

Structure of $[\text{Rh}_2\text{Cl}_2(\mu\text{-CF}_3\text{C}_2\text{CF}_3)(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_2]$: A Binuclear Complex Containing an Acetylene Molecule Bound as a Cis-Dimetalated Olefin and Accompanied by a Rhodium-Rhodium Bond

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Received October 9, 1980

The structure of $[\text{Rh}_2\text{Cl}_2(\mu\text{-CF}_3\text{C}_2\text{CF}_3)(\text{DPM})_2]$ (DPM = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) has been determined by X-ray crystallography. The complex crystallizes in the space group $P4_3$ with $a = 21.283$ (1) Å, $c = 14.255$ (1) Å, and $Z = 4$. On the basis of 5243 unique observed reflections, the structure was refined to $R = 0.040$ and $R_w = 0.055$. In the structure two rhodium atoms are bridged by two transoid DPM ligands, and in the equatorial plane, perpendicular to the metal phosphine plane, the acetylene molecule bridges the two metals, bound as a cis-dimetalated olefin. A terminal chloro ligand on each metal completes the metal coordinations. The Rh-Rh distance is 2.7447 (9) Å, indicating a metal-metal bond, and all parameters involving the acetylene ligand suggest sp^2 hybridization of the carbon atoms bound to rhodium. The metal-acetylene distances (average 1.996 (9) Å) are short for such bonds. Carbon monoxide reacts with the complex by insertion into the Rh-Rh bond, yielding $[\text{Rh}_2\text{Cl}_2(\mu\text{-CO})(\mu\text{-CF}_3\text{C}_2\text{CF}_3)(\text{DPM})_2]$: a species having a bridging carbonyl, an acetylene molecule bound as a cis-dimetalated olefin, and no metal-metal bond.

Introduction

Recent interest in binuclear complexes of acetylene stems in a large part from the possible relevance of such studies to metal surface catalysis.^{1,2} These relatively simple two-metal systems can yield valuable information regarding ligand rearrangements, the reactivity of metal-metal bonds, and the modes of acetylene coordination to metals, all of which are of importance in metal surface reactions. One of our interests in this regard concerns the mode of acetylene binding in binuclear systems and its relationship to the subsequent chemistry.

In binuclear complexes, two bonding modes for disubstituted acetylenes have been observed: the tetrahedral $\mu_2\text{-}\eta^2$ geometry in which the acetylene molecule lies perpendicular to the metal-metal axis^{1,3-13} and the cis-dimetalated olefinic mode¹⁴⁻¹⁸ having the acetylene parallel to the metal atoms. The transformation of one mode to the other has been observed

by Dickson and co-workers¹⁹ by the removal of a carbonyl ligand from $[\text{Rh}_2\text{Cp}_2(\text{CO})_2(\mu\text{-HFB})]$ (HFB = hexafluoro-2-butyne), yielding $[\text{Rh}_2\text{Cp}_2(\mu\text{-CO})(\mu\text{-HFB})]$ (the cis-dimetalated olefinic geometry was observed in the former¹⁵ and the $\mu_2\text{-}\eta^2$ geometry in the latter¹³). We have similarly effected the removal of CO from $[\text{Rh}_2\text{Cl}_2(\mu\text{-CO})(\mu\text{-HFB})(\text{DPM})_2]$ (**1**), yielding $[\text{Rh}_2\text{Cl}_2(\mu\text{-HFB})(\text{DPM})_2]$ ¹⁸ (**2**). This carbonyl-free species is analogous to $[\text{Pd}_2\text{Cl}_2(\mu\text{-HFB})(\text{DPM})_2]$,¹⁶ which contains a cis-dimetalated olefinic coordination mode of the acetylene ligand and no metal-metal bond, but differs from the palladium analogue in having two less electrons. As a consequence, if the acetylene molecule were bound as a cis-dimetalated olefin as in the palladium species, there would be a metal-metal bond, whereas if the $\mu_2\text{-}\eta^2$ mode were observed, there would be no accompanying metal-metal bond.

The structure determination of $[\text{Rh}_2\text{Cl}_2(\mu\text{-HFB})(\text{DPM})_2]$ (**2**) was therefore undertaken to determine the mode of acetylene binding in this complex in order to help establish the factors which favor each bonding mode. In addition a preparation of complex **2**, which is more direct than carbonyl removal from **1**, is reported.

Experimental Section

All solvents were dried over molecular sieves and degassed under dinitrogen prior to use. Reactions were performed under Schlenk conditions with use of atmospheres of either dinitrogen or the reactant gas. Bis(diphenylphosphino)methane (DPM)²⁰ was purchased from Strem Chemicals, hydrated rhodium chloride from Research Organic/Inorganic Chemicals, and hexafluoro-2-butyne (HFB) from Pierce Chemicals. These and other chemicals were used without further purification. $[\text{RhCl}(\text{C}_8\text{H}_{12})_2]$ was prepared by the reported procedure.²¹ Infrared spectra were run as Nujol mulls on KBr plates on a Perkin-Elmer Model 467 spectrometer, and ³¹P{¹H} NMR spectra were run at 36.4 MHz on a Bruker HFX-90 spectrometer at -40 °C.

Preparation of $[\text{Rh}_2\text{Cl}_2(\mu\text{-HFB})(\text{DPM})_2]$ (1**).** A 200-mg (0.406 mmol) sample of $[\text{RhCl}(\text{C}_8\text{H}_{12})_2]$ and 302 mg (0.786 mmol) of ground bis(diphenylphosphino)methane (DPM) were dissolved in 10 mL of CH_2Cl_2 and a stream of gaseous hexafluoro-2-butyne (HFB) was passed over the solution for 5 min with stirring. The orange solution turned dark green almost immediately but was left under an atmosphere of HFB for several hours. A green solid was precipitated in about 75% yield by addition of diethyl ether. Elemental analyses (C,

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- Abbreviations used are as follows: DPM = bis(diphenylphosphino)methane; HFB = hexafluoro-2-butyne; DMA = dimethyl acetylenedicarboxylate.
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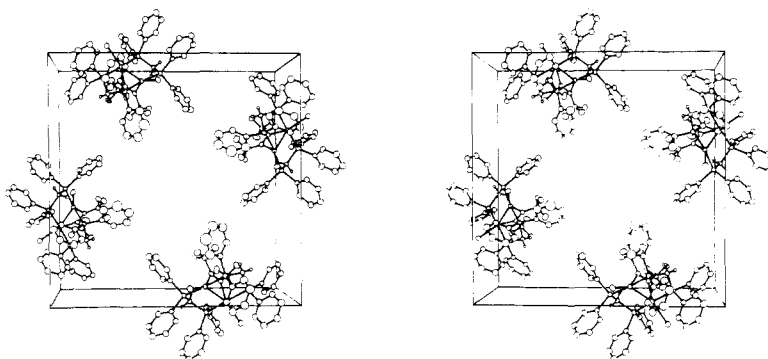


Figure 1. Stereoview of the unit cell of [Rh₂Cl₂(μ-HFB)(DPM)₂]. The x axis is from left to right, the y axis runs from bottom to top, and the z axis comes out of the page. 20% thermal ellipsoids are shown with the exception of the methylene hydrogen atoms which are drawn artificially small on this and all subsequent drawings.

