

Structure and ^{13}C Nuclear Magnetic Resonance Spectrum of Bis(cyclopentadienyl)ethyl(ethylene)niobium

L. J. Guggenberger,* P. Meakin, and F. N. Tebbe

Contribution No. 2048 from the Central Research Department,
E. I. du Pont de Nemours and Company, Experimental Section,
Wilmington, Delaware 19898. Received August 29, 1973

Abstract: The structure of $(\text{C}_5\text{H}_5)_2\text{Nb}(\text{C}_2\text{H}_5)(\text{C}_2\text{H}_4)$ was determined from room-temperature X-ray counter data. The molecular structure has the niobium bound to two nonparallel η^5 -cyclopentadienyl ligands and ethyl and ethylene ligands in the plane between the C_5H_5 rings; the resultant molecular symmetry is idealized $\text{C}_s(m)$. Both cyclopentadienyl rings are planar with a 47.6° dihedral angle between the rings. The mean Nb–C distances are 2.402 (5) Å to C_5H_5 , 2.316 (8) Å to C_2H_5 , and 2.299 (21) Å to C_2H_4 . The olefin C–C distance is 1.406 (13) Å. All hydrogen atom positions were refined; the ethylene hydrogens are bent significantly away from niobium, the dihedral angle between CH_2 's being 52° . The ^{13}C and ^1H nmr spectra of solutions of $(\text{C}_5\text{H}_5)_2\text{Nb}(\text{C}_2\text{H}_5)(\text{C}_2\text{H}_4)$ and $(\text{C}_5\text{H}_5)_2\text{Nb}(\text{C}_2\text{H}_4)$ in benzene- d_6 at room temperature have been recorded and analyzed. The nmr spectra indicate that the C_5H_5 ligands are fluxional at room temperature in both complexes. The exchange of the two distinct ends of the ethylene ligand is slow on the nmr time scale in both cases at 27° . The olefinic carbon resonances are shifted 94–115 ppm upfield on coordination to niobium. Crystals are tetragonal, space group $I4_1/a$, with $a = 16.481$ (2) and $c = 18.186$ (2) Å. The structure was solved by heavy-atom techniques and refined by least-squares to a conventional R of 0.044.

There has been a good deal of recent interest in bis(cyclopentadienyl)–transition metal complexes.^{1–3} Generally, the structures of these complexes are based on bent cyclopentadienyl rings with the remaining ligands bound in the horizontal mirror plane between the C_5H_5 rings. There is some controversy regarding the actual disposition of the hybridized valence orbitals available for bonding to other ligands in the horizontal mirror plane. The first bonding description, provided by the MO treatment of Ballhausen and Dahl,⁴ placed three orbitals in the horizontal mirror plane, two symmetric with respect to a vertical mirror plane for $(\text{C}_5\text{H}_5)_2\text{MX}_2$ complexes and the third (for a lone pair or ligand in $(\text{C}_5\text{H}_5)_2\text{MX}_3$ complexes) between these two, in the vertical mirror plane. Alcock⁵ suggested a different model with the lone pair orbital off to the side, in the same plane but 90° from the position in the Ballhausen and Dahl model. Recently there has been some additional evidence for the Alcock model.^{2,3} Green, *et al.*,² have proposed a model with features of both the Ballhausen–Dahl and Alcock models.

Bis(cyclopentadienyl)–metal complexes are very versatile structurally and chemically. In addition to the usual situation of two η^5 bonded C_5H_5 's, one may be of the C_5H_4 type, η^5 to one metal and η^1 to a second metal as in $[(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4)\text{NbH}]_2$.¹ Also, one of the C_5 rings may be part of a fulvalene ligand as in $[(\text{C}_5\text{H}_4)\text{Ti}]_2(\text{HAlEt}_2)(\text{C}_{10}\text{H}_8)$ and $[(\text{C}_5\text{H}_5)\text{Ti}]_2(\text{H})(\text{H}_2\text{AlEt}_2)(\text{C}_{10}\text{H}_8)$.⁶ The dihedral angles between the C_5 rings vary from 34 to 63° (117 – 146° between plane normals).¹ In addition to the general question of the ligand disposition in the horizontal mirror plane, we were specifically interested in the mode of attachment of ethylene to an early transition metal, niobium in this case. Would the

olefin be in the horizontal plane, perpendicular to it, or in some intermediate configuration? We felt intermediate geometries, or even the perpendicular geometry, might be feasible in view of the observed spread in the angles between C_5 rings in $(\text{C}_5\text{H}_5)_2\text{M}$ complexes. The analogy to the later transition metals is obvious; is the ethylene in the plane as in $\text{Ni}(0)$ – and $\text{Pt}(0)$ –olefin complexes or perpendicular to the plane as in $\text{Pt}(\text{II})$ –olefin complexes?⁷

The crystal structure of bis(cyclopentadienyl)ethyl(ethylene)niobium(III), $(\text{C}_5\text{H}_5)_2\text{Nb}(\text{C}_2\text{H}_5)(\text{C}_2\text{H}_4)$, was determined to establish the mode of the metal–olefin bonding. This structure also serves as a model for $(\text{C}_5\text{H}_5)_2\text{Nb}(\text{H})(\text{C}_2\text{H}_4)$ and its trialkylaluminum adducts.⁸ Initially we approached the problem by ^{13}C nmr. We would not expect to distinguish between the planar and perpendicular configurations with ^{13}C nmr, but we might identify an intermediate configuration. Our original efforts with CW ^{13}C nmr were not successful, but now with FT ^{13}C nmr we have good spectra of the $(\text{C}_5\text{H}_5)_2\text{Nb}(\text{C}_2\text{H}_5)(\text{C}_2\text{H}_4)$ and $(\text{C}_5\text{H}_5)_2\text{Nb}(\text{H})(\text{C}_2\text{H}_4)$ complexes. They are consistent with our structural data. The C_5H_5 rings are fluxional at room temperature. Spectra, chemical shifts, and coupling constants are presented for both complexes.

Experimental Section

The complex $(\text{C}_5\text{H}_5)_2\text{Nb}(\text{C}_2\text{H}_5)(\text{C}_2\text{H}_4)$ was prepared from $(\text{C}_5\text{H}_5)_2\text{NbH}_3$ and ethylene. The synthesis has been described⁹ and will be presented in more detail later.

Spectra. The ^{13}C nmr spectra were recorded for partially ^{13}C enriched samples in the CW mode using a Varian HA-100 spectrometer and for natural abundance samples in the Fourier mode using a Bruker HFX 90 spectrometer with a Digilab FTS/NMR-3 data system and a Digilab pulser. Benzene- d_6 was used as the solvent and as a deuterium lock for the time-shared deuterium lock on the Bruker spectrometer.

The spectra were first run in the CW and Fourier modes with

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- (3) J. L. Peterson and L. F. Dahl, *J. Amer. Chem. Soc.*, **96**, 2248 (1974).
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(8) F. N. Tebbe, *J. Amer. Chem. Soc.*, **95**, 5412 (1973).

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proton noise decoupling to simplify the spectra and to increase the signal-to-noise ratio *via* the Overhauser effect. Undecoupled spectra were then obtained on the Bruker spectrometer using the "alternately pulsed" or "gated decoupling" technique¹⁰⁻¹² in which the free induction decay following each pulse is recorded during the first part of the delay between pulses. During the remainder of the delay time between pulses, the decoupler is turned on to saturate the ¹H resonances in order to produce Overhauser enhancement of the ¹³C spectrum. In our experiments the total delay time between pulses was 2.0 sec, the first 0.8 sec of which was used to digitize the free induction decay. The decoupler was turned on for the remaining 1.2 sec.

