Journal of Organometallic Chemistry, 287 (1985) 265–273
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CRYSTAL STRUCTURE OF A METHYL(METHOXY)CARBENE COMPLEX OF NICKEL(II), *trans*-[Ni(C_6Cl_5)(PMe_2Ph)$_2${C(OMe)Me}]BF_4

DUANJUN XU *, KUNIO MIKI*, YASUSHI KAI, NOBUTAMI KASAI* and
MASANORI WADA

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565 (Japan)

(Received November 9th, 1984)

Summary

The structure of a nickel(II) complex, *trans*-[Ni(C_6Cl_5)(PMe_2-Ph)$_2${C(OMe)Me}]BF_4, containing the simplest alkyl(alkoxy)carbene ligand has been determined by X-ray crystallography ($R = 0.091$). The geometry around the nickel atom is square-planar. The comparatively short Ni–C(1) bond length of 1.843(10) Å showed the presence of π-bonding in the nickel–carbene bond.

Introduction

Transition metal–carbene complexes have received attention because of their importance as intermediates in organic reactions [1]. In addition, the bonding nature between the metal and the carbene ligand is of great interest from the viewpoint of structural chemistry. The preparation and characterization of a series of novel nickel(II) complexes of the type *trans*-[$NiRL_2$(carbene)]X (R = C_6Cl_5 or $C_6H_2Me_3$-2,4,6, L = PMe_3 or PMe_2Ph, and X = ClO_4 or BF_4) containing alkyl(alkoxy)carbene ligands have been reported [2–8]. The precise structure of one of these complexes, *trans*-[Ni(C_6Cl_5)(PMe_3)$_2$ ($\overline{CCH_2CH_2CH_2O}$)]$BF_4$ [8], containing a cyclic carbene ligand has already been determined by means of X-ray diffraction [9], comparison of which with the corresponding vinyl complex, *trans*-[Ni(C_6Cl_5)(PMe_3)$_2$-($\underline{C{=}CHCH_2CH_2O}$)], has clearly suggested a π-back-bonding contribution in the nickel–carbene bond [9]. We report here the molecular structure of one of the above nickel complexes, *trans*-[Ni(C_6Cl_5)(PMe_2Ph)$_2${C(OMe)Me}]BF_4, containing the simplest alkyl(alkoxy)carbene ligand, in order to elucidate the nature of the carbene ligand.

(Continued on p. 268)

---

* On leave from the Department of Chemistry, Zhejiang University, Hangzhou, China, 1981 Scholarship Fellow, Ministry of Education, Science and Culture, Japan.

