(7)	0.4111(8)	0.3797(4)	8.4
C(22)	0.1261(9)	0.5818(8)	0.4467(3)	7.8
C(23)	0.1158(9)	0.6308(8)	0.3438(3)	7.8
C(31)	0.4156(5)	0.4547(5)	0.3505(2)	3.0
C(32)	0.4080(5)	0.4646(6)	0.2983(2)	3.4
C(33)	0.4931(6)	0.5567(6)	0.2725(2)	3.4
C(34)	0.5932(5)	0.6465(6)	0.2993(2)	3.6
C(35)	0.6043(5)	0.6421(5)	0.3513(2)	3.0
C(36)	0.5164(5)	0.5473(5)	0.3755(2)	3.0
Cl(32)	0.28378(17)	0.35204(17)	0.26452(5)	5.2
Cl(33)	0.47618(18)	0.56372(18)	0.20777(5)	5.3
Cl(34)	0.69996(19)	0.76395(20)	0.26861(6)	6.4
Cl(35)	0.72633(14)	0.75419(14)	0.38526(5)	4.3
Cl(36)	0.53229(17)	0.54485(17)	0.44078(5)	5.0

All the computations were carried out on an ACOS 900, ACOS 850 or ACOS 930 computer and the low temperature data were collected on a diffractometer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

## Results and discussion

Crystal structures of both complexes are presented in Fig. 2. No unusually short contacts between adjacent molecules are observed in either complex. The shortest intermolecular distances between non-hydrogen atoms are 2.926(6) Å [Cl(35)(*x*, *y*, *z*)...F(2)(-1 + *x*, *y*, *z*)] for the carbene complex and 2.949(4) Å [O(*x*, *y*, *z*)...Cl(33)( $\frac{1}{2} - x$ ,  $-\frac{1}{2} + y$ ,  $\frac{1}{2} - z$ )] for the vinyl complex.

Molecular structures of the carbene and vinyl complexes are presented in Fig. 3 along with the atomic numbering, in which only the major component of the disordered carbene ligand is shown for the carbene complex. The most reliable model for the disordered structure obtained by the rigid-body group refinement is depicted in Fig. 1. Such a disordered structure of the methylmethoxycarbene ligand has not been observed in the PMe<sub>2</sub>Ph carbene complex [5], in which the phenyl group in the phosphine ligand probably plays a significant role in fixing the rotation of the carbene ligand. In view of this, the structure of the carbene complex is discussed in terms of this major component of the disordered model, because the minor component has less reliability owing to the low occupancy. Bond distances

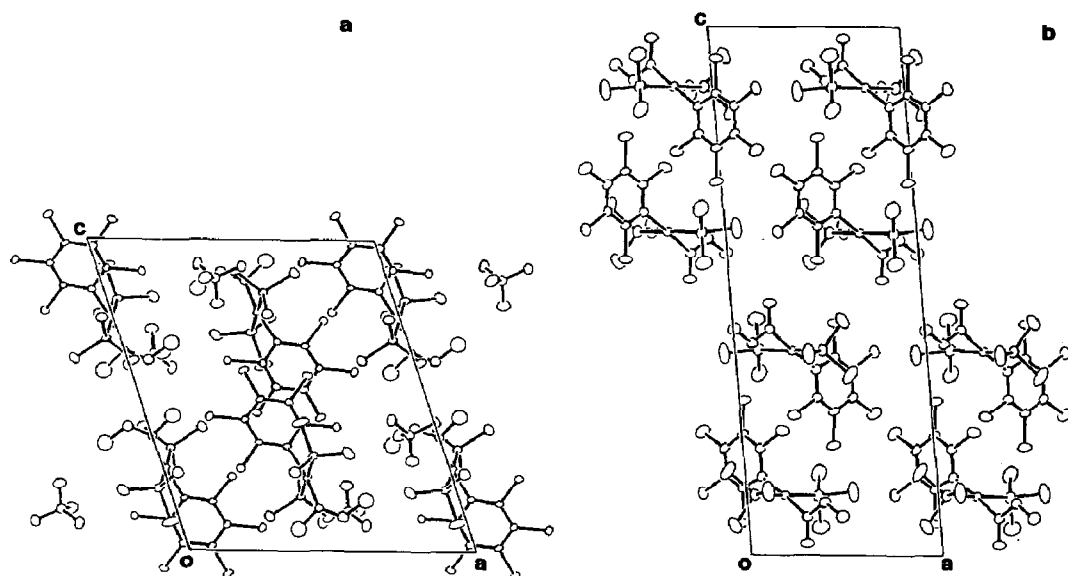


Fig. 2. Crystals structures by ORTEP drawings [11]. Non-hydrogen atoms are thermal ellipsoids at 30% probability levels, and hydrogen atoms are omitted for clarity. (a) the carbene complex viewed down the *b* axis. (b) the vinyl complex viewed down the *b* axis.

and angles of the both complexes are listed in Table 6, included in which are several selected values for the  $\text{PMe}_2\text{Ph}$  carbene complex [5] for the sake of comparison.