The proton spectra reported here were recorded in the CW mode at 100 MHz using the Varian HA 100 spectrometer and at 220 MHz using a Varian HR 220 spectrometer. Benzene-*d*₆ was again the solvent.

Crystal Data and Structure Determination. Crystals are tetragonal with cell dimensions of $a = 16.481(2)$ and $c = 18.186(2)$ Å. The cell parameters were refined from the angular positions of nine reflections carefully centered on the diffractometer. Crystals were enclosed in capillaries for all X-ray work. Precession and Weissenberg photographs showed that the diffraction symmetry is $C_{4h}(4/m)$, the lower symmetry tetragonal Laue group. The systematic absences of hkl ($h + k + l = 2n + 1$), $hk0$ ($h = 2n + 1$), and $00l$ (l not $4n$) established the space group as $I4_1/a$. The observed and calculated densities for 16 molecules per cell are 1.50 and 1.51 g/cm³, respectively. All atoms are in general space group positions,¹³ *i.e.*, there is no space group imposed molecular symmetry.

A prismatic crystal of dimensions $0.27 \times 0.27 \times 0.18$ mm was used in the data collection. The crystal was mounted on a Picker four-circled automatic diffractometer with the c^* axis coincident with the diffractometer ϕ axis. Data were measured out to $45^\circ 2\theta$ using the θ - 2θ scan technique and Zr-filtered Mo radiation (λ 0.7107 Å, takeoff angle of 3.0°). The scan rate was $1^\circ/\text{min}$ and the range for each reflection was 1.3° plus the $K\alpha_1$ - $K\alpha_2$ separation. Backgrounds of 20 sec were measured before and after each scan. A total of 1755 reflections were measured.

The data were corrected for Lorentz and polarization effects but not for absorption. The linear absorption coefficient for Mo radiation was 9.15 cm^{-1} . The maximum absorption effect observed (a ϕ scan at $\psi = 90^\circ$) was 4% in F_o . Structure factor errors were estimated as previously described with $F_o < 3\sigma(F_o)$ considered "unobserved."¹⁴

The structure was solved by conventional heavy-atom techniques. The R factor ($\sum ||F_o| - |F_c|| / \sum |F_o|$) with all nonhydrogen atoms in the model with isotropic thermal parameters was 0.082. The corresponding R_w , $[\sum w(|F_o| - |F_c|)^2 / \sum (F_o)^2]^{1/2}$, was 0.096. The R and R_w with anisotropic thermal parameters for the nonhydrogen atoms were 0.062 and 0.071, respectively. At this point general plane electron density maps were calculated through the C_5H_5 planes and sections parallel to the Nb-C₂ planes to search for the hydrogen atoms. All hydrogen atoms were clearly visible (0.3 - $0.5 \text{ e}/\text{Å}^3$); they were included in the refinement and their positional and thermal parameters were varied. The least-squares matrix was split into two blocks in intermediate refinements with the hydrogen atoms in the model. In the final refinements one block was used with all parameters varied except the hydrogen atom thermal parameters which were fixed at their refined values. The final R values for 1247 observed reflections were 0.044 for R and 0.049 for R_w . The values for all the data (1615 reflections) are 0.073 for R and 0.053 for R_w . The standard deviation of an observation of unit weight is 1.20.

Neutral atom form factors were used.¹⁵ The niobium atom was corrected for the real and imaginary parts of the anomalous scattering effect¹⁶ in the calculated structure factors. The function $\sum w(|F_o| - |F_c|)^2$ was minimized in the refinement.¹⁷

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The final positional parameters and isotropic thermal parameters for the hydrogen atoms are given in Table I. The hydrogen atoms

Table I. Positional Parameters for $(C_5H_5)_2Nb(C_2H_5)(C_2H_4)^a$

Atom	x	y	z	B (Å ²) ^b
Nb	0.21335 (4)	0.26243 (4)	0.45133 (4)	
C(1)	0.1305 (6)	0.1666 (6)	0.5181 (6)	
C(2)	0.1209 (6)	0.2393 (7)	0.5523 (6)	
C(3)	0.1930 (7)	0.2634 (7)	0.5818 (5)	
C(4)	0.2492 (6)	0.2034 (7)	0.5670 (5)	
C(5)	0.2117 (8)	0.1431 (6)	0.5267 (7)	
C(6)	0.2918 (6)	0.3254 (7)	0.3553 (5)	
C(7)	0.3432 (6)	0.2675 (6)	0.3910 (7)	
C(8)	0.3539 (5)	0.2951 (7)	0.4625 (6)	
C(9)	0.3109 (7)	0.3667 (7)	0.4691 (6)	
C(10)	0.2763 (6)	0.3848 (6)	0.4034 (6)	
C(11)	0.1370 (6)	0.2190 (6)	0.3546 (6)	
C(12)	0.1998 (6)	0.1619 (6)	0.3629 (6)	
C(13)	0.1106 (5)	0.3574 (5)	0.4397 (5)	
C(14)	0.1069 (8)	0.4267 (6)	0.4944 (6)	
H(1)	0.1015 (52)	0.1399 (50)	0.4875 (45)	2.0 (27)
H(2)	0.0763 (46)	0.2627 (45)	0.5580 (41)	0.9 (21)
H(3)	0.2000 (43)	0.3170 (47)	0.6127 (41)	1.6 (20)
H(4)	0.2994 (46)	0.2007 (46)	0.5760 (41)	0.9 (18)
H(5)	0.2338 (54)	0.1074 (49)	0.5057 (49)	2.0 (29)
H(6)	0.2781 (42)	0.3175 (43)	0.3074 (40)	1.0 (17)
H(7)	0.3603 (67)	0.2115 (69)	0.3689 (62)	7.2 (31)
H(8)	0.3945 (65)	0.2750 (55)	0.5126 (55)	5.8 (27)
H(9)	0.3110 (46)	0.3992 (44)	0.5028 (43)	1.0 (17)
H(10)	0.2450 (44)	0.4300 (47)	0.3979 (42)	1.4 (18)
H(11)C(11)	0.1383 (46)	0.2554 (44)	0.3132 (42)	1.4 (21)
H(12)C(11)	0.0834 (53)	0.2126 (51)	0.3633 (46)	2.7 (22)
H(13)C(12)	0.2379 (66)	0.1578 (69)	0.3305 (57)	5.8 (32)
H(14)C(12)	0.1929 (61)	0.0956 (63)	0.3862 (57)	6.4 (27)
H(15)C(13)	0.1189 (58)	0.3800 (56)	0.3982 (52)	3.9 (22)
H(16)C(13)	0.0559 (51)	0.3287 (49)	0.4418 (43)	3.0 (20)
H(17)C(14)	0.0655 (57)	0.4598 (55)	0.4834 (47)	3.4 (23)
H(18)C(14)	0.1215 (58)	0.4135 (55)	0.5385 (50)	3.3 (27)
H(19)C(14)	0.1556 (70)	0.4620 (68)	0.4926 (69)	7.5 (33)

^a The standard deviations here and in other tables are given in parentheses. ^b The refined isotropic thermal parameters are listed here.

are identified also by the carbon atoms to which they are attached. The thermal parameters for the nonhydrogen atoms are given in Table II. A list of observed and calculated structure factors ($\times 5$) is available.¹⁸

Results

¹³C Spectra. A portion of the room-temperature (27°) undecoupled Fourier mode natural abundance ¹³C nmr spectrum of a solution of $(C_5H_5)_2Nb(C_2H_5)(C_2H_4)$ in benzene-*d*₆ is shown in Figure 1. The ¹H noise decoupled spectrum consists of a strong single line to low field which is assigned to the cyclopentadienyl carbons and four lines in the region shown in Figure 1 which are assigned to the two ends of the ethylene ligand and to the CH₂ and CH₃ carbons of the ethyl group (a 1:1:1 triplet assigned to C₆D₆ is also observed). The spectrum in Figure 1 is assigned as follows: the triplets marked * ($J(^{13}C-^1H) = 153 \text{ Hz}$, δ 29.35 ppm downfield from internal TMS) and + ($J(^{13}C-^1H) = 154.5 \text{ Hz}$, δ 27.63 ppm downfield from TMS) are assigned to the two distinguishable ends of the ethylene ligand, the triplet marked Δ ($J(^{13}C-^1H) = 122 \text{ Hz}$, δ 11.18 ppm downfield from TMS) is assigned

(17) Computer programs used in addition to local programs were Prewitt's least-squares program SFLS5, the Busing-Levy error function program ORFFE, the Johnson plotting program ORTEP, and the Fourier program FOUR, a modification of a program written by C. J. Fritchie, Jr.

