resulted in the agreement factors[14] $R(F^2) = 0.074$ and $R(wF^2) = 0.059$. A final difference map was essentially featureless.

Discussion

A view of the $[HIr_4(CO)_{11}]^-$ anion is shown in Figure 2. The final atomic coordinates and selected bond distances are given in Tables II and III, respectively. The geometry of the $[BzPh_3]^+$ cation is entirely normal. Complete results from the X-ray and neutron analyses are available as supplementary material (see paragraph at end of paper).

In the preliminary X-ray analysis of $[BzPh_3P]^+[HIr_4(CO)_{11}]^-$, it was predicted[20] that the H atom would bridge the Ir(3)–Ir(4) edge of the tetrahedron, partly because of the Ir(3)–Ir(4) distance [2.795 (2) Å] being significantly longer than the others [mean 2.714 (7) Å] and partly because of the distortions of the Ir–Ir–C (terminal) angles about the Ir(3)–Ir(4) bond.[21] This prediction is confirmed by the present neutron analysis (Figure 2), which locates the hydride ligand in a nearly symmetrical position about this bond [Ir(3)–H(1) = 1.821 (3) Å, Ir(4)–H(1) = 1.847 (3) Å], making an Ir–H–Ir angle of 99.5 (1)°.

The anion has approximate C_s symmetry, with the pseudo mirror plane passing through Ir(1), Ir(2), H(1), C(12), O(13), C(20), O(21), C(22), and O(23) (Table IV). The two bridging carbonyl groups [C(230)O(231) and C(240)O(241)] are signficantly asymmetric, as has been found in other Ir_4 carbonyl complexes such as $[H_2Ir_4(CO)_{10}]^{2-}$ [10] and $[Ir_4(CO)_{11}Br]^-$.[9] The pattern of asymmetry, according to standard arguments,[9,22] suggests that the negative charge of the anion is predominantly associated with the Ir(2) atom.

The Ir–H(bridging) distance found here [average 1.834 (13) Å] is the most precise measured to date for a bond of this type. An earlier measurement by neutron diffraction, on the complex $[(C_5Me_5)Ir(\mu\text{-}H)_3Ir(C_5Me_5)]^+$, yielded an Ir–H(bridging) distance of 1.75 (3) Å,[23] but that value is probably less reliable because of disorder problems involving the $Ir(\mu\text{-}H)_3Ir$ portion of the molecule.

The structural analysis of the $[HIr_4(CO)_{11}]^-$ anion now completes the list of known structures of the isoelectronic series $Ir_4(CO)_{12}$, $[HIr_4(CO)_{11}]^-$, and $[H_2Ir_4(CO)_{10}]^{2-}$. All have different ligand arrangements about a common Ir_4 tetrahedral core: $Ir_4(CO)_{12}$ has exclusively terminal carbonyls;[3,4] $[HIr_4(CO)_{11}]^-$ has a bridging hydride ligand along with two bridging carbonyl groups, and $[H_2Ir_4(CO)_{10}]^{2-}$ has three bridging carbonyls but terminal hydrides.[10] Of the existing family of hydride/carbonyl Ir_4 clusters, only $H_2Ir_4(CO)_{11}$[1] remains structurally uncharacterized.

Acknowledgment. This research was supported by the National Sciences Foundation (Grant No. CHE-81-01122) and the Consiglio Nazionale delle Richerche (CNR), Rome. Work at Brookhaven National Laboratory was performed under contract with the U.S. Department of Energy. We wish to thank Joseph Henriques for technical assistance.

Registry No. $[BzPh_3P]^+[HIr_4(CO)_{11}]^-$, 92984-97-9; $[Ph_4P]^+[HIr_4(CO)_{11}]^-$, 92984-99-1; $[Ir_4(CO)_{11}]^{2-}$, 92984-98-0.

Supplementary Material Available: Listings of the anisotropic temperature factors (Table A), a complete set of interatomic distances (Table B) and bond angles (Table C), and the final observed and calculated squared structure factors for the neutron structural analysis (Table D) (62 pages). Ordering information is given on any current masthead page.

