Crystal and Molecular Structure of a Five-Coordinate Rhodium(I)–Diene Complex and the Correlation of Structural Parameters with Carbon-13 Nuclear Magnetic Resonance Shifts

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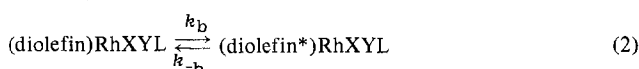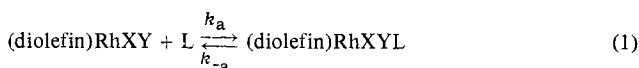and GRAHAM TURNER

The crystal and molecular structures of $(1,1,1,5,5,5$-hexafluoropentane-2,4-dionato)pyridine$(2,3,5,6-\eta^4$-2,3-dicarbomethoxybicyclo[2.2.1]heptadiene)rhodium(I), $Rh(C_5HF_6O_2)(C_5H_5N)(C_7H_6(CO_2CH_3)_2)$, have been measured by single-crystal x-ray diffraction. The orange crystals are monoclinic, space group $P2_1/c$, $Z = 4$, $a = 10.943$ (4) Å, $b = 12.861$ (8) Å, $c = 21.329$ (8) Å, and $\beta = 131.63$ (2)°. The calculated and observed densities are 1.77 and 1.73 (2) g cm^{-3}, respectively. Intensity data were collected on a Syntex $P\bar{1}$ diffractometer and a full-matrix least-squares refinement on 2786 significant reflections led to a conventional $R = 0.0772$. The structure can be related to a very rough trigonal bipyramid about the rhodium atom, with β-keto enolate oxygen atoms and one C–C double bond (attached to the carbomethoxy groups) filling the three equatorial positions and the other C–C double bond and the pyridine nitrogen atom filling the axial positions. The Rh–N distance (2.107 (8) Å) is normal although the Rh–O distances (2.217 (9), 2.235 (8) Å) are unusually long. The Rh–C(axial) distances (2.142 (10), 2.162 (10) Å) are significantly longer than the Rh–C(equatorial) distances (2.044 (13), 2.059 (14) Å). The corresponding C=C(axial) distance (1.390 (11) Å) is shorter than the C=C(equatorial) distance (1.448 (10) Å). ^{13}C NMR data indicate that the five-coordinate molecular geometry is maintained in solution. It is shown for a series of platinum– and rhodium–olefin complexes that the change in ^{13}C NMR shift of a carbon atom on coordination to the metal varies as the reciprocal of the metal–carbon distance cubed.
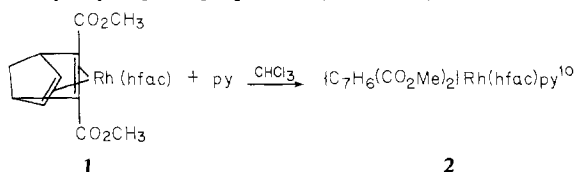
Introduction

A number of four-coordinate square-planar diolefin complexes of rhodium(I) exhibit temperature-dependent ^{1}H NMR spectra which have been interpreted in terms of an intramolecular exchange of olefin protons between nonequivalent sites.[1,2] The rate of this site exchange is enhanced by the addition of donor ligands such as organophosphines, organoarsines, dimethyl sulfoxide, and pyridine. An associative–dissociative mechanism involving (i) formation of a five-coordinate 1:1 adduct from a square-planar complex and base (eq 1) and (ii) an intramolecular rearrangement of the

$$(\text{diolefin})\text{RhXY} + \text{L} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} (\text{diolefin})\text{RhXYL} \qquad (1)$$

$$(\text{diolefin})\text{RhXYL} \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} (\text{diolefin*})\text{RhXYL} \qquad (2)$$

five-coordinate adduct (eq 2) provides a rationalization of the reported data.[2]

Several stable five-coordinate diolefin–rhodium(I)[3] and –iridium(I)[4] complexes that exhibit temperature-dependent ^{1}H NMR data consistent with rapid intramolecular rearrangements are known. However, none of these five-coordinate diolefin–rhodium(I) and –iridium(I) complexes[3-7] can be considered to be 1:1 adducts of the type postulated in eq 1, that is, products formed directly from a known square-planar diolefin–rhodium(I) complex and a simple nucleophile. More recently Shapley and Osborn[8] have reported NMR studies on complexes of the type in eq 1, and solid materials of the same type have been isolated and characterized but not studied by NMR.[9]

As part of a study of ligand substitution reactions of olefin complexes we have found that the four-coordinate complex, $(1,1,1,5,5,5$-hexafluoropentane-2,4-dionato)$(2,3$-dicarbomethoxybicyclo[2.2.1]heptadiene)rhodium(I), **1**, reacts with

CO₂CH₃

[structure diagram] Rh(hfac) + py $\xrightarrow{\text{CHCl}_3}$ {C₇H₆(CO₂Me)₂}Rh(hfac)py[10]

CO₂CH₃

        1   **2**

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one molecule of pyridine to give a five-coordinate 1:1 adduct, **2**, stable in both the solid state and solution. In this paper we report the structure of complex **2** determined by single-crystal x-ray diffraction. ^{13}C NMR data indicate that the molecular geometry found in the crystal is maintained in solution. A correlation between the ^{13}C chemical shift data and the structural data is presented.

