Table V. Structural and Magnetic Data for Hydroxo-Bridged Complexes

Complex	M–O–M, deg	$2J$, cm^{-1}
$[(dipy)Cu(OH)_2Cu(dipy)]SO_4 \cdot 5H_2O$	97^a	+48^b
$[(EAEP)Cu(OH)_2Cu(EAEP)](ClO_4)_2$	99.2 (3)^c	−130.4^d
$[(tmen)Cu(OH)_2Cu(tmen)]Br_2$	104.1 (2)^e	−509^f
$[(gly)_2Cr(OH)_2Cr(gly)_2]$	98.2 (2)^g	−8.4^{g,h}

[a] A. T. Casey, B. F. Hoskins, and F. D. Whillans, *Chem. Commun.*, 904 (1970). [b] Reference 3. [c] Reference 4. [d] Reference 5. [e] Reference 21. [f] Reference 20. [g] This work; ref 8. [h] Reference 7.

crystal field effects and dipole-dipole interactions as well as the exchange interaction contribute to the zero-field splitting, these contributions must be of opposite sign such that they are able to attenuate the overall value of the zero-field splitting.

We now consider the spin-spin coupling mechanism.[37] The structural data support a pseudotetrahedral geometry for the bridging oxygen atom. Thus there is an available lone pair of electrons in the nonbonding hybrid orbital on the oxygen which can interact with like pairs from the "t_{2g}" π orbitals[38] on each chromium ion. It is more difficult to account for the coupling of the remaining unpaired electron on each chromium without considering the effects of intraatomic exchange, since the in-plane π orbitals on each chromium are not advantageously oriented for a superexchange process. However, this latter process cannot be ruled out with certainty since these orbitals can mix with the σ orbitals of the bridging oxygen atom.

It is of interest to compare the structural and magnetic data for $[(gly)_2Cr(OH)_2Cr(gly)_2]$ with analogous data for hydroxo-bridged copper(II) complexes. These data are collected in Table V, where it may be seen that the singlet-triplet splittings in the copper(II) complexes correlate well with the Cu-O-Cu angle. The data for the chromium(III) complex are similar and it will be of considerable merit to characterize additional hydroxo-bridged chromium(III) and copper(II) complexes so that the structural factors which determine the magnitude of the spin-spin coupling can be identified.

Experimental Section

Magnetic Measurements. In the temperature range 77-296°K, magnetic susceptibilities of a powdered sample were determined using a Faraday balance.[39] A Foner-type vibrating sample magnetometer,[40] operating at a field strength of 10,000 G, was used to determine the magnetic susceptibilities in the 4.2-80°K temperature range. Mercury tetrathiocyanatocobaltate(II) was used as a magnetic susceptibility standard,[41] and diamagnetic corrections were estimated from Pascal's constants.[42]

Epr Measurements. The epr spectra of a powdered sample were obtained using a Varian V4502 X-band spectrometer equipped with a variable-temperature accessory.

Registry No. $[Cr(gly)_2OH]_2$, 36926-80-4.

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[37] For an early account see P. W. Anderson, *Magnetism*, 1, Chapter 2 (1963). For a recent review see A. P. Ginsberg, *Inorg. Chim. Acta Rev.*, 45 (1971).

[38] Specifically, with the z axis taken perpendicular to the Cr-O-Cr-O plane, these are the d_{xz}, d_{yz} orbitals.

[39] W. E. Hatfield, C. S. Fountain, and R. Whyman, *Inorg. Chem.*, 5, 1855 (1966).

[40] S. Foner, *Rev. Sci. Instr.*, 30, 548 (1959).

[41] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

[42] E. Konig, "Magnetic Properties of Transition Metal Compounds," Springer-Verlag, Berlin, 1966.

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Structure of π-$C_5H_5Rh(CH_2{=}CHF)_2$ and π-$C_5H_5Rh(CH_2{=}CHF)(CH_2{=}CH_2)$

RICHARD CRAMER* and G. S. REDDY

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A solution of π-$C_5H_5Rh(CH_2{=}CHF)_2$ contains six isomers as a consequence of differing orientations of the vinyl fluoride ligands. Two isomers of π-$C_5H_5Rh(CH_2{=}CH_2)(CH_2{=}CHF)$ were detected. The free energy difference of the isomers is small for both compounds (<1 kcal). The energy barrier to rotation of coordinated vinyl fluoride in π-$C_5H_5Rh(CH_2{=}CHF)_2$ appears to be slightly greater than that for ethylene in π-$C_5H_5Rh(CH_2{=}CH_2)_2$.