0022-328X/85/$03.30

TABLE 1

FINAL ATOMIC PARAMETERS WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
(a) Non-hydrogen atoms									
Positional parameters in fractions of the cell edges and thermal parameters in the form of $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl]$									
Ni	0.07483(10)	0.28212(5)	0.45166(7)	0.00581(9)	0.00133(3)	0.00275(4)	0.00042(8)	0.00109(10)	0.00009(5)
C(1)	0.0424(9)	0.3755(5)	0.4619(7)	0.0086(10)	0.0020(3)	0.0056(6)	0.0012(8)	0.0013(11)	0.0001(6)
C(2)	0.0330(12)	0.4070(6)	0.5518(7)	0.0183(16)	0.0027(3)	0.0042(5)	0.0033(11)	0.0031(14)	−0.0014(6)
C(3)	0.0338(12)	0.4030(6)	0.3132(6)	0.0178(15)	0.0028(3)	0.0031(4)	0.0027(11)	0.0044(13)	0.0013(6)
O	0.0274(7)	0.4225(4)	0.4047(5)	0.0142(9)	0.00174(17)	0.0060(4)	0.0013(7)	0.0034(10)	0.0009(4)
P(1)	0.2859(3)	0.30122(13)	0.47886(19)	0.0065(3)	0.00244(7)	0.00587(14)	−0.0009(2)	0.0002(3)	−0.00004(16)
C(11)	0.3399(13)	0.3146(8)	0.5974(9)	0.0132(15)	0.0057(6)	0.0070(8)	0.0019(15)	−0.0065(17)	−0.0053(11)
C(12)	0.3466(14)	0.3790(7)	0.4313(12)	0.0142(17)	0.0033(5)	0.0149(13)	−0.0042(13)	0.008(3)	0.0039(12)
C(13)	0.3845(8)	0.2294(5)	0.4483(6)	0.0045(8)	0.0036(4)	0.0046(5)	−0.0008(8)	−0.0002(9)	0.0002(6)
C(14)	0.4149(9)	0.1749(6)	0.5044(7)	0.0071(10)	0.0039(4)	0.0055(6)	0.0005(10)	−0.0008(12)	0.0011(8)
C(15)	0.4733(10)	0.1170(6)	0.4764(9)	0.0069(10)	0.0037(4)	0.0098(9)	0.0004(10)	−0.0011(15)	0.0011(10)
C(16)	0.5028(10)	0.1117(7)	0.3939(9)	0.0066(11)	0.0053(5)	0.0097(9)	0.0016(12)	0.0011(15)	−0.0046(11)
C(17)	0.4747(11)	0.1658(8)	0.3378(8)	0.0073(11)	0.0076(7)	0.0061(7)	0.0001(14)	0.0002(13)	−0.0030(11)
C(18)	0.4175(10)	0.2254(7)	0.3657(8)	0.0062(10)	0.0054(5)	0.0059(6)	0.0003(11)	0.0019(12)	0.0013(9)
P(2)	−0.1332(3)	0.25734(12)	0.42972(15)	0.0063(3)	0.00219(6)	0.00417(11)	0.00124(18)	0.0028(3)	0.00162(13)
C(21)	−0.2016(12)	0.2543(8)	0.5324(8)	0.0122(14)	0.0063(6)	0.0059(6)	0.0058(14)	0.0111(15)	0.0050(10)
C(22)	−0.1765(9)	0.1721(5)	0.3814(9)	0.0062(9)	0.0023(3)	0.0099(8)	−0.0013(8)	−0.0013(14)	−0.0005(8)
C(23)	−0.2369(8)	0.3175(5)	0.3613(6)	0.0057(8)	0.0029(3)	0.0042(5)	0.0004(8)	0.0010(9)	0.0023(6)
C(24)	−0.2842(10)	0.3769(6)	0.3943(8)	0.0087(11)	0.0031(4)	0.0074(7)	0.0017(10)	0.0042(14)	0.0016(8)
C(25)	−0.3645(11)	0.4209(6)	0.3424(9)	0.0101(12)	0.0031(4)	0.0101(9)	0.0037(11)	0.0065(17)	0.0038(9)
C(26)	−0.3977(12)	0.4051(7)	0.2551(9)	0.0103(13)	0.0054(6)	0.0087(8)	0.0014(13)	0.0009(16)	0.0073(11)
C(27)	−0.3554(13)	0.3472(8)	0.2208(8)	0.0141(15)	0.0056(6)	0.0061(7)	−0.0004(15)	−0.0021(16)	0.0054(10)
C(28)	−0.2731(10)	0.3025(6)	0.2745(8)	0.0086(11)	0.0040(4)	0.0060(6)	0.0016(10)	0.0012(13)	0.0020(8)