H, F, Cl) were consistent with the above formulation. The infrared spectrum showed an acetylene stretch at 1638 cm⁻¹, and the ³¹P{¹H} NMR spectrum displayed a resonance at 7.5 ppm (positive shifts are downfield of H₃PO₄) with $|^1J_{\text{Rh-P}} + ^2J_{\text{Rh-P}}| = 112.0$ Hz.²² Crystals of suitable quality for a single-crystal X-ray study were obtained by slow diethyl ether diffusion into a saturated CH₂Cl₂ solution of the complex under an atmosphere of HFB.

Reaction of [Rh₂Cl₂(μ-HFB)(DPM)₂] with CO. This reaction was monitored in an NMR tube by using a CD₂Cl₂ solution of **1**, prepared in situ, to which CO was slowly added. Upon CO addition, a new resonance at 8.9 ppm ($|^1J_{\text{Rh-P}} + ^2J_{\text{Rh-P}}| = 131.8$ Hz) immediately appeared. A comparison of the ³¹P{¹H} NMR spectrum of this new species with that of an authentic sample showed that it was [Rh₂Cl₂(μ-CO)(μ-HFB)(DPM)₂] (**1**). The infrared spectrum of this product showed a bridging carbonyl band at 1705 cm⁻¹, also consistent with complex **1**.

X-ray Data Collection

A dark green crystal of the title complex was mounted on a glass fiber. Preliminary film data showed that the crystal belonged to the tetragonal system with diffraction symmetry 4/m and extinctions (00: *l* ≠ 4*n*), characteristic of space groups P₄₁ and P₄₃. Accurate cell parameters were obtained by a least-squares analysis of 12 carefully centered reflections chosen from diverse regions of reciprocal space (50° ≤ 2θ ≤ 65°, Cu Kα radiation) and obtained with use of a narrow X-ray source. See Table I for pertinent crystal and data collection details. The width at half-height of several strong reflections (ω scan, open counter) lay in the range 0.08–0.09°.

Data were collected on an automated Picker four-circle diffractometer equipped with a scintillation counter and pulse-height analyser tuned to accept 90% of the Cu Kα peak. Background counts were measured at both ends of the scan range with crystal and counter stationary. The intensities of three standard reflections were measured every 100 reflections throughout the data collection. A second set of four standards was monitored twice a day. No significant decay of these standards was observed over the course of the data collection. The intensities of 5944 unique reflections (3° < 2θ < 120°) were measured with use of Cu Kα radiation, and the data were processed in the usual manner with $\sigma(F_o^2)$ calculated by using a value of 0.05 for *p*.²³ A total of 5243 reflections had $F_o^2 \geq 3\sigma(F_o^2)$ and were used in subsequent calculations. Absorption corrections were applied to the data by using Gaussian integration.²⁴

Structure Solution and Refinement

The structure was solved in space group P₄₁ with the use of a sharpened Patterson synthesis to locate the two independent Rh atoms. Subsequent refinements and difference Fourier syntheses led to the location of all remaining nonhydrogen atoms. Atomic scattering factors were taken from Cromer and Waber's tabulation²⁵ for all atoms except hydrogen, for which the values of Stewart et al.²⁶ were used.

Table I. Summary of Crystal Data and Intensity Collection

compd	Rh ₂ Cl ₂ (μ-HFB)(DPM) ₂
fw	1207.5
formula	Rh ₂ Cl ₂ P ₄ F ₆ C ₃₄ H ₄₄
cell parameters	
<i>a</i> , Å	21.283 (1) Å
<i>c</i> , Å	14.255 (1) Å
<i>Z</i>	4
<i>V</i> , Å ³	6457.3
density, g/cm ³	1.242 (calcd), 1.244 (measd by flotation)
space group	P ₄ ₁
crystal dimens, mm	0.28 × 0.40 × 0.42
crystal shape	tetragonal prism with 20 faces of the form: {100}, {110}, {101}, {111}, {310}, {410}, {122}, {113}
cryst vol, mm ³	0.0213
temp, °C	23
radiation	Cu Kα
μ, cm ⁻¹	63.587
range in absorption	0.179–0.341
corr factors	
receiving aperture, mm	3 × 4 (at 30 cm from cryst)
takeoff angle, deg	3.0
scan speed, deg/min	2 in 2θ
scan range, deg	0.95 below Kα ₁ to 0.95 above Kα ₂
bkgd counting times, s	2.5° ≤ 2θ ≤ 61°, 10; 61° < 2θ ≤ 95°, 20; 95° < 2θ ≤ 120°, 40
2θ limits, deg	2.5 ≤ 2θ ≤ 120
unique data used	5243
($F_o^2 \geq 3\sigma(F_o^2)$)	
final no. of parameters	278
varied	
error in observn of unit weight	1.530
<i>R</i>	0.040
<i>R</i> _w	0.055

Anomalous dispersion terms²⁷ for Rh, Cl, P, and F were included in *F_c*. All phenyl ring carbon atoms were refined as rigid groups having idealized *D*_{6h} symmetry and C–C distances of 1.392 Å. These carbon atoms were given independent isotropic thermal parameters. On one of the phenyl groups (ring 7) the thermal parameters of several carbon atoms became unusually large so this group was removed and refinement continued. A subsequent difference Fourier map reaffirmed the location of this group, but peaks corresponding to the carbon atoms near the para position were quite diffuse and about half the intensity of C(71) which is bonded to P(4). No indication of a simple disorder of these carbon atoms was obtained, so the group was reinserted and

(22) This is the separation between the two major peaks.

