The plot of pH *vs.* $E_{1/2}$ for the reduction of Mo(VI) to Mo(V) indicates two electrode reactions are involved, depending on pH. From pH 2.5 to 5.0 it is probable that two hydrogen ions are involved in the reduction (slope = 1.82) while from pH 5.0 to 7.0 only one hydrogen ion is involved (slope = 0.88). This difference undoubtedly reflects changes in the state of polymerization of molybdate with pH. A similar phenomenon was observed by Pecsok and Sawyer[3] with EDTA complexes of Mo(VI).

It is clear that under the proper conditions of pH and ligand concentration, gluconic acid will serve satisfactorily in the polarographic determination of Mo(VI). Furthermore, the data reported here indicate the possibility of the existence of other complexes with α-hydroxy acids, some of which may be of biochemical significance.

Acknowledgment.—Thanks are expressed by the authors to the Public Health Service (Grant GM-08347-1, Division of General Medical Sciences) for financial support.

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Structure and Nature of Bonding of $C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$[1]

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Received December 21, 1962

The structure of $C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$ has been determined from an X-ray analysis. The crystals contain four molecules in a monoclinic unit cell of symmetry Cc and dimensions $a = 13.40 \pm 0.02$ Å., $b = 13.78 \pm 0.02$ Å., $c = 7.88 \pm 0.01$ Å., and $\beta = 94°45' \pm 10'$. Final least-squares refinement has yielded discrepancy factors of $R_1 = 6.8\%$ and $R_2 = 7.5\%$ for 978 observed reflections. The structure consists of discrete molecules in which a Ni(II) is covalently bonded to a π-cyclopentadienyl anion and a bicyclo[2.2.1]heptadienyl (*i.e.*, norbornadienyl) anion which coördinates to the metal *via* a σ-bond from the bridged carbon atom and a μ-bond from the olefinic group to which the methyl carboxylate substituents are attached. The $C_5H_5NiC_5H_5C_2$ fragment possesses an approximate mirror plane which passes through the nickel, one carbon of the cyclopentadienyl ring, and the bridge carbon and mid-points of the olefinic bonds of the norbornadienyl moiety. The Ni(II)–bridged carbon distance of 1.964 ± 0.012 Å. represents the first known value for a nickel bonded to a tetrahedral carbon atom. The unconjugated olefinic bond is symmetrically linked to the Ni(II) with an average Ni–C distance of 1.970 ± 0.009 Å.; the nickel distance to the mid-point of the olefinic bond is 1.83 Å. The olefinic C–C distance of 1.450 ± 0.016 Å. is significantly longer than the C–C distance of 1.330 ± 0.021 Å. for the uncoördinated olefin (of normal double bond length). A detailed comparison of the structural features of the norbornadienyl group in $C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$ is made with those of the norbornadiene molecule itself and the molecule in chelated form as norbornadienedichloropalladium(II). Structural evidence for a small localized interaction between the Ni(II) and the cyclopentadienyl anion is given from the bond lengths and resulting molecular conformation. This specific interaction is ascribed to the perturbation of the π-electron density on the $C_5H_5^-$ anion by the ring's MO interaction with the dsp^2-type hybrid orbitals of the Ni(II). The nature of this bonding is discussed with respect to recently found localized metal interactions with other π-organic systems.

Introduction

Alkyne complexes of binuclear cyclopentadienylnickel have been reported[3-5] in which an alkyne group as a distinct molecular entity utilizes its π-orbitals for bonding to each of the two nickel atoms by an electron-pair μ-type bond.[6] More recently a second type of cyclopentadienylnickel alkyne complex has been prepared by Dubeck[7] by the reaction of dicyclopentadienylnickel with dimethylacetylene dicarboxylate. Elemental analysis and molecular weight measurements suggested a mononuclear nickel complex formed by a bimolecular coupling of the two reactants. On the basis of the compound's diamagnetism, n.m.r. spectrum, and degradative products, Dubeck[7] proposed a molecular model arising from the interaction of a nickel(II) with a π-cyclopentadienyl anion and with two electron-pair donors, one donor an aliphatic carbon (formerly a cyclopentadienyl carbon atom) and the other a nonconjugated olefinic group (formerly the alkyne).

The present X-ray study of $C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$ has confirmed the over-all configuration of Dubeck's model. The molecular geometry provides evidence for a small localized interaction between the Ni(II) and the cyclopentadienyl anion. The nature of this bonding is described, and the criteria presumably necessary for the formation of similarly localized cyclopentadienyl–metal interactions are given. A detailed comparison of the molecular features of the compound with those of norbornadiene[8] and norbornadienedichloropalladium(II)[9] is made.

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(1) Presented in part at the 7th International Conference on Coördination Chemistry, Stockholm and Uppsala, Sweden, June, 1962.

(2) Based in part on a dissertation submitted by Chin Hsuan Wei to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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Experimental Procedure

The compound was generously made available to us by Drs. Filbey and Dubeck of the Ethyl Corporation. The sample was recrystallized from toluene, and a small needle crystal of average width 0.06 mm. and length 0.26 mm. was used for obtaining intensity data without absorption correction. The density of the crystal was measured by flotation in both 2-iodopropane–tetrachloroethane solutions and 2-iodopropane–carbon tetrachloride solutions.

The unit cell lengths were determined from both Weissenberg and precession photographs; β was measured from precession photographs.

Multiple-film equiinclination photographs were obtained for nine reciprocal levels ($hk0$ through $hk8$) with Zr-filtered Mo Kα radiation. Timed-exposure precession photographs of $0kl$ data also were obtained with Mo Kα radiation. Both Weissenberg and precession intensity data consisting of 978 independent reflections were estimated visually with the aid of an internal standard and then corrected for Lorentz polarization effects. The corrected precession intensity data were used to place the corrected Weissenberg intensity data on a common scale. Final adjustment of scale factors for different Weissenberg levels was made by least-squares refinement.

Results

Unit Cell and Space Group.—Crystals of $C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$ (mol. wt. 331.0; m.p. *ca.* 85°) are monoclinic with $a = 13.40 \pm 0.02$ Å., $b = 13.78 \pm 0.02$ Å., $c = 7.88 \pm 0.01$ Å., $\beta = 94°45' \pm 10'$; volume of unit cell = 1450 Å.^{3}; $\rho_{\text{obsd}} = 1.50$ g. cm.$^{-3}$ *vs.* $\rho_{\text{calcd}} = 1.52$ g. cm.$^{-3}$ for four molecules per unit cell. The total number of electrons per unit cell, $F(000) = 688$. The linear absorption coefficient for Mo Kα radiation ($\lambda = 0.7107$ Å.) is 14 cm.$^{-1}$. Systematic absences, $\{hkl\}$ for $h + k$ odd, $\{h0l\}$ for l odd, and $\{0k0\}$ for k odd, indicate either Cc or C2/c as the probable space group; the choice of Cc(C_s^4) was confirmed by the structural determination. All atoms occupy the general fourfold set of positions (4a): $x, y, z;\ x, -y, {}^1/_2 + z;\ +$C centering.[10]

Determination of the Structure.—The structural analysis of the compound required the location of one nickel, sixteen carbon, and four oxygen atoms (and ideally the sixteen hydrogen atoms) which correspond to one molecule. The other three molecules in the unit cell are related by the space group symmetry.