Complexes of ethylene with rhodium(I) undergo a change of configuration through a propeller-like rotation of the ethylene ligand with the olefin-rhodium bond as its axis.[1] The energy barriers to rotation of coordinated ethylene in π-$C_5H_5Rh(C_2H_4)_2$ (15.0 ± 0.2 kcal[1b]) and some of its analogs have been evaluated,[1b,c] but, aside from data for C_2F_4 in π-$C_5H_5Rh(C_2H_4)(C_2F_4)$[1b] (no rotation detected), corresponding data for rhodium complexes of substituted olefins have not been reported. Accordingly the temperature dependence of the ^1H and ^{19}F nmr spectra of π-$C_5H_5Rh(CH_2{=}CHF)_2$ was studied.

Initiation of rapid rotation of ethylene in π-$C_5H_5Rh(C_2H_4)_2$ on raising the temperature is indicated by the nmr spectrum in the following manner. At low temperature the hydrogen of coordinated ethylene is responsible for two characteristically complex upfield absorptions centered at −2.89 and −1.00 ppm. These are attributed respectively to "outside" (H^o) and "inside" (H^i) locations (see Figure 1). At high temperatures fast rotation exchanges H^o and H^i and these absorptions broaden and, finally, coalesce.

Absorptions in the proton nmr spectrum of π-C_5H_5Rh-

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[1] (a) R. Cramer, *J. Amer. Chem. Soc.*, 86, 217 (1964); (b) R. Cramer, J. B. Kline, and J. D. Roberts, *ibid.*, 91, 2519 (1969); (c) R. Cramer and J. J. Mrowca, *Inorg. Chim. Acta*, 5, 528 (1971).

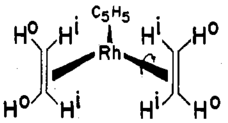


Figure 1.

$(CH_2{=}CHF)_2$ occur in four groups at 0°: −5.3 ppm (sharp, π-C_5H_5); −7.4 to −4.6 (broad, =CHF protons, both "inside" and "outside"); −3.6 to −2.4 (broad, outside protons of $=CH_2$); −1.7 to −0.8 (broad, inside protons of $=CH_2$). The chemical shift of $=CH_2$ protons is determined primarily by whether they are H^i or H^o (Figure 1) and secondarily by whether they are cis or trans to fluorine. As the temperature is raised the fine structure of proton absorptions attributed to vinyl fluoride disappears and absorptions for H^i and H^o begin to coalesce. On a 100-MHz spectrometer, these absorptions, whose centers were separated by 180 Hz at 0°, coalesce at about 68°.

The ^{19}F spectrum contains complex absorptions in two areas located (with respect to internal C_6F_6) at −12.0 to −9.0 ppm (F^o) and +17.0 to +25.0 ppm (F^i). (F^o and F^i are "outside" and "inside" F atoms; *cf.* Figure 1.) These absorptions become indistinguishable from the base line at 120° (HA-100 spectrometer with 12 accumulated signals on CAT).

The results suggest that the energy barrier for rotation of vinyl fluoride in π-$C_5H_5Rh(CH_2{=}CHF)_2$ is a little larger than for ethylene in π-$C_5H_5Rh(C_2H_4)_2$. A calculation based upon the coalescence temperature of the proton spectrum using eq 1[2] yields a value for $\Delta F_T^{\ddagger}$ of 16 kcal. $\Delta F_T^{\ddagger}$

$$\Delta F_T^{\ddagger} = -RT \ln \frac{\pi \Delta \nu h}{\sqrt{2}\, kT} \qquad (1)$$

is free energy of activation for rotation, $\Delta\nu$ is the separation of centers of absorption of H^i and H^o in the absence of exchange (cps), h is Planck's constant, k is Boltzmann's constant, and T is the coalescence temperature (°K). A similar calculation (based on the assumption that flattening of the ^{19}F spectrum at 120° indicates coalescence) gives 17 kcal for $\Delta F_T^{\ddagger}$.

