

**X-Ray Crystal Structure of the Cationic Cyclic Alkyl(alkoxy)carbene Complex of Nickel(II),  $trans$ -[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> and the Corresponding Alkoxy Vinyl Complex,  $trans$ -[Ni(C<sub>6</sub>Cl<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>(C=CHCH<sub>2</sub>CH<sub>2</sub>O)]; Evidence for Strong  $\pi$ -Bonding in the Nickel–Carbene Bond**

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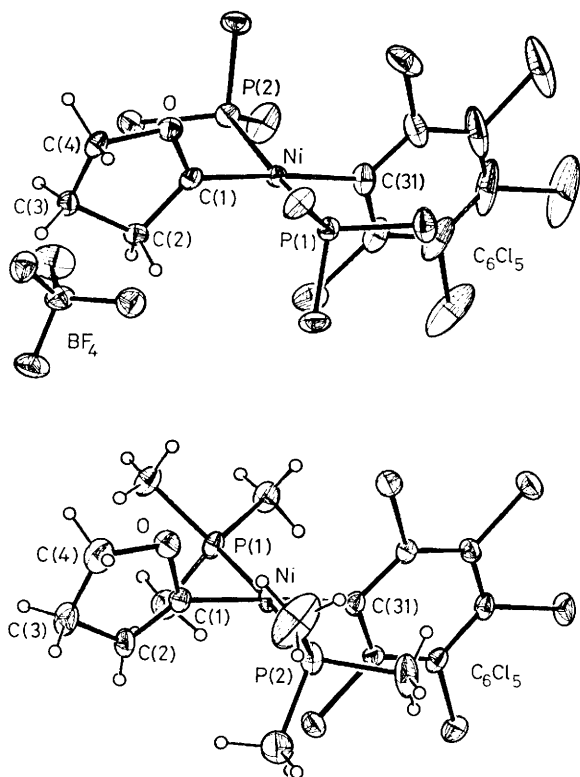
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The molecular structures of the cationic cyclic alkyl(alkoxy)carbene- and the corresponding alkoxyvinyl-nickel(II) complexes  $trans$ -[NiRL<sub>2</sub>(CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O)]BF<sub>4</sub> and  $trans$ -[NiRL<sub>2</sub>(C=CHCH<sub>2</sub>CH<sub>2</sub>O)] (R = C<sub>6</sub>Cl<sub>5</sub> and L = PMe<sub>3</sub>) have been determined by X-ray crystal structure analysis; a comparison of the structures suggests strong  $\pi$ -bonding in the nickel–carbene bond.

The nature of the transition metal–carbene bond is of great interest owing to its importance in transition metal complexes which are intermediates in a variety of organic reactions.<sup>1</sup> However, it is not yet well characterized structurally. A series of organo–nickel(II) carbene 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</sub>-2,4,6, L = PMe<sub>3</sub> or PMe<sub>2</sub>Ph, X = BF<sub>4</sub> or ClO<sub>4</sub>, and carbene = alkyl(alkoxy)carbene] have been prepared and characterized.<sup>2,3</sup> A series of X-ray structure analyses of these com-

plexes was carried out in order to establish the bonding nature of the nickel(II)–carbene bond. We report here the structure of the cationic cyclic alkyl(alkoxy)carbene complex,  $trans$ -[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> (**1**)<sup>3†</sup> and the

<sup>†</sup> After several attempts to obtain good single crystals, the BF<sub>4</sub><sup>-</sup> salt was found to be the most suitable, with respect to size, shape, and quality for an X-ray diffraction study.



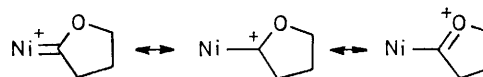
**Figure 1.** The molecular structures of *trans*-[Ni(C<sub>6</sub>Cl<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>(CCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O)]BF<sub>4</sub> (**1**) (upper) and *trans*-[Ni(C<sub>6</sub>Cl<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>(C=CHCH<sub>2</sub>CH<sub>2</sub>O)] (**2**) (lower).

corresponding alkoxyvinyl complex, *trans*-[Ni(C<sub>6</sub>Cl<sub>5</sub>)(PMe<sub>3</sub>)<sub>2</sub>(C=CHCH<sub>2</sub>CH<sub>2</sub>O)] (**2**).<sup>3</sup>