A three-dimensional Patterson function was computed from the corrected intensities. An interpretation of the resulting maps revealed the positions of the nickel atoms in the unit cell. Since the symmetry requirements of the space group Cc do not specify the origin of the unit cell in the a and c lattice-vector directions, the x and z coördinates of the asymmetric nickel atom arbitrarily were chosen at ${}^1/_4a$ and ${}^1/_2c$, respectively, and were not varied. A three-dimensional isotropic least-squares refinement of the nickel's y coordinate and its thermal parameter (initially given an estimated value of 2.0 Å.^{2}) was carried out. After two cycles a discrepancy index, $R_1 = [\Sigma||F_0| - |F_c||/\Sigma|F_0|] \times 100$, of 26.9% was obtained, which indicated that the nickel atoms were placed correctly in the unit cell.

A three-dimensional Fourier synthesis based only on the phases of the nickel atoms was computed next. A fundamental difficulty arose concerning the interpretation of the peaks obtained on the maps. Although the structure is not centrosymmetric, the nickel atoms are related to one another by centers of symmetry, and hence their phase contributions to the structure factors are such as to result in a superposition of electron-density peaks for two structures—the partially correct structure and its centrosymmetrically related image. On the basis of presumed bond distances and probable conformation, an assignment of eight Fourier peaks as a nickel atom, a five-membered cyclopentadienyl ring, and two carbon atoms was made. Two cycles of least-squares refinement of the positional and thermal parameters of these eight atoms resulted in a decrease of R_1 to 22.1%. Another three-dimensional Fourier function was computed from the refined phases for the eight atoms. By this procedure, which magnifies the peaks corresponding to the coördinates of the other atoms in the correct structure and eliminates the pseudosymmetrically related images, nine new peaks were identified. This "true-structure magnifying" procedure was repeated once more to locate the remaining atoms. Finally, another isotropic least-squares refinement was carried out for all twenty-one non-hydrogen atoms. After six cycles positional and thermal parameters remained constant well within the limits of their standard deviations. The final discrepancy values, R_1 and $R_2 = [\Sigma w||F_0| - |F_c||^2/\Sigma w|F_0|^2]^{1/2} \times 100$, are 6.8 and 7.5%, respectively, for the 978 non-zero reflections; the final value of the error of fit function, $[w||F_0| - |F_c||^2/(m - n)]^{1/2}$, is 1.157.[11] In these calculations the Sly–Shoemaker Fourier program[12] was used for the Patterson and Fourier syntheses, and the Busing–Levy full matrix least-squares program[13] was employed for the least-squares refinements. The weights[14] for the individual reflections were assigned as

$$\sqrt{w} = 10/F_0 \qquad \text{if } F_0 \geq 4F_{0,\min}$$
$$\sqrt{w} = F_0/1.6F_0{}^2{}_{,\min} \qquad \text{if } F_0 < 4F_{0,\min}$$

The refined structure was confirmed by a calculation of a three-dimensional difference synthesis which revealed no residual peak heights greater than 0.6 electron/Å.^{3}. No attempt was made to identify any of these peaks as due to hydrogen atoms. For the calculation of structure factors the atomic scattering factors of

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(10) "International Tables for X-Ray Crystallography," Vol. I The Kynoch Press, Birmingham, England, 1952, p. 89.

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TABLE I

FINAL ATOMIC PARAMETERS AND STANDARD DEVIATIONS

Atom	x	y	z	B, Å.^{2}	$10^4\sigma_x$	$10^4\sigma_y$	$10^4\sigma_z$	σB, Å.^{2}
Ni	0.2500	0.1864	0.5000	2.28	0	1	0	0.05
C_1	.2467	.2496	.1952	3.28	10	12	13	.24
C_2	.1582	.2135	.2977	3.02	11	9	14	.22
C_3	.1500	.2866	.4283	2.82	11	9	13	.21
C_4	.2321	.3628	.3996	3.70	11	12	15	.24
C_5	.2052	.4139	.2298	4.90	13	13	17	.31
C_6	.2146	.3457	.1127	4.25	12	12	16	.29
C_7	.3082	.2839	.3551	3.17	11	10	14	.23
C_8	.0783	.1539	.2215	2.80	10	9	13	.21
C_9	− .0404	.0187	.2519	7.36	19	18	25	.48
C_{10}	.0675	.2990	.5348	3.33	11	11	14	.23
C_{11}	.0061	.3894	.7615	4.89	14	13	19	.30
C_{12}	.3766	.1317	.6426	3.62	12	12	14	.24
C_{13}	.3248	.0549	.5498	3.55	11	11	14	.23
C_{14}	.2279	.0431	.6110	4.04	12	12	16	.27
C_{15}	.2202	.1206	.7378	4.21	13	12	16	.27
C_{16}	.3122	.1678	.7546	3.65	12	11	16	.26
O_1	.0483	.1614	.0751	4.55	9	9	12	.21
O_2	.0464	.0820	.3198	4.55	9	9	12	.20
O_3	− .0086	.2483	.5284	5.60	10	12	14	.27
O_4	.0844	.3706	.6436	4.39	8	9	11	.19

Thomas and Umeda[15] were used for nickel while those of Berghuis, *et al.*,[16] were used for carbon and oxygen.

Table I shows the final positional and isotropic thermal parameters together with their standard deviations obtained from the last cycle of least-squares refinement. The intramolecular distances, bond angles, and intermolecular distances less than 4.0 Å., which were calculated from the positional parameters of the last least-squares cycle with the Busing–Levy function and Error program,[17] are listed in Tables II, III, and IV, respectively. With the aid of the Smith program[18] the equations of planes formed by several sets of atoms and the separations of these and other atoms from the planes were calculated and are given in Table V. Individual weights were assigned to the atoms which form the planes according to the relation $w_k = [a\sigma(x_k)b\sigma\cdot(y_k)c\sigma(z_k)]^{-2/3}$, where $\sigma(x)_k$, $\sigma(y_k)$, and $\sigma(z_k)$ are standard deviations expressed as fractional coördinates of the final positional parameters x_k, y_k, and z_k, respectively. The equation of the least-squares plane is expressed in orthogonal coördinates X, Y, and Z, which are related to the monoclinic cell coördinates by the transformation $X_k = ax_k + cz_k \cos \beta$, $Y_k = by_k$, and $Z_k = cz_k \sin \beta$.

Discussion

The structure, defined by the parameters of Table I and by the coördinates of the equivalent positions of the space group, consists of discrete $C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$ molecules of the configuration shown in Fig. 1. The molecular complex is formed by a Diels–Alder type addition of the dimethylacetylene dicarboxylate molecule to the non-adjacent carbon atoms of one cyclopentadienyl ring of nickelocene such that the acetylene fragment emerges as an olefinic coördinating group. The resulting bicyclo[2.2.1]heptadienyl moiety coördinates to the Ni(II) *via* a σ-bond from the bridged carbon atom (C_7) and a μ-bond from the olefinic group. The over-all configuration suggested by Dubeck[7] is substantiated and hence the complex is correctly named as [2,3-bis-(methoxycarbonyl)-2π,5-norbornadien-7-yl]-(π-cyclopentadienyl)-nickel(II).