C(31)	0.1072(7)	0.1836(4)	0.4498(5)	0.0049(7)	0.00130(18)	0.0030(4)	0.0001(6)	0.0016(8)	0.0002(4)
C(32)	0.1225(8)	0.1398(4)	0.5221(5)	0.0073(8)	0.0022(3)	0.0017(3)	0.0003(7)	0.0024(8)	−0.0001(4)
C(33)	0.1513(8)	0.0697(4)	0.5188(5)	0.0087(9)	0.0016(2)	0.0023(3)	0.0017(7)	0.0007(8)	0.0005(4)
C(34)	0.1664(8)	0.0401(4)	0.4384(6)	0.0057(8)	0.00127(19)	0.0044(4)	0.0007(6)	0.0002(9)	0.0001(5)
C(35)	0.1519(8)	0.0818(4)	0.3642(5)	0.0069(8)	0.0017(3)	0.0031(4)	0.0010(7)	0.0010(9)	−0.0004(5)
C(36)	0.1218(8)	0.1517(4)	0.3712(5)	0.0063(8)	0.0017(2)	0.0025(4)	−0.0004(6)	0.0007(8)	0.0009(4)
Cl(32)	0.1069(3)	0.17641(13)	0.62258(14)	0.0164(4)	0.00262(7)	0.00271(9)	0.0025(3)	0.0027(3)	−0.00021(13)
Cl(33)	0.1757(3)	0.02026(13)	0.61174(15)	0.0163(4)	0.00254(7)	0.00368(10)	0.0039(3)	0.0028(3)	0.00265(14)
Cl(34)	0.2034(3)	−0.04590(12)	0.43080(17)	0.0159(4)	0.00170(6)	0.00565(13)	0.0033(3)	0.0041(4)	0.00034(14)
Cl(35)	0.1766(3)	0.04659(13)	0.26549(15)	0.0168(4)	0.00262(7)	0.00320(10)	0.0022(3)	0.0033(3)	−0.00135(13)
Cl(36)	0.1015(3)	0.20294(11)	0.27687(13)	0.0112(3)	0.00231(6)	0.00268(8)	0.00111(19)	0.0016(3)	0.00139(11)
B	−0.3179(14)	0.0721(7)	0.1586(8)	0.0150(17)	0.0034(4)	0.0046(6)	0.0023(13)	0.0074(16)	0.0010(8)
F(1)	−0.1989(15)	0.0621(11)	0.1873(15)	0.028(3)	0.0190(14)	0.038(3)	0.022(4)	0.027(4)	0.012(3)
F(2)	−0.323(3)	0.0491(7)	0.0820(7)	0.108(6)	0.0076(6)	0.0054(5)	−0.015(3)	0.005(3)	−0.0017(9)
F(3)	−0.3741(16)	0.0383(8)	0.2105(9)	0.056(4)	0.0106(7)	0.0153(10)	−0.022(3)	0.032(3)	0.0028(14)
F(4)	−0.3339(12)	0.1388(5)	0.1612(8)	0.037(3)	0.0042(4)	0.0148(9)	0.0029(13)	0.011(3)	−0.0004(9)

(b) Hydrogen atoms

Positional parameters in fractions of the cell edges and thermal parameters in the form of $\exp[-B(\sin\theta/\lambda)^2]$

Atom	x	y	z	B
H(14)	0.392(8)	0.177(4)	0.566(5)	3.(2)
H(15)	0.495(9)	0.078(5)	0.520(6)	5.(3)
H(16)	0.540(9)	0.068(5)	0.376(6)	5.(3)
H(17)	0.494(9)	0.165(5)	0.277(6)	5.(3)
H(18)	0.401(9)	0.265(5)	0.325(6)	5.(3)
H(24)	−0.259(9)	0.386(5)	0.456(6)	4.(2)
H(25)	−0.393(9)	0.461(5)	0.369(6)	5.(3)
H(26)	−0.452(9)	0.438(5)	0.218(6)	5.(3)
H(27)	−0.381(9)	0.335(5)	0.155(6)	5.(3)
H(28)	−0.239(9)	0.258(5)	0.252(6)	4.(3)

Experimental

The title compound was prepared according to the method reported previously [3], where the BF_4 anion was employed as the counter-anion instead of the ClO_4 anion.

Crystal data. $C_{25}H_{28}Cl_5NiOP_2BF_4$, $M = 729.2$, monoclinic, space group $P2_1/c$, a 10.531(2), b 19.262(6), c 15.495(4) Å, β 98.38(2)°, U 3109.5(13) Å^3, $Z = 4$, D_c 1.558, D_m 1.56 g cm^{-3}, $F(000)$ 1480, μ(Mo-K_α) 12.0 cm^{-1}.

A yellow prismatic crystal with approximate dimensions of 0.20 × 0.25 × 0.33 mm was mounted on a Rigaku automated four-circle diffractometer. Intensity data were collected up to a 2θ value of 54.0° with graphite-monochromatized Mo-K_α radiation (λ 0.71069 Å). The θ–2θ scan technique was employed at a 2θ scan rate of 4° min^{-1} with a scan width of $\Delta 2\theta = (2.0 + 0.70 \tan \theta)°$. Background intensities were measured for 7.5 s at both ends of a scan. The scan was repeated twice for weak reflections ($F < 3\sigma(F)$). Four standard reflections (400, 080, 006 and 036) measured at regular intervals showed no intensity decrease throughout the data collection. A total of 6800 independent reflections was collected, 4808 of which were considered as observed ($|F_o| > 3\sigma(|F_o|)$) and used for the structure determination and refinement. Usual Lp corrections were applied but corrections for absorption and extinction effects were ignored.