The complex ^{19}F signals of π-$C_5H_5Rh(CH_2{=}CHF)_2$ are the consequence of splitting by protons and by rhodium. Through proton decoupling both the upfield and downfield regions of the ^{19}F spectrum were resolved to four doublets. This indicates four species with "inside" fluorine and four with "outside" fluorine. It thus appears that the sample of π-$C_5H_5Rh(CH_2{=}CHF)_2$ contains all six of the possible stereoisomers (Figure 2).

At the temperature of these experiments vinyl fluoride ligands can reorient rapidly by rotation[3] but not by dissociation.[1a,4] Consequently two sets of stereoisomers are present (designated A and B in Figure 2). The members of each set interconvert readily by rotation but the exchange A ⇌ B requires dissociation and occurs rapidly only at higher temperatures. The amounts of the different isomers were estimated from the signal areas. Since the maximum ratio of any two different species over the temperature range −25 to +40° is about 1/4, the maximum free energy difference between these stereoisomers is 0.8 kcal.

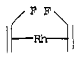
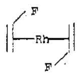
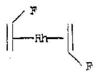
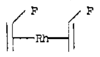
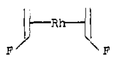
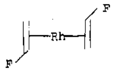
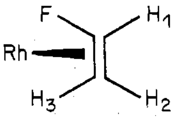
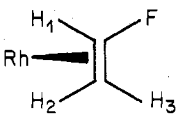
Set A			Set B		
	Expected Doublets			Expected Doublets	
Isomer	Low Field	High Field	Isomer	Low Field	High Field
	0	1		0	1
	1	1		1	1
	1	0		1	0

Figure 2. Stereoisomers of π-$C_5H_5Rh(CH_2{=}CHF)_2$.

Table I. Chemical Shifts (Ppm) and Coupling Constants (Hz) for H and F of Coordinated Vinyl Fluoride in π-$C_5H_5Rh(CH_2{=}CHF)(C_2H_4)$ (in $CDCl_3$)

	$\delta_1 = -6.61$ $\delta_2 = -2.64$ $\delta_3 = -1.21$ $\delta_F = +189.6$ (from F-11)	$J_{12} = 4.4$ $J_{13} = 7.4$ $J_{23} = 4.1$ $J_{1F} = 73.8\ (73.5)^a$ $J_{2F} = 24.2\ (24.2)^a$ $J_{3F} = 20.8\ (21.0)^a$ $J_{1Rh} = 3.7$ $J_{2Rh} = 3.0$ $J_{3Rh} = 1.8$ $J_{FRh} = (12.5)^a$
	$\delta_1 = -5.42$ $\delta_2 = -0.76$ $\delta_3 = -3.02$ $\delta_F = +153.7$ (from F-11)	$J_{12} = 4.1$ $J_{13} = 7.1$ $J_{23} = 4.1$ $J_{1F} = 71.0\ (71.0)^a$ $\left.\begin{matrix} J_{2F} = 22.0 \\ J_{3F} = 20.5 \end{matrix}\right\\}(21.0)^a$ $J_{1Rh} = 2.9$ $J_{2Rh} = 2.4$ $J_{3Rh} = 3.0$ $J_{FRh} = (6.2)^a$

[a] These values are from the undecoupled ^{19}F spectrum.

In order to verify our conclusions concerning the structure of π-$C_5H_5Rh(CH_2{=}CHF)_2$, the preparation and study of π-$C_5H_5Rh(CH_2{=}CHF)(C_2H_4)$ was undertaken. It was expected that only two isomers would be present—corresponding to "inside" or "outside" location of F in the vinyl fluoride ligand. π-$C_5H_5Rh(CH_2{=}CHF)(C_2H_4)$ was isolated by thin layer chromatography from its mixture with π-$C_5H_5Rh(C_2H_4)_2$ and π-$C_5H_5Rh(CH_2{=}CHF)_2$. As expected, in the proton-decoupled ^{19}F spectrum, only two doublets were observed (at −9.25 and +26.73 ppm from internal C_6F_6). The doublet structure is due to spin-spin coupling of rhodium and fluorine. The upfield absorption is assigned to the isomer with an "inside" fluorine.[5] On this basis the ratio of "inside" F/"outside" F isomers is 4/5 at 25° which corresponds to a free energy difference of 0.1 kcal. Analysis of the 100- and 220-MHz spectra yielded all the chemical shifts and H-F, H-H, and H-Rh coupling constants for both isomers (Table I). It can be seen that the H-H coupling constants do not differ appreciably in the two isomers whereas the H-F coupling constants are generally higher when F is "inside."