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Table II. Positional and Thermal Parameters for the Nongroup Atoms of $[\text{Rh}_2\text{Cl}_2(\mu\text{-HFB})(\text{DPM})_2]$

Atom	a			b					
	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Rh(1)	-0.00175(3)	0.28686(3)	0	4.62(4)	3.64(4)	4.55(4)	-0.08(3)	0.01(3)	0.08(3)
Rh(2)	0.06543(3)	0.37793(3)	0.09233(6)	5.45(4)	3.74(4)	4.13(4)	0.15(3)	-0.16(3)	-0.24(3)
Cl(1)	-0.0941(1)	0.2242(1)	-0.0144(2)	5.8(1)	5.0(1)	7.6(2)	-0.9(1)	-1.1(1)	0.3(1)
Cl(2)	0.0686(1)	0.4453(1)	0.2252(2)	9.4(2)	5.6(1)	5.3(2)	0.8(1)	-0.9(1)	-1.4(1)
P(1)	-0.0545(1)	0.3638(1)	-0.0838(2)	5.2(1)	4.1(1)	4.4(1)	-0.0(1)	-0.2(1)	0.3(1)
P(2)	0.0258(1)	0.46142(10)	0.0027(2)	5.8(1)	3.8(1)	4.3(1)	-0.24(9)	-0.0(1)	0.2(1)
P(3)	0.0494(1)	0.2027(1)	0.0739(2)	4.7(1)	3.8(1)	4.8(1)	0.18(9)	0.1(1)	-0.0(1)
P(4)	0.1156(1)	0.3027(1)	0.1819(2)	6.3(2)	4.3(1)	5.0(2)	0.5(1)	-1.1(1)	-0.1(1)
F(1)	0.1158(4)	0.3113(3)	-0.2223(4)	17.2(7)	7.0(4)	5.6(4)	-1.8(4)	4.1(4)	0.0(3)
F(2)	0.0458(3)	0.2424(3)	-0.1952(4)	8.6(4)	9.3(4)	7.1(4)	-1.4(4)	0.2(3)	-3.1(4)
F(3)	0.1389(3)	0.2292(3)	-0.1460(5)	8.4(4)	7.9(4)	9.1(5)	1.9(3)	2.1(4)	-1.3(4)
F(4)	0.1757(3)	0.4098(3)	-0.1192(5)	8.2(4)	9.4(5)	9.4(5)	-2.4(4)	1.7(4)	2.0(4)
F(5)	0.2161(3)	0.3251(3)	-0.0660(6)	6.2(4)	8.2(4)	17.9(8)	0.6(3)	2.7(5)	-2.4(5)
F(6)	0.2028(3)	0.4041(3)	0.0220(5)	6.4(4)	8.7(4)	10.6(5)	-2.7(3)	0.3(4)	-1.3(4)
C(1)	0.0942(5)	0.2734(4)	-0.1563(8)	7.9(7)	5.2(6)	5.3(6)	0.1(5)	0.8(6)	0.1(5)
C(2)	0.0784(4)	0.3056(4)	-0.0668(7)	5.5(5)	4.4(5)	5.5(6)	0.8(4)	0.8(5)	-0.0(4)
C(3)	0.1117(4)	0.3474(4)	-0.0207(6)	4.3(5)	4.9(5)	5.3(6)	0.4(4)	-0.7(4)	-0.2(4)
C(4)	0.1758(5)	0.3714(5)	-0.0448(8)	6.7(6)	5.4(6)	6.3(7)	0.8(5)	1.2(6)	-0.7(5)
C(5)	-0.0070(4)	0.4328(4)	-0.1082(6)	6.0(5)	3.8(4)	4.3(5)	-0.4(4)	0.2(4)	0.5(4)
C(6)	0.1244(4)	0.2278(4)	0.1228(6)	4.5(5)	3.9(4)	4.4(5)	0.4(4)	-0.1(4)	0.3(4)

^a Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. ^b The form of the thermal ellipsoid is $\exp[-2\pi^2(a^*U_{11}h^2 + b^*U_{22}k^2 + c^*U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$. The quantities given in the table are the thermal coefficients $\times 10^2$.

refinement was continued. It should be noted that the badly behaved group aims into the large cavity in the center of the cell as can be seen in the packing diagram (Figure 1). Apart from two hydrogens on the badly behaved group, all other hydrogen atoms were located but were input as fixed contributions and not refined. Their idealized positions were calculated after each cycle of refinement from the geometries of their attached carbon atoms by using a C-H distance of 0.95 Å. These hydrogen atoms were assigned isotropic thermal parameters of 1 Å² greater than those of their attached carbon atoms. All other nongroup atoms were refined individually with anisotropic thermal parameters. Initial refinements were carried out in space group $P4_1$, converging to $R = 0.056$ and $R_w = 0.082$.²⁸ Refining in the enantiomeric space group $P4_3$ resulted in crystallographic residuals of $R = 0.044$ and 0.062, indicating that the latter was probably the correct choice. Since these space groups are polar and, with atoms displaying high anomalous scattering, can give rise to polar dispersion errors,²⁹ significant differences in bond lengths were observed between the two space groups. In $P4_3$ the chemically equivalent P-C_{phenyl} distances, for example, show a narrower range (1.822 (5)–1.844 (5) Å) than the equivalent distances in $P4_1$ (1.808 (7)–1.852 (7) Å), adding further confirmation that $P4_3$ is the correct choice. At this stage of refinement, a comparison of the observed and calculated structure amplitudes of strong, low-angle reflections suggested that they suffered from extinction effects. Application of an isotropic secondary extinction correction³⁰ yielded $R = 0.040$ and $R_w = 0.055$ and greatly improved the agreement between $|F_o|$ and $|F_c|$ in these reflections. The highest 20 residual peaks on a final electron density difference map (0.78–0.50 e/Å³) were all in the vicinities of the phenyl groups, and most were in the vicinities of groups 7 and 8. A typical carbon atom on earlier Fourier syntheses had an electron density of about 2.3 e/Å³.