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[19] Other details of the neutron least-squares refinement: Due to the large number of variable parameters (677), parameters were grouped in blocks of ca. 225, and these blocks refined alternately to convergence. The isotropic extinction parameter, g, converged to a value of 0.49 (2) $\times 10^4$ [see: Zachariasen, W. H. *Acta Crystallogr.* **1967**, *23*, 558], with the most significant extinction correction being 0.864 dividing F_o^2 for the (163) reflection. Neutron-scattering lengths ($b \times 10^{-12}$ cm) used in the refinement were $b_{Ir} = 1.06$, $b_P = 0.513$, $b_C = 0.6648$, $b_O = 0.5803$, and $b_H = -0.3741$ [see: Koester, L. In "Neutron Physics"; Koester, L., Steyerl, A., Eds.; Springer-Verlag: Berlin, Heidelberg, New York, 1977; p 36].

[20] Wei, C. Y. Ph.D. Dissertation, University of Southern California, 1981; Chapter 2.

[21] The use of molecular distortions to infer H positions in metal hydride complexes is common. See, for example: Churchill, M. R.; Bird, P. H.; Kaesz, H. D.; Bau, R.; Fontal, B. *J. Am. Chem. Soc.* **1968**, *90*, 7135.

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[23] (a) Bau, R.; Carroll, W. E.; Hart, D. W.; Teller, R. G.; Koetzle, T. F. *Adv. Chem. Ser.* **1978**, *No. 167*, 73. (b) Teller, R. G. Ph.D. Dissertation, University of Southern California, 1978, Chapter 3.

[24] The molecular drawing was generated by the program ORTEP-II: Johnson, C. K. "ORTEP-II", Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

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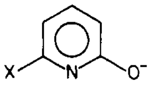
Preparation, Structure, and Properties of the Polar Dirhodium(II) Tetrakis(6-fluoro-2-oxypyridinate) Molecule

F. Albert Cotton,* Scott Han, and Wenning Wang

Received April 9, 1984

Since the discovery[1] of the $M_2(mhp)_4$ compounds (M = Cr, Mo, W; mhp = **1b**), it has been found that ligands of type **1**, which are derivatives or relatives of the 2-oxypyridinate ion (or that ion itself), are broadly useful for stabilizing dimetal units with a wide range of metallic elements and metal–metal bonds of orders from 1 to 4.[2]



1a (X=H), hp
1b (X=CH_3), mhp
1c (X=Cl), chp
1d (X=F), fhp

We recently reported[3] the first compounds containing the ligand **1d**, fhp, these being the three $M_2(fhp)_4(C_4H_8O)$ molecules in which M = Cr, Mo, and W. While in virtually all previous cases the arrangement of the four ligands on the M_2 core was such that each metal atom formed two M–N bonds and two M–O bonds (the only exceptions being a few cases where the ligand orientations were in a 3:1 ratio), the $M_2(fhp)_4(C_4H_8O)$ molecules had the fhp ligands all oriented in the same direction. This results in one metal atom having only M–N bonds while the other has four M–O bonds, plus an axial bond to the tetrahydrofuran molecule. It was not (and still is not) evident why this completely polar arrangement occurs. Since in the first study we dealt only with the quadruply bonded group 6 M_2^{4+} units, we felt it would be of value to determine how the fhp ligand would behave with an entirely different, but nevertheless stable and important, dimetal unit, namely, Rh_2^{4+}. We have succeeded in preparing several $Rh_2(fhp)_4L$ compounds, where L is C_2H_5OH, C_4H_8O, or $(CH_3)_2SO$, and have studied them structurally and spectroscopically.

Experimental Section

Preparation. A solution of the sodium salt of the 6-fluoro-2-hydroxypyridine anion (Na(fhp)) was prepared by dissolving 0.082

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[1] Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekutowski, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4725.

[2] Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982.