Only qualitative observations can be made concerning

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[2] (a) A. Allerhand, H. S. Gutowsky, J. Jonas and R. Meinzer, *J. Amer. Chem. Soc.*, 88, 3185 (1966); (b) C. E. Holloway, G. Hulley, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc. A*, 53 (1969).

[3] Using the equation $k = A \exp(-E_a/RT)$, with a value of 3×10^{12} sec^{-1} for A[1b] and 17 kcal for E_a, it is calculated that the half-life of a configuration of π-$C_5H_5Rh(CH_2{=}CHF)_2$ is about 3 min at −30° and 5 sec at 0°.

[4] Ethylene dissociates from π-$C_5H_5Rh(C_2H_4)_2$ at a rate that corresponds to a half-life of 30 min for π-$C_5H_5Rh(C_2H_4)_2$ at 130°: R. Cramer, *J. Amer. Chem. Soc.*, 94, 5681 (1972). Dissociative disproportionation of π-$C_5H_5Rh(CH_2{=}CHF)(C_2H_4)$ at 130° is described later in this paper.

[5] This assignment is based on an analogy with the assignment for proton nmr signals. It was deduced[1a] that in π-C_5H_5Rh(1,5-hexadiene) the absorption of the "inside" methylene protons is upfield from that of the "outside" methylene protons.

the rotation of olefin ligands in π-$C_5H_5Rh(CH_2{=}CHF)(C_2H_4)$. With a 220-MHz spectrometer, absorptions due to protons of coordinated $CH_2{=}CHF$ and C_2H_4 can be distinguished and rotations of both are frozen out at −20°. At +22° the signals due to H^i and H^o of C_2H_4 are broad and featureless (but not merged) while those of H^i and H^o on $CH_2{=}CHF$ retain fine structure. At +33° the fine structure of $CH_2{=}CHF$ proton signals has begun to disappear. At +40° there are two broad, featureless absorptions corresponding to H^i and H^o protons (of both ligands). At +50° there is only one broad absorption for protons of $CH_2{=}CHF$ and C_2H_4.

The pair of doublets in the proton-decoupled ^{19}F spectrum corresponding to F^i and F^o become broad singlets at 60° but are still distinguishable as separate, broad absorptions at 110°. After a solution of π-$C_5H_5Rh(CH_2{=}CHF)(C_2H_4)$ is heated at 130° for 10 min, the ^{19}F spectrum of the cooled solution is changed as a consequence of partial disproportionation to π-$C_5H_5Rh(CH_2{=}CHF)_2$ and π-$C_5H_5Rh(C_2H_4)_2$. This conclusion was substantiated by separation of the components using thin layer chromatography.

Experimental Section

Synthesis of acacRh($CH_2{=}CHF$)$_2$. The reaction was conducted in a 50-ml graduated cylinder containing a magnetic stirrer bar and surrounded by a cooling bath. A solution of 2.0 g of acacRh(C_2H_4)$_2$[1a] in 20 ml of CH_2Cl_2 was charged into the graduated cylinder, blanketed with nitrogen, and chilled to −50°. Vinyl fluoride was condensed into the solution to effect a volume change of 5 ml and the mixture was warmed during 15 min to −30°; a vigorous evolution of gas ensued. The solution was treated four times more with vinyl fluoride; the last two times the temperature was allowed to rise to 0°. A sample of the reaction solution was evaporated to dryness and the residue was treated with 1,5-cyclooctadiene. The infrared spectrum of the evolved gas showed no evidence of ethylene so it was presumed that displacement by vinyl fluoride was complete. Evaporation of solvent from the remainder of the solution gave 2.1 g of crude acacRh($CH_2{=}CHF$)$_2$ (92% yield).