Experimental Section

Preparation of $(1,1,1,5,5,5$-Hexafluoropentane-2,4-dionato)-pyridine$(2,3,5,6-\eta^4$-2,3-dicarbomethoxybicyclo[2.2.1]heptadiene)-rhodium(I), $C_{21}H_{18}F_6NO_6Rh$, $Rh(hfac)py(C_7H_6(CO_2Me)_2)$ (2). To di-μ-chloro-tetraethylenedirhodium(I)[11] (1.36 g) suspended in pentane was added 2,3-dicarbomethoxybicyclo[2.2.1]heptadiene (2.0 g). The reaction mixture was stirred at room temperature for 30 min. Evaporation to dryness gave di-μ-chloro-bis(2,3-dicarbomethoxybicyclo[2.2.1]heptadiene)dirhodium(I) (**3**) as an oily residue which recrystallized from dichloromethane–pentane as orange-yellow prisms (1.97 g, 81%), mp 178–180 °C.

Reaction of **3** (0.90 g) with Tl(hfac) (1.10 g) in dichloromethane for $^1/_2$ h, followed by filtration and evaporation to dryness, gave an oily residue. Extraction with pentane and evaporation to dryness gave $Rh(hfac)(C_7H_6(CO_2Me)_2)$ (**1**) as an orange oil (1.17 g, 87%), which slowly solidified on standing. Pyridine (0.18 g) was added to a solution of **1** (1.17 g) in pentane (10 ml). On cooling of the required product, **2** was obtained as fine yellow needles (1.12 g, 85%), mp 110–115 °C. Anal. Calcd for $C_{21}H_{18}F_6NO_6Rh$: C, 42.24; H, 3.04; mol wt 597. Found: C, 42.05; H, 3.11; mol wt (osmometrically in chloroform) 578. Crystals for x-ray studies were obtained from a dichloromethane–ether recrystallization.

Crystal Data. Two crystals, one a small fragment, 0.19 × 0.16 × 0.11 mm³, and the other a crystal ground to a sphere of radius 0.15 mm, were used for x-ray studies. Preliminary precession film data, on crystal 1, showed the crystal was monoclinic, and systematic absences of the type $0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$, were observed on the $hk0$ and $h0l$ photographs and uniquely defined the space group as $P2_1/c$. Cell parameters were obtained at 21 °C for the second crystal by least-squares refinement of the setting angles of 15 higher order reflections using Mo Kα radiation (λ 0.710 69 Å) and a Syntex $P\bar{1}$ diffractometer and were $a = 10.943$ (4) Å, $b = 12.861$ (8) Å, $c = 21.329$ (8) Å, $\beta = 131.63$ (2)°, $d = 1.77$ g cm^{-3}, $Z = 4$. The density measured by flotation in bromobenzene–diiodomethane was 1.73 (2) g cm^{-3}.

Intensities were measured on a Syntex $P\bar{1}$ diffractometer using graphite monochromatized Mo Kα radiation and a coupled θ(crystal)–2θ(counter) scan. Scans were made from 1.0° below the Kα_1 position to 1.0° above the Kα_2 position. The scan rate was chosen
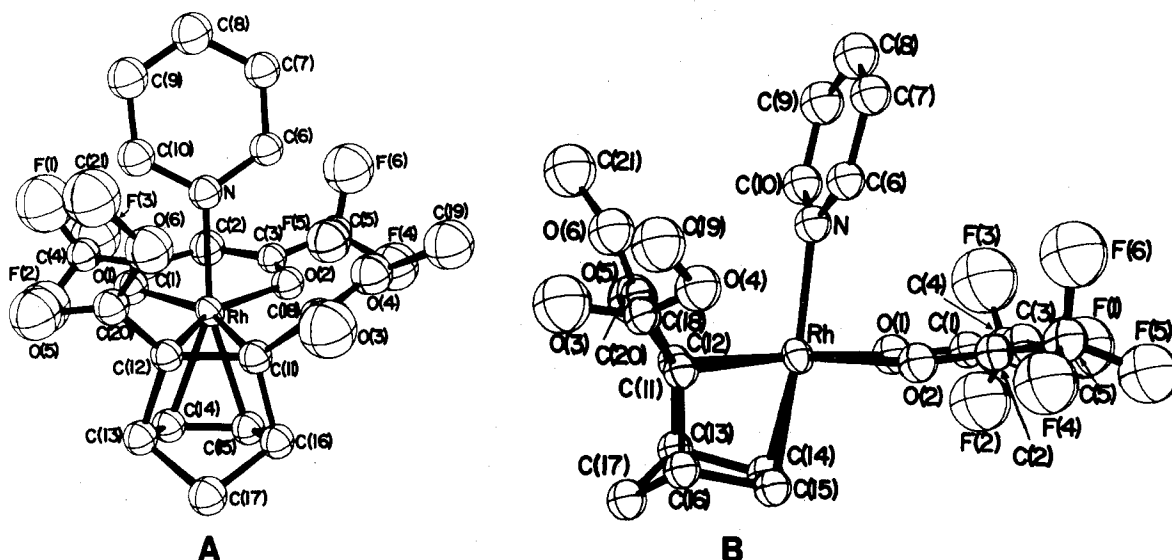
Figure 1. ORTEP[56] drawing of the molecule showing the numbering of the atoms.

for each reflection by the program supplied with the instrument and ranged from 4 to 24° min⁻¹. Stationary counts at the limits of each scan were made for half the scan time to establish the background. The intensity of a reflection was taken as $I = N_T - N_{BG1} - N_{BG2}$, where N_T is the total peak count and N_{BG1} and N_{BG2} are the background counts. $\sigma(I)$'s were taken as $(N_T + N_{BG1} + N_{BG2})^{1/2}$.

The orientation of crystal 1 was such that the a^* axis was roughly (±3°) collinear with the ϕ axis and intensities were measured to 2θ = 45°. The linear absorption coefficient was 8.4 cm⁻¹ and no corrections were made for absorption. After averaging of equivalent reflections, 2953 unique positive reflections remained, of which 1872 had $I > 3\sigma(I)$ and were considered significant. This data set was used to solve the crystal structure.