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Table I. Crystallographic Data for $Rh_2(fhp)_4(Me_2SO)$

formula	$Rh_2(C_5H_3NOF)_4((CH_3)_2SO)$
fw	732.28
space group	$P2_1/n$
systematic absences	$h0l$, $h + l = 2n$; $0k0$, $k = 2n$
a, Å	17.031 (6)
b, Å	9.177 (9)
c, Å	17.993 (6)
α, deg	90.0
β, deg	117.15 (4)
γ, deg	90.0
V, Å^3	2502 (5)
Z	4
d_{calcd}, g/cm^3	1.944
cryst size, mm	0.5 × 0.3 × 0.1
μ(Mo Kα), cm^{-1}	14.482
data colln instrument	Enraf-Nonius CAD-4
radiation (monochromated in incident beam)	Mo Kα (λ = 0.710 73 Å)
orientation reflcns: no.; range (2θ), deg	25; 25-35
temp, °C	25 ± 1
scan method	θ, 2θ
data colln range (2θ), deg	4.0-50.0
total no. of unique data	4832
no. of unique data with $F_o^2 > 3\sigma(F_o^2)$	2149
no. of params refined	343
transmission factors, %: max, min	99.58, 88.72
R^a	0.049
$R_w{}^b$	0.054
quality-of-fit indicator^c	1.3002
largest shift/esd, final cycle	0.02
largest peak, e/Å^3	1.088

[a] $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w |F_o|^2]^{1/2}$; $w = 1/\sigma(|F_o|^2)$. [c] Quality of fit = $[\Sigma w(|\Sigma_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$.

g (1.5 mmol) of $NaOCH_3$ and 0.17 g (1.5 mmol) of Hfhp in 20 mL of methanol. To this solution was added 0.2 g (0.76 n mol) of $RhCl_3 \cdot 3H_2O$, and this mixture was refluxed for 36 h. A bright green precipitate formed along with black rhodium metal. The solid was filtered and washed with 20 mL of distilled water. The product was then extracted from the metal with hot 95% ethanol. Evaporation of the solvent gave a bright green solid in 35% yield based on $RhCl_3 \cdot 3H_2O$. The compound was soluble in a variety of solvents including ethanol, tetrahydrofuran (THF), and acetone. The THF adduct was crystallized by slow evaporation of a solution in THF. The dimethyl sulfoxide adduct was prepared by dissolving 0.05 g of the compound in 25 mL of ethanol and adding two drops of Me_2SO. The resultant red-purple solution, upon slow evaporation, yielded platelike crystals suitable for X-ray diffraction studies.

X-ray Crystallography. A single crystal of the Me_2SO adduct was mounted with epoxy into a glass capillary. Measurement of unit cell constants and data collection were performed on an Enraf-Nonius CAD-4 autodiffractometer equipped with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. Lorentz, polarization, and absorption corrections were applied to the data.

The heavy-atom positions were determined by the direct-methods program MULTAN 11/82. The remaining non-hydrogen atoms were found by using alternate cycles of least squares and difference Fourier maps. Of 4852 unique data collected, those 2149 with $I > 3\sigma(I)$ were used to refine 343 parameters to final values of $R = 0.049$ and $R_w = 0.054$. Pertinent crystallographic data as well as expressions for R, R_w, and w are given in Table I. Only one peak in the final difference map was over 1.0 e/Å^3 (1.088), and this peak was a ghost peak extremely close to a rhodium atom.[4]

Crystals of the THF adduct were also studied crystallographically. Unit cell constants were measured on two crystals, with the following results. Crystal 1: a = 9.308 (2) Å, b = 14.748 (5) Å, c = 17.106 (5) Å, $\alpha = \beta = \gamma$ = 90.0°, V = 2348 (1) Å^3. Crystal 2: a = 9.303 (3) Å, b = 17.093 (6) Å, c = 14.762 (5) Å, $\alpha = \gamma$ = 90.0°, β = 90.14 (3)°, V = 2347 (1) Å^3.