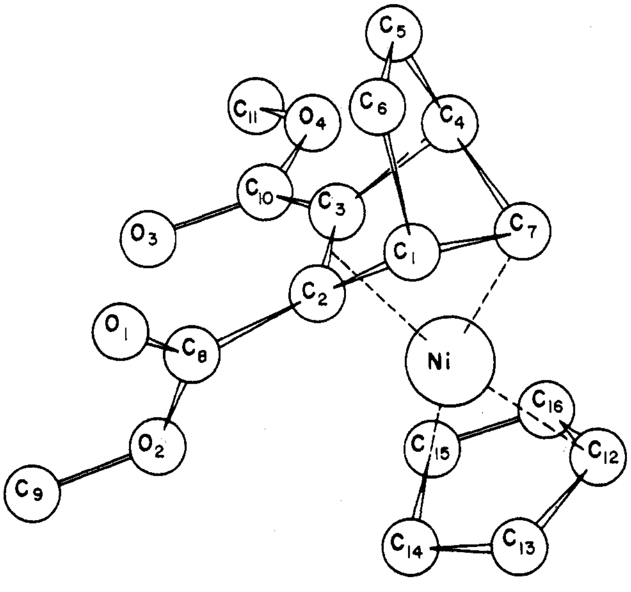

Fig. 1.—The molecular configuration of $C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$

A geometric feature of prime importance to the description of the bonding in the molecule (discussed later) is the orientation of the cyclopentadienyl ring about the nickel(II) with respect to the organometallic coördinating groups of the norbornadienyl system (see Fig. 1). The C_{14} and C_{15} atoms (taken as a pair) and

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TABLE II

INTRAMOLECULAR DISTANCES WITH STANDARD DEVIATIONS

Bond	Distance, Å.	Bond	Distance, Å.
Ni–C_1	2.552 ± 0.011	C_7–C_1	1.522 ± 0.016
–C_2	1.965 ± 0.012	–C_4	1.550 ± 0.020
–C_3	1.975 ± 0.013	C_1–C_6	1.522 ± 0.020
–C_4	2.561 ± 0.015	C_4–C_5	1.529 ± 0.019
–C_5	3.809 ± 0.016	C_6–C_5	1.330 ± 0.021
–C_6	3.759 ± 0.014	C_2–C_3	1.450 ± 0.016
–C_7	1.964 ± 0.012		
–C_{12}	2.096 ± 0.015	C_1–C_2	1.569 ± 0.017
–C_{13}	2.091 ± 0.014	C_4–C_3	1.551 ± 0.019
–C_{14}	2.191 ± 0.016	C_2–C_8	1.442 ± 0.015
–C_{15}	2.148 ± 0.013	C_3–C_{10}	1.450 ± 0.017
–C_{16}	2.122 ± 0.012	C_8–O_1	1.193 ± 0.014
–M[a]	2.041 ± 0.012	C_{10}–O_3	1.235 ± 0.018
–N[a]	1.831 ± 0.011	C_8–O_2	1.350 ± 0.015
C_{12}–C_{13}	1.433 ± 0.019	C_{10}–O_4	1.314 ± 0.016
C_{13}–C_{14}	1.432 ± 0.021	O_2–C_9	1.513 ± 0.025
C_{14}–C_{15}	1.472 ± 0.019	O_4–C_{11}	1.479 ± 0.018
C_{15}–C_{16}	1.394 ± 0.021		
C_{16}–C_{12}	1.375 ± 0.019		

[a] M and N denote the mid-points of the C_{14}–C_{15} and C_2–C_3 bonds, respectively.

TABLE III

BOND ANGLES WITH STANDARD DEVIATIONS

Angle	Degrees	Angle	Degrees
C_{12}–Ni–C_{13}	40.0 ± 0.5	C_6–Ni–C_2	37.1 ± 0.4
C_{13}–Ni–C_{14}	39.0 ± 0.6	C_5–Ni–C_3	36.1 ± 0.4
C_{14}–Ni–C_{15}	39.6 ± 0.5	Ni–C_7–C_1	93.2 ± 0.8
C_{15}–Ni–C_{16}	38.1 ± 0.6	–C_4	92.8 ± 0.8
C_{16}–Ni–C_{12}	38.0 ± 0.5		
		Ni–C_1–C_6	133.0 ± 0.8
C_{12}–C_{13}–C_{14}	109.0 ± 1.2	–C_4–C_5	135.8 ± 1.0
C_{13}–C_{14}–C_{15}	105.3 ± 1.2		
C_{14}–C_{15}–C_{16}	106.9 ± 1.3	Ni–C_6–C_5	82.0 ± 0.9
C_{15}–C_{16}–C_{12}	111.5 ± 1.3	–C_5–C_6	77.7 ± 0.9
C_{16}–C_{12}–C_{13}	107.1 ± 1.3		
C_1–C_7–C_4	94.8 ± 1.1	Ni–C_2–C_3	68.8 ± 0.6
C_7–C_1–C_6	101.5 ± 1.1	–C_3–C_2	68.0 ± 0.7
C_7–C_4–C_5	103.7 ± 1.0		
C_1–C_6–C_5	110.9 ± 1.2	C_7–C_2–C_3	71.2 ± 0.8
C_4–C_5–C_6	104.7 ± 1.4	–C_3–C_2	71.1 ± 0.8
		C_1–C_2–C_3	104.5 ± 1.0
C_7–Ni–C_{12}	102.4 ± 0.5	C_4–C_3–C_2	105.6 ± 1.0
–C_{13}	119.6 ± 0.6		
–C_{14}	157.1 ± 0.5	C_6–C_1–C_2	107.3 ± 1.1
–C_{15}	155.0 ± 0.5	C_5–C_4–C_3	108.6 ± 1.2
–C_{16}	119.1 ± 0.5		
		Ni–C_2–C_7	55.2 ± 0.5
C_2–Ni–C_{12}	158.0 ± 0.5	–C_3–C_7	55.1 ± 0.5
–C_{13}	125.1 ± 0.5	C_2–C_7–C_3	37.7 ± 0.5
–C_{14}	113.6 ± 0.5		
–C_{15}	129.6 ± 0.6	Ni–C_2–C_8	128.6 ± 0.8
–C_{16}	163.6 ± 0.5	–C_3–C_{10}	116.5 ± 0.8
C_3–Ni–C_{12}	154.8 ± 0.5		
–C_{13}	164.4 ± 0.5	C_2–C_8–O_1	122.3 ± 1.0
–C_{14}	129.4 ± 0.5	C_3–C_{10}–O_3	125.3 ± 1.2
–C_{15}	111.9 ± 0.5		
–C_{16}	124.0 ± 0.5	C_2–C_8–O_2	116.0 ± 0.9
		C_3–C_{10}–O_4	111.6 ± 1.2
C_7–C_1–C_2	92.9 ± 0.9	O_1–C_8–O_2	121.3 ± 1.0
–C_4–C_3	92.6 ± 1.1	O_3–C_{10}–O_4	123.1 ± 1.3
C_2–Ni–C_3	43.2 ± 0.5	C_8–O_2–C_9	119.2 ± 1.1
		C_{10}–O_4–C_{11}	116.9 ± 1.2
C_7–Ni–C_2	69.5 ± 0.5	C_1–C_2–C_8	122.2 ± 0.9
–C_3	69.4 ± 0.6	C_4–C_3–C_{10}	126.1 ± 1.1
C_1–Ni–C_2	37.9 ± 0.5	C_2–C_3–C_{10}	126.8 ± 1.2
C_4–Ni–C_3	37.2 ± 0.5	C_3–C_2–C_8	126.3 ± 1.1

the C_{12} atom of the cyclopentadienyl ring form an approximately eclipsed configuration with the olefinic bond atoms (C_2 and C_3) and the bridged alkyl atom (C_7), respectively, of the norbornadienyl group.