Because over one-third of the reflections recorded for the first crystal could not be considered significant and the bond length errors were quite large, another set of data was collected for the second crystal which was mounted roughly along its c axis. A total of 3581 independent reflections were observed of which 2786 were considered significant. The stability of the system was monitored by measuring a standard reflection, $2\bar{2}2$, after every 49 reflections. The counting esd of the standard was 1.3%, and the fluctuation was random (Gaussian). The data were treated as above. No correction was made for absorption, since $\mu r = 0.13$, and this will introduce an error in F of less than 1%. Unscaled structure factor amplitudes, F, and their standard deviations, $\sigma(F)$, were calculated from the expressions $F = (I/Lp)^{1/2}$ and $\sigma(F) = [1/^1/_2(Lp)^{1/2}][(\sigma(I)^2)^{1/2}/I]$. Lp, the Lorentz–polarization factor, is $(1 + \cos^2 2\theta)/(2 \sin 2\theta)$. The X-ray 71 programs DATCO3 and DATRDN were used to average data, to correct the intensity data for Lorentz and polarization effects, and to convert them to structure factors.

Solution of the Structure

The main features of the structure were found from the intensities measured for crystal 1. The position of the rhodium atom was found from a three-dimensional Patterson synthesis. Subsequent electron density synthesis and difference cycles (SYMFOU)[12] and the full-matrix least-squares refinement (CUDLS)[12] revealed the positions of all nonhydrogen atoms. In all further cycles of refinement the temperature factor of the rhodium atom, which was previously isotropic, was made anisotropic. Refinement was terminated at $R_1 = 0.0849$ and $R_2 = 0.1016$.[13]

At this stage it became apparent that the data were unable to supply the accuracy required, so a second data set was obtained from crystal 2. Refinement was continued using the final parameters obtained above. Refinement for the second crystal was terminated at $R_1 = 0.0772$ and $R_2 = 0.0087$. Scattering factors used throughout were those for neutral atoms from ref 14. The scattering factor for rhodium was modified to include anomalous dispersion terms.[15] The weighting scheme used in the final stages of full-matrix least-squares refinement was of the form $w = 1/[9.585 - 0.071\,52|F_o| + 0.002\,388|F_o|^2]$ and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The maximum shift per error in the final cycle of refinement was 0.03. The electron density

difference map showed several diffuse peaks around C(4), of magnitude 0.8–1.46 electrons/Å³, suggesting that this CF₃ group was partially disordered. A refinement with two CF₃ groups around C(4), each with occupancy 0.5, produced no significant improvement in the refinement. The large temperature factors of the fluorine atoms attached to C(4), (F(1), F(2), F(3)) reflect this disorder. The electron density difference map showed no peaks greater than 1.46 electrons/Å³ at −0.35, 0.27, 0.30 (close to C(4)) or valleys less than −0.88 electron/Å³ at −0.13, 0.22, 0.11 (close to the rhodium atom). The atomic coordinates for the nonhydrogen atoms are listed in Table I.

Results and Discussion

Crystal Structure. The molecule is pictured in Figure 1 and selected interatomic distances and angles are given in Table II. It can be seen in Figure 1A that, considering only the main groups attached to the rhodium atom, the molecule has roughly C_s symmetry. The CF₃ and carbomethoxy groups are not related by this plane and we assume that the orientation of these groups is determined by the exigencies of crystal packing. The arrangement of nearest-neighbor atoms around the rhodium atom can best be considered in terms of a trigonal bipyramid (although seven atoms are within bonding distance of the rhodium atom) with pyridine and one of the olefin groups occupying the axial positions and the other olefin group and oxygen atoms of the chelated β-keto enolate group occupying the equatorial positions. The structure is thus very similar to those of the series of iridium compounds studied by Churchill and Bezman.[5]

The Rh–C distances are within the range expected[7,17–23] but the distances from the rhodium atom to the equatorial olefin carbon atoms (2.044 (13), 2.059 (14) Å) are shorter than those to the axial olefin carbon atoms (2.142 (10), 2.162 (10) Å). In addition, the equatorial C(11)–C(12) distance (1.448 (10) Å), is longer than the axial C(14)–C(15) distance (1.390 (11) Å). This relationship between the M—C distances and the C=C distances is what would be expected from the Chatt–Dewar–Duncanson bonding model[24,25] and the difference in the axial and equatorial distances is in the same direction as was observed by Churchill and Bezman.[5] One major difference between the iridium and rhodium structures is that the rhodium atom is displaced 0.09 Å from the equatorial plane defined by O(1)O(2)C(11)C(12) away from the axial olefin rather than toward it as can be seen in Figure 1B.

The distances and angles within the pyridine ring are insignificantly different from those in the free pyridine molecule[26] and the Rh–N distance is as expected.[27–29] The β-keto enolate ring has dimensions very similar to the average values found by Lingafelter and Braun[30] but the Rh–O distances (2.235 (8),

Table I. Positional and Thermal[a] Parameters for
$Rh(C_5H_5N)(C_5HF_6O_2)(C_7H_6(CO_2CH_3)_2)$ ($\times 10^3$)