The structure was solved by the conventional Patterson and Fourier methods. The structure refinement was carried out by the block-diagonal least-squares procedure (HBLS-V [10]), the function minimized being $\Sigma w(|F_o| - |F_c|)^2$. The isotropic refinements including all the non-hydrogen atoms converged to an R value of 0.150, where $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. After several cycles of anisotropic refinements, 12 hydrogen atoms in the phenyl groups were included and refined isotropically. At the final stages of the refinement, three strong reflections (100, 011 and $\bar{1}23$), which were considered as highly affected by extinction, were omitted. The final R and R_w indices were 0.091 and 0.111 for 4805 observed reflections, respectively, where R_w is defined as $\{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$. The weighting scheme used was $w = (\sigma_{cs}^2 + 0.25|F_o|)^{-1}$, where σ_{cs} is the standard deviation obtained from the counting statistics, although unit weights were employed throughout the early stages of refinements. Atomic scattering factors were taken from International Tables for X-Ray Crystallography [11]. The final atomic parameters are presented in Table 1.

A table of the observed and calculated structure factors is available upon request from the authors.

All computations were carried out on an ACOS 900 computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University.

Results and discussion

A stereoscopic view of the molecular packing in the unit cell as viewed along the c^* axis is illustrated in Fig. 1 (ORTEP drawing [12]). No abnormally short intermolecular atomic contacts are observed, the shortest contact between non-hydrogen atoms being 3.29(3) Å [F(2)(x,y,z)...C(12)($-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$)].

The molecular structure (ORTEP drawing [12]) is shown in Fig. 2. The geometry around the nickel atom is square-planar, the maximum deviation from the least-squares coordination-plane being 0.045 Å. The plane of the carbene ligand defined

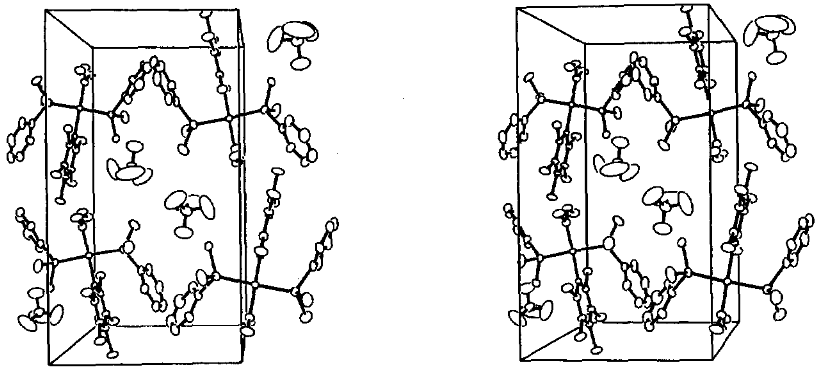


Fig. 1. Stereoscopic view of the molecular packing in the unit cell as viewed along the c^* axis.

by the C(1), C(2) and O atoms is almost perpendicular to the coordination plane, the dihedral angle between these two planes being 88.4°. The ^{1}H NMR study shows that two isomers of the carbene ligand exist in solution owing to hindered rotation about