(18) See paragraph at end of paper regarding supplementary material.

Table II. Thermal Parameters ($\times 10^4$) for $(C_5H_5)_2Nb(C_2H_5)(C_2H_4)^a$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Nb	25.4 (3)	26.0 (3)	24.4 (3)	-0.3 (2)	0.5 (2)	1.7 (2)
C(1)	51 (6)	39 (5)	58 (5)	-17 (4)	2 (4)	16 (4)
C(2)	42 (5)	71 (7)	40 (4)	-1 (4)	12 (4)	26 (4)
C(3)	67 (6)	54 (5)	25 (3)	-1 (5)	5 (3)	8 (3)
C(4)	41 (4)	73 (6)	37 (4)	-7 (5)	-6 (3)	21 (4)
C(5)	78 (7)	37 (5)	57 (5)	4 (5)	10 (5)	18 (4)
C(6)	56 (5)	73 (6)	26 (3)	-14 (5)	20 (4)	-5 (4)
C(7)	40 (4)	53 (5)	63 (5)	-1 (4)	16 (4)	-13 (4)
C(8)	27 (4)	72 (6)	55 (5)	-19 (4)	0 (3)	7 (5)
C(9)	61 (5)	54 (6)	37 (4)	-30 (5)	2 (4)	-8 (4)
C(10)	51 (5)	43 (5)	45 (4)	-7 (3)	11 (4)	9 (4)
C(11)	57 (5)	53 (5)	38 (4)	-1 (4)	-12 (4)	-14 (3)
C(12)	43 (5)	55 (5)	53 (5)	15 (4)	-13 (3)	-28 (4)
C(13)	39 (4)	36 (4)	35 (3)	8 (3)	2 (3)	1 (3)
C(14)	74 (7)	45 (5)	44 (4)	23 (4)	7 (5)	-4 (4)

^a The anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

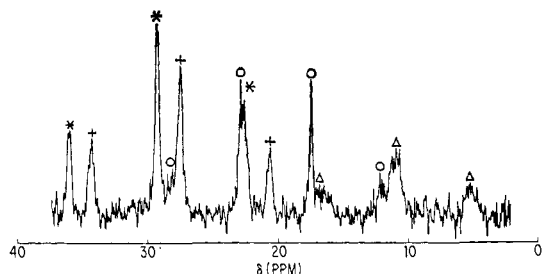


Figure 1. Part of the undecoupled Fourier mode ^{13}C nmr spectrum of $(C_5H_5)_2Nb(C_2H_5)(C_2H_4)$.

to the methylene carbon in the ethyl group, and the quartet marked \circ ($J(^{13}C-^1H) = 130.5$ Hz, δ 20.25 ppm downfield from TMS) is assigned to the methyl carbon. The linewidth effects observed in the spectrum shown in Figure 1 and more evident in the proton noise decoupled ^{13}C nmr spectra (ethyl CH_2 $^{13}C >$ ethylene CH_2 $^{13}C_1$, ethylene CH_2 $^{13}C_2 >$ methyl ^{13}C) are attributed to scalar coupling to the ^{93}Nb nucleus ($J = 9/2$, 100% natural abundance) combined with a partial "decoupling" of the ^{93}Nb nucleus due to quadrupole relaxation. Under conditions where the quadrupole relaxation is fast compared to the $^{13}C-^{93}Nb$ coupling constant, this contribution to the linewidth is proportional to $(J(^{13}C-^{93}Nb))^2$. Consequently the ordering of the linewidths given above is also the ordering for the $^{13}C-^{93}Nb$ coupling constants.

The resonances assigned to the undecoupled cyclopentadienyl carbons consist of a doublet ($J = 174$ Hz) of quintets ($J = 7$ Hz); the chemical shift is 97.57 ppm downfield from TMS. This spectrum and the proton noise decoupled ^{13}C spectrum indicate that all five cyclopentadienyl carbons are equivalent on the nmr time scale at room temperature (27°). This result is taken to imply a rapid rotation of the C_5H_5 ligand about its C_5 axis.

Figure 2 shows part of the undecoupled ^{13}C nmr spectrum of $(C_5H_5)_2Nb(H)(C_2H_4)$; the two triplets marked $*$ ($J = 153$ Hz, δ 13.44 ppm downfield from TMS) and $+$ ($J = 156$ Hz, δ 7.96 ppm) are assigned to the two distinguishable ethylenic carbons. The similarity between these $^{13}C-^1H$ coupling constants and those assigned to the ethylene carbons in $(C_5H_5)_2Nb(C_2H_5)(C_2H_4)$ confirms the assignment in $(C_5H_5)_2Nb(C_2H_5)(C_2H_4)$. Again the undecoupled cyclopentadi-

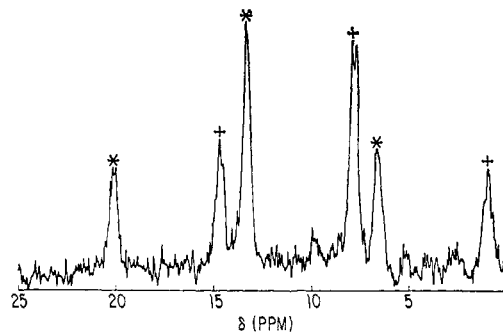


Figure 2. Part of the undecoupled Fourier mode ^{13}C nmr spectrum of $(C_5H_5)_2Nb(H)(C_2H_4)$.

enyl resonances consist of a doublet ($J = 176$ Hz) of quintets ($J = 7$ Hz) and the decoupled spectrum is a single line. Here too a rapid internal rotation of the C_5H_5 ligand is indicated. The chemical shift for the cyclopentadienyl carbons is 91.11 ppm downfield from TMS.

1H Spectra. The 220-MHz 1H nmr spectrum of $(C_5H_5)_2Nb(H)(C_2H_4)$ in benzene- d_6 consists of three regions. (1) An unresolved single line is observed 4.44 ppm downfield from TMS assigned to the cyclopentadienyl protons. (2) Two "triplets" of equal intensity, " J " = 11 Hz, δ 0.65 and 1.14 ppm, are observed downfield from TMS. This part of the spectrum is an AA'-BB' pattern approaching the AA'XX' limit and is assigned to the four protons on the two inequivalent ends of the ethylene ligand. (3) An unresolved single line at 2.93 ppm upfield from TMS is assigned to the hydride proton. The ratio of the integrated intensities for the three parts of the spectrum was determined to be 10:3.89:0.93 in very good agreement with the ratio of 10:4:1 expected for $(C_5H_5)_2Nb(H)(C_2H_4)$.