Atom	x	y	z	U, Å^2
Rh	−163.47 (8)[b]	206.59 (5)	93.11 (4)	a
O(1)	−300.3 (8)	213.7 (5)	−44.2 (4)	44 (2)
C(1)	−249 (1)	199.7 (7)	−80.2 (6)	36 (2)
C(2)	−95 (1)	172.2 (8)	−47.9 (6)	50 (3)
C(3)	32 (1)	150 (7)	37.7 (6)	33 (2)
O(2)	31.0 (7)	150.0 (5)	95.5 (4)	38 (1)
C(4)	−376 (1)	215.4 (8)	−173.4 (6)	46 (2)
F(1)	−334 (1)	195.7 (7)	−216.2 (6)	108 (3)
F(2)	−511 (1)	165.3 (8)	−208.1 (6)	113 (3)
F(3)	−417 (1)	315.4 (9)	−189.7 (7)	132 (4)
C(5)	202 (1)	129.0 (8)	68.5 (6)	43 (2)
F(4)	294 (1)	69.8 (6)	136.2 (5)	87 (2)
F(5)	198 (1)	77.4 (6)	13.3 (5)	81 (2)
F(6)	282 (1)	214.1 (7)	88.2 (6)	99 (3)
N	−80 (1)	356.7 (6)	98.5 (5)	36 (2)
C(6)	77 (1)	375.1 (7)	140.2 (6)	36 (2)
C(7)	132 (1)	468.2 (7)	133.6 (6)	41 (2)
C(8)	19 (1)	546.8 (9)	83.6 (7)	55 (3)
C(9)	−144 (1)	528.4 (8)	40.8 (7)	53 (2)
C(10)	−190 (1)	432.0 (8)	48.8 (6)	44 (2)
C(11)	−121 (1)	200.4 (7)	201.8 (5)	32 (2)
C(12)	−285 (1)	238.9 (7)	134.1 (5)	30 (2)
C(13)	−397 (1)	142.3 (7)	98.0 (5)	35 (2)
C(14)	−335 (1)	87.3 (7)	59.1 (5)	36 (2)
C(15)	−179 (1)	50.4 (7)	125.1 (5)	35 (2)
C(16)	−141 (1)	82.9 (7)	206.1 (5)	34 (2)
C(17)	−312 (1)	76.6 (7)	178.2 (6)	42 (2)
C(18)	16 (1)	251.2 (7)	281.6 (5)	33 (2)
O(3)	9 (1)	278.9 (7)	334.3 (6)	82 (3)
O(4)	153 (1)	251.8 (5)	297.4 (4)	48 (2)
C(19)	299 (2)	281 (1)	382.9 (8)	64 (3)
C(20)	−352 (1)	341.2 (7)	124.1 (6)	36 (2)
O(5)	−495 (1)	363.9 (7)	67.2 (5)	74 (2)
O(6)	−244 (1)	410.0 (6)	181.3 (5)	60 (2)
C(21)	−310 (2)	512 (1)	177 (1)	81 (4)

^{a} The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \ldots + 2\beta_{12}hk + \ldots)]$ and U_{ij} was obtained from $\beta_{ij} = 2\pi^2 b_i b_j U_{ij}$ where b_i are the reciprocal lattice vectors. Values of U_{ij} ($\times 10^4$) for Rh are as follows: U_{11}, 248 (4); U_{22}, 360 (5); U_{33}, 289 (4); U_{12}, −25 (3); U_{13}, 186 (4); U_{23}, −10 (3). ^{b} Standard deviations of the least significant figure are given here and in subsequent tables in parentheses.

2.217 (9) Å) are very long compared to other Rh–O values in similar compounds (1.98–2.06 Å).[19,22,31,32] An examination of the nonbonding distances in Table II shows that all distances between pairs of atoms bonded to the metal (except C–C distances) are as long as van der Waals contact distances, so that it appears that steric crowding around the metal cannot be responsible for the long Rh–O distances. It is possible that the pyridine group may be the cause of the long bonds. The O(1)–C(10) and O(2)–C(6) distances (2.98 (1), 3.18 (1) Å) are close to the van der Waals contact distance between a pyridine ring and an oxygen atom (3.1 Å),[33] and any shortening of the Rh–O bonds will shorten this distance, causing an increase in steric repulsion. Similar steric distortions caused by pyridine groups have been observed by us previously.[34] An alternative explanation may be that the long bonds are caused by the strong trans influence of an olefin group in this particular geometry. Clearly geometry is all-important, since the effect is not observed when the same diene is present in the square-planar complex pentane-2,4-dionato(2,3,5,6-η^4-2,3-dicarbomethoxybicyclo[2.2.1]heptadiene)-rhodium(I), **6**, where the Rh–O bond lengths (2.037 (5), 2.025 (5) Å) are normal.[35]

In the β-keto enolate group some small angular distortions are observed which we assume are caused by packing considerations. The main ring of the β-keto enolate group (O(1)C(1)C(2)C(3)O(2)) makes a dihedral angle of 7° with the RhO(1)O(2) plane and is bent away from the axial C=C group. The pyridine ring is arranged so that it is roughly

parallel to O(1)O(2) and C(11)C(12) and makes a dihedral angle of 76° with the plane formed by these four atoms such that the pyridine ring is bent away from the equatorial C=C group as can be seen in Figure 1B. There is a slight twist of the pyridine ring toward O(2) and C(12) and away from O(1) and C(11). This is probably caused by crystal packing. The atoms C(4) and C(5) are markedly out of the plane of the β-keto enolate ring (0.10 (2) and 0.16 (2) Å, respectively), C(4) being bent away from and C(5) being bent toward the pyridine ring and the rhodium atom, which lies 0.21 (1) Å out of the plane of the β-keto enolate ring.