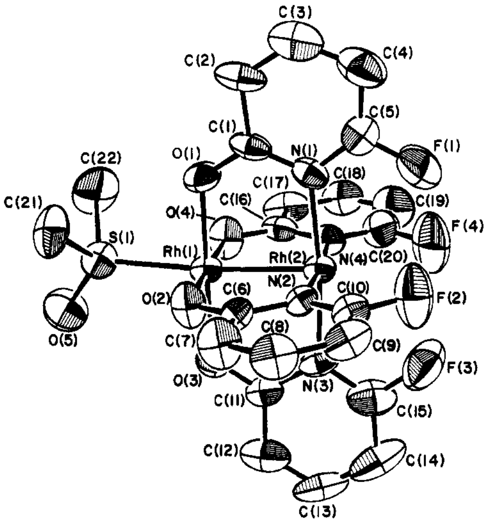

Figure 1. ORTEP representation of the $Rh_2(fhp)_4(Me_2SO)$ molecule. Thermal ellipsoids are at the 50% probability level. The atom-numbering scheme is defined.

The only systematic absence observed for crystal 1, $00l$, $l = 2n$, was indicative of the space group $P222_1$. However, no satisfactory solution could be obtained in this space group. The Patterson function seemed more consistent with the space group $P2_12_12_1$ and was solved in this space group for a linear set of three "rhodium" atoms, which gave a residual of ca. 26%, with an average "Rh-Rh" distance of ca. 2.34 Å. Direct methods gave the same solution. Least-squares refinement of these three atoms as rhodium atoms led to unreasonably high thermal parameters for the two outer atoms. A difference electron density map suggested a disordered array of ligands that all seemed to be attached to the central "rhodium" atom, but pointing in opposite directions. No model we could revise refined to better than 12%.

For crystal 2, the lone systematic absence was $0k0$, $k = 2n$; the centrosymmetric space group $P2_1/m$ gave unsuccessful results. In space group $P2_1$, the only Patterson and direct-methods solution was the same one (or its symmetry-related equivalent) seen in the case of crystal 1. A similar disordered arrangement was observed. Again the most satisfactory model could not be refined under 12% and was unsatisfactory in other respects, as well.

Spectroscopic Measurements. The UV-visible spectra were measured on a Cary 17D spectrophotometer at room temperature (ethanol and ethanol/Me_2SO solutions).

Results and Discussion

Table II gives the final positional parameters for $Rh_2(fhp)_4(Me_2SO)$, and Table III lists selected bond lengths and angles. Figure 1 shows an ORTEP plot of the $Rh_2(fhp)_4(Me_2SO)$ molecule.

As in the case of the previously reported[3] $M_2(fhp)_4(THF)$ structures, where M = Cr, Mo, or W, the ligand arrangement around the metal-metal bond in $Rh_2(fhp)_4(Me_2SO)$ is quite unusual. Again, the four fhp ligands have aligned in one direction along the Rh-Rh axis so that the four fluorine atoms form a square around, and completely screen, one axial position. The average Rh-F distance is 2.959 [5] Å, and the average of the four shortest F···F distances is 2.925 [7] Å.[5,6]

At the other axial position, a dimethyl sulfoxide molecule is coordinated to the dirhodium unit through the sulfur atom with a Rh-S distance of 2.332 (3) Å. This distance is much shorter, i.e., by ca. 0.12 Å, than the Rh-S axial distances of 2.449 (1) and 2.451 (2) Å seen in the molecules Rh_2-

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(4) Crystallographic computations were performed on a VAX 11/780 computer equipped with the Enraf-Nonius Structure Determination Package (VAXSDP) at the Department of Chemistry, Texas A&M University, College Station, Texas.

(5) A ( ) represents an esd for an individual value and a [ ] is defined as $[\sum_n \Delta_i^2/n(n-1)]^{1/2}$, where Δ_i is the deviation of the ith value in a set of n such values from the arithmetic mean of the n values.

(6) The van der Waals radius of the fluorine atom is ca. 1.35 Å, so that these contacts are quite acceptable.