Synthesis of π-$C_5H_5Rh(CH_2{=}CHF)_2$. A solution of cyclopentadienyllithium was prepared under nitrogen from 44 ml of tetrahydrofuran, 2.75 ml of cyclopentadiene, and 14 ml of 1.6 *M* *n*-butyllithium in hexane. This was chilled to −80° and 2.1 g of crude acacRh($CH_2{=}CHF$)$_2$ was added. The stirred solution was warmed to 25° for 45 min and the solvent was removed under vacuum at or below 25°. Crude product was sublimed from the residue (45–72° (0.1 mm)). This was crystallized twice from methanol and resublimed to obtain 1.44 g of π-$C_5H_5Rh(CH_2{=}CHF)_2$ (77% yield). *Anal.* Calcd for $C_9H_{11}RhF_2$: C, 41.56; H, 4.26; F, 14.61. Found: C, 42.28; H, 4.31; F, 14.42.

Synthesis of π-$C_5H_5Rh(CH_2{=}CHF)(C_2H_4)$. A solution of 5.0 g of acacRh(C_2H_4)$_2$ in 70 ml of CH_2Cl_2 was treated three times with 5 ml of $CH_2{=}CHF$ as described above. Evaporation of solvent gave 5.4 g of a mixture of acacRh(C_2H_4)$_2$, acacRh($CH_2{=}CHF$)$_2$, and acacRh($CH_2{=}CHF$)(C_2H_4). The gas displaced by treating a sample with 1,5-cyclooctadiene had an infrared spectrum that matched closely a mixture of 80% $CH_2{=}CHF$ and 20% C_2H_4. A solution of 5.0 g of the solid residue and 3.0 g of acacRh(C_2H_4)$_2$ in 30 ml of tetrahydrofuran was calculated to contain equimolar amounts of coordinated C_2H_4 and $CH_2{=}CHF$. It was added to a solution of cyclopentadienyllithium (at −40°) prepared from 40 ml of tetrahydrofuran, 4.8 ml of cyclopentadiene, and 33 ml of 1.6 *M* *n*-butyllithium in hexane. The mixture was warmed to +5° during 1.5 hr and the solvent was distilled at reduced pressure. The product was extracted from the residue with diethyl ether (300 ml in five portions). This extract was concentrated under nitrogen to a brown oil. It was crystallized by chilling to −80° a concentrated solution in methanol to give 6.3 g of solids.

Chromatography of this solid on alumina-coated plates using hexane to elute showed it contained three species. The minor components were identified as π-$C_5H_5Rh(C_2H_4)_2$ (R_f ~7.8) and π-$C_5H_5Rh(CH_2{=}CHF)_2$ (R_f ~5.6). The principal species is π-$C_5H_5Rh(CH_2{=}CHF)(C_2H_4)$ (R_f ~6.7).

A typical separation on preparative scale was conducted as follows. A solution of 0.091 g of the mixture of π-C_5H_5Rh(olefin)$_2$ compounds in 1 ml of CH_2Cl_2 was applied to an 8 in. × 8 in. aluminum oxide coated plate (Brinkman Instruments Co., Catalog No. 681400) by a mechanical applicator. The chromatogram was developed with hexane and the products were recovered by extraction from alumina with ether. Evaporation of ether gave 0.013 g of π-$C_5H_5Rh(C_2H_4)_2$, 0.015 g of π-$C_5H_5Rh(CH_2{=}CHF)_2$, and 0.040 g of π-$C_5H_5Rh(CH_2{=}CHF)(C_2H_4)$ (mp 50.5–51°). This corresponds to 40% conversion of "acacRh($CH_2{=}CHF$)(C_2H_4)" to π-$C_5H_5Rh(CH_2{=}CHF)(C_2H_4)$ and 14% conversions to both π-$C_5H_5Rh(C_2H_4)_2$ and π-$C_5H_5Rh(CH_2{=}CHF)_2$. *Anal.* Calcd for $C_9H_{12}RhF$: C, 44.65; H, 5.00; F, 7.85. Found: C, 44.89; H, 5.21; F, 8.03.

Registry No. acacRh($CH_2{=}CHF$)$_2$, 12282-05-2; π-$C_5H_5Rh(CH_2{=}CHF)_2$, 36118-17-9; i-[π-$C_5H_5Rh(CH_2{=}CHF)(C_2H_4)$], 36974-36-4; o-[$\pi$-$C_5H_5Rh(CH_2{=}CHF)(C_2H_4)$], 36974-37-5.