Apart from the lengthening of the C=C distances to 1.448 (10) and 1.390 (11) Å from 1.343 (3) Å in free norbornadiene, the distances and angles observed in the norbornadiene group do not differ significantly from those found in free norbornadiene,[36,37] in a norbornadiene–palladium complex,[38] or in the rhodium complex, **6**.[35]

The packing of the molecules in the crystal can be described in terms of a double chain along the c direction. Pairs of molecules in the two chains are related by the inversion center and contact is between the hydrogen atoms of the norbornadiene group on one molecule and a fluorine atom and oxygen atom of the β-keto enolate group and a hydrogen of the norbornadiene group on the other molecule. Within either chain, in the c direction, contact is between the bridgehead hydrogen atoms of the norbornadiene group and an oxygen atom on a carbomethoxy group of one molecule and the CF$_3$ groups on the next molecule. Contact between the double chains in the a direction is primarily an interaction between CF$_3$ groups and pyridine groups on different molecules; also there are carbomethoxy–carbomethoxy contacts. In the b direction contacts are again between the various CF$_3$, CH$_3$OCO, and pyridine groups. One important contact is between pairs of pyridine groups on two different molecules, which are arranged such that they are parallel to each other. All of the contact distances mentioned above are equal to or slightly larger than the expected van der Waals contact distances. See Figure 2 for a stereogram of the contents of the unit cell.

NMR Studies. ^{13}C NMR data (CDCl$_3$ solutions) for the series of (2,3-dicarbomethoxynorbornadiene)rhodium(I) complexes **1–7** are shown in Table III. The resonances corresponding to the various carbon nuclei were assigned on the basis of their ^{13}C–H couplings and by comparison with reported data for norbornenyl complexes.[39] For the square-planar complexes **1**, **3**, **4**, and **6** δ[C(1)] and δ[C(3)] are both shifted markedly upfield relative to the free dienes (ca. 85–87 and ca. 102 ppm, respectively). Similar large upfield shifts for olefin–rhodium(I) complexes have been previously reported.[40,41] δ[C(4)] shifts somewhat less (ca. 12 ppm upfield), but the magnitude is still fairly large considering the distance of C(4) from the metal atom. A similar shift to high field for the central methylene carbon nucleus along with a large metal–^{13}C(4) coupling has been previously noted for norbornenyl derivatives of palladium and platinum.[41] Coordination of the diene to rhodium(I) results in a small downfield shift for C(2) and C(5) (1–2 and 3–4 ppm, respectively) and δ[C(6)] is hardly affected. The iodo complex **5** provides a notable exception to otherwise reasonably consistent data in that the observed upfield shift for C(3) (114 ppm) is significantly greater than those observed for the other planar complexes.

Two pyridine adducts **2** and **7** have been studied by ^{13}C NMR. Molecular weight studies of the chloro complex **7**, formed by addition of pyridine to the dimer **3**, indicate a monomeric structure which would be expected for a pyridine cleavage[2] of the chloride bridges of **3**. Consistent with this the ^{13}C NMR data for **7** are very similar to those of the planar

Table II. Selected Distances (Å) and Angles (deg) in $Rh(C_5H_5N)(C_5HF_6O_2)(C_7H_6(CO_2CH_3)_2)$

Distances

Rh–N	2.107 (8)	O(2)–C(3)	1.24 (2)	C(12)–C(13)	1.54 (1)
Rh–O(1)	2.235 (8)	C(1)–C(2)	1.38 (2)	C(15)–C(16)	1.55 (2)
Rh–O(2)	2.217 (9)	C(2)–C(3)	1.40 (1)	C(13)–C(14)	1.55 (2)
Rh–C(11)	2.044 (13)	C(1)–C(4)	1.50 (1)	C(11)–C(18)	1.48 (1)
Rh–C(12)	2.059 (14)	C(3)–C(5)	1.53 (2)	C(12)–C(20)	1.45 (1)
Rh–C(14)	2.142 (10)	C(4)–F(1)	1.28 (2)	C(18)–O(3)	1.23 (2)
Rh–C(15)	2.162 (10)	C(4)–F(2)	1.31 (2)	C(20)–O(5)	1.22 (1)
N–C(6)	1.33 (1)	C(4)–F(3)	1.33 (2)	C(18)–O(4)	1.30 (2)
N–C(10)	1.35 (1)	C(5)–F(4)	1.32 (1)	C(20)–O(6)	1.32 (1)
C(6)–C(7)	1.39 (2)	C(5)–F(5)	1.33 (2)	O(4)–C(19)	1.47 (1)
C(9)–C(10)	1.39 (2)	C(5)–F(6)	1.29 (1)	O(6)–C(21)	1.48 (2)
C(7)–C(8)	1.39 (1)	C(11)–C(12)	1.448 (10)	C(13)–C(17)	1.55 (1)
C(8)–C(9)	1.37 (2)	C(14)–C(15)	1.390 (11)	C(16)–C(17)	1.54 (2)
O(1)–C(1)	1.23 (2)	C(11)–C(16)	1.54 (1)		

Nonbonded Distances

N–O(2)	2.94 (1)	N–O(1)	2.95 (1)	N–C(12)	3.19 (1)
N–C(11)	3.23 (1)	O(1)–O(2)	2.89 (1)	O(1)–C(12)	3.71 (1)
O(2)–C(11)	3.65 (1)	O(1)–C(14)	2.96 (1)	O(2)–C(15)	3.04 (1)
C(12)–C(14)	2.34 (1)	C(11)–C(15)	2.33 (1)	O(2)–C(6)	2.98 (1)
O(1)–C(10)	3.18 (1)	C(6)–C(18)	3.84 (1)	C(10)–C(20)	3.30 (1)
C(6)–O(4)	3.28 (1)	C(10)–O(6)	3.26 (1)		