The least-squares plane (Table V(f)) formed by C_{12}, M (the mid-point of C_{14}–C_{15}), C_7, and N (the mid-point of C_2–C_3) passes within 0.007 Å. of these four points and within 0.02 Å. of the nickel(II). Moreover, the C_{14}–C_{15} and C_2–C_3 bonds are nearly perpendicular to this best plane (88 and 89°, respectively). As seen from Table V(f), to a first approximation all the other atoms of the cyclopentadienyl ring, the norbornadienyl group, and the two carboxyl carbons are related in pairs on both sides of this plane by a mirror plane operation. Hence, the norbornadienyl fragment possesses *idealized* C_s-m symmetry.

The Ni(II)–C_7 distance of 1.96 ± 0.01 Å. represents the first known value for a nickel attached *via* a σ-bond to a tetrahedral carbon atom. This distance is close to the predicted single bond length of 1.92 Å. based on the accepted covalent radii of nickel (1.15 Å.) and a tetrahedrally hybridized carbon atom (0.77 Å.).

The nickel(II) is symmetrically linked to the two olefinic carbon atoms, C_2 (1.965 Å.) and C_3 (1.975 Å.). The mean Ni–C distance is 1.970 ± 0.009 Å.; the nickel distance to the mid-point of C_2–C_3 is 1.83 Å. As expected, the C_2–C_3 distance of 1.450 ± 0.016 Å. for the olefin coördinated to the Ni(II) is significantly longer than the C_6–C_5 distance of 1.330 ± 0.021 Å. for the uncoördinated olefin which is of normal double bond length. Similarly increased C–C bond lengths in olefinic groups coördinated to metals have been observed for $C_7H_8PdCl_2$ (1.460 ± 0.036 Å. and 1.460 ± 0.038 Å.),[9] $[C_8H_8PdCl_2]_2$ (1.45 ± 0.07 Å.),[9] $K(PtCl_3{\cdot}C_2H_4)H_2O$ (*ca.* 1.5 Å.),[19] *trans*-$[Pt(C_2H_4)(CH(CH_3)_2)Cl_2]$ (1.47 ± 0.18 Å.),[20] and $Co_4(CO)_{10}(C_2H_5C_2C_2H_5)$ (1.440 ± 0.020 Å.).[21]

The four carbon atoms (C_1, C_4, C_8, and C_{10}) attached to the olefinic group (C_2 and C_3) are displaced away from the nickel atom. The carbon atoms C_2 and C_3 are located 0.29 and 0.20 Å. from the least-squares plane formed by C_1, C_4, C_8, and C_{10} (Table V(e)). The dihedral angle between the two planes each formed by the olefinic carbons (C_2 and C_3) and two *cis*-bonded carbons (*i.e.*, one mean plane formed from C_2, C_3, C_1, C_4, and the other mean plane formed from C_2, C_3, C_8, C_{10}) is approximately 158°.

This distortion of the σ-framework of the normally sp^2 hybrid orbitals of C_2 and C_3 arising from the donation of the two π-electrons to the nickel(II) also is re-

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[19] J. A. Wunderlich and D. P. Mellor, *Acta Cryst.*, **7**, 130 (1954); J. A. Wunderlich and D. P. Mellor, *ibid.*, **8**, 57 (1955).

[20] P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *ibid.*, **13**, 149 (1960).

[21] L. F. Dahl and D. L. Smith, *J. Am. Chem. Soc.*, **84**, 2450 (1962).

TABLE IV

INTERMOLECULAR DISTANCES LESS THAN 4.0 Å.[a]

Atoms	Distance, Å.	Atoms	Distance, Å.
$C_{16}\ldots O_3^{III}$	3.301	$C_{12}\ldots O_1^{III}$	3.730
$O_4\ldots C_5^{I}$	3.426	$C_6\ldots C_{11}^{VII}$	3.812
$C_{14}\ldots O_2^{VI}$	3.501	$C_1\ldots C_{16}^{VII}$	3.823
$C_{14}\ldots C_8^{VI}$	3.526	$C_{11}\ldots C_5^{I}$	3.825
$C_{11}\ldots C_{13}^{V}$	3.544	$C_{14}\ldots C_{13}^{VI}$	3.836
$C_{11}\ldots C_{12}^{V}$	3.604	$C_{11}\ldots C_{12}^{IV}$	3.845
$C_7\ldots O_1^{III}$	3.606	$C_{16}\ldots C_{13}^{VI}$	3.849
$O_3\ldots C_1^{V}$	3.632	$O_2\ldots O_1^{VI}$	3.909
$C_{11}\ldots C_{13}^{IV}$	3.638	$O_2\ldots C_9^{VI}$	3.940
$C_{15}\ldots C_{13}^{VI}$	3.647	$C_{16}\ldots C_{10}^{III}$	3.943
$C_{12}\ldots O_3^{III}$	3.682	$C_{14}\ldots C_9^{VI}$	3.944
$C_9\ldots O_1^{VI}$	3.686	$C_7\ldots C_9^{II}$	3.945
$C_{11}\ldots C_7^{V}$	3.689	$C_{12}\ldots C_{10}^{III}$	3.962
$C_5\ldots C_9^{II}$	3.695	$C_{11}\ldots C_1^{V}$	3.967
$C_{14}\ldots O_1^{VI}$	3.701	$C_{14}\ldots C_2^{VI}$	3.970
$C_{15}\ldots C_{14}^{VI}$	3.701	$C_6\ldots O_4^{VII}$	3.972
$O_1\ldots C_{15}^{VII}$	3.702	$C_9\ldots C_9^{VI}$	3.975
$C_{15}\ldots O_2^{VI}$	3.724	$C_4\ldots C_9^{II}$	3.985
$O_3\ldots C_7^{V}$	3.729	$C_{15}\ldots C_9^{VI}$	3.995

[a] Superscripts refer to the following positions

I	$x,$	$-y,$	$1/2+z$
II	$1/2+x,$	$1/2+y,$	z
III	$1/2+x,$	$1/2-y,$	$1/2+z$
IV	$-1/2+x,$	$1/2+y,$	z
V	$-1/2+x,$	$1/2-y,$	$1/2+z$
VI	$x,$	$-1-y,$	$1/2+z$
VII	$x,$	$y,$	$-1+z$

TABLE V

EQUATIONS OF MOLECULAR PLANES AND DISTANCES OF ATOMS FROM THESE PLANES (IN Å.) FOR $C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$[a]

