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THE THREE-DIMENSIONAL STRUCTURE OF *trans,trans,trans*-1,5,9-CYCLODODECATRIENENICKEL

D. J. BRAUER and C. KRÜGER
Max-Planck Institut für Kohlenforschung, Lembkestrasse 5, 4330 Mülheim-Ruhr (Germany)

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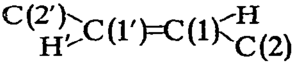
SUMMARY

The crystal structure of all-*trans*-1,5,9-cyclododecatrienenickel, $C_{12}H_{18}Ni$, has been determined from three-dimensional X-ray data collected at room temperature by counter methods. The compound crystallizes in the space group C^6_{2h}–$C2/c$ with four molecules in a unit cell with the dimensions: $a = 14.409(4)$Å, $b = 8.473(1)$Å, $c = 9.001(2)$Å, $\beta = 108.66(3)°$. The calculated density is 1.41 g/cm^3. Full-matrix least-squares refinement yielded a conventional R value of 0.039 based on 581 reflections above background. If one assigns one coordination position to each olefinic double bond, the coordination about the Ni atom is trigonal. The molecule possesses rigorous C_2 crystallographic symmetry; in addition, the molecular dimensions do not deviate significantly from D_3 symmetry. The Ni–C(sp^2) bond lengths average 2.024(2)Å, and the C(sp^2)–C(sp^2) bond lengths average 1.372(5)Å. The  ${}^{C(2')}_{H'}{>}C(1'){=}C(1){<}^{H}_{C(2)}$ fragments are not planar, the C(1)[C(2)]H groups being bent 8(2)° away from the Ni atom. The twelve membered ring shows some signs of angular strain; in particular, the C(1')=C(1)–C(2) angles average 127.5(3)°. The C(1')–C(1) vector forms a 32(1)° angle with the Ni coordination plane.

INTRODUCTION

The coordination of olefins to transition metals has received a great deal of interest. Of particular interest has been the charge distribution in formally zerovalent, trigonal transition metal olefin complexes. The most widely accepted metal olefin bonding scheme is that of Dewar–Chatt–Duncanson: a σ-bond formed by an empty metal hybrid orbital and the π-orbital of the olefin and a π-bond formed by a filled metal d orbital and the π^*-orbital of the olefin[1,2]. The hybridization of and the charge on the metal and carbon atoms has been studied by molecular orbital calculations[3a–c]. Thus in planar, trigonal complexes, the metal atom appears to be dp^2 hybridized, and the olefin receives a small, negative charge. The results are in partial agreement with electron spectroscopy studies of the charge on the metal and carbon atoms in similar complexes[4]. Distortions in the bonded olefin have been inferred from IR studies of Zeise's salt analogs[5] and from NMR studies of Pt^0 complexes[6]. These inferences have been confirmed by a number of X-ray crystal structure investigations of complexes formed with olefin derivatives[7]. The distortions, the bending back of the substituents on the olefin carbon atoms from the metal atom, have been shown by molecular orbital calculations to be consistent with the above bonding model[3c,8]. An additional feature of these structures, the twisting of the olefin out of the coordination plane[7,9a,9b], has received some theoretical attention[3b,10]. Both theoretical studies[3b] and NMR investigations[11] indicate low barriers for these distortions; therefore, the twist angles found in various X-ray structures should also reflect the solid state packing environment of the molecule[7].

The olefinic double bonds of all-*trans*-1,5,9-cyclododecatrienenickel (I) are constrained by the ligand geometry to be twisted out of the coordination plane. If one assigns one coordination position for each double bond, (I) is a trigonal Ni^0 complex[12]. The two-dimensional structural determination of (I) by Dietrich and Schmidt showed that the nickel atom occupies a position very close to the C_3 axis of the ligand[13]. In order to obtain more accurate molecular parameters for this compound, we have determined the crystal structure from a three-dimensional set of X-ray data.

RESULTS AND DISCUSSION

The structure of (I) is shown in Fig. 1. While the crystallographic symmetry of the compound is C_2, the observed molecular symmetry shows no significant deviations from D_3 symmetry. In the following discussions, therefore, we will only refer to the averaged values of the molecular parameters. The same symmetry is reported for the free ligand (II)[14].