Angles

N–Rh–O(1)	85.6 (3)	O(1)–C(1)–C(2)	130 (1)	Rh–O(2)–C(3)	128.2 (5)
N–Rh–O(2)	85.6 (3)	O(2)–C(3)–C(2)	130 (1)	Rh–C(15)–C(14)	70.4 (6)
N–Rh–C(11)	102.3 (4)	C(1)–C(2)–C(3)	122 (1)	Rh–C(14)–C(13)	95.1 (6)
N–Rh–C(12)	99.9 (4)	O(1)–C(1)–C(4)	114 (1)	Rh–C(15)–C(16)	94.7 (6)
N–RhC(14)	157.8 (3)	O(2)–C(3)–C(5)	112.6 (7)	C(11)–C(16)–C(15)	98 (1)
N–Rh–C(15)	162.8 (2)	C(2)–C(1)–C(4)	116 (1)	C(12)–C(13)–C(14)	99 (1)
O(1)–Rh–O(2)	80.9 (3)	C(2)–C(3)–C(5)	118 (1)	C(11)–C(16)–C(17)	102.1 (8)
O(1)–Rh–C(14)	84.9 (4)	C(1)–C(4)–F(1)	118 (1)	C(15)–C(16)–C(17)	101.6 (7)
O(2)–Rh–C(15)	87.8 (4)	C(1)–C(4)–F(2)	113 (1)	C(12)–C(13)–C(17)	101.2 (6)
O(1)–Rh–C(12)	119.2 (3)	C(1)–C(4)–F(3)	109 (1)	C(14)–C(13)–C(17)	100.8 (8)
O(2)–Rh–C(11)	118.2 (3)	C(3)–C(5)–F(4)	114 (1)	C(13)–C(17)–C(16)	95 (1)
C(11)–Rh–C(12)	41.3 (3)	C(3)–C(5)–F(5)	114 (1)	Rh–C(11)–C(18)	125 (1)
C(14)–Rh–C(15)	37.7 (3)	C(3)–C(5)–F(6)	111 (1)	Rh–C(12)–C(20)	122 (1)
C(11)–Rh–C(15)	67.2 (4)	F(1)–C(4)–F(2)	108 (1)	C(11)–C(18)–O(3)	123 (1)
C(12)–Rh–C(14)	67.8 (4)	F(1)–C(4)–F(3)	103 (1)	C(12)–C(20)–O(5)	124 (1)
Rh–N–C(6)	121.4 (6)	F(2)–C(4)–F(3)	105 (1)	C(11)–C(18)–O(4)	115 (1)
Rh–N–C(10)	119.1 (7)	F(4)–C(4)–F(5)	103 (1)	C(12)–C(20)–O(6)	115 (1)
C(6)–N–C(10)	118.7 (9)	F(4)–C(4)–F(6)	106 (1)	O(3)–C(18)–O(4)	121.3 (8)
N–C(6)–C(7)	122.6 (8)	F(5)–C(4)–F(6)	109 (1)	O(5)–C(20)–O(6)	122 (1)
N–C(10)–C(9)	121 (1)	Rh–C(11)–C(12)	69.9 (7)	C(18)–O(4)–C(19)	117 (1)
C(6)–C(7)–C(8)	119 (1)	Rh–C(12)–C(11)	68.8 (8)	C(20)–O(6)–C(21)	116.0 (8)
C(10)–C(9)–C(8)	119 (1)	Rh–C(11)–C(16)	99.8 (7)	C(13)–C(14)–C(15)	107.2 (9)
C(7)–C(8)–C(9)	119 (1)	Rh–C(12)–C(13)	98.6 (8)	C(16)–C(15)–C(14)	107 (1)
Rh–O(1)–C(1)	128.8 (5)	Rh–C(14)–C(15)	71.9 (6)	C(13)–C(12)–C(11)	105.5 (6)
				C(16)–C(11)–C(12)	105.5 (7)

Table III. ^{13}C NMR Data for Rhodium(I)–Dicarbomethoxynorbornadiene Complexes
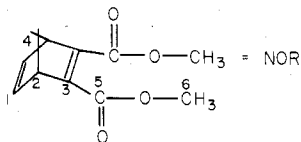
Compd	$\delta[C(1)]^a$	$\delta[C(2)]$	$\delta[C(3)]$	$\delta[C(4)]$	$\delta[C(5)]$	$\delta[C(6)]$
Free diene	142.41	51.94	152.45	72.96	165.42	52.53
			$[(NOR)RhX]_2^c$			
3, X = Cl	$55.9 (10.1)^b$	53.9 (2.6)	50.3 (12.1)	60.2 (6.1)	169.0 (?)	52.3
4, X = Br	55.6 (10.1)	54.2 (2.5)	50.5 (11.4)	60.6 (6.1)	169.0 (2.4)	52.1
5, X = I	~52.8 (?)	~52.8 (?)	38.3 (11.5)	57.8 (2.5)	172.9 (2.3)	52.9
			$(NOR)Rh(dik)^c$			
1, dik = hfac	58.4 (10.4)	53.4 (2.4)	~52 (?)	60.1 (6.0)	108.8 (2.2)	52.0
6, dik = acac	57.1 (11.0)	53.4 (2.6)	50.9 (12.5)	59.8 (5.4)	170.0 (2.4)	51.9
			Pyridine Adducts			
2	62.29 (8.0)	52.21 (2.2)	28.99 (14.0)	56.43 (5.5)	172.25 (2.4)	51.72
7	63.86 (8.8)	53.72 (2.7)	47.98 (12.5)	60.76 (4.9)	169.22 (2.0)	51.37