Similarly the 220-MHz 1H nmr spectrum for a solution of $(C_5H_5)_2Nb(C_2H_5)(C_2H_4)$ in benzene- d_6 can be divided into two regions: (1) an unresolved singlet at 4.46 ppm downfield from TMS assigned to the cyclopentadienyl protons and (2) a region closer to TMS consisting of (A) an AA'BB' pattern which has the appearance of two asymmetric triplets. The nmr parameters for this part of the pattern which is assigned to the four protons at the two inequivalent ends of the ethylene ligand are δ_A 1.31 ppm downfield from TMS and δ_B 0.90 ppm downfield from TMS, " J " \sim 7 Hz.

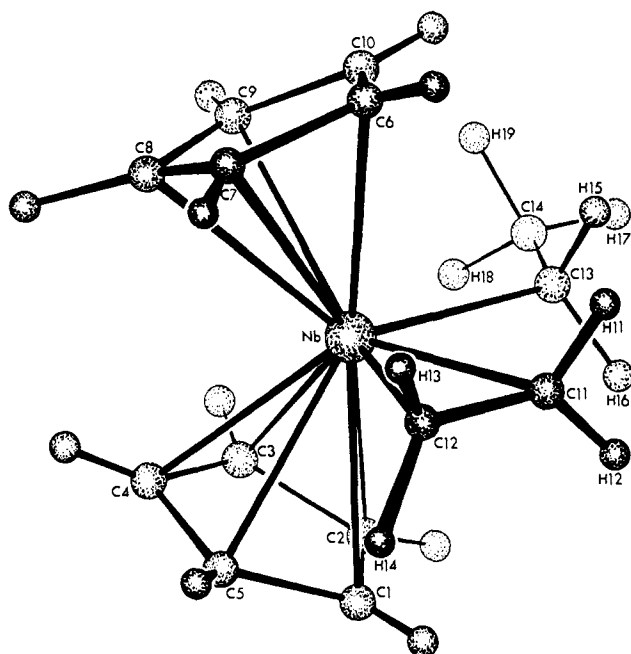


Figure 3. Molecular structure of $(C_5H_5)_2Nb(C_2H_5)(C_2H_4)$ illustrating the numbering used.

(B) An A_2B_3 pattern approaching the A_2X_3 limit with the nmr parameters δ_A 1.30 ppm, δ_B 1.83 ppm, and $J_{AB} = 7$ Hz. These resonances are assigned to the ethyl protons. The intensity ratio measured for $2C_5H_5:CH_3:CH_2$ (ethyl) + CH_2 (ethylene, downfield half): CH_2 (ethylene, upfield half) is 10:3.1:4.4:2.1, in fairly good agreement with the ratio 10:3:4:2 calculated from our assignment.

Structure Description. The crystal structure of $(C_5H_5)_2Nb(C_2H_5)(C_2H_4)$ consists of the packing of discrete molecules separated by van der Waals contacts. The molecular structure illustrating the numbering system used here is shown in Figure 3. Each Nb atom is η^5 bonded to two C_5H_5 rings that are bent back to make room in the horizontal mirror plane (molecular plane) for a σ -bonded ethyl and a " σ - π "-bonded ethylene ligand. Another view of the molecule, normal to the molecular plane, is shown in Figure 4. The molecule has no crystallographic symmetry but very nearly has $C_s(m)$ idealized point symmetry, even when the hydrogen atoms are included. The $C_s(m)$ point symmetry requires eclipsing of the C_5H_5 rings as shown in Figure 4.

Selected sets of interatomic distances and angles are given in Tables III and IV, respectively. All the Nb-C(C_5H_5) distances are equivalent, at 2.402 (5) Å, within experimental error. A case might be made for possible systematic differences in these distances with 2.418 (5) Å for the Nb-C(1), C(2) type, 2.393 (7) Å for the Nb-C(3), C(5) type, and 2.389 (3) Å for the Nb-C(4) type, the implication being perhaps that the steric interactions between the C_5H_5 's and C_2H_5 and C_2H_4 are stronger than between the two C_5H_5 ligands. However, there do not appear to be any compensating systematic differences in C-C distances in the rings, which might be expected for genuine differences in the Nb-C(C_5H_5) bonds. These Nb-C distances are very close to the 2.398 (4) Å value found in $[(C_5H_5)(C_5H_4)NbH]_2$,¹ other distances for comparison are 2.44 Å in $(C_5H_5)Nb-$

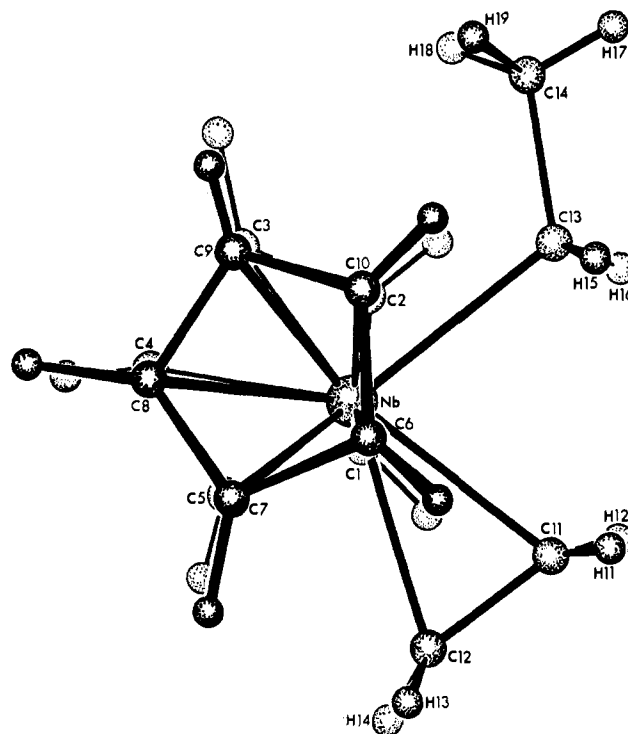


Figure 4. View of the molecular structure normal to the molecular plane.

Table III. Interatomic Distances for $(C_5H_5)_2Nb(C_2H_5)(C_2H_4)^a$

Bonding (Å)			
Nb-C(11)	2.277 (9)	C(1)-C(2)	1.359 (14)
Nb-C(12)	2.320 (9)	C(2)-C(3)	1.363 (13)
Av	2.299 (21)	C(3)-C(4)	1.381 (13)
Nb-C(13)	2.316 (8)	C(4)-C(5)	1.382 (15)
Nb-C(1)	2.416 (8)	C(5)-C(1)	1.402 (15)
Nb-C(2)	2.416 (9)	C(6)-C(7)	1.430 (14)
Nb-C(3)	2.396 (8)	C(7)-C(8)	1.389 (14)
Nb-C(4)	2.392 (9)	C(8)-C(9)	1.382 (14)
Nb-C(5)	2.397 (10)	C(9)-C(10)	1.355 (14)
Nb-C(6)	2.408 (8)	C(10)-C(6)	1.388 (13)
Nb-C(7)	2.407 (9)	Av	1.383 (7)
Nb-C(8)	2.386 (8)	C(11)-H(11)	0.96 (7)
Nb-C(9)	2.374 (9)	C(11)-H(12)	0.90 (8)
Nb-C(10)	2.430 (9)	C(12)-H(13)	0.86 (10)
Av	2.402 (5)	C(12)-H(14)	1.18 (10)
C(11)-C(12)	1.406 (13)	C(13)-H(15)	0.85 (9)
C(13)-C(14)	1.515 (13)	C(13)-H(16)	1.02 (8)
		C(14)-H(17)	0.90 (9)
		C(14)-H(18)	0.86 (9)
		C(14)-H(19)	0.99 (11)
			0.95 (4)
Nonbonding (Å)			
Nb-C(14)	3.319 (10)	C(12)-C(7)	2.979 (14)
Nb-H(11)	2.80 (8)	C(13)-C(2)	2.831 (13)
Nb-H(12)	2.80 (9)	C(13)-C(10)	2.847 (13)
Nb-H(13)	2.82 (11)	C(3)-C(9)	3.297 (13)
Nb-H(14)	3.01 (10)	C(4)-C(8)	2.979 (13)
Nb-H(15)	2.67 (10)	H(11)-C(6)	2.88 (7)
Nb-H(16)	2.82 (8)	H(12)-C(1)	3.02 (9)
C(11)-C(13)	2.791 (13)	H(13)-C(7)	2.74 (11)
C(11)-C(1)	3.098 (15)	H(14)-C(5)	2.69 (10)
C(11)-C(6)	3.095 (14)	H(15)-C(10)	2.60 (10)
C(12)-C(5)	3.002 (16)	H(16)-C(2)	2.71 (8)
		H(4)-H(8)	2.30 (12)