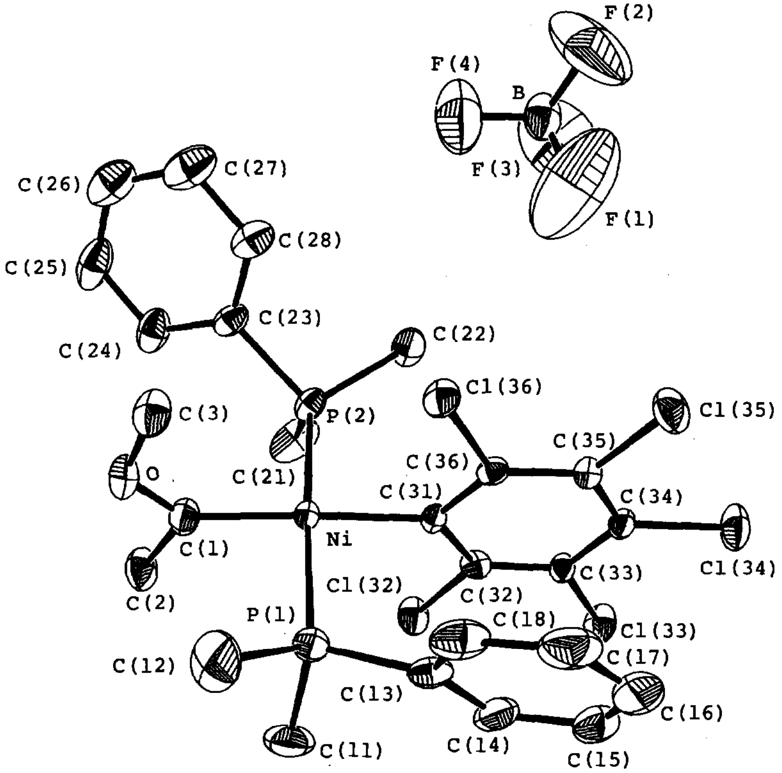
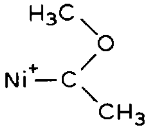
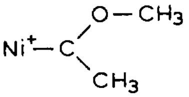


Fig. 2. The molecular structure together with atomic numbering system. Atoms are represented by thermal ellipsoids at 30% probability levels. Hydrogen atoms are omitted for clarity.

the C–O bond, as presented below [3].



(*Z*)



(*E*)

As shown in Fig. 2, the *Z* isomer is observed in the crystal structure, which is consistent with the ^1H NMR spectrum of the fresh solution [3]. In the chromium complex [$Cr(CO)_4(PPh_3)\{C(OMe)Me\}$] containing the present carbene ligand, the methyl(methoxy)carbene ligand takes the *E*-configuration [13], while the *Z* isomer was observed in the platinum complex [$Pt(Me)(PMe_2Ph)_2\{C(OMe)Me\}$]$PF_6$, although the carbene ligand was highly disordered [14]. The pentachlorophenyl group is also located almost perpendicular to the coordination plane (dihedral angle 89.6°). Two dimethylphenylphosphine groups take an eclipsed conformation to each other, with the two phenyl groups lying on opposite sides about the P(1)–Ni–P(2) bonds.

The bond distances and bond angles are listed in Tables 2 and 3, respectively. Table 4 summarizes the Ni^{II}–$C(sp^2)$ bond lengths in the known square-planar

TABLE 2

BOND DISTANCES (Å) WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Ni–C(1)	1.843(10)	Ni–C(31)	1.928(7)
Ni–P(1)	2.232(3)	Ni–P(2)	2.219(3)
C(1)–C(2)	1.536(16)		
C(1)–O	1.261(12)	O–C(3)	1.479(14)
P(1)–C(11)	1.860(14)	P(2)–C(21)	1.840(14)
P(1)–C(12)	1.826(18)	P(2)–C(22)	1.835(13)
P(1)–C(13)	1.833(10)	P(2)–C(23)	1.823(9)
C(13)–C(14)	1.371(14)	C(23)–C(24)	1.377(15)
C(14)–C(15)	1.373(17)	C(24)–C(25)	1.372(18)
C(15)–C(16)	1.362(19)	C(25)–C(26)	1.381(19)
C(16)–C(17)	1.362(20)	C(26)–C(27)	1.339(19)
C(17)–C(18)	1.394(19)	C(27)–C(28)	1.405(18)
C(18)–C(13)	1.377(16)	C(28)–C(23)	1.374(14)
C(31)–C(32)	1.394(11)	C(32)–C(33)	1.387(11)
C(33)–C(34)	1.399(12)	C(34)–C(35)	1.392(11)
C(35)–C(36)	1.391(11)	C(36)–C(31)	1.392(10)
C(32)–Cl(32)	1.739(8)	C(33)–Cl(33)	1.715(9)
C(34)–Cl(34)	1.710(9)	C(35)–Cl(35)	1.727(8)
C(36)–Cl(36)	1.751(8)		
B–F(1)	1.28(3)	B–F(2)	1.26(3)
B–F(3)	1.25(3)	B–F(4)	1.30(2)
C(14)–H(14)	1.02(8)	C(24)–H(24)	0.97(9)
C(15)–H(15)	1.02(10)	C(25)–H(25)	0.95(10)
C(16)–H(16)	0.98(10)	C(26)–H(26)	0.98(10)
C(17)–H(17)	1.00(10)	C(27)–H(27)	1.04(10)
C(18)–H(18)	0.99(10)	C(28)–H(28)	1.01(9)