(a) Plane through C_{12}, C_{13}, C_{14}, C_{15}, and C_{16}

$$-0.301X + 0.648Y - 0.700Z + 3.749 = 0$$

C_{12}	−0.002	C_{16}	−0.014
C_{13}	0.014	Ni	1.75
C_{14}	−0.025		
C_{15}	0.025		

(b) Plane through C_1, C_4, C_2, and C_3

$$-0.600X + 0.509Y - 0.617Z + 1.101 = 0$$

C_1	−0.001	Ni	−1.82
C_4	0.001	C_7	−0.97
C_2	0.001	C_8	0.56
C_3	−0.001	C_{10}	0.28

(c) Plane through C_1, C_4, C_6, and C_5

$$0.967X + 0.252Y - 0.047Z - 3.869 = 0$$

C_1	−0.000	Ni	−0.48
C_4	0.000	C_7	0.76
C_6	0.001		
C_5	−0.001		

(d) Plane through C_2, C_3, C_8, and C_{10}

$$-0.280X + 0.714Y - 0.642Z - 0.119 = 0$$

C_2	−0.060	Ni	−1.65
C_3	0.055	C_1	0.46
C_8	0.025	C_4	0.64
C_{10}	−0.030		

(e) Plane through C_1, C_4, C_8, and C_{10}

$$-0.471X + 0.631Y - 0.617Z + 0.204 = 0$$

C_1	−0.069	C_2	−0.29
C_4	0.079	C_3	−0.20
C_8	0.042		
C_{10}	−0.052		

(f) Plane through C_{12}, M (the mid-point of C_{14}–C_{15}), C_7, and N (the mid-point of C_2–C_3)

$$0.142X - 0.699Y - 0.701Z + 4.143 = 0$$

C_{12}	−0.007	C_1	1.11
M	0.007	C_4	−1.15
C_7	0.006	C_6	0.59
N	0.005	C_5	−0.74
		C_2	0.72
Ni	0.02	C_3	−0.73
C_{13}	1.15	C_8	1.57
C_{16}	−1.10	C_{10}	−1.60
C_{14}	0.74		
C_{15}	−0.73		

(g) Plane through C_7, C_1, and C_4

$$0.510X + 0.667Y - 0.543Z - 3.082 = 0$$

C_6	1.04	C_2	−1.41
C_5	1.07	C_3	−1.39

(h) Plane through C_2, C_8, O_1, O_2, and C_9

$$0.713X - 0.639Y - 0.288Z + 1.178 = 0$$

C_2	−0.002	O_2	0.027
C_8	−0.033	C_9	−0.060
O_1	0.014		

(i) Plane through C_3, C_{10}, O_3, O_4, and C_{11}

$$-0.393X + 0.633Y - 0.667Z + 0.416 = 0$$

C_3	−0.005	O_4	0.002
C_{10}	0.008	C_{11}	−0.008
O_3	−0.002		

[a] X, Y, and Z are othogonal coördinates expressed in Å.

flected in the bond angles of the carbon atoms attached to C_2 and C_3. The magnitudes of these angles (Table III) can be explained by the interaction between the olefinic bond and nickel(II) which causes an unsymmetrical charge distribution, thereby destroying the geometrical restrictions which the olefinic double bond places upon attached substituents.

Both of the methyl carboxylate substituents and the carbons to which they are attached are approximately planar. Although least-squares calculations show the methyl carbon (C_9) of one methyl carboxylate to be 0.06 Å. from the mean plane formed by atoms C_2, C_8, O_1, O_2, and C_9 (Table V(h)), all the atoms of the other methyl carboxylate are within 0.008 Å. of the mean plane formed by C_3, C_{10}, O_3, O_4, and C_{11} (Table V(i)). The methyl carboxylate group comprised of atoms C_{10}, O_3, O_4, and C_{11} lies approximately in a plane with the olefinic carbons (C_2 and C_3), while the other methyl carboxylate group comprised of atoms C_8, O_1, O_2, and C_9 is twisted out of the mean plane of the first methyl carboxylate group by a rotation of 119.5° about the C_2–C_8 bond. The resulting orientations of the two methyl carboxylate groups, which can be attributed to steric factors, destroys the idealized C_s-m symmetry for the whole molecule.

The corresponding C_2–C_8 and C_3–C_{10} distances of 1.44 ± 0.01 and 1.45 ± 0.01 Å., respectively, are comparable to the single bond distance of 1.48 Å. for trigonally hybridized carbon atoms.[22–24] The average distances of 1.22 ± 0.01 and 1.33 ± 0.01 Å. for the shorter and longer C–O bonds, respectively, in the carboxylate groups are close to the accepted values[25] of

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(22 D. R. Lide, Jr., *Tetrahedron*, **17**, 125 (1962).

(23) B. P. Stoicheff, *ibid.*, **17**, 135 (1962).

(24) O. Bastiansen and M. Traetteberg, *ibid.*, **17**, 147 (1962).

(25) "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, 1958, p. S17.

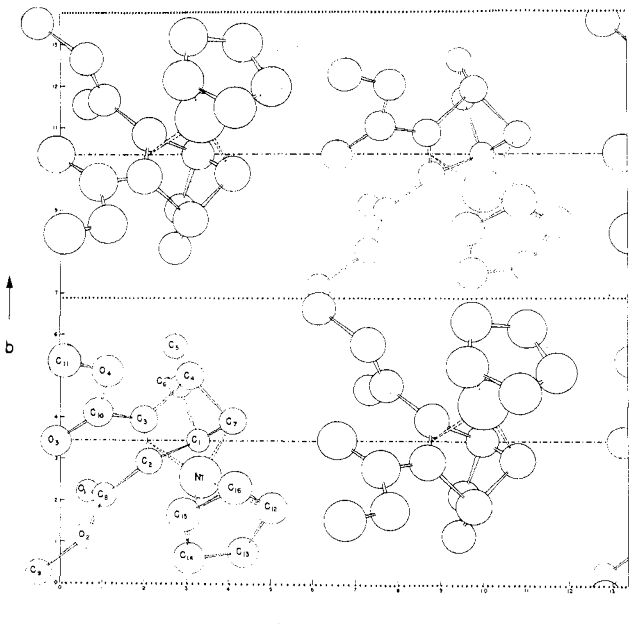

Fig. 2.—[001] projection of the unit cell.

1.23 ± 0.01 and 1.36 ± 0.01 Å., respectively. The O–CH_3 bond lengths of 1.51 ± 0.2 and 1.48 ± 0.02 Å. are compatible with those found in methyl formate (1.47 ± 0.04 Å.)[26] and methyl acetate (1.46 ± 0.04 Å.).[26]

The [001] projection of the unit cell shown in Fig. 2 indicates the packing in the molecular crystal as determined by the symmetry operations of the space group Cc. The closest intermolecular contacts (Table IV) of 3.3 Å. indicate no abnormal interactions between molecules.