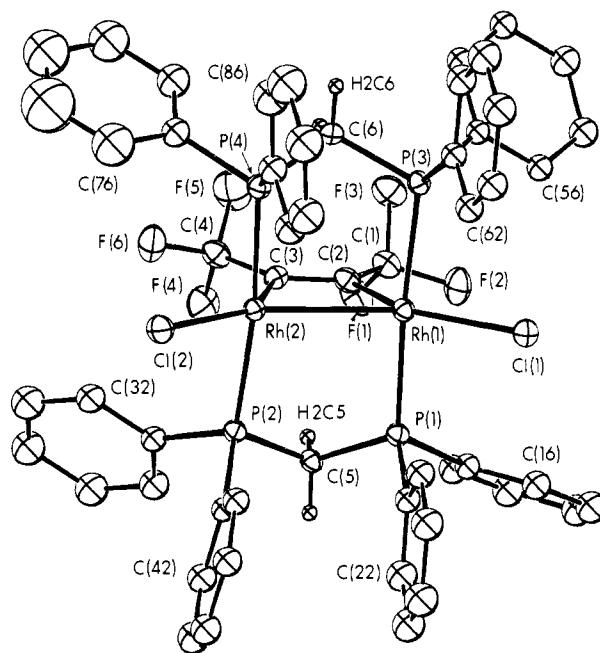


Figure 2. Perspective view of $[\text{Rh}_2\text{Cl}_2(\mu\text{-HFB})(\text{DPM})_2]$, showing the numbering scheme. The numbering on the phenyl carbon atoms starts at the carbon bonded to phosphorus and increases sequentially around the ring. 20% ellipsoids are shown.

(28) $R = \sum |F_o| - |F_c| / \sum |F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$.

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The final positional and thermal parameters of the nonhydrogen atoms and the group atoms are given in Tables II and III, respectively. The idealized hydrogen parameters and a listing of the observed and calculated structure amplitudes are available.³¹

Table III. Derived Parameters for the Rigid-Group Atoms of [Rh₂Cl₂(μ-HFB)(DPM)₂]

Atom	x	y	z	B(A ²)	Atom	x	y	z	B(A ²)
C(11)	-0.0831(8)	0.3406(3)	-0.1992(9)	4.3(2)	C(51)	0.0720(4)	0.1380(3)	-0.0032(5)	3.7(2)
C(12)	-0.0479(3)	0.3525(3)	-0.280(1)	5.2(2)	C(52)	0.1298(3)	0.1081(3)	0.0052(5)	4.3(2)
C(13)	-0.0696(8)	0.3323(4)	-0.3667(5)	6.2(3)	C(53)	0.1468(2)	0.0614(3)	-0.0583(4)	4.8(2)
C(14)	-0.1264(8)	0.3004(3)	-0.3734(9)	6.3(3)	C(54)	0.1058(4)	0.0446(3)	-0.1302(5)	5.6(2)
C(15)	-0.1616(3)	0.2885(3)	-0.293(1)	6.3(3)	C(55)	0.0479(3)	0.0746(3)	-0.1386(5)	5.5(2)
C(16)	-0.1400(8)	0.3086(4)	-0.2059(5)	5.3(2)	C(56)	0.0310(2)	0.1213(3)	-0.0751(4)	4.4(2)
C(21)	-0.1254(5)	0.3945(3)	-0.0281(4)	4.3(2)	C(61)	0.0106(5)	0.1636(3)	0.1737(6)	4.3(2)
C(22)	-0.1589(6)	0.4427(3)	-0.0711(6)	6.3(3)	C(62)	-0.0473(4)	0.1839(3)	0.2072(6)	5.1(2)
C(23)	-0.2126(4)	0.4669(3)	-0.0286(7)	7.0(3)	C(63)	-0.0740(5)	0.1554(3)	0.2855(4)	6.0(3)
C(24)	-0.2328(5)	0.4427(3)	0.0570(4)	7.6(3)	C(64)	-0.0427(5)	0.1065(3)	0.3304(6)	7.1(3)
C(25)	-0.1994(6)	0.3945(3)	0.1000(6)	6.8(3)	C(65)	0.0153(4)	0.0861(3)	0.2969(6)	7.2(3)
C(26)	-0.1457(4)	0.3703(3)	0.0574(7)	5.2(2)	C(66)	0.0420(5)	0.1147(3)	0.2186(4)	5.9(3)
C(31)	0.0867(3)	0.5169(3)	-0.0337(8)	4.1(2)	C(71)	0.1958(6)	0.3224(5)	0.2167(9)	5.3(2)
C(32)	0.1348(5)	0.5313(3)	0.0288(8)	5.3(2)	C(72)	0.2475(7)	0.2945(5)	0.1735(7)	7.1(3)
C(33)	0.1820(3)	0.5731(4)	0.0027(4)	7.3(3)	C(73)	0.3081(6)	0.3113(5)	0.2005(8)	10.7(5)
C(34)	0.1810(3)	0.6006(3)	-0.0859(8)	7.3(3)	C(74)	0.3170(6)	0.3559(5)	0.2706(9)	13.8(6)
C(35)	0.1328(5)	0.5862(3)	-0.1484(8)	7.0(3)	C(75)	0.2654(7)	0.3838(5)	0.3137(7)	19.0(9)
C(36)	0.0857(3)	0.5444(4)	-0.1223(4)	5.7(2)	C(76)	0.2048(6)	0.3670(5)	0.2868(8)	11.8(6)
C(41)	-0.0358(3)	0.5133(3)	0.0470(4)	3.7(2)	C(81)	0.0793(8)	0.2822(4)	0.2942(8)	5.3(2)
C(42)	-0.0515(4)	0.5670(3)	-0.0034(4)	5.5(2)	C(82)	0.0197(6)	0.3053(4)	0.3153(9)	6.2(3)
C(43)	-0.0985(3)	0.6069(3)	0.0294(6)	6.4(3)	C(83)	-0.0102(7)	0.2869(4)	0.3976(5)	8.4(4)
C(44)	-0.1298(3)	0.5929(3)	0.1126(4)	6.0(3)	C(84)	0.0194(8)	0.2454(4)	0.4588(8)	9.0(4)
C(45)	-0.1140(4)	0.5392(3)	0.1630(4)	5.4(2)	C(85)	0.0789(6)	0.2223(4)	0.4377(9)	9.8(4)
C(46)	-0.0670(3)	0.4993(3)	0.1302(6)	4.6(2)	C(86)	0.1088(7)	0.2407(4)	0.3553(5)	8.5(4)