nickel(II) complexes. The Ni–C(1) bond length in the present complex, which is almost compatible to the Ni–C(carbene) bond length in *trans*-$[\mathrm{Ni}(\mathrm{C_6Cl_5})(\mathrm{PMe_3})_2(\overline{\mathrm{CCH_2CH_2CH_2O}})]\mathrm{BF_4}$ (1.837(7) Å) [9], is one of the shortest $\mathrm{Ni^{II}}$–C(sp^2) bond lengths listed in Table 4. These facts imply that the π-back-bonding from the metal atom to the carbene ligand contributes significantly in the nickel–carbene bond. On the other hand, little π-interaction in the metal–carbene bond was suggested in both $[\mathrm{Cr(CO)_4(PPh_3)}\{\mathrm{C(OMe)Me}\}]$ [13] and $[\mathrm{Pt(Me)(PMe_2Ph)_2}\{\mathrm{C(OMe)Me}\}]\mathrm{PF_6}$ [14]. The Ni–C(31) bond length falls into the range found for the bonds between the nickel and $\mathrm{C_6R_5}$ group (1.88–1.98 Å) in Table 4. Of the bond angles around the C(1) atom, the Ni–C(1)–O angle is quite a bit larger and the O–C(1)–C(2) angle is smaller than the expected value for an sp^2 carbon atom. This may be due to the repulsion between the Ni atom and the C(3) methyl group. The C(1)–O bond distance is much shorter than the normal C–O single bond length, which suggests partial double-bond character due to the resonance structure (c) shown below.

TABLE 3

BOND ANGLES (°) WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

C(1)–Ni–P(1)	90.8(4)	C(1)–Ni–P(2)	91.8(4)
P(1)–Ni–C(31)	89.5(3)	P(2)–Ni–C(31)	87.6(3)
P(1)–Ni–P(2)	176.5(2)	C(1)–Ni–C(31)	175.8(4)
Ni–C(1)–C(2)	120.1(8)	Ni–C(1)–O	130.3(8)
O–C(1)–C(2)	109.6(9)	C(1)–O–C(3)	118.3(9)
Ni–P(1)–C(11)	111.2(5)	Ni–P(2)–C(21)	112.1(5)
Ni–P(1)–C(12)	117.2(6)	Ni–P(2)–C(22)	115.9(5)
Ni–P(1)–C(13)	114.4(4)	Ni–P(2)–C(23)	116.6(4)
C(11)–P(1)–C(12)	102.1(8)	C(21)–P(2)–C(22)	102.7(6)
C(11)–P(1)–C(13)	104.8(6)	C(21)–P(2)–C(23)	104.3(6)
C(12)–P(1)–C(13)	105.7(7)	C(22)–P(2)–C(23)	103.8(6)
P(1)–C(13)–C(14)	120.3(8)	P(2)–C(23)–C(24)	122.0(8)
P(1)–C(13)–C(18)	120.7(8)	P(2)–C(23)–C(28)	119.6(8)
C(14)–C(13)–C(18)	118.6(10)	C(24)–C(23)–C(28)	118.3(10)
C(13)–C(14)–C(15)	119.7(11)	C(23)–C(24)–C(25)	121.4(11)
C(14)–C(15)–C(16)	122.1(13)	C(24)–C(25)–C(26)	119.0(13)
C(15)–C(16)–C(17)	118.9(14)	C(25)–C(26)–C(27)	121.4(13)
C(16)–C(17)–C(18)	119.7(14)	C(26)–C(27)–C(28)	119.1(13)
C(17)–C(18)–C(13)	120.9(12)	C(27)–C(28)–C(23)	120.7(11)
Ni–C(31)–C(32)	125.7(6)	Ni–C(31)–C(36)	119.3(6)
C(36)–C(31)–C(32)	114.9(7)	C(31)–C(32)–C(33)	124.1(8)
C(32)–C(33)–C(34)	118.9(8)	C(33)–C(34)–C(35)	119.2(8)
C(34)–C(35)–C(36)	119.5(8)	C(35)–C(36)–C(31)	123.5(7)
C(31)–C(32)–Cl(32)	117.3(6)	C(33)–C(32)–Cl(32)	118.6(7)
C(32)–C(33)–Cl(33)	121.1(7)	C(34)–C(33)–Cl(33)	120.0(7)
C(33)–C(34)–Cl(34)	120.8(7)	C(35)–C(34)–Cl(34)	120.1(7)
C(34)–C(35)–Cl(35)	119.5(7)	C(36)–C(35)–Cl(35)	121.0(7)
C(35)–C(36)–Cl(36)	118.8(6)	C(31)–C(36)–Cl(36)	117.8(6)
F(1)–B–F(2)	100.6(18)	F(1)–B–F(3)	103.2(17)
F(1)–B–F(4)	105.3(16)	F(2)–B–F(3)	117.5(17)
F(2)–B–F(4)	112.9(16)	F(3)–B–F(4)	114.8(15)