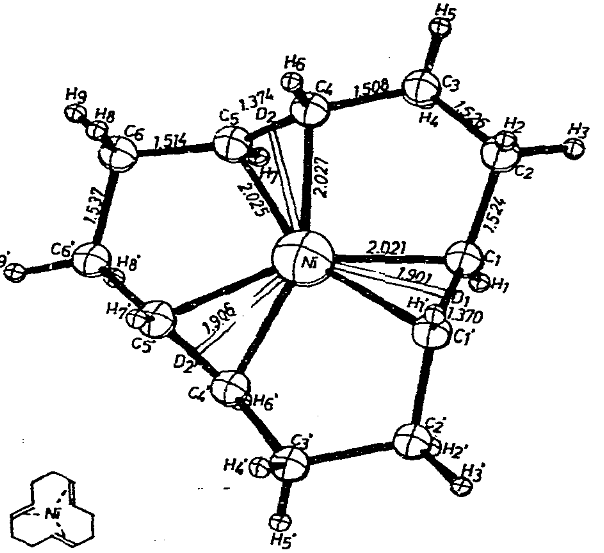
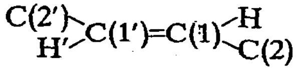


Fig. 1. A perspective drawing of all-*trans*-1,5,9-cyclododecatrienenickel. The standard deviations of the individual bond lengths are: C–C 0.007 Å; Ni–C 0.004 Å.

Best plane calculations show that the ${}^{C(2')}_{H'}\!>\!C(1')=C(1)\!<^{H}_{C(2)}$ fragments of (I)



are significantly nonplanar with the H(1′), C(2′), C(2), H(1) atoms located on the opposite side of the plane with respect to the nickel atom. In the free ligand (II), the analogous fragments are slightly nonplanar as shown by their average torsion angle of 176.9(8)°[14]. The average value of the corresponding torsion angle in (I) is −169.5(5)°. The C=C fragments are buckled towards the center of the molecule in (I) and away from the center of the molecule in (II). The angles formed by the C(1)–C(1′) vectors with the planes C(1), C(2), H(1) average 8(2)°. This small amount of bending back of the C(1), C(2), H(1) groups is consistent with the small difference of the average C=C bond lengths in (I) [1.372(5) Å] and the C=C bond length in *trans*-2-butene [1.347(3) Å][15].

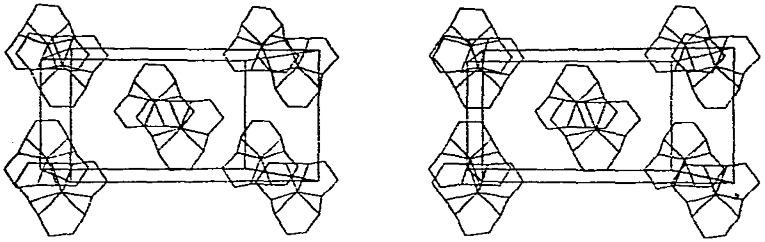


Fig. 2. A stereographic drawing of the all-*trans*-1,5,9-cyclododecatrienenickel unit cell contents as viewed with the *a* axis horizontal and the *b* axis vertical.

TABLE 1

POSITIONAL PARAMETERS FOR $C_{12}H_{18}Ni$

Atom	*x*	*y*	*z*
Ni	0.5000	0.6164(1)[a]	0.2500
C(1)	0.5403(3)	0.3920(5)	0.2255(6)
C(2)	0.6472(3)	0.3784(5)	0.3273(6)
C(3)	0.6993(3)	0.5315(5)	0.3128(6)
C(4)	0.6438(3)	0.6681(5)	0.3510(6)
C(5)	0.5979(3)	0.7887(5)	0.2530(6)
C(6)	0.5551(3)	0.9388(6)	0.2953(7)
H(1)	0.528(4)	0.376(5)	0.101(8)
H(2)	0.649(4)	0.363(6)	0.433(8)
H(3)	0.675(4)	0.285(6)	0.289(7)
H(4)	0.705(4)	0.544(7)	0.197(7)
H(5)	0.758(4)	0.524(7)	0.372(7)
H(6)	0.654(4)	0.676(6)	0.471(7)
H(7)	0.602(4)	0.779(7)	0.139(7)
H(8)	0.565(4)	0.938(7)	0.410(7)
H(9)	0.589(4)	1.039(7)	0.282(6)

[a] Numbers in parentheses throughout the paper represent the estimated standard deviation in the least significant figure.