Table II. Final Positional Parameters for $Rh_2(fhp)_4(Me_2SO)$[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Rh(1)	0.90788 (5)	0.02772 (9)	0.22355 (4)	C(4)	1.1842 (9)	0.386 (2)	0.4075 (8)
Rh(2)	1.06347 (5)	−0.00761 (9)	0.26974 (4)	C(5)	1.1597 (7)	0.256 (1)	0.3622 (7)
S(1)	0.7598 (2)	0.0836 (4)	0.1801 (2)	C(6)	0.9971 (6)	−0.103 (1)	0.3888 (5)
F(1)	1.2244 (5)	0.175 (1)	0.3595 (5)	C(7)	1.0025 (7)	−0.167 (1)	0.4634 (6)
F(2)	1.2159 (4)	−0.112 (1)	0.4244 (4)	C(8)	1.0815 (8)	−0.212 (1)	0.5238 (6)
F(3)	1.1744 (5)	−0.246 (1)	0.2630 (5)	C(9)	1.1604 (8)	−0.195 (1)	0.5138 (6)
F(4)	1.1865 (4)	0.036 (1)	0.1973 (4)	C(10)	1.1461 (6)	−0.132 (1)	0.4405 (6)
O(1)	0.9362 (5)	0.2243 (8)	0.2784 (4)	C(11)	0.9467 (6)	−0.258 (1)	0.1791 (6)
O(2)	0.9222 (4)	−0.064 (1)	0.3308 (4)	C(12)	0.9266 (8)	−0.401 (1)	0.1463 (6)
O(3)	0.8839 (5)	−0.1731 (9)	0.1700 (5)	C(13)	0.994 (1)	−0.489 (1)	0.1537 (8)
O(4)	0.8980 (4)	0.1160 (9)	0.1157 (4)	C(14)	1.083 (1)	−0.444 (2)	0.1941 (8)
O(5)	0.6886 (5)	−0.013 (1)	0.1296 (6)	C(15)	1.0942 (8)	−0.303 (1)	0.2235 (7)
N(1)	1.0815 (5)	0.196 (1)	0.3206 (5)	C(16)	0.9657 (7)	0.126 (1)	0.1031 (6)
N(2)	1.0719 (5)	−0.0886 (9)	0.3800 (4)	C(17)	0.9524 (8)	0.193 (1)	0.0251 (6)
N(3)	1.0321 (5)	−0.2096 (9)	0.2186 (5)	C(18)	1.0261 (7)	0.205 (1)	0.0121 (6)
N(4)	1.0448 (5)	0.077 (1)	0.1579 (4)	C(19)	1.1095 (8)	0.155 (2)	0.0687 (7)
C(1)	1.0132 (7)	0.270 (1)	0.3192 (6)	C(20)	1.1088 (7)	0.092 (1)	0.1391 (7)
C(2)	1.0256 (8)	0.408 (1)	0.3628 (7)	C(21)	0.7435 (7)	0.140 (2)	0.2673 (6)
C(3)	1.1103 (9)	0.456 (2)	0.4063 (8)	C(22)	0.7418 (9)	0.258 (2)	0.1261 (8)

[a] Numbers in parentheses are estimated standard deviations in the least significant figures.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for $Rh_2(fhp)_4(Me_2SO)$[a]

Bond Lengths

Rh(1)-Rh(2)	2.410 (1)	S(1)-O(5)	1.443 (8)
-S(1)	2.332 (3)	-C(21)	1.789 (11)
-O(1)	2.007 (7)	-C(22)	1.822 (13)
-O(2)	2.013 (7)	F(1)-C(5)	1.351 (14)
-O(3)	2.033 (8)	F(2)-C(10)	1.357 (12)
-O(4)	2.038 (7)	F(3)-C(15)	1.326 (15)
Rh(2)-N(1)	2.045 (9)	F(4)-C(20)	1.358 (14)
-N(2)	2.061 (8)		
-N(3)	2.030 (9)		
-N(4)	2.042 (9)		

Bond Angles

Rh(2)-Rh(1)-S(1)	175.02 (9)	Rh(1)-Rh(2)-N(4)	87.5 (3)
-O(1)	88.4 (2)	Rh(1)-S(1)-O(5)	123.0 (4)
-O(2)	88.8 (2)	-C(21)	110.3 (4)
-O(3)	89.6 (2)	-C(22)	105.3 (5)
-O(4)	89.0 (2)	O(5)-S(1)-C(21)	108.0 (6)
Rh(1)-Rh(2)-N(1)	87.0 (3)	-C(22)	108.5 (7)
-N(2)	87.9 (2)	C(21)-S(1)-C(22)	99.2 (7)
-N(3)	86.9 (3)		

[a] Numbers in parentheses are estimated standard deviations in the least significant figures.