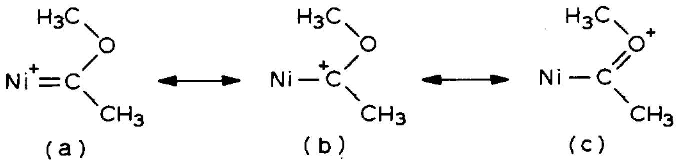


TABLE 4

NICKEL(II)-CARBON (sp^2) BOND LENGTHS IN SQUARE-PLANAR NICKEL(II) COMPLEXES

Complex	Ligand	Length (Å)	Reference
trans-$[Ni(C_6Cl_5)(PMe_3)_2(CCH_2CH_2CH_2O)]BF_4$	$CCH_2CH_2CH_2O$	1.837(7)	9
trans-$[Ni\{C(=O)Me\}Cl(PMe_3)_2]$	$C(=O)Me$	1.84(1)	15
trans-$[Ni(C_6Cl_5)(PMe_2Ph)_2\{C(OMe)Me\}]BF_4$	$C(OMe)Me$	1.843(10)	this work
$[Ni(S{=}CNMe_2)\{C(NMe_2)SC(NMe_2){=}S\}]BPh_4$	$S{=}CNMe_2$	1.854(11)	16
trans-$[Ni(C_6F_5)Br(PPh_2Me)_2]$	C_6F_5	1.880(5)	17
$[Ni(Ph)(PPh_3)\{PPh_2CH{=}C(Ph)O\}]$	C_6H_5	1.893	18
$[Ni\{PhC{=}C(Ph)Me\}(PPh_3)(acac)]$	$PhC{=}C(Ph)Me$	1.897	19
trans-$[Ni(C_6Cl_5)(C_6F_5)(PPh_2Me)_2]$	C_6Cl_5	1.905(10)	20
$[Ni(S{=}CNMe_2)\{C(NMe_2)SC(NMe_2){=}S\}]BPh_4$	$C(NMe_2)SC(NMe_2){=}S$	1.909(10)	16
trans-$[Ni(C_6Cl_5)(PMe_3)_2(C{=}CHCH_2CH_2O)]$	$C{=}CHCH_2CH_2O$	1.909(3)	9
trans-$[Ni(C_6Cl_5)(PMe_3)_2(CCH_2CH_2CH_2O)]BF_4$	C_6Cl_5	1.912(9)	9
trans-$[Ni(C_6Cl_5)(PMe_2Ph)_2\{C(OMe)Me\}]BF_4$	C_6Cl_5	1.928(7)	this work
trans-$[Ni(C_6Cl_5)(PMe_3)_2(C{=}CHCH_2CH_2O)]$	C_6Cl_5	1.930(3)	9
trans-$[Ni\{C_6H_3(OMe)_2\text{-}2,6\}_2(PMe_2Ph)_2]$	$C_6H_3(OMe)_2\text{-}2,6$	1.928(5) 1.931(5) 1.951(5)	21
trans-$[Ni(C_6F_5)_2(PPh_2Me)_2]$	C_6F_5	1.939(3)	22
trans-$[Ni\{C_6H_3(OMe)_2\text{-}2,6\}_2(PMe_3)_2]$	$C_6H_3(OMe)_2\text{-}2,6$	1.933(5) 1.954(5)	21
trans-$[Ni\{C_6H(OMe)_2\text{-}2,6\text{-}Br_2\text{-}3,5\}_2(PMe_2Ph)_2]$	$C_6H(OMe)_2\text{-}2,6\text{-}Br_2\text{-}3,5$	1.945(5)	21
trans-$[Ni\{C_6H(OMe)_2\text{-}2,6\text{-}Br_2\text{-}3,5\}_2(PMe_3)_2]$	$C_6H(OMe)_2\text{-}2,6\text{-}Br_2\text{-}3,5$	1.962(8)	21
trans-$[Ni(C_6Cl_5)(C_6F_5)(PPh_2Me)_2]$	C_6F_5	1.978(10)	20