The coordination geometry around the Ni atom is typically square-planar in each complex. The maximum deviations from the least-squares coordination planes are 0.12 and 0.07 Å for the carbene and vinyl complexes, respectively. The planes of the carbene and vinyl ligands defined by the C(1), C(2), O and C(3) atoms are almost perpendicular to the coordination planes, the dihedral angles being 88.6 and 89.9°,

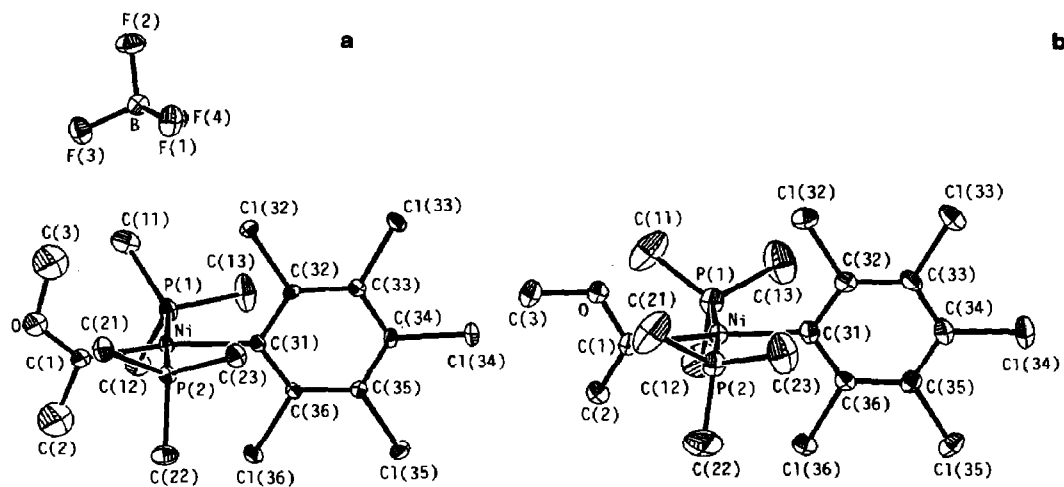


Fig. 3. Molecular structures by ORTEP drawings [11] along with atomic numbering systems. Non-hydrogen atoms are thermal ellipsoids at 30% probability levels, and hydrogen atoms are omitted for clarity. (a) the carbene complex. (b) the vinyl complex.

Table 6

Bond distances (Å) and angles (°) for the carbene and vinyl complexes, *trans*-[Ni(C<sub>6</sub>Cl<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>{C(OMe)Me}]BF<sub>4</sub> and *trans*-[Ni(C<sub>6</sub>Cl<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>{C(OMe)=CH<sub>2</sub>}] along with several selected values for the PMe<sub>2</sub>Ph carbene complex, *trans*-[Ni(C<sub>6</sub>Cl<sub>5</sub>)(PMe<sub>2</sub>Ph)<sub>2</sub>{C(OMe)Me}]BF<sub>4</sub> [5]