$(O_2CC_2H_5)_4(Me_2SO)_2$[7] and $Rh_2(O_2CCH_3)_4(Me_2SO)_2$,[8] respectively. The S–O distance is 1.443 (8) Å, and the two independent S–C distances are 1.789 (11) and 1.822 (13) Å.

The Rh–Rh bond length at 2.410 (1) Å fits well with the distances reported for dirhodium(II) compounds in general. This distance is not significantly different from the metal–metal separations seen in the tetracarboxylato-bridged dirhodium(II) compounds with axial sulfur coordination: $Rh_2(O_2CC_2H_5)_4(Me_2SO)_2$, 2.407 (1) Å;[7] $Rh_2(O_2CCH_3)_4(Me_2SO)_2$, 2.406 (1) Å.[8] The average Rh–O and Rh–N distances are 2.023 [4] and 2.045 [5] Å, respectively, and the Rh–Rh–O and Rh–Rh–N angles are 89.0 [1] and 87.3 [2]°, respectively. The remaining bond lengths and angles are all typical of these systems and warrant no further discussion. Complete tables of bond lengths and angles are available as supplementary material.

The electronic spectra of the $Rh_2(fhp)_4$ species in various solvents are similar to spectra observed for other dirhodium(II) compounds. An ethanol solution of the compound gives the three distinct peaks in the 400–800-nm range (769 nm, 13 000 cm^{-1}, $\epsilon = 29$; 615 nm, 16 300 cm^{-1}, $\epsilon = 172$; 467 nm (sh), 21 400 cm^{-1}, $\epsilon = 38$) seen for the dirhodium tetracarboxylato compounds with axial oxygen donors. In a solution of ethanol containing a few drops of Me_2SO, $Rh_2(fhp)_4$ gives a small distinct peak at 773 nm (12 900 cm^{-1}, $\epsilon = 17$) and a large peak centered at 523 nm (19 100 cm^{-1}, $\epsilon = 260$). This large peak is not inconsistent with the peak observed at 500 nm (20 000 cm^{-1}, $\epsilon = 275$) for $Rh_2(O_2CCH_3)_4(Me_2SO)_2$.[9] There also appears to be a broad band that begins at ca. 700 nm but is overlapped by the transition at 523 nm. The spectra described are depicted in Figure 2.

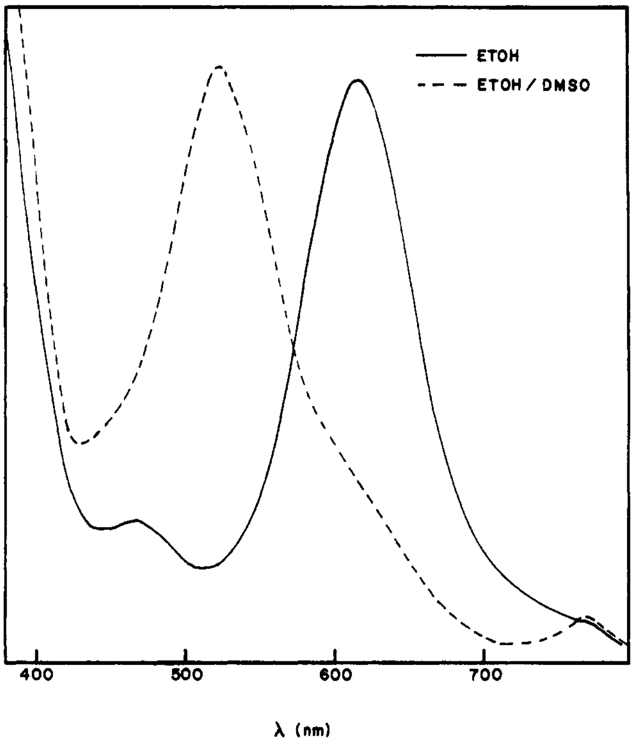

Figure 2. Electronic spectra of $Rh_2(fhp)_4$ in ethanol and ethanol/dimethyl sulfoxide solutions.