^a The errors for the mean values are calculated according to $[\Sigma(d_i - \bar{d})^2/n(n-1)]^{1/2}$ where d_i and \bar{d} are the distance and mean distance, respectively.

Table IV. Interatomic Angles for $(C_5H_5)_2Nb(C_2H_5)(C_2H_4)^a$

C(11)-Nb-C(12)	35.6 (3)	C(1)-C(2)-C(3)	109.6 (10)
C(11)-Nb-C(13)	74.8 (3)	C(2)-C(3)-C(4)	107.4 (10)
		C(3)-C(4)-C(5)	108.5 (10)
Nb-C(11)-C(12)	73.8 (5)	C(4)-C(5)-C(1)	106.8 (9)
Nb-C(11)-H(11)	113 (5)	C(5)-C(1)-C(2)	107.6 (10)
Nb-C(11)-H(12)	116 (6)	C(6)-C(7)-C(8)	106.3 (9)
C(12)-C(11)-H(11)	119 (5)	C(7)-C(8)-C(9)	107.2 (10)
C(12)-C(11)-H(12)	128 (6)	C(8)-C(9)-C(10)	109.1 (10)
H(11)-C(11)-H(12)	103 (7)	C(9)-C(10)-C(6)	109.5 (10)
		C(10)-C(6)-C(7)	107.8 (9)
Nb-C(12)-C(11)	70.5 (5)	Av	108.0 (4)
Nb-C(12)-H(13)	117 (8)	H(1)-C(1)-C(2)	133 (6)
Nb-C(12)-H(14)	115 (5)	H(1)-C(1)-C(5)	118 (6)
C(11)-C(12)-H(13)	121 (8)	H(2)-C(2)-C(1)	124 (6)
C(11)-C(12)-H(14)	126 (5)	H(2)-C(2)-C(3)	126 (6)
H(13)-C(12)-H(14)	104 (9)	H(3)-C(3)-C(2)	123 (4)
		H(3)-C(3)-C(4)	129 (4)
Nb-C(13)-C(14)	118.6 (7)	H(4)-C(4)-C(3)	131 (5)
Nb-C(13)-H(15)	105 (7)	H(4)-C(4)-C(5)	120 (5)
Nb-C(13)-H(16)	109 (5)	H(5)-C(5)-C(4)	126 (7)
C(14)-C(13)-H(15)	105 (6)	H(5)-C(5)-C(1)	126 (7)
C(14)-C(13)-H(16)	107 (5)	H(6)-C(6)-C(7)	119 (5)
H(15)-C(13)-H(16)	112 (8)	H(6)-C(6)-C(10)	133 (5)
		H(7)-C(7)-C(6)	125 (6)
C(13)-C(14)-H(17)	110 (6)	H(7)-C(7)-C(8)	128 (6)
C(13)-C(14)-H(18)	114 (6)	H(8)-C(8)-C(7)	135 (5)
C(13)-C(14)-H(19)	113 (7)	H(8)-C(8)-C(9)	118 (5)
H(17)-C(14)-H(18)	125 (9)	H(9)-C(9)-C(8)	129 (6)
H(17)-C(14)-H(19)	105 (9)	H(9)-C(9)-C(10)	121 (6)
H(18)-C(14)-H(19)	87 (9)	H(10)-C(10)-C(9)	121 (5)
		H(10)-C(10)-C(6)	129 (5)
		Av	126 (1)

^a The footnote to Table III applies here also.

$(CO)[(C_5H_5)_4C_4][(C_5H_5)_2C_2]$,¹⁹ 2.45 Å in $\{(C_5H_5)Nb(CO)[(C_5H_5)_2C_2]\}_2$,²⁰ and 2.46 Å in $(C_5H_5)Nb(CO)-[(C_5H_5)_2C_2]$.²¹

We consider the C-C distances in the rings to be essentially equivalent at 1.383 (7) Å. The only possible systematic variation is that the C(1)-C(5)[C(6)-C(7)] type is longer than the mean and the C(2)-C(3)-[C(9)-C(10)] type is shorter, but this does not correlate with Nb-C(C₅H₅) distances or make sense chemically. The values observed are in the range frequently found for cyclopentadienyl ligands.²² The average C-C-C angle of 108.0 (4)° in the C₅H₅ rings is right on the ideal value for a regular pentagon. The mean H-C-C angle of 126 (1)° is also right on the ideal value obtained from bisecting the external C-C-C angle. Likewise, the mean C-H value of 0.95 (4) Å is similar to that frequently found in X-ray determinations.

There are no direct literature comparisons for Nb-C distances to either the C₂H₅ or C₂H₄ ligands. A formally Nb-C(σ C₅H₄) bond value of 2.232 (7) Å was found in $[(C_5H_5)(C_5H_4)NbH]_2$ ¹ but that is a poor comparison because the C₅H₄ ligand was both η^5 and η^1 bonded with an unusual bridging geometry. The olefin and

(19) A. I. Gusev and Yu. T. Struchkov, *Zh. Strukt. Khim.*, **10**, 515 (1969); A. N. Nesmeyanov, A. I. Gusev, A. A. Pasynskii, K. N. Anisimov, N. E. Kolobova, and Yu. T. Struchkov, *Chem. Commun.*, 739 (1969).

(20) A. I. Gusev and Yu. T. Struchkov, *Zh. Strukt. Khim.*, **10**, 107 (1969); A. N. Nesmeyanov, A. I. Gusev, A. A. Pasynskii, K. N. Anisimov, N. E. Kolobova, and Yu. T. Struchkov, *Chem. Commun.*, 1365 (1968).

(21) A. I. Gusev and Yu. T. Struchkov, *Zh. Strukt. Khim.*, **10**, 294 (1969); A. N. Nesmeyanov, A. I. Gusev, A. A. Pasynskii, K. N. Anisimov, N. E. Kolobova, and Yu. T. Struchkov, *Chem. Commun.*, 277 (1969).

(22) P. J. Wheatley, *Perspect. Struct. Chem.*, **1**, 9 (1967).

ethyl bonding to Nb will be discussed further in the discussion section.