	Carbene complex <sup>a</sup>	PMe <sub>2</sub> Ph carbene complex [5]	Vinyl complex
Ni–C(1)	1.848	1.843(10)	1.916(5)
Ni–P(1)	2.214(2)	2.232(3)	2.178(2)
Ni–P(2)	2.210(2)	2.219(3)	2.178(2)
Ni–C(31)	1.934(6)	1.928(7)	1.930(5)
C(1)–C(2)	1.54 <sup>b</sup>	1.536(16)	1.335(8)
C(1)–O	1.25 <sup>b</sup>	1.261(12)	1.382(6)
C(3)–O	1.48 <sup>b</sup>	1.479(14)	1.425(8)
P(1)–C(11)	1.802(9)		1.798(10)
P(1)–C(12)	1.826(8)		1.822(9)
P(1)–C(13)	1.812(13)		1.814(10)
P(2)–C(21)	1.821(8)		1.811(10)
P(2)–C(22)	1.827(8)		1.811(9)
P(2)–C(23)	1.806(8)		1.808(9)
C(31)–C(32)	1.400(8)		1.398(7)
C(31)–C(36)	1.384(8)		1.394(7)
C(32)–C(33)	1.394(8)		1.387(7)
C(32)–Cl(32)	1.736(6)		1.744(5)
C(33)–C(34)	1.398(8)		1.396(7)
C(33)–Cl(33)	1.724(6)		1.727(6)
C(34)–C(35)	1.388(8)		1.389(7)
C(34)–Cl(34)	1.724(6)		1.726(6)
C(35)–C(36)	1.394(8)		1.394(7)
C(35)–Cl(35)	1.729(6)		1.732(5)
C(36)–Cl(36)	1.750(6)		1.742(5)
B–F(1)	1.393(10)		
B–F(2)	1.390(10)		
B–F(3)	1.365(10)		
B–F(4)	1.384(9)		
C(1)–Ni–P(1)	90.9	90.8(4)	87.08(14)
C(1)–Ni–P(2)	91.0	91.8(4)	87.37(14)
C(1)–Ni–C(31)	169.9	175.8(4)	175.29(19)
P(1)–Ni–P(2)	177.67(8)	176.5(2)	173.80(7)
P(1)–Ni–C(31)	88.68(17)	89.5(3)	92.95(14)
P(2)–Ni–C(31)	89.68(17)	87.6(3)	92.81(14)
Ni–C(1)–C(2)	120.7	120.1(8)	125.8(4)
Ni–C(1)–O	128.9	130.3(8)	112.2(3)
C(2)–C(1)–O	110.3 <sup>b</sup>	109.6(9)	122.0(5)
C(1)–O–C(3)	118.4 <sup>b</sup>	118.3(9)	117.7(4)
Ni–P(1)–C(11)	115.4(3)		116.4(4)
Ni–P(1)–C(12)	113.3(3)		113.1(3)
Ni–P(1)–C(13)	117.1(4)		118.6(3)
C(11)–P(1)–C(12)	105.5(4)		103.4(4)
C(11)–P(1)–C(13)	102.2(5)		102.4(5)
C(12)–P(1)–C(13)	101.6(5)		100.7(4)
Ni–P(2)–C(21)	116.7(3)		115.9(4)
Ni–P(2)–C(22)	112.4(3)		113.3(3)
Ni–P(2)–C(23)	116.8(3)		118.7(3)
C(21)–P(2)–C(22)	104.7(4)		103.7(5)
C(21)–P(2)–C(23)	101.8(4)		102.4(5)
C(22)–P(2)–C(23)	102.6(4)		100.7(4)



Table 6 (continued)

	Carbene complex <sup>a</sup>	PMe <sub>2</sub> Ph carbene complex [5]	Vinyl complex
Ni–C(31)–C(32)	121.5(4)		124.5(4)
Ni–C(31)–C(36)	122.8(4)		121.2(4)
C(32)–C(31)–C(36)	115.4(5)		114.3(4)
C(31)–C(32)–C(33)	122.9(5)		123.9(5)
C(31)–C(32)–Cl(32)	117.5(5)		116.9(4)
C(33)–C(32)–Cl(32)	119.5(5)		119.2(4)
C(32)–C(33)–C(34)	119.1(5)		119.4(5)
C(32)–C(33)–Cl(33)	120.8(5)		121.2(4)
C(34)–C(33)–Cl(33)	120.1(5)		119.5(4)
C(33)–C(34)–C(35)	119.9(6)		119.1(5)
C(33)–C(34)–Cl(34)	120.0(5)		120.8(4)
C(35)–C(34)–Cl(34)	120.2(5)		120.1(4)
C(34)–C(35)–C(36)	118.7(5)		119.3(5)
C(34)–C(35)–Cl(35)	120.1(5)		119.7(4)
C(36)–C(35)–Cl(35)	121.1(4)		121.0(4)
C(31)–C(36)–C(35)	124.0(5)		124.0(5)
C(31)–C(36)–Cl(36)	117.7(5)		117.8(4)
C(35)–C(36)–Cl(36)	118.3(4)		118.2(4)
F(1)–B–F(2)	109.9(7)		
F(1)–B–F(3)	109.2(7)		
F(1)–B–F(4)	108.6(6)		
F(2)–B–F(3)	109.6(7)		
F(2)–B–F(4)	108.5(6)		
F(3)–B–F(4)	110.8(6)		