Rigid Group Parameters

	a			b		
	Xc	Yc	Zc	Delta	Epsilon	Eta
Ring1	-0.1048(2)	0.3205(2)	-0.2863(4)	4.196(4)	1.322(9)	3.813(9)
Ring2	-0.1791(2)	0.4186(2)	0.0144(4)	-0.741(4)	0.859(6)	5.760(6)
Ring3	0.1338(2)	0.5587(2)	-0.0598(4)	4.005(4)	2.160(7)	1.392(7)
Ring4	-0.0828(2)	0.5531(2)	0.0798(3)	-0.549(4)	0.926(5)	5.488(4)
Ring5	0.0889(2)	0.0913(2)	-0.0667(3)	-0.762(4)	2.531(6)	1.732(5)
Ring6	-0.0160(2)	0.1350(2)	0.2520(4)	-0.721(4)	0.661(6)	0.620(6)
Ring7	0.2564(3)	0.3392(3)	0.2436(5)	2.332(6)	3.134(9)	0.381(1)
Ring8	0.0493(3)	0.2638(3)	0.3765(4)	-0.881(5)	0.709(9)	0.459(9)

^a X_c, Y_c, and Z_c are the fractional coordinates of the centroid of the rigid group. ^b The rigid group orientation angles δ, ε, and η (radians) are the angles by which the rigid body is rotated with respect to a set of axes X, Y, and Z. The origin is the center of the ring; X is parallel to a*, Z is parallel to c, and Y is parallel to the line defined by the intersection of the plane containing a* and b* with the plane containing b and c.

Table IV. Selected Distances (Å) in [Rh₂Cl₂(μ-HFB)(DPM)₂]

Bonding Distances			
Rh(1)-Rh(2)	2.7447(9)	C(4)-F(4)	1.34(1)
Rh(1)-Cl(1)	2.384(2)	C(4)-F(5)	1.34(1)
Rh(2)-Cl(2)	2.377(2)	C(4)-F(6)	1.31(1)
Rh(1)-P(1)	2.318(2)	P(1)-C(5)	1.816(8)
Rh(1)-P(3)	2.345(2)	P(2)-C(5)	1.831(9)
Rh(2)-P(2)	2.346(2)	P(3)-C(6)	1.823(8)
Rh(2)-P(4)	2.309(2)	P(4)-C(6)	1.813(8)
Rh(1)-C(2)	1.994(9)	P(1)-C(11)	1.822(5)
Rh(2)-C(3)	1.997(9)	P(1)-C(21)	1.826(5)
C(2)-C(3)	1.315(12)	P(2)-C(31)	1.828(5)
C(1)-C(2)	1.49(1)	P(2)-C(41)	1.827(5)
C(3)-C(4)	1.50(1)	P(3)-C(51)	1.826(5)
C(1)-F(1)	1.32(1)	P(3)-C(61)	1.844(5)
C(1)-F(2)	1.34(1)	P(4)-C(71)	1.827(7)
C(1)-F(3)	1.35(1)	P(4)-C(81)	1.830(6)
Nonbonding Distances			
P(1)-P(2)	2.959(3)	Cl(2)-H(76)	2.80
P(3)-P(4)	2.981(3)	Cl(2)-H(46)	2.82
Cl(1)-H(56)	2.70	H(72)-H(126)	2.11
Cl(1)-H(62)	2.78	H(12)-H(2C5)	2.18
Cl(2)-H(32)	2.80		

Description of Structure and Discussion

The unit cell of [Rh₂Cl₂(μ-HFB)(DPM)₂] consists of four discrete molecules of the complex as shown in Figure 1. There are no unusually short intermolecular contacts (Table IV). A

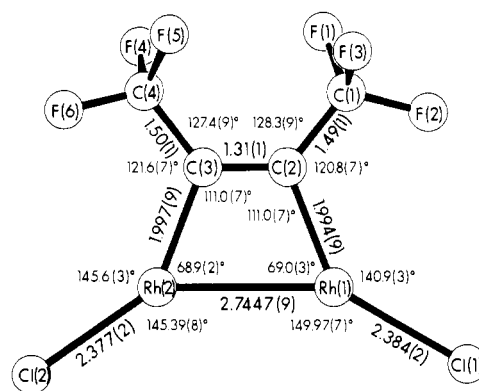


Figure 3. Representation of the metal coordination in the plane of the metal atoms and the acetylene molecule. Some relevant bond lengths and angles are shown.

perspective view of the molecule together with the numbering scheme is presented in Figure 2 (phenyl hydrogens have the same number as their attached carbon atoms), and a representation of the inner coordination sphere in the plane of the rhodium atoms and the acetylene molecule is shown in Figure 3.

The complex has a geometry typical of DPM-bridged binuclear complexes, having two rhodium atoms bridged by two transoid DPM ligands. In the equatorial plane, approximately perpendicular to the Rh-P vectors, the metals are bridged by a hexafluoro-2-butyne molecule, coordinated as a cis-dimetalated olefin. A terminal chloro ligand on each metal and

Table V. Selected Angles (Deg) in $[\text{Rh}_2\text{Cl}_2(\mu\text{-HFB})(\text{DPM})_2]$