Concluding Remarks. The chief result of this study is that it provides another example of the unidirectional orientation of all four fhp ligands, but with a dimetal unit distinctly different, in an electronic sense, from the group 6 units Cr_2^{4+}, Mo_2^{4+}, and W_2^{4+}. Again, there is an axial ligand at the

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(7) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1980**, *19*, 2347.

(8) Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1980**, *19*, 323.

(9) Johnson, S. A.; Hunt, H. R.; Neumann, H. M. *Inorg. Chem.* **1963**, *2*, 960.

unencumbered end, viz., on the metal atom bonded to the four fhp oxygen atoms. The question of why this arrangement is so preferred by this ligand whereas it has not been observed for any other similar ligand is still unanswered, but attention is now directed toward the properties of the ligand itself as well as the properties of the dimetal unit itself.

One possible explanation might be the following. Of the four ligands **1a–1d**, the fhp ligand may be unique in its steric requirements. Ligand **1a** has been relatively little studied, but it is certainly clear, by example ($Os_2(hp)_4Cl_2$[10]), that four of these may be arranged in a two-vs.-two (i.e., two pointing one way and two the other) fashion and still leave room at each end for an axial ligand. The H atoms at the 6-positions are too small to block these positions in a major way. Thus, an $M_2(hp)_4L_2$ species is possible in which the symmetrical arrangement of bridging ligands (assuming that this is inherently favorable) and the formation of two axial M–L bonds can be achieved at the same time. For all other type **1** ligands, **1b–d**, the size of the substituents at the 6-position is such that, in a two-vs.-two arrangement, no axial M–L bonds could be formed. In the case of fhp the unidirectional arrangement is possible since four fluorine atoms can fit at one end without repulsive contact, as noted earlier. It is then possible to form a good M–L axial bond at the other end. On the other hand, for **1b** and **1c**, a unidirectional arrangement would result in large repulsive interactions between methyl groups or chlorine atoms. A simple graphical estimate shows that adjacent pairs of these groups would make contacts that are 0.3–0.5 Å less than the sums of van der Waals radii.

This analysis still leaves open a possibility that merits experimental study. If the axial ligand molecules could be removed and the remaining $M_2(fhp)_4$ compound dissolved in a noncoordinating solvent, would rearrangement to a two-vs.-two structure take place? Preliminary experiments have been done on all of the $M_2(fhp)_4L$ systems but have not yielded any clean-cut results.

Acknowledgment. We are grateful to the National Science Foundation for financial support.

Registry No. $Rh_2(fhp)_4(Me_2SO)$, 93426-94-9; $Rh_2(fhp)_4(C_4H_8O)$, 93426-95-0; $Rh_2(fhp)_4(C_2H_5OH)$, 93426-96-1; Rh, 7440-16-6.

Supplementary Material Available: Tables of general temperature factor expressions (*B*'s and *U*'s), refined temperature factor expressions (*B*'s), root-mean-square amplitudes of thermal vibration, bond lengths, bond angles, final atomic coordinates, and structure factors for all observed data (26 pages). Ordering information is given on any current masthead page.

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(10) Cotton, F. A.; Thompson, J. L. *J. Am. Chem. Soc.* **1980**, *102*, 6437.

Contribution No. 3471 from the Central Research
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Esters of Phosphotungstic Acid. Anhydrous Phosphotungstic Acid

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Preparations of the neutral methyl and ethyl esters of phosphotungstic acid were undertaken following the earlier preparations of $CH_3OW_{12}PO_{39}{}^{2-}$ and $C_2H_5OW_{12}PO_{39}{}^{2-}$ reported from this laboratory.[1] The route chosen was vacuum thermolysis of the corresponding trialkyloxonium salts, $[(CH_3)_3O]_3W_{12}PO_{40}$ and $[(C_2H_5)_3O]_3W_{12}PO_{40}$. The desired esters, in slightly impure form, were obtained at 150 °C. Unfortunately, these esters do not sublime, and no inert solvent for them has been found, so that characterization had to be done on the crude products.