^{a} Shifts are from tetramethylsilane in ppm. ^{b} Values in parentheses are Rh–^{13}C coupling constants in Hz. ^{c} $[(NOR)RhX]_2$ represents a halogen-bridged dimer where X is the halogen atom, dik is a β-keto enolate anion, acac is the corresponding anion of acetylacetone, and hfac is the anion of 1,1,1,5,5,5-hexafluoroacetylacetone. ^{13}C NMR spectra were obtained using a Varian Associates XL-100-15 spectrometer operating in the Fourier transform mode and utilizing a Varian 620/i computer with 16K memory.
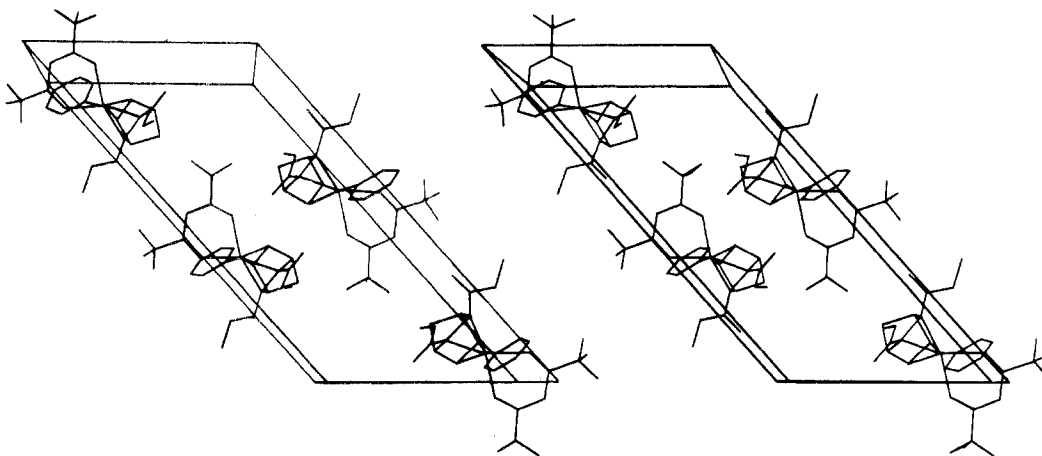
Figure 2. Stereogram (stereoscopic pair of perspective projections) of the contents of the unit cell viewed down the *b* axis. The *c** axis is parallel to the side of the page and the *a* axis to the top of the page.

complexes discussed above. However, the pyridine adduct **2**, which we have shown to have a pseudo-trigonal-bipyramidal structure in the solid state, gives ^{13}C data which are considerably different from those observed for the planar complexes. Most affected is $\delta[C(3)]$ which is shifted upfield by 123.5 ppm relative to the free diene compared to an upfield shift of ca. 102 ppm for the planar complexes. On the other hand, $\delta[C(1)]$ is shifted somewhat less to high field compared to the parent complex **1**. The marked difference observed for $\delta[C(3)]$ of **2** relative to those of the square-planar complexes **1**, **3**, **4**, and **6** strongly suggests that the solution structure of **2** is nonplanar and most probably has a five-coordinate geometry similar to that observed in the solid state. The reaction of (COD)Rh(hfac) or (NBD)Rh(hfac) with pyridine results in the formation of $(COD)Rh(py)_2{}^+hfac^-$ or $(NBD)Rh-(py)_2{}^+hfac^-$, respectively[42] (COD = 1,5-cyclooctadiene; NBD = norbornadiene). ^1H and ^{13}C NMR studies provide no evidence for formation of intermediate 1:1 adducts in these systems. In contrast, reaction of **1** with excess pyridine yields the 1:1 adduct **2** as the only product. It would appear therefore that either electronic or steric effects associated with the carbomethoxy substituents are responsible for stabilization of the five-coordinate 1:1 adduct **2**.

We have noted the anomaly of the iodo complex **5** with respect to observed ^{13}C shifts, and a comparison of the data with those observed for the hfac–py adduct **2** shows considerable similarities. In particular, $\delta[C(3)]$ of **5** is much closer to that observed in the hfac–py adduct **2** than in the square-planar complexes. $\delta[C(2)]$, $\delta[C(4)]$, and $\delta[C(5)]$ are very close for the two compounds. Only $\delta[C(1)]$ shows a shift which does not correspond. The data do not necessarily suggest that in the iodo complex the rhodium atom is five-coordinate, though by coordination of a solvent molecule it could be. Nevertheless, there appear to be differences between the solution structure of the iodo complex and the other halogen complexes and it will be of interest to study the iodo complex by single-crystal x-ray diffraction.

Correlation of Structural Parameters with ^{13}C NMR Data. The observed upfield shifts of the olefinic carbons in **2** and **6** may be correlated with the Rh–C distance: the shorter this distance the greater the observed upfield shift. In a related x-ray–^{13}C NMR study of a series of styrene–platinum(II) complexes we have observed a correlation between $\Delta\delta(C)$, the coordination upfield shifts, and the Pt–C distances.[43,44] It is thought that both changes in the nature of the olefin–metal bond and neighbor anisotropy effects (shielding by the metal) are responsible for the increase in $\Delta\delta(C)$.[45-47] Least-squares analysis of various inverse relationships suggests that $\Delta\delta(C)$ correlates *approximately* with r^{-3} (*r* is the metal–carbon
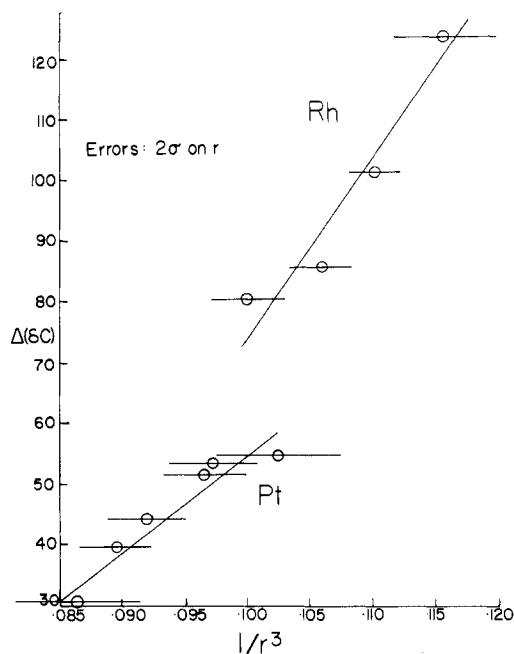