The data for the least-squares planes through the C₅H₅ rings are given in Table V; included also is the

Table V. Least-Squares Planes for $(C_5H_5)_2Nb(C_2H_5)(C_2H_4)^a$

Plane 1. C₅H₅: $-0.2376X - 0.4684Y + 0.8510Z - 6.222 = 0$
Plane 2. C₅H₅: $0.8143X + 0.5038Y - 0.2884Z - 4.770 = 0$
Plane 3. Molecular plane: $-0.5728X - 0.5299Y + 0.6253Z - 8.263 = 0$

Nb(0.000), C₁₁(0.000), C₁₂(0.000), C₁₃(0.009), C₁₄(0.060)

Atom	Plane 1 (n = 1)	Plane 2 (n = 2)
Nb	-2.098	-2.095
C(n)	0.000	-0.015
C(n + 1)	0.005	0.007
C(n + 2)	-0.008	0.004
C(n + 3)	0.007	-0.013
C(n + 4)	-0.004	0.018
H(n)	-0.16	-0.01
H(n + 1)	0.09	-0.11
H(n + 2)	0.03	0.12
H(n + 3)	-0.03	0.08
H(n + 4)	-0.14	0.00

Dihedral Angles (deg)		
Plane 1	47.6	β { C(12)H(13)H(14) 63.9
Plane 2		{ C(12)C(11)
α { C(11)H(12)H(11)	52.5	β { C(11)H(12)H(11) 63.6
{ C(12)H(13)H(14)		{ C(11)C(12)

^a The equations are based on Cartesian coordinates (a, b, c*). Only the carbon atoms were included in the C₅H₅ planes calculations. Only the Nb, C(11), and C(12) atoms were used to define plane 3.

equation of the Nb-olefin plane (plane 3). The perpendicular Nb-C₅H₅ distance (mean 2.096 Å) is similar to that observed in $[(C_5H_5)(C_5H_4)NbH]_2$ ¹ where a range of 2.025-2.091 Å was found for 12 independently determined distances. Both C₅H₅ rings here are clearly very planar. There does not appear to be any systematic displacement of hydrogen atoms from the ring planes. The C₂H₅ ligand is nearly in the metal-olefin plane. In fact, all five atoms (Nb, C(11), C(12), C(13), C(14)) are planar to within 0.02 Å.

A 010 projection of the crystal structure is shown in Figure 5 with the thermal ellipsoids plotted at the 50% probability level. This view shows only half (in the b direction) of the molecules for this body-centered cell. There is another set of symmetry-related molecules nearly directly below those shown in Figure 5. The data for the thermal ellipsoids are given in Table VI. The C₅H₅ rings are fairly rigid, perhaps because of contacts with the H's of the C₂H₄ and C₂H₅ ligands. There are no unusually short intermolecular contacts, the shortest contacts by type being 2.55 Å for H···H and 2.79 Å for C···H; there were no C···C contacts less than 3.25 Å.

Discussion

Spectra. It is interesting to compare the chemical shifts and coupling constants observed in $(C_5H_5)_2Nb(C_2H_5)(C_2H_4)$ and $(C_5H_5)_2Nb(H)(C_2H_4)$ with those observed in simple alkanes and alkenes. In ethylene the ¹³C-¹H coupling constant is 156.4 Hz,²³ which is only slightly larger than the ¹³C-H coupling constants ob-

(23) R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc., Ser. A*, **269**, 385 (1962).

Table VI. Root-Mean-Square Amplitudes of Vibration (Å) for $(C_5H_5)_2Nb(C_2H_5)(C_2H_4)$

Atom	Min	Inter	Max
Nb	0.185 (1)	0.188 (1)	0.205 (1)
C(1)	0.171 (15)	0.285 (15)	0.331 (15)
C(2)	0.176 (14)	0.257 (13)	0.353 (15)
C(3)	0.191 (13)	0.280 (13)	0.305 (14)
C(4)	0.206 (14)	0.235 (13)	0.348 (14)
C(5)	0.195 (15)	0.303 (15)	0.351 (15)
C(6)	0.161 (15)	0.280 (13)	0.344 (14)
C(7)	0.208 (14)	0.259 (13)	0.350 (14)
C(8)	0.163 (14)	0.297 (13)	0.337 (14)
C(9)	0.188 (14)	0.252 (14)	0.351 (15)
C(10)	0.201 (13)	0.272 (13)	0.301 (14)
C(11)	0.198 (13)	0.279 (14)	0.312 (14)
C(12)	0.196 (14)	0.220 (13)	0.369 (14)
C(13)	0.199 (12)	0.238 (12)	0.255 (11)
C(14)	0.202 (14)	0.277 (13)	0.348 (14)

served for coordinated ethylene in the two complexes studied here ($J(^{13}C-H) = 153-156$ Hz). The change in chemical shift on coordination is quite large, however. The ^{13}C chemical shift in free ethylene is 123.3 ppm downfield from TMS²⁴ compared to 7–30 ppm downfield from TMS in the complexes reported here. The ^{13}C chemical shift in cyclopropane is 3.5 ppm upfield from TMS²⁵ and the $^{13}C-H$ coupling constant is 161 Hz.²⁶ The $^{13}C-H$ coupling constant is about 125 Hz for methane and simple alkanes.²⁴ The coupling constants observed in the ethyl group in $(C_5H_5)_2Nb(C_2H_5)(C_2H_4)$ are quite close to this value and are much smaller than the $^{13}C-H$ coupling constants in ethylene thus supporting the assignment given above. The shifts assigned to the ethyl group in $(C_5H_5)_2Nb(C_2H_5)(C_2H_4)$ are typical of aliphatic ^{13}C nuclei.

It is important to notice that the olefin carbon atoms experience a rather large increase in shielding on coordination to niobium. The ΔC (ppm, upfield on coordination) varies from 94.0 in $(C_5H_5)_2Nb(C_2H_5)(C_2H_4)$ to 115.3 in $(C_5H_5)_2Nb(H)(C_2H_4)$. The same effect was found with rhodium²⁷ and platinum²⁸ complexes; the magnitudes observed were also comparable. This is suggestive at least of a fairly substantial metal to olefin interaction.

Structure. Our main interest in this structure was to elucidate the nature of the Nb–ethylene bonding. We have seen how the ethylene is in the molecular plane, the mirror plane of the molecule. In a sense then the geometry is like that in Ni(0) and Pt(0) complexes where the olefins are bound in the molecular plane. This is stretching the analog, however, since in the usual Ni(0) and Pt(0) cases the other ligands (phosphines) are also in the molecular plane. In Pt(II)–olefin complexes the olefins are normal to the molecular plane, as in Zeise's salt.

From spectral correlations we know that the $(C_5H_5)_2Nb(H)(C_2H_4)$ structure is like $(C_5H_5)_2Nb(C_2H_5)(C_2H_4)$ with the hydride replacing the ethyl ligand. The tri-

(24) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York, N. Y., 1972.

(25) J. J. Burke and P. C. Lauterbur, *J. Amer. Chem. Soc.*, **86**, 1870 (1964).

(26) K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2769 (1965).

(27) G. M. Bodner, B. N. Storhoff, D. Doddrell, and L. J. Tood, *Chem. Commun.*, 1530 (1970).

(28) M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, *J. Amer. Chem. Soc.*, **94**, 5087 (1972).