Of interest is a comparison of the structural features of the norbornadienyl group in $C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$ with those of the norbornadiene molecule itself[8] and the molecule in chelated form as the norbornadiene–dichloropalladium(II) complex.[9] Partial results of an unpublished electron diffraction study of the norbornadiene molecule carried out by Schomaker are reported by Wilcox, *et al.*,[8] in their MO calculations of the ground state of the bicycloheptadiene molecule. A careful X-ray examination of $C_7H_8PdCl_2$ by Baenziger and co-workers[9] showed the palladium(II) to be symmetrically linked to the two double bonds of the norbornadiene, whereas in the nickel(II) complex the nickel(II) is bonded to the bridged carbon and one double bond of the norbornadienyl moiety. The molecular configuration of the palladium(II) complex (Fig. 3) is required by space group symmetry to possess a vertical mirror plane which passes through the bridged carbon (C_7) and the mid-points of the double bonds of the norbornadiene as well as through the palladium and chlorine atoms. The norbornadiene unit in $C_7H_8PdCl_2$, like the norbornadiene molecule itself, possesses *idealized* C_{2v} symmetry within the limits of accuracy imposed by the standard deviations of the final positional parameters and resulting bond lengths and angles. Unlike the symmetrically bonded palladium complex, the unsymmetrically bonded norbornadienyl fragment in $C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$ necessarily is distorted, and hence, as mentioned earlier, possesses only *idealized* C_s-m symmetry with the approximate mirror plane passing through the bridged carbon atom and mid-points of the olefinic bonds.

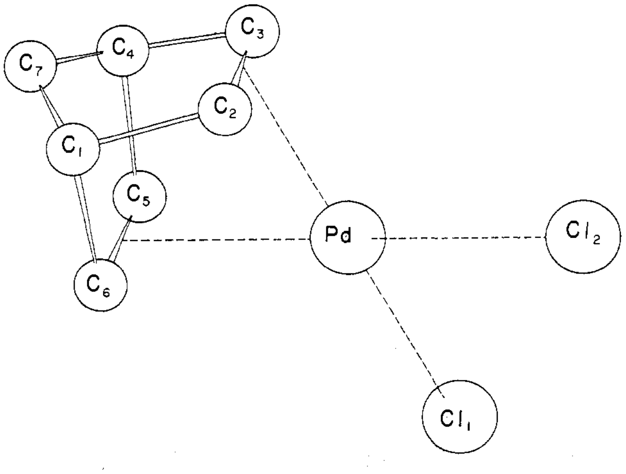

Fig. 3.—The molecular configuration of $C_7H_8PdCl_2$.

The corresponding intramolecular distances, bond angles, and dihedral angles for the three compounds are listed in Table VI. As a whole the agreement of equivalent distances and angles is good. Although there are significant differences in the C–C bond lengths in the metal-coördinated and uncoördinated olefinic groups, the other differences in corresponding norbornadienyl distances do not appear to be physically meaningful. The similar values (2.26–2.30 Å.) for the non-bonding distance between the bridgehead carbons show the apparent insensitivity of the bridged group to differences of 0.13 Å. in the olefinic bond length. The close agreement between the C–C bond lengths in the coördinated olefinic groups in the palladium (both 1.46 Å.) and nickel (1.45 Å.) complexes indicates similar electronic interaction of the olefinic groups with the two metals. As expected, the average palladium distance (2.04 Å.) to the mid-point of the two double bonds is 0.21 Å. longer than the corresponding nickel distance (1.83 Å.) to the mid-point of C_2–C_3; the difference in single-bond covalent radii for palladium (1.28 Å.) and nickel (1.15 Å.) is 0.13 Å.

A comparison of the norbornadienyl bond angles is more informative. The similar magnitudes of the sharp bridge angle in the norbornadiene molecule (95.4°) and those in the nickel (94.8°) and palladium (93.0°) complexes indicates considerable molecular strain of the bicyclic ring system in all three compounds in accord with the known stereochemistry of norbornadiene.[27] Additional evidence for the strained character of the normally tetrahedrally coördinated bridge carbon (C_7) in the nickel complex is given by the still sharper Ni–C_7–C_1 and Ni–C_7–C_4 bond angles of 93.2 and 92.8°, respectively.

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(26) J. M. O'Gorman, W. Shad, and V. Schomaker, *J. Am. Chem. Soc.*, **72** 4222 (1950).

(27) *Cf.* E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 303.

TABLE VI[a]

COMPARISON OF NORBORNADIENYL GEOMETRY IN $C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$, $C_7H_8PdCl_2$,[9] AND C_7H_8[8]

(a) Intramolecular distances, Å.

Atoms	$C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$	$C_7H_8PdCl_2$ (C_s symm.)	C_7H_8 (C_{2v} symm.)
C_1–C_7	1.52 ± 0.02	1.55 ± 0.02	1.56
C_4–C_7	1.55 ± 0.02		
C_1–C_6	1.52 ± 0.02	1.50 ± 0.02	1.52
C_4–C_5	1.53 ± 0.02		
C_1–C_2	1.57 ± 0.02	1.54 ± 0.02	1.52
C_4–C_3	1.55 ± 0.02		
C_2–C_3	1.45 ± 0.02	1.46 ± 0.04	1.33
C_6–C_5	1.33 ± 0.02	1.46 ± 0.04	
$C_1 \ldots C_4$	2.26 ± 0.02	2.25	2.30
$C_2 \ldots C_6$	2.49 ± 0.02	2.37	2.37
$C_3 \ldots C_5$	2.50 ± 0.02		
Metal–N	1.83 ± 0.01	2.04 (av.)	

(b) Bond angles, deg.

Angle	$C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$	$C_7H_8PdCl_2$ (C_s symm.)	C_7H_8 (C_{2v} symm.)
C_1–C_7–C_4	94.8 ± 1.1	93.0	95.4
C_7–C_1–C_6	101.5 ± 1.1	102.1	96.4
–C_4–C_5	103.7 ± 1.0		
C_7–C_1–C_2	92.9 ± 0.9	101.6	96.4
–C_4–C_3	92.6 ± 1.1		
C_2–C_1–C_6	107.3 ± 1.1	102.1	102.2
C_3–C_4–C_5	108.6 ± 1.2		
C_1–C_2–C_3	104.5 ± 1.0	104.9	109.1
C_4–C_3–C_2	105.6 ± 1.0		
C_1–C_6–C_5	110.9 ± 1.2	105.3	109.1
C_4–C_5–C_6	104.7 ± 1.4		

(c) Dihedral angle between two planes of non-bridged carbon atoms of two bicyclic rings, deg.

Planes	$C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$	$C_7H_8PdCl_2$	C_7H_8
C_2, C_3, C_1, C_4 and C_6, C_5, C_1, C_4	115.0	107.5	110.8

[a] N denotes both the mid-point of the C_2–C_3 bond in $C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$ and the mid-points of the C_2–C_3 and C_5–C_6 bonds in $C_7H_8PdCl_2$. The non-bonding intramolecular distances and dihedral angle of C_7H_8 were calculated from Schomaker's electron diffraction data (reported by Wilcox, *et al.*[8]) for which no standard deviations were given. The non-bonding intramolecular distances, bond angles, and dihedral angle in $C_7H_8PdCl_2$ were calculated from the final positional parameters reported by Baenziger, *et al.*[9]

For both metal complexes, the six angles (only four of which are crystallographically independent) adjacent to a double bond coördinated to the metal range from 104.5 to 105.6°. For the nickel complex the angles adjacent to the normal double bond average 108° compared to 109° for norbornadiene, still considerably less than the normally trigonal coplanar angle of 120°.