In Table 2 the average relevant bonded and non-bonded distances and bond angles of (I) and (II) are compared. Upon coordination, the sp^2 carbon atoms are drawn in 0.07(1) Å towards the metal atom, the paraffinic carbon atoms are moved

TABLE 2

A COMPARISON OF THE AVERAGE[a] DISTANCES AND ANGLES IN $C_{12}H_{18}Ni$ WITH THOSE OF THE FREE $C_{12}H_{18}$ LIGAND

	$C_{12}H_{18}Ni$[b]	$C_{12}H_{18}$[c]
Ni–C(sp^2)	2.024(2) Å	2.09(1) Å[d]
Ni–C(sp^2)	2.841(3) Å	2.75(1) Å
C(sp^2)–C(sp^2)	1.372(5) Å	1.32(2) Å
C(sp^2)–C(sp^3)	1.515(4) Å	1.49(2) Å
C(sp^3)–C(sp^3)	1.531(6) Å	1.54(2) Å
C(sp^2)–C(sp^2)–C(sp^3)	127.5(3)°	124.3(3)°
C(sp^2)–C(sp^3)–C(sp^3)	108.2(7)°	111.2(3)°
C–H	1.01(3) Å	
H–C–H	106(4)°	
C–C–H	111(3)°	
Twist angle[e]	32(1)°	33(1)°
ω(C–C=C–C)[f]	−169.5(5)°	176.9(8)°

[a] Weighted average values were taken since the individual values did not show a significant deviation from D_3 symmetry. [b] This work. [c] Ref. 14. [d] The Ni–C contacts for the free ligand were calculated by locating the point along the crystallographic C_2 axis of the molecule equidistant from the midpoints of C(1)–C(1') [M(1)] and C(4)–C(5) [M(2)]. [e] The twist angle is defined as the dihedral angle between the planes Ni, M(1), M(2) and Ni, C(sp^2), C(sp^2) where the sp^2 carbon atoms are bonded to each other. [f] The signs of the torsion angles have been determined according to the convention of Klyne and Prelog[20].

0.09(1) Å away from the nickel atom, and the olefin bond lengths increase by 0.05(2) Å. Since the twist angles, as defined in Table 2, are not significantly different, the observed changes in the two types of C–C–C bond angles may be the result of the minimization of the ring torsional strain induced by the previously described deformations of the ${}^{\text{C(2')}}_{\text{H'}}\!>\!\text{C(1')=C(1)}\!<^{\text{H}}_{\text{C(2)}}$ fragments. In particular, the large C(1')=C(1)–C(2) bond angles of 127.5(3)° must represent some steric strain considering that the free ligand value is 124.3(3)°[14], which is essentially the same as in *trans*-2-butene [123.8(4)°][15], and that some closing of this angle is to be expected upon coordination.

The coordinated C=C bond length is 1.372(5) Å. This distance is somewhat shorter than the corresponding bond lengths observed in $[(C_6H_5)_3P]_2NiC_2H_4$ (IV) [1.431(15) Å][9a] and $(C_6H_{11})_3PNi(C_2H_4)_2$ (III) [1.401(14) Å][16], both of which are essentially planar, trigonal Ni^0 structures. The shortening may result from reduced back donation from the nickel atom to the olefin both because of the greater number of olefins sharing the available electrons for back bonding and because of the twist angle [32(1)°], which probably reduces the chances for strong d_π–$p_{\pi*}$ overlap[3b]. Interestingly, if the latter factor is important in determining the coordinated C=C bond length, attempts at the calculation of the barriers to rotation of coordinated olefins by calculations of the total energy for different twist angles, without optimization of the C=C bond length, should overestimate the barrier.