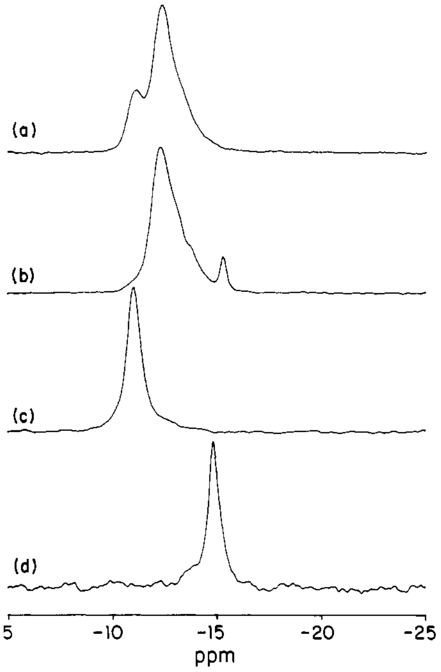

Figure 1. ^{31}P MAS NMR spectra: (a) $(C_2H_5O)_3W_{12}PO_{37}$ (90° pulse, 10-s recycle, 32 scans); (b) $(CH_3O)_3W_{12}PO_{37}$ (30° pulse, 10-s recycle, 52 scans); (c) $(HO)_3W_{12}PO_{37}$ (90° pulse, 10-s recycle, 4 scans); (d) $[(C_2H_5)_3O]_3W_{12}PO_{40}$ (90° pulse, 4-s recycle, 1375 scans).

The 150 °C thermolysate of $[(C_2H_5)_3O]_3W_{12}PO_{40}$ analyzed satisfactorily for $(C_2H_5O)_3W_{12}PO_{37}$. The ^{31}P MAS (magic-angle-spinning) NMR spectrum (Figure 1a) consisted of a major line at −12.3 ppm, assigned to the ester, and a minor line at −11.0 ppm, which is assigned to a small amount of anhydrous phosphotungstic acid, discussed in more detail below. The ^{31}P MAS spectrum of the 150 °C thermolysate of $[(CH_3)_3O]_3W_{12}PO_{40}$ (Figure 1b) also included a major line at −12.3 ppm, assigned to $(CH_3O)_3W_{12}PO_{37}$, but analysis showed an unsatisfactorily high carbon content. This is rationalized by the two minor lines at −15.2 and −13.7 ppm that are assigned to residual $[(CH_3)_3O]_3W_{12}PO_{40}$ and $[(CH_3)_3O]_2CH_3OW_{12}PO_{39}$, respectively. We find a ^{31}P MAS NMR line at −14.8 ppm for $[(C_2H_5)_3O]_3W_{12}PO_{40}$, consistent with assignment of the −15.2 ppm line; assignment of the −13.7 ppm line is based on earlier work[1] that reported a ^{31}P chemical shift of −13.9 ppm for $[(n\text{-}C_6H_{13})_4N]_2CH_3OW_{12}PO_{39}$ in dichloroethane.

Thermolysis of either of the tris(trialkyloxonium) salts or their 150 °C thermolysates at 215 °C under vacuum gave anhydrous phosphotungstic acid, $(HO)_3W_{12}PO_{37}$.[2] These samples all had a major ^{31}P MAS NMR line at −11.0 ppm and minor lines at −12.5 and/or −13.7 and/or −15.2 ppm, which are assigned as discussed above.

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(1) Knoth, W. H.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 4265–4266.

(2) (a) Characterization (GC/MS) of the volatile products from the 215 °C thermolysis of crude $(CH_3O)_3W_{12}PO_{37}$ revealed trace amounts of ethylene and propylene, larger amounts of C_3–C_7 hydrocarbons (butanes dominant), and dimethyl ether. These results correlate roughly with reported studies[2b] on the conversion of methanol and dimethyl ether to hydrocarbons by heteropolyacids. (b) Ono, Y.; Baba, T.; Sakai, J.; Keii, T. *J. Chem. Soc., Chem. Commun.* **1981**, 400. Hayashi, H.; Moffat, J. B. *J. Catal.* **1982**, *77*, 473–484. Okuhara, T.; Hibi, T.; Takahashi, K.; Tatematsu, S.; Misono, M. *J. Chem. Soc., Chem. Commun.* **1984**, 697–698.

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