Bond Angles			
P(1)-Rh(1)-Rh(2)	90.02 (6)	C(21)-P(1)-C(5)	104.7 (4)
P(3)-Rh(1)-Rh(2)	94.71 (6)	C(31)-P(2)-C(41)	102.5 (3)
P(2)-Rh(2)-Rh(1)	94.95 (6)	C(31)-P(2)-C(5)	103.9 (4)
P(4)-Rh(2)-Rh(1)	90.94 (6)	C(41)-P(2)-C(5)	103.0 (4)
P(1)-Rh(1)-P(3)	174.87 (9)	C(51)-P(3)-C(61)	104.0 (3)
P(2)-Rh(2)-P(4)	173.03 (9)	C(51)-P(3)-C(6)	102.7 (3)
Cl(1)-Rh(1)-Rh(2)	149.97 (7)	C(61)-P(3)-C(6)	103.3 (4)
Cl(2)-Rh(2)-Rh(1)	145.39 (8)	C(71)-P(4)-C(81)	102.2 (4)
P(1)-Rh(1)-Cl(1)	87.21 (8)	C(71)-P(4)-C(6)	103.3 (4)
P(3)-Rh(1)-Cl(1)	89.68 (8)	C(81)-P(4)-C(6)	103.9 (4)
P(2)-Rh(2)-Cl(2)	89.28 (9)	Rh(1)-P(1)-C(11)	115.8 (2)
P(4)-Rh(2)-Cl(2)	87.96 (9)	Rh(1)-P(1)-C(21)	115.4 (2)
P(1)-Rh(1)-C(2)	91.5 (3)	Rh(1)-P(1)-C(5)	113.6 (3)
P(3)-Rh(1)-C(2)	88.3 (3)	Rh(2)-P(2)-C(31)	112.9 (2)
P(2)-Rh(2)-C(3)	89.1 (2)	Rh(2)-P(2)-C(41)	121.8 (2)
P(4)-Rh(2)-C(3)	89.6 (2)	Rh(2)-P(2)-C(5)	110.8 (3)
Cl(1)-Rh(1)-C(2)	140.9 (3)	Rh(1)-P(3)-C(51)	115.3 (2)
Cl(2)-Rh(2)-C(3)	145.6 (3)	Rh(1)-P(3)-C(61)	119.0 (2)
C(2)-Rh(1)-Rh(2)	69.0 (3)	Rh(1)-P(3)-C(6)	110.8 (3)
C(3)-Rh(2)-Rh(1)	68.9 (2)	Rh(2)-P(4)-C(71)	115.1 (3)
Rh(1)-C(2)-C(3)	111.0 (7)	Rh(2)-P(4)-C(81)	117.0 (3)
Rh(2)-C(3)-C(2)	111.0 (7)	Rh(2)-P(4)-C(6)	113.6 (3)
Rh(1)-C(2)-C(1)	120.8 (7)	P(1)-C(5)-P(2)	108.4 (4)
Rh(2)-C(3)-C(4)	121.6 (7)	P(3)-C(6)-P(4)	110.1 (4)
C(1)-C(2)-C(3)	128.3 (9)	P(1)-C(11)-C(12)	120.9 (4)
C(4)-C(3)-C(2)	127.4 (9)	P(1)-C(11)-C(16)	119.0 (4)
F(1)-C(1)-C(2)	114.0 (8)	P(1)-C(21)-C(22)	119.6 (4)
F(2)-C(1)-C(2)	114.0 (8)	P(1)-C(21)-C(26)	120.4 (4)
F(3)-C(1)-C(2)	112.9 (9)	P(2)-C(31)-C(32)	118.8 (4)
F(4)-C(4)-C(3)	112.9 (9)	P(2)-C(31)-C(36)	121.2 (4)
F(5)-C(4)-C(3)	112.6 (8)	P(2)-C(41)-C(42)	119.4 (4)
F(6)-C(4)-C(3)	114.5 (8)	P(2)-C(41)-C(46)	120.6 (4)
F(1)-C(1)-F(2)	105.8 (9)	P(3)-C(51)-C(52)	121.8 (3)
F(1)-C(1)-F(3)	105.0 (9)	P(3)-C(51)-C(56)	118.1 (3)
F(2)-C(1)-F(3)	104.2 (8)	P(3)-C(61)-C(62)	121.3 (4)
F(4)-C(4)-F(5)	105.7 (9)	P(3)-C(61)-C(66)	118.6 (4)
F(4)-C(4)-F(6)	104.6 (8)	P(4)-C(71)-C(72)	121.4 (7)
F(5)-C(4)-F(6)	105.9 (9)	P(4)-C(71)-C(76)	118.6 (7)
C(11)-P(1)-C(21)	102.3 (3)	P(4)-C(81)-C(82)	119.3 (5)
C(11)-P(1)-C(5)	103.5 (4)	P(4)-C(81)-C(86)	120.5 (5)
Torsion Angles			
P(1)-Rh(1)-Rh(2)-P(2)	-6.16 (8)	C(51)-P(3)-Rh(1)-Cl(1)	73.7 (2)
P(3)-Rh(1)-Rh(2)-P(4)	-4.43 (9)	C(61)-P(3)-Rh(1)-Cl(1)	-50.9 (3)
P(1)-Rh(1)-Rh(2)-P(4)	177.56 (9)	C(31)-P(2)-Rh(2)-Cl(2)	78.8 (3)
P(2)-Rh(2)-Rh(1)-P(3)	171.85 (8)	C(41)-P(2)-Rh(2)-Cl(2)	-43.8 (3)
C(5)-P(1)-P(3)-C(6)	13.1 (4)	C(71)-P(4)-Rh(2)-Cl(2)	-66.1 (4)
C(5)-P(2)-P(4)-C(6)	10.3 (4)	C(81)-P(4)-Rh(2)-Cl(2)	53.9 (3)
C(11)-P(1)-P(3)-C(51)	16.0 (3)	C(11)-P(1)-Rh(1)-C(2)	83.4 (4)
C(21)-P(1)-P(3)-C(61)	11.5 (4)	C(21)-P(1)-Rh(1)-C(2)	-157.1 (4)
C(31)-P(2)-P(4)-C(71)	12.4 (4)	C(51)-P(3)-Rh(1)-C(2)	-67.2 (3)
C(41)-P(2)-P(4)-C(81)	10.6 (4)	C(61)-P(3)-Rh(1)-C(2)	168.2 (4)
C(1)-C(2)-C(3)-C(4)	-2.8 (1.6)	C(31)-P(2)-Rh(2)-C(3)	-66.9 (3)
Rh(1)-C(2)-C(3)-Rh(2)	-3.4 (8)	C(41)-P(2)-Rh(2)-C(3)	170.6 (4)
Cl(1)-Rh(1)-Rh(2)-Cl(2)	5.3 (2)	C(71)-P(4)-Rh(2)-C(3)	79.6 (4)
C(11)-P(1)-P(2)-C(31)	-19.3 (5)	C(81)-P(4)-Rh(2)-C(3)	-160.4 (4)
C(21)-P(1)-P(2)-C(41)	-11.7 (3)	C(5)-P(1)-Rh(1)-C(2)	-36.1 (4)
C(51)-P(3)-P(4)-C(71)	-11.2 (6)	C(5)-P(2)-Rh(2)-C(3)	49.2 (4)
C(61)-P(3)-P(4)-C(81)	-5.7 (4)	C(6)-P(3)-Rh(1)-C(2)	48.8 (4)
C(11)-P(1)-Rh(1)-Cl(1)	-57.5 (3)	C(6)-P(4)-Rh(2)-C(3)	-39.3 (4)
C(21)-P(1)-Rh(1)-Cl(1)	62.0 (3)		

a rhodium-rhodium bond complete the rhodium coordinations. The molecule has approximate C_{2v} symmetry with one pseudomirror plane bisecting the Rh-Rh bond and the other lying in the metal-acetylene plane. Each rhodium has a somewhat distorted trigonal-bipyramidal coordination with the trans phosphines in the axial sites and the chloro ligand, an acetylenic carbon atom, and the other metal occupying the three equatorial sites. The major distortion from idealized trigonal-bipyramidal geometry results from the acute $C_{\text{acetylene}}\text{-Rh-Rh}$ angles (Figure 3) and the concomitant larger angles involving the chloro ligands. These acute angles at rhodium are typical for metal-metal bonded complexes which are

bridged by acetylenes in the cis-dimetalated olefinic geometry.^{15,17}

Within the DPM framework, the parameters are essentially as expected: the Rh-P distances (range 2.309 (2)-2.346 (2) Å) compare well with other determinations as do the phosphorus-carbon distances (both methylene and phenyl). Similarly all angles within the DPM ligand are normal. As is often observed in these systems, the bridging methylene groups of the DPM ligand are both bent in the direction of the bulkier equatorial ligand (the acetylene ligand) allowing the phenyl groups to minimize their nonbonded contacts with this group. All phenyl groups are essentially staggered with regard to the