**Crystal data:** (**1**), C<sub>16</sub>H<sub>24</sub>Cl<sub>5</sub>NiOP<sub>2</sub>.BF<sub>4</sub>, *M* = 616.95, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 19.565(4), *b* = 10.552(3), *c* = 13.305(3) Å, β = 109.83(2)°, *U* = 2584.0(10) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.586, *D*<sub>m</sub> = 1.59 g cm<sup>-3</sup>, μ(Mo-*K*<sub>α</sub>) = 14.2 cm<sup>-1</sup>; (**2**), C<sub>16</sub>H<sub>23</sub>Cl<sub>5</sub>NiOP<sub>2</sub>, *M* = 529.15, triclinic, *P*1̄, *a* = 8.945(2), *b* = 11.162(3), *c* = 13.456(3) Å, α = 71.16(3), β = 94.00(2), γ = 114.44(2)°, *U* = 1154.4(5) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.522, *D*<sub>m</sub> = 1.53 g cm<sup>-3</sup>, μ(Mo-*K*<sub>α</sub>) = 15.5 cm<sup>-1</sup>. Intensity data were collected by the θ-2θ scan technique with 2θ up to 54.0°. A Rigaku automated four-circle diffractometer with graphite monochromatised Mo-*K*<sub>α</sub> radiation was used. Both structures were solved by the heavy-atom method and refined anisotropically by the block-diagonal least-squares procedure.‡ All the hydrogen atoms were located on difference Fourier maps except for the methyl hydrogens in (**1**). The final *R* indices for (**1**) and (**2**) are 0.083 and 0.043 for 4096 and 4151 [|*F*<sub>0</sub>| > 3σ(|*F*<sub>0</sub>|)] reflexions, respectively.§

‡ All computations were carried out on an ACOS 700S computer at the Crystallographic Research Centre, Institute for Protein Research, Osaka University.

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.



**Figure 2**

The molecular structures of (**1**) and (**2**) are shown in Figure 1. Selected bond lengths and bond angles are given for comparison in Table 1. The geometry around the nickel atom is square-planar for both complexes. The cyclic carbene ligand in (**1**), the cyclic vinyl group in (**2**), and the pentachlorophenyl groups are almost perpendicular to the coordination plane of the nickel.

On comparison of the two molecular structures the most remarkable feature is that the Ni-C(1) (carbene) bond in (**1**) is about 0.07 Å shorter than the corresponding Ni-C(1) (vinyl) bond in (**2**) and the Ni-C(31) (phenyl) bond in both complexes. The shortening of the Ni-C(1) bond in (**1**) indicates the presence of π-bonding in the nickel-carbene bond. This Ni-C bond length is the shortest Ni-C(sp<sup>2</sup>) bond to be reported, the shortest hitherto being 1.84(1) Å in the nickel-acyl bond of *trans*-[NiCl(PMe<sub>3</sub>)<sub>2</sub>(MeCO)].<sup>4</sup> The C(1)-O bond length in the carbene ligand of (**1**) is significantly shorter than the expected C-O single bond length or the C(4)-O bond length, which suggests a partial double-bond character in the C(1)-O bond due to the resonance structures shown in Figure 2.<sup>2</sup> On the other hand, both the C(1)-O and C(4)-O bond lengths of the vinyl group in (**2**) correspond to the range expected for C-O single bonds. The vinyl C(1)-C(2) bond length is also as expected for a C=C double bond. The Ni-C(31) bond length in (**1**) is slightly shorter than that in (**2**), and this may be due to the difference in *trans*-influence between the carbene and vinyl groups. The Ni-P bond lengths in (**1**) are longer than those in (**2**), which can be understood either by assuming a stronger d<sub>π</sub>-p<sub>π</sub> double bond character in the Ni-P bonding of (**2**) than in (**1**), or by assuming a larger steric interaction between the tertiary-phosphines and the *cis*-organic ligands in (**1**) than in (**2**).

Comparison of the structural parameters of (**1**) and (**2**) revealed the presence of π-bonding in the nickel-carbene bond. This is the first clear evidence for such π-bonding

**Table 1.** A comparison between the selected bond lengths and angles of the carbene complex (**1**) and the vinyl complex (**2**).

	(1)	(2)
	Bond lengths/Å	
Ni-C(1)	1.837(7)	1.909(3)
Ni-P(1)	2.210(2)	2.182(1)
Ni-P(2)	2.206(2)	2.172(1)
Ni-C(31)	1.912(9)	1.930(3)
C(1)-C(2)	1.482(10)	1.326(5)
C(1)-O	1.297(8)	1.402(4)
C(2)-C(3)	1.534(10)	1.499(6)
C(3)-C(4)	1.502(11)	1.463(7)
C(4)-O	1.529(9)	1.443(6)
	Bond angles/deg.	
C(1)-Ni-P(1)	90.3(3)	87.6(1)
C(1)-Ni-P(2)	90.4(3)	87.5(1)
C(31)-Ni-P(1)	89.7(3)	92.4(1)
C(31)-Ni-P(2)	90.0(3)	92.4(1)
Ni-C(1)-C(2)	127.4(6)	133.4(3)
Ni-C(1)-O	122.6(5)	116.4(3)
C(2)-C(1)-O	110.0(6)	110.2(3)
C(1)-C(2)-C(3)	105.9(6)	111.9(4)
C(2)-C(3)-C(4)	102.5(6)	101.3(4)
C(4)-O-C(1)	111.7(6)	107.2(3)

from precise X-ray structure analyses of the carbene and corresponding vinyl complexes of nickel(II).

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