Although the three independent bond angles involving the vertex bridgehead carbons (C_1 and C_4) are equal within 1° and average 102° for $C_7H_8PdCl_2$ (of *idealized* C_{2v} symmetry), the corresponding bridgehead bond angles in $C_5H_5NiC_5H_5C_2(CO_2CH_3)_2$ (of *idealized* C_s-m symmetry) are not similar to one another. The equivalent C_2–C_1–C_6 and C_3–C_4–C_5 angles average 108°. However, the average value of 93° for the equivalent C_7–C_1–C_2 and C_7–C_4–C_3 angles is significantly less than the average value of 103° for the equivalent C_7–C_1–C_6 and C_7–C_4–C_5 angles. This latter difference in bond angles can be ascribed primarily to the deformation of the bridged carbon by the Ni–C_7 σ-bond interaction. The plane (Table V(g)) formed by the nickel-bonded bridged carbon atom (C_7) and the two attached bridgehead carbons (C_1 and C_4) is bent at the bridgehead carbons toward the nickel(II) such that the coördinated olefinic carbon atoms (C_2 and C_3) both are approximately 0.35 Å. further away (1.40 Å. (av.) *vs.* 1.055 Å. (av.)) from this plane than the uncoördinated olefinic carbon atoms (C_6 and C_5). The six non-bridged carbon atoms of the two bicyclic rings form two planes (Tables V(b) and V(c)) within 0.001 Å. which intersect along a line through the bridgehead carbons with a dihedral angle of 115.0°. The bridged carbon (C_7) is displaced 0.97 and 0.76 Å., respectively, from these planes.

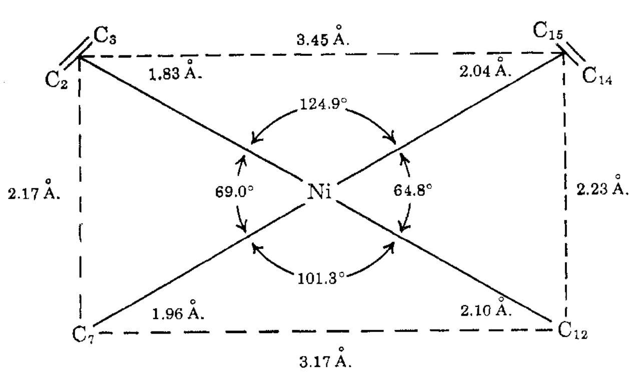
For $C_7H_8PdCl_2$ a least-squares plane calculation from the final data of Baenziger, *et al.*,[9] yielded a dihedral angle of 107.5°, which is only 7.5° smaller than the value for the nickel compound. Since the corresponding dihedral angle for the norbornadiene molecule itself was determined to be 110.8°, which is approximately midway between the values for the metal complexes, it can be concluded that the organometallic μ-bond interaction for the metal complexes, which occurs on opposite sides of the bicycloheptadienyl ring, causes *at most* a symmetric deformation of the six non-bridged carbon atoms of only 4°. For the palladium complex the bridged carbon (C_7) was found to be symmetrically displaced (mean value 0.86 Å.) by 0.87 Å. out of the mean plane formed by the C_1, C_4, C_2, and C_3 atoms and by 0.85 Å. out of the mean plane formed by the C_1, C_4, C_6, and C_5 atoms. Another "best" plane calculation for the palladium complex revealed that the two pairs of corresponding atoms (C_2 and C_6, C_3 and C_5) which under *idealized* C_{2v} symmetry are all equivalent, are separated by an average distance of 1.185 Å. (the mean of 1.16 and 1.21 Å.) from the plane formed by the three carbon atoms (C_7, C_1, and C_4) common to both cyclopentene rings. It should be noted that these mean values of 0.86 and 1.185 Å. agree well with the average values (0.865 and 1.23 Å.) of the unsymmetrical distances in the nickel complex. The above results show that, aside from the obvious change in double bond length due to coördination to a metal, the basic carbon skeleton of the norbornadienyl ring is essentially unaltered in all three compounds. For the nickel compound the symmetrical deformation of the bridged carbon and the difference in olefinic bond distances for the norbornadienyl fragment with subsequent loss of *idealized* C_{2v} symmetry and with the retention of only the *idealized* vertical mirror are readily understood from organometallic bonding considerations.

The present widely accepted view of the organometallic interaction of a π-cyclopentadienyl ring with a metal is that in all cases the entire ring is bonded uniformly to the metal atom by the overlap of a circularly symmetric set of π-type orbitals on the $C_5H_5^{-1}$ anion with a corresponding circularly symmetric set of orbitals on the metal atom. Structural evidence for a small localized interaction between the nickel(II) and the cyclopentadienyl anion is given from the bond lengths and resulting molecular conformation cited previously. This specific interaction can be ascribed to the perturbation of the π-electron density on the $C_5H_5^{-1}$ anion by the ring's interaction with the dsp^2-type hybrid orbitals of the nickel(II). The tendency of four-coordinated Ni(II) complexes to form tetragonal complexes is well known. Presumably, the influence of the two ligands (*e.g.*, the olefinic bond and bridged carbon (C_7) of the norbornadienyl fragment) attached on one side of the nickel(II) can induce the formation of dsp^2-type hybrid Ni(II) orbitals; the other two hybrid orbitals are directed toward C_{12} and the mid-point of the C_{14}–C_{15} bond of the cyclopentadienyl ring.

In accord with this proposed localized interaction, the C_{14}–C_{15} bond (1.47 Å.) is somewhat longer than the other C–C cyclopentadienyl ring bonds (C_{12}–C_{13}, 1.43 Å.; C_{13}–C_{14}, 1.43 Å.; C_{15}–C_{16}, 1.39 Å.; C_{16}–C_{12}, 1.38 Å.). Of greater significance is that the Ni–C distances to C_{14} (2.19 Å.) and C_{15} (2.15 Å.) are longer than those to C_{12} (2.10 Å.), C_{13} (2.09 Å.), and C_{16} (2.12 Å.); the nickel distance to the mid-point of C_{14}–C_{15} is approximately 2.04 Å. The maximum deviations of the five cyclopentadienyl ring carbons from the best plane formed by these carbon atoms (Table V(a)) is 0.025 Å.

Although the proton n.m.r. spectrum of the nickel complex in solution shows only a single resonance line for the $C_5H_5^{-1}$ group with an intensity signifying five equivalent hydrogens, it should be noted that a similar difference between the n.m.r. and X-ray results exists for the molecular conformation of (COT)-$Fe(CO)_3$[28,29] which has been attributed[29] to a dynamical effect involving internal ring rotation relative to the $Fe(CO)_3$ group.

The distances and angles of the four ligands which interact with the dsp^2-type hybrid orbitals of the nickel(II) are indicated below in a schematic diagram.



The angle of 14° formed by the line from the Ni(II) to the center of the olefinic bond, C_2–C_3, and the normal to the plane formed by the four carbons attached to the olefinic carbons (*i.e.*, the normal of the best plane comprised of the two bridgehead carbons, C_1 and C_4, and the two carboxyl carbons, C_8 and C_{10}, presumably represents the direction of the π-orbitals of the olefin; an angle of only 4° results when the π-orbital direction is assumed to be given by the normal to the plane formed by C_1, C_4, C_2, and C_3) shows to a first approximation that the π-bonding MO of the olefin is pointed almost directly at the Ni(II). The larger angle of 31° formed by the line from the Ni(II) to the center of C_{14}–C_{15} and the normal of the mean plane of the cyclopentadienyl ring carbons indicates that the π-AO's of the C_{14}–C_{15} carbons (and likewise the π-AO of C_{12}) would form bent bonds with the dsp^2-type hybrid orbitals of the Ni(II). A similar "bent" bond can be rationalized for the Ni–C_7 interaction. Hence, the bond angles given in the above sketch do not coincide with the directions of the hybrid orbitals of Ni(II).