Table VI

Least-Squares Planes Calculations ^a								
plane no.		eq		plane no.		eq		
1	-0.4482X + 0.7081Y - 0.5457Z - 4.3442 = 0	3	-0.4534X + 0.7049Y - 0.5455Z - 4.3207 = 0	2	-0.4200X + 0.7420Y - 0.5225Z - 4.6334 = 0	4	-0.4469X + 0.7078Y - 0.5471Z - 4.3422 = 0	
Distances from Planes (Å)								
plane no.	Rh(1)	Rh(2)	Cl(1)	Cl(2)	C(1)	C(2)	C(3)	C(4)
1	-0.0045 (5)	0.0089 (7)	0.045 (2)	-0.040 (3)	0.093 (10)	0.033 (9)	-0.013 (9)	-0.076 (10)
2					0.006 (10)	-0.010 (9)	0.009 (9)	-0.006 (10)
3	0.0000 (5)	0.0001 (7)			0.087 (10) ^b	0.027 (9)	-0.025 (9)	-0.096 (10) ^b
4	-0.0041 (5)	0.0088 (7)	0.043 (2)	-0.043 (3)		0.037 (9) ^b	-0.009 (9) ^b	
Dihedral Angles between Planes (Deg)								
plane no.		angle	plane no.		angle	plane no.		angle
1	2	2.86	1	4	0.12	2	4	2.86
1	3	0.35	2	3	3.15	3	4	0.42

^a X, Y, and Z are orthogonal coordinates in Å with X along the a axis, Y in the ab plane, and Z along the c* axis. ^b Not included in least-squares plane calculation.

equatorial ligands (as shown by the torsion angles in Table V), again minimizing contacts.

The Rh-Rh distance, at 2.7447 (9) Å, is typical for a Rh-Rh single bond, being comparable to the range observed (2.7566 (9)-2.8415 (7) Å) in analogous systems.³²⁻³⁵ This metal-metal distance is significantly shorter than the intraligand P-P distances (2.959 (3) and 2.981 (3) Å), indicating a mutual attraction by the metals. The resulting compression of the rhodium-rhodium axis is clearly evident in Figure 2. Both Rh-Cl distances (2.377 (2), 2.384 (2) Å) are normal for terminal chlorides and are significantly shorter than those observed in an analogous carbonyl adduct, [Rh₂Cl₂(μ-CO)(μ-DMA)(DPM)₂],¹⁸ where these bonds are nearly trans to a σ-alkenyl group of high trans influence. In the present compound the rhodium alkenyl bonds (Rh(1)-C(2) and Rh(2)-C(3)) are inclined to the Rh-Cl bonds by 140.9 (3)° and 145.6 (3)°, respectively, significantly bent from the trans geometry.

The hexafluoro-2-butyne group is bound to the metals as a cis-dimetalated olefin; therefore, all angles about C(2) and C(3) are close to 120° as expected for sp² hybridization of these atoms. The distortion from idealized sp² hybridization results from the strain imposed by the Rh-Rh bond which compresses the Rh(1)-C(2)-C(3) and Rh(2)-C(3)-C(2) angles to 110.0 (7)°. In other metal-metal bonded species having analogously bound acetylene ligands, similar distortions were observed,^{15,17} whereas when no metal-metal bond is present (as in [Pd₂Cl₂(μ-HFB)(DPM)₂]¹⁶ and [Rh₂Cl₂(μ-CO)(μ-HFB)(DPM)₂]¹⁸), the acetylene ligands are found to approach more closely the olefin geometry. In spite of the strain in the acetylene molecule, imposed by the short Rh-Rh distance, the rhodium atoms and the carbon atom framework of the acetylene ligand are quite planar (Table VI). On the basis of the observed strain in the molecule, one might expect that the resulting metal-acetylene orbital overlap would be less than in unstrained cases, resulting in less activation of the acetylene. However, the other structural parameters in the ligand do not confirm this expectation. The rhodium-acetylene bonds (average 1.996 (9) Å) are among the shortest observed for second- or third-row, acetylene-bridged complexes and the C(2)-C(3) bond, although somewhat shorter than those in the

complexes without metal-metal bonds, is not significantly different. Only the C(1)-C(2)-C(3) and C(4)-C(3)-C(2) angles, at 128.3 (9) and 127.4 (9)°, respectively, indicate a tendency toward a more linear acetylenic geometry, compared to the species without metal-metal bonds.

The C(1)-C(2) and C(3)-C(4) bonds are exactly as expected for single bonds between an sp²- and an sp³-hybridized³⁶ carbon atom and agree well with the analogous distances in other binuclear HFB complexes.^{13,14,16} Similarly the C-F distances and all angles at the CF₃ groups are normal.

[Rh₂Cl₂(μ-HFB)(DPM)₂] is now the third member of a series of complexes, which we have structurally characterized, containing a rhodium-rhodium bond, terminal halide ligands, and a bridging π-acceptor ligand; the other members are [Rh₂Cl₂(μ-SO₂)(DPM)₂]³³ and [Rh₂Br₂(μ-CO)(DPM)₂].³⁴ Structurally these three species are remarkably similar, having very similar Rh-Rh distances, similar rhodium-DPM frameworks, and even similar orientations of the DPM phenyl groups. Significantly, all display short bonds between the metals and the bridging small molecules, implying strong back-donation from the metals to these ligands. Although this activation of these small molecules was not obvious structurally for the carbonyl and sulfur dioxide molecules, the acetylene molecule is obviously activated, resembling as it does a dimetalated olefin.