<sup>a</sup> For the carbene ligand, bond lengths and angles for the major component (labeled as **a**) are listed. Those for the minor component (labeled as **b**) of the carbene ligand obtained by rigid-body group refinement are: Ni–C(1b) 1.890 Å, C(1b)–Ni–P(1) 90.8°, C(1b)–Ni–P(2) 90.5°, C(1b)–Bi–C(31) 171.2°, Ni–C(1b)–C(2b) 122.2° and Ni–C(1b)–O(b) 127.4°. <sup>b</sup> Bond distances and angles are fixed as a rigid-body group.

respectively. The arrangements of other ligands around the Ni atom, including the eclipsed conformation about the P–Ni–P axis, are very similar to each other in both complexes. However, a comparison of valence angles around the Ni atom, shows the deviation from the ideal square-planar arrangement to be significantly larger in the vinyl complex than in the carbene complex; the C(1)–Ni–P angles are (on average) 5.6° smaller than the C(31)–Ni–P angles in the vinyl complex, whereas in the carbene complex the former angles are (on average) 1.8° larger than the latter angles. There are two rotational isomers possible because of the hindered rotation about the C(1)–O bond. The *Z* isomer is observed in the carbene complex as reported in the complexes containing the same carbene ligand, the PMe<sub>2</sub>Ph carbene complex [5] and [Pt(Me)(PMe<sub>2</sub>Ph)<sub>2</sub>{C(OMe)Me}]PF<sub>6</sub> [8]. The *E* isomer of this carbene ligand is also known in [Cr(CO)<sub>4</sub>(PPh<sub>3</sub>){C(OMe)Me}] [12]. On the other hand, the vinyl ligand takes an *E* configuration as shown in Fig. 2b. In the carbene and vinyl complexes, the planes of pentachlorophenyl groups are approximately perpendicular to the coordination planes, the dihedral angles being 89.8 and 89.4° for the carbene and vinyl complexes, respectively.

Of the bond distances and angles listed in Table 6, the most valuable parameter is, of course, the metal–carbene carbon bond length. Unfortunately the accuracy of

this parameter in the present carbene complex is not sufficiently high owing to the disordered structure. However, it must be pointed out that the Ni–C(1) bond length in the present carbene complex as well as that in the  $\text{PMe}_2\text{Ph}$  carbene complex [5] is about 0.07 Å shorter than the corresponding length in the vinyl complex. The Ni<sup>II</sup>–C(*sp*<sup>2</sup>) bond lengths in the known square-planar nickel(II) complexes lie between 1.84 and 1.98 Å [4,5,13–24]. The Ni–C(carbene) bond lengths in the present and the  $\text{PMe}_2\text{Ph}$  carbene complexes are among the shortest of the Ni<sup>II</sup>–C(*sp*<sup>2</sup>) bonds. This fact suggests the presence of significant  $\pi$  back-bonding from the metal atom to the carbene ligand. The Ni–C(31) bond lengths are almost the same in both the carbene and the vinyl complexes and lie between 1.88 and 1.98 Å for the Ni<sup>II</sup>–C(aromatics) bond [4,5,16–24]. The significantly large difference in bond lengths between the carbene and vinyl complexes is also evident in the Ni–P bonds. The Ni–P bond lengths in the carbene complex are about 0.03 Å longer than those in the vinyl complex, probably because of the larger steric hindrance between the *cis*-ligands in the carbene complex owing to the shorter Ni–C(carbene) bond. However, if we assume *d* $\pi$ –*d* $\pi$  double bond character in the Ni–P bonds, then another interpretation is possible; i.e., there is less Ni–P  $\pi$ -bond character in the carbene complex than in the vinyl complex, which is expected to be caused by the considerable  $\pi$  back-bonding contribution from the metal atom to the carbene ligand. This also supports the presence of the strong  $\pi$  back-bonding in the nickel–carbene bond mentioned above.

In contrast to the conclusion that little  $\pi$ -bond interaction is observed in the metal–carbene bond, as revealed by structural studies on  $[\text{Pt}(\text{Me})(\text{PMe}_2\text{Ph})_2\{\text{C}(\text{OMe})\text{Me}\}]\text{PF}_6$  [8] and  $[\text{Cr}(\text{CO})_4(\text{PPh}_3)\{\text{C}(\text{OMe})\text{Me}\}]$  [12], the present study indicates that significant  $\pi$ -bonding character exists in the present carbene complex, which is consistent with results previously obtained for the nickel(II) complex containing a cyclic alkylalkoxycarbene ligand [4].

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