The differences in the Ni–C and C–C bond lengths for the cyclopentadienyl ring are on the borderline of statistical significance. However, it should be expected that this σ-bond perturbation can be small and that the C_5H_5 ring remains aromatic to a large degree.[30,31] This localized metal–C_5H_5 interaction presumably may be found for cyclopentadienyl compounds (*e.g.*, $C_5H_6RhC_5H_5$ and $C_8H_{12}RhC_5H_5$) of other metals besides Ni(II), such as Rh(I) and Ir(I), which have a characteristic tendency to use dsp^2-type hybrid orbitals for σ-bonding. Only relatively unstable cyclopentadienyl compounds have been reported for Pd(II) and attempts to isolate cyclopentadienyls of Pt(II) which form very stable σ-type organic compounds thus far have been unsuccessful.[32] Additional X-ray work on other cyclopentadienyl compounds is in progress to confirm the proposed structural principle of localized metal–C_5H_5 bonding.

This proposed localized bonding between the π-orbitals of the organic system and the transition metal is not without precedent. A structural determination of 2,4,6-triphenylcycloheptatrienoneiron tricarbonyl[33] conclusively showed the bonding of a diene group to $Fe(CO)_3$ to involve a three-point Diels–Alder type interaction in which the $Fe(CO)_3$ fragment is linked to the terminal carbon atoms by two σ-bonds and to the central double bond by a μ-bond. The non-planarity of the cyclopentadienone ring in $C_5H_5Co(CH_3C_2CH_3)_2$-CO[34] can be explained by a small contribution of a similarly localized metal interaction with the cyclic diene group. Still another example of a three-point localized interaction involving a cyclopentadiene ring with a metal has been found for $C_5H_5Co(C_5H_5C_6H_5)$,[35] whereas for $(C_6H_5C_2C_6H_5)_2Fe(CO)_3$[36] and $[(CH_3C_2CH_3)_2$-$NiCl_2]_2{\cdot}C_6H_6$[37] structural evidence points to a four-point interaction of the metal with the cyclobutadiene group for which the bonding presumably is of a de-

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[28] B. Dickens and W. N. Lipscomb, *J. Am. Chem. Soc.*, **83**, 4862 (1961).

[29] B. Dickens and W. N. Lipscomb, *J. Chem. Phys.*, **37**, 2084 (1962).

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localized nature. Clearly more structural work on these types of complexes is needed before more definite ideas of bonding can be systematized.

Acknowledgment.—We are indebted to the National Science Foundation (Grant No. 86-3474) for the financial support of this work and to the Numerical Analysis Laboratory of the University of Wisconsin for the use of the CDC 1604 computer.

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The Cation Dicyclopentadienyldicarbonylvanadium(III)

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Received December 10, 1962

Vanadium hexacarbonyl behaves as an oxidizing agent in non-polar solvents. The reaction at 15° of $V(CO)_6$ with dicyclopentadienylvanadium(II) and CO at atmospheric pressure gives the hexacarbonylvanadate of the new cationic species $[V(C_5H_5)_2(CO)_2]^+$. Yields of the diamagnetic solid are almost quantitative. The cation is isoelectronic with the neutral compound $Ti(C_5H_5)_2(CO)_2$.

Introduction

Calderazzo and Calvi[1] recently have isolated the hexacarbonylvanadate of the cation vanadium(0) π-tropylium-π-cycloheptatriene, $[V(C_7H_7)(C_7H_8)]$-$[V(CO)_6]$ in the course of the reaction between $V(CO)_6$ and C_7H_8. It was suggested also that the compound could be formed by a mechanism of intermolecular hydride elimination involving a molecule of $V(CO)_6$ from an intermediate $V(C_7H_8)(CO)_3$, followed by further substitution of carbon monoxide.

This suggestion has led us to study the reaction of vanadium hexacarbonyl with dicyclopentadienylvanadium in an attempt to prove that vanadium hexacarbonyl can act, in some cases, as an oxidizing agent in non-polar solvents. Such a reaction would provide additional evidence relative to the proposed mechanism of reaction.

Results

Preliminary experiments had shown that equimolecular quantities of $V(CO)_6$ and $V(C_5H_5)_2$ dissolved in heptane or toluene reacted readily at room temperature *under a nitrogen atmosphere*, with formation of nonvolatile brown-red compounds. However, the infrared spectra and analyses of reaction products clearly showed that a mixture of at least two different compounds was formed.

Further and similar experiments, carried out at 15° *under an atmosphere of carbon monoxide* in a gas-volumetric apparatus, led to a very brisk uptake of two moles of CO per mole of $V(C_5H_5)_2$ employed. An orange precipitate of $[V(C_5H_5)_2(CO)_2][V(CO)_6]$ (I) was formed in a high yield according to the scheme

$$V^{II}(C_5H_5)_2 + V^0(CO)_6 + 2CO \longrightarrow [V^{III}(C_5H_5)_2(CO)_2][V^{I-}(CO)_6]$$

The hexacarbonylvanadate of the new cationic species $[V(C_5H_5)_2(CO)_2]^+$ is moderately stable in air in the dry state, whereas its solutions in tetrahydrofuran or acetone must be handled under nitrogen. It is not sublimable, it is insoluble in H_2O and aliphatic and aromatic solvents, and sparingly soluble in CS_2. It is diamagnetic either in solution (sharpness of the peaks in the n.m.r. spectrum) or in the solid state (magnetic susceptibility measurements).

The infrared spectra of I showed three bands in the carbonyl stretching region at about 2050 (s), 2010 (s), and 1860 (ss) cm.$^{-1}$, the latter one being attributed[2-4] to the anion $[V(CO)_6]^-$.

A single C–H stretching frequency was found at about 3120 cm.$^{-1}$, while other infrared absorptions due to π-bonded cyclopentadienyl rings were located in the region between 7 and 12 μ as outlined in the Experimental section. The n.m.r. spectrum of I in acetone (10% solution by weight) showed only one sharp proton resonance peak centered at 1.48 ± 0.02 p.p.m. from benzene to high fields. π-Bonded cyclopentadienyl rings in diamagnetic dicyclopentadienyl metals and cyclopentadienyl metal carbonyls dissolved in toluene[5] or tetrahydrofuran[6] have a single proton resonance peak between 2.5 and 3.2 p.p.m. relative to benzene. The lower shift found in our case does not seem to be due only to a solvent effect; a decreased electron density in the rings therefore probably is responsible for the unusually low value of the chemical shift.

The salt-like character of I was demonstrated by preparing from it some derivatives of the cationic component.

By treatment of I with iodine in toluene the anionic carbon monoxide was quantitatively displaced at room temperature, whereas pyridine as a solvent, higher temperatures, very long reaction times, and a strong

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