Figure 3. Plot of the change in the ^{13}C chemical shift (ppm) of a carbon atom in an olefin complex on bonding to a metal vs. the reciprocal of the cube of the metal–carbon distances (Å^{-3}): Pt, platinum–styrene complexes;[43,44] Rh, complexes **2** and **6**.

distance) for the styrene–platinum(II) complexes *trans*-[(p-Y-C$_6$H$_4$CH=CH$_2$)PtCl$_2$(NC$_5$H$_4$Me)] and for the rhodium complexes **2** and **6** (within the obvious limitations of only four data points) (see Figure 3). Previous studies have indicated an approximately rectilinear correlation between the chemical shifts of π-bonded olefinic and σ-bonded methyl carbon nuclei in similar coordination sites on platinum(II).[46,47] The σ-bonded ^{13}C nuclei were found to be more sensitive to changes in trans ligands. The slopes of the plots (0.75–0.87) were in the range expected assuming an r^{-3} relationship.[46] It is interesting to note that the expression derived by Buckingham and Stephens[48] for the paramagnetic shielding of a hydridic proton by the platinum d electrons approximates to

$$\sigma_{xx}{}^p \approx \frac{-2e^2\hbar^2}{m^2c^2r^3\Delta E_E}$$

when $2kr > 16$[48,49] (i.e., for $k = 3$–4, $r \leq 3$ au; for Pt–C bonds $r \approx 4$ au). Thus $\sigma_{xx}{}^p$ varies as r^{-3}. However, this predicts far too small a shift for ^{13}C nuclei directly bound to platinum(II). A comparison of $\delta[C(\text{methyl})]$ vs. $\delta[H(\text{hydrido})]$ in analogous

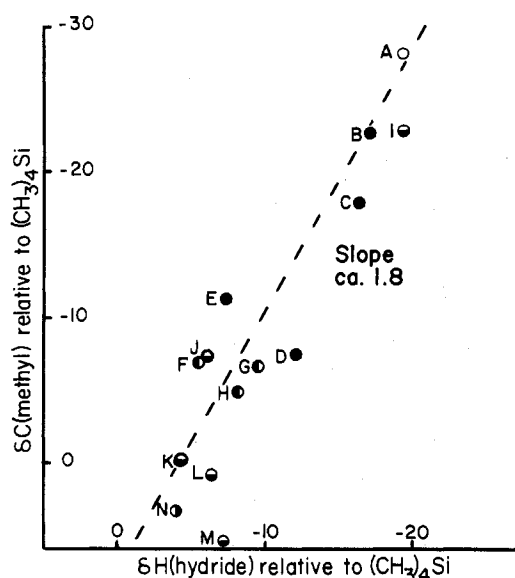**Figure 4.** Plot of $\delta[^{13}C(methyl)]$ vs. $\delta[^{1}H(hydride)]$ in similar coordination sites: O, *trans*-[CH$_3$PtCl(AsMe$_3$)$_2$][52] vs. *trans*-[HPtCl(AsEt$_3$)$_2$][53] (A); ●, *trans*-[CH$_3$PtX(PMe$_2$Ph)$_2$][52] vs. *trans*-[HPtX(PEt$_3$)$_2$],[53] X = NCS (B), Cl (C), I (D), CN (E); ◐, *trans*-[CH$_3$Pt(AsMe$_3$)$_2$L]PF$_6$[52] vs. *trans*-[HPt(AsEt$_3$)$_2$L]ClO$_4$, L = Co (F), AsPh$_3$ for ^{13}C and AsEt$_3$ for ^{1}H (G), EtNC for ^{13}C and *t*-BuNC for ^{1}H (H); ◓, *trans*-[CH$_3$Pt(PMe$_2$Ph)$_2$L]PF$_6$[52] vs. *trans*-[HPt(PEt$_3$)$_2$L]ClO$_4$,[53] L = pyridine (I), EtNC vs. *t*-BuNC (J), CO (K), PMe$_2$Ph vs. PEt$_3$ (L), C$_2$H$_4$ (M); ◑, *cis*-[Me$_2$Pt(PMe$_2$Ph)$_2$][54] vs. [H$_2$Pt{((*t*-Bu)$_2$PCH$_2$)$_2$C$_6$H$_4$}][55] (N).

coordination sites on platinum(II) (Figure 4) indicates that the chemical shifts of ^{13}C nuclei are about twice as sensitive to changes at the metal compared to protons. By assuming an r^{-3} relationship and allowing for the difference in r_{Pt-C} and r_{Pt-H}, this would indicate that, under identical conditions, the ^{13}C nucleus is about 4 times as sensitive to changes at the metal as the protons. Through-space neighbor anisotropy effects would be expected to induce the same shift for ^{1}H as for ^{13}C nuclei.[50] In contrast, for comparable changes in charge density at ^{1}H and ^{13}C, one would anticipate that the ^{13}C nucleus would be about 10–12 times more sensitive than the ^{1}H nucleus.[51] On the basis of these observations, one would have to concur with the rather pessimistic view of Evans and Norton[45] regarding the current level of understanding of the ^{13}C chemical shift data of carbon nuclei bonded to transition metals. We conclude, however, that our studies, while still limited, suggest the possibility of an r^{-3} relationship for the chemical shift data when studying closely related series of compounds.

Registry No. 1, 60840-38-2; 2, 60840-39-3; 3, 32714-40-2; 4, 60840-40-6; 5, 60861-09-8; 6, 57342-19-5; 7, 60861-10-1; di-μ-chloro-tetraethylenedirhodium(I), 12081-16-2; ^{13}C, 14762-74-4.

Supplementary Material Available: Table of the moduli of observed and calculated structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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