In spite of their structural similarities, these complexes differ significantly in their reactions with carbon monoxide.^{33,37} All react readily with CO but only in the acetylene species does the evidence suggest CO insertion into the metal-metal bond and certainly only this species gives a complex containing a bridging carbonyl with no accompanying metal-metal bond. Carbon monoxide attack in the other species seems to be terminal with subsequent rearrangement. Possibly in [Rh₂Cl₂(μ-HFB)(DPM)₂] the CF₃ groups block the terminal sites leaving only the bridging site open. An inspection of Figures 2 and 3 seems to support this suggestion. Furthermore, apart from the obvious differences resulting from the different bonding modes of SO₂, CO, and CF₃C₂CF₃, the major differences in the three related compounds is found in the Rh-Rh-halide angles. In the acetylene complex these angles (ca. 148°) are significantly less than those in the SO₂ and CO analogues (ca. 166°), suggesting that this distortion results from the crowding of the terminal sites by the CF₃ groups.

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An analogous series of palladium complexes, $[\text{Pd}_2\text{Cl}_2(\mu\text{-CO})(\text{DPM})_2]$,³⁸ $[\text{Pd}_2\text{Cl}_2(\mu\text{-SO}_2)(\text{DPM})_2]$,³⁹ and $[\text{Pd}_2\text{Cl}_2(\mu\text{-HFB})(\text{DPM})_2]$,¹⁶ has also been structurally characterized and differs from the rhodium series most significantly in the absence of metal-metal bonds. Although not much of the chemistry of these species has been reported, it seems that the palladium complexes, which lack the metal-metal bonds, are less reactive than their rhodium counterparts.

The chemistry of $[\text{Rh}_2\text{Cl}_2(\mu\text{-HFB})(\text{DPM})_2]$ is now currently under investigation to see whether small molecules other than

CO will insert into the Rh-Rh bond. In addition, since $[\text{Pd}_2\text{Cl}_2(\mu\text{-HFB})(\text{DPM})_2]$ ¹⁶ was found to cyclotrimerize hexafluoro-2-butyne, the present species will also be tested as a cyclotrimerization catalyst.

Acknowledgment. We thank the University of Alberta and the Natural Sciences and Engineering Research Council of Canada for financial support and NSERC for a scholarship to R.S.D.

Registry No. 1, 75503-68-3; 2, 77590-00-2; $[\text{RhCl}(\text{C}_8\text{H}_{12})]_2$, 12092-47-6.

Supplementary Material Available: Listings of the idealized hydrogen parameters and the observed and calculated structure amplitudes (17 pages). Ordering information is given on any current masthead page.

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Crystal Structure and Paramagnetic Properties of $[\text{Ni}(\text{C}_5\text{H}_5\text{NO})_6](\text{BrO}_3)_2$

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Received November 24, 1980

The compound $[\text{Ni}(\text{C}_5\text{H}_5\text{NO})_6](\text{BrO}_3)_2$ crystallizes in the space group $R\bar{3}$, with the metal atom at the center of the unit cell, which imposes a center of inversion and a threefold rotation axis at the metal atom. The coordination sphere of the nickel is rigorously octahedral; the unit cell parameters are $a = 9.513(1) \text{ \AA}$ and $\alpha = 84.58(1)^\circ$. The analysis of the susceptibilities measured at zero field yields the magnetic parameters $g_{\parallel} = 2.26 \pm 0.02$, $g_{\perp} = 2.33 \pm 0.02$, $D/k_B = 4.55 \pm 0.10 \text{ K}$, and $zJ/k_B = -0.10 \pm 0.05 \text{ K}$. The level-crossing field is found to be 31.0 kOe, and field-induced magnetic ordering in that external field is found not to occur down to at least 500 mK.

The magnetic properties of $S = 1$ spin-singlet ground-state systems have recently been of interest. The relevant compounds contain either trivalent vanadium¹⁻⁴ or divalent nickel⁵⁻¹⁰ in sites of uniaxial symmetry. In the examples to which we refer, a spin doublet is found above a singlet, and the zero-field splitting of the two states is so much larger than the exchange interaction that magnetic ordering does not occur spontaneously in the absence of a parallel applied magnetic field. Because of the symmetry of the systems, an applied field can cause one component of the doublet to drop in energy, and a level crossing can thereby occur eventually. This puts a double degeneracy into the ground state of the system so that when the exchange interaction is also large enough and the temperature is low enough, magnetic ordering can occur. The first example of such a field-induced magnetic ordering was provided by $[\text{Ni}(\text{C}_5\text{H}_5\text{NO})_6](\text{ClO}_4)_2$, where $\text{C}_5\text{H}_5\text{NO}$ is pyridine *N*-oxide. Magnetic ordering occurs in this system at 0.75 K in an applied field of 48 kOe. The complete phase diagrams for this salt as well as the isostructural nitrate analogue have also been determined and have been found to be quite similar.¹⁰ The subject has recently been reviewed.¹¹

One of the fascinating sidelights of this research has been the discovery that the salts $[\text{Ni}(\text{C}_5\text{H}_5\text{NO})_6]\text{X}_2$ are all found to be isostructural when X is ClO_4^- , BF_4^- , as well as NO_3^- . The iodide salt probably¹² is isostructural also. We now report the preparation, crystal structure, and susceptibility behavior of $[\text{Ni}(\text{C}_5\text{H}_5\text{NO})_6](\text{BrO}_3)_2$. It has been found that the substitution of even the large bromate ion allows the integrity of the crystal lattice symmetry of this system to remain intact. Furthermore, the magnetic properties are found to be quali-

tatively similar to those of the other systems but differ interestingly in quantitative detail.

Experimental Section

Hydrated nickel bromate was prepared from reagent grade nickel sulfate and barium bromate. The pyridine *N*-oxide complex was prepared in the usual fashion.¹³ Susceptibilities both at zero field and in an applied field have been measured in a fashion similar to that described earlier.⁹ Our crystal structure analysis procedures have also been described.¹⁴

Crystal Data for $[\text{Ni}(\text{C}_5\text{H}_5\text{NO})_6](\text{BrO}_3)_2$: $\text{NiBr}_2\text{N}_6\text{O}_{12}\text{C}_{30}\text{H}_{30}$, mol wt 885, space group $R\bar{3}$, $Z = 1$, $a = 9.513(1) \text{ \AA}$, $\alpha = 84.58(1)^\circ$,

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