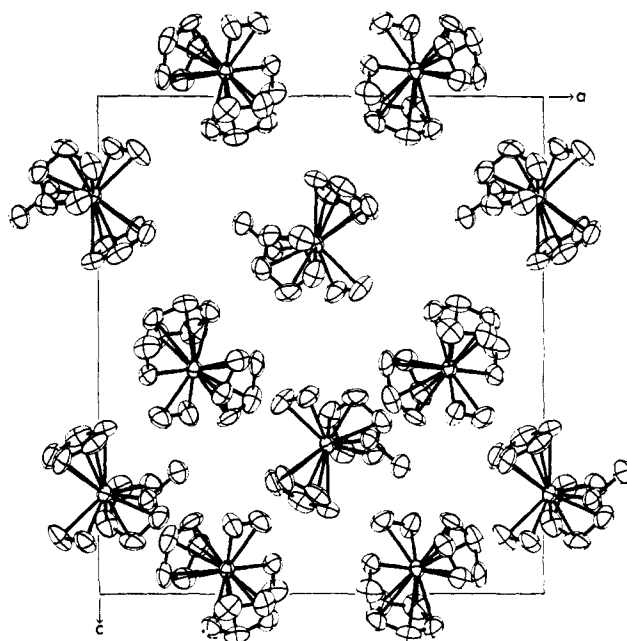
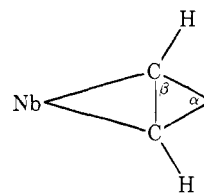


Figure 5. The 010 projection of the crystal structure of $(C_5H_5)_2Nb(C_2H_5)(C_2H_4)$; only half the cell in the b direction is shown (see text).

alkylaluminum adducts with $(C_5H_5)_2Nb(H)(C_2H_4)$ are presumably also based on this structure with aluminum adding to the hydride ($-Nb-H-Al-$).⁸

A question we can ask is whether the ethylene is in the molecular plane primarily because of steric effects or might electronic effects be involved as well. On first sight there appears to be a compelling steric reason for having the ethylene in the molecular plane. But if your look at accurate models, it seems that ethylene could fit in perpendicular to the plane if the angle were increased between the C_5H_5 rings (bent back further). We are talking about an ethylene shape difference of about 1 Å (1.54 Å width *vs.* 2.49 Å height, from $H \cdots H$ contacts). The observed angle between the C_5H_5 planes is 47.6°. This is in the middle of the range of dihedral angles between C_5H_5 rings observed generally (range is 34–63°); ref 1 gives a list of angles for many observed structures. Thus it appears that the C_5H_5 plane could bend back further. The point is that the ethylene position in the molecular plane might be at least partly favored for electronic as well as steric reasons. This argument is further enhanced if one considers that the olefin π^* orbital is in the molecular plane in this configuration. Thus the configuration in the plane should enhance electron metal– π^* overlap (*vide infra*).

In order to study the Nb– C_2H_4 geometry in more detail, we define the angles α and β following the convention of Ibers and coworkers.^{29,30} The angle α is



(29) J. K. Stalick and J. A. Ibers, *J. Amer. Chem. Soc.*, **92**, 5333 (1970).

(30) L. J. Guggenberger and R. Cramer, *J. Amer. Chem. Soc.*, **94**, 3779 (1972).

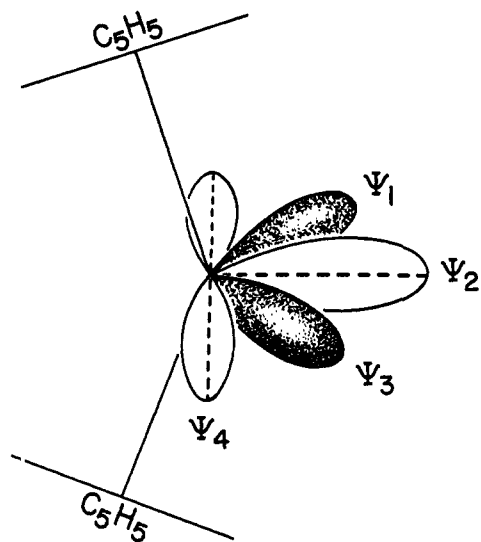


Figure 6. Orbitals used for bonding in bis(cyclopentadienyl)-transition metal complexes.

the angle between the plane normals, where the planes are defined by the olefin carbon atoms and their hydrogen substituents; β is the angle between the olefin C-C bond and the plane normal (Table V). For increasing bending back of the CH₂ planes, α increases from 0° and β decreases from 90°. We know of only two other structures where hydrogen atom positions were found and refined for metal-olefin structures—(C₅H₅)Rh(C₂F₄)(C₂H₄)³⁰ and KPtCl₃(C₂H₄)·H₂O³¹ (Zeise's salt). The work on the ethylene geometry in Zeise's salt is a neutron diffraction study, but the space group was not correct. There is a recent X-ray study of Zeise's salt in the correct space group,³² but the hydrogen atoms were not located; however, the molecular geometry did *not* change much from the neutron diffraction study. A comparison of α , β , and C-C bond distances in the three metal-ethylene structures is given in Table VII. The ethylene hydrogens in this

Table VII. Comparison of M-C₂H₄ Geometries

Compound	α (deg)	β (deg)	C-C (Å)
KPtCl ₃ (C ₂ H ₄)·H ₂ O	34.7	72.7	1.354 (15) neutron ^a 1.37 (3) X-rays ^b
(C ₅ H ₅)Rh(C ₂ F ₄)(C ₂ H ₄)	42.4	69.1	1.358 (9) ^c
(C ₅ H ₅) ₂ Nb(C ₂ H ₅)(C ₂ H ₄)	52.5	63.7	1.406 (13)

^a Reference 31. ^b Reference 32. ^c Reference 30.

structure are bent back further than in the previous two. This would be consistent with some shift in electron density from Nb to the olefin π^* orbital resulting in a lengthening of the C-C bond. This is supported by the ¹³C nmr parameters (*vide supra*). In fact, the ethylene geometry here is approaching the geometry of metal-tetracyanoethylene complexes; for example, α is 56.8° and β is 61.6° in (C₄H₉NC)₂Ni-

(31) W. C. Hamilton, K. A. Klanderman, and R. Spratley, *Acta Crystallogr., Sect. A*, **25**, S172 (1969).

(32) For the recent refinement and an explanation of the space group problem, see J. A. J. Jarvis, B. J. Kilbourn, and P. G. Owston, *Acta Crystallogr., Sect. B*, **27**, 366 (1971).

[C₂(CN)₄].²⁹ The α and β 's for other compounds are listed for comparison in ref 30.

The ethylene C-C distance of 1.406 (13) Å is similar to the values found generally for metal-olefin structures where the olefins do not have CN substituents. The C-C distances are longer when there are CN substituents on the olefin, but there are a few exceptions to this (for example, the 1.40 (2) Å value in (C₂H₃CN)Fe(CO)₄).³³ The observed C-C distances in metal-olefins range from 1.354 (15) Å in Zeise's salt³¹ to 1.526 (12) Å in [C₂(CN)₄]Ir(C₆N₄H)(CO)[(C₆H₅)₃P]₂.^{34, 35} This is discussed in more detail in ref 7 where a list of 27 observed C-C distances in metal-olefin structures is given. We conclude from the structural and ¹³C nmr parameters that the niobium-ethylene bond is comparable to that frequently observed for the later transition metals.

The Nb-C₂H₅ geometry is interesting in its own right because of the general lack of stability of transition metal σ -bonded alkyls. There is a good review available on the structural aspects of transition metal σ -bonded carbon atoms by Churchill.³⁶ The position of the ethyl group in the molecular plane as well as the Nb-C-C angle of 118.6 (7)° most likely result from net intramolecular steric effects. The C-C distance of 1.515 (13) Å is only slightly less than the C-C single bond value of 1.54 Å. There are no group V M-C σ -bonds for comparison with the Nb-C distance of 2.316 (8) Å. However, we might compare it with the Mo-CH₂ distances of 2.397 (19) Å in (C₅H₅)Mo(CO)₃-C₂H₅.^{36, 37} and 2.36 (2) Å in (C₅H₅)Mo(CO)₃(CH₂-COOH).³⁸ Proceeding to the right of the periodic table the M- σ -C bond lengths decrease dramatically (many in the 2.0-2.1 Å range).