In conclusion, it is clearly suggested that both the resonance structures (a) and (c) play significant roles in the bonding between the metal and the carbene ligand in the present complex.

References

1 For example, C.P. Casy, H. Alper (Ed.) Transition Metal Organometallics in Organic Synthesis, Vol. 1, Academic Press, New York, 1976, p. 190.
2 M. Wada, N. Asada and K. Oguro, Inorg. Chem., 17 (1978) 2353.
3 K. Oguro, M. Wada and R. Okawara, J. Organomet. Chem., 159 (1978) 417.
4 M. Wada, K. Oguro and Y. Kawasaki, J. Organomet. Chem., 178 (1979) 261.
5 M. Wada, S. Kanai, R. Maeda, M. Kinoshita and K. Oguro, Inorg. Chem., 18 (1979) 417.
6 M. Wada and Y. Koyama, J. Organomet. Chem., 201 (1980) 477.
7 M. Wada, Y. Koyama and K. Sameshima, J. Organomet. Chem., 209 (1981) 115.
8 M. Wada, K. Sameshima, K. Nishiwaki and Y. Kawasaki, J. Chem. Soc., Dalton Trans., (1982) 793.
9 K. Miki, H. Taniguchi, Y. Kai, N. Kasai, K. Nishiwaki and M. Wada, J. Chem. Soc., Chem. Commun., (1982) 1178.
10 T. Ashida, The Universal Crystallographic Computing System-Osaka, The Computation Center, Osaka University, 1979, p. 53.

11 International Tables for X-Ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974, p. 71.
12 C.K. Johnson, ORTEP-II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, 1976.
13 O.S. Mills and A.D. Redhouse, J. Chem. Soc., A, (1969) 1274.
14 R.F. Stepaniak and N.C. Payne, J. Organomet. Chem., 57 (1973) 213.
15 G. Huttner, O. Orama and V. Bejenke, Chem. Ber., 109 (1976) 2533.
16 W.K. Dean, R.S. Charles and D.G. van Derveer, Inorg. Chem., 16 (1977) 3328.
17 M.R. Churchill, K.L. Kalra and M.V. Veidis, Inorg. Chem., 12 (1973) 1656.
18 W. Keim, F.H. Kowaldt, R. Goddard and C. Krüger, Angew. Chem., 90 (1978) 493.
19 J.M. Huggins and R.G. Bergman, J. Am. Chem. Soc., 101 (1979) 4410.
20 M.R. Churchill and M.V. Veidis, J. Chem. Soc., A, (1971) 3463.
21 D. Xu, Y. Kai, K. Miki, N. Kasai, K. Nishiwaki and M. Wada, Bull. Chem. Soc. Jpn., 57 (1984) 1459.
22 M.R. Churchill and M.V. Veidis, J. Chem. Soc., Dalton Trans., (1972) 670.