One might assume that the lengthening of the C=C bond upon coordination to the nickel atom would be correlated with a shortening of the Ni–C bond lengths. For compounds (I), (III) and (IV) the Ni–C bond lengths are 2.024(2) Å, 2.014(12) Å and 1.991(11) Å, respectively. While the variation is in the proper direction, the overall change in the Ni–C values is hardly significant. This observation is surprising since the total of 0.059(16) Å variation in the C=C bond lengths in the series (I), (III) and (IV) represents a change of 0.40(10) in the olefin π-bond-order (calculated with the formula of Cruickshank[17]). Interestingly, in the compound bis-(1,5-cyclooctadiene)-nickel (V), which contains a nickel atom coordinated to four olefinic double bonds, the average coordinated C=C bond length is 1.39(1) Å and the average Ni–C bond length is 2.12(1) Å[18]. Although the D_2 symmetry and the four-coordination of the nickel atom in (V) preclude a strict comparison with (I), (III) and (IV), the point is that the coordinated C=C bond lengths do not appear to reflect the changes in the Ni–C bond lengths.

EXPERIMENTAL

A single crystal of the highly oxygen and moisture sensitive compound (I) was mounted in a dry argon-filled glass capillary*. Weissenberg and precession photographs confirmed that the space group was either C_s^4–Cc or C_{2h}^6–$C2/c$[13]. The crystal data as determined with a diffractometer are: $a=14.409$ (4) Å, $b=8.473$ (1) Å, $c=9.001$ (2) Å, $\beta=108.66$ (3)°, $Z=4$, $D_c=1.41$ g/cm^3. A total of 684 reflections (hkl, $\bar{h}kl$) were measured on a diffractometer (Ni filtered Cu-K_α, $\lambda=1.54178$ Å, $\theta \leq 60°$) and processed as described previously[19]. The variations in the intensity of the monitor reflection, measured after each twenty reflections, indicated that decomposition of the crystal was no more than 5%. The surface of the crystal, however, quickly became obscured by deposits of elemental nickel, and this fact precluded the measurement of the crystal for an absorption correction ($\mu=21.4$ cm^{-1}). The 581 independent observed reflections [$I>2\sigma(I)$] were assigned weights [$w^{-1}=\sigma^2$ (counting)$+(0.3I)^2$] and used in the solution and refinement of the structure. Unobserved reflections were given zero weights.

We assumed that the true space group was $C2/c$. With the aid of a sharpened Patterson map, a position for the nickel atom was located on the C_2 symmetry axis. A subsequent difference Fourier synthesis revealed the positions of the six carbon atoms in the asymmetric unit. The structure was refined by full-matrix least-squares techniques. The function minimized was $\Sigma w \cdot \Delta^2$, $\Delta=||F_0|-|F_c||$. After anisotropic refinement of the nickel and six carbon atoms, the values of the discrepancy indices $R_1=\Sigma\Delta/\Sigma|F_0|$ and $R_2=[\Sigma w \cdot \Delta^2/\Sigma w \cdot |F_0|^2]^{\frac{1}{2}}$ were 0.063 and 0.089, respectively. A difference Fourier synthesis clearly revealed the positions of the nine hydrogen atoms (0.29–0.51 e/Å^3). These atoms were assigned temperature factors of $U=0.07$ Å. Positional parameters for all atoms and anisotropic thermal parameters for the non-hydrogen atoms were refined smoothly to yield 0.039 for R_1 and 0.051 for R_2. The error of fit was 1.91. On the final least-square cycle, the shifts of the non-hydrogen atom parameters were all less than a tenth of their corresponding standard deviations, and the shifts of the hydrogen atom parameters were all less than seven tenths of their corresponding standard deviations. Least-squares refinement of the structure in the polar space group Cc did not yield a reasonable structure even though somewhat lower discrepancy indices were obtained. We conclude that the low discrepancy indices and the reasonable structure obtained are good evidence for the space group

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* The crystalline material was prepared according to the published procedure[12] by Dr. P. W. Jolly of this Institute.

being *C2/c*. The final positional parameters are listed in Table 1. The numbering scheme is shown in Fig. 1*.

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* After completion of this work, Dr. Dietrich communicated to us the results of his successful three-dimensional Fourier refinement of (I) using film data obtained from a twinned crystal. Having obtained single crystals of this compound and having used diffractometer data, we have been able to obtain more precise molecular parameters.