The Nb-C(C₂H₅) distance is essentially equivalent to the Nb-C(C₂H₄) distance; this is surprising in view of the very different bonding considerations involved. To examine the generality of this comparison, we looked at Pt(II) complexes, which seemed to be a good test since there are several Pt- σ -CH₂ distances and Pt-C₂(olefin) distances available. An average Pt-C(olefin) distance is 2.13 Å, taken from 2.127 (X-rays)³² and 2.14 Å (neutron)³¹ in KPtCl₃(C₂H₄)·H₂O, 2.16 Å in [C₂H₂(CH₃)₂]PtCl₂(phenethylamine),³⁹ 2.11 Å in PtCl(OCH₃)(dicyclopentadiene),⁴⁰ and 2.130 Å in [(C₄H₁₂N₂)-PtCl₃]Cl· $\frac{1}{2}$ H₂O.⁴¹ An average Pt- σ -CH₂ distance is 2.08 Å, taken from 2.106 (17) Å in K[Pt(acac)₂Cl]⁴² (acac = acetylacetonate), 2.10 (3) Å in [(CH₃)₃C₆H₂-PtCl]₂,^{36, 43} 2.07 Å in [PtCl(OCH₃)(dicyclopentadiene)]₂,⁴⁰

(33) A. R. Luxmoore and M. R. Truter, *Acta Crystallogr.*, **15**, 1117 (1962).

(34) J. S. Ricci and J. A. Ibers, *J. Amer. Chem. Soc.*, **93**, 2391 (1971).

(35) We are ignoring the probably anomalous value of 1.62 (3) Å in [C₂(Cl₄)Pt(C₆H₅)₃P]₂ where there was a disorder problem: J. N. Francis, A. McAdam, and J. A. Ibers, *J. Organometal. Chem.*, **29**, 131 (1971).

(36) M. R. Churchill, *Perspect. Struct. Chem.*, **3**, 91 (1970).

(37) M. J. Bennett and R. Mason, *Proc. Chem. Soc.*, 273 (1963).

(38) J. K. P. Ariyaratne, A. M. Bierrum, M. L. H. Green, M. Ishaq, C. K. Prout, and M. G. Swanwick, *J. Chem. Soc.*, 1309 (1969).

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(40) W. A. Whitla, H. M. Powell, and L. M. Venanzi, *Chem. Commun.*, 310 (1966).

(41) R. Spagna and L. Zambonelli, *J. Chem. Soc. A*, 2544 (1971).

(42) R. Mason, G. B. Robertson, and P. J. Pauling, *J. Chem. Soc. A*, 485 (1969).

(43) R. Mason, G. B. Robertson, P. O. Whimp, B. L. Shaw, and G. Shaw, *Chem. Commun.*, 868 (1968).

and 2.04 (3) Å in PtCl(OCH₃)(1,5-C₈H₁₂)(pyridine).⁴⁴ Thus in general M–C(olefin) distances may not be much different from M–C(σ-bonded) distances. There are bound to be many exceptions though since both M–C(olefin) and σ-M–C distances are influenced by substituent effects. Consider (C₅H₅)Rh(C₂F₄)(C₂H₄),³⁰ for example, where Rh–C(C₂F₄) is 2.024 (2) Å and Rh–C(C₂H₄) is 2.167 (2) Å; the Rh^{III}–σ-C distance is about 2.07 Å.³⁶

The current bonding ideas in bis(cyclopentadienyl)–transition metal complexes will be outlined very briefly with respect to the model in Figure 6. Ballhausen and Dahl⁴ suggested that ligands in (C₅H₅)₂MX₂ complexes would use orbitals ψ₁ and ψ₃ for ligand bonding and ψ₂ for lone pairs. Alcock⁵ suggested a similar model except that ψ₄ would be used for lone pairs instead of ψ₃. Green, *et al.*,² developed a model in MO terms extrapolated from the ferrocene model by “bending” the ferrocene MO’s under C_{2v}(2mm) symmetry. They proposed that either ψ₂ or ψ₄ might be used depending on the number of ligand orbitals and electrons available for bonding. The structure of (C₅H₅)₂Nb(C₂H₅)(C₂H₄)

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can be rationalized in the simplest possible way in terms of the original Ballhausen–Dahl model using only one metal orbital for bonding to ethylene. However, the Green, *et al.*, model is more attractive in that it allows more flexibility in the bonding description. Accordingly we can use ψ₁ to bond to C₂H₅ and ψ₃ for the σ bond to C₂H₄. Then ψ₂ and ψ₄ are available for possible Nb–π* back-bonding to C₂H₄; both ψ₂ and ψ₄ are of the same symmetry under the local C_s(m) point symmetry. As discussed above, this could provide an electronic reason for favoring the olefin configuration in the molecular plane. Further MO calculations³ on (C₅H₅)₂MX₂ complexes are in progress which might shed more light on the nature of the bonding in these complexes.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-5420.

Preparation and Structural Characterization of Transition Metal–Zinc Chloride Derivatives. The Crystal and Molecular Structure of [π-C₅H₅(CO)₃MoZnCl·O(C₂H₅)₂]₂ and [π-C₅H₅(CO)₃Mo]₂Zn

J. St. Denis, W. Butler, M. D. Glick, and J. P. Oliver*

Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. Received March 5, 1974

Abstract: The preparation and characterization of compounds of the general formula [π-C₅H₅(CO)₃MZnCl·O(C₂H₅)₂]₂ and [π-C₅H₅(CO)₃MZnCl]_x (M = Mo, W) are reported. The structures of [π-C₅H₅(CO)₃MoZnCl·O(C₂H₅)₂]₂ and of [π-C₅H₅(CO)₃Mo]₂Zn have been determined from single-crystal X-ray data collected by counter methods. [π-C₅H₅(CO)₃MoZnCl·O(C₂H₅)₂]₂ crystallizes in space group P $\bar{1}$ with one dimer molecule per unit cell of dimensions *a* = 8.524 (3) Å, *b* = 9.090 (3) Å, *c* = 13.152 (4) Å, α = 56.03 (2)°, β = 110.13 (2)°, and γ = 103.96 (2)°. Full-matrix least-squares refinement gave final discrepancy factors of *R*₁ = 0.043 and *R*₂ = 0.052 for 2578 data having *F*² > 3σ(*F*²). The molecular structure consists of a centrosymmetric dimer with chloride atoms bridging the zinc atoms and a π-C₅H₅(CO)₃Mo ligand and a diethyl ether molecule completing the four-coordination sphere of each zinc atom. The molybdenum–zinc bond distance is 2.632 (1) Å. [π-C₅H₅(CO)₃Mo]₂Zn crystallizes in space group P2₁/n with two centrosymmetric molecules per unit cell of dimensions *a* = 11.101 (4) Å, *b* = 7.548 (2) Å, *c* = 11.726 (4) Å, and β = 64.43 (2)°. Full-matrix least-squares refinement gave discrepancy factors of *R*₁ = 0.040 and *R*₂ = 0.058 for 2101 reflections with *F*² > 3σ(*F*²). The molecule has a linear molybdenum–zinc–molybdenum bond with a molybdenum–zinc distance of 2.538 (1) Å. The solvated derivatives may be converted to the nonsolvated species of the general formula [π-C₅H₅(CO)₃MZnCl]_x (M = Mo, W) by heating under a dynamic vacuum. Infrared spectral data are interpreted in terms of a polymeric structure with carbonyl oxygen–zinc interactions supporting a polymer framework for the nonsolvated compounds.

The organometallic structural chemistry of complexes containing group II or group III metals and transition metal carbonyl derivatives has recently taken on importance because of the recognized ability of the transition metal moiety to exhibit two different modes of bond formation with a main group metal.

The first mode of bonding, exemplified by Zn[Co(CO)₄]₂¹ and [π-C₅H₅(CO)₃Mo]₃Tl² involves direct metal–metal bonding. Many complexes of this type

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